INVESTIGATIONS OF SOME COMPLEXES
OF TRANSITION METALS WITH
SULPHUR DONOR LIGANDS

A thesis presented to the University of Surrey
for the degree of Doctor of Philosophy in the
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by

DARYOUSH SATTARI

The Joseph Kenyon Research Laboratories
Department of Chemistry
University of Surrey
Guildford, Surrey, England

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ABSTRACT

Complexes of several bivalent metals of the first transition series, and of gold(I), with some S-donor ligands have been synthesised.

A series of complexes of thiomalic acid \( \text{HO}_2\text{CCH(SH)CH}_2\text{CO}_2\text{H}, \text{tmH}_3 \) and some divalent metals, \( \text{Ni(tmH}_2)_2\cdot2\text{H}_2\text{O}, \text{Fe(tmH)} \) (pyridine), \( \text{M(tmH)}\cdot\text{nH}_2\text{O} \) (\( \text{M} = \text{Mn, Fe or Co} \)) and the salts \( \text{A[M}^{\text{II}}(\text{tm})]\cdot\text{nH}_2\text{O} \) (\( \text{A} = \text{Li, Na or K and M}^{\text{II}} = \text{Mn, Fe, Co or Ni} \)) has been prepared. The complexes, except of nickel(II), are air-sensitive, and were handled under nitrogen or in vacuo.

One nickel(II) complex, \( \text{Ni(tmH}_2)_2\cdot2\text{H}_2\text{O} \), has a normal magnetic moment for an octahedral complex while the others show temperature-dependence arising from weak ferromagnetic interactions.

All the iron(II)-thiomalates except \( \text{Fe(tmH)}(\text{py}) \), which is antiferromagnetic, also exhibited weak ferromagnetism. The temperature variation of the magnetic moment of \( \text{Co(tmH)}\cdot3\text{H}_2\text{O} \) was typical for a distorted octahedral monomeric structure, but the remaining cobalt(II) complexes and the manganese(II) complexes also showed antiferromagnetic interaction.

Octahedral configurations were assigned to all the transition metal ions from their reflectance spectra, and this, combined with the magnetic data, indicates that all except \( \text{Ni(tmH}_2)_2\cdot2\text{H}_2\text{O} \) and \( \text{Co(tmH)}\cdot3\text{H}_2\text{O} \) are polymeric.

Mössbauer spectra confirmed the oxidation and spin states and distorted octahedral stereochemistry of the iron(II) complexes.
From the infrared investigations it was found that the A[M\textsuperscript{II}(tm)]\cdot nH\textsubscript{2}O complexes contain bidentate carboxylate groups and coordinated -S as -SH bands are absent, whereas M(tmH)\cdot nH\textsubscript{2}O (M = Mn or Fe) contain one free carboxylic acid group and one bidentate carboxylate group. In Ni(tmH\textsubscript{2})\cdot 2H\textsubscript{2}O, unionised, and coordinated, and unionised, and uncoordinated carboxylic acid groups are present.

Similar investigations have been carried out with K\textsubscript{2}[Co(thiop)]\cdot H\textsubscript{2}O (thiop = thiopropionic acid), Co(cysH)\cdot 2H\textsubscript{2}O and A [Co(cys)\textsubscript{2}]\cdot 3H\textsubscript{2}O (A = Li, Na or K) (cysH = cysteine). These complexes contain transition metal ions in distorted octahedral configurations, and are believed to be polymeric.

Iron(II) complexes of the Schiff bases NN'-ethylenebis(monothio-acetylacetonime), (Sacac)\textsubscript{2}enH\textsubscript{2}, and 2-salicylideneaminobenzenethiol, (H\textsubscript{2}SalABT) have been prepared. The spin state of Fe[(Sacac)\textsubscript{2}en] has not been established because its magnetic moment (1.7 B.M.) is between the values expected for high-spin and low-spin iron(II). The black complex Fe(SalABT) is antiferromagnetic and is believed to have a six-coordinate structure involving bridging sulphur atoms.

A number of new transition metal nitrosyls have been obtained by reaction of the above complexes with nitric oxide. The infrared spectra of the diamagnetic dinitrosyls Fe(tmH)(NO)\textsubscript{2}, Co(tm)(NO)\textsubscript{2} and Fe(thiop)(NO)\textsubscript{2}\cdot CH\textsubscript{3}OH suggest coordinated NO\textsuperscript{+}. The related complex K[Fe(tm)]NO\cdot 2H\textsubscript{2}O is paramagnetic with magnetic moments close to the value expected for two unpaired electrons. It is believed that the complex contains S = 3/2 and S = 1/2 spin isomers in equilibrium. A nitrosyl Fe(trp)\textsubscript{2}NO\cdot 2H\textsubscript{2}O, obtained by reaction of Fe(trp)\textsubscript{2}H\textsubscript{2}O (trp = tryptophan) with nitric oxide, is similar in magnetic behaviour.
Some complexes of gold(I) with thiomalic acid have been isolated. These are \( \text{Au(tmH}_2\), \( \text{Na}_2[\text{Au(tm)}], \text{Ca[Au(tm)]\cdot2H}_2\text{O}\) and \( \text{Ba[Au(tm)]\cdotH}_2\text{O}\). They have polymeric structures involving bridging-sulphur atoms.

Reactions between thiomalatogold(I) and sulphur-containing ligands lead to the release of some or all of the coordinated thiomalic acid from thiomalatogold(I). In the reaction of glutathione and cysteine with thiomalatogold(I) polymeric, mixed ligand complexes, i.e. bis(glutathionato)mono(thiomalato)trigold(I) and (cysteinato)-(thiomalato)digold(I), were obtained. In the reaction with sodium diethylidithiocarbamate all the thiomalic acid was released and diethylidithiocarbamatogold(I) was precipitated. Albumin also produced a precipitate with thiomalatogold(I), but the thioether methionine did not.
. To Shahin and Mariam
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ABBREVIATIONS

$\text{tmH}_3$  thiomalic acid (mercaptosuccinic acid)
$\text{thiopH}_2$ thiopropionic acid
$cysH$ L-cysteine
$\text{trpH}$ tryptophan
$L\text{-metH}$ L-methionine
$\text{ethH}$ DL-ethionine
$\text{GluH}_3$ glutathione
$\text{PenH}$ penicillamine
$\text{SmcH}$ S-methylcysteine
$\text{gly}$ glycine
$\text{histH}$ histidine
$\text{py}$ pyridine
$\text{ABT}$ o-aminobenzenethiol
$\text{AET}$ aminoethanethiol
$\text{tsch}$ thiosemicarbazide
$\text{H}_2\text{SalABT}$ 2-salicylideneaminobenzenethiol
$\text{H}_2\text{AMT}$ 4-amino-3,5-dimercapto-1,2,4-triazole
$(\text{Sacac})_2\text{enH}_2$ NN'-ethylenediaminobis(monothioacetylaceton) imine
$\text{C.N.}$ coordination number
$\text{B.M.}$ Bohr magneton
$\text{C.T.}$ charge transfer
$\text{M.W.}$ molecular weight
$\text{O.D.}$ optical density
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CHAPTER I

INTRODUCTION
Introduction

Ligands containing sulphur donor atoms have been less extensively studied than their oxygen analogues, but more interest\textsuperscript{1-3} has been shown in metal complexes of such ligands in recent years, and the field has been reviewed.\textsuperscript{4} The affinity of metal ions for ligands depends, among other factors, on the type of donor atom, and Ahrland, Chatt and Davies\textsuperscript{5} have divided the metals into two classes: Class A, those that form more stable complexes with ligands in which the donor atom is the first member of group V B, VI B or VII B of the periodic table, i.e. N, O or F; and Class B, those that form stable complexes with the second or subsequent atoms of these groups as donors, i.e. P, S or Cl etc. For instance, mercury forms more stable complexes with ligands containing sulphur donor atoms than with their oxygen analogues. Class B behaviour is restricted to an area near the centre of the periodic table, most metals being in Class A. More recently, reviews\textsuperscript{6,7} have appeared on reactions involving metal complexes of sulphur-donor ligands.

1. Ligands containing sulphur donor atoms

Complexes of ligands which contain only sulphur donor atoms, and complexes in which ligands are apparently bonded to the metal atom only through sulphur in spite of the presence of other types of donor atom, are reviewed in this section, but as no dithiols were investigated their coordination chemistry has been omitted.

Class B metals form stable sulphite complexes, and the infrared spectra of complexes support the presence of metal-sulphur bonds,\textsuperscript{8,9}
e.g. with mercury(II), a typical Class B metal. Aromatic and aliphatic thiols can form complexes with metal ions. Divalent nickel forms a diamagnetic, polymeric complex (I) with ethanethiol, and a similar structure has been reported for the divalent palladium complex.

![Diagram of complex (I)](image)

Hexameric bis(ethanethiolato)nickel(II) is also known. Bridging thiol groups have been reported in some binuclear platinum and palladium complexes, whilst a polymeric structure has been suggested for the cobalt(III)-hexanethiol complex. Complexes of nickel(II) and palladium(II) with thiophenol have also been reported.

Polymeric d8-d10 metal ion complexes of sulphur-containing ligands have been recently reviewed. Mechanisms of reactions involving the mercapto group have been studied in recent years, interest being stimulated by the biological importance of SH-containing compounds such as cysteine. X-ray structural studies of two crystalline forms (II) of mercury(II) cysteinate showed that sulphur is coordinated to the mercury in each case, and the ligands contain -NH3+ groups and unionised and/or ionised carboxyl groups.
Copper is readily reduced to copper(I) by mercaptans such as L-cysteine which forms the polymeric complex $[\text{Cu}^{\text{I}}\text{SCH}_2\text{CH(NH}_3^+\text{)CO}_2^+]_n$.\textsuperscript{21,22} A silver-cysteine complex in which cysteine is monodentate is known.\textsuperscript{18}

The reaction of Cu(II) with thiomalic acid (HSR) in deaerated water is said\textsuperscript{23} to produce the mixed valence complex ion $[\text{Cu}^{\text{II}}(\text{Cu}^{\text{I}}\text{SR})_4]^{2+}$.
and the disulphide RSSR. On the other hand Hemmerich et al.\textsuperscript{24} did not find a mixed valence complex ion in the copper(I) cysteamine system, but from pH titrations and ESR measurements postulated that \([\text{Cu}^{II}\text{SR}]^{2+}\) ions are produced in solution, where \(\text{SR} = \text{SCH}_2\text{CH}_2\text{NH}_2\).

Silver(I) reacts with mercapto-containing carboxylic acids such as thiomalic acid to release protons and form Ag-S bonds.\textsuperscript{25,26} The carboxylate groups do not bind to the silver in these complexes. This information was deduced from pH, potentiometric and conductiometric titrations, and is supported by recent NMR evidence concerning the silver(I) complexes of L-cysteine and related ligands.\textsuperscript{27}

2. **Ligands containing sulphur and oxygen donor atoms**

Divalent nickel\textsuperscript{28} forms a monomeric and several sulphur-bridged, polymeric complexes with mercaptoacetic acid (HSCH\(_2\)COOH). Two forms of iron(II) mercaptoacetate were obtained, an air-unstable pale yellow form,\textsuperscript{29} and an air-stable, orange-yellow form obtained by warming the solution containing the yellow one. A single crystal X-ray study on the orange-yellow form has shown a polymeric structure (III) containing distorted [FeO\(_4\)S\(_2\)] octahedra bridged by sulphur and oxygen atoms of the mercaptoacetate ligand.\textsuperscript{30}

Infrared, UV and magnetic measurements on the solid complexes formed by bivalent metal ions and various alkylmercaptoacetic acids indicated that the sulphur atom (as well as the carboxylate group) was bound to the divalent cation.\textsuperscript{31-33}
Other aliphatic acids containing a thiol group have also been used as chelating ligands. β-Thiopropionic acid (HSCH₂CH₂COOH) forms complexes with d¹⁰ metal ions like Ag⁺, Cd²⁺, Hg²⁺ and also UO₂²⁺, in which the ligand is coordinated through the ionised sulphydryl group and the carbonyl oxygen of the unionised carboxyl group, except in the case of the cadmium(II) complex when the ligand is binegative and bidentate. Complexes of chromium(III), manganese(II), cobalt(II) and nickel(II) with α-thiopropionic acid have been prepared. Square-planar stereochemistry has been proposed for the manganese(II) complexes, and octahedral stereochemistry for cobalt(II) and chromium(III) complexes. With nickel(II), two types of complex, green and brown, were formed. The former has been assigned an octahedral structure, while the latter contains both octahedral and
square-planar nickel(II) units. Complex formation between cadmium(II) and α-thiopropionic acid\textsuperscript{36} gives the species $[\text{CdA}_2\text{]}^{2-}$, $[\text{Cd}_2\text{A}_3\text{]}^{2-}$ (IV), and $[\text{Cd}_3\text{A}_4\text{]}^{2-}$ (V) in solution.

Thiomalic acid forms complexes with a number of transition metal ions.\textsuperscript{26,37-40} From proton NMR spectra it is suggested that a 1:2 distorted octahedral complex is formed between $\text{WO}_4^{2-}$ and thiomalic acid in which the W-O bonds are almost co-planar.\textsuperscript{39} Panchal and co-workers\textsuperscript{37} have obtained solid $[\text{Cd}(\text{tmH})_2]\text{Cd}$, which has a 1:1 stoichiometry and is diamagnetic, and also $[\text{Ag}(\text{tmH})]\text{Ag}\cdot\text{H}_2\text{O}$. The structures are unknown. Complexes of thiomalic acid $\text{M(tmH)}$, where $\text{M} = \text{Zn(II)}, \text{Cd(II)}, \text{Hg(II)}$ and $\text{Pb(II)}$, have been isolated,\textsuperscript{41} and characterised by their infrared spectra. It is shown that doubly charged thiomalate anions are coordinated through sulphur and through oxygen atoms of the carboxylate groups. Potentiometric titrations of lead(II) nitrate with thiomalic acid and thiopropionic acid revealed
the formation of 1:1 complexes in solution.\textsuperscript{42}

The mechanism of oxidation of the mercapto group has been the subject of many recent papers.\textsuperscript{43,44} Amjad et al\textsuperscript{40} have found that the oxidation of thiomalic acid with thallium(III) takes place through a sulphur-bonded thallium(III) intermediate. With the one-electron oxidant\textsuperscript{45} iron(III), a rate-determining dimerisation is considered to take place with a two-electron transfer leading directly to the disulphide. Ready oxidation of the mercapto group means that complexes of mercapto-containing carboxylic acids are mainly restricted to metal ions in non-oxidising oxidation states, e.g. nickel(II), zinc(II), cadmium(II), mercury(II) and silver(I).\textsuperscript{36,46-48}

A single crystal X-ray study\textsuperscript{49} of diaqua(ethylenedithiodiacetato)-nickel(II) [Ni(-CH\textsubscript{2}SCH\textsubscript{2}COO\textsubscript{2} \cdot 2H\textsubscript{2}O] shows that the complex has the distorted octahedral structure (VI).

\begin{center}
\includegraphics{structure.png}
\end{center}
Some cobalt(III) and iron(III) complexes of α, β-unsaturated β-mercaptoesters are also known. \(^50\) Infrared spectra have been used to determine the donor atoms in many of these compounds. \(^51\)

q-Methylmercaptobenzoic acid (VII) forms complexes with several Class B metals. \(^52,53\) Halogen-bridged, binuclear complexes of several q-alkylmercaptobenzoic acids (VIII) have also been reported, \(^54,55\) including some containing two different metal ions. \(^53\)

![Diagram](image)

(VII)  (VIII)

From infrared and magnetic investigations the complexes M[OOC\(_2\)S(CH\(_2\)\(_n\))\(_n\)SCH\(_2\)COO]\(_n\)•2H\(_2\)O (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)) have been found\(^56\) to be octahedral, with coordinated water molecules and the ligand bonded through two oxygen and two sulphur atoms.

3. **Sulphur-nitrogen chelates containing thiol groups**

The chemistry of sulphur-nitrogen chelating agents has been recently reviewed. \(^57\) 2-Aminoethanethiol is the simplest representative of this class of ligand. Jensen\(^58\) observed the formation of nickel
complexes of this ligand in solution. Jicha and Busch\textsuperscript{59,60} found that two types of complex are formed with transition metal ions, monomeric bis-ligand complexes $\text{M(H}_2\text{NCH}_2\text{CH}_2\text{S)}_2$ (M = Ni, Pd), and trinuclear cationic complexes, $\text{M\{M(H}_2\text{NCH}_2\text{CH}_2\text{S)}_2\}_2\text{Cl}_2$ (IX) (M = Co, Ni and Pd), the structure of which has been confirmed for the nickel complex by X-ray diffraction.\textsuperscript{61}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{complex.png}
\caption{(IX)}
\end{figure}

The ligand 2-(2-mercaptoethyl)pyridine forms the mononuclear complexes $\text{M(N-S)}_2$ (M = Co, Ni, Pd and Pt), and trinuclear complexes\textsuperscript{62} $\text{M}_3\text{(N-S)}_3\text{X}_2$, similar to those obtained with 2-aminoethanethiol. However, these trinuclear complexes can only be isolated if the anion X is of low coordinating power. In the presence of halide ions, thiol-bridged, neutral, binuclear complexes $\text{M}_2\text{(N-S)}_2\text{X}_2$ are obtained.\textsuperscript{62,63} 2-Aminobenzenethiol forms inner complexes with cobalt(II), cobalt(III), nickel(II) and palladium(II).\textsuperscript{64,65}
A blue diamagnetic solid, first obtained by Hieber and Brück on reaction of a nickel(II) salt and the ligand in strong alkaline solution in the presence of air, was considered to be an oxo-bridged dimeric complex \([\text{NiO(C}_6\text{H}_4\text{SNH}_2)_2]_2\) (X).

Later it was shown\(^6^5,6^6\) to be \(\text{Ni(C}_6\text{H}_4\text{SNH}_2)_2\) (XI).

Larkworthy et al\(^6^7\) synthesised complexes with the general formula \(\text{M(C}_6\text{H}_4\text{SNH}_2)_2\) (M is vanadyl(IV), chromium(II), manganese(II), iron(II), cobalt(II), nickel(II) and zinc(II)) under anaerobic conditions, and showed that the cobalt(II) and nickel(II) complexes had been incorrectly described earlier. The manganese(II), iron(II) and cobalt(II) complexes
are antiferromagnetic, and the nickel(II) complex diamagnetic.

8-Mercaptoquinoline (XII), a similar ligand to 2-aminoethanethiol, forms very stable chelates with Class B metal ions.\(^{68-70}\)

![Diagram of 8-Mercaptoquinoline (XII)](image)

\[
\text{H}_2\text{N}-\text{C} \quad \text{SH} \quad \text{N} \quad \text{NH}_2 \\
\begin{align*}
\text{(XIII)} \\
\text{H}_2\text{N}-\text{C} \quad \text{SH} \\
\end{align*}

\[
\begin{align*}
\text{NH} \quad \text{NH}_2 \\
\text{H}_2\text{N}-\text{C} \quad \text{S} \\
\end{align*}
\]

\[
\begin{align*}
\text{(XIV)} \\
\end{align*}

Thiosemicarbazide(tscH) can exist in the tautomeric forms (XIII) and (XIV), and can act as a neutral, or, by loss of a proton as a charged, bidentate ligand. The complexes M(tsc\(_2\)) (M is nickel(II), palladium(II) and platinum(II)) have been obtained in two forms assumed to be cis-trans isomers.\(^{71,72}\)

Bertini et al\(^{73}\) obtained nickel(II) and cobalt(II) complexes of the Schiff bases formed from o-mercaptopbenzaldehyde and mono- or poly-amines having donor sets, SN (XV), S\(_2\)N\(_2\) (XVI), and S\(_2\)N\(_3\) (XVII). Zinc(II) complexes of (XV) (R = Me, Bu\(^n\), Hex) are also known.\(^{74}\)

![Diagram of Schiff bases](image)

\[
\begin{align*}
\text{R} \\
\text{H} \\
\text{C} \quad \text{N} \\
\text{SH} \\
\end{align*}
\]

\[
(R = \text{Me, Et, Pr, Bu}^s \text{ or Bu}^t) \\
\text{(XV)}
\]
Square-planar NN'-ethylenebis(methyl-2-amino-1-cyclopentenedithio-carboxylato (XVIII) complexes of nickel(II), palladium(II), cobalt(II) and copper(II) have been reported. The nickel(II) and palladium(II) complexes are diamagnetic, and the magnetic moments of the cobalt(II) and copper(II) complexes are 2.02 and 1.93 B.M. respectively.
Tetradentate NN'-ethylenebis(monothioacetylaceton imine) (XIX) \((\text{Sacac})_2\text{enH}_2\) reacts with divalent metals\(^76\) to form the complexes M(Sacac)_2en, where M is nickel(II), copper(II), cobalt(II), iron(II), zinc(II), palladium(II) and cadmium(II). The iron(II), cobalt(II) and copper(II) complexes exhibit room temperature magnetic moments of 3.69, 2.19 and 2.09 B.M. respectively, while those of nickel(II), zinc(II), palladium(II) and cadmium(II) are diamagnetic. Copper(II) complexes of tridentate sulphur- or oxygen-donor Schiff bases (XX) have been reported.\(^77\)

High-spin sulphur-bridged iron(II) complexes (FeL)_2 (XXI) and (FeL')_2 (XXII) were reported.\(^78\) \((\text{LH}_2 = \text{NN'}-\text{dimethyl-NN'}-\text{bis}(2-\text{mercaptoethyl})\text{ethylenediamine and } \text{L'H}_2 = \text{NN'}-\text{dimethyl-NN'}-\text{bis}(2-\text{mercaptoethyl})-1,3-\text{propanediamine).\n\)
4-Amino-3,5-dimercapto-1,2,4-triazole (H$_2$AMT) forms several types of complex with bivalent metal ions, i.e. [M(H-AMT)$_2$], [M(H-AMT)$_2$(H$_2$O)$_2$] (XXIII) and M(AMT)$_n$H$_2$O, where M is nickel(II), cobalt(II), copper(II), zinc(II), palladium(II), cadmium(II) and platinum(II).
In bis(2-mercapto-2,2-dimethylethylamino) cobalt(II) 
Co(SC(CH₃)₂CH₂NH₂)₂ the CoS₂N₂ unit is reported to be a slightly flattened tetrahedron. The cadmium(II) complex [Cd(SC(CH₃)₂CH₂NH₂)₂-CdCl₂]₂·2H₂O consists of centrosymmetric cadmium(II) tetrameric units containing both four and six coordinate cadmium ions.

The ligand (C₂H₂N₂S₃) (XXIV) forms complexes of general formula M(C₂HN₂S₃)₂ (M = Co(II), Ni(II), Zn(II), Cd(II) and Hg(II)), in which it can act as a sulphur donor, or a nitrogen and sulphur donor.

The cobalt and nickel complexes have been found to be square-planar, with a ligand bridge, which suggests that coordination occurs only
through the sulphur atoms. The weak paramagnetism of the nickel complex ($\mu_{\text{eff}} = 1.4$ B.M.), however suggests that the complex has some nickel ions in an octahedral environment. The zinc(II), cadmium(II) and mercury(II) complexes are polymeric and tetrahedral, involving coordination through the sulphur atoms and the nitrogen atoms.

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{O} \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{CNHCHCNHCH}_2\text{C} & \quad \text{O} \\
\text{OOC} & \quad \text{CH}_2 \\
\text{SH} &
\end{align*}
\]  

(XXV)

Stability constants for cadmium(II) and zinc(II) with the peptide glutathione (XXV) have been measured, and it was suggested that the metal complexes are tetrahedral in solution. McAuliffe et al have isolated complexes of glutathione with nickel(II), cobalt(II), palladium(II) and copper(II). The room temperature magnetic moments of the copper(II) and cobalt(II) complexes are 2.1 and 2.5 B.M. respectively, but the other compounds are diamagnetic. The complexes are polymeric with coordinated nitrogen and sulphur.

Cysteine complexes of a number of divalent metals have been isolated, and in most cases the ligand is coordinated through nitrogen and sulphur. Brown, diamagnetic potassium bis(cysteinato)nickelate(II) (XXVI), which is square planar, has been reported.

\[
\begin{align*}
2\text{K}^+ & \quad \text{O}_2\text{C}--\text{CH}--\text{NH}_2 \\
& \quad \text{S} \quad \text{Ni} \\
& \quad \text{NH}_2--\text{CH}_2 \\
& \quad \text{CH}_2--\text{S}
\end{align*}
\]  

(XXVI)
while two palladium(II)-cysteinate complexes were obtained, a halid-bridged form (XXVII) in which the Pd-C£-Pd linkage was identified by a $\nu$(Pd-C£) band at 276 cm$^{-1}$, the structure being analogous to that assigned to $\left[\text{Pd(penH)}_2\text{C£}\right]_2$ (penH = penicillamine),$^{84}$ and a substance of the formula Pd$_2$(cysH)$_3$C£$\cdot$2H$_2$O which was not investigated structurally. Iron(II)-cysteine complexes of 1:1 (XXVIII) and 1:2 (XXIX) stoichiometry have been isolated$^{29}$ which are extremely air-unstable.
They are believed to have polymeric structures of the type indicated, but no X-ray investigations have been reported.

In planar dichloro(DL-methionine)palladium(II)\(^{86}\) the methionine is bidentate through the sulphur and nitrogen atoms. Methyl-L-cysteine (N-SH) forms complexes\(^{87}\) \(M^{II}(N-S)_2\) (XXX) where \(M\) is zinc, nickel, mercury, cadmium and palladium.
4. Amino acids as nitrogen and oxygen donor ligands

Although this thesis is mainly concerned with metal complexes of S-donor ligands, some complexes of amino acids besides cysteine have been prepared and amino acid complexes are reviewed briefly here.

Simple amino acids exist as zwitterions $\text{LH}^{+}$ (XXXI) in the solid state, but almost invariably coordinate as the anionic species $\text{L}^{-}$ (XXXII).

\[
\begin{align*}
\text{RCHCOO}^{-} & \quad \text{RCHCOO}^{-} \\
\downarrow & \quad \downarrow \\
\text{NH}_3 & \quad \text{NH}_2
\end{align*}
\]

(XXXI) (XXXII)

There are numerous examples of complexes of transition-metal ions with amino acids and peptides. The simplest amino acid is glycine ($\text{H}_2\text{NCH}_2\text{COOH}$). X-ray crystal structures of diaquabis(glycinato)-nickel(II), bis(glycylglycinato)nickel(II) and triglycylglycinato-nickel(II) have been reported (XXXIII, XXXIV and XXXV).
It is thought that the \( \alpha \)-amino acid anion can act as a tridentate ligand in a bridging polymeric system of the type (XXXVI) in the solid.\(^8\)\(^9\)\(^{90}\)
Stability constants for complexes formed between a variety of metal ions (e.g. Cd(II), Co(II), Cr(II), Cu(II), Fe(II), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II), Zn(II), Al(III), Cr(III), Fe(III) and Ti(III)) and most amino acids have been determined. Of all \( \alpha \)-amino acids, histidine complexes have been among the most intensively studied. Bis(L-histidinato)nickel(II) monohydrate is monoclinic, and the structure is isomorphous with that of bis(L-histidinato)cobalt(II) monohydrate. These complexes are octahedral with nitrogen and oxygen coordinated to the metal (XXXVII).

\[
\text{(XXXVI)}
\]

\[
\text{(XXXVII)}
\]

\( M = \text{Ni}, \text{Co} \)
Bis(L-histidinato)zinc(II) dihydrate\textsuperscript{97,98} and bis(L-histidinato)-cadmium(II) dihydrate\textsuperscript{99} have the related trans-structures (XXXVIII).

In the complex bis(L-histidine)copper(II) nitrate-dihydrate\textsuperscript{100} histidine is bidentate, with two neutral histidine molecules coordinated to the central copper(II) atom through their amino nitrogen and carboxylate oxygen atoms arranged in a square plane. In Hg\textsuperscript{II}(histH\textsubscript{2})C\textsubscript{3}\textsuperscript{101} three chlorides and one carboxyl oxygen of the histidine are bonded to mercury. In histidinatomolybdenum(V) each molybdenum is bonded to a tridentate histidinate, an oxygen atom and a bis(oxo) bridging unit.\textsuperscript{102}

Cobalt(II), nickel(II) and zinc(II) complexes of aspartic acid are isomorphous (XXXIX).\textsuperscript{103}
The L-serinato complexes of copper(II) and zinc(II)\textsuperscript{104,106} have a square-pyramidal configuration; two chelate rings in the zinc complex occupy three points in the basal plane and the top of the pyramid (XL) whereas the copper atom is bound to two chelate rings in the basal plane (XLI). In diaquabis(serinato)nickel(II), nickel(II) is octahedral\textsuperscript{105} with two ligands in a cis-configuration with two water molecules completing the octahedron. The complex bis(2,3-diaminopropionato)cobalt(III) bromide is a distorted octahedron.\textsuperscript{107} The α-amino groups occupy trans positions and the carboxylate groups are cis as are the terminal amine groups (XLII).
The crystal structures of the copper(II)\textsuperscript{108} and zinc(II)\textsuperscript{109} hydrated complexes of glutamate, $\text{M}($\text{OOOCCH}_{2}\text{CH}($\text{NH}_{2})\text{COO})\cdot 2\text{H}_{2}\text{O}$ ($\text{M} = \text{Zn}, \text{Cu}$), are similar. In the copper compound, the copper atom is approximately square-planar, involving two oxygen atoms and a nitrogen atom of glutamate and a water molecule, but the zinc atom is surrounded by a more nearly square pyramidal arrangement. NMR investigations of ferrous ion and $\alpha$-amino acids (glycine, alanine, valine, leucine, serine, threonine, methionine, lysine hydrochloride, proline and histidine) suggest that coordination may take place through a carboxyl group or a carboxyl group and nitrogen, and in serine and threonine the hydroxyl group is coordinated to the ferrous ion.\textsuperscript{110}

Livingstone et al.\textsuperscript{111} have synthesized many complexes of the type $\text{ML}_{2}$ where $\text{L} = \text{DL-ethionine and S-methylcysteine}$, and $\text{M} = \text{Mn, Co, Ni, Cu, Zn or Cd}$. These complexes are polymeric, and the metal ions are six-coordinate through coordination to the amino groups and bidentate bridging carboxylato groups. Other metal complexes are the planar $[\text{M(UH)}\text{X}_{2}]$ ($\text{M} = \text{Pd, Pt}$; $\text{X} = \text{Cl, Br}$) in which the ligand donors are thioether and amino groups, and $[\text{Cu(Smc)}_{2}\text{Ag}]\text{NO}_{3}$, which involves ligand coordination to copper via oxygen and nitrogen donor atoms, and to silver via the sulphur atom. Recently, complexes of S-methylcysteine with zinc(II) and cadmium(II) have been synthesized,\textsuperscript{112} and their crystal structures have been determined. Cadmium is coordinated to nitrogen and carboxylate oxygen, in a slightly distorted octahedron, and zinc is similarly coordinated.

Although the amino acids histidine (XLIII) and tryptophan (XLIV) have similar structures in that their primary amine, carboxyl, and pyrrole-type nitrogen groups are the same, they differ in that
histidine has a pyridine-type nitrogen whilst tryptophan has a fused benzocOMPONENT. Williams\textsuperscript{113} has studied metal complexation of histidine and tryptophan with divalent metals (manganese, iron, cobalt, nickel, copper and zinc) in solution, and he found that histidine acts as a tridentate ligand with manganese(II), iron(II), cobalt(II) and nickel(II), while tryptophan acts as a bidentate ligand. In the zinc compound the carboxyl group is not coordinated and the zinc ion is tetrahedral. Where comparison is possible, the results are in good agreement with those in the solid state.\textsuperscript{95,96,100}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{molecules.png}
\caption{(XLIV) (XLIII)}
\end{figure}

Stability constants of tyrosine and tryptophan with some bivalent metals (cadmium, copper, nickel, lead and zinc) have been measured,\textsuperscript{114} and it was reported that the indole nitrogen in the case of tryptophan and the oxygen of the p-hydroxyphenyl group in the case of tyrosine do not take part in the formation of an additional chelate ring. The structures of complexes of L-methionine (L-metH) with divalent metals ML\textsubscript{2} (L = L-met; M = Cd, Zn and Cu) have been reported.\textsuperscript{115-117} In Cd(L-met)\textsubscript{2} the cadmium atom is six-coordinate\textsuperscript{115} through coordination to the amino group and bidentate, bridging carboxylato group; and the zinc\textsuperscript{116} and copper\textsuperscript{117} compounds are similar.
General properties of nitric oxide and its complexes with transition metals

Nitric oxide in the gaseous state is paramagnetic and colourless, and under normal conditions it behaves as a stable free radical. Its molecular orbital configuration: \(((1s\sigma)^2(1s\sigma^*)^2(2s\sigma)^2(2s\sigma^*)^2(2p_x\pi)^2(2p_y\pi^*)^2 = 2p_z\pi^*)^2\) shows that the unpaired electron is housed in an antibonding molecular orbital and can be lost relatively easily to give NO\(^+\), a species isoelectronic with carbon monoxide as well as with molecular nitrogen. In comparison with similar diatomic molecules such as \(N_2\) (1399 kJ mole\(^{-1}\)) or \(CO\) (1360 kJ mole\(^{-1}\)) the first ionization potential of nitric oxide molecules is low (916 kJ mole\(^{-1}\)) because it corresponds to the loss of an electron from an antibonding orbital.

The bond distance of 1.14 Å lies between the values of 1.18 and 1.06 Å for double and triple bonds respectively,\(^{119}\) and agrees with the bond order of 2.5 indicated by m.o. theory. The removal of an electron from the antibonding orbitals in nitric oxide leads to an increase\(^{120}\) in the N-O stretching frequency from 1875 cm\(^{-1}\) in NO to 2220 cm\(^{-1}\) in various nitrosonium salts.\(^{121}\) The electron affinity of nitric oxide is not known. The compounds formed between nitric oxide and sodium, potassium and barium, originally formulated\(^{122}\) as anionic nitrosyls, e.g. Na\(^+\)NO\(^-\), have been shown\(^{123}\) to contain the hyponitrite ion N\(_2\)O\(_2\)\(^-\).

Nitric oxide complexes

Depending on the nature and valence of the metal and the type of ligand present, nitric oxide compounds of transition metals may be
neutral, cationic or anionic. It is simplest to use hybridisation theory to visualise the different ways in which nitric oxide can combine with transition metals:

(a) An electron pair of neutral nitric oxide is shared with the metal, and a paramagnetic complex is obtained.

\[ M \rightarrow N = 0 \]

In this case the N-O stretching frequency should not be far removed from that of nitric oxide at 1878 cm\(^{-1}\), and the M-N-O angle should be less than 180°.

(b) Donation of one electron from nitric oxide to a metal results in the formation of NO\(^+\). In NO\(^+\) the nitrogen atom has sp-hybridisation so that subsequent donation of an electron pair to the metal results in the formation of an M-N-O bond angle of 180°.

\[ M \rightarrow N = 0 \leftrightarrow M = N = 0 \quad (i) \quad (ii) \]

Resonance structure (ii) indicates that d\(\pi\) - p\(\pi\) back bonding is considered to be important in linear M-N-O systems.

(c) An electron is transferred from the metal to nitric oxide to give NO\(^-\) which then coordinates. The nitrogen atom is sp\(^2\)-hybridised so that donation of an electron pair by NO\(^-\) results in an M-N-O bond angle of 120°.

\[ M \rightarrow N \rightarrow O \]

Sidgwick\(^{124}\) has suggested that coordination by NO\(^-\) is analogous
to that by the halide ion and the M-N-O system is structurally similar to organic nitroso compounds. Up to 1960, there was a view that in all but a few systems the linear mode of coordination was followed as in the nitroprusside ion \( \text{Fe(NO)(CN)_5}^{2-} \). A significant turning point in nitrosyl chemistry was achieved in 1967 when Ibers and Hodgson reported the first structurally bent nitrosyl complex.

(d) The nitric oxide group is not bonded linearly to the metal, but is held at some angle via the \( \pi \)-electron density.

\[
\begin{array}{c}
\text{N} \\
\vdots \\
\text{M}
\end{array}
\]

(e) Nitric oxide is bonded in a bridging position.

\[
\begin{array}{c}
\text{M} \\
\text{N} = 0 \\
\text{M}
\end{array}
\]

The ion \( \text{NO}^- \) is isoelectronic with oxygen, which absorbs\(^{128}\) at 1555 cm\(^{-1}\) and \( \text{NO}^+ \) is isoelectronic with nitrogen which absorbs at 2331 cm\(^{-1}\). Examples of nitrosyls with different types of M-N-O bonds, and the associated infrared stretching frequencies and bond angles are given in Table 1.1. The oxidation states given for the coordinated NO groups are those suggested in the references, and the bond angles often show departures from the idealised values above.

There are reviews on the preparation,\(^{142}\) structure\(^{143}\) and nature of bonding\(^{144,145}\) of transition-metal nitrosyls, and the following accounts, except for iron nitrosyls, refer only to more recently
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(NO) cm$^{-1}$</th>
<th>Bond angle</th>
<th>NO-oxidn. state</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(NO)$_2$SEt]$_2$</td>
<td>1773 1748</td>
<td>167°</td>
<td>NO$^+$</td>
<td>156</td>
</tr>
<tr>
<td>[Cr(CN)$_5$NO]$_3^-$</td>
<td>1645</td>
<td>Bent</td>
<td>NO$^-$</td>
<td>129</td>
</tr>
<tr>
<td>[CoNO($S_2$CNMe$_2$)$_2$]</td>
<td>1626</td>
<td>139°</td>
<td>NO</td>
<td>152</td>
</tr>
<tr>
<td>[(NO)$_2$FeS]$_2$K$_2$</td>
<td>1716</td>
<td>Bent</td>
<td>NO$^-$</td>
<td>156</td>
</tr>
<tr>
<td>(Et$_4$N)$_2$[Ru(NO)Cl$_5$]</td>
<td>1830</td>
<td>NO$^+$</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>[RuNO($S_2$CN)Et$_2$]$_3$</td>
<td>1803</td>
<td>180°</td>
<td>NO$^+$</td>
<td>133</td>
</tr>
<tr>
<td>[CoCl$_2$(NO)(PR$_3$)$_2$]</td>
<td>~1750</td>
<td>Linear</td>
<td>NO$^+$</td>
<td>139</td>
</tr>
<tr>
<td>(NH$_4$)$_2$[Fe(NO)S$_4$C$_4$(CN)$_4$]</td>
<td>1650</td>
<td>168°</td>
<td>NO</td>
<td>140</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_5$NO]Cl$_2$</td>
<td>1045</td>
<td>119°</td>
<td>NO$^-$</td>
<td>135</td>
</tr>
<tr>
<td>[IrNO(PPh$_3$)$_2$]</td>
<td>1660</td>
<td>180°</td>
<td>NO$^+$</td>
<td>136</td>
</tr>
<tr>
<td>[Fe(NO)$_2$I]$_2$</td>
<td>1818 1771</td>
<td>161°</td>
<td>NO$^+$</td>
<td>155</td>
</tr>
<tr>
<td>[Co(NO)$_2$Cl]$_2$</td>
<td>1859 1790</td>
<td>166°</td>
<td>NO$^+$</td>
<td>130</td>
</tr>
<tr>
<td>(Et$_4$N)$_2$[Pt$_2$(NO)$_2$Cl$_6$]</td>
<td>122°</td>
<td>NO$^a$</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>$\pi$C$_5$H$_5$NiNO</td>
<td>1820</td>
<td>180°</td>
<td>NO$^+$</td>
<td>138</td>
</tr>
<tr>
<td>Ru$<em>3$(CO)$</em>{10}$(NO)$_2$</td>
<td>1517 1500</td>
<td>NO$^a$</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>(C$_5$H$_5$)$_2$Cr$_2$(NO)$_3$(NH$_2$)</td>
<td>1684 1644 1505</td>
<td>172°</td>
<td>NO$^a$</td>
<td>134</td>
</tr>
<tr>
<td>Os$<em>3$(CO)$</em>{10}$(NO)$_2$</td>
<td>1503 1484</td>
<td>NO$^a$</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_5$Cr(NO)$_2$NCO</td>
<td>1818 1783</td>
<td>171°</td>
<td>NO</td>
<td>137</td>
</tr>
<tr>
<td>[C$_5$H$_5$Cr(NO)$_2$NMe$_2$]$_2$</td>
<td>1634</td>
<td>169°</td>
<td>NO</td>
<td>137</td>
</tr>
<tr>
<td>[CoCl$_2$(NO)(PR$_3$)$_2$]</td>
<td>~1650</td>
<td>Bent</td>
<td>NO$^-$</td>
<td>139</td>
</tr>
</tbody>
</table>

a - bridging nitrosyl
prepared metal nitrosyls. Collman et al\textsuperscript{146} have prepared
\[ \text{Mn(NO)\{HN\[(\text{CH}_2)_3\text{NCH}_3\text{H}_3(Z)\text{O}\}_2\}(\text{CHCl}_3), \]
where \( Z = \text{H}, \text{5-Br} \) or \( \text{5-NO}_2 \),
for which the NO stretching frequency is at about 1715 cm\textsuperscript{-1}.

Nitrosyl complexes with the general formula \( \text{M(NO)(CH}_3\text{CN)_2L}_2^{2+} \) (\( \text{M} = \text{Rh}, \text{Ir}; L = \text{P(C}_6\text{H}_5\text{)_3} \) and \( \text{As(C}_6\text{H}_5\text{)_3} \)) have\textsuperscript{147} nitrosyl absorptions between
1610 and 1650 cm\textsuperscript{-1}. Busch et al\textsuperscript{148} have reported the synthesis and
characterization of Cr(I) nitrosyl complexes with macrocyclic ligands,
in which the M-NO group is linear. Novel cationic dinitrosyl
compounds of general formula \( [\text{Mn(NO)_2L}_3]\text{BF}_4 \) (\( L = \text{PMe}_2\text{Ph, P(OMe)_3Ph and P(OMe)_3} \)) have been prepared.\textsuperscript{149} The structure of \( [\text{Mn(NO)_2(P(OMe)_3Ph)_2Cl}_2] \)
is trigonal bipyramidal\textsuperscript{150} (XLV), containing phosphonite groups in
the axial positions and nitrosyl groups which are not completely linear,
the M-N-O angles being 165 and 166\textdegree.  

![Diagram](image)

Thomas et al\textsuperscript{151} have obtained monomeric \( \text{CoL}_2\text{(NO)} \) (\( \text{HL} = \text{monothio-
dibenzoylethane or N-}(\text{morpholinothiocarbonylbenzamide}) \) which is
Nitrosylbis(N,N-dimethyldithiocarbamato)cobalt-[CoNO(Me₂dtc)₂], is an example of a class (d) nitrosyl as the crystal structure determination showed that this complex has a square-pyramidal structure with the NO molecule inclined at an angle of 139° to the pyramidal axis.

Iron nitrosyls

The black, unstable iron tetranitrosyl, Fe(NO)₄, was prepared by heating nitric oxide with iron pentacarbonyl under pressure. The infrared spectrum showed two N-O stretching frequencies in the NO⁺ region and one at 1150 cm⁻¹ assigned to NO⁻. The structure suggested was tetrahedral with three nitric oxide groups coordinated as NO⁺ and one coordinated as NO⁻. In compounds of the general series, Fe(NO)₃X (X = Cl, Br or I), which were shown to be monomeric, diamagnetic and unstable, the nitric oxide is assumed to be coordinated as NO⁺. These compounds lose nitric oxide easily to give the dinitrosyl halides [Fe(NO)₂X]₂ (X = Cl, Br or I) which are dimeric, diamagnetic and stable. The Fe-N-O grouping has been shown to be slightly bent in [Fe(NO)₂I]₂. (XLVI).
Related to the nitrosyl halides are some sulphur-containing iron nitrosyls of which Roussin's red and black salts are the best known examples. A series of dark red, diamagnetic esters of general formula $[\text{Fe(NO)}_2\text{SR}]_2$ ($R = \text{CH}_3$, $\text{C}_2\text{H}_5$, and $\text{C}_6\text{H}_5$) have been prepared from the red salt, $\text{K}_2[\text{Fe(NO)}_2\text{S}]_2$, and X-ray examination of $[\text{Fe(NO)}_2\text{SEt}]_2$ (XLVII) has shown that the Fe-N-O groupings are slightly bent. Related selenium and tellurium derivatives, $[\text{Fe(NO)}_2\text{MR}]_2$ (M = Se or Te) are also known. Roussin's black salts are diamagnetic and contain the anion $[\text{Fe}_4(\text{NO})_7\text{S}_3]^{-}$. Lewis et al. have suggested that the unstable brown ring compounds $[\text{Fe(H}_2\text{O)}_3\text{NO}]^{2+}$ and $[\text{Fe(NH}_3)_5\text{NO}]^{2+}$ have the formal structure $\text{Fe}^{1}\text{NO}^{+}$. The room temperature magnetic susceptibilities were independent of concentration and correspond to three unpaired electrons, a high-spin d$^7$ configuration. The dinitrosyl $\text{Fe(NO)}_2[S_2\text{CN(C}_2\text{H}_5)_2]$, has been found to be essentially diamagnetic at room temperature ($\mu_{\text{eff}} = 0.8$ B.M.). Infrared studies showed two bands in the region expected for $\text{NO}^{+}$. 

\[
\text{Fe} - \text{N} - \text{O}
\]
(1820 s, 1842 sh) from which it was concluded that the nitric oxide groups were cis. A more careful examination of the infrared spectrum of this compound showed the presence of bands at 814, 1419 and 1470 cm$^{-1}$ which are characteristic of an NO$_2$ group, from which it was concluded that this compound was in fact a nitro derivative of a mononitrosyl iron complex. Five coordinate mononitrosyl-1,2-dithiolene complexes of the general formula $[MNO(S_2C_2R_2)_2]^{n-}$ (M = Co or Fe; R = CN, CF$_3$ or C$_6$H$_5$; n = -2, -1, 0) have been prepared; these complexes have very similar physical and structural data to the nitrosyl bis(dialkylthiocarbamato)iron complexes.

Mononitrosyls of tetradeutate Schiff base cobalt(II) and iron(II) complexes have been studied. The N-O stretching frequencies in the iron complexes occurred from 1670 to 1790 cm$^{-1}$, within the range proposed for NO$. These complexes have been assigned the formal structure Fe(III) NO$-$ and the electronic configuration $(d_{xz}, d_{yz})^4(d_{xy})^1 (\pi^*\text{NO})^2$. The cobalt compounds are essentially diamagnetic. The mononitrosyl salen and salphen iron complexes have room temperature magnetic moments corresponding to three unpaired electrons, but on cooling to near 180° K the moments change abruptly to values corresponding to one unpaired electron. The NO stretching frequency also altered at this point from 1715 cm$^{-1}$ to 1630 cm$^{-1}$, suggesting that a change from a linear to bent Fe-N-O system might have occurred. FeNO(S$_2$CN(CH$_3$)$_2$)$_2$ is paramagnetic and has square-pyramidal geometry (XLVIII) with a nearly linear NO group in the axial position. Feltham et al have prepared numerous mononitrosyl iron $\sigma$-phenylenebis(dimethylarsine) complexes in which the nitrosyl stretching frequencies are in the range 1620-1860 cm$^{-1}$. 
Pentacoordinate mononitrosyl complexes of the general formula Fe(NO)[SCH₂CH₂N(R)(CH₂)ₙN(R)CH₂CH₂S] (n = 1, 2; R = CH₃) have been prepared. The crystal structure determination showed that the nitrosyl ligand occupies the apex of a distorted square pyramid. The Fe-N-O angles in two crystallographically independent molecules are 155° and 158° for n = 1 and 2 respectively.

The compounds Fe(NO)X[S₂CN(CH₃)₂]₂, where X = Cl, Br, I, SCN or NO₂, have been prepared. In cis-Fe(NO)S₂CN(C₂H₅)₂NO₂ (XLIX) the iron atom is hexacoordinate with an Fe-N-O angle of 175° and an (O)N-Fe-N(O₂) angle of 91°. Nitrosyl compounds FeL₂(NO) (HL = N-(morpholinothiocarbonyl)benzamide or monothiodibenzoylmethane) have been prepared. The iron atom is hexacoordinate in an S-bridged dimer.
Larkworthy et al. have reported some mono- and di-nitrosyl iron-amino acid complexes in which the nitrosyl stretching frequencies are between 1730 and 1760 cm$^{-1}$. Rabinowitz et al. have reacted nitrosonium salts with some binuclear iron(II) and cobalt(II) complexes:

$$ \text{(MI : E L}_2 \text{ + NO}^+ \rightarrow [(\text{MI}_2 \text{L})_2 \text{NO}]^+ $$

(L = NN'-dimethyl-NN'-bis(2-mercaptoethyl)ethylenediamine). X-ray diffraction results show the product to consist of two distorted octahedra sharing a common face through two bridging thiolate sulphur atoms and a symmetrically-bridging nitrosyl ligand. The NO stretching frequency is at about 1550 cm$^{-1}$. Scheidt et al. have reported the
preparation and molecular structure of nitrosyl (α,β,γ,δ-tetraphenyl-porphinato)(1-methylimidazole)iron(II). Equatorial bond distances in the FeN₆ coordination group average to 2.00 Å and FeN_NO is 1.73 Å. The Fe-N-0 bond angle is about 140°. Complexes formed by iron(II) and NO, and cysteine, cysteine ethylester, or β-mercaptoethanol, in neutral aqueous solution, have been investigated by e.s.r. methods.
Magnetochemistry

Only a brief account is given here. Further details are available elsewhere.

Magnetic effects are taken to be of two types: one, paramagnetism and its extensions - ferromagnetism and antiferromagnetism - arising from the spin and orbital angular momenta of unpaired electrons, and diamagnetism, arising from the motion of electrons as charged particles in filled shells. A paramagnetic substance is one which experiences a force towards the stronger part of a non-uniform magnetic field, and a diamagnetic substance being one which experiences a force in a direction opposite to that of the magnetic field gradient. Ferromagnetism and antiferromagnetism are the results of interactions between the magnetic dipoles on neighbouring atoms.

If a substance is placed in a field of H oersteds then B, the magnetic induction, or the number of lines of force per unit area within the substance, is given by:

\[ B = H + 4\pi I \]

where \( I \) is the intensity of magnetization corresponding to the induced magnetic moment per unit volume. Dividing through by \( H \),

\[ P = 1 + 4\pi k \]

where \( P \) and \( k \) are the permeability and susceptibility per unit volume respectively.

Susceptibility is usually more conveniently expressed per unit mass (\( \chi_g \), gram susceptibility) than per unit volume:
where $d$ is the density. The molar susceptibility is defined as:

$$X_M = X_g \times M$$

where $M$ is the molecular weight. However, paramagnetic substances will be composed of paramagnetic centres and diamagnetic groups for which a correction must be applied. The susceptibility per gram atom which has been corrected for the presence of diamagnetic components is defined as $X_A$, thus:

$$X_A = X_M - \Sigma X_L$$

where $X_L$ is the diamagnetism of the ions or atoms in the compound.

The diamagnetism of molecules can be measured directly or estimated with reasonable accuracy from Pascal's constants:\textsuperscript{187}

$$X_L = \Sigma n x_i^A + \lambda$$

where $x_i^A$ is the atomic susceptibility of an atom and $\lambda$ is a 'constitutive correction' which depends on the nature of the bonds involved in the molecule.

Curie found that for a number of paramagnetic substances, $X_A$ and $T$ were inversely proportional:

$$X_A = \frac{C}{T} \quad (C = \text{constant})$$

The theoretical derivation of the Curie law is based on several assumptions: paramagnetic substances contain atoms which behave as
small magnetic dipoles of magnetic moment $\mu$; the magnetic dipoles are independent of each other, i.e. the substance is said to be magnetically dilute; in the absence of a magnetic field there is no magnetization, but on application of the field the dipoles line up with the field and reinforce it; the thermal motion opposes this alignment; and the magnitude of the magnetic dipoles is independent of temperature.

It was deduced that the susceptibility $\chi_A$ is related to the magnetic moment $\mu$ by the expression

$$\chi_A = \frac{N\mu^2}{3kT}$$

where $k$ is Boltzmann's constant, and $N$ is the Avogadro constant.

The expression can be re-arranged to give the magnetic moment in Bohr magnetons (1 Bohr magneton, $\beta = \frac{\hbar}{4\pi mc}$):

$$\mu = \left(\frac{3k}{N\beta^2}\right)^\frac{1}{2} (\chi_A T)^\frac{1}{2} = 2.828\sqrt{\chi_A T}$$

Substitution of experimental values of $\chi_A$ and $T$ is said to give the effective magnetic moment $\mu_e$:

$$\mu_e = 2.828\sqrt{\chi_A T} \quad \text{B.M.}$$

In practice, deviations occur from ideal behaviour and many substances obey the Curie-Weiss law:

$$\chi_A = \frac{C}{T + \theta}$$

where $\theta$ is a measure of the departure from ideal behaviour, and $\mu_e$ will vary with temperature. The theoretical magnetic moments for 'free' ions
in the first transition series are given by

\[ \mu = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.} \]

where \( L \) is the resultant orbital angular momentum quantum number, and \( S \) is the resultant spin quantum number. In practice, for most compounds it is found that the experimental values of magnetic moment differ greatly from values predicted by this formula. However, it appears that the orbital momentum is often quenched \((L = 0)\) by the ligand field, and then the above equation reduces to the 'spin-only' formula:

\[ \mu_{s.o.} = \sqrt{4S(S+1)} \text{ B.M.} \]

If \( n \) is the number of unpaired electrons, \( S = \frac{n}{2} \), and \( \mu_{s.o.} \) is given by

\[ \mu_{s.o.} = \sqrt{n(n+2)} \text{ B.M.} \]

If \( n = 1, 2, 3, 4 \) and \( 5 \), \( \mu_{s.o.} = 1.73, 2.83, 3.88, 4.90 \) and \( 5.92 \) B.M. respectively. The effective magnetic moments \( (\mu_{\text{eff}}) \) of most magnetically dilute compounds of the first transition series are within 10% of the values predicted by the spin-only formula.

**Ferromagnetism and antiferromagnetism**

Substances are said to be 'magnetically dilute' if the magnetic ions are separated by diamagnetic atoms which are not capable of transmitting magnetic effects from one ion to another. In this class the magnetic properties of the whole system are the sum of the properties of the individual centres. This is no longer true when
there is interaction between the magnetic dipoles. Substances in which this occurs are said to exhibit magnetic exchange. Two possibilities are obvious: adjacent dipoles either tend to align themselves in opposite directions, or tend to align themselves in the same direction. The first of these possibilities leads to anti-ferromagnetism; the second to ferromagnetism. In the ferromagnetic state, the susceptibility increases rapidly at a critical temperature as the temperature is lowered; this temperature is known as the Curie temperature. For antiferromagnetic substances the magnetization begins to decrease to zero at a critical temperature called the Néel temperature. Normal paramagnetic behaviour occurs well above the Curie or Néel temperatures.

High spin and low spin complexes

Ions of the d⁴, d⁵, d⁶ and d⁷ configurations in the octahedral field may give high-spin or low spin complexes depending on the strength (10 Dq or Δ) of the ligand field. The five d-orbitals of 'free' transition metal ions are split into two or more sets of levels on the application of the field, when the ligand field reaches a critical value π, the high-spin and low-spin forms are equal in energy, and the low-spin form is more stable when 10 Dq > π. A chemical equilibrium of the two forms (spin-isomerism) might occur at a particular temperature, when the difference in energy between the high-spin and low-spin forms is comparable to the thermal energy kT (Fig. 1.1).
Since the position of equilibrium varies with temperature, this behaviour leads to a complicated variation of molar susceptibility and magnetic moment with temperature, and has been found in several classes of compound including some metal nitrosyls.
Mössbauer effect

The recoilless emission of γ-rays from nuclear excited states and subsequent resonant absorption by the same type of nuclei in their ground states was discovered by Rudolf Mössbauer in 1958. The Mössbauer effect is used to investigate comparatively weak interactions between the nucleus and surrounding electrons in the solid state. The elements for which the Mössbauer effect has been observed are shown in Table 1.2, and these include iron and gold. Mössbauer spectra of the iron complexes described in this work were obtained through the courtesy of Dr B W Fitzsimmons, Birkbeck College, London.

The suitability of an isotope for Mössbauer studies is influenced by the following:

(a) The life-time of the excited state should be in the range \(10^{-6}\) to \(10^{-12}\) seconds. The line widths become very narrow if the life-time is longer, making experimental conditions difficult, and shorter life-times lead to line widths which are too broad.

(b) The energies of the Mössbauer transition should be in the range 5 to 250 Kev.

(c) The abundance of the ground-state absorber nucleus should be as high as possible. In some cases, isotopic enrichment is desirable.

(d) The precursor which feeds the Mössbauer excited state should be long-lived. Some common half-lives are: \(^{57}\)Co, 267 days; \(^{119}\)Sn, 250 days; \(^{129}\)Te, 70 minutes.
**TABLE 1.2**

Elements showing the Mössbauer effect

```
<table>
<thead>
<tr>
<th>K</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
<th>Ge</th>
<th>kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc</td>
<td>Ru</td>
<td>Ag</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
</tr>
<tr>
<td>Cs</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
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<tr>
<td>Ra</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Pr</td>
<td>Nd</td>
<td>Sm</td>
<td>Eu</td>
<td>Gd</td>
</tr>
<tr>
<td></td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
</tr>
</tbody>
</table>
```
(e) Interfering radiation should be absent in order to maximise the resonance effect.

Chemical isomer shift

The source of γ-rays in $^{57}$Fe Mössbauer spectroscopy is $^{57}$Co incorporated in a solid such as stainless steel or palladium. The $^{57}$Co decays according to the scheme shown in Fig. 1.2. The $\gamma_3$ emission is that used in Mössbauer investigation. The absorber is a sample of the iron complex under investigation.

\[ \text{FIGURE 1.2 Decay scheme for } ^{57}\text{Co} \rightarrow ^{57}\text{Fe} \]
When the source is moved with respect to the absorber over a range of relative velocities, and the number of γ-rays transmitted through the absorber at each velocity is counted, absorption of γ-rays occurs when the Doppler effect has modified the energy of the emitted γ-rays so that it equals the difference in energy between the ground and first excited nuclear levels of the absorber nuclei. If the source and absorber nuclei are in a symmetrical environment a one-line spectrum results. If a single minimum is found at zero relative velocity as in Fig. 1.3 the nuclear energy levels of source and absorber (and, of course, the differences in energy between ground and excited states) are identical. This means that the source and absorber nuclei are in the identical surroundings. When the chemical environment of the source and the absorber differ, the Mössbauer resonance line recorded by such velocity scanning is displaced from zero velocity. This displacement is called the chemical isomer shift, $\delta$,.
The chemical isomer shift can be shown to be proportional to the s-electron density at the nucleus. This arises because the nucleus occupies a finite volume.

For example, if $a_{E_{\gamma}} > s_{E_{\gamma}}$, the nuclear energy levels are as shown in Fig. 1.4 in the source and the absorber, i.e. the source must be driven towards the absorber to increase the $\gamma$-ray energy so that absorption takes place at a positive relative velocity.

To a first approximation, the electron density about the nucleus is appreciably large only for s-electrons. During the course of a nuclear $\gamma$-transition it is usual for the effective nuclear size to
alter, thereby changing the nucleus-electron interaction energy by an amount proportional to the isomer shift. The energy change cannot be measured directly, but it is possible to compare isomer shifts referred to a suitable reference, in this thesis, natural iron foil.

It is found that for iron the greater the s-electron density at the nucleus the smaller is the isomer shift. Iron(III) has greater s-density at the nucleus than iron(II) because there is one less d-electron to penetrate the 3s\(^2\) shell and shield the s-electrons from the nucleus. As a result, high spin iron(III) complexes have smaller isomer shifts (~0.4 mm s\(^{-1}\)) than high-spin iron(II) complexes (~1.1 mm s\(^{-1}\)). In the case of low-spin complexes back donation of d-electrons to the ligands makes the s-density and the isomer shift depend little on oxidation state. The variation of isomer shift with the oxidation state is summarised in Fig. 1.5.

**Quadrupole splitting**

The quadrupole splitting arises from the interaction between the nuclear quadrupole moment (when the nuclear spin quantum number I > \(\frac{1}{2}\) the nucleus has a quadrupole moment) and the electric field gradient, generated by the electronic environment of the nucleus. The interaction of a non-cubic extranuclear electric field with the nuclear quadrupole moment results in a splitting of the excited nuclear energy level for which I = \(\frac{3}{2}\), and a characteristic two-line spectrum is obtained (Fig. 1.6). The separation of the peaks is the quadrupole splitting, \(\Delta E\) and the centroid of the two peaks relative to zero velocity is the chemical isomer shift, \(\delta\).
FIGURE 1.5 Approximate representation of the ranges of chemical isomer shifts found in iron complexes

- Fe(I) $S = \frac{3}{2}$
- Fe(I) $S = \frac{1}{2}$
- Fe(II) $S = 2$
- Fe(II) $S = 1$
- Fe(II) $S = 0$
- Fe(III) $S = \frac{5}{2}$
- Fe(III) $S = \frac{3}{2}$
- Fe(III) $S = \frac{1}{2}$
- Fe(IV) $S = 2$
- Fe(IV) $S = 1$
- Fe(VI) $S = 1$

Isomer shift (mm s$^{-1}$)

(relative to iron metal at RT)
FIGURE 1.6 Origin of quadrupole splitting, $\Delta E$

Diagram showing the splitting of levels for cubic and non-cubic cases, with quantum numbers $m_I$ for different states.

- Cubic: $I = \frac{3}{2}$
- Non-cubic: $m_I = \pm \frac{3}{2}$, $m_I = \pm \frac{1}{2}$

Graphs showing count rate and velocity variations with $\delta$ and $\Delta E$.
A simplified expression for the quadrupole splitting is
\[ \Delta E = \frac{1}{2} e^2 Q q \]
where \( Q \) is the nuclear quadrupole moment, \( e \) is the electronic charge and \( q \) is the electric field gradient at the nucleus. If the electric charge distribution around the nucleus is spherically symmetrical \( q = 0 \) and \( \Delta E = 0 \). Usually, \( q \) arises partly from the valence electrons \( (q_{\text{val}}) \) and the lattice charges \( (q_{\text{lat}}) \).

\[ q = q_{\text{val}} + q_{\text{lat}} \]

(a) **Low-spin iron(II) and high-spin iron(III) systems**

An octahedral, high-spin 3d\(^5\) (\(^6\)S) iron(III) ion with its half-filled shell is spherically symmetrical as is the low-spin t\(^5\)g\(^1\)A iron(II) configuration. The electron distributions are shown in Fig. 1.7(a) and (b). These configurations give no valence contribution to the electric field gradient,\(^{182}\) and thus:

\[ q = q_{\text{lat}} \]

The small value of quadrupole splitting which may be observed in high-spin 3d\(^5\) or low-spin 3d\(^6\) complexes is due to the small electric field gradient which arises from \( q_{\text{lat}} \), i.e. from small departures from a cubic environment. Values of \( \Delta E \) range from zero for a cubic environment to \(-1.5 \text{ mm s}^{-1}\) for a non-cubic one, the usual range being from 0.3 to 0.7 mm s\(^{-1}\).

(b) **Low-spin iron(III) and high-spin iron(II) systems**

The half-filled shell of a high-spin 3d\(^6\) (\(^5\)D) iron(II) ion has
one electron outside the spherically symmetrical shell shown in Fig. 1.7(c). Large \( \Delta E \) values ranging from 1.5 to 3.6 mm s\(^{-1}\) are obtained as this valence electron gives rise to a large electric field gradient (\( q_{\text{val}} \)). Similarly, a single electron hole can be visualised in low-spin d\(^5\) iron(III) ions (i.e. an electron is missing from a complete \( t_{2g} \) level) as shown in Fig. 1.7(d); \( q_{\text{val}} \) is large, and a large \( \Delta E \) is also expected for low-spin iron(III) complexes.

---

**FIGURE 1.7** Energies of d-orbitals, and the ground state occupancy schemes for octahedral coordination
Although low-spin iron(II) and low-spin iron(III) complexes give similar isomer shifts the latter are expected to give greater quadrupole splittings.
CHAPTER II

EXPERIMENTAL TECHNIQUES
1. Apparatus and preparative methods

Due to the high sensitivity of cobalt(II), iron(II) and manganese(II) compounds towards oxygen in solution and as solids, it was necessary to deoxygenate all solvents before use and carry out preparations and manipulations under nitrogen or vacuum using the apparatus (Fig. 2.1) described previously.\textsuperscript{183,184}

Nitrogen was passed through a glass tube about 50 cm in length and 5 cm in diameter, containing a slightly crushed BTS catalyst (supplied by B.A.S.F. Co Ltd) to remove any traces of oxygen from the nitrogen.

The catalyst was composed essentially of finely-divided copper deposited on an inert carrier and activated by various reagents. It was supplied in the oxidised form. After crushing it was placed in the tube, heated to 140-160\textdegree{}C with a heating tape and reduced by purging with hydrogen. The water formed drained from the column into a container as the reduction proceeded. If necessary the nitrogen, which entered the main apparatus at C, could be dried by passage through a column containing anhydrous magnesium perchlorate. The apparatus was evacuated and filled with nitrogen three times before any operations were carried out. The apparatus shown in Fig. 2.2 was used to filter off air-sensitive complexes. The suspension was allowed to pass down the hollow plunger of a greased glass syringe, B. The solid was collected on the filter pad, A, washed and dried, and the dry solid was broken up with the paddle which was rotated laterally and vertically using the syringe. The powdered solid was shaken into the pig, G, and packed into tubes which were then sealed off under vacuum.
FIGURE 2.1 Apparatus for preparing air-sensitive complexes
FIGURE 2.2 Filtration apparatus
2. Analytical methods

Nickel

The complex (0.2–0.4 g) was destroyed by evaporation to dryness with concentrated sulphuric acid (10 cm³), concentrated nitric acid (5 cm³) and concentrated perchloric acid (2 cm³). The residue was dissolved in water (200 cm³) and dilute hydrochloric acid (10 cm³) added. A slight excess of a solution of dimethylglyoxime reagent was added to the solution at 80°C and immediately dilute ammonia was added dropwise until it was in slight excess. The resulting suspension was heated at 100°C for thirty minutes, tested for complete precipitation, allowed to cool and then filtered through a sintered glass crucible. The precipitate was washed with water and dried to constant weight at 120°C.

Cobalt

The complex (about 0.2 g) was destroyed as in the nickel determination. The residue was dissolved in water and AR ammonium thiocyanate (1.0 g for each 0.1 g of cobalt) added, the solution was then heated to boiling, and pyridine (2 cm³) was added. In this way the cobalt was precipitated as the complex Co(C₅H₅N)₄(SCN)₂. This was filtered off on a sintered glass crucible, washed with solutions specified by Vogel and dried in a vacuum desiccator for 30–50 minutes to constant weight.

Manganese

The complex (about 0.2 g) was destroyed as in the nickel determination and the residue dissolved in water. The pH was
adjusted to 4 to 5 with dilute ammonia solution using methyl red as indicator. Rochelle salt (0.3 g), to prevent oxidation of manganese to the dioxide, and a two- to three-fold excess of 0.01 M EDTA, were added. The solution was adjusted to pH 10 with dilute ammonia solution, and a few drops of Eriochrome Black T indicator were added. The excess EDTA was then back titrated against standard 0.01 M zinc sulphate solution until the colour changed from blue to red.

Iron

Most iron analyses were carried out by direct ignition of the complex to the oxide Fe₂O₃ in silica crucibles at 800°C. The method was accurate to within 1-2%. However, in complexes containing an alkali metal the iron was estimated gravimetrically as the oxinate. The compound (0.1 g) was destroyed as for nickel and the residue was redissolved in water. A small excess of oxine was added and the pH of the solution was adjusted to 3.5-4.0 with ammonium acetate, the oxinate being precipitated as a black solid. The reaction mixture was digested for 20 minutes to coagulate the precipitate, cooled, and the oxinate was filtered off in sintered glass crucibles. The precipitate was washed with very dilute acetic acid and water, and the crucibles dried to constant weight at 110°C.

Gold

Gold analyses were carried out by direct ignition of the complex to the metal in silica crucibles at 700°C. The method described by Vogel was found not to be accurate because of the small amounts of gold complexes available for analysis.
Microanalyses

The carbon, hydrogen and nitrogen analyses were carried out by the University of Surrey Microanalytical Laboratory.

3. Magnetic measurements

The Gouy method was used to measure magnetic susceptibilities, usually over the temperature range 90°-300° K, of the compounds prepared in this work. The air-sensitive solids were sealed under vacuum in flat-bottomed pyrex glass tubes (Fig. 2.4). The construction of the magnetic balance has been described previously; the sample tube was suspended as shown in Fig. 2.3.

The tubes were calibrated for their diamagnetism over the temperature range above. The molar susceptibility $\chi_M$ was calculated from the formula:

$$\chi_M = \frac{2MgLw}{WH^2}$$

where

- $M$ = the molecular weight of the compound;
- $g$ = the acceleration due to gravity;
- $L$ = the length of the sample;
- $w$ = the change in weight on application of the field (allowing for the diamagnetism of the glass tube);
- $W$ = weight of sample;
- $H$ = the magnetic field experienced by the sample.
FIGURE 2.3 Variable temperature Gouy balance with cryostat
The atomic susceptibility $X_A$ of the metal ion was obtained by correcting $X_M$ for the diamagnetism of the ligands and ions present in the compound. The corrections for the diamagnetism of the ligands were obtained from Pascal's constants. The effective magnetic moment $\mu_e$ was then calculated from the formula:

$$\mu_e = 2.828 \sqrt{X_A \cdot T} \text{ B.M.}$$

where T is the absolute temperature.

4. **Infra-red measurements**

Infra-red spectra of nujol or hexachlorobutadiene mulls were recorded on a Perkin-Elmer 577 spectrophotometer, over the range 4000-200 cm\(^{-1}\). Air-sensitive complexes were mulled inside a plastic bag flushed out with nitrogen. The samples were placed between potassium bromide, sodium chloride, or polythene discs.

5. **Ultra-violet and visible spectra**

A Unicam SP 700C or a Beckman Acta M IV spectrophotometer was used to record the reflectance spectra of the compounds over the range 45,000-5,000 cm\(^{-1}\). Air-sensitive complexes were sealed under vacuum in a 2 mm silica cell using apparatus shown in Fig. 2.4. Lithium fluoride was used as a reference.
FIGURE 2.4 Apparatus for breaking sample tube under nitrogen
6. Molecular weight measurements

The instrument used was a Perkin-Elmer molecular weight apparatus Model 115. This instrument is made up of the following component units: an oven assembly, a measuring chamber, a sample chamber, and an electrical system (Fig. 2.5). The determination of molecular weight could be based upon the vapour pressure differences between two solutions, or between a solution and a pure solvent. The vapour pressure differences are not measured directly, but lead to a greater rate of condensation of vapour from the saturated thermostated measuring chamber on to a solution drop, because of its lower vapour pressure, than on to an adjacent solvent drop. The solution and solvent are placed on separate thermistors, and the difference in resistance between the thermistors, ΔR, is proportional to the molar concentration of the solution. If a substance of known molecular weight is used, and the results are plotted in the form of ΔR against C', where C' is the molar concentration and ΔR is the resistance difference, the intercept will yield the calibration constant K for the particular solvent. To determine an unknown molecular weight, it is then necessary to plot ΔR/C versus C, and to divide the intercept into the calibration constant:

\[ M = \frac{K}{\lim (\Delta R/C)} \]

\[ C \to 0 \]

where

M is the molecular weight of the solute;
K is a constant involving temperature;
ΔR is the resistance difference at each molar concentration.
FIGURE 2.5  Perkin-Elmer Model 115 molecular weight apparatus
7. Mössbauer measurements

All Mössbauer spectra were recorded at Birkbeck College, University of London, and the chemical isomer shifts are given with respect to iron foil.

8. Solvents and reagents

All solvents and reagents were technical grade, and were used without further purification except for deoxygenation.

The gold compounds were obtained from Johnson Matthey Chemicals Ltd., and all other metal salts were obtained from B.D.H. Ltd. Nitric oxide cylinders were obtained from B.D.H. Ltd. The nitric oxide was purified by passage through a dricold/methylated spirit trap, and the uptake of gas was measured with a gas burette. 188

All ligands except o-aminobenzenethiol, salicylaldehyde, \( \alpha \)-thiopropionic acid and glutathione were purchased from B.D.H. Ltd. o-aminobenzenethiol was obtained from Koch-Light Laboratories Ltd., salicylaldehyde from Fisons Scientific Apparatus Ltd., \( \alpha \)-thiopropionic acid from Aldrich Chemical Co. Ltd. and glutathione from Sigma. N N'-ethylene bis(monothioacetylacetonimine) was prepared by J. P. Rogers. 189
CHAPTER III

PREPARATION OF METAL COMPLEXES
Preparation of metal complexes

In the preparation of cobalt(II), iron(II) and manganese(II) complexes all manipulations were carried out under nitrogen or in vacuum. Because each complex, generally, was isolated in several sealed tubes, and some complexes remained in the filter unit and elsewhere, the yields were not measured accurately but were usually of the order of 60%. All complexes of thiomalate and cysteinate are soluble in water and insoluble in methanol and ethanol except Fe(cys).1.5H₂O and A[Mn(tm)]·nH₂O (A = Li, Na or K) which are insoluble in water.

1. Bis(thiomalato)nickel(II) dihydrate

A solution of nickel(II) acetate tetrahydrate in ethanol (2.48 g, 30 cm³) was slowly added to a solution of thiomalic acid in ethanol (3.00 g, 10 cm³). The dark green precipitate separated quickly, leaving the solution clear. The compound was filtered off, washed with hot ethanol and dried over calcium chloride.

   Found: C, 24.8; H, 3.5; Ni, 15.2%
   NiC₈H₁₀O₅S₂·2H₂O requires: C, 24.4; H, 3.5; Ni, 15.0%

2. Lithium thiomalatonickelate(II) trihydrate

Nickel(II) acetate tetrahydrate (2.49 g, 0.01 mole) was dissolved in ethanol (40 cm³). This solution was added slowly to thiomalic acid (1.50 g, 0.01 mole) in water (30 cm³) containing lithium hydroxide (1.26 g, 0.03 mole). A pink colour developed initially which changed to green when precipitation occurred. The solid was then isolated by filtration, washed with hot ethanol and dried over calcium chloride.
3. Sodium thiomalatonicelate(II) trihydrate

To a solution of thiomalic acid (1.50 g, 0.01 mole) in water (20 cm³) containing sodium hydroxide (1.20 g, 0.03 mole) a solution of nickel(II) acetate tetrahydrate (2.49 g, 0.01 mole) in ethanol (50 cm³) was added slowly. A deep pink colour appeared which changed to green when precipitation occurred. The green precipitate was filtered off, washed with hot ethanol and dried over calcium chloride.

Found: C, 17.3; H, 2.5; Ni, 20.4%
Na[NiC₄H₃O₄S]•3H₂O requires: C, 17.0; H, 3.1; Ni, 20.8%

4. Potassium thiomalatonicelate(II) dihydrate

A solution of nickel(II) acetate tetrahydrate (2.49 g, 0.01 mole) in ethanol (50 cm³) was treated with a solution of thiomalic acid (1.50 g, 0.01 mole) in water (20 cm³) containing potassium hydroxide (1.68 g, 0.03 mole) with stirring. A deep pink colour appeared which changed to green when precipitation occurred. The green precipitate was filtered off, washed with hot ethanol, and dried over calcium chloride.

Found: C, 17.7; H, 2.3; Ni, 20.5%
K[NiC₄H₃O₄S]•2H₂O requires: C, 17.1; H, 2.5; Ni, 21.0%
5. **Thiomalatocobalt(II) trihydrate**

Cobalt(II) acetate tetrahydrate (2.82 g, 0.0132 mole) was dissolved in absolute ethanol (40 cm³) with stirring, and the solution was filtered. To the filtrate was added thiomalic acid (1.50 g, 0.01 mole) in absolute ethanol (20 cm³); a red precipitate was formed. It was filtered off, washed twice with absolute ethanol, and dried under vacuum for 8 hours.

Found: C, 18.5; H, 3.3; Co, 22.5%

Co[C₄H₄O₄S]·2H₂O requires: C, 18.4; H, 3.8; Co, 22.7%

6. **Lithium thiomalatocobaltate(II) dihydrate**

A solution of thiomalic acid (2.25 g, 0.015 mole) in water (30 cm³) containing lithium hydroxide (2.60 g, 0.06 mole) was heated on a steam bath for 20 minutes and allowed to cool. To it was added hydrochloric acid (5.5 cm³, 3 M); this solution was then added to cobalt(II) chloride hexahydrate (3.57 g, 0.015 mole) in water (20 cm³). A green colour developed immediately. Addition of absolute ethanol (60 cm³) precipitated a green solid which was filtered off, washed with absolute ethanol and dried under vacuum for 8 hours.

Found: C, 19.4; H, 3.0; Co, 23.4%

Li[CoC₄H₄O₄S]·2H₂O requires: C, 19.3; H, 2.8; Co, 23.7%

7. **Sodium thiomalatocobaltate(II) trihydrate**

To a solution of thiomalic acid (2.25 g, 0.015 mole) in water (20 cm³) containing sodium hydroxide (2.16 g, 0.054 mole) was added hydrochloric acid (3 cm³, 3 M); the mixture was heated on a steam bath for 20 minutes, and allowed to cool. This solution was then added to
cobalt(II) chloride hexahydrate (3.57 g, 0.015 mole) in water (20 cm³).
A green colour developed immediately. To this solution absolute ethanol
(60 cm³) was added; the green precipitate formed was filtered off, washed
twice with absolute ethanol and dried under vacuum for 6 hours.

Found:  C, 17.3;  H, 2.0;  Co, 21.0%
Na[CoC₆H₃O₄S]·3H₂O requires:  C, 17.0;  H, 3.1;  Co, 20.8%

8. Potassium thiomalatocobaltate(II) trihydrate

A solution of potassium hydroxide (3.00 g, 0.054 mole) in water
(10 cm³) was added to a solution of thiomalic acid (2.25 g, 0.015 mole)
in water (15 cm³); then hydrochloric acid (3 cm³, 3 M) was added to the
mixture. This was heated on a steam bath for 20 minutes, and allowed
to cool. This solution was then added to cobalt(II) chloride hexahydrate
(3.57 g, 0.015 mole) in water (20 cm³). A green colour developed
immediately, and a dark green solid separated on addition of absolute
ethanol (80 cm³). The precipitate was filtered off, washed twice with
absolute ethanol and dried under vacuum for 6 hours.

Found:  C, 15.6;  H, 2.8;  Co, 19.7%
K[CoC₆H₃O₄S]·3H₂O requires:  C, 16.0;  H, 3.0;  Co, 19.7%

9. Bis(acetato)iron(II) dihydrate

This compound was used in the preparation of certain iron(II)
complexes and its preparation is given here.

An excess of iron powder was heated in aqueous 1:1 acetic acid
until the evolution of hydrogen ceased. The solution was cooled, the excess of iron filtered off and the filtrate evaporated to dryness. Iron(II) acetate was obtained as a pale green powder which was shaken with acetone so as to remove it from the walls of the flask, filtered off, dried by continuous pumping and sealed in glass tubes under vacuum. The dry compound was white. The whole operation was carried out under nitrogen since the product is extremely air sensitive, rapidly turning brown.

Found: Fe, 26.7%
Fe(CH$_3$COO)$_2$•2H$_2$O requires: Fe, 26.6%

10. **Thiomalatoiron(II) trihydrate**

Iron(II) chloride tetrahydrate (3.96 g, 0.02 mole) in methanol (50 cm$^3$) was added to an aqueous solution of thiomalic acid (3.00 g, 0.02 mole) in water (30 cm$^3$) containing sodium hydroxide (1.60 g, 0.04 mole). The fine yellow precipitate which formed was very difficult to filter off. After washing with methanol and acetone it was dried in vacuo for 6 hours. The complex was highly air sensitive and lost weight during weighing for microanalysis.

Found: C, 17.0; H, 3.0; Fe, 21.9%
FeC$_6$H$_4$O$_4$S•3H$_2$O requires: C, 18.6; H, 3.8; Fe, 21.7%

11. **Lithium thiomalatoferate(II) trihydrate**

Addition of iron(II) chloride tetrahydrate (3.96 g, 0.02 mole) in methanol (40 cm$^3$) to a solution of thiomalic acid (3.00 g, 0.02 mole) in
water (40 cm³) containing lithium hydroxide (2.52 g, 0.06 mole) with stirring produced a green solid. The suspension was heated at 60°C for 20 minutes and allowed to cool. The precipitate was filtered off, washed with methanol and once with acetone, and dried under vacuum for 5 hours.

| Found:   | C, 17.1; H, 3.1; Fe, 21.6% |
| Li[FeC₄H₃O₄S]·3H₂O requires: | C, 18.2; H, 3.4; Fe, 21.2% |

12. **Sodium thiomalatoferrate(II) monohydrate**

Thiomalic acid (2.25 g, 0.015 mole) was dissolved in water (10 cm³) and to it was added a solution of sodium hydroxide (1.80 g, 0.045 mole) in water (10 cm³). The mixture was heated on a steam bath for 15 minutes and allowed to cool. To this solution, with stirring, a solution of iron(II) chloride tetrahydrate (2.98 g, 0.015 mole) in methanol (50 cm³) was added. A yellow solid appeared and the suspension was heated at 50°C for 15 minutes and allowed to cool, filtered, and the solid washed once with methanol, twice with acetone, and dried under vacuum.

| Found:   | C, 20.1; H, 2.5; Fe, 22.8% |
| Na[FeC₄H₃O₄S]·H₂O requires: | C, 19.8; H, 2.1; Fe, 22.9% |

13. **Potassium thiomalatoferrate(II) trihydrate**

An aqueous solution of thiomalic acid (3.00 g, 0.02 mole) in water (20 cm³) containing potassium hydroxide (3.36 g, 0.06 mole) was heated on a steam bath for 15 minutes and allowed to cool. When aqueous iron(II) chloride tetrahydrate (3.96 g, 0.02 mole) in 80% methanol (60 cm³)
was added with stirring, a yellowish-green solid appeared. The suspension was heated at 50°C for 15 minutes, and allowed to cool. The solid was filtered off, washed once with methanol, then twice with acetone, and dried under vacuum.

Found:  C, 15.6; H, 1.8; Fe, 18.8%
K[FeC₄H₇O₄S]·3H₂O requires:  C, 16.2; H, 3.0; Fe, 18.9%

14. Pyridinethiomalatoiron(II)

Thiomalic acid (1.50 g, 0.01 mole) in absolute ethanol (20 cm³) was added slowly to a solution of iron(II) acetate dihydrate preparation 9 (1.68 g, 0.008 mole) in the same solvent containing pyridine (20 cm³). A yellow precipitate was formed. The precipitate was filtered off, washed with absolute ethanol containing 10% pyridine and dried under vacuum. The dry compound was extremely air-sensitive, turning dark green immediately on exposure to the atmosphere.

Found:  C, 38.0; H, 3.2; N, 4.9; Fe, 20.0%
FeC₅H₉O₄NS requires:  C, 38.2; H, 3.2; N, 4.9; Fe, 19.8%

15. Thiomalatomanganese(II) dihydrate

Manganese(II) acetate tetrahydrate (3.675 g, 0.015 mole) in water (20 cm³) was added to a solution of thiomalic acid (2.25 g, 0.015 mole) in the same solvent (15 cm³). Addition of absolute ethanol (80 cm³) produced a light blue precipitate. This was filtered off, washed with absolute ethanol and then with acetone, and dried under vacuum for 6 hours.
16. Lithium thiomalatomanganate(II) trihydrate

Thiomalic acid (2.25 g, 0.015 mole) in water (40 cm³) containing lithium hydroxide (1.89 g, 0.045 mole) was added to a solution of manganese(II) acetate tetrahydrate (3.67 g, 0.015 mole) in the same solvent (20 cm³) with stirring. The suspension was heated at 60°C for 20 minutes and allowed to cool. The precipitate was filtered off, washed first with water, then acetone and vacuum-dried for 5 hours. The dry solid was pale blue.

Found: C, 18.9; H, 2.8; Mn, 21.2%
Li[MnC₆H₄O₄S]·2H₂O requires: C, 18.4; H, 2.7; Mn, 21.1%

17. Sodium thiomalatomanganate(II) dihydrate

Manganese(II) acetate tetrahydrate (2.45 g, 0.01 mole) in water (20 cm³) was added with stirring to a solution of thiomalic acid (1.50 g, 0.01 mole) in water (30 cm³) containing sodium hydroxide (1.20 g, 0.03 mole). A blue precipitate separated quickly. The suspension was heated at 60°C for 20 minutes and allowed to cool. The precipitate was filtered off, washed first with water, then acetone and vacuum-dried for five hours. The dry solid was pale blue.

Found: C, 18.9; H, 2.8; Mn, 21.2%
Na[MnC₆H₄O₄S]·2H₂O requires: C, 18.4; H, 2.7; Mn, 21.1%
18. Potassium thiomalatomanganate(II) dihydrate

Addition of a solution of manganese(II) acetate tetrahydrate (2.45 g, 0.01 mole) in water (20 cm³) to a solution of thiomalic acid (1.50 g, 0.01 mole) in water (30 cm³) containing potassium hydroxide (1.68 g, 0.03 mole) gave a blue precipitate. The suspension was heated at 50°C for 15 minutes and allowed to cool. The solid was filtered off, washed with water, and then with acetone, and dried under vacuum for 6 hours. The dry solid was light blue.

Found: C, 17.4; H, 2.3; Mn, 19.8%
K[MnC₄H₃O₄S]·2H₂O requires: C, 17.3; H, 2.5; Mn, 19.8%

19. Bis(4-aminobenzenethiolato)iron(II)

This complex and the next were prepared as it was intended to react them with salicylaldehyde to form tridentate Schiff bases by a template synthesis. However, these reactions did not give pure products, and the iron(II) complex of one tridentate Schiff's base was obtained from the pre-formed ligand in solution (preparation 21).

Iron(II) sulphate heptahydrate was used for the preparation of bis(4-aminobenzenethiolato)iron(II), and it was necessary to remove the sulphuric acid formed in the reaction in order to obtain a pure product; however, to avoid the formation of hydrated oxides of iron from any slight excess of sodium hydroxide, a 20% deficiency of sodium hydroxide was used and the remaining sulphuric acid neutralized with excess sodium acetate.

A solution of 4-aminobenzenethiol (4.21 g, 0.0393 mole) sodium
hydroxide (1.28 g, 0.032 mole), and sodium acetate (1.63 g, 0.012 mole) in 30% ethanol (150 cm³) was slowly added to a solution of iron(II) sulphate heptahydrate (5.56 g, 0.02 mole) in 30% ethanol (150 cm³) at 35°C. After shaking for forty minutes at 35°C, the pale yellow precipitate obtained was filtered off, washed with distilled water, absolute ethanol and acetone, and dried under vacuum for 7 hours.

Found: C, 48.0; H, 4.4; N, 9.1; Fe, 18.2%

FeC₁₂H₁₂N₂S₂ requires: C, 47.4; H, 4.0; N, 9.2; Fe, 18.3%

20. Bis(2-aminoethanethiolato)iron(II) dihydrate

2-Aminoethanethiol hydrochloride (4.54 g, 0.04 mole) and sodium hydroxide (3.20 g, 0.08 mole) were dissolved in distilled water (200 cm³). This solution was added slowly with shaking to iron(II) sulphate heptahydrate (5.56 g, 0.02 mole) in distilled water (100 cm³). A deep red colour developed initially but quickly faded upon addition of all the ligand solution. Green crystals formed when the solution was allowed to stand overnight at room temperature. The solid was then isolated by filtration, washed twice with 50 cm³ portions of absolute ethanol and dried under vacuum for 6 hours.

Found: C, 19.0; H, 6.1; N, 11.2; Fe, 22.4%

FeC₄H₁₂N₂S₂·2H₂O requires: C, 19.6; H, 6.5; N, 11.4; Fe, 22.9%

21. 2-Salicylideneaminobenzenethiolatoiron(II)

Salicylaldehyde (2.44 g, 0.02 mole) was added to o-aminobenzene-thiol (2.50 g, 0.02 mole) in ethanol (150 cm³). The alcoholic solution of the resulting Schiff base was added to a solution of iron(II) acetate
dihydrate (2.00 g) in water (15 cm³) with shaking. A dark colour developed, and the black precipitate which formed was filtered off, washed with ethanol and dried under vacuum for 6 hours.

Found: C, 54.2; H, 3.0; N, 5.1%
FeC₁₃H₉NOS requires: C, 55.1; H, 3.2; N, 4.9%

22. NN'-Ethylenebis(monothioacetylacetoniminato)iron(II)

A solution of NN'-ethylenebis(monothioacetylacetonimine) (1.28 g, 0.005 mole) in methanol (60 cm³) containing iron(II) acetate dihydrate (1.00 g, 0.005 mole) was heated at 50-60°C for 30 minutes with stirring. A black colour developed and a black precipitate soon separated. It was filtered off, washed with methanol and dried under vacuum for 5 hours. The dry compound was fairly stable, turning brown very slowly when exposed to air.

Found: C, 44.9; N, 5.7; N, 8.6; Fe, 19.2%
FeC₁₂H₁₈N₂S₂ requires: C, 46.4; H, 5.8; N, 9.0; Fe, 18.0%

23. NN'-Ethylenebis(monothioacetylacetoniminato)cobalt(II)

A solution of cobalt(II) acetate tetrahydrate (1.25 g, 0.005 mole) in methanol (60 cm³) containing NN'-ethylenebis(monothioacetylacetonimine) (1.28 g, 0.005 mole) was heated for 30 minutes with stirring at 50-60°C. The solution turned to deep red and a light red precipitate was formed. This was filtered off, washed with methanol and dried under vacuum for 6 hrs.

Found: C, 45.7; H, 5.9; N, 8.9%
CoC₁₂H₁₈N₂S₂ requires: C, 46.0; H, 5.7; N, 8.9%
24. **Bis(tryptophanato)iron(II) monohydrate**

Sodium tryptophanate was prepared by heating a suspension of DL-tryptophan (4.80 g, 0.0235 mole) with sodium hydroxide (0.86 g, 0.0215 mole) in water (200 cm³) for 40 minutes on a steam bath. The solution was cooled and then excess tryptophan was filtered off, and the filtrate was slowly added to a solution of iron(II) sulphate heptahydrate (3.00 g, 0.0108 mole) in water (60 cm³) with shaking. A grey-blue precipitate separated, which was filtered off. For no obvious reason, a brown colour appeared on the surface of the solid. This was removed by washing with a large quantity of water, which became coloured. The white solid was washed with acetone and dried under vacuum for 3 hours. The compound was not very air-sensitive and there was little change in colour on extended exposure to air.

Found:  C, 54.0;  H, 4.6;  N, 11.3;  Fe, 11.9%

FeC₂H₂O₂N₄•H₂O requires:  C, 54.9;  H, 4.9;  N, 11.6;  Fe, 11.6%

25. **Cysteinatoiron(II) hydrate**

Iron(II) sulphate heptahydrate (2.78 g, 0.01 mole) was dissolved in water (10 cm³). To this was added L-cysteine (2.42 g, 0.02 mole) in water (10 cm³). On addition of sodium hydroxide (6 M) dropwise with shaking, a brown colour developed initially and a brown precipitate appeared when the ratio of metal ion and sodium hydroxide was 1:2. The precipitate was filtered off, washed with water and absolute ethanol and dried over P₂O₅ in vacuum. The dry compound was extremely air-sensitive, turning grey immediately on exposure to the atmosphere.

Found:  C, 19.5;  H, 4.2;  N, 6.6;  Fe, 26.1%

FeC₃H₅O₂NS•1.5H₂O requires:  C, 17.8;  H, 4.0;  N, 6.9;  Fe, 27.7%
The analytical data are not very satisfactory, and attempts to prepare Li₂[Fe(cys)₂], K₂[Fe(cys)₂] and Li₂[Mn(cys)₂] gave products with poor analyses.

26. Potassium bis(α-thiopropionato)cobaltate(II) monohydrate

Cobalt(II) chloride hexahydrate (3.57 g, 0.015 mole) in absolute ethanol (30 cm³) was added to a solution of α-thiopropionic acid (3.18 g, 0.03 mole) in 60% ethanol (50 cm³). Addition of potassium hydroxide (3.36 g, 0.06 mole) in 60% ethanol (50 cm³) with shaking produced a green precipitate which was filtered off, washed with absolute ethanol and dried in vacuum for 6 hours.

Found: C, 19.5; H, 2.7; Co, 16.3%

K₂[CoC₆H₅O₄S₂]·H₂O requires: C, 19.8; H, 2.7; Co, 16.2%

27. Lithium bis(cysteinato)cobaltate(III) trihydrate

L-Cysteine (2.42 g, 0.02 mole) was dissolved in water (30 cm³), and to it was added an aqueous solution of lithium hydroxide (10 cm³, 4.4 M) followed by a solution of hydrochloric acid (1 cm³, 3 M); the mixture was then heated on a steam bath for 30 minutes and allowed to cool. To it was added a solution of cobalt(II) chloride hexahydrate (2.38 g, 0.01 mole) in water (20 cm³). This gave a blue solution which quickly turned to brownish-blue. The mixture was heated at 80-90°C for 30 minutes and allowed to cool. To this solution absolute ethanol was added with shaking, and this immediately produced a brownish-blue precipitate which was filtered off, washed with absolute ethanol and dried under vacuum. Although the preparation was carried out under nitrogen a cobalt(III)
complex was isolated.

*Found: C, 20.3; H, 4.7; N, 7.6; Co, 16.2%*

Li\([\text{CoC}_6\text{H}_{10}\text{O}_2\text{N}_2\text{S}_2]\)•2\(\text{H}_2\text{O}\) requires: C, 20.1; H, 4.5; N, 7.8; Co, 16.5%

28. **Bis(cysteinato)cobalt(II) dihydrate**

To a solution of L-cysteine (2.42 g, 0.02 mole) in water (20 cm³) containing lithium hydroxide (1.30 g, 0.03 mole) was added a solution of hydrochloric acid (4 cm³, 3 M). To this was added cobalt(II) acetate tetrahydrate (2.49 g, 0.01 mole) in 70% ethanol (60 cm³). On mixing the two solutions a green solution was formed which, on cooling, gave a greenish-red precipitate. This was filtered off, washed with absolute ethanol and dried under vacuum for 7 hours. The dry, greenish-red solid turned red after several days in sealed tubes, but analyses and physical measurements were carried out before the colour change had become apparent.

*Found: C, 21.0; H, 4.8; N, 8.4; Co, 17.7%*

\(\text{CoC}_6\text{H}_{12}\text{O}_2\text{N}_2\text{S}_2\)•2\(\text{H}_2\text{O}\) requires: C, 21.5; H, 4.8; N, 8.3; Co, 17.6%

29. **Lithium bis(cysteinato)cobaltate(II) trihydrate**

Hydrochloric acid (1 cm³, 3 M) was added to a solution of L-cysteine (2.42 g, 0.02 mole) in water (30 cm³) containing lithium hydroxide monohydrate (1.90 g, 0.045 mole). The mixture was heated on a steam bath for 20 minutes and allowed to cool. To the solution was added cobalt(II) chloride hexahydrate (2.38 g, 0.01 mole) in water (20 cm³). The blue colour which first appeared changed rapidly to green. The mixture was heated for 30 minutes at 70-80°C and allowed to cool. The brown solid
which separated on addition of absolute ethanol (100 cm$^3$) was filtered off, washed with absolute ethanol and dried under vacuum for 7 hours.

Found: C, 19.9; H, 4.5; N, 7.2; Co, 15.9%

Li$_2$[CoC$_6$H$_{10}$O$_4$N$_2$S$_2$]$\cdot$3H$_2$O requires: C, 19.7; H, 4.4; N, 7.7; Co, 16.2%

30. Sodium bis(cysteinato)cobaltate(II) trihydrate

L-cysteine (2.42 g, 0.02 mole) was dissolved in water (20 cm$^3$) containing sodium hydroxide (1.80 g, 0.045 mole), and to the solution was added hydrochloric acid (1 cm$^3$, 3 M). The solution was heated on a steam bath for 20 minutes and allowed to cool. Then cobalt(II) chloride hexahydrate (2.38 g, 0.01 mole) in water (10 cm$^3$) was added, and on mixing the two solutions a blue colour was formed which rapidly changed to green. The mixture was heated for 30 minutes at 80°C, and allowed to cool. On addition of absolute ethanol (80 cm$^3$) a green precipitate was separated. This was filtered off, washed with absolute ethanol and dried under vacuum for 7 hours.

Found: C, 18.4; H, 3.9; N, 6.8; Co, 14.8%

Na$_2$[CoC$_6$H$_{10}$O$_4$N$_2$S$_2$]$\cdot$3H$_2$O requires: C, 18.1; H, 4.0; N, 7.0; Co, 14.8%

31. Potassium bis(cysteinato)cobaltate(II) trihydrate

To a solution of L-cysteine (2.42 g, 0.02 mole) in water (20 cm$^3$) was added potassium hydroxide (2.52 g, 0.045 mole) in water (10 cm$^3$) and then hydrochloric acid (1 cm$^3$, 3 M). The mixture was heated on a steam bath for 20 minutes and allowed to cool. To this solution was added cobalt(II)-chloride hexahydrate (2.38 g, 0.01 mole) in water (20 cm$^3$). A blue colour developed initially but quickly changed to green. The mixture was heated
for 30 minutes at 80-90°C and allowed to cool. To this solution absolute ethanol (80 cm³) was added, and the dark green precipitate was filtered off, washed with absolute ethanol and dried under vacuum for 7 hours.

\[ \text{Found: C, 16.8; H, 3.2; N, 6.5; Co, 13.9\%} \]

\[ \text{K}_2[\text{CoC}_6\text{H}_{10}\text{O}_4\text{N}_2\text{S}_2]\cdot3\text{H}_2\text{O requires: C, 16.8; H, 3.7; N, 6.5; Co, 13.7\%} \]

32. **Bis(nitrosyl)thiomalatocobalt**

A solution of thiomalic acid (2.25 g, 0.015 mole) in water (30 cm³) was added to a solution of cobalt(II) chloridehexahydrate (3.57 g, 0.015 mole) in water (40 cm³) in a flat-bottomed flask containing a magnetic stirrer. A dark red solution was formed. The nitrogen atmosphere was replaced by nitric oxide at room temperature, and nitric oxide was slowly absorbed, approximately two moles of which was absorbed per mole of cobalt. The dark red solution changed first to brown and finally a green precipitate was formed. The precipitate was filtered off, washed with water and 50% methanol and dried under vacuum for 8 hours. The solid is stable in air.

\[ \text{Found: C, 19.0; H, 2.3; N, 10.5; Co, 21.8\%} \]

\[ \text{CoC}_8\text{H}_4\text{O}_4\text{S(NO)}_2\text{ requires: C, 18.0; H, 1.5; N, 10.5; Co, 22.1\%} \]

33. **Bis(nitrosyl)thiopropionatoiron methanol**

Thiopropionic acid (2.12 g, 0.02 mole) in methanol (20 cm³) was added with constant stirring to a solution of iron(II) chloride tetrahydrate (3.98 g, 0.02 mole) in water (100 cm³). The nitrogen atmosphere was replaced by nitric oxide. The reaction was carried out at room temperature, the solution gradually darkened and when the nitric oxide up-take was complete (2 moles of nitric
oxide per mole of iron), the dark red precipitate was filtered off, washed with water and then with methanol and dried under vacuum.

Found: C, 19.0; H, 2.7; N, 11.3; Fe, 22.3%

FeC₃H₄O₂S(NO)₂ requires: C, 19.0; H, 3.1; N, 11.1; Fe, 22.2%

34. Bis(nitrosyl)thiomalatoiron

A solution of thiomalic acid (3.00 g, 0.02 mole) in water (20 cm³) was added to a solution of iron(II) chloride tetrahydrate (3.98 g, 0.02 mole) in water (60 cm³), in a flat-bottomed flask containing a magnetic stirrer. The absorption of nitric oxide was measured at room temperature; two moles of nitric oxide was absorbed per mole of iron. When the absorption was complete a dark red precipitate separated. This was filtered off, washed with water and dried under vacuum. The dry solid was reddish-brown.

Found: C, 18.1; H, 1.7; N, 10.4; Fe, 21.3%

FeC₄H₄O₄S(NO)₂ requires: C, 18.2; H, 1.5; N, 10.6; Fe, 21.2%

35. Sodium heminitrosylthiomalato ferrate methanol monohydrate

Sodium thiomalato ferrate(II) monohydrate was prepared by the method described in preparation 12. The compound (0.015 mole) was suspended in 80% methanol (120 cm³) in a flat-bottomed flask containing a magnetic stirrer. The nitrogen atmosphere was replaced by nitric oxide at room temperature. The sodium thiomalato ferrate(II) monohydrate gradually darkened, and when the nitric oxide up-take was complete, approximately half a mole of nitric oxide had been absorbed per mole of iron(II), and the brown compound which separated was filtered off, washed with water and methanol and dried under vacuum for 6 hours.


36. **Potassium nitrosylthiomalatoferate dihydrate**

Potassium thiomalatoiron(II) hydrate was obtained as in preparation 13. The yellowish-green precipitate was filtered off and re-suspended in 80% methanol in a flat-bottomed flask containing a magnetic stirrer. The nitrogen atmosphere was replaced by nitric oxide. The reaction was carried out at room temperature. The potassium thiomalatoiron(II) hydrate gradually darkened and when the nitric oxide up-take was complete one mole of nitric oxide had been absorbed per mole of iron(II) and the brown precipitate which separated was filtered off, washed twice with 30 cm$^3$ portions of distilled water, followed by two 50 cm$^3$ portions of methanol, and dried under vacuum.

\[
\text{Found: C, 14.9; H, 1.6; N, 4.3; Fe, 18.5}\%
\]

\[
\text{KFeC_6H_8O_8S(NO)_2H_2O requires: C, 15.5; H, 2.2; N, 4.5; Fe, 18.2}\%
\]

37. **Nitrosylbis(tryptophanato)iron dihydrate**

Bis(tryptophanato)iron(II) monohydrate was prepared from iron(II) chloride tetrahydrate, DL-tryptophan and lithium hydroxide monohydrate by the method described in preparation 24. The precipitate formed was filtered off and washed thoroughly with water to remove any lithium chloride, and then transferred, under nitrogen, into a reaction vessel containing water. The flask was evacuated, filled with nitric oxide, and the mixture was
stirred under nitric oxide until no further gas was absorbed. The reaction was completed within 5 hours, the initial white precipitate becoming dark brown as the reaction proceeded. Because the reaction was slow, the up-take of nitric oxide could not be measured accurately. The brown compound was filtered off, washed with methanol and dried under vacuum with constant pumping for 6 hours. The dry compound appeared stable on exposure to the air.

Found: C, 49.1; H, 4.7; N, 12.8; Fe, 11.0%

FeC₂₂H₂₂O₄N₄(NO)·2H₂O requires: C, 49.8; H, 4.9; N, 13.2; Fe, 10.6%

38. Bis(glycinato)nitrosyliron

A saturated solution of lithium glycinate was prepared by heating a suspension of glycine (4.50 g) containing lithium hydroxide monohydrate (2.0 g) in methanol (200 cm³) for 30 minutes on a steam bath. After cooling, the solution was filtered off and the filtrate was added to a solution of iron(II) chloride tetrahydrate (5.00 g) in methanol (60 cm³). A creamy precipitate came down which was filtered off and washed with methanol. The precipitate was then transferred, under nitrogen, into a reaction vessel containing methanol. The flask was evacuated, filled with nitric oxide and the mixture was stirred under nitric oxide until no further gas was absorbed. The reaction was complete in 30 minutes, approximately one mole of nitric oxide being absorbed per mole of iron. The white precipitate became dark green as the reaction proceeded. The solid was filtered off, washed with methanol and dried. The dry compound appeared stable on exposure to the atmosphere.

Found: C, 20.7; H, 3.7; N, 16.4; Fe, 24.4%

FeC₆H₉O₄N₂(NO) requires: C, 20.5; H, 3.4; N, 17.9; Fe, 23.9%
39. **NN'-Ethylenebis(monothioacetylacetatoiminato)nitrosyliron**

NN'-ethylenbis(monothioacetylacetatoiminato)iron(II) was prepared as in preparation 22. The compound (0.005 mole), suspended in methanol, was left under nitric oxide at room temperature with constant stirring. Approximately one mole of nitric oxide was absorbed per mole of iron. The deep dark green precipitate was filtered off, washed with methanol and dried under vacuum for 5 hours. The dry compound appeared stable on exposure to the atmosphere.

Found: C, 40.9; H, 5.3; N, 12.4%

FeC₁₂H₁₈N₂S₂(NO) requires: C, 42.3; H, 5.3; N, 12.3%

40. **Thiomalatogold(I)**

Potassium aurocyanide (1.44 g, 0.005 mole) was dissolved in water (20 cm³) and to it hydrochloric acid (3 cm³, 3 M) was added. The mixture was heated on a steam bath. The gold(I) cyanide which precipitated was filtered off, washed with water and suspended in water (30 cm³), and a solution of thiomalic acid (1.20 g, 0.008 mole) in water (20 cm³) was added. The mixture was heated on a steam bath until practically all the solid material had dissolved, and allowed to cool. After filtration, the filtrate was evaporated to dryness on a steam bath, and the residue tritured with hot ethyl acetate on the steam bath. The white solid was then filtered off, washed three times with hot ethyl acetate to remove unreacted thiomalic acid, and dried in a vacuum oven at 100°C for 4 hours.

Found: C, 13.9; H, 1.4; Au, 56.3%

AuC₄H₅O₄S requires: C, 13.9; H, 1.4; Au, 56.9%
41. **Sodium thiomalatoaurate(I)**

Sodium hydroxide (0.08 g, 0.002 mole) in water (5 cm$^3$) was added to a solution of thiomalatogold(I) prepared as above (0.346 g, 0.001 mole) in water (10 cm$^3$). The mixture was heated on a steam bath for a short time and allowed to cool. When absolute ethanol was added dropwise a very pale yellow precipitate appeared. This solid was filtered off, washed with absolute ethanol and dried in a vacuum oven at 90°C for 2 hours. This compound was then crystallised from water. Long shining needles separated from the aqueous solution, but these became a yellow-white powder during drying. The compound was further recrystallised by adding alcohol to a solution in a minimum of hot water.

**Found:** C, 11.5; H, 0.4%

Na$_2$[AuC$_4$H$_3$O$_4$S] requires: C, 12.3; H, 0.7%

42. **Cysteinatogold(I)**

Hydrogen tetrachloroaurate(III) (0.2 g) in water (10 cm$^3$) was added to a solution of sodium bisulphate (0.053 g) in water (10 cm$^3$) containing potassium hydroxide (0.124 g) and potassium cyanide (0.065 g). This mixture, which contained [KAu(CN)$_2$], was added to a solution of L-cysteine (0.062 g) in water (5 cm$^3$) which had been acidified with hydrochloric acid. The solution was heated on a steam bath for one hour and allowed to cool. The yellow powder cysteinatoaurate(I) was precipitated from the solution. It was filtered off, washed with water and dried under vacuum.

**Found:** C, 11.1; H, 1.9; N, 4.2; Au, 61.4;

AuC$_3$H$_6$O$_2$NS requires: C, 11.3; H, 1.9; N, 4.4; Au, 62.1;
43. **Cysteinatothiomalatodigold(I)**

A solution of thiomalatogold(I), prepared as in 40 above (0.07 g) in water (5 cm³) was added to a solution of L-cysteine (0.025 g) in water (4 cm³). The fine white precipitate which formed was very difficult to filter off. It was washed with water and dried under vacuum.

Found: C, 12.5; H, 1.9; N, 2.5; Au, 59.2%

\[
\text{Au}_2\text{C}_9\text{H}_{11}\text{O}_2\text{NS requires: C, 12.7; H, 1.6; N, 2.1; Au, 59.4%}
\]

44. **Bis(glutathionato)thiomalatotrigold(I)**

Thiomalatogold(I) (0.07 g) in water (5 cm³) was added to a solution of glutathione (0.062 g) in water (6 cm³). The white precipitate which formed on the addition of methanol was filtered off, washed with 70% methanol and dried under vacuum.

Found: C, 21.0; H, 2.7; N, 6.2; Au, 43.6%

\[
\text{Au}_3\text{C}_{24}\text{H}_{37}\text{O}_{16}\text{N}_6\text{S}_2 \text{ requires: C, 21.2; H, 2.6; N, 6.4; Au, 43.1%}
\]

45. **(NN-Diethyldithiocarbamato)gold(I)**

This pale yellow compound was prepared by adding a solution of thiomalatogold(I) (0.07 g) in water (4 cm³) to a solution of sodium diethyldithiocarbamate (0.05 g) in water (5 cm³). A yellow solid separated immediately. This was filtered off, washed with water and dried under vacuum. The dry compound was pale yellow.

Found: C, 18.3; H, 2.8; N, 4.1; Au, 57.2%

\[
\text{AuC}_5\text{H}_{10}\text{NS}_2 \text{ requires: C, 17.4; H, 2.9; N, 4.0; Au, 57.1%}
\]
46. Calcium thiomalatoaurate(I) dihydrate

Sodium thiomalatoaurate(I) (0.078 g) was prepared as in 41. The precipitate was filtered off and washed with ethanol. It was dissolved in water (4 cm³). To the solution sodium hydroxide (1.5 ml, 0.1 N) was added, followed by thiomalic acid (0.022 g) in water (3 cm³). To this a solution (0.038 g) of calcium hydroxide in water (4 cm³) was added. A pale yellow precipitate was formed which was filtered off, washed with water and dried under vacuum.

Found: C, 10.8; H, 1.4%
CaAuC₄H₃O₄S·2H₂O requires: C, 11.4; H, 1.6%

47. Barium thiomalatoaurate(I) monohydrate

Sodium thiomalatoaurate(I) (0.078 g) was dissolved in water (4 cm³). To the solution thiomalic acid (0.022 g) in water (3 cm³) was added, followed by sodium hydroxide (0.1 M) to adjust the pH to 7.0. A solution of barium chloride dihydrate in water (0.085 g, 5 cm³) was then added. The pH fell to 6.92, and a pale yellow precipitate was formed. It was filtered off, washed with water and dried under vacuum.

Found: C, 9.6; H, 0.9%
BaAuC₄H₃O₄S·H₂O requires: C, 9.6; H, 1.0%
CHAPTER IV

RESULTS AND DISCUSSION
Metal complexes of thiomalic acid

Several different types of complex of thiomalic acid (H₂CCH₂CHSHCO₂H₄tmH₃) with nickel(II), cobalt(II), iron(II) and manganese(II) have been prepared. The complexes are Fe(tmH)py, Ni(tmH)₂·₂H₂O, M(tmH)·nH₂O and A[M'(tm)]·nH₂O, where M = Co, Fe or Mn and M' = Ni, Co, Fe or Mn, A = Li, Na or K and n varies. These complexes are new, previous work on thiomalic acid complexes of the first transition series being restricted to measurements in solution, except for a very recent report of the preparation and infrared spectra of the complexes M(tmH), where M = Zn, Cd, Hg and Pb. The infrared spectra, electronic spectra, and magnetic properties of the complexes are presented in this chapter, and tentative structures assigned.

Infrared spectra

The most diagnostic region in the infrared spectra of metal carboxylates lies between 1300 cm⁻¹ and 1700 cm⁻¹ where the OCO stretching frequencies occur. As the strength of the M-O bond increases (structure B) the carboxylate group becomes more asymmetric, resulting in an increase in Δ (where Δ is the separation between the symmetric and asymmetric carboxylate stretching frequencies) compared to the free ion (structure A). Structure C shows symmetrical bidentate coordination of the carboxyl group for which Δ is smaller and of the same order as in the free ion. Structure D shows a bridging bidentate carboxyl group, and as the strength of the bond to the second metal atom increases, the symmetry of the carboxyl group increases and Δ decreases.
The infrared spectra of the complexes A[Ni(tm)]\text{\textperiodcentered}n\text{H}_2\text{O}, A[Co(tm)]\text{\textperiodcentered}n\text{H}_2\text{O}, A[Fe(tm)]\text{\textperiodcentered}n\text{H}_2\text{O} and A[Mn(tm)]\text{\textperiodcentered}n\text{H}_2\text{O} (Table 4.1) show a value for $\Delta$ within the range found for bidentate carboxylate groups (140-180 cm$^{-1}$). The band assigned to $\nu$(S-H) in the free acid at 2560 cm$^{-1}$ is absent from the spectra of the complexes as expected. The C-S stretching frequency generally appears as a band of weak or moderate intensity in the range 720-570 cm$^{-1}$ and it becomes even weaker on complex formation. The band due to $\nu$(C-S) in thiomalic acid at 678 cm$^{-1}$ (Table 4.1) has moved to lower frequency in the metal complexes, indicating the formation of metal-sulphur bonds in the complexes. All hydrated complexes have very broad bands at about 3400 cm$^{-1}$ which are assigned to the $\nu$(O-H) vibration of hydrogen-bonded water. The $\delta$(OH$_2$) absorptions expected at about 1630 cm$^{-1}$ are obscured by the bands of the ionised carboxylic groups.

In the infrared spectra of M(tmH)\text{\textperiodcentered}n\text{H}_2\text{O} (M = Co, Fe and Mn) (Table 4.1), the asymmetric carboxylate stretching absorption is split, indicating the presence of unionised and ionised carboxylic acid groups in the compounds. The most probable explanation is the presence of
TABLE 4.1

Selected infrared bands of the thiomalic acid complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption maxima (cm(^{-1}))</th>
<th>(v_{as}(\text{OCO}))</th>
<th>(v_{s}(\text{OCO}))</th>
<th>(\Delta)</th>
<th>(v(\text{S-H}))</th>
<th>(v(\text{C-S}))</th>
<th>(v(\text{OH}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{tmH}_3)</td>
<td></td>
<td>1690 vs, vb</td>
<td>1425 vs, b</td>
<td>265</td>
<td>2560 w</td>
<td>678 m</td>
<td>3000 vb</td>
</tr>
<tr>
<td>(\text{Ni(tmH}_2\cdot2\text{H}_2\text{O})</td>
<td>1715 s</td>
<td>1400 s, b</td>
<td>315</td>
<td>-</td>
<td>645 m</td>
<td>3350 vb</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1660 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1550 s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Li[Ni(tm)]\cdot3H}_2\text{O})</td>
<td>1550 b</td>
<td>1410 s, b</td>
<td>140</td>
<td>-</td>
<td>650 sh</td>
<td>3400 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{Na[Ni(tm)]\cdot3H}_2\text{O})</td>
<td>1550 b</td>
<td>1410 s, b</td>
<td>140</td>
<td>-</td>
<td>648 w</td>
<td>3400 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{K[Ni(tm)]\cdot2H}_2\text{O})</td>
<td>1560 b</td>
<td>1410 s, b</td>
<td>150</td>
<td>-</td>
<td>650 w</td>
<td>3390 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{Co(tm)}\cdot3\text{H}_2\text{O})</td>
<td>1720 sh</td>
<td>1390 s, b</td>
<td>230</td>
<td>-</td>
<td>642 s</td>
<td>3400 vb</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1550 b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Li[Co(tm)]\cdot2H}_2\text{O})</td>
<td>1540 b</td>
<td>1400 s, b</td>
<td>140</td>
<td>-</td>
<td>645 sh</td>
<td>3380 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{Na[Co(tm)]\cdot3H}_2\text{O})</td>
<td>1550 b</td>
<td>1370 s, b</td>
<td>180</td>
<td>-</td>
<td>642 sh</td>
<td>3370 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{K[Co(tm)]\cdot3H}_2\text{O})</td>
<td>1550 b</td>
<td>1400 s, b</td>
<td>150</td>
<td>-</td>
<td>660 sh</td>
<td>3360 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{Fe(tm)}\cdot3\text{H}_2\text{O})</td>
<td>1720 sh</td>
<td>1400 s, b</td>
<td>320</td>
<td>-</td>
<td>635 m</td>
<td>3400 vb</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1570 b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Li[Fe(tm)]\cdot3H}_2\text{O})</td>
<td>1565 b</td>
<td>1400 s, b</td>
<td>165</td>
<td>-</td>
<td>635 sh</td>
<td>3350 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{Na[Fe(tm)]\cdot2H}_2\text{O})</td>
<td>1580 b</td>
<td>1400 s, b</td>
<td>180</td>
<td>-</td>
<td>637 m</td>
<td>3380 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{K[Fe(tm)]\cdot3H}_2\text{O})</td>
<td>1570 b</td>
<td>1390 s, b</td>
<td>180</td>
<td>-</td>
<td>636 m</td>
<td>3350 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{Mn(tm)}\cdot2\text{H}_2\text{O})</td>
<td>1710 sh</td>
<td>1400 s, b</td>
<td>310</td>
<td>-</td>
<td>662 s</td>
<td>3300 vb</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1550 b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Li[Mn(tm)]\cdot3H}_2\text{O})</td>
<td>1550 b</td>
<td>1410 s, b</td>
<td>140</td>
<td>-</td>
<td>635 m</td>
<td>3380 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{Na[Mn(tm)]\cdot2H}_2\text{O})</td>
<td>1550 b</td>
<td>1410 s, b</td>
<td>140</td>
<td>-</td>
<td>640 sh</td>
<td>3300 vb</td>
<td></td>
</tr>
<tr>
<td>(\text{K[Mn(tm)]\cdot2H}_2\text{O})</td>
<td>1550 b</td>
<td>1410 s, b</td>
<td>140</td>
<td>-</td>
<td>635 sh</td>
<td>3320 vb</td>
<td></td>
</tr>
</tbody>
</table>
uncoordinated carboxylic acid groups for which $\Delta = 320 \text{ cm}^{-1}$ and coordinated carboxylate groups for which $\Delta = 160 \text{ cm}^{-1}$. Unionised, uncoordinated carboxylic acid groups, and coordinated carboxylic acid groups are present in $\text{Ni(tmH}_2\text{)}_2 \cdot 2\text{H}_2\text{O}$ as the infrared spectra show bands at $1715$ and $1660 \text{ cm}^{-1}$. Similar splittings of the asymmetric carboxylate stretches have led other workers to deduce the presence of uncoordinated or coordinated carboxylic acid groups or uncoordinated carboxylate groups. 196

Nickel-thiomalate complexes

Reflectance spectra

The UV spectra (Table 4.2, Figs. 4.1 and 4.2) of the nickel thiomalate complexes are dominated by an intense broad band between $38000$ and $30000 \text{ cm}^{-1}$, presumably due to charge transfer transitions. The bands at ca $9100$ and $14800 \text{ cm}^{-1}$, and the shoulders at ca $24400 \text{ cm}^{-1}$ in the visible spectra of $\text{Ni(tmH}_2\text{)}_2 \cdot 2\text{H}_2\text{O}$, $\text{Li[Ni(tm)] \cdot 3H}_2\text{O}$, $\text{Na[Ni(tm)] \cdot 3H}_2\text{O}$ and $\text{K[Ni(tm)] \cdot 2H}_2\text{O}$ can be assigned to the $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}$ (F) and $^3A_{2g} \rightarrow ^3T_{1g}$ (P) transitions respectively. 197 An octahedral environment is suggested by the electronic spectra (Table 4.2), which yield values for $D_q$ and $B$ which are reasonable for octahedral complexes in which a mixture of O- and S-donors is present. The calculated values for $v_3$ are in good agreement with the experimental values, suggesting that there is little distortion from octahedral symmetry. The values of $D_q$, $B$ and $v_3$ for Ni$^{2+}$ were calculated by the methods of Lever. 198 (The equations are given in Table 4.2, footnote (b).) Corresponding calculations for tetrahedral ions led to unrealistic values of $B$. 
### Table 4.2
Electronic spectra\(^a\) of nickel thiomalato complexes and calculated\(^b\) values for Dq, B and \(\nu_3\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(3^3A_{2g} \rightarrow 3^3T_{2g}(\nu_1))</th>
<th>(3^3A_{2g} \rightarrow 3^3T_{1g}(F)(\nu_2))</th>
<th>(3^3A_{2g} \rightarrow 3^3T_{1g}(P)(\nu_3))</th>
<th>Charge</th>
<th>Dq</th>
<th>B</th>
<th>(\nu_3) (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(tmH(_2))(_2)\cdot2H(_2)O</td>
<td>9100 b</td>
<td>14800 b</td>
<td>24000 sh</td>
<td>30000 vb</td>
<td>910</td>
<td>766</td>
<td>24100</td>
</tr>
<tr>
<td>Li[Ni(tm)](_3)H(_2)O</td>
<td>9200 b</td>
<td>14800 b</td>
<td>24400 sh</td>
<td>32700 s</td>
<td>920</td>
<td>773</td>
<td>24800</td>
</tr>
<tr>
<td>Na[Ni(tm)](_3)H(_2)O</td>
<td>9100 b</td>
<td>14800 b</td>
<td>24400 sh</td>
<td>32300 s</td>
<td>910</td>
<td>793</td>
<td>24900</td>
</tr>
<tr>
<td>K[Ni(tm)](_3)H(_2)O</td>
<td>9100 b</td>
<td>14900 b</td>
<td>24300 sh</td>
<td>33300 s</td>
<td>910</td>
<td>793</td>
<td>24900</td>
</tr>
</tbody>
</table>

(a) All frequencies in cm\(^{-1}\).

(b) The equations used in the calculations are:
\[
\begin{align*}
\nu_1 & = 10 \text{ Dq} \\
\nu_3 + \nu_2 - 3\nu_1 & = 15 \text{ B} \\
\nu_3 & = 7.5 \text{ B} + 15 \text{ Dq} + \frac{1}{2}(225 \text{ B}^2 + 100 \text{ Dq}^2 - 180 \text{ Dq} \text{ B})^{\frac{1}{2}}
\end{align*}
\]
Figure 4.1

- Ni(tmH₂)₂·2H₂O
- Li[Ni(tm)]·3H₂O

O.D.

wavelength (nm)
FIGURE 4.2

- K[Ni(tm)]•2H₂O
- Na[Ni(tm)]•3H₂O

wavelength (nm)
Magnetism

Expected magnetic moments at room temperature for nickel(II) complexes are: octahedral, ~3.2 B.M., independent of temperature; tetrahedral, ~3.5 B.M., temperature-dependent; and planar, ~0.0 B.M.

The magnetic properties (Tables 4.3 and 4.4 and Figs. 4.3 and 4.4) over the temperature range 80° to 300° K confirm the octahedral nature of the nickel-thiomalates, suggested by the reflectance data. The complex Ni(tmH₂)₂·2H₂O has a temperature-independent magnetic moment of 3.26 B.M. which is indicative of octahedral nickel(II) with a ³A₂ ground state;¹⁹⁹ and the other salts A[Ni(tm)]·nH₂O have similar magnetic moments at room temperature. However, these magnetic moments increased slightly as the temperature was lowered, showing that weak ferromagnetic interactions are present. It is believed that the salts have polymeric (I) structures as have other nickel compounds²⁰⁰ in which weak ferromagnetism is found, whereas Ni(tmH₂)₂·2H₂O is a monomer (II).

![Chemical structure of Ni(tmH₂)₂·2H₂O](attachment:image.png)
TABLE 4.3
Lithium thiomalatonickeal(II) trihydrate

<table>
<thead>
<tr>
<th>(10^6 x_A)</th>
<th>(10^{-2} x_A^{-1})</th>
<th>(T(°K))</th>
<th>(μ_e(\text{B.M.}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4260</td>
<td>2.347</td>
<td>295.0</td>
<td>3.16</td>
</tr>
<tr>
<td>4740</td>
<td>2.108</td>
<td>263.0</td>
<td>3.15</td>
</tr>
<tr>
<td>5390</td>
<td>1.856</td>
<td>230.5</td>
<td>3.15</td>
</tr>
<tr>
<td>6410</td>
<td>1.561</td>
<td>198.0</td>
<td>3.18</td>
</tr>
<tr>
<td>7730</td>
<td>1.294</td>
<td>166.0</td>
<td>3.20</td>
</tr>
<tr>
<td>9620</td>
<td>1.039</td>
<td>135.0</td>
<td>3.22</td>
</tr>
<tr>
<td>12830</td>
<td>0.779</td>
<td>103.5</td>
<td>3.25</td>
</tr>
<tr>
<td>15190</td>
<td>0.658</td>
<td>90.0</td>
<td>3.30</td>
</tr>
</tbody>
</table>

\(θ = -2°\)

Diamagnetic correction = \(-105 \times 10^{-6}\) c.g.s.u.

Bis(thiomalato)nickel(II) dihydrate

<table>
<thead>
<tr>
<th>(10^6 x_A)</th>
<th>(10^{-2} x_A^{-1})</th>
<th>(T(°K))</th>
<th>(μ_e(\text{B.M.}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4510</td>
<td>2.217</td>
<td>295.0</td>
<td>3.26</td>
</tr>
<tr>
<td>5060</td>
<td>1.976</td>
<td>262.5</td>
<td>3.25</td>
</tr>
<tr>
<td>5770</td>
<td>1.733</td>
<td>230.0</td>
<td>3.25</td>
</tr>
<tr>
<td>6690</td>
<td>1.494</td>
<td>198.5</td>
<td>3.25</td>
</tr>
<tr>
<td>8010</td>
<td>1.248</td>
<td>166.5</td>
<td>3.26</td>
</tr>
<tr>
<td>9830</td>
<td>1.017</td>
<td>135.0</td>
<td>3.25</td>
</tr>
<tr>
<td>12780</td>
<td>0.782</td>
<td>104.0</td>
<td>3.26</td>
</tr>
<tr>
<td>14790</td>
<td>0.676</td>
<td>90.0</td>
<td>3.26</td>
</tr>
</tbody>
</table>

\(θ = 0°\)

Diamagnetic corrections = \(-163 \times 10^{-6}\) c.g.s.u.
TABLE 4.4
Sodium thiomalatonickelate(II) trihydrate

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>T(°K)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4140</td>
<td>2.415</td>
<td>295.0</td>
<td>3.12</td>
</tr>
<tr>
<td>4600</td>
<td>2.173</td>
<td>265.0</td>
<td>3.12</td>
</tr>
<tr>
<td>5300</td>
<td>1.886</td>
<td>230.5</td>
<td>3.12</td>
</tr>
<tr>
<td>6160</td>
<td>1.663</td>
<td>198.5</td>
<td>3.12</td>
</tr>
<tr>
<td>7400</td>
<td>1.351</td>
<td>166.0</td>
<td>3.13</td>
</tr>
<tr>
<td>9230</td>
<td>1.083</td>
<td>135.0</td>
<td>3.15</td>
</tr>
<tr>
<td>12280</td>
<td>0.811</td>
<td>103.5</td>
<td>3.18</td>
</tr>
<tr>
<td>14400</td>
<td>0.694</td>
<td>90.0</td>
<td>3.21</td>
</tr>
</tbody>
</table>

$\theta = -3^\circ$  Diamagnetic correction = $-105 \times 10^{-6}$  c.g.s.u.

Potassium thiomalatonickelate(II) dihydrate

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>T(°K)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4430</td>
<td>2.259</td>
<td>295.0</td>
<td>3.23</td>
</tr>
<tr>
<td>5030</td>
<td>1.986</td>
<td>262.5</td>
<td>3.24</td>
</tr>
<tr>
<td>5860</td>
<td>1.701</td>
<td>229.0</td>
<td>3.27</td>
</tr>
<tr>
<td>6750</td>
<td>1.481</td>
<td>198.5</td>
<td>3.27</td>
</tr>
<tr>
<td>8090</td>
<td>1.167</td>
<td>166.0</td>
<td>3.27</td>
</tr>
<tr>
<td>10170</td>
<td>0.984</td>
<td>135.0</td>
<td>3.31</td>
</tr>
<tr>
<td>13370</td>
<td>0.748</td>
<td>103.5</td>
<td>3.32</td>
</tr>
<tr>
<td>15780</td>
<td>0.634</td>
<td>89.5</td>
<td>3.36</td>
</tr>
</tbody>
</table>

$\theta = -6^\circ$

Diamagnetic correction = $-92 \times 10^{-6}$  c.g.s.u.
Throughout the thesis, the behavior of $\chi_A$ and $\mu_e$ is depicted for Ni(tmH$_2$)$_2$·2H$_2$O and Li[Ni(tm)]·3H$_2$O.
FIGURE 4.4

K[Ni(tm)] • 2H₂O

Na[Ni(tm)] • 3H₂O
Cobalt(II)-thiomalate complexes

Magnetism

The ranges of magnetic moments for magnetically-dilute cobalt(II) complexes of different stereochemistry at room temperature are shown in Table 4.5:

TABLE 4.5

<table>
<thead>
<tr>
<th>Cobalt(II)</th>
<th>C.N.6</th>
<th>C.N.5</th>
<th>C.N.4</th>
<th>C.N.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-spin</td>
<td>4.8-5.2</td>
<td>4.2-4.6</td>
<td>4.2-4.8</td>
<td></td>
</tr>
<tr>
<td>Low-spin</td>
<td>1.8-2.0</td>
<td>1.7-2.1</td>
<td>2.1-2.9</td>
<td></td>
</tr>
</tbody>
</table>

Most octahedral cobalt(II) compounds can be classified as either high-spin or low-spin with magnetic moments in the ranges 4.8-5.2 B.M. and 1.8-2.0 B.M. respectively.202 In order of decreasing energy, an octahedral crystal field splits the \(^4\text{F}\) ground term into the levels \(^4\text{A}_2\), \(^4\text{T}_2\) and \(^4\text{T}_{1g}\). The \(^4\text{T}_{1g}\) ground term will possess some orbital angular momentum and the magnetic moment varies between the spin-only value 172,204

\[
\mu_{\text{s.o.}} = \left[4S(S + 1)\right]^\frac{1}{2} = 3.87 \text{ B.M. , } S = \frac{3}{2}
\]

and

\[
\mu = \left[4S(S + 1) + L(L + 1)\right]^\frac{1}{2} = 5.2 \text{ B.M. , } L = 3
\]

and is temperature-dependent.

Tables 4.6, 4.7 and Figs. 4.5 and 4.6 show the magnetic behaviour
of the cobalt(II) thiomalate complexes. The magnitude and variation of magnetic moment with temperature for $\text{Co}^{\text{II}}(\text{tmH}) \cdot 3\text{H}_2\text{O}$ (5.03(295° K) and 4.56(90° K)) suggest an octahedral monomeric structure (III) because this type of magnetic behaviour is found for magnetically-dilute, high-spin octahedral cobalt(II) complexes. The magnetic moment decreases at lower temperatures because of the smaller first order orbital contribution.

![Structure](image)

(III)

The magnetic moments for the complexes $\text{A}[\text{Co}(\text{tm})] \cdot n\text{H}_2\text{O}$, where $\text{A} = \text{Li, Na, K}$ and $n = 2, 3$ and 3 respectively, are somewhat lower at room temperature than for many magnetically-normal, octahedral complexes and they decrease markedly at lower temperatures, in one case to well below the spin-only value, and the Curie-Weiss law is obeyed with large $\theta$ values. However, hexacoordinated cobalt(II) complexes of low symmetry, e.g. with substituted phenols, reportedly exhibit low magnetic moments relative to those of regular octahedral complexes. It is therefore assumed that the complexes have polymeric octahedral structures (I), and the temperature variation of magnetic moment arises from a combination of antiferromagnetic interaction and varying orbital contribution. Tetrahedral structures are unlikely because temperature-independent moments would be expected.
<table>
<thead>
<tr>
<th>$10^6\chi_A$</th>
<th>$10^{-2}\chi_A^{-1}$</th>
<th>$T(\text{K})$</th>
<th>$\mu_e(\text{B.M.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10750</td>
<td>0.930</td>
<td>295.0</td>
<td>5.03</td>
</tr>
<tr>
<td>11920</td>
<td>0.839</td>
<td>263.0</td>
<td>5.00</td>
</tr>
<tr>
<td>13530</td>
<td>0.739</td>
<td>230.5</td>
<td>4.99</td>
</tr>
<tr>
<td>15410</td>
<td>0.649</td>
<td>198.5</td>
<td>4.94</td>
</tr>
<tr>
<td>17900</td>
<td>0.559</td>
<td>166.5</td>
<td>4.88</td>
</tr>
<tr>
<td>21150</td>
<td>0.473</td>
<td>135.0</td>
<td>4.77</td>
</tr>
<tr>
<td>25950</td>
<td>0.385</td>
<td>103.5</td>
<td>4.64</td>
</tr>
<tr>
<td>29010</td>
<td>0.345</td>
<td>90.0</td>
<td>4.56</td>
</tr>
</tbody>
</table>

$\theta = +6^\circ$

Diamagnetic correction = $-108 \times 10^{-6}$ c.g.s.u.

<table>
<thead>
<tr>
<th>$10^6\chi_A$</th>
<th>$10^{-2}\chi_A^{-1}$</th>
<th>$T(\text{K})$</th>
<th>$\mu_e(\text{B.M.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8900</td>
<td>1.124</td>
<td>295.0</td>
<td>4.58</td>
</tr>
<tr>
<td>9810</td>
<td>1.019</td>
<td>263.0</td>
<td>4.54</td>
</tr>
<tr>
<td>11000</td>
<td>0.909</td>
<td>230.0</td>
<td>4.49</td>
</tr>
<tr>
<td>12500</td>
<td>0.800</td>
<td>198.5</td>
<td>4.45</td>
</tr>
<tr>
<td>14430</td>
<td>0.693</td>
<td>166.5</td>
<td>4.38</td>
</tr>
<tr>
<td>17100</td>
<td>0.585</td>
<td>135.0</td>
<td>4.29</td>
</tr>
<tr>
<td>20940</td>
<td>0.478</td>
<td>103.5</td>
<td>4.16</td>
</tr>
<tr>
<td>22690</td>
<td>0.441</td>
<td>91.5</td>
<td>4.07</td>
</tr>
</tbody>
</table>

$\theta = +10^\circ$

Diamagnetic correction = $105 \times 10^{-6}$ c.g.s.u.
TABLE 4.7
Sodium thiomalatocobaltate(II) trihydrate

<table>
<thead>
<tr>
<th>$10^6 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>T(°k)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7230</td>
<td>1.383</td>
<td>295.5</td>
<td>4.13</td>
</tr>
<tr>
<td>7860</td>
<td>1.272</td>
<td>262.5</td>
<td>4.06</td>
</tr>
<tr>
<td>8430</td>
<td>1.186</td>
<td>230.5</td>
<td>3.94</td>
</tr>
<tr>
<td>9290</td>
<td>1.076</td>
<td>198.5</td>
<td>3.84</td>
</tr>
<tr>
<td>10400</td>
<td>0.961</td>
<td>166.5</td>
<td>3.72</td>
</tr>
<tr>
<td>11810</td>
<td>0.846</td>
<td>135.0</td>
<td>3.57</td>
</tr>
<tr>
<td>13980</td>
<td>0.715</td>
<td>103.5</td>
<td>3.40</td>
</tr>
<tr>
<td>15340</td>
<td>0.651</td>
<td>90.0</td>
<td>3.32</td>
</tr>
</tbody>
</table>

$\theta = +8^0$

Diamagnetic correction = 105 x 10^{-6} c.g.s.u.

Potassium thiomalatocobaltate(II) trihydrate

<table>
<thead>
<tr>
<th>$10^6 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>T(°k)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7670</td>
<td>1.303</td>
<td>295.0</td>
<td>4.25</td>
</tr>
<tr>
<td>8470</td>
<td>1.180</td>
<td>263.0</td>
<td>4.22</td>
</tr>
<tr>
<td>9520</td>
<td>1.050</td>
<td>230.0</td>
<td>4.18</td>
</tr>
<tr>
<td>10850</td>
<td>0.921</td>
<td>198.5</td>
<td>4.15</td>
</tr>
<tr>
<td>12610</td>
<td>0.793</td>
<td>166.5</td>
<td>4.09</td>
</tr>
<tr>
<td>15310</td>
<td>0.659</td>
<td>135.5</td>
<td>4.07</td>
</tr>
<tr>
<td>19950</td>
<td>0.501</td>
<td>103.5</td>
<td>4.06</td>
</tr>
<tr>
<td>23450</td>
<td>0.426</td>
<td>90.0</td>
<td>4.10</td>
</tr>
</tbody>
</table>

$\theta = +5^0$

Diamagnetic correction = 105 x 10^{-6} c.g.s.u.
FIGURE 4.5

Co(tmH)·3H₂O

Li[Co(tm)]·2H₂O
**FIGURE 4.6**

\[ \text{Na[Co(tm)] \cdot 3H}_2\text{O} \]

\[ 10^{-2} \chi_A^{-1} \quad \mu_e (\text{B.M.}) \]

\[ T^0 \text{K} \]

\[ 0 \quad 100 \quad 200 \quad 300 \]

\[ 0.7 \quad 1.4 \quad 4.5 \]

\[ 300 \quad 200 \quad 100 \quad 0 \]

\[ 3.0 \quad 1.5 \quad -1.5 \]

\[ \text{K[Co(tm)] \cdot 3H}_2\text{O} \]

\[ 10^{-2} \chi_A^{-1} \quad \mu_e (\text{B.M.}) \]

\[ T^0 \text{K} \]

\[ 0 \quad 100 \quad 200 \quad 300 \]

\[ 0.7 \quad 1.4 \quad 4.5 \]

\[ 300 \quad 200 \quad 100 \quad 0 \]

\[ 3.0 \quad 1.5 \quad -1.5 \]
Reflectance spectra

The most common geometries of cobalt(II) complexes are four coordinate tetrahedral and six-coordinate octahedral. Furthermore, true cubic symmetry is lost immediately when more than one type of ligand enters the coordination sphere. The colour of the complex is not always a useful criterion of stereochemistry, e.g. Co₂SiO₄ is purple and octahedral, and cobalt(II)-dipivaloylmethanide is pink and tetrahedral. The most careful theoretical explanation of the spectra of cobalt(II) complexes is due to Liehr. The spectra of the cobalt(II) complexes are difficult to assign, because the absorption bands are generally broad and ill-defined, but they indicate that the complex anions have a distorted octahedral stereochemistry. For regular octahedral cobalt(II) three spin-allowed transitions are expected, "T₁g + T₂g (ν₁), "Aₐ (ν₂) and "T₁g (P)(ν₃), but ν₁ is usually weak compared with ν₃, and ν₂ is often unobserved. The ν₁ absorption near 8000 cm⁻¹ (Table 4.8) is split as happens on distortion from octahedral symmetry. The transitions ν₂ (which is usually ca 2ν₁) and ν₃ cannot be distinguished among the broad bands to higher wavenumber (Figs. 4.7 and 4.8).

Iron thiomalate complexes

Magnetism

The results of variable temperature magnetic susceptibility measurements on the thiomalate-iron complexes are given in Tables 4.9 - 4.11. The plots of reciprocal atomic susceptibility and effective magnetic moment against temperature are shown in Figs. 4.9 - 4.11. The room temperature magnetic moments are in the
### TABLE 4.8

Electronic spectra (cm⁻¹) of cobalt thiomalate complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(tmm) • 3H₂O</td>
<td></td>
</tr>
<tr>
<td>7100 sh</td>
<td>7800 s</td>
</tr>
<tr>
<td>8100 s,b</td>
<td>8700 sh</td>
</tr>
<tr>
<td>11900 vw</td>
<td>12000 vw</td>
</tr>
<tr>
<td>14000 sh</td>
<td>14300 sh</td>
</tr>
<tr>
<td>15400 sh</td>
<td>15200 sh</td>
</tr>
<tr>
<td>18500 sh</td>
<td>17500 s</td>
</tr>
<tr>
<td>20500 sb</td>
<td>24400 sh</td>
</tr>
<tr>
<td>28600 s,vb</td>
<td>29500 s</td>
</tr>
</tbody>
</table>

| Li[Co(tm)] • 2H₂O         |             |
| 7800 s                    |             |
| 8900 sh                   |             |
| 12000 vw                  |             |
| 14700 vb                  |             |

| Na[Co(tm)] • 3H₂O         |             |
| 7800 s                    |             |
| 9000 sh                   |             |
| 11900 vw                  |             |
| 16700 vb                  |             |

| K[Co(tm)] • 3H₂O          |             |
| 7800 s                    | \( \nu_1 \) |
| 9000 sh                   |             |
| 11900 vw                  |             |
| 14700 vb                  |             |
| 16700 vb                  | \( \nu_2 \) |
| 22000 s,vb                | \( \nu_3 \) |
| 29000 s,vb                | \( \text{C.T.} \) |
FIGURE 4.7

- Li[Co(tm)]·2H₂O
- Co(tmH)·3H₂O

O.D.

wavelength (nm)
FIGURE 4.8

- Na[Co(tm)]•3H₂O
- K[Co(tm)]•3H₂O

wavelength (nm)

O.D.
range normally expected for octahedral high-spin iron(II) ($^5T_{2g}$ ground term, 4.9-5.5 B.M.). Increasing electron delocalisation and distortion from cubic symmetry can cause the magnetic moments of high-spin 3d$^6$ ions ($t_{2g}^4e_{g}^2$) to be closer to the spin-only value 4.90 B.M. than is the case with regular octahedral complexes.

For pyridinethiomalatoiron(II), the magnetic moment is below the spin-only value at room temperature and decreases still further as the temperature is lowered. This is believed to be due to antiferromagnetic interaction in a polymeric structure. In the cases of Fe(tmH)$\cdot$3H$_2$O and A[Fe(tm)l$\cdot$nH$_2$O where A = Li, Na or K, the moments increased as the temperature was lowered, the Curie-Weiss law being obeyed with high negative Weiss constants $\theta$ (positive intercept, Figs. 4.9, 4.10), which are indicative of weak ferromagnetic interaction presumably arising through polymerization structures (IV, I). Ferromagnetic interaction is uncommon in iron(II) complexes, but similar behaviour has been reported for the linear chain polymers Fe(phenanthroline)Cl$_2$, Fe(bipyridine)Cl$_2$ $^{209,210}$ and AFeCl$_3$ (A = K, Rb and Cs). $^{211}$

Reflectance spectra

Octahedral high-spin, divalent iron has a $t_{2g}^4e_{g}^2$ configuration and the electronic ground term $^5D$. No other quintet state is present. In octahedral symmetry the $^5D$ level will split into an orbital triplet $^5T_{2g}$ ground level and an orbital doublet $^5E_{g}$ excited level. Usually octahedral, high-spin divalent iron complexes show one weak transition, $^5T_{2g} \rightarrow ^5E_{g}$, in the near infrared region, but distortion from octahedral symmetry frequently causes two bands or one very broad and asymmetric band to be present. $^{208}$
<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>$T(\text{o}k)$</th>
<th>$\mu_e (\text{B.M.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12640</td>
<td>0.791</td>
<td>295.0</td>
<td>5.46</td>
</tr>
<tr>
<td>14440</td>
<td>0.692</td>
<td>262.5</td>
<td>5.50</td>
</tr>
<tr>
<td>16610</td>
<td>0.602</td>
<td>230.0</td>
<td>5.52</td>
</tr>
<tr>
<td>19660</td>
<td>0.508</td>
<td>198.5</td>
<td>5.58</td>
</tr>
<tr>
<td>24090</td>
<td>0.415</td>
<td>166.5</td>
<td>5.66</td>
</tr>
<tr>
<td>30920</td>
<td>0.323</td>
<td>135.0</td>
<td>5.77</td>
</tr>
<tr>
<td>44020</td>
<td>0.227</td>
<td>103.5</td>
<td>6.03</td>
</tr>
<tr>
<td>55390</td>
<td>0.180</td>
<td>90.0</td>
<td>6.31</td>
</tr>
</tbody>
</table>

$\theta = -25^\circ$

Diamagnetic correction = $-108 \times 10^{-6}$ c.g.s.u.

---

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>$T(\text{o}k)$</th>
<th>$\mu_e (\text{B.M.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9750</td>
<td>1.025</td>
<td>295.0</td>
<td>4.80</td>
</tr>
<tr>
<td>11270</td>
<td>0.887</td>
<td>262.5</td>
<td>4.86</td>
</tr>
<tr>
<td>12920</td>
<td>0.774</td>
<td>230.0</td>
<td>4.87</td>
</tr>
<tr>
<td>15060</td>
<td>0.664</td>
<td>198.5</td>
<td>4.88</td>
</tr>
<tr>
<td>18760</td>
<td>0.533</td>
<td>166.5</td>
<td>4.99</td>
</tr>
<tr>
<td>23260</td>
<td>0.430</td>
<td>135.5</td>
<td>5.01</td>
</tr>
<tr>
<td>33980</td>
<td>0.294</td>
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</tr>
<tr>
<td>41300</td>
<td>0.242</td>
<td>90.0</td>
<td>5.45</td>
</tr>
</tbody>
</table>

$\theta = -30^\circ$

Diamagnetic correction = $-105 \times 10^{-6}$ c.g.s.u.
## Table 4.10

### Sodium thiomalatoferrate(II) monohydrate

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$\chi_A^{-1}$</th>
<th>$T(°k)$</th>
<th>$\mu_e (B.M.)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9870</td>
<td>1.013</td>
<td>295.0</td>
<td>4.82</td>
</tr>
<tr>
<td>11640</td>
<td>0.859</td>
<td>262.5</td>
<td>4.94</td>
</tr>
<tr>
<td>13010</td>
<td>0.768</td>
<td>230.0</td>
<td>4.89</td>
</tr>
<tr>
<td>16100</td>
<td>0.621</td>
<td>198.5</td>
<td>5.05</td>
</tr>
<tr>
<td>19350</td>
<td>0.516</td>
<td>166.5</td>
<td>5.07</td>
</tr>
<tr>
<td>27010</td>
<td>0.370</td>
<td>135.0</td>
<td>5.40</td>
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<tr>
<td>39480</td>
<td>0.253</td>
<td>103.5</td>
<td>5.71</td>
</tr>
<tr>
<td>49300</td>
<td>0.203</td>
<td>90.0</td>
<td>5.95</td>
</tr>
</tbody>
</table>

$\theta = -40°$

Diamagnetic correction = $-78 \times 10^{-6}$ c.g.s.u.

### Potassium thiomalatoferrate(II) trihydrate

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$\chi_A^{-1}$</th>
<th>$T(°k)$</th>
<th>$\mu_e (B.M.)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11800</td>
<td>0.847</td>
<td>295.0</td>
<td>5.27</td>
</tr>
<tr>
<td>13060</td>
<td>0.766</td>
<td>262.5</td>
<td>5.23</td>
</tr>
<tr>
<td>14780</td>
<td>0.676</td>
<td>230.0</td>
<td>5.21</td>
</tr>
<tr>
<td>18320</td>
<td>0.548</td>
<td>198.5</td>
<td>5.37</td>
</tr>
<tr>
<td>22580</td>
<td>0.443</td>
<td>166.5</td>
<td>5.48</td>
</tr>
<tr>
<td>30000</td>
<td>0.333</td>
<td>135.0</td>
<td>5.69</td>
</tr>
<tr>
<td>44340</td>
<td>0.225</td>
<td>103.5</td>
<td>6.05</td>
</tr>
<tr>
<td>53820</td>
<td>0.186</td>
<td>90.0</td>
<td>6.22</td>
</tr>
</tbody>
</table>

$\theta = -37°$

Diamagnetic correction = $105 \times 10^{-6}$ c.g.s.u.
### TABLE 4.11
Pyridinethiomalatoiron(II)

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>$T(\text{o}K)$</th>
<th>$\mu_e (\text{B.M.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9330</td>
<td>1.070</td>
<td>295.0</td>
<td>4.69</td>
</tr>
<tr>
<td>10350</td>
<td>0.966</td>
<td>262.5</td>
<td>4.66</td>
</tr>
<tr>
<td>11440</td>
<td>0.874</td>
<td>230.0</td>
<td>4.58</td>
</tr>
<tr>
<td>12910</td>
<td>0.774</td>
<td>198.5</td>
<td>4.52</td>
</tr>
<tr>
<td>14690</td>
<td>0.680</td>
<td>166.5</td>
<td>4.42</td>
</tr>
<tr>
<td>17860</td>
<td>0.559</td>
<td>135.0</td>
<td>4.39</td>
</tr>
<tr>
<td>22000</td>
<td>0.454</td>
<td>103.5</td>
<td>4.26</td>
</tr>
<tr>
<td>25160</td>
<td>0.397</td>
<td>90.0</td>
<td>4.25</td>
</tr>
</tbody>
</table>

$\theta = +8^0$

Diamagnetic correction = $-118 \times 10^{-6}$ c.g.s.u.
FIGURE 4.10

Na[Fe(tm)]·H₂O

\[10^{-2} \chi_A \]

\[\mu_e (B.M.)\]

T°K

K[Fe(tm)]·3H₂O

\[10^{-2} \chi_A \]

\[\mu_e (B.M.)\]

T°K
FIGURE 4.11

Fe(tmlH)·Py

$10^{-2} X_A$

$\mu_{e,(B.M.)}$
(IV) $M(tmH) \cdot nH_2O$

($M = Fe^{II}$ or $Mn^{II}$)
The spectra of thiomalatoiron complexes contained two bands in the region of 10000 cm$^{-1}$ (Table 4.12 and Figs. 4.12 and 4.13) indicating some distortion in the octahedral polymers.

**TABLE 4.12**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{5}<em>{T_2g} - ^{5}</em>{E_g}$ (cm$^{-1}$)</th>
<th>C.T. (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(tmH) $\cdot 3\text{H}_2\text{O}$</td>
<td>7800 m 10650 m 18800 b 21000 vb</td>
<td></td>
</tr>
<tr>
<td>Fe(tmH) $\cdot \text{py}$</td>
<td>7700 m 10500 m 17400 sh 20400 sh 26700 b</td>
<td></td>
</tr>
<tr>
<td>Li[Fe(tm)] $\cdot 3\text{H}_2\text{O}$</td>
<td>7900 m 10900 b 17400 sh 20200 sh 28100 b</td>
<td></td>
</tr>
<tr>
<td>Na[Fe(tm)] $\cdot \text{H}_2\text{O}$</td>
<td>7800 m 10600 b 17000 sh 20600 sh 28000 b</td>
<td></td>
</tr>
<tr>
<td>K[Fe(tm)] $\cdot 3\text{H}_2\text{O}$</td>
<td>8600 m 10900 b 17600 sh 20800 sh 27000 b</td>
<td></td>
</tr>
</tbody>
</table>

**Mössbauer effects**

Mössbauer measurements were carried out at $78^0\text{K}$. The parameters are given in Table 4.13. The isomer shifts, $\delta$, are typical of high-spin iron(II) compounds, and no iron(III) absorptions were present in the spectrum, indicating that oxidation had not occurred during the preparations or later handling. The values of $\Delta E$, the quadrupole splitting, are of the magnitude usually found for high-spin octahedral iron(II) complexes in which some distortion is present, but where the main contribution to the magnitude of $\Delta E$ comes from the disymmetry of the d-electron configurations. Highly distorted complexes, for example those which are pentacoordinate, have larger quadrupole splittings of about 4 mm s$^{-1}$.  


FIGURE 4.12
FIGURE 4.13

- Li[Fe(tm)]·3H₂O
- K[Fe(tm)]·3H₂O
- Na[Fe(tm)]·H₂O
As the values of $\delta$ and $\Delta E$ vary so little with the complexes it can be assumed that the iron(II) environment is almost identical throughout.

**TABLE 4.13**

Mössbauer parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^a$ (mm s$^{-1}$)</th>
<th>$\Delta E$ (mm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li[Fe(tm)]·3H$_2$O</td>
<td>1.035</td>
<td>2.951</td>
</tr>
<tr>
<td>Na[Fe(tm)]·H$_2$O</td>
<td>1.042</td>
<td>2.951</td>
</tr>
<tr>
<td>K[Fe(tm)]·3H$_2$O</td>
<td>1.019</td>
<td>2.935</td>
</tr>
</tbody>
</table>

$a$ - The isomer shifts are given with respect to natural iron.

**Manganese-thiomalate complexes**

**Magnetism**

Manganese(II) has the electronic configuration [Ar]3d$^5$, and most manganese(II) compounds are high-spin octahedral or tetrahedral ($S = \frac{5}{2}$), a few are low-spin octahedral ($S = \frac{1}{2}$), and, in principle, square planar complexes with $S = \frac{3}{2}$ or $S = \frac{1}{2}$ could exist. Magnetic moment measurements can help to distinguish between these geometries.
Manganese(II) has a free ion ground term $^6S$ which is not split by crystal fields, irrespective of the symmetry of the complex in which the metal ion occurs, but gives rise to a $^6A_{1g}$ term in an octahedral environment. Being an orbital singlet, the ground term has no orbital angular momentum or magnetic moment associated with it. Since there are no higher energy excited terms possessing the same multiplicity as the ground term, second order mixing due to spin-orbit coupling cannot arise, nor can any second order Zeeman effects occur. Hence, the magnetic behaviour for manganese(II) complexes results only from the spin contribution and is described by the spin-only formula

$$\mu_{\text{s.o.}} = \left[4S(S+1)\right]^{\frac{1}{2}} = 5.92 \text{ B.M. for } S = \frac{5}{2}$$
### TABLE 4.14

<table>
<thead>
<tr>
<th>10^6(\chi_A)</th>
<th>10^{-2}(\chi_A^{-1})</th>
<th>T(°k)</th>
<th>(\mu_e)(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14790</td>
<td>0.676</td>
<td>295.0</td>
<td>5.90</td>
</tr>
<tr>
<td>16270</td>
<td>0.615</td>
<td>262.5</td>
<td>5.84</td>
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<tr>
<td>18130</td>
<td>0.552</td>
<td>230.5</td>
<td>5.78</td>
</tr>
<tr>
<td>20500</td>
<td>0.488</td>
<td>198.5</td>
<td>5.70</td>
</tr>
<tr>
<td>23540</td>
<td>0.428</td>
<td>166.5</td>
<td>5.60</td>
</tr>
<tr>
<td>27770</td>
<td>0.360</td>
<td>135.0</td>
<td>5.47</td>
</tr>
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<td>33610</td>
<td>0.297</td>
<td>103.5</td>
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</tr>
<tr>
<td>37290</td>
<td>0.268</td>
<td>90.0</td>
<td>5.18</td>
</tr>
</tbody>
</table>

\(\theta = +45^\circ\)

Diamagnetic correction = \(-95 \times 10^{-6}\) c.g.s.u.

---

<table>
<thead>
<tr>
<th>10^6(\chi_A)</th>
<th>10^{-2}(\chi_A^{-1})</th>
<th>T(°k)</th>
<th>(\mu_e)(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15020</td>
<td>0.665</td>
<td>295.0</td>
<td>5.95</td>
</tr>
<tr>
<td>16710</td>
<td>0.598</td>
<td>262.5</td>
<td>5.92</td>
</tr>
<tr>
<td>18320</td>
<td>0.545</td>
<td>230.0</td>
<td>5.80</td>
</tr>
<tr>
<td>20410</td>
<td>0.489</td>
<td>198.5</td>
<td>5.69</td>
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<td>0.371</td>
<td>135.0</td>
<td>5.39</td>
</tr>
<tr>
<td>32210</td>
<td>0.310</td>
<td>103.5</td>
<td>5.19</td>
</tr>
<tr>
<td>35320</td>
<td>0.283</td>
<td>90.0</td>
<td>5.04</td>
</tr>
</tbody>
</table>

\(\theta = +57^\circ\)

Diamagnetic correction = \(-92 \times 10^{-6}\) c.g.s.u.
### Lithium thiomalatomanganate(II) trihydrate

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>T(°k)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16500</td>
<td>0.606</td>
<td>295.0</td>
<td>6.23</td>
</tr>
<tr>
<td>18090</td>
<td>0.553</td>
<td>262.5</td>
<td>6.16</td>
</tr>
<tr>
<td>19820</td>
<td>0.507</td>
<td>231.0</td>
<td>6.05</td>
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<tr>
<td>22370</td>
<td>0.447</td>
<td>198.5</td>
<td>5.95</td>
</tr>
<tr>
<td>25380</td>
<td>0.394</td>
<td>166.5</td>
<td>5.81</td>
</tr>
<tr>
<td>28900</td>
<td>0.346</td>
<td>135.0</td>
<td>5.58</td>
</tr>
<tr>
<td>33940</td>
<td>0.295</td>
<td>103.5</td>
<td>5.30</td>
</tr>
<tr>
<td>35870</td>
<td>0.279</td>
<td>90.0</td>
<td>5.08</td>
</tr>
</tbody>
</table>

$\theta = 79^\circ$

Diamagnetic correction = $-105 \times 10^{-6}$ c.g.s.u.

### Potassium thiomalatomanganate(II) dihydrate

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>T(°k)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15580</td>
<td>0.642</td>
<td>295.0</td>
<td>6.06</td>
</tr>
<tr>
<td>17250</td>
<td>0.579</td>
<td>262.5</td>
<td>6.01</td>
</tr>
<tr>
<td>18840</td>
<td>0.530</td>
<td>230.0</td>
<td>5.88</td>
</tr>
<tr>
<td>21010</td>
<td>0.475</td>
<td>198.5</td>
<td>5.77</td>
</tr>
<tr>
<td>24060</td>
<td>0.416</td>
<td>166.5</td>
<td>5.66</td>
</tr>
<tr>
<td>27920</td>
<td>0.358</td>
<td>135.0</td>
<td>5.49</td>
</tr>
<tr>
<td>32840</td>
<td>0.304</td>
<td>103.5</td>
<td>5.21</td>
</tr>
<tr>
<td>35990</td>
<td>0.278</td>
<td>90.0</td>
<td>5.08</td>
</tr>
</tbody>
</table>

$\theta = 58^\circ$

Diamagnetic correction = $-92 \times 10^{-6}$ c.g.s.u.
FIGURE 4.14

\[ 0.80 - 0.40 \]

\[ 10^{-2} \chi_A^{-1} \]

\[ 0.70 - 0.35 \]

\[ 10^{-2} \chi_A^{-1} \]

\[ \mu_e (\text{B.M.}) \]

\[ \mu_e (\text{B.M.}) \]

\( T_0 K \)

\( T_0 K \)

\( \text{Mn(tmH)} \cdot 2\text{H}_2\text{O} \)

\( \text{Na}[\text{Mn(tm)}] \cdot 2\text{H}_2\text{O} \)
FIGURE 4.15

$K[Mn(tm)] \cdot 2H_2O$

$10^{-2} \chi_A^{-1}$ vs $T^0_K$

$\mu_e$(B.M.)

$K[Mn(tm)] \cdot 2H_2O$

$10^{-2} \chi_A^{-1}$ vs $T^0_K$

$\mu_e$(B.M.)
Therefore, in the absence of antiferromagnetism, the experimental magnetic moments should closely approach the spin-only value and be invariant with temperature. In thiomalatomanganese(II) dihydrate structure (IV) and sodium thiomalatomanganate(II) dihydrate structure (I), the value of $\mu_e$ decreases with temperature from approximately 5.9 B.M. at 295° K to approximately 5.1 B.M. at 90° K (Table 4.14 and Fig. 4.14). The room temperature values are close to the spin-only value for five unpaired electrons \( S = \frac{5}{2} \). The magnetic moments are as expected for octahedral complexes in which there are appreciable antiferromagnetic interactions. It is suggested that compounds are polymerised. Room temperature magnetic moments for lithium thiomalatomanganate(II) trihydrate and potassium thiomalatomanganate dihydrate are somewhat high (Table 4.15); the reason for this is not known. However, the magnetic moments decreased at lower temperature (Fig. 4.15), apparently due to antiferromagnetic interactions in polymeric structures (I).

**Reflectance spectra**

The reflectance spectra given in Table 4.16 and Figs. 4.16 and 4.17 are in good agreement for octahedral configurations and are quite similar to each other except for an additional band at 18700 cm\(^{-1}\) for Na[Mn(tm)]\(\cdot\)2H\(_2\)O and at 21700 cm\(^{-1}\) for Li[Mn(tm)]\(\cdot\)3H\(_2\)O.

**Structures of complexes of formula A[M\(^{II}\)(tm)]\(\cdot\)nH\(_2\)O**

The complexes of manganese(II), iron(II), cobalt(II) and nickel(II) of the general formula A[M\(^{II}\)(tm)]\(\cdot\)nH\(_2\)O have very similar
TABLE 4.16
Electronic spectra of manganese-thiomalate complexes
(all frequencies in cm⁻¹)

<table>
<thead>
<tr>
<th>Mn(tmH)</th>
<th>Li[Mn(tm)]</th>
<th>Na[Mn(tm)]</th>
<th>K[Mn(tm)]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H₂O</td>
<td>3H₂O</td>
<td>2H₂O</td>
<td>2H₂O</td>
<td></td>
</tr>
<tr>
<td>16000 m</td>
<td>16500 m, vb</td>
<td>17200 sh</td>
<td>16000 b</td>
<td>⁶A₁g → ⁴T₁g ('G)</td>
</tr>
<tr>
<td>17500 m</td>
<td>17400 sh</td>
<td>17400 m</td>
<td>17500 sh</td>
<td>⁶A₁g → ⁴T₂g ('G)</td>
</tr>
<tr>
<td>20900 m</td>
<td>21500 sh</td>
<td>18700 vv</td>
<td>20800 m</td>
<td>⁶A₁g → ⁴A₂g ('G)</td>
</tr>
<tr>
<td>23100 m</td>
<td>21700 sh</td>
<td>23100 m</td>
<td>23100 m</td>
<td>⁶A₁g → ⁴E₂g ('G)</td>
</tr>
<tr>
<td>23700 m</td>
<td>23700 m</td>
<td>23500 m</td>
<td>23500 m</td>
<td>⁶A₁g → ⁴T₂g ('D)</td>
</tr>
<tr>
<td>26500 m</td>
<td>26300 m</td>
<td>26300 sh</td>
<td>26400 m</td>
<td>⁶A₁g → ⁴E₂g ('D)</td>
</tr>
<tr>
<td>27900 m</td>
<td>27900 m</td>
<td>28000 sh</td>
<td>28000 m</td>
<td>⁶A₁g → ⁴T₁g ('P)</td>
</tr>
</tbody>
</table>

infrared spectra, and all have electronic spectra indicative of distorted octahedral coordination. They are therefore believed to have polymeric anions as indicated in the structures (I). The presence of magnetic interaction in the manganese(II), iron(II) and nickel(II) complexes, where little or no first order orbital contribution is expected, confirms the polymeric nature of the complexes. In the case of the cobalt(II) complexes the presence of first-order orbital contribution makes the magnetic behaviour more complicated, but the structures of the cobalt(II) complexes would be expected to be the same. The magnitudes of the quadrupole splittings for iron(II) salts also are as expected for hexacoordinate structures.
FIGURE 4.17

- - - Na[Mn(tm)] • 2H₂O

K[Mn(tm)] • 2H₂O

wavelength (nm)
Metal complexes of L-cysteine

Schubert\textsuperscript{214,215} was the first to describe the isolation in the solid state of some L-cysteine complexes of cobalt(II) and iron(II), but little information was given about their structures or properties, so these and related complexes have been re-investigated. The complexes, especially of iron(II), were found to be very air-sensitive.

Several new complexes formed between L-cysteine and cobalt(II) have been isolated, but the known iron(II) complex Fe(cys)\cdot1.5H\textsubscript{2}O could not be isolated pure. The complex Li\textsubscript{2}[Fe(cys)\textsubscript{2}] and a similar manganese(II) complex and K\textsubscript{2}[Fe(cys)\textsubscript{2}] could also not be obtained, although several attempts were made in each case. Other recent attempts\textsuperscript{216} to prepare pure iron(II) complexes of cysteine have also been unsuccessful.

Infrared spectra

The complexes M\textsubscript{2}[Co(cys)\textsubscript{2}]\cdot3H\textsubscript{2}O, where M = Li, Na or K, and Co(cysH)\textsubscript{2}\cdot2H\textsubscript{2}O have been prepared. The infrared spectra (Table 4.17) show that the band at 2540 cm\textsuperscript{-1} assigned\textsuperscript{217} to v(S-H) in the free acid is absent from the spectra of the metal complexes except in the case of Co(cysH)\textsubscript{2}\cdot2H\textsubscript{2}O, the infrared spectrum of which shows a weak absorption at 2530 cm\textsuperscript{-1}. The bands at 3400 cm\textsuperscript{-1}, assigned to v(OH), confirm the presence of water molecules. The band assigned\textsuperscript{48} as v(N-H) in the infrared spectrum of cysteine is shifted from 3200 cm\textsuperscript{-1} to about 3300 cm\textsuperscript{-1} in the spectra of the complexes. This is consistent with a change from -NH\textsuperscript{+} in the free acid to coordinated-NH\textsubscript{2} in the complexes, although hydrogen bonding complicates the infrared spectra
of complexes of amino acids and makes assignment difficult. The \( \text{NH}_2 \) deformation mode (\( \delta \text{NH}_2 \)) is obscured by the \( \nu_{\text{as}}(\text{OCO}) \) band in all cobalt complexes and no assignment has been made.

Nakamoto et al\textsuperscript{218} have demonstrated that hydrogen bonding is important with amino acid complexes and can affect the \( \Delta \) value, so great care must be exercised in predicting the nature of the carboxylate coordination.

It is suggested that in \( \text{Co(cysH)}_2 \cdot 2\text{H}_2\text{O} \) coordination is through nitrogen and bidentate bridging-carboxylate groups (V), because the infrared spectrum shows the presence of unionised sulphydryl groups, and in the case of \( \text{M}_2[\text{Co(cys)}_2] \cdot 3\text{H}_2\text{O} \) (\( \text{M} = \text{Li}, \text{Na} \) or \( \text{K} \)) coordination is through nitrogen and bridging-sulphur atoms. Similar suggestions have been made by others. Mitchell and Kay\textsuperscript{219} have proposed that in sodium di-\( \mu \)-sulphido-bis[oxo(L-cysteine)molybdate(V)] trihydrate, the coordination is through sulphur and nitrogen of L-cysteine, but others found that monodentate carboxylate groups were present.\textsuperscript{220} Also, in the sodium or potassium salts of \([\text{Fe(cys)}_2]^{2-}\), \([\text{Zn(cys)}_2]^{2-}\) and \([\text{Ni(cys)}_2]^{2-}\) the anion is said to be a bidentate sulphur and nitrogen donor,\textsuperscript{29,48,85} with S bridges in the iron complex.
<table>
<thead>
<tr>
<th>Compound</th>
<th>ν&lt;sub&gt;OH&lt;/sub&gt;</th>
<th>ν&lt;sub&gt;S-H&lt;/sub&gt;</th>
<th>ν&lt;sub&gt;as (CO)&lt;/sub&gt;</th>
<th>ν&lt;sub&gt;s (CO)&lt;/sub&gt;</th>
<th>Δ</th>
<th>ν(NH&lt;sub&gt;2&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-cysteine</td>
<td>3400 b</td>
<td>3330 m</td>
<td>1600 s</td>
<td>1580 s</td>
<td>160</td>
<td>3290 m</td>
</tr>
<tr>
<td>Co(C2H5)(CYS)&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2540 m</td>
<td>1590 s</td>
<td>1402 s</td>
<td>1400 s</td>
<td>188</td>
<td>3200 m</td>
</tr>
<tr>
<td>Li&lt;sub&gt;2&lt;/sub&gt;(Co(CYS)&lt;sub&gt;2&lt;/sub&gt;·3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>3450 b</td>
<td>-</td>
<td>1380 s</td>
<td>1380 s</td>
<td>220</td>
<td>3460 m</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;(Co(CYS)&lt;sub&gt;2&lt;/sub&gt;·3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>3440 b</td>
<td>-</td>
<td>1380 s</td>
<td>1380 s</td>
<td>205</td>
<td>3310 m</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;(Co(CYS)&lt;sub&gt;2&lt;/sub&gt;·3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>3400 b</td>
<td>-</td>
<td>1380 s</td>
<td>1380 s</td>
<td>200</td>
<td>3290 m</td>
</tr>
</tbody>
</table>
Reflectance spectra

The results of reflectance spectral investigations of the cobalt complexes are shown in Table 4.18 and Figs. 4.18 and 4.19. The spectra of the cobalt(II) complexes are difficult to assign, because the absorption bands are generally broad and ill-defined, but they indicate that the metal ion has a distorted octahedral stereochemistry. The $v_1$ absorption near 8000 cm$^{-1}$ (Table 4.18) is split as happens on distortion from octahedral symmetry. The low intensity band, appearing as a shoulder between 14000 to 17000 cm$^{-1}$, is identified as the transition $^{4}A_2 \rightarrow ^{4}T_1$ (which is usually ca 2$v_1$) and as in the thiomalate-complexes, $v_3$ cannot be distinguished among the broad bands to higher wavenumber.

Magnetism

As with the thiomalatocobaltate(II) salts the magnetic moments for these cobalt complexes are somewhat lower than for many magnetically-normal, octahedral complexes (4.8-5.2 B.M.).

The magnetic moments of the complexes $M_2[Co(\text{cys})_2] \cdot 3\text{H}_2\text{O}$ are shown in Tables 4.19 and 4.20 and Figs. 4.20 and 4.21. They decrease markedly at lower temperature and the Curie-Weiss law is obeyed with large $\theta$ values. It is therefore possible that the complexes have polymeric octahedral structures of the type shown in (VI).

The effective magnetic moments for $Co(\text{cysH})_2 \cdot 2\text{H}_2\text{O}$ are 3.45 B.M. and 2.91 B.M. at 295° K and 90° K respectively, with $\theta = 30^\circ$ K, and these low values suggest that the complex is polymeric and may have weak antiferromagnetic interactions (see thiomalic acid complexes).
<table>
<thead>
<tr>
<th>TABLE 4.18 Reflectance spectra</th>
<th>Co((\text{cysH})_2)</th>
<th>Li$_2${Co((\text{cysH})_2)</th>
<th>Na$_2${Co((\text{cysH})_2)</th>
<th>K$_2${Co((\text{cysH})_2)</th>
<th>H$_2$O</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2H$_2$O</td>
<td>3H$_2$O</td>
<td>3H$_2$O</td>
<td>3H$_2$O</td>
<td>H$_2$O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7700 s</td>
<td>7700 s</td>
<td>7700 s</td>
<td>7700 s</td>
<td>8300 s, b</td>
<td>v$_1$</td>
</tr>
<tr>
<td></td>
<td>8700 sh</td>
<td>9100 sh</td>
<td>8500 sh</td>
<td>9100 sh</td>
<td>8850 sh</td>
<td>v$_1$</td>
</tr>
<tr>
<td></td>
<td>11900 wv</td>
<td>12900 sh</td>
<td>13400 sh</td>
<td>14700 s, b</td>
<td>14700 s, b</td>
<td>v$_2$</td>
</tr>
<tr>
<td></td>
<td>13100 sh</td>
<td>14200 sh</td>
<td>15700 sh</td>
<td>14300 b</td>
<td>14300 b</td>
<td>v$_2$</td>
</tr>
<tr>
<td></td>
<td>16700 sh</td>
<td>17200 s, b</td>
<td>17500 s, b</td>
<td>16000 s, b</td>
<td>16000 s, b</td>
<td>v$_3$ +</td>
</tr>
<tr>
<td></td>
<td>20400 s, b</td>
<td>22000 vb</td>
<td>22500 s, b</td>
<td>21000 sh</td>
<td>21000 sh</td>
<td>v$_3$ +</td>
</tr>
<tr>
<td></td>
<td>25000 b</td>
<td>26300 b</td>
<td>29000 b</td>
<td>24100 b</td>
<td>28600 b</td>
<td>C.T.</td>
</tr>
</tbody>
</table>
The magnetic moment at room temperature of cobalt(II) in an aqueous 1:3 mixture of cobalt(II) chloride and cysteine has been reported to be 3.86 B.M. As this is low for high-spin cobalt(II) it may be that polymeric species are present in solution.

In one preparation a product which could be formulated as Li[Co$^{III}_2$(cys)$_2$] was obtained. It was found to be diamagnetic, and as it was prepared under nitrogen by the same method which gave Li$_2$[Co(cys)$_2$]·3H$_2$O, it is not understood how oxidation occurred. The reflectance spectrum showed absorption bands at 7900 sh, 9600 s, 15000 sh and 20000 vb.
TABLE 4.19

Bis(cysteinato)cobalt(II) dihydrate

<table>
<thead>
<tr>
<th>$10^6 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>$T$(°K)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5070</td>
<td>1.972</td>
<td>295.0</td>
<td>3.45</td>
</tr>
<tr>
<td>5610</td>
<td>1.782</td>
<td>262.5</td>
<td>3.43</td>
</tr>
<tr>
<td>6050</td>
<td>1.650</td>
<td>230.0</td>
<td>3.33</td>
</tr>
<tr>
<td>6550</td>
<td>1.526</td>
<td>198.5</td>
<td>3.22</td>
</tr>
<tr>
<td>7745</td>
<td>1.291</td>
<td>166.5</td>
<td>3.21</td>
</tr>
<tr>
<td>8970</td>
<td>1.114</td>
<td>135.0</td>
<td>3.11</td>
</tr>
<tr>
<td>10570</td>
<td>0.946</td>
<td>103.5</td>
<td>2.95</td>
</tr>
<tr>
<td>11780</td>
<td>0.848</td>
<td>90.0</td>
<td>2.91</td>
</tr>
</tbody>
</table>

$\theta = 30^0$

Diamagnetic correction = $-156 \times 10^{-6}$ c.g.s.u.

Lithium bis(cysteinato)cobaltate(II) trihydrate

<table>
<thead>
<tr>
<th>$10^6 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>$T$(°K)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6820</td>
<td>1.466</td>
<td>295.0</td>
<td>4.01</td>
</tr>
<tr>
<td>7640</td>
<td>1.309</td>
<td>262.5</td>
<td>4.00</td>
</tr>
<tr>
<td>8750</td>
<td>1.143</td>
<td>230.0</td>
<td>4.01</td>
</tr>
<tr>
<td>10120</td>
<td>0.988</td>
<td>198.5</td>
<td>4.00</td>
</tr>
<tr>
<td>11600</td>
<td>0.862</td>
<td>166.5</td>
<td>3.93</td>
</tr>
<tr>
<td>13450</td>
<td>0.743</td>
<td>135.0</td>
<td>3.81</td>
</tr>
<tr>
<td>16700</td>
<td>0.598</td>
<td>103.5</td>
<td>3.72</td>
</tr>
<tr>
<td>11850</td>
<td>0.530</td>
<td>90.0</td>
<td>3.68</td>
</tr>
</tbody>
</table>

$\theta = 26^0$

Diamagnetic correction = $-164 \times 10^{-6}$ c.g.s.u.
### Sodium bis(cysteinato)cobaltate(II) trihydrate

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>$T(\circ K)$</th>
<th>$\mu_e (\text{B.M.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7040</td>
<td>1.441</td>
<td>295.0</td>
<td>4.04</td>
</tr>
<tr>
<td>7680</td>
<td>1.302</td>
<td>262.5</td>
<td>4.01</td>
</tr>
<tr>
<td>8680</td>
<td>1.152</td>
<td>230.5</td>
<td>4.00</td>
</tr>
<tr>
<td>9650</td>
<td>1.036</td>
<td>198.5</td>
<td>3.91</td>
</tr>
<tr>
<td>11040</td>
<td>0.906</td>
<td>166.5</td>
<td>3.83</td>
</tr>
<tr>
<td>13030</td>
<td>0.767</td>
<td>135.0</td>
<td>3.75</td>
</tr>
<tr>
<td>15830</td>
<td>0.632</td>
<td>103.5</td>
<td>3.61</td>
</tr>
<tr>
<td>17730</td>
<td>0.564</td>
<td>89.5</td>
<td>3.56</td>
</tr>
</tbody>
</table>

$\theta = +38^\circ$

Diamagnetic corrections = $-164 \times 10^{-6}$ c.g.s.u.

### Potassium bis(cysteinato)cobaltate(II) trihydrate

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2} \chi_A^{-1}$</th>
<th>$T(\circ K)$</th>
<th>$\mu_e (\text{B.M.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7580</td>
<td>1.32</td>
<td>295.0</td>
<td>4.22</td>
</tr>
<tr>
<td>8360</td>
<td>1.196</td>
<td>262.0</td>
<td>4.19</td>
</tr>
<tr>
<td>9380</td>
<td>1.066</td>
<td>230.5</td>
<td>4.16</td>
</tr>
<tr>
<td>10580</td>
<td>0.945</td>
<td>199.0</td>
<td>4.10</td>
</tr>
<tr>
<td>12050</td>
<td>0.830</td>
<td>166.5</td>
<td>4.00</td>
</tr>
<tr>
<td>13780</td>
<td>0.721</td>
<td>135.0</td>
<td>3.87</td>
</tr>
<tr>
<td>15720</td>
<td>0.636</td>
<td>103.5</td>
<td>3.60</td>
</tr>
<tr>
<td>18270</td>
<td>0.547</td>
<td>90.0</td>
<td>3.62</td>
</tr>
</tbody>
</table>

$\theta = +62^\circ$

Diamagnetic corrections = $-164 \times 10^{-6}$ c.g.s.u.
FIGURE 4.20

Co(cysH)₂ \cdot 2H₂O

\begin{align*}
10^{-2} & \chi_\mathcal{A} \\
T^\circ & K
\end{align*}

Li₂[Co(cys)₂] \cdot 3H₂O

\begin{align*}
10^{-2} & \chi_\mathcal{A} \\
T^\circ & K
\end{align*}
Investigation of potassium bis(α-thiopropionato)cobaltate(II) monohydrate

It was mentioned in the Introduction that thiopropionic acid, a sulphur-oxygen donor like thiomalic acid, forms complexes with many divalent metals. Sodium bis(thiopropionato)cobalt(II), which was prepared in air, was reported\textsuperscript{35} to have a low magnetic moment of 2.09 B.M. at room temperature. From experience with the cobalt(II) thiomalates it would be expected that cobalt(II)-thiopropionates would oxidise readily. This has been found because the related salt, potassium bis(α-thiopropionato)cobaltate(II) K\textsubscript{2}[Co(thiop)\textsubscript{2}]\textcdot H\textsubscript{2}O, is very readily oxidised, so that the earlier work appears to be in error.

Infrared spectra

The infrared spectrum (Table 4.21) does not contain a band assignable to ν(S-H) of K\textsubscript{2}[Co(thiop)\textsubscript{2}]\textcdot H\textsubscript{2}O so that the thiol group is ionised and presumably coordinated; and a broad band at 3400 cm\textsuperscript{-1}, assigned to ν(O-H), confirms the presence of water. The value of Δ (ν\textsubscript{as}(OCO)-ν\textsubscript{s}(OCO)) is in the range found for monodentate carboxylate groups (Table 4.21) and is 40-50 cm\textsuperscript{-1} larger than the Δ values found for the metal complexes of thiomalic acid which are believed to contain bidentate carboxylate groups.
TABLE 4.21
Selected infrared data of α-thiopropionic acid and its cobalt complex

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(OH)</th>
<th>ν(S-H)</th>
<th>ν_{as}(OCO)</th>
<th>ν_{s}(OCO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>thiop H_2</td>
<td>3000</td>
<td>2580</td>
<td>1715 s,b</td>
<td>1420 s</td>
</tr>
<tr>
<td>K_2[Co(thiop)_2]·H_2O</td>
<td>3400 b</td>
<td>-</td>
<td>1570 vb</td>
<td>1380 b</td>
</tr>
</tbody>
</table>

Reflectance spectra

The bands at 20000 cm\(^{-1}\) and 14700 cm\(^{-1}\) in the visible spectrum of K_2[Co(thiop)_2]·H_2O (Table 4.18) can be assigned to the \(^4T_{1g}(F)\rightarrow^4T_{1g}(P)\) (ν_3) and \(^4T_{1g}(F)\rightarrow^4A_{2g}(F)\) (ν_2) transitions respectively, and the band due to the \(^4T_{1g}(F)\rightarrow^4T_{2g}(F)\) (ν_1) transition is split into two absorptions at 7700 and 8850 cm\(^{-1}\) (Fig.4.19). There is an additional absorption at 13400 cm\(^{-1}\), possibly due to a spin forbidden transition. This is good evidence for an octahedral environment with low symmetry.

Magnetism

The magnetic moment of K_2[Co(thiop)_2]·H_2O (Table 4.22) falls from a high-spin value of 4.59 B.M. at 295\(^\circ\) K to 3.56 at 90\(^\circ\) K with a large θ value of +122\(^\circ\) K (Fig. 4.22). The magnetic moment for the closely related complex Na_2[Co(thiop)_2] was reported to be 2.09 B.M. at room temperature, and it was deduced from this that the complex was low-spin. The low moment seems, from the present work, to be due to the presence of cobalt(III) in the complex as no precautions were taken to exclude air.
Octahedral cobalt(II) complexes with a $^4T_g$ ground state\textsuperscript{223,224} do not usually show such a great decrease of magnetic moment with decrease of magnetic moment with decreasing temperature so it is possible that some antiferromagnetic interaction is present, and a polymeric structure of the type shown in (VII) is suggested.

As in all the cobalt(II) complexes reported here, the low magnetic moments seem to confirm low-symmetry six-coordination with some antiferromagnetic interaction.


<table>
<thead>
<tr>
<th>$10^6 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>$T(°K)$</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8960</td>
<td>1.110</td>
<td>295.0</td>
<td>4.59</td>
</tr>
<tr>
<td>9410</td>
<td>1.060</td>
<td>262.5</td>
<td>4.44</td>
</tr>
<tr>
<td>10300</td>
<td>0.970</td>
<td>230.0</td>
<td>4.35</td>
</tr>
<tr>
<td>11100</td>
<td>0.901</td>
<td>198.5</td>
<td>4.19</td>
</tr>
<tr>
<td>12760</td>
<td>0.784</td>
<td>166.5</td>
<td>4.12</td>
</tr>
<tr>
<td>14170</td>
<td>0.706</td>
<td>135.0</td>
<td>3.91</td>
</tr>
<tr>
<td>16390</td>
<td>0.610</td>
<td>103.5</td>
<td>3.68</td>
</tr>
<tr>
<td>17620</td>
<td>0.567</td>
<td>90.0</td>
<td>3.56</td>
</tr>
</tbody>
</table>

$\theta = +122°$

Diamagnetic correction = $-121 \times 10^{-6}$ c.g.s.u.

<table>
<thead>
<tr>
<th>$10^5 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>$T(°K)$</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22550</td>
<td>0.443</td>
<td>295.0</td>
<td>7.29</td>
</tr>
<tr>
<td>24440</td>
<td>0.409</td>
<td>262.5</td>
<td>7.16</td>
</tr>
<tr>
<td>27230</td>
<td>0.367</td>
<td>230.0</td>
<td>7.07</td>
</tr>
<tr>
<td>30180</td>
<td>0.331</td>
<td>198.5</td>
<td>6.92</td>
</tr>
<tr>
<td>34770</td>
<td>0.287</td>
<td>166.5</td>
<td>6.80</td>
</tr>
<tr>
<td>41000</td>
<td>0.244</td>
<td>135.0</td>
<td>6.65</td>
</tr>
<tr>
<td>48220</td>
<td>0.207</td>
<td>104.0</td>
<td>6.33</td>
</tr>
<tr>
<td>54452</td>
<td>0.184</td>
<td>90.0</td>
<td>6.26</td>
</tr>
</tbody>
</table>

$\theta = +48°$

Diamagnetic correction = $-250 \times 10^{-6}$ c.g.s.u.

The measurements in the Table were carried out at 2060 gauss. Room temperature moments at 3300 and 4740 gauss were 6.79 and 6.45 B.M. respectively.
Figure 4.22

$K_2[Co(thiop)_2] \cdot H_2O$

$10^{-2} \chi_A$

$\mu_e (\text{B.M.})$

$T^\circ K$

0

100

200

300

0.70

1.40

5.0

2.5
Investigation of bis(tryptophanato)iron(II)

Infrared spectra

The zwitter-ionic character of amino acids in the crystalline state has been established beyond any doubt. The infrared spectra of free tryptophan and the iron(II) complex are similar (Table 4.23), except for the presence of an additional band at 3298 cm\(^{-1}\) which is assigned to the coordinated NH\(_2\) stretching vibration since the \(v\text{NH}\) vibration of the free NH\(_2\) group has been observed at 3360 cm\(^{-1}\).

**TABLE 4.23**

Selected infrared bands (cm\(^{-1}\)) of trpH and Fe(trp)\(_2\)•H\(_2\)O

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v\text{NH}(\text{indole}))</th>
<th>(v\text{NH})</th>
<th>(v\text{OH})</th>
<th>(v_{\text{as}}(\text{OCO}))</th>
<th>(v_{\text{s}}(\text{OCO}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>trpH</td>
<td>3410 s</td>
<td>-</td>
<td>1610 s,b</td>
<td>1415 s</td>
<td></td>
</tr>
<tr>
<td>Fe(trp)(_2)•H(_2)O</td>
<td>3400 s</td>
<td>3298 m</td>
<td>3360 m</td>
<td>1580 s,b</td>
<td>1417 s</td>
</tr>
</tbody>
</table>

Bonding through the N-H group of the indole ring is ruled out, as no significant shift is observed in the band (3400 cm\(^{-1}\)) due to the stretching vibration of this group. The band at 1610 cm\(^{-1}\) in free tryptophan has moved to 1580 cm\(^{-1}\) which indicates bonding to the metal ion through the oxygen atom of the ionized carboxylic group. So tryptophanate is coordinated to iron through the nitrogen and oxygen atoms of the ionised carboxylic group, and tryptophanate acts as a bidentate ligand in bis(tryptophanato)iron(II) monohydrate. The band around 3360 cm\(^{-1}\) in the spectrum of the complex is assigned to the \(v\text{OH}\) of water. The NH\(_2\) deformation mode (\(\delta\text{NH}_2\)) is obscured by the \(v_{\text{as}}(\text{OCO})\) band in Fe(tryp)\(_2\)•H\(_2\)O and no assignment has been made.
Reflectance spectra

Bis(tryptophanato)iron(II) monohydrate shows a very broad band at 10000 cm\(^{-1}\) (Fig. 4.23) which could be due to the transition \(\text{^5T}_{2g} \rightarrow \text{^5E}_g\) in octahedral symmetry\(^{228}\) and bands at 17700, 20600 and 24100 cm\(^{-1}\) which are assigned to charge transfer transitions.

Magnetism

Magnetic measurements on bis(tryptophanato) iron(II) monohydrate were carried out over the temperature range 295-90° K. The results are given in Table 4.22. The plots of reciprocal atomic susceptibility and effective magnetic moment against temperature are shown in Fig. 4.24. The magnetic moment for this compound is much higher than expected for four unpaired electrons (4.9-5.6 B.M.). This appears to be due to traces of ferromagnetic impurities because the magnetic moment varied with field strength (footnote, Table 4.22). However, the magnetic moment decreased as the temperature was lowered and this may be due to antiferromagnetic interaction in the compound. It may be that the ferromagnetic impurities were introduced during the unexplained colour change in the reaction. It is strange that the nitrosyl prepared from this complex (p.176) did not have a field-dependent magnetic moment.
FIGURE 4.23

Fe(SalABT)
Fe(trp)$_2$$ \cdot $H$_2$O
Fe(Sacac)$_2$en
Figure 4.24

Fe(trp)$_2$$\cdot$H$_2$O

$10^{-2} \chi_A$ vs. $T_\text{OK}$

$\mu_e (B.M.)$ vs. $T_\text{OK}$
Iron(II) complexes of some Schiff bases

As mentioned in the Introduction, the tetradeinate Schiff base NN'-ethylenbis(monothioacetylacetonimine) forms complexes with many divalent metals. The iron(II) complex is reported to have an unusual magnetic moment of 3.69 B.M. at room temperature. Because of this, and to investigate its reactions with molecules such as nitric oxide and oxygen, this compound has been re-investigated.

The 1:1 iron(II) complex of the doubly charged anion of the tridentate Schiff base 2-salicylideneaminobenzenethiol(H₂SalABT) (VIII) has not been reported, and because it would be expected to have a dimeric structure with bridging S atoms in which magnetic interaction would occur, it has been prepared.

![Chemical Structure](image)

(VIII)

The complexes Fe(ABT)₂ and Fe(AET)₂ were also prepared because it was intended to react these with salicylaldehyde to form iron(II) complexes of this Schiff's base through condensation with the coordinated o-aminobenzenethiol, but there was insufficient time to investigate this reaction. The Fe(ABT)₂ and Fe(AET)₂ showed the same Mössbauer behaviour as reported earlier.¹⁸⁸
Magnetism

The magnetic data for Fe(SalABT) and Fe[(Sacac)₂en] are given in Table 4.24 and Fig. 4.25.

The complex Fe(SalABT) is apparently antiferromagnetic as expected with a Néel point at about 110 K. It is believed that this compound has a structure (IX) involving bridging sulphur atoms.

The complex Fe[(Sacac)₂en] has a much lower moment at room temperature than reported earlier. As the magnetic moment decreased further as the temperature was reduced, it may be that a spin-equilibrium is present. On the other hand the low moment could be due to antiferromagnetic interactions in a polymeric or dimeric structure (X), or to the presence of temperature-independent paramagnetism and paramagnetic impurities in a low-spin compound.
TABLE 4.24
2-Salicylideneaminobenzenethiolatoiron(II)

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2}\chi_A^{-1}$</th>
<th>$T(°K)$</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4740</td>
<td>2.10</td>
<td>295.0</td>
<td>3.34</td>
</tr>
<tr>
<td>4950</td>
<td>2.02</td>
<td>262.5</td>
<td>3.22</td>
</tr>
<tr>
<td>5370</td>
<td>1.86</td>
<td>230.0</td>
<td>3.14</td>
</tr>
<tr>
<td>5560</td>
<td>1.77</td>
<td>198.0</td>
<td>2.97</td>
</tr>
<tr>
<td>5780</td>
<td>1.73</td>
<td>166.5</td>
<td>2.77</td>
</tr>
<tr>
<td>6063</td>
<td>1.66</td>
<td>135.0</td>
<td>2.55</td>
</tr>
<tr>
<td>5990</td>
<td>1.66</td>
<td>103.5</td>
<td>2.22</td>
</tr>
<tr>
<td>5870</td>
<td>1.70</td>
<td>90.0</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-130 \times 10^{-6}$ c.g.s.u.

NN'-Ethylenebis(monothioacetylacetoniminato)iron(II)

<table>
<thead>
<tr>
<th>$10^6 \chi_A$</th>
<th>$10^{-2}\chi_A^{-1}$</th>
<th>$T(°K)$</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>1319</td>
<td>1605</td>
<td>7.58</td>
<td>6.23</td>
</tr>
<tr>
<td>1000</td>
<td>1605</td>
<td>10.0</td>
<td>6.23</td>
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<tr>
<td>1055</td>
<td>1625</td>
<td>10.78</td>
<td>6.15</td>
</tr>
<tr>
<td>1108</td>
<td>1715</td>
<td>9.02</td>
<td>5.83</td>
</tr>
<tr>
<td>1236</td>
<td>1595</td>
<td>8.09</td>
<td>6.27</td>
</tr>
<tr>
<td>1444</td>
<td>1745</td>
<td>6.92</td>
<td>5.73</td>
</tr>
<tr>
<td>1514</td>
<td>1835</td>
<td>6.60</td>
<td>5.45</td>
</tr>
<tr>
<td>1444</td>
<td>1765</td>
<td>6.92</td>
<td>5.66</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-166 \times 10^{-6}$ c.g.s.u.
FIGURE 4.25

Fe(Sacac)$_2$en

$10^{-2} \chi^1_A$

$T^oK$

Fe(SalABT)

$10^{-2} \chi^1_A$

$T^oK$

$\mu_e$ (B.M.)

$\mu_e$ (B.M.)

(1)

(2)
It is not easy to account for the marked changes in the slopes of the temperature-susceptibility curves shown in Fig. 4.25 for duplicate preparations which had reasonable analyses. The changes in weight were small so that the accuracy of the measurements is low.

The much higher magnetic moment of 3.69 B.M. reported earlier is close to a spin-only value for three unpaired electrons which is unlikely for iron(II). It is possible that the earlier measurement had been carried out on a partly oxidised sample and it is hoped that Mössbauer data will help to distinguish between the possibilities by identifying whether or not more than one iron species is present.

The reflectance spectra at room temperature of the complexes Fe[(Sacac)\textsubscript{2}en] and Fe(SalABT) are shown in Fig. 4.23 and Table 4.25, but no assignments have been possible.
### Reflectance spectra

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reflectance</th>
<th></th>
<th>Reflectance</th>
<th></th>
<th>Reflectance</th>
<th></th>
<th>Reflectance</th>
<th></th>
<th>Reflectance</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe[(Sacac)₂en]</td>
<td>23500 sh</td>
<td>18200 s, vb</td>
<td>14800 sh</td>
<td>9800 sh</td>
<td>8400 s, b</td>
<td>7100 sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(SalABT)</td>
<td>23500 sh</td>
<td>18200 vb</td>
<td>16000 sh</td>
<td>11600 sb</td>
<td>9600 sh</td>
<td>7700 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Metal nitrosyls

Complexes which are reactive towards oxygen often give stable nitrosyls. Thus the reactions between several of the complexes described earlier in the thesis and nitric oxide have been studied in the hope of obtaining new metal nitrosyls.

Reactions with nitric oxide

Per mole of complex thiomalatoiron(II) trihydrate, thiomalatocobalt(II) trihydrate and thiopropionatoiron(II) absorbed two moles of nitric oxide; potassium thiomalatoiron(II) trihydrate, bis(glycinato)iron(II), bis(tryptophanato)iron(II) monohydrate, NN'-ethylenebis(monothioacetylacetoniminato)cobalt(II) absorbed one mole of nitric oxide (Table 4.26). Mononitrosyl NN'-ethylenebis (monothioacetylacetoniminato)cobalt was prepared during an undergraduate project and was known before.

In all cases the measured molar uptake agreed with the analyses of the products.
TABLE 4.26

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Product</th>
<th>Solvent</th>
<th>Molar up-take</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl$_2$ + tmH$_3^a$</td>
<td>Fe(tmH)(NO)$_2$</td>
<td>water</td>
<td>2.0 mole</td>
</tr>
<tr>
<td>CoCl$_2$ + tmH$_3^a$</td>
<td>Co(tm)(NO)$_2$</td>
<td>water</td>
<td>2.0 mole</td>
</tr>
<tr>
<td>FeCl$_2$ + thiophH$_2^a$</td>
<td>Fe(thip)(NO)$_2$</td>
<td>16% methanol</td>
<td>2.0 mole</td>
</tr>
<tr>
<td>K[Fe(tm)].3H$_2$O$^b$</td>
<td>K Fe(tm)NO</td>
<td>80% methanol</td>
<td>1.1 mole</td>
</tr>
<tr>
<td>Fe(gly)$_2^b$</td>
<td>Fe(gly)$_2$NO</td>
<td>methanol</td>
<td>1.0 mole</td>
</tr>
<tr>
<td>Fe(trp)$_2$.H$_2$O$^b$</td>
<td>Fe(trp)$_2$NO</td>
<td>water</td>
<td>1.0 mole</td>
</tr>
<tr>
<td>Fe(Sacac)$_2$en$^b$</td>
<td>Fe (Sacac)$_2$en NO</td>
<td>methanol</td>
<td>1.0 mole</td>
</tr>
<tr>
<td>Co(CH$_2$COO)$_2$ + H$_2$(Sacac)$_2$en$^c$</td>
<td>Co (Sacac)$_2$en NO</td>
<td>methanol</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) Metal chloride was first mixed with ligand under nitrogen which was then replaced with nitric oxide.

(b) Complexes were prepared, filtered off, and suspended in solvent nitrogen which was then replaced with nitric oxide.

(c) Metal acetate and ligand were mixed under nitric oxide.
Investigation of Nitrosyl Complexes

Infrared Spectra

By comparing the spectra of the nitrosyls and parent complexes in the NO stretching region (shown in Figures 4.26-4.29), the frequencies given in Table 4.27 have been assigned to the nitrosyl stretching vibrations.

**TABLE 4.27**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$ NO (cm$^{-1}$)</th>
<th>$\nu$ (CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(tmH)(NO)$_2$</td>
<td>1808 s</td>
<td>1718 sh</td>
</tr>
<tr>
<td></td>
<td>1735 s,b</td>
<td>1690 m</td>
</tr>
<tr>
<td>Co(tm)(NO)$_2$</td>
<td>1845 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1820 s</td>
<td>1708 sh</td>
</tr>
<tr>
<td></td>
<td>1790 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1764 m</td>
<td>1688 s</td>
</tr>
<tr>
<td></td>
<td>1750 m</td>
<td></td>
</tr>
<tr>
<td>Fe(thiop)(NO)$_2$CH$_3$OH</td>
<td>1790 m</td>
<td>1690 s</td>
</tr>
<tr>
<td></td>
<td>1760 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1726 m</td>
<td></td>
</tr>
<tr>
<td>K Fe(tm)NO .2H$_2$O</td>
<td>1785 s</td>
<td>1600 s,b</td>
</tr>
<tr>
<td></td>
<td>1750 s,b</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 4.27

Co(tml) • 3H₂O

Co(tml) • (NO)₂

wavenumber (cm⁻¹)
FIGURE 4.28

Fe(thiop)(NO)$_2$$^*$$\text{CH}_3\text{OH}$

wavenumber (cm$^{-1}$)
FIGURE 4.29

$K[\text{Fe(tm)}] \cdot 3\text{H}_2\text{O}$

$K[\text{Fe(tm)}](\text{NO}) \cdot 2\text{H}_2\text{O}$

wavenumber (cm$^{-1}$)
The N-O stretching frequencies of the thiomalato-iron nitrosyls occur in the range 1850 to 1750 cm\(^{-1}\), previously assigned to coordinated \(\text{NO}^+\). Dinitrosylthiomalatoiron could then be said to contain iron (O) and \(\text{NO}^+\), and this would agree with its diamagnetism.

The complex \(\text{Fe(tmh).3H}_2\text{O}\) has an absorption at 1570 cm\(^{-1}\) which is indicative of ionised and bidentate carboxylate groups; and this absorption has moved to higher frequency at 1690 cm\(^{-1}\) in the spectrum of dinitrosylthiomalatoiron. This suggests the presence of ionised and coordinated carboxylate groups in dinitrosylthiomalatoiron which could have the tetrahedral structure (XI).

\[
\text{O} \quad \text{NO} \\
\text{CH}_2 \quad \text{CO} \quad \text{Fe} \quad \text{NO} \\
\text{HC} \quad \text{S} \\
\text{CO}_2\text{H} \\
\text{XI}
\]

Since an absorption at 3100 cm\(^{-1}\) assigned to \(\nu(\text{OH})\) was observed, this further supports the proposed structure. The Mössbauer isomer shifts are compatible with the iron (O) formulation.\(^\text{212}\)

Dinitrosylthiopropionatoiron has three absorptions in the \(\text{NO}^+\) region and dinitrosylthiomalato-cobalt has a complicated series of absorptions in this region (Table 4.27).
The absorption at 1550 cm$^{-1}$ in the spectrum of Co(tmH)$\cdot$3H$_2$O which indicated bidentate carboxylate groups has moved to higher frequency at 1688 cm$^{-1}$ indicative of the presence of ionised and monodentate carboxylate groups in the dinitrosyl-cobalt complex (XII). As no absorption is observed for v(OH) of carboxylic acid in this compound, it was believed that both carboxylic acid groups are ionised and coordinated.

![Diagram](image)

The complex K[Fe(tm)NO]$\cdot$2H$_2$O has two absorptions at 1785 and 1750 cm$^{-1}$, and as this is a mononitrosyl the presence of two bands is presumably due to solid state effects.

**Magnetic properties**

Magnetic susceptibility measurements showed that Co(tm)(NO)$_2$, Fe(tmH)(NO)$_2$ and Fe(thiop)(NO)$_2$$\cdot$CH$_3$OH are diamagnetic. Dinitrosyliron complexes are known to be diamagnetic.\(^{173}\) In the case of the cobalt complex, it is possible that cobalt is present as Co$^1$ (d$^8$ configuration).
Potassium mononitrosylthiomalatoiron dihydrate has a magnetic moment below the spin-only value for two unpaired electrons ($S = 1$, $\mu_{s.o.} = 2.83$ B.M.) which decreased to a value close to that expected for one unpaired electron ($S = \frac{1}{2}$, $\mu_{s.o.} = 1.73$ B.M.) as the temperature was lowered (Table 4.28 and Fig. 4.30). If it is assumed that reaction of $K[Fe^{II}(tm)]\cdot3H_2O$ with nitric oxide produces a nitrosyl containing coordinated $NO^+$ and iron(I) ($3d^7$), one or three ($S = \frac{3}{2}$, $\mu_{s.o.} = 3.87$ B.M.) unpaired electrons can be present. It is difficult to see how two unpaired electrons could be present or to explain the temperature-dependent moment, except by assuming that the complex contains $S = \frac{3}{2}$ and $S = \frac{1}{2}$ spin isomers in equilibrium. This type of behaviour has been found in other iron mononitrosyls\textsuperscript{165} where coordination of nitric oxide brings the ligand field close to the crossover value.

Although reaction of a suspension of $K[Fe(tm)]\cdot3H_2O$ in aqueous methanol with nitric oxide gave the mononitrosyl $K[Fe(tm)]NO\cdot2H_2O$, the reaction of the corresponding sodium salt resulted in the absorption of 0.6 mole of nitric oxide per mole of complex. The product had $\nu(NO)$ absorptions at 1780 and 1750 cm$^{-1}$ but the analysis could only be fitted to the unsatisfactory formula $Na[Fe(tm)](NO)_{\frac{1}{2}}\cdotCH_3OH,H_2O$.

**Investigation of Fe[ ([Sacac]$_2$en)NO ]**

Nitrosyl$([Sacac]_2$en)$iron$ was prepared by reaction of $([Sacac]_2$en)$iron(II)$ with nitric oxide. Mononitrosyl $([Sacac]_2$en)cobalt
### TABLE 4.28

Potassium nitrosothiomalatoferate dihydrate

<table>
<thead>
<tr>
<th>$10^6 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>$T(°K)$</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3320</td>
<td>3.012</td>
<td>295.0</td>
<td>2.79</td>
</tr>
<tr>
<td>3460</td>
<td>2.890</td>
<td>262.5</td>
<td>2.69</td>
</tr>
<tr>
<td>3765</td>
<td>2.656</td>
<td>230.0</td>
<td>2.63</td>
</tr>
<tr>
<td>4020</td>
<td>2.487</td>
<td>198.5</td>
<td>2.52</td>
</tr>
<tr>
<td>4430</td>
<td>2.257</td>
<td>166.5</td>
<td>2.42</td>
</tr>
<tr>
<td>4760</td>
<td>2.100</td>
<td>135.0</td>
<td>2.26</td>
</tr>
<tr>
<td>5560</td>
<td>1.798</td>
<td>104.0</td>
<td>2.15</td>
</tr>
<tr>
<td>5860</td>
<td>1.706</td>
<td>90.0</td>
<td>2.05</td>
</tr>
</tbody>
</table>

$\theta = +114°$

Diamagnetic correction = $-103 \times 10^{-6}$ c.g.s.u.
has also been prepared. The NO stretching frequency of the cobalt complex is at 1638 cm\(^{-1}\), so it can be considered formally to contain cobalt(III) and NO\(^{-}\). It is diamagnetic, in agreement with this formulation.

In mononitrosyl[(Sacac)\(_2\)en]iron, the NO stretching frequency occurs at 1630 cm\(^{-1}\) (Fig. 4.31), which is in the range expected for NO\(^{-}\). From its magnetic moment, which is essentially independent of temperature (Table 4.29 and Fig. 4.32), this nitrosyl exists only in the \(S = \frac{1}{2}\) form unlike iron mononitrosyls of the tetradeinate ligand Salen\(^{163}\) and K[Fe(tml)]NO. It is believed that the compound contains formally Fe(III) and NO\(^{-}\), and it is expected to have a square-pyramidal structure (XIII), with a bent Fe-N-O group.

![Chemical structure](image)
FIGURE 4.31

Fe\{(Sacac)\textsubscript{2}en\}

Fe\{(Sacac)\textsubscript{2}en\}(NO)

wavenumber (cm\textsuperscript{-1})
### TABLE 4.29

Nitrosylbis(trp) iron dihydrate

<table>
<thead>
<tr>
<th>$10^6 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>T(°K)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7520</td>
<td>1.329</td>
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<td>4.21</td>
</tr>
<tr>
<td>7800</td>
<td>1.282</td>
<td>262.5</td>
<td>4.06</td>
</tr>
<tr>
<td>8440</td>
<td>1.184</td>
<td>230.0</td>
<td>3.94</td>
</tr>
<tr>
<td>8910</td>
<td>1.122</td>
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</tr>
<tr>
<td>8960</td>
<td>1.116</td>
<td>166.5</td>
<td>3.45</td>
</tr>
<tr>
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<td>1.077</td>
<td>135.0</td>
<td>3.16</td>
</tr>
<tr>
<td>9500</td>
<td>1.052</td>
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</tr>
<tr>
<td>9660</td>
<td>1.035</td>
<td>90.0</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-280 \times 10^{-6}$ c.g.s.u.

Nitrosyl[(Sacac)$_2$en]iron

<table>
<thead>
<tr>
<th>$10^6 x_A$</th>
<th>$10^{-2} x_A^{-1}$</th>
<th>T(°K)</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1487</td>
<td>6.724</td>
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</tr>
<tr>
<td>1717</td>
<td>5.824</td>
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<td>1.89</td>
</tr>
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<td>1933</td>
<td>5.173</td>
<td>230.0</td>
<td>1.88</td>
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<td>2126</td>
<td>4.703</td>
<td>198.5</td>
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<td>2500</td>
<td>4.000</td>
<td>166.0</td>
<td>1.82</td>
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<td>2990</td>
<td>3.344</td>
<td>135.0</td>
<td>1.79</td>
</tr>
<tr>
<td>3815</td>
<td>2.621</td>
<td>104.0</td>
<td>1.78</td>
</tr>
<tr>
<td>4360</td>
<td>2.293</td>
<td>90.0</td>
<td>1.77</td>
</tr>
</tbody>
</table>

$\theta = +50$

Diamagnetic correction = $-176 \times 10^{-6}$ c.g.s.u.
Fe(trp)_2(NO), 2H_2O

Fe[(Sacac)_2en]NO

\(10^{-2} \chi_\alpha^{-1}\)

\(\mu(e_{B.M.})\)

\(T^0K\)
Investigation of Nitrosyl(aminoacid)iron Complexes

Mononitrosyl bis(glycinato)iron and mononitrosyl bis(tryp tophanato)iron complexes have been prepared because preliminary work suggested that these are further examples of nitrosyls with the unusual $S = \frac{3}{2}$ configuration, for which little magnetic or Mössbauer data are available.

The NO stretching frequencies of Fe(gly)$_2$NO and Fe(trp)$_2$NO.2H$_2$O are at 1750 and 1778 cm$^{-1}$ respectively (Figures 4.33 and 4.34).

Magnetic Susceptibility Measurements

A magnetic susceptibility measurement on mononitrosyl(tryp tophanato)iron dihydrate was carried out over the temperature range 300-900 K and the results are given in Table 4.29 and Fig. 4.32.

The magnetic moment of the compound at room temperature is 4.21 B.M., slightly higher than spin-only value for three unpaired electrons, confirming the preliminary work. The magnetic moment decreased as the temperature was lowered to approximately that for one unpaired electron ($S = \frac{1}{2}$, $\mu_{s.o.} = 1.73$ B.M.). This compound is similar in behaviour to other complexes in which spin equilibria occur. Mononitrosyl bis(glycinato)iron$^{168}$ has a room temperature magnetic moment of 3.8 B.M., but this did not change on cooling, so that this nitrosyl exists only as the $S = \frac{3}{2}$ form over the available temperature range.
Figure 4.33

Fe(gly)$_2$

Fe(gly)$_2$NO

wavenumber (cm$^{-1}$)
FIGURE 4.34

Fe(try)₂·H₂O

[Fe(try)₂]NO₂·2H₂O

wavenumber (cm⁻¹)
CHAPTER V

GOLD COMPLEXES
Introduction

Gold ($5d^{10}6s^1$) can exist in four oxidation states, the most important of these being gold(I) ($5d^{10}$) and gold(III) ($5d^8$). Gold(III) is the most stable state in aqueous solution; it forms many diamagnetic, usually coloured, compounds in which it exhibits a wide range of stereochemistries.

Gold(I) has a closed shell configuration and its compounds are diamagnetic and colourless, except in cases where colour results from the anion or charge transfer bands. A few compounds of gold(II) and gold(V) are known, but these are unstable in aqueous solution.

Gold(III) complexes

Gold trihalides are dimers\(^{231-233}\) with chloride and bromide, whereas AuF\(_3\) exists as a fluoride-bridged polymer.\(^{234}\) The planar complex anions $[\text{AuX}_4]^-\)$ can be prepared by dissolving AuX in alkali metal halides ($X = \text{Cl}$ or Br). Beurskens et al\(^{235}\) have reported the preparation, structure and properties of dithiocarbamate complexes of formula $[\text{Au}(\text{S}_2\text{CN}(n-\text{C}_4\text{H}_9)_2][\text{AuX}_2]$, where $X = \text{Cl}$, Br, I or CN. The chloride, bromide and iodide are isomorphous, and the crystal structure of the bromide has been determined. Au(I) is linearly coordinated in the $\text{AuX}_2^-$ ion, and Au(III) is in planar coordination with four sulphur atoms. The structures of $\text{MBr}_2\text{S}_2\text{CN}(n-\text{C}_4\text{H}_9)_2$, where $\text{M} = \text{Au(III)}$ or Cu(III), have been determined.\(^{236}\) In these complexes copper(III) and gold(III) are in planar coordination, and the diamagnetic behaviour of these compounds is in accord with low-spin d\(^8\)
configurations. Four-, five- and six-coordinated Au(III) chelates with o-phenylenebisdimethylarsine (as) have been prepared from aqueous solution. Duckworth et al. have reported the structures in Table 5.1 for these complexes.

**TABLE 5.1**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Coordination No.</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Au(as)₂]³⁺</td>
<td>4</td>
<td>planar</td>
</tr>
<tr>
<td>[Au(as)₂I]²⁺</td>
<td>5</td>
<td>trigonal bipyramidal</td>
</tr>
<tr>
<td>[Au(as)₂I₂]⁺</td>
<td>6</td>
<td>octahedral</td>
</tr>
</tbody>
</table>

**Gold(I) complexes**

Gold(I) generally exhibits linear two-fold coordination because the relatively small energy difference between the filled 5d and the unfilled 6s orbitals permits extensive hybridisation to give linear sp-hybrids. The classical examples are AuX (X = CN, C₂, Br, I), in which, as in many gold(I) complexes, the metal atom achieves linear coordination through polymerization (I).

(I)
Gold(I) can also form trigonal planar complexes\textsuperscript{242}, e.g. chlorobis(triphenylphosphine)gold(I), which is formed when an excess of PPh\textsubscript{3} is refluxed with C\&AuPPh\textsubscript{3} in benzene (II).

\begin{center}
\begin{tikzpicture}
  \node (1) at (0,0) {Au};
  \node (2) at (-1,-1) {Ph\textsubscript{3}P};
  \node (3) at (1,-1) {PPh\textsubscript{3}};
  \draw (1) -- (2);
  \draw (1) -- (3);
  \node (4) at (-2,0) {Cl};
  \draw (1) -- (4);
\end{tikzpicture}
\end{center}

(II)

From measurements in aqueous alcohol gold(I) is thought to be tetrahedrally coordinated in complexes\textsuperscript{243,244} of type (III)

\begin{center}
\begin{tikzpicture}
  \node (1) at (0,0) {Au};
  \node (2) at (-1,-1) {As};
  \node (3) at (-2,-2) {As};
  \node (4) at (-1,-2) {Et\textsubscript{2}};
  \node (5) at (1,-1) {As};
  \node (6) at (2,-2) {As};
  \node (7) at (1,-2) {Et\textsubscript{2}};
  \node (8) at (0,0) {X (X = halide)};
  \draw (1) -- (2);
  \draw (1) -- (3);
  \draw (1) -- (4);
  \draw (1) -- (5);
  \draw (1) -- (6);
  \draw (1) -- (7);
\end{tikzpicture}
\end{center}

(III)

In the complex \([\text{Au(III)}(\text{dimethylglyoximate})_2][\text{AuCl}_2]\), the ion AuCl\textsubscript{2}\textsuperscript{−} is linear, but if Au-Au bonding is included then the Au(I)
must be considered square-planar, and the configuration about Au(III) is octahedral. The structure of Na$_3$[Au(S$_2$O$_3$)$_2$] • 2H$_2$O (IV) shows the preference of Au(I) for S- rather than O-coordination.

Water molecules are hydrogen-bonded to the sulphur and oxygen atoms of the thiosulphate ligands. Gold(I)NN'-dipropydithiocarbamate has a dimer structure (V).

Gold(I) complexes of β-D-thioglucose, thiomalic acid, glutathione, L-cysteine and D-pencillamine have been prepared, but their structures
are not known. The first two compounds have been used in the treatment of rheumatoid arthritis. The physiological action of these gold drugs is unknown, although from its general chemistry gold is likely to be associated with sulphur-containing proteins. The structure of the drugs is also unknown, and so thiomalatogold(I) complexes have been synthesised, and some reactions with S-donor ligands investigated in this work.
RESULTS AND DISCUSSION

Thiomalatogold(I) Complexes

Mixing equimolar solutions of gold(I) cyanide and thiomalic acid (tmH₃) resulted in the formation of Au(tmH₂). The infrared spectrum of Au(tmH₂) (Table 5.2) shows that the band at 2560 cm⁻¹ assigned as $\nu$(S-H) in the spectrum of the free acid is absent. The bands due to the $\nu_{as}$(0CO) and $\nu_{s}$(0CO) vibrations of the carboxylate groups are almost unaffected by complex formation, and a broad $\nu$(OH) absorption was found at 3100cm⁻¹. Thus it would appear that the complex Au(tmH₂) contains an Au-S bond, and that the carboxylate groups are not ionised and do not complex with the gold.

The infrared spectra of the complex salts, Na₂[Au(tm)], Ca[Au(tm)]₂H₂O and Ba[Au(tm)]₂H₂O (Table 5.2) do not show $\nu$(S-H) peaks. The values of $\Delta$, where $\Delta = \nu_{as}$(0CO) - $\nu_{s}$(0CO), vary from 190 to 160cm⁻¹, and are thus in the range found for complexes containing ionic carboxylate groups. The spectra of calcium and barium thiomalatoaurates (I) have very broad bands at about 3400cm⁻¹ which are assigned to the $\nu$(O-H) stretches of hydrogen-bonded water.

Molecular Weight Measurement

Since gold(I) is generally linearly coordinated the formulae (A) and (B) cannot accurately represent the environment of the Au(I) ions.
### TABLE 5.2
Selected infrared bands of thiomalic acid and its gold complexes

<table>
<thead>
<tr>
<th></th>
<th>(\nu_{\text{OH}})</th>
<th>(\nu_{\text{SH}})</th>
<th>(\nu_{\text{as}(\text{OCO})})</th>
<th>(\nu_{\text{s}(\text{OCO})})</th>
<th>(\Delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{tmH}_3)</td>
<td>3000 vb</td>
<td>2560 m</td>
<td>1690 s,b</td>
<td>1425 s</td>
<td>265</td>
</tr>
<tr>
<td>(\text{AutmH}_2)</td>
<td>3100 vb</td>
<td>-</td>
<td>1700 s,b</td>
<td>1410 s</td>
<td>290</td>
</tr>
<tr>
<td>(\text{Na}_2[\text{Autm}])</td>
<td>-</td>
<td>-</td>
<td>1580 b</td>
<td>1390 m</td>
<td>190</td>
</tr>
<tr>
<td>(\text{Ca}[\text{Au(tm)}] \cdot \text{H}_2\text{O})</td>
<td>3400 vb</td>
<td>-</td>
<td>1570 b</td>
<td>1390 s</td>
<td>180</td>
</tr>
<tr>
<td>(\text{Ba}[\text{Au(tm)}] \cdot \text{H}_2\text{O})</td>
<td>3400 vb</td>
<td>-</td>
<td>1565 b</td>
<td>1405 m</td>
<td>160</td>
</tr>
<tr>
<td>(\text{Au}_2\text{tmH}_2 \cdot \text{cys})</td>
<td>-</td>
<td>-</td>
<td>1700 m</td>
<td>1390 m</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1610 s</td>
<td></td>
<td>220</td>
</tr>
</tbody>
</table>

### TABLE 5.3
Selected infrared bands of cysteine and cysteinategold(I)

<table>
<thead>
<tr>
<th></th>
<th>(\nu_{\text{S-H}})</th>
<th>(\nu_{\text{as}(\text{OCO})})</th>
<th>(\nu_{\text{s}(\text{OCO})})</th>
<th>(\Delta)</th>
<th>(\nu_{\text{NH}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CysH})</td>
<td>2540 m</td>
<td>1590 s</td>
<td>1402 s</td>
<td>188</td>
<td>3200 m</td>
</tr>
<tr>
<td>(\text{AuCys})</td>
<td>-</td>
<td>1580 b</td>
<td>1380 s</td>
<td>200</td>
<td>3150 m</td>
</tr>
</tbody>
</table>
Thus, molecular weight measurements were carried out on thiomalic acid, thiomalatogold(I) and sodium thiomalatogold(I) in water in an attempt to determine the degree of polymerisation, and the results are given in Table 5.4 and Fig. 5.1.

The pK₁ and pK₂ values for thiomalic acid are 3.64 and 4.64 respectively. From these it can be calculated that a molecular weight of 147.8 would be expected for thiomalic acid, allowing for dissociation. The experimental results (Table 5.4) gave molecular weight of 148.0. This compares favourably with the formula molecular weight of 150 confirming that dissociation of protons does not affect very much the molecular weight determinations.

In the case of thiomalatogold(I), the experimental molecular weight is 665, about twice the formula molecular weight of 346. Coordination of gold to the sulphur atom of thiomalic acid would not be expected to increase the dissociation of the -CO₂H groups greatly because the gold ion is some distance from them. However, its effect is unknown, but it can be concluded that thiomalatogold(I) is at least a dimer in solution.
<table>
<thead>
<tr>
<th></th>
<th>AR (g/Kg)</th>
<th>C (g/Kg)</th>
<th>AR/C</th>
<th>M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{tmH}_3)^a</td>
<td>211.5</td>
<td>10.7</td>
<td>19.76</td>
<td>146.2</td>
</tr>
<tr>
<td>(M.W. 150)</td>
<td>201.0</td>
<td>10.2</td>
<td>19.70</td>
<td>150.8</td>
</tr>
<tr>
<td></td>
<td>164.0</td>
<td>8.3</td>
<td>19.75</td>
<td>133.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19.73</td>
<td>148.0</td>
</tr>
<tr>
<td>(\text{Au(tmH}_2))</td>
<td>30.0</td>
<td>1.55</td>
<td>19.35</td>
<td>672.0</td>
</tr>
<tr>
<td>(M.W. 346)</td>
<td>33.0</td>
<td>1.70</td>
<td>19.41</td>
<td>622.0</td>
</tr>
<tr>
<td></td>
<td>31.5</td>
<td>1.61</td>
<td>19.56</td>
<td>589.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19.40</td>
<td>665.0</td>
</tr>
<tr>
<td>(\text{Na}_{2}\text{Au(tm)})</td>
<td>54.0</td>
<td>2.77</td>
<td>19.49</td>
<td>79.2</td>
</tr>
<tr>
<td>(M.W. 390)</td>
<td>45.0</td>
<td>2.31</td>
<td>19.48</td>
<td>77.7</td>
</tr>
<tr>
<td></td>
<td>36.5</td>
<td>2.15</td>
<td>16.97</td>
<td>62.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.00</td>
<td>80.1</td>
</tr>
</tbody>
</table>

\(a - pK_1 = 3.64;\) \(pK_2 = 4.64;\) \(pK_3 = 10.37\)
FIG. 5.1

**tmH$_3$**

\[ \Delta R/C \]

\[ C(\text{g/kg}) \]

**Au(tmH$_2$)**

\[ \Delta R/C \]

\[ C(\text{g/kg}) \]

**Na$_2[Au(tm)]$**

\[ \Delta R/C \]

\[ C(\text{g/kg}) \]
The experimental molecular weight for sodium thiomalatogold(I) is 80.1, the formula value is 390, and the experimental value is even less than that (130) expected for complete dissociation into three ions. Hydrolysis of the carboxylate groups by water could occur to produce hydroxyl ions and the thiomalatogold(I) in equilibrium. This would cause the molecular weight to be lower than expected.

A $^{13}$C n.m.r. investigation of aqueous sodium thiomalatogold(I) in excess thiomalic acid reported during the course of the present work has demonstrated$^{248}$ the presence of the species $\text{Au}_4\text{(SR)}^{17-}$ in solution, \{SR = \[(\text{SCH}_2\text{COO})_2\]\}. From the available evidence, it can be concluded that Au(I)-thiomalates are polymerised.

In view of the low affinity of Au(I) for oxygen ligands, the problem of how Au(I) attains a higher coordination number in Au(I)-thiomalate can be examined by comparison with the 1:1 Ag(I) alkylthiolates which have been studied crystallographically$^{249}$. Ag(I)-cyclohexanethiolate has an infinite Ag-S framework with a combination of trigonal-planar AgS$_3$ and linear AgS$_2$ units. Possible structures using these types of unit for gold(I)-thiomalate in solution are:
Cysteinategold(I)

Cysteinategold(I) was prepared as it was a possible product of reaction between thiomalategold(I) and cysteine. It was isolated by mixing equimolar amounts of potassium aurocyanide and L-cysteine in acid solution. The infrared spectrum of Au(cys) shows that the band at 2545 cm$^{-1}$ assigned$^{216}$ to $\nu$(S-H) in the free acid is absent. Thus, it is believed that the sulphur atom is bonded to the gold(I). The infrared spectrum of Au(cys) shows some differences from that of L-cysteine in the $\nu_{as}$(OOC) and $\delta$NH regions (Table 5.3). Amino acids such as L-cysteine exist as zwitterions, and strong hydrogen bonding exists in the crystal$^{250}$. Possibly in solid Au(cys) the zwitter-ionic form is present, and the gold atom may be weakly coordinated to the carboxylate group, thus increasing $\Delta$. 
Reaction of thiomalatogold(I) with sulphur-containing ligands

It has been discussed earlier that thiomalatogold(I) forms a low molecular weight polymer in solution. This is because gold(I) cannot be linearly coordinated in a monomeric 1:1 Au(I)-to-thiomalate complex, and interaction between thiomalatogold(I) units can be anticipated. The coordination of other sulphur donor ligands to gold(I)-thiomalates can also be anticipated, and as glutathione, cysteine and SH-containing proteins such as haemoglobin and serum albumin are available in vivo such reactions can be important in drug action. Several workers have indeed shown that thiomalatogold(I) interacts with SH-containing proteins. It is not certain whether thiomalate is displaced, and the products of reaction are not known, and thiol exchange reactions between thiomalatogold(I) and small S- and SH-containing ligands could be models for biologically-important reactions.

Thiomalatogold(I) was titrated with cysteine, glutathione and thiomalic acid using sodium nitroprusside as indicator for free SH groups. The colour change from orange to pale orange is not sharp so it was difficult to detect the end point accurately. However, the colour change occurred at approximately 1:1 molar ratios (Table 5.5), and a permanent precipitate appeared with cysteine.

Larger quantities of reactants were then used to try to isolate the species present in solutions with 1:1 molar ratios of reactants. The reactions between thiomalatogold(I) and various sulphur-donor
ligands were carried out in water. With glutathione it was necessary to add methanol to obtain a solid, and the details are given in Table 5.5.

The displacement of some or all of the thiomalate from thiomalatogold(I) on addition of different thiols appears to have occurred from identification of the different precipitates by infrared spectroscopy and elemental analysis. Sodium diethyldithiocarbamate released all of the thiomalic acid from thiomalatogold(I) in aqueous solution and diethyldithiocabamatogold(I) was formed. However, in the reaction with cysteine only half of the thiomalic acid was released and cysteinatothiomalatodigold(I) was formed. The infrared spectrum (Table 5.2) shows, in the carboxylic group region, an absorption at 1700 cm\(^{-1}\) belonging to the \(\nu_{as}(\text{OCO})\) of thiomalic acid; this band has been identified for thiomalatogold(I) previously; and a band at 1610 cm\(^{-1}\) which was previously assigned to the ionised carboxyl group of cysteine in cysteinatogold(I); the \(\delta(NH_3^+)\) absorptions are obscured by the \(\nu(\text{OCO})\) bands. In the reaction of glutathione with thiomalatogold(I) only two-thirds of the thiomalate was released because bis(glutathionato)mono-(thiomalato)triaurate(I) was obtained on the addition of methanol to the aqueous solution. The infrared spectrum of this compound has three absorption bands between 1500-1800 cm\(^{-1}\), the band at 1720 cm\(^{-1}\) being assigned to \(\nu_{as}(\text{OCO})\) of the unionised carboxyl group of thiomalic acid and those at 1630 and 1530 cm\(^{-1}\) are assigned to the \(\delta(NH_2)\) and \(\nu_{as}(\text{CO}_2^-)\) groups of glutathione. No precipitate was formed on the addition L-methionine to an
TABLE 5.5

Reaction of aqueous thiomalatogold(I) with R-SH, RSR', and NaS₂CN(C₂H₅)₂

<table>
<thead>
<tr>
<th>Added ligand</th>
<th>Wt. (a) of added ligand (mg)</th>
<th>Wt. (a) of thiomalatogold(I) (mg)</th>
<th>Molar ratio</th>
<th>Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cysteine</td>
<td>24.2</td>
<td>69.2</td>
<td>1:1</td>
<td>white</td>
</tr>
<tr>
<td>2 glutathione</td>
<td>61.4</td>
<td>69.2</td>
<td>1:1</td>
<td>white</td>
</tr>
<tr>
<td>3 methionine</td>
<td>14.92</td>
<td>34.6</td>
<td>1:1</td>
<td>-</td>
</tr>
<tr>
<td>4 thiomalic acid</td>
<td>15.0</td>
<td>34.6</td>
<td>1:1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>17.3</td>
<td>2:1</td>
<td>-</td>
</tr>
<tr>
<td>5 albumin</td>
<td>20.0</td>
<td>38.0</td>
<td>-</td>
<td>white</td>
</tr>
<tr>
<td>6 sodium diethyl dithiocarbamate</td>
<td>24.7</td>
<td>30.0</td>
<td>1:1</td>
<td>yellow</td>
</tr>
</tbody>
</table>

(a) In 10 cm³ of water
aqueous solution of thiomalatogold(I) even when methanol, ethanol or acetone was added to the mixture. This suggests that unlike thiols, a thioether does not interact with thiomalatogold(I).

Rabenstein\textsuperscript{254} has found that in the Hg(II)-glutathione complex the binding is almost exclusively to sulphur. So in the mixed ligand complexes cysteinatothiomalatodiaurate(I) and bis(glutathionato) mono(thiomalate)triaurate(I), cysteine and glutathione are likely to be bonded through the sulphur. Isab and Sadler reported\textsuperscript{248} that reaction of mercaptoacetic acid or N-acetyl-L-cysteine with thiomalatogold(I) leads to release of some of the thiomalate.

When barium chloride and calcium hydroxide were reacted with sodium thiomalatoaurate(I) at pH 7 in the presence of sodium thiomalate, i.e. in the conditions in which Au\textsubscript{4}(tm)\textsuperscript{3-} is said to exist, Ca[Au(tm)].2H\textsubscript{2}O and Ba[Au(tm)].H\textsubscript{2}O respectively were precipitated. This means either that Au\textsubscript{4}(tm)\textsuperscript{3-} is not present in solution or the cluster is broken up to give the calcium or barium salt.

From the reactions studied in the present work it is concluded that the 1:1 complex thiomalatogold(I) reacts with SH-containing molecules which bind more strongly to Au(I) than a ligand having an-SCH\textsubscript{3} group. It is likely that the exchange reactions of thiols with Au(I) take place via the sulphur only, and the NH\textsubscript{2} and CO\textsubscript{2}\textsuperscript{-} groups are usually not involved. From the exchange reaction of diethyldithiocarbamate with thiomalatogold(I) it appears that diethyldithiocarbamatogold(I) is the more stable complex.
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