METAL COMPLEXES OF AMINOACID ESTERS AND AMIDES

A thesis presented to the University of Surrey for the degree of Master of Philosophy in the Faculty of Biological and Chemical Sciences.

by

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ABSTRACT

Complexes of ethylenediaminetetraacetamide with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Mg(II), Ca(II), Ba(II), Zn(II), Cd(II), Hg(II) and La(III) have been prepared as chloride salts (and perchlorate in the case of Cu(II)) and characterised on the basis of microanalytical, spectral, magnetic and conductivity data. The corresponding N-deuterated complexes have also been prepared and their spectral properties have been used in the characterisation of the undeuterated complexes. In aqueous solution the Cu(II) complex behaves as a dibasic acid and ionisation constants for the deprotonation of two amide groups in this complex have been obtained by potentiometric methods. In addition the conjugate base complex has been isolated from solution. Complexes of the tetramethylester of Edta with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cd(II), Hg(II) and Sn(II) have also been prepared and characterised using the above methods.

The reactions between trans-[Co(en)$_2$Cl$_2$]Cl (en = ethylenediamine) and ethylenediaminemonoacetic acid (EdmaH) and its ethyl ester (EdmaEt) have been found to give the products trans-[Co(en)$_2$Cl(EdmaH)]$^{2+}$ and cis-[Co(en)$_2$Cl(EdmaEt)]$^{2+}$ respectively. In the former the amino acid is monodentate and bonded through its carboxylate group to the metal ion while in the latter the amino acid ester behaves as a monodentate N-bonded ligand. The kinetics of the Hg(II) promoted acid hydrolysis, in which Cl$^-$ is replaced by H$_2$O, and base hydrolysis, in which Cl$^-$ is replaced by OH$^-$ have been inves-
tigated at 25±0.1°C in both cases. The hydrolysis of EdmaEt in the presence of some metal ions has also been studied at 25±0.1°C and the order in which these metal ions promote ester hydrolysis is Cu(II) > Co(II) > Ni(II).

Finally the synthesis and properties of a number of divalent metal ion (Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)) complexes of the ligand 2-carboethoxy-1,10-phenanthroline have been investigated.
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INTRODUCTION
Investigations of metal complexes with amino acid ester, amide and peptide ligands have been widespread over the last two decades. These investigations have included not only the preparation and structural elucidation of the complexes but also the hydrolysis of the ester, amide and peptide ligands. The impetus for this work has arisen from the realization that such compounds serve as excellent models for the action of the complex esterase and peptidase metallo-enzymes in biological systems, e.g. carboxypeptidase A, leucine aminopeptidase and glycylglycine dipeptidase.

Earlier kinetic investigations of the hydrolysis of coordinated substrates have been hampered by the difficulty in identifying the hydrolytically most active species in solution. The difficulty arises from the fact that solutions containing metal ions (M\(^{n+}\)) and ester, amide or peptide ligands (L) may contain a large number of complex species e.g. ML\(^{n+}\), ML\(_2^{n+}\), ML\(_3^{n+}\) etc. In addition the mixed ligand complexes [M(L)(A)]\((n-1)^+\), [M(L)]\(_2(A)^{(n-1)^+}\) etc. will also form in solution as hydrolysis of the ligand proceeds. (A is the hydrolysis product). This problem has partly been resolved by using polydentate ligands which form only 1:1 complexes with metal ions e.g. the tetramethyl ester of Edta (I).
This approach has considerably simplified the treatment of kinetic data. Another recent development in this field has involved the use of inert cobalt(III) systems, containing the substrate as one of the ligands\(^6,7\) This has helped to resolve mechanistic ambiguities arising from the use of labile metal ion complexes.

This thesis describes the preparation and properties of both types of complexes as well as some kinetic investigations of hydrolysis reactions of the ligands.

1. Aminoacid Ester Complexes Containing Coordinated Ester Groups.

In 1952 Kroll discovered that the hydrolysis of aminoacid esters was catalysed by metal ions\(^8\) He found that the complexes of ethylglycinate with copper(II), cobalt(II) and manganese(II) underwent relatively rapid base hydrolysis at pH 7, conditions under which hydrolysis of the free ester was unobserved. Kroll explained the catalytic behaviour of the metal ion in terms of its ability to polarize the ester carboxyl group (II) and consequently to increase its susceptibility to attack by the nucleophilic hydroxide ion.

\[
\begin{align*}
\text{CH}_2\text{C-OR'}^+ \\
\text{H}_2\text{N} \\
\text{M} \\
\end{align*}
\]
This mechanism is similar to that involved in the acid catalysed hydrolysis of esters. Such polarization of the carbonyl group by metal ions has since been verified by infrared spectral studies of metal complexes containing glycine ester and \( \alpha \)-alanine ester ligands\(^9,10\)

Thus, whereas the free amino acid esters and complexes containing monodentate N-coordinated amino acid esters (III) show \(-C=O\) stretching frequencies in the 1740 cm\(^{-1}\) region of their infrared spectra, metal ion complexes containing the aminoacid esters as bidentate ligands (IV, V) have carbonyl stretching frequencies as much as 90 cm\(^{-1}\) lower. This indicates that the electron density in the carbonyl group is considerably distorted by the metal ions.
(a) Formation and Reactions of $\text{[Co(en)}_2\text{glyOEt]}^{3+}$ (V).

The ester complex (V) was first identified in aqueous solution as a product of the Hg(II) assisted removal of $\text{Cl}^-$ from the complex cis-$\text{[Co(en)}_2\text{glyOEtCl]}^2+$ (VI). This complex loses $\text{Cl}^-$ (as HgCl$^+$) in a rate determining step giving a five coordinated intermediate (VII).

\[
\begin{align*}
\text{(VI)} & \\
\text{(en)}_2\text{-Co} & \begin{array}{c}
\text{NH}_2\text{-CH}_2\text{-C}^\text{\textcircled{O}}\text{C}_2\text{H}_5
\end{array} \text{Cl} + \text{Hg(II)} \\
& \xrightarrow{\text{slow}} -\text{HgCl}^+
\end{align*}
\]

\[
\begin{align*}
\text{(VII)} & \\
\text{(en)}_2\text{-Co} & \begin{array}{c}
\text{NH}_2\text{-CH}_2\text{-C}^\text{\textcircled{O}}\text{C}_2\text{H}_5
\end{array} \\
& \rightarrow \text{(en)}_2\text{-Co} \begin{array}{c}
\text{NH}_2\text{-CH}_2\text{-C}^\text{\textcircled{O}}\text{C}_2\text{H}_5
\end{array}
\]
\]

\[
\begin{align*}
\text{(V)} & \\
\text{(en)}_2\text{-Co} & \begin{array}{c}
\text{NH}_2\text{-CH}_2\text{-C}^\text{\textcircled{O}}\text{C}_2\text{H}_5
\end{array}
\]
\]

In a subsequent rapid step the ester carbonyl group enters the vacant coordination site (in preference to water) giving the chelated ester product (V). This complex, on standing, undergoes a reaction involving hydrolysis of the highly activated ester group. In acidic solutions ($\text{pH} < 4$) the rate expression for the hydrolysis reaction is
indicating that attack by the relatively weak nucleophile, H₂O, occurs. In solutions of pH > 7 however, hydroxide ion is the attacking nucleophile and the rate expression

\[
\text{Rate} = k_2 \text{[Ester complex (V)]} [\text{OH}^-]
\]

is observed for the hydrolysis reaction, which is very rapid under these conditions (reaction (2)).
Metal ion activation of ester groups with respect to attack by nucleophiles has also proved extremely useful synthetically. Thus chelated ester complexes like (V) in nonaqueous media are attacked by aminoacid esters (reaction (3)), amines, and alcohols to give complexes containing peptide ester, amide and transesterifed ligands respectively.

\[
\text{(en)}_2^+\text{CoO}^+\text{NH}-\text{CH}_2-\text{CO}_2\text{R} + \text{NH}_2-\text{CH}_2-\text{CO}_2\text{R} \rightarrow \text{(V)}
\]

\[
\text{(en)}_2^+\text{CoO}^+\text{NH}-\text{CH}_2-\text{CO}_2\text{R} + \text{NH}_2-\text{CH}_2-\text{CO}_2\text{R} \rightarrow \text{(IX)}
\]

Reaction (3) provides an example of a situation where a metal ion singularly plays the role of two reagents commonly used in peptide synthesis. It activates the carbonyl group to nucleophilic attack, fulfilling the role of coupling agents such as dicyclohexylcarbodiimide. Secondly it protects the
sensitive amino group on the coordinated aminoacid ester and in this way functions like N-protecting groups such as carboxbenzoxo and dimerone (5,5-dimethylcyclohexane-1,3-dione).

(b) The Cu(II) Complex of the Tetramethyl Ester of EDTA.

In aqueous solution Cu(II) forms a 1:1 complex with the tetramethyl ester of Edta (EdtaMe₄)⁵. On the basis of infrared spectral evidence it appears that two of the methoxy carbonyl groups are strongly coordinated to the metal ion (X).

The coordinated ester groups give rise to carbonyl stretching frequencies at 1705 cm⁻¹ in the infrared spectrum of the complex, while the remaining two ester groups have carbonyl stretching frequencies at 1730 cm⁻¹. Since the carbonyl stretching frequencies of the free ligand EdtaMe₄ occur at 1740 cm⁻¹, it may be that the latter two ester groups are weakly coordinated in axial positions to the metal ion, in which case the ligand is hexadentate. Alternatively the ligand may be quadridentate.
with these ester groups remaining uncoordinated and aquo ligands occupying the fifth and sixth coordination sites of the metal ion. Direct coordination to the metal ion results in two of the ester carbonyl groups in the above complex being highly activated to attack by nucleophiles e.g. OH\(^-\) and H\(_2\)O. Consequently the tetraester complex is rapidly base hydrolysed to the corresponding diesterdicarboxylato complex (XII), even in aqueous solutions of very low hydroxide ion concentrations (pH < 6). Parallel hydrolytic pathways involving attack by the weak nucleophile, H\(_2\)O on the coordinated ester groups was also observed. The hydrolysis of the tetraester complex is summarised in reaction sequence (4)
The second order rate constants $k_1$ and $k_2$ for bimolecular hydroxide ion attack on the above substrates are both some $10^5$ times faster than the second order rate constants for hydrolysis of two ester groups in the free ligand EdtaMe$_4$. Further evidence for metal ion activation of the ester groups is that attack by H$_2$O, although slow on the complexes (the nucleophilicity of H$_2$O is a factor of $10^{11}$ smaller than the nucleophilicity of OH$^-$ with respect to complexes (X) and (XII)), is unobservable for the free ligand.

In more alkaline solutions (pH $> 7$) the ester groups in the diesterdicarboxylato complex (XII) are base hydrolysed in a two step process yielding the Cu(II) complex of Edta as product. Rate constants for these steps are about $10^3$ greater than the rate constants for the hydrolysis of the corresponding ligand.
2. Aminoacid Ester Complexes Containing Uncoordinated Ester Groups.

Springer and Curran\textsuperscript{9} prepared and characterised a number of divalent metal ion complexes of ethyl and methyl glycinate and methyl $\alpha$-alaninate. Many of these complexes are of the type $\text{MX}_2(\text{NH}_2-\text{CHR-CO}_2\text{R'})_2$ ($X=\text{Cl}^-,\text{Br}^-$) in which the ester ligand is monodentate and bonded to the metal through the amino group. Investigations of such systems are mainly confined to infrared spectroscopic studies, while the kinetics of ester hydrolysis have received little attention. Indeed the few available results\textsuperscript{8,14} on these kinetic studies are inconclusive and conflicting, due in part to the low stability constants of the complexes in aqueous solution. One exception to this is provided by the complex cis- $\text{[Co(en)}_2(\text{glyOR})\text{OH}]^{2+}$ (XIII), ($R=-\text{CH}_2(\text{CH}_3)_2$), which is a product of $\text{Br}^-$ removal from cis- $\text{[Co(en)}_2(\text{glyOR})\text{Br}]^{2+}$ in weakly alkaline solutions.\textsuperscript{7} The ester group in this complex, although not directly coordinated to the metal ion, is nevertheless very sensitive to base hydrolysis. This occurs by a mechanism involving attack by neighbouring coordinated $\text{OH}^-$ on the carbonyl group (reaction (5)).

\[
\begin{align*}
\text{(en)}_2\text{-Co}\begin{array}{c}
\text{NH}_2\text{-CH}_2\text{-C-OR} \\
\text{OH}
\end{array} & \quad 2^+ \\
\text{(en)}_2\text{-Co}\begin{array}{c}
\text{NH}_2\text{-CH}_2\text{-C}\text{-O} \\
\text{C}=\text{O}
\end{array} & \quad \text{+ ROH} \\
\text{(XIII) } & \quad \text{........ (5)}
\end{align*}
\]
The rate enhancement for this process over the hydrolysis of the free ester is comparable in magnitude to those earlier encountered for directly coordinated esters. The metal ion presumably contributes to the ease of the reaction by holding the two reactants in juxtaposition. Moreover chelate ring formation helps to stabilise the transition state of the reaction relative to the ground state, thus lowering the energy of activation. These factors lead to an extraordinary efficient process in view of the fact that the nucleophilicity of $\text{OH}^-$ is decreased by a factor at least $10^7$ on coordination to the metal ion.

In a similar type of reaction, the complex $\left[\text{Co(NH}_3\right]_5(\text{NH}_2^-\text{CH}_2^-\text{CO}_2\text{C}_2\text{H}_5)^\text{3+}$ undergoes intramolecular amidolysis in alkaline solutions. The product $\left[\text{Co(NH}_3\right]_4(\text{NH}_2^-\text{CH}_2^-\text{CONH})^\text{2+}$, which contains glycine imide chelated through both nitrogen atoms, results from intramolecular attack by coordinated $\text{NH}_2^-$ (conjugate base of an $\text{NH}_3^-$ ligand) on the ester carbonyl group with concomitant loss of $\text{C}_2\text{H}_5\text{OH}$.

Complexes of amino acid esters containing two or more nitrogen, sulphur or oxygen donor atoms have been widely investigated from both structural and kinetic viewpoints. These complexes are in general thermodynamically more stable in solution than complexes containing monodentate aminoacid esters and as a result ester hydrolysis reactions in these systems are more amenable to kinetic study.
Methyl histidinate (XIV)\textsuperscript{16-18}, methyl 2,3-diamino-propionate (XV)\textsuperscript{19} and the methyl cysteinate anion (XVI)\textsuperscript{10,17,21-23} form 1:1; or 2:1 complexes with metal ions under appropriate conditions. Infrared spectral measurements provide no evidence for methoxycarbonyl bonding to the metal ions either in the solid state or in solution. As expected the neutral bis(methylcysteinate) complexes undergo base hydrolysis reactions more slowly than the analogous positively charged complexes of the other ligands.\textsuperscript{24} Rate enhancements of the order 1.5x10\textsuperscript{2} have been reported for ester hydrolysis in methyl cysteinate complexes over the free ligand. The relative abilities of metal ions to promote hydrolysis follow the general order \textit{Ni(II)} > \textit{Pb(II)} > \textit{Zn(II)} > \textit{Cd(II)} > \textit{Hg(II)}. This correlates well with the order of metal nitrogen bond strengths inferred from infrared spectral measurements.\textsuperscript{17,20} This implies that the catalytic effect of the metal ion depends largely on its inductive effect, acting through the amino group. Withdrawal of electrons from the acyl carbon atom facilitates nucleophilic attack by OH\textsuperscript{-}.

The bis-(methylhistidinate)copper(II) complex cation undergoes hydrolysis 265 times more rapidly than the free ester, even after the statistical advantage is accounted for. The rate enhancement however is less than 4 relative to the monoprotonated ester.\textsuperscript{19}

\begin{align*}
\text{CH}_2\text{-CH-CO}_2\text{CH}_3 & \quad \text{CH}_2\text{-CH-CO}_2\text{CH}_3 & \quad \text{CH}_2\text{-CH-CO}_2\text{CH}_3 \\
\text{NH}_2 & \quad \text{NH}_2 & \quad \text{S}^- \\
\text{N} & & \text{NH}_2 \\
\text{H} & & \\
\text{(XIV)} & \text{(XV)} & \text{(XVI)}
\end{align*}
Angelici and coworkers\textsuperscript{4,25,26} have prepared a series of polydentate amino acid ester N,N-diacetic acid ligands and studied the behaviour of their complexes with metal ions (XVII) in aqueous solutions. These complexes undergo base hydrolysis (reaction 6) in solutions of pH as low as 4.

\[
\begin{align*}
\text{Cu} & \text{R-CH R-CH} \\
& \text{O} \quad \text{OH}_2 \\
\text{N} & \text{Cu} \\
& \text{R-CH} \quad \text{COOC}_2\text{H}_5 \\
\end{align*}
\]

\[
\begin{align*}
\text{Cu} & \text{R-CH R-CH} \\
& \text{O} \quad \text{OH}_2 \\
\text{N} & \text{Cu} \\
& \text{R-CH} \quad \text{COOC}_2\text{H}_5 + \text{CH}_3\text{OH} \\
\end{align*}
\]

(XVII) \quad (XVIII)

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} \\
\end{align*}
\]

\[\text{Cu} \text{R-CH R-CH} \quad \text{O} \quad \text{OH}_2 \\
\text{N} \quad \text{Cu} \\
\text{R-CH} \quad \text{COOC}_2\text{H}_5 + \text{CH}_3\text{OH} \quad \text{C}_2\text{H}_5\text{OH} \quad \text{... ... (6)}
\]

Infrared spectroscopic studies indicate that little or no ester carbonyl to metal bonding is present in the ester complexes. Rates of ester hydrolysis reactions are greater for lanthanide(III) complexes than for divalent d-block metal ion complexes and within the lanthanide group catalytic properties of the metal ions increase almost regularly with increasing atomic number.
3. Metal Complexes of Aminoacid Amides and Peptides.

Metal complexes of peptide and amide ligands have been extensively investigated both in the solid state and in aqueous solution in recent years.\textsuperscript{27,28} This is mainly because of their biological significance particularly in relation to some enzyme reactions. Thus for example the peptidase activity of carboxypeptidase A is dependent on the presence of one of the metal ions Co(II), Ni(II), Zn(II) (which is present in the native enzyme), Mn(II) or Fe(II) at the active site of the enzyme.\textsuperscript{29} The apoenzyme is peptidase inactive as is its Cu(II) complex.


The amide group has been widely studied as a unidentate donor in simple species such as acetamide and dimethylformamide\textsuperscript{30} and in cyclic systems such as $\gamma$-butyrolactam.\textsuperscript{31} More recently however considerable attention has been focused on bidentate and tridentate amide ligands containing nitrogen donor atoms additional to the amide group.

(a) Pyridine-2-carboxamides

Pyridine-2-carboxamide (picolinic acid amide, piaH) behaves as a bidentate ligand forming two types of chelates, one cationic $\left[M \left(\text{H}_2\text{O}\right)_2\text{piaH} \right] \text{Cl}_2$, and the other neutral, $M\text{pia}_2$, with various metal ions.\textsuperscript{32} The crystal structures of the Ni(II) complexes have been determined.\textsuperscript{33} The cationic complex, (XIX) is octahedral with the amide ligands in trans positions. The neutral chelate (XX), which is square planar, is formed by ionization of the
amide groups in the octahedral complex. A concomitant change in donor atoms from oxygen to amidate nitrogen occurs during ionization. Magnetic and visible spectral data ( (XIX) is paramagnetic and blue coloured, whereas (XX) is diamagnetic and yellow coloured ) are consistent with these structures.32

\[
\begin{align*}
\text{(XIX)} & \quad \text{2+} & \quad \text{(XX)} \\
\end{align*}
\]

Infrared spectroscopic comparisons of the ligand, its complexes and their \(^{15}\)N and \(^2\)H substituted analogues provide further evidence for N,O coordination in the octahedral complex and N,N coordination in the square planar complexes.34

Divalent metal ion complexes (both 1:1 and 2:1) of the bidentate ligands N-methyl(mepiaH) and N,N-dimethyl(dimepia)pyridine-2-carboxamide have been prepared.35 Diffuse reflectance and infrared spectra indicate that the amide oxygen is again the donor atom in preference to the amide nitrogen.
In alkaline solutions the Cu(II), Ni(II) and Pd(II) complexes with mepiaH undergo deprotonation but only Pd(mepia)$_2$.2H$_2$O was isolated from solution.

The ligand N-(2-picoly)-2-pyridylacetamide,(ppaH,(XXI)), acts as an N,0 bidentate ligand in the complexes Ni(ppaH)$_2$X$_2$H$_2$O (X=Cl$, Br$, NCS$^-$) and [Co(ppaH)$_2$H$_2$O](ClO$_4$)$_2$. It also forms the complex Cu(ppa)Cl in which it behaves as an N,N,N-terdentate anionic ligand.

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{CH}_2-\text{CONH-CH}_2 \\
\text{O} \\
\end{array}
\]

(XXI)

(b) Phenanthroline-2-carboxamide

Incorporation of an amide group into the 2-position of 1,10-phenanthroline provides a tridentate chelating agent, which forms 2:1 complexes with Fe(II), Ni(II), Co(II) and Cu(II). Infrared spectral evidence shows that the amide group is coordinated to the metal ions through its oxygen atom. Electronic spectral and magnetic data indicates that the ligand produces a relatively weak ligand field and that the Fe(II) complex is high spin. In this respect its behaviour is similar to the structurally related 1,10-phenanthroline-2-carboxylate which also has a 2N,0 donor sequence, but unlike 1,10-phenanthroline-2-amidoxime, a 3N donor ligand which forms a low spin bis complex with Fe(II). On treating the bis
complex with base one of the ligands undergoes amide group deprotonation. This surprisingly produces little change in the magnetic and spectral properties of the complexes. Deprotonation of the second amide ligand does not occur, presumably because of the low solubility of the singly ionized species, which separates from solution immediately on the addition of base.

(c) Glycinamide and Related Complexes

A neutral reddish-blue 2:1, copper(II) complex of glycinamidate was first isolated by Rising and Yang in 1932.\(^{40}\) Neutrality was assumed to be achieved by ionization of the amide group of glycinamide. This was later confirmed by potentiometric titration results\(^{41}\) which showed that an aqueous solution mixture of glycinamide and Cu(II), present in a 2:1 molar ratio, consumed two moles of base per mole of metal ion. A similar Cu(II) complex of 1-leucinamide was also isolated.\(^{42}\)

Several planar 2:1 aminoacid amidate complexes of Ni(II) and Pd(II) have also been synthesised and characterised spectroscopically.\(^{43}\) Pd(II) forms both cis and trans complexes with 1-alanine and 1-leucine amidates but only a trans complex with glycinamidate (XXII)

\[
\text{(XXII)}
\]
Ni(II) forms only trans complexes with these ligands. Cationic complexes of Ni(II) with aminoacid amides have also been isolated under neutral conditions.

The effect of Cu(II) on the hydrolysis of glycinamide has been investigated in the pH range 6 - 12. In near neutral solutions the metal ion promotes the hydrolysis of the amide, by forming the hydrolytically active cationic complex \( \text{[Cu(NH}_2\text{-CH}_2\text{-CONH}_2\text{)]}^{2+} \). At high pH however this complex is converted to the neutral glycinamidate complex \( \text{Cu(NH}_2\text{-CH}_2\text{-CONH}_2\text{)} \) which is insensitive to base hydrolysis.

A variety of N,O chelated glycinamide complexes \( \text{[Co(en)}_2\text{(NH}_2\text{-CH}_2\text{-CONRR')}\text{]}(\text{NO}_3)_2\text{ClO}_4 \) ( \( R=\text{H,CH}_3; R'=\text{H,CH}_3 \) ) have been prepared and hydrolysis of the amide ligands investigated in the pH range 8 - 14. In the case of the \( R=R'=\text{H} \) and \( R=\text{H}, R'=\text{CH}_3 \) complexes ionization of the amide groups \( (\text{pK}_a \approx 11) \) occurs in this pH range and the kinetic data have been interpreted in terms of equilibria involving the hydrolytically active amide complexes and their amidate conjugate bases, which are hydrolytically inactive. As a result the rate of base hydrolysis shows a first order dependence on \( [\text{OH}^-] \) at low pH (where only the conjugate acid is present) but an independence of \( [\text{OH}^-] \) at high pH. In the \( N,N \)-dimethylglycinamide complex ( \( R=R'=\text{CH}_3 \) ) the absence of an amide proton rules out the possibility of amide group ionization and a first order dependence on \( [\text{OH}^-] \) was observed for base hydrolysis of this complex over the entire pH range. In the case of all three amides however the metal ion causes a rate enhancement of about \( 10^6 \) for base hydrolysis.
The complex cis-\([\text{Co(en)}_2(\text{NH}_2\text{CH}_2\text{CONH}_2)(\text{OH})]\)\(^2+\), (XXIII), which contains the monodentate glycinamide ligand, has been identified as one of the products of \(\text{Br}^-\) removal from the complex cis-\([\text{Co(en)}_2(\text{NH}_2\text{CH}_2\text{CONH}_2)\text{Br}]\)\(^2+\) in aqueous base\(^{45}\). The hydroxy complex undergoes a rapid intramolecular hydrolysis reaction involving attack by coordinated \(\text{OH}^-\) on the adjacent amide group (reaction 8).

\[
\begin{align*}
\text{cis-}[\text{Co(en)}_2(\text{NH}_2\text{CH}_2\text{CONH}_2)(\text{OH})]^{2+} \quad &\xrightarrow{-\text{NH}_3} \quad \text{cis-}[\text{Co(en)}_2(\text{NH}_2\text{CH}_2\text{CONH}_2)]^{2+} \\
\text{(XXIII)} &\quad \\
\end{align*}
\]

\[\text{............}(8)\]

5. Peptide Complexes.

Using a combination of aqueous \((\text{D}_2\text{O})\) infrared spectroscopy, potentiometric titrations and visible spectroscopy Kim and Martell have studied solution equilibria involving the formation of Cu(II) complexes with glycyglycine.\(^{46}\) The ionization equilibria of the ligand as well as the \(-\text{C}=\text{O}\) stretching frequencies of the peptide and carboxylic acid (or carboxylate) groups are summarised in the reaction scheme 9.
Thus at pH 3.58 the infrared spectrum of the ligand exhibits bands at 1720, 1675 and 1595 cm⁻¹ due to the equilibrium

\[
\text{(XXIV)} \rightleftharpoons \text{(XXV)} + \text{H}^+ 
\]

In the presence of an equimolar amount of Cu(II), equilibrium 10 is established

\[
\text{(XXIV)} + \text{Cu(II)} \rightleftharpoons \left[ \begin{array}{c} \text{H}_2\text{N} \\ \text{CH}_2 \end{array} \right]^{+} \text{Cu} \begin{array}{c} O \\ O \end{array} \text{C=NH} \text{CH}_2 \text{C=O} \rightleftharpoons x\text{H}^+
\]

and the infrared spectrum of the aqueous solution at pH 3.58 shows an additional absorption at 1625 cm⁻¹ due to the Cu(II) coordinated amide carbonyl group. On raising the pH of the solution to 5.18 the above equilibrium shifts completely to
the right, amide group ionization occurs \( (pK_a = 4) \) and the site of coordination shifts from O to N. The infrared spectrum of the solution at this pD shows only two absorptions one at 1610 cm\(^{-1}\) (due to the amidate carbonyl group) and the other at 1598 cm\(^{-1}\) (due to the coordinated carboxylate group).

The complex diaquoglycylglycinato-copper(II) hydrate has been crystallised from solution and its crystal structure determined.\(^4\) The peptide dianion behaves as a N,N,O tridentate ligand with a water molecule completing the square planar structure. A loosely bound water molecule lies perpendicular to this plane and a third water molecule links the structure by hydrogen bonding.

Ni(II) also induces the ionization of amide linkages in peptides \( (pK_a \approx 10) \) to give complexes with peptide nitrogen donors.\(^4\) During this ionization Ni(II) complexes of glycyl peptides with three or more residues change colour from blue to yellow corresponding to a transition from a paramagnetic, octahedral to a diamagnetic square planar species. In the case of the glycylglycine complex however, no such colour change is observed on amide group ionization and the conjugate base was shown to be the octahedral complex sodium bisglycylglycinato-nickel(II) in which the glycylglycinato dianion acts as an N,N,O tridentate ligand. Pd(II) is more effective than either Ni(II) or Cu(II) in promoting peptide group ionization \( (pK_a \approx 3.5) \) and complexes of this metal ion containing peptide nitrogen donor atoms are readily obtained.\(^4\)
Oxidation of Co(II) complexes of glycylglycine (glyglyH₂) led to the isolation of the crystalline complexes \([\text{Co(H}_2\text{O})_6] \cdot [\text{Co(glygly)}_2]_2 \cdot 12\text{H}_2\text{O}\), \([\text{Co(H}_2\text{O})_6][\text{Co(glygly)}_2]_2 \cdot 6\text{H}_2\text{O}\) and \(\text{Ba}[\text{Co(glygly)}_2]_2 \cdot n\text{H}_2\text{O} (n=12-17)\). All three complexes contain chemically identical \([\text{Co(glygly)}_2]^−\) anions in which the ligand is tridentate through two nitrogen and one oxygen donor atoms. Acidification of solutions containing \([\text{Co(glygly)}_2]^−\) leads to the rapid and reversible uptake of the two protons by the peptide oxygen atoms yielding the cationic complex \([\text{Co(glyglyH)}_2]^+\).

6. Metal Ion Promoted Peptide Hydrolysis.

The Cu(II) catalysed hydrolysis of glycylglycine had been studied in some detail. The pH rate profile for the reaction displays a maximum at pH 4.2 consistent with the view that the catalytically active species in the reaction is the peptide oxygen bonded complex. The lowering in the rate at higher pH values is due to the formation of the inactive deprotonated complex produced by ionization of the peptide hydrogen atom.

It has been found that a number of complexes of the type \(\text{cis-}[\text{CoN}_4(\text{OH})(\text{OH}_2)]^{2+} (N_4 = \text{a system of four nitrogen donor atoms})\) stoichiometrically and rapidly cleave the N-terminal aminoacids from di- and tri-peptides. The proposed mechanism for this reaction involves replacement of the aquo ligand by the peptide (through its amino group) followed by intramolecular attack by the adjacent hydroxyl ligand on the N-terminal peptide carbonyl group. Evidence for this pathway
is provided by the fact that the trans isomer of the above complex is inactive and N-protected peptides are not hydrolysed.

A number of N,O chelated complexes of the type $[\text{CoN}_4(\text{gly-glyH}_2)]^{3+}$ have been prepared and their base hydrolysis reactions studied. The metal ion causes rate enhancements of $\sim 10^5$ relative to base hydrolysis of the free ligand. As in the case of Cu(II) the complexes $[\text{CoN}_4(\text{glyglyH})]^{2+}$ obtained by peptide group ionization are insensitive to base hydrolyses.
CHAPTER 2

EXPERIMENTAL TECHNIQUES
1. Spectroscopic Methods.

The infrared spectra of the ligands and their complexes were recorded as nujol mulls (or liquid films when appropriate) between sodium chloride plates in the wavenumber range 625 - 4000 cm\(^{-1}\). A Perkin Elmer Model 577, Grating Infrared Spectrometer was used for this purpose.

Diffuse reflectance spectra of the complexes were recorded in the range 12,000 - 50,000 cm\(^{-1}\) on a Unicam SP700C spectrophotometer fitted with an SP735 diffuse reflectance accessory. The samples were contained in a special cell and pure lithium fluoride was used as a reference.

Electronic solution spectra were recorded on either Unicam SP800B or SP8000 spectrophotometers. The solutions of the complexes were contained in 1cm silica cells. Kinetics of hydrolysis reactions of the cobalt(III) complexes described in this thesis, were studied spectrophotometrically on a Unicam SP500 spectrophotometer coupled to a Venture RE541.20 potentiometric recorder.

2. Potentiometric Methods.

Acid ionization constants of ligands in metal complexes were obtained by potentiometric titrations. In addition the kinetics of base hydrolysis of ester complexes were investigated by the pH-stat technique. These operations were carried out using a Radiometer pH Meter 26, with an automatic Titrator 11. An autoburette unit ABU12 was used to deliver the titrant
and a Titrigraph SBR2 monitored the addition of titrant versus 

\[ \text{pH} \text{ (in potentiometric titrations) or time (in pH-stat kinetics).} \]

A high alkalinity glass electrode type G202B was used as 

indicator and a saturated calomel electrode with diffusion 

filter type K401 as reference. The electrode system was 

standardised at 25±0.1°C with 0.05M potassium hydrogen phtha-

late (pH=4.008) and 0.01M disodium tetraborate (pH=9.185) 

buffers. The reaction solution was contained in a 150cm³ 

vessel fitted with a cover which was designed to accomo-

date the electrode system, nitrogen inlet and outlet tubes, a 

titrant inlet tube, a thermometer and a stirrer. The beaker 

was lowered into a water bath thermostatted at 25±0.1°C , so 

that the reaction solution was fully immersed.


Magnetic susceptibilities of the metal complexes at room 

temperature were measured by the Gouy method, using the equation

\[
\chi_g = \frac{\kappa V + \beta w}{W}
\]

\[.........(11)\]

where \(\chi_g\) is the gram susceptibility of the specimen, \(\kappa\) is 

the volume susceptibility of air (0.029x10^{-6} \text{ c.g.s.u.}), \(V\) is 

the volume of the specimen of weight \(W\), \(w\) is the change in 

specimen weight as a result of applying a magnetic field and \(\beta\) 

is a constant involving the dimensions of the specimen and the 

field strength. The apparatus used consists of a balance,
from the left hand pan of which the cylindrical specimen was suspended and an electromagnet. The specimen and suspension were surrounded by glass to exclude draughts and a thermometer was arranged close to the specimen to give its temperature.

The constant $\beta$ was obtained using a calibrant (Ni(en)$_3$S$_2$O$_3$) of known susceptibility ($\chi_g = 1.104 \times 10^{-5}$ at $20^\circ$C, $\frac{d\chi_g}{dT} = -0.04 \times 10^{-6}$). This was packed into a glass tube of predetermined volume (using distilled water) and weighed in the absence of (W) and in the presence of an applied magnetic field. The increase in weight of the calibrant (w) was calculated after correcting for the diamagnetism of the glass tube. This was obtained by finding the decrease in weight of the empty tube resulting from the applied field. The gram susceptibilities of the complexes were similarly obtained at various applied field strengths using equation (11) and the appropriate values of $\beta$. The molar susceptibility $\chi_M$ of each complex was calculated using the expression

$$\chi_M = \chi_g \cdot M \quad \text{(12)}$$

where $M$ is the molecular weight of the complex. The molar susceptibility of the metal ion, $\chi_A$, was calculated by allowing for the additive diamagnetic susceptibility of the rest of the molecule,$^{54}$ ($\chi_L$), viz.

$$\chi_A = \chi_M - \chi_L \quad \text{(13)}$$
The effective magnetic moment of the metal ion, $\mu_e$, in Bohr Magnetons, was obtained using the expression

$$\mu_e = 2.828 \sqrt{\chi_A \cdot T}$$

........... (14)

where $T$ is the absolute temperature.


Molar conductivities of the complexes were measured at 25±0.1°C using a Phillips PR9500 conductance bridge with a dip-type cell. The cell constant, $b$, was determined by measuring the resistance of a standard solution of KCl (7.4789 g. of AR KCl per 1000 g. of deionized water), $R_{KCl}$. The specific conductance, $\kappa$, of this solution is known and is related to the cell constant by the expression

$$\kappa = C_{KCl} \cdot b$$

........... (15)

where $C_{KCl}$ (conductance of KCl) = \left( \frac{1}{R_{KCl}} - \frac{1}{R_{H_2O}} \right)

........... (16)

and $R_{H_2O}$ is the resistance of water. The molar conductance values, $\kappa_M$, for the complexes were obtained using the equation

$$\kappa_M = \frac{\kappa \times 1000}{\text{Molarity}}$$

........... (17)
where
\[ \kappa = C_{\text{complex}} \cdot b \] 
............ (18)

and
\[ C_{\text{complex}} = \frac{1}{R_{\text{complex}}} - \frac{1}{R_{\text{solvent}}} \] 
............ (19)

The molar conductance values thus determined were compared with those similarly obtained for known electrolytes under the same conditions. The electrolyte type of each complex was in this way established.

5. Kinetic Methods.

(a) Ester Hydrolysis.

The base catalysed hydrolysis of an amino acid ester, whether complexed or uncomplexed may be represented by the general equation

\[ R - \text{CO}_2\text{R'} + \text{OH}^- \rightarrow \text{RCO}_2^- + \text{R'}\text{OH} \] 
............ (20)

where R is a metal ion containing radical in the case of an ester complex. This reaction is bimolecular and obeys the rate expression

\[ \text{Rate} = k_2 [R-\text{COOR}] [\text{OH}^-] \] 
............ (21)

If [OH\(^-\)] is maintained constant, pseudo first order conditions are satisfied and the rate equation simplified to

\[ \text{Rate} = k_{\text{obs.}} [R-\text{COOR}] \] 
............ (22)
where \( k_{\text{obs.}} = k_2 [\text{OH}^-] \) is the pseudo first order rate constant.

During reaction (20) \( \text{OH}^- \) is consumed and the progress of the reaction may be followed by the pH-stat kinetic method which monitors the rate of hydroxide ion consumption at constant pH. From the plots of \( \ln(V_\infty - V_t) \) versus time where \( V_\infty \) is the total volume of alkali consumed and \( V_t \) is the total volume consumed at time \( t \), values of \( k_{\text{obs.}} \) were obtained in a series of experiments at different pH values. A series of independent values of \( k_2 \), the second order rate constant was then calculated.

(b) **Hydrolysis of Co(III) Complexes.**

Halopentamminecobalt(III) complexes such as those described in chapter 4 of this thesis undergo two types of reactions in aqueous solution. These are acid hydrolysis during which the halide ligand is replaced by water viz.

\[
[\text{CoN}_5\text{X}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{CoN}_5(\text{H}_2\text{O})]^3+ + \text{X}^- \tag{23}
\]

and base hydrolysis during which the halide ligand is replaced by hydroxide ion viz.

\[
[\text{CoN}_5\text{X}]^{2+} + \text{OH}^- \rightarrow [\text{CoN}_5\text{OH}]^{2+} + \text{X}^- \tag{24}
\]

Since aquo and hydroxo ligands occupy higher positions in the spectrochemical series than halide ligands the above hydrolysis
reactions are characterised by marked UV-visible spectral changes, with $\lambda_{\text{max}}$ values shifting to shorter wavelengths. This allows the reaction kinetics to be studied spectrophotometrically by monitoring the absorbance change at a suitable wavelength as a function of time.
CHAPTER 3

METAL COMPLEXES OF THE
TETRAAMIDE AND TETRAMETHYL ESTER OF
ETHYLENEDIAMINETETRAACETIC ACID
1. Introduction.

In view of its many applications as an analytical reagent for metal ions it is not surprising that complexes of ethylenediaminetetraacetate(Edta) and its conjugate acids have been widely studied. Complexes containing hexadentate Edta, pentadentate Edta and Hedta, tetradaentate Edta and H$_2$edta and bidentate H$_4$edta have been identified in the solid state and in solution.$^{57,58,59}$

Despite the generally accepted chemical importance of Edta very little attention has been directed towards the complexing behaviour of its derivatives. A few complexes of its tetraethylester, EdtaEt$_4$, have been reported$^{60}$ and the Cu(II) promoted hydrolysis of this ligand has been investigated in some detail.$^5$ The synthesis of partly esterified Edta derivatives, EdtaMe$_n$ (n=1 - 3), has been conveniently achieved by selective hydrolysis of Cu(II)-EdtaMe$_4$ complex.$^5$ In this chapter the synthesis and characterisation of metal complexes of the tetramethylester and the tetraamide, Edta(NH$_2$)$_4$, of Edta are reported.

2. Experimental.

(a) Preparation of the tetramethylester of Edta, EdtaMe$_4$. $^5$

A solution of ethylenediaminetetraacetic acid, H$_4$Edta (30g.) in dry methanol (100cm$^3$) was cooled in an ice bath and thionyl chloride (10cm$^3$) added dropwise with stirring. During the addition the temperature of the reaction mixture was
maintained below 10°C. The suspension was stirred overnight and then refluxed until all the solid had completely dissolved. The solution was basified with a saturated sodium bicarbonate solution and the ester was extracted into ether. The ether phase was dried over anhydrous sodium sulphate and the solvent removed under reduced pressure. The tetraester was obtained as a residual light yellow coloured oil (b.p. 189-191°C, 3 mm Hg) in 80 - 90% yield.

Found: C, 48.2%; H, 7.0%; N, 7.9%. C_{14}H_{24}N_{2}O_{8} requires C, 48.3%; H, 7.0%; N, 8.0%

A liquid film IR spectrum of the product showed a -C=O stretching frequency at 1740 cm⁻¹ which is typical of an aliphatic ester, and the ¹H NMR spectrum of a CCl₄ solution displayed signals at δ = 3.59 ppm (12 carbomethoxy protons), 3.49 ppm (8 acetato methylene protons) and 2.79 ppm (4 ethylenediamine methylene protons) downfield from TMS.

(b) Preparation of the Tetraamide of Edta, Edta(NH₂)₄.

A previously reported method for the preparation of this compound resulted in only a modest yield after a preparative time of one month. The following method gave an improved yield after only three hours. A stirred solution of EdtaMe₄ (8 g.) in dry methanol (50 cm³) at room temperature was saturated with ammonia at time intervals of 30 mins. After about three hours the tetraamide crystallised from solution. A single recrystallisation from a minimum volume of boiling water gave a pure product in 80% yield.
Found  C, 41.7% ; H, 6.8% ; N, 28.9%.  

requires  C, 41.7% ; H, 7.0% ; N, 29.2%.

The IR spectrum of the amide (nujol mull) shows broad absorptions at 3380, 3200 cm\(^{-1}\) (NH\(_2\) stretching frequencies), 1660 cm\(^{-1}\) (amide I band), and 1580 cm\(^{-1}\) (amide II band). The N-deuterated amide, C\(_{10}H_{12}D_6N_6O_4\), was prepared by recrystallising the parent amide from a minimum volume of hot D\(_2\)O (80°C). The IR spectrum of the N-deuterated amide shows strong broad absorptions at 2530, 2360 cm\(^{-1}\) (ND\(_2\) stretching frequencies) and 1640 cm\(^{-1}\) (amide I band). No absorption is observed at 1580 cm\(^{-1}\) but instead a band of medium intensity occurs at 1165 cm\(^{-1}\). This may be assigned to an N-D bending vibration (amide II band).

(c) Preparation of Metal Complexes of Edta(NH\(_2\))\(_4\),

\[ M(C_{10}H_{20}N_6O_4)Cl_n \cdot xH_2O. \]

A solution of Edta(NH\(_2\))\(_4\) (5x10\(^{-3}\) mol) in a minimum volume of hot water was added dropwise with stirring to a solution of the metal chloride (5x10\(^{-3}\) mol) in hot methanol. In most cases the complexes crystallised on cooling the solution to room temperature, otherwise crystallisation was initiated by the addition of diethylether. Using Cu(ClO\(_4\))\(_2\)\( \cdot \)6H\(_2\)O as starting material a copper(II) complex of Edta(NH\(_2\))\(_4\) was isolated as its perchlorate salt. Analytical, spectral (IR and diffuse reflectance) magnetic (at room temperature) and conductivity data for these complexes are presented in Tables 1 - 5.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Calc.%</th>
<th>Found%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Mn(C_{10}H_{20}N_{6}O_{4})Cl_{2}·\frac{1}{2}H_{2}O</td>
<td>28.4</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe(C_{10}H_{20}N_{6}O_{4})Cl_{2}</td>
<td>28.9</td>
<td>4.8</td>
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<tr>
<td>Co(C_{10}H_{20}N_{6}O_{4})Cl_{2}·\frac{1}{2}H_{2}O</td>
<td>28.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Ni(C_{10}H_{20}N_{6}O_{4})Cl_{2}·3H_{2}O</td>
<td>25.0</td>
<td>5.6</td>
</tr>
<tr>
<td>Cu(C_{10}H_{20}N_{6}O_{4})Cl_{2}·3H_{2}O</td>
<td>25.2</td>
<td>5.4</td>
</tr>
<tr>
<td>Cu(C_{10}H_{20}N_{6}O_{4})Cl_{10}O_{4}</td>
<td>21.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Cu(C_{10}H_{20}N_{6}O_{4})·2H_{2}O</td>
<td>31.4</td>
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</tr>
<tr>
<td>Mg(C_{10}H_{18}N_{6}O_{4})Cl_{2}</td>
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<td>5.3</td>
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<tr>
<td>Ca(C_{10}H_{20}N_{6}O_{4})Cl_{2}·2H_{2}O</td>
<td>27.6</td>
<td>5.6</td>
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<tr>
<td>Ba(C_{10}H_{20}N_{6}O_{4})Cl_{2}·4H_{2}O</td>
<td>21.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn(C_{10}H_{20}N_{6}O_{4})Cl_{2}·3H_{2}O</td>
<td>25.2</td>
<td>5.5</td>
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<tr>
<td>Cd(C_{10}H_{20}N_{6}O_{4})Cl_{2}·4H_{2}O</td>
<td>22.1</td>
<td>5.2</td>
</tr>
<tr>
<td>Hg(C_{10}H_{20}N_{6}O_{4})Cl_{2}·5H_{2}O</td>
<td>18.5</td>
<td>4.6</td>
</tr>
<tr>
<td>La(C_{10}H_{20}N_{6}O_{4})Cl_{3}·7H_{2}O</td>
<td>18.2</td>
<td>5.2</td>
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</table>
Table 2 Salient IR Spectral Bands of Ethylenediaminetetraacetamide, Edta(NH$_2$)$_4$ and its Metal Complexes (cm$^{-1}$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amide I($\nu$(C=O)) and Amide II($\nu$(NH$_2$)) bands</th>
<th>$\nu_s$(NH$<em>2$), $\nu</em>{as}$(NH$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edta(NH$_2$)$_4$</td>
<td>1660 ; 1580</td>
<td>3240 ; 3380</td>
</tr>
<tr>
<td>MnEdta(NH$_2$)$_4$Cl$_2$·$\frac{3}{2}$H$_2$O</td>
<td>1660 ; 1605 ; 1560</td>
<td>3120 ; 3250</td>
</tr>
<tr>
<td>FeEdta(NH$_2$)$_4$Cl$_2$</td>
<td>1663 ; 1612 ; 1555</td>
<td>3120 ; 3250</td>
</tr>
<tr>
<td>CoEdta(NH$_2$)$_4$Cl$_2$·$\frac{3}{2}$H$_2$O</td>
<td>1662 ; 1611 ; 1555</td>
<td>3125 ; 3250</td>
</tr>
<tr>
<td>NiEdta(NH$_2$)$_4$Cl$_2$·3H$_2$O</td>
<td>1675 ; 1610 ; 1590</td>
<td>3100 ; 3190 ; 3360</td>
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<tr>
<td>CuEdta(NH$_2$)$_4$Cl$_2$·3H$_2$O</td>
<td>1685 ; 1615 ; 1570</td>
<td>3060 ; 3180 ; 3350</td>
</tr>
<tr>
<td>CuEdta(NH$_2$)$_2$(ClO$_4$)$_2$</td>
<td>1670 ; 1615 ; 1595</td>
<td>3060 ; 3170 ; 3335</td>
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<tr>
<td>CuEdta(NH$_2$)$_2$(NH)$_2$·2H$_2$O</td>
<td>1675 ; 1570</td>
<td>3160 ; 3300</td>
</tr>
<tr>
<td>MgEdta(NH$_2$)$_4$Cl$_2$</td>
<td>1690 ; 1660 ; 1610</td>
<td>3080 ; 3160 ; 3250 ; 3340 ; 3380 ; 3440</td>
</tr>
<tr>
<td>CaEdta(NH$_2$)$_4$Cl$_2$·2H$_2$O</td>
<td>1670vB</td>
<td>3180 ; 3280vB</td>
</tr>
<tr>
<td>BaEdta(NH$_2$)$_4$Cl$_2$·4H$_2$O</td>
<td>1665 ; 1615</td>
<td>3150 ; 3300</td>
</tr>
<tr>
<td>ZnEdta(NH$_2$)$_4$Cl$_2$·3H$_2$O</td>
<td>1670 ; 1625 ; 1612</td>
<td>3195 ; 3230 ; 3285 ; 3350 ; 3385</td>
</tr>
<tr>
<td>CdEdta(NH$_2$)$_4$Cl$_2$·4H$_2$O</td>
<td>1665 ; 1605</td>
<td>3175 ; 3280 ; 3340</td>
</tr>
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<td>HgEdta(NH$_2$)$_4$Cl$_2$·5H$_2$O</td>
<td>1690 ; 1670 ; 1648 ; 1615</td>
<td>3190 ; 3225 ; 3290 ; 3370 ; 3450</td>
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<tr>
<td>LaEdta(NH$_2$)$_4$Cl$_2$·7H$_2$O</td>
<td>1680vB ; 1650 ; 1610vB</td>
<td></td>
</tr>
</tbody>
</table>

b = broad ; vb = very broad
Table 3 - Salient IR Spectral Bands for N-deuterated Ethylenediaminetetraacetamide, Edta(ND$_2$)$_2$, and its Metal Complexes (cm$^{-1}$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CO)</th>
<th>$\nu_{s}$(ND$_2$)</th>
<th>$\nu_{as}$(ND$_2$)</th>
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</thead>
<tbody>
<tr>
<td>Edta(ND$_2$)$_4$</td>
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<td>2360</td>
<td>2530</td>
</tr>
<tr>
<td>MnEdta(ND$_2$)$_4$Cl$_2$·$\frac{3}{2}$D$_2$O</td>
<td>1625</td>
<td>2390</td>
<td>2475</td>
</tr>
<tr>
<td>FeEdta(ND$_2$)$_4$Cl$_2$</td>
<td>1625</td>
<td>2290</td>
<td>2470</td>
</tr>
<tr>
<td>CoEdta(ND$_2$)$_4$Cl$_2$·$\frac{3}{2}$D$_2$O</td>
<td>1620</td>
<td>2270</td>
<td>2490</td>
</tr>
<tr>
<td>NiEdta(ND$_2$)$_4$Cl$_2$·$\frac{7}{2}$D$_2$O</td>
<td>1650,1600</td>
<td>2290,2350</td>
<td>2500$^b$</td>
</tr>
<tr>
<td>CuEdta(ND$_2$)$_4$Cl$_2$·3D$_2$O</td>
<td>1630$^b$</td>
<td>2310</td>
<td>2500$^b$</td>
</tr>
<tr>
<td>CuEdta(ND$_2$)$_4$(ClO$_4$)$_2$</td>
<td>1630$^b$</td>
<td>2310</td>
<td>2480</td>
</tr>
<tr>
<td>CuEdta(ND$_2$)$_2$(ND)$_2$·2D$_2$O</td>
<td>1630,1600</td>
<td>2290$^b$</td>
<td>2470$^b$</td>
</tr>
<tr>
<td>MgEdta(ND$_2$)$_4$Cl$_2$</td>
<td>1625</td>
<td>2280</td>
<td>2460</td>
</tr>
<tr>
<td>CaEdta(ND$_2$)$_4$Cl$_2$·2D$_2$O</td>
<td>1630</td>
<td>2300$^b$</td>
<td>2510</td>
</tr>
<tr>
<td>BaEdta(ND$_2$)$_4$Cl$_2$</td>
<td>1630</td>
<td>2200-2500$^{vb}$</td>
<td></td>
</tr>
<tr>
<td>ZnEdta(ND$_2$)$_4$Cl$_2$·3D$_2$O</td>
<td>1640</td>
<td>2370</td>
<td>2540</td>
</tr>
<tr>
<td>CdEdta(ND$_2$)$_4$Cl$_2$·4D$_2$O</td>
<td>1640</td>
<td>2360</td>
<td>2540</td>
</tr>
<tr>
<td>HgEdta(ND$_2$)$_4$Cl$_2$·5D$_2$O</td>
<td>1640</td>
<td>2360</td>
<td>2540</td>
</tr>
<tr>
<td>LaEdta(ND$_2$)$_4$Cl$_3$·7D$_2$O</td>
<td>1650,1610</td>
<td>2200-2500$^{vb}$</td>
<td></td>
</tr>
</tbody>
</table>
Table 4  Room Temperature Magnetic Moments of Paramagnetic Metal Complexes of Ethylenediaminetetraacetamide, Edta(NH$_2$)$_4$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Current (amps.)</th>
<th>$10^6 \chi_g$ (c.g.s.)</th>
<th>$10^3 \chi_M$ (c.g.s.)</th>
<th>$10^3 \chi_A$ (c.g.s.)</th>
<th>$\mu_e$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnEdta(NH$_2$)$_4$Cl$_2$$\cdot$$\frac{1}{2}$H$_2$O</td>
<td>0.5</td>
<td>37.08</td>
<td>15.69</td>
<td>15.87</td>
<td>6.10</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>34.62</td>
<td>14.65</td>
<td>14.84</td>
<td>5.99</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>36.63</td>
<td>15.50</td>
<td>15.69</td>
<td>6.06</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>35.05</td>
<td>14.83</td>
<td>15.01</td>
<td>5.94</td>
</tr>
<tr>
<td>FeEdta(NH$_2$)$_4$Cl$_2$</td>
<td>0.5</td>
<td>30.28</td>
<td>12.56</td>
<td>12.75</td>
<td>5.47</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>28.88</td>
<td>11.99</td>
<td>12.17</td>
<td>5.34</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>27.42</td>
<td>11.38</td>
<td>11.56</td>
<td>5.21</td>
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<td>2.0</td>
<td>28.72</td>
<td>11.92</td>
<td>12.11</td>
<td>5.33</td>
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<tr>
<td>CoEdta(NH$_2$)$_4$Cl$_2$$\cdot$$\frac{1}{2}$H$_2$O</td>
<td>0.5</td>
<td>17.98</td>
<td>7.84</td>
<td>8.03</td>
<td>4.34</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>17.94</td>
<td>7.83</td>
<td>8.01</td>
<td>4.33</td>
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<td>1.5</td>
<td>17.97</td>
<td>7.84</td>
<td>8.02</td>
<td>4.34</td>
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<tr>
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<td>2.0</td>
<td>18.08</td>
<td>7.88</td>
<td>8.07</td>
<td>4.35</td>
</tr>
<tr>
<td>NiEdta(NH$_2$)$_4$Cl$_2$$\cdot$$\frac{3}{2}$H$_2$O</td>
<td>-0.5</td>
<td>9.23</td>
<td>4.36</td>
<td>4.54</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>9.17</td>
<td>4.33</td>
<td>4.51</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>9.66</td>
<td>4.56</td>
<td>4.75</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>9.07</td>
<td>4.28</td>
<td>4.47</td>
<td>3.26</td>
</tr>
<tr>
<td>CuEdta(NH$_2$)$_4$Cl$_2$$\cdot$3H$_2$O</td>
<td>0.5</td>
<td>2.42</td>
<td>1.15</td>
<td>1.34</td>
<td>1.77</td>
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<td>1.0</td>
<td>2.41</td>
<td>1.15</td>
<td>1.33</td>
<td>1.77</td>
</tr>
<tr>
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<td>1.5</td>
<td>2.52</td>
<td>1.20</td>
<td>1.39</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2.52</td>
<td>1.20</td>
<td>1.39</td>
<td>1.80</td>
</tr>
<tr>
<td>CuEdta(NH$_2$)$_4$(ClO$_4$)$_2$</td>
<td>0.5</td>
<td>1.99</td>
<td>1.10</td>
<td>1.29</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.99</td>
<td>1.10</td>
<td>1.29</td>
<td>1.74</td>
</tr>
<tr>
<td>CuEdta(NH$_2$)$_2$(NH)$_2$·2H$_2$O</td>
<td>0.5</td>
<td>2.86</td>
<td>1.10</td>
<td>1.29</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2.71</td>
<td>1.04</td>
<td>1.23</td>
<td>1.70</td>
</tr>
</tbody>
</table>
Table 5 - Conductivity and Diffuse Reflectance Spectral Data for Metal Complexes of Ethylenediaminetetraacetamide, Edta(NH$_2$)$_4$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar Conductivities, $\Lambda^+_M$ (ohm$^{-1}$cm$^2$mol$^{-1}$)</th>
<th>Diffuse Reflectance Spectra (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnEdta(NH$_2$)$_4$Cl$_2$•$\frac{1}{2}$H$_2$O</td>
<td>insoluble</td>
<td>very weak bands</td>
</tr>
<tr>
<td>FeEdta(NH$_2$)$_4$Cl$_2$</td>
<td>146 (2:1)</td>
<td>9000 ; 26000 ; 35000</td>
</tr>
<tr>
<td>CoEdta(NH$_2$)$_4$Cl$_2$•$\frac{1}{2}$H$_2$O</td>
<td>149 (2:1)</td>
<td>9000$^w$ ; 15700$^w$ ; 19500$^s$</td>
</tr>
<tr>
<td>NiEdta(NH$_2$)$_4$Cl$_2$•$\frac{3}{2}$H$_2$O</td>
<td>157 (2:1)</td>
<td>9500 ; 15500 ; 25000</td>
</tr>
<tr>
<td>CuEdta(NH$_2$)$_4$Cl$_2$•$3$H$_2$O</td>
<td>139 (2:1)</td>
<td>13000 ; 6500$^t$</td>
</tr>
<tr>
<td>CuEdta(NH$_2$)$_4$(ClO$_4$)$_2$</td>
<td>154 (2:1)</td>
<td>13000 ; 6500$^t$</td>
</tr>
<tr>
<td>CuEdta(NH$_2$)$_4$(NH)$_2$•$2$H$_2$O</td>
<td>non-electrolyte</td>
<td>15500 ; 7700$^t$</td>
</tr>
<tr>
<td>MgEdta(NH$_2$)$_4$Cl$_2$</td>
<td>146 (2:1)</td>
<td></td>
</tr>
<tr>
<td>CaEdta(NH$_2$)$_4$Cl$_2$•$2$H$_2$O</td>
<td>137 (2:1)</td>
<td></td>
</tr>
<tr>
<td>BaEdta(NH$_2$)$_4$Cl$_2$•$4$H$_2$O</td>
<td>156 (2:1)</td>
<td></td>
</tr>
<tr>
<td>ZnEdta(NH$_2$)$_4$Cl$_2$•$3$H$_2$O</td>
<td>155 (2:1)</td>
<td></td>
</tr>
<tr>
<td>CdEdta(NH$_2$)$_4$Cl$_2$•$3$H$_2$O</td>
<td>146 (2:1)</td>
<td></td>
</tr>
<tr>
<td>HgEdta(NH$_2$)$_4$Cl$_2$•$5$H$_2$O</td>
<td>non-electrolyte</td>
<td></td>
</tr>
<tr>
<td>LaEdta(NH$_2$)$_4$Cl$_3$•$7$H$_2$O</td>
<td>213 (3:1)</td>
<td></td>
</tr>
</tbody>
</table>

* obtained using $1 \times 10^{-3}$M solutions of the complexes in anhydrous methanol.

+ Electrolyte type in brackets.

$s$ = strong ; $w$ = weak ; $b$ = broad ; $t$ = tail

$\Lambda^+_M$ (CaCl$_2$) = 149ohms$^{-1}$cm$^2$mol$^{-1}$

$\Lambda^+_M$ (LaCl$_3$) = 237ohms$^{-1}$cm$^2$mol$^{-1}$
The N-deuterated complexes, $M(C_{10}H_{12}D_8N_6O_4)Cl_n \cdot xD_2O$, were prepared by dissolving the parent complexes in a minimum volume of hot $D_2O$ and evaporating the resulting solutions to dryness under reduced pressure.

(d) **Preparation of the Deprotonated Complex**, $Cu(C_{10}H_{13}N_6O_4) \cdot 2H_2O$.

An aqueous solution containing equimolar amounts of Edta$(NH_2)_4$ and $Cu(ClO_4)_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$ (5x10$^{-3}$mol) was titrated with an NaOH solution (1.2x10$^{-2}$moles). During the titration the solution developed an intense blue colour. The solution was then evaporated to dryness and redissolved in a minimum volume of hot methanol. Crystallisation of the complex was induced by the addition of a small volume of diethylether. Data relevant to the characterisation of this product are presented in Tables 1 - 5.

(e) **Preparation of Metal Complexes of EdtaMe$_4$**, $M(C_{14}H_{24}N_8O_8)Cl_n \cdot xH_2O$.

A stirred solution of the metal chloride (0.005mol) in anhydrous methanol (40cm$^3$) was treated dropwise with a solution of EdtaMe$_4$ (0.005mol) also in dry methanol (40cm$^3$). In many cases the desired complexes crystallised from solution on standing, otherwise crystallisation was induced by the addition of ether. Analytical, spectral (IR and diffuse reflectance), magnetic (at room temperature) and conductivity data for these complexes are presented in Tables 6 - 9.
Table 6 - Analytical Data for Metal Complexes of the Tetramethylester of Edta, EdtaMe₄, C₁₄H₂₄N₂O₈.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Calc. %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Mn(C₁₄H₂₄N₂O₈)Cl₂</td>
<td>35.4</td>
<td>5.1</td>
</tr>
<tr>
<td>Fe(C₁₄H₂₁N₂O₈)Cl₂</td>
<td>35.4</td>
<td>5.1</td>
</tr>
<tr>
<td>Co(C₁₄H₂₄N₂O₈)Cl₂</td>
<td>35.1</td>
<td>5.1</td>
</tr>
<tr>
<td>Ni(C₁₄H₂₄N₂O₈)Cl₂•H₂O</td>
<td>33.9</td>
<td>5.3</td>
</tr>
<tr>
<td>Cu(C₁₄H₂₄N₂O₈)Cl₂•H₂O</td>
<td>34.8</td>
<td>5.0</td>
</tr>
<tr>
<td>Cd(C₁₄H₂₄N₂O₈)Cl₂•H₂O</td>
<td>30.6</td>
<td>4.8</td>
</tr>
<tr>
<td>Hg(C₁₄H₂₄N₂O₈)Cl₂</td>
<td>27.1</td>
<td>3.9</td>
</tr>
<tr>
<td>Sn(C₁₄H₂₄N₂O₈)Cl₂•9H₂O</td>
<td>24.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Table 7  Principal IR Spectral Bands of the Tetramethylester of Edta, EdtaMe₄ and its Metal Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{as}(H_2O),\nu_{s}(H_2O)$</th>
<th>$\nu(C=O)$</th>
<th>$\nu(CN), \nu(CO)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EdtaMe₄</td>
<td></td>
<td>1740s,b</td>
<td>1200s,b</td>
</tr>
<tr>
<td>Mn(EdtaMe₄)Cl₂</td>
<td></td>
<td>1740;1725;1690</td>
<td>1250;1235;1220</td>
</tr>
<tr>
<td>Fe(EdtaMe₄)Cl₂</td>
<td></td>
<td>1745;1735;1730;1685</td>
<td>1255;1242;1235;1212</td>
</tr>
<tr>
<td>Co(EdtaMe₄)Cl₂</td>
<td></td>
<td>1745;1690</td>
<td>1248;1237;1220;1212</td>
</tr>
<tr>
<td>Ni(EdtaMe₄)Cl₂·H₂O</td>
<td>3460;3200b</td>
<td>1740;1680</td>
<td>1255;1240;1215</td>
</tr>
<tr>
<td>Cu(EdtaMe₄)Cl₂</td>
<td></td>
<td>1745;1720</td>
<td>1245;1235;1215</td>
</tr>
<tr>
<td>Cd(EdtaMe₄)Cl₂·H₂O</td>
<td>3580;3530</td>
<td>1740;1727;1695</td>
<td>1245;1210</td>
</tr>
<tr>
<td>Hg(EdtaMe₄)Cl₂</td>
<td></td>
<td>1745;1725</td>
<td>1227;1205;1185</td>
</tr>
<tr>
<td>Sn(EdtaMe₄)Cl₂·9H₂O</td>
<td>3000-3600b</td>
<td>1735</td>
<td>1260;1245;1210</td>
</tr>
<tr>
<td>Complex</td>
<td>Current ((\text{amps.}))</td>
<td>(10^6 \chi_g)</td>
<td>(10^3 \chi_M)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>(\text{Mn(EdtaMe}_4\text{)Cl}_2)</td>
<td>0.5</td>
<td>33.52</td>
<td>15.89</td>
</tr>
<tr>
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<td>1.5</td>
<td>35.28</td>
<td>17.72</td>
</tr>
<tr>
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<td>2.0</td>
<td>33.82</td>
<td>16.04</td>
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<td>(\text{Fe(EdtaMe}_4\text{)Cl}_2)</td>
<td>0.5</td>
<td>25.10</td>
<td>11.92</td>
</tr>
<tr>
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<td>1.0</td>
<td>24.23</td>
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<td>12.63</td>
</tr>
<tr>
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<td>2.0</td>
<td>25.93</td>
<td>12.32</td>
</tr>
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</tr>
<tr>
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<td>2.0</td>
<td>15.87</td>
<td>7.58</td>
</tr>
<tr>
<td>(\text{Ni(EdtaMe}_4\text{)Cl}_2\cdot\text{H}_2\text{O})</td>
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<td>4.12</td>
</tr>
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<td>8.37</td>
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<td>4.51</td>
</tr>
<tr>
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<td>2.0</td>
<td>8.70</td>
<td>4.31</td>
</tr>
<tr>
<td>(\text{Cu(EdtaMe}_4\text{)Cl}_2)</td>
<td>0.5</td>
<td>2.75</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.81</td>
<td>1.35</td>
</tr>
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<td>1.5</td>
<td>2.99</td>
<td>1.44</td>
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<tr>
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<td>2.0</td>
<td>2.71</td>
<td>1.31</td>
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</table>
Table 9  Conductivity and Diffuse Reflectance Spectral Data for Metal Complexes of Ethylenediaminetetramethylester, EdtaMe₄.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar Conductivities (ohms⁻¹cm²mol⁻¹) *</th>
<th>Diffuse Reflectance Spectra (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(EdtaMe₄)Cl₂</td>
<td>128 (2:1)</td>
<td>v. weak bands at 17000; 19000; 23000</td>
</tr>
<tr>
<td>Fe(EdtaMe₄)Cl₂</td>
<td>131 (2:1)</td>
<td>8500; 14200; 26000</td>
</tr>
<tr>
<td>Co(EdtaMe₄)Cl₂</td>
<td>122 (2:1)</td>
<td>7000; 14500w; 17500s; 20000w</td>
</tr>
<tr>
<td>Ni(EdtaMe₄)Cl₂·H₂O</td>
<td>85 (1:1)</td>
<td>8600; 14500; 24000</td>
</tr>
<tr>
<td>Cu(EdtaMe₄)Cl₂</td>
<td>71 (1:1)</td>
<td>6500w; 13000s</td>
</tr>
<tr>
<td>Cd(EdtaMe₄)Cl₂·½H₂O</td>
<td>63 (1:1)</td>
<td></td>
</tr>
<tr>
<td>Hg(EdtaMe₄)Cl₂</td>
<td>non-electrolyte</td>
<td></td>
</tr>
<tr>
<td>Sn(EdtaMe₄)Cl₂·9H₂O</td>
<td>94 (1:1)</td>
<td></td>
</tr>
</tbody>
</table>

* Electrolyte type in brackets

Obtained using 1x10⁻³M solutions of the complexes in anhydrous methanol

s = strong; w = weak; b = broad

Λₘ(NaCl) = 70ohms⁻¹cm²mol⁻¹, Λₘ(CaCl₂) = 149ohms⁻¹cm²mol⁻¹

Λₘ(LaCl₃) = 237ohm⁻¹cm²mol⁻¹
3. Results and Discussion.

(a) **Potentiometric and Spectrophotometric Titrations of the Cu(II) - Edta(NH₂)₄ Complex.**

Aqueous solutions containing equimolar amounts of Edta(NH₂)₄ and Cu(II) are diacidic and consume two moles of alkali per mole of metal ion (or ligand) in a potentiometric titration. This is consistent with the generally observed acidic behaviour of amide groups coordinated to Cu(II) (briefly reviewed in Chapter 1 p.22 et seq.). The ionizations relevant to base consumption are represented in equation (25).

Preliminary potentiometric investigations indicated that the ionization constants $K_1$ and $K_2$ overlap ($K_1/K_2 < 10^{2.5}$) and the Noyes treatment of potentiometric data was used in the determination of these constants. Data relevant to these calculations are presented in Table 10. At 25±0.1°C and ionic strength 0.1M (NaClO₄) the mixed ionization constants $pK_1^M = 6.45±0.01$ ; $pK_2^M = 8.00±0.02$ were obtained. These values compare satisfactorily with the ionization constants of the amide groups in the related bis-(glyginamido)copper(II) complex for which $pK_a$ values of 6.91 and 8.12 have been reported. Amide groups in Cu(II) peptide complexes are generally more acidic than the complexes just discussed.

An equimolar aqueous solution of Edta(NH₂)₄ and Cu(II) was also titrated spectrophotometrically in the pH range 4.4 - 10. Visible spectra at different pH values are shown in Fig. 1.
\[
\begin{align*}
\text{(XXX)} & \quad \frac{\text{[Cu(H2N-CH2-CO-NH2)2]}}{}^{2+} \\
\quad & \quad \xrightleftharpoons[K_1]{H^+} \\
\text{(XXXI)} & \quad \frac{\text{[Cu(H2N-CH2-CO-NH2)2]}}{}^{+} \\
\quad & \quad \xrightleftharpoons[K_2]{H^+} \\
\text{(XXXII)} & \quad \frac{\text{[Cu(H2N-CH2-CO-NH2)2]}}{}
\end{align*}
\]

\[\ldots\ldots (25)\]
Table 10 Data Pertinent to the Calculation of the Ionization
Constants for the Cu-Edta(NH$_3$)$_4$ Complex (5.0x10$^{-3}$M)
in Aqueous Solution(50.0cm$^3$) at 25±0.1°C and Ionic
Strength 0.1M(NaClO$_4$); Method of Albert and Serjeant

<table>
<thead>
<tr>
<th>Vol. of titrant (0.20M NaOH) added</th>
<th>pH</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>pk$_1^M$</th>
<th>pk$_2^M$</th>
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<tr>
<td>0.4</td>
<td>5.730</td>
<td>-7.79x10$^{-9}$</td>
<td>9.16x10$^{-3}$</td>
<td>2.72x10$^{-15}$</td>
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<td>4.6</td>
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<td>0.8</td>
<td>6.099</td>
<td>-2.68x10$^{-9}$</td>
<td>8.33x10$^{-3}$</td>
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<td>4.2</td>
<td>8.359</td>
<td>1.43x10$^{-11}$</td>
<td>1.54x10$^{-3}$</td>
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<td>2.6</td>
<td>7.289</td>
<td>1.03x10$^{-11}$</td>
<td>4.67x10$^{-3}$</td>
<td>1.34x10$^{-17}$</td>
<td>6.44</td>
<td>7.99</td>
</tr>
</tbody>
</table>

\[ \begin{align*}
X &= (B-C)(H^+) ; \quad Y = 2C-B ; \quad Z = (H^+)^2B \\
K_1^M &= \frac{Y_1Z_2-Z_2Y_1}{X_1Y_2-X_2Y_1} ; \quad K_2^M = \frac{X_1Z_2-X_2Z_1}{Y_1Z_2-Y_2Z_1}
\end{align*} \]

Where \( B \) is the concentration of complex being titrated and \( C \) is the concentration of base added. The subscripts 1,2 refer to pairs of readings symmetrical about the point at which one equivalent of base has been added (2.5cm$^3$). \( X_1, Y_1, Z_1 \) refer to readings in each pair below 2.5cm$^3$ and \( X_2, Y_2, Z_2 \) refer to readings in each pair above 2.5cm$^3$. 
Fig. 1 Visible Spectra of Aqueous Solutions Containing Cu(II) \((5.0 \times 10^{-3} \text{M})\) and Edta(NH₂)₄ \((5.0 \times 10^{-3} \text{M})\) at pH (a) 4.8 (b) 6.1 (c) 7.1 (d) 8.0 (e) 10.0
Spectra of solutions of pH< 5 show a broad absorption with $\lambda_{\text{max}} = 780\text{nm}$. On the addition of alkali however this absorption shifts to shorter wavelengths (pH7, $\lambda_{\text{max}} = 695\text{nm}$; pH9.8, $\lambda_{\text{max}} = 640\text{nm}$) and undergoes appreciable intensification. These spectral changes are very similar to those observed in the spectrophotometric titrations of the Cu(II) complexes of glycylglycine and aminoacid amides. This similarity strongly suggests that a change in donor atoms from amide oxygen to amidate nitrogen occurs as a result of amide ligand deprotonation. Aqueous IR spectroscopy proved uninformative with respect to this process because of the breadth of the absorptions in the 1550 - 1700cm$^{-1}$ region. The visible spectral results also eliminate the possibility that aquo ligands and not amide ligands are being neutralized at pH< 10. This follows from the fact that OH$^-$ and H$_2$O are closely positioned in the spectrochemical series and ionization of aquo copper(II) complexes give rise to only small changes in the visible spectra.

The foregoing potentiometric and spectrophotometric evidence suggests that in aqueous solution of pH< 4 the Cu(II) - Edta(NH$_2$)$_4$ complex has structure (XXX). The conjugate base of this complex has structure (XXXI) and reaches maximum concentration in solution at pH near 7.5. At pH >10 the main species in solution, Cu(II)Edta(NH$_2$)(NH)$_2$ has structure (XXXII). In all case aquo ligands or the nonacidic amide ligands are probably weakly bonded in axial positions to the metal ion.
(b) Structures of the Metal Complexes of Edta(NH$_2$)$_4$ Inferred from Spectral, Magnetic and Conductivity Data.

The IR spectrum of the ligand shows broad absorption bands at 3380 and 3200 cm$^{-1}$ which may be assigned to asymmetric and symmetric NH$_2$ stretching vibrations respectively. Both absorptions shift to much lower wavenumbers on deuteration of the amide hydrogens $\nu_{as}(\text{ND}_2)$, 2530 cm$^{-1}$; $\nu_s(\text{ND}_2)$, 2360 cm$^{-1}$. The ligand also shows a broad absorption at 1660 cm$^{-1}$ shouldered by a weaker absorption at 1580 cm$^{-1}$. These are the amide I, $\nu$(CO), and amide II, $\nu$(NH$_2$), bands respectively. The former band which is normally the more intense is only slightly affected by N-deuteration, while the latter disappears and is replaced by a new absorption band at 1155 cm$^{-1}$, $\nu$(ND$_2$). The broadness of these bands is probably due to the presence of extensive hydrogen bonding. In the ligand intramolecular and intermolecular hydrogen bonding is possible with the amide and amine nitrogen atoms as well as the amide oxygen atom all potential hydrogen acceptors in hydrogen bonding. As well as band broadening hydrogen bonding also causes shifts to lower wavenumbers in the absorptions under discussion. When the ligand forms complexes with metal ions some of the hydrogen bonds are broken. Metal ions however also cause shifts to lower frequencies in the above bands. Therefore the positions of the absorptions in the complexes relative to the free ligands are difficult to predict since this largely depends on the relative effects of metal ions and hydrogen bonding in lowering band frequencies.
The IR spectra of the complexes consist of intense broad absorptions in the regions 3000 - 3500cm\(^{-1}\) and 1500 - 1700cm\(^{-1}\). The former region contains in addition to NH\(_2\) stretching bands, absorptions due to lattice and coordinated water molecules. The NH\(_2\) stretching bands are shifted to the region 2200 - 2500 cm\(^{-1}\) on N-deuteration. In all complexes the ND\(_2\) stretching vibrations occur at lower wavenumbers than in the free ligand. The 1500 - 1700cm\(^{-1}\) region of the IR spectra of the complexes contain a number of absorptions due to amide I and amide II bands. The IR spectra of the N-deuterated complexes in this region are much simpler and show only an amide I band, which gives rise to a broad absorption near 1600cm\(^{-1}\). The \(v(\text{NH}_2)\) bands in the parent complexes are replaced at much lower wavenumbers by \(v(\text{ND}_2)\) bands in their N-deuterated derivatives. The amide I bands in the N-deuterated complexes all appear at slightly lower wavenumbers than the amide I band of the ligand.

The conductivity data for nearly all the divalent metal ion complexes in dry methanol give molar conductivity values close to that measured for the 2:1 electrolyte CaCl\(_2\) (\(\Lambda_M = 149\text{ohms}^{-1}\text{cm}^2\text{mol}^{-1}\)) under similar conditions. The visible spectra of the methanol solutions were found to be very similar to the diffuse reflectance spectra of the complexes, in situations where the latter could be recorded. It can therefore be assumed that Cl\(^-\) is not coordinated to the metal ion in these complexes. The La(III) complex was found to behave as a 3:1 electrolyte.
The diffuse reflectance spectrum of the Ni(II) complex, NiEdta(NH₂)₄Cl₂·3½H₂O, shows three bands characteristic of the $^3A_2g \rightarrow ^3T_2g$ (9500 cm⁻¹), $^3A_2g \rightarrow ^3T_1g(\Pi)$ (15500 cm⁻¹) $^3A_2g \rightarrow ^3T_1g(\Pi)$ (25000 cm⁻¹) transitions generally observed in octahedral Ni complexes. The energy levels involved in these transitions are shown in the partial energy level diagram for Ni(II) in an octahedral environment (Fig. 2). Only triplet states and the low energy singlet state derived from the Russell Saunders $^1D$ state of the free ion are represented in this diagram.

Fig. 2 Partial Energy Level Diagram for Ni(II) in an Octahedral Field.
Applying the rule of average environments to reflectance data for NiO₆ (the corresponding bands appear around 9000, 14000 and 25000 cm⁻¹) and NiN₆ (11000, 18500 and 30000 cm⁻¹) systems, the observed spectrum agrees quite well with that predicted for an NiO₄N₂ chromophore. The room temperature magnetic moment (3.27 B.M.) is also consistent with octahedral stereochemistry. In an octahedral complex the metal ion has two unpaired electrons and its ground state is a spin triplet. The spin only formula predicts a value of 2.8 B.M. for the magnetic moment but the observed value generally exceeds this value due to a partial orbital contribution to the total magnetic moment. The IR spectrum of the Ni(II) complex in the 1500 - 1700 cm⁻¹ region is complicated but greatly simplified by N-deuteration which removes the √(NH₂) bands. The N-deuterated derivative shows two distinct C=O stretching bands at 1660 and 1600 cm⁻¹, which may be assigned to coordinated and uncoordinated amide groups respectively. On the basis of the magnetic, conductivity and spectral data, the Ni(II) complex may therefore be formulated as [NiEdta-(NH₂)₄(H₂O)₂]Cl₂·1½H₂O in which the amide is present as a 2N(amine), 2O tetradentate ligand, with two aquo ligands completing octahedral coordination (XXXIII).
The room temperature magnetic moments of the Cu(II) complexes (ca. 1.7B.M.) are consistent with square planar, square pyramidal or octahedral geometries, but give little further information other than to indicate they are magnetically dilute. Detailed interpretations of the reflectance spectra of Cu(II) complexes are usually complicated because of the relatively low symmetry environments surrounding the metal ion. The diffuse reflectance spectrum of CuEdta(NH₂)₄-Cl₂·3H₂O shows a band at about 13000cm⁻¹ with a broad 'tail' into the near infrared region. This is a characteristic feature of the many known Jahn-Teller distorted six coordinated Cu(II) complexes. The main band is resolvable into at least three components ascribable to $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{z^2}$.
and \( d_{x^2-y^2} \rightarrow d_{xz, yz} \) 'hole' transitions. The energy level diagram for the 3d orbitals of Cu(II) in a distorted octahedral field is shown in Fig. 3. The transitions just mentioned involve the 'hole' in the \( d_{x^2-y^2} \) orbital.

\[
\begin{array}{c}
\text{Fig. 3 Energy Level Diagram for Cu(II) in a Distorted Octahedral Field.}
\end{array}
\]

The aqueous solution spectrum of CuEdta(NH\(_2\))\(_4\)Cl\(_2\).3H\(_2\)O is strikingly similar to the diffuse reflectance spectrum of CuEdta(NH\(_2\))\(_4\)Cl\(_2\).3H\(_2\)O. On the basis of the foregoing evidence this complex may be formulated as \( [\text{CuEdta(NH}_2\text{)}_4] \text{Cl}_2 \cdot 3\text{H}_2\text{O} \) in which the amide acts as an 2N, 4O hexadentate donor with two of the amide groups weakly bonded in axial positions to the metal ion (XXXIV).
The alternative formulation \[ \text{CuEdta(NH}_2\text{)}_4\cdot(\text{H}_2\text{O})_2 \text{Cl}_2\cdot\text{H}_2\text{O} \]
in which the amide is tetradentate was disfavoured since the complex when heated at 100°C in vacuo loses its water molecules but showed no change in its diffuse reflectance spectrum. In addition the deuterated complex CuEdta(ND\text{2})_4\text{Cl}_2, which was obtained from CuEdta(ND\text{2})_4\text{Cl}_2\cdot3\text{D}_2\text{O} under the same conditions was found to have an IR spectrum identical to the trideuterate in the 2300 - 2500 and 1600 - 1700 cm\text{^{-1}} regions. Additional evidence for the former structure is provided by the fact that the diffuse reflectance spectrum of the complex
\[
\left[ \text{CuEdta(NH}_2\text{)}_4 \right] (\text{ClO}_4)_2 \quad \text{(XXXIV)}
\]
which contains no water molecule is identical to the spectrum of the complex chloride trihydrate. The reflectance spectrum of \( \text{CuEdta(NH}_2\text{)}_2^-(\text{NH}_3)_2 \cdot 2\text{H}_2\text{O} \) is identical to the solution spectrum of the amide complex in base, conditions under which the metal ion is surrounded in a square plane by \( N_4 \) donor system (Chapter 3, section 2(a)). The unionized amide groups or aquo ligands may be weakly bonded to the axial position of the metal ion.

The diffuse reflectance spectrum of the complex \( \text{CoEdta(NH}_2\text{)}_4\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O} \) is characteristic of six coordinate Co(II), showing three bands at around \( 9000\text{cm}^{-1} \) (weak), \( 15700\text{cm}^{-1} \) (weak) and \( 19500\text{cm}^{-1} \) (strong). For octahedral \( (O_h) \) high spin Co(II) complexes three spin allowed transitions are expected: 
\[
^4T_{1g}(F) \rightarrow ^4T_{2g} \quad (v_1 \approx 8000 - 10000\text{cm}^{-1}),
\]
\[
^4T_{1g}(F) \rightarrow ^4A_{2g} \quad (v_2)
\]
and 
\[
^4T_{1g}(F) \rightarrow ^4T_{1g}(P) \quad (v_3, \text{ca. 20000cm}^{-1}).
\]

The energy levels involved in these transitions are shown in the partial energy level diagram for a high spin octahedral Co(II) complex (Fig.4). For \( O_h \) symmetry the first band is usually weaker than the third and the second is often unobserved. However a marked increase in the intensity of the \( v_1 \) and \( v_2 \) bands has been reported for some Co(II) complexes which deviate from \( O_h \) symmetry. The observed room temperature magnetic moment (4.34\text{B.M.}) for \( \text{CoEdta(NH}_2\text{)}_4\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O} \) is significantly outside the range of values normally observed for octahedral Co(II) complexes.
In high spin octahedral complexes the ground state is $^{4}{T}_{1g}$ and observed magnetic moments are much higher than spin only values (3.87B.M.) due to a considerable orbital contribution. In fields of less than $O_h$ symmetry the ground state is split with concomitant reduction in the orbital contribution. On the basis of the evidence discussed it appears that the amide ligand is hexadentate in the Co(II) complex which consequently may be written as $[\text{CoEdta(NH}_2\text{)}_4]\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$ (XXXV).
The diffuse reflectance spectrum of the complex FeEdta(NH$_2$)$_4$·Cl$_2$ contains a band at 9000cm$^{-1}$ which appears to be split. In a high spin octahedral field the ground state of Fe(II) is $^5T_{2g}$ and the 9000cm$^{-1}$ band is due to the spin allowed transition to the $^5E_g$ state, the degeneracy of which should be lifted by the Jahn-Teller effect. The observed room temperature magnetic moment (5.36B.M.) is typical of a magnetically dilute Fe(II) complex in a high spin octahedral field. On the basis of conductivity, magnetic and spectral data it would therefore appear that the amide ligand is also hexadentate in this complex, viz. [FeEdta(NH$_2$)$_4$]Cl$_2$. 

(XXXV)
The room temperature magnetic moment of the complex \( \text{MnEdta(NH}_2\text{)}_4\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O} \) (6.02B.M.) is consistent with a high spin octahedral complex\(^7\). For Mn(II) the ground state is \( ^6\text{S} \) for which there is no orbital angular momentum.\(^7\) Because of orbital nondegeneracy this state cannot be split by a crystal field of any symmetry. Therefore the observed magnetic moments of Mn(II) complexes are nearly always as predicted by the spin only formula (5.92B.M.).\(^7\) In some cases however small deviations are observed due to covalence in the metal ligand bonds. The absence of any other spin sextet terms implies that all electronic transitions from the \( ^6\text{S} \) ground state will be spin as well as parity forbidden. The d-d spectra of high spin Mn(II) complexes therefore are very weak, which explains the weak colours of these complexes.

Since the insolubility of the complex \( \text{MnEdta(NH}_2\text{)}_4\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O} \) in methanol did not permit conductance measurements, it can be concluded that the amide ligand in this complex is hexadentate only on the basis that the IR spectrum in the 1600 - 1700cm\(^{-1}\) region is virtually identical with the analogous Fe(II) complex.

The alkaline earth metal ion complexes of \( \text{Edta(NH}_2\text{)}_4 \) when N-deuterated show IR absorption bands similar to the d-block octahedral complexes in the 1600cm\(^{-1}\) region. The spectrum of the complex \( \text{MgEdta(ND}_2\text{)}_4\text{Cl}_2 \) in the 2200 - 2600 cm\(^{-1}\) (\( \nu(\text{ND}_2) \)) region is also very similar to the spectra of octahedral complexes e.g. \( \text{FeEdta(ND}_2\text{)}_4\text{Cl}_2 \). On the basis of these similarities as well as conductance data it seems likely that these complexes are octahedral with the amide behaving as a hexadentate ligand.
The complex $\text{HgEdta}(\text{NH}_2)_4\text{Cl}_2\cdot5\text{H}_2\text{O}$ is non-conducting in methanol which implies $\text{Cl}^-$ coordination to the metal ion in this complex. The IR spectrum of the complex shows only two absorptions in the $1600 - 1700\text{cm}^{-1}$ region and the positions and the relative intensities of the bands ($1660, 1605\text{cm}^{-1}$) are very similar to those of the ligand ($1660, 1580\text{cm}^{-1}$). As in the case of the free amide the $1660\text{cm}^{-1}$ band is slightly shifted to lower wavenumber as a result of N-deuteration whereas the $1605\text{cm}^{-1}$ band disappears from this region. The similarities strongly suggest that the amide groups are uncoordinated in the Hg(II) complex. In view of the generally observed tendency of Hg(II) to form tetrahedral rather than octahedral complexes\textsuperscript{71} it seems likely that the Hg(II) complex may be represented as tetrahedral $\left[\text{HgEdta}(\text{NH}_2)_4\text{Cl}_2\right]\cdot5\text{H}_2\text{O}$ (XXXVI) in which Edta($\text{NH}_2)_4$ exists as a bidentate ligand coordinated through its amine nitrogen atoms.

\begin{center}
(XXXVI)
\end{center}
The complexes ZnEdta(NH$_2$)$_4$Cl$_2$·3H$_2$O and CdEdta(NH$_2$)$_4$Cl$_2$·4H$_2$O differ from the Hg(II) complex in that both behave as 2:1 electrolytes in methanol, which implies that Cl$^-$ is uncoordinated under these conditions. This contrasting behaviour is not surprising in view of the fact that Hg(II) complexes with halide ligands are generally much more stable (sometimes by factors as great as $10^{30}$ in aqueous solution) than their Zn(II) and Cd(II) analogous. The IR spectra of the Zn(II) and Cd(II) complexes are almost identical in band positions and relative intensities with the spectrum of the Hg(II) complex in the 1600 - 1700 cm$^{-1}$ region. It therefore seems likely that in both cases Edta(NH$_2$)$_4$ is again bidentate with the amide groups all uncoordinated. Likely structures for these complexes are tetrahedral with two aquo ligands completing the coordination requirements of the metal ion i.e. 

\[ [\text{ZnEdta(NH}_2\text{)}_4(\text{H}_2\text{O})_2] \text{Cl}_2 \cdot \text{H}_2\text{O} \quad \text{and} \quad [\text{CdEdta(NH}_2\text{)}_4(\text{H}_2\text{O})_2] \text{Cl}_2 \text{H}_2\text{O}. \]

The complex LaEdta(NH$_2$)$_4$Cl$_3$·7H$_2$O behaves as a 3:1 electrolyte in methanol. The IR spectrum of the complex shows a broad absorption band in the 1600 - 1700 cm$^{-1}$ region. The spectrum of the N-deuterated complex shows bands of roughly equal intensity at 1610 and 1650 cm$^{-1}$ indicative of the presence of coordinated and uncoordinated amide groups. The NH$_2$ and ND$_2$ stretching vibration bands are swamped by intense broad absorptions associated with coordinated and uncoordinated water molecules. Due to the limited data available the exact structure of this complex is difficult to predict although it seems likely that the amide is present as a tetradeutate ligand viz. 

\[ [\text{LaEdta(NH}_2\text{)}_4(\text{H}_2\text{O})_x] \cdot (7-x)\text{H}_2\text{O} \]


The infrared spectrum of a liquid film of EdtaMe\textsubscript{4} shows an absorption of medium intensity at 2950 cm\textsuperscript{-1} which may be assigned to CH stretching vibrations, and a strong absorption at 1740 cm\textsuperscript{-1} which is typical of a carbonyl stretching absorption in a saturated aliphatic ester.\textsuperscript{61} A strong absorption band at 1200 cm\textsuperscript{-1} is probably due to a C–O asymmetric stretching vibration, although the shoulders on this band at 1175 and 1140 cm\textsuperscript{-1} may be due to C–N stretching vibrations.

The IR spectra of the d-block metal ion complexes investigated show two or more absorption bands in the 1650 - 1750 cm\textsuperscript{-1} region. In all cases an absorption is observed in the 1740 cm\textsuperscript{-1} region almost in an identical position to the ν(CO) band in the spectrum of the ligand. This is consistent with the presence in the complexes of uncoordinated or very weakly coordinated ester groups.\textsuperscript{9,10}

The complex Ni(EdtaMe\textsubscript{4})Cl\textsubscript{2}·H\textsubscript{2}O shows C=O stretching bands of roughly equal intensities at 1740 and 1680 cm\textsuperscript{-1}. The symmetric and asymmetric OH stretching bands occur in the 3100 - 3460 cm\textsuperscript{-1} region. This complex behaves as a 1:1 electrolyte in methanol which suggests that one of the Cl\textsuperscript{-} groups is coordinated to the metal ion. The diffuse reflectance spectrum of the complex is very similar to that of NiEdta(NH\textsubscript{2})\textsubscript{4}Cl\textsubscript{2}·3½H\textsubscript{2}O (Chapter 3, 3(b)) in that it contains three main bands with comparable relative intensities. The positions of these bands
(8600, 14500 and 24000 cm\(^{-1}\)) however are at slightly lower wavenumbers than the corresponding bands in the amide complexes (9500, 15000 and 25000 cm\(^{-1}\)). The observed shift to lower wavenumber is approximately that expected when an O donor ligand is replaced by a Cl\(^-\) ligand, which occupies a lower position in the spectrochemical series.\(^{71}\) These spectral similarities strongly suggest that the Ni(II)-ester complex is also octahedral. The room temperature magnetic moment (3.25 B.M.) of the complex is also consistent with octahedral stereochemistry around the metal ion, as discussed in section 3(b) of this chapter. From the data just discussed it seems likely that the Ni(II) complex may be formulated as \([\text{Ni(EdtaMe}_4]\text{(Cl)}\text{H}_2\text{O}][\text{Cl}]\) in which the ester ligand is a tetradentate 2 N, 2 O donor (XXXVII).

![Chemical structure of Ni(II) complex](image-url)
The complex \( \text{Cu(EdtaMe}_4\text{)}\text{Cl}_2 \) also behaves as a 1:1 electrolyte in methanol. Its IR spectrum shows C=O stretching absorptions, one at 1745\( \text{cm}^{-1} \) and another which is much more intense at 1720\( \text{cm}^{-1} \). The latter band carries a shoulder at 1730\( \text{cm}^{-1} \). The diffuse reflectance spectrum of the complex consists of a broad band at 13000\( \text{cm}^{-1} \), with a much less pronounced tail into the near IR region than that observed for the amide complex \( \text{CuEdta(NH}_2)_4\text{Cl}_2\cdot3\text{H}_2\text{O} \) (Chapter 3,3(b)). The room temperature magnetic moment of the complex is 1.94B.M. On the basis of the available data the most likely structure for this complex seems to be (XXXVIII).

\[
\text{XXXVIII}
\]
The uncoordinated ester group accounts for the IR band at 1745 cm\(^{-1}\) while the axially bonded ester group could be responsible for the shoulder at 1730 cm\(^{-1}\) on the main \(-\text{C}=\text{O}\) stretching band at 1720 cm\(^{-1}\).

The complex \(\text{Co(EdtaMe}_4)\text{Cl}_2\) behaves as a 2:1 electrolyte in methanol. Its diffuse reflectance spectrum shows the three bands (7000, 14500, 17500 cm\(^{-1}\)) characteristic of high spin distorted octahedral Co(II) complexes (Chapter 3, 3(b)) although all three appear at lower wavenumbers than the corresponding bands in \(\text{CoEdta(NH}_2)_4\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}\) (9000, 15700, 19500 cm\(^{-1}\)). The room temperature magnetic moment (4.23 B.M.) is also consistent with a distorted octahedral complex as discussed in section 3(b) of this chapter. The IR spectrum of the complex indicates the presence of coordinated, \(\nu(\text{CO}) = 1690\text{ cm}^{-1}\), and uncoordinated or very weakly coordinated, \(\nu(\text{CO}) = 1745\text{ cm}^{-1}\), ester groups. On the basis of the foregoing data it appears that EdtaMe\(_4\) is hexadentate in the complex \([\text{Co(EdtaMe}_4)]\text{Cl}_2\) but that some of the ester groups are much more weakly coordinated to the metal ion than the others.

The complexes Mn(EdtaMe\(_4\))\text{Cl}_2 and Fe(EdtaMe\(_4\))\text{Cl}_2 both behave as 2:1 electrolytes in methanol, indicating that Cl\(^{-}\) is uncoordinated in both cases. The IR spectra of the complexes in the C=O stretching region show bands at 1685 and 1725 - 1745 cm\(^{-1}\). The Mn(II) complex is extremely pale coloured, a property which is common to high spin octahedral complexes of this metal ion.\(^{71}\) The room temperature magnetic moment (6.18 B.M.) is also indicative of a high spin octahedral
complex, if allowance is made for some covalence in the metal ligand bonds (Chapter 3,3(b)). The diffuse reflectance spectrum of the Fe(II) complex has a band at 8800 cm\(^{-1}\) (split) and is similar to the spectrum of FeEdta(NH\(_2\))\(_4\)Cl\(_2\) which was shown to be octahedral (Chapter 3,3(b)). The room temperature magnetic moment (5.35 B.M.) is consistent with a magnetically dilute high spin octahedral Fe(II) complex. It therefore appears likely that both the above complexes are octahedral with EdtaMe\(_4\) acting as a 2 N, 4 O donor. Again, however, in order to explain the IR data it must be assumed that some of the ester groups are much more weakly coordinated than the others.

The complex Hg(EdtaMe\(_4\))Cl\(_2\) is a non-electrolyte in methanol which indicates that Cl\(^-\) is coordinated to the metal ion. The IR spectrum of the complex shows a split C=O stretching band in the 1725 - 1745 cm\(^{-1}\) region. As in the case of HgEdta(NH\(_2\))\(_4\)Cl\(_2\)·5H\(_2\)O (Chapter 3, 3(b)) it appears that the above complex is tetrahedral and that EdtaMe\(_4\) acts as a bidentate ligand through its nitrogen atoms with its ester groups uncoordinated.

The complex Cd(EdtaMe\(_4\))Cl\(_2\)·H\(_2\)O is a 1:1 electrolyte in methanol. Its IR spectrum in the C=O stretching region shows absorptions at 1695, 1725 and 1740 cm\(^{-1}\). The OH stretching bands occur in the 3520 - 3580 cm\(^{-1}\) region, which indicates the presence of lattice rather than coordinated water. It seems likely that the Cd(II) complex is octahedral with EdtaMe\(_4\) acting as a pentadentate ligand. The uncoordinated ester group would account for the 1740 cm\(^{-1}\) absorption and
the remaining bands could be attributed to the coordinated ester groups in the plane of the nitrogen atom and the metal ion and to the axially bonded ester group trans to coordinated Cl⁻.

The complex Sn(EdtaMe₄)Cl₂·9H₂O is a 1:1 electrolyte in methanol. The IR spectrum of this complex is identical to that of EdtaMe₄ in the C=O stretching region. It therefore seems that this ligand is bidentate in the above complex with Cl⁻ and aquo ligands completing the coordination requirements of the metal ion.
CHAPTER 4

METAL COMPLEXES OF

ETHYLENEDIAMINEMONOACETIC ACID

AND ITS ETHYL ESTER
1. Introduction.

Ethylendiaminemonoacetic acid (EdmaH) is a simple artificial, aminoacid the conjugate base (Edma) of which is potentially a 2 N, 0 tridentate ligand. Despite this only a few reports are available on metal complexes of this ligand. A 1:1:1 mixed ligand complex is formed between bidentate EdmaH, a naphtholazopyrazolone dye and Cr(III). The octahedral complexes [Co(Edma)₂]Cl₂H₂O and [Cr(Edma)₂]Cl₃H₂O have also been reported. In theory six geometrical isomers are possible for each of these complexes depending on the relative positions in the octahedron of the carboxylate oxygen atoms and the secondary and primary nitrogen atoms. However, only two isomers were isolated for the Co(III) complex, one of which has the carboxylate groups trans and the other cis. Only one Cr(III) isomer was isolated and this was shown to have a trans configuration with respect to the carboxylate groups. EdmaH also reacts with K₂PtCl₄ to give the complex Pt(EdmaH)Cl₂ in which the aminoacid is bidentate through its nitrogen atoms. In aqueous solution this complex undergoes a reaction, the rate of which is pH dependent, and the product of which is Pt(Edma)Cl.

In this chapter the preparation, characterisation and some reactions of Co(III) complexes of EdmaH and its ethyl ester are reported. The hydrolysis of the ester (EdmaEt) in the presence of various divalent metal ions is also described.
2. Experimental.

(a) Preparation of Ethylenediaminemonoacetic Acid Dihydrochloride (EdmaH₂HCl).

This compound was prepared by a modification of a previously reported method.⁷⁴

A solution of chloroacetic acid (94.5g.) in water (100cm³) was neutralized with an equimolar quantity of solid sodium bicarbonate. Ethylenediamine (60g.) was added dropwise to the solution, which was then treated with a solution (80cm³) of sodium hydroxide (40g.). The final solution was evaporated to dryness on a rotary evaporator. The residue was dissolved in a minimum quantity of hot water and acidified to pH 3 with concentrated HCl. The solvent was then removed under reduced pressure, the oily residue was washed with ethanol, and treated with concentrated HCl (350cm³). After the addition of an equal volume of ethanol/ether (1:1) the solution was cooled overnight in an ice bath whereupon EdmaH₂HCl was obtained as a white crystalline product. It was recrystallised from a minimum amount of ethanol.

The IR spectrum of the product showed a -C=O stretching absorption at 1720cm⁻¹ characteristic of a carboxylic acid group.⁶¹ The melting point (144°C) agrees quite well with that reported in the literature (145°C).⁷⁶
(b) Preparation of the Ethyl Ester of Ethylenediaminemonoaetic Acid Dihydrochloride (EdmaEt.2HCl).

Dry HCl gas was passed through a stirred suspension of EdmaH.2HCl (10g.) in absolute ethanol (250cm$^3$). After some time the acid dissolved and the resulting solution was further treated with HCl and cooled, whereupon a white precipitate was obtained. The IR spectrum of the product showed a C=O stretching band at 1740cm$^{-1}$, typical of an aliphatic ester.

(c) Preparation of Chlorobis(ethylenediamine)(ethylenediaminemonoaetic Acid)cobalt(III) Chloride.

A 1:1 mole ratio of trans [Co(en)$_2$Cl$_2$]Cl and EdmaH.2HCl were ground together and the mixture made into a paste by the addition of a few drops of water. Triethylamine was added dropwise to the paste until the colour changed from green to mauve. The mixture was then treated with a few drops of concentrated HCl. Upon addition of methanol a mauve coloured precipitate was obtained. This was suction filtered, washed with acetone and dried in a vacuum oven at 60$^\circ$C. Found: C,24.4% ; H,6.1% ; N,20.5%. $C_{26}H_{26}N_6O_2Cl_3Co$ requires C,23.8% ; H,6.5% ; N,20.8%.

The IR spectrum of the complex, as a nujol mull, shows a -C=O stretching band at 1620cm$^{-1}$ characteristic of a coordinated carboxylate group. The electronic spectrum of an aqueous solution of the complex showed absorption bands at 555,460 and 365nm.
(d) Preparation of Chlorobis(ethylenediamine)(ethylenediamine-
monoethylacetate)cobalt(III) Chloride.

A 1:1 mole ratio of trans \([\text{Co(en)}_2\text{Cl}_2]\)Cl and EdmaEt.2HCl were ground together and made into a paste by the addition of a few drops of water. The paste was treated dropwise with triethylamine until the colour change to purple was complete. The mixture was treated with concentrated HCl, followed by methanol whereupon a purple precipitate was obtained. This was filtered, washed with acetone and dried in a vacuum oven at 60°C.

Found: C,27.1% ; H,7.6% ; N,19.5%. \( C_{10}H_{30}N_6O_2Cl_3\)Co requires C,27.8% ; H,7.0% ; N,19.5%

The IR spectrum of the complex showed a C=O stretching band at 1740cm\(^{-1}\). The electronic spectrum of an aqueous solution of the complex had bands at 525 and 365nm.
3. Results and Discussion.

(a) Structures of Complexes $[\text{Co(en)}_2\text{Cl(EdmaH)}]\text{Cl}_2$ and $[\text{Co(en)}_2\text{Cl(EdmaEt)}]\text{Cl}_2$.

Trans- $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$ is a useful starting material from which many other Co(III) complexes can be prepared. This is because the Cl$^-$ ligands are relatively labile and can be substituted by a variety of nucleophiles. Reactions between trans- $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$ and amines have been extensively studied since first investigated by Meisenheimer. Despite much qualitative study the influence of the nature of the amine on the product of the reaction remains speculative, since any of the products in the reaction scheme 26 - 28 may be obtained.

\[
\begin{align*}
\text{trans-} [\text{Co(en)}_2\text{Cl}_2]^+ & \rightarrow \text{cis-} [\text{Co(en)}_2\text{Cl(A)}]^2+ \ldots (26) \\
\text{trans-} [\text{Co(en)}_2\text{Cl}_2]^+ & \rightarrow \text{cis-} [\text{Co(en)}_2\text{Cl(OH)}]^+ \ldots (27) \\
& \rightarrow \text{trans-} [\text{Co(en)}_2\text{Cl(OH)}]^+ 
\end{align*}
\]

Reaction (26) seems to occur mainly with sterically hindered or weakly basic amines, reaction (27) occurs almost exclusively in the case of primary aliphatic amines, and the cis configurations of the products have been unambiguously established by resolution of the racemic mixture (a trans configuration would be achiral).
Reactions of trans $\text{[Co(en)$_2$Cl$_2$]}^+$ and aminoacids have not been reported but are currently being investigated. However, a number of products of the type cis- $\text{[Co(en)$_2$Cl(NH$_2$-CH$_2$-CO$_2$R)]}^{3+}$ (R=-CH$_3$, -C$_2$H$_5$, -C$_3$H$_7$) have been prepared using glycine esters as incoming nucleophiles.

The product of the reaction between trans- $\text{[Co(en)$_2$Cl$_2$]}^+$ and EdmaEt (2(d)) seems to have structure (XXXIX).

![Chemical structure](XXXIX)

Its IR spectrum has a $\text{C=O}$ stretching band at 1740 cm$^{-1}$ characteristic of an uncoordinated ester group, and its electronic spectrum ($\lambda_{\text{max}}$ 525,365 nm) is similar to that of cis- $\text{[Co(en)$_2$Cl(A)]}^{2+}$ complexes and indicative of a CoN$_5$Cl chromophore. The product of the reaction between trans- $\text{[Co(en)$_2$Cl$_2$]}^+$ and EdmaEt seems to have structure (XL).
The IR band at 1640 cm\(^{-1}\) (coordinated carboxylate) is consistent with this assignment, as is the three-band electronic spectrum in the 350 - 600 nm region (\(\lambda_{\text{max}}\) 555, 460 and 356 nm).

For most octahedral Co(III) complexes with the exception of [CoF\(_6\)]\(^{3-}\) and Co(H\(_2\)O)\(_3\)F\(_3\), the ground state is \(^1A_{1g}\) and consequently these complexes are diamagnetic. The electronic absorption spectra of these Co(III) complexes in regular octahedral environments results from transitions from this state to the singlet states \(^1T_{1g}\) and \(^1T_{2g}\).

Complexes of the type CoX\(_4\)YA can exist in cis or trans configurations. The lowering of symmetry (from O\(_h\)) causes negligible splitting of the \(^1T_{2g}\) state but appreciable splitting of the \(^1T_{1g}\) state in the trans isomer. In the cis isomer the \(^1T_{1g}\) state is also split but to a much smaller extent. The electronic spectra of the cis complexes therefore consist of three bands, two of which are almost superimposed. In the trans isomer three distinct bands may be observed. On this basis, the trans configuration has been assigned to the complex [Co(en)\(_2\)Cl(EdmaH)]\(^{2+}\) and the cis configuration to the complex [Co(en)\(_2\)Cl(EdmaEt)]\(^{2+}\).

Their electronic spectra are similar to those of trans [Co-(en)\(_2\)Cl\(_2\)]\(^+\) (\(\lambda_{\text{max}}\) 610, 453, 385 nm) and cis- [Co(en)\(_2\)Cl\(_2\)]\(^+\) (\(\lambda_{\text{max}}\) 535, 380 nm) except that the bands are shifted towards shorter wavelengths due to the higher positions of O and N donors compared to Cl\(^-\) in the spectrochemical series.
(b) Reactions of the Complexes $[\text{Co(en)}_2\text{Cl(EdmaH)}]\text{Cl}_2$ and $[\text{Co(en)}_2\text{Cl(EdmaEt)}]\text{Cl}_2$ in Aqueous Solution.

It has been well established that Co(III) complexes undergo three types of ligand substitution reaction in aqueous solution.\(^{83}\) These are: (i) base hydrolysis in which the overall reaction involves replacement of the leaving ligand by hydroxide ion e.g.

$$\text{[Co(NH}_3)_5\text{X}]^{2+} + \text{OH}^- \rightarrow \text{[Co(NH}_3)_5\text{OH}]^{2+} + \text{X}^-$$

\[\text{..} \ldots \text{..} \ldots \text{..} \ldots (29)\]

(ii) acid hydrolysis in which the leaving ligand is replaced by water e.g.

$$\text{[Co(NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \rightarrow \text{[Co(NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{X}^-$$

\[\text{..} \ldots \text{..} \ldots \text{..} \ldots (30)\]

and (iii) anation reactions in which aquo ligands are replaced by incoming nucleophiles. Acid hydrolysis reactions are so called because they are usually performed under acidic conditions in order to suppress the much more rapid base hydrolysis reactions.

All the available experimental data correlating various effects on rates are compatible with the assignment of an $S_N^1$ mechanism for acid hydrolysis reactions.\(^{83}\) This mechanism is outlined using the substrate $[\text{Co(NH}_3)_5\text{Cl}]^{2+}$ as an example.
\[
\text{[Co(NH}_3\text{)}_5\text{Cl]}^{2+} \xrightarrow{\text{slow}} \text{[Co(NH}_3\text{)}_5\text{]}^{3+} + \text{Cl}^- \]

five coordinate intermediate

\[
+ \text{H}_2\text{O} \; \text{fast}
\]

\[
\text{[Co(NH}_3\text{)}_5(\text{H}_2\text{O})]^{3+}
\]

\[
\text{(31)}
\]

The rate expression for this process is

\[
\text{Rate} = k\text{[Co(NH}_3\text{)}_5\text{Cl]}^{2+}
\]

\[
\text{(32)}
\]

When halide is the leaving group rates of reaction are considerably enhanced by the presence of halide abstractors e.g. Hg(II), Tl(III) or Ag(I). These metal ions give rise to species which are better as leaving groups than halide

\[
\text{[Co(NH}_3\text{)}_5\text{Cl]}^{2+} + \text{Hg(II)} \xrightarrow{K} \text{[Co(NH}_3\text{)}_5\text{Cl} \rightarrow \text{Hg(II)}]}^{4+}
\]

\[
\text{slow} \; k'
\]

\[
\text{[Co(NH}_3\text{)}_5\text{OH}_2\text{]}^{3+} \xleftarrow{\text{fast} \; \text{H}_2\text{O}} \text{[Co(NH}_3\text{)}_5\text{]}^{3+} + \text{HgCl}^+
\]

\[
\text{(33)}
\]

These metal ions are technically not catalysts as the initial and final states of the added reagent are different but this term has crept into the literature. The rate expression for the above reaction is
\[
\text{Rate} = k_2 [\text{Co(NH}_3\text{)}_5\text{Cl}] [\text{Hg(II)}] \\

\text{..... (34)}
\]

assuming a steady state approximation for the Cl\(^-\) bridged complex and \(K[\text{Hg(II)}] << 1\).

The nature of the five coordinate transition state in the acid hydrolysis of Co(III) complexes remains speculative.\(^{84}\) This may be either trigonal bipyramidal in which case extensive stereochemical change may occur between reactant and product or square pyramidal in which case the reaction proceeds with retention of configuration.

Over the years four different mechanisms have been proposed for the base hydrolysis reactions of Co(III) complexes.\(^{83}\) However it is now generally regarded that an \(S_N1CB\) mechanism is probably the closest approach to the truth. This mechanism is illustrated using \([\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}\) as an example

\[
\begin{align*}
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} &+ \text{OH}^- &\xrightarrow{K} &[\text{Co(NH}_3\text{)}_4(\text{NH}_2)\text{Cl}]^{+} &+ \text{H}_2\text{O} \\
\downarrow & & & &\downarrow k, \text{ slow} \\
[\text{Co(NH}_3\text{)}_5(\text{OH})]^{2+} &\xrightarrow{+\text{H}_2\text{O}} &[\text{Co(NH}_3\text{)}_4(\text{NH}_2)]^{2+} &+ \text{Cl}^- \\
\text{five coordinate intermediate} & & & &\text{..... (35)}
\end{align*}
\]

The application of a steady state approximation to \([\text{Co(NH}_3\text{)}_4^- (\text{NH}_2)\text{Cl} ]^+\) and the assumption that \(K[\text{OH}] << 1\) leads to the rate expression

\[
\text{Rate} = k_2 [\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} [\text{OH}^-] \\

\text{..... (36)}
\]
where $k_2 = kK$. For Co(III) amine complexes it seems valid to assume that $K [OH^-]$ is usually much less than 1. Recently a $pK_a$ value of 14.9 has been reported for $[Co(en)_3]^{3+}$ in aqueous hydroxide-dimethylsulphoxide mixtures.\(^{85}\)

The $S_{N1CB}$ mechanism involves a rapid pre-equilibrium between the reacting complex and its conjugate base, followed by rate determining dissociation of the latter to a five coordinate intermediate, which rapidly reacts with water to give the hydroxide product. The formation of an amide conjugate base requires the presence of an amine proton in the reacting complexes. It has been found that complexes without those acidic protons e.g. trans- $[Co(bipy)_2Cl_2]^{+}$\(^{86}\) and trans- $[Co(tep)_2Cl_2]^{+}$\(^{56}\) are insensitive to base hydrolysis.

In perchloric acid solutions containing Hg(II) salts the complex trans- $[Co(en)_2Cl(EdmaH)]^{2+}$ undergoes a reaction characterised by marked spectral changes in the 350 - 600nm region Fig. 5. The absorption at 550nm in the reactant disappears and is replaced by a more intense absorption at 490nm, in the product. Well defined isosbestic points occur at 545, 415 and 362nm. Attempts to isolate the product from solution were unsuccessful but the electronic spectrum of the product ($\lambda_{max}$ 492, 355nm) is consistent with the structure cis- $[Co-(en)_2OH_2(EdmaH)]^{2+}$ in which EdmaH is bonded to the metal ion through its carboxylate group. The spectral intensification is also consistent with a change from a trans to a cis configuration occurring during the reaction, since the spectra of cis complexes are generally more intense than trans complexes because of lower symmetry.
Fig. 5 Solution Spectra of trans-[Co(en)$_2$(Cl)$_2$(Bdmah)]$^{2+}$ in 0.5M HCIO$_4$

Containing 0.2M Hg(II)

Scanned after (a) 5mins., (b) 10mins., (c) 17mins.,
(d) 26mins., (e) 45mins.

Wavelength nm

0.2 0.4 0.6 0.8

Absorbance

400 450 500 550 600
The kinetics of the Hg(II) protonated acid hydrolysis of trans- \([\text{Co(en)}_2\text{Cl(EdmaH)}]^{2+}\) were investigated at 25±0.1°C by following the absorbance increase during the reaction at 492nm. In all cases the [Hg(II)] was in vast excess over the complex concentration and therefore remained constant during each reaction. Under these conditions rate expression (34) simplifies to

\[
\text{Rate} = k_{\text{obs}}[\text{Co(en)}_2\text{Cl(EdmaH)}]^{2+}
\]  

...... (37)

where \(k_{\text{obs}}\) is the pseudo first order rate constant and is equal to \(k_2 [\text{Hg(II)}]\). Plots of \(\ln(\text{Abs}_\infty - \text{Abs}_t)\) versus time were linear for three half lives. The slopes of these plots are equal to \(-k_{\text{obs}}\). Values of \(k_2\) obtained for various Hg(II) concentrations are presented in Table 11. The [HClO₄] in all experiments was 1M.

### Table 11 Rate Constants for the Hg(II) Promoted Acid Hydrolysis of cis-\([\text{Co(en)}_2\text{Cl(EdmaEt)}]^{2+}\) at 25±0.1°C.

<table>
<thead>
<tr>
<th>Hg(II)</th>
<th>(k_{\text{obs}}/\text{s}^{-1})</th>
<th>(k_{\text{obs}}/ [\text{Hg(II)}].(=k_2)\text{M}^{-1}\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20M</td>
<td>1.16x10⁻³</td>
<td>5.8x10⁻³</td>
</tr>
<tr>
<td>0.10M</td>
<td>5.92x10⁻³</td>
<td>5.9x10⁻³</td>
</tr>
<tr>
<td>0.05M</td>
<td>2.92x10⁻⁴</td>
<td>5.8x10⁻³</td>
</tr>
</tbody>
</table>
These values of $k_2$ are similar to those obtained for other cis-[Co(en)$_2$Cl(N-donor)] systems. (Table 12).

Table 12 Some Second-Order Rate Constants for Hg(II) Promoted Acid Hydrolysis of cis [Co(en)$_2$Cl-(N-donor)]$^{2+}$ Systems.

<table>
<thead>
<tr>
<th>N donor</th>
<th>$k_2$/M$^{-1}$s$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>5.66x10$^{-3}$</td>
<td>87, 88</td>
</tr>
<tr>
<td>NH$_2$-CH$_2$-CH$_3$</td>
<td>8.83x10$^{-3}$</td>
<td>87, 88</td>
</tr>
<tr>
<td>NH$_2$-(CH$_2$)$_2$-O-COCH$_3$</td>
<td>8.00x10$^{-3}$</td>
<td>89</td>
</tr>
</tbody>
</table>

The complex cis-[Co(en)$_2$Cl(EdmaEt)]$^{2+}$ also undergoes a Hg(II) promoted acid hydrolysis reaction during which $\lambda_{\text{max}}$ shifts from 525 and 365 to 487 and 355nm (Fig.6). Well defined isosbestic points were observed at 520 and 415nm. The wavelength shift is characteristic of replacement of Cl$^-$ by H$_2$O and the product of the reaction seems to be cis-[Co(en)$_2$-(OH$_2$)(EdmaEt)]$^{3+}$. The relative positions of $\lambda_{\text{max}}$ for cis-[Co(en)$_2$OH$_2$(EdmaEt)]$^{3+}$ (487nm) which is a CoN$_5$O chromophore and cis-[Co(en)$_2$OH$_2$(EdmaH)]$^{3+}$ (492nm) which is a CoN$_4$O$_2$ chromophore are consistent with an N donor atom being higher in the spectrochemical series than an O donor atom. The kinetics of the Hg(II) promoted acid hydrolysis of cis-[Co(en)$_2$Cl(EdmaEt)]$^{2+}$ at 25±0.1°C were followed
Fig. 6 Solution Spectra of cis-[Co(en)$_2$Cl(EdmaEt)]$^{2+}$ in 0.5M HClO$_4$

Containing 0.2M Hg(II).

Scanned after (a) 2mins.
(b) 4mins.
(c) 6mins.
(d) 11mins.
(e) 20mins.
spectrophotometrically at 487nm. Values of the second order rate constant obtained at different Hg(II) concentrations are presented in Table 13.

Table 13 Rate Constants for the Hg(II) Promoted Acid Hydrolysis of trans-[Co(en)₂Cl(EdmaH)]^3+ at 25±0.1°C.

<table>
<thead>
<tr>
<th>Hg(II)</th>
<th>kₐ /s⁻¹</th>
<th>k₂/M⁻¹s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20M</td>
<td>7.59x10⁻⁴</td>
<td>3.8x10⁻⁴</td>
</tr>
<tr>
<td>0.10M</td>
<td>3.77x10⁻⁴</td>
<td>3.8x10⁻⁴</td>
</tr>
<tr>
<td>0.05M</td>
<td>1.98x10⁻⁴</td>
<td>4.0x10⁻⁴</td>
</tr>
</tbody>
</table>

The value of k₂ is similar to those obtained for other trans-[Co(en)₂Cl(N-donor)] complexes.⁸²

The complex trans [Co(en)₂Cl(EdmaH)]²⁺ is a monobasic acid with a pKₐ for ionization of the ammonium group of about 8.8

\[
\begin{align*}
[\text{Co(en)}₂\text{Cl(EdmaH)}]^{2+} & \rightleftharpoons [\text{Co(en)}₂\text{Cl(EdmaH)}]^+ + \text{H}^+ \\
[\text{trans-Co(en)}₂\text{Cl(EdmaH)}]^{2+} & \rightleftharpoons [\text{trans-Co(en)}₂\text{Cl(EdmaH)}]^+ + \text{H}^+ 
\end{align*}
\]
This value is approximate since attempts to obtain an accurate value by potentiometric titration were hampered by base hydrolysis of the complex in alkaline solutions. Therefore in neutral and weakly alkaline solutions (pH 7 - 11) the complex trans- \([\text{Co(en)}_2\text{Cl(EdmaH)}]^2+\) exists in equilibrium with its conjugate base, trans- \([\text{Co(en)}_2\text{Cl(Edma)}]^+\). In alkaline solutions (pH >9) the electronic spectrum of the equilibrium mixture of the complex undergoes considerable change as base hydrolysis occurs (Fig. 7). During this reaction the absorption at 555nm disappears and is replaced by a new absorption of greater intensity at 505nm. The electronic spectrum (\(\lambda_{\text{max}}\) 505, 362nm) indicates that the hydroxo product has the cis configuration. The base hydrolysis reaction is summarized in reaction scheme (39)

\[
\begin{align*}
\text{trans- } [\text{Co(en)}_2\text{Cl(EdmaH)}]^2+ & \rightleftharpoons \text{trans- } [\text{Co(en)}_2\text{Cl(Edma)}]^2+ \\
\downarrow & \\
\text{cis- } [\text{Co(en)}_2\text{OH(EdmaH)}]^2+ & \rightleftharpoons \text{cis- } [\text{Co(en)}_2\text{OH(Edma)}]^2+
\end{align*}
\]

(39)

In 0.1M NaOH solution the equilibrium lies almost completely in favour of cis- \([\text{Co(en)}_2\text{OH(Edma)}]^2+\). The relative positions of \(\lambda_{\text{max}}\) in the electronic spectrum of this complex (505, 362nm) and in the spectrum of the complex cis- \([\text{Co(en)}_2\text{OH}_2-\text{(EdmaH)}]^2+\) (492,355nm), which was a product of the Hg(II) promoted acid hydrolysis of trans- \([\text{Co(en)}_2\text{Cl(EdmaH)}]^2+\) is
Fig. 7 Solution Spectra of trans-\([\text{Co}(\text{en})_2\text{Cl(Edma)}]^{+}\) in 0.1M Triethylamine Buffer (pH 10.3).

Scanned after (a) 2mins., (b) 4mins., (c) 7mins., (d) 12mins., (e) 20mins.
consistent with $H_2O$ being higher in the spectrochemical series than $OH^-$. The kinetics of base hydrolysis were investigated at pH values where the conjugate base is the predominant species in solution. Reactions were investigated spectrophotometrically by monitoring the absorbance increase at 505nm. During each reaction constant pH was maintained by the use of n-butylamine/n-butylamine. hydrogen perchlorate buffers ([n-BuNH$_2$] + [n-BuNH$_3^+$] = 0.1M). All solutions were at 1M (NaClO$_4$) constant ionic strength. Under these conditions rate expression (36) for base hydrolysis reactions simplifies to

$$\text{Rate} = k_{\text{obs}} [\text{Co(\text{en})}_2\text{Cl(Edma)}]^+$$

where $k_{\text{obs}}$, the pseudo first order rate constant equals $k_2[OH^-]$. The values of $k_{\text{obs}}$ obtained using solutions of different pH as well as the corresponding $k_2$ values (in units of activity$^{-1}$s$^{-1}$) are presented in Table 14.

The complex cis- [Co(\text{en})$_2$Cl(EdmaEt)]$^{2+}$ also undergoes base hydrolysis in alkaline solutions. This reaction is accompanied by electronic spectral changes during which $\lambda_{\text{max}}$ shifts from 525 to 500nm (Fig. 8). This wavelength shift is due to Cl$^-$ being replaced by $OH^-$ which is more highly placed in the spectrochemical series. The position of $\lambda_{\text{max}}$ for the complex cis- [Co(\text{en})$_2$OH(EdmaEt)]$^{2+}$ is, as expected, higher than for its conjugate acid cis- [Co(\text{en})$_2$OH$_2$(EdmaEt)]$^{3+}$.
Fig. 8 Solution Spectra of cis- [Co(en)$_2$Cl(EdmaEt)]$^{2+}$ in 0.1M Triethylamine Buffer (pH 10.3).

Scanned after (a) 4mins., (b) 8mins.,
(c) 13mins., (d) 26mins.
(487 nm). The kinetics of base hydrolysis of the above complex were studied by following the absorbance increase at 500 nm. A borax buffer solution (0.01 M) was used at the lower pH, and an n-butylamine/n-butylamine hydrogen perchlorate buffer was used at the higher pH. Values of $k_{obs}$ as a function of pH and the corresponding $k_2$ values are presented in Table 15.

Table 14 Rate Data for the Base Hydrolysis of trans-[Co(en)$_2$-Cl(Edma)$_{1}$]$_{1}^{+}$ at 25±0.1°C.

<table>
<thead>
<tr>
<th>pH</th>
<th>(OH$^{-}$)</th>
<th>$k_{obs}$/s$^{-1}$</th>
<th>$k_2$/A$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.62</td>
<td>4.17x10$^{-5}$</td>
<td>3.48x10$^{-4}$</td>
<td>8.27</td>
</tr>
<tr>
<td>10.18</td>
<td>1.51x10$^{-4}$</td>
<td>1.32x10$^{-3}$</td>
<td>8.74</td>
</tr>
<tr>
<td>10.45</td>
<td>2.82x10$^{-4}$</td>
<td>2.23x10$^{-3}$</td>
<td>7.91</td>
</tr>
<tr>
<td>10.62</td>
<td>4.17x10$^{-4}$</td>
<td>3.41x10$^{-3}$</td>
<td>8.18</td>
</tr>
</tbody>
</table>

Table 15 Rate Data for the Base Hydrolysis of cis-[Co(en)$_2$-Cl(EdmaEt)$_{2}$]$_{2}^{+}$ at 25±0.1°C.

<table>
<thead>
<tr>
<th>pH</th>
<th>(OH$^{-}$)</th>
<th>$k_{obs}$/s$^{-1}$</th>
<th>$k_2$/A$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td>1.58x10$^{-5}$</td>
<td>2.53x10$^{-4}$</td>
<td>16.0</td>
</tr>
<tr>
<td>10.10</td>
<td>1.26x10$^{-4}$</td>
<td>1.93x10$^{-4}$</td>
<td>15.3</td>
</tr>
</tbody>
</table>
The complex cis- $[\text{Co(en)}_2\text{Cl(EdmaEt)}]^ {2+}$ undergoes base hydrolysis approximately twice as fast as trans- $[\text{Co(en)}_2\text{Cl-} (\text{Edma})] ^+$. A contributing factor to this rate enhancement is the increased positive charge on the ester complex, which would cause amine ligands in this complex to be more acidic ($K$ and therefore $k_2$ in rate expression (36) larger) than the amine ligands in the trans complex.

(c) Metal Ion Promoted Hydrolysis of Ethylenediaminemonoethylacetate (EdmaEt).

The base hydrolysis of EdmaEt has been shown to proceed in either of two ways:

\[
\begin{align*}
\text{NH}_2-(\text{CH}_2)_2-\text{NH}-\text{CH}_2-\text{CO}_2\text{Et} \\
\text{(i)} & \quad \text{(ii)} \\
\text{NH}_2-(\text{CH}_2)_2-\text{NH}_2-\text{CH}_2-\text{CO}_2^- \\
\end{align*}
\]

........ (41)

The formation of 2-ketopiperazine occurs by the following mechanism:

........ (42)
Rate constants for the disappearance of ester i.e. the sum of the rate constants for the two pathways have been reported. Rate constants for the base hydrolysis of the conjugate acids of ethylenediaminemonoethylacetate, $\text{HEDmaEt}^+ = \text{NH}_3-(\text{CH}_2)_2-\text{NH-CH}_2-\text{CO}_2\text{Et}$, $\text{H}_2\text{EdmaEt}^{2+} = \text{NH}_3-(\text{CH}_2)_2-\text{NH}_2-\text{CH}_2-\text{CO}_2\text{Et}$, neither of which give rise to ring closure have also been determined.

In the presence of Cu(II) cyclisation of EdmaEt is prevented due to the formation of complex (XLI)

\[
\begin{array}{c}
\text{CH}_2 \quad \text{CH}_2 \\
\downarrow \\
\text{H}_2\text{N} \quad \text{NH} \quad \text{CH}_2 \\
\downarrow \\
\text{Cu} \quad \text{O} = \text{C} - \text{OEt}
\end{array}
\]

(XLI)

However hydrolytic pathways (ii) of reaction (41) is promoted by this metal ion.

The Co(II), Ni(II) and Cu(II) promoted hydrolyses of EdmaEt (reaction (43)) were investigated by the pH-stat technique at $25 \pm 0.1^\circ\text{C}$. Metal ion and ligand concentrations were all $5.0 \times 10^{-3}\text{M}$ and the solutions were also $0.1\text{M}$ in NaClO$_4$ to maintain constant ionic strength. Values of $k_{\text{obs}}$ (see equation (22), Chapter 2) as a function of pH are presented in Tables 16 - 18. Values of $[\text{OH}^-]$ were obtained from $[\text{OH}^-]$ using an activity coefficient value for OH$^-$ of 0.772.
Table 16  Co(II)-Promoted Hydrolysis of EdmaEt at 25±0.1°C.

<table>
<thead>
<tr>
<th>pH</th>
<th>(OH(^{-}))</th>
<th>[OH(^{-})]</th>
<th>k(_{obs}/s^{-1})</th>
<th>k(_2/M^{-1}s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.35</td>
<td>2.24x10^{-7}</td>
<td>2.90x10^{-7}</td>
<td>1.35x10^{-4}</td>
<td>4.66x10^{2}</td>
</tr>
<tr>
<td>7.455</td>
<td>2.85x10^{-7}</td>
<td>3.69x10^{-7}</td>
<td>1.74x10^{-4}</td>
<td>4.72x10^{2}</td>
</tr>
<tr>
<td>7.80</td>
<td>6.31x10^{-7}</td>
<td>8.17x10^{-7}</td>
<td>3.43x10^{-4}</td>
<td>4.20x10^{2}</td>
</tr>
</tbody>
</table>

Table 17  Ni(II)-Promoted Hydrolysis of EdmaEt at 25±0.1°C.

<table>
<thead>
<tr>
<th>pH</th>
<th>(OH(^{-}))</th>
<th>[OH(^{-})]</th>
<th>k(_{obs}/s^{-1})</th>
<th>k(_2/M^{-1}s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.44</td>
<td>2.75x10^{-7}</td>
<td>3.56x10^{-7}</td>
<td>6.16x10^{-5}</td>
<td>1.73x10^{2}</td>
</tr>
<tr>
<td>7.78</td>
<td>6.03x10^{-7}</td>
<td>7.81x10^{-7}</td>
<td>1.46x10^{-4}</td>
<td>1.87x10^{2}</td>
</tr>
</tbody>
</table>

Table 18  Cu(II)-Promoted Hydrolysis of EdmaEt at 25±0.1°C.

<table>
<thead>
<tr>
<th>pH</th>
<th>(OH(^{-}))</th>
<th>[OH(^{-})]</th>
<th>k(_{obs}/s^{-1})</th>
<th>k(_2/M^{-1}s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.89</td>
<td>7.80x10^{-9}</td>
<td>1.01x10^{-8}</td>
<td>2.76x10^{-4}</td>
<td>2.73x10^{4}</td>
</tr>
<tr>
<td>6.04</td>
<td>1.10x10^{-8}</td>
<td>1.42x10^{-8}</td>
<td>4.06x10^{-4}</td>
<td>2.86x10^{4}</td>
</tr>
<tr>
<td>6.71</td>
<td>5.13x10^{-8}</td>
<td>6.65x10^{-8}</td>
<td>1.78x10^{-3}</td>
<td>2.68x10^{4}</td>
</tr>
<tr>
<td>7.74</td>
<td>5.49x10^{-7}</td>
<td>7.11x10^{-8}</td>
<td>2.23x10^{-4}</td>
<td>3.14x10^{4}</td>
</tr>
</tbody>
</table>
From the data in Tables 16 - 18 it can be seen that the metal ion promoted ester hydrolysis of EdmaEt is in the order Cu(II) >> Co(II) > Ni(II). This trend is similar to that observed in the metal ion promoted hydrolysis of other esters. Hence Cu(II) is more effective than Ni(II) in promoting the hydrolysis of the methyl esters of L-histidine\(^{18}\) and 2,3-diaminopropionic acid.\(^ {19}\) Co(II) on the other hand is more effective than Ni(II) in promoting the base hydrolysis of some aminoacid esters of N,N-diacetic acids.\(^ {4}\)

The value of \(k_2\) for the Cu(II) promoted hydrolysis of EdmaEt is greater than that reported in the literature \((1.8 \times 10^4 M^{-1} s^{-1})\).\(^ {76}\) This may be due to the fact that the reported value is only approximate since only 2 - 10% of the reaction was followed. In addition in the pH range investigated it is likely that hydroxy complexes of Cu(II), e.g. (XLII) are present

\[
\begin{array}{c}
\text{CH}_2 - \text{CH}_2 \\
| \\
\text{H}_2\text{N} - \text{NH} - \text{CH}_2 \\
| \\
\text{Ho} - \text{Cu} - \\
| \\
\text{O} = \text{C} - \text{OEt}
\end{array}
\]

(XLII)

This would be less susceptible than the aquo complex to attack by \(\text{OH}^-\) due to its lower charge.
CHAPTER 5

METAL COMPLEXES OF

2-CARBOETHOXY-1,10-PHENANTHROLINE
1. Introduction.

The ability of the bidentate ligand 1,10-phenanthroline to form stable complexes with a variety of metal ions is well established. The stability constants of many metal complexes of this ligand have been determined and found to be consistently greater than those of analogous bipyridyl complexes. This increased stability is apparently due to greater resonance in the more highly conjugated phenanthroline complexes.

Substitution in the 2-position of 1,10-phenanthroline by potential donors provides a system capable of behaving as a tridentate chelating agent. A large number of 2-substituted phenanthrolines and their metal complexes have been reported. In 1966 Corey reported the synthesis of 2-cyano-1,10-phenanthroline and from this material a variety of 2-substituted 1,10-phenanthrolines have been prepared. These include the tridentate ligands 2-carboxy-1,10-phenanthroline, its amide, thioamide, amidoxime, carbaldehyde imines, carbaldehyde hydrazones and thiazo1.

\[ (X = -\text{CO}^-, -\text{CONH}_2, \]
\[ -\text{CSNH}_2, -\text{C=NOH}, \]
\[ -\text{NH}_2, -\text{CH=NR}, \text{CH=N-NRR'} ) \]

(XLIII)
The metal complexes of these substituted phenanthrolines have been investigated by Goodwin and co-workers. The interest in these systems has centred mainly on the structural features of the complexes resulting from steric effects of the substituent groups, or on the changes in basic strength of the nitrogen atoms in the phenanthroline ring, induced by substitution in the heterocyclic nucleus and the consequent effect on the stability of derived metal complexes.

2. Experimental.

1,10-phenanthroline monohydrate ($C_{12}H_{8}N_2\cdot H_2O$) was obtained from Aldrich Chemical Company and used without further purification. This was converted to 2-cyano-1,10-phenanthroline according to the reaction scheme (43).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{COCl} & \quad \rightarrow \\
\text{C}_6\text{H}_5\text{CN} & \quad \leftarrow \\
\end{align*}
\]
(a) **1,10-Phenanthroline-1-oxide.**

To a solution of 1,10-phenanthroline monohydrate (0.10ml) in 120cm$^3$ of glacial acetic acid was added dropwise with stirring 12.0cm$^3$ of 30% hydrogen peroxide. The temperature of the solution was maintained at 70 - 75°C for 3 hours, after which time an additional 12.0cm$^3$ of hydrogen peroxide was added. Heating was continued for a further 3 hours. The solution was then concentrated to a volume of approximately 30cm$^3$ on a rotary evaporator, 30cm$^3$ of water was added and the solution finally concentrated to a volume of approximately 20cm$^3$. The mixture was neutralized with a sodium carbonate/water paste. The solid mass was extracted with chloroform and the combined extracts evaporated to dryness. The resulting residue was dried in an oven at 50°C, ground to a fine powder, and extracted into chloroform. The combined chloroform extracts were boiled with decolorizing charcoal filtered, and the filtrate evaporated to dryness. The tan yellow product of 1,10-phenanthroline-1-oxide was obtained in 80% yield.

(b) **2-Cyano-1,10-phenanthroline.**

A stirred solution of 1,10-phenanthroline-1-oxide (0.07mol) and potassium cyanide (0.25mol) in distilled water (250cm$^3$) was treated with benzoyl chloride (15.0cm$^3$) over a period of 15 minutes. During the addition, 2-cyano-1,10-phenanthroline precipitated from solution. The precipitate was suction filtered, washed with water and dried. Recrystallization from acetonitrile gave light tan needles with melting point 334°C, in 70% yield.
This product was used to prepare 2-carboethoxy-1,10-phenanthroline according to reaction scheme (44)

\[
\begin{align*}
R-CN & \overset{OH^-}{\underset{R-COO^-} \longrightarrow} \overset{OH^-}{\underset{H^+} \longrightarrow} \overset{R-COOH}{\underset{EtOH,H^+} \downarrow} \\
& \text{NH}_3 + \text{R-COO}^-
\end{align*}
\]

(c) 2-Carboxy-1,10-phenanthroline.

To a solution of 2-cyano-1,10-phenanthroline (0.148 mol) in 95% ethanol (100 cm\(^3\)) was added a solution of 10.0 g. of sodium hydroxide (0.25 mol) in water (40 cm\(^3\)). The mixture was refluxed for 2 hours (until evolution of ammonia ceased). The solution was cooled to room temperature and made slightly acidic with concentrated hydrochloric acid. The solvent was removed, using a rotary evaporator, and the residue was dried in a vacuum oven at 30°C. The IR spectrum of the product showed a strong absorption at 1700 cm\(^{-1}\) characteristic of an unionized -COOH group.

(d) 2-Carboethoxy-1,10-phenanthroline.

A suspension of 2-carboxy-1,10-phenanthroline (8.93x10\(^{-3}\) mol) in absolute ethanol (10 cm\(^3\)) was treated with concentrated H\(_2\)SO\(_4\) (5 cm\(^3\)) and refluxed for 5 hours. The
solution was then basified with concentrated aqueous ammonia and cooled in an ice-bath. Water (200 cm$^3$) was then added. The tarry precipitate was extracted into acetone and decolorized by charcoal. The ester was precipitated from acetone by the addition of water. The IR spectrum of the product showed $\nu$ (C=O) at 1734 cm$^{-1}$ indicative of a completely esterified product. The melting point of the product was 133°C. Found: C, 71.14%; H, 4.72%; N, 11.01%  $\text{C}_{15}\text{H}_{12}\text{N}_{2}\text{O}_{2}$ requires  
C, 71.40%; H, 4.79%; N, 11.01%

(e) **Preparation of Metal Complexes of 2-Carboethoxy-1,10-phenanthroline, $\text{M(C}_{15}\text{H}_{12}\text{N}_{2}\text{O}_{2})\text{Cl}_{2}$**.

To a solution of 2-carboethoxy-1,10-phenanthroline ($1\times10^{-3}$ mol) in hot ethanol (70 cm$^3$) was added dropwise with stirring a solution of the metal chloride ($1\times10^{-3}$ mol) in hot ethanol (10 cm$^3$). The metal complexes crystallized from solution on cooling. The products were washed with a little ethanol and dried in a vacuum oven at 40°C. Analytical, spectral and magnetic data for the complexes are presented in Tables 19 - 22.
Table 19 Analytical Data for Metal Complexes of 2-Carboethoxy-1,10-phenanthroline.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calculated %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Mn((\text{C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2)\text{Cl}_2)</td>
<td>47.61</td>
<td>3.20</td>
</tr>
<tr>
<td>Fe((\text{C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2)\text{Cl}_2\cdot2\text{H}_2\text{O})</td>
<td>43.48</td>
<td>3.52</td>
</tr>
<tr>
<td>Co((\text{C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2)\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O})</td>
<td>46.03</td>
<td>3.35</td>
</tr>
<tr>
<td>Ni((\text{C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2)\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O})</td>
<td>46.06</td>
<td>3.35</td>
</tr>
<tr>
<td>Cu((\text{C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2)\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O})</td>
<td>45.50</td>
<td>3.31</td>
</tr>
<tr>
<td>Zn((\text{C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2)\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O})</td>
<td>45.29</td>
<td>3.29</td>
</tr>
<tr>
<td>Compound</td>
<td>$\nu(C=O)$ cm$^{-1}$</td>
<td>$\nu(C-O)$ cm$^{-1}$</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>$\text{C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2$</td>
<td>1734</td>
<td>1270</td>
</tr>
<tr>
<td>$\text{Cu(C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2\text{)Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$</td>
<td>1730</td>
<td>1285 1310</td>
</tr>
<tr>
<td>$\text{Co(C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2\text{)Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$</td>
<td>1725</td>
<td>1280 1300</td>
</tr>
<tr>
<td>$\text{Ni(C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2\text{)Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$</td>
<td>1730; 1690</td>
<td>1280 1300</td>
</tr>
<tr>
<td>$\text{Fe(C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2\text{)Cl}_2\cdot2\text{H}_2\text{O}$</td>
<td>1730</td>
<td>1280 1300</td>
</tr>
<tr>
<td>$\text{Mn(C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2\text{)Cl}_2$</td>
<td>1730; 1695</td>
<td>1280 1300</td>
</tr>
<tr>
<td>$\text{Zn(C}<em>{15}\text{H}</em>{12}\text{N}_2\text{O}_2\text{)Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$</td>
<td>1725</td>
<td>1285 1305</td>
</tr>
<tr>
<td>Complex</td>
<td>Current in amps</td>
<td>$10^6 \chi_{g}$ c.g.s.</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Mn(C$<em>{15}$H$</em>{12}$N$_2$O$_2$)Cl$_2$</td>
<td>0.5</td>
<td>42.29</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>43.01</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>42.65</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>42.42</td>
</tr>
<tr>
<td>Fe(C$<em>{15}$H$</em>{12}$N$_2$O$_2$)Cl$_2$·2H$_2$O</td>
<td>0.5</td>
<td>31.12</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>31.79</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>31.39</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>30.97</td>
</tr>
<tr>
<td>Co(C$<em>{15}$H$</em>{12}$N$_2$O$_2$)Cl$_2$·½H$_2$O</td>
<td>0.5</td>
<td>25.23</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>24.23</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>25.52</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>25.77</td>
</tr>
<tr>
<td>Ni(C$<em>{15}$H$</em>{12}$N$_2$O$_2$)Cl$_2$·½H$_2$O</td>
<td>0.5</td>
<td>12.95</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>12.69</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>12.89</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>12.84</td>
</tr>
<tr>
<td>Cu(C$<em>{15}$H$</em>{12}$N$_2$O$_2$)Cl$_2$·½H$_2$O</td>
<td>0.5</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>3.53</td>
</tr>
<tr>
<td>Complex</td>
<td>Spectrum</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>Mn(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>v.weak bands at 28000, 17000, 8500, 6000</td>
<td></td>
</tr>
<tr>
<td>Fe(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)Cl&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>20000, 11500, 6400</td>
<td></td>
</tr>
<tr>
<td>Co(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)Cl&lt;sub&gt;2&lt;/sub&gt;·½H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>25500, 19500, 16500, 6500</td>
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<td>Ni(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)Cl&lt;sub&gt;2&lt;/sub&gt;·½H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>23500, 13500, 8000</td>
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<td>Cu(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)Cl&lt;sub&gt;2&lt;/sub&gt;·½H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>13000</td>
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3. Results and Discussion.

All the metal complexes of 2-carboethoxy-1,10-phenanthroline which were investigated behave as non-electrolytes in ethanol. This indicates that Cl\(^-\) is coordinated in all these complexes.

The IR spectrum of the ligand shows a -C=O stretching absorption at 1734 cm\(^{-1}\), which is shifted to lower frequencies in the metal complexes. This is indicative of either direct carbonyl coordination to the metal ions or alternatively may be due to the inductive effect of the metal ions, coordinated through the ring nitrogen atoms, being transmitted to the ester group. The phenanthroline ring vibrations \(\gamma(C\equiv C)\), \(\gamma(C\equiv N)\) and the C=O stretching vibrations are observed at slightly higher frequencies in the complexes compared to the free ligand.

The room temperature magnetic moment of the manganese(II) complex (5.94 B.M.) is close to the spin only value predicted for high spin octahedral complexes of this metal ion. It therefore seems likely that 2-carboethoxy-1,10-phenanthroline behaves as a 2 N, 0 tridentate ligand in this complex and that one of the Cl\(^-\) groups acts as a bridging ligand. The extremely pale colour of the compound is also indicative of an octahedral complex and allows the alternative possibility of tetrahedral coordination (in which 2-carboethoxy-1,10-phenanthroline is bidentate) to be disfavoured. This is because in tetrahedral complexes of Mn(II) the electronic transitions are spin but not parity forbidden and the complexes usually have a noticeable yellow colour.
The diffuse reflectance spectrum of the iron(II) complex shows a doublet band (11500, 6400 cm$^{-1}$) which is characteristic of octahedral iron(II) complexes. The band at 20000 cm$^{-1}$ is probably due to metal to ligand charge transfer since similar bands are observed in the spectra of iron(II) complexes of 1,10-phenanthroline. The room temperature magnetic moment (5.11 B.M.) is consistent with a high spin octahedral magnetically-dilute iron(II) complex. It therefore appears that 2-carboethoxy-1,10-phenanthroline is tridentate in this complex, and that the two Cl$^-$ ligands and an aquo ligand complete octahedral geometry around the metal ion.

The intense blue colour of the cobalt(II) complex suggests a tetrahedral environment around this metal ion. The ground state of Co(II) in a tetrahedral field is $^4A_2$ and the electronic transitions $^4A_2 \to ^4T_1(P)(v_2)$, $^4T_2 \to ^4T_1(F)(v_2)$, $^4A_2 \to ^4T_1(F_1)(v_1)$ are all spin allowed. The highest energy transition, to the $^4T_1(F)$ excited state, usually dominates the visible spectra of tetrahedral Co(II) complexes. The transition from the ground state to the $^4T_1(F)$ state generally occurs in the near IR region, while the lowest energy transition i.e. to the $^4T_2$ state is seldom observed due to it being in an inconvenient region of the spectrum (1 - 2 microns) and also because it is weak. The $v_2$ and $v_3$ bands are usually split, and $v_3$ normally has the greater intensity. The reflectance spectrum of the Co(II) complex of 2-carboethoxy-1,10-phenanthroline shows two bands, one of which is observed at
6500 cm\(^{-1}\) (\(v_2\)). The other band (\(v_3\)) which occurs in the visible region is more intense and is split with maxima at 16500 and 19500 cm\(^{-1}\). The room temperature magnetic moment (4.79 B.M.) of the Co(II) complex indicates significant orbital contribution to the total angular momentum. It therefore seems likely that the Co(II) complex is tetrahedral with 2-carboethoxy-1,10-phenanthroline acting as a 2 N bidentate ligand and two chloride ligands completing the polyhedron.

The diffuse reflectance spectrum of the nickel(II) complex displays three bands characteristic of octahedral Ni(II). These bands occur at 8000 cm\(^{-1}\) (\(^3A_2g \rightarrow ^3T_2g\)), 13500 cm\(^{-1}\) (\(^3A_2g \rightarrow ^3T_1g(P)\)) and 23500 cm\(^{-1}\) (\(^3A_2g \rightarrow ^3T_1g(P)\)).\(^{69}\) The positions of these bands are at slightly lower energies than the corresponding bands in the spectrum of the complex NiEdta(NH\(_2\)\(_4\)Cl\(_2\) \(\cdot\)\(\frac{3}{2}\)H\(_2\)O. The room temperature magnetic moment (3.45 B.M.) is also consistent with octahedral stereochemistry.\(^{71}\) It seems likely that 2-carboethoxy-1,10-phenanthroline behaves as a tridentate ligand in the Ni(II) complex and that one of the chloride ions is present as a bridging ligand. The resulting chromophore involving Ni(II) surrounded by an N\(_2\)OCl\(_2\) donor system would be expected to show bands at lower energies than the NiN\(_2\)O\(_4\) chromophore in the ethylenediaminetetraacetamide complex.

The diffuse reflectance spectrum of the copper(II) complex shows a broad unsymmetrical band at 13000 cm\(^{-1}\) characteristic of a distorted octahedral complex.\(^{69}\) The room temperature magnetic moment is 1.93 B.M. It appears likely that in this
complex 2-carboethoxy-1,10-phenanthroline is tridentate and that one of the chloride ions behaves as a bridging ligand. A similar structure is possible for Zn(II) complex although the available data does not allow tetrahedral geometry with a donor atom arrangement as is present in the Co(II) complex to be ruled out.
REFERENCES


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