Synthetic and Solution Studies on Metal Complexes of *N,N,N',N'*-Tetrakis(2-carbamoylethyl)ethylenediamine

Robert W. Hay,* Mahesh P. Pujari, and (in part) Norman Govan
Chemistry Department, University of Stirling, Stirling FK9 4LA
Angelo Perotti *
Dipartimento di Chimica Generale, Università di Pavia, viale Taramelli 12, 27100 Pavia, Italy

The preparation of the tetra-amide ligand *N,N,N',N'*-tetrakis(2-carbamoylethyl)ethylenediamine (H_2L) by Michael addition of ethylenediamine to acrylamide is described. The ligand forms complexes with Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, Ba^{II}, Zn^{II}, Cd^{II}, Hg^{II}, and La^{III}, which have been characterised in the solid state. With Cu^{II}, Ni^{II}, and Pd^{II}, deprotonated complexes [ML] can be prepared in solution and the solid state. For the other metal ions the complexes can be formulated as $M^{n+}(H_2L)Cl_n{\cdot}xH_2O$. The stepwise protonation of the ligand has been studied by potentiometric titration, giving $\log K_1 = 7.20(1)$ and $\log K_2 = 3.25(2)$ at 25 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$). Titration data for the molar ratio $H_2L/M^{II} = 1:1$ ($M^{II} = Cu^{II}$, Ni^{II}, or Pd^{II}) can be fitted to the stepwise equilibria (i)—(iii) and the corresponding log β values are reported.

$$M^{2+} + H_2L \overset{\beta_{110}}{\rightleftharpoons} [M(H_2L)]^{2+} \tag{i}$$

$$M^{2+} + H_2L \overset{\beta_{11-1}}{\rightleftharpoons} [M(HL)]^{+} + H^{+} \tag{ii}$$

$$M^{2+} + H_2L \overset{\beta_{11-2}}{\rightleftharpoons} [ML] + 2H^{+} \tag{iii}$$

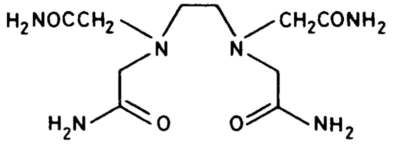
The co-ordination chemistry of linear and macrocyclic amides has attracted considerable attention in recent years and the topic has been reviewed.[1] Deprotonation of the amide nitrogen is known to occur with various metal ions such as Cu^{II}, Ni^{II}, Pd^{II}, Co^{II}, Co^{III},[1] and possibly Zn^{II}.[2] There is a general consensus that the site of co-ordination in the complexes prior to deprotonation is the carbonyl oxygen,[1,3–6] although claims that the intact amide nitrogen can serve as the donor occur in the literature.[7–9] Recent e.s.r. data[6] on copper(II) complexes provide strong evidence for oxygen co-ordination prior to amide deprotonation.

A previous paper[10] has dealt with metal complexes of ethylenediaminetetra-acetamide (**I**). The present paper describes the synthesis of *N,N,N',N'*-tetrakis(2-carbamoylethyl)ethylenediamine (**II**) and studies of its complexes with a series of metal ions. Copper(II) complexes of *N,N'*-bis(2-carbamoylethyl)ethylenediamine (**III**) and *N,N'*-bis(2-carbamoylethyl)trimethylenediamine (**IV**) have previously been described.[11,12] A very recent paper[13] deals with nickel(II) complexes of the last two ligands.

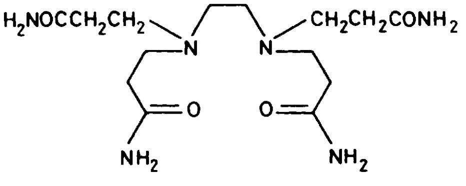
Experimental

The ligand *N,N,N',N'*-tetrakis(2-carbamoylethyl)ethylenediamine (H_2L) was prepared as follows. Ethylenediamine (6.7 cm^3, 0.1 mol) was slowly added to a solution of acrylamide (28.4 g, 0.4 mol) in acetonitrile (150 cm^3) and the solution refluxed for *ca.* 3 h. On cooling, the product was filtered off, and recrystallised from dry ethanol–chloroform.[2,3] The resulting colourless crystals were collected, washed several times with cold diethyl ether, and dried *in vacuo*, m.p. 170—172 °C (Found: C, 48.8; H, 8.2; N, 24.8. $C_{14}H_{28}N_6O_4$ requires C, 48.8; H, 8.2; N, 24.4%). The i.r. spectrum (KBr disc) has a series of four sharp ν(NH) bands at 3 200, 3 300, 3 390, and 3 430 cm^{-1} and the amide I band at 1 660 cm^{-1}. The ^{13}C n.m.r. spectrum has the expected four signals at 34.7, 51.7, 52.6, and 180.3 p.p.m. in D_2O solvent.

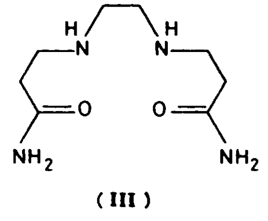
Metal Complexes.—The deprotonated complex $[CuL]{\cdot}H_2O$ was prepared as follows. An aqueous solution containing equimolar amounts of the ligand and $Cu(ClO_4)_2{\cdot}6H_2O$ (5×10^{-3} mol) was titrated with sodium hydroxide solution



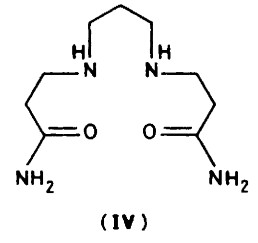
(I)



(II) = H_2L



(III)



(IV)

Table 1. Analytical and conductivity data for metal complexes of *N,N,N′,N′*-tetrakis(2-carbamoylethyl)ethylenediamine

		Analysis[a]/%			
Compound	Colour	C	H	N	Λ_M[b]/S cm^2 mol^{-1}
H_2L	Colourless	48.8 (48.8)	8.2 (8.2)	24.85 (24.4)	—
$Cu(H_2L)Cl_2\cdot3H_2O$	Green	31.65 (31.55)	6.45 (6.45)	15.8 (15.75)	144 (2:1)
$Ni(H_2L)Cl_2\cdot3H_2O$	Green	31.85 (31.85)	6.5 (6.5)	15.6 (15.9)	141 (2:1)
$Co(H_2L)Cl_2\cdot H_2O$	Pink	34.25 (34.15)	6.1 (6.15)	17.1 (17.05)	156 (2:1)
$Fe(H_2L)Cl_2\cdot H_2O$	Brown	34.1 (34.3)	6.15 (6.15)	17.1 (17.15)	140 (2:1)
$Mn(H_2L)Cl_2$	Colourless	35.85 (35.75)	5.85 (6.0)	17.7 (17.85)	152 (2:1)
$Ba(H_2L)Cl_2\cdot2.5H_2O$	Colourless	28.3 (28.15)	5.55 (5.55)	13.95 (14.05)	149 (2:1)
$Zn(H_2L)Cl_2\cdot2H_2O$	Colourless	32.65 (32.0)	6.25 (6.35)	16.2 (16.0)	156 (2:1)
$Cd(H_2L)Cl_2\cdot3.5H_2O$	Colourless	28.65 (28.45)	6.0 (5.95)	14.15 (14.25)	144 (2:1)
$Hg(H_2L)Cl_2\cdot H_2O$	Colourless	26.75 (26.55)	4.7 (4.75)	13.35 (13.25)	non-electrolyte
$La(H_2L)Cl_3\cdot5H_2O$	Colourless	25.0 (24.75)	5.5 (5.65)	12.45 (12.35)	232 (3:1)
$Cu(H_2L)(ClO_4)_2\cdot0.5H_2O$	Blue	27.55 (27.3)	4.75 (4.75)	13.7 (13.65)	149 (2:1)
$CuL\cdot H_2O$	Dark bluish violet	39.75 (39.65)	6.65 (6.65)	19.8 (19.8)	non-electrolyte

[a] Calculated figures in parentheses. [b] Conductivities obtained using 1×10^{-3} mol dm^{-3} solutions of the complexes in absolute MeOH at 25 °C. In this solvent $\Lambda_M(CaCl_2) = 149$ S cm^2 mol^{-1} and $\Lambda_M(LaCl_3) = 237$ S cm^2 mol^{-1}.

(1.5×10^{-2} mol dm^{-3}). During the titration the solution developed an intense blue colour (pH *ca.* 9). The solution was then slowly evaporated to dryness and the residue dissolved in the minimum volume of ethanol. Addition of a few drops of diethyl ether led to immediate crystallisation of the complex. It is important that, during evaporation of the basic solution, the temperature is kept below 60 °C. Higher temperatures lead to decomposition of the complex.

The protonated complexes which may be formulated as $M(H_2L)Cl_n\cdot xH_2O$ ($H_2L = C_{14}H_{28}N_6O_4$) were prepared by the following general method. The ligand H_2L (5×10^{-3} mol) was dissolved in the minimum volume of hot water and treated with the appropriate metal chloride (5×10^{-3} mol) in ethanol (*ca.* 20 cm^3) with constant stirring. In most cases the complexes slowly crystallised on cooling the solution to room temperature. In some cases (Cu^{II}, Ni^{II}, and Ca^{II}), it was necessary to initiate crystallisation by the addition of a few drops of diethyl ether. The use of $Cu(ClO_4)_2\cdot6H_2O$ in the above preparation gave $[Cu(H_2L)][ClO_4]_2\cdot0.5H_2O$. Analytical data for the various complexes are summarised in Table 1. The complexes are very hygroscopic and were immediately stored in a vacuum desiccator. The calcium(II) complex absorbs water very rapidly from the atmosphere and as a result analytical data were not obtained.

Physical Measurements.—Visible spectra were determined using a Perkin-Elmer Lambda 5 spectrophotometer. I.r. measurements (KBr discs) were made with a Perkin-Elmer 577 instrument. Conductivity measurements were carried out using a PTI-18 digital conductivity meter employing 1×10^{-3} mol dm^{-3} solutions of the complexes in absolute methanol.

Potentiometric titrations of the ligand in the absence and in the presence of copper(II) (as the perchlorate salt), nickel(II) (perchlorate salt), or palladium(II) [as $Pd(NO_3)_2\cdot2H_2O$] were carried out in an automatic system controlled by an Apple IIe computer. The system consisted of: (*i*) a Radiometer PHM84 research pH-meter, using a Beckman Futura glass electrode and an Ingold saturated chloride–calomel reference electrode, fitted in an Ingold cell system; (*ii*) a Radiometer ABU80 autoburette; (*iii*) a Metrohm thermostatted cell; and (*iv*) a Huber MINISTAT digital thermostat. The temperature was maintained at 25.0 ± 0.1 °C, and each titration was performed in a solution of 50 cm^3 adjusted to an ionic strength of 0.1 mol dm^{-3} with $NaClO_4$. The electrode system was standardised prior to each titration in terms of hydrogen-ion concentrations and all equilibrium constants are expressed in concentration units. The β values are expressed in terms of *l*, *m*, and *h*, representing ligand, metal, and proton respectively.

Typical concentrations of the ligand and of the metal ion (in a 1:1 molar ratio) were in the range 0.5×10^{-3}—1.0×10^{-3} mol dm^{-3}. Details of the experimental procedure have been extensively described elsewhere.[14] The data were processed on a VAX 11/780 computer, using the MINIQUAD program[15] and the results were graphically displayed using the DISPLO[16] and GRAPH[17] programs.

In the titration curves, $-\log [H^+]$ *versus* B/H_2L, B/H_2L is the number of moles of the standard base, B, per mole of the ligand H_2L. Negative values indicate an excess of acid, and positive values an excess of base (*e.g.* −2 represents 2 equivalents of standard acid).

Results and Discussion

The ligand *N,N,N′,N′*-tetrakis(2-carbamoylethyl)ethylenediamine (H_2L) is readily prepared by Michael addition of ethylenediamine to acrylamide.

The stepwise protonation equilibria of the ligand [equations (1) and (2)] were studied by potentiometric titration giving log

$$H^+ + H_2L \xrightleftharpoons{K_1} H_3L^+ \qquad (1)$$

$$H^+ + H_3L^+ \xrightleftharpoons{K_2} H_4L^{2+} \qquad (2)$$

$K_1 = 7.20(1)$ and $\log K_2 = 3.25(2)$ at 25 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$). Comparisons of log *K* values with those of ethylenediamine (en) ($\log K_1 = 9.98$, $\log K_2 = 7.28$)[18] and *N,N′*-bis(2-carbamoylethyl)ethylenediamine ($\log K_1 = 8.81$, $\log K_2 = 5.84$)[12] indicate that both $\log K_1$ and $\log K_2$ decrease as substitution on the amino nitrogen atoms increases. Presumably both steric effects and inductive effects of the substituent lead to a reduction in the basicity of the nitrogen donors. The ratio K_1/K_2 is quite large due to electrostatic repulsive effects in H_4L^{2+}.

The interaction of copper(II) with the ligand was studied by potentiometric titration (with standard base) of solutions of the ligand and copper(II) perchlorate (molar ratio $H_2L/Cu^{II} = 1:1$), containing an excess of acid ($HClO_4$), Figure 1. The titration data can be fitted to the set of equilibria (3)—(5). The

$$Cu^{2+} + H_2L \rightleftharpoons [Cu(H_2L)]^{2+}; \log \beta_{110} = 8.15(1) \qquad (3)$$

$$Cu^{2+} + H_2L \rightleftharpoons [Cu(HL)]^+ + H^+; \quad \log \beta_{11-1} = 0.85(2) \qquad (4)$$

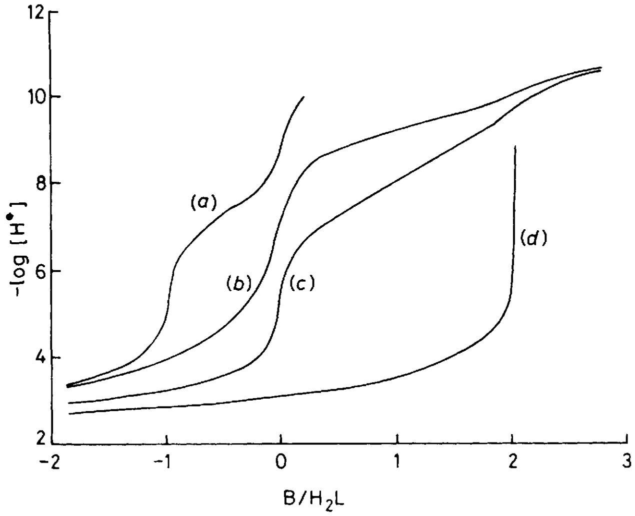


Figure 1. Titration curves for (*a*) $H_2L + H^+$, (*b*) $H_2L + H^+ + Ni^{2+}$, (*c*) $H_2L + H^+ + Cu^{2+}$, and (*d*) $H_2L + H^+ + Pd^{2+}$

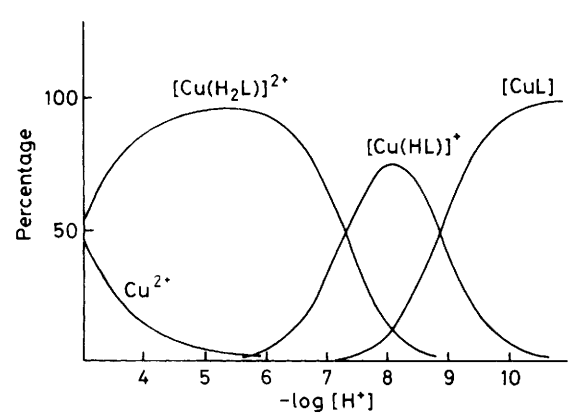


Figure 2. Species distribution curve for copper(II) complexes of H_2L (1 : 1 molar ratio)

$$Cu^{2+} + H_2L \rightleftharpoons [CuL] + 2H^+; \quad \log \beta_{11-2} = -8.02(2) \quad (5)$$

constants β_{lmh} are the formation constants, where l is the stoicheiometric coefficient of the ligand, m that of the metal, and h that of the proton in the complex species. Negative values of h indicate deprotonation of the complex.

The species $[Cu(H_2L)]^{2+}$ which predominates in the $-\log [H^+]$ range 3.0—7.0, Figure 2, corresponds to a complex in which the Cu^{II} is chelated by the neutral ligand. The β_{110} value is somewhat lower than that for $[Cu(en)]^{2+}$ (10.58 log units)[18] suggesting that only the two amino groups act as donors. However, structures of type (**V**) cannot be ruled out. A structure of type (**VI**) is highly unlikely as delocalisation of the lone pairs on nitrogen onto oxygen will greatly reduce the σ-donor capacity of the nitrogen atoms.

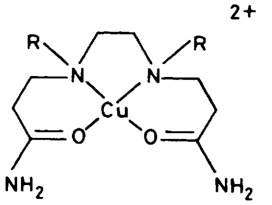
Recent measurements[6] (potentiometric titration, spectrophotometry, and e.s.r.) on the complexes formed between copper(II) and 3,8-dimethyl-4,7-diazadeca-3,7-dienediamide have established the equilibria shown in Scheme 1; $pK_1 = 7.35$ and $pK_2 = 8.76$ at 25 °C. Species (**VII**) has $\lambda_{max.}$ 624 nm and displays five superhyperfine lines in its e.s.r. spectrum, whereas (**IX**) has $\lambda_{max.}$ 522 nm and has nine superhyperfine lines in its e.s.r. spectrum.

Deprotonation of $[Cu(H_2L)]^{2+}$ occurs in two consecutive steps to give $[Cu(HL)]^+$ and [CuL]. The monodeprotonated species reaches its maximum percentage (75%) at $-\log [H^+] = 8$, while the doubly deprotonated complex is 100% abundant at pH 11. The pK_a values for the ionisation [equations (6) and (7)]

$$[Cu(H_2L)]^{2+} \overset{K_a'}{\rightleftharpoons} [Cu(HL)]^+ + H^+ \quad (6)$$

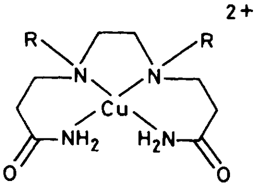
$$[Cu(HL)]^+ \overset{K_a''}{\rightleftharpoons} [CuL] + H^+ \quad (7)$$

of $[Cu(H_2L)]^{2+}$ and $[Cu(HL)]^+$ can readily be derived as $pK_a' = \log \beta_{110} - \log \beta_{11-1}$ and $pK_a'' = \log \beta_{11-1} - \log \beta_{11-2}$, giving $pK_a' = 7.30$ and $pK_a'' = 8.87$ at 25 °C. These values are very comparable with those obtained in the copper(II)–3,8-dimethyl-4,7-diazadeca-3,7-dienediamide system. The various equilibria involved in the present system are

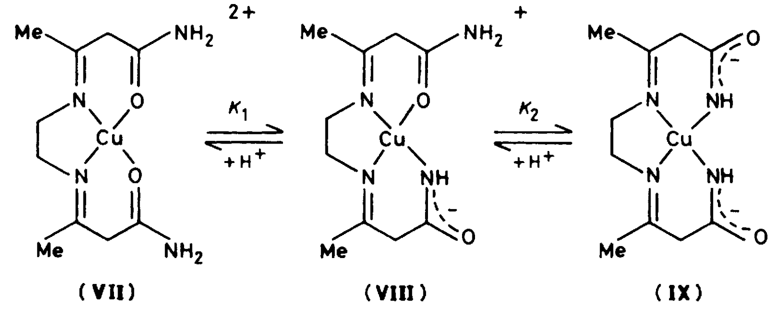


(**V**)

R = $CH_2CH_2CONH_2$

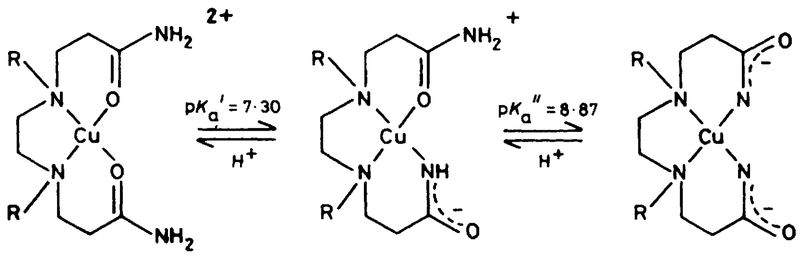


(**VI**)



(**VII**) (**VIII**) (**IX**)

Scheme 1.



Scheme 2. R = $CH_2CH_2CONH_2$

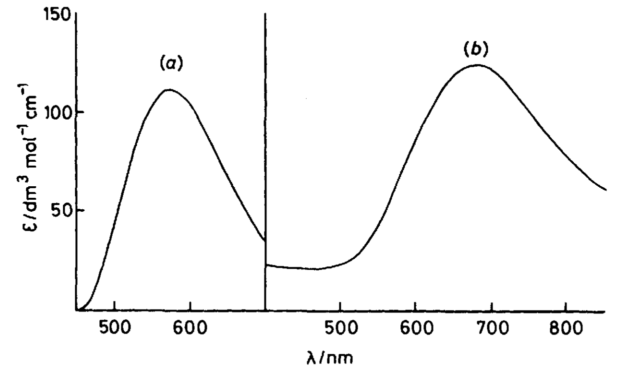
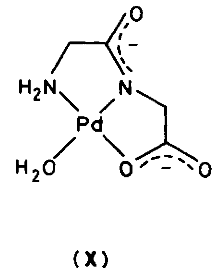
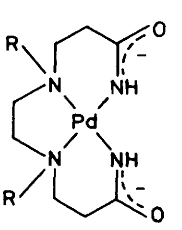


Figure 3. Visible spectra of (*a*) [CuL] at pH 11.43, $\lambda_{max.}$ 573 nm (ε = 111 dm^3 mol^{-1} cm^{-1}) and (*b*) $[Cu(H_2L)]^{2+}$ at pH 5.53, $\lambda_{max.}$ 679 nm (ε = 125 dm^3 mol^{-1} cm^{-1}). The spectra were determined using 1:1 molar ratios of the ligand and copper(II) perchlorate, each 1 × 10^{-3} mol dm^{-3}



(**X**)



(**XI**)

R = $CH_2CH_2CONH_2$

summarised in Scheme 2. Spectrophotometric titrations of equimolar mixtures of *N,N,N',N'*-tetrakis(2-carbamoylethyl)ethylenediamine and copper(II) perchlorate establish that at pH 5.53 where $[Cu(H_2L)]^{2+}$ is *ca.* 100% abundant there is a broad absorption band at 679 nm (ε = 125 dm^3 mol^{-1} cm^{-1}) which, on addition of base, moves to shorter wavelength as ligand deprotonation occurs. The complex [CuL] has $\lambda_{max.}$ 573 nm (ε = 111 dm^3 mol^{-1} cm^{-1}) at pH 11.43, Figure 3.

The complex $[CuL]\cdot H_2O$ which is dark bluish violet in colour was characterised in the solid state. Conductivity measurements (methanol solvent) confirmed that it was a non-electrolyte. The solid-state spectrum (Nujol mull) has a *d–d* band at 571 nm, very comparable with the value of 573 nm observed in solution.

Palladium(II) is known to promote the deprotonation of amides at relatively low pH values. Thus at pH 4 dipeptides form a tridentate chelate about palladium(II) consisting of two five-membered rings with amino, deprotonated amide, and carboxylato-oxygen donor atoms.[19] A representative structure involving glycylglycine is shown in (**X**). Potentiometric titration of a mixture containing a 1:1 molar ratio of $Pd(NO_3)_2$ and H_2L

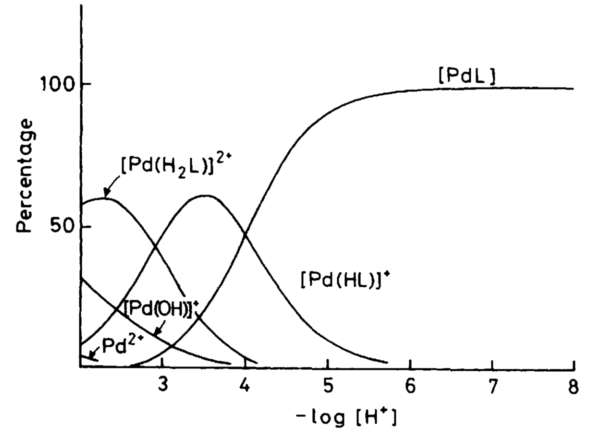


Figure 4. Species distribution curve for palladium(II) complexes of H_2L (1:1 molar ratio)

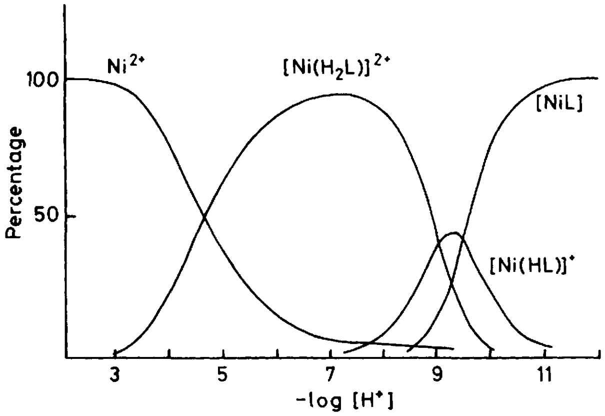


Figure 5. Species distribution curve for nickel(II) complexes of H_2L (1:1 molar ratio)

indicates the release of two protons, Figure 1. The deprotonated complex, [PdL] (**XI**), is completely formed by pH 7. The system is complicated by the hydrolysis equilibria of Pd^{II}. If $[Pd(OH)]^+$ is the only hydrolysed species present, the potentiometric data can be fitted to the set of equilibria (8)—(10). The formation

$$Pd^{2+} + H_2L \rightleftharpoons [Pd(H_2L)]^{2+};\ \log \beta_{110} = 11.24(3) \quad (8)$$

$$Pd^{2+} + H_2L \rightleftharpoons [Pd(HL)]^+ + H^+;\ \log \beta_{11-1} = 8.35(2) \quad (9)$$

$$Pd^{2+} + H_2L \rightleftharpoons [PdL] + 2H^+;\ \log \beta_{11-2} = 4.37(3) \quad (10)$$

constants give pK_a values for $[Pd(H_2L)]^{2+}$ and $[Pd(HL)]^+$ of 2.89 and 3.98 respectively. The speciation plot for the system is shown in Figure 4.

Nickel(II), like copper(II) and palladium(II), can also induce ionisation of the amide protons. The titration data for $H_2L/Ni^{II} = 1:1$ can be fitted to the set of equilibria (11)—(13),

$$Ni^{2+} + H_2L \rightleftharpoons [Ni(H_2L)]^{2+};\ \log \beta_{110} = 5.99(2) \quad (11)$$

$$Ni^{2+} + H_2L \rightleftharpoons [Ni(HL)]^{+} + H^{+};\quad \log \beta_{11-1} = -3.04(3) \quad (12)$$

$$Ni^{2+} + H_2L \rightleftharpoons [NiL] + 2H^{+};\quad \log \beta_{11-2} = -12.50(3) \quad (13)$$

giving pK_a values for $[Ni(H_2L)]^{2+}$ and $[Ni(HL)]^{+}$ of 9.03 and 9.46 respectively. The speciation curve for this system is shown in Figure 5. Deprotonation at the two amide sites occurs with increasing pH to give the yellow square-planar [NiL] which has $\lambda_{max.}$ 461 nm (ε = 93 dm^3 mol^{-1} cm^{-1}) at pH 12. Similar observations have been made with Ni^{II} and *N*,*N*′-bis(2-carbamoylethyl)ethylenediamine (**III**).[13] In this case the complex [NiL′] is also completely formed by pH 12, with the ${}^1A_{1g} \longrightarrow {}^1E_g$ transition of the singlet-ground-state nickel occurring at 440 nm (ε = 102 dm^3 mol^{-1} cm^{-1}).

The formation-constant data are summarised in Table 2, and the pK_a data for the $[M(H_2L)]^{2+}$ and $[M(HL)]^{+}$ species in Table 3. The very low p*K* values observed with Pd^{II} are comparable with values obtained for palladium(II) complexes of peptides, indicating the very strong affinity of Pd^{II} for nitrogen donors.

A variety of complexes of the general formulation $M^{n+}(H_2L)Cl_n{\cdot}xH_2O$ (M = Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, Ba^{II}, Zn^{II}, Hg^{II}, or La^{III}) have been characterised in the solid state, Table 1. The i.r. spectrum of the free ligand H_2L has four sharp absorption bands at 3 430, 3 390, 3 300, and 3 200 cm^{-1}, Table 4, which may be assigned to asymmetric and symmetric NH_2 stretching vibrations respectively.[20] It also displays a broad band at 1 660 cm^{-1}, with a weaker shoulder at 1 620 cm^{-1} which can be assigned to the amide I [ν(CO)] and the amide II [$\delta(NH_2)$] bands respectively.

Table 2. Summary of the formation-constant data at 25 °C and *I* = 0.1 mol dm^3 ($NaClO_4$)

Equilibrium	Cu^{2+}	Ni^{2+}	Pd^{2+}
$M^{2+} + H_2L \rightleftharpoons [M(H_2L)]^{2+}$	8.15(1)	5.99(2)	11.24(3)
$M^{2+} + H_2L \rightleftharpoons [M(HL)]^{+} + H^{+}$	0.85(2)	−3.04(3)	8.35(2)
$M^{2+} + H_2L \rightleftharpoons [ML] + 2H^{+}$	−8.02(2)	−12.50(3)	4.37(3)

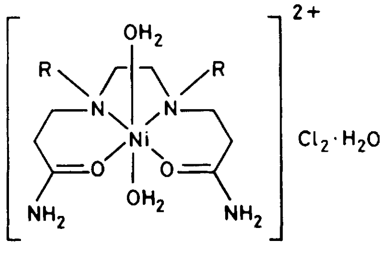
Table 3. The pK_a values for $[M(H_2L)]^{2+}$ (pK_a') and $[M(HL)]^{+}$ (pK_a'') at 25 °C and *I* = 0.1 mol dm^{-3} ($NaClO_4$)

	Cu^{2+}	Ni^{2+}	Pd^{2+}
pK_a'	7.30	9.03	2.89
pK_a''	8.87	9.46	3.98

The i.r. spectra of the complexes, Table 4, display broad absorptions in the regions 3 000—3 500 and 1 500—1 700 cm^{-1}. The former region contains, in addition to NH_2 stretching bands, absorptions due to lattice and co-ordinated water molecules.

The conductivities of all the metal(II) complexes (with the exception of that of Hg^{II}) in dry methanol fall within the range 140—160 S cm^2 mol^{-1}, Table 1, consistent with 2:1 electrolytes and indicate the presence of ionic chloride. In addition, the visible spectra of the methanol solutions were found to be very similar to the solid-state (Nujol mull) spectra where the former could be recorded.

It is difficult to assign definitive structures to some of these compounds on the basis of the available structural data, but some general conclusions can be drawn. The Nujol-mull spectrum of green $Ni(H_2L)Cl_2{\cdot}3H_2O$ has bands characteristic of the ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ (628 nm) and the ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ (380 nm) transitions normally observed in octahedral nickel(II) complexes. The observed spectrum agrees quite well with that predicted for a NiO_4N_2 chromophore.[10] On the basis of the conductivity and spectral data, the nickel(II) complex can probably be formulated as $[Ni(H_2L)(H_2O)_2]Cl_2{\cdot}H_2O$ in which the ligand acts as a 2N (amine) and 2O (amide) tetradentate ligand with two aquo ligands completing the octahedral co-ordination sphere, (**XII**).



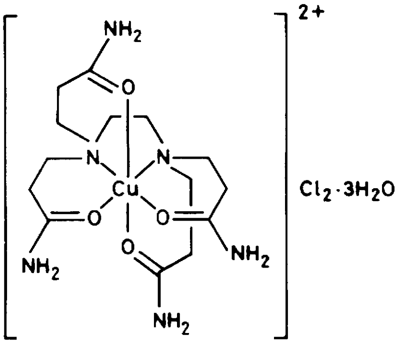
(**XII**) R = $CH_2CH_2CONH_2$

The Nujol-mull spectrum of $Cu(H_2L)Cl_2{\cdot}3H_2O$ has a broad band at *ca.* 670 nm very comparable with the value of 679 nm determined for aqueous solutions at pH 5.5 where the $[Cu(H_2L)]^{2+}$ is almost 100% abundant, Figure 4. The spectra have a broad 'tail' into the near-i.r. region, behaviour which is characteristic of many Jahn-Teller distorted six-co-ordinate

Table 4. Infrared data (cm^{-1}) for *N*,*N*,*N*′,*N*′-tetrakis(2-carbamoylethyl)ethylenediamine and its metal complexes (KBr discs)

Compound	Amide I [ν(CO)] and II [$\delta(NH_2)$]		$\nu_{sym}(NH_2)$	$\nu_{asym}(NH_2)$	ν(C–N)
H_2L	1 660	1 620	3 200	3 390	1 370
$Cu(H_2L)Cl_2{\cdot}3H_2O$	1 672	1 620(sh)	3 180	3 350	1 355
$Ni(H_2L)Cl_2{\cdot}3H_2O$	1 660	1 600	obscured by H_2O band		1 320
$Co(H_2L)Cl_2{\cdot}H_2O$	1 665	1 600(sh)	3 180	3 380	1 330
$Fe(H_2L)Cl_2{\cdot}H_2O$	1 665	1 620(sh)	3 180	3 360	1 360
$Mn(H_2L)Cl_2$	1 660	1 620	obscured by H_2O band		1 325
$Ba(H_2L)Cl_2{\cdot}2.5H_2O$	1 640	1 610	obscured by H_2O band		1 370
$Zn(H_2L)Cl_2{\cdot}2H_2O$	1 665	1 625	3 420, 3 180, 3 120, 3 020		1 328
$Cd(H_2L)Cl_2{\cdot}3.5H_2O$	1 670	1 625	3 480, 3 180, 3 120, 3 020		1 329
$Hg(H_2L)Cl_2{\cdot}H_2O$	1 660	1 610	3 185	3 340	1 345
$La(H_2L)Cl_3{\cdot}5H_2O$	1 670	1 620(sh)	obscured by H_2O band		1 328
$Cu(H_2L)(ClO_4)_2{\cdot}0.5H_2O$	1 660	1 580	3 180	3 380	1 328
$CuL{\cdot}H_2O$	1 675	1 620(sh)	3 170	3 385	1 325

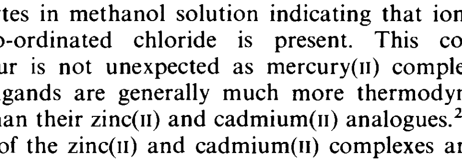
copper(II) complexes.[21] It is likely that the amide ligand acts as a hexadentate N_2O_4 donor with the two additional amide groups weakly bonded in the axial positions to the metal, (**XIII**), to give



(XIII)

$[Cu(H_2L)]Cl_2{\cdot}3H_2O$. The $[Cu(H_2L)(OH_2)_2]Cl_2{\cdot}H_2O$ formulation in which the amide is tetradentate is less likely since the complex on heating to 100 °C *in vacuo* loses three water molecules and there is no change in the reflectance spectrum.

The complex $Hg(H_2L)Cl_2{\cdot}H_2O$ is a non-electrolyte in methanol, indicating chloride co-ordination. The i.r. spectrum displays only two absorptions in the 1 600—1 700 cm^{-1} region and the positions and relative intensities of the bands (1 660, 1 610 cm^{-1}) are very similar to those observed for the free ligand (1 660 and 1 620 cm^{-1}). These similarities strongly suggest that the amide groups are unco-ordinated in the mercury(II) complex. As mercury(II) generally forms tetrahedral rather than octahedral complexes,[22] it is likely that the mercury(II) complex can be represented as $[Hg(H_2L)Cl_2]{\cdot}H_2O$ (**XIV**) in which the ligand is bidentate *via* the two amino nitrogen donors.



(XIV)

The $Zn(H_2L)Cl_2{\cdot}2H_2O$ and $Cd(H_2L)Cl_2{\cdot}3.5H_2O$ complexes differ from the mercury(II) complex in that they are both 2:1 electrolytes in methanol solution indicating that ionic rather than co-ordinated chloride is present. This contrasting behaviour is not unexpected as mercury(II) complexes with halide ligands are generally much more thermodynamically stable than their zinc(II) and cadmium(II) analogues.[22] The i.r. spectra of the zinc(II) and cadmium(II) complexes are almost identical (both in band positions and relative intensities) with the spectrum of the mercury(II) complex in the 1 600—1 700 cm^{-1} region. It is therefore probable that in both cases the ligand is again bidentate with the amide groups unco-ordinated. Likely structures for these complexes are tetrahedral with two aquo ligands completing the co-ordination sphere of the metal ion, *i.e.* $[Zn(H_2L)(H_2O)_2]Cl_2$ and $[Cd(H_2L)(H_2O)_2]Cl_2{\cdot}1.5H_2O$.

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