

Studies on a Dioxotetraamine Macrocyclic Ligand, its Copper(II) and Nickel(II) Complexes and Solution Equilibria*

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Reaction of diethyl 2-(4-nitrobenzyl)malonate with triethylenetetraamine yielded the macrocycle 12-(4-nitrobenzyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (L). Its complexes with Cu^{II} and Ni^{II}, *i.e.* [MH₂L] and [ML]²⁺, were synthesised and characterized. Detailed studies have been made on the solution equilibria of L with five transition-metal and three rare-earth-metal ions. The stability of the transition-metal complexes accords with the Irving–William series and that of the rare-earth-metal complexes increases with decreasing metal-ion radii. The crystal structure of [H₂L][NO₃]₂·H₂O has been determined.

The macrocyclic dioxotetraamine ligands have distinctive co-ordination behaviours and are similar to structures of polypeptides. The hydrogen of the amide is lost upon co-ordination of divalent metal ions, and the ligands are able to stabilize Cu^{III} and Ni^{III}.¹ Their complexes function as models of enzymes; for example, copper(II) complexes are used to model superoxide dismutase² and have anti-inflammatory and other actions.³ Other divalent metal complexes are able to model mono-oxygenase⁴ and to carry oxygen reversibly.⁵ Furthermore, the dioxotetraamine compounds are able to extract selectively noble metals. Their nickel(II) complexes oxidize olefins to cyclic alkoxy compounds.^{6,7}

Much work has been done on the synthesis of these compounds and on the properties of their complexes, but until now mainly in solution.^{8,9} For example, only the crystal structure of a platinum(II) complex of a dioxotetraamine has been reported.¹⁰ We have reported the structure, properties and physiological activities of complexes of dioxotetraamines.^{11–15} The present paper reports the synthesis and crystal structure of a new dioxotetraamine, 12-(4-nitrobenzyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione, L. This is the first report of the crystal structure of a substituted dioxotetraamine. In addition, we studied the properties of their four MH₂L and ML complexes (M = Cu^{II} or Ni^{II}) and the solution equilibrium of L with five transition-metal and three rare-earth-metal ions. The significant results obtained might provide new clues to the synthesis of new complexes and the separation of metal ions.

Experimental

Materials.—The reagents used were chemically pure and triethylenetetraamine was purified by traditional methods. Diethyl 2-(4-nitrobenzyl)malonate was obtained by reaction of diethyl malonate with 4-nitrobenzyl chloride, m.p. 62–63 °C (lit.,¹⁶ 63 °C). Sodium carbonate free NaOH for pH titration was obtained by Powell's method.¹⁷ Metal salts (AnalaR grade) were recrystallized from twice distilled water and their solutions were standardized. The acid content of solutions of metal salts was measured by ion exchange.

Preparation of Compounds.—12-(4-Nitrobenzyl)-1,4,7,10-

tetraazacyclotridecane-11,13-dione (L). To a solution of diethyl 2-(4-nitrobenzyl)malonate (0.74 g, 2.5 mmol) in absolute alcohol (500 cm³) was added triethylenetetraamine (0.37 g, 2.5 mmol). After refluxing for 1 week, the solution was reduced in volume to 50 cm³, and upon cooling a pale yellow powder was isolated. It was washed with alcohol and dried, yield 0.13 g (15%) (Found: C, 55.15; H, 6.75; N, 19.80. C₁₆H₂₃N₅O₄ requires C, 55.00; H, 6.65; N, 20.05%). ν_{\max} (KBr) 3319 (NH), 1666 (C=O); 1514, 1343 cm⁻¹ (NO₂).

[H₂L][NO₃]₂·H₂O. Compound L (1.0 g, 2.9 mmol) was dissolved in nitric acid (6.0 mmol), to give a volume of 5 cm³. Pale yellow crystals were isolated from the filtered solution after being allowed to stand undisturbed for several days, yield 1.1 g (76%) (Found: C, 38.90; H, 5.70; N, 19.50; H₂O, 3.9. C₁₆H₂₇N₇O₁₁ requires C, 38.90; H, 5.50; N, 19.85; H₂O, 3.7%). ν_{\max} (KBr) 3562 (OH); 3388, 3289 (NH); 1679 (C=O); 1514, 1344 (NO₂); 1384, 829 cm⁻¹ (NO₃⁻) cm⁻¹. Λ (water) 250.8 S cm² mol⁻¹.

[CuH₂L]·H₂O 1. To an aqueous solution (5 cm³) of CuSO₄·5H₂O (0.73 g, 2.9 mmol) was added compound L (1.0 g, 2.9 mmol) and then saturated Ba(OH)₂ solution was added dropwise until completion of BaSO₄ precipitation. The solution was filtered and evaporated to dryness, leaving a purple-red solid. The solid was recrystallized from methanol, yield 0.66 g (47%) (Found: C, 39.55; H, 5.80; Cu, 13.40; N, 14.95; H₂O, 14.1. C₁₆H₂₉CuN₅O₈ requires C, 39.80; H, 6.05; Cu, 13.10; N, 14.50; H₂O, 14.9%). λ_{\max} 502 nm (ϵ 84 dm³ mol⁻¹ cm⁻¹). ν_{\max} (KBr) 3600–3100 (NH, OH); 1585 (C=O); 1510, 1340 cm⁻¹ (NO₂). Λ (water) 9.34 S cm² mol⁻¹.

[NiH₂L]·6H₂O 2. To an aqueous solution (5 cm³) of NiSO₄·6H₂O (0.76 g, 2.9 mmol) was added compound L (1.0 g, 2.9 mmol). The solution was treated in a similar manner to that of complex 1. Yellow crystals were obtained, yield 0.83 g (56%) (Found: C, 37.55; H, 6.20; N, 13.45; Ni 11.50; H₂O, 20.5. C₁₆H₃₃N₅NiO₁₀ requires C, 37.40; H, 6.45; N, 13.60; Ni, 11.40; H₂O, 21.0%). ν_{\max} (KBr) 3500–3300 (OH); 1585 (C=O); 1518, 1344 cm⁻¹ (NO₂). Λ (water) 24.1 S cm² mol⁻¹.

[CuL]SO₄·H₂O 3. To an aqueous solution (5 cm³) of CuSO₄·5H₂O (0.73 g, 2.9 mmol) was added compound L (1.0 g, 2.9 mmol). Pale purple crystals were isolated from the filtered solution upon standing, yield 0.9 g (59%) (Found: C, 36.80; H, 5.20; Cu, 10.50; N, 13.45; H₂O, 3.4. C₁₆H₂₅CuN₅O₆S requires C, 36.50; H, 4.85; Cu, 10.60; N, 13.30; H₂O, 3.41%). ν_{\max} (KBr) 3500–3330 (OH); 1675 (C=O); 1516, 1343 (NO₂); 1121, 619 cm⁻¹ (SO₄²⁻). Λ (water) 148 S cm² mol⁻¹.

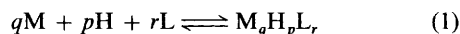
* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

[CuL(O₂CMe)][O₂CMe]·H₂O **4**. This complex was prepared by a similar procedure as that for **3**. A blue-purple solid was obtained, yield 0.97 g (61%) (Found: C, 44.05; H, 5.45; Cu, 11.70; N, 12.30; H₂O, 3.0. C₂₀H₃₁CuN₅O₉ requires C, 43.75; H, 5.70; Cu, 11.60; N, 12.75; H₂O, 3.3%). ν_{\max} (KBr) 3496–3419 (OH); 1635 (C=O); 1586 (MeCO₂[−]); 1512, 1344 cm^{−1} (NO₂). Λ (water) 90.3 S cm² mol^{−1}.

Measurements.—Infrared spectra were obtained on a Nicolet 170 SXFT spectrophotometer, X-band EPR spectra on a Bruker ER 420 spectrophotometer with frequency modulation (100 kHz) operated at room temperature and 77 K (frozen MeOH solution).

pH Titrations.—An aqueous solution (20 cm³) containing L and salt (both 1.00 × 10³ mol dm^{−3}) and HClO₄ (2.00 × 10^{−3} mol dm^{−3}) was titrated with carbonate-free 0.100 mol dm^{−3} NaOH by using a microsyringe with precision ± 2 µl. pH Values were measured by a Corning pH meter equipped with a glass–silver–silver chloride combination electrode, precision ± 0.001 pH. The electrode was standardized by buffer solutions of potassium hydrogen-phthalate and mixed phosphates. The ionic strength was kept at 0.1 mol dm^{−3} with NaClO₄ and the temperature of solutions was kept at 30 ± 0.01 °C. The solutions were deoxidized with pure nitrogen gas. The pH values were recorded when the recording changed by not more than 0.005 pH unit during titration. The protonation constant of compound L was determined under the same conditions.

The equilibria in the systems can be written as in equation (1) where $\beta_{pqr} = [M_qH_pL_r]/[M]^q[H]^p[L]^r$ and charges are



omitted for simplicity; square brackets denote equilibrium concentrations and q , p and r the numbers of metal ions, hydrogen ions and ligand molecules bound in the complex; p has a negative value because H⁺ is released during coordination.

Applying the law of mass action to each experimental point i ($= 1, 2, \dots, n$), we obtain equations (2)–(4) where j denotes the

$$c_{H_i} = [H]_i + \sum_{j=1}^n p_j \beta_{p,q,r,j} [H]_i^{p_j} [M]_i^{q_j} [L]_i^{r_j} \quad (2)$$

$$c_{M_i} = [M]_i + \sum_{j=1}^n q_j \beta_{p,q,r,j} [H]_i^{p_j} [M]_i^{q_j} [L]_i^{r_j} \quad (3)$$

$$c_{L_i} = [L]_i + \sum_{j=1}^n r_j \beta_{p,q,r,j} [H]_i^{p_j} [M]_i^{q_j} [L]_i^{r_j} \quad (4)$$

number complexes ($j = 1, 2, \dots, n$) and c_{H_i} , c_{M_i} , c_{L_i} denote the total concentrations of hydrogen ions, metal ions and ligand in solutions at experimental point i respectively. The values of β_{pqr} were calculated by an IBM PS/2-80 computer using the program LEMIT^{17–19} which is based on the Newton–Raphson and Gauss–Newton method so minimizing U in equation (5)

$$U = \sum_{i=1}^n (c_{H_i}^{\text{calc}} - c_{H_i}^{\text{exptl}})^2 \quad (5)$$

where $c_{H_i}^{\text{calc}}$ and $c_{H_i}^{\text{exptl}}$ denote calculated and experimental values at the i th point.

Crystal Structure Determination of L·2HNO₃·H₂O.—*Crystal data.* C₁₆H₂₇N₇O₁₁, $M = 493.43$, triclinic, space group $P\bar{1}$, $a = 9.803(2)$, $b = 10.485(4)$, $c = 11.078(4)$ Å, $\alpha = 82.49(3)$, $\beta = 83.94(2)$, $\gamma = 78.90(2)^\circ$, $U = 1103.9(6)$ Å³, $D_m = 1.49$ g cm^{−3}, $Z = 2$, $D_c = 1.48$ g cm^{−3}, $F(000) = 520$, $\mu(\text{Mo–K}\alpha) = 1.18$ cm^{−1}, $\lambda = 0.71069$ Å, crystal dimensions $0.4 \times 0.3 \times 0.3$ mm.

Data collection and processing. A pale yellow rhomboidal crystal was mounted on an Enraf–Nonius CAD4 diffractometer equipped with graphite-monochromated Mo–K α radiation and using a ω – 2θ scan technique with scan width = $0.85 + 0.350 \tan \theta$. The scan rate was 5.5° min^{−1} (in ω). 3884 Reflections were collected in the range of $3 < 2\theta < 50^\circ$, of which 2532 having $I > 3\sigma(I)$ were used in the structure determination. Lorentz polarization and empirical absorption corrections were applied using the DIFABS procedure.²⁰ The structure was solved by direct methods using the MITHRIL program.²¹ Most of the non-hydrogen atoms were located from an E map; the remaining non-hydrogen atoms were determined with successive Fourier difference syntheses. The hydrogen atoms were obtained from a difference electron-density map. The structure was refined by full-matrix least squares and converged with unweighted and weighted agreement factors of $R = \Sigma |F_o - F_c| / \Sigma |F_o| = 0.054$, $R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.063$, $w = 1/\sigma^2(F)$. The maximum and minimum residuals had heights of +0.24 and −0.28 e Å^{−3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Positional parameters of [H₂L][NO₃]₂·H₂O with estimated standard deviations (e.s.d.s) in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.9480(4)	0.5460(3)	−0.2117(3)	C(11)	0.6691(4)	−0.0237(4)	0.7412(3)
O(2)	0.7791(5)	0.6838(4)	−0.1431(4)	C(12)	0.8453(4)	0.0836(4)	0.8219(3)
O(3)	0.7391(2)	−0.0195(2)	0.4474(2)	C(13)	0.8804(4)	0.1692(4)	0.7069(4)
O(4)	0.9790(2)	0.1078(3)	0.3442(2)	C(14)	1.0676(4)	0.2917(4)	0.6088(3)
N(1)	0.8480(5)	0.5754(4)	−0.1396(3)	C(15)	1.0609(4)	0.2903(4)	0.4736(3)
N(2)	0.6103(3)	0.1329(3)	0.5571(2)	C(16)	0.8916(3)	0.1982(3)	0.3807(3)
N(3)	0.6958(3)	0.0675(3)	0.8274(3)	O(O1)	1.1590(3)	0.0919(3)	0.9255(2)
N(4)	1.0328(3)	0.1719(3)	0.6864(3)	O(O2)	1.3772(2)	0.0820(3)	0.9484(2)
N(5)	0.9209(3)	0.2905(3)	0.4404(3)	O(O3)	1.2712(3)	0.2301(3)	0.8192(3)
C(1)	0.8127(4)	0.4760(4)	−0.0419(3)	N(O1)	1.2694(3)	0.1354(3)	0.8985(3)
C(2)	0.6870(5)	0.4996(4)	0.0273(4)	O(O4)	0.434(1)	0.386(1)	0.3641(8)
C(3)	0.6555(4)	0.4036(4)	0.1175(4)	O(O5)	0.3800(7)	0.3902(8)	0.5512(7)
C(4)	0.7479(3)	0.2871(3)	0.1402(3)	O(O6)	0.294(2)	0.546(1)	0.421(1)
C(5)	0.8738(4)	0.2699(4)	0.0699(3)	O(O4')	0.430(2)	0.356(2)	0.434(2)
C(6)	0.9072(4)	0.3627(4)	−0.0214(3)	O(O5')	0.306(1)	0.467(1)	0.565(2)
C(7)	0.7099(4)	0.1823(4)	0.2374(3)	O(O6')	0.299(3)	0.533(3)	0.374(3)
C(8)	0.7368(3)	0.2041(3)	0.3663(3)	N(O2)	0.3636(4)	0.4437(4)	0.4493(4)
C(9)	0.6939(3)	0.0969(3)	0.4593(3)	O(1w)	0.5421(4)	0.3140(3)	0.7849(4)
C(10)	0.5635(4)	0.0367(4)	0.6511(3)				

Results and Discussion

Crystal Structure of $[\text{H}_2\text{L}][\text{NO}_3]_2 \cdot \text{H}_2\text{O}$.—The crystal structure of ligand L is shown in Fig. 1. The atomic coordinates and selected bond distances and angles are given in Tables 1 and 2. The geometrical parameters are in the normal ranges. The C–N bond distances of the amide are about 1.35 Å, being shorter than that of a normal C–N single bond (1.47 Å), implying partial double-bond character, *i.e.* O(3)–C(9)–N(2) and O(4)–C(16)–N(5) comprise conjugated systems. The hydrogen-bond distance between O(3) and H(20) is 2.114 Å, the N(4)–H(20)···O(3) distance being 2.880(4) Å. The hydrogen bonds stabilize the conformation of the ring. Atoms O(3), N(2), C(9) and C(10) comprise a plane, and O(4), N(5), C(15) and C(16) another, the two planes are not coplanar and have a dihedral angle of 103.10°. All atoms of the benzene ring and of the nitro group are approximately in the same plane, as a result of the conjugated system they comprise. Atoms N(2), N(3), N(4) and N(5) deviate from their least-squares plane by about +0.16 Å in the free dioxotetraamine, but they are coplanar in analogous macrocyclic metal complexes.^{10–12} The dihedral angle between the plane of the benzene ring and that of the four nitrogen atoms is 121.39°; this differs from that of 1,4,8,11-tetraazacyclotetradecane with benzene side groups,²² where the

two planes are perpendicular to each other. In addition, atoms H(O2) and O(1w) of the water molecule are linked to O(O3) of NO_3^- and to H(13) on N(3) by hydrogen bonds (Table 3). Atom O(O6) in another NO_3^- is similarly linked to H(25) on N(5). Atoms H(14) and H(19) in two HNO_3 are bound to N(3) and N(4) respectively, with bond lengths of about 1.0 Å. Thus the ligand has charge 2+, and the two hydrogen atoms form hydrogen bonds with O(O2) O(O1) in NO_3^- , so the complex is electroneutral. The many hydrogen bonds in the complex stabilize the crystal structure, similar to what was found previously for a platinum(II) complex of a tetraamine.¹⁰

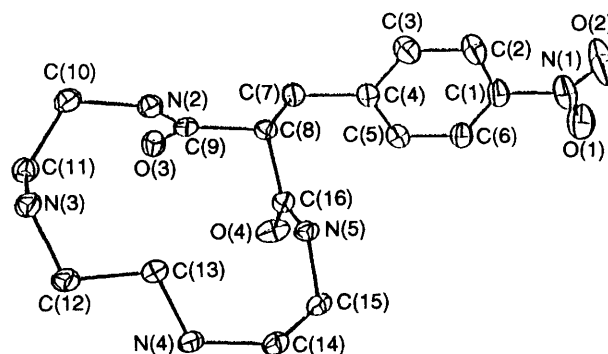


Fig. 1 Molecular structure and crystallographic numbering of the cation of $[\text{H}_2\text{L}][\text{NO}_3]_2 \cdot \text{H}_2\text{O}$

Table 2 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

O(1)–N(1)	1.215(4)	O(3)···N(4)	2.880(4)
O(2)–N(1)	1.204(4)	C(4)–C(7)	1.507(5)
O(3)–C(9)	1.235(4)	C(7)–C(8)	1.553(5)
O(4)–C(16)	1.229(4)	C(8)–C(9)	1.514(5)
N(1)–C(1)	1.463(5)	C(8)–C(16)	1.532(4)
N(2)–C(9)	1.337(4)	C(10)–C(11)	1.507(5)
N(2)–C(10)	1.454(5)	C(12)–C(13)	1.508(5)
N(3)–C(12)	1.502(4)	C(14)–C(15)	1.508(5)
N(3)–C(11)	1.511(5)	O(O3)···O(1w)	2.928(5)
N(4)–C(13)	1.493(4)	O(O6)···O(1w)	3.03(2)
N(4)–C(14)	1.501(4)	O(O6')···O(1w)	2.78(3)
N(5)–C(16)	1.331(4)	N(2)–H(8)	0.87(4)
N(5)–C(15)	1.458(4)	N(3)–H(13)	0.98(4)
C(1)–C(6)	1.369(5)	N(3)–H(14)	1.00(4)
N(3)···O(1w)	2.739(5)	N(4)–H(20)	0.90(5)
N(3)···O(O2)	2.859(4)	N(4)–H(19)	0.94(5)
N(4)···O(O1)	2.993(4)	N(5)–H(25)	0.77(4)
C(4)–C(7)–C(8)	113.4(3)	H(8)–N(2)–C(9)	118(3)
C(9)–C(8)–C(16)	105.0(2)	H(8)–N(2)–C(10)	120(3)
C(9)–C(8)–C(7)	110.5(3)	H(13)–N(3)–H(14)	113(3)
C(16)–C(8)–C(7)	112.7(3)	H(13)–N(3)–C(12)	108(2)
O(3)–C(9)–N(2)	121.3(3)	H(13)–N(3)–C(11)	108(2)
O(3)–C(9)–C(8)	121.0(3)	H(14)–N(3)–C(12)	108(2)
N(2)–C(9)–C(8)	117.6(3)	H(14)–N(3)–C(11)	106(2)
N(2)–C(10)–C(11)	114.4(3)	H(20)–N(4)–H(19)	103(4)
C(10)–C(11)–N(3)	114.8(3)	H(20)–N(4)–C(13)	109(3)
N(3)–C(12)–C(13)	109.7(3)	H(20)–N(4)–C(14)	111(3)
N(4)–C(13)–C(12)	112.1(3)	H(19)–N(4)–C(13)	105(2)
N(4)–C(14)–C(15)	114.5(3)	H(19)–N(4)–C(14)	115(3)
N(5)–C(15)–C(16)	113.1(3)	H(25)–N(5)–C(16)	118(3)
O(4)–C(16)–N(5)	124.1(3)	H(25)–N(5)–C(15)	119(3)
O(4)–C(16)–C(8)	120.0(3)	H(22)–C(14)–N(4)	104(2)
N(5)–C(16)–C(8)	115.7(3)		

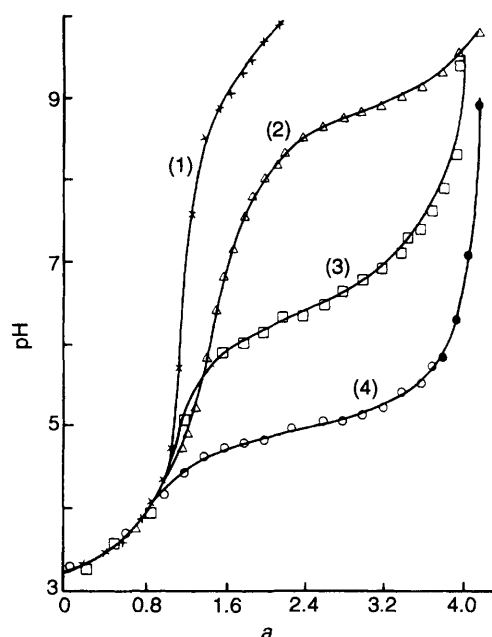


Fig. 2 Potentiometric titration curves of ligand and transition-metal ions: (1), L; (2), L + Co^{2+} ; (3), L + Ni^{2+} ; (4), L + Cu^{2+}

Table 3 Hydrogen-bond distances (Å) and angles (°)

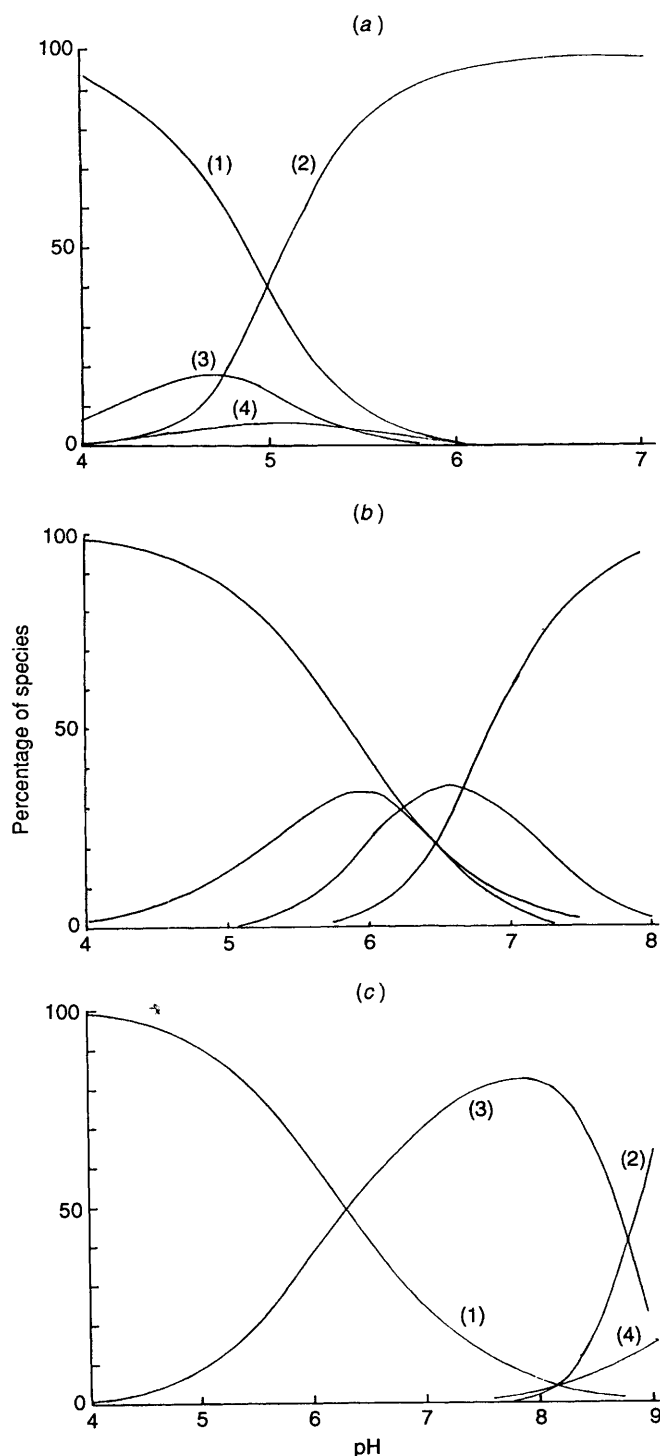
Hydrogen bond	A–H	H···O	A–H···O	A–H···O
N(3)–H(14)···O(O2 ^{III})	1.000	1.876	2.859(4)	166.87
N(3)–H(13)···O(1w)	0.977	1.768	2.739(4)	172.59
N(4)–H(19)···O(O1)	0.938	2.071	2.993(4)	167.52
N(5)–H(25)···O(O6 ^{II})	0.774	2.184	2.89(1)	152.67
O(1w)–H(O2)···O(O3 ^{IV})	0.949	2.024	2.928(5)	158.49
N(4)–H(20)···O(3 ^I)	0.900	2.114	2.880(4)	142.37

Symmetry operations: I 2 – x, – y, 1 – z; II 1 – x, 1 – y, 1 – z; III 2 – x, – y, 2 – z; IV 1 + x, y, z.

Table 4 The EPR parameters of some copper(II) complexes

Ligand	g_{\parallel}	g_{\perp}	$10^4 A_{\parallel}/\text{cm}^{-1}$	$g_{\parallel}/A_{\parallel}$	g_{calc}	g_{iso}	$10^4 A_{\text{iso}}/\text{cm}^{-1}$
12-(4-Nitrobenzyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione	2.166	2.049	213.6	101.4	2.088	2.083	88.30
1,4,7,10-Tetraazacyclotridecane-11,13-dione*	2.179	2.044	222	101.8	2.089	2.090	91.3
12-Benzyl-1,4,7,10-tetraazacyclotridecane-11,13-dione*	2.153	2.051	225	95.7	2.085	2.087	91.3

* Ref. 23, in aqueous solution, 123 K.

**Fig. 3** Species distribution curves for the copper(II)–(a), nickel(II)–(b) and cobalt(II)–ligand systems (c), species: (1), M^{2+} ; (2), $[MH_2L]$; (3), $[ML]^{2+}$; (4) $[MH_1L]^+$

Characterization of Complexes. The molar conductivity at 23 °C showed that complex 3 has the formula $[CuL]SO_4 \cdot H_2O$. The conductivity of $[H_2L][NO_3]_2$ showed that it is a 1:2 electrolyte. Therefore the H^+ of HNO_3 binds to L to form $[H_2L][NO_3]_2 \cdot H_2O$ in agreement with the results of the crystal structure determination. The conductivity of $[CuL(O_2CMe)] \cdot [O_2CMe] \cdot H_2O$ indicated one acetate group co-ordinated to Cu^{II} and another located in the outer sphere. The conductivity of the other complexes is very small, therefore they are non-dissociated. The small values may result from weak inner-sphere dissociation.

From IR data it is seen that the C=O stretching vibration of free L occurs at 1666 cm^{-1} and those of $[CuH_2L]$ and of $[NiH_2L]$ at 1585 cm^{-1} , i.e. a shift of about 80 cm^{-1} toward low wavenumber. This shows that the conjugation effect is strengthened, i.e. co-ordination of Cu^{II} or Ni^{II} made the amide proton dissociate, leaving O–C–N conjugated. The shifts of the C=O stretching vibrations of $[CuL]SO_4 \cdot H_2O$ and $[CuL(O_2CMe)][O_2CMe] \cdot H_2O$ are smaller and the IR spectra contain absorptions due to the anions, implying that the amide protons have not dissociated.

EPR Spectra.—Table 4 shows the EPR parameters of $[CuH_2L] \cdot H_2O$ 1 in methanol solution at 110 K. It is seen that they are very similar to those of its parent copper complexes of 1,4,7,10-tetraazacyclotridecane-11,13-dione and 12-benzyl-1,4,7,10-tetraazacyclotridecane-11,13-dione, in which Cu^{II} has a planar-square geometry. The $g_{\parallel}/A_{\parallel}$ values show that all three complexes are tetragonally distorted; g_{iso} values obtained from spectra at room temperature are in agreement with g_{calc} calculated from anisotropic spectra.

Solution Chemistry.—Fig. 2 shows the titration curves of the ligand L and L plus metal ions ($a = c_{OH}/c_L$). The buffer regions of the copper and nickel systems are rather long, with a rapid increase at about $a = 4$. The crystal structure showed that when the molar ratio of H^+ to L was 2:1 two H^+ were bound to N atom of NH groups to give N–H bond lengths of 0.77–0.87 Å. Therefore in solution these two H^+ are neutralized by NaOH first and thereafter the two NH protons, giving the stable complex $[MH_2L]$. The other complexes have comparatively poor stability. With the transition-metal ions, not only $[MH_2L]$, but also $[MH_1L]$ and $[ML]$ were formed. The equilibrium constants obtained are given in Tables 5 and 6. The stability sequence is: $Zn^{II} < Cu^{II} > Ni^{II} > Co^{II} > Mn^{II}$, in agreement with the Irving–William series. For the rare-earth-metal ions the stability sequence is $Yb^{III} > Sm^{III} > Pr^{III}$, i.e. decreasing with increasing ion radii. This is because the small cavity of the 13-membered cyclic ligand favours ions with small radii. The equilibrium constants for the complexes $[MH_2L]$ ($M = Cu$ or Ni) are smaller than those of 1,4,7,10-tetraazacyclotridecane-11,13-dione complexes [$\log \beta(CuH_2L) = -2.22$, $\log \beta(NiH_2L) = -6.05$]²⁴ due to electron withdrawal of the nitro group. Fig. 3 shows the distribution curves of Cu^{II} , Ni^{II} and rare-earth metal ions. In neutral and weakly basic solutions, the species $[MH_2L]$ predominate, amounting to almost 100% at pH 7–8, for Cu^{II} and Ni^{II} . In contrast, $[ML]$ predominate for Co^{II} , Zn^{II} and Mn^{II} . Other species exist only in

Table 5 Equilibrium constants at 30 ± 0.01 °C, $I = 0.10$ mol dm⁻³ (NaClO₄), for transition-metal complexes

Reaction	M = Cu	Ni	Co	Zn	Mn
$M^{2+} + L \rightleftharpoons [MH_{-2}L] + 2H^+$	-2.96 ± 0.02	-7.09 ± 0.04	-11.90 ± 0.10	-10.93 ± 0.07	-15.54 ± 0.08
$M^{2+} + L \rightleftharpoons [MH_{-1}L]^+ + H^+$	-1.22 ± 0.08	-0.41 ± 0.11	-4.08 ± 0.12	-6.78 ± 0.10	-9.48 ± 0.17
$M^{2+} + L \rightleftharpoons [ML]^{2+}$	6.56 ± 0.03	5.86 ± 0.05	5.66 ± 0.05	5.22 ± 0.04	3.15 ± 0.08
$M^{2+} + OH^- \rightleftharpoons [M(OH)]^+$	-7.88 ± 0.10				

For $H^+ + L \rightleftharpoons HL^+$, $\log \beta = 8.63 \pm 0.01$; for $2H^+ + L \rightleftharpoons H_2L^{2+}$, $\log \beta = 11.63 \pm 0.03$.

Table 6 Equilibrium constants at 30 ± 0.01 °C, $I = 0.10$ mol dm⁻³ (NaClO₄), for rare-earth-metal complexes

Reaction	M = Yb
$M^{3+} + L \rightleftharpoons [MH_{-2}L]^+ + 2H^+*$	-10.10 ± 0.3
$M^{3+} + L \rightleftharpoons [MH_{-1}L]^{2+} + H^+$	-5.54 ± 0.10
$M^{3+} + L \rightleftharpoons [ML]^{3+}$	-1.05 ± 0.06

* For Sm^{3+} , $\log \beta = -11.04 \pm 0.03$; for Pr^{3+} , $\log \beta = -12.5 \pm 0.04$

strongly basic solutions, but in such solutions hydrolysis occurs and it is not easy to obtain pure complexes. We were able to isolate only copper(II) and nickel(II) complexes.

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