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Aqueous Solution Equilibria Involving the Ligand 2,2,4-Trimethyl-1,5,9-triazacyclododecane and Nickel(II), Copper(II), and Zinc(II)

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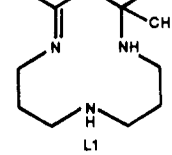
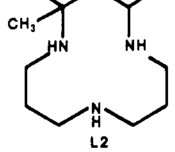
Complexes formed in aqueous solution by the ligand 2,2,4-trimethyl-1,5,9-triazacyclododecane with nickel(II), copper(II) and zinc(II) have been investigated potentiometrically and spectrophotometrically. The nickel(II) complexes are shown to be five-coordinate. Acid dissociation constants (pK_a values) of the ligand are 2.51, 7.34 and 12.3 at 25.0 °C; $I = 0.1$ mol dm^{-3} ($NaNO_3$). Formation of the nickel(II) complex was too slow to be investigated potentiometrically; the formation constants for the copper(II) and zinc(II) complexes are log $K = 11.58$ and 7.68, respectively. Formation of the copper complex was catalyzed by bromide ions, and bromide complexes were observed in solution. The complexes of all three metals readily lose a proton from a coordinated water molecule; pK_a for the reaction $ML(H_2O)_2^{2+} \rightleftharpoons ML(OH)(H_2O)^+ + H^+$ is 9.81 (Ni), 8.48 (Cu), and 9.56 (Zn). The species $[M_2L_2(OH)_2]^{2+}$ is also shown to exist for M = Ni and Cu. The equilibrium constants (log K values) for the reaction $2ML(OH)^+ \rightleftharpoons M_2L_2(OH)_2^{2+}$ are 2.44 (Ni) and 2.00 (Cu). At high pH, the species $CuL(OH)_2$ was also formed; pK_a = 11.9. Nickel complexes with the ligand 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene have also been investigated.

Introduction

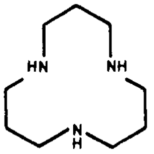
Martin et al.[1] have shown that the product of the Schiff base condensation of acetone with the nickel(II) and copper(II) complexes of 4-azaheptane-1,7-diamine (dipropylenetriamine, dpt) is the metal complex of the macrocyclic ligand 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (L1).



L1



L2



L3

The complex α-Ni(L1)$(NCS)_2$[2] has been shown to be five-coordinate in the solid with an approximately square-pyramidal arrangement of the five donor nitrogens around the nickel ion.[1] In this paper we report studies on the aqueous solution equilibria involving nickel(II), copper(II), and zinc(II) complexes of the ligand 2,2,4-trimethyl-1,5,9-triazacyclododecane (L2) which is prepared by reducing L1. The nickel(II) complexes formed by L2 are five-coordinate in aqueous solution with the tridentate ligand and two water molecules in the coordination sphere. In the solid state both five- and six-coordinate complexes can be prepared. The stereochemistries of the copper(II) and zinc(II) complexes are not known but the ligand must coordinate facially and so the structures are probably similar. We also report our studies on the aqueous solution equilibria of the nickel(II) complexes with L1. These studies are possible with the nickel complex because hydrolysis of the imine bond in this complex is slow.

Triaza macrocycles with varying ring sizes have been reported to form both five- and six-coordinate solid-state complexes.[3,4] The results in the present study are compared with those reported for the ligand 1,5,9-triazacyclododecane (L3)[5-7] which forms octahedral nickel(II) complexes in solution. Also, the pK_a values for hydrolysis of the coordinated water molecules are compared with those reported for the few five-coordinate complexes stable in aqueous solution.[8-11]

Experimental Section

Spectral Measurements. Ultraviolet and visible spectra were measured on Unicam SP700 (diffuse reflectance spectra, reference magnesium carbonate) and Perkin-Elmer 402 spectrophotometers. In the solution spectra, matched silica cells were used, path length varying from 0.2 to 5.0 cm. Infrared spectra were measured on a Grubb Parsons GS 8 spectrophotometer in the range 4000–600 cm^{-1} by using mulls with Nujol and hexachlorobutadiene. ^{1}H NMR spectra were recorded with a Perkin-Elmer (Hitachi R20) 60 MHz NMR spectrometer with D_2O as solvent and with sodium (3-trimethylsilyl)propane)sulfonate as internal standard.

Preparation of Compounds. Bis(isothiocyanato)(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)nickel(II)–Hemiacetone, $[Ni(L1)(NCS)_2]\cdot{}^1/_2(CH_3)_2CO$. This was prepared by a modification of the method described by Martin et al.[1] Methanol was added to solubilize the $Ni(dpt)_2(NCS)_2$ in the acetone, and the reaction mixture was warmed to about 30 °C. Within 45 min the product precipitated. The compound crystallizes with half a molecule of acetone of crystallization; yield 70%.

Di-μ-hydroxo-bis[(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)-nickel(II)] Perchlorate, $[Ni_2(L1)_2(OH)_2](ClO_4)_2$. The μ-hydroxo dimer was prepared by the method of Martin et al.[1] Again the preparation was accelerated if $Ni(dpt)_2(ClO_4)_2$ was dissolved in a methanol/acetone mixture and heated to 30 °C.

Aquo(nitrato)(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)-nickel(II) Nitrate, $[Ni(L1)(NO_3)H_2O]NO_3$. A direct condensation reaction between $Ni(dpt)_2(NO_3)_2$ and acetone does not yield the desired product.[12] Instead the following method was adopted. Nitric acid (1.1 equiv) was added to a slurry of $[Ni_2(L1)_2(OH)_2](ClO_4)_2$ (5.0 g) and KNO_3 (3.3 g) in methanol (30 cm^3). The volume was reduced to 10–15 cm^3, cooled, and then filtered. Propan-2-ol (10 cm^3) was added to the filtrate and the volume again reduced until the product precipitated. The product was recrystallized from an ethanol/methanol mixture; yield 90%. Anal. Calcd for $C_{12}H_{27}N_5O_7Ni$: C, 34.98; H, 6.60; N, 17.00. Found: C, 35.03; H, 6.60; N, 17.20.

In the reflectance spectrum band maxima were observed at 9800 (ν_1), 16 900 (ν_2), and 27 000 (ν_3) cm^{-1}.[13] The ratio ν_2/ν_1 of 1.72 is typical of octahedral nickel(II).[14,15]

Infrared spectra indicated both bidentate and ionic nitrate were present:[16] ν(O–H) 3450 (bd, m, sh) cm^{-1}, ν(N–H) 3222 and 3248 (s, sp) cm^{-1}, ν(C=N) 1650 (s) cm^{-1}; bidentate nitrate ν_2 810 (m, sp), ν_3 1293 (s) and 1479 (s) cm^{-1}; ν_1 and ν_4 not observed; combination bands (bidentate) ($\nu_1 + \nu_3$) 2303 and 2508 cm^{-1}, ($\nu_1 + \nu_4$) 1729 and 1771 cm^{-1}, 2ν_1 2060 (vw) cm^{-1}; combination bands (ionic) ($\nu_1 + \nu_3$) 2375 and 2393 cm^{-1}, ($\nu_1 + \nu_4$) 1761 cm^{-1}.

(μ-Oxalato)-bis(isothiocyanato)bis[(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)nickel(II)], $Ni_2(L1)_2(NCS)_2(C_2O_4)$. This complex was prepared by using the method described by Martin et al.[1]

In the reflectance spectrum band maxima were observed at 10 300, 17 100 and 27 800 cm^{-1}. The ratio ν_2/ν_1 of 1.66 is typical of octahedral nickel(II).

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Infrared spectra: ν(N–H) 3276 (m) cm^{-1}, ν(C=N) 1657 (s, sh) cm^{-1}; coordinated isothiocyanate 2080 (vs) cm^{-1}; bidentate bridging oxalate ν_{as}(OCO) 1633 (vs) cm^{-1}, ν_s(OCO) 1353 (ms) and 1304 (m) cm^{-1}, δ(OCO) 793 (m) cm^{-1}.

2,2,4-Trimethyl-1,5,9-triazacyclododecane, L2. [Ni(L1)(NCS)$_2$]$\cdot{}^1/_2$(CH$_3$)$_2$CO (10.0 g) and sodium cyanide (5.0 g) in absolute ethanol were stirred vigorously until the blue color disappeared. The solution was cooled in an ice–salt mixture and then filtered. Sodium borohydride (1.0 g) and dry methanol (15 cm^3) were added and the mixture was stirred for 40 min. The solution was filtered, 500 cm^3 of ether was added, and the solution was cooled in an ice–salt bath for 3 h. Addition of HBr (5 cm^3, 46%) to the filtered solution gave impure L2$\cdot$3HBr. The free amine was extracted from a saturated NaOH solution (15 cm^3) into ether (300 cm^3). The ether was dried (MgSO$_4$) and then removed. Vacuum distillation (0.2 mmHg, 105–110 °C) gave the ligand monohydrate (oil). Dehydration of this oil gave a deliquescent solid, mp 28–32 °C. Addition of HBr or HNO$_3$ to the ether solution gave the appropriate acid salts which were recrystallized from methanol. Steam distillation of the reaction mixture left after NaBH$_4$ reduction gave similar yields and purity: yield 60%, L2$\cdot$3HBr mp 266–270 °C; L2$\cdot$3HNO$_3$ mp 173–174 °C. Anal. Calcd for $C_{12}H_{27}N_3\cdot H_2O$: C, 62.29; H, 12.63; N, 18.16. Found: C, 62.33; H, 12.36; N, 18.00. Calcd for $C_{12}H_{27}N_3\cdot 3HBr$: C, 31.60; H, 6.63; N, 9.21; Br, 52.56. Found: C, 31.59; H, 6.71; N, 9.42; Br, 52.44. Calcd for $C_{12}H_{27}N_3\cdot 3HNO_3$: C, 35.77; H, 7.84; N, 20.57. Found: C, 35.82; H, 7.51; N, 20.88.

Infrared spectra: L2$\cdot$H$_2$O ν(O–H) 3500 (bd), δ(O–H) 1633 (w, bd) cm^{-1}, ν(N–H) 3253 (s, bd), δ(N–H) 1466 and 1472 (s, bd) cm^{-1}; L2$\cdot$3HBr ν(NH) 3146 and 3183 (m, sp), δ(NH$_3$) 1575 (s, sp) and 1589 (m, sp) cm^{-1}; L2$\cdot$3HNO$_3$ ν(N–H) 3180 (s, bd), δ(NH$_3$) 1606 (m, sp) and 1629 (m, sp) cm^{-1}.

NMR spectra: L2 (0.075 g in 0.7 cm^3 of D$_2$O, pD = pH meter reading + 0.40 = 13.3[17]) δ_{Me_4Si} 2.60 (t, 8 H, α-CH$_2$ groups), 1.60 (m, 6 H, β-CH$_2$ groups), 1.08 and 0.91 (d, J_{CH_3-H} = 9.5 Hz, 4-methyl), 1.00 (s, 6 H, geminal dimethyls); L2$\cdot$3HNO$_3$ (0.10 g in 0.7 cm^3 of D$_2$O, pD = 2.2) δ_{Me_4Si} 3.32 (m, 8 H, α-CH$_2$ groups), 2.22 (m, 6 H, β-CH$_2$ groups), 1.56 and 1.46 (d, J_{CH_3-H} = 6.2 Hz, 4-methyl), 1.50 and 1.40 (s, geminal dimethyls).

Bis(nitrato)(2,2,4-trimethyl-1,5,9-triazacyclododecane)nickel(II), [Ni(L2)(NO$_3$)$_2$]. A solution of nickel nitrate (1.3 g) in dry ethanol (25 cm^3) was added dropwise to a dry boiling ethanol solution (25 cm^3) of L2$\cdot$H$_2$O (1.1 g). The volume was reduced to 5 cm^3 and propan-2-ol (5 cm^3) added to give a blue oil which solidified on the addition of acetone. This was recrystallized twice from ethanol; yield 75%. Anal. Calcd for $C_{12}H_{27}N_5O_6Ni$: C, 36.39; H, 6.87; N, 17.68. Found: C, 36.77; H, 6.83; N, 17.92.

In the reflectance spectrum band maxima were observed at 9500, 16 400, and 26 600 cm^{-1}. The ratio ν_2/ν_1 of 1.73 suggests a six-coordinate geometry.

The infrared spectra indicated the presence of both bidentate and monodentate nitrate:[16] ν(N–H) 3206 and 3249 (m) cm^{-1}; bidentate nitrate ν_2 808 (m, sp) cm^{-1}, ν_3 1308 (s) and 1487 (s) cm^{-1}; monodentate nitrate ν_2 820 (w, sp) cm^{-1}, ν_3 1315 (s) and 1413 (s) cm^{-1}; ν_1 and ν_4 not observed; combination bands (bidentate) ($\nu_1 + \nu_3$) 2301 and 2503 cm^{-1}; combination bands (monodentate) ($\nu_1 + \nu_3$) 2325 and 2450 cm^{-1}, ($\nu_1 + \nu_4$) 1715 and 1762 (bd) cm^{-1}.

Bis(nitrato)(2,2,4-trimethyl-1,5,9-triazacyclododecane)copper(II), [Cu(L2)(NO$_3$)$_2$]. This complex was prepared as was the nickel complex. The product was recrystallized twice from ethanol; yield 80%. Anal. Calcd for $C_{12}H_{27}N_5O_6Cu$: C, 35.95; H, 6.79; N, 17.47. Found: C, 35.89; H, 6.82; N, 17.26.

In the reflectance spectrum band maxima were observed at 8800 and 1500 cm^{-1}.

Infrared spectra indicated the presence of monodentate nitrate: ν(N–H) 3245 (s) and 3321 (m, sp) cm^{-1}; monodentate nitrate ν_2 (816 (m) cm^{-1}, ν_3 1312 (s, bd), 1484 (s), 1312 (s, bd), and 1428 cm^{-1}, ν_4 708 (w, sp) and 736 (w, sp) cm^{-1}; combination bands 2ν_1 2014 and 2048 (w) cm^{-1}, ($\nu_1 + \nu_3$) 2298 and 2453 (sp) cm^{-1}, ($\nu_1 + \nu_4$) 1731 and 1741 (w) cm^{-1}.

Potentiometric Titrations. Solutions of the triamine and the metal complexes were prepared from weighed samples of pure analyzed L2$\cdot$3HNO$_3$, L2$\cdot$3HBr, Ni(L1)(NO$_3$)$_2\cdot$H$_2$O, Ni(L2)(NO$_3$)$_2$, and Cu(L2)(NO$_3$)$_2$. The concentrations of the ligand solutions were further checked by titration against standardized sodium hydroxide. Analytical grade copper and zinc nitrates were used without further purification. Copper nitrate solutions were standardized either by electrodeposition or by EDTA titration. Zinc nitrate solutions were standardized by EDTA titration. The ionic strength of the solutions was controlled by the addition of sodium nitrate to give a total ionic strength at the start of the titration of 0.10 mol dm^{-3}. Sodium perchlorate could not be used to control the ionic strength because of the insolubility of the hydroxoperchlorate complexes.

Potentiometric measurements were made with a Radiometer 4d pH meter, Beckman E2 glass electrode, and a saturated KCl calomel electrode. The NBS buffers phthalate, phosphate, and borate were used to linearize the pH meter. All titrations were performed with NaOH under a nitrogen atmosphere in a thermostated vessel maintained at 25.0 °C. In the batch titrations where a halide-free solution was required, leakage of halide ions from the electrode was avoided by isolating the calomel electrode from the test solution. Electrical contact was maintained via a saturated KNO$_3$ salt bridge.

Acid Dissociation Constants. The values of pK_{a1} and pK_{a2} of L2 were determined potentiometrically at concentrations of 5.000 × 10^{-3} and 1.000 × 10^{-2} mol dm^{-3}; however, pK_{a3} was too high to be determined accurately by potentiometric titrations which indicated pK_{a3} > 12. The value of pK_{a3} was determined spectrophotometrically by using an indicator (tropaeolin OOO, BDH). The absorbance of a series of solutions of known hydroxide concentration (3 × 10^{-3}–3 × 10^{-2} mol dm^{-3}) and indicator (7 × 10^{-5} mol dm^{-3}) was measured and then compared with that of similar solutions containing the amine (1.00 × 10^{-2} mol dm^{-3}). The value of pK_{a3} was calculated on the assumption that the only species present in solution were L and HL$^+$. Absorbance readings were made on a single-beam Uvispek H700 spectrophotometer at 500 nm by using 1-cm silica cells thermostated at 25.0 °C.

Metal Complex Formation Constants. Initially the formation constants were determined with L2$\cdot$3HBr as the source of the ligand (concentration in the range 5 × 10^{-3}–1.4 × 10^{-2} mol dm^{-3}). Under these circumstances it was possible to perform "normal" potentiometric titrations with copper as complex formation was reasonably rapid (metal concentration in the range 3.6 × 10^{-3}–1.2 × 10^{-2} mol dm^{-3}). With zinc, the solutions apparently reached equilibrium after about 10 min and so a number of potentiometric titrations were performed. However experiments described below indicated that equilibrium had not been reached in these solutions. Attempted titrations with nickel(II) and cobalt(II) were not successful because complex formation was too slow in the case of nickel and was either too slow or did not occur thermodynamically with cobalt(II). Spectrophotometric studies with the solutions of the copper complexes revealed that bromide complexes were formed with Cu(L2)$^{2+}$. In order to avoid interference by the bromide complexes, it was decided to use L2$\cdot$3HNO$_3$ as the source of ligand. When this salt was used, the formation of the copper and zinc complexes was very slow so that formation constants had to be determined by a "batch" method. Solutions of the ligand, metal ion, and various amounts of hydroxide ion (pH range 4.7–5.7 for copper and 6.8–9.7 for zinc) were prepared and equilibrated under a nitrogen atmosphere at 25.0 °C for 3 days in the case of copper and between 14 and 67 days for zinc before the pH of the solution was measured. A total of 15 different copper solutions at three different concentrations ((1.90–9.99) × 10^{-3} mol dm^{-3}) and 32 different zinc solutions at four different zinc concentrations (2.00 × 10^{-3}–1.39 × 10^{-2} mol dm^{-3}) were used. In order to prevent the precipitation of the metal hydroxides from these solutions, an excess of ligand (up to threefold) was used and the sodium hydroxide was added to the solutions slowly.

The results obtained from the batch titration of the zinc complex did not agree with the results obtained from the potentiometric titrations. A batch titration with L2$\cdot$3HBr as the source of the ligand (threefold excess of ligand) and a potentiometric titration performed under exactly the same conditions indicated the solutions had not reached equilibrium until 11 days after the solutions were prepared.

Hydrolysis of the Metal Complexes. The hydrolysis of the nickel and copper complexes was studied in the absence of bromide ions by titrating solutions of the nitrate salts of the metal complexes (concentration range 2 × 10^{-3}–1.4 × 10^{-2} mol dm^{-3}). The zinc hydrolysis was studied by the batch titrations described above. The hydrolysis equilibria were rapid in all cases. It was also possible to study the hydrolysis of the Ni(L1)$^{2+}$ complex because hydrolysis of the imine bond in this species is slow. In Cu(L1)$^{2+}$ the imine bond hydrolyzes too rapidly to be studied by this method.

Calculations. Ligand acid dissociation constants were determined by using a computer program described earlier.[18] The formation

Table I. Logarithms of the Equilibrium Constants for the Reactions of $L2 \cdot 3HNO_3$[c]

equilibrium		Ni^{2+}	Cu^{2+}	Zn^{2+}
$LH^+ \rightleftarrows L + H^+$	-12.3 ± 0.2[a]			
$LH_2^{2+} \rightleftarrows LH^+ + H^+$	-7.34 ± 0.02			
$LH_3^{3+} \rightleftarrows LH_2^{2+} + H^+$	-2.51 ± 0.06			
$M^{2+} + L \rightleftarrows ML^{2+}$			11.58 ± 0.06[b]	7.68 ± 0.06[b]
$ML^{2+} \rightleftarrows MLOH^+ + H^+$		-9.81 ± 0.1	-8.48 ± 0.02	-9.56 ± 0.2
$MLOH^+ \rightleftarrows ML(OH)_2 + H^+$			-11.9 ± 0.5	
$2MLOH^+ \rightleftarrows M_2L_2OH_2^{2+}$		2.44 ± 0.1	2.00 ± 0.05	

[a] All errors quoted are twice the standard deviations. [b] These figures represent the precision of the data. The errors are larger (see text). [c] Temperature 25.0 °C; $I = 0.1$ mol dm^{-3} ($NaNO_3$).

Table II. Acid Dissociation Constants for Some Triaza Ligands at 25.0 °C

ligand	pK_{a3}	pK_{a2}	pK_{a1}	ref
L2[a]	12.3	7.34	2.51	this work
L3[b]	12.6	7.57	2.41	7
c	13.15	7.97		6
[11]aneN_3[b]	11.96	7.61		7, 24
[10]aneN_3[c]	12.75	6.86		6
b	12.02	6.59		7
[9]aneN_3[b]	10.42	6.82		4
b	10.68	6.86	2.1	25
d	10.59	6.88		26
dien[b]	9.93	9.04	4.39	25, 27
2,3-tri[b]	10.22	9.18	6.13	25, 27
dpt[b]	10.75	9.60	7.71	25, 27

[a] $I = 0.1$ mol dm^{-3} ($NaNO_3$). [b] $I = 0.1$ mol dm^{-3} (KNO_3). [c] $I = 0.5$ mol dm^{-3} (KNO_3). [d] $I = 0.2$ mol dm^{-3} ($NaClO_4$).

constants and the hydrolysis constants of the metal complexes were initially calculated with the program SCOGS.[19] Calculations were also performed with the program MINIQUAD 75.[20] The results obtained by using the two programs were identical. In all calculations a value of 13.78 was employed for pK_w at 25.0 °C.[21] Measured pH values were converted to $-\log [H^+]$ values by subtracting 0.11 from the measured pH.[22] Absorption maxima and molar extinction coefficients of the absorption spectra were calculated with the program SPANA.[23]

Results and Discussion

The results for the formation of the 1:1 complexes of L2 with copper and zinc obtained in the absence of bromide ions are given in Table I. With $L2 \cdot 3HBr$ as the source of ligand, the following values of log *K* were obtained with copper(II): $Cu(L2)^{2+}$, 11.62 ± 0.06; $Cu(L2)(OH)^+$, −8.52 ± 0.26; $Cu_2(L2)_2(OH)_2^{2+}$, 2.3 ± 0.2. These results are in fair agreement with those in Table I. The larger errors are a reflection of the fact that bromide complexes are formed in solution (vide infra). With zinc(II) and $L2 \cdot 3HBr$ the results obtained were dependent on the time allowed for equilibration. The formation constants given in Table I were calculated by using the value of $pK_{a3} = 12.3$ for the ligand. There is a strong dependence of the formation constant upon the value of pK_{a3}, and as this value is not known accurately, the real error in the formation constants is probably ±0.2. The values obtained for the hydrolysis constants are not dependent upon the formation constants and so their errors are as stated in Table I.

Acid Dissociation Constants. The acid dissociation constants for L2 together with the values for some other triamines are given in Table II. The values obtained for L2 are very similar to the values obtained for L3 by Zompa[7] and differ considerably from the values reported by Riedo and Kaden[6] for L3 at a different ionic strength. The most noteworthy feature of the constants in Table II is the very high value of pK_{a3} of the triaza macrocycles ([9]aneN_3 is an exception). The most likely explanation for this phenomenon is that the proton (or H_3O^+ ion) is able to form hydrogen bonds to all three nitrogens of the ligand. The smaller ring size of [9]aneN_3 apparently prevents the formation of such strong hydrogen bonds. High pK_a values have also been reported for tetraaza macrocycles.[28] The large drop in pK_a value for the loss of the second proton can be attributed to the disruption of the strongly hydrogen-bonded structure, together with the strong electrostatic repulsion between the two protons constrained by the ligand structure to be in close proximity. This latter effect also accounts for the strongly acidic nature of the third proton.

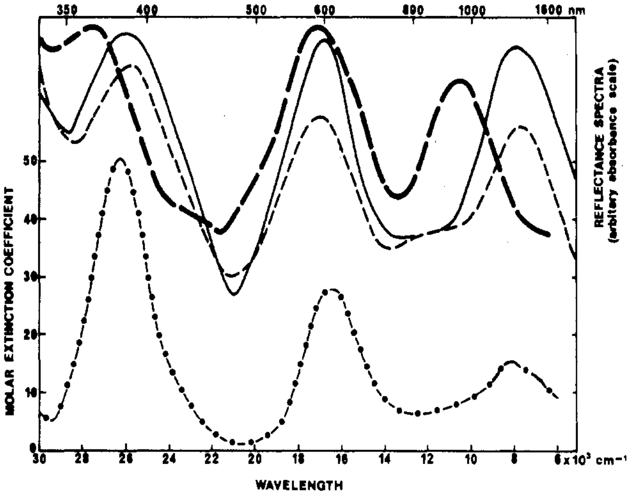

Figure 1. UV–visible spectra of the nickel complexes. Diffuse reflectance spectra: ---, $[Ni_2(L1)_2(NCS)_2(C_2O_4)]$ (octahedral); —, α-Ni(L1)(NCS)$_2$; - - -, Ni(L2)(NCS)$_2$ (five-coordinate). Absorption spectrum: ···, $[Ni_2(L1)_2(OH)_2](ClO_4)_2$ (in water with pH adjusted to 7.02).

In view of the large differences reported for the pK_a values of the ligand L3, which may be due to differences in ionic strength, it is not possible to comment on the effects that the methyl groups on L2 have on the acid dissociation constants of the ligand. If our results are compared with those of Zompa[7] obtained at the same ionic strength then the effect is small. Similar small effects have been observed with tetraaza macrocycles.[29]

Metal Complexes. The crystal structure of α-Ni(L1)(NCS)$_2$ establishes that the nickel is five-coordinate with one of the geminal methyl groups blocking the sixth coordination site.[1] The similarity of the reflectance spectra of α-Ni(L1)(NCS)$_2$ and Ni(L2)(NCS)$_2$ establishes that L2 also forms five-coordinate complexes (Figure 1 and Table (III)). It is possible to prepare complexes containing L1 and L2 where the nickel is apparently six-coordinate. The diffuse reflectance spectrum of $Ni_2(L1)_2(NCS)_2(C_2O_4)$ is typical of octahedral nickel; the ratio of ν_2/ν_1 is 1.66.[14,15] The infrared spectrum indicates that the oxalate acts as a bridging bidentate ligand and the thiocyanates are N-bound to the nickel.[1] The infrared and reflectance spectra of the complexes $Ni(L1)(NO_3)_2 \cdot H_2O$ and $Ni(L2)(NO_3)_2$ indicate that these complexes are also six-coordinate in the solid state. In aqueous solution these six-coordinate species revert to a spectrum typical of five-coordinate geometry.

Table III. d–d Absorption Spectra of Nickel and Copper Complexes[d]

complex	ν_1	ν_2	ν_3
Five-Coordinate Nickel Complexes			
β-Ni(L1)$(NCS)_2$[a]	7.2	16.7	26.0
Ni(L2)$(NCS)_2$[a]	7.4	17.3	26.3
Ni(L1)$(H_2O)_2^{2+}$[b]	8.2 (13)	16.4 (30)	26.3 (50)
Ni(L1)$(H_2O)(OH)^{+}$[b]	8.6 (33)	16.5 (39)	26.6 (73)
$Ni_2(L1)_2(OH)_2^{2+}$[b]	7.2 (44)	16.5 (68)	26.5 (156)
$[Ni_2(L1)_2(OH)_2](ClO_4)_2$[a]	7.4	16.4	26.4
Ni(L2)$(H_2O)_2^{2+}$[b]	8.0 (14)	16.2 (28)	26.1 (50)
Six-Coordinate Nickel Complexes			
$Ni_2(L1)_2(NCS)_2C_2O_4$[a]	10.3	17.1	27.8
[Ni(L1)$(NO_3)H_2O]NO_3$[a]	9.8	16.9	27.0
Ni(L2)$(NO_3)_2$[a]	9.5	16.4	26.6
Ni(dpt)$(H_2O)_3^{2+}$[b]	10.4 (2)	16.7 (7)	27.2 (15)
Copper Complexes			
Cu(L2)$(H_2O)_2^{2+}$[b]	8.5 (75)	14.1 (99)	35.1 (2810)
Cu(L2)$(H_2O)(OH)^{+}$[b]	c	15.0 (89)	36.4 (2660)
Cu(L2)$(OH)_2$[b]	c	14.9 (100)	36.4 (3390)
$Cu_2(L2)_2(OH)_2^{2+}$[b]	c	15.2 (220)	38.5 (10 000) 28.6 (1040)

[a] Diffuse-reflectance spectrum. [b] Aqueous solution spectrum. [c] Not measured. [d] The absorption maxima are $\times 10^3$ cm^{-1} with the molar extinction coefficients (dm^3 mol^{-1} cm^{-1}) given in parentheses.

The changes in the spectrum of Ni(L1)$^{2+}$(aq) with concentration (1.4–2 × 10^{-2} mol dm^{-3}) and pH (7–11) were used to calculate the absorption maxima and molar extinction coefficients of the species present in solution. The results of these calculations are given in Table III. The ratios ν_2/ν_1 of 2.00 for Ni(L1)$(H_2O)_2^{2+}$, 1.92 for Ni(L1)(OH)$(H_2O)^+$, and 2.29 for $Ni_2(L1)_2(OH)_2^{2+}$ are typical of five-coordinate nickel complexes[3] and lie outside the range of 1.6–1.8 observed with octahedral complexes. The high molar extinction coefficients are also typical of five-coordinate nickel;[14] compare Ni(L1)$(H_2O)_2^{2+}$ and Ni(dpt)$(H_2O)_3^{2+}$ (Table III).

Nickel Complexes. We were unable to determine the formation constants for Ni(L2)$^{2+}$ because complex formation in aqueous solution is extremely slow. Zompa[7] has determined the formation of the nickel complexes of L3 by waiting 3–4 months for equilibration, and L2 reacts much more slowly with metal ions than does L3. Titration of solutions of Ni(L1)$(NO_3)_2$ and Ni(L2)$(NO_3)_2$ (concentration range (1.95–9.76) × 10^{-3} mol dm^{-3}) in the pH range 7.0–11.0 allowed us to investigate the hydrolysis equilibria of the metal complexes. Above pH 11, nickel hydroxide precipitated.

The titrations showed that hydrolysis was occurring above pH 8. Calculations which included only the species NiL$(H_2O)(OH)^+$ yielded values for the acid dissociation constant which were concentration dependent. Above pH 9 the visible absorption spectrum of solutions of Ni(L1)$^{2+}$ and Ni(L2)$^{2+}$ also showed a concentration dependence indicative of the formation of polymeric species. If only the dimeric species $Ni_2L_2(OH)_2^{2+}$ was included in the calculations, the fit to the data was unsatisfactory below pH 9.3 but good above this pH. Inclusion of both species in the calculations produced a satisfactory fit to the data with the constants for Ni(L2)$^{2+}$ given in Table I. For Ni(L1)$^{2+}$ the results (log K values) were very similar: Ni(L1)(OH)$^+$, −9.85 ± 0.02; $Ni_2(L1)_2(OH)_2^{2+}$, 2.78 ± 0.04. The solid complex $[Ni_2(L1)_2(OH)_2](ClO_4)_2$ has been isolated, and the low magnetic moment of 2.94 is indicative of some nickel–nickel interaction.[1]

The calculated aqueous solution spectrum of $Ni_2(L1)_2(OH)_2^{2+}$, determined from the titration results, and the reflectance spectrum of $[Ni_2(L1)_2(OH)_2](ClO_4)_2$ are also very similar (vide supra) supporting assignment of the dimeric species in solution.

Table IV. Hydrolysis Constants for Some Selected Five- and Six-Coordinate Complexes

ligand	Ni(II)	Cu(II)	Zn(II)	ref
Five-Coordinate				
L2	9.81[a]	8.48	9.6	this work
Me_6tren	9.53[a]	8.52	9.00	8
dacoda	10.1, 10.55[a]	>13.0	8.59	11, 10
Six-Coordinate				
[9]aneN_3	c	7.9, 8.25	b	4, 24
L3	c	8.14	7.49	7
dien	c	9.29	b	31
2,3-tri	c	9.00	8.73	32
dpt	c	9.65	8.56	33
tren	11.98, 11.93[c]	9.37	10.26	8, 34
edda	11[c]		10.5	11
cis,cis-tach		7.70	7.93	35

[a] Five-coordinate in aqueous solution. [b] Hydrolysis was observed. [c] Six-coordinate in aqueous solution.

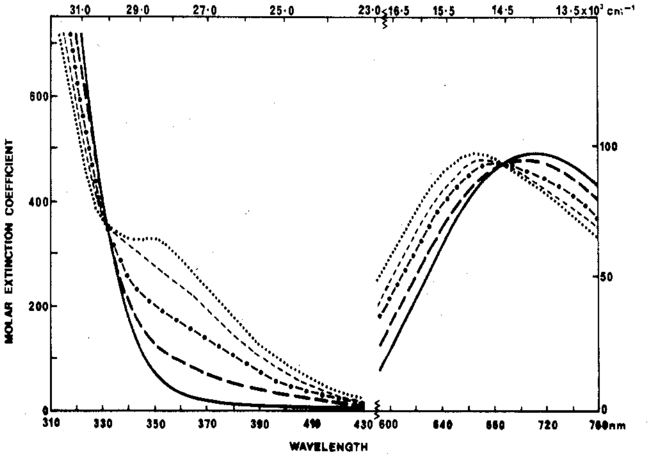

Figure 2. pH dependence of the absorption spectrum of the Cu–L2 system (0.009 975 mol dm^{-3}): —, pH 6.81; – – –, pH 8.01; -·-, pH 8.40; ---, pH 8.84; ···, pH 10.14.

The formation of hydroxonickel(II) complexes is somewhat unusual. Six-coordinate nickel complexes apparently only hydrolyze at quite high pH values (>pH 11) and have been little studied. Hydrolysis of five-coordinate nickel complexes is more facile, and the pK_a values reported here appear to be reasonably typical for such complexes (Table IV).

Hydroxo bridged complexes for nickel are very unusual, although such species are common for copper.[36] The only similar complexes of which we are aware are the complexes $Ni_2(tren)_2(OH)^{3+}$, $Ni_2(tren)_2(OH)_2^{2+}$, and $Ni_2(tren)_2(OH)_3^{+}$[37] which are apparently formed in strongly basic solution. Equilibrium constants for these species have not been reported. The unique combination of a relatively low pK_a value and the presence of two coordinated water molecules apparently favors the formation of the hydroxo-bridged species. Indeed our results show that the formation of the dimer $M_2(L2)_2(OH)_2^{2+}$ from the monomer M(L2)(OH)$^+$ is slightly more favored for nickel than for copper.

Copper Complexes. The formation of the copper complex Cu(L2)$^{2+}$ occurs slowly in the pH range 4–6, and hydrolysis of the complex occurs above pH 7. Again the data in the hydrolysis region could be fitted best by including both the species Cu(L2)(OH)$^+$ and $Cu_2(L2)_2(OH)_2^{2+}$ in the calculations. Above pH 10 there was a significant deviation of the calculated and experimental titers in the calculations using SCOGS, and it was evident that more protons were released above this pH. Inclusion of Cu(L2)$(OH)_2$ as a species in the SCOGS calculations improved the standard deviation in titer by a factor of 3. Attempts to include additional species such

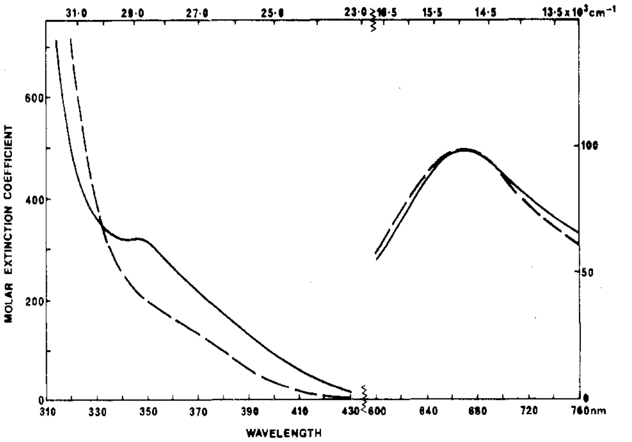

Figure 3. Concentration dependence of the absorption spectra for the Cu–L2 system (pH 10.1): ---, 0.000971 mol dm^{-3}; —, 0.009658 mol dm^{-3}.

as $Cu(L2)_2^{2+}$ in the calculations did not lead to significantly improved results.

Spectrophotometric evidence for the presence of these species is shown in Figure 2. The absorption maxima of solutions of $Cu(L2)^{2+}$ progressively shift to higher energy with increasing pH (refer to Figure 2 and Table III).

The spectra, especially in the region of the absorption shoulder at about 28600 cm^{-1}, were concentration dependent (Figure 3). An absorption band in the region 30000–20000 cm^{-1} has been observed in many dimeric copper complexes and has been assigned to a charge-transfer transition from the lone-pair electrons of the bridged hydroxo ligand to the copper ion.[38] Its appearance in solutions of $Cu(L2)^{2+}$ and the concentration dependence of the spectra are taken to indicate the existence of $Cu_2(L2)_2(OH)_2^{2+}$ in solution. The solid complex $[Cu_2(L2)_2(OH)_2](ClO_4)_2$ has an absorption band at 27200 cm^{-1} and a low magnetic moment (1.62 μ_B) indicative of some copper–copper interaction. The appearance of isosbestic points at 35300, 30100, and 14700 cm^{-1} over the pH range 6.8–10 (Figure 2) and their concentration independence (Figure 3) are consistent with the presence of the three species $Cu(L2)^{2+}$, $Cu(L2)(OH)^{+}$, and $Cu_2(L2)_2(OH)_2^{2+}$ in solution.[39] Above pH 10 there was a further change in the spectrum; the isosbestic points disappeared and the 350-nm absorption decreased in intensity consistent with the formation of the species $Cu(L2)(OH)_2$. Absorption maxima and molar extinction coefficients were calculated from the spectra and the equilibrium constants (concentration and pH ranges investigated were 2.5×10^{-3}–1.0×10^{-2} mol dm^{-3} and pH 6.5–11, respectively). The results are presented in Table III. These complexes also exhibit an absorption band in the region 10000–8000 cm^{-1}, but the pH dependence of this band was not investigated.

The shift of the absorption maxima to higher energy and the decrease in molar extinction coefficient on hydrolysis are consistent with hydrolysis of an equatorially coordinated water molecule.[40] Similar shifts in the visible absorption band have been observed on hydrolysis of $Cu([9]aneN_3)^{2+}$.[4] Higher molar extinction coefficients for the visible absorption band have been reported for the related copper complexes with L3, $Cu(L3)^{2+}$ 14500 cm^{-1} (ϵ 138) and $Cu_2(L3)_2(OH)_2^{2+}$ 15400 cm^{-1} (ϵ 285).[6] However, the shift of the visible absorption maxima to lower energy, with decreasing complex stability of the copper complexes with the triaza macrocycles, is consistent with previous observations.[5]

Hydrolysis of the coordinated water molecules in the copper complexes of triaza macrocycles appears to be only slightly affected by the size of the macrocyclic ring. The pK_a values reported in Table IV for the copper complexes with $[9]aneN_3$ and L2 are similar. The hydrolysis of solutions of $Cu(L3)^{2+}$ has been interpreted solely in terms of the species $Cu_2(L3)_2(OH)_2^{2+}$ with an equilibrium constant for the reaction

$$2Cu(L3)^{2+} + 2OH^- \rightleftharpoons Cu_2(L3)_2(OH)_2^{2+}$$

of log K = 13.23.[6] With L2, log K for this reaction is 12.6.

Table V. Logarithms of Formation Constants for Some Triamine Complexes with Copper(II) and Zinc(II)

ligand	Cu(II)	Zn(II)	ref
$[9]aneN_3$	15.1	11.7	4
	15.5	11.6	25
	16.2		26
$[10]aneN_3$	15.5	11.3	5
	16.1		6
$[11]aneN_3$	14.4	10.4	5
L3	12.6	8.8	5
	13.16		6
L2	11.6	7.7	this work

Bromide ions were found to catalyze the formation of $Cu(L2)^{2+}$. In addition, when bromide ions were present in solutions of $Cu(L2)^{2+}$ there is evidence that bromide complexes formed. The isosbestic points observed in the absence of bromide ions were not observed when bromide was present in solution, and an absorption shoulder at 405 nm, present above pH 7.5, was observed to be dependent on the pH and both bromide and $Cu(L2)^{2+}$ concentrations. This latter observation suggested formation of the bromide–hydroxo dimer $[Cu_2(L2)_2(OH)Br]^{2+}$. Below pH 7.5, addition of bromide caused an increase in the absorption bands. A plot of ϵ_{app} against $(\epsilon_{app} - \epsilon(Cu(L2)Br))/[Br^-]_T$ (ϵ_{app} is the apparent molar extinction coefficient, $\epsilon(Cu(L2)Br)$ is the molar extinction coefficient of the $Cu(L2)Br^+$ complex, and $[Br^-]_T$ is the total concentration of bromide ions in solution),[41] for $[Br^-]_T$ in the range 8.48×10^{-3}–4.24×10^{-2} mol dm^{-3} and a $Cu(L2)^{2+}$ concentration 2.119×10^{-3} mol dm^{-3} at 27000 cm^{-1}, pH 6.50, and 25.0 °C, gave a good straight line with slope $-1/K(Cu(L2)Br)$ corresponding to a $K(Cu(L2)Br)$ of 5.0 ± 0.8 and an intercept 81 ± 9 dm^3 mol^{-1} cm^{-1} corresponding to $\epsilon(Cu(L2)Br)$ at 27000 cm^{-1} ($\epsilon(Cu(L2))$ 12 dm^3 mol^{-1} cm^{-1}). Linearity of the plot suggested formation of the complex $Cu(L2)Br_2$ was not significant under the experimental conditions used. The value of $K(Cu(L2)Br)$ is lower than that reported for $[Cu(teta)Br]^{+}$[41] of 10.8 and is comparable to that of the aquated Cu(II) ion; $K(CuBr)$ = 5.0.[42]

Zinc Complexes. The equilibrium between zinc and L2 was slow. The results calculated from the batch titrations of zinc and $L2\cdot3HNO_3$ are given in Table I. Attempts to include $Zn(L2)_2^{2+}$ and $Zn_2(L2)_2(OH)_2^{2+}$ in the calculations did not lead to an improved fit of the experimental data. The batch titration performed with $L2\cdot3HBr$ indicated that bromide complexes of $Zn(L2)^{2+}$ are formed in solution. With this form of the ligand there was no evidence for the hydrolysis of the $Zn(L2)^{2+}$ complex up to pH 10. The formation constant calculated from the data (log $K(Zn(L2)^{2+})$ = 7.77 ± 0.08) is in good agreement with the value determined with $L2\cdot3HNO_3$ (Table I). The failure to observe the species $Zn_2(L2)_2(OH)_2^{2+}$ may indicate that the zinc complexes in aqueous solution are tetrahedral rather than five-coordinate.

Formation Constants of the Metal Complexes. Comparison of the formation constants for L2 with the constants for the other triaza macrocyclic ligands given in Table V reveals that L2 forms the least stable complexes of any triaza macrocycle measured to date. The decrease in stability with increasing size of the macrocyclic ring is possibly due to increased strain within the macrocyclic ring although other explanations, e.g., ligand preorientation prior to complexation, are possible. The decrease observed for L2 may be due to an increase in the ring strain arising from the methyl groups. We are reluctant to draw the conclusion that the decrease in the formation constants for the complexes of L2 compared to those of L3 is due to a change in the coordination number of the metal ion. Most copper(II) complexes may be five-coordinate in aqueous solution, and the $Zn(L3)^{2+}$ complex may also be five-coordinate.

Metal Complex Hydrolysis Constants. A number of workers have commented on the ease of hydrolysis of coordinated water molecules in five-coordinate complexes. Certainly in the case of nickel(II) where it is relatively easy to establish the coordination number from spectroscopic measurements it is clear that the value of the pK_a in five-coordinate complexes is lower than that for similar six-coordinate complexes (Table IV). The simplest interpretation would be to attribute the decrease in pK_a to stronger metal–oxygen binding due to a change in coordination number, and indeed, where a four-coordinate geometry can be adopted, e.g., $[Ni(dachen)(OH)]^+$, the value of pK_a (8.84) is the lowest reported for a nickel complex.[43] With copper(II) and zinc(II) complexes, where it is much more difficult to assign a coordination number in aqueous solution, it is clear from the data in Table IV that those ligands which impose a five-coordinate geometry on nickel(II) give rise to copper and zinc complexes which are relatively easy to hydrolyze. An exception is where the water molecule is a weakly bound axial group, e.g., $Cu(dacoda)H_2O$.

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Registry No. β-$Ni(L1)(NCS)_2$, 66540-28-1; $Ni(L2)(NCS)_2$, 69897-27-4; $Ni(L1)(H_2O)_2^{2+}$, 69897-28-5; $Ni(L1)(H_2O)(OH)^+$, 69927-40-8; $Ni_2(L1)_2(OH)_2^{2+}$, 66540-30-5; $[Ni_2(L1)_2(OH)_2](ClO_4)_2$, 66756-81-8; $Ni(L2)(H_2O)_2^{2+}$, 69897-29-6; $Ni_2(L1)_2(NCS)_2C_2O_4$, 69897-30-9; $[Ni(L1)(NO_3)H_2O]NO_3$, 69897-32-1; $Ni(L2)(NO_3)_2$, 69897-33-2; $Ni(dpt)(H_2O)_3^{2+}$, 69622-25-9; $Cu(L2)(H_2O)_2^{2+}$, 69897-34-3; $Cu(L2)(H_2O)(OH)^+$, 69897-35-4; $Cu(L2)(OH)_2$, 69897-36-5; $Cu_2(L2)_2(OH)_2^{2+}$, 69897-37-6; $Cu(L2)(NO_3)_2$, 69897-38-7; $Zn(L2)(H_2O)_2^{2+}$, 69897-39-8; L2, 69881-53-4; L2·3HBr, 69881-54-5; $L2{\cdot}3HNO_3$, 69881-55-6; $Ni(dpt)_2(NCS)_2$, 66540-29-2; $Ni(dpt)_2(NO_3)_2$, 49726-04-7; acetone, 67-64-1; propan-2-ol, 67-63-0.

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