compressed octahedral geometry. These complexes undergo an irreversible intramolecular rearrangement, which is acid-catalyzed, to form transient nickel(III) complexes, with EPR spectra characteristic of tetragonally elongated octahedral complexes. The rate of interconversion varies with the dipeptide in the order AlaGly > GlyGly > AibGly > GlyAla > AlaAla. The intermediate undergoes a loss of nickel(III) at a rate independent of acid concentration. Rate constants for the second step varies with the dipeptide in the order GlyGly > AlaGly ≅ AibGly > GlyAla > AlaAla.

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Registry No. 1, 89164-56-7; bis(L-alanylglycinato)nickelate(III), 89164-57-8; bis(L-alanyl-L-alaninato)nickelate(III), 89164-58-9; bis(glycyl-L-alaninato)nickelate(III), 89164-59-0; bis(α-aminoisobutyrylglycinato)nickelate(III), 89164-60-3.

Contribution from the Dipartimento di Chimica, Università di Firenze, and ISSECC (CNR), 50132 Florence, Italy, and Dipartimento di Chimica, Università della Calabria, Calabria, Italy

Coordination Tendencies of a Series of Tetraazacycloalkanes Related to 1,4,7,10-Tetraazadecane (trien): Synthetic, Thermodynamic, and Structural Aspects

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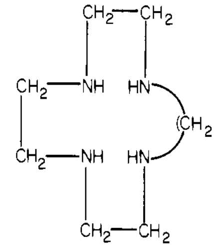
The macrocycle 1,4,7,10-tetraazacyclopentadecane (L5) has been synthesized. The basicity constants and the stability constants of the complexes $[ML5]^{2+}$ and $[MHL5]^{3+}$ (M = Cu(II), Ni(II)) have been determined by potentiometry at 25 °C in 0.5 mol dm^{-3} KNO_3. The enthalpies of formation of the Cu(II) and Ni(II) complexes of L5 have been determined by flow and batch microcalorimetry. The Cu(II) complex with 1,4,7,10-tetraazacyclotetradecane (L4) has been prepared and characterized by X-ray measurements. The compound $[CuL4](ClO_4)_2$ crystallizes in an orthorhombic unit cell ($P2_12_12$ space group) with lattice constants $a = 22.219$ (8) Å, $b = 13.753$ (5) Å, and $c = 9.097$ (4) Å, $D_{calcd} = 1.66$ g cm^{-3} for $Z = 6$, and $V = 2779.8$ Å^3. Least-squares refinement gave $R = 0.076$ for the 854 observed reflections. The unit cell contains two independent complex molecules. The copper atoms of both molecules are in a tetragonally distorted octahedral environment, where the four nitrogen atoms are in a planar arrangement and two oxygen atoms of two perchlorate ions in the apical positions. Among the macrocycles related to trien, L5 forms the weakest metal complexes.

Introduction

The open-chain tetraamine 1,4,7,10-tetraazadecane (trien) is one of the most familiar ligands. Many metal complexes of trien have been prepared and extensively studied both in the solid state and in aqueous solution.[2] Spectroscopic studies have shown that trien can adopt either the cis or trans configuration in octahedral complexes.[3] Beside these considerations it is also well-known that the chemistry of macrocyclic complexes has attracted considerable interest over recent years in an attempt to rationalize the special thermodynamic and kinetic properties of these complexes.[4-6] Tha aim of this work is to investigate the trends in coordination capabilities toward protons and metal ions such as Cu(II) and Ni(II) of a series of tetraazacycloalkane ligands that can be obtained by cyclization of the linear tetraamine 1,4,7,10-tetraazadecane (trien) with hydrocarbon bridges of different lengths (see structure).



$n = 0$: 1,4,7,10-tetraazadecane (L1)
$n = 2$: 1,4,7,10-tetraazacyclododecane (L2)
$n = 3$: 1,4,7,10-tetraazacyclotridecane (L3)
$n = 4$: 1,4,7,10-tetraazacyclotetradecane (L4)

This paper reports the synthesis and the coordination properties of the macrocyclic ligand 1,4,7,10-tetraazacyclopentadecane (L5) and the crystal structure of the complex $[CuL4](ClO_4)_2$. Thermodynamic and structural data have been discussed and compared with data for the other ligands of the series, taken from the literature.

Experimental Section

Preparation of 1,4,7,10-Tetraazacyclopentadecane (L5). The tosyl derivative of L5, 1,4,7,10-tetrakis(tolyl-*p*-sulfonyl)-1,4,7,10-tetraazacyclopentadecane (I), was obtained by adding dropwise to a solution (1.3 dm^3) of the disodium salt (120 g) of *N,N′,N″,N‴*-tetrakis(tolyl-*p*-sulfonyl)-1,4,7,10-tetraazadecane a solution (650 cm^3) of *O,O′*-bis(tolyl-*p*-sulfonyl)pentane-1,5-diol (53.2 g) in anhydrous DMF. The reaction mixture was refluxed for 1 h. The volume was reduced

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Table I. Positional Parameters (×10^4), Anisotropic Temperature Factors (×10^3),[a] and Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	−1671 (2)	−862 (3)	−1588 (6)	43 (3)	48 (3)	70 (4)	6 (3)	7 (3)	−8 (3)
Cu(2)	0	−5000	−6368 (6)	40 (4)	88 (6)	41 (5)	13 (4)	0	0
Cl(1)	−3051 (6)	−773 (10)	770 (17)	75 (8)	70 (9)	115 (12)	21 (8)	16 (8)	26 (10)
Cl(2)	−181 (6)	−1566 (11)	−3092 (25)	61 (11)	112 (12)	194 (20)	2 (8)	47 (12)	−28 (13)
Cl(3)	−1448 (4)	−3711 (8)	−6144 (13)	47 (7)	73 (8)	61 (10)	12 (6)	6 (6)	16 (8)

[a] Anisotropic thermal factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$.

by vacuum distillation, resulting in a white sticky precipitate to which water was added (1 dm^3). The product was recrystallized twice from ethanol; mp 237–238 °C. Anal. Calcd for $C_{39}H_{50}N_4O_8S_4$: C, 56.36; H, 6.06; N, 6.74. Found: C, 56.1; H, 6.4; N, 7.1. Infrared spectra showed that cyclization has occurred since no bands in the N–H region (3060–3500 cm^{-1}) were observed. The free ligand L5 was obtained by hydrolysis of the tetratosylate derivative (I), with concentrate H_2SO_4 solution, following the procedure already described.[7] The crude free amine was purified as the tetrahydrochloride monohydrate. Anal. Calcd for $C_{11}H_{32}N_4Cl_4O$: C, 34.93; H, 8.53; N, 14.81; Cl, 37.50. Found: C, 34.7; H, 8.2; N, 15.1; Cl, 37.6.

Complexes. The Ni(II) complex of ligand L5 was obtained by mixing equimolar solutions of $Ni(ClO_4)_2{\cdot}6H_2O$ and the ligand in hot butanol and recrystallizing the product from ethanol. The Cu(II) complex of L4 was obtained by mixing equimolar aqueous solutions of $Cu(ClO_4)_2{\cdot}6H_2O$ and the ligand L4 prepared as described in ref 8. The solution was heated and concentrated. As the solution was slowly cooled, blue crystals were obtained; these were filtered, washed with ethanol and ether, and dried. Anal. Calcd for $[NiL5](ClO_4)_2$: C, 27.99; H, 5.55; N, 11.87. Found: C, 28.0; H, 5.7; N, 12.0. Calcd for $[CuL_4](ClO_4)_2$: C, 25.96; H, 5.22; N, 12.11. Found: C, 25.8; H, 5.2; N, 11.9.

Materials. All potentiometric and calorimetric measurements were carried out in 0.5 mol dm^{-3} KNO_3 as ionic medium, using commercial KNO_3 (C. Erba ACS grade) without further purification. Standardized CO_2-free solutions of NaOH, used in the potentiometric and calorimetric experiments, were prepared according to the procedure already described.[9]

EMF Measurements. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, thermostated cell, etc.) that have been already described.[10] The titration system was controlled by an Apple II Europlus personal computer, equipped with a 9-in. video display, an impact printer, and one minifloppy disk driver. A computer program was written in Basic[11] to monitor, for each titration point, the emf value and the volume of titrant added. For the determination of the stability constants of Ni(II) complexes of L5, because of the long time required to reach chemical equilibrium, a "batchwise" potentiometric technique was employed as described elsewhere.[12] The computer program MINIQUAD[13] was used to process data and calculate both basicity and stability constants.

Calorimetric Measurements. For the calorimetric measurements, LKB BATCH Model 10700-2 and LKB FLOW Model 10700-1 microcalorimeters were used. The flow technique was employed to determine the enthalpy of formation of $[CuL5]^{2+}$. A full description of the apparatus and its calibrations has already reported.[14] In aqueous solutions of the macrocycles, the main species present is the diprotonated form $[H_2L]^{2+}$; the presence of two positive charges causes the metal–complex reaction to be rather slow. This problem can be avoided by working in strongly alkaline solution (0.5 mol dm^{-3} NaOH) where the ligand remains unprotonated. The enthalpy change can be related to that in neutral solution through appropriate dilution experiments (see ref 14). In a typical calorimetric experiment a solution of Cu(II) (1.2 × 10^{-4} mol dm^{-3}) in NaOH (0.5 mol dm^{-3}) and a solution of the ligand hydrochloride (1.3 × 10^{-4} mol dm^{-3}) in NaOH (0.5 mol dm^{-3}) were injected into the calorimeter; the flow rates were varied in such a way as to have a metal-to-ligand ratio ranging from 1:1 to 1:1.5.

The batch technique was used to determine the enthalpy of formation of $[NiL5]^{2+}$; the description of this apparatus, its calibrations, and its mode of operation for slow reactions has already reported.[15] The reaction for which ΔH° has been determined can be represented by eq 1, where L = L5. Values of ΔH° for L = $6H_2O$ have been

$$[NiL]^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-} + L \qquad (1)$$

reported previously.[15] A solution (0.4 cm^3) of $[NiL_5]^{2+}$ complex (0.01–0.02 mol dm^{-3}) was introduced by weight into one side of the calorimetric cell compartment; the NaOH–NaCN (2.5 cm^3) solution (0.4 mol dm^{-3} NaOH, 0.1 mol dm^{-3} NaCN) was introduced into the other by a precision pipet. The calorimeter was allowed to equilibrate, and then the measurement was started by mixing the reactants. The reaction was considered complete when no further heat change could be detected, after ca. 0.5 h. In order to confirm that the reaction was complete and the equilibrium had been reached, we determined the concentration of $[Ni(CN)_4]^{2-}$ spectrophotometrically in the reaction mixture just after the collection of the thermal data.

Spectrophotometric Measurements. Visible spectra at different temperatures were recorded on a Beckman DK 2A spectrophotometer.

X-ray Data Collection and Reduction. The blue crystal used for data collection was a parallelepiped of dimensions 0.25 × 0.15 × 0.10 mm. Crystals are orthorhombic and belong to the space group $P2_12_12$ with six units of the $[CuL4](ClO_4)$ formula in the unit cell. Dimensions are as follows: a = 22.219 (8), b = 13.753 (5), and c = 9.097 (4) Å ($\lambda_{Mo\,K\alpha}$ = 0.709 26 Å). The calculated density is 1.66 g cm^{-3}. Intensity data were collected at room temperature (about 21 °C) on a Philips PW 1100 computer-controlled diffractometer equipped with a graphite monochromator, using the same radiation. All reflections with $5° < 2\theta < 50°$ were measured by the ω–2θ scan technique at a scan speed of 0.07°/s (in ω) with a variable scan width of $(0.80 + 0.30 \tan \omega)°$ across the peak. Background counts were taken for a time equal to half the scan time on each side of the peak. The indexes of the collected reflections are all positive. Three standard reflections were measured every 120 min during data collection, but no significant variation was noticed in their intensities. The standard deviation $\sigma(I)$ was estimated as previously described[16] with an instability factor equal to 0.03. A reflection was considered unobserved if the net intensity I was $<3\sigma(I)$. Out of the 2797 total reflections, 854 had $I > 3\sigma(I)$. An absorption correction, μ(Mo Kα) = 9.76 cm^{-1}, was applied by using the appropriate routines of the SHELX 76 system of programs (transmission factors varied between 0.86 and 0.90).[17] The intensity data were then corrected for Lorentz and polarization effects. Atomic scattering factors were taken from ref 18 for nonhydrogen atoms and from ref 19 for hydrogen atoms. By application of the anomalous dispersion corrections, the absolute structure could be assigned.[18]

Solution and Refinement of the Structure. The positions of the two independent Cu atoms were obtained from a Patterson synthesis. The

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Table II. Positional Parameters ($\times 10^4$), Isotropic Temperature Factors ($\times 10^3$), and Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U, Å^2
N(1)	−1463 (14)	−1692 (21)	75 (38)	61 (11)
N(2)	−1899 (16)	−2053 (23)	−2574 (37)	75 (11)
N(3)	−2071 (14)	−228 (24)	−3176 (37)	70 (10)
N(4)	−1349 (16)	478 (23)	−1140 (40)	77 (11)
C(1)	−1535 (19)	−2757 (30)	−491 (48)	90 (15)
C(2)	−1966 (20)	−2848 (32)	−1520 (53)	91 (14)
C(3)	−2348 (19)	−1858 (30)	−3698 (50)	89 (15)
C(4)	−2193 (19)	−846 (32)	−4388 (49)	100 (14)
C(5)	−1770 (24)	728 (33)	−3629 (50)	114 (17)
C(6)	−1604 (20)	1190 (27)	−2133 (45)	79 (15)
C(7)	−1283 (20)	821 (38)	252 (52)	97 (16)
C(8)	−848 (20)	356 (31)	1322 (57)	118 (17)
C(9)	−1029 (22)	−628 (29)	1976 (50)	114 (17)
C(10)	−990 (17)	−1553 (29)	1160 (46)	84 (13)
N(5)	−284 (14)	−5866 (29)	−4770 (38)	88 (12)
N(6)	−504 (23)	−5878 (46)	−7697 (59)	165 (20)
C(11)	−818 (17)	−6457 (27)	−5136 (43)	72 (13)
C(12)	−737 (22)	−6874 (34)	−6589 (55)	123 (17)
C(13)	−359 (27)	−6359 (47)	−8639 (65)	163 (27)
C(14)	−53 (33)	−5452 (37)	−9191 (51)	178 (27)
C(15)	−298 (18)	−5313 (38)	−3470 (56)	112 (21)
O(1)	−2647 (17)	−204 (33)	−134 (51)	165 (15)
O(2)	−3540 (14)	−212 (24)	999 (33)	105 (11)
O(3)	−3297 (28)	−1469 (46)	−174 (74)	255 (28)
O(4)	−2833 (27)	−1293 (43)	1692 (77)	221 (28)
O(5)	−645 (17)	−995 (30)	−3030 (43)	124 (14)
O(6)	237 (21)	−1361 (34)	−4355 (57)	199 (21)
O(7)	−402 (17)	−2543 (30)	−3026 (46)	145 (15)
O(8)	44 (30)	−1415 (47)	−1895 (76)	242 (34)
O(9)	−829 (16)	−3586 (24)	−6469 (46)	126 (13)
O(10)	−1782 (15)	−2927 (24)	−6601 (42)	110 (11)
O(11)	−1617 (18)	−4551 (27)	−6993 (41)	147 (14)
O(12)	−1520 (15)	−3934 (27)	−4757 (42)	119 (12)

Table III. Basicity Constants at 25 °C and $I = 0.5$ mol dm^{-3}

	L1[a]	L2[b]	L3[b]	L4[c]	L5[d]
$\log K_1$	10.02	10.97	11.19	10.98	10.33 (1)[e]
$\log K_2$	9.39	9.87	10.12	9.75	9.48 (1)
$\log K_3$	7.00	<2	<2	4.86	5.71 (1)
$\log K_4$	4.00	<2	<2	2.00	1.28 (2)
$\log \beta_4$	30.41			27.59	26.80

[a] Reference 20. [b] Reference 21. [c] Reference 8. [d] This work. [e] Values in parentheses are standard deviations in the last significant figure.

positions of the other independent non-hydrogen atoms were obtained from successive Fourier maps. One of the two complex cations possesses a twofold symmetry axis passing through the Cu atom. The structure was refined by full-matrix least squares using the SHELX program.[17] The function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2(F_o)$. The hydrogen atoms were introduced in calculated positions (C–H distance of 1.08 Å), with an overall temperature factor U of 0.05 Å^2, and were not refined. Their positions were varied in every cycle on the basis of the shift of the linked atoms. Anisotropic temperature factors were used for the Cu and Cl atoms, whereas the other atoms were assigned isotropic thermal parameters. The final temperature factors of the oxygen atoms in the perchlorate ions and those of some nitrogen and carbon atoms of the ligand molecule were rather high. These values can be ascribed to some degree of disorder existing in the structure, which may have also caused the low number of observed reflections. The final refinement gave an R value of 0.076 and R_w defined as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0.072. A final ΔF Fourier synthesis did not show remarkable features except for some diffuse peaks in the zone of the perchlorate ions. Their height was, however, less than 1 e/Å.^{3} The final values of the atomic parameters are reported in Tables I and II. A listing of F_o and F_c is available as supplementary material.

Results and Discussion

Thermodynamic Aspects. Protonation. The stepwise protonation constants for L5 have been reported in Table III. For comparison, the protonation constants for trien and trien-like macrocycles have been also reported. The noncyclic polyamine trien shows the highest overall basicity;[20] the cyclization invariably reduces the overall basicity of cyclic polyamines. As has been already pointed out, the lower basicities for cyclic polyamines can be ascribed to the proximity of the NH_2^+ groups,[22] resulting in strong electrostatic repulsions. The effect of cyclization on the amine basicities is very strong in the third and fourth protonation constants (see Table III). Such a trend is more marked for the smaller macrocycles L2 and L3 whose third and fourth protonation constants are too small to be measured.[21]

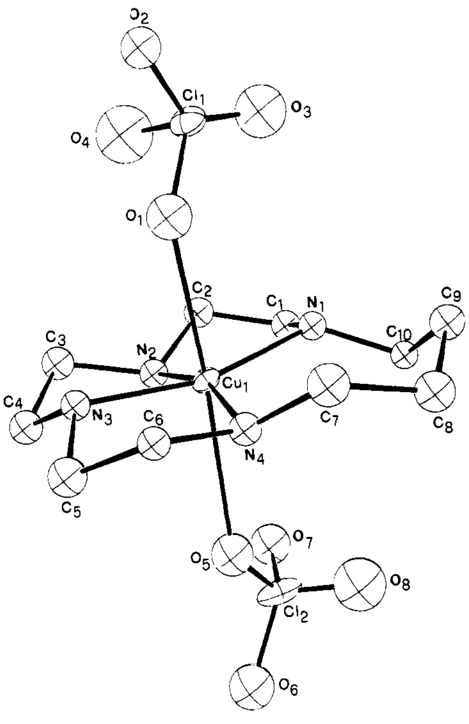

Figure 1. Molecular structure of [CuL4]$(ClO_4)_2$ showing all atoms other than hydrogen.

Cu(II) Complexes. The X-ray structure determination of [CuL4]$(ClO_4)_2$ has shown that the complex is octahedral (see Figure 1) with the metal ion in the least-squares N_4 plane but with a tetrahedrally distorted arrangement of the nitrogen atoms.

The presence of the seven-membered ring induces some strain in the N_4 plane, thus weakening the Cu–N interactions. As far as ligand L5 is concerned, because of the very long hydrocarbon chain bridging two adjacent nitrogen atoms one would expect the macrocycle to be very flexible and able to behave similarly to the open-chain counterpart L1 in metal complexation. Indeed, the stability of the [CuL1]$^{2+}$ complex[20,23] is very close to that of [CuL5]$^{2+}$ complex (see Figure 2 and Table IV), but the $\Delta H^\ominus$ and $T\Delta S^\ominus$ contributions to the overall stability are quite different for the two systems, indicating (a) that the macrocyclic complex is not strain free,

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Table IV. Thermodynamic Parameters of Formation of Cu(II) and Ni(II) Complexes with Ligand L5 (25 °C, $I = 0.5$ mol dm^{-3} (KNO_3), Standard State = 1 mol dm^{-3})

reaction	log *K*	$-\Delta G^\ominus$, kcal mol^{-1}	$-\Delta H^\ominus$, kcal mol^{-1}	$T\Delta S^\ominus$, kcal mol^{-1}
$Cu^{2+} + L5 \rightleftarrows [CuL5]^{2+}$	20.40 (1)[a]	27.83 (1)	19.2 (2)	8.6 (2)
$Cu^{2+} + L5 + H^+ \rightleftarrows [CuHL5]^{3+}$	22.35 (5)	30.49 (7)		
$[CuL5]^{2+} + H^+ \rightleftarrows [CuHL5]^{3+}$	1.95	2.66		
$Ni^{2+} + L5 \rightleftarrows [NiL5]_{oct}{}^{2+}$	11.75 (8)	16.0 (1)	11.4 (2)	4.6 (2)
$Ni^{2+} + L5 \rightleftarrows [NiL5]_{plan}{}^{2+}$	12.07 (8)	16.5 (1)	7.7 (2)	8.8 (2)
$Ni^{2+} + L5 + H^+ \rightleftarrows [NiHL5]^{3+}$	18.0 (1)	24.5 (1)	...	...
$[NiL5] + H^+ \rightleftarrows [NiHL5]^{3+}$	6.25	8.53	...	...
$[NiL5]_{oct}{}^{2+} \rightleftarrows [NiL5]_{plan}{}^{2+} + 2H_2O$	0.33 (2)	0.45 (2)	−3.7 (2)	4.1 (2)

[a] Values in parentheses are standard deviations in the last significant figure.

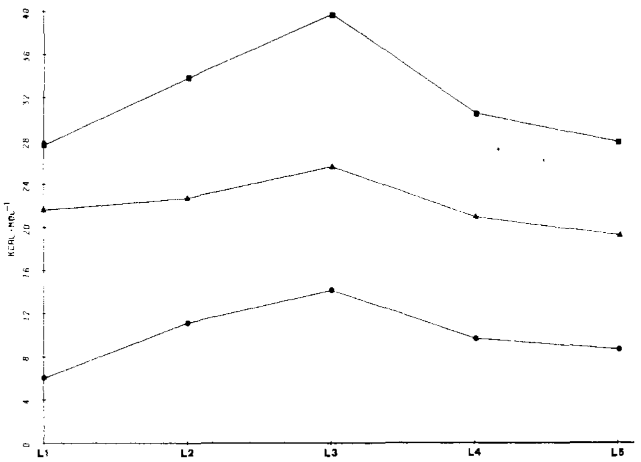

Figure 2. Enthalpic (▲) and entropic (●) contributions to the free energy (■) of formation for Cu(II) complexes of trien and trien-like macrocycles. Thermodynamic data for ligands L1, L2, L3, and L4 have been taken from ref 20, 23; 24, 25; 14, 26; and 8, respectively.

as the enthalpy of formation is the smallest among those of the complexes investigated, and (b) that the macrocyclic complex still has a large configurational entropy gain compared to the complex formed by the open-chain ligand.

Ni(II) Complexes. The stability constants of the Ni(II) complexes with L5 have been measured by a "batchwise" potentiometric technique, and the enthalpy of formation has been determined calorimetrically. These values are reported in Table IV. Many Ni(II) complexes with tetraaza macrocycles are present in aqueous solution as equilibrium mixtures of octahedral diaquo paramagnetic and square-planar diamagnetic forms.[8,12,15,27] The thermodynamic data for the above equilibrium for ligand L5 have been determined spectrophotometrically and are reported in Table IV. The octahedral forms of Ni(II) macrocyclic complexes can be compared with the $[NiL1]^{2+}$ complex. Moreover the high kinetic inertness of Ni(II) tetraaza macrocycles do not make available the stability constants for $[NiL2]^{2+}$ and $[NiL3]^{2+}$. The $[NiL]^{2+}$ complex (log $K = 14.4$)[20] is slightly less stable than $[NiL4]^{2+}$ (log $K = 14.81$)[12] and more stable than $[NiL5]^{2+}$ (see Table IV); this trend is the same as that observed for the analogous Cu(II) complexes. It seems reasonable to expect that also the stabilities of $[NiL2]^{2+}$ and $[NiL3]^{2+}$ should follow the same trend as the corresponding Cu(II) complexes, with the $[NiL3]^{2+}$ complex most stable and the $[NiL2]^{2+}$ one next. As far as the formation enthalpies of the octahedral Ni(II) complexes are concerned, it may be noted that $[NiL3]^{2+}$ is the most exothermic complex ($-\Delta H^\ominus = 20.0$ kcal mol^{-1});[28] either shortening or lengthening of the hydrocarbon chain that bridges two adjacent nitrogen atoms results in a strong reduction of the exothermicity of the formation reaction.

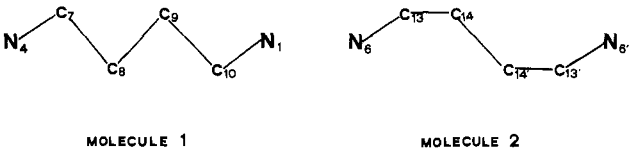

Figure 3. Representation of the butylenic bridge in molecule 1 and molecule 2.

An X-ray structural investigation on the low-spin $[NiL5](ClO_4)_2$ compound has shown that the nickel atom lies in the best plane defined by the four nitrogen atoms.[29] All of the carbon atoms in the eight-membered chelate ring lie on the same side with respect to the above least-squares plane.

Protonated Metal Complexes. Both Cu(II) and Ni(II) form with macrocycle L5 monopronated $[MHL5]^{3+}$ complexes. The constants for these are listed in Table IV. Formation of monoprotonated complexes is quite common for tetraaza macrocycles having 14 or higher membered rings.[12] The relative concentration of these interesting species, in which protonation of the nitrogen atom involves cleavage of a M–N bond with formation of a large chelate ring, is invariably small. The protonation reaction yielding the $[MHL5]^{3+}$ complex from $[ML5]^{2+}$ (see Table IV) is much easier for the Ni(II) complex (log $K = 6.25$) than for the Cu(II) one (log $K = 1.95$). This is consistent with the fact that the $[CuL5]^{2+}$ complex is more stable than the $[NiL5]^{2+}$ one. Such values of protonation constants are much smaller than that for protonation of the first nitrogen atom in the free ligand (log $K = 10.33$; see Table III). This may be considered as indirect evidence for the fact that the chelating ligand has no uncoordinated nitrogen atoms.

Description of the Structure of $[CuL4](ClO_4)_2$. The structure consists of monomeric complexes $[CuL4](ClO_4)_2$ in which the coordination polyhedron of Cu(II) is a tetragonally distorted octahedron. The unit cell contains two independent complex molecules. One of these (molecule 2) has a binary axis passing through the metal atom and the macrocycle. Since such a molecule is affected by disordering, which is particularly noticeable in the N–$(C)_4$–N moiety where some values of distances and angles are unrealistic, it may be used with caution to establish comparisons with the other molecule in the asymmetric unit (molecule 1), either with similar complexes reported in the literature. Figure 1 shows a perspective view of molecule 1. The copper atoms of both molecules lie in the mean plane of the four nitrogen atoms with two perchlorate oxygen atoms occupying the apical positions of a distorted octahedron about the metal atom (the Cu–O distances are in the range 2.64–2.70 Å). Selected values of bond distances and angles are reported in Table V. The four nitrogen atoms are displaced from their least-squares plane by 0.17–0.21 Å with an arrangement slightly distorted toward that of a tetrahedron. The 14 atoms in the macrocycle of molecule 1 lie alternatively

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Table V. Interatomic Distances (Å) and Angles (deg)

	Distances		
Cu(1)-N(1)	1.95 (3)	C(3)-C(4)	1.57 (5)
Cu(1)-N(2)	1.93 (3)	C(5)-C(6)	1.54 (5)
Cu(1)-N(3)	1.91 (3)	C(7)-C(8)	1.51 (5)
Cu(1)-N(4)	2.02 (3)	C(8)-C(9)	1.53 (4)
Cu(1)-O(1)	2.70 (4)	C(9)-C(10)	1.47 (4)
Cu(1)-O(5)	2.64 (4)	C(11)-C(12)	1.45 (5)
Cu(2)-N(5)	1.98 (3)	C(13)-C(14)	1.51 (6)
Cu(2)-N(6)	2.04 (5)	C(14)-C(14′)	1.27 (9)
Cu(2)-O(9)	2.68 (3)	C(15)-C(15′)	1.58 (7)
N(1)-C(1)	1.56 (4)	Cl(1)-O(1)	1.45 (4)
N(1)-C(10)	1.45 (4)	Cl(1)-O(2)	1.35 (3)
N(2)-C(2)	1.46 (4)	Cl(1)-O(3)	1.40 (6)
N(2)-C(3)	1.45 (4)	Cl(1)-O(4)	1.20 (6)
N(3)-C(4)	1.42 (4)	Cl(2)-O(5)	1.30 (4)
N(3)-C(5)	1.53 (4)	Cl(2)-O(6)	1.51 (5)
N(4)-C(6)	1.45 (4)	Cl(2)-O(7)	1.43 (4)
N(4)-C(7)	1.37 (4)	Cl(2)-O(8)	1.22 (6)
N(5)-C(11)	1.48 (4)	Cl(3)-O(9)	1.42 (3)
N(5)-C(15)	1.41 (5)	Cl(3)-O(10)	1.37 (3)
N(6)-C(12)	1.78 (5)	Cl(3)-O(11)	1.44 (3)
N(6)-C(13)	1.13 (6)	Cl(3)-O(12)	1.31 (3)
	Angles		
N(1)-Cu(1)-N(2)	85.7 (13)	Cu(1)-N(3)-C(4)	113.8 (23)
N(1)-Cu(1)-N(3)	164.9 (12)	Cu(1)-N(3)-C(5)	113.2 (24)
N(1)-Cu(1)-N(4)	107.1 (13)	C(4)-N(3)-C(5)	112.8 (28)
N(1)-Cu(1)-O(1)	90.3 (12)	Cu(1)-N(4)-C(6)	110.7 (22)
N(1)-Cu(1)-O(5)	98.1 (11)	Cu(1)-N(4)-C(7)	122.8 (28)
N(2)-Cu(1)-N(3)	85.1 (13)	C(6)-N(4)-C(7)	112.9 (31)
N(2)-Cu(1)-N(4)	163.6 (13)	Cu(2)-N(5)-C(11)	115.0 (25)
N(2)-Cu(1)-O(1)	107.5 (12)	Cu(2)-N(5)-C(15)	107.3 (30)
N(2)-Cu(1)-O(5)	86.4 (12)	C(11)-N(5)-C(15)	118.0 (32)
N(3)-Cu(1)-N(4)	84.2 (12)	Cu(2)-N(6)-C(12)	106.3 (30)
N(3)-Cu(1)-O(1)	81.0 (12)	Cu(2)-N(6)-C(13)	129.7 (48)
N(3)-Cu(1)-O(5)	93.3 (11)	C(12)-N(6)-C(13)	93.5 (53)
N(4)-Cu(1)-O(1)	83.1 (13)	Cu(1)-O(1)-Cl(1)	126.6 (22)
N(4)-Cu(1)-O(5)	81.8 (12)	Cu(1)-O(5)-Cl(2)	138.6 (23)
O(1)-Cu(1)-O(5)	164.3 (11)	Cu(2)-O(9)-Cl(3)	124.9 (17)
N(5)-Cu(2)-N(5′)	85.7 (15)	N(1)-C(1)-C(2)	112.9 (35)
N(5)-Cu(2)-N(6)	84.5 (19)	N(2)-C(2)-C(1)	108.3 (35)
N(5)-Cu(2)-N(6′)	164.5 (17)	N(2)-C(3)-C(4)	107.2 (31)
N(5)-Cu(2)-O(9)	104.0 (13)	N(3)-C(4)-C(3)	105.2 (32)
N(5)-Cu(2)-O(9′)	78.9 (13)	N(3)-C(5)-C(6)	102.6 (30)
N(6)-Cu(2)-N(6′)	107.5 (22)	N(4)-C(6)-C(5)	111.4 (29)
N(6)-Cu(2)-O(9)	91.8 (18)	N(4)-C(7)-C(8)	121.4 (40)
N(6)-Cu(2)-O(9′)	85.8 (18)	C(7)-C(8)-C(9)	117.1 (37)
O(9)-Cu(2)-O(9′)	176.1 (13)	C(8)-C(9)-C(10)	123.4 (34)
Cu(1)-N(1)-C(1)	105.7 (22)	N(1)-C(10)-C(9)	114.3 (33)
Cu(1)-N(1)-C(10)	128.4 (23)	N(5)-C(11)-C(12)	108.8 (34)
C(1)-N(1)-C(10)	114.8 (28)	N(6)-C(12)-C(11)	104.3 (36)
Cu(1)-N(2)-C(2)	110.9 (23)	N(6)-C(13)-C(14)	84.0 (49)
Cu(1)-N(2)-C(3)	110.4 (23)	C(13)-C(14)-C(14′)	153.8 (59)
C(2)-N(2)-C(3)	122.0 (30)	N(5)-C(15)-C(15′)	106.0 (36)

above and below the least-squares plane, so that the five-membered rings have a gauche configuration with a similar arrangement for the seven-membered ring. The configuration of the last ring is different in molecule 2, as is shown in Figure 3.

In both molecules, however, the nitrogen atoms are of the *R,S,R,S* type. An analogous conformation has been found for the Ni(II) complex formed by the same L4 ligand, having the formula $[NiCl_2L4]H_2O$.[29] The Cu–N distances, which are in the range 1.91–2.04 Å, are in agreement with the expected values for a geometry of this type.[30] The N–Cu–N angles in the five-membered rings are close to the expected values of about 85° (range 84.2–85.7°), whereas those formed by the seven-membered ring are 107.1 and 107.5° for molecules 1 and 2, respectively. These large values allow the metal atom to lie in the plane of the macrocycle. It should be noted that in the structure of the octahedral $[Cu(cyclam)](ClO_4)_2$ complex (cyclam = 1,4,7,11-tetraazacyclotetradecane), formed by the 14-membered cyclam ligand, there are two five-membered chelated rings in gauche configuration and two six-membered ones in chair configuration.[31] The largest differences between the cyclam derivative and the present complex are due both to the N–Cu–N angles involving nonadjacent nitrogen atoms, which in the former compound have the symmetry-imposed value of 180°, against values between 163.6 and 164.9°, and to the Cu–O distances, which are significantly shorter in the cyclam complex (whereas the Cu–N distances are slightly longer) than in the present one. As far as the complexes with analogous 13-membered ligands are concerned, structural studies on a C-dimethylated derivative of L3 have shown that the Ni(II) ion can fit inside the cavity of a 13-membered tetraaza macrocycle.[32] The conformation in this case is chair for the six-membered rings, gauche for two of the five-membered rings, and cis for the five-membered ring opposite to the six-membered one.

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Registry No. I, 84194-07-0; L5·4HCl, 88996-25-2; L5, 83616-30-2; $[NiL5](ClO_4)_2$, 84194-12-7; $[CuL5](ClO_4)_2$, 88996-24-1; *N,N′,N″,N‴*-tetrakis(tolyl-*p*-sulfonyl)-1,4,7,10-tetraazadecane, disodium salt, 56187-06-5; *O,O′*-bis(tolyl-*p*-sulfonyl)pentane-1,5-diol, 24293-28-5.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, deviations from least-squares planes, hydrogen atom coordinates, and bond angles (8 pages). Ordering information is given on any current masthead page.

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