1 are trivalent rather than divalent (as in **2** and **3**), and there is about twice the transition-metal ion load for **1** than for either **2** or **3**. Also, **1** has an additional water of hydration and perturbs the host structure to a greater degree than either **2** or **3**.

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Synthesis and Complexing Properties of the Large Polyazacycloalkane 1,4,7,10,13,16,19,22,25,28-Decaazacyclotriacontane (L). Crystal Structure of the Monoprotonated Dicopper(II) Complex [Cu2(L)HCl2](ClO4)3·4H2O

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The synthesis and characterization of the large aza macrocycle 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane (L) ([30]aneN$_{10}$) are described. Crystals of the compound [Cu$_2$(L)HCl$_2$](ClO$_4$)$_3$·4H$_2$O are monoclinic, space group $P2/n$, with $a = 21.491$ (5) Å, $b = 7.696$ (4) Å, $c = 12.210$ (4) Å, $\beta = 103.04$ (5)°, and $Z = 2$. Refinement of the atomic parameters by least-squares methods gave a final R factor of 0.097 ($R_w = 0.097$) for 1298 unique reflections with $I > 3\sigma(I)$. The structure consists of binuclear [Cu$_2$(L)HCl$_2$]$^{3+}$ cations and perchlorate anions; each half of the macrocycle is symmetry related by a twofold axis passing through its center. The copper atoms (Cu–Cu distance 7.26 (1) Å) are coordinated by four nitrogen atoms of the macrocycle ligand (average Cu–N = 2.03 (2) Å) and one chloride ion (Cu–Cl = 2.43 (1) Å) in a square-pyramidal geometry. One of the two uncoordinated nitrogen atoms is protonated. The basicity constants of the macrocycle and the stability constants of the copper(II) complexes were determined by potentiometry at 25 °C in 0.15 mol dm^{-3} NaClO$_4$. The formation enthalpy of the species [Cu$_2$(L)]$^{4+}$ was determined by batch microcalorimetry. Only binuclear species are formed; the stability of the binuclear [Cu$_2$(L)]$^{4+}$ species is high (log $K = 37.77$), and its formation is largely exothermic ($\Delta H° = -45.5$ kcal mol^{-1}). The thermodynamic quantities $\Delta G°$ and $\Delta H°$ as well as the electronic spectral features of the [Cu$_2$(L)]$^{4+}$ species indicate that all nitrogen atoms are coordinated to the copper(II) atoms. The [Cu$_2$(L)]$^{4+}$ macrocycle shows a great tendency to form protonated and hydroxo species: [Cu$_2$(L)H]$^{5+}$, [Cu$_2$(L)H$_2$]$^{6+}$, [Cu$_2$(L)H$_3$]$^{7+}$, and [Cu$_2$(L)OH]$^{3+}$ are the species present at equilibrium.

Introduction

Little investigative work has been done with large aza macrocycles.[2-4] The preferred binucleating tendency (rather than mononucleating) of these ligands, together with the possible suitability for "anion coordination" studies[5] and "supercomplex" formation,[6] provides confirmation that these macrocyclic ligands display some interesting complexation chemistry. The adjective "large" has been used to describe polyazacycloalkanes having more than six nitrogen donor atoms.[3] The largest polyazacycloalkane so far investigated contained nine nitrogen donor atoms and two copper(II) ions.[7] In recent papers, studies on the three large polyazacycloalkanes 1,4,7,10,13,16,19-heptaazacycloheneicosane ([21]aneN$_7$),[4] 1,4,7,10,13,16,19,22-octaazacyclotetracosane ([24]aneN$_8$),[3] and 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane ([27]aneN$_9$)[7] have been reported. We have now syn-

thesized and characterized the large polyazacycloalkane 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane ([30]aneN$_{10}$) (abbreviated as (L)) and studied its ligational behavior toward hydrogen (basicity) and copper(II) ions.


L
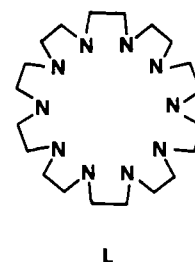
Experimental Section

Ligand Synthesis. The overall synthetic path followed to obtain the macrocyclic ligand is reported in Figure 1. All chemicals were reagent grade and were utilized without further purification.

1,4,7,10,13-Pentakis(p-tolylsulfonyl)-1,4,7,10,13-pentaazatridecane (b). The starting material was obtained from the commercial 1,4,7,10,13-pentaazatridecane (a) (Fluka product) by double distillation under reduced pressure. The fraction collected was that between 265 and 270 °C at 0.1 Torr. A solution of **a** (19.9 g, 0.105 mol) in 100 cm³ of pyridine was added to a solution of p-toluenesulfonyl chloride (100 g, 0.53 mol) in 300 cm³ of pyridine placed in a 1 dm³ four-necked round-bottom flask equipped with a mechanical stirrer. The addition of the pentaamine (**a**) solution was carried out in such a way that the reaction temperature was kept at 40–50 °C. After the addition, the reaction mixture was maintained at 50 °C for 2 h and then was allowed to cool at room temperature and added to a vigorously stirred mixture of water and ice (2.5 dm³) containing the amount of concentrated HCl necessary to

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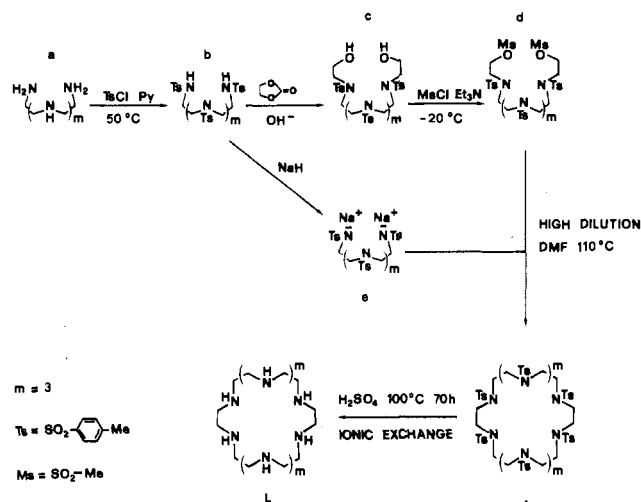
Figure 1. Reaction sequence for the synthesis of the large macrocycle [30]aneN$_{10}$ (L).

neutralize the pyridine. The product obtained was filtered off, washed with water and ethanol, and dissolved in 300 cm^3 of chloroform. The resulting solution was washed three times with 1 mol dm^{-3} HCl and three times with water and then dried over Na$_2$SO$_4$. To the filtered warm solution was added 1 dm^3 of hot ethanol. On cooling, a white product separated. The product was filtered off, washed with ethanol and diethyl ether, recrystallized from a chloroform/ethanol mixture (1:4), and then dried under vacuum at 50 °C: yield 40.7 g (40.5%); mp 173–175 °C; TLC,[8] one product with R_f 0.31. Anal. Calcd for C$_{43}$H$_{53}$N$_5$S$_5$O$_{10}$: C, 53.76; H, 5.77; N, 7.30; S, 16.70. Found: C, 53.6; H, 5.6; N, 7.2; S, 16.5.

3,6,9,12,15-Pentakis(p-tolylsulfonyl)-3,6,9,12,15-pentaazaheptade-cane-1,17-diol (c). A finely powdered mixture of **b** (50 g, 0.052 mol), ethylene carbonate (10.6 g, 0.12 mol), and KOH (0.5 g) was placed in a 1-dm^3 three-necked round-bottom flask equipped with a mechanical stirrer, condenser, and thermometer. The stirred mixture was heated on an oil bath until it melted and then kept at 170 °C for 4 h. The mixture was allowed to cool at 110 °C, and then 500 cm^3 of methanol was rapidly added. The solution was refluxed for 1 h and then cooled at room temperature with stirring overnight. The white crude product obtained was filtered, washed with methanol, and recrystallized from an etha-nol/methylene chloride mixture (4:1): yield 52.85 g (82.4%); mp 194–196 °C; TLC, one product with R_f 0.21. Anal. Calcd for C$_{47}$H$_{61}$N$_5$S$_5$O$_{12}$: C, 53.85; H, 5.86; N, 6.68. Found: C, 53.7; H, 5.8; N, 6.6.

O,O'-Bis(methylsulfonyl)-3,6,9,12,15-pentakis(p-tolylsulfonyl)-3,6,9,12,15-pentaazaheptadecane-1,17-diol (d). A solution of **c** (42 g, 0.04 mol) and 12.2 g of triethylamine in 500 cm^3 of anhydrous methylene chloride was cooled to −20 °C under nitrogen in a 1-dm^3 four-necked round-bottom flask equipped with a mechanical stirrer. To this solution was added dropwise over a period of 20 min, with stirring, a solution of 10.1 g (0.088 mol) of methanesulfonyl chloride in 50 cm^3 of dry methylene chloride. The reaction mixture was kept at −20 °C for 30 min; then, after being allowed to warm to room temperature, it was added to a vigorously stirred mixture of water and ice containing 50 cm^3 of concentrated HCl. The organic phase was separated, washed three times with water, and dried over anhydrous Na$_2$SO$_4$. The dry solution was reduced to 100 cm^3, and 500 cm^3 of hot methanol was added. By slow cooling, a white powder separated. The crude product was filtered off, washed with methanol, and recrystallized from a hot methylene chlo-ride/methanol mixture: yield 41 g of **d** (85%); mp 191–194 °C; TLC, one product with R_f 0.33. IR spectra demonstrated that mesylation had occurred, since no bands in the O–H region (3300–3500 cm^{-1}) were observed. Anal. Calcd for C$_{49}$H$_{65}$H$_5$S$_7$O$_{16}$: C, 48.86; H, 5.44; N, 5.81; S, 18.63. Found: C, 48.9; H, 5.4; N, 5.7; S, 18.6.

1,4,7,10,13,16,19,22,25,28-Decakis(p-tolylsulfonyl)-1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane (f). A solution of **b** (19.2 g, 0.02 mol) in 1 dm^3 of anhydrous DMF was treated with sodium hydride (10 g) in small portions under nitrogen. When the hydrogen evolution had ceased, the solution of **e** (see Figure 1) was filtered into one of the two additional funnels of a 3-dm^3 four-necked flask, equipped

also with a mechanical stirrer and condenser. In the second funnel was placed a solution of **d** (24.1 g, 0.02 mol) in 1 dm^3 of anhydrous DMF. The two solutions were added simultaneously at a constant rate to 0.5 dm^3 of anhydrous DMF vigorously stirred and heated at 110 °C in a 3-dm^3 round-bottom flask. The addition was carried out over 4 h and then the temperature maintained at 110 °C for a further 1 h. The resulting solution was reduced to 200 cm^3 and then added to a stirred mixture of water and ice (3 dm^3). The crude product obtained was filtered off, washed with water and ethanol, and dried under vacuum. The residue was chromatographed over a silica gel column (300 g, 8 cm in diameter) with chloroform. To the concentrated (150 cm^3) eluted solution was added 1 dm^3 of hot methanol, and the white product that separated on cooling was placed in the extraction thimble of a Soxhlet apparatus and washed with methanol for 24 h. The residue was re-crystallized from a toluene/benzene mixture (1:1) and dried at 50 °C under vacuum: yield 4.7 g of **f** (12%); mp 264–267 °C; TLC, one product with R_f 0.68. IR spectra demonstrated that cyclization had occurred, since no bands in the N–H region (3300–3500 cm^{-1}) were observed. Anal. Calcd for C$_{90}$H$_{110}$N$_{10}$S$_{10}$O$_{20}$: C, 54.80; H, 5.62; N, 7.10. Found: C, 54.7; H, 5.6; N, 7.0.

1,4,7,10,13,16,19,22,25,28-Decaazacyclotriacontane (L). The removal of tosyl groups from **f** was performed by the procedure as previously described for other similar compounds.[2] A 2.5-g sample of **f** (1.27 mmol) yielded 0.86 g (85%) of (L)·10HCl·2H$_2$O. Anal. Calcd for C$_{20}$H$_{64}$N$_{10}$Cl$_{10}$O$_2$: C, 28.90; H, 7.76; N, 16.85. Found: C, 29.1; H, 7.8; N, 16.8. The ^{13}C NMR spectrum of (L)·10HCl (water with 15% D$_2$O, 20 MHz) consists of only one signal at δ 44.6 (–CH$_2$–).

Synthesis of Copper(II) Complex. Well-formed blue prismatic crystals of the complex [Cu$_2$(L)HCl$_2$](ClO$_4$)$_3$·4H$_2$O were obtained by mixing 0.1 mmol of (L)·10HCl·2H$_2$O dissolved in 5 cm^3 of 0.2 mol dm^{-3} NaOH and a solution of Cu(ClO$_4$)$_2$·6H$_2$O (0.2 mmol in 2 cm^3 of water). With slow evaporation at room temperature of the resulting solution, crystals of the complex grew. The product was filtered, washed with aqueous ethanol (50%), and dried under vacuum at room temperature. (*Caution!* Per-chlorate salts of metal complexes can be explosive and must be handled with care. Compounds should not be heated as solids.) Anal. Calcd for C$_{20}$H$_{59}$N$_{10}$Cu$_2$Cl$_5$O$_{16}$: C, 24.02; H, 5.95; N, 14.01. Found: C, 23.9; H, 6.0; N, 13.9.

Materials. All potentiometric measurements were carried out in 0.15 mol dm^{-3} NaClO$_4$ (C. Erba ACS grade) and purified according to the procedure already described.[9] Standardized CO$_2$-free solutions of NaOH, used in the potentiometric titrations, were prepared by following the procedure described in ref 10.

Emf Measurements. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, cell, microcomputer, etc.) that has been fully described.[11] The computer program SUPER-QUAD[12] was used to process data and calculate both basicity and stability constants.

Calorimetric Measurements. All calorimetric measurements were performed with an LKB BATCH Model 10700-2 microcalorimeter. The direct reaction between copper(II) and the macrocycle (L) is fast; the heat of reaction was measured by mixing an aqueous solution of cop-per(II) with a solution containing the neutralized appropriate hydro-chloric macrocyclic salt. Under the reaction conditions and from the determined stability constants, the species present and their percentages at equilibrium before and after mixing were calculated by means of the DISPOL[13] computer program. The only significant species present at equilibrium before and after mixing were the free nonprotonated ligand and the complex [Cu$_2$(L)]$^{4+}$. Blank experiments were carried out to correct for the enthalpy of dilution of the NaOH solution.

Spectroscopy. Proton-decoupled ^{13}C NMR spectra were recorded with a Varian FT-80A spectrometer operating at 20.0 MHz and with water with 15% (w/w) D$_2$O as solvent; chemical shifts are reported in ppm from SiMe$_4$ with dioxane as the secondary reference standard [δ(dioxane) = δ(SiMe$_4$) + 67.4].

The electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer.

Collection and Reduction of X-ray Intensity Data. A blue elongated prism with approximate dimensions 0.4 × 0.2 × 0.1 mm was mounted on a Philips PW 1100 computer-controlled diffractometer and used for data collection. A summary of the crystallographic data is reported in

(8) TLC measurements were carried out on precoated TLC plates, silica gel 60 F-254 (Merk), with a chloroform/acetone (50:1) mixture as eluent. Only in the case of product **d** (see Figure 1) was the mixture (10:1) in the same components.

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Table I. Basicity and Formation Constants for the System Copper(II)/[30]aneN$_{10}$ in Aqueous Solution (25 °C in 0.15 mol dm^{-3} NaClO$_4$)

	log K	
reaction	L = [30]aneN$_{10}$	L = [27]aneN$_9$
H^a + L = HL	9.85 (3)^b	9.59^c
H + HL = H$_2$L	9.44 (3)	9.40
H + H$_2$L = H$_3$L	8.95 (3)	8.77
H + H$_3$L = H$_4$L	8.56 (3)	8.27
H + H$_4$L = H$_5$L	7.79 (3)	6.37
H + H$_5$L = H$_6$L	5.24 (3)	4.22
H + H$_6$L = H$_7$L	3.84 (3)	3.24
H + H$_7$L = H$_8$L	3.02 (2)	2.31
H + H$_8$L = H$_9$L	1.97 (1)	1.8
H + H$_9$L = H$_{10}$L	1.8 (1)	

reaction	log K
2Cu + (L) = Cu$_2$(L)	37.77 (4)^b
2Cu + (L) + H = Cu$_2$(L)H	43.36 (3)
2Cu + (L) + 2H = Cu$_2$(L)H$_2$	47.21 (3)
2Cu + (L) + 3H = Cu$_2$(L)H$_3$	50.52 (3)
Cu$_2$(L) + H = Cu$_2$(L)H	5.59
Cu$_2$(L)H + H = Cu$_2$(L)H$_2$	3.85
Cu$_2$(L)H$_2$ + H = Cu$_2$(L)H$_3$	3.31
2Cu + (L) + H$_2$O = Cu$_2$(L)OH + H	26.43 (5)
Cu$_2$(L) + OH = Cu$_2$(L)OH	2.39

^{a}Charges omitted for clarity. ^{b}Values in parentheses are standard deviations in the last significant figure. ^{c}Taken from ref 7.

Table III. Unit-cell dimensions were determined from the angular settings of 25 carefully centered reflections. Intensities were corrected for Lorentz, polarization, and absorption effects[14] (transmission factors ranged between 0.78 and 0.89). The intensities of three standard reflections were monitored periodically for stability control during data collection.

Solution and Refinement of the Structure. The systematic absences in the diffraction data were consistent with space group *Pn* or *P2/n*. *P2/n* was assumed on the basis of the centric distribution of *E* values and later confirmed by the successful refinement of the structure. The structure was solved by the heavy-atom technique, with the use of Patterson and electron-density syntheses. Refinement was performed by means of the full-matrix least-squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = a/(\sigma^2(F) + bF^2)$, where a and b are adjustable parameters. Anisotropic thermal parameters were refined for the copper atom, the atoms in its coordination sphere, and the chlorine atoms of perchlorates. Hydrogen atoms were included in calculated positions, and their parameters were not refined. The refinement of the perchlorate anions was troublesome because of high thermal motion and rotational disorder; rigid-group refinement was unsuccessful, so the atoms were allowed to move without constraints. One of the oxygen atoms (O(2)) of the perchlorate sitting on the twofold axis refined in an unreasonable position. All calculations were performed on an IBM 4361/3 computer with the SHELX-76 set of programs[14] that use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 15. Table IV reports the list of the final atomic coordinates for non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix. The molecular plots were produced by the program ORTEP.[16]

Results and Discussion

Protonation. The observed basicity constants for macrocycle L are reported in Table I. For the purpose of comparison the basicity constants of the similar large macrocycle [27]aneN$_9$ (L1) have been reported.[7] The results show that macrocycle L behaves as a relatively strong base in the first five protonation steps and as a weaker base in the last protonation steps. This grouping of the basicity constants is typical of aza macrocycles, and it has been explained in terms of charge-repulsion effects. In the case of large aza macrocycles, the positive charges that accumulate in the macrocyclic framework as the degree of protonation in-
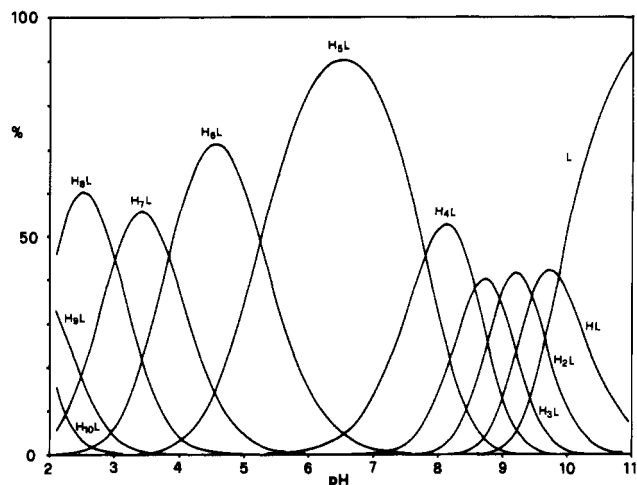

Figure 2. Distribution diagram for the system H/L (charges omitted).

creases experience smaller repulsions than those that accumulate on smaller macrocycles, thus making the difference between the two groups of basicity constants much larger for smaller macrocycles.[17] It should be noted that the larger macrocycle (L) is slightly more basic than L1 in each protonation step. At least in the first protonation step the greater basicity of L compared with that of L1 can be explained in terms of a statistical effect that is favorable to the larger macrocycle (L). Indeed, in macrocycle L there are ten equivalent sites where the first proton can be bound and one site from which the bound proton can be removed. In the case of the smaller macrocycle (L1), there are only nine equivalent positions where the first proton can be bound and one position from which it can be removed. In this situation the statistical factor that favors L should be $R \ln 10 - R \ln 9 \approx 0.2$, in agreement with what is experimentally found (see Table I). Of course statistical considerations can be applied also for the further protonation steps; however, as the macrocycle protonation degree increases, other factors like electrostatic repulsion, ligand stiffening, and hydrogen-bonding formation become important and overcome the statistical contribution. The distribution diagram for the system H$^+$/L (see Figure 2) shows that in the neutral pH region many highly charged (protonated) species are present, thus making this large macrocycle suitable for anion coordination studies.

Copper(II) Complexes. In Table I are reported the stability constants for the copper(II) complexes of L. For the complex [Cu$_2$(L)]$^{4+}$ the thermodynamic parameters $\Delta H°$ and $T\Delta S°$ are also reported in Table II. Macrocycle L forms only binuclear species with copper(II). Considering the series of large polyazacycloalkanes so far investigated, a trend appears for the formation reaction enthalpies of the binuclear species, which are more exothermic as the overall size of the macrocycle increases (see Table II). The formation reaction of the species [Cu$_2$(L)]$^{4+}$ is the most exothermic ($\Delta H° = -45.5$ kcal mol^{-1}) among the formation reactions of binuclear copper(II) complexes of large macrocycles so far investigated. The increase of the overall number of donor atoms involved in the coordination to the metal ions and the decrease of the electrostatic repulsions between the metal ions coordinated are the two most important factors that can be invoked to explain this trend. The aqueous solution of the complex [Cu$_2$(L)]$^{4+}$ shows a wide absorption band at 16 200 cm^{-1} ($\epsilon = 224$ dm^3 mol^{-1} cm^{-1}) and a shoulder in the 11 000-cm^{-1} region possibly indicating pentacoordination of the two copper(II) ions.[18] The poor tendency of the binuclear complex [Cu$_2$(L)]$^{4+}$ to protonate itself is shown by the equilibrium constant corresponding

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Table II. Stability Constants and Thermodynamic Parameters for the Binuclear Species $[Cu_2L]^{4+}$ with the Large Macrocycles [24]aneN$_8$ (bistrien), [27]aneN$_9$ (L1), and [30]aneN$_{10}$ (L)

macrocycle	log ($K[Cu_2L]$)	$-\Delta G°$ [a]	$-\Delta H°$	$T\Delta S°$
[24]aneN$_8$	36.63[b]	49.96[b]	39.0[b]	11.0[b]
[27]aneN$_9$	36.03[c]	49.14[c]	42.8[c]	6.3[c]
[30]aneN$_{10}$	37.77[d]	51.52[d]	45.5[d]	6.0[d]

[a] $\Delta G°$, $\Delta H°$, and $T\Delta S°$ in kcal mol^{-1}. [b] Taken from ref 3, $I = 0.5$ mol dm^{-3} (NaClO$_4$). [c] Taken from ref 7; $I = 0.15$ mol dm^{-3} (NaClO$_4$). [d] This work.

Table III. Crystal and Refinement Data

mol formula	Cu$_2$C$_{20}$H$_{59}$N$_{10}$O$_{16}$Cl$_5$
mol wt	1000.06
a, Å	21.491 (5)
b, Å	7.696 (4)
c, Å	12.210 (4)
β, deg	103.04 (5)
V, Å^3	1967.4
Z	2
space gp	$P2/n$[a]
d_{calcd}, g cm^{-3}	1.69
radiation	graphite monochromated; Mo Kα (λ = 0.7107 Å)
temp, °C	25
μ, cm^{-1}	12.2
scan tech	$\theta/2\theta$
scan speed, deg min^{-1}	3.6
scan width, deg	1.0 + 0.3 tan θ
scan range, deg	4.0 < 2θ < 48.0
total no. of ind reflcns	3483
cutoff of obsd data	3$\sigma(I)$
no. of obsd reflcns	1298
no. of refined params	149
R[b]	0.097
R_w[c]	0.097

[a] Based on a centric distribution of E values and later confirmed by the structural determination. [b] $R = \sum ||F_o| - |F_c||/\sum |F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

to the addition of one proton to the complex (see Table I). This constant is much smaller than the one related to the protonation of the first nitrogen in the free macrocycle and even smaller than that of the equally charged H$_4$(L)$^{4+}$ species (see Table I). A more detailed analysis of the measured values of formation enthalpies (−42.8 kcal mol^{-1} for $[Cu_2(L1)]^{4+}$ and −45.5 kcal mol^{-1} for $[Cu_2(L)]^{4+}$; see Table II) allows some considerations. The greater stability of the larger macrocycle complex $[Cu_2(L)]^{4+}$, compared with that of $[Cu_2(L1)]^{4+}$ (2.4 kcal mol^{-1}), is entirely due to a favorable enthalpy contribution (2.7 kcal mol^{-1}; see Table II), thus indicating that the overall metal to ligand donor atom interaction is stronger for macrocycle L, which has one more donor atom than L1. A similar increase in "exothermicity" (3.8 kcal mol^{-1}) was observed going from $[Cu_2(bistrien)]^{4+}$ to $[Cu_2(L1)]^{4+}$ (see Table II). We therefore conclude that, for the largest macrocycle (L) that we have investigated up to now, the ligand flexibility allows all nitrogen donor atoms present in the ligand to be involved in the formation of the binuclear species $[Cu_2(L)]^{4+}$.

Macrocycle L shows some tendency to form polyprotonated dicopper(II) species (see Table I). It is interesting to note that the stepwise protonation constants of the binuclear monoprotonated species $[Cu_2(L)H]^{5+}$ to form more protonated species $[Cu_2(L)H_2]^{6+}$ and $[Cu_2(L)H_3]^{7+}$ are similar: 3.85 and 3.31 log units, respectively. Such a behavior can be explained by assuming that the protonation sites in the complexes are far away and do not influence each other. As already found for other polyazacycloalkane macrocycles, L forms very stable binuclear hydroxo species $[Cu_2(L)OH]^{3+}$, as shown by the equilibrium constant for the addition of the hydroxide ion to the binuclear complex: log $K = 2.39$ (see Table I). In order to better understand the formation of protonated metal complexes, we have been able to grow good crystals for X-ray analysis of the monoprotonated binuclear species $[Cu_2(L)HCl_2](ClO_4)_3 \cdot 4H_2O$.

Table IV. Positional Parameters and Their Estimated Standard Deviations in Parentheses ($\times 10^4$)

atom	x/a	y/b	z/c
Cu	3832 (1)	−860 (3)	6124 (2)
Cl(1)	4400 (4)	1266 (10)	5254 (10)
N(1)	1861 (7)	1979 (20)	6086 (13)
C(2)	2112 (9)	2327 (26)	5099 (16)
C(3)	2792 (8)	1881 (24)	5308 (18)
N(4)	2928 (7)	−17 (19)	5471 (13)
C(5)	2711 (10)	−924 (30)	4336 (18)
C(6)	3008 (10)	−2678 (30)	4416 (21)
N(7)	3682 (8)	−2489 (20)	4782 (14)
C(8)	4086 (14)	−3997 (40)	5156 (25)
C(9)	4501 (13)	−4000 (39)	6106 (23)
N(10)	4578 (8)	−2419 (23)	6754 (14)
C(11)	4493 (16)	−2718 (43)	7863 (28)
C(12)	4371 (11)	−1287 (31)	8479 (19)
N(13)	3890 (7)	−111 (19)	7765 (13)
C(14)	4059 (10)	1702 (30)	8051 (19)
C(15)	1164 (10)	2219 (30)	5871 (17)
O(W1)	3142 (9)	3249 (25)	2720 (16)
O(W2)	4092 (12)	1111 (38)	3160 (22)
Cl(2)	2500 (0)	6410 (9)	7500 (0)
O(1)	2929 (7)	5454 (22)	7077 (13)
O(2)[a]	2357 (14)	8056 (38)	7091 (23)
O(2)[a]	2038 (15)	6870 (44)	6360 (29)
Cl(3)	963 (3)	7026 (10)	3336 (9)
O(3)	570 (13)	6106 (38)	3720 (22)
O(4)	943 (11)	8643 (37)	3718 (21)
O(5)	606 (14)	7472 (40)	2128 (28)
O(6)	1494 (12)	6580 (33)	2995 (21)

[a] Atoms with occupancy factor of 0.5.

Table V. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

Distances

Cu–Cl(1)	2.43 (1)	Cu–N(4)	2.03 (1)
Cu–N(7)	2.03 (2)	Cu–N(10)	2.01 (2)
Cu–N(13)	2.06 (1)	N(1)–C(2)	1.45 (2)
N(1)–C(15)	1.47 (2)	C(2)–C(3)	1.47 (2)
C(3)–N(4)	1.49 (2)	N(4)–C(5)	1.53 (2)
C(5)–C(6)	1.49 (3)	C(6)–N(7)	1.42 (2)
N(7)–C(8)	1.46 (3)	C(8)–C(9)	1.29 (3)
C(9)–N(10)	1.44 (3)	N(10)–C(11)	1.42 (3)
C(11)–C(12)	1.39 (3)	C(12)–N(13)	1.50 (2)
N(13)–C(14)	1.46 (2)	C(14)–C(15)	1.55 (2)

Angles

Cl(1)–Cu–N(4)	98.3 (5)	Cl(1)–Cu–N(7)	93.8 (6)
Cl(1)–Cu–N(10)	97.6 (6)	Cl(1)–Cu–N(13)	108.1 (5)
N(4)–Cu–N(7)	85.3 (6)	N(7)–Cu–N(10)	84.7 (6)
N(4)–Cu–N(13)	97.8 (6)	N(10)–Cu–N(13)	85.8 (6)
C(2)–N(1)–C(15)	112.5 (15)	N(1)–C(2)–C(3)	110.8 (16)
C(2)–C(3)–N(4)	114.2 (16)	Cu–N(4)–C(3)	120.4 (11)
Cu–N(4)–C(5)	106.2 (11)	C(3)–N(4)–C(5)	108.4 (16)
N(4)–C(5)–C(6)	108.4 (18)	C(5)–C(6)–C(7)	108.6 (18)
Cu–N(7)–C(6)	106.3 (13)	Cu–N(7)–C(8)	105.3 (15)
C(6)–N(7)–C(8)	120.6 (19)	N(7)–C(8)–C(9)	121.5 (29)
C(8)–C(9)–N(10)	117.5 (28)	Cu–N(10)–C(9)	108.1 (15)
Cu–N(10)–C(11)	101.4 (16)	C(9)–N(10)–C(11)	111.2 (23)
N(10)–C(11)–C(12)	117.8 (27)	C(11)–C(12)–N(13)	110.7 (22)
Cu–N(13)–C(12)	106.3 (11)	Cu–N(13)–C(14)	117.1 (14)
C(12)–N(13)–C(14)	109.7 (16)	N(13)–C(14)–C(15)	109.9 (15)
N(1)–C(15)–C(14)	108.2 (14)		

Description of the Structure of $[Cu_2(L)HCl_2](ClO_4)_3 \cdot 4H_2O$. The structure of the compound consists of $[Cu_2(L)HCl_2]^{3+}$ cations and disordered perchlorate anions. Four water molecules bridge the complex molecules in the crystal lattice by a hydrogen-bond chain of the type Cl···O(W2)···O(W1)···O(W1)[19]···O(W2)[19]···Cl[19]. The two halves of the macrocyclic cation are symmetry related by a twofold axis passing through its center.

In the binuclear unit each copper atom is coordinated by four nitrogen atoms of the macrocyclic ligand and one chloride ion
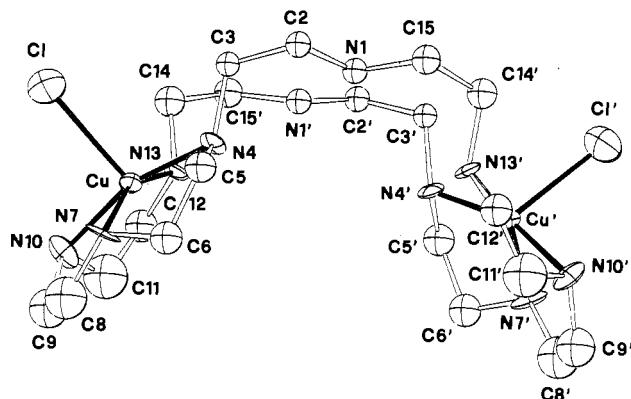
(19) Symmetry related by $^1/_2 - x$; y; $^1/_2 - z$.

Figure 3. ORTEP drawing of [Cu₂(L)HCl₂]³⁺ cation. Thermal ellipsoids are shown at 30% probability.

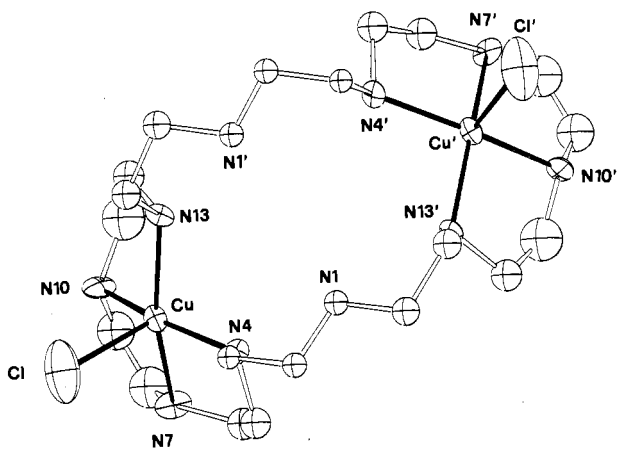**Figure 4.** Top view of [Cu₂(L)HCl₂]³⁺ cation. Thermal ellipsoids are shown at 30% probability.

forming a slightly distorted square pyramid (Figure 3). The site of protonation must be on the N(1) or N(1′) atom of the macrocycle, but owing to the presence of the twofold axis, the two nitrogen atoms are crystallographically equivalent and therefore the proton is statistically distributed between them. The distance of 3.90 (3) Å between N(1) and N(1′) (Figure 4) rules out any possibility of bridging for the hydrogen atom. The nitrogen atoms

lie in the basal plane with a maximum deviation of 0.05 Å from the least-squares plane through them. The copper atom is 0.34 Å out of the plane. Bond lengths and angles of the binuclear complex are reported in Table V. The mean Cu–N distance of 2.03 (2) Å is identical (within experimental error) with the analogous distance in the [Cu₂(bistrien)Cl₂](ClO₄)₂ complex³ whereas the Cu–Cl distance (2.43 (1) Å) is shorter than the Cu–Cl bond length found in the same complex (2.48 (1) Å), in which the copper atom interacts with a further chloride ion at 3.31 Å. The intramolecular Cu–Cu distance is 7.26 (1) Å compared to 6.138 (1) Å found in [Cu₂(bistrien)Cl₂](ClO₄)₂. The macrocycle has a saddle-shaped configuration; the two least-squares planes through the coordinating nitrogens form an angle of 83.8° (see supplementary material). As in the [Cu₂(bistrien)Cl₂](ClO₄)₂ compound, all the five-membered chelate rings are in the gauche configuration.

It should be noticed that crystal structures of protonated macrocyclic complexes are rare because protonated species are present as a small fraction and in a narrow pH range in the solution equilibria. In spite of the above considerations, a protonated complex species [Cu₂(L)H]Cl₂(ClO₄)₃·4H₂O crystallized in which one of the uncoordinated atoms is protonated. The occurrence of such monoprotonated species in the solid state can be attributed to various stabilizing effects such as chloride coordination and a hydrogen-bonding network. In solution the binuclear complex [Cu₂(L)]⁴⁺ seems to behave differently because as previously mentioned, the thermodynamic data suggest that a Cu–N bond is broken each time a proton is added to form [Cu₂(L)H]⁵⁺, [Cu₂(L)H₂]⁶⁺, and [Cu₂(L)H₃]⁷⁺ species.

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Protonation of Six-Coordinate Hydrido Complexes of Osmium(II). Examples of Seven-Coordination in Osmium Polypyridyl Chemistry

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The hydrido–osmium(II) complexes *trans*-[Os(chelate)(PPh₃)₂(CO)H](PF₆) (chelate = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 5,5′-dimethyl-2,2′-bipyridine) undergo protonation with trifluoromethanesulfonic acid (TFMSH) in CH₂Cl₂ or trifluoroacetic acid (TFAH) media to form the dihydrido complexes [Os(chelate)(PPh₃)₂(CO)H₂]²⁺. Through the interpretation of a series of NMR spectral experiments involving ¹H, ²H, and ³¹P nuclei, arguments are developed that implicate a pentagonal-bipyramidal solution structure for [Os(bpy)(PPh₃)₂(CO)H₂]²⁺ in 10% TFMSH–90% TFAH (by volume) solution. The proposed structure, which has PPh₃ ligands above and below the pentagonal plane but adjacent hydrido ligands, is consistent with a protonation mechanism involving the least molecular reorganization on going from octahedral *trans*-[Os(bpy)(PPh₃)₂(CO)H]⁺ to pentagonal-bipyramidal [Os(bpy)(PPh₃)₂(CO)H₂]²⁺.

Trifluoromethanesulfonate (TFMS; CF₃SO₃⁻) complexes of the transition metals are often of preparative value as intermediates

in net substitution reactions. The use of the TFMS ligand as a leaving group has been the theme of a series of kinetic¹ and