Synthesis of 1,10,19,28-Tetraoxa-4,7,13,16,22,25,31,34-octaazacyclohexatriacontane (L) and its Complex $[Cu_4L(OH)_4][ClO_4]_4 \cdot 2H_2O$

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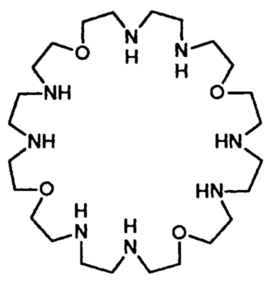
A 36-membered macrocycle with four ethylenediamine entities, 1,10,19,28-tetraoxa-4,7,13,16,22,25,31,34-octaazacyclohexatriacontane (L), has been synthesized and characterized by ^1H and ^{13}C NMR and fast atom bombardment (FAB) mass spectra. Its complexing behaviour toward copper(II) ion was investigated spectroscopically and the macrocycle shown to incorporate four copper(II) ions in the range pH 6–9. A tetranuclear complex $[Cu_4L(OH)_4][ClO_4]_4 \cdot 2H_2O$ was obtained and characterized to be of a cubane-type $Cu_4(OH)_4$ core surrounded by the macrocycle, according to IR, visible, FAB and ESR spectra, cyclic voltammetry, and cryomagnetic susceptibility.

The chemistry of polyazamacrocycles has been the subject of many recent studies because of interest in the organization of polynuclear metal structures as models of non-haem polymetallic proteins, molecular recognition, and 'supercomplex' formation.[1–3] Complexation of saturated polyazamacrocycles with seven to twelve nitrogen donor atoms separated by ethylene bridges was studied by Bencini *et al.*[4–6] and the macrocycles with eight or more nitrogen atoms were shown to afford dinuclear metal(II) (M = Cu, Ni or Zn) complexes.[7] Dinucleating complexations of macrocycles with two N_3 co-ordination sites separated by $[CH_2]_2O[CH_2]_2$ bridges were reported by Martell and co-workers[8,9] and Lippard and co-workers.[10–12] Martell and co-workers[13,14] also reported that macrobicycles with two N_4 sites separated by similar bridges form dinuclear copper and cobalt complexes. Larger macrocycles, 1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane and 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane,[15] are suggested to form trinuclear copper(II) complexes in solution. The first well characterized trinuclear copper(II) complex was reported by Lehn and co-workers[16] using a macrocycle containing three ethylenediamine (en) entities as donor sites separated by $[CH_2]_2O[CH_2]_2$ bridges. Single-crystal X-ray analysis revealed that the macrocycle surrounds a trinuclear core doubly bridged by hydroxide ions, $Cu_3(OH)_2$, each copper forming a chelate with each en site. However, to the best of our knowledge tetratopic polyazamacrocycles have not been reported so far, though some macrocycles possessing phenolic or alcoholic groups as intrinsic bridges[17,18] have been shown to co-ordinate to tetranuclear or more large cores.

The aim of this study was to synthesize a tetratopic polyazamacrocycle containing four symmetrically located en entities. Thus 1,10,19,28-tetraoxa-4,7,13,16,22,25,31,34-octaazacyclohexatriacontane (L) has been obtained in which the four en entities are separated by $[CH_2]_2O[CH_2]_2$ bridges. The synthesis and characterization of the macrocycle and its complexation to afford a tetracopper(II) complex $[Cu_4L(OH)_4][ClO_4]_4 \cdot 2H_2O$ are reported.

Experimental

Physical Measurements.—Elemental analyses of C, H and N were obtained at the Service Centre of Elemental Analysis of Kyushu University. Copper was analysed on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Proton and ^{13}C NMR spectra were recorded on a JNM GX-400 spectrometer, using tetramethylsilane (in $CDCl_3$) and sodium 3-(trimethylsilyl)propane-1-sulfonate (in D_2O) as the internal standard. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-DX300 spectrometer, infrared (IR) spectra on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls and electronic spectra on a Shimadzu UV-210 spectrometer at room temperature. Magnetic susceptibilities were measured in the range 80–300 K on a Faraday balance designed in our laboratory. Data were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants. Cyclic voltammograms were recorded on an apparatus comprised of a Hokuto Denki HA-501 potentiostat and a HB-104 function generator. Measurements were carried out in aqueous solutions (*ca.* 1 × 10^{-3} mol dm^{-3}) using sodium perchlorate as the supporting electrolyte. A three-electrode cell was used with a glassy-carbon working electrode, a platinum-coil auxiliary electrode, and a saturated calomel reference electrode (SCE). Controlled-potential electrolyses were made on the same instrument using a platinum net as the working electrode.



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Preparations.—1,14-*Dichloro*-6,9-*di*(*toluene*-p-*sulfonyl*)-3,12-*dioxa*-6,9-*diazatetradecane* **1**. To a stirred mixture of di(2-chloroethyl) ether (251.7 g, 1.76 mol) and powdered K_2CO_3 (121.6 g, 0.88 mol) in dry dimethylformamide (dmf, 135 cm^3) was added a dmf solution (200 cm^3) of ethylenediamine ditoluene-*p*-sulfonate[18] (65 g, 0.176 mol) at 80 °C in the course of 6 h. The solvent was evaporated to dryness under reduced pressure and the residue dissolved in dichloromethane (250 cm^3). The solution was washed with three portions (200 cm^3) of water and concentrated to give a crude product. It was dissolved in benzene (250 cm^3) and the solution diffused with hexane (15 cm^3), resulting in the precipitation of compound **1** as colourless microcrystals. Yield 74% (Found: C, 49.40; H, 5.90; N, 4.80. Calc. for $C_{24}H_{34}Cl_2N_2O_6S_2{\cdot}CH_2Cl_2$: C, 49.85; H, 6.00; N, 4.65%).

1,14-*Di(phthalimido)*-6,9-*di(toluene*-p-*sulfonyl)*-3,12-*dioxa*-6,9-*diazatetradecane* **2**. A dmf solution (160 cm^3) of potassium phthalimide (30 g, 0.162 mol) was stirred at 100 °C in the dark, and to this was added dropwise a dmf solution (130 cm^3) of compound **1** (31 g, 0.0533 mol) in the course of 3.5 h. After the addition was completed the stirring at 100 °C was continued for 4 h and the solution allowed to stand at ambient temperature overnight. The reaction mixture was poured onto ice–water, and the resulting colourless mass was separated and thoroughly washed with water. The product was dissolved in dichloromethane (200 cm^3) and the solution shaken three times with water (200 cm^3). The dichloromethane layer was dried with Na_2SO_4 and concentrated to dryness. To the resulting mass was added benzene (70 cm^3) and the solvent evaporated to dryness to give compound **2** as a colourless powder. Yield: 89.5%. It was used for the following reaction without further purification.

1,14-*Diamino*-6,9-*di(toluene*-p-*sulfonyl)*-3,12-*dioxa*-6,9-*diazatetradecane* **3**. Compound **2** (38.3 g, 0.0477 mol) was suspended in dry ethanol (230 cm^3) in a flask and the vessel purged thoroughly with argon. Dry hydrazine (5.3 cm^3, 0.165 mol) was added and the mixture was refluxed for 12 h. The reaction mixture was acidified to pH 1 with 6 mol dm^{-3} hydrochloric acid, refluxed for 1.5 h, and allowed to stand at room temperature to give a colourless solid. It was separated by filtration and washed with ethanol. The filtrate and the washings were combined, concentrated to dryness, made alkaline by adding an aqueous solution (370 cm^3) of sodium hydroxide (69.6 g), and extracted with three portions (150 cm^3) of chloroform. The extract was dried with Na_2SO_4 and evaporated to dryness to give compound **3** as a colourless crystalline powder. Yield: 81%. It was used for the following reaction without further purification.

6,9-*Di(toluene*-p-*sulfonyl)*-1,14-*di(toluene*-p-*sulfonylamino)*-3,12-*dioxa*-6,9-*diazatetradecane* **4**. A mixture of compound **3** (20.9 g, 0.0385 mol), dichloromethane (90 cm^3), and an aqueous solution (90 cm^3) of sodium hydroxide (4.9 g, 0.123 mol) was stirred on an ice-bath, and solid toluene-*p*-sulfonyl chloride (22.1 g, 0.116 mol) added little by little. After the addition was complete, the mixture was stirred at room temperature for 12 h. The dichloromethane solution was separated and the aqueous layer shaken with three portions (80 cm^3) of dichloromethane. The mother-liquor and the extracts were combined, dried over Na_2SO_4, and concentrated to give an oily substance. This was dissolved in dichloromethane and the solution subjected to silica gel column chromatography (2.7 × 47 cm). The elution was carried out successively with dichloromethane and then dichloromethane–ethyl acetate (20:1, 10:1, and 5:1 v/v). The eluates were combined and concentrated to dryness to give compound **4** as a colourless crystalline powder. Yield: 49% (Found: C, 52.95; H, 5.90; N, 6.40. Calc. for $C_{38}H_{50}N_4O_{10}S_4{\cdot}0.25CH_2Cl_2$: C, 52.70; H, 5.85; N, 6.40%).

3,9,12,18-*Tetra(toluene*-p-*sulfonyl)*-6,15-*dioxa*-3,9,12,18-*tetraazaicosane*-1,20-*diol* **5**. A sodium ethoxide solution was prepared by dissolving sodium (5 g, 0.217 mol) in absolute ethanol (100 cm^3) in a closed system filled with argon. 2-Aminoethanol *N*-toluene-*p*-sulfonate[19] (40 g, 0.20 mol) was added, and the mixture was stirred for 1 h at room temperature then concentrated to dryness. The residue and compound **1** (28.5 g, 0.049 mol) were dissolved in dry dmf (300 cm^3), and the mixture stirred at 90 °C under argon in the dark. It was concentrated under reduced pressure at 40 °C to give an oily substance which was dissolved in dichloromethane and subjected to silica gel column chromatography (2.7 × 52 cm). The elution was carried out first with chloroform and then chloroform–ethyl acetate (5:1 v/v) when the desired compound **5** started to elute [checked by silica gel thin-layer chromatography developed by chloroform–ethyl acetate (1:1 v/v)]. On evaporating the solvent compound **5** was obtained as a colourless crystalline powder. Yield: 87%. It was used for the following reaction without further purification.

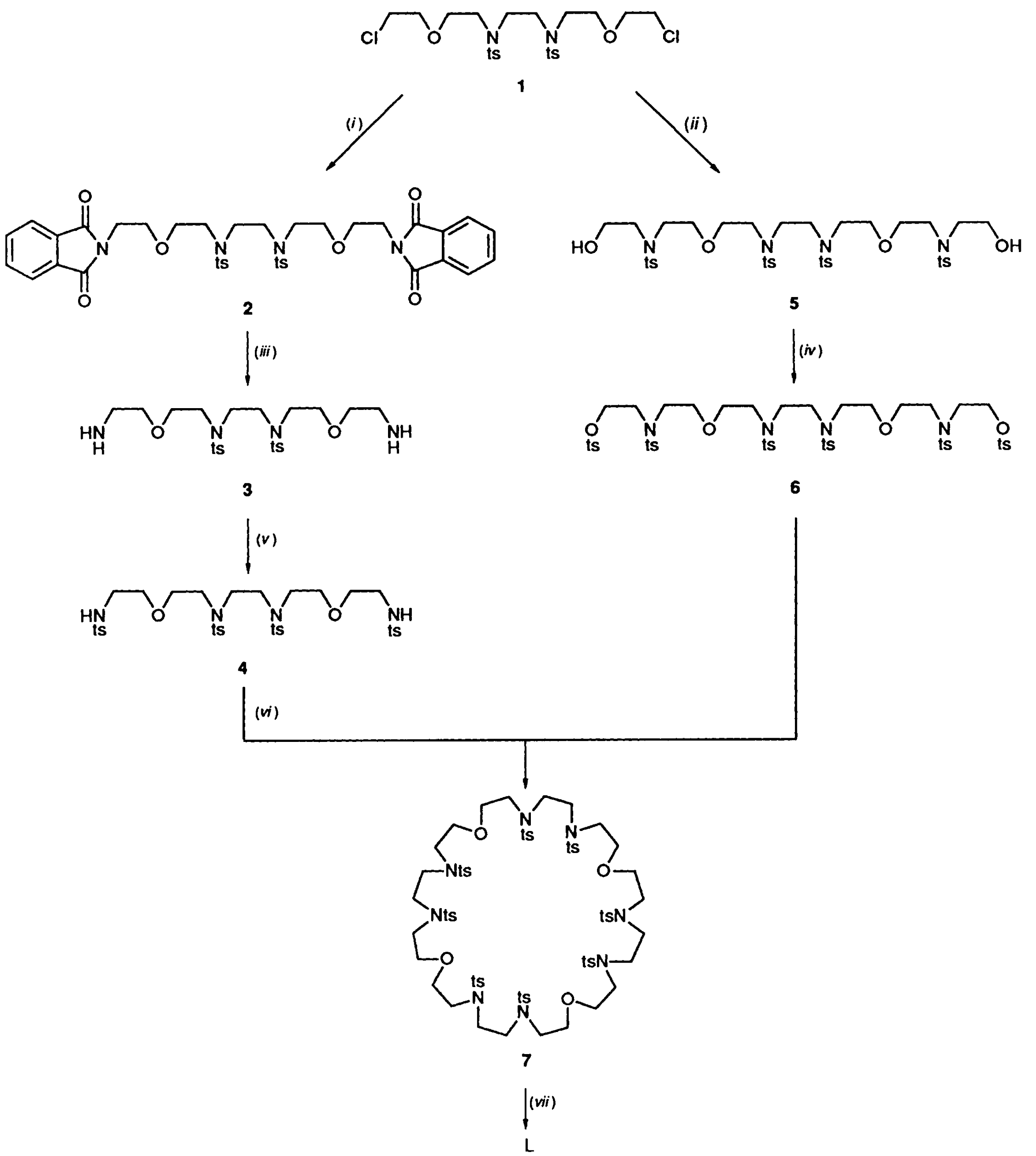
3,9,12,18-*Tetra(toluene*-p-*sulfonyl)*-1,20-*di(toluene*-p-*sulfonyloxy)*-6,15-*dioxa*-3,9,12,18-*tetraazaicosane* **6**. To a pyridine solution (35 cm^3) of toluene-*p*-sulfonyl chloride (6.1 g, 0.319 mol) was dropwise added a pyridine solution (25 cm^3) of compound **5** at 0 °C and the mixture stirred at this temperature overnight. It was then poured onto crushed ice (250 g), and the resulting oily substance extracted with dichloromethane (90 cm^3). The extract was washed with 5% hydrochloric acid and with water and dried with Na_2SO_4. On evaporating the solvent compound **6** was obtained as a colourless oily substance. Yield: 94% (Found: C, 53.85; H, 5.70; N, 4.65. Calc. for $C_{56}H_{70}N_4O_{16}S_6$: C, 53.90; H, 5.65; N, 4.50%).

1,10,19,28-*Tetraoxa*-4,7,13,16,22,25,31,34-*octa(toluene*-p-*sulfonyl)*-4,7,13,16,22,25,31,34-*octaazacyclohexatriacontane* **7**. To a sodium ethoxide solution prepared by dissolving sodium (0.62 g, 0.027 mol) in absolute ethanol (100 cm^3) under argon was added compound **2** (10 g, 0.012 mol), and the resulting solution stirred at 60 °C for 30 min then concentrated to dryness to give the disodium salt of **2** as a colourless solid.

In a three-necked flask (1 l) fitted with two dropping funnels and a reflux condenser was placed dry dmf (600 cm^3). In one dropping funnel was placed a dmf solution (70 cm^3) of the disodium salt of **2**. In the other was placed a dmf solution (70 cm^3) of compound **6** (16 g, 0.013 mol). The apparatus was thoroughly purged with dry argon and shielded from light. Its temperature was raised to 100 °C and the two solutions of the components were dropped in at the same rate in the course of 12 h. The solvent was removed under reduced pressure to give a small volume to which crushed ice (*ca.* 200 g) was added, resulting in the precipitation of a solid mass. This was dissolved in dichloromethane, and the solution shaken three times with water, dried with Na_2SO_4, and concentrated to give an oily substance. To the flask was added benzene (80 cm^3) and the mixture was concentrated to dryness. This operation was repeated to give compound **7** as a colourless crystalline powder melting at 205 °C. Yield: 45% (Found: C, 55.20; H, 6.05; N, 6.30. Calc. for $C_{80}H_{104}N_8O_{20}S_8{\cdot}0.3C_6H_6$: C, 55.25; H, 6.00; N, 6.30%). FAB mass spectrum: *m/z* 1753 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.67 (d, *J* = 8.3, 16 H, *o*-protons of tosyl group), 7.27 (d, *J* = 5.62, 16 H, *m*-protons of tosyl group), 3.51 [t, *J* = 5.62, 16 H, N(ts)C*H*$_2$C*H*$_2$N(ts)], 3.32 [t, *J* = 5.61, 16 H, N(ts)C*H*$_2$CH$_2$OCH$_2$C*H*$_2$N(ts)], 3.25 [t, *J* = 5.61 Hz, 16 H, N(ts)CH$_2$C*H*$_2$OC*H*$_2$CH$_2$N(ts)] and 2.38 (s, 24 H, CH$_3$).

1,10,19,28-*Tetraoxa*-4,7,13,16,22,25,31,34-*octaazacyclohexatriacontane* (L). A mixture of compound **7** (8 g, 0.004 56 mol), phenol (12.8 g), and hydrobromic acid solution in acetic acid (31%, 170 cm^3) was stirred at 80 °C for 14 h then concentrated to small volume. To this was added toluene (85 cm^3) and the mixture distilled under reduced pressure. This operation was repeated three times using 270 cm^3 of toluene in total. The residue was shaken with a mixture of dichloromethane (230 cm^3) and water (200 cm^3). The aqueous layer was separated, washed with three portions (50 cm^3) of dichloromethane, and concentrated to dryness. The resulting viscous material was dissolved in absolute ethanol and the solution concentrated to small volume to give L·8HBr as a highly hygroscopic, pale brown precipitate. Yield: 98%. The free form of the macrocycle (L) was obtained as a colourless oily substance by passing L·8HBr over a Dowex 50 W-X8 resin in its basic form. Yield: 98%. ^{13}C NMR (D_2O): δ 50.322 (NHC*H*$_2$C*H*$_2$NH), 50.018 (NHCH$_2$C*H*$_2$O) and 71.864 (NHC*H*$_2$CH$_2$O).

$[Cu_4L(OH)_4][ClO_4]_4{\cdot}2H_2O$. To an aqueous solution of the ligand (free form; 0.54 g, 1.04 mmol) was added dropwise an aqueous solution (5 cm^3) of copper(II) perchlorate hexahydrate



Scheme 1 (*i*) Potassium phthalimide; (*ii*) HO[CH$_2$]$_2$NH(ts); (*iii*) N$_2$H$_4$ in EtOH; (*iv*) tosyl chloride in dry pyridine; (*v*) tosyl chloride; (*vi*) NaOEt; (*vii*) hydrolysis

(1.73 g, 4.68 mmol). The resulting deep blue solution was made alkaline (pH 9) by adding an aqueous solution of sodium hydroxide (1 mol) and concentrated to small volume. Ethanol (2 cm^3) was added and the mixture concentrated to give a viscous oily substance. The addition and evaporation of ethanol were repeated three times to afford deep blue microcrystals, which were recrystallized from water. Yield: 55% (Found: C, 22.65; H, 4.95; Cu, 19.75; N, 8.50. Calc. for $C_{24}H_{64}Cl_4Cu_4N_8O_{26}$: C, 22.60; H, 4.75; Cu, 19.90; N, 8.80%. FAB mass spectrum: *m/z* 841 [$Cu_4L(OH)_4{}^+$].

In our attempts to grow large crystals a $NaClO_4$ adduct, [$Cu_4L(OH)_4$][ClO_4]$_4$·$NaClO_4$, was obtained as blue crystals when the complex was recrystallized from an aqueous solution containing excess of $NaClO_4$. Yield: 90% (Found: C, 21.15; H, 4.55; Cu, 18.25; N, 8.25. Calc. for $C_{24}H_{60}Cl_5Cu_4N_8NaO_{28}$: C, 21.15; H, 4.45; Cu, 18.65; N, 8.20%).

Results and Discussion

Synthesis and Characterization of Macrocycle L.—The synthesis of the macrocycle is summarized in Scheme 1. The key precursor compounds prior to the cyclization are **4** and **6**, both of which were derived from the same starting compound **1**. The starting compound was prepared in a tolerable yield by the reaction of the di(toluene-*p*-sulfonyl) derivative of ethylenediamine[19] and excess of di(2-chloroethyl) ether in dmf in the presence of K_2CO_3. The conversion of **1** into **4** was carried out *via* the Gabriel reaction and tosylation. Compound **1** was converted into **6** by reaction with 2-aminoethanol *N*-toluene-*p*-sulfonate,[20] followed by tosylation at the terminal alcoholic groups. The cyclization of **4** and **6** to form **7** was achieved by a modification of the method of Richman and Atkins.[21] The hydrolysis of **7** to L (as the octahydrobromide) was performed quantitatively by treatment with 31% hydrobromic acid in acetic acid in the presence of a large excess of phenol.[22,23]

Tetracopper(II) *Complex of the Macrocycle*.—Spectroscopic studies were performed in order to gain an insight into the complexing behaviour of the macrocycle L toward copper(II) ion (4.5 equivalents) in aqueous solution at various pH. As seen

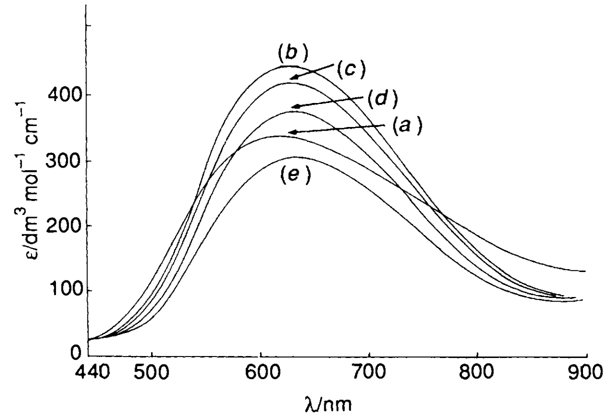


Fig. 1 The pH dependence of the complexation of Cu^{II} to L in water: [Cu] = 4.5×10^{-3} dm^{-3} mol and [L] = 1×10^{-3} dm^{-3} mol. pH 5.0 (*a*), 6.0–7.0 (*b*), 7.5 (*c*) 9.0 (*d*), and 11.0 (*e*)

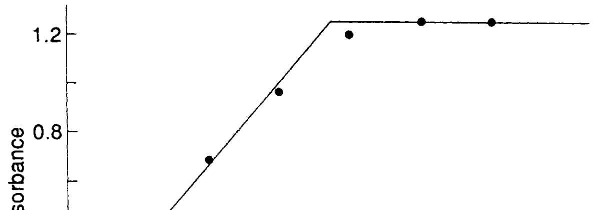


Fig. 2 Intensity changes at 630 nm at various [Cu]/[L] ratios. The concentration of the macrocycle is fixed at 3.37×10^{-3} mol dm^{-3}

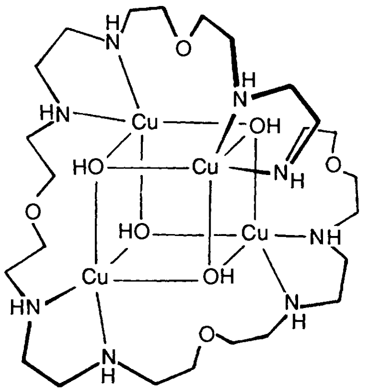


Fig. 3 Probable structure of $[Cu_4L(OH)_4]^{4+}$

in Fig. 1 the absorption spectra in the range pH 6–9 are similar except for a slight change in intensity, showing a band maximum at 633 nm. Under more acidic conditions ($pH < 6$) the spectra differ significantly with a band maximum at shorter wavelength. Under more alkaline conditions the band intensity gradually decreased and the precipitation of copper(II) hydroxide began near pH 12.

Spectroscopic investigations were made at 630 nm and pH 9 (buffered with boric acid) by changing the copper-to-L ratio (Fig. 2). The absorbance at 630 nm increased with increasing metal-to-L ratio up to 4:1 but became constant at >4:1 suggesting that the macrocycle can incorporate four copper(II) ions. This was confirmed by the isolation of $[Cu_4L(OH)_4][ClO_4]_4 \cdot 2H_2O$. The complex shows a sharp IR band at 3550 cm^{-1} which can be attributed to the ν(O–H) mode of bridging hydroxide ion.[24] The FAB mass spectrum shows a dominant peak at *m*/*z* 841 which corresponds to $Cu_4L(OH)_4$. Thus, the most plausible structure is a cubane-type $Cu_4(OH)_4$ core surrounded by the macrocycle (see Fig. 3). An $NaClO_4$ adduct of the complex, $[Cu_4L(OH)_4][ClO_4]_4 \cdot NaClO_4$ (see Experimental section), formed large crystals but our efforts to solve the crystal structure were in vain.

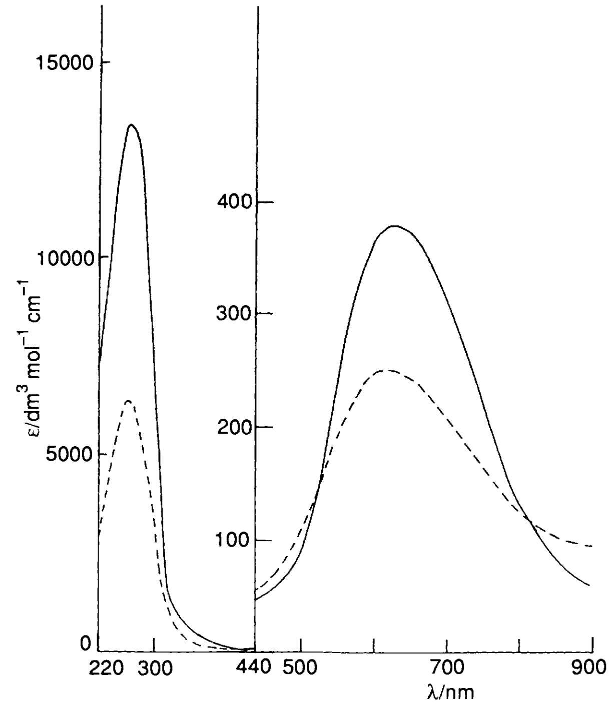


Fig. 4 Electronic spectra of $[Cu_4L(OH)_4]^{4+}$ in water (———) and of its reduced species (– – – –)

The electronic spectra of this complex in water and acetonitrile are similar. The spectrum in water is shown in Fig. 4. It resembles the spectra at pH 6–9 in Fig. 1, adding support to the conclusion that the macrocycle preferentially co-ordinates a tetranuclear copper(II) core near the neutral pH range. The d–d band maximum (633 nm) is low in energy compared with those of tetragonal copper(II) complexes. For example, di-μ-hydroxo-dicopper(II) complexes of *N*,*N*,*N*′,*N*′-substituted ethylenediamines show the d–d band maximum near 550 nm.[25] The spectrum of the present complex suggests a substantial distortion from planarity around the copper(II) ion. The intense absorption band at 265 nm (ε 13 500 dm^3 mol^{-1} cm^{-1}) is tentatively assigned to a charge-transfer (c.t.) transition from the bridging OH^- to the copper(II) ion.

The ESR spectra of the complex were measured on a powdered sample and in acetonitrile solution at room and liquid-nitrogen temperatures. Irrespective of the conditions of measurement the complex showed only a very broad signal centred around *g* 2.0 probably because of rapid intramolecular spin–spin relaxation. The magnetic moment is 1.90 μ_B per copper at room temperature, practically independent of temperature down to liquid-nitrogen temperature. This implies that the spin coupling in the $Cu_4(OH)_4$ core is very weak. It is known that the magnetic interaction in cubane-type tetranuclear copper(II) complexes is sensitive to the core structure[26–29] and is either weakly antiferromagnetic or ferromagnetic depending upon the core distortion.

A cyclic voltammogram of the complex in water is shown in Fig. 5. One redox couple is seen in the negative potential region whereas there is no redox wave in the positive potential region up to +1.0 V. The redox couple at −0.3 V is quasi-reversible (peak separation: *ca.* 120 mV) when measured in the range 0 to −0.6 V (see the insert). Controlled-potential electrolyses at

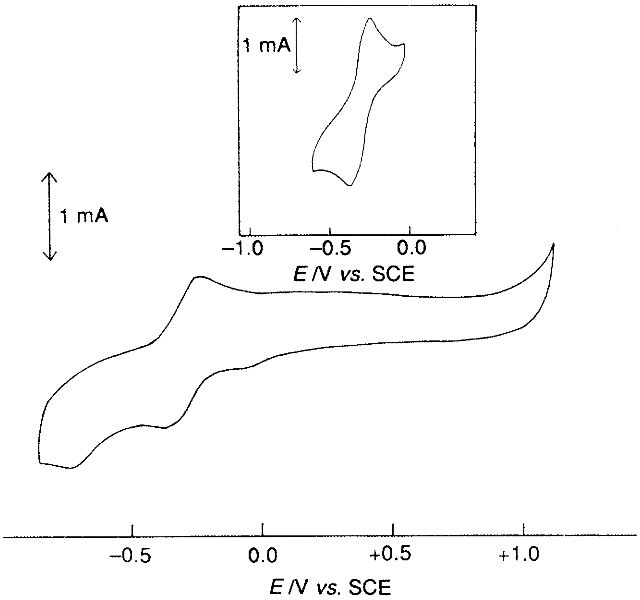


Fig. 5 Cyclic voltammogram of $[Cu_4L(OH)_4]^{4+}$. The insert is the sweep in the range 0 to −0.6 V: concentration = *ca.* 1×10^{-3} mol dm^{-3}, in water with $NaClO_4$ (1×10^{-1} mol dm^{-3}), glassy carbon electrode, scan rate 80 mV s^{-1}

−0.3 V revealed two electron transfers. We tentatively assign this wave to the process: $Cu^{II}_4 \rightleftharpoons Cu^{I}_2Cu^{II}_2$.

The electronic spectrum of the reduced species is given in Fig. 4. In accord with the reduction of two copper(II) ions, the intensity of the c.t. band at 265 nm (ε 6700 dm^3 mol^{-1} cm^{-1}) is nearly one half that of the parent complex. However, this is not the case of the d–d band which is shifted to shorter wavelength (620 nm) and the intensity is *ca.* two thirds of that of the parent complex. This result suggests a slight structural change around the copper(II) ion in the reduced species. Further, the spectrum suggests the presence of a new absorption band in the near-IR region. Such a band has been reported for mixed-valence copper(I,II) complexes and assigned to the intervalence transition band.[30,31]

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (No. 03241105).

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Received 2nd *July* 1991; *Paper* 1/03305K