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Copper(II) complexes of tetraaza macrocycles bearing pendant arms: syntheses, structures and properties

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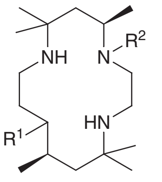
A new difunctionalized tetraaza macrocycle, 1,8-bis(2-hydroxyethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, H_2L^2 has been synthesized in one step by the reaction of ethylene oxide and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L^1). The crystal structure of $[Cu(H_2L^2)][ClO_4]_2$ **1** shows the metal ion in tetragonally elongated octahedral geometry, co-ordinated by the oxygen atoms of the pendant arms in the *trans*-axial position. Copper(II) complexes were also synthesized and characterized from other 1,8-disubstituted macrocyclic ligands L^3, L^4, HL^5, H_2L^6, L^8 and H_2L^9. The molecular structure of $[CuL^3][ClO_4]_2$ **2** ($R^1 = R^2 = CH_2CH_2CN$) and $[CuL^5]ClO_4$, **4** ($R^1 = H$, $R^2 = CH_2CO_2^-$) shows the macrocycle in *trans*-I configuration with square planar and distorted square pyramidal geometries respectively at the metal centers. The structures of complexes $[CuL^8][ClO_4]_2$ **6** [L^8 = 1,8-bis(2-cyanoethyl)-4,7,11,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane] and $[Cu(H_2L^9)][ClO_4]_2$ **7** (corresponding CH_2CO_2H derivative) show the macrocyclic ligand in the *trans*-III configuration. Interestingly the two pendant acetic acid groups of H_2L^9 in **7** remain protonated and co-ordinate through the carbonyl oxygen atoms in *trans*-octahedral geometry. The cyclic voltammetric studies of the complexes revealed that the copper(I) oxidation state is highly stabilized by the ligands L^3 and L^8. The pH dependent co-ordination geometry changes of complexes **4**, $[CuL^6]$ **5** ($R^1 = R^2 = CH_2CO_2^-$) and **7** based on the changes in their electronic spectra are discussed. The kinetics of acid promoted dissociation reactions of complexes **2** and **6** has been studied in HCl–NaCl solutions ($I = 5.0$ M). The possible mechanisms of the reactions, the factors influencing the rate and the relative importance of the solvent separation and protonation pathways are discussed.

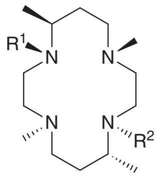
Introduction

The co-ordination chemistry of polyaza macrocycles has been studied extensively.[1] However, macrocycles bearing pendant co-ordinating groups[2–6] continue to attract attention largely due to their structures and properties which are different from their unsubstituted parent macrocycles.[7] Some of these ligands exhibit remarkable metal ion selectivity that is of interest in several areas.[8,9] Most of the studies involved completely N-alkylated macrocycles[10,11] with some reports on partially N-functionalized macrocycles.[12–14] The syntheses of these partially N-alkylated macrocycles is generally complicated, but the presence of alkyl or aryl substituents on the macrocyclic ring carbons next to the secondary amino groups facilitate syntheses, as alkylation takes place only on sterically less hindered nitrogen atoms.[15]

In continuation of our work on C-alkylated 1,4,8,11-tetraazacyclotetradecane complexes,[16–18] we now report syntheses, structural characterization and properties of copper(II) complexes of some N-functionalized tetraaza macrocycles. Reactions of *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane L^1 with alkylating agents gave partially N-alkylated products. Although the nitrogen atoms at 4 and 11 positions are more basic, they are sterically hindered and only 1,8 functionalization takes place. A new di-*N*-hydroxyethylated macrocycle, 1,8-bis(2-hydroxyethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane H_2L^2 has been isolated by the direct reaction of L^1 and ethylene oxide. The crystal structure of its copper complex, $[Cu(H_2L^2)][ClO_4]_2$ is reported. Macrocyclic ligands containing either one or two pendant acetic acid groups have also been synthesized. The structures of $[Cu(H_2L^9)][ClO_4]_2\cdot 2H_2O$ where the two pendant acetic acid groups of the macrocycle co-ordinate the metal ion through the carbonyl oxygen atoms, and $[CuL^5]ClO_4$, where the mono-*N*-acetic acid group co-ordinates the metal ion through a carboxylate oxygen atom, are also reported. The crystal structures of $[CuL^3][ClO_4]_2$ and $[CuL^8][ClO_4]_2$, where the macrocycle contains cyanoethyl groups are also reported.



$R^1 = R^2 = H$	L^1
$R^1 = R^2 = CH_2CH_2OH$	H_2L^2
$R^1 = R^2 = CH_2CH_2CN$	L^3
$R^1 = R^2 = CH_2CH_2CH_2NH_2$	L^4
$R^1 = H$ $R^2 = CH_2COOH$	HL^5
$R^1 = R^2 = CH_2COOH$	H_2L^6



$R^1 = R^2 = H$	L^7
$R^1 = R^2 = CH_2CH_2CN$	L^8
$R^1 = R^2 = CH_2COOH$	H_2L^9

Experimental

Materials

All the chemicals in the syntheses were of reagent grade used without further purification. The solvents were dried prior to use by standard procedures.[19] The ligands L^1 and L^7 were synthesized following the reported procedures.[20,21]

Syntheses of ligands

1,8-Bis(2-hydroxyethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, H_2L^2. To a solution of compound L^1 (2.84 g, 10 mmol) in 30 cm³ of dry ethanol was added 3 cm³ of cold liquefied ethylene oxide at 0 °C. The reaction mixture was maintained at this temperature for 4 h and at 5 °C for 12 h.

The solution was then slowly warmed to room temperature. Removal of solvent left a white residue that was recrystallized from ethanol–water mixture. Yield 60%. IR (KBr, cm^{-1}): 3380 [*ν*(O–H)] and 3240 [*ν*(N–H)]. ^{13}C NMR (CDCl$_3$): *δ* 14.1, 24.6, 28.4, 38.7, 46.7, 47.3, 49.4, 51.7, 53.4 and 61.3.

1,8-Bis(2-cyanoethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, L^3, and 1,8-bis(2-cyanoethyl)-4,7,11,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane, L^8. Acrylonitrile solution of ligands L^1 and L^7 were heated to reflux for 6 to10 h. The reaction mixture was cooled to room temperature, filtered and evaporated to dryness. The residue was dissolved in dichloromethane and ethanol mixture to give the corresponding ligands as white crystalline solids. Yield >90%. IR (KBr, cm^{-1}): 2250 [*ν*(C≡N)] and 3270 [*ν*(N–H)] (for ligand L^3). ^{13}C NMR (CDCl$_3$): L^3, *δ* 14.2, 17.2, 24.3, 28.5, 38.9, 46.2, 46.7, 49.7, 51.5, 52.9 and 119.1; L^8, *δ* 14.7, 18.7, 30.3, 43.3, 46.5, 47.4, 53.5, 53.6, 55.7 and 119.3.

1,8-Bis(3-aminopropyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, L^4. To a refluxing solution of compound L^3 (1 g, 2.6 mmol) in 60 cm^3 of dry toluene was added sodium metal (1.52 g, 66 mmol). Then 18 cm^3 of dry ethanol were added dropwise over a period of 1.5 h and the reaction mixture was refluxed for 3 h. It was cooled to room temperature and allowed to stand in a refrigerator for 12 h. Sodium ethoxide precipitated was removed by filtration. The precipitate was washed several times with toluene and the filtrate and washings were combined and evaporated to dryness. The pale yellow residue was then extracted into boiling benzene and evaporation of solvent gave the corresponding ligand in 65% yield. IR (cm^{-1}): 3280 and 3250 [*ν*(N–H)]. ^{13}C NMR (CDCl$_3$): *δ* 12.9, 23.8, 28.4, 32.3, 38.7, 40.4, 46.1, 46.9, 50.7 and 52.2.

5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-1-acetic acid, HL^5·2HClO$_4$. To a 10 cm^3 dry methanol solution of bromoacetic acid (1.4 g, 10 mmol) was added KOH (0.56 g, 10 mmol) in 10 cm^3 of methanol. Then L^1 (2.84 g, 10 mmol) in 20 cm^3 of dry methanol and anhydrous sodium carbonate (1.3 g, 12 mmol) were added. The mixture was stirred at 45 °C for 6 h and then at 60 °C for 16 h. It was cooled to room temperature and the precipitated sodium hydrogencarbonate was removed by filtration. The solvent was removed using a rotary evaporator and the residue dissolved in water and filtered. The unchanged starting material was separated from the water solution by extracting with dichloromethane. The water layer was acidified with concentrated perchloric acid to pH 4.5 and the product precipitated on standing. Yield 70% (Found: C, 39.3; H, 7.1; N, 10.1. $C_{18}H_{40}Cl_2N_4O_{10}$ requires C, 39.8; H, 7.4; N, 10.3%). IR (KBr, cm^{-1}): 3360 [*ν*(O–H)], 3210 [*ν*(N–H)], 1710 [*ν*(CO)] and 1120 [*ν*(ClO$_4$)].

5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-1,8-diacetic acid, H$_2$L^6·2HClO$_4$. To a 10 cm^3 dry methanol solution of bromoacetic acid (2.8 g, 20 mmol) was added KOH (1.12 g, 20 mmol) in 10 cm^3 of methanol. Then L^1 (2.84 g, 10 mmol) in 20 cm^3 of dry methanol and anhydrous sodium carbonate (2.6 g, 24 mmol) were added and the reaction mixture was stirred at 80 °C for 16 h. It was cooled to room temperature and the precipitated sodium hydrogencarbonate removed by filtration. The solvent was removed using a rotary evaporator and the residue dissolved in water and filtered. The unchanged starting material was separated from the water solution by extracting with dichloromethane. The water layer was acidified with concentrated perchloric acid to pH 4.5 and the product precipitated on standing. Yield 78% (Found: C, 39.5; H, 7.1; N, 8.9. $C_{20}H_{42}Cl_2N_4O_{12}$ requires C, 39.9; H, 7.0; N, 9.3%). IR (KBr, cm^{-1}): 3360 [*ν*(O–H)], 3215 [*ν*(N–H)], 1700 [*ν*(CO)] and 1120 [*ν*(ClO$_4$)].

4,7,11,14-Tetramethyl-1,4,8,11-tetraazacyclotetradecane-1,8-diacetic acid, H$_2$L^9·2HClO$_4$. This ligand was synthesized in the same way as H$_2$L^6. Yield 60% (Found: C, 37.2; H, 6.2; N, 9.5. $C_{18}H_{38}Cl_2N_4O_{12}$ requires C, 37.7; H, 6.6; N, 9.8%). IR (KBr, cm^{-1}): 3340 [*ν*(O–H)], 1700 [*ν*(CO)] and 1120 [*ν*(ClO$_4$)].

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Syntheses of complexes

[Cu(H$_2$L^2)][ClO$_4$]$_2$ 1. A 5 cm^3 methanol solution of copper perchlorate hexahydrate (0.37 g, 1 mmol) was added to a 20 cm^3 methanol solution of H$_2$L^2 (0.37 g, 1 mmol). The reaction mixture was refluxed for 1 h, cooled to room temperature and filtered. Slow evaporation of solvent at room temperature gave a blue crystalline product that was filtered off and air-dried. Yield 80% (Found: C, 37.6; H, 6.8; N, 8.7. $C_{20}H_{44}Cl_2CuN_4O_{10}$ requires C, 37.8; H, 6.9; N, 8.8%). IR (KBr, cm^{-1}): 3360 [*ν*(O–H)], 3210 [*ν*(N–H)] and 1120 [*ν*(ClO$_4$)].

[CuL^3][ClO$_4$]$_2$ 2. To a methanol solution (20 cm^3) of ligand (0.39 g, 1 mmol), copper perchlorate hexahydrate (0.37 g, 1 mmol) was added. The reaction mixture was refluxed for 15 min and cooled to room temperature. The violet precipitate obtained was filtered off and washed with methanol. The complex was recrystallized from acetonitrile solvent. Yield 90% (Found: C, 40.2; H, 6.3; N, 12.6. $C_{22}H_{42}Cl_2CuN_6O_8$ requires C, 40.5; H, 6.4; N, 12.9%). IR (KBr, cm^{-1}): 2250 [*ν*(C≡N)], 3195 [*ν*(N–H)] and 1116 [*ν*(ClO$_4$)].

[CuL^4][ClO$_4$]$_2$ 3. To an aqueous solution (10 cm^3) of ligand (0.4 g, 1 mmol), Cu(ClO$_4$)$_2$·6H$_2$O (0.37 g, 1 mmol) was added. The reaction mixture was warmed at 60° C for 2 h. The solution was filtered and the volume reduced to 5 cm^3. The pH of the solution was adjusted to 6. Slow evaporation at room temperature gave a purple product that was filtered off and air-dried. Yield 60% (Found: C, 39.7; H, 7.4; N, 12.5. $C_{22}H_{50}Cl_2CuN_6O_8$ requires C, 40.0; H, 7.6; N, 12.7%). IR (KBr, cm^{-1}): 3220 [*ν*(N–H)] and 1100 [*ν*(ClO$_4$)].

[CuL^5]ClO$_4$ 4. The salt Cu(ClO$_4$)$_2$·6H$_2$O (0.74 g, 2 mmol) was added to a 20 cm^3 aqueous solution of HL^5 (1.224 g, 2 mmol). The reaction mixture was refluxed for 2–3 h and the blue solution obtained concentrated on a water-bath. The pH of the solution was adjusted to 4. Slow evaporation at room temperature gave the crystalline complex in 70% yield (Found: C, 42.5; H, 7.4; N, 10.9. $C_{18}H_{37}ClCuN_4O_6$ requires C, 42.8; H, 7.5; N, 11.1%). IR (KBr, cm^{-1}): 1630 [*ν*(COO)] and 1100 [*ν*(ClO$_4$)].

[CuL^6] 5. This complex was synthesized in the same way as **4** in 70% yield. It was recrystallized from the aqueous perchloric acid solution (pH 4) (Found: C, 51.5; H, 8.5; N, 11.9. $C_{20}H_{40}CuN_4O_4$ requires C, 51.7; H, 8.6; N, 12.1%). IR (KBr, cm^{-1}): 1630 [*ν*(COO)].

[CuL^8][ClO$_4$]$_2$ 6. This complex was synthesized and recrystallized in the same way as complex **2** (Found: C, 38.1; H, 6.0; N, 13.3. $C_{20}H_{38}Cl_2CuN_6O_8$ requires C, 38.4; H, 6.1; N, 13.5%). IR (KBr, cm^{-1}): 2250 [*ν*(C≡N)] and 1116 [*ν*(ClO$_4$)].

[Cu(H$_2$L^9)][ClO$_4$]$_2$ 7. This complex was also synthesized in the same way as **4** in 60% yield. It was recrystallized from aqueous perchloric acid solution (pH 4) (Found: C, 33.7; H, 5.5; N, 8.6. $C_{18}H_{36}Cl_2CuN_4O_{12}$ requires C, 34.0; H, 5.7; N, 8.8%). IR (KBr, cm^{-1}): 3360 [*ν*(O–H)], 1680 [*ν*(C=O)] and 1100 [*ν*(ClO$_4$)].

Physical measurements

The carbon, hydrogen and nitrogen analyses were carried out on a Heraeus CHN elemental analyzer. Infrared spectra were recorded on a BOMEN (Hartmann-Braun MB series) FT-IR spectrophotometer as KBr pellets, electronic absorption spectra on a Hitachi U-3300 or U-3410 UV/VIS spectrophotometer, ^1H and ^{13}C NMR spectra on an AC Bruker 300 MHz NMR spectrometer. Cyclic voltammetric studies were carried out on a CH instruments, model 604A computer controlled electrochemical analyzer. All the experiments were performed under a dry nitrogen atmosphere in acetonitrile solvent using 0.1 M NBu_4ClO_4 as the supporting electrolyte. A three-electrode assembly comprising a platinum-working electrode, a platinum auxiliary electrode and Ag–AgCl reference electrode was used. The ferrocene–ferrocenium couple was used as the redox standard.

Kinetic studies. Kinetic measurements for acid catalysed dissociation reactions of complexes **2** and **6** were carried out in aqueous HCl–NaCl solutions of ionic strength 5.0 M at 25.0 ± 0.1 °C. Absorbance *vs.* time data were collected at 540 and 600 nm respectively using Hitachi U-3200 or U-3410 spectrophotometers. Good first order kinetics were observed for both complexes. The rate constants were obtained by linear least squares fit for the data by using a computer.

Crystallography

Single crystals of complex **1** were obtained by slow evaporation of its methanol solution, those of **2** and **6** by slow evaporation of their acetonitrile solutions and of **4** and **7** by slow evaporation of their aqueous perchloric acid solutions. Intensity data were collected on an Enraf-Nonius CAD4 or Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation (0.71073 Å). Data reduction and absorption corrections were performed using XTAL or NRCVAX programs.[22,23] Structures were solved by the heavy-atom methods with SHELXS 97[24] and refined by full matrix least-squares analysis on F^2 with SHELXL 97.[25]

$[Cu(H_2L^2)][ClO_4]_2$ 1. $C_{20}H_{44}Cl_2CuN_4O_{10}$, $M = 635.04$, monoclinic, space group $P2/n$, $a = 8.5256(5)$, $b = 15.5111(9)$, $c = 10.8567(6)$ Å, $\beta = 101.176(1)°$, $U = 1408.5(1)$ Å^3, $T = 296$ K, $Z = 2$, μ(Mo-Kα) = 10.22 cm^{-1}, 7673 reflections measured, 3845 unique (R(int) = 0.050) which were used in all calculations. The final $wR(F^2)$ was 0.132, $R1 = 0.050$.

$[CuL^3][ClO_4]_2$ 2. $C_{22}H_{42}Cl_2CuN_6O_8$, $M = 653.06$, orthorhombic, space group $Fdd2$, $a = 22.1089(9)$, $b = 30.5304(12)$, $c = 8.7632(4)$ Å, $U = 5915.1(4)$ Å^3, $T = 295$ K, $Z = 8$, μ(Mo-Kα) = 9.73 cm^{-1}, 8324 reflections measured, 2761 reflections unique (R(int) = 0.044) which were used in all calculations. The final $wR(F^2)$ was 0.120, $R1 = 0.049$.

$[CuL^5]ClO_4$ 4. $C_{18}H_{38}Cl_2CuN_4O_{9.33}$, $M = 594.3$, trigonal, space group $P3c1$, $a = 25.4777(2)$, $c = 16.1648(2)$ Å, $U = 9087.0(1)$ Å^3, $T = 295$ K, $Z = 12$, μ(Mo-Kα) = 9.44 cm^{-1}, 51015 reflections measured, 4060 unique which were used in all calculations. The final $wR(F^2)$ was 0.215, $R1 = 0.074$.

$[CuL^8][ClO_4]_2$ 6. $C_{20}H_{38}Cl_2CuN_6O_8$, $M = 625.00$, monoclinic, space group $P2_1/n$, $a = 9.2539(1)$, $b = 12.7198(1)$, $c = 11.8658(2)$ Å, $\beta = 103.187(1)°$, $U = 1359.87(3)$ Å^3, $T = 295$ K, $Z = 2$, μ(Mo-Kα) 10.54 cm^{-1}, 7438 reflections were measured, 2458 unique (R(int) = 0.022) which were used in all calculations. The final $wR(F^2)$ was 0.083, $R1 = 0.033$.

$[Cu(H_2L^9)][ClO_4]_2$ 7. $C_{18}H_{40}Cl_2CuN_4O_{14}$, $M = 670.98$, monoclinic, space group $P2_1/c$, $a = 8.833(2)$, $b = 9.881(1)$, $c = 16.168(2)$ Å, $\beta = 98.31(2)°$, $U = 1396.4(4)$ Å^3, $D_c = 1.596$ g cm^{-3}, μ(Mo-Kα) = 10.46 cm^{-1}, $T = 295$ K, $Z = 2$, 2442 reflections were measured, 1798 unique (R(int) = 0.015) which were used in all calculations. The final $wR(F^2)$ was 0.141, $R1 = 0.052$.

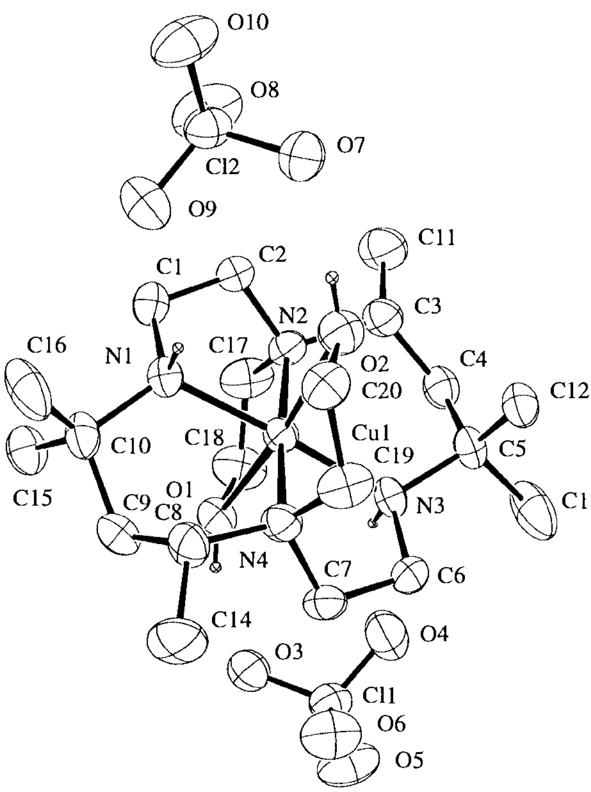


Fig. 1 An ORTEP drawing of the molecular structure of $[Cu(H_2L^2)][ClO_4]_2$ **1** along with the atom numbering scheme.

CCDC reference number 186/1537.

See http://www.rsc.org/suppdata/dt/1999/2885/ for crystallographic files in .cif format.

Results and discussion

Molecular structures of complexes

$[Cu(H_2L^2)][ClO_4]_2$ 1. The structure of the complex confirms that hydroxyethylation of L^1 takes place selectively on sterically less hindered 1,8 nitrogen atoms of the macrocycle. The metal ion is co-ordinated by the two oxygen atoms of the hydroxyethyl pendant arms and the four nitrogen atoms of the macrocycle in a tetragonally elongated octahedral geometry. The two *trans*-axial Cu–O bonds (2.535 and 2.603 Å) are considerably longer than the four Cu–N equatorial bonds and this distortion arises predominantly from the Jahn–Teller effect operative on the d^9 metal center. The Cu–O bond distances are comparable to those in $[CuL(H_2O)_2]^{2+}$ and $[Cu(H_2L)(ClO_4)_2]^{2+}$ complexes[26] (L = 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine). The average Cu–N (tertiary) bond distance of 2.076(8) Å is longer than the average Cu–N (secondary) bond distance (2.009(5) Å). The N–Cu–N angles of the five and six membered chelate rings are in the expected range and are given in Table 1. The ORTEP[27] drawing of the molecular structure along with the atom numbering scheme is shown in Fig. 1.

The macrocycle adopts *trans*-III stereochemistry where the two six-membered chelate rings are in the chair form and the two five-membered rings are in the *gauche* form.[28] The presence of one of the methyl groups, C(14), in the axial position on the six-membered chelate ring makes the chair unstable while the methyl group on the other ring is in the stable equatorial position. The hydroxyethyl group and the methyl group [C(14)] on the six-membered chelate ring are *anti* with respect to the plane while the methyl group [C(11)] on the other six-membered chelate ring and hydroxyethyl groups are *syn* to each other.

There is extensive hydrogen bonding where the protons of the pendant hydroxyethyl groups are bonded to the oxygen atoms of the two perchlorate ions and the O···O distances are

Table 1 Selected bond lengths (Å) and angles (°) for $[\mathrm{Cu(H_2L^2)}][\mathrm{ClO_4}]_2$ **1** and $[\mathrm{CuL^3}][\mathrm{ClO_4}]_2$ **2**

1			
Cu–N(1)	2.008(5)	Cu–N(2)	2.054(8)
Cu–N(3)	2.011(5)	Cu–N(4)	2.098(8)
Cu–O(1)	2.535(5)	Cu–O(2)	2.603(5)
N(1)–Cu–N(2)	87.2(2)	N(2)–Cu–N(3)	94.0(2)
N(1)–Cu–N(4)	93.3(2)	N(3)–Cu–N(4)	85.7(2)
O(1)–Cu–N(1)	94.8(2)	O(1)–Cu–N(2)	77.7(2)
O(1)–Cu–N(3)	82.9(2)	O(1)–Cu–N(4)	107.5(2)
O(2)–Cu–N(1)	80.6(2)	O(2)–Cu–N(2)	99.7(2)
O(2)–Cu–N(3)	101.7(2)	O(2)–Cu–N(4)	75.2(2)
N(1)–Cu–N(3)	177.1(3)	N(2)–Cu–N(4)	174.7(4)
O(1)–Cu–O(2)	174.9(2)		
2			
Cu–N(1)	1.976(3)	Cu–N(2)	2.079(3)
N(1)–Cu–N(2)	87.1(1)	N(1)–Cu–N(2′)	97.3(1)
N(1)–Cu–N(1′)	159.4(2)	N(2)–Cu–N(2′)	155.7(2)

Symmetry transformation used to generate equivalent atoms: (′) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$.

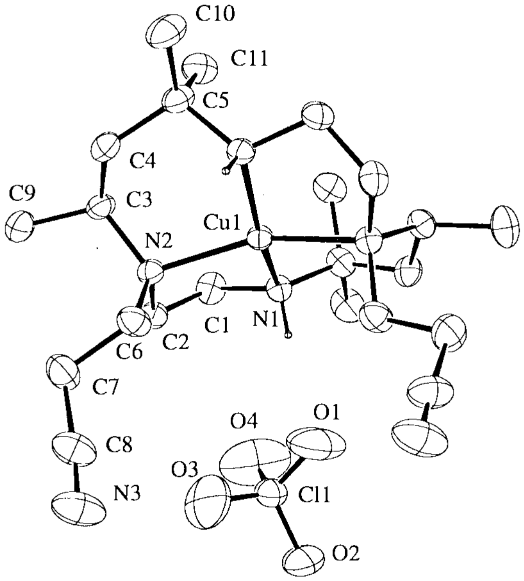


Fig. 2 An ORTEP drawing of the molecular structure of $[\mathrm{CuL^3}][\mathrm{ClO_4}]_2$ **2** along with the atom numbering scheme.

2.815(7) and 2.768(8) Å; H(1)–O(1) ··· O(3) 2.038 Å and H(1)–O(2) ··· O(7) 1.976 Å. The protons of the secondary amines form weak bifurcated hydrogen bonds with the oxygen atoms of hydroxyethyl groups and with perchlorate oxygens atoms and the N ··· O distances are in the range 3.017(8)–3.468(9) Å and the N–H ··· O angles are between 116.8 and 149.8°; H(1)–N(1) ··· O(2) 2.467, H(1)–N(1) ··· O(9) 2.657 and H(1)–N(3) ··· O(1) 2.514, H(1)–N(3) ··· O(4) 2.489 Å.

Thus crystal structure determination of the complex confirmed a six-co-ordinate geometry involving pendant hydroxyethyl groups rather than the proposed square planar geometry without involving pendant donors.[29]

$[\mathrm{CuL^3}][\mathrm{ClO_4}]_2$ 2. The crystal structure analysis of this complex (Fig. 2) shows the macrocycle in the *trans*-I stereochemistry[28] where the two six-membered chelate rings are in stable chair form and the two five-membered rings are in the eclipsed conformation. The four nitrogen atoms of the macrocylic ligand co-ordinate the metal ion in a distorted square planar geometry. The Cu–N bond lengths and the N–Cu–N bond angles of the five-membered chelate rings are in the expected range while the bond angles of the six-membered rings are slightly widened (97.3°) (Table 1). The N–Cu–N′ *trans* angles show large deviations from normal values (159.4(4)°). The least squares plane calculations shows the four nitrogen atoms to be deviated from the plane by ±0.39 Å. The methyl groups [C(9) and C(9′)] on the six-membered chelate rings are in the stable equatorial position and *syn* to the cyanoethyl groups.

Table 2 Selected bond lengths (Å) and angles (°) for $[\mathrm{CuL^5}]\mathrm{ClO_4}$ **4**

Cu–N(1)	2.067(5)	Cu–N(2)	2.011(6)
Cu–N(3)	2.001(5)	Cu–N(4)	2.011(6)
Cu–O(1)	2.252(4)		
N(1)–Cu–N(2)	88.1(2)	N(2)–Cu–N(3)	94.2(2)
N(1)–Cu–N(4)	93.5(2)	N(3)–Cu–N(4)	88.8(2)
O(1)–Cu–N(1)	77.7(2)	O(1)–Cu–N(2)	99.1(2)
O(1)–Cu–N(3)	90.5(2)	O(1)–Cu–N(4)	103.0(2)
N(1)–Cu–N(3)	168.2(2)	N(2)–Cu–N(4)	157.7(2)

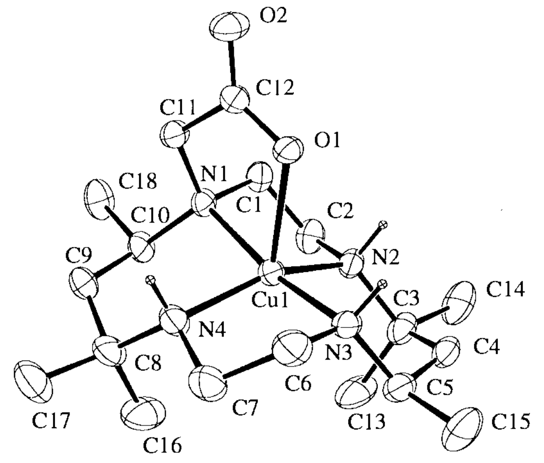


Fig. 3 An ORTEP drawing of the molecular structure of $[\mathrm{CuL^5}]\mathrm{ClO_4}$ **4** along with the atom numbering scheme.

$[\mathrm{CuL^5}]\mathrm{ClO_4}\cdot\mathrm{HClO_4}\cdot\frac{1}{2}\mathrm{HClO_4}\cdot\frac{1}{3}\mathrm{HClO_4}\cdot\frac{1}{6}\mathrm{H_2O}$ 4. The ORTEP drawing of the complex is in Fig. 3. The metal ion is co-ordinated by the nitrogen atoms of the macrocycle in the equatorial plane and the oxygen atom of the pendant carboxylate group at the apical position. The macrocycle is in the *trans*-I configuration[28] with the two five-membered rings in the eclipsed form. In the analogous mono *N*-acetato macrocyclic complex reported by our group recently the macrocycle adopted the *trans*-III configuration with all the four chelate rings in the stable form.[30]

The metal ion lies on the plane with the four nitrogen atoms deviating by ±0.30(3) Å from the mean plane. The Cu–N (tertiary) bond distance of 2.067(5) Å is longer than the Cu–N (secondary) bond distances. The Cu–O (axial) bond length of 2.252(4) Å is much longer than the Cu–N (equatorial) bonds. The N–Cu–N bond angles of five- and six-membered rings are in the expected range, but the N(4)–Cu–O(1) and N(1)–Cu–O(1) and the *trans* angles show large deviations from the ideal values (Table 2) making the geometry distorted square-pyramidal.

$[\mathrm{CuL^8}][\mathrm{ClO_4}]_2$ 6. The ORTEP drawing (Fig. 4) shows the complex cation on a center of symmetry. Unlike in complex **2**, here the macrocycle adopts the stable *trans*-III stereochemistry.[28] The metal ion is in a square planar geometry, co-ordinated by the four nitrogen atoms of the ring. The two Cu–N bonds where N is attached to the cyanoethyl groups are slightly longer (2.160(2) Å) than the other two Cu–N bonds (2.023(2) Å). The N–Cu–N bond angles of the five- and six-membered rings are in the expected range (Table 3). In this

Table 3 Selected bond lengths (Å) and angles (°) for $[CuL^8][ClO_4]_2$ **6** and $[Cu(H_2L^9)][ClO_4]_2 \cdot 2H_2O$ **7**

6			
Cu–N(1)	2.023(2)	Cu–N(2)	2.160(2)
N(1)–Cu–N(2)	86.9(1)	N(1)–Cu–N(2′)	93.1(1)
N(1)–Cu–N(1′)	180.0	N(2)–Cu–N(2′)	180.0
7			
Cu–N(1)	2.072(4)	Cu–N(2)	2.110(3)
Cu–O(2)	2.319(3)		
N(1)–Cu–N(2)	86.9(1)	N(1)–Cu–N(2′)	93.1(1)
N(1)–Cu–O(2)	87.6(1)	N(2)–Cu–O(2)	78.8(1)
O(2)–Cu–N(1′)	92.4(1)	O(2)–Cu–N(2′)	101.2(1)
O(2′)–Cu–N(2′)	101.2(1)	O(2)–Cu–O(2′)	180.0
N(1)–Cu–N(1′)	180.0	N(2)–Cu–N(2′)	180.0

Symmetry transformation used to generate equivalent atoms: (′) $-x$, $-y$, $-z$.

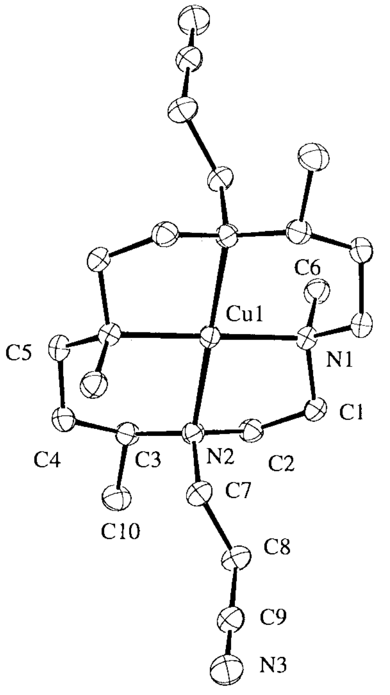


Fig. 4 An ORTEP drawing of the molecular structure of $[CuL^8]$-$[ClO_4]_2$ **6** along with the atom numbering scheme.

structure also the methyl groups on the six-membered chelate ring and cyanoethyl groups are *syn* to each other.

$[Cu(H_2L^9)][ClO_4]_2 \cdot 2H_2O$ 7. The ORTEP drawing of the molecular structure of the complex cation (Fig. 5) shows the metal ion in *trans*-octahedral geometry, co-ordinated by the four nitrogen atoms of the macrocycle in the equatorial plane and the two carbonyl oxygen donors rather than the usual carboxylate oxygens at the apical positions. This is clearly revealed by the comparison of the bond distances. The Cu–O(2) bond length is 2.319(3) Å and is comparable with the Cu–O bond distances of macrocycles bearing *N*-acetic acid groups.[14,31] However, the C(8)–O(2) bond distance is 1.206(5) Å and C(8)–O(1) 1.295(5) Å. These distances are shorter and longer respectively than the C–O bond distances (1.257(6) and 1.249(6) Å) found in macrocyclic complexes containing these pendant *N*-acetate groups.[14,31] Moreover C(8)–O(2) is typical of a localized C=O double bond and distinctly shorter than the C(8)–O(1) bond. These bond lengths are quite similar to the C=O and C–O single bond distances in the free ligand appended with pendant *N*-acetic acid groups.[15] All these comparisons confirm that the metal ion is co-ordinated by the carbonyl oxygen atoms.[32]

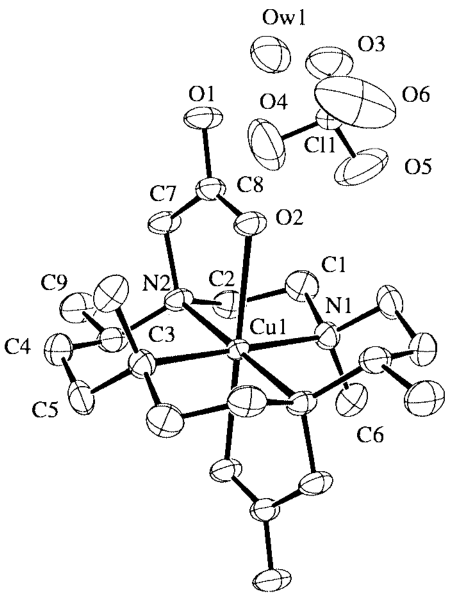


Fig. 5 An ORTEP drawing of the molecular structure of $[Cu(H_2L^9)]$-$[ClO_4]_2 \cdot 2H_2O$ **7** along with the atom numbering scheme.

The Cu–N(CH_2CO_2H) bond distance of 2.110(3) Å is longer than the Cu–N(CH_3) bond distance (2.072(4) Å) and this is due to the electron-attracting inductive effect of the acetic acid groups. The N–Cu–N angles of the five- and six-membered rings are typical of 14 membered tetraaza macrocyclic complexes and all the other angles around the metal ion are in the expected range. Selected bond distances and angles are given in Table 3.

The hydrogen atoms attached to O(1) and those of the water molecule were located in the Fourier difference map. There is a hydrogen bonding interaction between the hydrogen atoms of the water molecule and the carboxyl oxygen atom (the O···O distance is 2.538(5) Å, H(1)O(1)···O(W) 1.52 Å and the angle is 177.7°) and the water molecule is also involved in hydrogen bonding with the oxygen atom of the perchlorate ion.

Thus unlike in other polyaza macrocyclic complexes, the di-*N*-acetic acid pendant arms co-ordinate the metal ion through the carbonyl oxygen atoms rather than the common carboxylate oxygen atoms which remain protonated.

Spectral data of the complexes

The infrared spectrum of complex **1** shows the O–H stretching of the pendant arms at 3360 cm^{-1}. Complexes **2** and **6** showed $\nu(C \equiv N)$ stretching at 2250 cm^{-1}. The $\nu(CO_2^-)$ of complexes **4** and **5** was observed at ≈1630 cm^{-1} while **7** showed a sharp band at 1680 cm^{-1} corresponding to C=O stretching. In addition to these bands, all the complexes showed ν(N–H) of the co-ordinated secondary amines (except **6** and **7**) in the range of ≈3200 to ≈3230 cm^{-1} and broad bands corresponding to ionic perchlorates (except **5**) at ≈1100 cm^{-1}.

The electronic spectrum of complex **1** exhibited a broad band at 540 nm rather similar to the spectra of the square planar complexes of di-*N*-alkylated 14-membered tetraaza macrocyces.[13] This is due to the Jahn–Teller effect operative on the d^9 metal ion and also confirmed from the structure of the complex which shows two long *trans*-axial Cu–O bonds relative to the short equatorial Cu–N bonds. Complexes **2** and **6** showed broad bands at 548 nm and at 602 nm respectively. Complex **3** also exhibited a broad band at 530 nm close to that of **1**. Based on the spectral data and by analogy, octahedral geometry is proposed for complex **3** with the amino groups of the pendant

Table 4 Electronic spectral[a] and cyclic voltammetric data[b]

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Cu^{II}–Cu^{I} $E_{1/2}$/V (ΔE/mV)
$[Cu(H_2L^2)][ClO_4]_2$	540 (124)	−0.45 (180)
$[CuL^3][ClO_4]_2$	548 (621)	−0.05 (62)
$[CuL^4][ClO_4]_2$	530 (630)	—
$[CuL^5]ClO_4$	630 (144)	−0.97 (70)
$[CuL^6]$	608 (110)	−1.55 (175)
$[CuL^8][ClO_4]_2$	602 (206)	−0.15[c]
$[Cu(H_2L^9)][ClO_4]_2$	622 (27)	−0.98 (185)

[a] In water. [b] In CH_3CN at 298 K using 0.1 mol dm^{-3} NBu_4ClO_4 as supporting electrolyte at a platinum working electrode with Ag–AgCl as reference electrode. [c] Irreversible.

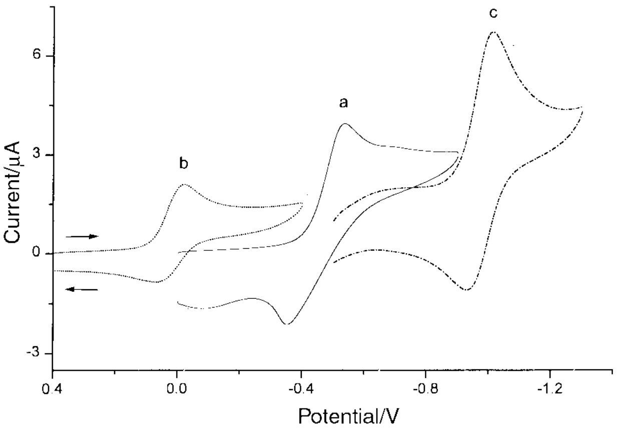


Fig. 6 Cyclic voltammograms at 298 K in CH_3CN solvent (0.1 mol dm^{-3} NBu_4ClO_4, Ag–AgCl reference electrode) at a platinum working electrode of complexes **1** (*a*), **2** (*b*) and **4** (*c*) at a scan rate of 100 mV s^{-1}.

arms in the *trans*-axial position. The spectral data of the complexes are presented in Table 4.

Redox properties of the complexes

The cyclic voltammetric studies of all the complexes were carried out in acetonitrile solvent at a platinum electrode. The copper(II) complexes of tetraaza macrocyclic ligands generally exhibit irreversible redox waves.[26] However most of the present set of complexes exhibited reversible to quasireversible redox waves corresponding to the reduction of Cu^{II} to Cu^{I}. Complex **1** exhibited a quasireversible peak at −0.45 V while **2** and **6** showed reversible and irreversible peaks respectively at −0.05 and −0.15 V. Macrocycle L^3 stabilizes the copper(I) oxidation state by almost 700 mV compared to the parent macrocycle L^1.[33] Relative to complex **2**, the redox process in **6** is shifted towards more cathodic potential due to the presence of electron donating methyl groups on the nitrogen atoms of the ring and the planar configuration of the macrocycle. The cyclic voltammograms of complexes **1**, **2** and **4** are shown in Fig. 6.

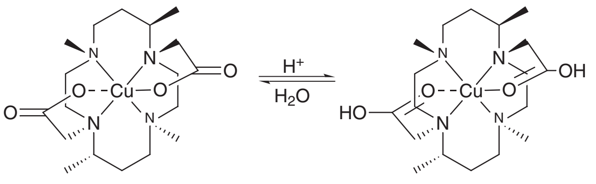
Ligands HL^5, H_2L^6 and H_2L^9 containing pendant acetic acid groups stabilize the copper(II) oxidation state. Complex **4** gave a reversible peak at −0.97 V. Complexes **5** and **7** exhibited quasireversible redox couples at −1.55 and at −0.98 V respectively. Comparison of the redox data of **5** and **7** shows that the copper(I) state is stabilized by almost 600 mV in **7** where the metal ion is co-ordinated by carbonyl oxygen atoms, *i.e.* the redox process in complex **5** is shifted towards more cathodic potential because of increase in the electron density due to the co-ordination of the metal ion with the electron rich carboxylate oxygen atoms leading to the stabilization of copper(II) state. Complex **3** exhibited only an ill defined peak probably corresponding to the ligand reduction and no metal centered reduction peak was observed. The $E_{1/2}$ values of the complexes are given in Table 4.

Co-ordination geometry changes of complexes 4, 5 and 7 in solution

The electronic spectrum of complex **4** in water exhibited a broad band at 630 nm. However addition of strong acids (0.1 M) such as perchloric to an aqueous solution of **4** shifts the band to shorter wavelength (565 nm). This spectrum is similar to those of the square-planar complexes, indicating protonation of the pendant arm resulting in the metal ion being co-ordinated by only the four nitrogen atoms of the macrocyclic ligand. In basic aqueous solutions (0.1 to 5 M) the spectra are essentially the same as that in pure water. This indicates that this complex exists as a five-co-ordinated species in solution also and that hydroxide ion is not involved in co-ordination even under the high basic conditions.

The pH dependent co-ordination geometry change was also accompanied by change in the electrochemical behavior. As discussed in the previous section complex **4** exhibits a reversible couple at −0.97 V in acetonitrile. When concentrated sulfuric acid was successively added to this solution a new couple at −0.17 V was observed with the couple at −0.97 V slowly disappearing. This potential is close to those of complexes **2** and **6**, where the macrocycle has non-co-ordinating electron withdrawing pendant arms. This couple probably corresponds to the square planar complex without involving an acetate donor.

Complexes **5** and **7** exhibited broad bands at 608 and 622 nm respectively in aqueous solutions. However in 0.1 M $HClO_4$ solution these bands are shifted to lower wavelength at 585 and 595 nm respectively. Interestingly no further spectral changes were observed and the spectra were essentially the same in 0.1 to 5 M solutions. Further the spectrum of complex **7** was similar to that measured in Nujol mull. In basic solution also the complexes exhibited bands at 608 and 622 nm only. These results indicate that in pure water complex **7** also exists in the deprotonated form, $[CuL^9]$ (Scheme 1), like **5**. However in acidic solutions, both the complexes exist in the protonated form, $[Cu(H_2L^5)][ClO_4]_2$ and $[Cu(H_2L^9)][ClO_4]_2$, where the pendant acetic acid group co-ordinates the metal ion through the carbonyl oxygen atom. The studies also reveal that unlike in complex **4** the acetic acid groups are not removed from the co-ordination sphere even in strong acid solutions to give square planar complexes.



Scheme 1 Structural rearrangement of $[Cu(H_2L^9)][ClO_4]_2$ in aqueous solution.

Kinetic studies

The dissociation kinetics of complexes **2** and **6** were studied in aqueous HCl and NaCl solutions. The reactions were found to occur in a single stage and with the rate equation (1). No

$$-d[CuL^{2+}]/dt = k_{obs}[CuL^{2+}] \qquad (1)$$

significant amounts of intermediates were formed in the solutions and the complexes dissociated with the observed pseudo-first-order rate constants showing an acid dependence as given in eqns. (2) and (6).

The plot of observed rate constants of complex **2** *vs.* $[H^+]$ (Fig. 7) gave a curve concave to the axis of the rate constant and passing through the origin. A plot of k_{obs} *vs.* $[H^+]^2$ gave a straight line and the rate law (2). The value of k obtained

$$k_{obs} = k[H^+]^2 \qquad (2)$$

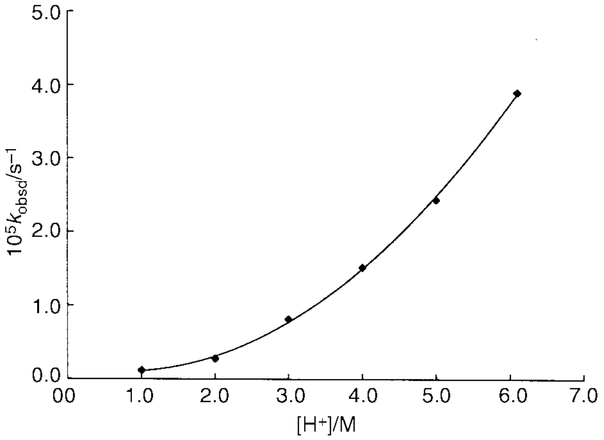


Fig. 7 Plot of k_{obs} *vs.* [H$^+$] for the dissociation of complex **2** at 25.0 ± 0.1 °C and $I = 5.0$ mol dm^{-3} (NaCl + HCl). The circles are the experimental results; the line is calculated from $k_{obs} = k_{67}K_{16}[H^+]^2$ with $k_{67}K_{16} = 1.10 \times 10^{-6}$ dm^6 mol^{-2} s^{-1}.

from the slope of this plot is 1.10×10^{-6} dm^6 mol^{-2} s^{-1}. The experimental rate law is in agreement with the mechanism [Scheme 2 and eqns. (3)–(5)]. For this mechanism the simple rate

$$\mathbf{i} + H^+ \xrightleftharpoons{K_{16}} \mathbf{vi} \qquad (3)$$

$$\mathbf{vi} + H^+ \xrightarrow{k_{67}} \mathbf{vii} \qquad (4)$$

$$\mathbf{vii} \xrightarrow{\text{fast}} \text{products} \qquad (5)$$

law $k_{obs} = k_{67}K_{16}[H^+]^2$ holds good with $k_{67}K_{16} = 1.10 \times 10^{-6}$ dm^6 mol^{-2} s^{-1}. Since there was no detectable intermediate found during the course of dissociation, $[Cu(HL^3)]^{3+}$ **v** is relatively unstable compared to $[CuL^3]^{2+}$. In the monoprotonated intermediate **v** the distance between the non-co-ordinated protonated amine and the metal ion is very small due to the cyclic constraints of the macrocycle. The instability of this species is due to the large electrostatic and inductive effects of copper(II) ion. Owing to the cyclic constraints of the ligand as well as the steric effects of the six methyl groups and the two cyanoethyl groups, the unco-ordinated donor atom in species **vi** is strongly restricted and unable to move out of the first co-ordination sphere. In this case the presence of acid has a very important effect and as a consequence the protonation pathway (4) is more important than the solvation pathway, **vi** + $H_2O \longrightarrow$ **ix**.

For complex **6** the plot of observed rate constant *vs.* [H$^+$] is a straight line (Fig. 8). This reaction obeys the simple rate law (6).

$$k_{obs} = k_H[H^+] + k_d \qquad (6)$$

The values of k_H and k_d obtained from the slope and intercept of the plot are 1.47×10^{-6} dm^3 mol^{-1} s^{-1} and 2.36×10^{-6} s^{-1} respectively. The quotient $k_H/k_d = 0.623$ dm^3 mol^{-1} represents the relative rate of dissociation by the protonation and solvation pathways. The experimental rate law is in accordance with the mechanism (Scheme 2) in eqns. (7)–(11). For this

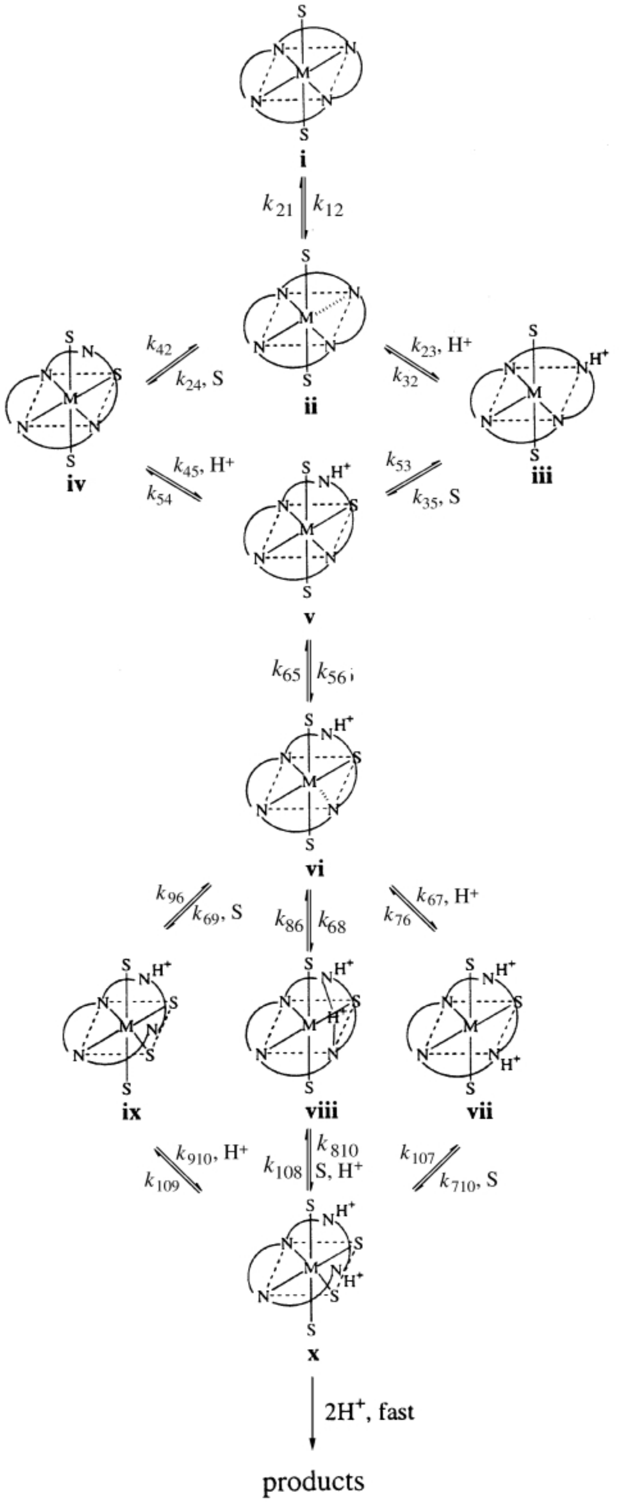
$$\mathbf{i} \xrightleftharpoons{K_{12}} \mathbf{ii} \qquad (7)$$

$$\mathbf{ii} + H^+ \xrightarrow{k_{23}} \mathbf{iii} \qquad (8)$$

$$\mathbf{iii} \xrightarrow{\text{fast}} \text{products} \qquad (9)$$

$$\mathbf{ii} + S \xrightarrow{k_{24}} \mathbf{iv} \qquad (10)$$

$$\mathbf{iv} \xrightarrow{\text{fast}} \text{products} \qquad (11)$$



Scheme 2 Proposed mechanism for the acid-catalysed dissociation of complexes **2** and **6** (S = solvent).

mechanism the simple rate law $k_{obs} = k_{23}K_{12}[H^+] + K_{12}k_{24}$ holds good where $k_{23}K_{12}$ is 1.47×10^{-6} dm^3 mol^{-1} s^{-1} and $K_{12}k_{24}$ is 2.36×10^{-6} s^{-1}. In this complex both solvation and protonation contributed to the rate as the unco-ordinated donor atom in **ii** is relatively less restricted as compared to **vi** and is able to move out of the first co-ordination sphere.

Conclusion

A new di-*N*-hydroxyethylated tetraaza macrocycle has been synthesized easily in one step by reaction of L^1 with ethylene oxide. The crystal structure of its copper complex showed that the oxygen atoms of the pendant arms co-ordinate the metal

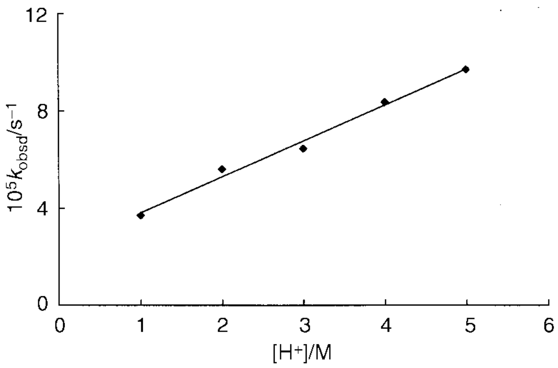


Fig. 8 Plot of k_{obs} *vs.* $[H^+]$ for the dissociation of complex **6** at 25.0 ± 0.1 °C and $I = 5.0$ mol dm^{-3} (NaCl + HCl). The circles are the experimental results; the line is calculated from $k_{obs} = k_{23}K_{12}[H^+] + k_{24}K_{12}$ with $k_{23}K_{12} = 1.47 \times 10^{-6}$ dm^3 mol^{-1} s^{-1} and $k_{24}K_{12} = 2.36 \times 10^{-6}$ s^{-1}.

ion to give a tetragonally elongated octahedral geometry. Complexes have also been synthesized and studied from other N-functionalized macrocycles. The structure of the copper(II) complex of that containing two pendant *N*-acetic acid groups, H_2L^9, showed carbonyl oxygen rather than the usual carboxylate oxygen co-ordination. Redox studies of the complexes revealed that macrocycles L^3 and L^8 highly stabilize the copper(I) oxidation state. Complex **4** showed a square pyramidal to square planar geometry change, while **5** and **7** exhibited a carboxylate to carbonyl oxygen co-ordination change from aqueous to acidic aqueous solutions.

Acknowledgements

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