New 1,4,7,10-Tetraazacyclotridecane-11,13-dione Ligands appended with Additional Donor(s) 8-Methylquinoline(s): Crystal Structures and Characterization of their Copper(II) Complexes†

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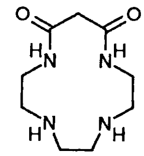
Two macrocyclic dioxotetraamine ligands 4-(quinolin-8-ylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (H_2L^1) and 4,7-bis(quinolin-8-ylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (H_2L^2) have been synthesized. The resulting dioxomacrocycles readily co-ordinate Cu^{2+} with concomitant double deprotonation of the ligands. The solution behaviour of the copper(II) complexes [CuL^1] **1** and [CuL^2] **2** has been studied by ESR, UV/VIS and cyclic voltammetric techniques. Remarkable red shifts were observed for the absorption band maxima of the electronic spectra of these copper(II) complexes (598 nm for **1** and 600 nm for **2**) in comparison to that of unsubstituted (1,4,7,10-tetraazacyclotridecane-11,13-dione)copper(II) species (516 nm). The crystal structures of **1** and **2** (which crystallised in the form [$(CuL^2)_2$]·$3H_2O$·MeCN) have been determined by X-ray diffraction analysis. Crystallographic data: **1**, orthorhombic, space group *Pcab*, $a = 16.260(3)$, $b = 7.739(2)$, $c = 27.530(9)$ Å, $Z = 8$, $R' = 0.061$ for 2594 observed reflections with $I > 3\sigma(I)$; **2**, triclinic, space group $P\bar{1}$, $a = 12.288(3)$, $b = 14.734(4)$, $c = 18.005(4)$ Å, $\alpha = 102.26(2)$, $\beta = 104.26(2)$, $\gamma = 107.02(2)°$, $Z = 2$, $R' = 0.090$ for 2284 observed reflections with $I > 3\sigma(I)$. In complex **1**, the Cu atom is five-co-ordinate and forms a distorted square pyramid in which N(11) of the quinoline pendant is at the apical site. The Cu–N(11) bond [2.266(3) Å] is longer than the basal Cu–N bond lengths [average 1.985(3) Å]. In complex **2**, the Cu^{II} centre is also five-co-ordinate, with one of the quinoline pendants co-ordinating to Cu^{II} from the apical position and the other pendant remaining unco-ordinated.

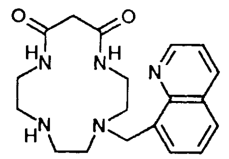
Macrocyclic dioxotetraamines H_2L have received much attention and have been extensively studied in recent years.[1–5] Such ligands are unique chelators for transition-metal ions, such as Cu^{II}, Ni^{II}, Co^{II} and Pt^{II} with simultaneous dissociation of the two amide protons, giving neutral complexes designated as $[M^{II}L]^0$ (L is the doubly deprotonated ligand).[1,2] Macrocyclic oxotetraamines bear dual structural features of macrocyclic tetraamines and oligopeptides and can stabilize higher oxidation states of some of these ions.[1,2a,6,7] These properties have been applied to superoxide dismutase-like catalysts.[8] Furthermore, some of these compounds have been used as metal-ion carriers.[2g,h]

So far, great effort has been made in the incorporation of functionalized pendant groups into a saturated macrocyclic tetraamine structure (*e.g.* cyclam = [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane) to modify its conformational and redox properties of the metal complexes.[9] However, up to now, only a few examples of the macrocyclic dioxotetraamines bearing functionalized pendant groups have been reported.[2j,k,10,11] Furthermore, most of them have been concerned with chemistry in solution. To our knowledge, only the crystal structures of the platinum(II) complexes of the monocyclic dioxotetraamine (1,4,8,11-tetraazacyclotetradecane-5,7-dione or dioxocyclam) have been reported.[2i]

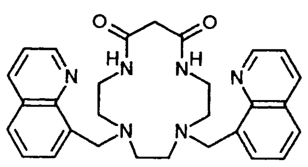
Herein, we report the synthesis and characterization of two new macrocyclic dioxotetraamine ligands bearing one and two quinolines as additional donor pendant(s), H_2L^1 and H_2L^2, and their complexation properties with Cu^{II} as well as the crystal structures of the copper(II) complexes, **1** and **2**. To our knowledge, this is the first report of crystal structures for 1,4,7,10-tetraazacyclotridecane-11,13-dione (dioxo[13]aneN_4) complexes.



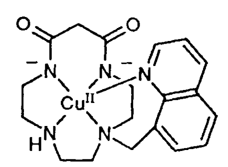
H_2L



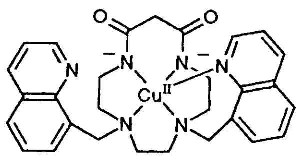
H_2L^1



H_2L^2



1 [$Cu^{II}L^1$]



2 [$Cu^{II}L^2$]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
Non-SI unit employed: G = 10^{-4} T.

Experimental

Materials and General Methods.—Most starting materials and solvents for syntheses were obtained commercially and purified by standard methods prior to use. The ligand H_2L, 1,4,7,10-tetraazacyclotridecane-11,13-dione, was prepared according to a modified literature method.[12] *N*-Bromosuccinimide (nbs) was recrystallized from distilled water, 8-Methylquinoline was purchased from BDH (England) and used without further purification. All the other reagents for syntheses and analyses were of analytical grade. The FT-IR spectra were recorded on a 170SX (Nicolet) spectrometer, EI-mass spectra (MS) on a VG ZAB-HS instrument. Elemental analysis was performed on a P-E 240C analyzer. Proton NMR spectra were recorded on a Bruker AC-P 200 spectrometer (200 MHz, 25 °C, in $CDCl_3$, with tetramethylsilane as the internal reference) and electronic absorption spectra were measured on a Shimadzu UV-240 spectrophotometer.

Syntheses of 4-(*Quinolin*-8-*ylmethyl*)-1,4,7,10-*tetraazacyclotridecane*-11,13-*dione* (H_2L^1) *and* 4,7-*Bis*(*quinolin*-8-*ylmethyl*)-1,4,7,10-*tetraazacyclotridecane*-11,13-*dione* (H_2L^2).—8-Methylquinoline (**3**, 3.6 g, 42 mmol), nbs (7.5 g, 42 mmol), and azobis(isobutyronitrile) (aibn, 50 mg) were dissolved in deoxygenated CCl_4 (40 cm^3). The resulting mixture was heated at reflux for *ca.* 36 h under Ar. After filtration and evaporation, the residue was treated with cyclohexane. 8-Bromomethylquinoline **4** was isolated as yellowish crystals. It was further purified by recrystallization from cyclohexane (6 g, 80%), m.p. 79.0–80.0 °C. ^1H NMR ($CDCl_3$): δ 5.25 (2 H, s), 7.41–7.55 (2 H, m), 7.79–7.82 (2 H, m), 8.14–8.19 (1 H, m) and 9.02 (1 H, s) (Found: C, 53.85; H, 3.50; N, 6.25. $C_{10}H_8BrN$ requires C, 54.10; H, 3.65; N, 6.30%).

For the synthesis of H_2L^1, a solution of **4** (650 mg, 2.93 mmol) in deoxygenated dimethylformamide (dmf) (20 cm^3) was added dropwise to a solution of H_2L (2.5 g, 11.7 mmol) in deoxygenated dmf (80 cm^3) in the presence of an excess amount of fine dried K_2CO_3 at *ca.* 80 °C. The resulting reaction mixture was heated at 80 °C for 10 h under Ar. After filtration of the reaction mixture, the filtrate was evaporated to dryness and then dissolved in water and then extracted with $CHCl_3$. The combined $CHCl_3$ solution was dried and evaporated, and then the residue was purified by column chromatography on silica gel by eluting with CH_2Cl_2–MeOH–NH_3(aq) (100:5:1). The product was finally recrystallized from CH_2Cl_2–MeCN as colourless needles (1.66 g, 40%). M.p. 142–144 °C, ^1H NMR ($CDCl_3$): δ 2.56–2.70 (8 H, m), 3.29 (2 H, m), 3.62 (2 H, qnt), 4.22 (2 H, s), 7.41–7.78 (4 H, m), 8.15–8.20 (1 H, m) and 8.92–8.95 (1 H, m). IR (KBr pellet): 614, 789, 1312, 1562, 1626; 1667, 2834, 2933 (C=O); and 3297 (NH) cm^{-1}. EI-MS: *m*/*z* 355 (*M* 355.44) (Found: C, 64.00; H, 6.85; N, 19.40. $C_{19}H_{26}N_5O_2$ requires C, 64.20; H, 7.10; N, 19.70%).

When 4 equivalents of **4** were used in the above reaction, H_2L^2 was obtained as colourless prisms (2.32 g, 40%). ^1H NMR ($CDCl_3$): δ 2.32–2.42 (8 H, m), 3.19–3.21 (4 H, m), 3.44 (2 H, s), 4.09 (4 H, s), 7.40–7.60 (6 H, m), 7.72–7.76 (2 H, m), 8.14–8.19 (2 H, m) and 8.86–8.90 (2 H, m). IR (KBr pellet): 786, 833, 1500, 1522, 1560, 1652; 1678, 2792, 3066 (C=O); and 3262 (NH) cm^{-1}, EI-MS: *m*/*z* 496 (*M* 496.61) (Found: C, 70.40; H, 6.35; N, 16.70. $C_{29}H_{32}N_6O_2$ requires C, 70.15; H, 6.50; N, 16.90%).

Preparation of [CuL^1] **1** *and* [CuL^2] **2**.—The complex [CuL^1] **1** was obtained by mixing a 1:1 molar ratio of $Cu(MeCO_2)_2$ and H_2L^1 in deoxygenated MeOH under reflux for 15 min. The blue reaction mixture was filtered and evaporated under Ar. The residue was then treated with MeCN. A crystal suitable for X-ray analysis was obtained from an MeCN–MeOH solution. IR (KBr pellet): 3400, 3164, 2921, 2872, 2832, 1578 (C=O), 1419, 1348 and 788 cm^{-1} (Found: C, 55.00; H, 5.40; N, 17.10. $C_{19}H_{23}CuN_5O_2$ requires C, 54.75; H, 5.55; N, 16.80%). The complex [CuL^2] **2** was obtained in a similar manner to that for complex **1** and crystallised in the form $[(CuL^2)_2]\cdot 3H_2O\cdot MeCN$. IR (KBr pellet): 3400, 2941, 2840, 1588 (C=O), 1461, 1380, 1075, 835 and 797 cm^{-1} (Found: C, 59.20; H, 5.60; N, 15.35. $C_{58}H_{60}Cu_2N_{12}O_4\cdot 3H_2O\cdot CH_3CN$ requires C, 59.50; H, 5.75; N, 15.05%).

ESR Studies.—ESR spectra were measured on a Bruker ER-200-D-SRC10 spectrophotometer. Methanol solutions of copper(II) complexes (obtained by mixing equimolar amounts of ligand and $Cu(NO_3)_2$, and 2 equivalents of NaOH for the neutralization of two dissociable amide protons) were prepared and spectra recorded at 298 and 112 K.

Electrochemical Studies.—Cyclic voltammetry (CV) measurements were performed with a PARC model 273 electrochemical apparatus in aqueous solution at 25.0 ± 0.05 °C with 0.50 mol dm^{-3} Na_2SO_4 as supporting electrolyte and the solution was bubbled with pure Ar gas. The concentrations of the complexes of **1** and **2** were kept at 2×10^{-3} and $\approx 1 \times 10^{-3}$ mol dm^{-3}, respectively. The pH was adjusted with concentrated NaOH or H_2SO_4 solution. The cyclic voltammograms at a scan rate of 100 or 200 mV s^{-1} were evaluated graphically. A three-electrode system was employed: glassy carbon as working electrode, saturated calomel electrode (SCE) as a reference and Pt coil as counter electrode.

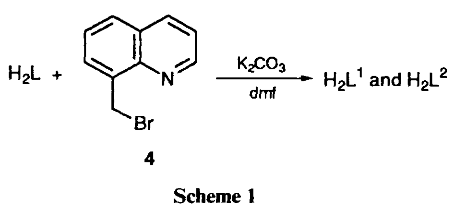
Crystallographic Studies.—Crystals were mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite-crystal monochromater situated in the incident beam for data collection. Unit-cell dimensions were obtained by least-squares refinements using 25 reflections. For **2**, a total of 7249 independent reflections were collected, of which, however, only 2284 reflections with $I > 3\sigma(I)$ could be considered to be observed and used because the crystal obtained was very thin in one dimension and the intensities of reflections in this dimension were lost. We tried to prepare better crystals of complex **2** using many solvents and procedures but failed. For both complexes, the correction for L_p factors was applied to the data, and the structures were solved by direct methods (MULTAN 82[13]). The Cu atom was located from *E*-maps. The other non-hydrogen atoms were located by successive Fourier difference syntheses. The final refinement was by full-matrix least-square methods with anisotropic thermal parameters for non-hydrogen atoms and converged with unweighed and weighted (unit weights for all observed reflections) agreement factors of 0.051 and 0.061 for **1**, and 0.081 and 0.090 for **2**, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis of Ligands.—The ligands were prepared according to Scheme 1. 8-Bromomethylquinoline **4** was easily isolated as crystals from cyclohexane in 80% yield after the reaction of 8-methylquinoline **3** with an equimolar amount of nbs in the presence of aibn in CCl_4 for *ca.* 36 h.

For the preparation of H_2L^1, **4** and an excess amount of H_2L were used to obtain the monoalkylated product. The main product H_2L^1 was purified by silica-gel column chromatography and recrystallized from CH_2Cl_2–MeCN as colourless



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Scheme 1

Table 1 Crystal data and data collection summary for complexes **1** and **2***

Compound	**1**	**2**
Formula	$C_{19}H_{23}CuN_5O_2$	$(C_{29}H_{30}CuN_6O_2)_2{\cdot}3H_2O{\cdot}MeCN$
M_r	416.97	1211.38
Crystal system	Orthorhombic	Triclinic
Space group	*Pcab*	$P\bar{1}$
a/Å	16.260(3)	12.288(3)
b/Å	7.739(2)	14.734(4)
c/Å	27.530(9)	18.005(4)
α/°	90	102.26(2)
β/°	90	104.26(2)
γ/°	90	107.02(2)
U/Å^3	3464(3)	2875(3)
Z	8	2
D_c/g cm^{-3}	1.595	1.388
μ(Mo-Kα)/cm^{-1}	12.88	8.04
F(000)	1736	1268
Crystal dimensions (mm)	0.2 × 0.2 × 0.3	0.1 × 0.2 × 0.3
Total reflections collected	5348	8113
Independent reflections (R_{int})	4808 (0.025)	7249 (0.062)
No. of independent reflections with $I > 3\sigma(I)$	2594	2284
No. of parameters refined	244	444
Scan speed/° min^{-1}	1.53–9.15	0.92–5.49
R	0.051	0.081
R'	0.061	0.090
Max. Δ/σ	0.04	1.27
Goodness of fit	4.17	8.82

* Details in common: deep blue crystals, T = 299 K, $2\theta_{max}$ = 46°, λ(Mo-Kα) = 0.710 73 Å, empirical absorption,[14] refinement by full-matrix least squares (MULTAN 82),[13] H atoms refined isotropically and allowed to ride on attached atoms, ω-2θ scan type, PDP 11/44 and IBM 486 computers using the SDP-PLUS program system.[15]

Table 2 Atomic coordinates for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Cu	0.078 53(4)	0.077 2(1)	0.099 33(3)
O(1)	−0.164 7(3)	−0.029 4(7)	0.077 3(2)
O(2)	0.007 1(3)	−0.426 3(6)	0.104 9(2)
N(1)	−0.037 9(3)	0.095 1(8)	0.084 2(2)
N(2)	0.078 0(3)	−0.171 0(7)	0.106 9(2)
N(3)	0.202 4(3)	0.052 8(7)	0.093 3(2)
N(4)	0.089 9(3)	0.286 3(7)	0.055 0(2)
N(11)	0.097 4(3)	0.187 9(8)	0.174 8(2)
C(11)	0.026 4(5)	0.217(1)	0.196 4(3)
C(12)	0.016 0(5)	0.197(1)	0.248 1(4)
C(13)	0.081 0(6)	0.148(1)	0.275 4(3)
C(14)	0.159 5(5)	0.117 1(9)	0.253 1(3)
C(15)	0.229 4(5)	0.069(1)	0.279 8(3)
C(16)	0.302 4(5)	0.040(1)	0.256 7(3)
C(17)	0.309 8(5)	0.069(1)	0.205 2(3)
C(18)	0.242 5(4)	0.118 3(9)	0.178 6(2)
C(19)	0.165 1(4)	0.143 2(9)	0.201 6(2)
C(21)	−0.093 0(4)	−0.025 7(8)	0.094 1(3)
C(22)	−0.065 4(4)	−0.170 1(9)	0.129 0(3)
C(23)	0.011 2(4)	−0.264 5(9)	0.111 8(2)
C(24)	0.153 1(4)	−0.253(1)	0.087 2(3)
C(25)	0.224 7(4)	−0.136 3(8)	0.100 4(3)
C(26)	0.214 4(4)	0.109(1)	0.041 5(2)
C(27)	0.175 1(4)	0.287 5(9)	0.033 6(3)
C(28)	0.023 9(4)	0.254(1)	0.018 1(3)
C(29)	−0.055 0(4)	0.225 5(9)	0.047 0(3)
C(30)	0.253 6(4)	0.163(1)	0.126 2(3)

needles in 40% yield. The dialkylated H_2L^2 was also obtained as the minor product which was eluted more rapidly than H_2L^1. When H_2L and 4 equivalents of **4** were used, the main product was H_2L^2. All the analytical and spectral data are in good agreement with the theoretical requirements of the two new ligands.

Crystal Structures.—The crystallographic data and data collections for complexes **1** and **2** are summarized in Table 1. The molecular structure of complex **1** is shown in Fig. 1. The atomic positional parameters, selected bond lengths, bond angles, and torsion angles are listed in Tables 2 and 3, respectively.

From Fig. 1, it can be seen that, in complex **1**, the Cu^{II} centre is five-co-ordinate [with N(1), N(2), N(3), N(4) and N(11)] and adopts a distorted square-pyramidal configuration. The two deprotonated amide nitrogens [N(1) and N(2)] have stronger co-ordination bonds (Cu–N$^-$ bonds 1.93–1.94 Å) than those for the secondary amine N(3) (2.03 Å) and the tertiary amine N(4) (2.04 Å). The four equatorial basal nitrogens [N(1), N(2) N(3) and N(4)] are not co-planar. The Cu^{II} ion deviates from the least-squares plane of the four basal nitrogens towards the pendant nitrogen[N(11)] by *ca.* 0.4 Å. This is probably due to the very tight cavity of the 13-membered ring for Cu^{II}. In the copper(II) complex of 14-membered dioxocyclam appended with 8-methylquinoline, the Cu^{II} ion is above the least-squares plane by *ca.* 0.3 Å and detailed data will be reported elsewhere. The Cu–N distances of the four basal nitrogens fall in the range of 1.93–2.0 Å, and can be considered as normal Cu–N co-ordination bonds.[11c,12] The apical Cu–N(11) distance of 2.266(3) Å is longer than those of the basal Cu–N distances, suggesting the weaker co-ordination of the pendant nitrogen due to a steric constraint or the Jahn–Teller effect. The distances C(21)–N(1) (1.32 Å) and C(23)–N(2) (1.31 Å) show their partial double bond characters which arise from conjugation in the O(1)–C(21)–N(1) and O(2)–C(23)–N(2) systems. The dihedral angle between the quinoline plane and the basal least-squares plane is 60.8°.

The structure of complex **2** is shown as the partial structure of $[(CuL^2)_2]{\cdot}3H_2O{\cdot}MeCN$ in Fig. 2. Selected atomic positional parameters, bond lengths and angles for **2** are listed in Tables 4 and 5, respectively. From Fig. 2, it is obvious that the co-ordination environment around the Cu atom is similar to that of complex **1**. The Cu atom is also five-co-ordinate with only one of the pendants interacting with the central Cu and the other pendant remaining unco-ordinated. The two quinoline pendants are in the same side of the N_4 square plane. It should be noted that two similar but different conformations were found to exist in a unit cell. They have similar configuration of

Table 3 Selected bond lengths (Å), bond angles (°), and torsion angles (°) for complex **1** with e.s.d.s in parentheses

Cu–N(1)	1.942(3)	O(1)–C(21)	1.252(4)	N(2)–C(23)	1.313(5)	N(3)–C(30)	1.494(5)
Cu–N(2)	1.933(3)	O(2)–C(23)	1.268(5)	N(2)–C(24)	1.481(4)	N(4)–C(27)	1.507(5)
Cu–N(3)	2.030(3)	N(1)–C(21)	1.324(5)	N(3)–C(25)	1.520(4)	N(4)–C(28)	1.495(4)
Cu–N(4)	2.035(3)	N(1)–C(29)	1.464(5)	N(3)–C(26)	1.506(4)	C(18)–C(30)	1.494(5)
Cu–N(11)	2.266(3)						
N(1)–Cu–N(2)	95.1(1)	N(2)–Cu–N(11)	106.1(1)	Cu–N(2)–C(23)	124.2(2)	Cu–N(4)–C(27)	108.9(3)
N(1)–Cu–N(3)	162.9(1)	N(3)–Cu–N(4)	86.1(1)	Cu–N(2)–C(24)	112.6(2)	Cu–N(4)–C(28)	102.0(3)
N(1)–Cu–N(4)	84.6(1)	N(3)–Cu–N(11)	88.8(2)	Cu–N(3)–C(25)	108.3(2)	Cu–N(11)–C(19)	120.3(2)
N(1)–Cu–N(11)	107.3(2)	N(4)–Cu–N(11)	103.8(2)	Cu–N(3)–C(26)	100.6(2)	N(3)–C(30)–C(18)	112.6(3)
N(2)–Cu–N(3)	85.5(1)	Cu–N(1)–C(21)	124.4(2)	Cu–N(3)–C(30)	116.6(2)	N(11)–C(19)–C(18)	120.3(4)
N(2)–Cu–N(4)	148.8(1)	Cu–N(1)–C(29)	112.4(3)				

N(1)–C(21)–C(22)–C(23)	−56.33(0.81)	C(30)–N(3)–C(25)–C(24)	153.92(0.57)	C(29)–N(1)–C(21)–O(1)	−7.45(1.02)
N(3)–C(26)–C(27)–N(4)	−47.33(0.68)	C(30)–N(3)–C(26)–C(27)	−69.57(0.64)	C(21)–N(1)–C(29)–C(28)	−139.51(0.61)
C(21)–C(22)–C(23)–N(2)	60.95(0.79)	C(26)–N(3)–C(30)–C(18)	−69.57(0.64)	C(24)–N(2)–C(23)–C(22)	−175.90(0.57)
O(1)–C(21)–C(22)–C(23)	123.61(0.68)	C(27)–N(4)–C(28)–C(29)	170.32(0.53)	C(26)–N(3)–C(25)–C(24)	−84.32(0.66)
C(29)–N(1)–C(21)–C(22)	172.79(0.57)	N(2)–C(24)–C(25)–N(4)	−41.74(0.75)	C(25)–N(3)–C(26)–C(27)	168.50(0.50)
C(24)–N(2)–C(23)–O(2)	6.70(1.02)	N(4)–C(28)–C(29)–N(1)	−51.04(0.69)	C(25)–N(3)–C(30)–C(18)	−59.06(0.69)
C(23)–N(2)–C(24)–C(25)	−162.50(0.61)	C(21)–C(22)–C(23)–O(2)	−121.48(0.67)	C(28)–N(4)–C(27)–C(26)	−97.62(0.63)
N(1)–Cu–N(2)–C(24)	141.62(0.44)	N(1)–Cu–N(4)–C(28)	−33.73(0.39)	N(1)–Cu–N(3)–C(30)	140.05(0.75)
N(1)–Cu–N(3)–C(26)	21.77(0.98)	N(1)–Cu–N(3)–C(25)	−95.45(0.87)	N(1)–Cu–N(2)–C(23)	−14.81(0.58)
N(1)–Cu–N(4)–C(27)	−153.59(0.43)				

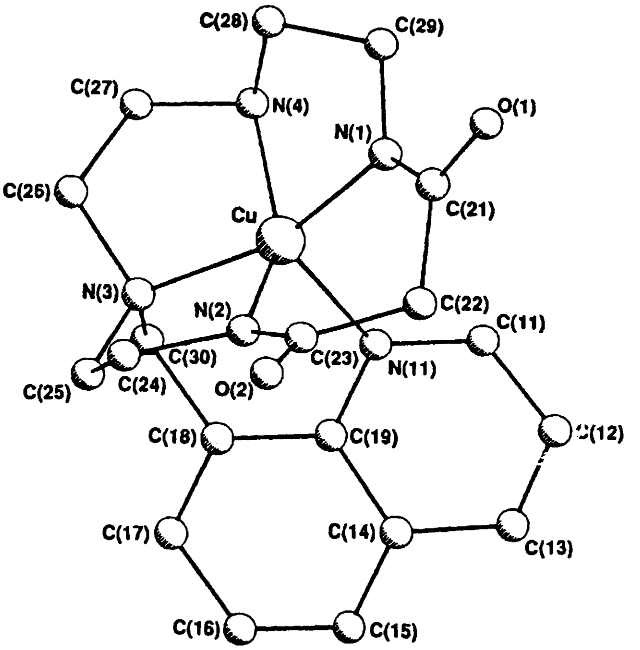

Fig. 1 Perspective drawing of complex **1**

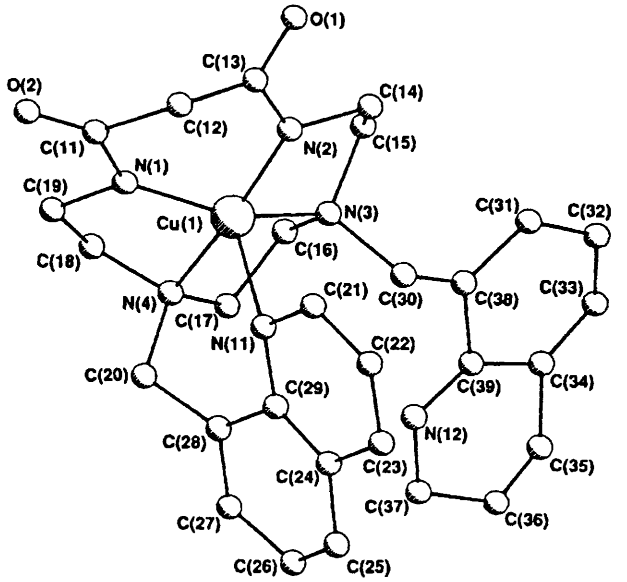

Fig. 2 Perspective drawing of complex **2**

the macrocycle with different dihedral angles, bond distances and angles. For example, in one molecule (see Fig. 3), the dihedral angle between the least-squares plane N(1)N(2)N(3)-N(4) and the co-ordinated quinoline plane N(11), C(21)–C(28) is 65.5°, whereas, in the other molecule, the corresponding angle is 56.0°. The two different subunits link each other with water through hydrogen bonding. In a unit cell (Fig. 3), four different molecules were linked with six water molecules and the structure was thus stabilized.

Electrochemical Studies.—The cyclic voltammograms of the copper(II) complexes with ligands L, L^1 and L^2 were examined in aqueous solution (0.5 mol dm^{-3}, Na_2SO_4, at 25 °C), and the electrochemical data are summarized in Table 6. All the cyclic voltammograms showed one quasi-reversible redox wave, and they were all pH sensitive and could be obtained only in a very narrow pH range. The Cu^{III}–Cu^{II} potential for the complex with L^1, $E_{\frac{1}{2}} = +0.78$ V *vs.* SCE, is 0.20 V more positive than that for [CuL] ($E_{\frac{1}{2}} = +0.58$ V) under the same conditions,[1a,2d,6d] implying that ligand L^1 appended with a quinoline pendant destabilizes the copper(III) state compared with unsubstituted L. This behaviour can be interpreted in terms of less favourable fitting of the d^8 Cu^{III} ion in a square-pyramidal cavity. The change from Cu^{II} to Cu^{III} state (d^8, low spin) involves drastic reduction of the ion radius.[3a] For a square-planar complex of Cu^{III} with a deprotonated tripeptide, a Cu^{III}–N (deprotonated amide) distance of 1.80 Å and a longer Cu^{III}–N (amine) distance of 1.90 Å have been found.[12] Such distances fit quite well with the 13-membered macrocyclic cavity. For both complexes, when Cu^{II} is oxidized to Cu^{III}, the ion would insert completely into the cavity rather than reside above the least-squares plane of the four basal nitrogens. Therefore, the co-ordination of quinoline pendant to the central Cu^{III} ion would become very difficult or impossible due to steric constraints. Furthermore, like Ni^{II} (d^8, low spin), Cu^{III} tends to adopt a square-planar co-ordination rather than be five-co-ordinate. Since *N*-substitution increases the steric constraint of

Table 4 Atomic coordinates for complex **2** with e.s.d.s in parentheses *

Atom	*x*	*y*	*z*
Cu(1)	0.9815(2)	0.3416(2)	0.8688(1)
Cu(2)	0.6684(2)	0.3686(2)	0.4197(2)
O(1)	0.6894(9)	0.390(1)	0.9130(8)
O(2)	0.894(1)	0.5504(8)	0.7742(8)
O(3)	0.479(2)	0.543(1)	0.7670(9)
O(4)	0.658(1)	0.649(1)	0.489(1)
N(1)	0.977(1)	0.444(1)	0.8242(9)
N(2)	0.844(1)	0.340(1)	0.9029(9)
N(3)	1.042(1)	0.2968(9)	0.9665(9)
N(4)	1.149(1)	0.368(1)	0.8595(8)
N(5)	0.663(1)	0.495(1)	0.479(1)
N(6)	0.602(1)	0.3800(9)	0.3141(9)
N(7)	0.584(1)	0.213(1)	0.3670(9)
N(8)	0.697(1)	0.3385(8)	0.5265(8)
N(11)	0.908(1)	0.205(1)	0.7620(8)
N(12)	1.183(2)	0.105(1)	0.937(1)
N(13)	0.863(1)	0.386(1)	0.428(1)
N(14)	0.602(1)	0.049(2)	0.297(1)
C(11)	0.891(1)	0.485(1)	0.801(1)
C(12)	0.768(2)	0.415(1)	0.810(1)
C(13)	0.767(1)	0.385(1)	0.879(1)
C(14)	0.847(2)	0.306(1)	0.975(1)
C(15)	0.979(1)	0.333(1)	1.027(1)
C(16)	1.177(2)	0.351(1)	0.997(1)
C(17)	1.223(2)	0.341(1)	0.926(1)
C(18)	1.196(2)	0.475(1)	0.871(1)
C(19)	1.093(2)	0.503(1)	0.818(1)
C(20)	1.152(2)	0.316(1)	0.778(1)
C(21)	0.785(2)	0.152(1)	0.745(1)
C(22)	0.733(2)	0.048(1)	0.707(1)
C(23)	0.796(2)	−0.009(2)	0.685(1)
C(24)	0.922(1)	0.047(1)	0.703(1)
C(25)	0.998(2)	−0.007(2)	0.684(2)
C(26)	1.116(2)	0.042(2)	0.705(2)
C(27)	1.167(2)	0.149(1)	0.736(1)
C(28)	1.096(1)	0.204(1)	0.753(1)
C(29)	0.977(1)	0.148(1)	0.744(1)
C(30)	1.009(2)	0.183(1)	0.949(1)
C(31)	1.023(2)	0.148(2)	1.079(2)
C(32)	1.079(3)	0.107(2)	1.141(2)
C(33)	1.164(2)	0.075(2)	1.132(2)
C(34)	1.202(3)	0.069(2)	1.071(2)
C(35)	1.290(3)	0.025(3)	1.051(2)
C(36)	1.308(3)	0.011(3)	0.988(2)
C(37)	1.265(3)	0.061(2)	0.924(2)
C(38)	1.069(2)	0.153(1)	1.014(1)
C(39)	1.157(2)	0.104(1)	1.001(1)
C(41)	0.658(2)	0.566(1)	0.449(1)
C(42)	0.666(2)	0.560(2)	0.364(1)
C(43)	0.587(2)	0.455(1)	0.299(1)
C(44)	0.531(2)	0.277(2)	0.254(1)
C(45)	0.491(2)	0.213(2)	0.293(1)
C(46)	0.537(2)	0.181(1)	0.428(1)
C(47)	0.639(1)	0.228(1)	0.515(1)
C(48)	0.630(2)	0.393(1)	0.565(1)
C(49)	0.667(2)	0.502(1)	0.562(1)
C(50)	0.826(2)	0.377(1)	0.581(1)
C(51)	0.889(2)	0.398(1)	0.363(1)
C(52)	0.969(2)	0.357(2)	0.331(1)
C(53)	1.019(2)	0.306(1)	0.376(1)
C(54)	1.002(1)	0.296(1)	0.444(1)
C(55)	1.050(2)	0.242(2)	0.489(1)
C(56)	1.027(2)	0.229(2)	0.556(1)
C(57)	0.946(2)	0.274(2)	0.585(1)
C(58)	0.902(1)	0.328(1)	0.541(1)
C(59)	0.919(1)	0.337(1)	0.473(1)
C(60)	0.667(1)	0.164(1)	0.342(1)
C(61)	0.552(2)	0.019(1)	0.215(1)
C(62)	0.499(2)	−0.088(1)	0.171(1)
C(63)	0.503(2)	−0.153(1)	0.212(1)
C(64)	0.559(2)	−0.123(1)	0.296(1)
C(65)	0.577(2)	−0.185(2)	0.341(2)
C(66)	0.635(3)	−0.159(2)	0.419(2)
C(67)	0.687(2)	−0.047(2)	0.463(2)
C(68)	0.667(1)	0.013(1)	0.422(1)
C(69)	0.611(2)	−0.021(1)	0.343(1)
O(21)	0.469(2)	0.400(2)	0.840(2)
O(22)	0.748(1)	0.759(1)	0.648(1)
O(23)	0.725(1)	0.644(1)	0.755(1)
C(1)	0.423(2)	0.739(2)	0.948(2)
C(2)	0.498(2)	0.685(2)	0.969(2)
N	0.366(2)	0.790(2)	0.932(1)

* Carbon atoms refined isotropically as was N atom of acetonitrile.

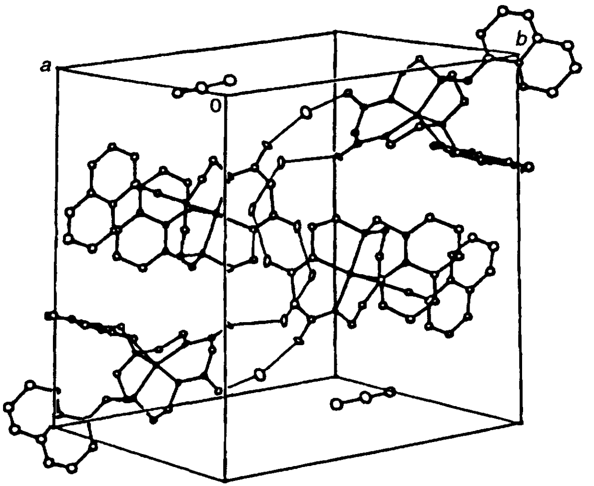

Fig. 3 Perspective drawing of molecular stacking in the unit cell of complex **2**

the dioxo[13]aneN_4 ring, Cu^{III} ions in the two complexes are not stabilized to the same extent as in the unsubstituted complex [CuL]. The Cu^{III}–Cu^{II} potentials for **1** and **2** are thus more positive than that for [CuL].

Spectroscopic Studies.—The absorption maxima data of the present copper(II) complexes in MeOH solution are listed in Table 6. The d–d transition bands for **1** and **2** (598 and 600 nm, respectively) are significantly shifted to higher wavelengths compared with that for [CuL] (516 nm). These values are nearly the same as that of the copper(II) complex of cyclen (600 nm) (cyclen = 1,4,7,10-tetraazacyclododecane).[1a] Since the d–d absorption band gives an empirical measure of the in-plane Cu^{II}–N interaction,[16] the remarkable red shifts observed for complexes **1** and **2** indicate weakened in-plane bonding of the two complexes compared with that of [CuL] due to the *N*-substitution and the axial co-ordination of the quinoline pendant.

ESR Studies.—Fig. 4 shows the ESR spectra of **1** in MeOH solution at 298 and 112 K. It can be seen that the spectrum of the complex at room temperature is split into four equally spaced absorptions by the interaction with the Cu^{II} nucleus ($I = \frac{3}{2}$) [Fig. 4(*a*)]. The isotropic ESR parameters are $g_{iso} = 2.095$ and $A_{iso} = 82$ G (8.07×10^{-3} cm^{-1}) (Table 7). When the solution is frozen at 112 K, an ESR spectrum characteristic of axial symmetry is observed, which is very similar to that of the [CuL] complex. The approximate ESR parameters of complex **1** are graphically evaluated as $g_{\parallel} = 2.184$, $g_{\perp} = 2.050$, $A_{\parallel} = 186$ G (1.90×10^{-2} cm^{-1}), and $A_{\perp} = 30$ G (2.90×10^{-3} cm^{-1}), where $g_{\perp} = (3g_{iso} - g_{\parallel})/2$ and $A_{\perp} = (3A_{iso} - A_{\parallel})/2$.[17]

Table 5 Selected bond lengths (Å), bond angles (°), and torsion angles (°) for complex **2** with e.s.d.s in parentheses

Cu(1)–N(1)	1.862(7)	N(2)–C(13)	1.332(9)
Cu(1)–N(2)	1.936(6)	N(2)–C(14)	1.49(2)
Cu(1)–N(3)	2.056(7)	N(3)–C(15)	1.574(9)
Cu(1)–N(4)	2.031(6)	N(3)–C(16)	1.510(9)
Cu(1)–N(11)	2.240(5)	N(3)–C(30)	1.540(9)
O(1)–C(13)	1.271(8)	N(4)–C(17)	1.53(1)
O(2)–C(11)	1.164(8)	N(4)–C(18)	1.46(1)
N(1)–C(11)	1.380(9)	N(4)–C(20)	1.527(9)
N(1)–C(19)	1.48(1)	N(11)–C(21)	1.399(9)
N(1)–Cu(1)–N(2)	93.2(2)	Cu(1)–N(1)–C(19)	115.4(4)
N(1)–Cu(1)–N(3)	149.4(2)	Cu(1)–N(2)–C(13)	125.8(5)
N(1)–Cu(1)–N(4)	86.5(2)	Cu(1)–N(2)–C(14)	112.5(5)
N(1)–Cu(1)–N(11)	104.2(2)	Cu(1)–N(3)–C(15)	104.1(4)
N(2)–Cu(1)–N(3)	86.9(2)	Cu(1)–N(3)–C(16)	104.5(5)
N(2)–Cu(1)–N(4)	166.1(2)	Cu(1)–N(3)–C(30)	114.8(4)
N(2)–Cu(1)–N(11)	103.7(2)	Cu(1)–N(4)–C(17)	108.4(5)
N(3)–Cu(1)–N(4)	86.4(2)	Cu(1)–N(4)–C(18)	104.3(4)
N(3)–Cu(1)–N(11)	105.5(3)	Cu(1)–N(11)–C(29)	122.4(4)
N(4)–Cu(1)–N(11)	89.8(3)	N(3)–C(30)–C(38)	114.7(5)
Cu(1)–N(1)–C(11)	134.6(6)		
N(1)–C(11)–C(12)–C(13)	46.22(2.33)	C(19)–N(1)–C(11)–O(2)	4.53(2.84)
C(19)–N(1)–C(11)–C(12)	−179.69(1.49)	C(11)–N(1)–C(19)–C(18)	162.70(1.54)
C(14)–N(2)–C(13)–O(1)	−6.21(2.57)	C(14)–N(2)–C(13)–C(12)	−179.82(1.70)
C(13)–N(2)–C(14)–C(15)	−137.31(1.71)	C(16)–N(3)–C(15)–C(14)	156.71(1.52)
C(30)–N(3)–C(16)–C(17)	78.43(1.87)	C(18)–N(4)–C(17)–C(16)	87.47(1.92)
C(20)–N(4)–C(17)–C(16)	−154.12(1.59)	C(17)–N(4)–C(20)–C(28)	64.05(1.99)
C(18)–N(4)–C(20)–C(28)	−174.65(1.60)	C(21)–C(22)–C(23)–C(24)	−1.64(3.06)
C(11)–C(12)–C(13)–O(1)	133.77(1.91)	C(11)–C(12)–C(13)–N(2)	−52.73(2.51)
N(2)–C(14)–C(15)–N(3)	−48.24(1.89)	N(3)–C(16)–C(17)–N(4)	49.60(2.03)
N(4)–C(18)–C(19)–N(1)	38.88(2.04)	O(2)–C(11)–C(12)–C(13)	46.22(2.33)

Table 6 Physical properties of the copper(II) complexes, [CuL], **1** and **2**

		[CuL]	**1**	**2**
CV[a,b]	Scan rate/mV s^{-1}	100	200	200
	pH	≈ 5.5	≈ 5	≈ 4.5
	E_{pa}/V	+0.54	+0.73	+0.79
	E_{pc}/V	+0.62	+0.82	+0.89
	ΔE_p/mV	80	90	90
	$E_{\frac{1}{2}}$/V	+0.58	+0.78	+0.84
UV/VIS[c]	λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1})	516 (100)	598 (170)	600 (230)

[a] In H_2O at 25 °C, *E*/V *vs.* SCE. [b] [CuL] and **1** were kept at 2×10^{-3} mol dm^{-3} and **2** was $\approx 1 \times 10^{-3}$ mol dm^{-3} owing to its low solubility in H_2O. [c] In MeOH at 25 °C with preneutralized solution (NaOH).

All the parameters for other complexes are also listed in Table 7. It is obvious that the observed $A_{\parallel}$ values decrease and $g_{\parallel}$ values increase from the copper(II) complexes with L to L^1 and L^2. The tendency for $A_{\parallel}$ to decrease and for $g_{\parallel}$ to increase can be taken as a measure of the lowering of the strength of in-plane ligand fields under the tetragonal basal square arrangement of copper(II) complexes.[18] Therefore, ESR spectra also reflect the weakened in-plane bonding in complexes **1** and **2** compared with that in [CuL]. This is also consistent with the results of electrochemical and UV/VIS measurements as well as the crystal structures of **1** and **2**, which show that the Cu^{II} ion is raised out of the plane of the equatorial ligands leading to a decrease in in-plane bonding. The ESR parameters for **1** and **2** also indicate a $d_{x^2-y^2}$ ground state of Cu^{II} in these complexes.

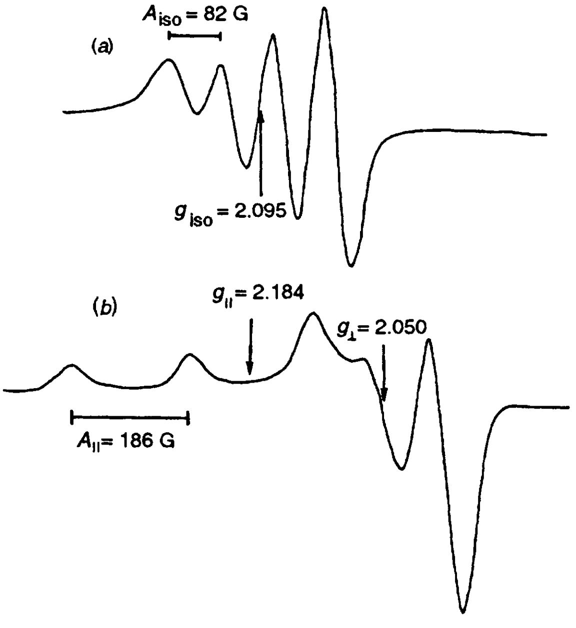

Fig. 4 X-Band ESR spectra of complex **1** in MeOH at (*a*) 298 K and (*b*) 112 K

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Table 7 The ESR parameters of [CuL], **1** and **2** in MeOH solution at 298 and 112 K *

	298 K		112 K			
Complex	g_{iso}	A_{iso}/G (10^{-3} cm^{-1})	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$/G (10^{-2} cm^{-1})	$A_{\perp}$/G (10^{-3} cm^{-1})
[CuL]	2.087	91 (8.92)	2.176	2.043	199 (2.022)	37 (3.37)
1	2.095	82 (8.07)	2.184	2.050	186 (1.897)	30 (2.90)
2	2.098	80 (7.88)	2.187	2.054	180 (1.894)	30 (2.85)

* $A_{\perp}$ was calculated according to formula $3A_{iso} = A_{\parallel} + 2A_{\perp}$ and $g_{\perp}$ according to formula $3g_{iso} = g_{\parallel} + 2g_{\perp}$.

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