The First Binuclear Copper(II) Complex of a Bibracchial Lariat Ether: Synthesis, Magnetic Susceptibility and Crystal Structure†

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A new bibracchial lariat ether, *N,N'*-bis(8-quinolylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L^1) and its dicopper(II) complex, $[Cu_2L^1(OH)][ClO_4]_3 \cdot Me_2CO$, were synthesized. The crystal structure and a variable-temperature magnetic susceptibility study reveal that the two copper atoms are bridged by an OH group and nearly completely diamagnetic. This is the first example of a binuclear copper(II) complex containing a bibracchial lariat ether.

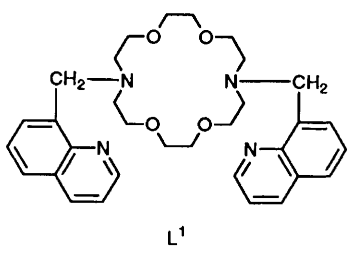
Bibracchial lariat ethers have attracted much attention in recent years. In the metal complexes of such compounds the guest cation trapped in the macrocyclic ring may be wrapped in such a way that the additional donor groups on the arms provide further co-ordination, forming a three-dimensional structure as in the cryptand. Donor-arm groups as 2-hydroxyethyl, 2-methoxyethyl, 2-methoxy-1-naphthylmethyl, carboxymethyl, ethoxycarbonylmethyl, 2-furylmethyl, 2-pyridylmethyl, phosphonomethyl, *etc.* and their complexes with alkali- or alkaline-earth metals,[1-4,5a] heavy metals,[6] lanthanides[7] and a few transition metals[8,9] have been reported. However, all these studies are concerned with mononuclear complexes.

In a previous communication[5] we reported the potassium and sodium complexes of *N,N'*-bis(2-methoxy-1-naphthylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L^2), in which the donor atoms of the macrocycle and side arms co-operatively complex with cations at the same side of macrocycle and both sides respectively forming a three-dimensional configuration as in the cryptate (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)potassium iodide.[5b] The cation-binding properties of bibracchial lariat ethers are controlled by the co-ordination characteristics of the parent macrocycles and of the donor side arms. Variation of the latter could offer new possibilities in designing specific host molecules for metal cations.

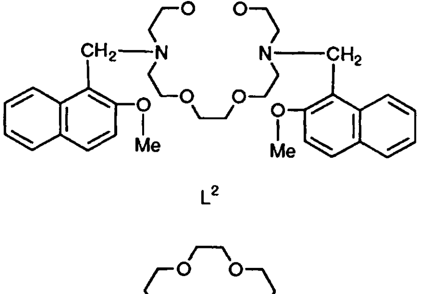
In this paper we report a new bibracchial lariat ether, *N,N'*-bis(8-quinolylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L^1) containing a soft nitrogen donor in each side arm, and the crystal structure of its copper(II) complex.

Results and Discussion

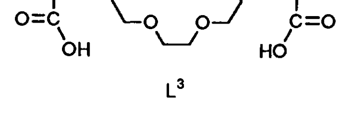
Compound L^1 was synthesized by treating 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane with 8-(bromomethyl)quinoline and anhydrous sodium carbonate in acetonitrile solution.[1,2] By refluxing L^1 with $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol a copper(II) complex **1** was obtained. As determined by elemental analyses, the molecular formula of **1** after recrystallization from acetone is $[Cu_2L^1(OH)][ClO_4]_3 \cdot Me_2CO$, *i.e.* a binuclear copper(II) complex with an acetone molecule trapped in the crystal lattice.



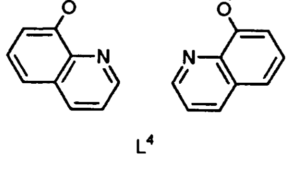
L^1



L^2



L^3



L^4

The IR spectrum of the complex exhibits a strong band at 1102 cm^{-1} is assigned to the bridging OH. The stretching vibration of the perchlorate ion appears as a single band around 1108; a band of 624 cm^{-1} implies that the ion is free and not co-ordinated to the copper(II) ion.[10,11] The band at 1713 cm^{-1} is due to the lattice acetone molecule. Comparing the IR spectrum of complex **1** with that of L^1, the C–N and C–O bands undergo bathochromic shifts due to withdrawal of electronic charge from the N and O atoms to the metal ion.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: emu = $4\pi \times 10^{-6}$ SI

Table 1 Atom coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Cu(1)	4748(1)	3356(1)	4256(1)
Cu(2)	6571(0)	3575(1)	4632(0)
Cl(1)	1865(2)	1483(2)	2333(2)
Cl(2)	4518(2)	5929(2)	4750(2)
Cl(3)	998(2)	5762(3)	2293(3)
N(1)	4280(4)	3555(6)	5341(5)
N(2)	3915(4)	2816(7)	3559(5)
N(3)	6987(4)	4834(6)	4928(5)
N(4)	7519(4)	3151(6)	4383(5)
O(1)	5656(3)	3810(4)	4757(4)
O(2)	4915(4)	1790(5)	4589(5)
O(3)	6456(4)	2200(4)	4874(4)
O(4)	6552(3)	3829(5)	3077(4)
O(5)	5046(4)	3380(5)	3000(4)
O(6)	2366(6)	857(9)	2715(10)
O(7)	1618(9)	1195(11)	1488(7)
O(8)	2138(8)	2316(8)	2224(17)
O(9)	1309(13)	1507(18)	2767(16)
O(10)	5037(5)	5556(7)	5416(6)
O(11)	4755(20)	6672(13)	4357(13)
O(12)	4351(6)	5250(7)	4052(6)
O(13)	3949(8)	6044(18)	5222(11)
O(14)	445(9)	5659(18)	2732(15)
O(15)	986(10)	5219(11)	1593(10)
O(16)	1244(10)	6604(10)	2144(15)
O(17)	1546(16)	5447(18)	2919(20)
O(18)	−667(8)	3555(23)	3246(18)
C(1)	4670(6)	3549(8)	6141(7)
C(2)	4435(7)	3706(9)	6947(7)
C(3)	3748(7)	3926(9)	6920(9)
C(4)	3296(7)	3955(8)	6093(9)
C(5)	2605(7)	4157(10)	6060(11)
C(6)	2182(7)	4144(9)	5278(14)
C(7)	2441(18)	3928(9)	4483(13)
C(8)	3134(5)	3714(7)	4470(7)
C(9)	3584(6)	3754(8)	5273(8)
C(10)	3363(6)	3500(9)	5395(7)
C(11)	3729(6)	1944(7)	3969(8)
C(12)	4340(5)	1286(8)	4154(8)
C(13)	5453(7)	1227(8)	4986(10)
C(14)	6031(6)	1790(8)	5495(7)
C(15)	7081(6)	1685(8)	4836(8)
C(16)	7458(6)	2163(9)	4172(8)
C(17)	7742(6)	3655(9)	3622(8)
C(18)	7203(5)	3651(9)	2786(8)
C(19)	6024(5)	3977(7)	2323(7)
C(20)	5383(6)	4249(8)	2649(7)
C(21)	4639(10)	3004(21)	2332(11)
C(22)	4006(4)	2640(11)	2653(7)
C(23)	6571(6)	5534(6)	4767(7)
C(24)	6756(8)	6429(9)	5042(7)
C(25)	7364(7)	6582(9)	5522(8)
C(26)	7856(5)	5858(7)	5742(6)
C(27)	8490(7)	5997(9)	6227(7)
C(28)	8956(7)	5297(11)	6387(9)
C(29)	8796(5)	4446(8)	6015(7)
C(30)	8145(5)	4261(7)	5537(7)
C(31)	7663(5)	4966(7)	5406(6)
C(32)	8014(5)	3294(8)	5251(8)
C(33)	463(11)	3296(18)	2921(17)
C(34)	−49(7)	3545(13)	3562(13)
C(35)	178(18)	3645(21)	4573(17)

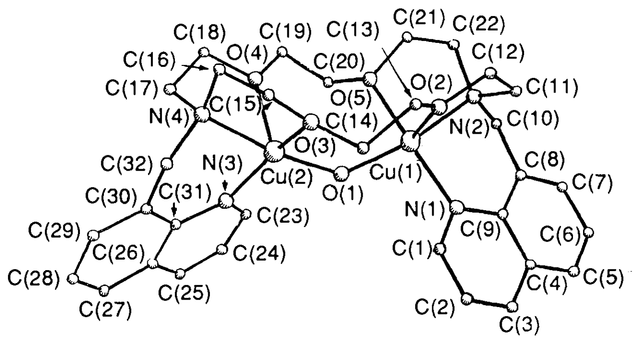

Fig. 1 Molecular structure of $[Cu_2L^1(OH)][ClO_4]_3{\cdot}Me_2CO$ and the atom numbering scheme used. Hydrogen atoms, the anions and lattice acetone molecule have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for complex **1** with estimated standard deviations in parentheses

Cu(1) ··· Cu(2)	3.526(3)	Cu(1)–N(1)	2.006(8)
Cu(1)–N(2)	1.962(8)	Cu(1)–O(1)	1.935(6)
Cu(1)–O(2)	2.361(7)	Cu(1)–O(5)	2.066(7)
Cu(2)–N(3)	2.037(8)	Cu(2)–N(4)	2.034(9)
Cu(2)–O(1)	1.852(6)	Cu(2)–O(3)	2.064(7)
Cu(2)–O(4)	2.365(7)		
N(1)–Cu(1)–N(2)	93.1(3)	N(1)–Cu(1)–O(1)	97.6(3)
N(1)–Cu(1)–O(2)	91.9(3)	N(1)–Cu(1)–O(5)	162.8(3)
N(2)–Cu(1)–O(1)	169.2(3)	N(2)–Cu(1)–O(2)	78.4(3)
N(2)–Cu(1)–O(5)	82.5(3)	O(1)–Cu(1)–O(2)	99.3(3)
N(1)–Cu(1)–O(5)	87.8(3)	O(2)–Cu(1)–O(5)	103.4(3)
N(3)–Cu(2)–N(4)	88.5(3)	N(3)–Cu(2)–O(1)	99.6(3)
N(3)–Cu(2)–O(4)	91.2(3)	N(3)–Cu(2)–O(3)	153.5(3)
N(4)–Cu(2)–O(1)	171.4(3)	N(4)–Cu(2)–O(4)	75.4(3)
N(4)–Cu(2)–O(3)	81.9(3)	O(1)–Cu(2)–O(3)	91.9(3)
O(1)–Cu(2)–O(4)	101.4(2)	O(3)–Cu(2)–O(4)	110.0(3)

The molecular structure of complex **1** is illustrated in Fig. 1. The atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. The two quinoline rings stack at the same side of the macrocycle (the angles between the two quinoline rings and the average plane of the macrocycle are 53.8 and 119.8° respectively), forming a basket-shaped structure which accommodates the two Cu^{2+} ions. The distances of the two copper atoms to the macrocycle plane are 1.2032 and 1.1888 Å respectively. The copper atoms are bridged by an OH group originating from the co-ordinated H_2O molecule, which might further co-ordinate to another Cu^{2+} ion, releasing an H^+ ion. There is an ionic interaction between Cu^{II} and the O (bridge) atom.

The atom Cu(1) is surrounded by N(1), N(2), O(5), O(2) and O(1). The Cu(1)–N(1), Cu(1)–N(2), Cu(1)–O(1) and Cu(1)–O(5) bond lengths are about 2 Å, while Cu(1)–O(2) is much longer (2.361 Å). The distance of Cu(1) to the N(1), N(2), O(1), O(5) plane is 0.1170 Å. Hence the co-ordination geometry of Cu(1) is a distorted square pyramid with the apex at O(2). The geometry of Cu(2) is also a distorted square pyramid, with the apex at O(4). The distance of Cu(2) to the base plane of the pyramid is 0.1772 Å. The shape and size of the two pyramids are quite similar but not identical. The Cu(1) ··· Cu(2) distance is 3.526(3) Å.

The released H^+ ion combines with ClO_4^- anion to form hydrogen perchlorate. Therefore there are three ClO_4^- counter ions. No intermolecular interaction is found between the complex and the acetone molecule.

In complex **1** the donor atoms of the quinoline ring and of the macrocycle co-operatively co-ordinate the two Cu^{2+} ions, forming a stable three-dimensional structure. So far as we know this is the first example of a binuclear transition-metal complex of a double-armed diaza crown ether.

Gluzinski *et al.*[12] determined the crystal structure of (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-*N*,*N*′-diacetato)-copper(II) **2** which is a centrosymmetric molecule containing

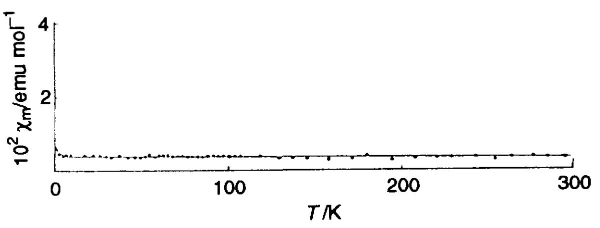

Fig. 2 Magnetic susceptibility data for $[Cu_2L^1(OH)][ClO_4]_3\cdot Me_2CO$. The solid line is calculated using the Bleaney–Bowers equation

Cu^{2+} inside the macrocycle. The copper atom is bonded to two carboxylic oxygen atoms and to two nitrogen and two oxygen atoms of the macrocycle. The Cu–O (carboxylic) and Cu–N (ring) bond lengths are about 2 Å, while the Cu–O (ring) bond lengths are rather long (2.645 Å). The two carboxylato oxygens and two N atoms form a square around the copper atom and the two oxygen atoms in the macrocycle are at the apical positions. The co-ordination geometry of this mononuclear complex is an elongated octahedron. The distance of the other two ring oxygen atoms from the copper is too large for them to take part in co-ordination.

The structure of L^1 is similar to L^3, the difference being the quinoline moieties instead of the acetato groups. In complex **1** all donor atoms in the ligand are co-ordinated and the long Cu(1)–O(2) bonds are much shorter than the Cu–O (ring) bonds in complex **2**. Therefore the ligand L^1 in **1** is more effectively co-ordinated than is L^3 in **2**. This is probably the reason why the quinoline side-armed diaza crown ether easily forms a binuclear copper(II) complex.

It appears that the two copper(II) ions can organize all the available donor atoms in L^1 so as to form the most favourable five-co-ordinated square-pyramidal structure. The open-chain analogue of L^1 is L^4, a podand with two 8-quinolyl end groups.[13] So far as we know, its copper complex has not been reported. This ligand which contains more ether oxygens seems to favour alkali-metal rather than transition-metal ions. In the RbI complex of L^4 the eight ether oxygen atoms are helically coiled around the Rb^+ cation in the equatorial plane, while two nitrogen atoms in the quinoline ring co-ordinate from above and below.

Instead of a flexible polyethylene glycol chain, L^1 contains a rather rigid macrocycle which in co-operation with the two rigid quinoline moieties could be arranged around two metal ions having smaller radius than that of Rb^+. In addition, the replacement of the oxygen atoms by the softer N atoms in the side arms increases the co-ordination ability toward transition-metal ions. Therefore, a binuclear copper(II) complex can be formed in which all the donor atoms in the ligand participate in co-ordination in a fashion which well suits the ionic configuration of Cu^{II} and makes the two metal ions five-co-ordinated.

Magnetic Properties.—A tiny positive susceptibility (*ca.* 0.004 emu mol^{-1}) was observed at 298 K, which was constant at lower temperature. There is a small increase in χ_m at 4.7 K probably due to contamination by a monomeric copper complex (Fig. 2).

The results show that the two copper(II) cations in complex **1** are very strongly antiferromagnetically coupled. Using the Bleaney–Bowers equation for a $S = \frac{1}{2}$ dimer, the $2J$ value will be about -1000 cm^{-1}, *i.e.* nearly completely diamagnetic. While many binuclear copper(II) complexes have been shown to exhibit antiferromagnetism, very few are diamagnetic at room temperature, especially for those with cyclic ligands. An analogous macrocyclic binuclear copper(II) complex in which the copper atoms are bridged by an azide ion has been reported to exhibit similar magnetic behaviour.[14]

The strong antiferromagnetic coupling in this μ-hydroxo system may be due to the angle Cu–O–Cu being approximately linear (136.7°) and the Cu–O bond lengths are rather short (1.935 Å and 1.852 Å); magnetic exchange interaction can take place through the OH bridge.

Experimental

General.—Microanalyses were performed using a Perkin-Elmer 240C elemental analyser; metal contents were determined by a J-A 1100 Mark III inductively coupled plasma atomic emission spectrometer. Infrared spectra were recorded on a Nicolet FTIR 170 SX spectrometer, ^1H NMR spectra using a JEOL 60 SI spectrometer and mass spectra on a VG-ZAB-HS spectrometer. Molar susceptibilities were measured on a powdered sample using a model CF-1 vibrating-sample magnetometer between 1.8 and 300 K.

Synthesis of N,N′-*Bis*(8-*quinolylmethyl*)-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* (L^1).—A mixture of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (1.31 g, 5 mmol), anhydrous sodium carbonate (2.65 g, 25 mmol), 8-(bromomethyl)quinoline (2.44 g, 11 mmol) and acetonitrile (50 cm^3) was refluxed with stirring for 18 h. The cooled reaction mixture was filtered and washed with acetonitrile. The combined filtrate was evaporated to give the crude product which was washed with light ligroin (b.p. 60–90 °C) and dried *in vacuo*. Recrystallization from light ligroin afford light yellow needles of L^1. Yield 3.59 g (66%), m.p. 100–101 °C (Found: C, 70.4; H, 7.30; N, 10.6. $C_{32}H_{40}N_4O_4$ requires C, 70.6; H, 7.35; N, 10.3%). ν_{max}(KBr) 2881, 2813, 1619, 1594, 1575, 1469, 1356, 1119, 834 and 794 cm^{-1}. δ_H(60 MHz, solvent $CDCl_3$, standard $SiMe_4$) 9.00–8.80 (2 H, m, quinoline H^2), 8.30–7.90 (4 H, m, quinoline $H^{3,4}$), 7.80–7.20 (6 H, m, quinoline H^{5-7}), 4.46 (4 H, s, $2CH_2$), 3.83–3.63 (16 H, m, $8OCH_2$) and 2.97 (8 H, t, J = 6 Hz, $4NCH_2$). *m/z* 544 (M^+, 4), 402 ($M^+ - C_{10}H_8N$, 29), 259 [$N(CH_2CH_2OCH_2CH_2OCH_2CH_2)NH$, 7] and 142 ($C_{10}H_8N$, 100%).

Synthesis of the Dicopper(II) *Complex.*—To an ethanolic solution of L^1 (0.05 g, 0.9 mmol, 20 cm^3) was added dropwise a solution of $Cu(ClO_4)_2\cdot 6H_2O$ in ethanol (5 cm^3) until no more precipitate was formed. The mixture was refluxed for 0.5 h. The precipitate was filtered off, washed three times with ethanol, dried *in vacuo* and recrystallized from acetone. Dark blue crystals of complex **1** were obtained. Yield 0.10 g (93%) (Found: C, 40.2; H, 4.35; Cu, 12.6; N, 5.05. $C_{35}H_{47}Cl_3Cu_2N_4O_{18}$ requires C, 40.2; H, 4.55; Cu, 12.2; N, 5.35%). ν_{max}(KBr) 1713 (CO), 1599, 1513, 1456, 1102 and 624 cm^{-1}.

When the crude product was recrystallized from dry ethanol, blue crystals were obtained. Yield 0.09 g (90%) (Found: C, 39.0; H, 4.20; Cu, 12.6; N, 5.50. $C_{32}H_{41}Cl_3Cu_2N_4O_{17}$ requires C, 38.9; H, 4.20; Cu, 12.9; N, 5.65%). In this case single crystals of suitable size for X-ray diffraction could not be obtained.

Crystallography.—*Crystal data.* $C_{35}H_{47}Cl_3Cu_2N_4O_{18}$, M = 1044.87, monoclinic, space group *Cc*, a = 19.477(3), b = 14.647(3), c = 15.053(3) Å, β = 98.53(1)°, U = 4247(1) Å^3, Z = 4, D_c = 1.64 g cm^{-3}, $F(000)$ = 2155.64. Crystal dimensions 0.30 × 0.30 × 0.40 mm, μ(Mo-Kα) = 12.71 cm^{-1}.

Data collection and processing. Nicolet R3m/E diffractometer, ω–2θ mode with ω scan width = 1.6°, ω scan speed 8° min^{-1}, graphite-monochromated Mo-Kα radiation; 5451 reflections measured ($1 \leqslant 2\theta \leqslant 43°$), 5341 unique giving 2306 with $I > 3\sigma(I)$.

Structure analysis and refinement. The coordinates of two Cu atoms were obtained by direct methods and all the non-hydrogen atoms were determined by several Fourier syntheses. The structure was refined by the block-diagonal-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms. The positions of hydrogen atoms of the diaza crown ring were located on a Fourier-difference map and the others by theoretical calculation. The hydrogen-atom positions were fixed in the last refinement. Final R and R' were 0.0500 and 0.0468 respectively. A weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.0001\ F^2$ was used.

All calculations were performed on an Eclipse S/40 computer using the SHELXTL program.[15]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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