Preparation of 1,4,8,11-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane (L^1) and a Binuclear Complex with Copper(II). *X*-Ray Structure of $[Cu_2L^1Br_2][ClO_4]_2$†

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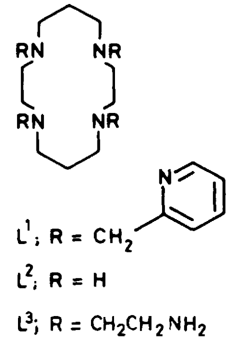
The 14-membered tetra-azamacrocyclic ligand 1,4,8,11-tetra-azacyclotetradecane has been functionalised at the four N atoms with pendant 2-pyridylmethyl groups to give a new potentially octadentate ligand, L^1. The binuclear copper(II) complex $[Cu_2L^1Br_2][ClO_4]_2$ has been isolated, and its structure determined by *X*-ray crystallography. The deep green crystals are monoclinic, space group $P2_1/c$, with $a = 9.029(1)$, $b = 21.120(5)$, $c = 11.376(2)$ Å, $\beta = 111.47(1)°$, and $Z = 2$. The structure was solved by the heavy-atom method to a final R value of 0.037 for 2 264 reflections with $I/\sigma(I) > 3.0$. All eight N atoms are co-ordinated in an *exo* structure in which each copper atom is five-co-ordinate, bonding to a bromide ion and four N atoms (two from adjacent pyridyl groups and two from one of the NCH_2CH_2N portions of the macrocyclic ring). The Cu–Br bond length is 2.412(1) Å and Cu–N bond lengths are in the range 1.996(4)—2.147(4) Å. The Cu–Cu distance is 5.74(1) Å, and this together with the magnetic susceptibility at room temperature indicates that there is no appreciable interaction between the two copper centres.

Kaden[1] has reviewed the methods available for the synthesis of *N*-functionalised azamacrocycles. Tetra-azamacrocycles modified at the N atoms with four pendant co-ordinating arms have been found to form metal complexes with two metal ions co-ordinated outside the macrocyclic ring ('exo' co-ordination).[2] The thermodynamically favourable 'endo' mode of co-ordination, with the metal ion inside the macrocyclic cavity, is presumably not formed for kinetic reasons, although in one case pendant $-CH_2CH_2OH$ groups have been found to increase the rate of incorporation of metal ions into the macrocyclic ring.[3]

We report here the synthesis of a new octa-azamacrocycle (L^1) with four pendant 2-pyridylmethyl groups attached to the four N atoms of 1,4,8,11-tetra-azacyclotetradecane (L^2). The isolation of a binuclear copper(II) complex of L^1 and its characterisation by *X*-ray crystallography are also reported.



Results and Discussion

The synthesis of L^1 in high yield from L^2 proceeds smoothly in a two-phase reaction between 2-(chloromethyl)pyridine and L^2 in a mixture of aqueous NaOH and dichloromethane, without any need for the addition of a phase-transfer catalyst. We have recently used this method to synthesise monofunctionalised tetra-azamacrocycles in good yield.[4] An ethanolic solution of L^1 when mixed with $[Cu(dmso)_6][ClO_4]_2$ (dmso = dimethyl sulphoxide) in a 1:2 molar ratio gives an immediate blue precipitate of $Cu_2L^1(ClO_4)_4$ (probably $[Cu_2L^1(ClO_4)_2][ClO_4]_2$ by analogy with the known compound of L^3).[2] All attempts to grow single crystals of this product from various solvents were unsuccessful. However, when 2 equivalents of bromide ion were added shiny green crystals suitable for *X*-ray diffraction were obtained from acetonitrile solution. Chemical analysis indicated a formula $[Cu_2L^1Br_2][ClO_4]_2$, which was confirmed by the structure determination. The complex shows a *d–d* band at 748 nm (ε = 498 dm^3 mol^{-1} cm^{-1}), and a magnetic moment per Cu^{II} of 2.2 B.M. Similar values are reported for binuclear copper(II) complexes in which there is no appreciable interaction between the two copper(II) ions.[5] This is also confirmed by the crystal structure.

The molecular structure is shown in the Figure. There is a crystallographic inversion centre, and consequently the environments of the two copper atoms are identical. Each copper atom is five-co-ordinate, to four N atoms (two from pendant pyridyl groups) and one bromide ion. The structure is midway between that of a trigonal bipyramid and a square pyramid. The atomic co-ordinates are in Table 1, and selected bond lengths and angles in Table 2. The structure is interestingly different from that reported for the analogous complex $[Cu_2L^3(ClO_4)_2]^{2+}$ in which *exo* co-ordination is also observed.[2] In the latter case six-membered chelate rings are present through bonding to

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† μ-[1,4,8,11-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane-$N^1N^4N'N''$(Cu^1):$N^8N^{11}N'''N''''$(Cu^2)]-bis[bromocopper(II)] diperchlorate.

Supplementary data available (No. SUP 56540, 2 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: B.M. = 9.27×10^{-24} A m^2.

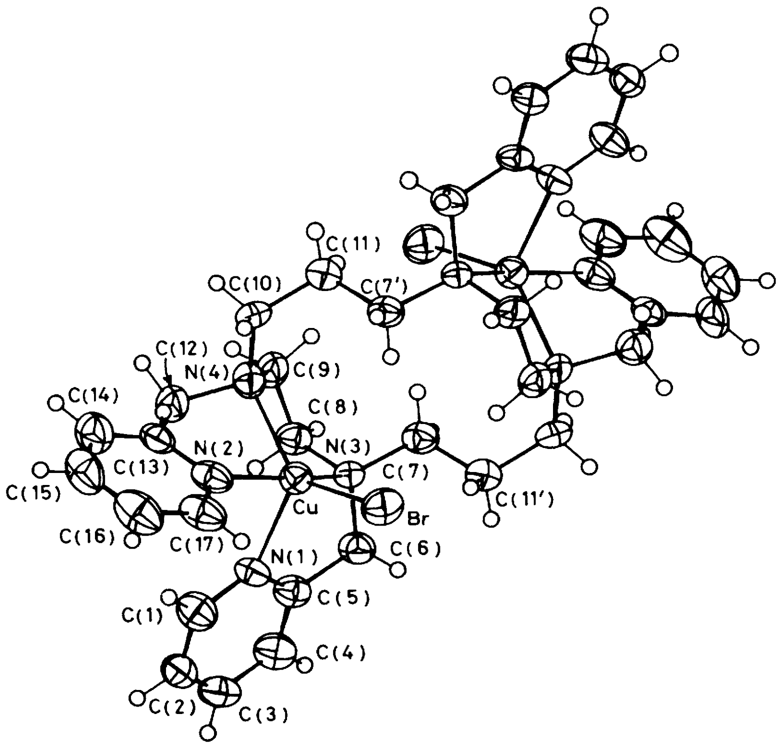

Figure. Molecular structure of $[Cu_2L^1Br_2]^{2+}$ ion, showing the atomic numbering. The molecule has an inversion, relating primed to unprimed atoms

Table 1. Atomic co-ordinates (× 10^4) for $[Cu_2L^1Br_2][ClO_4]_2$ with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Br	3 896.3(6)	5 380.5(3)	6 260.6(5)	C(4)	4 083(7)	3 609(3)	9 940(5)
Cu	2 893.3(6)	4 329.3(3)	6 339.6(5)	C(5)	3 411(5)	3 785(2)	8 706(5)
Cl	−5(2)	1 743(1)	5 577(1)	C(6)	1 871(5)	3 494(3)	7 747(5)
O(11)	−995(5)	1 958(3)	4 359(4)	C(7)	211(6)	4 404(2)	7 555(4)
O(12)	−782(5)	1 849(3)	6 445(4)	C(8)	−185(5)	3 705(2)	5 704(4)
O(13)	327(5)	1 089(2)	5 558(4)	C(9)	596(5)	3 540(2)	4 775(4)
O(14)	1 462(5)	2 083(2)	6 002(4)	C(10)	251(5)	4 552(2)	3 664(4)
N(1)	4 087(4)	4 215(2)	8 188(4)	C(11)	965(5)	5 087(2)	3 160(5)
N(2)	4 344(4)	3 614(2)	5 955(4)	C(12)	2 513(5)	3 871(3)	3 866(4)
N(3)	983(4)	4 001(2)	6 857(3)	C(13)	3 873(5)	3 490(2)	4 711(5)
N(4)	1 459(4)	4 094(2)	4 521(3)	C(14)	4 684(6)	3 061(2)	4 254(5)
C(1)	5 494(6)	4 463(3)	8 905(5)	C(15)	6 000(6)	2 763(3)	5 072(5)
C(2)	6 254(7)	4 285(3)	10 154(6)	C(16)	6 478(6)	2 885(3)	6 341(5)
C(3)	5 536(8)	3 863(3)	10 667(5)	C(17)	5 635(6)	3 311(3)	6 741(5)

-$NCH_2CH_2CH_2N$- fragments of the macrocyclic ring, whereas in the Figure the chelate rings are all five-membered. In both cases the copper(II) is five-co-ordinate with further bonding to two pendant arms and an anionic ligand (ClO_4^- or Br^-). The reason for the differences between these two structures is not obvious, although in general five-membered chelate rings are usually more stable than six-membered rings. Steric interactions between the bulkier pyridyl groups and the backbone propyl chains of the macrocyclic ring might aid the formation of five-membered chelate rings in our case. The Cu–N bond lengths (Table 2) are all in the expected range, as is Cu–Br. The Cu–Cu distance is 5.74 Å, and there is no interaction between the two copper atoms. The N(1)–Cu–N(4) bond angle (158°) is the largest at Cu and could be regarded as the axis of a distorted trigonal bipyramid; N(1)–Cu–N(2) is close to 90°, and the three angles at Cu in the 'trigonal plane' formed by N(2), N(3), and Br are in the range 112.0—131.5°. However, N(2)–Cu–N(4) and N(1)–Cu–N(3) are significantly less than 90°, with distortion of the trigonal bipyramid by displacement of Cu towards Br.

Experimental

4,7-Diazadecane-1,10-diamine was obtained from Aldrich, and other reagents were the most pure materials obtainable commerically. 1,4,8,11-Tetra-azacyclotetradecane (L^2) was prepared by a published method,[6] and the purity checked by ^{13}C and ^1H n.m.r. spectroscopy. Microanalyses were obtained commerically.

N.m.r. spectra were recorded with a Bruker WH180 Fourier-transform spectrometer at 298 K, and $SiMe_4$ was used as an internal standard ($\delta = 0$). Visible spectra were recorded with a Shimadzu model 365 spectrophotometer, and magnetic moments measured by the Evans method using a Bruker WH90 n.m.r. spectrometer.[7]

Table 2. Bond lengths (Å) and angles (°) around copper in $[Cu_2L^1Br_2][ClO_4]_2$

Cu–N(1)	1.996(4)	Cu–N(2)	2.147(4)
Cu–N(4)	2.060(3)	Cu–Br	2.412(1)
Cu–N(3)	2.132(4)		
Br–Cu–N(1)	94.9(1)	Br–Cu–N(2)	112.0(1)
Br–Cu–N(3)	131.5(1)	Br–Cu–N(4)	106.9(1)
N(1)–Cu–N(2)	89.7(2)	N(1)–Cu–N(3)	81.3(2)
N(2)–Cu–N(3)	116.3(2)	N(1)–Cu–N(4)	158.1(2)
N(2)–Cu–N(4)	80.3(1)	N(3)–Cu–N(4)	85.6(1)

Preparation of Compound L^1.—To a solution of L^2 (1 g, 5 mmol) in dichloromethane (25 cm^3) was added a solution of NaOH (1.6 g, 40 mmol) in water (50 cm^3). This two-phase mixture was stirred during the dropwise addition of a solution of 2-(chloromethyl)pyridine hydrochloride (3.2 g, 20 mmol) in dichloromethane (25 cm^3) over a period of 1 h. The stirring was continued at room temperature for a further 12 h and the organic layer was then separated. The aqueous layer was extracted with dichloromethane (3 × 150 cm^3), and the combined organic layers were evaporated to give a solid which was recrystallised from ethanol; yield 2 g (70%), m.p. 170 °C. Proton and proton-decoupled ^{13}C n.m.r. spectra were recorded in $CDCl_3$ solution (s = singlet, d = doublet, t = triplet, p = pentuplet); ^1H, δ 1.79 (4 H, p), 2.61 (8 H, t), 2.70 (8 H, s), 3.64 (8 H, t), 7.10 (4 H, t), 7.47 (4 H, d), 7.56 (4 H, t), and 8.48 (4 H, d); ^{13}C, 23.70 (2 C), 50.89 (4 C), 51.75 (4 C), 61.28 (4 C), 121.68 (4 C), 122.83 (4 C), 136.08 (4 C), 148.73 (4 C), and 160.34 (4 C).

Preparation of $[Cu_2L^1Br_2][ClO_4]_2$.—To a solution of L^1 (0.2 g, 0.35 mmol) in ethanol (50 cm^3) was added a solution of $[Cu(dmso)_6][ClO_4]_2$ (516 mg, 0.70 mmol) in ethanol (50 cm^3). The resulting blue precipitate was filtered off, washed with cold ethanol, and redissolved in a minimum amount of dry acetonitrile. Potassium bromide (82 mg, 0.70 mmol) was added and the solution allowed to evaporate slowly over a few days. Shiny green crystals of $[Cu_2L^1Br_2][ClO_4]_2$ were deposited (yield 250 mg, 72%) (Found: C, 38.2; H, 4.20; Br, 15.1; N, 10.65. Calc. for $C_{34}H_{44}Br_2Cl_2Cu_2N_8O_8$: C, 38.85; H, 4.20; Br, 15.2; N, 10.65%).

Crystallography.—Crystal data. The crystals form as deep green blocks which are monoclinic, space group $P2_1/c$, with a = 9.029(1), b = 21.120(5), c = 11.376(2) Å, β = 111.47(1)°, U = 2 018.6(7) $Å^3$, M = 1 050.6, Z = 2, D_c = 1.73 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 32.08 cm^{-1}, $F(000)$ = 1 059.76.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range from −0.9 to +1.0 (2θ) around the $K_{\alpha1}$–$K_{\alpha2}$ angles, scan speed 2—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed slight changes during the data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by a least-squares fit to 15 high-angle reflections. 2 264 Unique observed reflections $[I/\sigma(I) > 3.0]$ were used in the refinement (3 582 total), and corrected for Lorentz, polarisation and absorption effects, the last with ABSCOR;[8] maximum and minimum transmission factors were 0.74 and 0.59. The crystal dimensions were 0.20 × 0.12 × 0.40 mm. Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$ indicated space group $P2_1/c$.

The heavy atom was located by Patterson techniques, and light atoms were then found in successive Fourier syntheses. Hydrogen atoms were given fixed isotropic thermal parameters, U = 0.07 $Å^2$, and were inserted at calculated positions and not refined. Final refinement was by cascaded least-squares methods, with anisotropic thermal parameters for all atoms other than hydrogen. The largest peak on a final Fourier difference synthesis was of height 0.3 e $Å^{-3}$. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.0007 was used. This was shown to be satisfactory by a weight analysis. The final R value was 0.037 (R' = 0.039). Computing was with the SHELXTL system[9] on a Data General DG30 computer, following initial processing on a Burroughs B6700. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 10.

Acknowledgements

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