A dicopper(II) complex of a new octaaza macrocycle: a receptor in the entatic state

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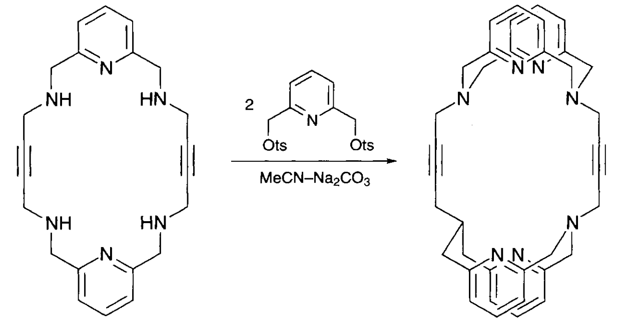
In the crystallographically characterized macrocyclic complex $[Cu_2L(MeCN)_2][F_3CSO_3]_4 \cdot 2$ MeCN the copper ions adopt a highly distorted five-coordinate geometry; relaxation to a more regular octahedral geometry on incorporation of a bridging substrate is demonstrated by the structure of $[Cu_2L(\mu\text{-}CN)(MeCN)_2][ClO_4]_3$.

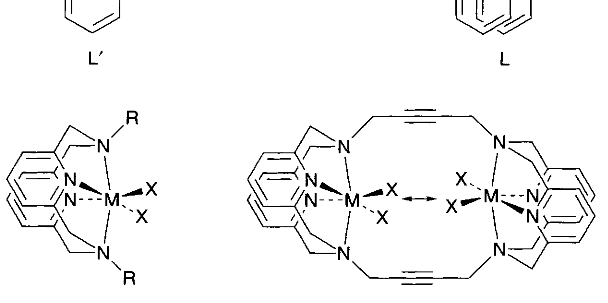
Dinuclear metal complexes of polyaza macrocycles are relevant to various aspects of coordination chemistry such as the selective binding of small bridging molecules in a 'cascade' fashion and the biomimesis of dinuclear sites in metalloenzymes.[1]

In solution, binding of a bridging substrate is in competition with solvent coordination. An interesting steric situation can be achieved utilising a dinuclear macrocyclic complex in which the metal ions are highly preorganised so that the coordinated solvent molecules of the different metals are oriented towards each other and fixed at a distance smaller than their van der Waals radii. For such an energetically unfavoured situation replacement of solvent molecules by a bridging substrate of appropriate geometry should be favoured by free energy considerations. To study this phenomenon we have designed the octaazamacrocycle L, readily prepared by reacting L′[2] with 2 equiv. of 2,6-pyridinedimethyl ditosylate.[3] L is composed of two 2,11-diaza[3.3](2,6)pyridinophane moieties linked by two linear but-2-yne spacers. The coordination chemistry of the tetradentate 2,11-diaza[3.3](2,6)pyridinophane unit has been explored with various transition metals.[4] In all cases this ligand forms octahedral 1 : 1 complexes in the crystalline state with two *cis*-oriented coordination sites occupied by anions, *e.g.* Cl^- (Scheme 1, left). Spectroscopic investigations of the Cu^{II} complex demonstrate that octahedral coordination is retained in solution when Cl^- is replaced by solvent molecules.[4d]



L′

L



Scheme 1 X = anion or solvent, R = alkyl

Force-field calculations† on hypothetical $[Cu_2LX_4]^{4+}$ complexes (X = H_2O, MeCN) indicate that no steric strain is imposed by the ligand framework itself upon connecting two octahedral {2,11-diaza[3.3](2,6)pyridinophane}copper fragments with two but-2-yne spacers. However, there is a significant steric hindrance between solvent molecules coordinated to the different metal ions (Scheme 1, right).

In order to characterize the dicopper(II) complex of **1** in the absence of a bridging substrate we reacted **1** and $Cu(F_3CSO_3)_2$ in acetonitrile. The tetrahedral RSO_3 moiety of the triflate counterion is too large to fit into the cavity between the but-2-yne spacers.[2] Green crystals of $[Cu_2L(MeCN)_2][F_3CSO_3]_4 \cdot 2$ MeCN **1** were obtained from acetonitrile–diethyl ether. The $[Cu_2L(MeCN)_2]^{4+}$ cation (Fig. 1) is crystallographically centrosymmetric with Cu···Cu = 5.02 Å.‡ The CuN_5 polyhedron is highly distorted from the usually encountered square-based pyramidal or trigonal bipyramidal geometries. The coordination can be considered as square pyramidal with a tetrahedrally distorted basal plane formed by N(2), N(3), N(4) and N(5). The apical Cu–N(1) bond length (2.07 Å) is nearly the same as average value of the four remaining Cu–N distances (2.03 Å). In general, the apical Cu–N bond of square-pyramidal CuN_5 complexes is 0.1–0.5 Å longer than the in-plane bonds.[6] A significant difference in the otherwise similar bonding parameters of the {2,11-diaza[3.3](2,6)pyridinophane}copper(II) moiety in **1** and in dichloro{*N*,*N*-dimethyl-2,11-diaza-[3.3](2,6)pyridinophane}copper(II)[4a] is revealed by the longer $Cu–N(sp^3)$ bonds of *ca.* 2.34 Å in the latter complex, which displays an octahedral geometry elongated along the $N(sp^3)–Cu–N(sp^3)$ axes.

It is probable that the unusual Cu coordination in **1** is energetically less favoured than an octahedral geometry. The advantage, however, is that each Cu coordinates only one MeCN coligand (instead of two in the octahedral case) so that

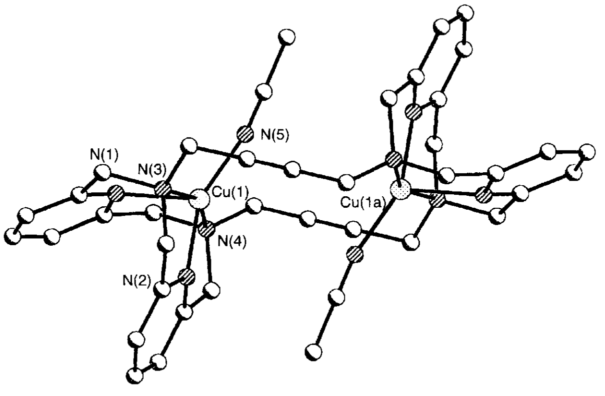


Fig. 1 Structure of the centrosymmetric $[Cu_2L(MeCN)_2]^{4+}$ cation of **1** with heteroatom labelling, hydrogen atoms omitted. Selected distances (Å) and angles (°): Cu(1)–N(1) 2.070(2), Cu(1)–N(2) 1.955(2), Cu(1)–N(3) 2.119(2), Cu(1)–N(4) 2.128(2), Cu(1)–N(5) 1.932(2), Cu(1)···Cu(1a) 5.02; N(3)–Cu(1)–N(4) 156.84(7), N(2)–Cu(1)–N(5) 153.49(9), N(2)–Cu(1)–N(3) 82.43(8), N(3)–Cu(1)–N(5) 101.21(8), N(4)–Cu(1)–N(5) 100.13(8), N(2)–Cu(1)–N(4) 82.51(8), N(1)–Cu(1)–N(2) 88.44(8), N(1)–Cu(1)–N(3) 81.21(8), N(1)–Cu(1)–N(4) 80.90(8), N(1)–Cu(1)–N(5) 118.06(8).

any steric hindrance of the coordinated solvent molecules is avoided and **1** can be regarded as a receptor which is in a stressed or 'entatic' state in the absence of a bridging substrate.

The optical spectrum of **1** in MeCN shows a much more intense d–d band (λ_{max} 707 nm, ε 440 dm^3 mol^{-1} cm^{-1}) compared to octahedral [{*N*,*N*-dimethyl-2,12-diaza-[3.3](2,6)pyridinophane}CuCl(MeOH)]$^+$ (λ_{max} 799 nm, ε 40 dm^3 mol^{-1} cm^{-1}).[4d] Since Cu in a non-centrosymmetric, square-pyramidal environment generally exhibits higher molar absorbances than in a centrosymmetric, octahedral ligand field,[8] the five-coordination of the Cu ions in **1** is probably retained in MeCN solution. Addition of potentially bridging substrates such as cyanide and carbonate readily results in a significant decrease of d–d band intensity (Fig. 2), suggesting the presence of octahedral Cu. Switching from five-coordination in the 'empty' receptor to six-coordination in the presence of a bridging substrate is confirmed by the crystal structures of Cu_2L complexes containing bridging 1,2-μ-cyanide and 1,1-μ-carbonate coligands. Fig. 3 shows the complex cation of [Cu_2L(μ-CN)$(MeCN)_2$][ClO_4]$_3$ **4**.‡ The elongated octahedral geometry of the Cu ions is comparable to that observed in dichloro{*N*,*N*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane}copper(II).[4a] The conformation of the macrocyclic framework and the Cu···Cu distance (**4**, 4.94 Å) are similar in **1** and **4**.

An aqueous solution of [Cu_2L][F_3CSO_3]$_4$ (2 mmol dm^{-3}) has pH 2.73(±0.02) and displays a low-intensity optical band (λ_{max} 697 nm, ε 79 dm^3 mol^{-1} cm^{-1}) indicative of octahedral coordination. We attribute this behaviour to the deprotonation of Cu-coordinated water followed by formation of an OH-bridged complex. Molecular modelling studies suggest that formation of a double OH-bridge [Cu(μ-OH)$_2$Cu] is sterically impossible, but that a single OH^- ion might indeed bridge the Cu ions in [Cu_2L]. The calculated pK_{a1} value of 1.6(±0.5) for [$Cu_2L(H_2O)_n$]$^{4+}$§ is extraordinarily low compared to other macrocyclic dicopper(II) complexes.[9] For [$Cu_2L'(H_2O)_n$]$^{4+}$ we have determined a pK_a of 6.4 by potentiometry. Spectrophotometric and crystallographic studies indicate that in dinuclear complexes of L′ the Cu ions prefer a square-pyramidal N_3X_2 coordination (X = donor atom of solvent or anion) either in the presence or absence of bridging coligands.[2] A ball-and-stick model of square-pyramidal [$Cu_2L'(H_2O)_4$]$^{4+}$ illustrates that the ligand can easily adopt various conformations which avoid any steric hindrance of the coordinated water molecules. In our view slightly different Lewis acidities or subtle differences in the steric preorganisation of the metal ions in [Cu_2L] and [Cu_2L'] would not account for the very different pK_a values of the complexes. This observation reflects the necessity of a bridging OH^- coligand for the stabilization of [Cu_2L] in aqueous solution.

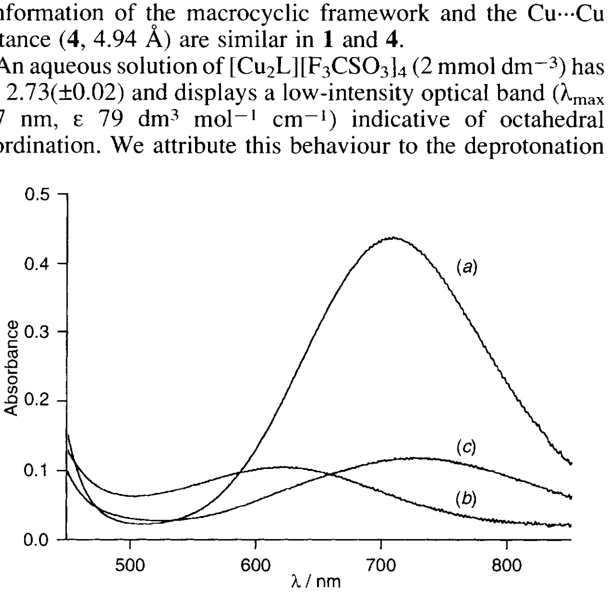


Fig. 2 (*a*) Optical absorbance of **3** (1 mmol dm^{-3}) in MeCN; (*b*) spectrum after addition of $NEt_4^+CN^-$ (1 equiv.); (*c*) spectrum after stirring with excess solid $NaHCO_3$

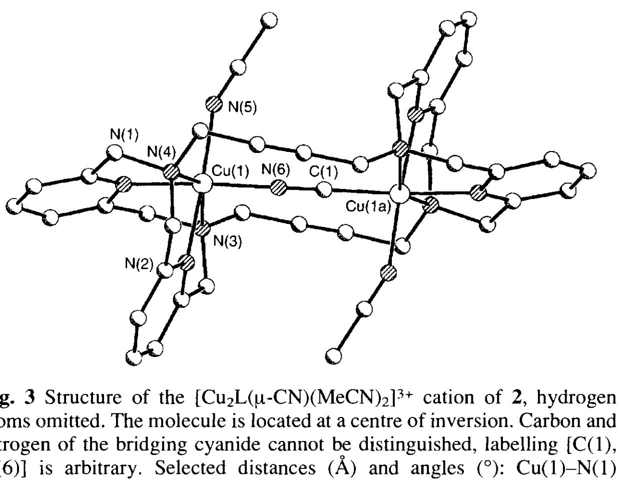


Fig. 3 Structure of the [Cu_2L(μ-CN)$(MeCN)_2$]$^{3+}$ cation of **2**, hydrogen atoms omitted. The molecule is located at a centre of inversion. Carbon and nitrogen of the bridging cyanide cannot be distinguished, labelling [C(1), N(6)] is arbitrary. Selected distances (Å) and angles (°): Cu(1)–N(1) 1.963(4), Cu(1)–N(2) 2.084(4), Cu(1)–N(3) 2.327(4), Cu(1)–N(4) 2.316(4), Cu(1)–N(5) 2.093(4), Cu(1)–C(1)/N(6) 1.907(4), C(1)–N(6) 1.124(8), Cu(1)···Cu(1a) 4.94; N(3)–Cu(1)–N(4) 151.65(13), N(2)–Cu(1)–N(5) 176.2(2), N(1)–Cu(1)–C(1)/N(6) 176.3(2), N(1)–Cu(1)–N(2) 81.43(15).

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Footnotes

† Force-field calculations were performed with the program MOBY.[7] The {2,11-diaza[3.3](2,6)pyridinophane}copper(II) unit was treated as a rigid fragment using the crystallographic bonding parmeters of {*N*,*N*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane}$CuCl_2$.[6a]

‡ *Crystal data* for **3**: monoclinic, space group $P2_1/n$, a = 13.662(3), b = 11.693(2), c = 18.809(4) Å, β = 97.39(3), U = 2979.8(10) Å^3, Z = 2, Mo-Kα radiation (0.71073 Å), no absorption correction, 6736 measured reflections, 5033 observed with $I > 2\sigma(I)$, 502 refined parameters, R (on F_o) = 0.0375, R_w (on F_o^2) = 0.0875, min., max. residual electron density −0.466, 0.415 e Å^{-3}. For **4**: the unit cell contains two different complex cations, [Cu_2L(μ-CN)$(MeCN)_2$]$^{3+}$ and [Cu_2L(μ-CN)$(OH_2)_2$]$^{3+}$; triclinic, space group $P\bar{1}$, a = 11.831(2), b = 13.038(3), c = 16.765(3) Å, α = 108.17(3), β = 96.72(3), γ = 95.22(3), U = 2417.8(8) Å^3, Z = 2, Mo-Kα radiation (0.71073 Å), no absorption correction, 10970 measured reflections, 7295 observed with $I > 2\sigma(I)$, 605 refined parameters, R (on F_o) = 0.0581, R_w (on F_o^2) = 0.1836, min., max. residual electron density −0.722, 2.775 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ At pH 2.7 no dissociation of [Cu_2L] (2 mmol dm^{-3}) into free metal ion and ligand, is detectable by spectrophotometry. pK_a = 1.6(±0.5) for [$Cu_2L(OH_2)_n$]$^{4+}$ was obtained from K_a = [$Cu_2L(OH)$]$^{3+}$[H^+]/[Cu_2L]$^{4+}$, setting [$Cu_2L(OH)$]$^{3+}$ = [H^+] = $10^{-2.73(\pm 0.2)}$ mol dm^{-3} and [Cu_2L]$^{4+}$ = (0.002 − [H^+]) mol dm^{-3}.

References

1 Reviews: (*a*) J.-M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441; (*b*) S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461; (*c*) A. E. Martell, R. J. Motekaitis, D. Chen and I. Murase, *Pure Appl. Chem.*, 1993, **65**, 959; (*d*) A. Bencini, A. Bianci and P. Paoletti, *Coord. Chem. Rev.*, 1992, **120**, 51.
2 S. Warzeska and R. Krämer, *Chem. Ber.*, 1995, **128**, 115.
3 J. S. Bradshaw, P. Huszthy, C. W. McDaniel, C. Y. Zhu, N. K. Dalley, R. M. Izatt and S. Lifson, *J. Org. Chem.*, 1990, **55**, 3129.
4 (*a*) F. R. Fronczek, A. Mamo and S. Pappalardo, *Inorg. Chem.*, 1989, **28**, 1419; (*b*) H. Sakaba, C. Kabuto, H. Horino and M. Arai, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1822; (*c*) C.-M. Che, Z.-Y. Li, K.-Y. Wong, C.-K. Poon, T. C. W. Mak and S.-M. Peng, *Polyhedron*, 1994, **13**, 771; (*d*) H.-J. Krüger, *Chem. Ber.*, 1995, **128**, 531.
5 U. Höweler, *MOBY Version 1.5*, Springer Verlag, Berlin, 1992.
6 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 6, pp. 606–610.
7 B. L. Vallee and R. J. P. Williams, *Biochemistry*, 1968, **59**, 498.
8 B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1972, 1196.
9 Among the lowest reported values is pK_a = 4.3 for the dicopper(II) complex of an octaaza macrobicycle: J. Motekaitis, A. E. Martell, J.-M. Lehn and E.-I. Watanabe, *Inorg. Chem.* 1982, **21**, 4253.

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