Template Synthesis of a Novel Macrobicyclic Ligand and the Crystal Structure of its Unique Dinuclear Copper(I) Complex

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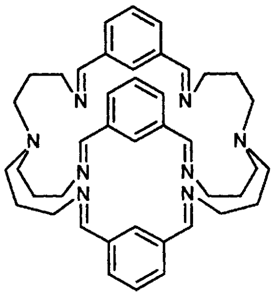
The condensation of a tris(3-aminopropyl)amine with benzene-1,3-dicarbaldehyde in the presence of $AgNO_3$ produces the dinuclear silver(I) complex of an octa-aza hexa Schiff's base macrobicyclic ligand, which is converted to a unique dinuclear copper(I) hexa Schiff's base cryptate complex by transmetallation.

In recent years considerable effort has been directed towards the synthesis of potential biological models of metalloproteins with dinuclear copper(I) active sites.[1] The motivating factor is the important role that copper(I) plays in oxygen transport and catalytic oxidation.[1,2—5] Much interest, thus far, has focused around those complexes in which the dicopper(I) ions are bound by ligands in a two-[3,4] or three-co-ordinate[5] fashion. While stable four-co-ordinate copper(I) complexes with all-sulphur[6] or mixed-donor atoms[7] as co-ordination sites are known, those involving all-nitrogen donor atoms are rare. We report here the synthesis of a very air-stable dicopper(I) complex of the macrobicyclic ligand mx_3trtn_2 (**1**). Both copper(I) centres are shown to be four-co-ordinate by single crystal *X*-ray structure determination. A satisfactory elemental analysis was obtained.

The dicopper(I) complex of mx_3trtn_2 was prepared *via* transmetallation of a silver(I) complex[8,9] which was originally obtained through the template reaction of the tripodal tris-(3-aminopropyl)amine with isophthalaldehyde in the presence of silver(I). To a stirred solution of the aldehyde (7.30 mmol) and $AgNO_3$ (5.89 mmol) in absolute methanol (200 cm^3) was added dropwise a solution of tris(3-aminopropyl)amine (4.89 mmol) in absolute methanol (100 cm^3) during 20 min. The mixture was then heated under reflux with stirring for 3 h, and $NaClO_4$ solution (50 cm^3; 14.24 mmol) was added. The mixture was further refluxed for an hour. The resulting yellow dinuclear silver(I) complex which precipitated was filtered off and recrystallized from acetonitrile (1.98 g, 75% yield). The dicopper complex was prepared by refluxing the Ag^I complex in a mixture of MeOH–MeCN (50 : 25 cm^3) with an excess of $Cu(MeCN)_4(ClO_4)$ or $Cu(ClO_4)\cdot 6H_2O$ during 1 h. Orange-red crystals suitable for an *X*-ray crystal structure determination† were obtained on allowing the solution to stand for 48 h. The crystal structure data were collected at 193 K.

The molecular structure of the cationic complex $[Cu_2(mx_3trtm_2)]^{2+}$ is shown in Figure 1. In the cation the two copper atoms are enclosed within the ligand. However there is no apparent interaction between the two metallic centres which are separated by 4.44(1) Å. Each copper atom is four-co-ordinate by three nitrogen atoms from the weakly basic imine-*m*-xylene moiety and one more basic tertiary bridgehead nitrogen from the tris(3-aminopropyl) moiety. There is no plane of symmetry within the molecule. The Cu–imine nitrogen distances are in good agreement with those of other Cu^I co-ordination compounds, falling within the



mx_3trtn_2 (**1**)

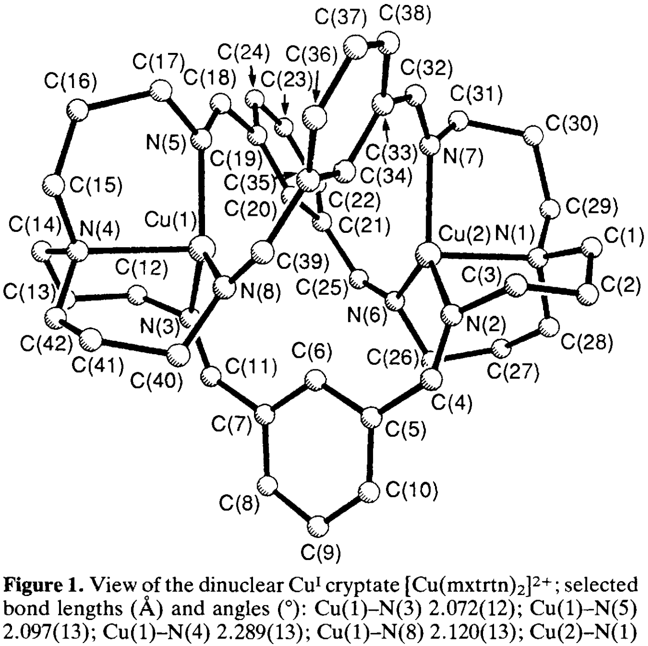


Figure 1. View of the dinuclear Cu^I cryptate $[Cu(mxtrtn)_2]^{2+}$; selected bond lengths (Å) and angles (°): Cu(1)–N(3) 2.072(12); Cu(1)–N(5) 2.097(13); Cu(1)–N(4) 2.289(13); Cu(1)–N(8) 2.120(13); Cu(2)–N(1) 2.27(12); Cu(2)–N(6) 2.054(11); Cu(2)–N(2) 2.106(14); Cu(2)–N(7) 2.077(11); N(3)–Cu(1)–N(4) 91.9(5); N(4)–Cu(1)–N(5) 92.3(5); N(4)–Cu(1)–N(8) 90.7(5); N(3)–Cu(1)–N(5) 119.7(5); N(3)–Cu(1)–N(8) 120.7(5); N(5)–Cu(1)–N(8) 119.3(5); N(1)–Cu(2)–N(2) 92.3(5); N(2)–Cu(2)–N(6) 120.7(5); N(2)–Cu(2)–N(7) 121.2(5); N(1)–Cu(2)–N(6) 91.9(4); N(1)–Cu(2)–N(7) 92.2(5); N(6)–Cu(2)–N(7) 117.7(5).

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† *Crystal data*: $[Cu_2(C_{42}H_{54}N_8)]\cdot 2(ClO_4)\cdot CH_3OH\cdot 1/2(CH_3CN)$, M_r = 1049.5, monoclinic, space group $P2_1/c$ (No. 14), a = 17.059(5), b = 14.676(6), c = 18.986(6) Å, β = 97.78(2)°; V = 4710 $Å^3$, Z = 4, D_c = 1.472 g cm^{-3}; T = 193 K; crystal dimensions 0.08 × 0.41 × 0.50 mm. Data collected with Mo-K_α (λ = 0.710 73 Å) radiation on a Nicolet R3m diffractometer; scan speed: variable 1.50—15.00 °/min, observed reflections: 3573 with $I \geqslant 3\sigma(I)$; absorption correction applied (T_{min} = 0.77, T_{max} = 0.93). The structure was solved by direct methods. Refinement conditions: hydrogens were placed at geometrically calculated positions with isotropic thermal parameters fixed at 0.08. All other non-hydrogen atoms were refined anisotropically. The acetonitrile was found to sit about a centre of symmetry with the central carbon atom at the special position (0,0,0). The terminal carbon and nitrogen atoms for the acetonitrile are disordered. At convergence R = 0.084, R_w = 0.086. The atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

range 2.05—2.10 Å.[1e,4,7,10] However, the Cu–N distances involving the tertiary nitrogen donor sites are longer than normal, with values of 2.29(1) Å for Cu(1)–N(4) and 2.27(1) Å for Cu(2)–N(1). This is indicative of weaker interaction between copper(I) and the hard, more strongly basic tertiary nitrogens. Cu^I, which is soft, binds strongly with the soft imine nitrogen sites. The average N–Cu–N angle involving the central (tertiary) nitrogen atoms is 91.8°, while that involving the remaining (imine) nitrogen atoms is 119.9°. Therefore, in the absence of the fourth co-ordination site, the co-ordination around each copper atom would be considered essentially trigonal planar. However, the presence of this site, even though the co-ordination is weak as indicated by the long apical bonds for the Cu(1)–N(4) and Cu(2)–N(1) distances, implies that the co-ordination geometry of each copper centre should be described as trigonal pyramidal.

The dicopper(I) complex is unusual in that it does not show any reactivity towards dioxygen, nor does it react with other well known donors such as carbon monoxide, iodide, sulphide, azide, cyanide, and thiocyanate. This cannot be attributed to the large spacing between the Cu^I centres (4.44 Å) because some of these donors are monodentate, while others seem to be large enough to be accommodated within the macrocyclic cavity. In addition, not even solvent molecules can be found in the cavity of the cryptate. On the basis of evidence currently available, we suggest that the low reactivity of Cu^I in this case is due to highly effective co-ordination by the four nitrogens, three of which are 'soft' imine nitrogens of very low basicity, but which form co-ordinate bonds with Cu^I having considerable covalent character.

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