Crystal Structures of Two Binuclear Cu^{2+} Complexes with 1,4,7,10-Tetra-azacyclododecane-*N,N',N'',N'''*-tetra-acetic Acid and 1,4,8,11-Tetra-azacyclotetradecane-*N,N',N'',N'''*-tetra-acetic Acid

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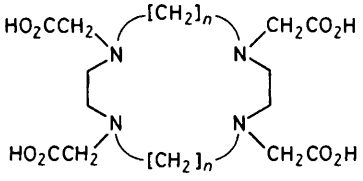
The structures of the binuclear Cu^{2+} complexes with the two title ligands are unexpected and completely different from each other, the 14-membered macrocycle giving a true binuclear species with two nearly identical Cu^{2+}–macrocycle units, whereas the 12-membered ligand binds one Cu^{2+} through the four nitrogens of the macrocycle and two carboxylates and the other one only through carboxylates with a similar structure to that found in many dicopper(II) tetracarboxylate systems.

The co-ordination chemistry of tetra-azacycloalkanetetra-acetic acids (H_4L) has been studied in several papers.[1] With transition metal ions it is known that these macrocycles form species with different stoicheiometry [$M(H_2L)$, $M(HL)^-$, $M(L)^{2-}$, or $M_2(L)$],[2] the structures of which are difficult to deduce from spectral data alone. Although binuclear species have not been observed in solution they can easily be prepared as solids by mixing the ligand with a twofold excess of the metal ion. The structures of two binuclear Cu^{2+} complexes with 1,4,7,10-tetra-azacyclododecane-*N,N',N'',N'''*-tetra-acetic acid (H_4dota) and with 1,4,8,11-tetra-azacyclotetradecane-*N,N',N'',N'''*-tetra-acetic acid (H_4teta) of the type Cu_2L have now been determined by *X*-ray crystallography.

Crystal data: $C_{16}H_{24}Cu_2N_4O_8 \cdot 5H_2O$ [Cu_2(dota)], M = 617.56, monoclinic, space group $P2_1/c$, a = 11.607(5), b = 16.953(5), c = 12.986(2) Å; β = 110.82(3)°; U = 2388.5 Å^3; D_c = 1.717, D_m = 1.70 g cm^{-3}; Z = 4, $F(000)$ = 1280. $C_{18}H_{28}Cu_2N_4O_8 \cdot 6H_2O$ [Cu_2(teta)], M = 663.62, triclinic, space group $P\bar{1}$, a = 9.254(4), b = 10.220(3), c = 15.937(2) Å; α = 92.01(2), β = 100.01(2), γ = 113.71(2)°; U = 1349.7 Å^3; D_c = 1.633, D_m = 1.63 g cm^{-3}; Z = 2, $F(000)$ = 664. Intensity data were collected with Mo-K_α radiation to θ = 27° (θ–2θ scan mode). Unit cell parameters were obtained from accurate centring of 25 reflections. Intensities of 3928 and 3469 independent reflections for structures (**1**) and (**2**), respectively, were measured with an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. No corrections for absorbance were applied. The structures were solved by Patterson and Fourier techniques. Structure (**1**) yielded 2368 reflections with $F_o > 2\sigma(F_o)$ and (**2**) 2214 reflections with $F_o > 2\sigma(F_o)$ respectively which were used in the anisotropic refinements with the weighting scheme $w = 1/\sigma^2(F)$. The final R indices were 0.0573 and 0.0556, respectively.†

The ligand dota gives a 2 : 1 Cu^{2+} complex in which the two Cu^{2+} ions are in completely different environments (Figure



H_4dota, n = 2

H_4teta, n = 3

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

1). Cu(1) is co-ordinated by two carboxylate oxygen and four nitrogen atoms of the macrocycle which is folded to give a *cis*-octahedral geometry. The pseudo-octahedral geometry is distorted since the axial Cu(1)–N bonds (2.326 and 2.298 Å) are distinctly longer than the equatorial Cu(1)–N bonds (2.119 and 2.116 Å). Additionally the N(2)–Cu(1)–N(4) angle is 151.3°, so that the linearity expected for an octahedron is not attained. This might be due to the strain imposed by the macrocycle, which because of its size does not allow the two nitrogens N(2) and N(4) to come exactly into the axial positions. The same geometry was also found in the mononuclear complex Cu(H_2dota).[3] The two carboxylates which are not involved in binding Cu(1) are used to co-ordinate to Cu(2). The structural entity which results is the same as that found in many dicopper tetracarboxylates. Two Cu(2) ions are bridged by four carboxylate groups which come from four different macrocycles, and each Cu^{2+} additionally binds a water molecule. The Cu(2)–Cu(2′) distance of 2.652 Å is practically the same as in Cu_2(acetate)$_4$ (2.65 Å).[4] Thus the Cu_2(dota) complex is composed of two structural elements which have both been found previously in other complexes.

For the binuclear complex with teta, however, the situation is completely different (Figure 2). Both Cu^{2+} ions have a relatively similar surrounding, being co-ordinated by two amino nitrogen atoms, two carboxylate oxygen atoms, and by an additional axial oxygen atom. It results in a square pyramidal geometry with Cu(1) and Cu(2) being out of the N_2O_2 plane by 0.17 and 0.22 Å, respectively. The two Cu^{2+} ions differ slightly from each other, however, the axial ligand being a water molecule [O(9)] and a carboxylate group [O(5)] for Cu(1) and Cu(2), respectively. The two Cu^{2+} ions belong to different macrocyclic units which are linked by a bridging carboxylate group. The distances between the two Cu^{2+} ions co-ordinated by the same macrocycle are 4.78 and 4.88 Å for Cu(1′)–Cu(1) and Cu(2)–Cu(2′), respectively, and for two Cu^{2+} ions of different macrocycles the distance is 5.53 Å, so that an antiferromagnetic interaction is expected. In some respects the structure described here resembles that found by Murase *et al.*[5] for the binuclear Cu^{2+} complex of tetrakis-*N*,*N*′,*N*″,*N*‴-(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane.

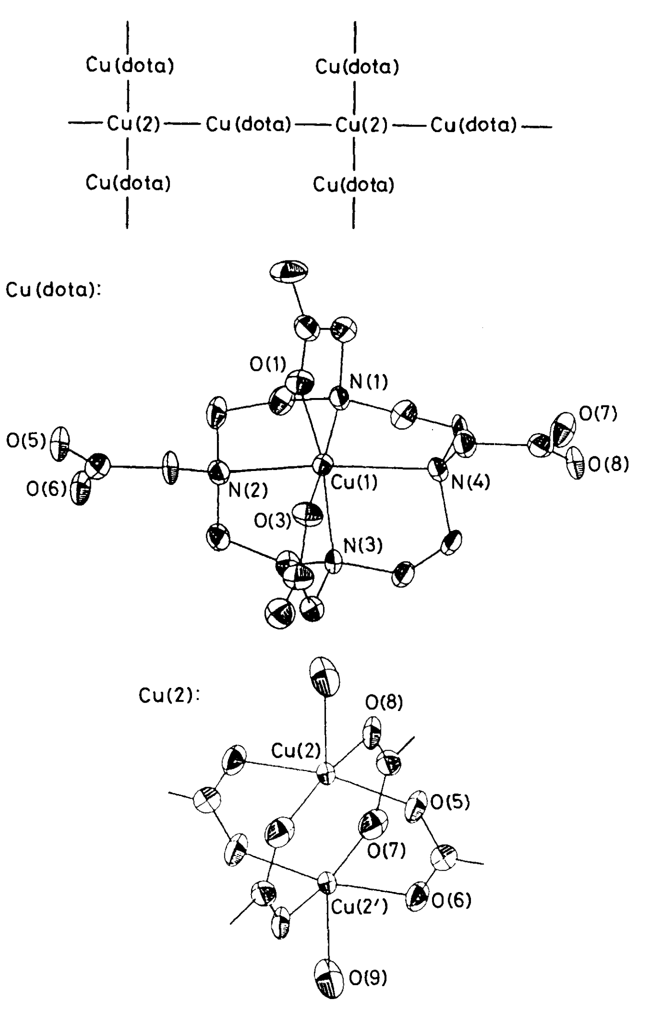

Figure 1. Structure of Cu_2(dota)·$5H_2O$ (**1**). Cu(1) co-ordination geometry: Cu(1)–O(1) 1.957(7), Cu(1)–O(3) 1.982(5), Cu(1)–N(1) 2.119(6), Cu(1)–N(2) 2.326(7), Cu(1)–N(3) 2.116(7), Cu(1)–N(4) 2.298(6) Å; ∠(2)-Cu(1)-N(4) 151.3(3)°. The Cu(2) co-ordination geometry: Cu(2)–Cu(2′) 2.652(2), Cu(2)–O(5) 1.954(8), Cu(2′)–O(6) 1.959(8), Cu(2′)–O(7) 1.962(8), Cu(2)–O(8) 1.969(8), Cu(2′)–O(9) 2.164(8) Å.

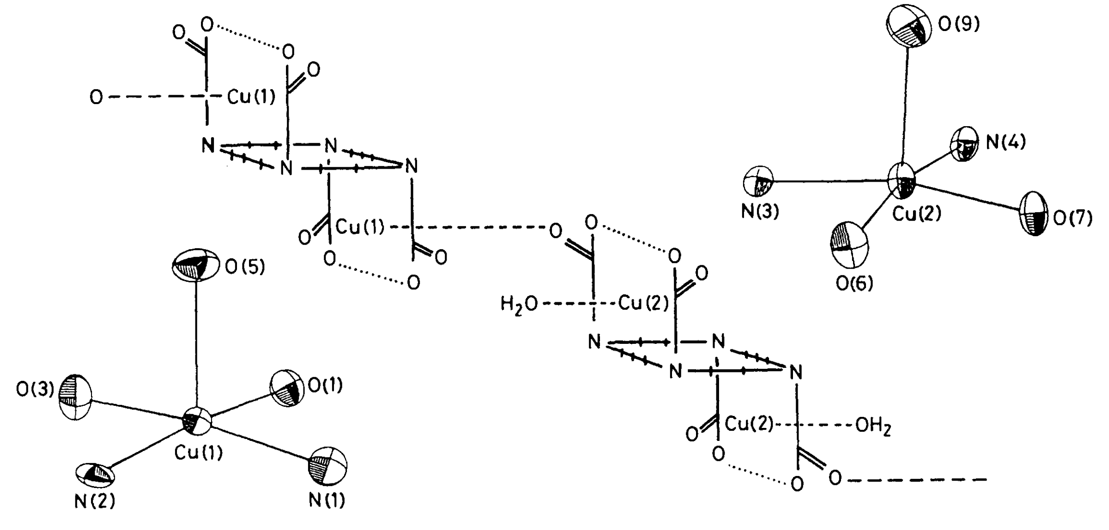

Figure 2. Structure of Cu_2(teta)·$6H_2O$ (**2**). Cu(1) environment: Cu(1)–O(1) 1.942(6), Cu(1)–O(3) 1.937(5), Cu(1)–O(5) 2.243(7), Cu(1)–N(1) 2.023(6), Cu(1)–N(2) 2.021(7) Å. Cu(2) environment: Cu(2)–O(6) 1.948(6), Cu(2)–O(7) 1.927(7), Cu(2)–O(9) 2.236(6), Cu(2)–N(3) 2.027(7), Cu(2)–N(4) 2.038(7) Å. Copper–copper distances Cu(1)–Cu(1′) 4.776, Cu(2)–Cu(2′) 4.878, Cu(1)–Cu(2) 5.532 Å.

Our results show how a subtle change from a 12-(dota) to a 14-(teta) membered ring strongly influences the structure of the binuclear complexes with Cu^{2+}.

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