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Quinquedentate "Wrap-around" Macrocyclic Ligands. The X-ray Structure Determination of {Dibenzo[*k*, *r*][1,5,9,13,17]-penta-azacyclo-eicosa[9,20]diene-N^1, N^5,N^9,N^{15},N^{19}}copper(II) Diperchlorate

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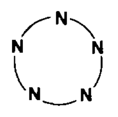
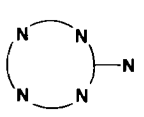
Most quinquedentate macrocyclic nitrogen ligands of the schematic type I adopt an approximately planar geometry when coordinated to a metal ion [1]. We have attempted to prepare comparable ligands which provide a 3-dimensional donor set and define 5-coordination sites at an octahedral metal ion, thus leaving the sixth site available for the coordination of small monodentate ligands. Bifurcated ligands of the type II have been used [2] previously to achieve such a coordination environment for transition metal ions.



I



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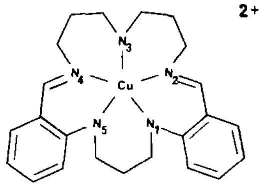
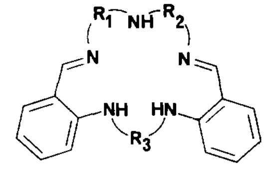


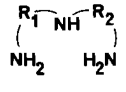
III

We report here the structure of an unusual copper(II) complex (III) of a 20-membered cyclic ligand. Penta-aza macrocycles of this type (IV) were obtained from condensation reactions of (V) and (VI) performed in the presence of zinc(II) acetate under conditions which had previously allowed the isolation of certain metal-free quadridentate [3] and sexidentate [4] ligands. Only the more flexible of the diimine macrocycles (IV) with at least 20-membered inner great rings were found to coordinate readily to ions of the first transition series.

{Dibenzo[*k*, *r*][1,5,9,13,17]-penta-azacyclo-eicosa[9,20]diene-N^1, N^5,N^9, N^{15}, N^{19}} copper(II) diperchlorate was prepared by mixing ethanol solutions of the free ligand and hydrated copper(II) perchlorate.



IV



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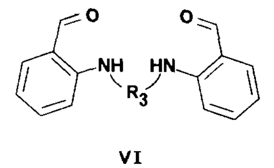
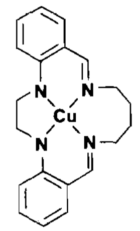


VI



VII

Slow evaporation of an acetone solution gave deep blue–purple prisms. $[CuC_{23}H_{31}N_5](ClO_4)_2$, M = 661.98, monoclinic, space group $P2_1/c$, $a = 9.170(4)$, $b = 17.059(6)$, $c = 19.026(4)$ Å, $\beta = 111.9(5)°$, U = 2763.6 Å^3, Z = 4. The structure determination was undertaken by using 1546 unique reflections with $I \geqslant 3\sigma(I)$ obtained on a Philips PW1100 4-circle diffractometer equipped with graphite monochromatized MoK_α radiation ($\lambda = 0.71069$ Å), collected using the space group $P2_1/n$, $c = 17.774(4)$ Å and $\beta = 96.30(5)°$.

The structure consists of a dicationic five-coordinate copper(II) complex of the macrocycle (Figure 1) which is well-separated from the ClO_4^- counterions. It became clear at an early stage of refinement that

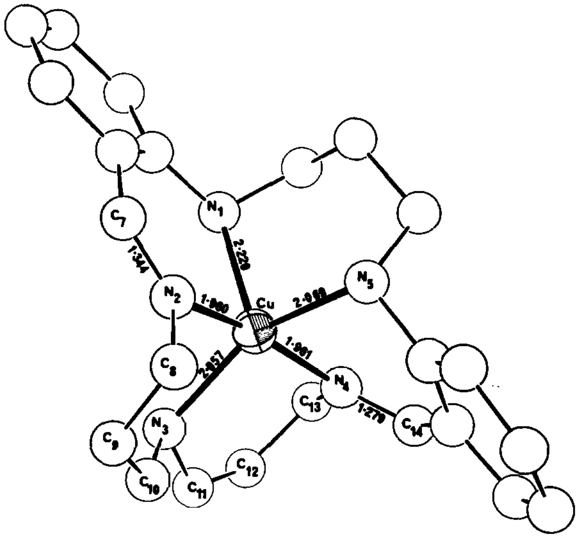


Figure 1. The macrocyclic dication. The conformation with the higher site occupation factors for the disordered chelate rings between N(2)–N(3) and N(3)–N(4) are shown.

disorder was present in both perchlorate ions and also in the trimethylene bridges between N(2)–N(3) and N(3)–N(4). Two independent ClO_4^- groups were found and refined [5] about each central chlorine atom. From an expanded difference Fourier map, two positions were resolved for each of the carbon atoms C(8) to C(12). The resulting two conformations of the trimethylene bridges were shown to have approximately equal population [6] and are illustrated in Figure 2. Neighbouring carbon atoms C(7), C(13) and C(14) showed high thermal parameters, and when refined anisotropically gave maximum vibrational amplitudes in directions consistent with the disorder (see Figure 2). Refinement of positional and thermal parameters (Cu, Cl and N atoms also anisotropic) for all non-hydrogen atoms was performed using full-matrix least-squares procedures [7] and has converged at a conventional R factor of 0.0957.

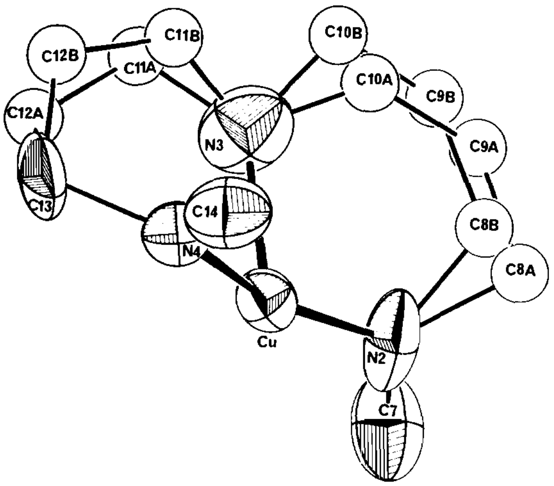


Figure 2. The disorder in the trimethylene chelate rings. The site occupation factors for the C(8)–C(10) atoms are: 0.53(4) (chain A) and 0.47(4) (chain B), and for the C(11) and C(12) atoms: 0.44(3) (chain A) and 0.56(3) (chain B).

The coordination polyhedron defined by the five nitrogen atoms is irregular. The main distortion from a square pyramidal arrangement (with N(2), N(3), N(4) and N(5) as the base) results from the nitrogen N(1) deviating from the apical position, apparently being constrained by the ligand bridges to approach the adjacent donor atoms N(2) and N(5) (see Table).

Coordinate bonds to the secondary amine nitrogen atoms are significantly longer than those found [8] in a copper complex (VII) of a comparable deprotonated quadridentate macrocycle. The variations in Cu–N lengths in III may be partially attributed to steric restrictions associated with the wrapping of the ligand about the five vertices of the coordination polyhedron. Such strain effects may partially account for the observation that the ligand can be relatively easily displaced from the copper ion on treatment with coordinating solvents such as dimethylformamide and dimethylsulphoxide.

TABLE. Interatomic Lengths and Angles in the Coordination Sphere.

Distances/Å		Angles/°	
Cu–N(1)	2.22(1)	N(1)–Cu–N(2)	91.0(6)
Cu–N(2)	1.96(1)	N(1)–Cu–N(3)	109.7(7)
Cu–N(3)	2.06(2)	N(1)–Cu–N(4)	104.2(6)
Cu–N(4)	1.96(1)	N(1)–Cu–N(5)	98.6(5)
Cu–N(5)	2.07(1)	N(2)–Cu–N(3)	87.9(8)
N(2)..N(3)	2.79	N(2)–Cu–N(4)	164.5(7)
N(3)..N(4)	2.84	N(2)–Cu–N(5)	87.9(7)
N(4)..N(5)	2.79	N(3)–Cu–N(4)	89.6(7)
N(5)..N(2)	2.79	N(3)–Cu–N(5)	151.5(7)
N(1)..N(2)	2.99	N(4)–Cu–N(5)	87.0(7)
N(1)..N(3)	3.51		
N(1)..N(4)	3.30		
N(1)..N(5)	3.25		

Acknowledgement

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5 Site occupation factors of 0.69(3) and 0.31(3) for one perchlorate and 0.65(1) and 0.35(1) for the other were obtained from the refinement of the ClO_4^- ions as rigid tetrahedra (O–Cl–O, 109.5(5)°) pivoting on their central Cl atoms, with all the Cl–O bonds refined as one variable to a value of 1.436(8).

6 Site occupation factors for equivalent atoms in the two conformations were refined such that their sum was fixed at 1.0, while constraining chemically equivalent bonds in the disordered chelate rings to have the same lengths, and with disordered pairs atoms having a common isotropic thermal parameter.

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