Dodeca(dimethylamido)cyclohexaphosphonitrile as a Macrocyclic Ligand

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Summary In the compound $[N_6P_6(NMe_2)_{12}CuCl]^+CuCl_2^-$, a 5-co-ordinated cupric ion is situated inside the 12-membered ring, the slight weakening of the ring bonds to the co-ordinating nitrogen atoms being partially compensated by increased exocyclic electron release.

DIMETHYLAMIDOCYCLOPHOSPHONITRILES, like other phosphonitriles carrying electron-releasing groups,[1] form complexes with metal ions, and the complexes are especially stable if the size of the ring is great enough for it to act as a macrocyclic ligand. Dodeca(dimethylamido)cyclohexaphosphonitrile $N_6P_6(NMe_2)_{12}$ reacts with $CuCl_2$ and with CuC separately, and with an equimolar mixture of the two forms a bright orange complex $N_6P_6(NMe_2)_{12}Cu_2Cl_3$, which gives a conducting solution in acetonitrile.

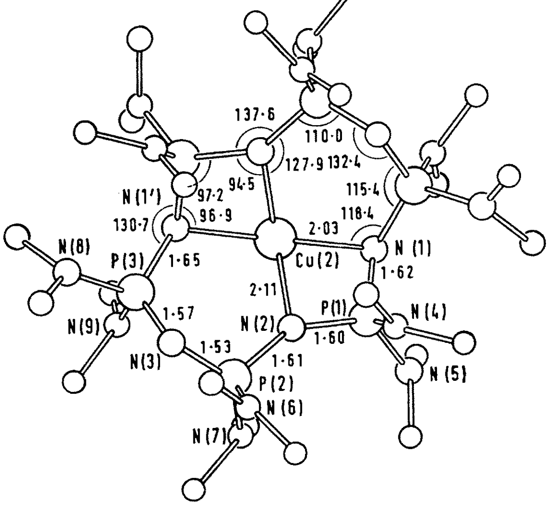

FIGURE. *General view of the* $N_6P_6(NMe_2)_{12}CuCl^+$ *ion. Mean standard deviations are* 0·02 Å *and* 1·1°.

Crystals of the complex are monoclinic, $a = 19{\cdot}352(8)$, $b = 8{\cdot}690(6)$, $c = 14{\cdot}069(7)$ Å, $\beta = 91{\cdot}04(4)°$, $Z = 2$, space group $P2/n$. The structure was determined with Mo-K_α diffractometer data from Patterson and electron-density maps; full-matrix least-squares refinement reduced R to 0·083 for 1103 observed reflections. The structure is ionic, and is formulated as $[N_6P_6(NMe_2)_{12}Cu^{II}Cl]^+Cu^ICl_2^-$. The $CuCl_2^-$ ion, hitherto unrecognised, is situated on a crystallographic C_2 axis and is linear, with Cu–Cl = 2·11(1) Å. The cation (Figure) is also situated on a crystallographic C_2 axis, and has Cu^{II} bonded to four nitrogen atoms of the phosphonitrilic ring and to one chlorine atom. The chlorine atom [obscured by Cu(2) in the Figure] can be regarded as occupying either the apical position of a distorted square pyramidor, since $\angle$N(1)Cu(2)N(1′) is large (160·9°), an equatorial position of a distorted trigonal bipyramid; neither idealised configuration is uncommon for Cu^{II}. Distortion is also evident at the co-ordinated nitrogen atoms, the N–Cu(2) bonds being imperfectly aligned with the conventional lone pair directions.

The geometry of the ring shows several points of contrast with that of $N_6P_6(NMe_2)_{12}$ itself.[2] It can be regarded as being derived from a planar arrangement, which is folded about the N(1) $\cdots\cdot$ N(1′) direction to give two approximately planar sections at a dihedral angle of 129°. Co-ordination tightens a ring already somewhat crowded in the uncomplexed state,[2] the mean angles at phosphorus and nitrogen being both reduced (Table; individual values are given in the Figure). The ring bond lengths are of two types, those from the co-ordinated nitrogen atoms being slightly longer (1·62 Å) than the others (1·55 Å), there being, as there is in complexes of $N_4P_4Me_8$,[3] some tendency to bond localisation. The withdrawal of the lone pairs on

Comparison of mean bond lengths and angles

	$N_6P_6(NMe_2)_{12}$[a]	$[N_6P_6(NMe_2)_{12}\cdot CuCl]^+$
Ring P–N (Å)	1·563(10)	1·597(20)
„ NPN (degrees)	120·1(5)	107·5(11)
„ PNP („)	147·5(7)	133·6(13)
Exocyclic P–N (Å)	1·669(10)	1·655(20)

[a] Reference 2. All standard deviations are of individual values.

the nitrogen atoms from the ring bonding system is partially compensated, as it is in $N_3P_3Cl_2(NHPr^i)_4,HCl$,[4] by electron release from the exocyclic nitrogen atoms. The shortest exocyclic bond lengths are, as expected, P(1)N(4) and P(1)N(5), mean 1·63(1) Å. The distribution of bond length as a whole provides further support for the concept of interacting endocyclic and exocyclic π-systems in phosphonitriles.

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