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Preliminary communication

Copper(I)–aryl bonds in cluster complexes: the structure of $[Cu(2\text{-}Me_2NC_6H_4)]_4(CuBr)_2 \cdot 1.5C_6H_6$

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SUMMARY

An X-ray diffraction analysis of $[Cu(2\text{-}Me_2NC_6H_4)]_4(CuBr)_2 \cdot 1.5C_6H_6$ shows the six copper atoms in a distorted octahedral arrangement; the bromine atoms bridge *trans*-equatorial edges, the 2-(dimethylamino)phenyl ligands bridging faces so that the complex has approximate C_2 symmetry.

The syntheses of the arylcopper complexes, Cu_4Ar_4 and $Cu_4Ar_4 \cdot Cu_2Br_2$, have been reported[1,2] and the analogous silver[3], lithium[4] and mixed metal complexes, $Cu_4Ar_4Ag_2Br_2$[2], and $Ar_4Cu_2Li_2$[4], have now been prepared. We have recently established[5] that (4-methyl-2-cupriobenzyl)dimethylamine is a tetranuclear species, the aryl ligands bridging copper atoms separated by 2.38Å. In view of the novelty of such complexes of transition metals and the probability of mixed arylcopper(I)–copper(I) halide clusters occurring as intermediates in the Ullmann biaryl synthesis, we proceeded to a structural analysis of $[Cu(2\text{-}Me_2NC_6H_4)]_4Cu_2Br_2 \cdot 1.5C_6H_6$.

The crystals (benzene) are triclinic with the Delaunay reduced cell, $a = 10.29$, $b = 13.27$, $c = 17.50$Å, $\alpha = 95.5°$, $\beta = 115.5°$, $\gamma = 98.3°$, space group $P\bar{1}$; $Z = 2$, $d_m = 1.79$, $d_c = 1.78$. 3355 reflexions having $F_{obs} > 10.0\ \sigma(F_{obs})$ were used in the X-ray analysis (Mo-K_α radiation; four circle diffractometry). The structure was determined by heavy atom methods; $R = 0.066$ with anisotropic temperature factors for the copper and bromine atoms and further refinement is proceeding. The stereochemistry is shown in Fig. 1.

The copper–copper distances depend markedly on the nature of the bridging ligand. The bromine-bridged atoms are separated by 2.70Å (Cu–Br–Cu = 66.7°). The apical and equatorial copper atoms bridged by the aryl ligands have a mean separation of 2.48Å, the corresponding unbridged atoms being separated by 2.64Å. The bond angles

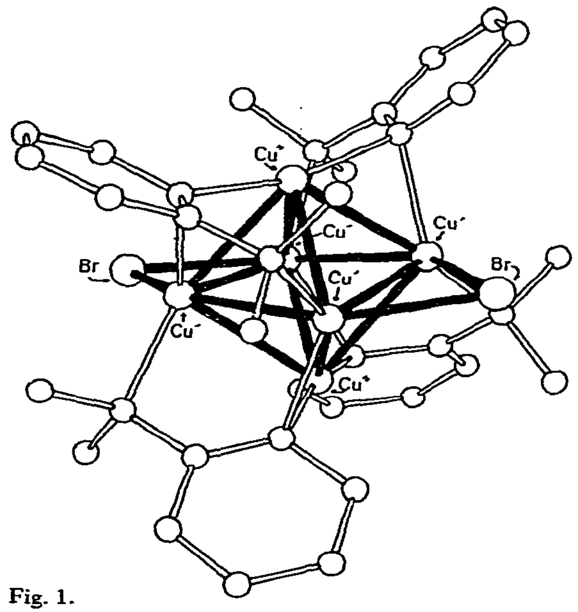

Fig. 1.

Cu–C(Ar)–Cu average 70.5° and 75.5° for the tetramer[5] and hexanuclear complexes. Elsewhere we have elaborated a theory which relates these bridge bond angles to electron deficiency in a wide range of complexes[6]. The difference between the mean Cu–N distance in the present complex (2.11Å) and that in the tetramer (2.21Å) may be related to the increased electronegativity of the bromine-bridged copper atoms.

Within the hexanuclear complex, bromine bridging of only four copper atoms implies asymmetric copper to aryl bonding (the mean lengths of Cu′–C and Cu″–C are 2.08Å and 1.97Å respectively). Without postulating direct metal-to-metal bonding, the coordination symmetry of the Cu′ atoms is roughly trigonal (average bond angles Br–Cu –C = 117°, Br–Cu′–N = 106°, N–Cu′–C = 120°) while that around the two Cu″ atoms is approximately linear (C–Cu″–C = 164°).

Our results suggest that bridging aryl ligands may form a systematic structural feature for Group IB aryl–metal complexes.

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