The Crystal Structure of the 2:1 Dimer [(Pyridine *N*-oxide)$_2$CuBr$_2$]$_2$

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Summary: The structure of the 2:1 dimer [(pyridine *N*-oxide)$_2$CuBr$_2$]$_2$ is reported and is shown to differ significantly from that of the corresponding chloride complex as well as from other structure types in the aromatic *N*-oxide series.

AROMATIC *N*-oxides of copper(II) complexes have recently been considered by Watson[1] in an effort to generalize the magnetic behaviour of more than a hundred of these complexes in terms of 12 idealized structure types. Dibromobis(pyridine *N*-oxide)Cu^{II}, [(C$_5$H$_5$NO)$_2$CuBr$_2$]$_2$, was cited as probably belonging to the same structure type and as having a considerably larger magnetic moment than the chloride analogue, [(C$_5$H$_5$NO)$_2$CuCl$_2$]$_2$. This magnetic result was unexpected because in the 1:1 series, bromide complexes exhibit smaller room temperature moments. We have determined the structure of the bromide complex and have found that, although the basic molecular unit is also a dimer, it differs markedly from the chloride compound. Moreover, the bromide complex does not fit any of the 12 structure types discussed by Watson.

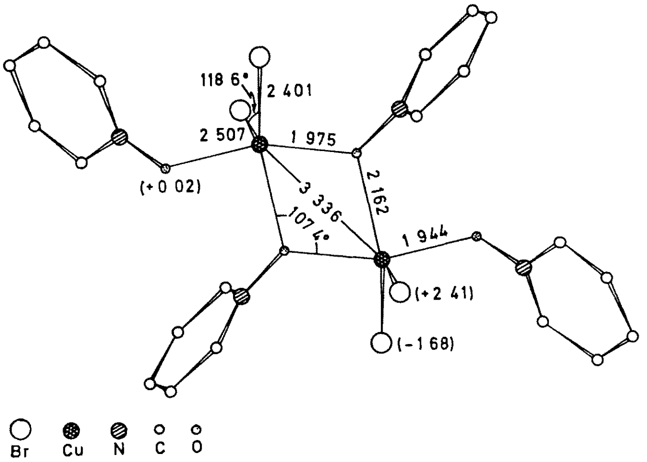

FIGURE. *Structure of the dimer* [(C$_5$H$_5$NO)$_2$CuBr$_2$]$_2$ *projected on the plane defined by the copper atoms and bridging oxygen atoms. Figures in parentheses indicate distances* (Å) *of atoms from this plane.*

Crystals of [(pyridine *N*-oxide)$_2$CuBr$_2$]$_2$ are triclinic with $a = 10{\cdot}510$, $b = 10{\cdot}882$, $c = 11{\cdot}818$ Å, $\alpha = 78{\cdot}572$, $\beta = 89{\cdot}880$, $\gamma = 81{\cdot}165°$, space group $P\bar{1}$, $D_m = 2{\cdot}08$, $D_c = 2{\cdot}10$ g cm^{-3}, and $Z = 2$. The intensities of 5958 reflections were measured on a diffractometer and the structure was solved by an analysis of the Patterson map. Block-matrix anisotropic least-squares refinement resulted in an R value of 0·046. The crystal structure consists of two centrosymmetric dimeric molecules per unit cell centred about (0,0,0) and (1/2,1/2,1/2). The structure of the dimer located about (0,0,0) is shown in the Figure. The dimer located about (1/2,1/2,1/2) is similar in all essential features except for a larger Br–Cu–Br angle (134·6°).

A comparison of this structure with that of the corresponding chloride complex shows that the co-ordination about the copper atoms differs significantly. The main features of these two structures can be summarized as follows—In the bromide complex the two non-bridging oxygen atoms lie nearly in the plane defined by the copper and bridging oxygen atoms with the bromine atoms above and below this plane. In the chloride complex,[2] the copper, bridging oxygen, and chlorine atoms are coplanar and the non-bridging oxygen atoms lie above and below this plane. Thus, for the bromide complex to fit the idealized structure type of the chloride complex, the plane of the copper and bridging oxygen atoms would have to be rotated with respect to the bromine atom *ca.* 90° about the Cu–Cu direction. Finally, the bromide complex reported here cannot be regarded as a minor variant of any other structure type described by Watson.

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[1] W. H. Watson, *Inorg. Chem.*, 1969, **8**, 1879.

[2] J. C. Morrow, presented at the National Meeting of the American Crystallographic Association, Gatlinburg, Tennessee, June 1965.