X-Ray Crystal Structure of a Dimeric Silver(I) Complex Containing Short Metal-Metal Separations

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Summary *X*-Ray analysis of bis(3-hydroxy-4-phenyl-2,2,3-trimethylcyclohexanecarboxylato)disilver(I) dihydrate shows that it contains centrosymmetric bridged dimers with short silver–silver distances of 2·778 and 2·834 ± 0·005 Å.

A NUMBER of *X*-ray single-crystal structure studies of metal carboxylates have revealed the presence of centrosymmetric dimers containing bridging carboxylate groups and a range of metal–metal separations the shortest of which are indicative of strong metal–metal interactions.[1] There have appeared several reports[2–4] of silver(I) carboxylates in which metal–metal separations similar to those found in silver metal[5] (2·89 Å) are present, and one occurrence of a shorter distance (2·80 Å) has been reported for the low temperature (−140 °C) ferroelectric complex, glycinesilver(I) nitrate.[3] We now report that room temperature (20 °C) *X*-ray analysis of bis(3-hydroxy-4-phenyl-2,2,3-trimethylcyclohexanecarboxylato)disilver(I) dihydrate shows that it contains centrosymmetric bridged dimers in which the silver–silver distances are significantly less than those in silver metal.

Crystals of $(C_{16}H_{21}AgO_3)_2 \cdot 2H_2O$ are monoclinic, space group $P2_1/c$, with $a = 15\cdot76$, $b = 18\cdot71$, $c = 12\cdot39$ Å, $\beta = 103\cdot1°$, $D_m = 1\cdot46$, $Z = 4$, $D_c = 1\cdot445$. Three-dimensional *X*-ray intensity data were recorded by equi-inclination multiple-film Weissenberg photography and visually estimated. The structure was solved by the heavy-atom method, and the atomic positional and thermal parameters (anisotropic Ag, isotropic C and O) were refined by full-matrix least-squares calculations to the present *R* of 0·117 for 2228 independent observed reflexions.

The asymmetric crystal unit contains two crystallographically independent centrosymmetric dimers, and consequently two estimates of all molecular dimensions are derived from the analysis. We record here the averaged molecular dimensions except where the individual values differ significantly. All the C–C and C–O distances lie satisfactorily close to their normal values. The silver atoms are held by two bridging carboxylate ligands with unequal Ag–O bonds of length 2·20 and 2·29 ± 0·02 Å, and O–Ag–O angles of 158 ± 1°. The longer of these distances is to that oxygen atom which is also involved in an intramolecular hydrogen bond with the hydroxy-group (O · · · O = 2·58 Å). The Ag–Ag separations at 2·778 and 2·834 ± 0·005 Å differ significantly as do the corresponding shortest Ag · · · C(Ph) distances of 2·92 and 2·76 ± 0·03 Å. The individual Ag–Ag distances in the complex are significantly less than in silver metal and thus are indicative of metal–metal interactions. The differences between these distances in the complex may arise from the presence of the proximate phenyl rings which are not equidistant from the silver atoms of each dimer. The phenyl groups may be weakly associated with the silver atoms[6] although this conclusion is not without some ambiguity for these phenyl groups are constrained to be close to the silver atoms owing to the organic ligand geometry. The silver atoms are co-ordinated also by the hydroxy-oxygen atoms of neighbouring molecules with Ag · · · O = 2·46 Å. A very distorted octahedral arrangement around the silver atoms is completed by disordered water molecules which are distributed over two sites for each silver atom with average Ag · · · O distances of 3·13 Å.

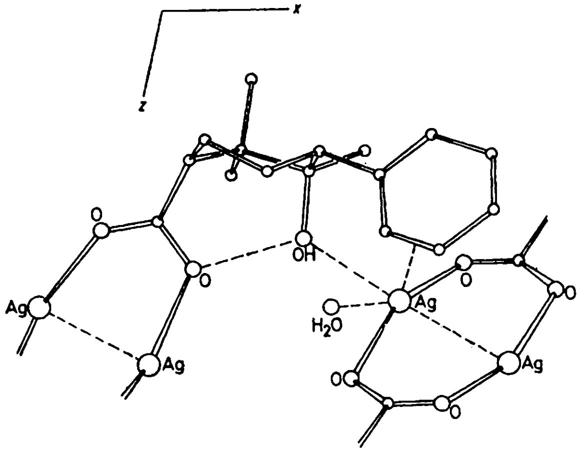

FIGURE. *The conformation of the organic ligand and its co-ordination to the silver atoms.*

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[1] F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *Acta Cryst.*, 1971, **B27**, 1664, and references therein.
[2] A. E. Blakeslee and J. L. Hoard, *J. Amer. Chem. Soc.*, 1956, **78**, 3029.
[3] R. S. Krishnan, J. K. M. Rao, and M. A. Viswamitra, *J. Phys. Soc. Japan Suppl.*, 1969, **28**, 298.
[4] C. B. Acland and H. C. Freeman, *Chem. Comm.*, 1971, 1016.
[5] 'International Tables for *X*-Ray Crystallography', vol. III, Kynoch Press, Birmingham, 1962.
[6] E. A. H. Griffith and E. L. Amma, *J. Amer. Chem. Soc.*, 1971, **93**, 3167.