The Crystal and Molecular Structure of the Bis-(*o*-xylene)silver Perchlorate Dimer

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Summary The crystal structure of the dimer of bis-(*o*-xylene)silver perchlorate has been determined by single-crystal methods: the dimer is made up of oxygen-bridged silver(I) with the fourfold co-ordination of the metal completed by interaction with the π-electrons of two aromatic entities.

THE crystal structures of a number of complexes between silver perchlorate and aromatic π-donors may be described as layer structures. The layers or sheets are composed of $AgClO_4$ (ionic material) and aromatic (organic material) which are alternately stacked to make the crystal structure. Examples of this type of layer are found in the crystal structures: benzenesilver perchlorate,[1] bis(cyclohexylbenzene)silver perchlorate,[2] bis-(*m*-xylene)silver perchlorate,[3] naphthalenetetrakis(silver perchlorate) tetrahydrate,[4] and anthracene-tetrakis(silver perchlorate) monohydrate. In these structures, Ag–O(perchlorate) distances range between 2·45—2·68 Å. We have maintained, in spite of the fact that these distances are long compared with single bond silver–oxygen distances as indicated by covalent radii (*ca.* 2·2Å), they are important interactions in the stabilization of the structure. We have now found strong support for this view in the oxygen-bridged dimeric structure of bis-(*o*-xylene)silver perchlorate. The geometric details of the dimer yield valuable information concerning the nature of the silver–aromatic bond.

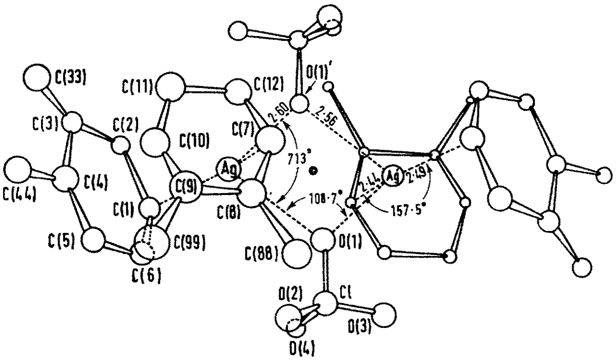

FIGURE. *Perspective view of the dimer of* bis-(*o*-xylene)·$AgClO_4$. *The two halves of the dimer are related by the centre of symmetry indicated. Bonded distances are shown by dotted lines. For simplicity the next nearest* Ag–C *are not dotted. They are*: Ag–C(6) 2·57, Ag–C(12) 2·53Å. *The rings are normal within experimental error and distances and angles are not shown. Maximum e.s.d.'s in distances are*: Ag–C,O ± 0·03; C–C, ±0·07; Cl–O ±0·04Å. *The maximum e.s.d.'s for the angles are*: Ag–O–Ag, ±1; O–Ag–O, ±1; C–Ag–C, ±1; C–C–Ag, ±2; C–C–C, ±4°. *The e.s.d.'s are relatively high due to large thermal motions of the rings, as expected for an isolated dimeric molecule.*

Bis-(*o*-xylene)silver(I) perchlorate $[o\text{-}MeC_6H_4Me]_2Ag^IClO_4$ forms colourless, hygroscopic, light-sensitive needles, stable only in sealed capillaries: M 420, triclinic $P\bar{1}$. With Mo-K_α (λ = 0·71068), a = 8·595(1), b = 10·766(1), c = 10·817(1) Å, α = 86·21(1), β = 103·28(1), γ = 113·70(1)°, Z = 2, D_c = 1·56; D_m could not be measured but, in general, for these types of compounds D varies between 1·6—1·8, μ = 12·6 cm^{-1} for Mo-K_α. Crystals were mounted in capillaries on an automated Picker full-circle diffractometer and aligned by standard methods.[6] 3500 independent *hkl* intensities were measured with Mo-K_α radiation, of which 1236 were non-zero. The structure was solved by standard heavy-atom techniques and refined by full-matrix least-squares with anisotropic temperature factors for Ag and Cl and four oxygens, but only isotropic for the remaining atoms, to a final R factor of 0·103.[6]

The structure consists of isolated oxygen-bridged dimers (Figure) in which each silver acquires its usual co-ordination number of four by forming bonds with the π-orbitals of two aromatic entities and two bridging oxygen atoms of perchlorate groups. The Ag–Ag distance within the dimer is 4·198(5) Å, *i.e.*, no metal–metal interaction. Whereas the Ag–O bridging distances within the dimer are *ca.* 2·6 Å, the next shortest Ag–O distance is 3·38 Å. There are no Ag–O distances less than 4 Å between dimers, and clearly no significant intermolecular Ag–O interaction exists. All other non-bonded interatomic distances are normal. In space group $P\bar{1}$ the centre of the Ag, O(1), O(1′), Ag′ four-membered ring lies on a centre of symmetry and therefore, this ring must be planar. The angle between Cl–O(1) and O(1)–(centre of Ag–Ag′ line) is 168°. This together with the Ag–O(1)–Ag′ angle of 109° indicates that each bridging oxygen contributes two electron pairs and two tetrahedral orbitals to the bridge bonding. The sharp O(1)–Ag–O(1′) angle indicates that Ag contributes almost pure *p*-orbital to the bridge. Therefore, the bridge-bonding is well described as four electron pair donor-acceptor bonds. On the other hand, the "broad" C(7)–Ag–C(1) angle indicates that Ag uses a considerable amount of 5*s*-orbital in its interaction with the aromatic moieties: this strongly supports our view[2–4] that the principal interaction between Ag^{I} and aromatic entities involves the silver 5*s*-orbital with the π-electrons.

Fukui *et al.*[7] predicted, based upon a MO charge-transfer model, that Ag^{I} would interact with the π-electrons of the C–C bond directly opposite to the methyl groups in *o*-xylene. We find this to be true for one ring but not the other. This may well be simply a reflection of non-bonded repulsions between methyl groups overcoming the electronic factors involved.

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