The Crystal and Molecular Structure of a Novel Silver Ion–Aromatic Complex, Bis(cyclohexylbenzene)silver(I) Perchlorate

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As part of a synthesis and structure determination of metal ion–aromatic complexes, we have prepared the 2 : 1 aromatic : silver(I) complex between cyclohexylbenzene and silver perchlorate and determined its crystal structure. The only structures known between Ag(I) and aromatic donors are the 1 : 1 complexes benzene·$AgClO_4$[1] and benzene·$AgAlCl_4$.[2] However, there have been reports of 2 : 1 complexes between benzene and $AgClO_4$[3] and between various xylenes and $AgClO_4$.[4,5] We prepared and determined the structure of a 2 : 1 complex.

Bis(cyclohexylbenzene)silver(I) perchlorate $(C_6H_{11}Ph)_2Ag(I)ClO_4$, forms colourless hygroscopic, light-sensitive needles, stable only in sealed capillaries under a positive vapour pressure of cyclohexylbenzene *M*, 347·8, orthorhombic *Pmcn*. With Mo-K_α ($\lambda = 0{\cdot}71069$), $a = 32{\cdot}17 \pm 0{\cdot}02$, $b = 5{\cdot}666 \pm 0{\cdot}003$, $c = 12{\cdot}67 \pm 0{\cdot}01$ Å, $Z = 4$,

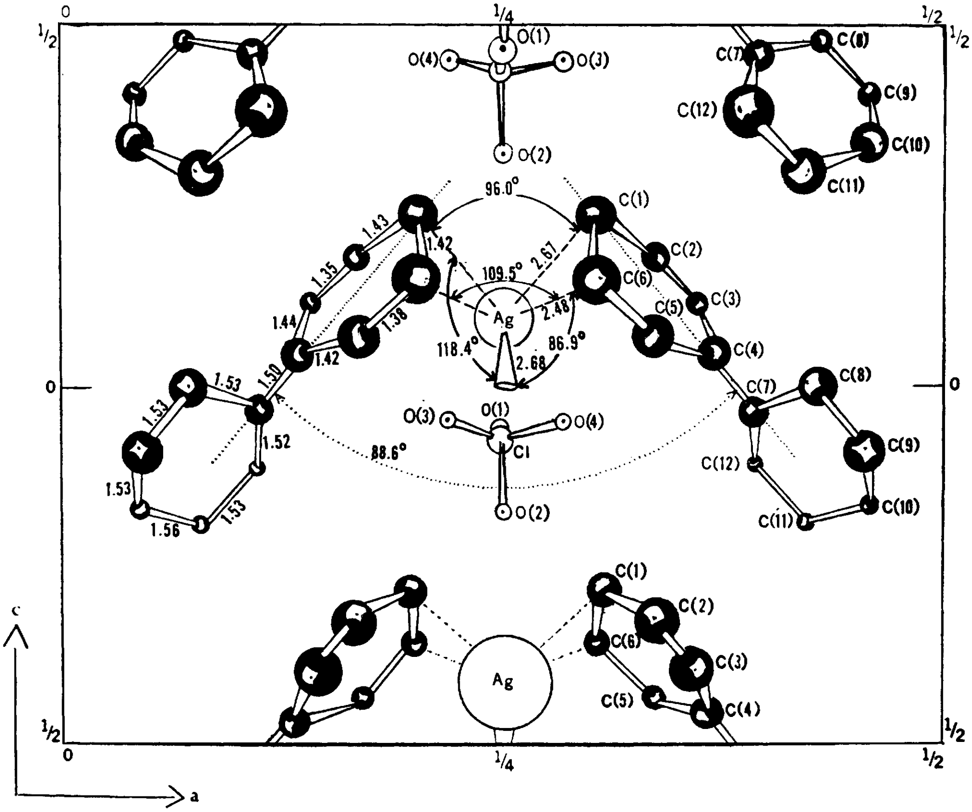

FIGURE. *View of the structure of* $(C_6H_{11}\text{–}C_6H_5)_2\cdot AgClO_4$ *down the* b *axis. The Ag is co-ordinated to two aromatic rings and to* O(1) *of the perchlorate group in the cell above that pictured. Estimated standard deviations in bond distances are:* Ag–C, ± 0·010; Ag–O, ± 0·015; C–C, ± 0·013 – 0·018 Å.

$D_c = 1{\cdot}52$, D_m *ca.* 1·4 g. cm.$^{-3}$ (could not be accurately measured). 1070 independent *hkl* reflections were measured manually with a Picker diffractometer using a G.E. single crystal orienter. The structure was solved by standard techniques† and refined by full matrix least-squares to a final *R*-value of 0·082.

The structure may be described as a distorted "half-open hinge" with the connecting section removed and replaced by Ag(I) displaced toward the open end of the hinge. The leaves of the hinge are the organic groups (Figure). The bisector of the "hinge" is a crystallographic mirror plane that contains the Ag(I) as well as the Cl and two O atoms of the perchlorate group. This mirror relates the two organic groups to one another. The Ag(I) is thus three-co-ordinate in an approximate trigonal pyramid arrangement with one donor bond from each aromatic ring and the third interaction with O(1) of the perchlorate group. This makes the complex a "molecular" unit $Ar_2\cdot AgClO_4$ in contrast to the previously known Ar·Ag(I) complexes.[1,2] The X–Ag–X (X = C,O) angles are such that it appears that Ag(I) is using either 5*p* or 5*s*5*p*^{3} orbitals as acceptors rather than the previously considered 5*s* orbitals.[6] Further, the shortest Ag–C distances are 2·48 and 2·67 Å, the shortest distance being within experimental error of that found in $C_6H_6\cdot AgClO_4$ and $C_6H_6\cdot AgAlCl_4$, and we now feel that a "normal" Ag–C [C(Aromatic)] distance should be 2·48 Å as this distance has been found in three radically different situations. The asymmetry in M–C distances has been noted as a characteristic feature of metal ion–aromatic complexes.[2,7]

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† For computer programmes and general techniques see: R. L. Girling and E. L. Amma, *Inorg. Chem.*, 1967, **6**, 2009.

The benzene ring is planar within experimental error, and although the ring seems to be systematically distorted toward the cyclohexadiene structure, the errors are such that this may not be statistically significant. Further, the C(1)–C(4)–C(7) angle is 180° within experimental error.

The cyclohexyl portion of the complex is in a chair configuration with normal C–C distances. The angle of twist between the benzene-ring plane and the C(4)–C(7)–C(12) plane is 50·2°.

The next closest Ag–X distance is Ag–O(4) at 2·83 Å. All other intermolecular distances are >4 Å. A "normal" Ag–O single bond[8] would be 2·18 Å. If one considers Ag–O(4) as a long covalent interaction, this would make an alternative description a five-co-ordinate silver. Another possibility might be an ion-pair surrounded by non-polar groups. We prefer the three-co-ordinate Ag(I) description.

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[1] H. G. Smith and R. E. Rundle, *J. Amer. Chem. Soc.*, 1958, **80**, 5075.
[2] R. W. Turner and E. L. Amma, *J. Amer. Chem. Soc.*, 1966, **88**, 3243.
[3] B. G. Torre-Mori, D. Janjic, and B. P. Susz, *Helv. Chim. Acta*, 1964, **47**, 1172.
[4] G. Peyronel, G. Belmondi, and I. M. Vezzosi, *J. Inorg. Nuclear Chem.*, 1958, **20**, 577.
[5] E. A. Hall and E. L. Amma, to be published.
[6] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.
[7] R. W. Turner and E. L. Amma, *J. Amer. Chem. Soc.*, 1966, **88**, 1877.
[8] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1960, p. 246.