The Crystal Structure of Tetrabutylammonium Tetraiodotriargentate $(C_4H_9)_4NAg_3I_4$; a Chain Structure with Short Ag–Ag Distances

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Summary The crystal structure of $(C_4H_9)_4NAg_3I_4$ reveals a composite Ag–I chain unlike that of any other silver–halogen complex; Ag–Ag distances of about 3 Å occur.

THE ADDITION of a saturated solution of silver acetate to tetrabutylammonium iodide in acetonitrile does not yield the expected precipitate of silver iodide. Instead, on standing, highly refracting crystals appear which, chemical analysis shows, have the formula $(C_4H_9)_4NAg_3I_4$. An *X*-ray crystallographic examination was undertaken to determine the relationship of this new compound with the known Cs_2AgI_3,[1] in which chains of AgI_4 tetrahedra occur, each tetrahedron sharing two corners; with $(CH_3)_4NAg_2I_3$[2] and $CsAg_2I_3$,[3] in which double chains of AgI_4 tetrahedra occur, each tetrahedron sharing three edges; and with $RbAg_4I_5$,[4] in which Ag^+ ions statistically occupy a proportion of tetrahedral sites in a three-dimensional array of Rb^+ and I^- ions having cubic symmetry.

Crystal data: $(C_4H_9)_4NAg_3I_4$, $M = 1073{\cdot}6$; monoclinic, $P2_1/c$, $a = 9{\cdot}45(0{\cdot}01)$, $b = 15{\cdot}77(0{\cdot}02)$, $c = 18{\cdot}88(0{\cdot}02)$ Å, $\beta = 101°\ 08'\ (15')$; $D_m = 2{\cdot}5$ g.cm.$^{-3}$ (by flotation), $D_c = 2{\cdot}58$ g.cm.$^{-3}$, $Z = 4$.

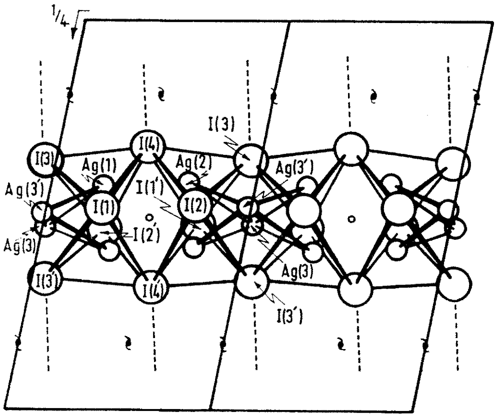

FIGURE. *The structure of the* $[Ag_3I_4]^-$ *ion; two unit cells shown in projection along* [010]. *The broken line represent planes of approximate mirror symmetry. Portions of other chains included in the unit cell, related by symmetry, have been omitted for clarity.*

A suitable crystal was ground until spherical. The intensities of 1293 non-zero diffracted beams were measured on a Buerger–Supper–Pace 0·01°-incrementing two-circle auto-diffractometer within the reciprocal layers 0*kl*—8*kl*. Mo-K_α radiation (Zr-filtered) equi-inclination geometry, and stationary background–ω–scan–stationary background mode were used throughout. The structure was solved by the symbolic addition method and refined by full-matrix least-squares analysis to $R = 0{\cdot}16$ for the Ag and I atoms only. Refinement of the N and C positions has not yet been attempted, but the most interesting features of the structure are already clear.

The $[Ag_3I_4]^-$ moiety comprises a chain structure in which all iodine atoms lie at the corners of slightly distorted tetrahedra. The chain is built up from pairs of tetrahedra sharing one edge symmetrically, and the four free corners of the resulting unit are shared with other similarly oriented units to extend into an infinite chain parallel to the crystallographic *a* axis. Every tetrahedron contains one Ag atom, and an octahedral hole is defined between every adjacent pair of double tetrahedra. Of these octahedral sites, *alternate* ones only are occupied by *two* silver atoms astride the symmetry centre, 3·13 Å apart, the others being empty. A "cluster" of six Ag atoms is thus produced, located at the apices of (again) two tetrahedra sharing one edge, the whole cluster having approximately C_{2v} (*mm*) symmetry. The Ag—Ag distances are not equal, however, and while the length of the shared edge is 3·13 Å, and of the opposite pair of edges is 3·06 Å, the lengths of the other edges of the tetrahedra range from 3·36 to 3·57 Å (see Table). Interpretation of these bond lengths in terms of chemical interaction is neither simple not certain.

Interatomic distances in the $[Ag_3I_4]^-$ *ion*

(a) Tetrahedron containing Ag (1)	
I (1)–I (2)′	4·92
I (1)–I (3)	4·62
I (1)–I (4)	4·71
I (3)–I (4)	4·67
Ag (1)–I (1)	2·90
Ag (1)–I (2)′	2·92
Ag (1)–I (3)	2·95
Ag (1)–I (4)	2·73
(b) Tetrahedron containing Ag (2)	
I (2)–I (1)′	4·92
I (2)–I (3)	4·46
I (2)–I (4)	4·53
I (4)–I (3)	4·90
Ag (2)–I (2)	2·90
Ag (2)–I (1)′	2·88
Ag (2)–I (3)	2·98
Ag (2)–I (4)	2·75
(c) Octahedron containing Ag (3) and Ag (3)′	
Ag (3)–Ag (3)′	3·13
Ag (3)–I (3)′	3·12
Ag (3)–I (3)	3·09
Ag (3)–I (1)′	2·75
Ag (3)–I (2)′	2·73
Ag (3)–Ag (1)	3·50
Ag (3)–Ag (2)′	3·57
Ag (3)–Ag (1)′	3·36
Ag (3)–Ag (2)	3·55

Standard deviations are at present all approximately ±0·01 Å including cell parameter errors.

The co-ordination state of the Ag atoms is likewise unusual. Ag(1) and Ag(2) are each surrounded by one I at *ca* 2·74, one Ag at 3·06, three I at *ca.* 2·9 and two Ag at *ca.* 3·5 Å; whereas Ag(3) is surrounded by two I at *ca.* 2·74, one Ag at 3·13, two I at 3·12 and 3·09, and four Ag at *ca.* 3·5 Å. The overall structure is thus quite different from the structure of any other known Ag–I complex, but is not unlike that of silver nitrate in having a large co-ordination site occupied by a *pair* of silver atoms.[5]

This salt was first prepared, from aqueous acetone rather than acetonitrile, by S. G. Smith.[6] We thank I. D. Page for preparing a sample at the suggestion of M. C. Whiting. We also thank the S.R.C. for financial support.

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