Tetramethylammonium Diiodoargentate(I), [N(CH₃)₄][AgI₂]

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Abstract. $M_r = 435 \cdot 825$, orthorhombic, *Immm*, $a = 9 \cdot 228$ (3), $b = 15 \cdot 353$ (6), $c = 6 \cdot 899$ (3) Å, $V = 977 \cdot 43$ (1) Å³, $Z = 4$, $D_x = 2 \cdot 961$ Mg m⁻³, λ(Mo $K\alpha$) $= 0 \cdot 71069$ Å, $\mu = 99 \cdot 69$ mm⁻¹, $F(000) = 1151 \cdot 87$, $R = 0 \cdot 082$ for 610 observed unique reflections measured at room temperature. The compound was crystallized from dimethylformamide. AgI_4 tetrahedra share edges only and form infinite chains parallel to the c axis. The mean Ag–I bond distance is $2 \cdot 781$ Å. The $N(CH_3)_4$ cations connect the infinite $_\infty^1[AgI_{4/2}]$ anions parallel to a.

Introduction. We have been able to detect polymeric anions $[Ag_nI_{n+1}]^-$ formed during the synthesis of complex silver iodides with large organic cations in organic bases. Structural studies revealed that in these anions AgI_4 tetrahedra are condensed to give one-dimensional infinite polyanions (Brink, Binnendijk & van de Linde, 1954; Meyer, 1963; Thackeray & Coetzer, 1975; Peters, Ott & von Schnering, 1982). $(CH_3)_4NAgI_2$ was formed from AgI and $(CH_3)_4NI$ by heating in dimethylformamide which yielded colourless needles.

Experimental. Needle-shaped single crystal, $0 \cdot 11 \times 0 \cdot 12 \times 2 \cdot 38$ mm, of title compound mounted on a glass capillary; Syntex *P*3 four-circle diffractometer, Mo $K\alpha$ radiation monochromated by graphite; 15 reflections with θ between 5 and 15° used for determination of lattice parameters; for final refinement of these parameters we used all symmetry-equivalent reflections of 064, 602, and 480; ψ-scan absorption correction applied using only reflections with χ between 40 and 90° as well as θ between 3 and 25°; $\sin\theta/\lambda \le 0 \cdot 65$ Å⁻¹, $0 \le h \le 11, 0 \le k \le 19, 0 \le l \le 8$; intensity of standard reflection 510 varied 4·5%; 610 unique reflections with $F \ge 3\sigma(F)$ used for structure determination, weak reflections suppressed by data-collection routine. *SHELXTL* system (Sheldrick, 1978) on an Eclipse S/250 employed to solve structure by direct-phase determination; phases of 96 strong reflections determined and on the resulting E map approximate

Table 1. *Final positional* ($\times 10^4$) *and equivalent isotropic thermal* (Å² $\times 10^3$) *parameters*

	Position	x	y	z	U_{eq}*
Ag	4(*j*)	5000	0	2634 (4)	50 (1)
I(1)	4(*h*)	0	6350 (2)	5000	80 (1)
I(2)	4(*f*)	7526 (2)	5000	0	58 (1)
N	4(*g*)	0	1951 (16)	0	42 (8)
C(1)	8(*n*)	8722 (33)	2594 (24)	0	88 (13)
C(2)	8(*l*)	0	8616 (23)	8274 (53)	124 (18)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°)

Ag–I(1)	2·756 (3) (2×)	N–C(1)	1·54 (4) (2×)
Ag–I(2)	2·806 (2) (2×)	N–C(2)	1·48 (4) (2×)
I(1)–Ag–I(1')	97·5 (1)	C(1)–N–C(1')	100 (3)
I(1)–Ag–I(2)	112·5 (1) (4×)	C(1)–N–C(2)	112 (1) (4×)
I(2)–Ag–I(2')	108·9 (1)	C(2)–N–C(2')	107 (3)

positions of the heavy atoms could be determined; positional and thermal parameters refined by anisotropic least-squares cycles using F^2 magnitudes to $R = 0 \cdot 082$, $R_w = 0 \cdot 083$, $w = 1/\sigma^2$. The positions of H atoms could not be confirmed, probably because of their marked thermal motion. $(\Delta/\sigma)_{max} = 0 \cdot 053$ for z of C(2). Max. and min. height in final difference synthesis $+2 \cdot 51$ and $-3 \cdot 44$ e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 contains final atomic parameters, Table 2 bond distances and angles.* Perspective drawings of the $(CH_3)_4N^+$ cation and a section of the $_\infty^1[AgI_2]^-$ anion can be seen in Fig. 1 and a stereoscopic view of the unit cell in Fig. 2.

One-dimensional infinite anionic chains $_\infty^1[AgI_{4/2}]$ parallel to **c** formed by AgI_4 tetrahedra sharing edges

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39182 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
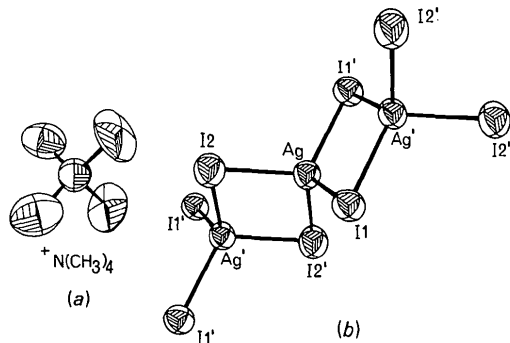
Fig. 1. Perspective drawings of (a) the cation $(CH_3)_4N^+$ and (b) a section of the anion $\frac{1}{\infty}[AgI_2]^-$, with the labelling of the atoms.
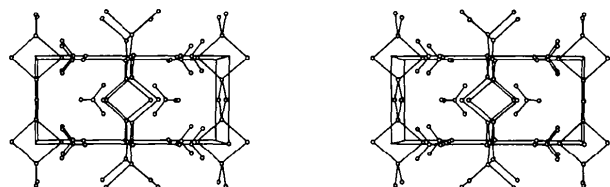

Fig. 2. Stereoscopic view of the unit cell.

only are the main structural feature of this compound. This polyanion is isostructural to the chains in the SiS_2 structure (Büssem, Fischer & Gruner, 1935). The mean Ag—I bond distance of 2·781 Å within these tetrahedra is shorter than that of 2·856 Å in $Ag_2I_4C_8H_{22}N_2$ (Thackeray & Coetzer, 1975) and that of 2·88 Å in $(CH_3)_4NAg_2I_3$ (Meyer, 1963). The $N(CH_3)_4$ tetrahedra are arranged between the infinite anions to form a zigzag chain of N and I(2) and to cause a connection of the anions parallel to **a**. The N atoms and the C atoms of the tetrahedral cations form planes parallel to *ab* as well as planes parallel to *bc*.

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The Structure of 1,2;3,4-Bis{μ-[bis(diphenylphosphino)methane]-*P,P'*}-1,2;2,4;4,1-tri-μ-carbonyl-1,2,3,3,4-pentacarbonyl-*tetrahedro*-tetrairidium(0), C58H44Ir4O8P4

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Abstract. $M_r = 1762$, monoclinic, $I2/a$, $a = 28·833$ (2), $b = 17·264$ (4), $c = 23·074$ (2) Å, $\beta = 97·00$ (1)°, $V = 11400$ Å³, $Z = 8$, $D_m = 2·2$ (1), $D_x = 2·05$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 9·11$ mm⁻¹, $F(000) = 6592$, $T = 298$ K, $R = 0·042$ for 4779 observed reflections. The Ir atoms form a nearly regular tetrahedron with Ir—Ir bonds in the range 2·692–2·746 (1) Å. Each dppm [dppm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$] ligand bridges two Ir atoms, with mean Ir—P = 2·297 (5) Å; the $Ir_4(dppm)_2$ portion has approximate, and non-crystallographic, symmetry $\bar{4}(S_4)$, but the carbonyl groups, three bridging and five terminal, do not conform to this.

Introduction. The crystal structures of several transition-metal cluster complexes containing dppm [bis(diphenylphosphino)methane] as a ligand have been determined by X-ray methods. Thus, for example, the structures of $Rh_4(CO)_8(dppm)_2$ (Carré, Cotton & Frenz, 1976), $Ru_3(CO)_8(dppm)_2$ (Lavigne, Lugan & Bonnet, 1982), and $Rh_6(CO)_{10}(dppm)_3$ (Ceriotti, Ciani,