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A novel tetranuclear iodoargentate(I) ion, $[Ag_4I_8]^{4-}$, with a cubane-type core

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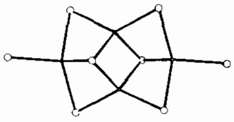
Abstract

A novel tetranuclear iodoargentate(I) anion, $[Ag_4I_8]^{4-}$, with a cubane-type Ag_4I_4 core has been isolated as the tetrapropylammonium salt and characterised by means of crystal structure determination. There are two crystallographically independent anions, each of which is situated around a two-fold axis. One of the terminal iodide ligands in one such $[Ag_4I_8]^{4-}$ anion is disordered, as are two of the tetrapropylammonium cations. The ordered terminal Ag–I bonds range from 2.748(2) to 2.765(2) Å and the bridging Ag–I from 2.897(2) to 2.932(3) Å, all four silver(I) centres exhibiting distorted tetrahedral coordination geometry. The compound crystallises in the monoclinic space group $C2$, with $a=26.836(6)$, $b=12.535(4)$, $c=24.509(6)$ Å, $\beta=118.54(2)°$, $V=7243(4)$ Å^3, at -120 °C, and $Z=4$. Full-matrix least-squares refinement yielded a final $R=0.042$ ($R_w=0.045$) for 333 parameters and 3784 observed reflections.

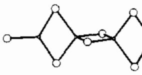
Key words: Crystal structures; Silver complexes; Iodide complexes; Cluster complexes

Introduction

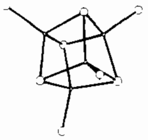
The coordination number of the coinage metal in crystalline halogenocuprates(I) and, to a somewhat lesser extent in halogenoargentates(I), has been shown to be dependent on the properties, and, in particular, on the size, of the cation with which it is co-precipitated [1]. Thus, in general, low metal(I) coordination numbers are obtained with bulky, unipositive cations such as tetraphenylarsonium, tetraphenylphosphonium and tetrabutylammonium, the metal attaining higher coordination numbers with decreasing size of the cation. Moreover, for a given cation, higher copper(I) or silver(I) coordination numbers tend to be favoured the heavier the halogenide ligand [1]. In the case of silver(I), a coordination number of four is, undoubtedly, that which is most commonly observed, usually resulting in polymeric anions, e.g. of stoichiometry $[Ag_2X_3]^-$ (X = Cl [2], Br [2, 3] or I [4–6]) or $[AgX_2]^-$ (X = Cl [7], Br [8, 9] or I [8, 10–12]). Hitherto, only two discrete halogenoargentate(I) ions composed solely of four-coordinated metal(I) centres have been described, viz. the dinuclear $[Ag_2I_6]^{4-}$ anion in $[Pt(C_2H_8N_2)_2I_2]_2[Ag_2I_6]$ [13], and the tetranuclear $[Ag_4I_8]^{4-}$ cluster in $[C_{15}H_{30}N_2]_2[Ag_4I_8]$ [14]. In this latter compound, four silver(I) iodide tetrahedra share edges, the four silver atoms in the resulting centrosymmetric cluster being co-planar, forming a rhombus with Ag–Ag edges of 3.125(4) and 3.283(4) Å and diagonals of 2.967(4) and 5.680(4) Å [14]. An iodoargentate(I) anion with the same stoichiometry as the latter anion has been prepared as the tetraphenylarsonium and tetraphenylphosphonium salts [15]; this ion contains, however, two three-coordinated and two four-coordinated silver(I) centres. The two known types of $[Ag_4I_8]^{4-}$ cluster are depicted schematically as **I** and **II**. In connection with an ongoing investigation of the role of cation size on the coordination number of silver(I) in halogenoargentates(I) crystallizing with symmetrically substituted tetraalkylammonium and related cations, we have prepared a third type of $[Ag_4I_8]^{4-}$ cluster with a cubane-type core (**III**). Although cubane cores are now a common feature in $[Ag_4I_4L_4]$ molecules where L is a Lewis base with, e.g. a nitrogen [16–18] or phosphorus [19, 20] donor, this type of core has not previously been documented for a simple iodoargentate(I) anion.



I



II



III

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Experimental

Preparation of $[N(C_3H_7)_4]_4[Ag_4I_8]$

Crystals of $[N(C_3H_7)_4]_4[Ag_4I_8]$ were prepared by dissolving 2.0 mmol (0.62 g) tetrapropylammonium iodide (Aldrich) in 5 ml dimethylformamide and adding 1.0 mmol (0.23 g) silver(I) iodide (ICN Biomedicals, K & K) which dissolved under stirring at ambient temperature. Colourless prisms of $[N(C_3H_7)_4]_4[Ag_4I_8]$ were deposited from the solution after slow evaporation of the solution over a period of 1–2 days.

Crystallography

Crystal and experimental data are summarised in Table 1. Diffracted intensities from a colourless, prismatic crystal were measured at −120 °C on a Rigaku AFC6R diffractometer using graphite-monochromated Mo Kα radiation from an RU200 rotating anode operated at 9 kW (50 kV; 180 mA) and the ω scan mode with a scan width of $(1.18+0.30 \tan \theta)°$ and a scan rate of 8° min^{-1}. Weak reflections ($I<10\sigma(I)$) were rescanned three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection, the ratio of peak counting time to background counting time being 2:1. Three reflections monitored at regular intervals (after every 150 reflections measured) showed no evidence of crystal decay. Of the 6689 unique reflections measured ($3.5<2\theta<50°$, h, k, $\pm l$), 3784 had $I>3.0\sigma(I)$ and were considered observed. Intensities were corrected for Lorentz and polarisation effects and an empirical correction based on azimuthal scans for several reflections was made for the effects of absorption (max., min. transmission factors: 1.00, 0.89). Cell constants were determined from the setting angles for 20 automatically centred reflections in the range $14.0<2\theta<15.9°$.

TABLE 1. Crystal and experimental data for $[N(C_3H_7)_4]_4[Ag_4I_8]$

Formula	$C_{48}H_{112}Ag_4I_8N_4$
Molecular weight	2192.1
Crystal system	monoclinic
Space group	$C2$ (No. 5)
Temperature (°C)	−120
a (Å)	26.836(6)
b (Å)	12.535(4)
c (Å)	24.509(6)
β (°)	118.54(2)
Volume (Å^3)	7243(4)
Z	4
Calculated density (g/cm^3)	2.01
$F(000)$	4160
μ (cm^{-1})	44.6
Approx. crystal dimensions (mm)	0.20×0.25×0.30
Radiation (Å)	graphite-monochromated Mo Kα (0.71069)
Data collected	h, k, $\pm l$
$2\theta_{max}$ (°)	50
Scan mode	ω
ω Scan rate (°/min)	8.0
No. unique reflections	6689
No observed reflections	3784
No. parameters refined	333
R	0.042
R_w	0.045
Max.; min. residual electron density (e/Å^3)	1.01; −0.78

The coordinates of the silver and seven of the iodine atoms were determined by direct methods (MITHRIL [21]) and those of the remaining atoms from subsequent electron density maps. The y coordinate of I(1) was used to fix the origin. I(8) was found to be disordered such that it was located in two positions I(8a) and I(8b), both being assigned site occupancy 0.5. Of the five crystallographically independent cations (two are situated on two-fold axes), two (cation 3 and cation 5, i.e. N(3) and N(5), respectively) were found to be associated with disorder. In both cases, this led to large temperature factors for some carbon atoms (see Table 2) and, for cation 5, also to one somewhat unrealistic C–C distance, viz. C(44)–C(45) = 1.88(6) Å. For this latter cation, two of the carbon atoms, C(47) and C(48), could be resolved into partially occupied sites (see Table 2). Full-matrix least-squares refinement, including anisotropic thermal parameters for the silver and iodine atoms and isotropic thermal parameters for the remaining atoms and with 91 hydrogen atoms bonded to carbons not associated with disorder included as a fixed contribution in calculated positions (C–H = 0.95 Å; $B=1.2B_{eq}$ of the carrying carbon atom), gave a final $R=0.042$ ($R_w=0.045$) for 333 parameters and 3784 reflections. The enantiomorph refined to identical R and R_w values. Maximum, minimum discrepancy in final difference map: 1.01, −0.78 e Å^{-3}. Weighting scheme: $w=[\sigma^2(F_o)]^{-1}$.

For atomic scattering factors, anomalous dispersion corrections, and computer programs used see ref. 22. The figures were drawn using ORTEP [23].

Results and discussion

Fractional coordinates for $[N(C_3H_7)_4]_4[Ag_4I_8]$ are given in Table 2 and bond lengths and angles within the two crystallographically independent $[Ag_4I_8]^{4-}$ anions in Table 3, the crystallographic numbering being as is shown in Fig. 1. Both $[Ag_4I_8]^{4-}$ anions are situated around two-fold axes. One of the iodide ligands (I(8)) in the second anion is disordered (see above) and, for clarity, only one of the two possible positions for this atom (I(8a)) is shown in Fig. 1. The bridging Ag–I bonds, which range from 2.901(2) to 2.930(2) Å (anion 1) and from 2.897(2) to 2.932(3) Å (anion 2), are typical

TABLE 2. Fractional atomic coordinates and B_{eq}[a] (for Ag and I) or B (Å^2) for the non-hydrogen atoms in $[N(C_3H_7)_4]_4[Ag_4I_8]$. Disordered atoms with occupancy 0.5 are denoted with an asterisk

Atom	x	y	z	B_{eq}/B
Ag(1)	0.04679(6)	0.0290(1)	0.57837(7)	3.45(6)
Ag(2)	−0.05822(6)	0.2302(1)	0.51687(7)	3.48(6)
I(1)	−0.07518(5)	0.0000	0.52097(5)	2.64(4)
I(2)	0.06178(5)	0.2564(1)	0.60276(5)	2.62(4)
I(3)	0.10083(6)	−0.1024(2)	0.68004(6)	4.37(6)
I(4)	−0.13197(5)	0.3651(1)	0.53100(6)	3.72(5)
Ag(3)	0.05605(6)	0.1140(2)	0.06950(7)	3.71(6)
Ag(4)	0.04693(7)	0.3243(2)	−0.03972(7)	4.52(7)
I(5)	0.05996(5)	0.0932(1)	−0.04636(5)	3.18(5)
I(6)	0.07596(5)	0.3416(1)	0.09096(6)	3.42(5)
I(7)	0.12852(5)	−0.0230(1)	0.16182(5)	3 25(5)
I(8a)*	0.1124(1)	0.4396(3)	−0.0730(2)	5.5(1)
I(8b)*	0.0880(1)	0.4734(3)	−0.0948(2)	5.2(1)
N(1)	0.5000	0.213(2)	1.0000	3.8(5)
C(1)	0.5455(7)	0.287(2)	1.0067(8)	3.5(4)
C(2)	0.6013(9)	0.232(2)	1.0181(10)	5.3(6)
C(3)	0.6460(10)	0.308(2)	1.0268(11)	6.0(6)
C(4)	0.5171(8)	0.141(2)	1.0552(8)	3.5(4)
C(5)	0.5347(10)	0.189(2)	1.1161(10)	5.2(6)
C(6)	0.5534(10)	0.112(2)	1.1683(10)	6.0(6)
N(2)	0.5000	0.126(2)	0.5000	2.5(4)
C(7)	0.4459(7)	0.197(2)	0 4735(7)	2.8(4)
C(8)	0.3923(8)	0.140(2)	0.4450(9)	4.2(5)
C(9)	0.3458(8)	0.218(2)	0.4212(9)	4.6(5)
C(10)	0.4996(8)	0.051(2)	0.4507(8)	3.6(4)
C(11)	0 4975(8)	0.113(2)	0.3946(9)	4.5(5)
C(12)	0.4891(10)	0.032(2)	0.3426(10)	6.0(6)
N(3)	0.0381(6)	0.137(1)	0.2709(7)	3.2(3)
C(13)	0.0854(7)	0.138(2)	0.3346(7)	2.6(4)
C(14)	0.1432(8)	0.112(2)	0.3433(9)	4.2(5)
C(15)	0.1876(9)	0.097(2)	0.4125(10)	5.5(6)
C(16)	0.0321(8)	0.027(2)	0.2376(9)	4.1(5)
C(17)	0.0306(13)	−0.056(3)	0.2787(14)	9.5(9)
C(18)	0.0357(17)	−0.165(4)	0.2468(18)	14.4(14)
C(19)	−0.0178(8)	0.149(2)	0.2706(9)	3.8(4)
C(20)	−0.0682(8)	0.167(2)	0.2109(9)	4.4(5)
C(21)	−0.1229(10)	0.165(2)	0.2181(11)	6.0(6)
C(22)	0.0492(8)	0.215(2)	0.2330(9)	3.8(5)
C(23)	0.0428(10)	0.337(2)	0.2495(11)	6.1(6)
C(24)	0.0990(10)	0.394(2)	0.2754(10)	6.0(6)
N(4)	0.7416(6)	0.170(1)	0.3399(6)	3.0(3)
C(25)	0.7754(8)	0.275(2)	0.3526(8)	3.5(4)
C(26)	0.7418(10)	0.368(2)	0.3194(11)	6.3(6)
C(27)	0.7816(11)	0.471(3)	0.3395(13)	8.2(8)
C(28)	0.7870(8)	0.086(2)	0.3801(9)	4.5(5)
C(29)	0.7643(9)	−0.024(2)	0.3706(10)	5.5(6)
C(30)	0.7493(10)	−0.062(2)	0.4178(11)	6.2(6)
C(31)	0.6948(8)	0.178(2)	0.3527(9)	3.9(5)
C(32)	0.7092(9)	0.216(2)	0.4167(9)	4.9(5)
C(33)	0.6565(11)	0.219(2)	0.4245(11)	7.1(7)
C(34)	0.7166(8)	0.140(2)	0.2716(8)	3.3(4)
C(35)	0.7592(9)	0.114(2)	0.2511(10)	5.4(6)
C(36)	0.7287(13)	0.091(3)	0.1809(14)	9.9(10)
N(5)	0.2700(7)	0.187(2)	0.1278(7)	4.0(4)
C(37)	0.2295(7)	0.210(2)	0.1543(8)	3.3(4)
C(38)	0.2580(8)	0.221(2)	0.2263(9)	4.1(5)
C(39)	0.2166(8)	0.256(2)	0.2450(8)	3.5(4)
C(40)	0.3068(10)	0.090(2)	0.1618(11)	6.5(7)
C(41)	0.2731(13)	−0.011(3)	0.1479(15)	10.3(10)
C(42)	0.3178(18)	−0.085(4)	0.2002(20)	16.0(16)
C(43)	0.3083(12)	0.289(3)	0.1396(13)	8.2(8)
C(44)	0.3512(18)	0.266(4)	0.1235(20)	20.6(17)
C(45)	0.4018(18)	0.382(4)	0.1469(20)	18.8(16)
C(46)	0.2333(9)	0.161(2)	0.0597(10)	5.5(6)
C(47a)*	0.2579(16)	0.136(3)	0.0217(16)	3.6(9)
C(48a)*	0.2185(24)	0.085(5)	−0.0433(26)	8.6(17)
C(47b)*	0.2271(23)	0.284(5)	0.0283(25)	8.3(16)
C(48b)*	0.2021(19)	0.224(4)	−0.0447(20)	5.9(12)

(continued)

TABLE 2. (continued)

[a] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

TABLE 3. Bond distances (Å) and angles (°) for the anions in $[N(C_3H_7)_4]_4[Ag_4I_8]$[a]

Anion 1			
Ag(1)–I(1)	2.903(2)	Ag(2)–I(1)	2.930(2)
Ag(1)–I(1')	2.901(2)	Ag(2)–I(2)	2.904(2)
Ag(1)–I(2)	2.901(2)	Ag(2)–I(2')	2.906(2)
Ag(1)–I(3)	2.752(2)	Ag(2)–I(4)	2.748(2)
Ag(1)···Ag(1')	3.442(3)	Ag(2)···Ag(2')	3.594(3)
Ag(1)···Ag(2)	3.537(2)	Ag(1)···Ag(2')	3.548(2)
I(1)···I(1')	4.616(3)	I(2)···I(2')	4.518(3)
I(1)···I(2)	4.563(2)	I(1)···I(2')	4.550(2)
I(1)–Ag(1)–I(1')	105.38(6)	I(1)–Ag(2)–I(2)	102.91(6)
I(1)–Ag(1)–I(2)	103.66(6)	I(1)–Ag(2)–I(2')	102.44(6)
I(1)–Ag(1)–I(3)	110.38(7)	I(1)–Ag(2)–I(4)	117.95(7)
I(1')–Ag(1)–I(2)	103.29(6)	I(2)–Ag(2)–I(2')	102.07(6)
I(1')–Ag(1)–I(3)	116.67(7)	I(2)–Ag(2)–I(4)	117.05(7)
I(2)–Ag(1)–I(3)	116.12(6)	I(2')–Ag(2)–I(4)	112.26(6)
Ag(1)–I(1)–Ag(1')	72.75(6)	Ag(1)–I(2)–Ag(2)	75.08(5)
Ag(1)–I(1)–Ag(2)	74.67(5)	Ag(1)–I(2)–Ag(2')	75.30(5)
Ag(1')–I(1)–Ag(2)	74.95(5)	Ag(2)–I(2)–Ag(2')	76.42(6)
Anion 2			
Ag(3)–I(5)	2.903(2)	Ag(4)–I(5)	2.932(3)
Ag(3)–I(5")	2.897(2)	Ag(4)–I(6)	2.920(2)
Ag(3)–I(6)	2.905(2)	Ag(4)–I(6")	2.923(2)
Ag(3)–I(7)	2.765(2)	Ag(4)–I(8a)	2.686(4)
		Ag(4)–I(8b)	2.821(4)
Ag(3)···Ag(3")	3.296(3)	Ag(4)···Ag(4")	3.850(3)
Ag(3)···Ag(4)	3.681(3)	Ag(3)···Ag(4")	3.632(3)
I(5)···I(5")	4.744(3)	I(6)···I(6")	4.374(3)
I(5)···I(6)	4.453(2)	I(5)···I(6")	4.515(2)
I(5)–Ag(3)–I(5")	109.75(6)	I(5)–Ag(4)–I(6)	99.10(7)
I(5)–Ag(3)–I(6)	100.14(6)	I(5)–Ag(4)–I(6")	100.93(7)
I(5)–Ag(3)–I(7)	113.87(7)	I(5)–Ag(4)–I(8a)	113.70(10)
		I(5)–Ag(4)–I(8b)	122.94(10)
I(5")–Ag(3)–I(6)	102.20(7)	I(6)–Ag(4)–I(6")	96.94(6)
I(5")–Ag(3)–I(7)	111.97(7)	I(6)–Ag(4)–I(8a)	115.00(10)
		I(6)–Ag(4)–I(8b)	121.02(10)
I(6)–Ag(3)–I(7)	117.73(6)	I(6")–Ag(4)–I(8a)	126.68(10)
		I(6")–Ag(4)–I(8b)	111.35(9)
Ag(3)–I(5)–Ag(3")	69.26(6)	Ag(3)–I(6)–Ag(4)	78.38(6)
Ag(3)–I(5)–Ag(4)	78.22(6)	Ag(3)–I(6)–Ag(4")	77.11(6)
Ag(3")–I(5)–Ag(4)	77.08(6)	Ag(4)–I(6)–Ag(4")	82.42(6)

[a] Symmetry code: i: $-x, y, 1-z$; ii: $-x, y, -z$.

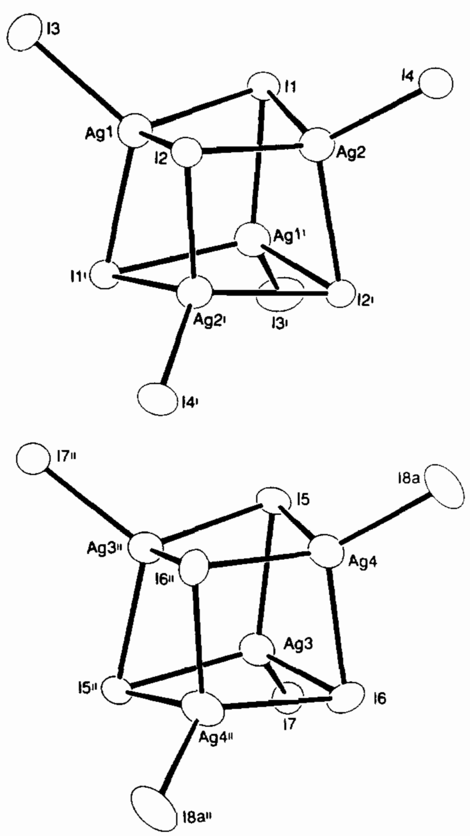

Fig. 1. The two crystallographically independent $[Ag_4I_8]^{4-}$ ions each viewed approximately down the two-fold axis. In anion 2 only one of the two positions of I(8), viz. I(8a), is shown for clarity. For symmetry codes see Table 3. Thermal ellipsoids enclose 50% probability.

of values observed for bridging Ag–I associated with four-coordinated silver(I) [1], whereas the Ag–I bonds involving the ordered terminal iodide ligands are appreciably shorter, viz. 2.748(2) and 2.752(2) Å (anion 1) and 2.765(2) Å (anion 2) and are of the same order as the bridging Ag–I distances determined for the three-coordinated silver(I) centre in the $[Ag_4I_8]^{4-}$ (**II**) cluster [15]. Although the individual Ag–I(8a) and Ag–I(8b) bond distances differ from one another and also from the remaining terminal Ag–I distances, presumably owing to inadequate resolution of the disorder, the mean value, 2.754 Å, is consistent with those values determined for the ordered terminal iodide ligands. Ag···Ag and I···I contacts range from 3.442(3) to 3.594(3) Å and 4.518(3) to 4.616(3) Å (anion 1) and 3.296(3) to 3.850(3) and 4.374(3) to 4.744(3) Å (anion 2), respectively, the cubane core of anion 2 thus being slightly more distorted than that of anion 1.

In the tetrameric complex between silver(I) iodide and tetrahydrothiophene [24], $[Ag_4I_4(C_4H_8S)_4]$, the core has been found to be of a stellar quadrangular type, a description shown [24] to be applicable also to $[Ag_4I_4(C_5H_{11}N)_4]$ [16] and $[Ag_4I_4(PEt_3)_4]$ [19], whereas the core in $[Ag_4I_4(PPh_3)_4]$ [20] is shown [24] to be closer to the cubane type. The Ag_4I_4 cores in both $[Ag_4I_8]^{4-}$ anions prepared in the present study are best described as being of cubane type, since the ratios between mean Ag···Ag and I···I distances are 0.77 and 0.80 for anion 1 and anion 2, respectively (cf. ref. 24).

For tetranuclear cubane-type copper(I) complexes, $[Cu_4X_4L_4]$ ($X=Cl^-$ or Br^-), it has been demonstrated that a regular cubic core is preferred when L is a pure σ donor ligand, but that two types of distortion in which four of the cube edges are appreciably elongated are favoured when L is a π acceptor, i.e. an olefin [25]. These approximately isoenergetic isomers differ solely in the spatial arrangement of the four long Cu–X bonds, such that either all four are parallel or that they are situated pairwise in two orthogonal planes [25]. It does not yet seem to be known whether or not Ag–X cores in analogous silver(I) complexes would distort in a similar manner. In the present silver(I) anion, $[Ag_4I_8]^{4-}$, in which L is not a π acceptor, the Ag–I distances within the cubane core are, however, similar in length.

An iodocuprate(I) analogue of the $[Ag_4I_8]^{4-}$ ion (**II**), composed of three- and four-coordinated metal centres, was the first halogenocuprate(I) or halogenoargentate(I) anion of this type to be reported [26]. As yet, there appears to be no example of a halogenocuprate(I) anion, $[Cu_4X_8]^{4-}$ (X=Cl, Br or I), with a cubane-type core; a $[Cu_4I_7]^{3-}$ cluster has, however, recently been prepared and characterised in $[N(C_4H_9)_4]_3[Cu_4I_7]$ [27]. This anion is composed of three edge-sharing Cu–I tetrahedra with a fourth copper(I) in a trigonal-planar site and may thus be envisaged as containing an extremely distorted cubane-type core.

As described above, two of the tetrapropylammonium cations are situated on two-fold axes, while the remaining three occupy general positions (see Table 2). Two of these latter cations are disordered with respect to the orientation of the propyl groups, a feature commonly observed for this cation [28] and analogues such as tetrabutylammonium [29]. Bond distances and angles within the ordered ions are normal (see, for example, refs. 28, 30–32). The closest packing distances are: I(1)···C(28ⁱⁱⁱ)=3.82(2) Å and I(7)···C(26ⁱᵛ)=3.85(2) Å, there being three shorter distances, viz. I(8a)···C(47b), I(8a)···C(48b) and I(8b)···C(6ᵛ) of 3.49(6), 3.47(5) and 3.76(2) Å, respectively, which can be attributed to artefacts of the disorder. (Symmetry code: iii: $x-1, y, z$; iv: $x-\frac{1}{2}, y-\frac{1}{2}, z$; v: $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$.)

The present investigation provides a further example illustrating the increase in silver(I) coordination number in a discrete iodoargentate(I) anion with decreasing size of the unipositive cation, i.e. from three and four in $[Ag_4I_8]^{4-}$, precipitated with tetraphenylarsonium and tetraphenylphosphonium, to four in the present tetrapropylammonium salt. As mentioned above, the correlation between metal(I) coordination number and cation size is, in general, less pronounced in halogenoargentates(I) than in halogenocuprates(I) [1], polymeric iodoargentate(I) species in which silver(I) is four-coordinated having also been obtained with the tetraphenylarsonium and tetraphenylphosphonium cations [15] and with tetrabutylammonium [33]. However, in the case of chloro- and bromoargentates(I), the principle of matching large cations with small anions in which silver(I) exhibits a low coordination number (contrary to the usual principle of matching small cations with small anions and vice versa) [34, 35] has been exploited for the preparation of discrete mononuclear trigonal $[AgCl_3]^{2-}$ and $[AgBr_3]^{2-}$ ions [36], and of an approximately linear $[AgCl_2]^-$ anion [37]. With the bulky $[KL]^+$ cation (L = cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)) used to precipitate $[AgCl_2]^-$ [37], a dinuclear $[Ag_2I_4]^{2-}$ anion, containing three-coordinated silver(I) was obtained [37]. An analogous anion has recently been isolated as $[CuL'_2][Ag_2I_4]$, where L′ = 1,1-di(2-pyridyl)ethyl methyl ether-*N*,*N*′,*O* [38] and a discrete approximately trigonal mononuclear $[AgI_3]^{2-}$ ion has been isolated as the methyltriphenylphosphonium salt [39, 40].

For crystalline halogenocuprates(I), it has been suggested that cation–halogenide packing is the primary process occurring during formation of the solid compound, copper(I) attaining the appropriate coordination number by occupation of available interstices, subsequent rearrangement then resulting in the specific anion [32]. The tuning of the metal(I) coordination environment in halogenocuprates(I) to cation properties, such as size, undoubtedly reflects the flexibility of the bonding requirements of both the metal [41–43] and the ligands [44]. A similar situation could be envisaged to be operative in the formation of crystalline halogenoargentates(I), although with iodide as ligand, the tuning of the silver(I) coordination number appears to be somewhat less sensitive in that extremely bulky unipositive cations are required to reduce the coordination number from four to three.

Supplementary material

Hydrogen atom coordinates, anisotropic thermal parameters for Ag and I, and bond distances and angles within the cations are available from the authors on request.

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References

1 S. Jagner and G. Helgesson, *Adv. Inorg. Chem.*, *37* (1991) 1, and refs. therein

2 G. Helgesson and S. Jagner, *Acta Crystallogr., Sect. C, 44* (1988) 2059.

3 S. Jagner, S. Olson and R. Stomberg, *Acta Chem Scand., Ser A, 40* (1986) 230.

4 C. Brink, N.F. Binnendijk and J. van de Linde, *Acta Crystallogr*, *5* (1954) 176.

5 H.-J. Meyer, *Acta Crystallogr., 16* (1963) 788.

6 J.D. Kildea, B.W. Skelton and A.H. White, *Aust. J. Chem*, *39* (1986) 171.

7 G. Helgesson, M. Josefsson and S. Jagner, *Acta Crystallogr., Sect. C, 44* (1988) 1729.

8 R. Stomberg, *Acta Chem Scand., 22* (1968) 2022; *23* (1969) 3498.

9 L.V. Shirshova, I.P. Lavrent'ev and V.I. Ponomarev, *Koord. Khim., 15* (1989) 1048.

10 M.M. Thackeray and J. Coetzer, *Acta Crystallogr., Sect. B, 31* (1975) 2341.

11 S. Geller and T.O. Dudley, *J. Solid State Chem., 26* (1978) 321.

12 K. Peters, H.-G. von Schnering, W. Ott and H.-M. Seidenspinner, *Acta Crystallogr., Sect C, 40* (1984) 789.

13 H.J. Keller, B. Keppler and H. Pritzkow, *Acta Crystallogr., Sect. B, 38* (1982) 1603.

14 J. Estienne, *Acta Crystallogr., Sect. C, 42* (1986) 1512.

15 G. Helgesson and S. Jagner, *J. Chem. Soc., Dalton Trans.*, (1990) 2413.

16 G.B. Ansell, *J. Chem. Soc B,* (1971) 443.

17 P.C. Healy, N.K. Mills and A.H. White, *Aust. J. Chem., 36* (1983) 1851.

18 L.M. Engelhardt, S Gotsis, P.C. Healy, J.D. Kildea, B.W. Skelton and A.H. White, *Aust. J. Chem., 42* (1989) 149.

19 M.R. Churchill and B.G. DeBoer, *Inorg Chem., 14* (1975) 2502.

20 B.-K. Teo and J.C. Calabrese, *Inorg Chem*, *15* (1976) 2474.

21 C.J. Gilmore, *J. Appl. Crystallogr., 17* (1984) 42.

22 *TEXSAN Structure Solution Package,* Molecular Structure Corporation, The Woodlands, TX, 1989.

23 C.J. Johnson, *ORTEP, ORNL Rep. 3794*, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

24 B. Norén and Å. Oskarsson, *Acta Chem Scand*, *Ser. A, 39* (1985) 701.

25 M. Håkansson, S. Jagner, E. Clot and O. Eisenstein, *Inorg. Chem*, *31* (1992) 5389, and refs. therein.

26 H. Hartl, *Angew. Chem*, *99* (1987) 925; *Angew. Chem., Int. Ed. Engl., 26* (1987) 927.

27 H. Hartl, I. Brüdgam and F. Mahdjour, *28th Int. Conf. Coord. Chem., Gera, Germany, 1990*, p. 5-34.

28 M. Asplund and S. Jagner, *Acta Chem Scand*, *Ser. A, 38* (1984) 725.

29 M. Langkjær, E. Larsen and S. Larsen, *Acta Chem. Scand., Ser. A, 39* (1985) 187, and refs. therein.

30 M. Asplund and S. Jagner, *Acta Chem. Scand*, *Ser. A, 38* (1984) 411.

31 S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A, 40* (1986) 52.

32 S. Andersson, M. Håkansson and S. Jagner, *J Crystallogr. Spectrosc. Res., 19* (1989) 147.

33 C.J. Gilmore, P.A. Tucker and P. Woodward, *J Chem Soc A,* (1971) 1337.

34 D.M.P. Mingos and A.L. Rohl, *Inorg Chem*, *30* (1991) 3769, and refs. therein.
35 D.M.P. Mingos and A.L. Rohl, *J. Chem. Soc, Dalton Trans*, (1991) 3419, and refs. therein.
36 G. Helgesson and S. Jagner, *J. Chem Soc., Dalton Trans*, (1993) 1069.
37 G. Helgesson and S. Jagner, *Inorg Chem.*, *31* (1991) 2574.
38 P.G. Jones, *Acta Crystallogr., Sect C*, *48* (1992) 1314.
39 G.A. Bowmaker, G.R. Clark, D.A. Rogers, A. Camus and N. Marsich, *J. Chem. Soc., Dalton Trans*, (1984) 37.
40 G.A. Bowmaker, A. Camus, B.W. Skelton and A.H. White, *J. Chem Soc., Dalton Trans*, (1990) 727.
41 K.M. Merz, Jr. and R. Hoffmann, *Inorg Chem.*, *27* (1988) 2120.
42 J K. Burdett and O. Eisenstein, *Inorg Chem.*, *31* (1992) 1758.
43 G.L. Soloveichik, O. Eisenstein, J.T. Poulton, W E. Streib, J.C. Huffman and K.G. Caulton, *Inorg Chem.*, *31* (1992) 3306.
44 L. Subramanian and R Hoffmann, *Inorg Chem.*, *31* (1992) 1021.