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Silver–iodocarbon complexes: crystal structures of eight compounds obtained from the reactions of $AgPF_6$ or $AgNO_3$ with CH_2I_2, $I(CH_2)_3I$ and simple aryl iodides

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Eight silver(I)–iodocarbon complexes have been prepared and structurally characterized by single-crystal X-ray diffraction. In $[Ag\{I(CH_2)_3I\}_2]PF_6$, $[Ag(ICH_2I)_2]PF_6$, $[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$ and $[Ag(1,2\text{-}BrIC_6H_4)_4]PF_6$ the silver ions are four-co-ordinate and bonded to four iodine atoms of four iodocarbon ligands, the co-ordination geometry varying from slightly distorted tetrahedral to trigonal pyramidal. Typical Ag–I bond lengths are in the range 2.8–2.9 Å though the axial Ag–I bond in $[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$ is significantly elongated to 3.2–3.3 Å. The diiodocarbons function as bridging ligands in $[Ag\{I(CH_2)_3I\}_2]PF_6$ and $[Ag(ICH_2I)_2]PF_6$. The structure of the former consists of a chain polymer built from $Ag[I(CH_2)_3I]_2Ag$ rings whilst the latter consists of $(AgICH_2I)_n$ chains cross-linked by $Ag(ICH_2I)_2Ag$ rings. The compound $[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$ is a tetrameric cyclic structure in which one-third of the $1,2\text{-}I_2C_6H_4$ ligands bridge two silvers *via* the two iodine atoms, the others functioning as monodentate to a silver atom *via* one of the iodine atoms. The compound $[Ag_2(O_2PF_2)_2(p\text{-}IC_6H_4Me)]$ contains a complex sheet $[Ag(O_2PF_2)]_n$ structure in which an iodotoluene bridges two silvers *via* an iodo and an η^2-arene linkage. Each difluorophosphate links four silvers *via* two μ-oxygen bridges. The compound $[Ag(O_2PF_2)(1,4\text{-}I_2C_6H_4)]$ contains $[Ag(O_2PF_2)]_n$ chains in which the difluorophosphate forms a three-atom O,O′ bridge. These chains are cross-linked *via* bridging $1,4\text{-}I_2C_6H_4$ ligands which co-ordinate to silver *via* the iodine atoms. The compound $[Ag(NO_3)(CH_2I_2)]$ is a sheet array derived from fused $Ag_4(\mu\text{-}NO_3)_2(\mu\text{-}ICH_2I)_2$ 16-atom rings with each silver bonded to two oxygen and two iodine atoms in a distorted-tetrahedral array. The compound $[Ag(NO_3)(1,2\text{-}I_2C_6H_4)]$ is composed of spiral chains of $[Ag(\mu\text{-}NO_3)]_n$ in which the nitrate uses only one oxygen atom to bridge two silvers. Each silver is bonded to two iodine and two oxygen atoms. The 'AgI_2O_2' bond angles range from 82 to 134°. The $1,2\text{-}I_2C_6H_4$ ligands bridge alternate first and third silvers along the chain and stack on either side of the $[Ag(NO_3)]_n$ chain to produce two complementary spiral arrays.

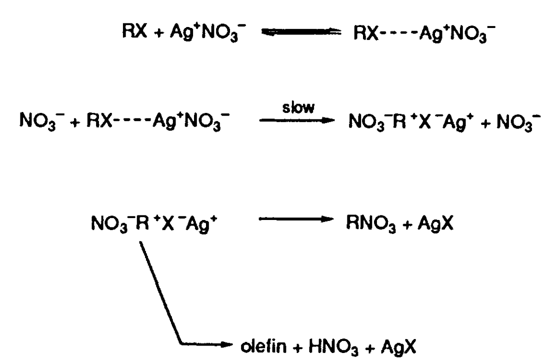
Compounds containing iodocarbon–silver(I) bonds ($RI\text{–}Ag^+$) have long been suspected as intermediates in the reactions of alkyl iodides with silver salts [*e.g.*, equation (1)].[1] For this

$$AgNO_2 + CH_3(CH_2)_3I \longrightarrow CH_3(CH_2)_3NO_2 + AgI \quad (1)$$

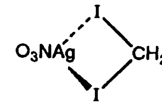
reaction class, Pocker and Kevill[2] proposed the general mechanism in Scheme 1 based on results obtained from studies on the kinetics of the reactions of $AgNO_3$ with 2-octyl halides. Here, a pre-equilibrium step is described in which the alkyl halide, RX, interacts with the Ag^+ cation to give the species $[RX\text{–}Ag^+NO_3^-]$. In a much earlier report (1906), Scholl and Steinkopf[3] prepared the compound $Ag(NO_3)(CH_2I_2)$ **1** for which they proposed the structure **I** which envisaged the co-ordination of the organic iodide to Ag^I.

In spite of these results, it is only recently that co-ordination compounds containing simple alkyl and aryl halides have been structurally characterized.[4–7] Notable examples of silver(I)–alkyl halide complexes include $[\{Ag(ClCH_2CH_2Cl)\}_2(\mu\text{-}OTeF_5)_2]$ **2**[8] and $[\{Ag(CH_2Cl_2)_2(\mu\text{-}OTeF_5)_2\}_2Pd]$ **3**.[9] Both **2** and **3** exhibit chelating α,ω-dichloroalkane ligands, which are among the world's weakest Lewis bases. Very recently, Strauss and co-workers[10] have structurally characterized $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$ and $[Ag(C_2H_4Br_2\text{-}1,2)_3][Sb(OTeF_5)_6]$. These and related chloroalkane complexes of silver are very air and moisture sensitive.

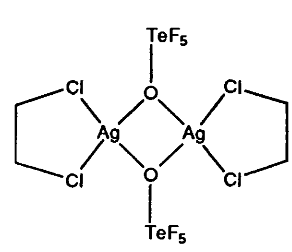
In this paper we report the synthesis and the crystal structural characterization of a series of crystalline silver(I)–iodocarbon complexes obtained from the reaction of $AgPF_6$ and $AgNO_3$ with diiodomethane, 1,3-diiodopropane and simple aryl iodides. These compounds are easily prepared without



Scheme 1 X = Halide



I



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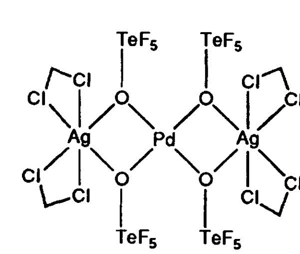


3

elaborate syntheses suggesting that the RI→Ag^+ bond is stronger than the RCl→Ag^+ bond as would be expected from the principle of 'hard' and 'soft' acids and bases. Some of this work has been previously reported in preliminary communications.[11,12]

Results and Discussion

A simple approach to obtaining crystalline samples of the complexes $[Ag\{I(CH_2)_3I\}_2]PF_6$ **4** and $[Ag(ICH_2I)_2]PF_6$ **5** in >85% isolated yields is shown in equation (2). Ethylene

$$AgPF_6 \xrightarrow[(ii)\ 2\ I(CH_2)_nI]{(i)\ C_2H_4\ \text{in}\ CH_2Cl_2} [Ag\{I(CH_2)_nI\}_2]PF_6 \qquad (2)$$

complexation of Ag^+ helps to solubilize the $AgPF_6$ in CH_2Cl_2 and also promotes the formation of large crystals of the complexes **4** and **5**, suitable for X-ray diffraction study, by slowing down the rate of silver(I)–alkyl iodide complexation. A similar reaction with 1,2-diiodobenzene in CH_2Cl_2 followed by the addition of pentanes gave the complex $[Ag(I_2C_6H_4)_3]PF_6$ **6**. Reaction of 4 equivalents of *p*-iodotoluene with $AgPF_6$, in an attempt to obtain $[Ag(IC_6H_4Me)_4]PF_6$, gave white cubic crystals which melted at ≈0 °C. A similar reaction with bromo-2-iodobenzene gave $[Ag(IBrC_6H_4)_4]PF_6$ **7** as a low-melting (≈0 °C) crystalline solid. When the presumed complex $[Ag(IC_6H_4Me)_4]PF_6$ was allowed to stand in a cold CH_2Cl_2 solution the crystals redissolved and after 24 h the complex $[Ag_2(O_2PF_2)_2(IC_6H_4Me)]$ **8** was obtained. A similar procedure using 1,4-diiodobenzene gave $[Ag(O_2PF_2)(1,4\text{-}I_2C_6H_4)]$ **9**. The formation of difluorophosphate involves a silver(I)-promoted hydrolysis of the hexafluorophosphate anion, a reaction that has recently been discussed in some detail.[13] Reaction of $AgNO_3$ in MeOH with CH_2I_2 gave the previously reported complex $[Ag(NO_3)(CH_2I_2)]$ **1** whilst reaction with 1,2-$I_2C_6H_4$ gave $[Ag(NO_3)(I_2C_6H_4)]$ **10**. Reaction of $AgNO_3$ with iodobenzene and *p*-iodotoluene resulted in the isolation of $AgNO_3$ upon crystallization. Reaction of simple alkyl iodides (*e.g.* propyl iodide) with $AgPF_6$, $AgBF_4$ or $AgNO_3$ results in the rapid formation of AgI at temperatures > −20 °C. Reaction of CH_2I_2 and $I(CH_2)_3I$ with $AgBF_4$ also resulted in the fairly rapid formation of AgI.

Silver(I) exhibits linear, trigonal, tetrahedral, pentagonal and even octahedral co-ordination (see complex **3**) and subtle changes readily influence the co-ordination geometry.[14] Consequently the primary method used structurally to characterize the compounds **1** and **4**–**10** is single-crystal X-ray diffraction.

The structure of $[Ag\{I(CH_2)_3I\}_2]PF_6$ **4** is shown in Fig. 1 (PF_6^- not shown). Selected bond distances and angles for complex **4** are listed in (Table 1). The silver atoms lie on two-fold axes. In the solid state the compound is composed of tetrahedrally co-ordinated Ag^+ and bridging 1,3-diiodopropane ligands which give rise to a chain polymer array. The Ag–I bond lengths range from 2.812(1) to 2.818(1) Å. The Ag–I–C and I–Ag–I bond angles range from 96.8(3)–97.4(4) and 106.6(1)–114.9(1)° respectively. There are no close contacts between Ag^+ and PF_6^-. While the solution structure of **4** is not known, its relative stability in CH_2Cl_2 (no formation of AgI after 24 h at 0 °C) strongly suggests that the 1,3-diiodopropane functions as a bidentate ligand. The lack of AgI formation also suggests that the most reactive alkyliodide–silver species contain only one RI–Ag^+ interaction consistent with previous mechanistic proposals.[2] A probable solution structure for the $[Ag\{I(CH_2)_3I\}_2]^+$ cation is **II**. Proton NMR studies indicate a downfield shift of 0.30 and 0.05 ppm for the ICH_2– and –CH_2– protons respectively *vis-à-vis* free 1,3-diiodopropane in CD_2Cl_2. Exchange between free (added) and co-ordinated diiodopropane is fast on the NMR time-scale even at −60 °C.

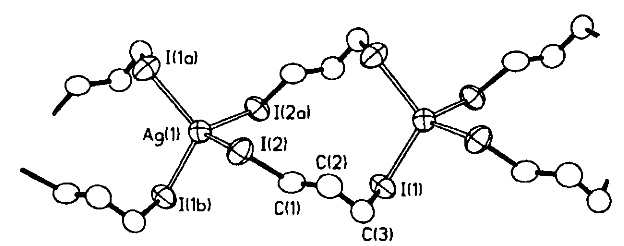
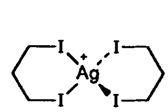


Fig. 1 The structure of $[Ag\{I(CH_2)_3I\}_2]PF_6$ **4** (PF_6^- not shown)



II

The structure of $[Ag(ICH_2I)_2]PF_6$ **5** is shown in Fig. 2 (PF_6^- not shown). Selected bond distances and angles are given in Table 2. In the solid state the compound consists of chains of $(AgICH_2I)_n$ units cross-linked by '$Ag(ICH_2I)_2Ag$ rings'. The co-ordination about Ag^+ is a distorted-tetrahedral array with I–Ag–I varying from 88.5(1) to 131.3(1)°. The Ag–I bond lengths vary from 2.811(1) to 2.921(1) Å with the longer ones being associated with the smallest I–Ag–I bond angle. The C–I bond lengths range from 2.115(12) to 2.139(9) Å and the Ag–I–C bond angles vary from 97.4(3) to 104.2(3)°. The ^1H NMR spectrum in CD_2Cl_2 exhibits a singlet at δ 3.98 which represents a downfield shift *vis-à-vis* free CH_2I_2 of 0.08 ppm. Whilst the solution structure of **5** is not known, exchange between free (added) and co-ordinated CH_2I_2 is fast on the NMR time-scale. Exchange between CH_2I_2 and CD_2Cl_2, a weaker ligand but present in large excess, could also be significant.

The molecular structure of $[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$ **6** is shown

Table 1 Selected bond lengths (Å) and angles (°) for $[Ag\{I(CH_2)_3I\}_2]PF_6$(**4**)

Ag(1)–I(2)	2.818(1)	Ag(1)–I(1a)	2.812(1)
Ag(1)–I(1b)	2.812(1)	Ag(1)–I(2a)	2.818(1)
I(1)–C(3)	2.159(11)	I(1)–Ag(1a)	2.812(1)
I(2)–C(1)	2.182(11)	C(1)–C(2)	1.507(15)
C(2)–C(3)	1.483(17)		
I(2)–Ag(1)–I(1a)	110.6(1)	I(2)–Ag(1)–I(1b)	106.6(1)
I(1a)–Ag(1)–I(1b)	114.9(1)	I(2)–Ag(1)–I(2a)	107.4(1)
I(1a)–Ag(1)–I(2a)	106.6(1)	I(1b)–Ag(1)–I(2a)	110.6(1)
C(3)–I(1)–Ag(1a)	97.4(4)	Ag(1)–I(2)–C(1)	96.8(3)
I(2)–C(1)–C(2)	109.9(6)	C(1)–C(2)–C(3)	111.9(9)
I(1)–C(3)–C(2)	113.1(8)		

Symmetry-related atoms: I(1a) $x, -1 + y, z$; I(1b) $-x, -1 + y, \frac{3}{2} - z$; Ag(1a) $x, 1 + y, z$; I(2a) $-x, y, \frac{3}{2} - z$.

Table 2 Selected bond lengths (Å) and angles (°) for $[Ag(ICH_2I)_2]PF_6$ **5**

Ag(1)–I(1)	2.921(1)	Ag(1)–I(2)	2.823(1)
Ag(1)–I(3a)	2.882(1)	Ag(1)–I(4a)	2.811(1)
I(1)–C(1)	2.115(9)	I(2)–C(2)	2.118(11)
I(3)–C(2)	2.139(9)	I(3)–Ag(1b)	2.882(1)
I(4)–C(1)	2.115(12)	I(4)–Ag(1a)	2.811(1)
I(1)–Ag(1)–I(2)	111.6(1)	I(1)–Ag(1)–I(3a)	88.5(1)
I(2)–Ag(1)–I(3a)	108.1(1)	I(1)–Ag(1)–I(4a)	109.8(1)
I(2)–Ag(1)–I(4a)	105.9(1)	I(3a)–Ag(1)–I(4a)	131.3(1)
Ag(1)–I(1)–C(1)	103.1(3)	Ag(1)–I(2)–C(2)	101.4(2)
C(2)–I(3)–Ag(1b)	104.2(3)	C(1)–I(4)–Ag(1a)	97.4(3)
I(1)–C(1)–I(4)	112.9(5)	I(2)–C(2)–I(3)	110.2(4)

Symmetry-related atoms: Ag(1a), I(4a) $x, 2 - y, 1 - z$; I(3a) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; Ag(1b) $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$.

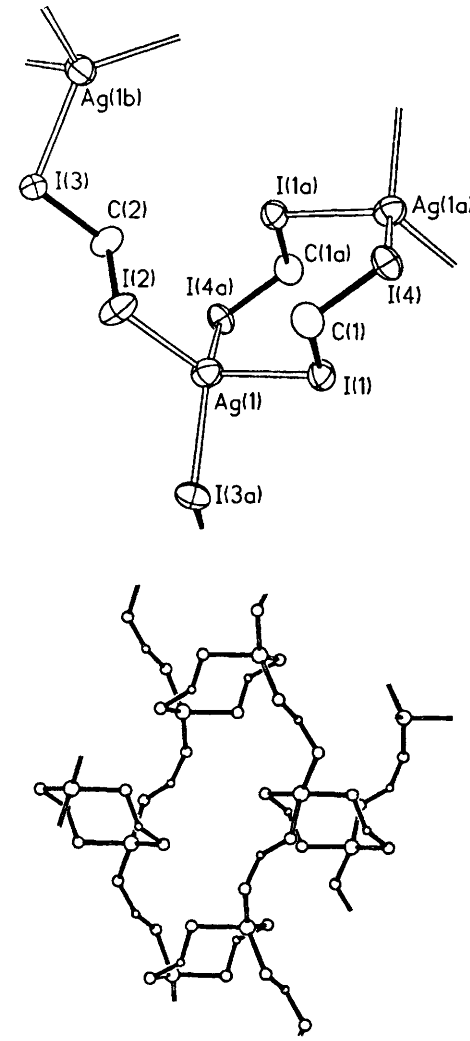


Fig. 2 Labelling scheme and structure of $[Ag(ICH_2I)_2]PF_6$ **5** (PF_6^- not shown)

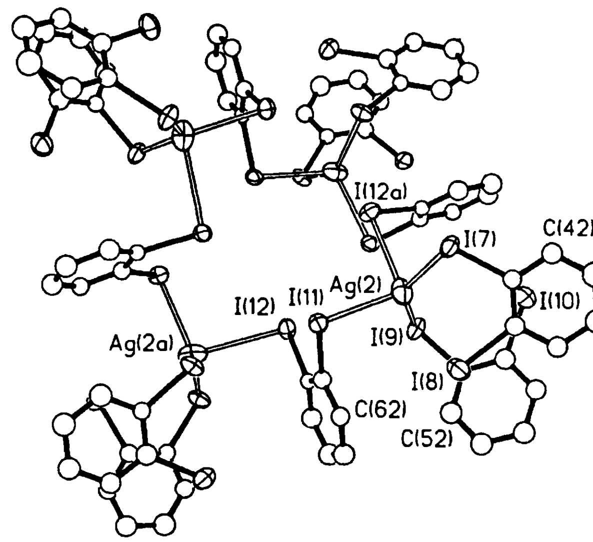


Fig. 3 The structure of $[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$ **6** (PF_6^- not shown)

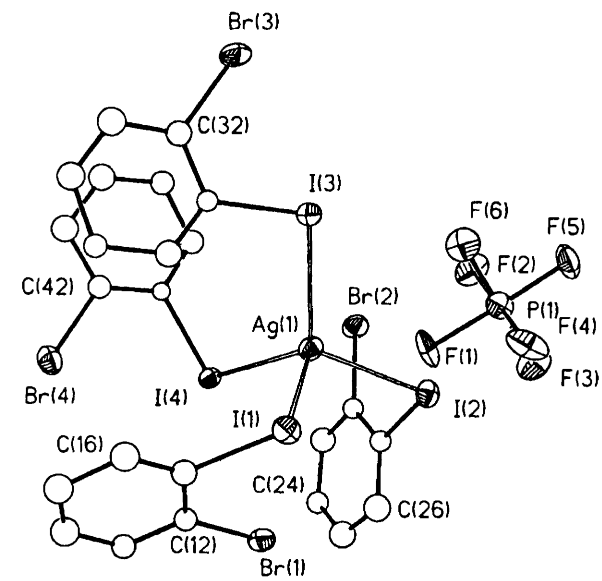


Fig. 4 The structure of $[Ag(1,2\text{-}BrIC_6H_4)_4]PF_6$ **7**

in Fig. 3. (PF_6^- not shown). Selected bond lengths and angles are given in Table 3. The structure has two independent cyclic tetrameric molecules in which two thirds of the 1,2-diiodobenzenes function as monodentate ligands, whilst the remaining third co-ordinate *via* both iodines and bridge two Ag^+ ions. The tetranuclear complexes have $\bar{4}$ symmetry. The coordination at Ag^+ can be considered as a highly distorted trigonal-pyramidal array. The I–Ag–I bond angles in the trigonal plane vary from 107.0(1) to 139.3(1)°. The axial Ag–I bond lengths, which vary from 3.155(5) to 3.306(5) Å are significantly longer than those in the trigonal plane which vary from 2.777(4) to 2.879(4) Å. The bridging $I_2C_6H_4$ ligands have one long and one short Ag–I bond. The Ag–I–C bond angles range from 94.8(5) to 104.2(6)°. The silver–iodine separation for the non-co-ordinated iodine of the monodentate $I_2C_6H_4$ ligands varies from 3.47 to 4.33 Å.

The molecular structure of $[Ag(1,2\text{-}BrIC_6H_4)_4]PF_6$ **7** is shown in Fig. 4. Selected bond lengths and angles are given in Table 4. The co-ordination at silver is a distorted-tetrahedral array with I–Ag–I bond angles ranging from approximately 105 to 117° whilst the Ag–I bond lengths are in the range 2.80–2.88 Å. The Ag–I–C bond angles vary from 95.3 to 102.2°. None of the bromine atoms is within bonding distance of the Ag^+ ion.

The structure of $[Ag_2(O_2PF_2)_2(p\text{-}IC_6H_4Me)]$ **8** is shown in Fig. 5. Selected bond lengths and angles are given in Table 5. The solid-state structure consists of an infinite sheet array of $[Ag(O_2PF_2)]_n$ in which each silver ion, which is five-coordinate, is bound to four oxygens of bridging difluorophosphate goups. Each *p*-iodotoluene bonds to two Ag^+ ions *via* one I–Ag bond and by an η^2-arene bond involving two of the carbons not bonded to I or Me. The iodotoluene ligands are equally distributed on either side of the $[Ag(O_2PF_2)]_n$ sheet. Each difluorophosphate group is bonded to four Ag^+ ions *via* two μ-oxygen atoms which gives rise to a structural array containing 'AgO_2Ag four-atom', '$AgO(O_2P)Ag$ six-atom' and '$Ag(O_2P)_2Ag$ eight-atom' rings. The Ag–O bond lengths vary from 2.351(12) to 2.554(13) Å and Ag–O–P angles from 116.1(7) to 134.7(9)°. At temperatures > 10 °C the iodotoluene slowly dissociates and the crystal collapses.

The structure of $[Ag(O_2PF_2)(1,4\text{-}I_2C_6H_4)]$ **9** is shown in Fig. 6. Selected bond lengths and angles are given in Table 6. The structure consists of $[Ag(O_2PF_2)]_n$ chains cross-linked by bridging $1,4\text{-}I_2C_6H_4$ ligands. The silver atoms lie on mirror planes and each is bound to two iodine and two oxygen atoms. The Ag–I bond lengths are 2.82 Å and the I–Ag–I angle is 123.2(1)°. The difluorophosphate group forms an unsymmetric O,O′-three atom bridge with Ag–O bond lengths of 2.243(10) and 2.379(8) Å and Ag–O–P bond angles of 165.6(8) and 121.8(5)° respectively.

The structure of the compound $[Ag(NO_3)(CH_2I_2)]$ **1** first reported in 1906,[3] is shown in Fig. 7. Bond lengths and angles are given in Table 7. The solid-state structure involves a sheet

Table 3 Selected bond lengths (Å) and angles (°) for $[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$ **6***

Ag(1)–I(1)	2.836(4)	Ag(1)–I(3)	2.823(5)
Ag(1)–I(5)	2.836(5)	Ag(1)–I(2a)	3.306(5)
Ag(2)–I(7)	2.790(4)	Ag(2)–I(9)	2.777(4)
Ag(2)–I(11)	2.879(4)	Ag(2)–I(12a)	3.155(5)
I(1)–C(11)	2.048(19)	I(2)–C(16)	2.062(20)
I(2)–Ag(1a)	3.306(5)	I(3)–C(21)	2.072(19)
I(4)–C(26)	2.084(20)	I(5)–C(32)	2.149(15)
I(5)–C(31)	2.335(19)	I(7)–C(41)	2.093(20)
I(8)–C(46)	2.115(21)	I(9)–C(51)	2.056(21)
I(10)–C(56)	2.080(21)	I(11)–C(61)	2.077(17)
I(12)–C(66)	2.105(19)	I(12)–Ag(2a)	3.155(5)
I(1)–Ag(1)–I(3)	119.3(1)	I(1)–Ag(1)–I(5)	103.5(1)
I(3)–Ag(1)–I(5)	137.2(1)	I(1)–Ag(1)–I(2a)	98.9(1)
I(3)–Ag(1)–I(2a)	87.8(1)	I(5)–Ag(1)–I(2a)	87.7(1)
I(7)–Ag(2)–I(9)	139.3(1)	I(7)–Ag(2)–I(11)	112.0(1)
I(9)–Ag(2)–I(11)	107.0(1)	I(7)–Ag(2)–I(12a)	96.6(1)
I(9)–Ag(2)–I(12a)	88.7(1)	I(11)–Ag(2)–I(12a)	98.3(1)
Ag(1)–I(1)–C(11)	98.5(6)	Ag(1)–I(3)–C(21)	98.2(6)
Ag(1)–I(5)–C(32)	96.9(7)	Ag(1)–I(5)–C(31)	99.9(7)
C(16)–I(2)–Ag(1a)	95.4(5)	Ag(2)–I(9)–C(51)	101.7(6)
Ag(2)–I(7)–C(41)	104.2(6)	C(66)–I(12)–Ag(2a)	95.9(5)
Ag(2)–I(11)–C(61)	94.8(5)		

* The unit cell contains two independent tetrameric molecules, one of which [Ag(1) data] has some disorder associated with a $C_6H_4I_2$ substituent. Symmetry-related atoms: Ag(1a) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$; I(2a) $\frac{1}{2} - y, -\frac{1}{2} + x, \frac{1}{2} - z$; Ag(2a) $y, -x, -z$; I(12a) $-y, x, -z$.

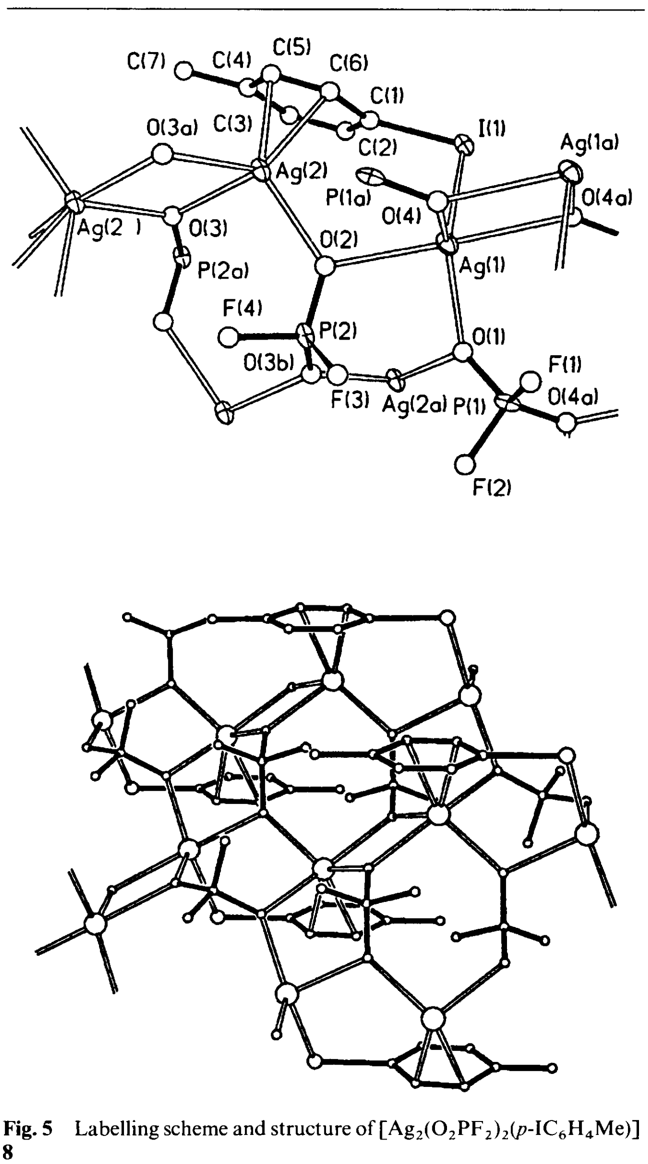


Fig. 5 Labelling scheme and structure of $[Ag_2(O_2PF_2)_2(p\text{-}IC_6H_4Me)]$ **8**

Table 4 Selected bond lengths (Å) and angles (°) for $[Ag(1,2\text{-}BrIC_6H_4)_4]PF_6$ **7**

Ag(1)–I(1)	2.883(4)	Ag(1)–I(2)	2.813(4)
Ag(1)–I(3)	2.799(4)	Ag(1)–I(4)	2.823(4)
I(1)–C(11)	2.156(31)	I(2)–C(21)	2.085(26)
I(3)–C(31)	2.088(29)	I(4)–C(41)	2.116(25)
I(1)–Ag(1)–I(2)	106.4(1)	I(1)–Ag(1)–I(3)	105.4(1)
I(2)–Ag(1)–I(3)	116.8(1)	I(1)–Ag(1)–I(4)	106.0(1)
I(2)–Ag(1)–I(4)	108.6(1)	I(3)–Ag(1)–I(4)	112.9(1)
Ag(1)–I(1)–C(11)	100.6(7)	Ag(1)–I(2)–C(21)	95.3(8)
Ag(1)–I(3)–C(31)	102.2(7)	Ag(1)–I(4)–C(41)	97.3(7)

Table 5 Selected bond lengths (Å) and angles (°) for $[Ag(O_2PF_2)_2(p\text{-}IC_6H_4Me)]$ **8**

I(1)–Ag(1)	2.790(2)	I(1)–C(1)	2.104(15)
Ag(2)–O(2)	2.351(12)	Ag(2)–O(3)	2.434(12)
Ag(2)–C(5)	2.581(15)	Ag(2)–C(6)	2.525(13)
Ag(2)–O(1a)	2.540(14)	Ag(2)–O(3a)	2.388(12)
Ag(1)–O(1)	2.377(11)	Ag(1)–O(2)	2.488(12)
Ag(1)–O(4)	2.400(16)	Ag(1)–O(4b)	2.554(13)
P(1)–F(1)	1.549(15)	P(1)–F(2)	1.549(10)
P(1)–O(1)	1.490(13)	P(1)–O(4a)	1.441(14)
P(2)–F(3)	1.532(13)	P(2)–F(4)	1.578(10)
P(2)–O(2)	1.474(11)	P(2)–O(3b)	1.449(14)
O(1)–Ag(2a)	2.540(14)	O(3)–Ag(2b)	2.388(12)
O(3)–P(2a)	1.449(14)	O(4)–Ag(1a)	2.554(13)
O(4)–P(1a)	1.441(14)		
Ag(1)–I(1)–C(1)	101.1(4)	O(2)–Ag(2)–O(3)	95.5(4)
O(2)–Ag(2)–C(5)	129.4(5)	O(3)–Ag(2)–C(5)	93.7(5)
O(2)–Ag(2)–C(6)	104.9(5)	O(3)–Ag(2)–C(6)	115.5(5)
C(5)–Ag(2)–C(6)	29.6(5)	O(2)–Ag(2)–O(1a)	88.9(4)
O(3)–Ag(2)–O(1a)	157.2(4)	C(5)–Ag(2)–O(1a)	100.8(5)
C(6)–Ag(2)–O(1a)	84.6(5)	O(2)–Ag(2)–O(3a)	121.5(4)
O(3)–Ag(2)–O(3a)	78.2(5)	C(5)–Ag(2)–O(3a)	109.1(5)
C(6)–Ag(2)–O(3a)	130.6(4)	O(1a)–Ag(2)–O(3a)	80.4(4)
I(1)–Ag(1)–O(1)	121.4(3)	I(1)–Ag(1)–O(2)	106.6(3)
O(1)–Ag(1)–O(2)	88.2(4)	I(1)–Ag(1)–O(4)	110.3(3)
O(1)–Ag(1)–O(4)	127.0(4)	O(2)–Ag(1)–O(4)	87.5(5)
I(1)–Ag(1)–O(4b)	77.9(3)	O(1)–Ag(1)–O(4b)	96.0(4)
O(2)–Ag(1)–O(4b)	171.0(5)	O(4)–Ag(1)–O(4b)	83.6(4)
Ag(1)–O(1)–P(1)	124.9(8)	Ag(1)–O(1)–Ag(2a)	115.1(5)
P(1)–O(1)–Ag(2a)	119.9(7)	Ag(2)–O(2)–Ag(1)	112.8(4)
Ag(2)–O(2)–P(2)	130.7(7)	Ag(1)–O(2)–P(2)	116.1(7)
Ag(2)–O(3)–Ag(2b)	101.8(5)	Ag(2)–O(3)–P(2a)	125.7(6)
Ag(2b)–O(3)–P(2a)	129.5(6)	Ag(1)–O(4)–Ag(1a)	96.4(4)
Ag(1)–O(4)–P(1a)	124.8(9)	Ag(1a)–O(4)–P(1a)	134.7(9)
Ag(2)–C(6)–C(5)	77.6(9)	Ag(2)–C(5)–C(6)	72.8(9)

Symmetry-related atoms: Ag(2a), O(4a) $-1 + x, y, z$; Ag(2b), O(3b) $1 - x, 1 - y, -z$; Ag(1a), O(4b) $-x, 1 - y, 1 - z$; P(1a), O(1a) $1 + x, 1 + y, z$; P(2a), O(3a) $-x, 1 - x, -z$.

Table 6 Selected bond lengths (Å) and angles (°) for $[Ag(O_2PF_2)(1,4\text{-}I_2C_6H_4)]$ **9**

Ag(1)–I(1)	2.821(1)	Ag(1)–O(1)	2.243(10)
Ag(1)–I(1a)	2.821(1)	Ag(1)–O(2a)	2.379(8)
I(1)–C(2)	2.106(7)	P(1)–O(1)	1.454(9)
P(1)–O(2)	1.455(9)	P(1)–F(1)	1.532(7)
P(1)–F(1a)	1.532(7)	O(2)–Ag(1a)	2.379(8)
I(1)–Ag(1)–O(1)	111.6(1)	I(1)–Ag(1)–I(1a)	123.2(1)
O(1)–Ag(1)–I(1a)	111.6(1)	I(1)–Ag(1)–O(2a)	102.7(1)
O(1)–Ag(1)–O(2a)	101.8(4)	I(1a)–Ag(1)–O(2a)	102.7(1)
Ag(1)–I(1)–C(2)	103.0(2)	Ag(1)–O(1)–P(1)	165.6(8)
P(1)–O(2)–Ag(1a)	121.8(5)		

Symmetry-related atoms: Ag(12a) $\frac{1}{2} + x, y, \frac{1}{2} - z$; I(1a) $\frac{1}{2} + x, \frac{3}{2} - y, z$; O(2a) $-\frac{1}{2} - x, y, \frac{1}{2} - z$; F(1a) $x, \frac{3}{2} - y, z$.

array of fused $Ag_4(\mu\text{-}NO_3)_2(\mu\text{-}CH_2I_2)_2$ 16-atom rings with each silver bonded to two oxygen and two iodine atoms in a distorted-tetrahedral array. The nitrate bridges two silver

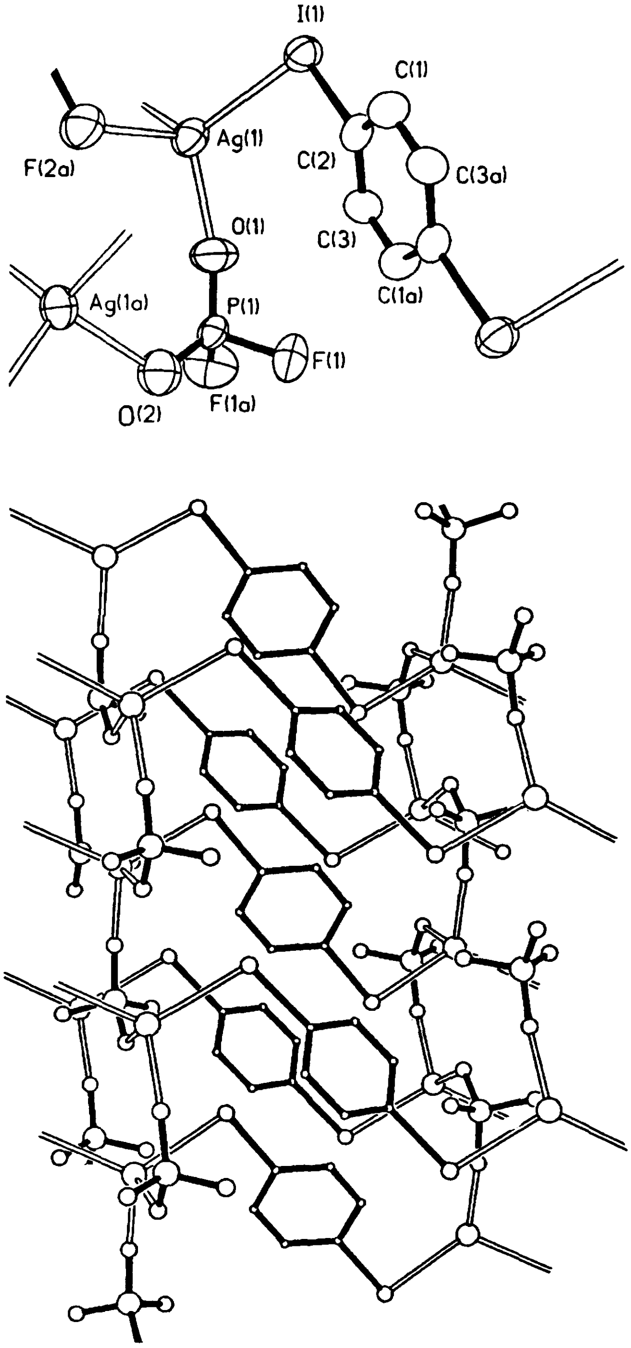


Fig. 6 Labelling scheme and structure of [$Ag(O_2PF_2)(1,4\text{-}I_2C_6H_4)$] **9**

atoms *via* two oxygen atoms. Angles vary from an O–Ag–O of 86.9(5)° to an I–Ag–I angle of 123.3(1)° and an I–Ag–O angle of 131.3(4)°. The Ag–I bond lengths are in the normal 2.8–2.9 Å range.

The structure of the compound [$Ag(NO_3)(1,2\text{-}I_2C_6H_4)$] **10** is given in Fig. 8. Bond lengths and angles are given in Table 8. This compound is composed of spiral chains of [$Ag(\mu\text{-}NO_3)$]$_n$ in which the nitrate uses only one oxygen atom to bridge two silvers. The 1,2-diiodobenzene ligands form bridges in a first and third Ag atom array thereby generating '$Ag_3O_2I_2C_2$' nine-atom rings. The $I_2C_6H_4$ ligands 'stack' on either side of the [$Ag(NO_3)$]$_n$ chain to produce two complementary spiral arrays. The AgI_2O_2 co-ordination about silver is highly distorted with bond angles in the range 82–134°. The Ag–I bond lengths are in the 'typical' 2.8–2.9 Å range. The Ag–O bond lengths are all close to 2.36 Å.

The complexes **4**–**7** and [$Ag(CH_2Cl_2)_3$]$_2$[$Ti(OTeF_5)_6$], [$Ag(CH_2Br_2)_3$][$Nb(OTeF_5)_6$] and [$Ag(C_2H_4Br_2\text{-}1,2)_3$][$Sb(OTeF_5)_6$][10] are the only known examples of homoleptic halogenocarbon co-ordination. The four-co-ordinate environments of **4**–**7** vary from a slightly distorted tetrahedral array, as observed in **7** to a trigonal-pyramidal array in **6** in which the axial Ag–I bond is 0.4–0.5 Å longer than the equatorial Ag–I bonds. Similar variations are observed in the solid-state structures of chalcogenides and halides of Ag^I and Cu^I and the trigonal-pyramidal array in which the axial bond is elongated, as observed in **6**, has been ascribed to a second-order Jahn–Teller effect.[14] It is noteworthy that in both the structure of **10** and that of **6** no chelating $1,2\text{-}I_2C_6H_4$ bonding mode is observed even though such a mode is observed in the iridium complex [$IrH_2(PPh_3)_2(1,2\text{-}I_2C_6H_4)$]$SbF_6$.[15]

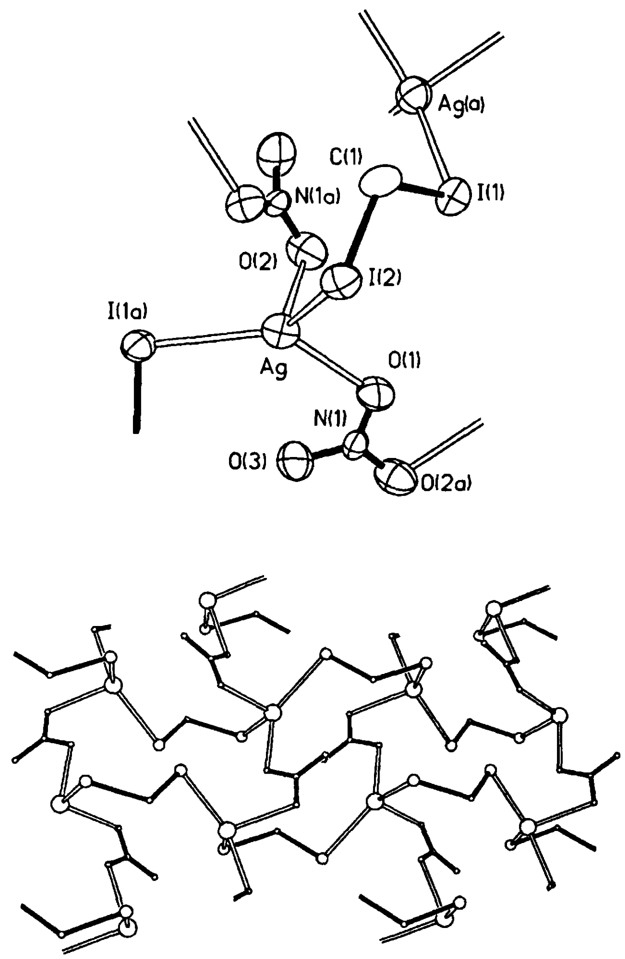


Fig. 7 Labelling scheme and structure of [$Ag(NO_3)(CH_2I_2)$] **1**

Table 7 Selected bond lengths (Å) and angles (°) for [$Ag(NO_3)(CH_2I_2)$] **1**

I(1)–C(1)	2.143(22)	I(1)–Ag(a)	2.819(2)
I(2)–Ag	2.868(3)	I(2)–C(1)	2.123(18)
Ag–O(1)	2.367(16)	Ag–O(2)	2.571(15)
Ag–I(1a)	2.819(2)	O(1)–N(1)	1.254(23)
O(2)–N(1a)	1.232(25)	O(3)–N(1)	1.245(22)
N(1)–O(2a)	1.232(25)		
C(1)–I(1)–Ag(a)	101.4(5)	Ag–I(2)–C(1)	99.3(6)
I(2)–Ag–O(1)	98.7(4)	I(2)–Ag–O(2)	111.6(4)
O(1)–Ag–O(2)	86.9(5)	I(2)–Ag–I(1a)	123.3(1)
O(1)–Ag–I(1a)	131.3(4)	O(2)–Ag–I(1a)	97.9(4)
Ag–O(1)–N(1)	110.9(11)	Ag–O(2)–N(1a)	99.0(12)
O(1)–N(1)–O(3)	121.0(17)	O(1)–N(1)–O(2a)	118.6(16)
O(3)–N(1)–O(2a)	120.4(17)	I(1)–C(1)–I(2)	112.2(10)

Symmetry-related atoms: Ag(a) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; I(1a) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; N(1a) $-x, -\frac{1}{2}-y, -\frac{1}{2}+z$; O(2a) $x, -\frac{1}{2}-y, \frac{1}{2}+z$.

Table 8 Selected bond lengths (Å) and angles (°) for $[Ag(NO_3)(1,2\text{-}I_2C_6H_4)]$ **10**

I(1)–Ag(1)	2.878(2)	I(1)–C(1)	2.074(13)
I(2)–Ag(1)	2.812(2)	I(2)–C(4)	2.126(12)
I(3)–Ag(2)	2.871(2)	I(3)–C(7)	2.100(13)
I(4)–Ag(2)	2.778(2)	I(4)–C(10)	2.088(13)
Ag(1)–O(1)	2.353(14)	Ag(1)–O(4)	2.352(13)
Ag(2)–O(1)	2.356(15)	Ag(2)–O(4a)	2.356(13)
O(1)–N(1)	1.261(22)	O(2)–N(1)	1.195(19)
O(3)–N(1)	1.205(22)	O(4)–N(2)	1.264(20)
O(4)–Ag(2a)	2.356(13)	O(5)–N(2)	1.240(21)
O(6)–N(2)	1.175(21)		
Ag(1)–I(1)–C(1)	108.2(3)	Ag(1)–I(2)–C(4)	99.9(4)
Ag(2)–I(3)–C(7)	103.8(4)	Ag(2)–I(4)–C(10)	107.1(4)
I(1)–Ag(1)–I(2)	106.7(1)	I(1)–Ag(1)–O(1)	98.0(4)
I(2)–Ag(1)–O(1)	127.9(5)	I(1)–Ag(1)–O(4)	114.5(4)
I(2)–Ag(1)–O(4)	124.5(3)	O(1)–Ag(1)–O(4)	81.8(5)
I(3)–Ag(2)–I(4)	102.5(1)	I(3)–Ag(2)–O(1)	111.2(5)
I(4)–Ag(2)–O(1)	112.4(4)	I(3)–Ag(2)–O(4a)	110.4(3)
I(4)–Ag(2)–O(4a)	134.4(4)	O(1)–Ag(2)–O(4a)	84.3(5)
Ag(1)–O(1)–Ag(2)	115.1(6)	Ag(1)–O(1)–N(1)	125.8(11)
Ag(2)–O(1)–N(1)	117.6(11)	Ag(1)–O(4)–N(2)	120.9(10)
Ag(1)–O(4)–Ag(2a)	123.3(6)	N(2)–O(4)–Ag(2a)	115.8(10)

Symmetry-related atoms: Ag(2a), C(4a), C(6a), C(10a), C(12a) $1 + x, y, z$; O(4a), C(1a), C(3a), C(7a), C(9a) $-1 + x, y, z$.

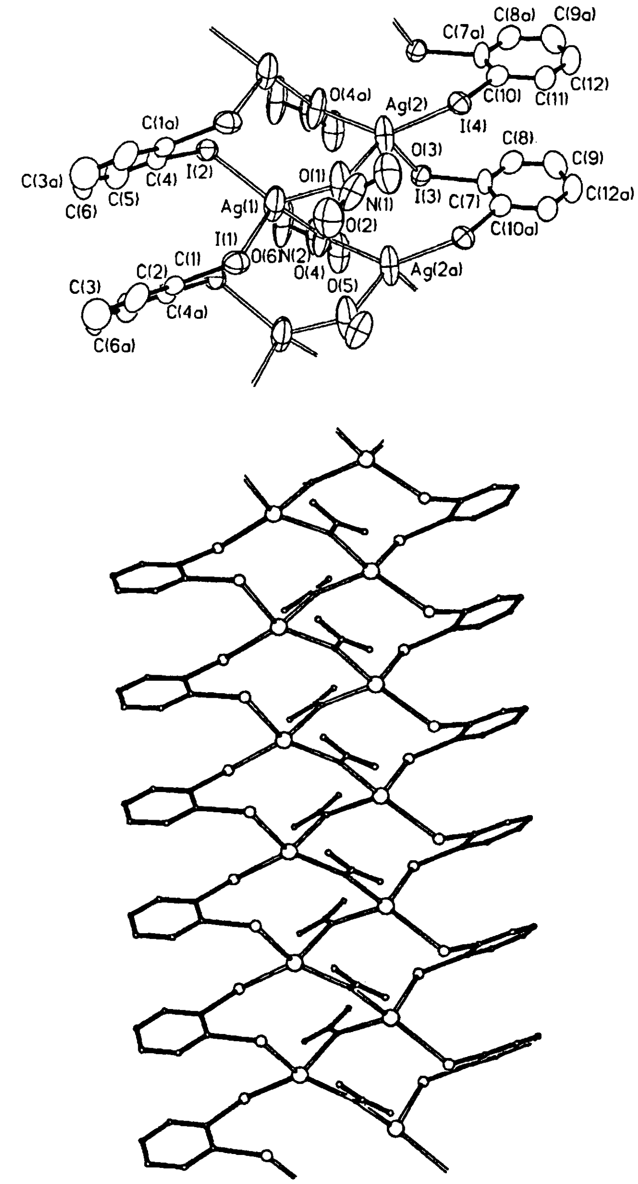


Fig. 8 Labelling scheme and structure of $[Ag(NO_3)(1,2\text{-}I_2C_6H_4)]$ **10**

Experimental

Preparations

$[Ag\{I(CH_2)_3I\}_2]PF_6$ 4. Ethylene was bubbled through a stirred mixture containing $AgPF_6$ (0.62 g, 2.45 mmol) in CH_2Cl_2 (15 cm^3) for 15 min. The resultant slightly turbid colourless solution was filtered into another flask and $I(CH_2)_3I$ (0.56 cm^3, 4.87 mmol) added slowly *via* syringe. After 2 h the pale tan-yellow crystals of complex **4** which formed were separated from the mother-liquor, washed with CH_2Cl_2 (2 × 5 cm^3), and dried *in vacuo* (yield 1.81 g, 87%), m.p. 83–89 °C (Found: C, 8.45; H, 1.35; I, 59.50. Calc. for $C_6H_{12}AgF_6I_4P$: C, 8.55; H, 1.45; I, 60.10%). Similarly prepared was $[Ag(ICH_2I)_2]PF_6$ **5** which was isolated as colourless needles (yield, 86%), m.p. 92–94 °C (decomp.) (Found: C, 2.85; H, 0.50; I, 65.00. Calc. for $C_2H_4AgF_6I_4P$: C, 3.05; H, 0.50; I, 64.40%).

The complexes $[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$ **6** and $[Ag(1,2\text{-}BrIC_6H_4)_4]PF_6$ **7** were similarly prepared but required the reduction of the volume of CH_2Cl_2 solvent followed by addition of dry hexanes and cooling to −20 °C to induce crystallization. Complex **6** was isolated as colourless needles (yield 30%), m.p. 89–94 °C (Found: C, 22.25; H, 1.35; I, 58.30. Calc. for $C_{18}H_{12}AgF_6I_6P$: C, 21.85; H, 1.1; I, 57.75%). Complex $[Ag(1,2\text{-}BrIC_6H_4)_4]PF_6$ **7** was isolated as white needles which melted at ≈0 °C.

The difluorophosphate complexes were prepared in a manner similar to that of **4** and isolated as crystalline products after the solution had been kept at ≈0 °C for 24–48 h. The complex $[Ag_2(O_2PF_2)_2(p\text{-}IC_6H_4Me)]$ **8** was isolated as white needles (yield 18%) which decompose with 'extrusion' of iodotoluene at room temperature (Found: C, 13.00; H, 1.05; I, 19.15. Calc. for $C_7H_7Ag_2F_4IO_4P_2$: C, 13.20; H, 1.10; I, 19.95%), $[Ag(O_2PF_2)(1,4\text{-}I_2C_6H_4)]$ **9** as white prisms (yield 70%).

Finely ground $AgNO_3$ (0.23 g) was dissolved in MeOH (15 cm^3). The solution was filtered and $1,2\text{-}I_2C_6H_4$ (0.16 cm^3) added. The solution was left to stand under a fast-flowing nitrogen atmosphere. Slow evaporative loss of the solvent gave complex **10** as white needles (yield 87%), m.p. 84–85 °C (Found: C, 13.85; H, 0.70; N, 2.90; I, 49.85. Calc. for $C_6H_4AgI_2NO_3$: C, 14.40; H, 0.80; N, 2.80; I, 50.80%).

The previously reported complex $[Ag(NO_3)(CH_2I_2)]$ **1**[3] was similarly prepared.

Crystallography

All data sets were collected on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) except that for complex **7** on a Siemens P4 diffractometer. Data were corrected for Lorentz-polarization and absorption effects.[16] The structures were solved and refined using the SHELXTL-PC package.[17] All refinements were by full-matrix least squares, minimizing $\Sigma w(F_o - F_c)^2$ [using data with $F > 4\sigma(F)$] where $w^{-1} = \sigma^2(F) + gF^2$. The refinement for compound **8** yielded a higher than normal *R* factor and some residual electron-density peaks around the I and Ag atoms. Our attempts to select other crystals and collect different data sets did not yield any improvement in the results. The structure of **6** has two independent, cyclic tetramer molecules. One has some disorder associated with a $C_6H_4I_2$ substituent. Two sites were refined for the disordered iodine atom and the phenyl ring was refined with fixed geometry. Crystal data and details of data collection and structure refinement are given in Table 9, and atomic coordinates in Table 10.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. Requests for data should also quote ref. 11. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Table 9 Crystal data and details of data collection and structure refinement for complexes **1** and **4–10**

	1	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Empirical formula	$CH_2AgI_2NO_3$	$C_6H_{12}AgF_6I_4P$	$C_2H_4AgF_6I_4P$	$C_{72}H_{48}Ag_4F_{24}I_{24}P_4$	$C_{24}H_{16}AgBr_4F_6I_4P$	$C_7H_7Ag_2FIO_4P$	$C_6H_4AgF_2I_2O_2P$	$C_6H_4AgI_2NO_3$
Crystal habit *	Needle	Needle	Plate	Needle	Plate	Needle	Plate	Needle
Crystal size/mm	0.32 × 0.20 × 0.15	0.30 × 0.25 × 0.35	0.32 × 0.26 × 0.12	0.24 × 0.32 × 0.42	0.60 × 0.50 × 0.16	0.43 × 0.21 × 0.15	0.08 × 0.25 × 0.23	0.30 × 0.22 × 0.18
M	437.7	844.6	788.5	4970.1	1384.4	635.7	538.7	499.8
Crystal class	Monoclinic	Monoclinic	Monoclinic	Tetragonal	Orthorhombic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	$I\bar{4}$	*Pbca*	$P\bar{1}$	*Pnma*	$P\bar{1}$
a/Å	7.307(2)	17.739(4)	8.584(3)	18.430(3)	21.012(9)	5.949(1)	7.769(2)	4.180(2)
b/Å	11.072(2)	7.481(2)	11.987(3)	18.430(3)	14.988(10)	10.776(1)	18.668(2)	11.510(2)
c/Å	8.931(2)	13.676(2)	13.458(4)	33.905(7)	21.20(2)	12.182(1)	7.865(2)	21.705(4)
α/°						69.71(1)		77.80(2)
β/°	99.31(3)	101.49(3)	102.58(4)			89.74(1)		89.71(2)
γ/°						75.39(1)		86.90(2)
U/Å^3	712.9(4)	1778.5(9)	1351.5(10)	11 521(6)	6714(12)	704.6(2)	1140.6(7)	1019.2(5)
Z	4	4	4	4	8	2	4	4
D_c/g cm^{-3}	4.078	3.154	3.875	2.865	2.739	2.996	3.137	3.257
μ(Mo-Kα)/mm^{-1}	11.418	8.204	10.780	7.232	9.138	5.248	7.318	8.010
F(000)	768	1504	1376	8864	5024	588	968	896
T/K	294	294	294	294	173	173	294	294
2θ range/°	3.7–45.0	3.0–54.0	3.1–50.0	2.4–50	6.0–40.0	3.6–45.0	2.2–54.0	3.6–45.0
Intensity decay	1.000–0.697	1.00–0.352	1.002–0.986	1.004–0.714	1.000–0.950	1.004–0.980	1.000–0.982	1.015–0.974
Minimum, maximum absorption correction	0.1237, 0.4437	0.1263, 0.6486	0.5053, 0.7428	0.2255, 0.5924	0.1086, 0.6658	0.130, 0.6812	0.1316, 0.5898	0.2168, 0.5603
No reflections collected	1073	2233	2630	5555	3361	1862	1513	3739
Unique reflections	928	1951	2368	5482	2968	1838	1272	2633
R_{int}	0.064	0.073	0.031	0.009	0.00	0.00	0.00	0.029
Observed reflections	663	1371	1944	3203	1828	1745	1 017	2159
Weighting g	0.0017	0.0025	0.0020	0.0004	0.008	0.0200	0.0017	0.0030
R	0.046	0.054	0.036	0.055	0.063	0.113	0.051	0.055
R'	0.057	0.079	0.055	0.057	0.068	0.180	0.073	0.080
Goodness of fit	1.06	1.35	1.01	1.66	1.33	1.29	1.55	1.38
Largest, mean Δ/σ	0.04, 0.00	0.09, 0.01	0.04, 0.00	0.02, 0.00	0.02, 0.00	0.08, 0.02	0.00, 0.00	0.01, 0.00
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	1.27, −1.04	1.09, −1.25	1.03, −1.36	1.42, −1.49	0.95, −1.36	6.57, −4.39	0.99, −1.30	1.54, −1.53

* All crystals were colourless.

Table 10 Atomic coordinates

Atom	x	y	z	Atom	x	y	z
$[Ag\{I(CH_2)_3I\}_2]PF_6$ **4**							
Ag(1)	0.0	−0.037 3(2)	0.75	P(1)	−0.25	−0.25	0.5
I(1)	0.018 9(1)	0.760 5(1)	0.583 2(1)	F(1)	−0.199 0(12)	−0.414 0(21)	0.523 8(13)
I(2)	0.128 3(0)	0.185 8(1)	0.814 0(1)	F(2)	−0.314 4(12)	−0.387 0(25)	0.514 5(14)
C(1)	0.101 4(6)	0.380 5(15)	0.693 3(8)	F(1*)	−0.167 0(9)	−0.301 8(35)	0.527 0(17)
C(2)	0.144 6(5)	0.551 8(14)	0.723 0(9)	F(2*)	−0.258 3(21)	−0.473 0(37)	0.537 5(25)
C(3)	0.136 4(6)	0.679 5(14)	0.638 6(10)	F(3)	−0.259 4(5)	−0.309 7(12)	0.387 8(6)
$[Ag(ICH_2I)_2]PF_6$ **5**							
Ag(1)	−0.029 2(1)	0.854 2(1)	0.660 1(1)	P(1)	−0.001 7(3)	0.501 4(2)	0.738 6(2)
I(1)	0.020 7(1)	1.092 8(1)	0.635 8(1)	F(1)	0.157 4(11)	0.482 5(12)	0.708 1(10)
I(2)	−0.343 0(1)	0.789 3(1)	0.566 3(1)	F(2)	−0.160 6(12)	0.517 0(11)	0.769 9(10)
I(3)	−0.518 6(1)	0.605 7(1)	0.372 7(1)	F(3)	−0.050 0(14)	0.377 1(7)	0.721 5(8)
I(4)	−0.173 6(1)	1.268 6(1)	0.437 1(1)	F(4)	0.042 9(13)	0.628 1(6)	0.756 5(7)
C(1)	−0.200 0(11)	1.146 4(10)	0.545 6(8)	F(5)	0.082 3(13)	0.477 0(8)	0.850 1(6)
C(2)	−0.300 4(11)	0.682 2(10)	0.449 8(8)	F(6)	−0.084 6(14)	0.527 2(8)	0.626 6(6)
$[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$ **6**							
Ag(1)	0.371 1(2)	0.181 9(2)	0.320 1(1)	C(13)	0.540 8	0.395 4	0.249 1
Ag(2)	0.159 4(2)	0.161 5(2)	0.066 0(1)	C(14)	0.535 4	0.374 2	0.209 7
I(1)	0.523 8(1)	0.197 7(1)	0.315 1(1)	C(15)	0.526 3	0.301 1	0.200 2
I(2)	0.512 9(1)	0.143 0(1)	0.211 7(1)	C(16)	0.522 4	0.249 3	0.230 1
I(3)	0.308 5(1)	0.135 3(1)	0.391 8(1)	C(21)	0.218 0	0.202 1	0.391 4
I(4)	0.320 1(1)	0.329 2(2)	0.369 1(1)	C(22)	0.150 4(11)	0.171 8(8)	0.399 9(6)
I(5)	0.321 9(2)	0.227 5(1)	0.244 8(1)	C(23)	0.088 2	0.214 9	0.398 5
I(6)	0.136 1(2)	0.235 9(3)	0.274 6(1)	C(24)	0.093 6	0.288 2	0.388 7
I(7)	0.133 5(1)	0.209 5(1)	0.142 7(1)	C(25)	0.161 2	0.318 5	0.380 3
I(8)	0.324 3(2)	0.203 3(1)	0.109 7(1)	C(26)	0.223 4	0.275 4	0.381 6
I(9)	0.189 4(1)	0.218 4(1)	−0 .008 1(1)	C(31)	0.250 0	0.326 1	0.263 3
I(10)	0.181 1(2)	0.391 6(2)	0.043 6(1)	C(32)	0.323 0(13)	0.342 1(8)	0.256 7(8)
I(11)	0.197 3(1)	0.010 1(1)	0.063 6(1)	C(33)	0.348 5	0.412 6	0.262 1
I(12)	0.147 3(1)	0.004 8(1)	−0 .040 7(1)	C(34)	0.300 9	0.467 3	0.274 0
P(1)	1.0	0.5	0.143 4(4)	C(35)	0.227 9	0.451 4	0.280 6
P(2)	0.0	0.0	0.134 4(3)	C(36)	0.202 5	0.380 8	0.275 2
P(3)	0.5	0.0	0.115 8(4)	C(41)	0.204 1	0.297 5	0.149 8
P(4)	0.5	0.5	0.104 8(5)	C(42)	0.177 1(9)	0.361 1(12)	0.166 5(6)
F(1)	0.940 7(14)	0.507 8(16)	0.176 2(10)	C(43)	0.221 9	0.421 7	0.170 4
F(2)	0.940 7(11)	0.510 2(11)	0.109 1(8)	C(44)	0.293 7	0.418 7	0.157 5
F(3)	0.986 6(14)	0.416 0(11)	0.142 1(9)	C(45)	0.320 7	0.355 0	0.140 7
F(4)	0.026 3(14)	0.078 6(11)	0.133 8(7)	C(46)	0.275 9	0.294 4	0.136 9
F(5)	0.0	0.0	0.087 6(8)	C(51)	0.280 0	0.280 1	0.003 2
F(6)	−0.080 6(11)	0.028 4(16)	0.135 7(7)	C(52)	0.346 8(12)	0.251 0(9)	−0.008 1(6)
F(7)	0.5	0.0	0.163 9(7)	C(53)	0.410 8	0.288 2	0.000 5
F(8)	0.0	0.0	0.180 2(7)	C(54)	0.408 0	0.354 5	0.020 4
F(9)	0.581 9(11)	0.025 0(16)	0.117 4(7)	C(55)	0.341 2	0.383 5	0.031 6
F(10)	0.477 1(15)	0.083 5(12)	0.116 6(7)	C(56)	0.277 2	0.346 3	0.023 0
F(11)	0.5	0.0	0.070 8(8)	C(61)	0.273 2	0.021 8	0.018 7
F(12)	0.557 7(12)	0.493 9(14)	0.073 7(7)	C(62)	0.344 8(10)	0.035 9(11)	0.029 7(4)
F(13)	0.441 8(12)	0.504 6(14)	0.136 4(8)	C(63)	0.398 1	0.044 4	0.000 9
F(14)	0.492 6(12)	0.414 3(11)	0.105 7(7)	C(64)	0.380 0	0.038 8	−0.038 9
C(11)	0.527 7	0.270 4	0.269 5	C(65)	0.308 5	0.024 7	−0.049 9
C(12)	0.536 9(11)	0.343 5(11)	0.279 0(5)	C(66)	0.255 1	0.016 2	−0.021 1
($\times 10^4$) $[Ag(1,2\text{-}BrIC_6H_4)_4]PF_6$ **7**							
Ag(1)	8 810(1)	−866(2)	6 059(1)	C(26)	7 015(15)	−842(22)	4 893(17)
I(1)	8 598(1)	−2 592(1)	6 620(1)	C(31)	10 107(11)	−422(18)	7 288(14)
I(2)	8 453(1)	−1 020(1)	4 785(1)	C(32)	10 638(13)	−63(17)	7 607(16)
I(3)	10 087(1)	−463(2)	6 303(1)	C(33)	10 679(14)	−66(18)	8 237(17)
I(4)	7 958(13)	311(1)	6 666(1)	C(34)	10 204(13)	−394(19)	8 561(17)
Br(1)	7 054(1)	−1 833(2)	6 342(2)	C(35)	9 658(12)	−762(17)	8 290(15)
Br(2)	8 322(2)	1 296(2)	4 959(2)	C(36)	9 641(13)	−751(19)	7 612(16)
Br(3)	11 336(1)	434(2)	7 134(2)	C(41)	8 643(11)	1 036(16)	7 187(14)
Br(4)	8 049(2)	302(2)	8 293(2)	C(42)	8 651(12)	992(19)	7 822(16)
C(11)	7 948(13)	−2 244(18)	7 368(16)	C(43)	9 111(13)	1 439(19)	8 191(18)
C(12)	7 327(12)	−1 980(18)	7 179(15)	C(44)	9 564(15)	1 893(21)	7 846(18)
C(13)	6 922(14)	−1 807(17)	7 663(15)	C(45)	9 547(13)	1 982(20)	7 210(17)
C(14)	7 113(14)	−1 905(19)	8 258(18)	C(46)	9 073(12)	1 500(18)	6 883(16)
C(15)	7 676(14)	−2 132(19)	8 443(18)	P(1)	10 017(4)	−2 592(5)	4 947(5)
C(16)	8 134(15)	−2 344(19)	7 962(17)	F(1)	9 511(8)	−2 551(12)	5 494(9)
C(21)	7 595(12)	−334(18)	4 884(14)	F(2)	10 010(8)	−1 537(10)	4 912(10)
C(22)	7 587(12)	606(18)	4 960(14)	F(3)	9 466(8)	−2 634(12)	4 440(10)
C(23)	7 014(14)	1 005(22)	5 066(16)	F(4)	10 022(7)	−3 655(10)	5 003(11)
C(24)	6 434(12)	516(19)	5 093(15)	F(5)	10 523(8)	−2 629(12)	4 432(10)
C(25)	6 470(14)	−407(21)	5 032(17)	F(6)	10 560(8)	−2 547(11)	5 452(9)

Table 10 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
$[Ag_2(O_2PF_2)_2(p\text{-}IC_6H_4Me)]$ **8**							
I(1)	0.144 2(2)	0.174 2(1)	0.484 8(1)	O(2)	0.017 8(21)	0.521 6(12)	0.169 8(10)
Ag(2)	0.414 9(2)	0.432 8(1)	0.153 1(1)	O(3)	0.356 2(19)	0.423 2(11)	−0.041 0(9)
Ag(1)	−0.082 3(2)	0.452 6(1)	0.377 0(1)	O(4)	0.154 0(22)	0.590 3(13)	0.407 7(10)
P(1)	−0.664 9(7)	0.630 0(4)	0.335 6(4)	C(1)	0.352 0(26)	0.139 0(15)	0.352 9(12)
P(2)	−0.170 3(8)	0.620 4(4)	0.080 6(3)	C(2)	0.314 6(31)	0.054 6(18)	0.295 0(15)
F(1)	−0.548 0(19)	0.706 8(11)	0.394 9(10)	C(3)	0.449 8(25)	0.035 1(15)	0.212 9(12)
F(2)	−0.771 9(20)	0.752 5(12)	0.221 1(9)	C(4)	0.633 6(33)	0.097 1(20)	0.178 3(15)
F(3)	−0.277 3(18)	0.747 6(11)	0.111 7(9)	C(5)	0.672 4(29)	0.183 2(18)	0.239 7(14)
F(4)	−0.045 7(17)	0.687 5(10)	−0.030 6(8)	C(6)	0.535 8(28)	0.203 4(16)	0.319 5(13)
O(1)	−0.482 4(20)	0.527 8(12)	0.304 4(10)	C(7)	0.781 9(37)	0.072 2(21)	0.084 1(18)
$[Ag(O_2PF_2)(1,4\text{-}I_2C_6H_4)]$ **9**							
Ag(1)	0.329 7(1)	0.75	0.382 6(1)	F(1)	0.814 1(7)	0.688 3(3)	0.665 4(10)
I(1)	0.161 7(1)	0.617 1(0)	0.422 8(1)	C(1)	0.362 2(10)	0.477 2(5)	0.405 2(10)
P(1)	0.773 0(4)	0.75	0.543 5(4)	C(2)	0.366 6(9)	0.545 8(4)	0.468 7(9)
O(1)	0.589 6(11)	0.75	0.506 9(16)	C(3)	0.503 9(10)	0.568 5(4)	0.564 2(10)
O(2)	0.903 6(12)	0.75	0.410 9(10)				
$[Ag(NO_3)(CH_2I_2)]$ **1**							
I(1)	−0.224 1(2)	−0.501 9(1)	0.096 6(2)	O(2)	0.216 4(24)	−0.351 5(13)	0.262 6(21)
I(2)	−0.364 2(2)	−0.203 2(1)	0.163 2(2)	O(3)	0.235 7(23)	−0.043 3(15)	−0.033 2(19)
Ag	0.026 3(3)	−0.159 2(2)	0.187 3(2)	N(1)	0.171 2(22)	−0.130 8(14)	−0.112 2(18)
O(1)	0.060 2(21)	−0.202 9(13)	−0.066 2(17)	C(1)	−0.356 2(32)	−0.385 4(16)	0.238 3(24)
$[Ag(NO_3)(1,2\text{-}I_2C_6H_4)]$ **10**							
I(1)	0.757 9(2)	0.522 1(1)	0.405 8(1)	N(2)	0.830 5(45)	0.646 2(12)	0.155 6(6)
I(2)	0.081 1(2)	0.390 8(1)	0.274 1(1)	C(1)	0.955 1(27)	0.349 5(11)	0.417 5(5)
I(3)	0.330 0(2)	0.956 7(1)	0.093 8(1)	C(2)	0.977 8(39)	0.280 0(15)	0.478 8(8)
I(4)	−0.345 0(2)	1.091 2(1)	0.222 4(1)	C(3)	1.117 0(48)	0.168 8(19)	0.488 0(8)
Ag(1)	0.445 0(5)	0.584 2(1)	0.284 6(1)	C(4)	0.094 1(29)	0.295 7(12)	0.369 4(6)
Ag(2)	−0.057 6(5)	0.878 8(1)	0.202 8(1)	C(5)	0.214 9(40)	0.182 8(14)	0.380 6(8)
O(1)	0.257 7(48)	0.778 5(11)	0.289 4(7)	C(6)	0.235 4(50)	0.122 6(15)	0.440 8(9)
O(2)	0.405 9(38)	0.770 4(12)	0.383 1(6)	C(7)	0.351 0(34)	1.140 5(11)	0.088 2(6)
O(3)	0.109 4(41)	0.916 2(13)	0.336 1(7)	C(8)	0.229 4(35)	1.214 5(14)	0.032 5(7)
O(4)	0.759 2(39)	0.688 6(10)	0.203 3(6)	C(9)	0.235 9(41)	1.337 7(15)	0.024 1(8)
O(5)	0.994 2(47)	0.705 6(12)	0.113 9(6)	C(10)	−0.517 0(31)	1.186 5(12)	0.135 2(6)
O(6)	0.743 5(56)	0.552 5(11)	0.151 8(6)	C(11)	−0.509 3(33)	1.313 2(12)	0.127 1(6)
N(1)	0.258 0(43)	0.822 9(14)	0.337 8(6)	C(12)	−0.628 1(41)	1.383 0(14)	0.071 3(7)

* Disorder components of F(1) and F(2), ratio 50:50.

Acknowledgements

We thank the Natural Science and Engineering Research Council for financial support of this work.

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Received 25*th September* 1995; *Paper* 5/06297G