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FULL PAPER

Synthetic and single-crystal X-ray diffraction studies of CH_2I_2 and aryl iodide complexes of silver carboxylates and β-diketonates

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The silver(I) iodocarbon complexes $[\{Ag_2(O_2CCF_3)_2(CH_2I_2)_2\}_n]$ **1**, $[\{Ag_2(O_2CCF_3)_2(1,2\text{-}I_2C_6H_4)_2\}_n]$ **2**, $[\{Ag_2(O_2CCF_3)_2(1,4\text{-}I_2C_6H_4)_2\}_n]$ **3**, $[\{Ag_2(O_2CCF_3)_2(IC_6H_5)\}_n]$ **4**, $[\{Ag_4(O_2CCF_3)_4(H_2O)_2(p\text{-}IC_6H_4Me)_2\}_n]$ **5**, $[\{Ag_2(O_2CCF_3)_2(1,2\text{-}I_2C_6H_4)\}_n]$ **6**, $[\{Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(1,2\text{-}I_2C_6H_4)\}_n]$ **7**, $[\{Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(IC_6H_5)\}_n]$ **8**, $[\{Ag_4(hfacac)_4(p\text{-}IC_6H_4Me)_2]$ **10** (hfacac = 1,1,1,5,5,5-hexafluoroaceylacetonate) and $[Ag_4(hfacac)_4(1,2\text{-}I_2C_6H_4)_3]$ **11** have been prepared and structurally characterized by single-crystal X-ray diffraction. The silver carboxylate complexes all contain carboxylate-bridged Ag_2(carboxylate-*O,O′*)$_2$ dimers (Ag–O 2.22–2.40 Å) with the intra-dimer Ag · · · Ag distance varying in the range 2.9106(12) to 3.1527(14) Å which are the values observed for the alternating dimer units $Ag_2(O_2CCF_3)_2(H_2O)_2$ and $Ag_2(O_2CCF_3)_2$ observed in **5**. In the complexes **1**–**3** the silver trifluoroacetate dimers are linked by I,I′-bridging I_2R ligands with one 'short' Ag–I bond (2.94–3.05 Å) and one 'long' Ag–I bond (3.13–3.14 Å) per silver. In **4**, **7** and **8** the Ag_2(carboxylate-*O,O′*)$_2$ dimers are extended into a chain polymer *via* Ag_2O_2 rings formed by co-ordination of each silver to an oxygen atom (Ag–O 2.33–2.51 Å) from an adjacent dimer. The $1,2\text{-}I_2C_6H_4$ forms an I,I′ bridge across the two silver atoms of the dimer unit in **7** [Ag–I 2.918(1) and 3.024(1) Å]. Complex **8** contains an acute angle bridging IC_6H_5 [Ag–I 2.927(2) and 2.970(2) Å, Ag–I–Ag 61.4(1)°], whilst in **4** the IC_6H_5 is semibridging [Ag–I 2.853(1) and 3.309(1) Å]. In complex **5** the two structurally different dimer units are bridged in a wide-angle fashion by $p\text{-}IC_6H_4Me$ [Ag–I 2.9200(9) and 2.9333(8) Å, Ag–I–Ag 144.53(3)°]. Complex **6** contains eight-atom $Ag_2(O_2CCF_3$-*O,O′*)$_2$ rings linked to six-atom $Ag_2(O_2CCF_3$-*O,O′*)(O_2CCF_3-*O,O*) rings which are interlinked to give an alternating 8646 ring chain polymer with I,I′-bridging $1,2\text{-}I_2C_6H_4$ across the two silvers of the six-atom rings [Ag–I 2.722(2) and 2.980(2) Å]. The hfacac complex **10** contains a tetranuclear unit in which the hfacac ligands both chelate and bridge whilst the *p*-iodotoluenes each bridge two silvers *via* η^1-iodocarbon and η^2-aryl co-ordination. Complex **11** is a tetranuclear unit in which three hfacac ligands both chelate and bridge whilst the fourth hfacac ligand bridges two silvers and forms a monodentate interaction with a third silver in a μ-O, η^1-O′ mode. One $1,2\text{-}I_2C_6H_4$ ligand forms a monodentate interaction with a silver atom [Ag–I 3.064(3) Å] whilst the other two $1,2\text{-}I_2C_6H_4$ molecules function as highly unsymmetrical bidentate ligands [Ag–I 2.691(2), 3.350(2) and 2.719(2) and 3.228(2) Å]. The Ag–I–C bond angles vary from 85.9(4)° in **11** to 108.70(12)° in **3**.

Strauss and co-workers[1,2] have pioneered the synthesis of silver-ion complexes of some of chemistry's weakest Lewis-base ligands, simple chlorocarbons such as CH_2Cl_2 and bromocarbons such as CH_2Br_2. These complexes are very air, light and moisture sensitive and require rigorously anhydrous methods of synthesis. In contrast some corresponding silver iodocarbon complexes can easily be prepared without elaborate syntheses, with the compound $[Ag(NO_3)(CH_2I_2)]$ being first reported in 1906.[3] We have previously reported the structural characterization of several CH_2I_2 and aryl iodide complexes of $AgNO_3$ and $AgPF_6$ as well as the 1,3-diiodopropane complex $[Ag\{I(CH_2)_3I\}_2]PF_6$.[4,5] However attempts to prepare structurally similar complexes using the simple alkyl iodides MeI, EtI and PrI all result in the expected rapid formation of AgI. We have now extended our studies to include silver carboxylate and β-diketonate systems and here report the synthesis and structural characterization of several aryl iodide and CH_2I_2 silver complexes derived from reactions with silver trifluoroacetate, silver oxide–trichloroacetic acid and silver oxide–hexafluoroacetylacetone (Hhfacac). Silver(I) exhibits linear, trigonal, tetrahedral, pentagonal and even octahedral co-ordination and subtle changes readily influence the co-ordination geometry. Consequently the primary method used structurally to characterize these new compounds is single-crystal X-ray diffraction. Two of the compounds reported here have been briefly described in a previous communication.[6]

Results and Discussion

Silver trifluoroacetate complexes

Crystalline products of the general form $[\{Ag_2(O_2CCF_3)_2(I_2R)_2\}_n]$ were readily obtained by adding 1 equivalent of diiodide to a suspension of $[Ag_2(O_2CCF_3)_2]$ in CH_2Cl_2 and cooling the resultant solution to −20 °C. Crystals suitable for single-crystal X-ray diffraction were obtained for $[\{Ag_2(O_2CCF_3)_2(CH_2I_2)_2\}_n]$ **1**, $[\{Ag_2(O_2CCF_3)_2(1,2\text{-}I_2C_6H_4)_2\}_n]$ **2** and $[\{Ag_2(O_2CCF_3)_2(1,4\text{-}I_2C_6H_4)_2\}_n]$ **3**. Complexes **1** and **2** melt at ≈10 °C. On standing complex **1** decomposed to give AgI. Similar synthetic procedures using iodobenzene gave $[\{Ag_2(O_2CCF_3)_2(IC_6H_5)\}_n]$ **4** whilst *p*-iodotoluene gave $[\{Ag_4(O_2CCF_3)_4(H_2O)_2(p\text{-}IC_6H_4Me)_2\}_n]$ **5**. Reaction of $[\{Ag_2(O_2CCF_3)_2\}]$ with $1,2\text{-}I_2C_6H_4$ using a 2 : 1 stoichiometry resulted in the isolation of $[\{Ag_2(O_2CCF_3)_2(1,2\text{-}I_2C_6H_4)\}_n]$ **6**.

Silver trichloroacetate complexes

The complexes $[\{Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(1,2\text{-}I_2C_6H_4)\}_n]$ **7**, $[\{Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(IC_6H_5)\}_n]$ **8** and $[\{Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(p\text{-}IC_6H_4Me)\}_n]$ **9** were obtained as white crystalline products from the reaction of Ag_2O with an excess of HO_2CCCl_3 in MeOH in the presence of the appropriate iodide.

Silver hexafluoroacetylacetonate complexes

Reaction of *p*-iodotoluene with Ag_2O and hexafluoroacetyl-

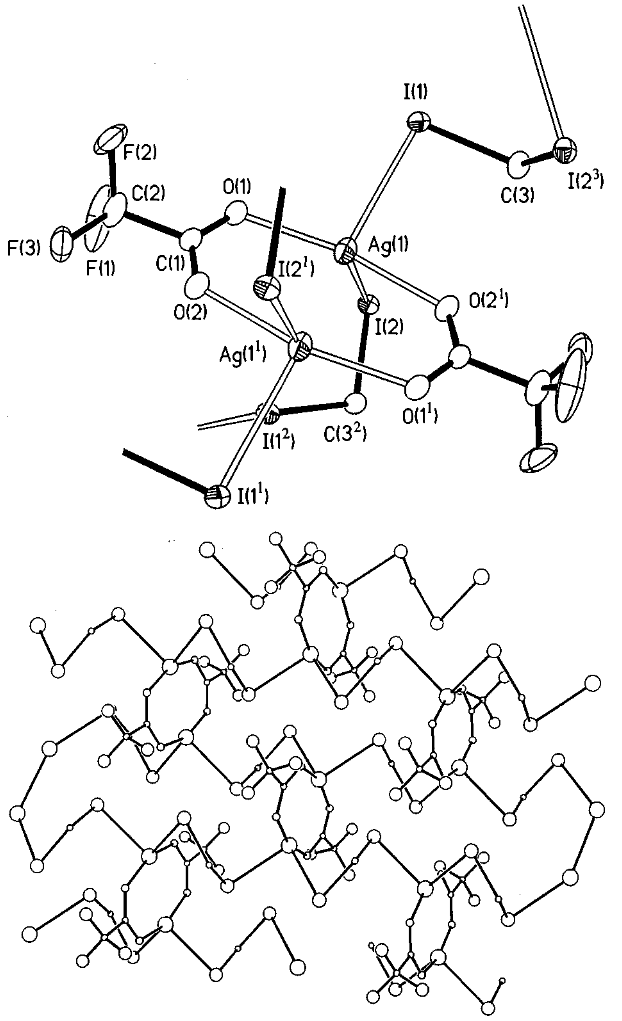

Fig. 1 Labelling scheme and structure of complex **1**. Where shown, probability ellipsoids are at the 30% level for all structures

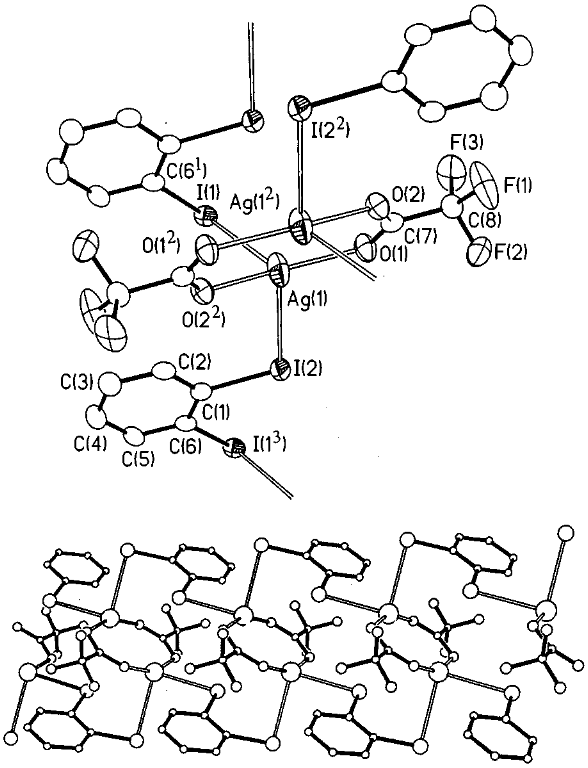

Fig. 2 Labelling scheme and structure of complex **2**

Table 1 Bond lengths (Å) and angles (°) for complex **1**

Ag(1)–O(1)	2.226(4)	Ag(1)–O(2^1)	2.251(4)
Ag(1)–I(2)	3.1446(7)	Ag(1)–I(1)	3.0054(7)
I(2)–C(3^2)	2.126(6)	I(1)–C(3)	2.137(6)
F(2)–C(2)	1.321(9)	F(1)–C(2)	1.327(8)
O(1)–C(1)	1.244(7)	F(3)–C(2)	1.337(8)
O(2)–Ag(1^1)	2.251(4)	O(2)–C(1)	1.245(7)
C(3)–I(2^3)	2.126(6)	C(1)–C(2)	1.541(8)
C(3)–H(3B)	0.96	C(3)–H(3A)	0.96
O(1)–Ag(1)–O(2^1)	160.6(2)	O(1)–Ag(1)–I(1)	101.75(12)
O(2^1)–Ag(1)–I(1)	93.40(12)	O(2^1)–Ag(1)–I(2)	84.28(12)
O(1)–Ag(1)–I(2)	108.38(13)	I(1)–Ag(1)–I(2)	86.53(2)
C(3)–I(1)–Ag(1)	93.3(2)	C(3^2)–I(2)–Ag(1)	85.4(2)
C(1)–O(1)–Ag(1)	121.7(4)	C(1)–O(2)–Ag(1^1)	127.5(4)
O(1)–C(1)–O(2)	129.9(5)	O(1)–C(1)–C(2)	113.5(5)
O(2)–C(1)–C(2)	116.6(5)	F(2)–C(2)–F(1)	107.9(6)
F(2)–C(2)–F(3)	106.6(5)	F(1)–C(2)–F(3)	107.4(6)
F(2)–C(2)–C(1)	110.4(6)	F(1)–C(2)–C(1)	111.6(5)
F(3)–C(2)–C(1)	112.6(5)	I(2^3)–C(3)–I(1)	112.6(3)

Symmetry transformations used to generate equivalent atoms: 1 $-x + 1$, $-y + 1$, $-z + 2$; 2 x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$; 3 x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$.

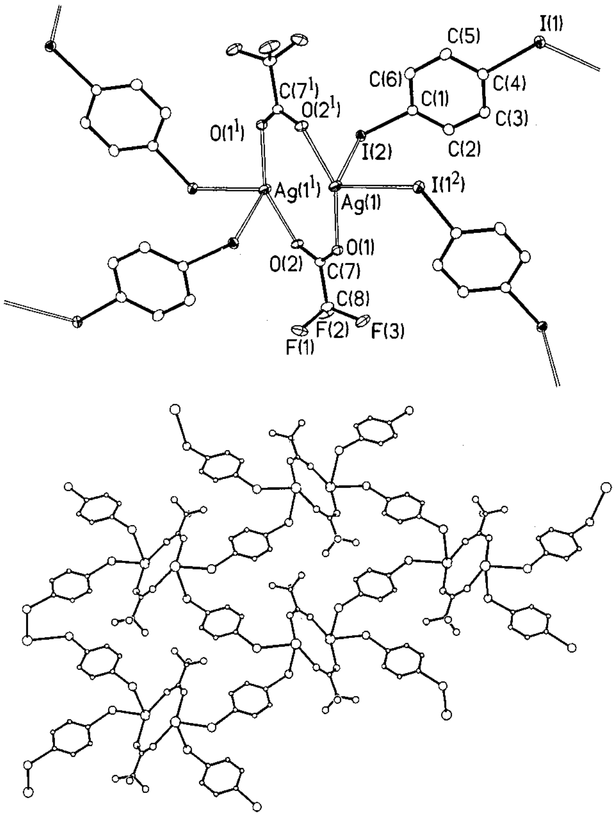

Fig. 3 Labelling scheme and structure of complex **3**

acetone in CH_2Cl_2 gave, on addition of pentane and cooling, the complex $[Ag_4(hfacac)_4(p\text{-}IC_6H_4Me)_2]$ **10** whilst a similar reaction with $1,2\text{-}I_2C_6H_4$ led to the isolation of $[Ag_4(hfacac)_4(1,2\text{-}I_2C_6H_4)_3]$ **11**.

Single-crystal X-ray diffraction studies

The solid-state structures of the compounds $\{Ag_2(O_2CCF_3)_2(CH_2I_2)_2\}_n]$ **1**, $[\{Ag_2(O_2CCF_3)_2(1,2\text{-}I_2C_6H_4)_2\}_n]$ **2** and $[\{Ag_2(O_2CCF_3)_2(1,4\text{-}I_2C_6H_4)_2\}_n]$ **3** are shown in Figs. 1–3. Selected bond lengths and bond angles are given in Tables 1–3. All three compounds contain '$I_2Ag(\mu\text{-}O_2CCF_3)_2AgI_2$' structural units. The three-atom trifluoroacetate bridges are almost coplanar (Ag–O 2.21–2.25 Å, O–Ag–O 153–161°) and each silver has one 'short' Ag–I bond length [3.0054(7) **1**, 3.0556(10) **2**, 2.9394(5) Å **3**] and one 'long' Ag–I bond length [3.1446(7) **1**, 3.1339(11) **2**,

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

I(1)–C(6^1)	2.094(6)	I(1)–Ag(1)	3.0556(10)
I(2)–C(1)	2.101(6)	I(2)–Ag(1)	3.1339(11)
Ag(1)–O(1)	2.213(5)	Ag(1)–O(2^2)	2.223(4)
C(6^1)–I(1)–Ag(1)	92.1(2)	C(1)–I(2)–Ag(1)	103.8(2)
O(1)–Ag(1)–O(2^2)	155.6(2)	O(1)–Ag(1)–I(1)	112.2(2)
O(2^2)–Ag(1)–I(1)	88.12(13)	O(1)–Ag(1)–I(2)	94.53(12)
O(2^2)–Ag(1)–I(2)	100.14(13)	I(1)–Ag(1)–I(2)	86.70(3)
C(7)–O(1)–Ag(1)	117.5(4)	C(7)–O(2)–Ag(1^2)	134.1(4)

Symmetry transformations used to generate equivalent atoms: 1 $x - 1, y, z$; 2 $-x + 1, -y + 1, -z + 1$; 3 $x + 1, y, z$.

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Ag(1)–O(1)	2.242(3)	Ag(1)–O(2^1)	2.271(3)
Ag(1)–I(1^2)	2.9394(5)	Ag(1)–I(2)	3.1375(6)
I(1)–C(4)	2.105(4)	I(1)–Ag(1^3)	2.9394(5)
I(2)–C(1)	2.099(4)	O(1)–C(7)	1.239(5)
O(2)–C(7)	1.245(5)	O(2)–Ag(1^1)	2.271(3)
O(1)–Ag(1)–O(2^1)	153.36(12)	O(1)–Ag(1)–I(1^2)	98.62(8)
O(2^1)–Ag(1)–I(1^2)	105.08(8)	O(1)–Ag(1)–I(2)	99.99(9)
O(2^1)–Ag(1)–I(2)	88.41(8)	I(1^2)–Ag(1)–I(2)	98.72(2)
C(4)–I(1)–Ag(1^3)	108.70(12)	C(1)–I(2)–Ag(1)	93.31(12)
C(7)–O(1)–Ag(1)	128.8(3)	C(7)–O(2)–Ag(1^1)	116.9(3)

Symmetry transformations used to generate equivalent atoms: 1 $-x + 1, -y + 1, -z + 1$; 2 $x, -y + \frac{1}{2}, z - \frac{1}{2}$; 3 $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

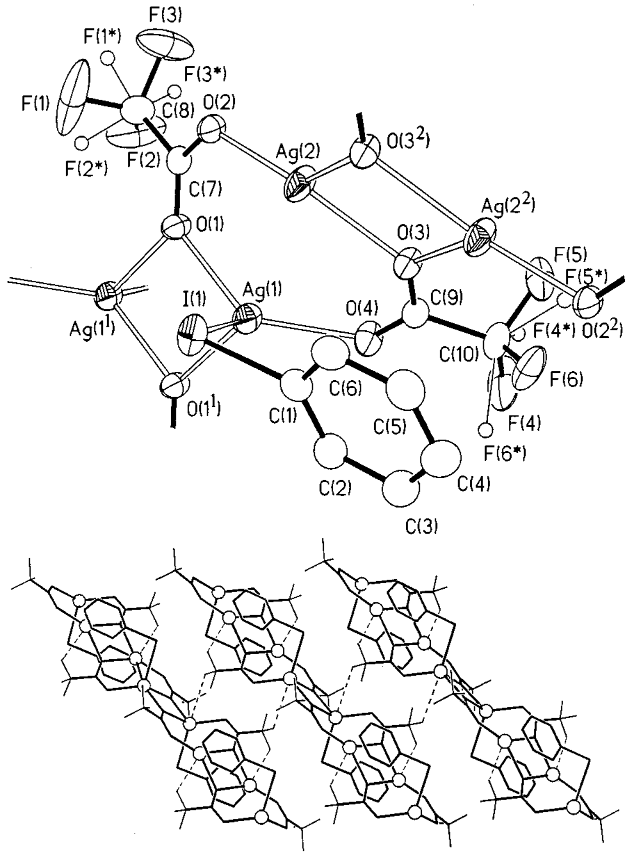

Fig. 4 Labelling scheme and structure of complex **4**. The CF_3 groups are disordered over two sites

Table 4 Selected bond lengths (Å) and angles (°) for complex **4**

Ag(1)–I(1)	2.853(1)	Ag(1)–O(1)	2.327(6)
Ag(1)–O(4)	2.250(7)	Ag(1)–O(1^1)	2.399(5)
Ag(2)–O(2)	2.223(6)	Ag(2)–O(3)	2.316(7)
Ag(2)–O(3^2)	2.397(5)	I(1)–C(1)	2.082(9)
O(1)–C(7)	1.234(9)	O(1)–Ag(1^1)	2.399(5)
O(2)–C(7)	1.237(8)	O(3)–C(9)	1.248(9)
O(3)–Ag(2^2)	2.397(5)	O(4)–C(9)	1.232(8)
I(1)–Ag(1)–O(1)	105.1(1)	I(1)–Ag(1)–O(4)	112.0(1)
O(1)–Ag(1)–O(4)	130.2(2)	I(1)–Ag(1)–O(1^1)	112.3(1)
O(1)–Ag(1)–O(1^1)	78.0(2)	O(4)–Ag(1)–O(1^1)	114.8(2)
O(2)–Ag(2)–O(3)	146.1(2)	O(2)–Ag(2)–O(3^2)	134.8(2)
O(3)–Ag(2)–O(3^2)	76.7(2)	Ag(1)–I(1)–C(1)	99.0(2)
Ag(1)–O(1)–C(7)	122.4(5)	Ag(1)–O(1)–Ag(1^1)	102.0(2)
C(7)–O(1)–Ag(1^1)	135.6(5)	Ag(2)–O(2)–C(7)	126.0(6)
Ag(2)–O(3)–C(9)	122.8(5)	Ag(2)–O(3)–Ag(2^2)	103.3(2)
C(9)–O(3)–Ag(2^2)	133.0(6)	Ag(1)–O(4)–C(9)	120.3(6)

Symmetry transformations used to generate equivalent atoms: 1 $1 - x, 1 - y, 1 - z$; 2 $-x, 2 - y, 1 - z$.

3.1375(6) Å **3**]. The shorter AgI is closer to being coplanar with the μ-carboxylate bridges whilst the longer AgI takes an 'axial' position. The silver–silver distances are 3.0030(11) **1**, 3.1163(14) **2** and 3.0300(8) Å **3**, somewhat longer than that observed in silver trifluoroacetate [2.967(3) Å] and structurally similar systems.[7,8] Complex **1** consists of spiral chains of $(AgICH_2I)_n$ units interlinked by '$Ag(O_2CCF_3)_2Ag$ rings'. Complex **2** is a ladder array in which two $[Ag(1,2\text{-}I_2C_6H_4)]_n$ chains are cross-linked by '$Ag(O_2CCF_3)_2Ag$ rings'. Complex **3** has a structural assembly similar to that of **1**. The I–Ag–I bond angles vary from *ca.* 86.5° for **1** and **2** to 98.72(2)° for **3**. The Ag–I–C bond angles vary considerably ranging from a low value of 85.4(2)° found in **1** to a high value of 108.70(12)° found in **3** consistent with relatively easy angular distortion (bond bending) of the weak $RI{-}Ag^+$ interactions.

Iodobenzene complexes. The solid-state structure of the complex $[\{Ag_2(O_2CCF_3)_2(IC_6H_5)\}_n]$ **4** is shown in Fig. 4. Selected bond lengths and bond angles are given in Table 4. Complex **4** contains a chain polymer array of interlinked $Ag_2(O_2CCF_3)_2$ dimers with an iodobenzene co-ordinated *via* the iodine atom to alternating silver atoms. The chain polymer is very similar to that observed in $[\{Ag_2(O_2CCF_3)_2\}_n]$ except that co-ordination of the iodobenzene is accompanied by a slight distortion away from coplanarity of the bridging carboxylates in **4**, *vis-à-vis* $[\{Ag_2(O_2CCF_3)_2\}_n]$.[7] The Ag···Ag separation in **4** [2.937(1) Å] is very similar to that of $[\{Ag_2(O_2CCF_3)_2\}_n]$ [2.967(3) Å]. The iodobenzene bonds to alternate Ag atoms with an Ag(1)–I bond length of 2.853(1) Å and with an Ag–I–C bond angle of 99.0(2)°. The distance between Ag(2) and I is 3.309(1) Å and the Ag(2)–Ag(1)–I bond angle is 69.7° suggestive of a weak Ag(2)···I interaction and a semibridging situation.

The structure of the trichlorocetate system $[\{Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(IC_6H_5)\}_n]$ **8** is shown in Fig. 5. Selected bond lengths and bond angles are given in Table 5. The solid-state structure of **8** consists of two silver atoms bridged by two trichloroacetates and by the iodine atom of the iodobenzene. The Ag–I bond lengths are 2.927(3) and 2.970(2) Å and the Ag–I–Ag bond angle is 61.4(1)°. One of the silver–oxygen bonds is bridged by a trichloroacetic acid molecule hydrogen bonded to the oxygen of a trichloroacetate bridge and with a long $CCl_3C(OH){=}O\cdots Ag$ interaction [O(6)···Ag(1)] of 2.861(10) Å. The $Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(IC_6H_5)$ units are linked *via* Ag_2O_2 interactions involving one of the oxygen atoms in each bridging trichloroacetate to give a chain structure very similar to that observed in **4**. The Ag···Ag separation is 3.014(1) Å and Ag–I–C bond angles are 94.4(7) and 102.3(8)°.

The structure of $[\{Ag_4(O_2CCF_3)_4(H_2O)_2(p\text{-}IC_6H_4Me)_2\}_n]$ **5** is shown in Fig. 6. Selected bond lengths and bond angles are given in Table 6. The structure is composed of alternating $Ag_2(O_2CCF_3)_2$ and $Ag_2(O_2CCF_3)_2(H_2O)_2$ dimers with Ag···Ag separations of 3.1527(4) and 2.9106(12) Å respectively. These dimers are linked by the bridging iodine atom of the *p*-iodotoluene. The Ag–I bond lengths are 2.9200(9) and 2.9333(8) Å and the Ag–I–Ag bond angle is 144.53(3)°. The

Table 5 Selected bond lengths (Å) and angles (°) for complex **8**

Ag(1)–I(1)	2.927(2)	Ag(1)–O(2)	2.379(12)
Ag(1)–O(3)	2.272(11)	Ag(1)–O(3^2)	2.465(11)
Ag(2)–I(1)	2.970(2)	Ag(2)–O(1)	2.301(12)
Ag(2)–O(4)	2.230(12)	Ag(2)–O(1^1)	2.534(11)
I(1)–C(11)	2.093(26)	O(1)–C(1)	1.264(20)
O(1)–Ag(2^1)	2.534(11)	O(2)–C(1)	1.232(20)
O(3)–C(3)	1.260(20)	O(3)–Ag(1^2)	2.465(11)
O(4)–C(3)	1.218(20)	C(5)–O(5)	1.293(29)
C(5)–O(6)	1.169(28)	O(5)–HO	0.70
HO···O(2)	2.25	O(2)···O(5)	2.685(15)

I(1)–Ag(1)–O(2)	101.7(3)	I(1)–Ag(1)–O(3)	109.5(3)
O(2)–Ag(1)–O(3)	123.5(4)	I(1)–Ag(1)–O(3^2)	98.9(3)
O(2)–Ag(1)–O(3^2)	138.4(4)	O(3)–Ag(1)–O(3^2)	81.7(4)
I(1)–Ag(2)–O(1)	100.0(3)	I(1)–Ag(2)–O(4)	107.9(3)
O(1)–Ag(2)–O(4)	131.3(5)	I(1)–Ag(2)–O(1^1)	106.9(3)
O(1)–Ag(2)–O(1^1)	75.2(5)	O(4)–Ag(2)–O(1^1)	129.6(4)
Ag(1)–I(1)–Ag(2)	61.4(1)	Ag(1)–I(1)–C(11)	102.3(7)
Ag(2)–I(1)–C(11)	94.4(7)	Ag(2)–O(1)–C(1)	120.6(10)
Ag(2)–O(1)–Ag(2^1)	104.8(5)	C(1)–O(1)–Ag(2^1)	133.9(11)
Ag(1)–O(2)–C(1)	132.8(12)	Ag(1)–O(3)–C(3)	121.0(10)
Ag(1)–O(3)–Ag(1^2)	98.3(4)	C(3)–O(3)–Ag(1^2)	134.6(10)
Ag(2)–O(4)–C(3)	132.8(10)		

Symmetry transformations used to generate equivalent atoms: 1 $\frac{1}{2} - x, \frac{1}{2} - y, -z$; 2 $-x, -y, -z$.

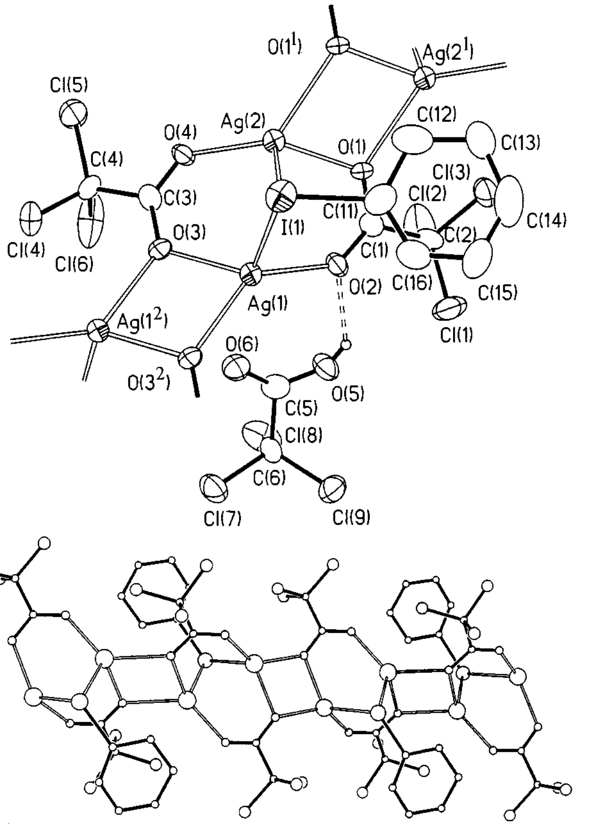

Fig. 5 Labelling scheme and structure of complex **8**. The hydrogen bond to the trichloroacetic acid solvate molecule is shown with broken lines

Table 6 Selected bond lengths (Å) and angles (°) for complex **5**

I(1)–C(1)	2.119(8)	I(1)–Ag(1)	2.9200(9)
I(1)–Ag(2)	2.9333(8)	Ag(1)–O(2^2)	2.231(6)
Ag(1)–O(1)	2.233(6)	Ag(2)–O(4^3)	2.256(6)
Ag(2)–O(3)	2.282(5)	Ag(2)–O(5)	2.512(6)
O(1)–C(8)	1.245(10)	O(1)···H(20^1)	2.07(11)
O(2)–C(8)	1.235(10)	O(2)–Ag(1^2)	2.231(6)
O(3)–C(10)	1.249(10)	O(3)–H(10^1)	2.17(8)
O(4)–C(10)	1.238(10)	O(5)–H(10)	0.72(8)

C(1)–I(1)–Ag(1)	102.2(2)	C(1)–I(1)–Ag(2)	101.2(2)
Ag(1)–I(1)–Ag(2)	144.53(3)	O(2^2)–Ag(1)–O(1)	146.6(2)
O(2^2)–Ag(1)–I(1)	110.65(14)	O(1)–Ag(1)–I(1)	97.14(14)
O(4^3)–Ag(2)–O(3)	151.2(2)	O(4^3)–Ag(2)–O(5)	93.9(2)
O(3)–Ag(2)–O(5)	99.7(2)	O(4^3)-Ag(2)–I(1)	102.1(2)
O(3)–Ag(2)–I(1)	101.80(14)	O(5)–Ag(2)–I(1)	95.3(2)
C(8)–O(1)–Ag(1)	125.0(5)	C(8)–O(2)–Ag(1^2)	123.2(5)
C(10)–O(3)–Ag(2)	117.2(5)	C(10)–O(4)–Ag(2^3)	124.7(5)

Symmetry transformations used to generate equivalent atoms: 1 $x - 1, y, z$; 2 $-x, -y + 1, -z + 1$; 3 $-x + 2, -y + 1, -z$.

Table 7 Selected bond lengths (Å) and angles (°) for complex **7**

Ag(2)–I(1)	2.9180(10)	Ag(2)–O(1)	2.226(6)
Ag(2)–O(4)	2.273(5)	Ag(2)–O(2^1)	2.466(7)
Ag(1)–I(2)	3.0240(10)	Ag(1)–O(2)	2.334(5)
Ag(1)–O(3)	2.317(5)	Ag(1)–O(4^2)	2.717(7)
I(1)–C(16)	2.109(7)	I(2)–C(11)	2.093(10)
O(1)–C(1)	1.214(11)	O(2)–C(1)	1.241(12)
O(2)–Ag(2^2)	2.466(7)	O(3)–C(3)	1.247(11)
O(4)–C(3)	1.239(11)	C(1)–C(2)	1.557(9)
O(6)–C(5)	1.185(10)	O(5)–C(5)	1.264(13)
O(3)···O(5)	2.715(9)	O(5)–HO	0.962(10)
HO···O(3)	1.75		

I(1)–Ag(2)–O(1)	103.0(2)	I(1)–Ag(2)–O(4)	106.5(2)
O(1)–Ag(2)–O(4)	137.9(2)	I(1)–Ag(2)–O(2^1)	115.2(1)
O(1)–Ag(2)–O(2^1)	114.3(2)	O(4)–Ag(2)–O(2^1)	78.9(2)
I(2)–Ag(1)–O(2)	84.3(1)	I(2)–Ag(1)–O(3)	120.0(2)
O(2)–Ag(1)–O(3)	149.4(2)	Ag(2)–I(1)–C(16)	96.3(2)
Ag(1)–I(2)–C(11)	97.4(2)	Ag(2)–O(1)–C(1)	131.3(6)
Ag(1)–O(2)–C(1)	122.0(5)	Ag(1)–O(2)–Ag(2^2)	100.4(3)
C(1)–O(2)–Ag(2^2)	136.2(4)	Ag(1)–O(3)–C(3)	126.8(5)
Ag(2)–O(4)–C(3)	121.6(5)	O(3)–Ag(1)–O(4^2)	122.8(5)
Ag(1)–O(4^2)–Ag(2^2)	94.9(5)	I(2)–Ag(1)–O(4^2)	87.1(5)

Symmetry transformations used to generate equivalent atoms: 1 $x, \frac{1}{2} - y, \frac{1}{2} + z$; 2 $x, \frac{1}{2} - y, -\frac{1}{2} - z$.

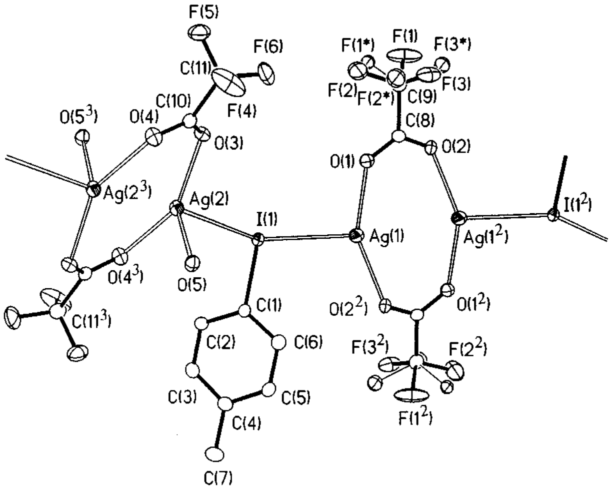

Fig. 6 Labelling scheme and structure of complex **5**. One of the CF_3 groups is disordered over two sites

Ag–I–C bond angles are 101.2(2) and 102.2 (2)°. The water molecules occupy axial sites on opposite faces of the $Ag_2(O_2CCF_3)_2(H_2O)_2$ unit. The Ag–O bond length for the co-ordinated H_2O is 2.512(6) Å which is significantly longer than the Ag–O carboxylate bonds (*ca.* 2.25 Å). The chain structures are cross-linked by hydrogen bonds between the H_2O molecules and carboxylate oxygens on neighbouring chains.

The structure of $[\{Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(1,2\text{-}I_2C_6H_4)\}_n]$ **7** is shown in Fig. 7. Selected bond lengths and bond angles are given in Table 7. The structure is very similar to that of compound **8**, Fig. 5. The polymer chain is composed of linked silver trichloroacetate dimers with the two silver atoms of the dimers being bridged by 1,2-diiodobenzene bonding to

Table 8 Selected bond lengths (Å) and angles (°) for complex **6**

I(1)–Ag(1)	2.722(2)	I(1)–C(1)	2.112(13)
I(2)–Ag(2)	2.980(2)	I(2)–C(2)	2.067(15)
Ag(1)–O(2)	2.288(12)	Ag(1)–O(4)	2.465(9)
Ag(2)–O(1)	2.275(15)	Ag(2)–O(2^1)	2.4039(10)
Ag(2)–O(4)	2.382(11)	Ag(2)–O(3^2)	2.343(10)
O(1)–C(7)	1.196(18)	O(2)–C(7)	1.230(18)
O(2)–Ag(1^1)	2.403(10)	O(3)–C(9)	1.230(14)
O(3)–Ag(2^2)	2.343(10)	O(4)–C(9)	1.219(16)
Ag(I)–I(1)–C(1)	97.4(4)	Ag(2)–I(2)–C(2)	102.9(4)
I(1)–Ag(1)–O(2)	140.2(3)	I(1)–Ag(1)–O(4)	98.7(3)
O(2)–Ag(1)–O(4)	98.0(4)	I(1)–Ag(1)–O(2^1)	123.9(3)
O(2)–Ag(1)–O(2^1)	79.4(4)	O(4)–Ag(1)–O(2^1)	115.5(4)
I(2)–Ag(2)–O(1)	148.3(4)	I(2)–Ag(2)–O(4)	90.1(3)
O(1)–Ag(2)–O(4)	95.2(4)	I(2)–Ag(2)–O(3^2)	83.0(3)
O(1)–Ag(2)–O(3^2)	98.9(4)	O(4)–Ag(2)–O(3^2)	163.0(3)
Ag(2)–O(1)–C(7)	137.8(13)	Ag(1)–O(2)–C(7)	116.6(10)
Ag(1)–O(2)–Ag(1^1)	100.6(4)	C(7)–O(2)–Ag(1^1)	140.3(11)
C(9)–O(3)–Ag(2^2)	118.6(9)	Ag(1)–O(4)–Ag(2)	88.7(3)
Ag(1)–O(4)–C(9)	141.7(10)	Ag(2)–O(4)–C(9)	128.0(8)

Symmetry transformations used to generate equivalent atoms: 1 $1 - x, -y, 1 - z$; 2 $-x, 1 - y, 1 - z$.

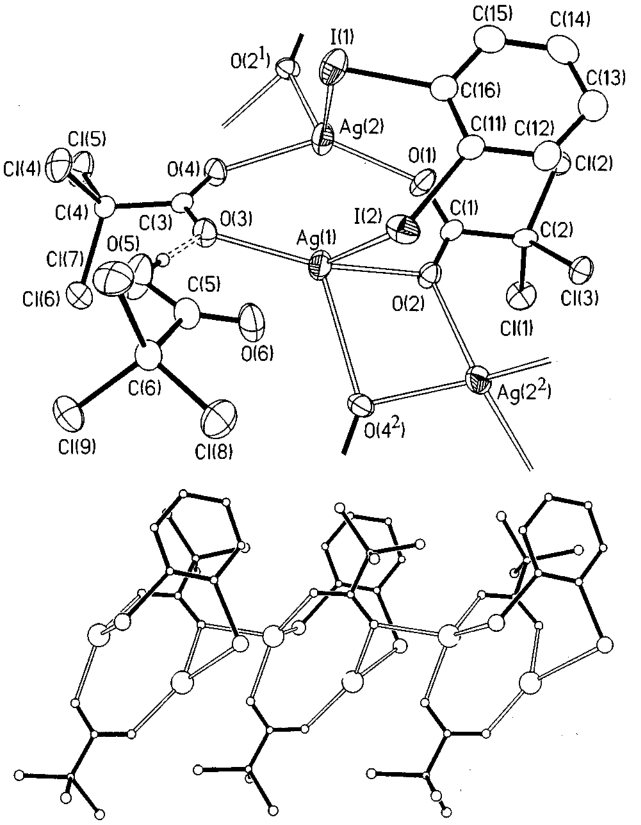

Fig. 7 Labelling scheme and structure of complex **7**. The hydrogen bond to the trichloroacetic acid solvate molecule is shown with broken lines

silver *via* η^1 co-ordination of the iodine atoms with Ag–I bond lengths of 2.918(1) and 3.024(1) Å and Ag–I–C bond angles of 96.3(2) and 97.4(2)°.

In comparison to the μ-IC_6H_5 complex **8** the co-ordination of the 1,2-diiodobenzene results in a slight twist of the $Ag_2(O_2CCCl_3)_2$ ring structure in **7** relative to **8**, which is reflected in larger O–Ag–O angles within the $Ag_2(O_2CCCl_3)_2$ ring [149.4(2) *vs.* 123.5(4)° for **8**]. This distortion is also reflected in the non-symmetry of the 1,2-diiodobenzene bridge which exhibits Ag–Ag–I angles of 77 [Ag(2)–Ag(1)–I(1)] and 109° [Ag(1)–Ag(2)–I(2)]. As with **8** the compound **7** contains a trichloroacetic acid molecule which bridges one of the silver–oxygen bonds of each $Ag_2(O_2CCCl_3)_2$ unit *via* a hydrogen bond to the oxygen and a long $CCl_3C(OH){=}O\cdots Ag$ interaction [2.799(11) Å].

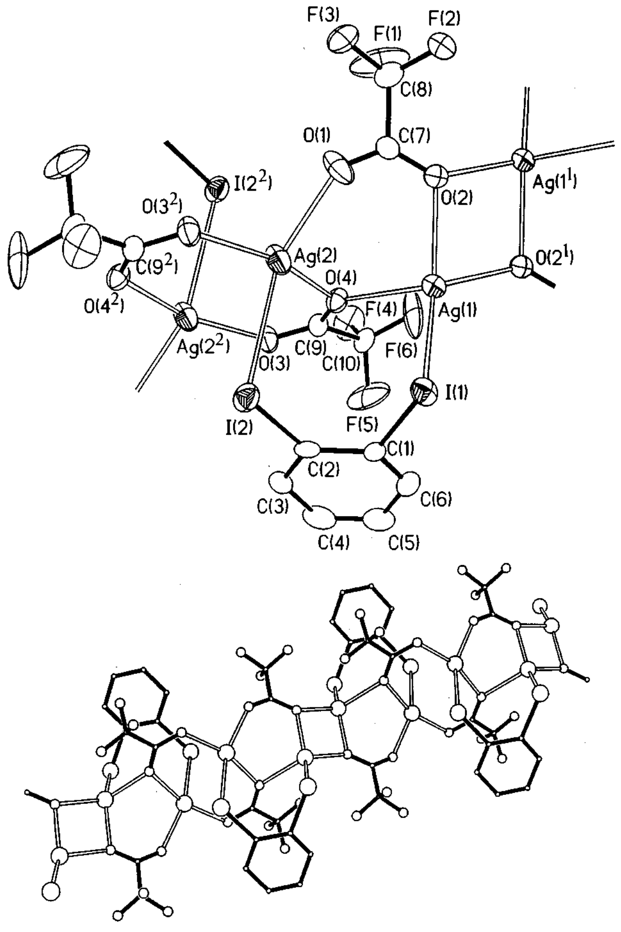

Fig. 8 Labelling scheme and structure of complex **6**

The structure of $[\{Ag_2(O_2CCF_3)_2(1,2\text{-}I_2C_6H_4)\}_n]$ **6** is shown in Fig. 8. Selected bond lengths and bond angles are given in Table 8. The compound is polymeric with bridging 1,2-diiodobenzenes η^1 co-ordinated to silver *via* the iodine atoms. The arrangement of the bridging carboxylates is unusual and different to those previously observed in other silver carboxylate compounds.[2] The polymer chain is composed of three different fused-ring structures. Two are the expected $Ag_2(O_2CCF_3)_2$ eight-atom ring and the Ag_2O_2 four-atom ring as observed in $[\{Ag_2(O_2CCF_3)_2\}_n]$ and $[\{Ag_2(O_2CCF_3)_2(IC_6H_5)\}_n]$ **4**. The third and structurally unusual is a six-atom ring $Ag_2(\mu\text{-}O_2CCF_3\text{-}O,O')(\mu\text{-}O_2CCF_3\text{-}O)$ in which one of the trifluoroacetate ligands bridges the two silver atoms *via* the same oxygen atom. The 1,2-diiodobenzene ligands bridge the two silver atoms of the six-atom ring on alternate sides of the silver carboxylate chain which is composed of fused '8 6 4 6 · · · atom rings'. Silver–silver separations are 2.923(3) (eight-atom ring), 3.389(1) (six-atom ring) and 3.611(1) Å (four-atom ring). The Ag–I bond lengths and Ag–I–C bond angles are 2.722(2) Å and 97.4(4)° for the silver that is part of both the six- and four-atom rings, and 2.980(2) and 102.9(4)° for the silver that is common to both six- and eight-atom rings.

The molecular structure of $[Ag_4(hfacac)_4(p\text{-}IC_6H_4Me)_2]$ **10** is shown in Fig. 9. Selected bond lengths and bond angles are given in Table 9. The compound is dimeric with four silver atoms per formula unit. There are two kinds of silver(I) atoms in each molecule; the outer silvers co-ordinate η^2 to an 'HCCH' unit of the *p*-iodotoluenes and three hfacac oxygen atoms whilst the inner two silvers are η^1 bonded to the iodide atoms and also co-ordinated to four 'hfacac oxygens'. The Ag–O distances are similar to those found in other silver hexafluoroacetylacetonates and vary from 2.322(14) to 2.650(14) Å. There

Table 9 Selected bond lengths (Å) and angles (°) for complex **10**

I(1)–Ag(1)	2.850(4)	I(1)–C(21)	2.062(11)	I(2)–Ag(3)	2.765(2)	I(2)–C(31)	2.073(16)
Ag(1)–O(1)	2.551(17)	Ag(1)–O(4)	2.426(14)	Ag(3)–O(5)	2.529(17)	Ag(3)–O(6)	2.347(11)
Ag(1)–O(1^1)	2.621(12)	Ag(1)–O(2^1)	2.545(18)	Ag(3)–O(8)	2.555(16)	Ag(3)–O(5^2)	2.650(14)
Ag(2)–O(3)	2.322(14)	Ag(2)–O(4)	2.436(23)	Ag(4)–O(6)	2.485(12)	Ag(4)–O(7)	2.334(20)
Ag(2)–O(2^1)	2.417(11)	C(22)–Ag(2^1)	2.531(20)	Ag(4)–O(8)	2.409(17)	C(36)–Ag(4^2)	2.518(21)
C(23)–Ag(2^1)	2.599(20)	C(24)–C(27)	1.538(27)	C(35)–Ag(4^2)	2.596(17)		
Ag(1)–I(1)–C(21)	104.9(6)	I(1)–Ag(1)–O(1)	127.2(4)	C(25)–C(24)–C(27)	122.5(15)	I(1)–C(21)–C(22)	119.8(4)
I(1)–Ag(1)–O(4)	107.9(5)	O(1)–Ag(1)–O(4)	76.6(5)	I(1)–C(21)–C(26)	120.2(4)	Ag(3)–I(2)–C(31)	103.8(4)
I(1)–Ag(1)–O(1^1)	103.9(4)	O(1)–Ag(1)–O(1^1)	103.5(4)	I(2)–Ag(3)–O(5)	108.5(2)	I(2)–Ag(3)–O(6)	174.7(4)
O(4)–Ag(1)–O(1^1)	139.2(6)	I(1)–Ag(1)–O(2^1)	159.7(3)	O(5)–Ag(3)–O(6)	70.3(4)	I(2)–Ag(3)–O(8)	106.9(3)
O(1)–Ag(1)–O(2^1)	73.1(5)	O(4)–Ag(1)–O(2^1)	75.7(6)	O(5)–Ag(3)–O(8)	143.6(4)	O(6)–Ag(3)–O(8)	73.6(5)
O(1^1)–Ag(1)–O(2^1)	65.8(5)	O(3)–Ag(2)–O(4)	78.0(7)	I(2)–Ag(3)–O(5^2)	106.6(3)	O(5)–Ag(3)–O(5^2)	98.8(4)
O(3)–Ag(2)–O(2^1)	126.3(5)	O(4)–Ag(2)–O(2^1)	77.9(5)	O(6)–Ag(3)–O(5^2)	78.7(4)	O(8)–Ag(3)–O(5^2)	78.8(5)
O(3)–Ag(2)–C(22^1)	121.2(6)	O(4)–Ag(2)–C(22^1)	153.4(5)	O(6)–Ag(4)–O(7)	121.8(5)	O(6)–Ag(4)–O(8)	73.9(5)
O(2^1)–Ag(2)–C(22^1)	100.3(5)	O(3)–Ag(2)–C(23^1)	90.2(6)	O(7)–Ag(4)–O(8)	78.2(6)	O(6)–Ag(4)–C(35^2)	128.7(6)
O(4)–Ag(2)–C(23^1)	151.8(4)	O(2^1)–Ag(2)–C(23^1)	128.4(5)	O(7)–Ag(4)–C(35^2)	95.3(6)	O(8)–Ag(4)–C(35^2)	154.3(4)
C(22^1)–Ag(2)–C(23^1)	31.5(3)	Ag(1)–O(1)–C(1)	117.0(18)	O(6)–Ag(4)–C(36^2)	99.3(5)	O(7)–Ag(4)–C(36^2)	125.5(5)
Ag(1)–O(1)–Ag(1^1)	76.5(4)	C(1)–O(1)–Ag(1^1)	124.5(11)	O(8)–Ag(4)–C(36^2)	152.8(4)	C(35^2–Ag(4)–C(36^2)	31.6(2)
C(3)–O(2)–Ag(1^1)	123.3(17)	C(3)–O(2)–Ag(2^1)	132.8(13)	Ag(3)–O(5)–C(11)	123.7(16)	Ag(3)–O(5)–Ag(3^2)	81.2(4)
Ag(1^1)–O(2)–Ag(2^1)	92.2(5)	Ag(2)–O(3)–C(6)	123.8(15)	C(11)–O(5)–Ag(3^2)	111.9(14)	Ag(3)–O(6)–Ag(4)	95.6(5)
Ag(1)–O(4)–Ag(2)	94.7(6)	Ag(1)–O(4)–C(8)	142.5(18)	Ag(3)–O(6)–C(13)	126.5(11)	Ag(4)–O(6)–C(13)	136.5(10)
Ag(2)–O(4)–C(8)	117.1(17)	C(23)–C(22)–Ag(2^1)	77.0(3)	Ag(4)–O(7)–C(16)	124.9(12)	Ag(3)–O(8)–Ag(4)	92.3(7)
C(21)–C(22)–Ag(2^1)	104.8(3)	C(22)–C(23)–Ag(2^1)	71.5(3)	Ag(3)–O(8)–C(18)	141.9(11)	Ag(4)–O(8)–C(18)	123.4(12)
C(24)–C(23)–Ag(2^1)	107.3(3)	C(23)–C(24)–C(27)	117.4(15)				

Symmetry transformations used to generate equivalent atoms: 1 1 − x, −y, −z; 2 1 − x, −y, 1 − z.

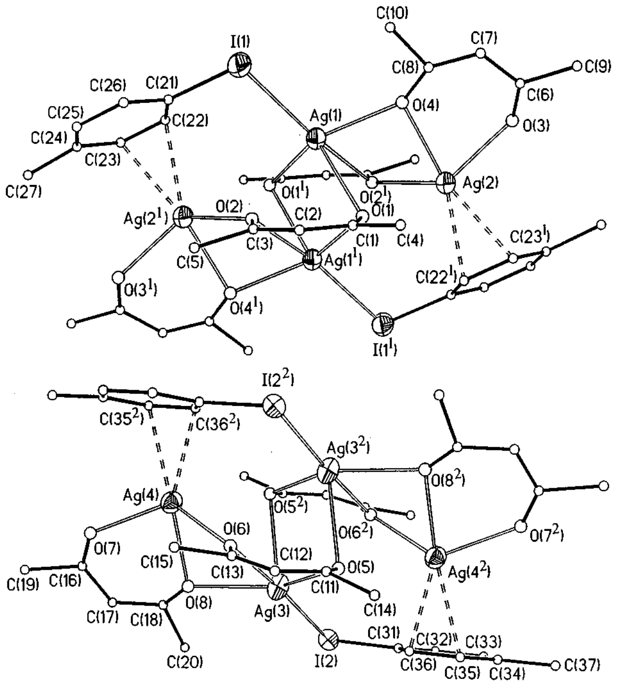

Fig. 9 Labelling scheme and structure of complex **10**. For clarity fluorine atoms have been omitted

Table 10 Selected bond lengths (Å) and angles (°) for complex **11**

Ag(1)–I(1)	3.064(3)	Ag(1)–O(1)	2.330(10)
Ag(1)–O(2)	2.465(12)	Ag(1)–O(3)	2.393(11)
Ag(1)–O(4)	2.506(8)	Ag(2)–I(3)	3.228(2)
Ag(2)–I(4)	2.719(2)	Ag(2)–O(3)	2.463(10)
Ag(2)–O(5)	2.390(11)	Ag(2)–O(7)	2.399(9)
Ag(3)–I(5)	2.691(2)	Ag(3)–O(2)	2.369(9)
Ag(3)–O(4)	2.387(11)	Ag(3)–O(6)	2.452(10)
Ag(4)–O(5)	2.575(8)	Ag(4)–O(6)	2.310(10)
Ag(4)–O(7)	2.388(12)	Ag(4)–O(8)	2.316(10)
Ag(3)···I(6)	3.350(2)	Ag(1)···I(3)	3.436(2)
I(1)–Ag(1)–O(1)	97.0(3)	I(1)–Ag(1)–O(2)	76.4(3)
O(1)–Ag(1)–O(2)	75.7(4)	I(1)–Ag(1)–O(3)	99.4(3)
O(1)–Ag(1)–O(3)	137.6(4)	O(2)–Ag(1)–O(3)	146.3(3)
I(1)–Ag(1)–O(4)	81.5(3)	O(1)–Ag(1)–O(4)	151.4(4)
O(2)–Ag(1)–O(4)	76.2(3)	O(3)–Ag(1)–O(4)	70.1(3)
I(3)–Ag(2)–I(4)	76.5(1)	I(3)–Ag(2)–O(3)	78.9(2)
I(4)–Ag(2)–O(3)	131.5(2)	I(3)–Ag(2)–O(5)	87.1(2)
I(4)–Ag(2)–O(5)	139.0(2)	O(3)–Ag(2)–O(5)	79.6(4)
I(3)–Ag(2)–O(7)	152.8(3)	I(4)–Ag(2)–O(7)	129.0(3)
O(3)–Ag(2)–O(7)	76.2(3)	O(5)–Ag(2)–O(7)	78.0(3)
I(5)–Ag(3)–O(2)	133.8(3)	I(5)–Ag(3)–O(4)	134.2(2)
O(2)–Ag(3)–O(4)	80.3(3)	I(5)–Ag(3)–O(6)	129.7(2)
O(2)–Ag(3)–O(6)	75.8(4)	O(4)–Ag(3)–O(6)	81.0(4)
O(5)–Ag(4)–O(6)	70.2(3)	O(5)–Ag(4)–O(7)	74.6(3)
O(6)–Ag(4)–O(7)	142.7(3)	O(5)–Ag(4)–O(8)	147.4(4)
O(6)–Ag(4)–O(8)	140.6(4)	O(7)–Ag(4)–O(8)	76.5(4)
Ag(1)–I(1)–C(31)	116.8(5)	Ag(2)–I(3)–C(41)	85.9(4)
Ag(2)–I(4)–C(46)	95.6(4)	Ag(3)–I(5)–C(51)	96.2(3)
Ag(1)–O(1)–C(1)	129.3(10)	Ag(1)–O(2)–Ag(3)	96.3(4)
Ag(1)–O(2)–C(3)	125.0(9)	Ag(3)–O(2)–C(3)	138.3(10)
Ag(1)–O(3)–Ag(2)	97.8(3)	Ag(1)–O(3)–C(6)	123.8(11)
Ag(2)–O(3)–C(6)	137.5(11)	Ag(1)–O(4)–Ag(3)	94.7(3)
Ag(1)–O(4)–C(8)	121.5(8)	Ag(3)–O(4)–C(8)	140.0(10)
Ag(2)–O(5)–Ag(4)	92.4(3)	Ag(2)–O(5)–C(11)	138.8(10)
Ag(4)–O(5)–C(11)	120.8(8)	Ag(3)–O(6)–Ag(4)	100.3(3)
Ag(3)–O(6)–C(13)	132.4(10)	Ag(4)–O(6)–C(13)	127.1(10)
Ag(2)–O(7)–Ag(4)	97.0(4)	Ag(2)–O(7)–C(16)	130.0(9)
Ag(4)–O(7)–C(16)	127.0(8)	Ag(4)–O(8)–C(18)	130.6(10)

exist two types of tridentate μ_3-bridging hfacac co-ordination modes, which are fairly similar to those observed in the norbornadiene (bicyclo[2.2.1]hepta-2,5-diene, nbd) complex [Ag$_4$(hfacac)$_4$(nbd)$_2$].[9] Unusual hfacac bridging modes have also recently been identified in the cyclooctadiene compound [Ag$_2$(hfacac)$_2$(cod)$_2$].[10] The Ag–I bond length is 2.850(4) Å and the Ag–I–C bond angle is 104.9(6)°. Several examples of η^2 co-ordination of arenes to Ag^I are known.[11]

The molecular structure of [Ag$_4$(hfacac)$_4$(1,2-I$_2$C$_6$H$_4$)$_3$] **11** is shown in Fig. 10. Selected bond lengths and bond angles are given in Table 10. All four silvers have different co-ordination environments. Two μ_3 and two μ_4 hfacac bonding modes are observed. The three 1,2-diiodobenzene ligands are each co-ordinated to a different silver *via* an iodine atom(s). The diiodobenzene co-ordinated to Ag(1) is clearly monodentate with an Ag(1)–I(1) bond length of 3.064(3) Å whilst the Ag(1)···I(2) separation is 5.80 Å. The diiodobenzene co-ordinated to Ag(3) has a rather short Ag(3)–I(5) bond distance of 2.691(2) Å together with an Ag(3)···I(6) separation of 3.350(2) Å suggestive of a very weak interaction between Ag(3) and the second iodine of the diiodobenzene ligand. The diiodobenzene

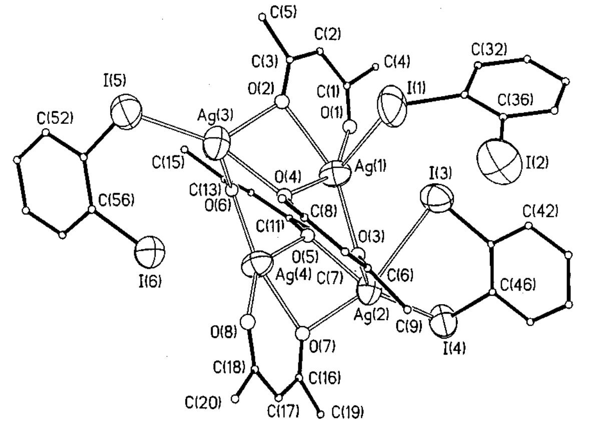

Fig. 10 Labelling scheme and structure of complex **11**. For clarity fluorine atoms and minor components of disorder have been omitted

bonded to Ag(2) exhibits a similar unsymmetrical bidentate interaction with Ag(2)–I(4) and Ag(2)···I(3) bond lengths of 2.719(2) and 3.228(2) Å respectively. The Ag(2)–I(3)–C(41) bond angle is 85.9(4)° whilst that of Ag(2)–I(4)–C(46) is 95.6(4)°. The silver is not coplanar with the $I_2C_6H_4$ ligand. The structural features of the $Ag(2)I_2C_6H_4$ unit are very similar to those reported for one of the ligands in the *exo*-dithio-7,8-dicarba-*nido*-undecaborate derivative $[NMe_4][Ag\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ where unsymmetric Ag–S bond lengths of 2.520(4) and 2.939(4) Å are observed.[12]

The molecular 'hfacac' complexes **10** and **11** were subjected to variable-temperature ^1H and $^{19}F\text{-}\{^1H\}$ NMR studies in CD_2Cl_2 solution. Signals associated with only one type of aryl iodide and one type of hfacac ligand were observed down to −70 °C. These observations, which are not consistent with the solid-state structures of **10** and **11**, are indicative of rapid intra- and/or inter-molecular exchange processes even at −70 °C and the structures of all of the above compounds in solution are not easily ascertained. Similar solution behaviour is observed for the norbornadiene complex $[Ag_4(hfacac)_4(nbd)_2]$.[9]

As expected for silver(I) co-ordination compounds, a range of co-ordination geometries are readily attained in complexes containing aromatic iodocarbons and/or CH_2I_2. Geometries have been realized that are close to ideal whilst in others large distortions are observed.[5] Co-ordination environments structurally characterized to date include $(RI)_4Ag^+$, $(RI)_2AgO_x$ ($x = 2$ or 3), $(RI)AgO_y$ ($y = 3$ or 4) and $(\mu\text{-}RI)Ag_2O_z$ ($z = 4$ or 6) where O is an oxygen atom of an oxyanion ($O_2CCF_3^-$, NO_3^-, $O_2PF_2^-$). The weakly bonded iodocarbon,[13] as expected, is easily distorted from ideal geometries exhibiting Ag–I–C bond angles ranging from 85.9(4) Å found in **11** to 108.70(12)° found in **3**. Particularly noteworthy is the ability of aromatic iodides to function as bridging ligands with complexes **8**, **5** and **4** being the first examples of this type of arrangement. For bridging μ-RI systems Ag–I–Ag bond angles vary from 61.4(1)° found in **8** to 144.53(3)° found in **5**. Silver–iodine bond distances for η^1-co-ordinated iodocarbons vary from 2.691(2) observed in **11** to 3.1446(7) Å observed in **1**. However weaker interactions are observed for the semi-bridging iodobenzene in **4** [2.853(1) and 3.309(1) Å] and for the semichelating $1,2\text{-}C_6H_4$ ligands in **11** [2.689(3) and 3.350(2), and 2.719(2) and 3.228(2) Å].

Experimental

Silver oxide, silver trifluoroacetate, hexafluoroacetylacetone, trichloroacetic acid, diiodomethane, iodobenzene, *p*-iodotoluene, 1,2- and 1,4-diiodobenzene were obtained from the Aldrich Chemical Co. Elemental analyses were done by Canadian Microanalytical Laboratories, Vancouver, British Columbia, Canada.

Syntheses

$[\{Ag_2(O_2CCF_3)_2(CH_2I_2)_2\}_n]$ 1. Silver trifluoroacetate (0.341 g) was dissolved in CH_2Cl_2 (15 cm^3). The solution was filtered and CH_2I_2 (0.4 cm^3; a CH_2I_2:Ag ratio of *ca.* 3 : 1) added. Addition of pentanes (10 cm^3) and cooling to 0 °C gave complex **1** as white plate-like crystals (35% yield) which melted at room temperature.

The complexes $[\{Ag_2(O_2CCF_3)_2(1,2\text{-}I_2C_6H_4)_2\}_n]$ **2** and $[\{Ag_2(O_2CCF_3)_2(1,4\text{-}I_2C_6H_4)_2\}_n]$ **3** were similarly prepared. Complex **2** was obtained as low melting (≈10 °C) pale yellow plates (Yield 40%), **3** as white needles (yield 62%), m.p. 41–42 °C (Found: C, 16.92; H, 0.94; I, 45.35. Calc. for $C_8H_4AgF_3I_2O_2$: C, 17.45; H, 0.73; I, 46.08%).

$[\{Ag_2(O_2CCF_3)_2(IC_6H_5)\}_n]$ 4. Iodobenzene (0.2 cm^3) was added to silver trifluoroacetate (0.192 g) in CH_2Cl_2 (15 cm^3). The solution was filtered and the volume reduced *in vacuo*. On cooling to 0 °C complex **4** was obtained as white prisms (28% yield), m.p. 122–128 °C (Found: C, 18.29; H, 0.95; I, 20.14. Calc. for $C_{10}H_5Ag_2F_6IO_4$: C, 18.60; H, 0.78; I, 19.65%). The complex $[\{Ag_4(O_2CCF_3)_4(H_2O)_2(p\text{-}IC_6H_4Me)_2\}_n]$ **5** was similarly prepared and isolated as white needles (25% yield), m.p. 59–63 °C (Found: C, 19.15; H, 1.58; I, 18.24. Calc. for $C_{11}H_9Ag_2F_6IO_5$: C, 19.49; H, 1.34; I, 18.72%). The complex $[\{Ag_2(O_2CCF_3)_2(1,2\text{-}I_2C_6H_4)\}_n]$ **6** was isolated as white prisms (yield 48%) (Found: C, 15.21; H, 0.64; I, 35.52. Calc. for $C_5H_2AgF_3IO_2$: C, 15.56; H, 0.52; I, 32.89%).

$[\{Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(1,2\text{-}I_2C_6H_4)\}_n]$ 7. Silver oxide (0.28 g) and 1,2-diiodobenzene (0.31 cm^3) were added to CH_2Cl_2 (50 cm^3). Trichloroacetic acid (*ca.* 1 g) was slowly added to the stirred suspension until all the silver oxide was consumed. The mixture was then filtered, the volume of the filtrate reduced to 10 cm^3, pentane (10 cm^3) added and the solution cooled to 0 °C. Complex **7** crystallized as white needles (yield 47%), m.p. 100–103 °C (Found: C, 13.73; H, 0.62; I, 25.12. Calc. for $C_{12}H_5Ag_2Cl_9I_2O_6$: C, 13.94; H, 0.49; I, 24.55%). The iodobenzene and *p*-iodotoluene complexes **8**, m.p. 100–102 °C, and **9**, m.p. 75–78 °C, were similarly prepared (Found for **8**: C, 15.63; H, 1.00; I, 13.85. Calc. for $C_{12}H_6Ag_2Cl_9IO_6$: C, 15.85; H, 0.67; I, 13.97. Found for **9**: C, 16.47; H, 0.92; I, 13.36. Calc. for $C_{13}H_8Ag_2Cl_9IO_6$: C, 16.94; H, 0.87; I, 13.77%).

$[\{Ag_4(hfacac)_4(IC_6H_4Me)_2\}_n]$ 10. Silver oxide (0.51 g) and hexafluoroacetylacetone (0.31 cm^3) were added to CH_2Cl_2 (50 cm^3). *p*-Iodotoluene (0.484 g) was added and the resultant solution filtered and the volume reduced *in vacuo* to ≈8 cm^3. Pentane (5 cm^3) was added and the solution allowed to stand at 0 °C for several days. Complex **10** was obtained as off-white prisms (yield 38%), m.p. 81–84 °C (Found: C, 24.31; H, 1.29; I, 14.78. Calc. for $C_{17}H_9Ag_2F_{12}IO_4$: C, 24.08; H, 1.07; I, 14.97%). The complex $[Ag_4(hfacac)_4(1,2\text{-}I_2C_6H_4)_3]$ **11** was similarly prepared (Found: C, 20.41; H, 0.84; I, 33.61. Calc. for $C_{19}H_8Ag_2F_{12}I_3O_4$: C, 20.29; H, 0.72; I, 33.85%).

Crystallography

Crystal data and details of the data collection and structure refinement for compounds **1**–**11** can be found in Table 11. Each compound yielded colourless crystals which darkened on prolonged exposure to light. Generally the data sets collected at room temperature were subject to linear intensity decay and this was corrected for. No significant decay was noticed in the case of the low-temperature data sets. Low-temperature data collection was not available for all the complexes. All data sets were collected using Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz-polarization and for absorption.[14] The structures were solved and refined using the SHELXTL PC package.[15] All refinements on *F* were by full-matrix least

Table 11 Crystal data and details of data collection and structure refinement for complexes **1**–**8**, **10** and **11**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**10**	**11**
Emprical formula	$C_3H_2AgF_3I_2O_2$	$C_8H_4AgF_3I_2O_2$	$C_8H_4AgF_3I_2O_2$	$C_{10}H_5Ag_2F_6IO_4$	$C_{11}H_9Ag_2F_6IO_5$	$C_{10}H_4Ag_2F_6I_2O_4$	$C_{12}H_5Ag_2Cl_9I_2O_6$	$C_{12}H_6Ag_2Cl_9IO_6$	$C_{34}H_{18}Ag_4F_{24}I_2O_8$	$C_{38}H_{16}Ag_4F_{24}I_6O_8$
Crystal size/mm	0.15 × 0.12 × 0.14	0.52 × 0.23 × 0.48	0.35 × 0.15 × 0.13	0.62 × 0.46 × 0.26	0.25 × 0.18 × 0.30	0.32 × 0.14 × 0.15	0.31 × 0.22 × 0.21	0.23 × 0.30 × 0.20	0.25 × 0.45 × 0.32	0.28 × 0.23 × 0.42
M	488.72	550.8	550.8	645.8	677.8	771.7	1033.8	907.9	1695.8	2249.4
Crystal class	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	9.928(1)	6.533(2)	5.509(1)	8.513(2)	5.222(1)	7.843(2)	13.755(3)	16.235(3)	10.782(2)	11.621(2)
b/Å	7.756(1)	24.493(5)	20.877(2)	9.123(2)	11.340(3)	9.329(3)	17.999(2)	16.994(3)	14.716(2)	12.479(2)
c/Å	11.439(1)	8.224(2)	10.296(1)	10.793(2)	14.172(3)	11.604(3)	11.344(2)	17.968(4)	16.976(2)	22.076(4)
α/°				69.09(2)	81.95(2)	85.25(2)			71.30(2)	91.71(3)
β/°	96.89(3)	113.00(1)	92.25(1)	80.21(2)	84.60(2)	83.80(2)	113.59(5)	94.90(3)	75.51(2)	103.66(3)
γ/°				78.52(2)	86.94(2)	79.92(2)			68.60(2)	111.55(3)
U/Å^3	878.6(2)	1211.3(5)	1179.2(3)	762.9(3)	826.6(3)	829.3(5)	2573.8(8)	4939.2(10)	2348.2(8)	2869.2(2)
Z	4	4	4	2	2	2	4	8	2	2
D_c/g cm^{-3}	3.685	3.020	3.875	2.811	2.723	3.090	2.668	2.442	2.398	2.604
μ(Mo-Kα)/mm^{-1}	9.322	6.781	6.965	4.669	4.320	6.159	4.883	3.837	3.100	4.696
F(000)	864	992	992	596	632	700	1912	3408	1582	2060
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Enraf-Nonius CAD4	Siemens P4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
T/K	153	173	173	294	173	294	294	294	294	294
2θ range/°	3.2–30.0	3.2–54.0	7.0–60.0	4.8–52.7	6.4–50.0	3.0–60.0	2.3–45.0	2.3–50.0	2.6–45	3.5–45.0
Intensity decay (%)	<2	<2	<2	1.000, 0.676	<2%	1.000–0.0783	1.000–1.041	1.009–0.345	1.000–0.727	1.002–0.890
Minimum, maximum absorption correction	0.2175, 0.5160	0.1335, 0.6123	0.1911, 0.6056	0.5700, 0.91 200	0.2942, 0.7953	0.729, 1.353	0.2525, 0.6632	0.1234, 0.7730	0.2468, 0.7436	0.0036, 0.7084
No. reflections collected	2685	2870	3746	3366	3247	4904	3695	4722	4155	7597
Unique reflections	2554	2651	3434	3097	2901	4633	3353	4325	4065	7502
R_{int}	0.062	0.018	0.024	0.029	0.047	0.116	0.024	0.152	0.000	0.000
Observed reflections [$F > 4\sigma(F)$]	2255	2403	3111	2323	2458	2327	2722	2592	2966	5558
Refinement on	F^2	F^2	F^2	F	F^2	F	F	F	F	F
Weighting g or a,b	0.0467, 4.59	0.0668, 5.97	0.0135, 5.02	0.0020	0.1000. 0.00	0.0008	0.0035	0.0100	0.0061	0.0004
$R1$ or R	$R1 = 0.0347$	$R1 = 0.0406$	$R1 = 0.0281$	$R = 0.0425$	$R1 = 0.0509$	$R = 0.0631$	$R = 0.0368$	$R = 0.0802$	$R = 0.0599$	$R = 0.0709$
$wR2$ or R'	$wR2 = 0.0996$	$wR2 = 0.1135$	$wR2 = 0.0696$	$R' = 0.0686$	$wR2 = 0.1327$	$R = 0.0945$	$R' = 0.0650$	$R' = 0.1283$	$R' = 0.0994$	$R' = 0.0087$
Goodness of fit	1.16	1.08	1.19	1.29	1.019	2.27	1.03	1.16	1.19	3.24
Largest, mean Δ/σ	0.002, 0.000	0.015, 0.001	0.006, 0.001	0.080, 0.010	0.002, 0.000	0.52, 0.02	0.000, 0.000	0.52, 0.03	0.12, 0.01	0.26, 0.07
$\Delta\rho$ Maximum, minimum e Å^{-3}	1.44, −1.85	1.56, −1.93	0.93, −1.02	0.77, −0.66	1.97, −1.80	1.25, −1.41	1.01, 1.69	1.54, −1.09	1.09, 0.81	1.92, −1.61

$R = \Sigma(F_o - F_c)/\Sigma(F_o)$, $R' = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, $R1 = \Sigma(F_o - F_c)/\Sigma(F_o)$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; R, R' and $R1$ are calculated with $F > 4\sigma(F)$ while $wR2$ is calculated using all data.

squares [using data with $F > 4\sigma(F)$] with weights of $w^{-1} = \sigma^2(F) + gF^2$. The F^2 refinements were carried out using all data and the weighting scheme was $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. H-atoms were placed in calculated positions and included in the refinements as riding atoms.

In compound **11** two iodine atoms [(I(1)/I(1*) and I(2)/C(34)] are disordered over two sites and the minor component of I(2) lies on the same site as C(34). The disorder is not shown in Fig. 10.

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