Alkyl and Aryl Iodide Complexes of Silver(I)

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The first structurally characterized examples of alkyl and aryl iodide complexes of silver are reported; similar compounds have long been thought to be intermediates in the reactions of alkyl iodides with silver salts.

In 1906 Scholl and Steinkopf[1] reported the preparation of the compound $AgNO_3 \cdot CH_2I_2$ for which they proposed the structure **1**[1] which envisioned the coordination of the organic iodide. However, it is only recently that coordination compounds containing simple alkyl and aryl iodides have been structurally characterized.[2–5] We report here on the synthesis and structural characterization of several alkyl and aryl iodide complexes of silver(I).

A simple approach to obtaining crystalline products in >60% isolated yields is given in eqn. (1). (Ethylene complexation of Ag^+ helps to solubilize the silver salts).

$$AgX \xrightarrow[\text{ii, + RI}]{\text{i, } C_2H_4 \text{ in } CH_2Cl_2 \text{ or MeOH}} (RI)_x(AgX)_y \qquad (1)$$
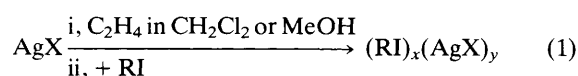
e.g. $X^- = BF_4^-$, PF_6^-, NO_3^-, $O_2CCF_3^-$, $O_2CCCl_3^-$, hexafluoroacetylacetonate. $RI = CH_2I_2$, $I(CH_2)_3I$, aromatic iodides.

The ratio of the organic iodide to AgX in the isolated white crystalline products varies from system to system, as does the thermal stability and susceptibility to nucleophilic displacement of AgI by X^-. (In some systems either thermal dissociative loss of the aryl iodide or precipitation of AgI (alkyl systems) occurs quite rapidly at 20 °C†). Reaction of 1,3-diiodopropane with $AgPF_6$ gives [{$I(CH_2)_3I$}$_2$Ag]PF_6 the solid-state structure of which is constructed from tetrahedrally coordinated Ag^+ and bridging 1,3-diiodopropane ligands to

1   **2**
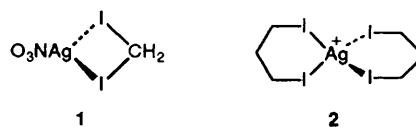
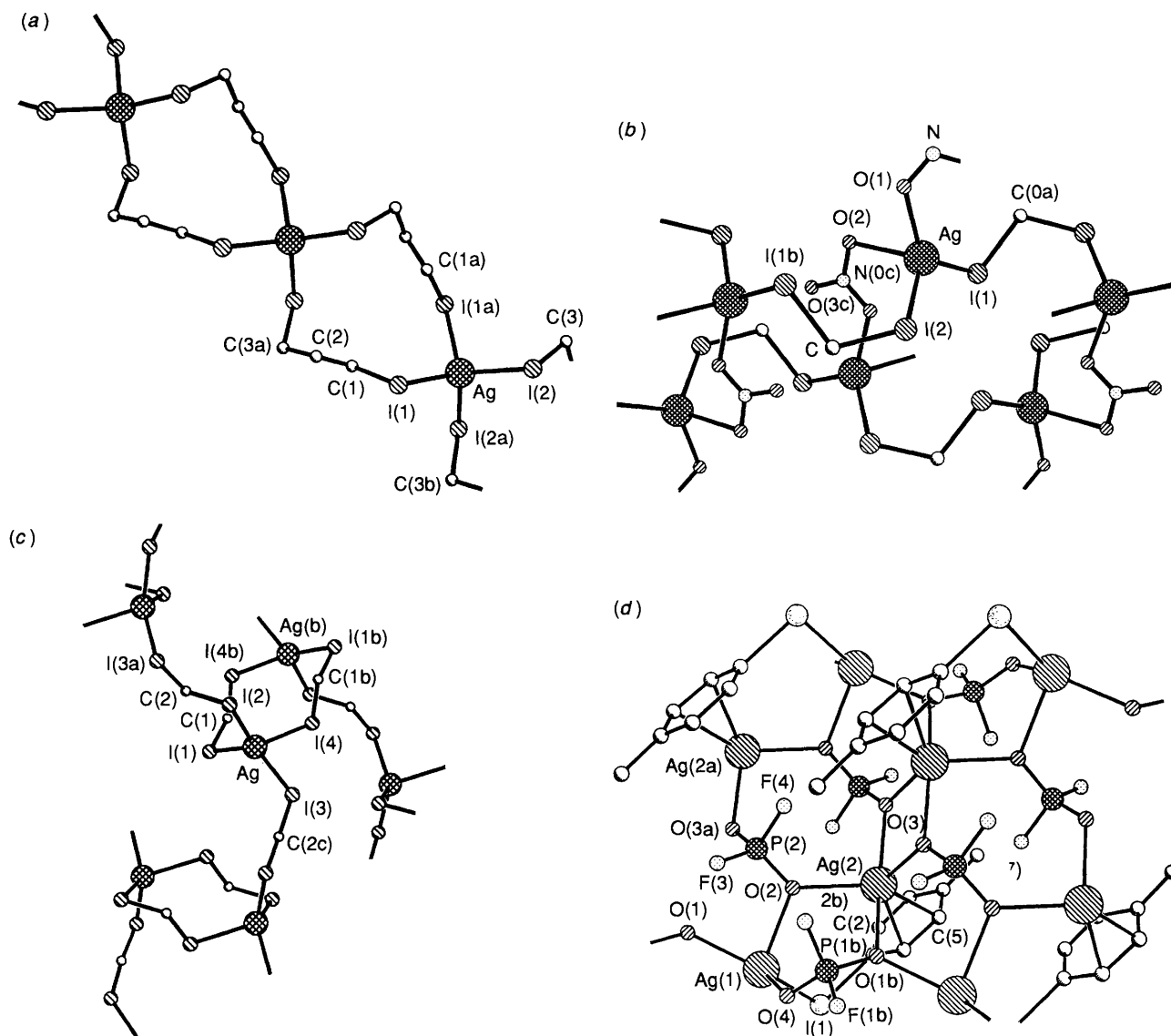† Formation of AgI from the reaction of methyliodide with $AgPF_6$–C_2H_4–CH_2Cl_2 is rapid at 20 °C.

Fig. 1 Structural features as determined by single-crystal X-ray diffraction of (a) [{I(CH₂)₃I}₂]AgPF₆ (PF₆⁻ not shown); (b) AgNO₃·CH₂I₂;[1] (c) [(CH₂I₂)₂Ag]PF₆ (PF₆⁻ not shown) and (d) (C₇H₇I)(AgO₂PF₂)₂. Typically Ag–I bond lengths are 2.80–2.92 Å, Ag–I C bond angles are 96–104° and Ag–O bond lengths are 2.37–2.56 Å.

give a chain polymer array [Fig. 1(a); PF₆⁻ not shown].‡ From ¹H NMR studies it is probable that the structure in CD₂Cl₂

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‡ *Crystal data* for [{I(CH₂)₃I}₂Ag]PF₆: C₆H₁₂AgF₆I₄P, M = 844.6, monoclinic, space group C2/c, a = 17.739(4), b = 7.481(1), c = 13.676(3) Å, β = 101.49(3)°, U = 1783.9(9) Å³ and Dᴄ = 3.15 g cm⁻³ for Z = 4. μ(Mo-Kα) = 81.8 cm⁻¹.

For AgNO₃·CH₂I₂: CH₂AgI₂NO₃, M = 437.7, monoclinic, space group P2₁/c, a = 7.306(1), b = 11.072(2), c = 8.931(2) Å, β = 99.31(3)°, U = 712.9(4) Å³ and Dᴄ = 4.08 g cm⁻³ for Z = 4. μ(Mo-Kα) = 114.2 cm⁻¹.

For [{CH₂I₂}₂Ag]PF₆: C₂H₄AgF₆I₄P, M = 788.5, monoclinic, space group P2₁/n, a = 8.584(3), b = 11.987(3), c = 13.458(4) Å, β = 102.58(4)°, U = 1351.5(7) Å³ and Dᴄ = 3.86 g cm⁻³ for Z = 4. μ(Mo-Kα) = 107.8 cm⁻¹.

For (CH₃C₆H₄I)(AgO₂PF₂)₂: C₇H₇Ag₂F₄IO₄P₂, M = 635.7, triclinic, space group P1̄, a = 5.9486(5), b = 10.7762(13), c = 12.1281(15) Å, α = 69.706(10), β = 87.743(9), γ = 75.393(9)°, U = 705.8(4) and Dᴄ = 2.99 g cm⁻³ for Z = 2. μ(Mo-Kα) = 52.4 cm⁻¹. Intensity data collected on an Enraf-Nonius CAD-4 diffractometer, Mo-Kα (λ = 0.71073 Å). Refinement was by full-matrix least-squares to minimize Σw(Fₒ-Fᴄ)², where w⁻¹ = σ²(F) + gF². Hydrogen atoms were positioned on geometric grounds (C–H 0.96 Å).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

solution is mononuclear with chelating 1,3-diiodopropane (*i.e.* 2).§ At 20 °C exchange between free and the coordinated 1,3-diiodopropane of 2 is fast on the NMR time-scale.§

The compound AgNO₃·CH₂I₂ reported by Scholl and Steinkopf[1] does indeed contain coordinated diiodomethane. The structure is in essence a sheet consisting of μ₂-bridging NO₃⁻ and CH₂I₂ ligands and tetrahedrally coordinated Ag⁺, [Fig. 1(b)].‡ The solid-state structure of the complex [(CH₂I₂)₂Ag]PF₆ exhibits a cross-linked polymeric chain array composed of μ₂-bridging CH₂I₂ and a distorted tetrahedral coordination of Ag⁺ [Fig. 1(c);‡ PF₆⁻ not shown]. Whilst the solution structure of [(CH₂I₂)₂Ag]PF₆ is not known, exchange between free and coordinated CH₂I₂ is fast on the NMR time-scale (200 MHz, 20 °C, CD₂Cl₂).

Finally, it should be noted that aryl iodides also have the

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§ ¹H NMR (200 MHz, 20 °C) shifts for I(CH₂)₃I in CD₂Cl₂: δ 3.28 (4H), 2.23 (2H); for [{(CH₂)₃I}₂Ag]PF₆: 3.58(4H), 2.28(2H), calc. (found) for C₆H₁₂AgF₆I₄P : C, 8.53 (8.47); H, 1.43 (1.36); I, 60.10 (59.50).

potential of η^2-arene coordination to Ag$^+$.[6] Reaction of 4-iodotoluene with $AgPF_6$–C_2H_4–CH_2Cl_2 followed by addition of pentane and slow crystallization (non-anhydrous conditions) gave a low yield (18%) of the compound $(CH_3C_6H_4I)(AgO_2PF_2)_2$ as white needles which rapidly lose the iodotoluene at room temperature. Low temperature structural characterization [Fig. 1(d)]‡ indicates a coordinated η^1-iodide linkage to one silver and an η^2-bond between the arene ring and the second silver. The difluorophosphates (hydrolysis product of the PF_6^-) function as μ_4-bridging ligands (each oxygen is μ_2) and both Ag$^+$ ions can be considered to be five-coordinate (approximately trigonal bipyramidally bonded to four O atoms and either I or the arene ring). These results, which include the first examples of homoleptic halocarbon coordination complement the recent studies of chloroalkane complexes of $AgOTeF_5$ reported by Strauss et al.[7]

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