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Preliminary Communication

$\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{IC}_6\text{H}_5)$, The first example of a complex containing a bridging iodo carbon ligand

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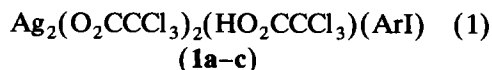
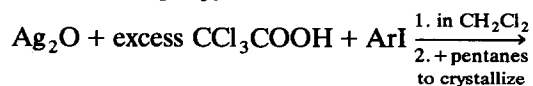
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Abstract

The preparation and molecular structures, as determined by single crystal X-ray diffraction, of the complexes $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{IAr})$, where IAr = iodobenzene and 1,2-diiodobenzene, are reported. In the former the iodobenzene functions as a μ_2 -bridge.

Whilst halocarbon–metal bonds have long been suspected to be important intermediates in organometallic chemistry, it is only recently that coordination compounds containing simple alkyl and aryl iodides functioning as η^1 -ligands have been structurally characterized [1–5]. We here report on the isolation of the complex $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{IC}_6\text{H}_5)$ which is the first example of a simple iodo-carbon compound functioning as a μ_2 -bridge. The only other example of a halo-carbon functioning as a bridging ligand is to be found in the complex $\text{Ag}(\text{OTeF}_5)(1,2\text{-C}_2\text{H}_4\text{Cl}_2)$ reported by Strauss et al. [6].

Aryliodide complexes of silver trichloroacetate can be isolated as white crystalline compounds following the simple procedure described in eqn. (1). {e.g. ArI = iodobenzene (**1a**), 1,2-diiodobenzene (**1b**) and 4-iodotoluene (**1c**) [7*].}



The molecular structure of the iodobenzene complex (**1a**) and the 1,2-diiodobenzene complex (**1b**) have

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* Reference number with asterisk indicates a note in the list of references.

been determined by single crystal X-ray diffraction [8*]. The solid state structure of $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\mu_2\text{-IC}_6\text{H}_5)$ (**1a** see Fig. 1) consists of two silver atoms bridged by two trichloroacetates and by the iodine atom of the iodobenzene { $\text{Ag–I–Ag} = 61.4(1)^\circ$ }. 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 $\text{CCl}_3\text{C}(\text{OH}) = \text{O} \cdots \text{Ag}$ interaction of 2.779(11) Å. The $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{IC}_6\text{H}_5)$ unit is linked to other units via the oxygen of the trichloroacetate linkages to give a chain structure. A very similar structural array is observed for the 1,2-diiodobenzene complex $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{I}_2\text{C}_6\text{H}_4)$ (**1b** see Fig. 2) except that the 1,2-diiodobenzene forms a bridge structure involving η^1 -coordination of iodides to separate silver atoms. In comparison to the $\mu_2\text{-IC}_6\text{H}_5$ complex coordination of the 1,2-diiodobenzene results in a slight twist of the $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2$ ring structure in **1b** relative to **1a**, which is reflected in larger O–Ag–O angles

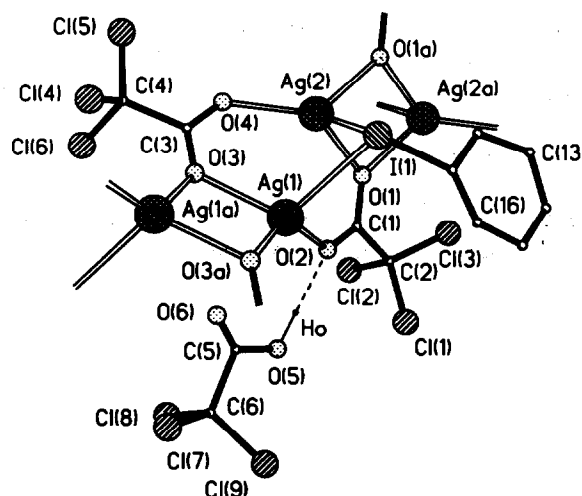


Fig. 1. The structural features as determined by single crystal X-ray diffraction of $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{IC}_6\text{H}_5)$. For the sake of clarity atoms have been drawn as spheres of arbitrary radii and hydrogen atoms have been omitted. Weak interactions are indicated by a dashed line. Selected bond lengths (Å): $\text{Ag}(1)\text{--I}(1)$ 2.929(3), $\text{Ag}(2)\text{--I}(1)$ 2.971(2), $\text{Ag}(1)\text{--O}(2)$ 2.379(12), $\text{Ag}(1)\text{--O}(3)$ 2.275(11), $\text{Ag}(1)\text{--O}(3a)$ 2.453(11), $\text{Ag}(2)\text{--O}(1)$ 2.307(11), $\text{Ag}(2)\text{--O}(4)$ 2.232(12), $\text{Ag}(2)\text{--O}(1a)$ 2.528(11). Bond angles ($^\circ$): $\text{Ag}(1)\text{--I}(1)\text{--Ag}(2)$ 61.4(1), $\text{Ag}(1)\text{--I}(1)\text{--C}(11)$ 101.6(8), $\text{Ag}(2)\text{--I}(1)\text{--C}(11)$ 93.9(7). The $\text{Ag}(1)\text{--Ag}(2)$ separation is 3.014(1) Å.

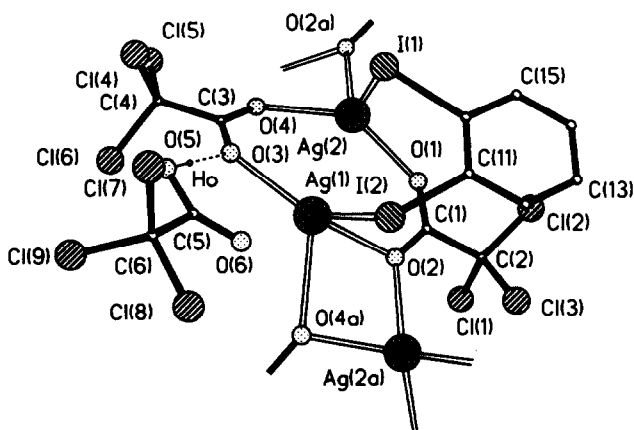


Fig. 2. The structural features as determined by single crystal X-ray diffraction of $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{I}_2\text{C}_6\text{H}_4)$. Selected bond lengths (Å): $\text{Ag}(1)-\text{I}(2)$ 3.025(1), $\text{Ag}(2)-\text{I}(1)$ 2.919(1). Bond angles (°): $\text{Ag}(1)-\text{I}(2)-\text{C}(11)$ 97.4(2), $\text{Ag}(2)-\text{I}(1)-\text{C}(16)$ 96.2.

within the $(\mu_2\text{-O}_2\text{CCCl}_3)_2$ unit and nonsymmetry of the 1,2-diiodobenzene bridge which exhibits Ag–Ag–I angles of 77° [$\text{Ag}(2)-\text{Ag}(1)-\text{I}(1)$] and 109° [$\text{Ag}(1)-\text{Ag}(2)-\text{I}(2)$]. This is accompanied by a slight elongation of the $\text{Ag} \cdots \text{Ag}$ separation [2.929(3) Å, **1a**; 3.078(1) Å, **1b**]. Silver-iodide bond distances and the average Ag–I–C bond angles are similar in the two complexes. The above results constitute a further development in the identification of the bonding modes available to weakly ligating halo-carbon compounds and complement the recent studies of iodoalkane complexes of AgPF_6 [9], a dichloromethane Ru_3 cluster [10] and the extensive studies of chloroalkane complexes of AgOTeF_5 , reported by Strauss *et al.* [6,11].

Acknowledgements

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References and notes

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- 7 Silver oxide (0.246 g) and *para*-iodotoluene (0.46 g) were added to CH_2Cl_2 (50 ml). Trichloroacetic acid was slowly added to the stirred suspension until all of the silver oxide was consumed. The reaction was then filtered, the volume of the filtrate reduced to 10 ml, pentane (10 ml) added and the solution cooled to 0°C . $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{IC}_6\text{H}_4\text{CH}_3)$ (**1c**) crystallized from solution as white fibrous needles (0.66 g, 68%) m.p. $75\text{--}78^\circ\text{C}$. Calcd. (found) for $\text{C}_{13}\text{H}_8\text{Ag}_2\text{Cl}_9\text{IO}_6$ (**1c**): C, 16.94 (16.47); H, 0.87 (0.92); I, 13.77 (13.36)%. Complexes **1a** and **1b** were similarly prepared.
- 8 Crystal data for $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{IC}_6\text{H}_5)$: $\text{C}_{12}\text{H}_6\text{Ag}_2\text{Cl}_9\text{IO}_6$, $M = 907.9$, monoclinic, space group $C2/c$, $a = 16.235(3)$, $b = 16.994(3)$, $c = 17.968(4)$ Å $\beta = 94.90(3)^\circ$, $U = 4939.2(17)$ Å³, and $D_c = 2.442$ g cm⁻³ for $Z = 8$. $\mu(\text{Mo-K}\alpha) = 38.37$ cm⁻¹, $R = 0.079$ for 2420 reflections with $F > 6.0\sigma(F)$. For $\text{Ag}_2(\text{O}_2\text{CCCl}_3)_2(\text{HO}_2\text{CCCl}_3)(\text{I}_2\text{C}_6\text{H}_4)$: $\text{C}_{12}\text{H}_5\text{Ag}_2\text{Cl}_9\text{I}_2\text{O}_6$, $M = 1033.8$, monoclinic, space group $P2_1/c$, $a = 13.755(3)$, $b = 17.999(2)$, $c = 11.3440(10)$ Å, $\beta = 113.59(5)^\circ$, $U = 2574.0$ Å³, and $D_c = 2.668$ g cm⁻³ for $Z = 4$. $\mu(\text{Mo-K}\alpha) = 48.82$ cm⁻¹, $R = 0.037$ for 2670 reflections with $F > 6.0\sigma(F)$. Intensity data collected on an Enraf-Nonius CAD-4 diffractometer, $\text{Mo-K}\alpha(\lambda = 0.71073$ Å). Empirical absorption corrections were carried out using the program DIFABS [8b]. Structures were solved by direct methods using SHELXTL PC [8c]. Refinement was by full-matrix least squares to minimize $\sum w(F_0 - F_c)^2$ where $w^{-1} = \sigma^2(F) + gF^2$. (b) N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, **39** (1983) 158; (c) G.M. Sheldrick, SHELXTL PC, Siemens Analytical X-ray Instruments, Inc., 1990 Karlsruhe, Germany.
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