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Tetramethylammonium *catena*-Di-μ-chloro-argentate(I)

BY GÖRAN HELGESSON, MAGDALENA JOSEFSSON AND SUSAN JAGNER*

Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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Abstract. $[N(CH_3)_4][AgCl_2]$, $M_r = 252{\cdot}9$, orthorhombic, *Immm*, $a = 8{\cdot}825\,(3)$, $b = 14{\cdot}526\,(4)$, $c = 6{\cdot}570\,(2)$ Å, $V = 842{\cdot}2\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}99$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}93$ mm^{-1}, $F(000) = 496$, $T = 170$ K, $R = 0{\cdot}032$ for 549 unique observed $[I \geq 3\sigma(I)]$ reflections and 43 parameters. The $[AgCl_2]^-$ anion is a one-dimensional infinite polymeric chain composed of edge-sharing $AgCl_4$ tetrahedra, in which the Ag—Cl distances are 2·599 (1) and 2·618 (1) Å and the Ag···Ag contacts are 3·137 (1) and 3·433 (1) Å.

Introduction. In halocuprates(I) crystallizing with symmetrically substituted tetraalkylammonium and related unipositive cations, the coordination number of copper(I) in the anion has been found to increase regularly with decreasing size of the cation (Andersson & Jagner, 1986, 1987). Previous crystallographic studies on haloargentates(I) containing tetraalkylammonium cations have been mainly concerned with iodoargentates(I), which have been shown to contain infinite polymeric species based on silver(I) iodide tetrahedra, *viz* $[N(C_4H_9)_4][Ag_3I_4]$(Gilmore, Tucker & Woodward, 1971), $[N(CH_3)_4]_2[Ag_{13}I_{15}]$ (Geller & Lind, 1970), $[N(CH_3)_4][Ag_2I_3]$ (Meyer, 1963; Kildea, Skelton & White, 1986) and $[N(CH_3)_4][AgI_2]$ (Peters, von Schnering, Ott & Seidenspinner, 1984). A double chain composed of edge-sharing silver(I) bromide tetrahedra, analogous to the $[Ag_2I_3]^-$ chain in $[N(CH_3)_4][Ag_2I_3]$ (Meyer, 1963; Kildea, Skelton & White, 1986), occurs in $[N(CH_3)_4][Ag_2Br_3]$ (Jagner, Olson & Stomberg, 1986). There would appear to be no previous crystallographic investigation of chloroargentates(I) crystallizing with tetraalkylammonium cations; far-IR spectroscopic studies on the tetraethylammonium and tetramethylammonium compounds, however, indicate the presence of infinite chain anions of stoichiometry $[Ag_2Cl_3]^-$ and $[AgCl_2]^-$, respectively (Bottger & Geddes, 1967). As part of an investigation of the dependency of the coordination of silver(I) in chloroargentates(I) on cation size, we have determined the structure of $[N(CH_3)_4][AgCl_2]$.

Experimental. The compound was prepared according to the method of Kuhn & Schretzmann (1955, 1957), using 0·10 g (0·7 mmol) AgCl [ICN Biomedicals, K & K], 0·076 g (0·7 mmol) tetramethylammonium chloride [Fluka] and 15 ml dimethylformamide; colourless elongated prisms, m.p. 566–568 K, being obtained after a few days. Preliminary unit-cell dimensions and space group from rotation and Weissenberg films, suggesting isostructurality with $[N(CH_3)_4][AgI_2]$ (Peters *et al.*, 1984); intensity data collected on a Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation; crystal dimensions (distance to faces from vertex chosen as origin for absorption correction): 0·000 $(001, 0\bar{1}0, 1\bar{1}0)$, 0·389 $(00\bar{1})$, 0·261 $(\bar{1}10)$, 0·164 (010), 0·109 (120), 0·129 $(\bar{1}\bar{2}0)$ mm. 15 reflections used to determine unit-cell parameters; $3{\cdot}5 \leq 2\theta \leq 55°$; $0 \leq h \leq 11$; $0 \leq k \leq 18$; $0 \leq l \leq 8$; ω–2θ scan mode, variable 2θ scan rate: 2·5–20·0 °min^{-1}; 96-step profiles; Lehmann & Larsen (1974) profile-analysis method used to calculate the intensities (Lindqvist & Ljungström, 1979); variation in intensity of 2 standard reflections, measured every 48 reflections, < 2%, 583 unique non-systematically absent reflections measured, of which 549 with $I \geq 3\sigma(I)$; absorption correction with *ABSORB* (DeTitta, 1985), transmission factors 0·481–0·652. The coordinates of $[N(CH_3)_4][AgI_2]$ (Peters *et al.*, 1984) were checked against the Patterson function and used as starting point for the refinement. H atoms located from difference map; non-H atoms refined with anisotropic and H atoms with isotropic thermal parameters. Full-matrix least-squares refinement based on F gave final $R = 0{\cdot}032$ (549 reflections; 43 parameters), $wR = 0{\cdot}043$, $w = [\sigma^2(F_o) + 0{\cdot}0002F_o^2]^{-1}$;

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* To whom correspondence should be addressed.

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non*-H *atoms*

E.s.d.'s are given in parentheses

$$B_{eq} = (8\pi^2/3)\sum_{ij}U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	B_{eq}
Ag	4(*j*)	0·5000	0·0000	0·26124 (6)	2·30 (1)
Cl(1)	4(*h*)	0·5000	0·13612 (8)	0·0000	2·09 (3)
Cl(2)	4(*f*)	0·2652 (1)	0·0000	0·5000	2·18 (3)
N	4(*g*)	0·0000	0·1968 (3)	0·0000	1·67 (8)
C(1)	8(*n*)	0·1368 (4)	0·2573 (3)	0·0000	2·71 (9)
C(2)	8(*l*)	0·0000	0·1383 (3)	0·1883 (8)	3·63 (12)

$(\Delta/\sigma)_{max} < 0{\cdot}012$; final difference electron density: max. 1·50, min. $-1{\cdot}47$ e Å^{-3}. Anomalous-dispersion correction for all non-H atoms. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs described by Lindgren (1977) and Andersen (1985). Atomic coordinates are listed in Table 1.*

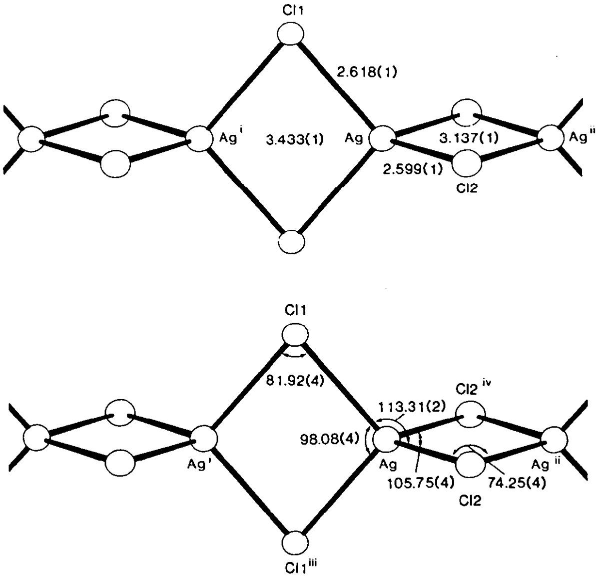

Fig. 1. Connectivity relationships within the [AgCl$_2$]$^-$ anion. E.s.d.'s are given in parentheses. The thermal ellipsoids enclose 50% probability (Johnson, 1965). Symmetry code: (i) x, y, $-z$; (ii) x, y, $1-z$; (iii) x, $-y$, z; (iv) $1-x$, y, z.

Discussion. [N(CH$_3$)$_4$][AgCl$_2$] is isostructural with [N(CH$_3$)$_4$][AgI$_2$] (Peters *et al.*, 1984), the anion being an infinite chain of edge-sharing silver(I) chloride tetrahedra extending parallel to the *c* axis. The structure of the anion is in accordance with the far-IR spectroscopic studies of Bottger & Geddes (1967). Bond distances and angles within the ion are given in Fig. 1. The silver(I)–chloride distances, 2·599 (1) and 2·618 (1) Å, are intermediate between those reported for the polymeric anion in Cs[AgCl$_2$], *viz* 2·49–2·87 Å, in which silver(I) is trigonal-bipyramidally coordinated (Gaebell, Meyer & Hoppe, 1983). In the dinuclear [Ag$_2$Cl$_5$]$^{3-}$ anion, which can be described in terms of chlorine-bridged AgCl$_2^-$ ions, silver(I) exhibiting distorted trigonal-planar coordination geometry, terminal Ag—Cl distances are 2·46 Å and bridging 2·69 Å (Bowles & Hall, 1971, 1975). The di-μ-chloro-dichlorodiargentate(I) ion in [P(C$_6$H$_5$)$_4$]$_2$[Ag$_2$Cl$_4$], which can also be described in terms of two bent [AgCl$_2$]$^-$ moities joined *via* weak Ag—Cl interactions, *i.e.* containing pseudo three-coordinated silver(I), exhibits Ag—Cl distances of 2·358 (2), 2·447 (1) and 2·792 (2) Å (Helgesson & Jagner, 1988).

While both the tetramethylammonium dichloroargentate(I) and the tetramethylammonium diiodoargentate(I) (Peters *et al.*, 1984) contain infinite chain anions of stoichiometry [AgX_2]$^-$, the corresponding bromoargentate(I) crystallizes as a double chain of edge-sharing silver(I) bromide tetrahedra of stoichiometry [Ag$_2$Br$_3$]$^-$ (Jagner, Olson & Stomberg, 1986). This type of chain has also been found in a second modification of the tetramethylammonium iodoargentate(I), [N(CH$_3$)$_4$][Ag$_2$I$_3$] (Meyer, 1963; Kildea, Skelton & White, 1986). It has been suggested (Bottger & Geddes, 1967) that tetramethylammonium dibromoargentate(I) might also crystallize with [AgBr$_2$]$^-$ chains of the type described here, but no crystallographic evidence has yet been provided to support this. Nor has the existence of [N(CH$_3$)$_4$][Ag$_2$Cl$_3$], the chloroargentate(I) analogue of [N(CH$_3$)$_4$][Ag$_2$Br$_3$] and [N(CH$_3$)$_4$][Ag$_2$I$_3$], been documented.

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* Lists of structure factors, anisotropic thermal parameters for the non-H atoms, fractional coordinates and thermal parameters for the H atoms, and bond distances and angles within the tetramethylammonium cation have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51100 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Metal Complexes of Sulfur–Nitrogen Ligands: the Structure of Amino(triphenyl)phosphonium [Di(thiazane)-3-eno](thiosulfato)(triphenylphosphine)platinate

BY MICHAEL B. HURSTHOUSE AND RICHARD L. SHORT

Department of Chemistry, Queen Mary College, London E1 4NS, England

AND PAUL F. KELLY AND J. DEREK WOOLLINS

Department of Chemistry, Imperial College, London SW7 2AY, England

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Abstract. $[P(C_6H_5)_3(NH_2)][Pt(S_2N_2H)(S_2O_3)(C_{18}H_{15}P)]$, $M_r = 940·96$, monoclinic, $P2_1/n$, $a = 12·222\,(4)$, $b = 17·155\,(4)$, $c = 18·126\,(5)$ Å, $\beta = 100·63\,(2)°$, $V = 3735\,(2)$ Å^3, $Z = 4$, $D_x = 1·674$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71073$ Å, $\mu = 39·18$ cm^{-1}, $F(000) = 1864$, $T = 298$ K, $R = 0·0444$ for 3015 observed reflections. The Pt atom is in a square-planar environment, coordinated to S and N atoms of the chelating S_2N_2H ligand, a thiosulfate S atom *trans* to S and triphenylphosphine. There are H-bonding interactions between the S_2O_3 ligand, the S_2N_2H hydrogen and the amine hydrogens of the $Ph_3PNH_2^+$ cation.

Introduction. A number of metal–sulfur–nitrogen complexes are known (Kelly & Woollins, 1986) but, to date, there are no structurally characterized examples of mixed-ligand complexes containing S_2N_2H– and phosphine ligands. Compounds of this type may be of use as sulfur–nitrogen reagents in syntheses.

Experimental. The compound (1) was prepared by reaction of S_4N_4 with $Pt(PPh_3)_3$ in air, the crystals being obtained from THF/petroleum ether (Kelly, 1987). Crystal size $0·20 \times 0·15 \times 0·25$ mm. Data collected on Enraf–Nonius CAD-4 diffractometer, lattice parameters from 25 reflections, $24 < 2\theta < 26°$. Total of 4705 reflections measured using $\omega/2\theta$ scan mode, $3 < 2\theta < 44°$, in the range h: 0→12, k: 0→18, l: −19→19. Intensities of three standard reflections (162, 081, $\bar{1}6\bar{2}$) measured every 1 h showed no decay during data collection, orientation standards checked every 100 reflections. Corrections for Lorentz, polarization and absorption (North, Phillips & Mathews, 1968) applied; max. and min. relative transmission factors 99·9 and 83·6%. 4520 unique reflections with 1505 considered unobserved $[I < 3\sigma(I)]$, systematic absences $h0l$, $h + l = 2n$ and $0k0$, $k = 2n + 1$ uniquely indicate $P2_1/n$. Position of Pt atom located from Patterson synthesis and all non-H atoms found from successive Fourier difference syntheses. Anisotropic displacement factor coefficients for all non-H atoms, phenyl rings refined as rigid group with refined group $U_{\rm iso}$ values for hydrogens. Other hydrogens refined freely with isotropic coefficients. Final refinement on F by full-matrix least-squares methods. Largest peak in final difference Fourier map 0·97 e Å^{-3} close to Pt. Weighting scheme $w = 1/(\sigma^2F + gF^2)$ where $g = 0·0001$ applied. Max. Δ/σ in final cycle 0·08. Final $R = 0·0444$, $wR = 0·0389$. Computing with *SHELX*80 (Sheldrick, 1980) on

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