X-Ray Crystal Structure Identification of the Ternary Complex $MgCl_2 \cdot 2SbCl_3 \cdot 6MeCN$ *

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The solid-state structure of $MgCl_2 \cdot 2SbCl_3 \cdot 6MeCN$ has been determined by *X*-ray diffraction studies as the ionic salt $[Mg(MeCN)_6][(SbCl_4)_2]$. Crystals of hexakis(acetonitrile)magnesium(II) bis[tetrachloroantimonate(III)] are triclinic, space group $P\bar{1}$ with a = 8.968(8), b = 10.220(11), c = 8.389(9) Å, α = 97.1(1), β = 79.8(1), γ = 78.1(1)°, and Z = 1. 2 165 Independent reflections above background have been measured on a diffractometer and the structure refined to R 0.070. In the centrosymmetric $[Mg(MeCN)_6]^{2+}$ cation, the six-co-ordinate magnesium atom has a regular octahedral geometry with independent Mg–N distances of 2.136(9), 2.134(7), and 2.179(8) Å. The $[SbCl_4]^-$ units are polymeric. There are three short Sb–Cl bonds in a *fac* arrangement [Sb–Cl(1) 2.433(2), Sb–Cl(3) 2.431(2), Sb–Cl(4) 2.367(3) Å]. Two $SbCl_3$ moieties are bridged *via* two weaker bonds [Sb–Cl(2) 3.006(3), Sb–Cl(2′) 2.822(4) Å] over a centre of symmetry to give $[Sb_2Cl_8]^{2-}$ units. These units are connected *via* a further weak contact Sb–Cl(1″) 3.580(2) Å to give a polymeric chain. The environment of the antimony atom is distorted octahedral and there is no evidence for a stereochemically active lone pair of electrons around the antimony centres.

The ability of antimony(III) to act as a halide acceptor is a recognised feature of antimony chemistry. Depending on the source of halide ion and, by inference, the choice of cation, a range of complex halide ions has been isolated and structurally characterised, namely $[SbCl_4]^-$,[1–4] $[SbCl_5]^{2-}$,[2,5–8] $[SbCl_6]^{3-}$,[3,9] $[Sb_2Cl_8]^{2-}$,[10] $[Sb_2Cl_9]^{3-}$,[11,12] and $[Sb_4Cl_{16}]^{4-}$.[10]

The usual preparation involves direct mixing with a quaternary ammonium (or related) salt. As an alternative approach we are investigating the possible use of electropositive metal halides as the source of halide ion(s) thereby giving rise to antimonate(III) salts involving metal cationic species which themselves may be of some chemical interest. The first such choice was $MgCl_2$. In this report we describe the crystal structure of $MgCl_2 \cdot 2SbCl_3 \cdot 6MeCN$ (1) as obtained from the reaction of $SbCl_3$ with $MgCl_2$ in acetonitrile solution.

Experimental

After allowing several hours mixing with stirring at room temperature, slow evaporation of an acetonitrile solution containing equimolar amounts of $MgCl_2$ and $SbCl_3$ gave a crop of transparent needles of the ternary complex $MgCl_2 \cdot 2SbCl_3 \cdot 6MeCN$ (1) (Found: C, 18.6; H, 2.4; Cl, 35.5; N, 10.9. Calc. for $C_{12}H_{18}Cl_8MgN_6Sb_2$: C, 18.1; H, 2.3; Cl, 35.6; N, 10.5%). The i.r. spectrum shows characteristic stretching vibrations for ν(CN) 2 292, 2 328 cm^{-1} and ν(SbCl) 278, 334 cm^{-1}. Although sensitive to air–moisture hydrolysis the product can be safely handled under conventional N_2 dry-box conditions.

X-Ray Crystallography.—*Crystal data*. $C_{12}H_{18}Cl_8MgN_6Sb_2$, M = 797.7, triclinic, space group $P\bar{1}$, a = 8.968(8), b = 10.220(11), c = 8.389(9) Å, α = 97.1(1), β = 79.8(1), γ = 78.1(1)°, Z = 1, D_m = 1.75 g cm^{-3}, D_c = 1.80 g cm^{-3}, $F(000)$ = 382, μ = 26.1 cm^{-1}, $\lambda(Mo\text{-}K_\alpha)$ = 0.710 7 Å.

A crystal of approximate size 0.25 × 0.15 × 0.25 mm was mounted on a Stoe Stadi-2 diffractometer and data collected *via* a variable width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of (2.0 + sin μ/tanθ). 2 365 Independent reflections were measured with $2\theta < 50°$ of which 2 165 with $I > 3\sigma(I)$ were used in the subsequent refinement. An empirical absorption correction was applied.[13] The structure was determined by the usual heavy-atom method and all non-hydrogen atoms were refined anisotropically. The methyl hydrogen atoms were refined as rigid groups, each with a common thermal parameter. The structure was refined by full-matrix least squares to R 0.070 (R' 0.078). Calculations were carried out using SHELX 76[14] on the Amdahl V7 at the University of Reading. Positional parameters are given in Table 1 and bond lengths and angles in Table 2.

Table 1. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	x	y	z
Sb(1)	4 985(1)	934(1)	2 822(1)
Cl(1)	3 226(3)	1 342(3)	942(3)
Cl(2)	6 943(3)	453(4)	5 350(4)
Cl(3)	6 698(3)	2 276(3)	1 627(4)
Cl(4)	3 499(3)	2 897(3)	4 671(4)
Mg	0*	5 000*	0*
N(1)	−74(12)	3 025(10)	−1 114(10)
C(2)	−155(10)	1 966(10)	−1 502(10)
C(3)	−280(14)	592(12)	−2 028(16)
N(4)	−45(9)	4 249(9)	2 267(9)
C(5)	−278(12)	3 693(10)	3 331(11)
C(6)	−540(19)	2 975(14)	4 678(15)
N(7)	2 533(10)	4 398(9)	−696(10)
C(8)	3 774(11)	4 123(11)	−1 300(12)
C(9)	5 363(14)	3 789(15)	−2 040(19)

* Parameter fixed.

Results and Discussion

The structure of $MgCl_2 \cdot 2SbCl_3 \cdot 6MeCN$ (1) shows $[Mg(MeCN)_6]^{2+}$ cations are present together with a rather complex polymeric chain of $[SbCl_4]^-$ ions in accord with an ionic

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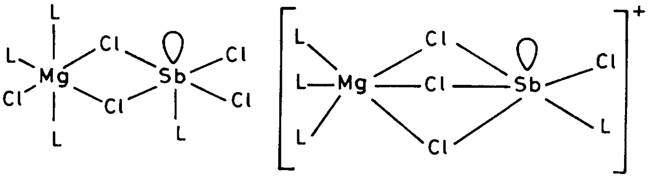
* Hexakis(acetonitrile)magnesium(II) di-μ-chloro-bis[trichloroantimonate(III)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

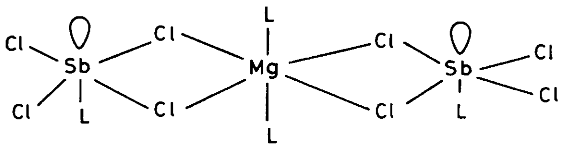
Table 2. Bond distances (Å) and angles (°) for $[Mg(MeCN)_6]^{2+}[Sb_2Cl_8]^{2-}$

Dimensions in the cation					
Mg–N(1)	2.136(9)	N(1)–C(2)	1.112(13)	C(5)–C(6)	1.433(14)
Mg–N(4)	2.134(7)	C(2)–C(3)	1.452(15)	N(7)–C(8)	1.101(13)
Mg–N(7)	2.179(8)	N(4)–C(5)	1.128(12)	C(8)–C(9)	1.402(16)
N(1)–Mg–N(4)	87.8(3)	Mg–N(1)–C(2)	171.4(7)	N(4)–C(5)–C(6)	178.8(12)
N(1)–Mg–N(7)	88.6(4)	N(1)–C(2)–C(3)	179.0(10)	Mg–N(7)–C(8)	168.3(8)
N(4)–Mg–N(7)	92.8(3)	Mg–N(4)–C(5)	164.7(8)	N(7)–C(8)–C(9)	178.7(10)
Dimensions in the anion					
Sb(1)–Cl(1)	2.433(2)	Sb(1)–Cl(4)	2.367(3)		
Sb(1)–Cl(2)	3.006(3)	Sb(1)–Cl(2′)	2.822(4)		
Sb(1)–Cl(3)	2.431(2)	Sb(1)–Cl(1″)	3.580(2)		
Cl(1)–Sb(1)–Cl(2)	175.62(8)	Cl(1)–Sb(1)–Cl(2′)	92.25(10)	Cl(4)–Sb(1)–Cl(2′)	85.10(10)
Cl(1)–Sb(1)–Cl(3)	94.02(10)	Cl(1)–Sb(1)–Cl(1″)	73.20(7)	Cl(4)–Sb(1)–Cl(1″)	160.52(9)
Cl(2)–Sb(1)–Cl(3)	89.37(10)	Cl(2)–Sb(1)–Cl(2′)	84.13(10)	Cl(2′)–Sb(1)–Cl(1″)	105.34(8)
Cl(1)–Sb(1)–Cl(4)	90.26(10)	Cl(2)–Sb(1)–Cl(1″)	110.11(7)	Sb(1)–Cl(1)–Sb(1″)	106.80(8)
Cl(2)–Sb(1)–Cl(4)	86.98(10)	Cl(3)–Sb(1)–Cl(2′)	171.76(11)	Sb(1)–Cl(2)–Sb(1′)	95.87(10)
Cl(3)–Sb(1)–Cl(4)	89.52(12)	Cl(3)–Sb(1)–Cl(1″)	81.64(8)		

Symmetry elements: (′); $1 - x, -y, 1 - z$: (″); $1 - x, -y, -z$.



Type (**A**)



Type (**B**)

formulation (see later discussion). Since the initial presence of $[SbCl_4]^-$ ions, arising from self-ionisation of $SbCl_3$, can be dismissed,[15] the transfer of chloride ions from Mg^{II} to Sb^{III} is most likely to occur by a molecular mechanism. Halogen-bridged intermediates of binuclear [(**A**)] or even trinuclear [(**B**)] types can be proposed; the lone pair associated with Sb^{III} may not show stereochemical activity as depicted and the number and arrangement of co-ordinated ligand molecules, L = MeCN, around each metal centre can vary.

The ability of $MgCl_2$ to give bimetallic complexes incorporating halogen bridging is well known, *e.g.* $[TiCl_4(\mu\text{-}Cl)_2MgL_4]$ [L = EtO_2CMe or[16] thf (tetrahydrofuran)[17]], $[FeCl_2(\mu\text{-}Cl)_2Mg(thf)_4]$,[18] or $[Mg_2(\mu\text{-}Cl)_3(thf)_6]^+$.[19] Equally there are precedents[17,20] for halide transfer as in the reaction of $[MgCl_2(thf)_2]$ with $[Mo(O)Cl_3(thf)_2]$ where removal of both chlorine atoms from Mg^{II} results in the formation of $[Mg(thf)_6][Mo(O)Cl_4(thf)]_2$. Again, $[MCl_4(thf)_2]$ (M = Ti or Zr) can act as the effective Lewis acid to remove the chlorine atoms from $[MgCl_2(thf)_2]$ to give $[Mg(thf)_6]^{2+}$ and either $[MCl_6]^{2-}$ or $[MCl_5(thf)]^-$ depending on the molar ratio of reactants and the actual conditions used.

Discussion of the Structure.—The unit cell of (**1**) is shown in Figure 1 as the *b* projection. The structure contains $[Mg(MeCN)_6]^{2+}$ cations and polymeric $[Sb_2Cl_8]^{2-}$ anions. The $[Mg(MeCN)_6]^{2+}$ cations are centrosymmetric with three independent Mg–N distances of 2.136(9), 2.134(7), and 2.179(8) Å. The dimensions of the Mg–N–C–Me units are similar and indicate that co-ordination to the metal has little effect on the linear geometry of the acetonitrile molecule.[21] Presumably the subtle differences in the bond lengths and angles, more noticeably Mg–N–C [171.4(7), 164.7(8), and 168.3(8)°] are due to packing effects. A search of the Cambridge Data Centre files shows that the observed Mg–N bond lengths are as expected: we noted 45 structures which contained an Mg–N–C fragment of which the average Mg–N distance was 2.17 Å, with a minimum value of 2.00 Å. Although $[Mg(MeCN)_6]^{2+}$ has been mentioned in terms of solution studies[22] there is no previous report of the structure of this cation. The structure of $[Mg(MeCN)_6]^{2+}2[AlCl_4]^-$ has been investigated[23] but it proved impossible to solve because of twinning and disorder. The structure of the isomorphous Fe^{II}–Fe^{III} salt was however determined.[23]

The $[SbCl_4]^-$ units are polymeric. There are three short Sb–Cl bonds in a *fac* arrangement [Sb–Cl(1) 2.433(2), Sb–Cl(3) 2.431(2), and Sb–Cl(4) 2.367(3) Å]. Two $SbCl_3$ moieties are bridged *via* two weaker bonds [Sb–Cl(2) 3.006(3) and Sb–Cl(2′) 2.822(4) Å] over a centre of symmetry to give $[Sb_2Cl_8]^{2-}$ units. These units are connected *via* a further weak contact [Sb–Cl(1″) 3.580(2) Å] to give a polymeric chain. An overall picture of the polymeric $[SbCl_4]^-$ units showing the centres of symmetry along the chain is given in Figure 2. The environment of the antimony atom is distorted octahedral and there is no evidence for a stereochemically active lone pair of electrons around antimony centres. As is apparent from Table 2, there are some distortions in Cl–Sb–Cl angles from 90° but these can be ascribed to bridging requirements rather than any lone-pair activity.

Previous structure determinations of $[SbCl_4]^-$ point to the fact that this particular anion can exist in various arrangements but seldom monomeric (C_{2v}). The observed structures are invariably polymeric with one feature in common, namely, a *fac* arrangement of three short Sb–Cl bonds. Thus, in pyridinium tetrachloroantimonate,[1] the Sb atom occupies an octahedral environment with Sb–Cl distances (2 ×) 2.38, (2 ×) 2.63, and (2 ×) 3.13 Å. In $[NH_3(C_6H_5)][SbCl_4]$,[2] there are two distinct

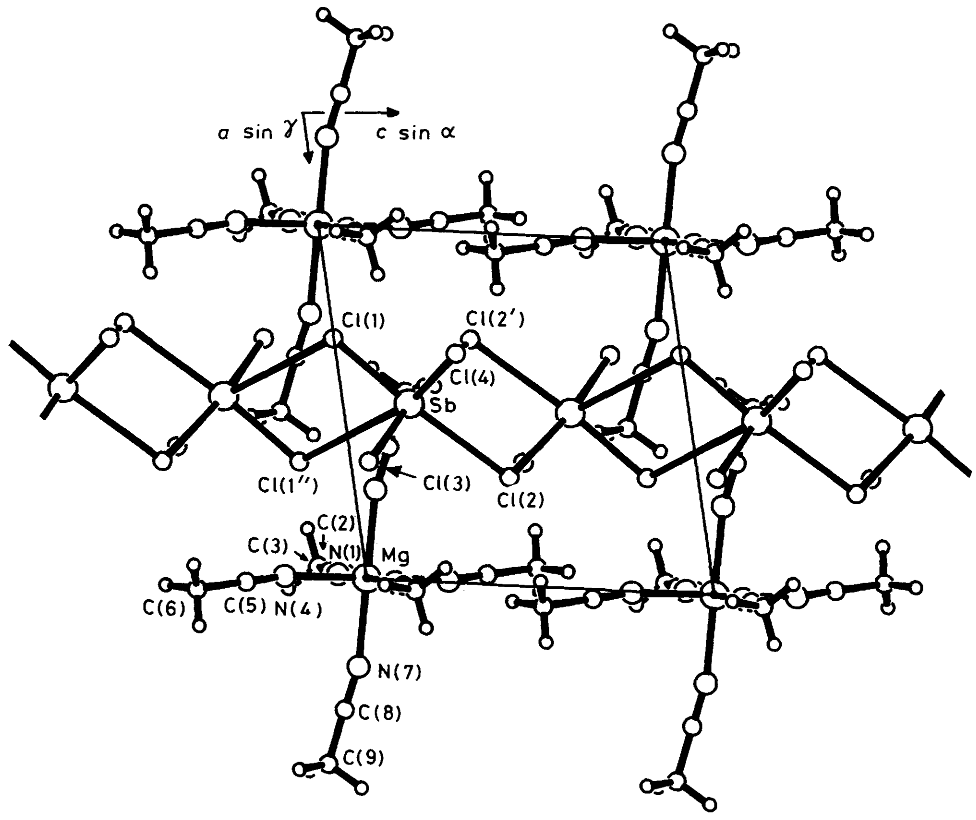


Figure 1. The unit cell of $[Mg(MeCN)_6]^{2+}[Sb_2Cl_8]^{2-}$ in the *b* projection

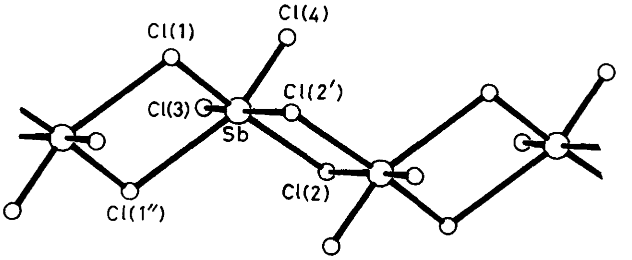


Figure 2. The polymeric structure of $[Sb_2Cl_8]^{2-}$ extending along the *c* direction. All Sb_2Cl_2 bridges are centrosymmetric

Sb atoms which form polymeric chains bridged by chlorine atoms. Each Sb atom occupies an octahedral environment with Sb–Cl distances of 2.38, 3.40, 2.50, 2.87, 3.23, and 3.37 Å and 2.43, 2.43, 2.59, 2.74, 3.05, and 3.02 Å respectively. On the other hand, in $[NHEt_3][SbCl_4]$,[3] the two independent Sb atoms are described as five-co-ordinate square pyramidal with three short Sb–Cl bonds (2.38—2.46 Å) and two long Sb–Cl bonds (2.82—2.95 Å).* In $[NHMe_3][SbCl_4]$,[4] the Sb atoms are octahedral with three short Sb–Cl bonds in a *fac* arrangement (2.48—2.57 Å) and three long Sb–Cl bonds (2.72—2.92 Å). In none of these structures is there any clear indication of stereochemical lone-pair activity.

The wide range of different structures suggests that the *fac* $SbCl_3$ moiety is the important part of the structure and this unit forms weak chlorine bridges the nature of which is dependent more upon packing forces than any stereochemical preferences of the metal atom.

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* In this particular structure the next closest chlorine atoms are at 3.86 and 3.50 Å in the two co-ordination spheres. The geometry of the co-ordination sphere of the second Sb is therefore very similar to that in the present molecule, which we prefer to describe as six-co-ordinate.

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