Halide Abstraction by Antimony(v): a Convenient Route to Antimonate(v) Salts involving Cationic Transition Metal Species. Crystal and Molecular Structure of *fac*-$[TiCl_3(MeCN)_3][SbCl_6]$

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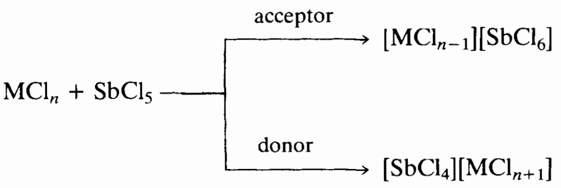
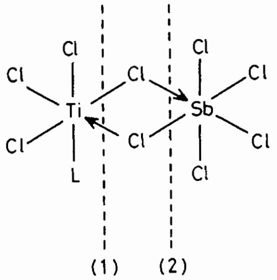
Treatment of the transition metal halides MCl_n (M = Ti, n = 4; M = V or Fe, n = 3; M = Fe, n = 2) with antimony(v) chloride in acetonitrile (L) provides antimonate(v) salts of the type $[MCl_{n-1}L_{7-n}][SbCl_6]$, characterised by ^{121}Sb n.m.r.; the structure of the product with M = Ti, n = 4 has been established by *X*-ray diffraction.

Early observations on the use of antimony(v) chloride as a non-aqueous solvent indicate that many covalent chlorides dissolve readily to give conducting solutions.[1] Evidently ionic species are formed, and since self-ionisation is almost negligible formation of charged chloro-antimony(v) species can only result from halide transfer either by acceptance on the part of Sb^V to give the $SbCl_6^-$ anion or by expulsion giving rise to the $SbCl_4^+$ cation (Scheme 1). Our interest lies in the exploitation of the acceptor (Lewis acid) role to remove halide ion(s) from transition metal (M) halides as a direct route to



Scheme 1



Scheme 2

antimonate(v) salts involving cationic species which may in themselves be of chemical interest and in some cases be otherwise 'inaccessible'.

Antimony(v) chloride dissolved in MeCN reacts with $TiCl_4$ in MeCN to give a bright yellow solid of composition $TiCl_4{\cdot}SbCl_5{\cdot}3MeCN$. This ternary complex has been identified by *X*-ray crystallography as the ionic salt $[TiCl_3(MeCN)_3][SbCl_6]{\cdot}CH_2Cl_2$.† The solvent dichloromethane molecule in the unit cell results from recrystallisation. The structure consists of discrete *fac*-$[TiCl_3(MeCN)_3]^+$ cations and $[SbCl_6]^-$ anions, both with crystallographically imposed *m* symmetry. In the six-co-ordinate Ti^{IV} cation (Figure 1) the independent Ti–Cl distances are 2.195(5) and 2.176(3) Å and Ti–N distances 2.160(9) and 2.172(3) Å. The structure is very much distorted from octahedral with Cl–Ti–Cl angles close to 100° and N–Ti–N angles close to 80°. The magnitude of the distortion is surprising, but as there are no obvious intermolecular causes or crystal field effects (d^0) it must be caused by the difference in size between the chlorine and nitrogen atoms. As expected the $[SbCl_6]^-$ anion is much more regular, with Sb–Cl distances in the range 2.330(3) to 2.360(3) Å and angles within 1° of the ideal.

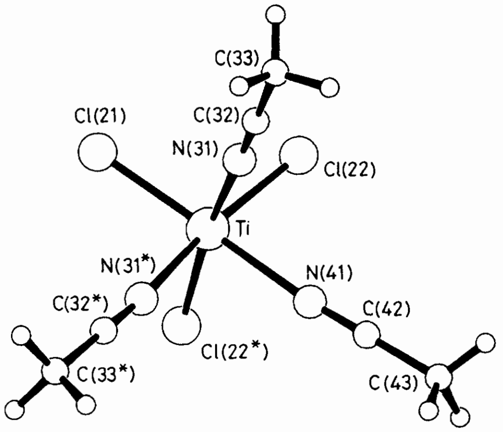


Figure 1. Molecular structure (with atom labelling) of the cation $[TiCl_3(MeCN)_3]^+$

Table 1. Antimonate(v) salts prepared.

Compound	Colour	M.p./°C	^{121}Sb N.m.r.^{a} δ (p.p.m.)	^{121}Sb N.m.r.^{a} $W_{\frac{1}{2}}$/Hz
(**1**) $[TiCl_3(MeCN)_3][SbCl_6]$	Yellow	95—96	−0.2	191
(**2**) $[VCl_2(MeCN)_4][SbCl_6]$	Green	156—158	+1.3	196
(**3**) $[FeCl_2(MeCN)_4][SbCl_6]$	Yellow	160—161	−2.3	182
(**4**) $[FeCl(MeCN)_5][SbCl_6]$	Yellow	155—157	−1.7	172

^{a} MeCN solutions (*ca.* 10^{-2} M) doped with 10% (by volume) of CD_3CN with $[Et_4N][SbCl_6]$ (δ 0, $W_{\frac{1}{2}}$ 190 Hz) as external reference.

The general applicability of this approach is demonstrated by the preparation of other antimonate(v) salts (V^{III}, Fe^{III}, and Fe^{II}) listed in Table 1. Compounds (**1**)—(**4**) give satisfactory microanalytical data, and positive identification of $[SbCl_6]^-$ ions is provided by the ^{121}Sb n.m.r. (95.73 MHz) data. All show one symmetrical signal and there is an evident shift independence with respect to counter-ion even when paramagnetic species are involved. An *X*-ray structure determination programme is under way to resolve the question of *cis*/*trans* geometry of the $[MCl_2(MeCN)_4]^+$ cations. The i.r. spectra of compounds (**2**) and (**3**) contain a sharp ν(CN) doublet profile, *e.g.* V^{III} 2321 and 2296 cm^{-1}, Fe^{III} 2302 and 2278 cm^{-1}, and the electronic spectrum of compound (**2**) shows bands at 14 388, 28 248 (pronounced shoulder), and 31 152 cm^{-1}, which can be assigned as $^3T_{1g}(^3A_{2g}) \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(^3A_{2g}) \rightarrow {}^3T_{1g}(P)(^3E_g)$, and $^3T_{1g}(^3A_{2g}) \rightarrow {}^3T_{1g}(P)(^3A_{2g})$, respectively, for a tetragonally distorted (D_{4h}) d^2 octahedral system, *cf.* $[V(H_2O)_4Cl_2]^+$.[2,3] We take this to indicate a common *trans*-structure. The formation of the solvated cation $[FeCl_2(MeCN)_4]^+$ from the $SbCl_5/FeCl_3$ system rather than anionic $FeCl_4^-$ as observed for the $PCl_5/FeCl_3$[4] and $MgCl_2/FeCl_3$[5] systems serves to emphasize the rapacious Lewis acid capacity of Sb^V.

The transfer of halide ion from M to Sb most likely proceeds by a molecular mechanism involving halogen-bridged intermediate(s), *e.g.* for the $TiCl_4/SbCl_5$ reaction we can postulate the cleavages shown in Scheme 2. Asymmetric cleavage (1) implicates Sb^V as the preferred halogen acceptor and the choice of L = MeCN as a strongly co-ordinating aprotic solvent not only allows solvent occupancy of vacant co-ordination sites created on the titanium centre following halide expulsion but also avoids problems of Sb–Cl/Ti–Cl solvolysis side reactions. The (unlikely) reverse situation, asymmetric cleavage (2), offers a route to $SbCl_4^+$ but with the daunting proviso that the chosen metal M exceeds Sb^V in Lewis acid character.

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† *Crystal data*: $C_7H_{11}N_3Cl_{11}SbTi$, M = 696.8, orthorhombic, space group *Pmnb* (No. 62), Z = 4, a = 10.456(8), b = 23.527(22), c = 9.654(8) Å, U = 2374.9 Å^3, D_c = 1.95 g cm^{-3}, $F(000)$ = 1336, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 27.2 cm^{-1}; 2435 independent reflections with $2\theta_{max}$ 50° were measured on a diffractometer, of which 1439 with $I > 3\sigma(I)$ were used in the calculations. An empirical absorption correction was applied. The structure was solved by heavy atom methods and refined (Sb, Ti, Cl, N, and C anisotropic, H isotropic as part of rigid groups) to R 0.061. The final difference Fourier map showed no significant peaks (max. 0.76, min. −0.98 e Å^{-3}). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The isolation and structural characterisation of $MgCl_2{\cdot}2SbCl_3{\cdot}6MeCN$ as the antimonate(III) salt $[Mg(MeCN)_6]^{2+}[Sb_2Cl_8]^{2-}$ indicates that Sb^{III} is equally effective in selective halide ion abstraction from covalent metal halides.[6]

We thank Dr. A. Harrison for the ^{121}Sb n.m.r. measurements, S.E.R.C. for funds for the diffractometer, and Mr. A. W. Johans for assistance with the crystallographic investigations.

Received, 23rd March 1987; Com. 370

References

1 D. S. Payne, 'Halides and Oxyhalides of Group V Elements as Solvents,' in 'Nonaqueous Solvent Systems,' ed. T. C. Waddington, Academic Press, London, 1965, ch. 8.
2 P. J. McCarthy, J. C. Lauffenburger, M. M. Schreiner, and D. C. Rohrer, *Inorg. Chem.*, 1981, **20**, 1571.
3 W. F. Donovan and P. W. Smith, *J. Chem. Soc., Dalton Trans.*, 1975, 894.
4 T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, 1968, **7**, 2150.
5 P. Sobota, T. Pluzinski, and T. Lis, *Polyhedron*, 1984, **3**, 45.
6 P. P. K. Claire, G. R. Willey, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, in the press.