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The Crystal and Molecular Structure of Diethylenetriammonium Hexachloroantimonate(III)

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A compound of the type [DenH$_3$]SbCl$_6$ (DenH$_3$ = diethylenetriammonium cation) was prepared and characterized by means of structural and vibrational measurements. The structure consists of monomeric SbCl$_6$$^{3-}$ anions and triprotonated diethylenetriammonium cations. The SbCl$_6$$^{3-}$ anion has a strongly distorted octahedral geometry, presenting three short (2.415–2.495 Å) and three long (2.836–3.114 Å) Sb–Cl bonds. The presence of multiple hydrogen bonds, mainly involving the counterion and the three long-bonded chlorine atoms, is considered to be responsible for the octahedral distortion. Vibrational properties of the complex are discussed in the light of its known crystal structure.

Introduction

The great interest in haloantimonates(III) derives from the fact that they may assume various structural geometries, depending on the role of the lone pair on the metal ion. Among them the octahedral coordination, although unexpected on the basis of the valence-shell electron-pair repulsion (VSEPR) model of Sidgwick and Powell [1] and of Gillespie and Nyholm [2, 3], is not unusual, although generally obtained by the presence of bridging halogen atoms giving rise to infinite chains [4, 5]. Only one compound, $Co(NH_3)_6SbCl_6$, is known to contain perfectly octahedral discrete $SbCl_6^{3-}$ units [6].

In an effort to explore in more detail the competitive role of lone pairs and of hydrogen bonding between ligand and counterion in deforming the octahedral configuration in discrete: ML_6^{3-} units, we have now investigated the vibrational and structural properties of a diethylenetriammonium hexachloroantimonate(III) compound. This compound represents the first case of discrete $SbCl_6^{3-}$ units having an organic molecule (triprotonated) as a counterion.

Experimental

Preparation of the Diethylenetriammonium Hexachloroantimonate(III)

By mixing diethylenetriamine and $SbCl_3$ (ligand to metal molar ratio of 1:1) in methanol and by adding concentrated hydrogen chloride until the white precipitate disappears and by slow evaporating white crystals separated. The compound may be recrystallized from methanol. Found: C, 11.04; H, 3.73; N, 9.59. Calc. for $C_4H_{16}N_3SbCl_6$: C, 11.04; H, 3.71; N, 9.67.

Physical Measurements

Infrared spectra were recorded with a Perkin Elmer spectrophotometer in nujol mull on polythene. Raman spectra were recorded for solid samples with a Jobin–Yvon instrument equipped with an argon laser.

Structure Determination

A colourless crystal of the title compound was mounted on a Philips PW 1100 four circle diffractometer in a random orientation, using Mo-Kα radiation. Crystal data and details of parameters associated with collection and refinement of the structure are given in Table I. Cell dimensions were determined by diffractometry using 25 reflections in the range $16° \leqslant \theta \leqslant 20°$. The intensities of 2565 reflections were collected using the θ–2θ scan technique with individual profile analysis [7]; 2288 reflections having $I > 3\sigma(I)$ were considered as 'observed' and were used in the analysis. Data reduction included correction for Lorentz, polarization and absorption effects (an empirical absorption correction was applied).

The centrosymmetric space group was assumed and confirmed by successful refinement. Location of the antimony atom from the Patterson map led to the full structure by standard Fourier methods. Refinement was carried out by full matrix least squares,

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TABLE I. Summary of Crystal Data Collection.

Molecular formula	$C_4H_{16}Cl_6N_3Sb$
Mol. wt.	440.7
a, Å	10.016(3)
b, Å	10.076(3)
c, Å	8.123(2)
α, deg	67.96(3)
β, deg	105.88(3)
γ, deg	100.03(3)
V, Å^3	728.5(4)
d_{obs} (by flotation), g cm^{-3}	2.00
d_{calc}, g cm^{-3}	2.01
Z	2
Crystal size, mm	0.20 × 0.29 × 0.62
Radiation (λ, Å)	Mo-Kα ($\bar{\lambda}$ = 0.710688)
2θ, limits, deg	5–50
Temp., °C	20
Abs. coeff., cm^{-1}	29.91
F(000), electrons	428
Reflections collected	2656
Unique data used (I > 3σ(I))	2288
No. of variables	144
R ($R = \Sigma\Delta F/\Sigma\|F_o\|$)	0.0365
R_w ($R_w = [\Sigma w\|\Delta F\|^2/\Sigma w F_o^2]^{1/2}$	0.042
GOF (GOF = $[\Sigma w\|\Delta F\|^2/(NO - NV)]^{1/2}$	0.54
(NO = No. of observed reflections	
NV = No. of variables refined)	

anisotropically for Sb, Cl, C and N; isotropically for hydrogen atoms which were fixed in the calculated positions. The refinement converged at $R = 0.0365$, $R_w = 0.042$ using the weighting scheme $w^{-1} = \sigma^2 F_o + 0.01088\ F_o^2$. The atomic scattering factors and correction for anomalous dispersion were applied using the values given in the International Tables of X-ray Crystallography [8]. Final atomic coordinates and thermal parameters are reported in Table II and III. Interatomic distances and angles are given in Table IV.

All the calculations were performed by using a CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale, Bologna with the SHELX system of programs and the financial support of the University of Parma.

Results and Discussion

Crystal Structure of the Compound

The structure of the title compound consists of monomeric $SbCl_6^{3-}$ anions and triprotonated diethylenetriammonium cations. The $SbCl_6^{3-}$ configuration is distorted octahedral, in which the different Sb–Cl bonds are present. The shortening of Sb–Cl(1) = 2.495(1), Sb–Cl(2) = 2.521(2), Sb–Cl(3) = 2.415(1) Å bonds appears to be a *trans* effect in response to the lengthening of the Sb–Cl(4) = 2.836(1), Sb–Cl(5) = 2.846(2), Sb–Cl(6) = 3.114(2) Å, respectively. The angles involving atoms mutually *cis* (Fig. 1) range from 81.73(6) to 97.97(6)°, while the *trans* angles are 174.47(7), 173.3(1), 170.50(6), the last involving Cl(3) and Cl(6) atoms. The deviations of these bond angles from the ideal values of 90 and 180° are consistent with the presence of the long bonds, the largest deviations from 90° involving the chlorine atoms more weakly bonded, Cl(4)–Sb–Cl(5) = 97.97(6)°, Cl(5)–Sb–Cl(6) = 81.7(1)°. This kind of coordination is different with respect to that found in other chloroantimonate anions. In fact in K_2SbCl_5 [9] and $(NH_4)_2SbCl_5$ [10] the chloroantimonate(III) anions are square-pyramidal coordinated, in agreement to that suggested by Gillespie and Nyholm [3] for AB_5E system (A = central atom; B = ligand; E = unshared electron pair). In $Co(NH_3)_6$-

TABLE II. Fractional Atomic Coordinates (×10^4).

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Sb	2476(0)	2635(0)	2260(0)	H2	7213(50)	−773(50)	11979(50)
Cl1	3485(1)	5131(1)	873(1)	H3	7184(50)	675(50)	12684(60)
Cl2	1482(2)	2615(2)	−937(2)	H4	8736(50)	521(60)	10006(70)
Cl3	449(1)	3562(1)	2375(1)	H5	8511(50)	2100(60)	10320(70)
Cl4	1094(1)	−130(1)	3565(2)	H6	6127(50)	144(60)	9145(70)
Cl5	3833(1)	2913(1)	5698(2)	H7	6059(50)	1883(60)	9136(70)
Cl6	5316(2)	1525(2)	2719(2)	H8	5886(40)	1912(40)	6087(50)
N1	7789(5)	183(5)	12185(6)	H9	7485(40)	1125(40)	6846(50)
C1	8046(5)	1046(6)	10338(7)	H10	7047(50)	4001(50)	6762(70)
C2	6673(5)	1195(5)	8944(6)	H11	8648(50)	3212(50)	7589(70)
N2	6890(4)	1833(4)	7033(5)	H12	8288(60)	3101(60)	4424(70)
C3	7658(5)	3287(5)	6614(7)	H13	8705(60)	4808(60)	4647(70)
C4	7919(6)	3921(6)	4707(7)	H14	7014(50)	4999(40)	2037(70)
N3	6649(5)	4443(5)	3275(6)	H15	6206(50)	5191(50)	3602(60)
H1	8760(50)	−97(50)	13170(50)	H16	5865(50)	3599(50)	3082(60)

TABLE III. Anisotropic Thermal (×10^4) Parameters for Sb, Cl, N and C with E.s.d.'s in Parentheses.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sb	233(3)	268(3)	243(3)	−120(2)	84(2)	5(1)
Cl(1)	443(8)	335(7)	349(7)	−153(6)	180(6)	−47(6)
Cl(2)	471(8)	459(8)	290(7)	−194(6)	85(6)	−65(6)
Cl(3)	294(7)	459(8)	568(9)	−232(7)	163(6)	54(6)
Cl(4)	313(7)	373(7)	370(7)	−140(6)	107(6)	65(5)
Cl(5)	352(7)	399(8)	324(7)	−164(6)	48(5)	76(6)
Cl(6)	405(8)	409(8)	563(9)	−251(7)	177(7)	16(6)
N(1)	328(25)	462(28)	210(22)	−55(20)	74(18)	48(20)
N(2)	288(22)	287(21)	275(20)	−111(17)	90(17)	24(17)
N(3)	463(29)	328(25)	330(23)	−113(20)	55(21)	46(20)
C(1)	208(25)	457(32)	244(24)	−80(23)	80(19)	−13(21)
C(2)	260(26)	375(29)	227(24)	−103(21)	72(20)	43(21)
C(3)	296(27)	312(27)	380(28)	−159(22)	74(22)	−66(21)
C(4)	344(30)	429(31)	316(29)	−51(24)	153(23)	40(24)

TABLE IV. Bond Distances (Å) and Angles (deg).

a) In the coordination polyhedron			
Sb–Cl(1)	2.495(1)	Sb–Cl(4)	2.836(2)
Sb–Cl(2)	2.521(2)	Sb–Cl(5)	2.846(2)
Sb–Cl(3)	2.415(1)	Sb–Cl(6)	3.114(2)
Cl(1)–Sb–Cl(2)	87.47(6)	Cl(2)–Sb–Cl(6)	95.50(8)
Cl(1)–Sb–Cl(3)	90.39(7)	Cl(3)–Sb–Cl(4)	86.27(7)
Cl(1)–Sb–Cl(4)	174.47(7)	Cl(3)–Sb–Cl(5)	88.78(6)
Cl(1)–Sb–Cl(5)	86.36(6)	Cl(3)–Sb–Cl(6)	170.50(6)
Cl(1)–Sb–Cl(6)	88.59(7)	Cl(4)–Sb–Cl(5)	97.97(6)
Cl(2)–Sb–Cl(3)	93.89(7)	Cl(4)–Sb–Cl(6)	95.42(7)
Cl(2)–Sb–Cl(4)	88.35(7)	Cl(5)–Sb–Cl(6)	81.73(6)
Cl(2)–Sb–Cl(5)	173.29(9)		
b) In the aliphatic amine			
N(1)–C(1)	1.493(7)	N(2)–C(3)	1.494(6)
C(1)–C(2)	1.513(6)	C(3)–C(4)	1.516(8)
C(2)–N(2)	1.502(6)	C(4)–N(3)	1.487(7)
N(1)–C(1)–C(2)	109.1(4)	N(2)–C(3)–C(4)	114.2(4)
C(1)–C(2)–N(2)	111.3(4)	C(3)–C(4)–N(3)	113.1(5)

SbCl$_6$, discrete SbCl$_6^{3-}$ anions with regular octahedral coordination geometry, unusual for AB$_6$E complexes [3], are present [6].

In the present compound the geometry of the SbCl$_6^{3-}$ octahedron is very similar to that found in chloroantimonate(III) salts with organic cations [4, 5], although in theses compounds the chloroantimonate(III) anions build up chains, or dimers, by bridging chlorine atoms. The presence of monomeric units in our compound can be ascribed to the triprotonated aliphatic amine, which, involving the chlorine atoms in hydrogen bonds (Table V), makes it impossible to connect the coordination polyhedra with bridging chlorine atoms. Only Cl(3), which exhibits the shortest Sb–Cl bond distance, is not involved in hydrogen bonds.

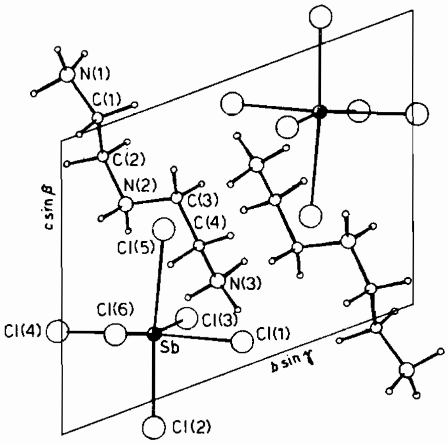

Fig. 1. Projection of the structure along [100] axis.

Distortion from octahedral geometry in our SbCl$_6^{3-}$ anion may also be ascribed to the strong hydrogen bonding, which involves five of the six coordinated chlorine atoms. The polyhedron distortion is caused by lengthening of distances of Cl(4), Cl(5) and Cl(6) atoms, which present the strongest multiple (Cl(5) and Cl(6) trifurcated) hydrogen bonds. For this compound the antimony lone pair may therefore be considered stereochemically inactive.

Bond distances and angles in the aliphatic amine are regular for C(sp^3)–C(sp^3) and C(sp^3)–N(sp^3) bonds [11], the torsion angles around C–C and C–N bonds being:

N(1)–C(1)–C(2)–N(2) = −170.3(4)°

C(1)–C(2)–N(2)–C(3) = −59.2(6)°

C(2)–N(2)–C(3)–C(4) = 178.3(4)°

N(2)–C(3)–C(4)–N(3) = 74.6(6)°

TABLE V. Possible Hydrogen Bonds.

Donor–H		Donor···Acceptor		H···Acceptor		Donor–H···Acceptor	
N(2)–H(8)	1.08(4)	N(2)···Cl(5)^{i}	3.193(4)	H(8)···Cl(5)^{i}	2.34(4)	N(2)–H(8)···Cl(5)^{i}	135(2)
N(3)–H(16)	1.08(5)	N(3)···Cl(6)^{i}	3.151(6)	H(16)···Cl(6)^{i}	2.18(5)	N(3)–H(16)···Cl(6)^{i}	149(4)
N(1)–H(1)	1.08(4)	N(1)···Cl(4)^{ii}	3.222(4)	H(1)···Cl(4)^{ii}	2.28(5)	N(1)–H(1)···Cl(4)^{ii}	145(3)
N(1)–H(2)	1.08(5)	N(1)···Cl(5)^{iii}	3.326(5)	H(2)···Cl(5)^{iii}	2.56(4)	N(1)–H(2)···Cl(5)^{iii}	127(3)
N(1)–H(3)	1.08(6)	N(1)···Cl(6)^{iv}	3.217(6)	H(3)···Cl(6)^{iv}	2.20(6)	N(1)–H(3)···Cl(6)^{iv}	156(4)
N(2)–H(9)	1.08(5)	N(2)···Cl(4)^{v}	3.103(5)	H(9)···Cl(4)^{v}	2.04(5)	N(2)–H(9)···Cl(4)^{v}	168(3)
N(3)–H(15)	1.08(6)	N(3)···Cl(5)^{vi}	3.219(6)	H(15)···Cl(5)^{vi}	2.20(6)	N(3)–H(15)···Cl(5)^{vi}	157(4)
N(3)–H(14)	1.08(5)	N(3)···Cl(1)^{vii}	3.200(5)	H(14)···Cl(1)^{vii}	2.33(6)	N(3)–H(14)···Cl(1)^{vii}	137(3)
N(3)–		N(3)···Cl(2)^{vii}	3.418(5)	H(14)···Cl(2)^{vii}	2.59(4)	N(3)–H(14)···Cl(2)^{vii}	133(3)

Equivalent positions:
i = x, y, z
ii = x + 1, y, z + 1
iii = –x + 1, –y, –z + 2
iv = x, y, z + 1
v = –x + 1, –y, –z + 1
vi = –x + 1, –y + 1, –z + 1
vii = –x + 1, –y + 1, –z

TABLE VI. Assignments of the Sb–Cl bands in [DenH$_3$]SbCl$_6$ Compound.

	O_h	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$
	C_{3v}	A_1	E	$A_1 + E$	$A_1 + E$	$A_1 + E$	$A_2^{a} + E$
[DenH$_3$]SbCl$_6$	R	307vs	258s			145m	132sh
	IR		245sh	260s,br,as	155s,br,as	140sh	

^{a}Inactive.

Vibrational Spectra

The far-I.R. and Raman spectra of the [DenH$_3$]-SbCl$_6$ compound (Table VI) are compatible with the presence of distorted octahedral antimony sites. A regular octahedral molecule gives rise to six normal modes of vibration, of these $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(E_{2g})$ are Raman active, $\nu_3(F_{1u})$ and $\nu_4(F_{1u})$ are infrared active, and $\nu_6(F_{2u})$ is inactive, which are easily assigned assuming the usual ordering $\nu_1 > \nu_2 > \nu_5$ and $\nu_3 > \nu_4$. For our compound the broad asymmetric nature of the infrared active bands and the coincidences in the infrared and Raman spectra suggest the lowering of the O_h symmetry. This agrees with the structural results reported above, namely that although the environment of Sb atoms in the SbCl$_6^{3-}$ units is based on an octahedron, there is considerable displacement of the Sb atoms along three-fold axis for the presence of three short and three long Sb–Cl bonds. Therefore the vibrational data may be better interpreted in terms of C_{3v} symmetry.

The comparison of the assignments of the Sb–Cl bands in our compound with those reported in the literature for other similarly distorted compounds, interpreted in terms of C_{3v} symmetry [12–14], supports our considerations.

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Supplementary Material Available

Listings of observed and calculated structure factors and of isotropic thermal parameters for hydrogen atoms (14 pages) are available from the Editor on request.

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