The First Simple, Donor-Free Salt of the $Sb(OTeF_5)_6^-$ Anion: Synthesis, Structure, Characterization, and Thermochemistry of $Cs[Sb(OTeF_5)_6]$

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Received February 23, 2001

Introduction

Highly resistant and weakly coordinating anions have been the focus of much recent work,[2] and, therefore, a series of hexateflatometalates $M(OTeF_5)_6^-$ (M = As, Sb, Bi, Nb) has been prepared as NR_4^+ (R = Me, Et)[3] and silver salts.[4] However, we showed that for $Ag[Sb(OTeF_5)_6]$ the silver cation remained coordinated by a small but undetermined number of CH_2Cl_2 solvent molecules, which reacted with some of our desired products.[5] When SO_2ClF was used as a solvent, incomplete substitution and formation of $Ag[Sb(Cl_x)(OTeF_5)_{6-x}]$ resulted.[6] Cationic silver−chalcogen complexes such as $[Ag_2Se_6(SO_2)_2][Sb(OTeF_5)_6]_2$ were formed from mixtures of $Ag[Sb(OTeF_5)_6]$ and chalcogen halides E_nHal_2 (E = S, Se, n = 3−5),[7] presumably due to the highly polarizing nature of the Ag^+ cation. In fact, it is so polarizing that the Ag^+ cation in $Ag[Sb(OTeF_5)_6]$ is sufficient to oxidize elemental tellurium to give $[Te_4][Sb(OTeF_5)_6]_2$.[5] Therefore, an alternative starting material was needed to introduce the $Sb(OTeF_5)_6^-$ anion by a metathesis reaction. Herein, we present the synthesis, characterization, and X-ray crystal structure of unsolvated $Cs[Sb(OTeF_5)_6]$, **1**. Cs^+ is less polarizing than Ag^+, and so this salt is highly useful in introducing the $Sb(OTeF_5)_6^-$ anion by a metathesis reaction with halides or hexafluorometalates MF_6^- (M = As, Sb), especially since $CsMF_6$ is poorly soluble in SO_2, our standard solvent for reactions.

Experimental Section

Reactions were carried out in thick-walled 10 mm (o.d.) NMR tubes fitted with a special J. Young NMR valve. General techniques and methods have been described elsewhere.[8] Additional information is found in the Supporting Information.

Reaction Utilizing CsBr. Anhydrous CsBr (0.165 g, 0.775 mmol) was weighed into a 10 mm (o.d.) thick-walled NMR tube, and a stock solution of $Ag[Sb(OTeF_5)_6]$ in SO_2 (2.0 mL, 0.319 M, 0.638 mmol) was transferred[9] onto the CsBr. Immediately, a yellow beige precipitate formed that is likely AgBr; see below. Additional SO_2 was condensed up to a height of 5.5 cm onto the frozen mixture, and NMR spectra were obtained. The solution was then decanted[10] into a one bulb vessel. The remaining material (insoluble in SO_2) was soluble in aqueous $Na_2S_2O_3$ solution and weighed 0.193 g (calcd for AgBr, 0.120 g). Successive reduction of the solvent of the filtrate and cooling to 4 °C afforded colorless crystals of $Cs[Sb(OTeF_5)_6]$, which were isolated (0.88 g, 81%).

Reaction Utilizing CsI. Solid beige $Ag[Sb(OTeF_5)_6]$ (1.727 g, 1.040 mmol) and anhydrous CsI (0.330 g, 1.269 mmol) were weighed into a 10 mm (o.d.) thick-walled NMR tube. Immediately after the mixing, a reaction occurred at some spots (brownish color). Approximately 4 g of SO_2 (5.5 cm height) was condensed onto the solid mixture and immediately gave a dark violet solution (iodine color) over a yellow precipitate. All volatiles were removed in vacuo, and the solid residue was exposed to a dynamic vacuum for 2 h. However, after redissolution in approximately 4 g of SO_2, the color of the solution was only slightly less intense, but further evacuation to remove the last traces of iodine was avoided in order not to risk decomposition as observed in the case of the silver salt. A ^{19}F NMR spectrum of this sample only showed lines attributable to the $Sb(OTeF_5)_6^-$ anion [$\delta^{19}F = -40.7$, $^1J(^{19}F-^{125}Te) = 3597$ Hz]. Decantation by a direct connection[10] and removal of all volatiles led to a grayish/metallic appearing microcrystalline material that a gave a very intense Raman spectrum identical to that of solid iodine ($\nu = 181$ cm^{-1}).

Results and Discussion

$Ag[Sb(OTeF_5)_6]$[11] reacted cleanly with CsBr in SO_2 solution to give insoluble AgBr and the very SO_2-soluble $Cs[Sb(OTeF_5)_6]$ (**1**) salt in 81% recovered yield (eq 1).

$$CsBr + Ag[Sb(OTeF_5)_6] \rightarrow Cs[Sb(OTeF_5)_6]\ (\mathbf{1}) + AgBr \qquad (1)$$

The in situ ^{19}F NMR spectrum of this reaction only showed a signal attributable to the $Sb(OTeF_5)_6^-$ anion at $\delta^{19}F = -40.7$ [$^1J(^{19}F-^{125}Te) = 3565$ Hz), which is unchanged compared to the original signal of $Ag[Sb(OTeF_5)_6]$ in SO_2 ($\delta^{19}F = -40.6$)[5] and comparable to those reported for the $Sb(OTeF_5)_6^-$ anion in CH_2Cl_2 ($\delta^{19}F = -41.4$ to -41.8).[3,4] The expected AB_4 spin system of the $OTeF_5$ group was not observed; rather, the spectrum collapsed to a single line, in agreement with earlier findings.[3−5]

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[‡] Part of this work has been presented at the 5th RSC/GDCh conference (Inorganic Chemistry) in Brighton, U.K., 1999.

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(1) X-ray crystal structure determination.

(2) For recent reviews, see: (a) Reed, C. *Acc. Chem. Res.* **1998**, *31*, 133. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

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(9) The transfer vessel was built from a graded cylinder glass blown onto a J. Young valve and a glass tube suitably equipped to attach the valve of a 10 mm NMR tube. The latter connection includes a Rotoflo valve to flame dry the evacuated connection prior to use. To ensure complete transfer of the stock solution, small amounts of the solvent were condensed three times into the cylinder and poured back to the reaction vessel.

(10) Direct connection: A 0.25 in. glass tubing incorporating one valve to allow flame drying. The reaction vessels were connected to the direct connection by Gyro Lock fittings (Swage Lock Corp.). A short (2 cm) Teflon tubing was inserted into the glass tubing within the Gyro Lock to avoid contact of metal and solution. A variation of this device is described in ref 8.

(11) Containing a small but undetermined number of CH_2Cl_2 molecules.

10.1021/ic010217+ CCC: $20.00

Table 1. Observed Raman Frequencies (Relative Areas under the Peak) of the $Sb(OTeF_5)_6^-$ Anion in **1** Compared to and Assigned on the Basis of Those Found in $[NMe_4][Sb(OTeF_5)_6]^3$

assignment	$[NMe_4][Sb(OTeF_5)_6]$	$Cs[Sb(OTeF_5)_6]$
$\nu_{as}(TeF_4)$	737 (8)	707 (12)
	731 (9)	693 (3)
	722 (sh)	
$\nu_s(Te-F)$	706 (50)	723 (50)
$\nu_{sym}(TeF_4)$	659 (100)	666 (100)
$\nu_{as}(TeF_4)$	643 (18)	633 (13)
$\nu_{as}(Te-O)^a$	426 (8)	409 ± 20 (20, broad)
	397 (22)	
$\delta_{as}(F-TeF_4)$	334 (19)	337 (17)
$\delta_{sym}(F-TeF_4)$	304 (16)	305 (11)
$\delta_{ciss}(TeF_4)$	236 (14)	239 (15)
$\delta(Te-O-Sb)$	139 (34)	140 (15)
	130 (17, sh)	
$\delta(Te-O-Sb)$	108 (15)	110 (sh)
and lattice modes	90 (9)	85 (3)

[a] Coupled with Sb−O.[3]

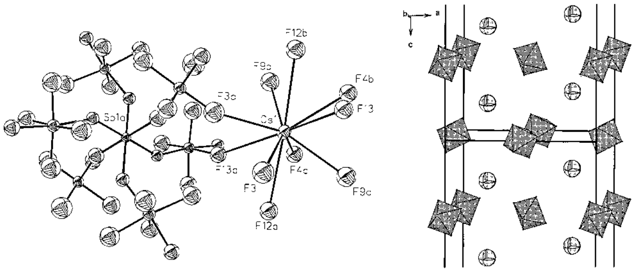

Figure 1. Section of the solid-state structure of $Cs[Sb(OTeF_5)_6]$ (**1**). One $Sb(OTeF_5)_6^-$ anion and all Cs- -F contacts are shown on the left; thermal ellipsoids are drawn at the 25% probability level. The solid-state packing omitting all Te and F atoms is shown on the right (SbO_6 octahedra and Cs ellipsoids).

However, when CsBr was replaced by CsI, an intensely red violet colored solution resulted (color of iodine). The Raman spectrum of the soluble material of this reaction was identical to that of elemental iodine, which implies that the I^- in CsI was oxidized to I_2, and indeed, a thermochemical evaluation of this reaction showed that the oxidation of I^- by Ag^+ (in SO_2) is exothermic but that of Br^- [12] is endothermic. The in situ ^{19}F NMR spectrum of the last reaction only showed a signal attributable to the $Sb(OTeF_5)_6^-$ anion at $\delta^{19}F = -40.7$ [$^1J(^{19}F-^{125}Te) = 3597$ Hz); no other fluorine containing species were found. In this case, Raman spectroscopy showed only a very intense iodine band. However, for **1** the Raman spectrum of $Cs[Sb(OTeF_5)_6]$ (actual spectrum deposited) exclusively showed bands attributable to the $Sb(OTeF_5)_6^-$ anion indicating an unsolvated Cs^+ cation. The Raman bands of the $Sb(OTeF_5)_6^-$ anion are collected in Table 1 and are compared to and assigned on the basis of those reported for $[N(CH_3)_4^+][Sb(OTeF_5)_6^-]^3$.

The bands of both anions are in very good agreement. The asymmetric stretching vibrations $\nu_{as}(TeF_4)$ in **1** are at lower energy than those in the NMe_4^+ salt. No indication of coordinated solvent SO_2 was found in $Cs[Sb(OTeF_5)_6]$ (**1**).

The solid-state structure of a colorless single crystal of $Cs[Sb(OTeF_5)_6]$ was determined.[13,14] Due to the small size of the crystal, the collected data set was weak, and consequently, the data-parameter ratio was only 4:1 rendering extensive structural discussions inadequate. However, we can reasonably give a general description of the structure and obtain thermochemical volumes and radii. Compound **1** forms an ionic lattice built from unsolvated Cs^+ cations and $Sb(OTeF_5)_6^-$ anions that adopt a zinc blend type structure. The Cs atom is coordinated by six stronger Cs- -F contacts at 3.09−3.14 Å and four weaker contacts at 3.42−3.43 Å that are below the sum of their respective van der Waals radii of 3.60 Å (see Figure 1). Utilizing the Brown approach,[15] the sum of the valency units (vu) of the Cs^+ ion was estimated as +0.90 vu, which is in good agreement with the univalent character of the Cs^+ monocation.

The Cs^+ ion in this structure is tetrahedrally coordinated by four $Sb(OTeF_5)_6^-$ anions. Two of the anions coordinate with two different $OTeF_5$ groups monodentate to the Cs^+ ion, and the other two anions coordinate with three different $OTeF_5$ groups monodentate to the Cs^+ ion. The Cs−F contacts in **1** may be compared to those found in $Cs(LiF_2)$[16] [and $Cs(SbF_6)$].[17] In these salts, the Cs atom is coordinated by six shorter Cs- -F contacts at 2.96−3.15 Å (3.12 Å) and two (six) longer contacts

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(12) The oxidation of gaseous I^- ($\Delta_fH = -188$ kJ/mol) by Ag^+ ($\Delta_fH = +1017$ kJ/mol) with formation of Ag^0 ($\Delta_fH = +285$ kJ/mol) and 0.5 I_2 ($\Delta_fH = 31$ kJ/mol) is thermochemically possible ($\Delta_rH = -513$ kJ/mol). Adding the calculated [Born equation, dielectric constant 14 (SO_2 at room temperature)] solvation energies of Ag^+ ($r = 1.29$ Å; 501 kJ/mol) and I^- ($r = 2.06$ Å; 313 kJ/mol) as well as the experimental atomization energy of Ag^0 (285 kJ/mol) and the experimental sublimation enthalpy of 0.5 I_2 (31 kJ/mol) into a suitable Born−Fajans−Haber cycle allows the estimation of the heat of the reaction $Ag^+_{(solv)} + I^-_{(solv)} \rightarrow Ag^0_{(c)} + 0.5\ I_{2\ (c)}$ as slightly exothermic ($\Delta_rH = -13$ kJ/mol). Due to the higher electron affinity of bromine (325 vs 294 kJ/mol for iodine) and the higher solvation energy of the smaller $Br^-_{(solv)}$ ion ($r = 1.82$ Å, 354 vs 313 kJ/mol for $I^-_{(solv)}$) the homologous reaction (giving liquid Br_2) is endothermic for bromine ($\Delta_rH = +54$ kJ/mol).

(13) A crystal of **1** (0.03 × 0.06 × 0.08 mm) was mounted on a RIGAKU AFC5R diffractometer, and subsequent measurements were performed at 213 ± 1 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å). Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of 25 carefully centered reflections in the range of $15.97° < 2\Theta < 28.81°$ and correspond to a tetragonal primitive unit cell with $a = 14.260(3)$ Å, $c = 14.618(5)$ Å, and $V = 2972.8(8)$ Å^3 ($Z = 4$, $CsF_{30}O_6SbTe_6$, FW = 1686.20, $d = 3.77$ g/cm^3). Data were collected in the $\omega - 2\Theta$ scan technique up to a maximum of 2Θ of 50.1° with an ω-scan width of $1.37 + 0.35 \tan \Theta°$ at a scan speed of 8° min^{-1}. Weak reflections ($I < 15\sigma$) were rescanned up to a maximum of six scans and the counts were accumulated. Stationary background counts were recorded on each side of the reflection with a peak/background counting time ratio of 2: 1. Of the 2682 reflections recorded, 2474 were unique ($R_{int} = 0.042$), equivalent reflections were merged. The intensities of three representative standard reflections were measured every 150 reflections and decreased during the data collection by 11.9%. A linear correction factor was applied to account for this phenomenon. An empirical absorption correction correction ($\mu = 81.13$ cm^{-1}) based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.81 to 1.00. Data were corrected for Lorentz and polarization effects. The systematic absences uniquely determined the space group to be $P4_2/n$. The structure was solved using direct methods and all atom positions were identified by interpretation of the subsequent difference Fourier maps using the TEXSAN[14] crystallographic software package of Molecular Structure Corp. Only the Cs atom was refined anisotropically; all other atoms were refined isotropically. The final cycle of the full-matrix least-squares refinements on F was based on 366 observed reflections [$I > 3\sigma(I)$] and 92 variable parameters and converged with weighted and unweighted agreement factors of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|) = 0.058$ and $R_w = \Sigma(w|F_o| - |F_c|)^2/\ \Sigma w|F_o|^2) = 0.051$ (GOF = 1.77, $\Delta\rho = +1.37/-1.22$ e$^-$/A^3).

(14) Molecular Structure Corp. (1997−1999). teXsan for Windows. Single-Crystal Structure Analysis Software. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381.

(15) The contacts s (in valency units vu) have been defined as $s = (R/R_0)^{-N}$, where R is the observed distance, R_0 is the covalent bond distance (bond order = 1) of the bond in question, and N is a empirically derived constant. For Cs- -F contacts $N = 4.61$ and $R_0 = 1.904$ Å, see: Brown, I. D. In *Structure and Bonding in Crystals*; M. O'Keefe, M., Navrotsky, A., Eds.; Academic Press: London, 1981; Vol. 2, 1.

(16) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984.

(17) Nolte, M. J.; de Beer, H. J. *Acta Crystallogr. B* **1979**, 1208.

at 3.50 and 3.53 Å (3.38 Å) that are similar to the distances found in ***1*** (3.04−3.14 and 3.42−3.49 Å). The geometry of the $Sb(OTeF_5)_6^-$ anion is unremarkable. Average bond lengths and bond angles are $d(\mathrm{Sb-O})_{av} = 1.90(5)$ Å, $d(\mathrm{Te-O})_{a.} = 1.81(5)$ Å, $d(\mathrm{Te-F})_{av} = 1.74(6)$ Å and $(\mathrm{Sb-O-Te})_{av} = 149(3)°$ and agree well with those reported for other $Sb(OTeF_5)_6^-$ anions, e.g., in $[NMe_4][Sb(OTeF_5)_6]$ with $d(\mathrm{Sb-O})_{avg} = 1.91(1)$ Å, $d(\mathrm{Te-O})_{av} = 1.78(1)$ Å, $d(\mathrm{Te-F})_{avg} = 1.75(2)$ Å, and $(\mathrm{Sb-O-Te})_{av} = 150.9(8)°$[3]. The crystal packing is best described as a cubic close packing of the large spherical $Sb(OTeF_5)_6^-$ anions (radius 4.79 Å, see below) where the Cs^+ ions [Goldschmidt radius: 1.65 Å] occupy every second tetrahedral hole ($r_{cat}/r_{an} = 0.344$) (see Figure 1). The zinc blend structure is in agreement with the radius ratio rules, which require a cation−anion radius ratio between 0.225 and 0.414 for this lattice type.

The unsolvated nature of the cation in this crystal structure allowed us to establish the thermochemical volume (radius) of the $Sb(OTeF_5)_6^-$ anion, which is needed to obtain lattice potential enthalpy estimates of known and unknown $Sb(OTeF_5)_6^-$ salts. The volume (radius) of the Cs^+ cation is 19 Å^3 (1.65 Å),[18] and therefore, the volume (radius) of the $Sb(OTeF_5)_6^-$ anion followed as

$$\boldsymbol{V[\mathrm{Sb(OTeF_5)_6}^-]} = [(\text{unit cell volume}/Z) - V(\mathrm{Cs}^+)] = [(2973/4) - 19] = \mathbf{724\ Å^3}$$

$$\boldsymbol{r[\mathrm{Sb(OTeF_5)_6}^-]} = d(\mathrm{Cs-Sb}) - r(\mathrm{Cs}^+) = 6.44 - 1.65 = \mathbf{4.79\ Å}$$

Using Jenkins, Passmore, et al.'s generalized volume-based Kapustinskii equation,[18] the lattice potential enthalpy of the $Cs[Sb(OTeF_5)_6]$ salt was estimated as 363 kJ/mol. Utilizing the known lattice potential enthalpies of CsBr ($\Delta H_{Latt} = 647$ kJ/mol) and AgBr ($\Delta H_{Latt} = 905$ kJ/mol)[19] and estimating that of $Ag[Sb(OTeF_5)_6]$ ($\Delta H_{Latt} = 365$ kJ/mol)[18] allowed us to establish the solid-state enthalpy of eq 1 as exothermic by 256 kJ/mol $\{[Sb] = Sb(OTeF_5)_6\}$:

$$\Delta H(\text{eq 1}) = \Delta H_{Latt}(\mathrm{CsBr}) + \Delta H_{Latt}\{\mathrm{Ag[Sb]}\} - \Delta H_{Latt}(\mathrm{AgBr}) - \Delta H_{Latt}\{\mathrm{Cs[Sb]}\} =$$

$$\Delta H(\text{eq 1}) = 647 + 365 - 905 - 363 =$$

$$\boldsymbol{\Delta H}\mathbf{(eq\ 1) = -256\ kJ/mol}$$

Concluding Remarks

The synthesis of the unsolvated $Cs[Sb(OTeF_5)_6]$ salt was achieved in good yield and is exothermic by 256 kJ/mol. The $Sb(OTeF_5)_6^-$ anion may then be introduced into other salts by a metathesis reaction with halides or hexafluorometalates MF_6^- (M = As, Sb). Due to the large size of the $Sb(OTeF_5)_6^-$ anion, the lattice potential energies of the resulting species are dramatically decreased and may lead to hitherto unknown species and structures.

Acknowledgment. This work was supported by the Natural Science and Engineering Research Council of Canada NSERC (J.P., T.S.C.). We thank Isabelle Dionne M.Sc. for the Raman spectra. Dr. Ingo Krossing is grateful to the Alexander von Humboldt Foundation in Bonn, Germany, for providing a Feodor−Lynen Fellowship.

Supporting Information Available: Details of the Experimental Section and a copy of the Raman spectrum of **1**. A CIF File containing details of the X-ray structure determination is also deposited. This material is available free of charge via the Internet at http://pubs.acs.org.

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