Weakly Coordinating Anions $M(OTeF_5)_6^-$ (M = Nb, Sb) and $M(OTeF_5)_6^{2-}$ (M = Ti, Zr, Hf): Two-Step Synthesis, Characterization, Stability, and Use in the Isolation of the Dihaloalkane Complex Cations $Ag(CH_2Cl_2)_3^+$, $Ag(CH_2Br_2)_3^+$, and *catena*-poly[$Ag(1,2\text{-}C_2H_4Br_2)_2$-*μ*-($1,2\text{-}C_2H_4Br_2$)-*Br*:*Br′*]$^+$

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The syntheses of silver(I) salts of the weakly coordinating anions $Nb(OTeF_5)_6^-$, $Sb(OTeF_5)_6^-$, $Ti(OTeF_5)_6^{2-}$, $Zr(OTeF_5)_6^{2-}$, and $Hf(OTeF_5)_6^{2-}$ are reported. The reactions took place in high yields in two steps using commerically available $HOTeF_5$, AgF, and either $NbCl_5$, $SbCl_5$, $TiCl_4$, $ZrCl_4$, or $HfCl_4$. Metathesis reactions of some of the silver(I) salts with CPh_3Cl and $[N(n\text{-}Bu)_4][Cl]$ afforded $[CPh_3][Nb(OTeF_5)_6]$, $[CPh_3][Sb(OTeF_5)_6]$, $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$, $[N(n\text{-}Bu)_4][Sb(OTeF_5)_6]$, and $[N(n\text{-}Bu)_4]_2[Ti(OTeF_5)_6]$. Recrystallization of $Ag_2Ti(OTeF_5)_6$, $AgNb(OTeF_5)_6$, and $AgSb(OTeF_5)_6$ from dichloromethane, dibromomethane, and 1,2-dibromoethane, respectively, afforded diffraction-quality crystals of the dihaloalkane complexes $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$, and [*catena*-poly[$Ag(1,2\text{-}C_2H_4Br_2)_2$-*μ*-($1,2\text{-}C_2H_4Br_2$)-*Br*:*Br′*]][$Sb(OTeF_5)_6$]. Crystallographic data for $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$: triclinic, $P\bar{1}$, $a = 10.944(2)$ Å, $b = 10.989(2)$ Å, $c = 11.144(2)$ Å, $\alpha = 66.83(3)°$, $\beta = 75.09(3)°$, $\gamma = 83.44(3)°$, $Z = 1$, $T = -135(1)$ °C, $R = 0.068$. Crystalloographic data for $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$: monoclinic, $C2/c$, $a = 14.302(3)$ Å, $b = 13.224(3)$ Å, $c = 21.537(4)$ Å, $\beta = 96.16(3)°$, $Z = 4$, $T = -128(1)$°C, $R = 0.059$. Crystallographic data for [*catena*-poly[$Ag(1,2\text{-}C_2H_4Br_2)_2$-*μ*-($1,2\text{-}C_2H_4Br_2$)-*Br*:*Br′*]][$Sb(OTeF_5)_6$]: triclinic, $P\bar{1}$, $a = 9.772(1)$ Å, $b = 9.784(1)$ Å, $c = 10.992(1)$ Å, $\alpha = 86.85(1)°$, $\beta = 87.07(1)°$, $\gamma = 84.21(1)°$, $Z = 1$, $T = -97(1)$ °C, $R = 0.062$. The latter two structures, with $AgBr_6$ coordination spheres, are the first two examples of bromoalkane complexes of any metal. The stability of the anions toward reaction with various solvents, other weakly coordinating anions, and the electrophiles $HOTeF_5$ and $AgOTeF_5$ was investigated. The $Nb(OTeF_5)_6^-$ anion reacted with acetonitrile or $OTeF_5^-$ to form $F_5TeOTeF_5$ and $NbO(OTeF_5)_4(CH_3CN)^-$ or $NbO(OTeF_5)_5^{2-}$, respectively. The order of stability of the anions with respect to the electrophiles is $Sb(OTeF_5)_6^- > Nb(OTeF_5)_6^- \gg Ti(OTeF_5)_6^{2-} \sim B(OTeF_5)_4^-$. It was concluded that the $Sb(OTeF_5)_6^-$ anion will probably be the most useful weakly coordinating anion in its class.

Introduction

An important goal of our research program is to enhance the chemical reactivity of soluble d-block metal complexes. Cationic metal complexes with vacant, virtual, or latent coordination sites[1,2] would have extremely high Lewis acidities and/or electrophilicities, two important measures of reactivity that could be utilized for catalysis, for stoichiometric synthesis, or for generating new and unusual species. Consequently, there is a great deal of interest in the synthesis of new classes of anions that are much less coordinating than ClO_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^-, BPh_4^-, etc.[3] To be most useful, the new anions will need to share several common features, including a large effective radius. A large anion made up of many atoms will have its charge either buried in the interior or widely distributed on the periphery, and it will be sterically hindered from making a close approach to a given cation. In addition, by the positioning of hard, weakly basic fluorine or hydrogen atoms on the periphery of the anion, there will be weaker bonding between the anion and an electrophilic cation. Any useful new anion will also need to be kinetically stable: it must not rapidly fragment into more strongly coordinating moieties. Last, it will need to be stable with respect to oxidation, since many very acidic cations are also strong oxidants.

One new class of anions includes fluorinated derivatives of BPh_4^-, including $B(C_6F_5)_4^-$ and $B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$.[3–8] Another class includes several carborane anions, including $CB_9H_{10}^-$ and $CB_{11}H_{12}^-$, and their halogenated derivatives.[3,9–15] The class of anions that we have been investigating is based on the

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(1) Virtual, *adjective*: being such practically or in effect, although not in actual fact or name. Latent, *adjective*: present but invisible or inactive; lying hidden and undeveloped. Our definition of a virtual coordination site is a weakly ligated (e.g., weakly solvated) coordination site.[20] A latent coordination site is neither geometrically conspicuous nor occupied except in the presence of a relatively strong ligand (e.g., six-coordinate ReF_6^+, which has O_h symmetry, has a latent coordination site to which F^- can bind to form seven-coordinate ReF_7).[2]

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pentafluorooxotellurate (teflate) moiety.[3,16] The electronic similarity between the $OTeF_5$ substituent and a fluorine atom has been recognized for quite some time. The $OTeF_5$ radical possesses an electronegativity rivaling that of fluorine.[17] The $OTeF_5^-$ anion (Te$-$O = 1.786(3) Å, Te$-$F(av) = 1.853(3) Å, O$-$Te$-$F$_{eq}$(av) = 95.2(2)° [18]) is nearly isostructural with SbF_6^- (Sb$-$F(av) = 1.844(3) Å in $KSbF_6$[19]). Approximately 50% of the negative charge on the $OTeF_5^-$ anion has been calculated to reside on the oxygen atom, with the remaining 50% distributed among the five fluorine atoms.[18] The stability of teflate compounds with respect to fluoride abstraction[20] is an important advantage they possess (BF_4^-, PF_6^-, and SbF_6^- are known to transfer a fluoride ion to strong cationic electrophiles[21]).

The first teflate-based anions to be studied as weakly coordinating anions were $Pd(OTeF_5)_4^{2-}$ [22] and $B(OTeF_5)_4^-$.[23] Although these counterions have their negative charges distributed over a large number of fluorine atoms, diminishing the interaction between any given fluorine atom and a cationic center, it was found that some cations, such as Ag^+, could coordinate to the oxygen atoms. In these cases, relatively strong Ag$-$O(Te)$-$M bridges (M = Pd,[22] B[23b,d]), as well as the weaker Ag$-$F(Te) bonds, were formed. In addition, it was found that the putative cations $[SiR_3]^+$ and [Fe(porphyrin)]$^+$ rapidly abstracted an intact teflate anion from $B(OTeF_5)_4^-$, presumably via formation of Si$-$O(Te)$-$B and Fe$-$O(Te)$-$B bridges.[23b] Simple dissociation of $OTeF_5^-$ from the borate anion was ruled out because no isotope exchange occurred, even after many days, when $[N(n\text{-Bu})_4][^{17}OTeF_5]$ was mixed with $[N(n\text{-Bu})_4][B(^{16}OTeF_5)_4]$. The presence of an electrophile such as H^+ or Ag^+ was required to effect rapid (< 1 h) isotope scrambling.

In this paper we describe a study of even larger teflate-based anions, $M(OTeF_5)_6^{n-}$ (M = Nb, Sb, n = 1; M = Ti, Zr, Hf, n = 2). We have found that these hexakis(pentafluorooxotellurato)metalate anions are (i) straightforward to prepare, (ii) much less coordinating, (iii) much more stable in the presence of electrophiles, and (iv) much more solubilizing in weakly coordinating solvents than either $B(OTeF_5)_4^-$ or $Pd(OTeF_5)_4^{2-}$. While NR_4^+ and/or Cs^+ salts of $Ti(OTeF_5)_6^{2-}$,[24] $Nb(OTeF_5)_6^-$,[25] and $Sb(OTeF_5)_6^-$ [26] had already been prepared by others, the new synthetic route is general, uses fewer steps, and yields Ag^+ salts of the $M(OTeF_5)_6^{n-}$ anions, which can be used as metathesis reagents. We also report the structural characterization of three unprecedented dihaloalkane complexes of silver(I), $Ag(CH_2Cl_2)_3^+$, $Ag(CH_2Br_2)_3^+$, and *catena*-poly[Ag(1,2-$C_2H_4Br_2)_2$-μ-(1,2-$C_2H_4Br_2$)-*Br:Br′*]$^+$ (Ag(1,2-$C_2H_4Br_2)_3^+$).[27] Some of these results have been communicated earlier.[28]

Results and Discussion

Synthesis and Spectroscopic Characterization of $Ag_nM(OTeF_5)_6$ (M = Nb, Sb, n = 1; M = Ti, Zr, Hf, n = 2). Our synthetic procedures are based on teflate/chloride metathesis reactions between $AgOTeF_5$[29] and MCl_5 (M = Nb, Sb) or MCl_4 (M = Ti, Zr, Hf) in the weakly coordinating solvents dichloromethane or 1,1,2-trichlorotrifluoroethane (F-113), shown as follows:

$$6\text{AgOTeF}_5 + \text{MCl}_{6-n} \xrightarrow[\text{or F-113}]{\text{CH}_2\text{Cl}_2} \text{Ag}_n\text{M(OTeF}_5)_6 + (6-n)\text{AgCl}$$

These particular solvents were chosen because they coordinate only weakly to Ag^+, allowing the solid-state transformations

$$[\text{Ag(solv)}_x]_n[\text{M(OTeF}_5)_6] \xrightarrow[-nx\text{ solv}]{\text{vacuum}} \text{Ag}_n\text{M(OTeF}_5)_6$$

to proceed at room temperature within several hours (compare $[Ag(CH_2Cl_2)_2]_2[Pd(OTeF_5)_4]$,[22] which loses all traces of dichloromethane under vacuum in 24 h at room temperature). Since $AgOTeF_5$ can be prepared in high yield from $HOTeF_5$,[29] all of the silver(I) salts reported in this paper can be prepared in a generic two-step procedure starting with $HOTeF_5$, the parent compound from which all teflates are made.[30] The strong acid $HOTeF_5$ is now commerically available (Aldrich).

The most straightforward reaction was that between $AgOTeF_5$ and $NbCl_5$ in F-113, since the product, $AgNb(OTeF_5)_6$, is quite soluble in this solvent (see below) and can be crystallized directly from the reaction mixture. The reaction proceeds to completion (no $AgOTeF_5$ is observed in the product) during several hours at room temperature. The syntheses of $[N(n\text{-Bu})_4][Nb(OTeF_5)_6]$ and $[Ph_3C][Nb(OTeF_5)_6]$ were straightforward metathesis reactions between $AgNb(OTeF_5)_6$ and either $[N(n\text{-Bu})_4][Cl]$ or Ph_3CCl, respectively, and gave high yields after crystallization. The syntheses of $AgSb(OTeF_5)_6$ and Ag_2Ti-

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Scheme 1

This work:

$$HOTeF_5 + AgF \longrightarrow AgOTeF_5 + HF$$

$$6AgOTeF_5 + MCl_{6-n} \longrightarrow Ag_nM(OTeF_5)_6 + (6-n)AgCl$$

M = Nb, Sb; n = 1
M = Ti, Zr, Hf; n = 2

Sladky et al. (ref 24):

$$HOTeF_5 + CsCl \longrightarrow [Cs][OTeF_5] + HCl$$

$$4HOTeF_5 + TiCl_4 \longrightarrow Ti(OTeF_5)_4 + 4HCl$$

$$Ti(OTeF_5)_4 + 2[Cs][OTeF_5] \longrightarrow [Cs]_2[Ti(OTeF_5)_6]$$

Seppelt et al. (ref 25):

$$HOTeF_5 + [NR_4][Cl] \longrightarrow [NR_4][OTeF_5] + HCl$$

$$HOTeF_5 + NbCl_5 \longrightarrow Nb(OTeF_5)_5 + 5HCl$$

$$Nb(OTeF_5)_5 + [NR_4][OTeF_5] \longrightarrow [NR_4][Nb(OTeF_5)_6]$$

Schrobilgen et al. (ref 26):

$$3HOTeF_5 + BCl_3 \longrightarrow B(OTeF_5)_3 + 3HCl$$

$$HOTeF_5 + [NR_4][Cl] \longrightarrow [NR_4][OTeF_5] + HCl$$

$$B(OTeF_5)_3 + SbF_3 \longrightarrow Sb(OTeF_5)_3 + BF_3$$

$$2B(OTeF_5)_3 + 3XeF_2 \longrightarrow 3Xe(OTeF_5)_2 + 2BF_3$$

$$Sb(OTeF_5)_3 + [NR_4][OTeF_5] \longrightarrow [NR_4][Sb(OTeF_5)_4]$$

$$[NR_4][Sb(OTeF_5)_4] + Xe(OTeF_5)_2 \longrightarrow [NR_4][Sb(OTeF_5)_6] + Xe$$

$(OTeF_5)_6$ were similar to that of $AgNb(OTeF_5)_6$. However, since these compounds are not very soluble in F-113, they were extracted into and crystallized from dichloromethane after the teflate/chloride metathesis reaction was complete. No $AgOTeF_5$ was observed by ^{19}F NMR spectroscopy in the purified products. The syntheses of $[N(n\text{-}Bu)_4][Sb(OTeF_5)_6]$, $[Ph_3C][Sb(OTeF_5)_6]$, and $[N(n\text{-}Bu)_4]_2[Ti(OTeF_5)_6]$ were also straightforward metathesis reactions.

The compounds $Ag_2Zr(OTeF_5)_6$ and $Ag_2Hf(OTeF_5)_6$ could not be readily prepared using F-113 as the solvent. For example, stirring $ZrCl_4$ and 6 equivs of $AgOTeF_5$ in F-113 for 28 h at 22 °C resulted in the recovery of only 65% of the expected AgCl. Furthermore, IR and ^{19}F NMR spectra of the products showed the presence of unreacted $AgOTeF_5$. Heating these reactants in F-113 for 39 h (the temperature ranged from 55 to 78 °C) did not drive the reaction to completion. Instead, $Ag_2Zr(OTeF_5)_6$ and $Ag_2Hf(OTeF_5)_6$ were prepared either by refluxing the reactants in 1,2-dichloroethane (~80 °C) or by heating them in dichloromethane at 80 °C in a vessel equipped to handle pressures of at least 4 atm. The advantage of the latter method is that coordinated dichloromethane can be removed from the compounds by placing them under dynamic vacuum for 48 h at room temperature. In contrast, 1,2-dichloroethane binds more strongly to the silver ions and cannot be removed under vacuum in a reasonable amount of time. The compounds $Ag_2Zr(OTeF_5)_6$ and $Ag_2Hf(OTeF_5)_6$ are the first examples of salts of the previously unknown $Zr(OTeF_5)_6^{2-}$ and $Hf(OTeF_5)_6^{2-}$ anions.

The $Ta(OTeF_5)_6^-$ anion had previously been prepared by Moock and Seppelt and isolated as its Cs^+ and NR_4^+ salts.[25] Nevertheless, our attempts to prepare $AgTa(OTeF_5)_6$ were unsuccessful. No solvent system could be found that would allow the chloride/teflate metathesis of $TaCl_5$ and $AgOTeF_5$ to proceed to completion. The use of refluxing 1,2-dichloroethane resulted in the formation of an insoluble product.

Our general, two-step synthetic procedure for the synthesis of $Ag_nM(OTeF_5)_6$ salts is summarized in Scheme 1, which also shows the published synthetic schemes for the preparation of $Cs_2Ti(OTeF_5)_6$,[24] $[NR_4][Nb(OTeF_5)_6]$,[25] and $[NR_4][Sb(OTeF_5)_6]$.[26] The advantages of our new procedure are severalfold. First and foremost, none of the previously published procedures yield Ag^+ salts. Second, the published procedures are not general and require more steps. Third, the preparation of $Ti(OTeF_5)_4$,[24] $Nb(OTeF_5)_5$,[25] and $CsOTeF_5$[31] requires large excesses of expensive $HOTeF_5$ (e.g., a 10-fold excess for the synthesis of $Nb(OTeF_5)_5$). Our procedure uses $AgOTeF_5$, which can be prepared in large quantities in greater than 80% yield from stoichiometric amounts of AgF and $HOTeF_5$.[29] Fourth, we have found that the reactions of metal chlorides such as $TiCl_4$ or $NbCl_5$ with $HOTeF_5$ do not go to completion even when large excesses of $HOTeF_5$ are used. This necessitates a separate purification of the intermediates $Ti(OTeF_5)_4$ and $Nb(OTeF_5)_5$. Finally, $Nb(OTeF_5)_5$ is an unstable compound, making a procedure dependent on its synthesis and purification problematic. Seppelt and co-workers reported than it slowly decomposes at room temperature to NbF_5 and polymeric $(TeOF_4)_n$.[32] Similarly, $Sb(OTeF_5)_5$ is also an unstable compound,[33] which is why Schrobilgen and co-workers developed their elegant but lengthy procedure for the synthesis of $[NR_4][Sb(OTeF_5)_6]$ salts.[26]

Table 1. ^{19}F NMR Spectral Data[a]

compd	δ_A	δ_B	J_{AB}, Hz	J_{AX}, Hz	J_{BX}, Hz
$AgNb(OTeF_5)_6$	−41.4	−47.1	195	3490	3650
$[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$	−41.3	−47.0	187	3330	3440
$[CPh_3][Nb(OTeF_5)_6]$	−41.4	−47.1	195	3490	3650
$AgSb(OTeF_5)_6$	−41.4[b]			3560[b]	
$[N(n\text{-}Bu)_4][Sb(OTeF_5)_6]$	−41.4[b]			3560[b]	
$[CPh_3][Sb(OTeF_5)_6]$	−41.4[b]			3560[b]	
$Ag_2Ti(OTeF_5)_6$	−34.7	−46.8	186	3210	3520
$[N(n\text{-}Bu)_4]_2[Ti(OTeF_5)_6]$	−34.6	−46.6	182	3140	3490
$Ag_2Zr(OTeF_5)_6$	−35.2	−47.3	187	3180	3490
$Ag_2Hf(OTeF_5)_6$	−35.2	−47.0	187	3190	3480

[a] 188.3, 282.4, or 470.5 MHz; AB_4X patterns (X = ^{125}Te, 7.5% NA, $I = {}^1/_2$); $\delta(CFCl_3) = 0$; solvent is dichloromethane. [b] Cannot distinguish between δ_A and δ_B or between J_{AX} and J_{BX} (see text).

All of our new compounds were characterized by ^{19}F NMR spectroscopy and exhibited resonances due to a single type of $OTeF_5$ group. As is the case with ^{19}F NMR spectra of most teflate compounds,[34] the spectra were second order AB_4X patterns shielded relative to $CFCl_3$ (X = ^{125}Te, 7.0% natural abundance, $I = {}^1/_2$). When the signal/noise ratio was high, ^{123}Te satellites were also observed (0.91% natural abundance, $I = {}^1/_2$). The results are listed in Table 1. Values of δ_A, δ_B, and J_{AB} were determined by comparing the experimental spectra to simulated spectra that were calculated using the computer program LAOCOON PC.[35] Values of J_{AX} and J_{BX} were measured directly from the experimental spectra. There is excellent agreement with appropriate literature data. For example, Moock and Seppelt reported δ_A −41.4, δ_B −46.2, and J_{AB} = 180 Hz for $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$ in dichloromethane,[25] and Schrobilgen and co-workers reported δ −41.8 for $[NMe_4][Sb(OTeF_5)_6]$ in dichloromethane.[26] Spectra of $Ag_2Zr(OTeF_5)_6$ and $Ag_2Hf(OTeF_5)_6$ dissolved in dichloromethane-d_2 are shown in Figure 1. The group of resonances at ca. −33 to −37 ppm in each spectrum is due to the unique axial fluorine atom in each of the six equiv teflate groups. The intense resonances at ca. −47 ppm in each spectrum are due to the four equatorial fluorine atoms. Very small amounts of one or more impurities can be seen at the base of the equatorial fluorine atom

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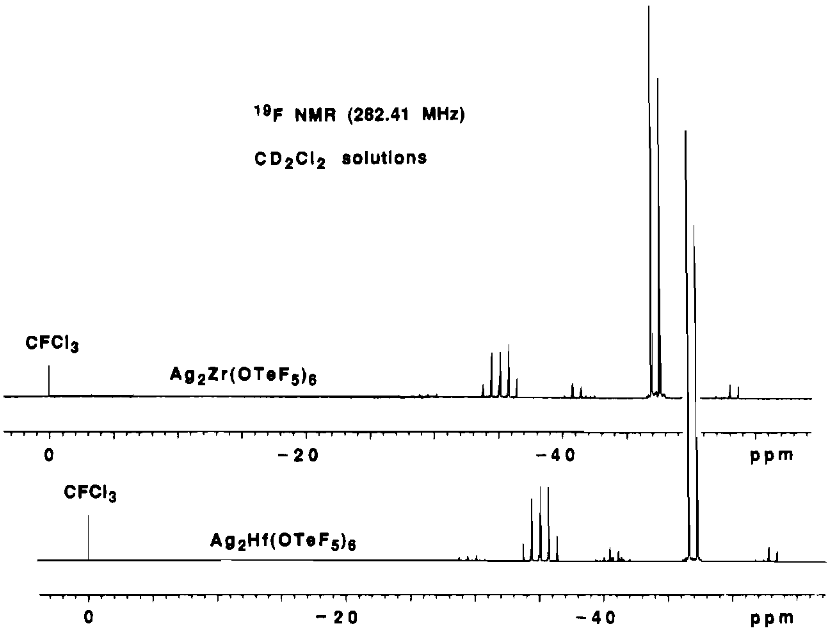

Figure 1. 282.41 MHz ^{19}F NMR spectra of $Ag_2Zr(OTeF_5)_6$ and $Ag_2Hf(OTeF_5)_6$ ($CFCl_3$ internal standard).

Table 2. Infrared Spectral Data (cm^{-1})[a]

compd	ν(TeO)	ν(TeF)	ν(MO)
$AgNb(OTeF_5)_6$	830	726, 701, 674	440
$AgSb(OTeF_5)_6$	874	722, 702, 682	467
$Ag_2Ti(OTeF_5)_6$	830 (bd)	717, 690, 623	448
$Ag_2Zr(OTeF_5)_6$	861	705, 682, 637	430
$Ag_2Hf(OTeF_5)_6$	870	707, 682, 637	420

[a] Samples were Nujol mulls between AgBr windows; bd = broad.

"doublets." All other observed resonances are either ^{123}Te or ^{125}Te satellites.

Infrared spectra of the five silver salts were recorded as Nujol mulls between AgBr windows. Bands attibutable to Te−O, Te−F, and M−O stretching vibrations are listed in Table 2. The assignments follow an earlier study.[18] Assuming idealized octahedral symmetry for the hexakis(teflate) anions, the ν(TeO) and ν(MO) values listed represent T_{1u} vibrations.

The solubility of $AgNb(OTeF_5)_6$ in the weakly coordinating, low dielectric solvent F-113 ($\epsilon \sim 2.4$) is 0.40 M. This is relatively high compared with the silver salts of other teflate-based anions: $Ag_2Ti(OTeF_5)_6$, 0.009 M; $AgB(OTeF_5)_4$, 0.004 M;[85b] and $AgOTeF_5$, 0 M (i.e., no detectable solubility).[85b] The high solubility of $AgNb(OTeF_5)_6$ in such a weakly donating solvent will enable the exploration of solution chemistry which could not be carried out using dichloromethane as the solvent. For example, the compounds $[Ag(CO)_n][Nb(OTeF_5)_6]$ ($n = 1$, 2, 3) are also soluble in F-113,[36] and this will allow the catalytic activity of the carbonyl cations to be studied in solution. When these silver(I) carbonyls were dissolved in dichloromethane, the carbonyl ligands were rapidly and completely replaced by dichloromethane ligands.[36]

Structures of $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$, and [*catena*-poly[$Ag(1,2\text{-}C_2H_4Br_2)_2$-$\mu$-($1,2\text{-}C_2H_4Br_2$)-*Br*:*Br'*]][$Sb(OTeF_5)_6$]. Experimental parameters for the crystallographic studies are listed in Table 3. Interatomic distances and angles are listed in Table 4. Drawings of the anions and cations are shown in Figures 2 and 3, respectively. The structure of $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$ consists of centrosymmetric $Ti(OTeF_5)_6^{2-}$ anions that are weakly bonded to two $Ag(CH_2Cl_2)_3^+$ cations via two weak Ag•••F contacts at 3.029(8) and 3.033(6) Å (the sum of the van der Waals radii for Ag and F is 3.15 ± 0.08 Å [37]). The structure of $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$ consists of discrete $Ag(CH_2Br_2)_3^+$ cations and $Nb(OTeF_5)_6^-$ anions. The closest Ag•••F contact is 4.152(9) Å. The structure of [*catena*-poly[$Ag(1,2\text{-}C_2H_4Br_2)_2$-$\mu$-($1,2\text{-}C_2H_4Br_2$)-*Br*:*Br'*]][$Sb(OTeF_5)_6$] consists of single-strand polycationic $[-(1,2\text{-}C_2H_4Br_2)_2Ag-BrC_2H_4Br-]_n^{n+}$ chains and discrete $Sb(OTeF_5)_6^-$ anions. The closest Ag•••F contact is 3.196(7) Å.

(a) Structures of the Anions. The $Ti(OTeF_5)_6^{2-}$, $Nb(OTeF_5)_6^-$, and $Sb(OTeF_5)_6^-$ anions all display very similar structures: an octahedral array of octahedral teflate groups surrounding a central metal or metalloid atom. This structural motif has also been observed in the neutral compounds $Mo(OTeF_5)_6$,[38] $U(OTeF_5)_6$,[39] and $Te(OTeF_5)_6$[40] and in NR_4^+ salts of the $As(OTeF_5)_6^-$, $Sb(OTeF_5)_6^-$, and $Bi(OTeF_5)_6^-$ anions.[26] Other structural motifs that have been observed for homoleptic teflate species include linear ($Xe(OTeF_5)_2$[41,42]), trigonal planar ($B(OTeF_5)_3$[43]), square planar ($Pd(OTeF_5)_4^{2-}$,[22] $I(OTeF_5)_4^-$,[44] and $Au_2(OTeF_5)_6$[45]), and tetrahedral ($B(OTeF_5)_4^-$ [23]). Since the M−O−Te linkages are bent (ca. 140−160°) in $Ti(OTeF_5)_6^{2-}$, $Nb(OTeF_5)_6^-$, and $Sb(OTeF_5)_6^-$, these anions cannot have rigorous O_h symmetry. Their highest possible symmetry is S_6, but their actual symmetry in $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$, and [*catena*-poly[$Ag(1,2\text{-}C_2H_4Br_2)_2$-$\mu$-($1,2\text{-}C_2H_4Br_2$)-*Br*:*Br'*]][$Sb(OTeF_5)_6$] is only C_i. In a S_6 conformation, two of the eight O_3 faces of the MO_6 octahedron are much less sterically encumbered than the other six. These two parallel faces are perpendicular to the S_6 axis, as shown in Figure 5.

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Table 3. Details of the X-ray Diffraction Study of $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$, and $[Ag(1,2\text{-}C_2H_4Br_2)_3][Sb(OTeF_5)_6]^a$

compd	$[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$	$[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$	$[Ag(1,2\text{-}C_2H_4Br_2)_3][Sb(OTeF_5)_6]^a$
molecular formula	$C_6H_{12}Ag_2Cl_6F_{30}O_6Te_6Ti$	$C_3H_6AgBr_6F_{30}O_6NbTe_6$	$C_6H_{12}AgBr_6F_{30}O_6SbTe_6$
fw	2204.8	2152.9	2224.8
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
unit cell dimens			
a, Å	10.944(2)	14.302(3)	9.772(1)
b, Å	10.989(2)	13.224(3)	9.784(1)
c, Å	11.144(2)	21.537(4)	10.992(1)
α, deg	66.83(3)	90	86.85(1)
β, deg	75.09(3)	96.16(3)	87.07(1)
γ, deg	83.44(3)	90	84.21(1)
unit cell volume, Å^3	1190.3(4)	4049.7(7)	1042.9(2)
Z	1	4	1
calcd density, g cm^{-3}	3.08	3.53	3.54
cryst dimens, mm	0.80 × 0.40 × 0.35	0.40 × 0.20 × 0.05	0.08 × 0.08 × 0.24
data collcn temp, °C	−135(1)	−128(1)	−97(1)
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)	Mo Kα (0.7107)
monochromator	graphite	graphite	graphite
abs coeff, cm^{-1}	54.01	11.085	11.138
scan type	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
scan speed, deg min^{-1}	variable (3−30)	variable (4−60)	variable (4−60)
2θ range, deg	4−50	4−55	4−55
reflcns	$\pm h,\pm k,-l$	$h,k,\pm l$	$h,\pm k,\pm l$
tot. no. of reflcns measd	4396	4651	4796
no. of obsd reflcns, $\lvert F_o\rvert > n\sigma(F_o)$	3786 ($n = 2.5$)	3183 ($n = 2.0$)	3984 ($n = 2.0$)
data/param ratio	13.2	14.7	16.4
R ($\lvert F_o\rvert > 4\sigma(F_o)$)	0.068	0.059	0.062
R_w	0.098	0.158	0.178
GOF	1.02	1.05	1.06
g (refined)	0.00046		

[a] $[Ag(1,2\text{-}C_2H_4Br_2)_3][Sb(OTeF_5)_6]$ = [*catena*-poly$[Ag(1,2\text{-}C_2H_4Br_2)_2\text{-}\mu\text{-}(1,2\text{-}C_2H_4Br_2)\text{-}Br{:}Br']][Sb(OTeF_5)_6]$.

The teflate groups are no more crowded in the hexakis(teflate) species than they are in the more open structures (e.g., $B(OTeF_5)_4^-$ or $Pd(OTeF_5)_4^{2-}$), as judged by F•••F contacts between teflate groups and by the lack of distortion within teflate groups (i.e., the Te−O and Te−F bond distances and the angles within the teflate groups of the three hexakis(teflate) anions are normal[18]). The oxygen atoms of the hexakis(teflate) species are, however, much more shielded from the surrounding medium than in the more open structures, as judged by space-filling models and especially by the lack of Ag−O(Te)−M bridges in the three compounds examined here. It will be seen (below) that this additional steric hindrance has a profound effect on the reactivity of the anions in the presence of electrophiles.

Anion radii, M−O distances, and M−O−Te angles for $Ti(OTeF_5)_6^{2-}$, $Nb(OTeF_5)_6^-$, and $Sb(OTeF_5)_6^-$ are listed in Table 5, along with values for structurally related species. The radius is defined as the average of the sums of the distance between the cental atom and each of the six axial fluorine atoms and the van der Waals radius of a fluorine atom (1.40 Å).[37] It can be seen that all of the anion radii are roughly the same, 6.8 ± 0.2 Å. The average M−O distances for the three anions examined here are 1.936(12) Å for $Ti(OTeF_5)_6^{2-}$, 1.933(16) Å for $Nb(OTeF_5)_6^-$, and 1.949(11) Å for $Sb(OTeF_5)_6^-$, which are not statistically different. For comparison, the average of two Sb−O distances in $Rb_2Sb_2OF_{11}$ is 1.91(3) Å[46] and the average Nb−O distance involving nonbridging oxygen atoms in $LiNb(OEt)_6$ is 1.88(2) Å.[47]

The U−O−Te angle in $U(OTeF_5)_6$ is 170°. It has been suggested that the larger U−O−Te angle might be due to O→U p→f π-bonding.[39] The range of M−O−Te angles in the group of transition metal hexakis(teflate) compounds which have now been structurally characterized are 145.6(2)−146.2(2)° for $Mo(OTeF_5)_6$, 142.3(4)−145.2(5)° for $Ti(OTeF_5)_6^{2-}$, and 148.4(5)−158.0(8)° for $Nb(OTeF_5)_6^-$. These d^0 central metal ions, which are capable of forming O→M p→d π-bonds, do not exhibit the nearly linear M−O−Te angles found in the uranium compound. In fact, the range of M−O−Te angles of the main group derivatives $Te(OTeF_5)_6$, $As(OTeF_5)_6^-$, $Sb(OTeF_5)_6^-$, and $Bi(OTeF_5)_6^-$ are not that different from those of the above transition metal derivatives. The ranges for the antimonate anions in the three compounds are 138.5(4)−141.6(4)° in the *catena*-poly$[Ag(1,2\text{-}C_2H_4Br_2)_2\text{-}\mu\text{-}(1,2\text{-}C_2H_4Br_2)\text{-}Br{:}Br']^+$ salt, 148.4(8)−153.4(8)° in the NMe_4^+ salt, and 160.7(9)−167(1)° in the NEt_4^+ salt. It is sensible to conclude that there is a relatively wide range of M−O−Te angles (ca. 140−170°) accessible to the anions in the solid state and in solution. The observed angles in a given structure are probably determined more by intermolecular than intramolecular forces.

(b) Structures of the Silver(I)−Dihaloalkane Complex Cations. There is an excellent review of the coordination chemistry of neutral haloalkanes (i.e., neutral molecules containing only carbon, hydrogen, and halogen atoms),[48] but this field is still not very well developed. Several years ago we reported a structural study of a series of silver(I) complexes of dichloromethane and 1,2-dichloroethane.[22,49] Since that time, only three other chloroalkane complexes have been structurally characterized, one of ruthenium,[50] one of thallium,[23c] and another of silver.[51] Recently, a series of iodoalkane and diiodoalkane complexes of silver(I) have been structurally characterized.[52]

The $Ag(CH_2Cl_2)_3^+$ cation in $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$ consists of three dichloromethane ligands coordinated in bi-

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Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$, and $[Ag(1,2\text{-}C_2H_4Br_2)_3][Sb(OTeF_5)_6]$[a]

	$[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$	$[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$	$[Ag(1,2\text{-}C_2H_4Br_2)_3][Sb(OTeF_5)_6]$[a]
M−O1	1.935(6)[b]	1.918(10)[c]	1.951(7)[d]
M−O2	1.939(9)[b]	1.949(8)[c]	1.938(6)[d]
M−O3	1.933(6)[b]	1.931(9)[c]	1.958(6)[d]
Te−O	1.812(9)−1.822(7)	1.806(9)−1.824(7)	1.832(7)−1.849(7)
Te−F	1.822(7)−1.861(8)	1.782(12)−1.832(7)	1.810(7)−1.835(6)
Ag−X1	2.702(3)[e]	2.847(2)[f]	3.081(2)[f]
Ag−X2	2.856(5)[e]	2.932(2)[f]	2.702(1)[f]
Ag−X3	2.656(3)[e]	2.816(2)[f]	2.874(1)[f]
Ag−Cl4	3.049(4)		
Ag−Cl5	2.719(4)		
Ag−Cl6	3.030(6)		
Ag−F1	3.029(8)		
Ag−F6	3.033(6)		
C−X	1.72(1)−1.79(1)[e]	1.91(2)−1.92(2)[f]	1.94(1)−1.96(1)[f]
C1−C1′			1.51(3)
C2−C3			1.48(2)
O−M−O	90.7(3)−90.8(3)[b]	89.1(4)−90.9(4)[c]	88.5(3)−91.5(3)[d]
M−O−Te	142.3(4)−145.2(5)[b]	148.4(5)−158.0(8)[c]	138.5(4)−141.6(4)[d]
O−Te−F_{eq}	91.5(3)−96.0(3)	89.6(5)−93.7(6)	89.3(3)−96.7(3)
O−Te−F_{ax}	177.5(4)−177.8(3)	178.1(6)−179.0(4)	176.0(3)−178.2(3)
X−C−X	110.2(7)−113.2(6)[e]	111.1(8)−112.2(7)[f]	
Br−C−C			107(1)−113.3(8)
X1−Ag−X2	63.3(1)[e]	96.62(5)[f]	93.32(5)[f]
X1−Ag−X3	140.5(1)[e]	98.68(5)[f]	86.45(5)[f]
X2−Ag−X3	101.6(1)[e]	67.05(5)[f]	97.14(4)[f]
Br1−Ag−Br1′		67.74(7)	180
Br1−Ag−Br2′		163.81(6)	86.68(5)
Br1−Ag−Br3′		109.85(5)	93.55(5)
Br2−Ag−Br2′		99.26(9)	180
Br2−Ag−Br3′		90.42(6)	82.86(4)
Br3−Ag−Br3′		145.64(9)	180
Cl1−Ag−Cl4	139.7(1)		
Cl1−Ag−Cl5	113.4(1)		
Cl1−Ag−Cl6	82.0(1)		
Cl2−Ag−Cl4	80.8(1)		
Cl2−Ag−Cl5	145.4(1)		
Cl2−Ag−Cl6	85.9(1)		
Cl3−Ag−Cl4	60.8(1)		
Cl3−Ag−Cl5	99.2(1)		
Cl3−Ag−Cl6	135.5(1)		
Cl4−Ag−Cl5	85.6(1)		
Cl4−Ag−Cl6	77.7(1)		
Cl5−Ag−Cl6	60.1(1)		
Ag−Cl−C	88.5(4)−97.9(5)		
Ag−Br−C		87.6(4)−91.2(5)	113.0(4),[g] 100.3(4),[h] 94.1(4)[i]

[a] $[Ag(1,2\text{-}C_2H_4Br_2)_3][Sb(OTeF_5)_6]$ = [*catena*-poly$[Ag(1,2\text{-}C_2H_4Br_2)_2\text{-}\mu\text{-}(1,2\text{-}C_2H_4Br_2)$-*Br*:*Br′*]][$Sb(OTeF_5)_6$]. [b] M = Ti. [c] M = Nb. [d] M = Sb. [e] X = Cl. [f] X = Br. [g] Br = Br1. [h] Br = Br2. [i] Br = Br3.

dentate fashion to the d^{10} silver(I) ion. The Ag−Cl distances range from 2.656(5) to 3.049(4) Å. For comparison, the Ag−Cl distances in $[Ag(CH_2Cl_2)_2]_2[Pd(OTeF_5)_4]$ range from 2.775(2) to 2.882(2) Å,[22] and the sum of van der Waals radii for silver and chlorine is 3.45 ± 0.05 Å.[37] The dichloromethane molecules have Cl−Ag−Cl bite angles that range from 60.1(1) to 63.3(1)°. The Ag−Cl−C−Cl chelate rings are nearly planar. The average deviations from the least-squares planes of the four atoms are 0.007, 0.082, and 0.110 Å for the chelate rings containing C1, C2, and C3, respectively. Ideally, one would expect three mutually perpendicular chelate rings for a tris(chelate) complex with four-membered, planar chelate rings. The least-squares plane of the chelate ring containing C3 makes angles of 92.8 and 87.9° with the planes of the rings containing C1 and C2, respectively. However, the planes of the C1 and C2 chelate rings make an angle of only 70.6°, allowing F1 and F6 to make a closer approach to the silver atom than would be otherwise possible. The Ag··F interactions are so long (>3 Å) that they are best thought of as weak ion−dipole interactions.

The $Ag(CH_2Br_2)_3{}^+$ cation in $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$ has a structure similar to that of $Ag(CH_2Cl_2)_3{}^+$: it consists of three dibromomethane ligands coordinated to the silver ion in bidentate fashion. This is the first example of a structurally characterized bromoalkane complex of any metal. The Ag−Br distances range from 2.816(2) to 2.932(2) Å. For comparison, the Ag−Br distances in $Ag(BrCH_2SO_3)$,[53] Ag_2NO_3Br,[54] and AgBr[55] are 2.9709(5), 2.665(1)−2.959(1), and 2.88738(5) Å, respectively, and the sum of van der Waals radii for silver and bromine is 3.55 ± 0.05 Å.[37] The silver ion in $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$ lies on a crystallographic 2-fold axis that also passes through C1. Therefore, the Ag−Br−C−Br chelate ring containing C1 is rigorously planar. The pair of symmetry-related chelate rings are nearly planar: the average deviation of the four atoms from the least-squares plane containing Ag, C2, Br2, and Br3 is 0.091 Å. The three chelate rings are not strictly mutually perpendicular, although they approach it, lying at angles of 80.6, 87.0, and 99.4° to each other. These deviations may be due to packing forces, since the closest Ag··F contact is greater than 4 Å. The dibromomethane molecules

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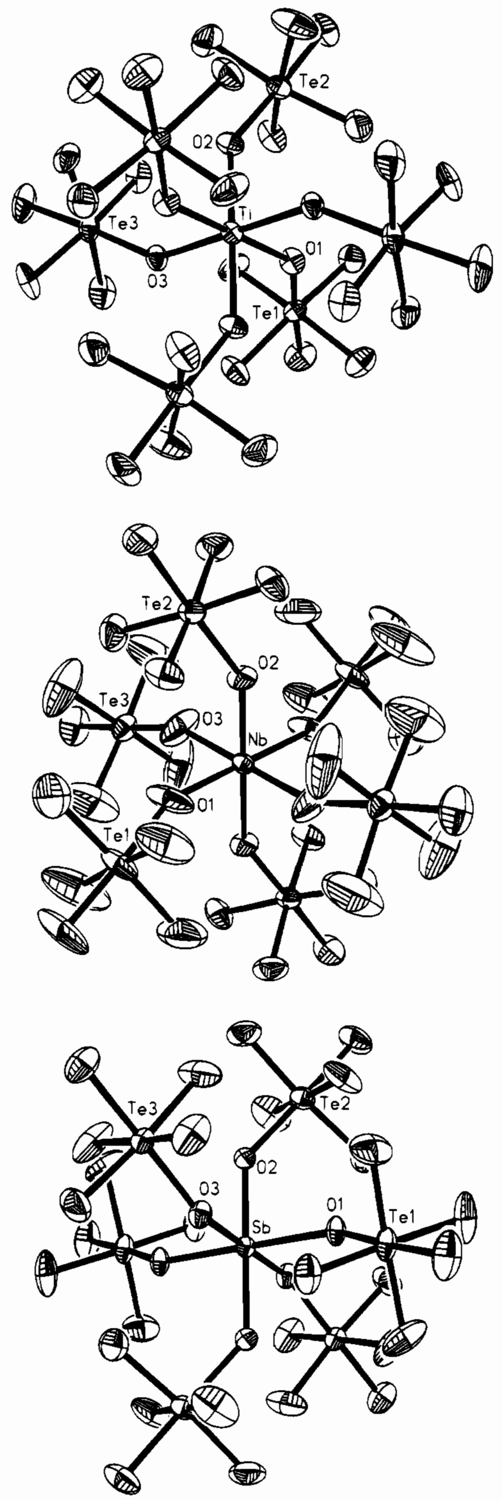

Figure 2. Drawings of the $Ti(OTeF_5)_6^{2-}$ (top), $Nb(OTeF_5)_6^-$ (middle), and $Sb(OTeF_5)_6^-$ (bottom) anions (50% probability ellipsoids).

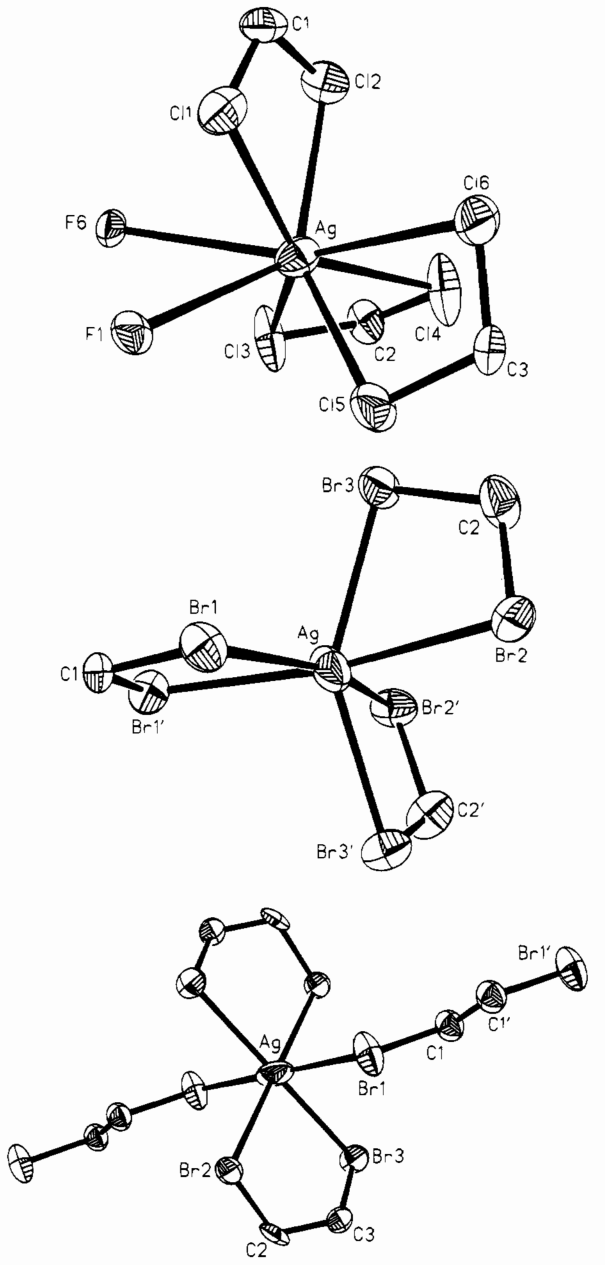

Figure 3. Drawings of the $Ag(CH_2Cl_2)_3^+$ (top), $Ag(CH_2Br_2)_3^+$ (middle), and *catena*-poly[$Ag(1,2\text{-}C_2H_4Br_2)_2$-$\mu$-$(1,2\text{-}C_2H_4Br_2)$-*Br*:*Br′*]$^+$ (bottom) cations (50% probability ellipsoids).

have Br−Ag−Br bite angles that are 67.74(7) and 67.05(5)°, several degrees larger than in the dichloromethane complex $Ag(CH_2Cl_2)_3^+$. Interestingly, the diiodomethane ligands in $[Ag(CH_2I_2)][NO_3]$ and $[Ag(CH_2I_2)_2][PF_6]$ are not bidentate: instead they bridge pairs of silver(I) ions.[52a] This is probably because a bidentate diiodomethane ligand would necessitate Ag−I−C bond angles of less than 90°, as shown in Figure 6. Angles less than 90° are probably less than optimal for metal−haloalkane bonding: a theoretical study led to a predicted angle of 100° for a $Pt-I-CH_3$ linkage.[56] Actual M−I−C angles for coordinated monodentate iodoalkanes are 99.4° (M = Ag(I); average over several structures),[52a] 106.9(8)° (M = Ir(III); average of two values),[57] 102.5(5)° (M = Re(I)),[58] 101.8(2)° (M = Ru(II)),[59] and 104.9(7)° (M = Ru(II)).[60] The one example of a monodentate chloroalkane contains a M−Cl−C angle of 105.9(2)°.[51]

The structure of [*catena*-poly[$Ag(1,2\text{-}C_2H_4Br_2)_2$-$\mu$-$(1,2\text{-}C_2H_4Br_2)$-*Br*:*Br′*]][$Sb(OTeF_5)_6$] is significantly different than the other two structures described above. The centrosymmetric silver(I) ion is bound to two symmetry related bidentate 1,2-dibromoethane ligands. Two more 1,2-dibromomethane ligands, each of which donates one bromine atom to the silver ion, round out the approximately octahedral $AgBr_6$ coordination sphere. The second bromine atoms on these two terminal ligands bridge to

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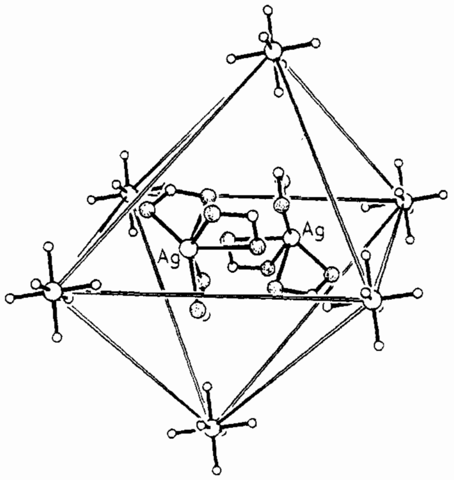

Figure 4. Drawing of the distorted octahedral arrangement of $Ti(OTeF_5)_6^{2-}$ anions about centrosymmetrically related pairs of $Ag(CH_2Cl_2)_3^+$ cations in $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$. For clarity, the anions are shown only as TiO_6 octahedra and the cations are shown without hydrogen atoms.

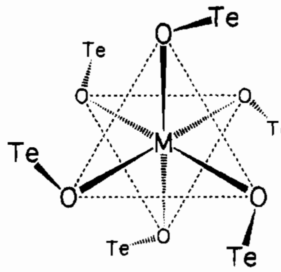

Figure 5. View down the S_6 axis of an idealized S_6-symmetry $M(OTeF_5)_6$ species (fluorine atoms have been omitted for clarity). The two parallel O_3 faces indicated with dashed lines are the two most open faces in the MO_6 octahedron.

adjacent silver ions, forming single-strand $[-(1,2\text{-}C_2H_4Br_2)_2\text{-}Ag-BrC_2H_4Br-]_n^{n+}$ chains. The Ag−Br distances within the chelate rings are 2.702(1) and 2.874(1) Å. The terminal Ag−Br distance is 3.081(2) Å. The Br−Ag−Br angles range from 82.86(4) to 97.14(4)°. The Br1−Ag−Br2 bite angle of 97.14(4)° is much larger than the bite angles of the chelating 1,2-dichloroethane ligands found in the structures of $[Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)]_2$ and $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(OTeF_5)_4$ (74.8(1)−78.0(1)°).[22] The Br−C−C−Br torsional angle within the chelate rings is 105.6°. The torsional angle for the bridging 1,2-dibromoethane ligand is 180°. For comparison, the Cl−C−C−Cl torsional angles in $Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)$ and $[Ag(1,2\text{-}C_2H_4Cl_2)_2]_2[Pd(OTeF_5)_4]$ range from 66.4 to 70.0°.

The C−Br bond distances of the 1,2-dibromoethane ligands in *catena*-poly$[Ag(1,2\text{-}C_2H_4Br_2)_2\text{-}\mu\text{-}(1,2\text{-}C_2H_4Br_2)\text{-}$*Br*:*Br′* range from 1.94(1) to 1.96(1) Å. No simple comparison can be made, since neither the structure of 1,2-dibromoethane nor the structure of a 1,2-dibromoethane solvate has been reported in the literature. The structure of 2-hydroxy-3,4,5-tribromopentanoic acid exhibits C−Br distances that range from 1.938(8) to 1.974(6) Å.[61] Therefore, no elongation of the C−Br bonds in 1,2-dibromoethane is apparent when the molecule coordinates to silver(I). A similar conclusion can be reached regarding the C−Br bonds in dibromomethane: the distances in $Ag(CH_2Br_2)_3^+$ range from 1.91(2) to 1.92(2) Å while the distance in gaseous dibromomethane is 1.91(2) Å.[62] Although silver(I) is known to activate carbon−halogen bonds, its role is apparently to stabilize the $(\delta+)C\cdots X(\delta-)\cdots Ag^+$ transition state, since elongation of a haloalkane C−X bond upon coordination to a metal ion has never been observed for any of the halogens.[22,48]

The homoleptic complexes $Ag(CH_2Br_2)_3^+$ and *catena*-poly$[Ag(1,2\text{-}C_2H_4Br_2)_2\text{-}\mu\text{-}(1,2\text{-}C_2H_4Br_2)\text{-}$*Br*:*Br′*$]^+$ are two examples of structurally characterized metal complexes in which the metal-ion coordination spheres are filled exclusively with haloalkane ligands (two others are known, involving silver(I) and iodocarbon ligands (see above)[52a]).

(c) Solid-State Packing. The very large $Ti(OTeF_5)_6^{2-}$ anions in $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$ are arranged in a highly distorted, but recognizable, version of a cubic close-packed array. Similar anion packing arrangements were found for the trigonal form of $Te(OTeF_5)_6$,[40] for $[N(Me)_4][As(OTeF_5)_6]$,[26] and for $[N(Et)_4][Sb(OTeF_5)_6]$.[26] The magnitude of the distortions may be judged from the 10.9−14.6 Å range of distances from any given titanate anion to the 12 anions closest to it. Interestingly, the $Ag(CH_2Cl_2)_3^+$ cations do not occupy the positions that would correspond to the tetrahedral holes in the idealized close-packed array of anions (i.e., an antifluorite-type lattice is not observed). Instead, centrosymmetrically related pairs of cations, with two Cl···Cl van der Waals contacts of 3.43 Å, occupy positions corresponding to octahedral holes, as shown in Figure 4. The observed packing arrangement is therefore a distorted version of the sodium chloride structure, with "2+" cations and 2− anions. If the geometric center of the $[Ag(CH_2Cl_2)_3]_2^{2+}$ dication is defined as Ct, the Ti···Ct distances range from 7.63 to 9.63 Å and the Ti···Ct···Ti angles range from 74.6 to 105.4°. The magnitude of the Ti···Ct distances suggests that the anion radius of 6.8 Å listed in Table 5 overestimates the effective radius of the $Ti(OTeF_5)_6^{2-}$ anion.

The $Nb(OTeF_5)_6^-$ anions in $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$ do not pack in a manner that can be represented as close-packed. Instead, each niobate anion is surrounded by six other niobate anions in a distorted octahedral array (four Nb···Nb distances are 9.80 Å and two are 10.77 Å), resulting in a distorted version of simple cubic anion packing. The $Ag(CH_2Br_2)_3^+$ cations are arranged in a similar distorted cubic array that interpenetrates the anion array in a manner best described as a variant of the cesium chloride structure. The eight Ag···Nb nearest neighbor distances range from 8.43 to 9.39 Å. Similar packing was observed for $[N(Me)_4][Bi(OTeF_5)_6]$[26] but was incorrectly described as resulting from "two interpenetrating cubic closest packed lattices of cations and anions." In no sense can the packing in $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$ or in the bismuth compound be described as close-packed. The packing of the $Sb(OTeF_5)_6^-$ anions in [*catena*-poly$[Ag(1,2\text{-}C_2H_4Br_2)_2\text{-}\mu\text{-}(1,2\text{-}C_2H_4Br_2)\text{-}$*Br*:*Br′*]$[Sb(OTeF_5)_6]$ is similar to that found in $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$, despite the obvious differences in the crystal systems and unit cells adopted by the two compounds.

Stability of $M(OTeF_5)_6^{n-}$ Anions. (a) Stability to Hydrolysis. The efficacy of $M(OTeF_5)_6^{n-}$ anions as weakly coordinating anions depends in large part on their stability under a variety of conditions. All of the compounds reported in this paper undergo hydrolysis when exposed to even trace amounts of moisture. However, this is only a limitation as far as synthesis and handling is concerned. As far as applications are concerned, there would be no reason to study reactive cations with vacant, virtual, or latent coordination sites except under the strictest anaerobic and anhydrous conditions.

(b) Stability in the Presence of Solvents and Other Weak Nucleophiles. Intrinsic stability in solution is an important issue because some hexakis(teflate) compounds have been observed to decompose as follows (M = Mo(VI), m = 0, solvent = $CFCl_3$;[38] M = Os(VI), m = 0, no solvent;[63] M = Bi(V), m = 1−, solvents = SO_2ClF and CH_3CN;[26] M = I(V), m = 1−,

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Table 5. Structural Parameters for $M(OTeF_5)_6^{0/n-}$ Species[a]

species	cation	M–O dist, Å	M–O–Te angle, deg	radius, Å[b]	ref
$Ti(OTeF_5)_6^{2-}$	$[Ag(CH_2Cl_2)_3]^+$	1.933(6) 1.935(6) 1.939(9)	142.3(4) 142.8(4) 145.2(5)	6.75	this work
$Nb(OTeF_5)_6^-$	$[Ag(CH_2Br_2)_3]^+$	1.92(1) 1.931(9) 1.949(8)	148.4(5) 157.8(7) 158.0(8)	6.85	this work
$Mo(OTeF_5)_6$		1.860(4) 1.865(4) 1.870(4)	145.6(2) 146.0(2) 146.2(2)	6.75	38
$U(OTeF_5)_6$		2.04(3) 2.05(2)	170(2) 171(1)	7.02	39
$As(OTeF_5)_6^-$[c]	NMe_4^+	1.70(8) 1.77(4) 1.79(3)	139.9(9) 140(4) 141(2)	6.63	26
$Sb(OTeF_5)_6^-$	$[Ag(1,2\text{-}C_2H_4Br_2)_3]^+$[d]	1.938(6) 1.951(7) 1.958(6)	138.5(4) 139.3(4) 141.6(4)	6.73	this work
$Sb(OTeF_5)_6^-$	NMe_4^+	1.90(1) 1.90(1) 1.92(1)	148.4(8) 150.9(7) 153.4(8)	6.72	26
$Sb(OTeF_5)_6^-$	NEt_4^+	1.87(1) 1.87(1) 1.88(2)	160.7(9) 160.8(9) 167(1)	6.71	26
$Te(OTeF_5)_6$[e]		1.906(3) 1.901(3) 1.900(3)	138.9(2) 139.0(2) 139.1(2)	6.71	40
$Bi(OTeF_5)_6^-$	NMe_4^+	2.052(6) 2.054(6) 2.064(5)	135.3(3) 135.7(3) 137.1(3)	6.76	26

[a] M–O distances and M–O–Te angles are listed in ascending order and do not necessarily correlate with one another. [b] Defined as the average $M\cdots F_{ax}$ distance (in Å) + 1.40 Å. [c] There were two crystallographically unique $As(OTeF_5)_6^-$ anions in this structure, one of which was disordered. [d] $Ag(1,2\text{-}C_2H_4Br_2)_3^+$ = *catena*-poly$[Ag(1,2\text{-}C_2H_4Br_2)_2\text{-}\mu\text{-}(1,2\text{-}C_2H_4Br_2)\text{-}Br{:}Br']^+$. [e] Triclinic modification.

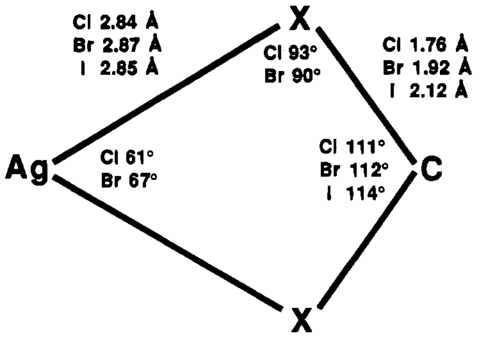

Figure 6. Average structural parameters for the relatively planar four-membered chelate rings in $Ag(CH_2X_2)_3^+$ cations (X = Cl, Br; this work) and in $Ag(CH_2I_2)_n^+$ cations with monodentate, bridging diiodomethane ligands (*n* = 1, 2; ref 52a).

solvent = CH_2Cl_2[44]):

$$M(OTeF_5)_6^{m} \rightarrow O{=}M(OTeF_5)_4^{m} + F_5TeOTeF_5$$

The structures of $MoO(OTeF_5)_4$,[38] $WO(OTeF_5)_4$,[63] and $OsO(OTeF_5)_4$[63] reveal pseudo-octahedral coordination geometries around the metal ions. Each structure consists of pairs of square-pyramidal $MO(OTeF_5)_4$ moieties (apical oxo ligand) with pairs of weak intermolecular $M\cdots F$ contacts. The structure of $IO(OTeF_5)_4^-$ consists of discrete square-pyramidal molecular ions, with no intermolecular $I\cdots F$ contacts.[44]

Fluorine-19 NMR spectra demonstrate that $Nb(OTeF_5)_6^-$, $Sb(OTeF_5)_6^-$, $Ti(OTeF_5)_6^{2-}$, $Zr(OTeF_5)_6^{2-}$, and $Hf(OTeF_5)_6^{2-}$ are stable indefinitely in dichloromethane solution. We confirm the report by Schrobilgen and co-workers[26] that $Sb(OTeF_5)_6^-$ is also stable indefinitely in acetonitrile, a solvent that caused the decomposition of $Bi(OTeF_5)_6^-$ (see reaction above). However, acetonitrile causes the rapid decomposition of $Nb(OTeF_5)_6^-$: ^{19}F NMR spectra of either $AgNb(OTeF_5)_6$ or $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$ in a mixture of dichloromethane and acetonitrile show the formation of two new teflate AB_4 patterns in an approximately 2:1 ratio. In the experiment with $AgNb(OTeF_5)_6$, the chemical shifts of the more intense AB_4 pattern are δ_A −35.1 and δ_B −47.5, while those of the less intense AB_4 pattern are δ_A −46.9 and δ_B −36.9. A ^{19}F NMR spectrum of the volatile components of this reaction mixture consists of only the δ_A −46.9, δ_B −36.9 AB_4 pattern. The volatility of this reaction product and a comparison of chemical shifts suggests that it is $F_5TeOTeF_5$ (literature values for the neat liquid:[64] δ_A −48.1, δ_B −37.5). We conclude that the following reaction had occurred:

$$Nb(OTeF_5)_6^- + CH_3CN \rightarrow \\ trans\text{-}NbO(OTeF_5)_4(CH_3CN)^- + F_5TeOTeF_5$$

The AB_4 pattern at δ_A −35.1, δ_B −47.5 is assigned to the four equiv equatorial teflate groups in the *trans*-$NbO(OTeF_5)_4(CH_3CN)^-$ complex ion.

NMR spectra, shown in Figure 7, demonstrate conclusively that a similar decomposition occurred when $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$ was treated with $[N(n\text{-}Bu)_4][OTeF_5]$ in dichloromethane. Once again resonances attributable to $F_5TeOTeF_5$ were observed (these are labeled with open circles in Figure 7), along with two new AB_4 patterns in an approximately 4:1 ratio (the chemical shifts of the more intense AB_4 pattern, labeled with solid circles, are δ_A −35.7 and δ_B −48.6, while those of the less intense AB_4 pattern, labeled with asterisks, are δ_A −27.3 and δ_B −42.6). On the basis of this evidence, we conclude that the following reaction had occurred:

$$Nb(OTeF_5)_6^- + OTeF_5^- \rightarrow NbO(OTeF_5)_5^{2-} + F_5TeOTeF_5$$

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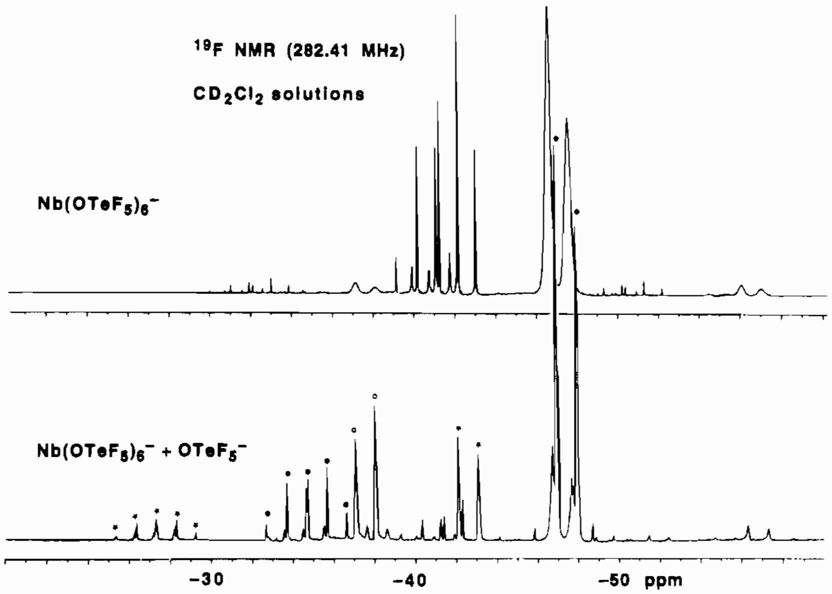


Figure 7. 282.41 MHz ^{19}F NMR spectra of $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$ (upper spectrum) and a mixture of $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$ and $[N(n\text{-}Bu)_4][OTeF_5]$ (lower spectrum) that had equilibrated for several hours ($CFCl_3$ internal standard). Resonances due to a small amount of $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$ can be observed in the lower spectrum, along with three new AB_4X patterns assigned to the axial (asterisks) and equatorial (solid circles) teflate groups of $NbO(OTeF_5)_5^{2-}$ and to $F_5TeOTeF_5$ (open circles).

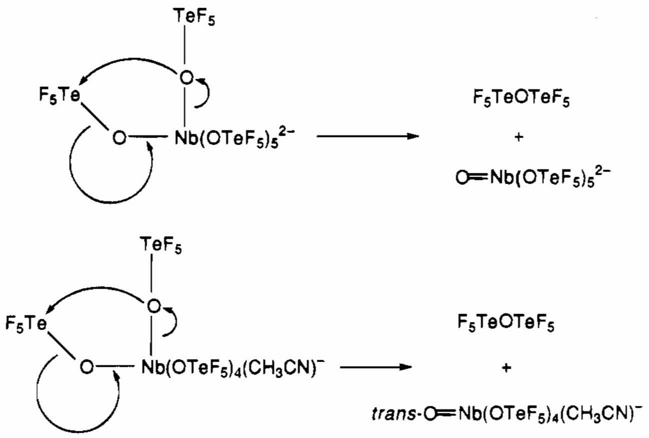
The two AB_4 patterns in a 4:1 ratio are assigned to the four equiv equatorial teflate groups and to the unique axial teflate group in the $NbO(OTeF_5)_5^{2-}$ complex ion, respectively. The proposed product $NbO(OTeF_5)_5^{2-}$ is structurally analogous to the C_{4v} $NbOF_5^{2-}$ ion.[65]

The $Nb(OTeF_5)_6^-$ anion also reacted with PF_6^- in dichloromethane. After 7.5 h, in addition to the ^{19}F NMR doublet due to the hexafluorophosphate anion at δ −72.4, two doublets appeared at δ −84.4 and δ −88.5, indicating the formation of new species with P−F bonds. A new AB_4 pattern with δ_A −35.1 and δ_B −45.8 was also present. No resonances due to $F_5TeOTeF_5$ were observed.

In contrast to the behavior of the $Nb(OTeF_5)_6^-$ anion, $Sb(OTeF_5)_6^-$ was found to be stable indefinitely in the presence of acetonitrile, $OTeF_5^-$, or PF_6^-. The difference in reactivities may be due to the greater tendency of Nb(V) to achieve seven-coordination relative to Sb(V) . We speculate that, in the presence of acetonitrile or $OTeF_5^-$, the seven-coordinate complexes $Nb(OTeF_5)_6(CH_3CN)^-$ or $Nb(OTeF_5)_7^{2-}$ are formed and that these intermediates decompose by means of intramolecular formation of $F_5TeOTeF_5$, as shown in Scheme 2.

(c) Stability in the Presence of Electrophiles. The abstraction of a relatively strongly coordinating $OTeF_5^-$ anion from a weakly coordinating $M(OTeF_5)_6^{n-}$ anion by an electrophile could severely restrict the use of that anion in demanding situations. In an earlier study, we found that the $B(OTeF_5)_4^-$ anion underwent complete isotope scrambling within 1 h when it was treated with ^{17}O- or ^{18}O-labeled $HOTeF_5$ or $AgOTeF_5$ in dichloromethane.[23b] Simple dissociation of a teflate anion from $B(OTeF_5)_4^-$ was ruled out. We proposed that the electrophiles H^+ and Ag^+ attacked the borate anion at one of its most basic sites, the four oxygen atoms, producing intermediates with H−O(Te)−B or Ag−O(Te)−B bridges that rapidly underwent labeled/unlabeled teflate group exchange. The observation that there are no Ag−O(Te)−M bridges in $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$, and $[catena\text{-}poly\text{-}[Ag(1,2\text{-}C_2H_4Br_2)_2\text{-}\mu\text{-}(1,2\text{-}C_2H_4Br_2)\text{-}Br{:}Br']][Sb(OTeF_5)_6]$ suggested to us that the hexakis(teflate) anions may be more stable in the presence of electrophiles than are the tetrakis(teflate) anions $B(OTeF_5)_4^-$ and $Pd(OTeF_5)_4^{2-}$. This was found to be the case for the uninegative anions $Nb(OTeF_5)_6^-$ and $Sb(OTeF_5)_6^-$.

Scheme 2



The $N(n\text{-}Bu)_4^+$ salts of natural abundance $Ti(OTeF_5)_6^{2-}$, $Nb(OTeF_5)_6^-$, and $Sb(OTeF_5)_6^-$ were treated with 1 equiv of $H^{18}OTeF_5$ (77% ^{18}O) in dichloromethane. Fluorine-19 NMR spectra demonstrated that no net chemical reaction, other than possible isotope scrambling, occurred during these experiments (i.e., these hexakis(teflate) anions are stable indefinitely in the presence of $HOTeF_5$). After various time intervals, in separate experiments, the volatile components CH_2Cl_2 and H^*OTeF_5 were removed from the reaction mixture and treated with pyridine, which formed $[pyH][^*OTeF_5]$ quantitatively. The degree of isotope scrambling was determined by comparing the absorbances of bands in infrared spectra of $[pyH^+][^*OTeF_5]$ dissolved in dichloromethane at 834 cm^{-1} ($\nu(Te^{16}O)$) and 793 cm^{-1} ($\nu(Te^{18}O)$). A typical set of results is shown in Figure 8. The dashed line is the spectrum of 0.128 M $[pyH][^{18}OTeF_5]$ (77% ^{18}O) in dichloromethane. The solid line is the spectrum of 0.128 M $[pyH][^*OTeF_5]$ made from H^*OTeF_5 recovered from a 1:1 mixture of $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$ and $H^{18}OTeF_5$ (77% ^{18}O) that had equilibrated in dichloromethane for 47 h. The decrease in absorbance at 793 cm^{-1} and the increase in absorbance at 834 cm^{-1} correspond to approximately 22%

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(65) (a) Rakov, I. E.; Gorbunova, Y. E.; Kokunov, Y. V.; Mikhailov, Y. N. *Koord. Khim.* **1993**, *19*, 759. (b) von Barner, J. H.; Christensen, E.; Bjerrum, N. J.; Gilbert, B. *Inorg. Chem.* **1991**, *30*, 561.

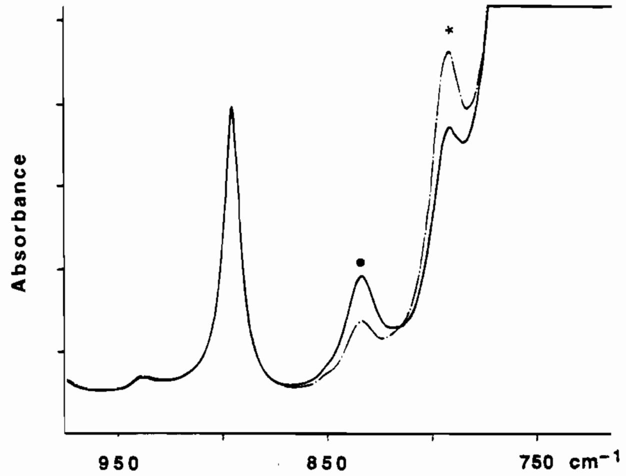

Figure 8. Infrared spectra of 0.128 M dichloromethane solutions of $[pyH][^{18}OTeF_5]$ (77% ^{18}O) (dashed line) and $[pyH][^*OTeF_5]$ made from H^*OTeF_5 recovered from a 1:1 mixture of $[N(n\text{-}Bu)_4][Nb(OTeF_5)_6]$ and $H^{18}OTeF_5$ (77% ^{18}O) that had equilibrated for 47 h (solid line). The band at 896 cm^{-1} and the absorption below 775 cm^{-1} are due to solvent. The bands at 834 cm^{-1} (solid circle) and 793 cm^{-1} (asterisk) are assigned to $\nu(Te^{16}O)$ and $\nu(Te^{18}O)$, respectively.

isotope scrambling after this time interval (this assumes statistical scrambling, i.e., 100% isotope scrambling for this 1:1 mixture would result in 14.3% of the ^{18}O label in H^*OTeF_5 and 85.7% in $Nb(OTeF_5)_6^-$). Thus, the $Nb(OTeF_5)_6^-$ anion is much more stable than $B(OTeF_5)_4^-$ in the presence of $HOTeF_5$. In contrast, a mixture of $[N(n\text{-}Bu)_4]_2[Ti(OTeF_5)_6]$ and $H^{18}OTeF_5$ in dichloromethane resulted in complete isotope scrambling after only 1 h. A mixture of $[N(n\text{-}Bu)_4][Sb(OTeF_5)_6]$ and $H^{18}OTeF_5$ in dichloromethane resulted in no detectable isotope scrambling, even after 168 h.

The exchange of teflate groups between the silver(I) salts of $Ti(OTeF_5)_6^{2-}$ and $Nb(OTeF_5)_6^-$ and $Ag^{18}OTeF_5$ (77% ^{18}O) in dichloromethane was also monitored by infrared spectroscopy. After 1 h, complete isotope scrambling had occurred between $Ag_2Ti(OTeF_5)_6$ and $Ag^{18}OTeF_5$. However, after 72 h no detectable isotope scrambling had occurred between $Ag^{18}OTeF_5$ and $AgNb(OTeF_5)_6$.

The stability with respect to $OTeF_5^-$ abstraction in the presence of electrophiles, as monitored by teflate group exchange reactions, follows the order $Sb(OTeF_5)_6^- > Nb(OTeF_5)_6^- \gg Ti(OTeF_5)_6^{2-} \sim B(OTeF_5)_4^-$. It still seems sensible to conclude that coordination of an electrophile to one of the teflate oxygen atoms must precede teflate group abstraction. The greater accessibility of the teflate oxygen atoms in $B(OTeF_5)_4^-$, relative to the sterically more congested $Nb(OTeF_5)_6^-$ and $Sb(OTeF_5)_6^-$ anions, is commensurate with the greater reactivity of the $B(OTeF_5)_4^-$ anion. Nevertheless, the structures of the $M(OTeF_5)_6^{n-}$ anions, which are very similar, do not provide any clues to the observed differences in reactivity within the class of hexakis(teflate) anions. In the case of $Ti(OTeF_5)_6^{2-}$, the greater negative charge may account for its greater rate of exchange in the presence of electrophiles relative to either of the two uninegative hexakis(teflate) anions. The difference in reactivity of $Nb(OTeF_5)_6^-$ in the presence of $HOTeF_5$ or $AgOTeF_5$ may be due to the great difference in size between the proton and the Ag^+ ion. However, it is not clear from the structures why $Nb(OTeF_5)_6^-$, but not $Sb(OTeF_5)_6^-$, undergoes exchange (albeit slow exchange) with labeled $HOTeF_5$. Perhaps a seven coordinate species such as $Nb(OTeF_5)_6(HOTeF_5)^-$ is formed prior to proton transfer. Nevertheless, it is clear from these results that the $Sb(OTeF_5)_6^-$ anion is the most stable of the hexakis(teflate) anions in the presence of electrophiles and, therefore, is probably the most useful weakly coordinating anion in its class.

Experimental Section

Inert Atmosphere. None of the new compounds appeared to be oxygen sensitive, but all were extremely moisture sensitive. Therefore, all preparations and physical measurements were carried out with rigorous exclusion of air and water. Schlenk, glovebox, and high-vacuum techniques were employed, with purified nitrogen or argon used when an inert atmosphere was required.[66]

Reagents and Solvents. These were reagent grade or better. The following compounds were used as received: $ZrCl_4$ (Strem), $HfCl_4$ (Strem). Niobium pentachloride and $TaCl_5$ (Johnson Mathey) were sublimed. Antimony pentachloride (MCB) and $TiCl_4$ (Strem) were vacuum distilled. Tetra-*n*-butylammonium chloride (Aldrich) was recrystallized from acetone and diethyl ether. Three-times recrystallized $[N(n\text{-}Bu)_4][PF_6]$ was a gift from Professor C. M. Elliott. The following compounds were prepared by following literature procedures: $HOTeF_5$,[67] $H^{18}OTeF_5$,[18] $AgOTeF_5$,[23e] $[N(n\text{-}Bu)_4][OTeF_5]$.[67] The following solvents were dried by distillation from sodium metal, P_2O_5, CaH_2, and/or activated 4 Å molecular sieves: acetone, acetonitrile, 1,2-dibromoethane, dibromomethane, diethyl ether, 1,2-dichloroethane, dichloromethane, dichloromethane-d_2, toluene, and 1,1,2-trichlorotrifluoroethane.

Preparation of New Compounds. $Ag_2Ti(OTeF_5)_6$. A mixture of $TiCl_4$ (0.074 g, 0.39 mmol), $AgOTeF_5$ (0.810 g, 2.34 mmol), and 1,1,2-trichlorotrifluoroethane (2 mL), which was originally brown in color, was stirred for 12 h. The resulting reaction mixture was filtered through a fine-porosity glass frit yielding a white solid (AgCl) and a clear, colorless solution. Removal of solvent gave an extremely hygroscopic, free-flowing white solid in >70% yield. The compound was judged >98% pure by ^{19}F NMR spectroscopy.

$[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$. A 4 mL solution of $Ag_2Ti(OTeF_5)_6$ (1.20 g, 0.709 mmol) in dichloromethane (4 mL) was reduced to one-half volume under vacuum, causing clear, colorless crystals of $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$ to form. The coordinated dichloromethane molecules are readily lost from the crystals at room temperature.

$[N(n\text{-}Bu)_4]_2[Ti(OTeF_5)_6]$. A 1 equiv amount of $Ag_2Ti(OTeF_5)_6$ and 2 equiv of $[N(n\text{-}Bu)_4][Cl]$ were mixed in dichloromethane and stirred for at least 1 h. The AgCl precipitate was removed by filtration. All traces of solvent were removed from the filtrate under vacuum, leaving a free-flowing white solid that was judged >98% pure by ^{19}F NMR spectroscopy.

$Ag_2Zr(OTeF_5)_6$ and $Ag_2Hf(OTeF_5)_6$. A 6 equiv amount of $AgOTeF_5$ and 1 equiv of either $ZrCl_4$ or $HfCl_4$ were heated to 80 °C in dichloromethane using a glass pressure vessel (*Caution*: the pressure in the glass vessel exceeds 3 atm; the normal boiling point of dichloromethane is 40 °C). The slurry was filtered through a fine-porosity glass frit to remove AgCl. The filtrate volume was reduced and cooled to −20 °C. After several hours large, colorless, rectangular crystals formed. The crystals were isolated and placed under dynamic vacuum for 48 h to remove solvent molecules that were bound to the silver(I) ions, giving extremely hygroscopic, free-flowing white solids (42% yield for $Ag_2Zr(OTeF_5)_6$, 70% yield for $Ag_2Hf(OTeF_5)_6$). Infrared spectra showed no traces of dichloromethane bound to the silver(I) ions. The compounds were judged >98% pure by ^{19}F NMR spectroscopy (see Figure 1).

$AgNb(OTeF_5)_6$. A 1 equiv amount of $NbCl_5$, 6 equiv of $AgOTeF_5$, and F-113 were charged to a glass reaction vessel containing a stir bar. The reaction mixture was stirred for 4 h. The AgCl precipitate was removed by filtration using a medium-porosity glass frit. The filtrate volume was reduced and cooled to −20 °C. After a period of hours colorless crystals formed. The crystals were isolated and placed under dynamic vacuum for several hours to remove solvent molecules that were bound to the silver(I) ions, giving an extremely hygroscopic, free-flowing white solid in 32% yield. The compound was judged >98% pure by ^{19}F NMR spectroscopy. Further concentration of the supernatant produced additional crystalline product, giving total yields

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(66) (a) Wayda, A. L.; Darensbourg, M. Y. *Experimental Organometallic Chemistry*; American Chemical Society: Washington, DC, 1987. (b) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(67) Strauss, S. H.; Abney, K. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 2806.

as high as 85%, although trace amounts of impurities were present when this much product was recovered.

[Ag(CH_2Br_2)$_3$][Nb($OTeF_5$)$_6$]. The compound AgNb($OTeF_5$)$_6$ (~0.05 g) was dissolved in dibromomethane (~0.35 mL; mp −52 °C) which had been dried over 4 Å molecular sieves and purified by fractional distillation. After 1 week colorless crystals formed.

[N(*n*-Bu)$_4$][Nb($OTeF_5$)$_6$]. A 1 equiv amount of AgNb($OTeF_5$)$_6$ and 1 equiv of [N(*n*-Bu)$_4$][Cl] were mixed in dichloromethane and stirred for 1 h. The AgCl was removed by filtration and the filtrate cooled to −20 °C. Colorless crystals were isolated in 58% yield. The compound was judged >98% pure by ^{19}F NMR spectroscopy.

[Ph_3C][Nb($OTeF_5$)$_6$]. A 1 equiv amount of Ph_3CCl and 1 equiv of AgNb($OTeF_5$)$_6$ were placed in a flask. A bright yellow color developed where the two colorless solids were in contact. Dichloromethane was added to the flask, and the bright yellow mixture was stirred for 1−3 h, wrapped in foil. The suspension was then filtered through a medium-porosity glass frit. The volume of the yellow filtrate was reduced and cooled to −20 °C. Many small yellow crystals formed within hours. The crystals were isolated and placed under dynamic vacuum to give a fine yellow powder in 77% yield. The compound, which was judged >98% pure by ^{19}F NMR spectroscopy, darkened upon exposure to light and was kept wrapped in foil whenever possible.

AgSb($OTeF_5$)$_6$. A 6 equiv amount of $AgOTeF_5$, F-113, and a stir bar were degassed in a glass reaction vessel. A 1 equiv amount of $SbCl_5$ was transferred under vacuum into the reaction vessel. The reaction mixture was stirred overnight. After the F-113 was removed under vacuum, the solid mixture was extracted with dichloromethane. The dichloromethane solution was cooled to −20 °C. After several hours colorless crystals formed. The crystals were isolated and were placed under dynamic vacuum for several hours to remove solvent molecules that were bound to the silver(I) ions, giving an extremely hygroscopic, free-flowing white solid in 66% yield. The compound was judged >98% pure by ^{19}F NMR spectroscopy.

[Ag(1,2-$C_2H_4Br_2$)$_3$][Sb($OTeF_5$)$_6$].[27] The compound AgSb($OTeF_5$)$_6$ was dissolved in 1,2-dibromoethane that had been dried over 4 Å molecular sieves and purified by fractional distillation. After several weeks colorless rectangular crystals formed.

[N(*n*-Bu)$_4$][Sb($OTeF_5$)$_6$]. A 1 equiv amount of AgSb($OTeF_5$)$_6$ and 1 equiv of N(*n*-Bu)$_4$Cl were mixed in dichloromethane and stirred overnight. The AgCl was removed by filtration and the filtrate cooled to −20 °C. Colorless crystals were isolated in 69% yield. The compound was judged >98% pure by ^{19}F NMR spectroscopy.

[Ph_3C][Sb($OTeF_5$)$_6$]. A 1 equiv amount of Ph_3CCl and 1 equiv of AgSb($OTeF_5$)$_6$ were mixed in dichloromethane. The bright yellow suspension was stirred for 1-2 h and filtered through a medium-porosity glass frit. The filtrate volume was reduced and cooled to −20 °C. After several hours small dark yellow crystals formed. These were isolated in 82% yield. The compound, which was judged >98% pure by ^{19}F NMR spectroscopy, darkened upon exposure to light and was kept in the dark whenever possible.

Spectroscopic Measurements. Samples for IR spectroscopy were either Nujol mulls between AgBr windows or dichloromethane solutions in 0.2-mm path length cells with KBr windows. Spectra were recorded at room temperature on a Perkin-Elmer 983 infrared spectrometer. Samples for ^{19}F NMR spectroscopy were dichloromethane or dichloromethane-d_2 solutions in 5-mm glass tubes. Spectra were recorded on a Bruker SY-200 or WP-300 spectrometer. Chemical shifts (δ scale) are relative to internal $CFCl_3$ (^{19}F). All ^{19}F NMR spectra were AB_4X patterns shielded relative to $CFCl_3$ (X = ^{125}Te, $I = {}^1/_2$, 7% natural abundance). In some cases ^{123}Te satellites could also be observed.

Crystallographic Study. A Siemens *R*3*m* diffractometer equipped with a LT-2 variable-temperature accessory was used. Crystals of [Ag(CH_2Cl_2)$_3$]$_2$[Ti($OTeF_5$)$_6$], [Ag(CH_2Br_2)$_3$][Nb($OTeF_5$)$_6$], and [Ag(1,2-$C_2H_4Br_2$)$_3$][Sb($OTeF_5$)$_6$] were examined at −20 °C or colder using an apparatus previously described.[22] When a suitable crystal was found, it was embedded in Silicone or Halocarbon 25-5S grease at the end of a glass fiber and quickly placed in the cold nitrogen stream of the LT-2 unit.

Centering of 25 reflections allowed least-squares calculation[68] of the cell constants given in Table 3, which also lists other experimental parameters. The intensities of three control reflections monitored every 97 reflections showed no significant trend during the course of the data collections. Empirical absorption corrections, based on intensity profiles for 16 reflections over a range of setting angles (ψ) for the diffraction vector, were applied to the observed data for all three compounds. The transmission factors ranged from 0.192 to 0.466 for [Ag(CH_2Cl_2)$_3$]$_2$[Ti($OTeF_5$)$_6$], from 0.371 to 0.968 for [Ag(CH_2Br_2)$_3$][Nb($OTeF_5$)$_6$], and from 0.214 to 0.481 for [Ag(1,2-$C_2H_4Br_2$)$_3$][Sb($OTeF_5$)$_6$].[27] Lorentz and polarization corrections were applied to the data.

The structures were solved by direct methods for [Ag(CH_2Cl_2)$_3$]$_2$[Ti($OTeF_5$)$_6$] or by interpretation of Patterson maps for [Ag(CH_2Br_2)$_3$][Nb($OTeF_5$)$_6$] and [Ag(1,2-$C_2H_4Br_2$)$_3$][Sb($OTeF_5$)$_6$].[69] The refinements involved anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (C−H = 0.96 Å, U(H) = $1.2U_{iso}$(C)). Neutral-atom scattering factors (including anomalous scattering) were taken from ref 69. The weighted least-squares refinements converged (weights were calculated as $(\sigma^2(F) + |g|F_o^2)^{-1})$ for [Ag(CH_2Cl_2)$_3$]$_2$[Ti($OTeF_5$)$_6$], $(\sigma^2(F_o) + (0.0755P)^2 + 53.05P^{-1}$ for [Ag(CH_2Br_2)$_3$][Nb($OTeF_5$)$_6$] ($P = (\max(F_o^2,0) + 2F_c^2)/3$), and $(\sigma^2(F_o) + (0.1253P)^2 + 1.96P^{-1}$ for [Ag(1,2-$C_2H_4Br_2$)$_3$][Sb($OTeF_5$)$_6$] ($P = (\max(F_o^2,0) + 2F_c^2)/3$). In the final difference Fourier maps, the maximum and minimum electron densities were 4.50 and −2.49 e Å^{-3} for [Ag(CH_2Cl_2)$_3$]$_2$[Ti($OTeF_5$)$_6$], 2.67 and −1.44 e Å^{-3} for [Ag(CH_2Br_2)$_3$][Nb($OTeF_5$)$_6$], and 3.71 and −3.79 e Å^{-3} for [Ag(1,2-$C_2H_4Br_2$)$_3$][Sb($OTeF_5$)$_6$]. Analysis of variance as a function of Bragg angle, magnitude of F_o, reflection indices, etc., showed no significant trends.

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Supplementary Material Available: Complete tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters for [Ag(CH_2Br_2)$_3$][Nb($OTeF_5$)$_6$] and [*catena*-poly[Ag(1,2-$C_2H_4Br_2$)$_2$-μ-(1,2-$C_2H_4Br_2$)-*Br*:*Br*′]][Sb($OTeF_5$)$_6$] (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Similar information is available for [Ag(CH_2Cl_2)$_3$]$_2$[Ti($OTeF_5$)$_6$]: see the supplementary material paragraph at the end of ref 28.

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(68) Calculations for diffractometer operations were performed by using software supplied with the Siemens *R*3*m* diffractometer. All structural calculations were performed in the X−ray laboratory at Colorado State University with the SHELXTL program library written by Professor G. M. Sheldrick and supplied by Siemens.

(69) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.