The addition of water or 48% aqueous hydrofluoric acid to AgSbF$_6$ in acetonitrile showed similarly broadened lines. In the absence of information concerning possible exchange processes involving fluoride ion and viscosity and dielectric constant changes in these solutions, we are unable to account for the observed multiplet broadening.

Experimental Section

Sample Preparation.—AgSbF$_6$ and NaSbF$_6$ were obtained from Alfa Inorganics and used without further purification. Spectro Grade solvents were used.

Solutions were normally prepared in the air although unnecessary exposure of reagents to the atmosphere was avoided. The possible effects of moisture absorbed from the atmosphere were tested by preparing a sample solution under dry nitrogen. Acetonitrile was dried by distillation from calcium hydride under nitrogen and a previously unopened sample of AgSgF$_6$ was recrystallized from this solvent. The ^{19}F nmr of this solution showed no significant difference compared to that of a similar solution prepared in the air with spectroscopic grade solvent.

On exposure to light, freshly prepared solutions of AgSbF$_6$ produced a black material, presumably metallic silver, after a few minutes. This did not appear to affect the nmr spectra in any way other than to decrease signal intensity after exposure to light for several days.

Nmr Spectra.—The ^{19}F spectra were obtained using a Varian HA-100 spectrometer operating at 94.1 MHz. The spectrum illustrated in Figure 1 was obtained using a modified HA field-sweep mode. The lock was switched off and the manual oscillator was replaced by an external oscillator generating about 15,000 Hz. We were unable to obtain a symmetrical intensity pattern using this mode. The coupling constants were determined by scanning each component separately in an HA frequency-sweep mode using trifluoroacetic acid to provide a lock signal Considerable difficulty was experienced in correctly phasing the broad (100–200 Hz) components in this mode. Consequently, each value was obtained from measurements on the two appropriate components with the best line shapes. The precision is a subjective estimate of the accuracy in determining the band maxima.

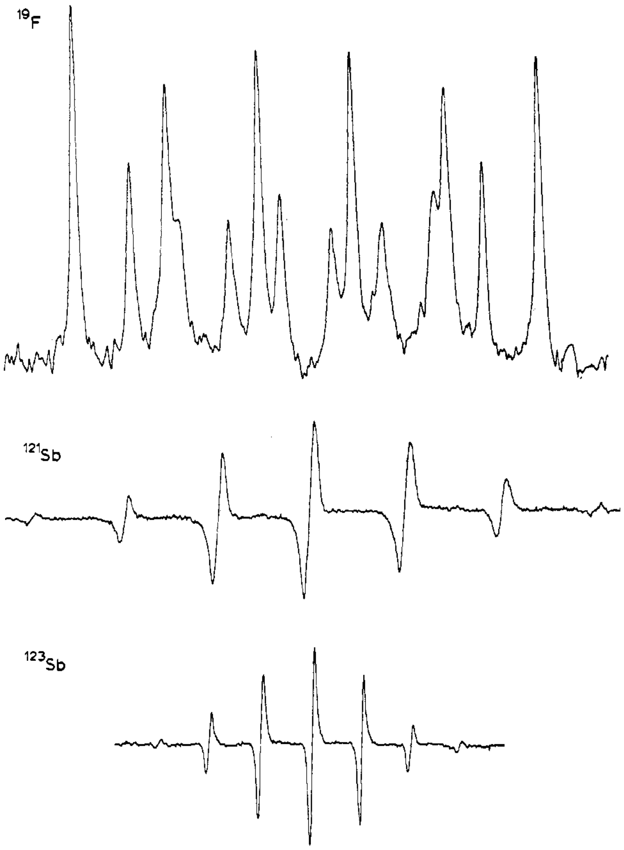

Figure 1—The ^{19}F, ^{121}Sb, and ^{123}Sb nmr spectra of the SbF$_6^-$ ion. The spectra are shown relative to a common frequency scale.

The ^{12}Sb and ^{123}Sb nmr spectra were obtained with a Varian 4200B wide-line spectrometer combined with a 9-in. magnet. In a field of 14.1 kG, frequencies of 14.4 and 7.8 MHz were used for ^{121}Sb and ^{123}Sb, respectively. The spectra shown in Fgure 1 were recorded as the derivative of the absorption mode.

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Tellurates of the Type A^{2+}TeO$_4$

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Although sulfates and selenates of the A^{2+}SO$_4$ and A^{2+}SeO$_4$ types are well known, little is known about anhydrous A^{2+}TeO$_4$ tellurates. Only BaTeO$_4$ is well established.[1,2] We have now prepared and characterized tellurates of this type where A is Mg, Ca, Sr, Ba, Cd, or Pb.

Experimental Section

The reactants were reagent grade or better. The syntheses were generally carried out at high pressure and temperature. Appropriate quantities of the reactants were intimately mixed, sealed in gold tubes, and heated at 700° with 3000 atm of supporting pressure for 8 hr. The reactant mixtures were of the types $\mathrm{ACl_2}\cdot x\mathrm{H_2O{-}Na_2TeO_4\cdot 2H_2O}$, $\mathrm{AO{-}H_2TeO_4\cdot 2H_2O}$, or $\mathrm{A(OH)_2}\cdot x\mathrm{H_2O{-}H_2TeO_4\cdot 2H_2O}$. A mixture of PbO$_2$ and TeO$_2$ could also be used to prepare PbTeO$_4$. Preparations at 600° under 1 atm of flowing oxygen were successful for making polycrystalline samples of BaTeO$_4$, SrTeO$_4$, and CdTeO$_4$.

Anal. Calcd for MgTeO$_4$: Mg, 11.3; Te, 59.1; O, 29.6. Found: Mg, 11.5; Te, 58.7; O, 29.4. Calcd for CdTeO$_4$: Cd, 37.0; Te, 42.0; O, 21.0. Found: Cd, 36.8; Te, 42.3; O, 21.4. Calcd for CaTeO$_4$: Ca, 17.3; Te, 55.1; O, 27.6. Found: Ca, 17.2; Te, 55.4; O, 27.3. Calcd for SrTeO$_4$: Sr, 31.4; Te, 45.7; O, 22.9. Found: Sr, 31.4; Te, 45.5; O, 22.8. Calcd for BaTeO$_4$: Ba, 41.8; Te, 38.8; O, 19.5. Found: Ba, 41.9; Te, 38.4; O, 19.1. Calcd for PbTeO$_4$: Pb, 52.0; Te, 32.0; O, 16.0. Found: Pb, 52.4; Te, 29.9; O, 16.2.

X-Ray powder patterns were obtained on all products at 25° using a Guinier–Hägg camera with Cu Kα_1 radiation and an internal standard of KCl (a = 6.2931 Å). Single-crystal photographs were taken with a precession camera using Mo radiation. Cell dimensions were refined by least squares using the Guinier data.

Thermogravimetric analyses (tga) employed a Du Pont 900 thermal analyzer and a heating rate of 10°/min.

Results

The A^{2+}TeO$_4$ tellurates where A^{2+} is Mg, Ca, Sr, Ba, or Cd are white, and PbTeO$_4$ is light yellow. They

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(2) R. N. Knyazeva and A. P. Kurapova, *Russ. J. Inorg. Chem.*, **14**, 1220 (1969).

all lose oxygen before melting when heated in air; the temperatures at which oxygen loss begins is indicated in Table I. Reactions between $Na_2TeO_4 \cdot 2H_2O$ and a chloride gave small crystals which were suitable for single-crystal X-ray diffraction studies.

TABLE I

CRYSTALLOGRAPHIC[a] AND STABILITY DATA

Compound	a, Å	b, Å	c, Å	Angle,[b] deg	d_x[c]	d_m	Dec pt,[d] °C
$MgTeO_4$	4.6860	5.5848	5.0198	93.211	5.466	5.43	630
$CdTeO_4$	5.0036	12.5254	4.9881		6.458	6.43	630
$CaTeO_4$	5.2299	12.6785	4.9809		4.658	4.64	700
$SrTeO_4$	5.5757	13.1144	5.0032		5.068	5.02	730
$BaTeO_4$	5.9224	13.5117	5.0230	93.483	5.444	5.49	790
$PbTeO_4$	5.4129	4.9471	6.0185	99.596	8.333	8.28	740

[a] Errors estimated from standard deviations are ±0.0004 Å for the 4–5 Å edges, ±0.0008 Å for 12–13 Å edges, and ±0.006° on the angles. [b] The angle is β for $MgTeO_4$ and $PbTeO_4$ but γ for $BaTeO_4$. [c] Calculated density based on crystallographic data. [d] Decomposition temperature by tga.

Single crystals of $SrTeO_4$ were found to be orthorhombic with a space group of $Pca2_1$ or $Pcam$. The refined cell dimensions are given in Table I. $CaTeO_4$ and $CdTeO_4$ were judged isomorphous with $SrTeO_4$ by comparison of their X-ray powder patterns; the refined cell dimensions of $CaTeO_4$ and $CdTeO_4$ are given in Table I. Density measurements (Table I) indicate four formula units per unit cell for these tellurates.

Single crystals of $BaTeO_4$ found to be monoclinic with a space group of $P2_1/c$ where a = 5.9225 Å, b = 5.0229 Å, c = 15.0796 Å, and β = 116.56°. The cell may also be described by a = 5.9225 Å, b = 5.0229 Å, c = 13.5117 Å, β = 93.48°, and a space group of $P2_1/n$. This cell has an obvious similarity to the cells of $CdTeO_4$, $CaTeO_4$, and $SrTeO_4$. Consequently, in Table I the cell dimensions have been rearranged to facilitate comparison. It appears that $BaTeO_4$ has a distorted version of the structure which exists for $CdTeO_4$, $CaTeO_4$, and $SrTeO_4$.

Single crystals of $PbTeO_4$ were found to be monoclinic, and the refined cell dimensions are given in Table I. The space group is $C2$, Cm, or $C2/m$, and there are two formula units per unit cell.

The powder pattern of $MgTeO_4$ was readily indexed by assuming it had a wolframite-type structure. Intensities were calculated using the published[3] positional parameters for $NiWO_4$, and a comparison of observed and calculated intensities supports this structure type for $MgTeO_4$.

Discussion

Of the tellurates prepared only $MgTeO_4$ appears to be of a known structure type. These tellurates are clearly not isostructural with the analogous sulfates and selenates. This is probably due to the preference of Te^{6+} for octahedral rather than tetrahedral coordination to oxygen. $MgTeO_4$ is isostructural with several tungstates; however, in this structure all cations are six-coordinated to oxygen. The other A^{2+}-TeO_4 tellurates are not isostructural with known structures of analogous tungstates, molybdates, or uranates.

X-Ray powder patterns of $BaTeO_4$ have been given by Engelbrecht and Sladky[1] and by Knyazeva and Kurapova.[2] These agree very well with our powder pattern, and thus it is certain that we all have the same phase.

Knyazeva and Kalugina[4] have reported the preparation of $SrTeO_4$; however, their powder pattern is entirely different than ours. Furthermore, their preparation temperature (750°) is very close to the decomposition temperature of $SrTeO_4$.

Natansohn[5,6] has reported the preparation of $MgTeO_4$, $CaTeO_4$, $SrTeO_4$, and $BaTeO_4$. However, preparative temperatures of 900–1000° were used, and such tellurates are not stable under these conditions.

It is possible that the valence states in $PbTeO_4$ are 4–4 instead of 2–6. However, $PbTeO_4$ is not merely a solid solution of PbO_2 and TeO_2 because it is not isomorphous with any form of PbO_2 or TeO_2. Furthermore, varying the reactant ratios in the PbO_2–TeO_2 system did not indicate a significant range of stoichiometry for $PbTeO_4$.

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The Application of Symmetry Ascent Selection Rules to a Factor Group Analysis of Red Mercuric Iodide

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The study of metal–ligand vibrations[1,2] has played an important role in the development of coordination chemistry. However ambiguity in band assignment has often vitiated the value of such studies. Recently single-crystal infrared and Raman studies, *e.g.*,[3,4] have become more common and present the possibility of unambiguous band assignment. However, even in such cases where high-resolution polarized data are obtained, the number of observed vibrations may be less than that calculated on the basis of a factor group analysis. In such circumstances the polarization data may allow assignment of a vibration to a particular symmetry species but it may be impossible to distinguish whether the vibration concerned is internal to a molecular species in the crystal or is external thereto, *i.e.*, is a lattice mode.

For example, vibrational studies of red mercuric iodide[5,6] were recently substantiated by a single-crystal Raman study.[7] This revealed only four of the six expected Raman-active transitions down to an ob-

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