step is attack of the ligand onto the four-coordinated Ag(III) with expansion of the inner coordination sphere of the metal. Although we are dealing with a very few reactions involving metal and ligand species for which no analogous kinetic data are available, the foregoing characterizations seem most reasonable at the present time.

We may now say that each of the second-order rate constants listed in Tables I and II represents the forward rate constant for direct ligand replacement on square-planar Ag(III) with no observable contribution from a "solvent path"[28] or reverse reaction. It remains for us to attempt an association between these values of k_f and k_s and the constants k_1 and k_2. The ratio of the observed rate constants k_f/k_s at 25° is similar and quite moderate for both periodate (~4.8) and tellurate (~3.3) with the periodate system reacting somewhat faster. However, the temperature dependence and resultant activation parameters (Table III) exhibit different trends for the two systems.

The difference in $\Delta S^{\ddagger}$ is sufficiently large for the two periodate complexations that we make the assignments $k_1 \equiv k_f$ and $k_2 \equiv k_s$ for periodate in accordance with statistical and steric considerations. That is (assuming similar solvation effects), a more negative activation entropy is expected for the second step because of a reduced number of possible coordinating sites and increased hindrance to ligand attack on the monoperiodate complex compared to the $Ag(OH)_4^-$ anion. In addition, even if no periodate protons are lost upon complexation, the mono(periodato)argentate(III) anion will be more negatively charged than $Ag(OH)_4^-$ (eq 2, 2′). Although this does not necessarily lead to a decrease in $\Delta S^{\ddagger}$,[30,31] increased electron density on the mono complex might play some part in reducing the activation enthalpy for the second step.

In the case of tellurate complexation, there is no large difference in either $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ for the two steps. As noted above, $\Delta S^{\ddagger}$ for the second complexation would be expected to be more negative than for the first step. We thus tend to favor the association $k_1 \equiv k_s$ and $k_2 \equiv k_f$ for tellurate, although this must be considered a very tenuous assignment. A more negative $\Delta S^{\ddagger}$ for substitution on Ag(III) by tellurate as compared to periodate might be due in part to the higher degree of protonation on $H_4TeO_6^{2-}$ resulting in a decrease in the number of possible attacking sites.

Because of the limited stability of the tetrahydroxoargentate(III) anion and the dearth of well-characterized silver(III) complexes, we have chosen ligands for this initial study of Ag(III) substitution rates which have not previously been used in complexation kinetics studies. Thus, until data on analogous reactions are available, no meaningful comparison of the rates of Ag(III) substitution reactions with those of other square-planar d^8 systems can be made. It is interesting to note, however, that, in spite of possibly unfavorable electrostatic interactions between $Ag(OH)_4^-$ and the incoming ligand, the reactions of this study are more rapid than typical substitution rates on gold(III) or palladium(II)—both of which, in turn, react faster than platinum(II).[28]

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Registry No. $Ag(OH)_4^-$, 23172-26-1; $H_2IO_6^{3-}$, 23470-68-0; $H_4TeO_6^{2-}$, 41673-77-2.

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Synthesis and Reactions of Aminotellurium Pentafluoride

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$R_3SiNHTeF_5$ ($R = CH_3$) is produced by reaction of $(R_3Si)_2NH$ with tellurium hexafluoride. *N*-Trimethylsilylaminotellurium pentafluoride reacts with hydrogen fluoride to yield the title compound. The preparation of the derivatives $H_2NTeF_5 \cdot AsF_5$, $Cs^+NHTeF_5^-$, and $[-HgN(TeF_5)-]_x$ is described.

Aminosulfur pentafluoride (H_2NSF_5) is not stable toward hydrogen fluoride elimination.[1] The existence of H_2NSeF_5 seems to be unlikely, considering the oxidation potential of selenium in the VI valence state. Known derivatives, R_2NTeF_5,[2] decompose rapidly above 35°, suggesting that only limited stability can be expected for H_2NTeF_5.

In the present work, aminotellurium pentafluoride is produced by a double silicon–nitrogen cleavage reaction. Contrary to the suggestions described above, H_2NTeF_5 was found to be stable up to 150°. Further, its behavior as acid or base was studied. The base character of H_2NTeF_5 is lower than that of H_2NSF_5, and some acid character is proved by the existence of the salts $Cs^+NHTeF_5^-$ and $[-HgN(TeF_5)-]_x$, both of which were made by cleavage of $R_3SiNHTeF_5$[1] with cesium fluoride and mercuric fluoride.

Experimental Section

General Information. Fluorine and proton nmr spectra were taken on a JEOL 60 HL instrument, using $CFCl_3$ as an internal reference. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer with KBr windows. Raman spectra were taken on a Coderc PH 1 instrument, using a He–Ne laser for excitation, 190 mW. Mass spectra were recorded on a Varian CH 7 instrument with 70-eV excitation energy.

Materials. Bis(trimethylsilyl)amine was prepared by ammonolysis of chlorotrimethylsilane.[3] Fluorination of elemental tellurium, ar-

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senic trifluoride, and mercuric chloride gave tellurium hexafluoride, arsenic pentafluoride, and mercuric fluoride, respectively. Cesium fluoride was taken as it was purchased from the Ozark-Mahoning Co.

***N*-Trimethylsilylaminotellurium Pentafluoride.** On 0.1 mol of $(R_3Si)_2NH$, placed in a 250-ml stainless steel vessel and cooled to liquid nitrogen temperature, was condensed 0.13 mol of TeF_6. The mixture was warmed up to room temperature and stirred for 12 hr. The volatile compounds were trapped at −196°; only a small residue remained in the pressure vessel. The volatile materials were distilled in a glass apparatus. Trimethylsilylaminotellurium pentafluoride is a colorless liquid, slowly turning yellow at temperatures above 100°, mp 9°, bp 58° (12 mm). The yield is almost quantitative. *Anal.* Calcd for $C_3H_{10}SiNTeF_5$: C, 11.6; H, 3.2; N, 4.5; Te, 40.9; F, 30.6. Found: C, 11.5; H, 3.1; N, 4.7; Te, 41.5; F, 30.4.

The ir spectrum shows absorptions at 3361 (s) (N–H stretch), 2968 (m) and 2908 (w) (C–H stretch), 1417 (m) (N–H bend), 1261 (s) and 1236 (m) (C–H bend), 855 (vs), 768 (m), 690 (vs), 641 (m), 620 (w), 345 (m), 330 cm^{-1} (s). Raman bands occur at 3360 (w, p), 2965 (w, dp), 2910 (m, p), 1428 (w, dp), 1270 (w, dp), 1246 (w, sh), 848 (s, p), 767 (m, p), 698 (vs, p) (TeF_4 symmetric stretch), 647 (sh), 632 (vs, p), 580 (s, p), 352 (s, p), 336 (sh), 300 (s, p), 256 (s, p), 235 (s, p), 200 (s, p), 178 cm^{-1} (s, p).

^1H nmr (TMS internal standard): τ 9.21 (CH) and 5.88 (NH), ratio 9:1. ^{19}F nmr ($CFCl_3$ internal standard, 56.4 MHz): ab_4 pattern, δ_a 31.1 ppm, δ_b 37.0 ppm, $J_{ab} = 173$ Hz, $J_{^{125}Te\text{-}a} = 3245$ Hz, $J_{^{125}Te\text{-}b} = 3375$ Hz.

The mass spectrum gave evidence for the ions $R_2SiNHTeF_5^+$, $RSiNHTeF_4^+$, $RSiNTeF_3^+$, TeF_3^+, $NHTeF^+$ or $RTeF^+$, TeF^+, TeN^+, $RSiF_2^+$, and R_2SiF^+.

Aminotellurium Pentafluoride. $R_3SiNHTeF_5$ (0.1 mol) was placed into a quartz tube (4-in. length, $^1/_2$-in. inner diameter) and frozen by cooling with ice. A small excess of anhydrous hydrogen fluoride (0.1 mol) was added slowly by a plastic pipet. A strongly exothermic reaction occurred immediately. After cooling to Dry Ice temperature, most of R_3SiF was pumped off under high vacuum. The solid residue was sublimed under vacuum onto a −30° cold finger. The yield was quantitative. H_2NTeF_5 is a colorless, crystalline solid, mp 82.5°, bp 121°. *Anal.* Calcd for H_2NTeF_5: H, 1.2; N, 5.9; Te, 53.3; F, 39.8. Found: H, 0.9; N, 5.8; Te, 52.1; F, 40.0.

Ir spectrum (methylene chloride solution): 3380 (s) and 3295 (s) (N–H stretch), 1514 (m) (N–H bend), 839 (m), 692 (vs) and 624 (s) (Te–F and Te–N stretch), 322 cm^{-1} (vs) (Te–F bend). Raman spectrum (methylene chloride solution): 684 (vs, p), 631 (vs, p), and 600 (s, p) (Te–F and Te–N stretch), 333 (m, dp), 283 (s, p), 250 (s, dp), 193 cm^{-1} (m, dp).

^1H nmr (methylene chloride solution): τ 5.20 (NH). ^{19}F nmr: ab_4 pattern, δ_a 37.2 ppm, δ_b 43.2 ppm, $J_{ab} = 176$ Hz, $J_{^{125}Te\text{-}a} = 3290$ Hz, $J_{^{125}Te\text{-}b} = 3565$ Hz.

Mass spectrum: $H_2NTeF_5^+$, TeF_5^+, $H_2NTeF_4^+$, TeF_4^+, $H_2NTeF_3^+$, TeF_3^+, TeF_2^+, TeF^+, Te^+.

Attempted Preparation of $HN(TeF_5)_2$. $R_3SiNHTeF_5$ was allowed to react in a stainless steel vessel with an excess of TeF_6 at 80° for 1 hr. The volatile products consisted of N_2, TeF_6, and R_3SiF, identified by usual methods. Large amounts of a yellow, nonvolatile solid remained in the vessel, but could not be identified as $HN(TeF_5)_2$.

Attempted Preparation of $(R_3Si)_2NTeF_5$. $(R_3Si)_2NLi$[4] (0.12 mol) was dissolved in 70 ml of chlorotrifluoromethane. This solution was placed into a stainless steel vessel; then at −196° an excess of TeF_6 (0.15 mol) was condensed onto it. The mixture was warmed up to room temperature with magnetic stirring. Ir analysis of the gas phase showed some TeF_6 and a small amount of R_3SiF. More than 90% of the reacted tellurium was found in a yellow, insoluble, and nonvolatile solid. The $CFCl_3$ solution contained a yellow compound. Its ^{19}F nmr showed a typical TeF_5 group; its ^1H nmr, R_3Si protons. This compound, probably $(R_3Si)_2NTeF_5$, decomposed even in dilute solution to the yellow solid.

Reaction of Aminotellurium Pentafluoride with Arsenic Pentafluoride. A mixture of aminotellurium pentafluoride, methylene chloride as solvent, and arsenic pentafluoride was condensed into a glass trap using an all-glass vacuum line. Reaction occurred even at −78°. The excess AsF_5 and CH_2Cl_2 were pumped off at room temperature. A nonvolatile white solid remained which decomposed at about 130°. *Anal.* Calcd for $H_2NTeAsF_{10}$: H, 0.5; N, 3.4; Te, 31.1; As, 18.4; F, 46.5. Found: H, 0.7; N, 3.4; Te, 30.0; As, 17.5; F, 44.6.

Ir spectrum: 3340 (m), 3298 (m), 1105 (s), 701 (vs), 612 (m), 388 cm^{-1} (vs).

Reaction of Aminotellurium Pentafluoride with Boron Trifluoride. A methylene chloride solution, containing H_2NTeF_5 and BF_3 in a 1:1 mole ratio, gave a crystalline product when cooled to −78°, but decomposition with loss of BF_3 was observed when the compound was warmed above −60°.

Cesium Amidotellurium Pentafluoride, $Cs^+NHTeF_5^-$. Cesium fluoride (10 mmol) was placed in a 50-ml glass bulb under a dry atmosphere; then methylene chloride was added (20 ml). A small excess of $R_3SiNHTeF_5$ (11 mmol) was added dropwise under magnetic stirring. The progress of the reaction was controlled by ^1H nmr: the singlet of $R_3SiNHTeF_5$ decreased and the doublet of R_3SiF increased. The colorless solid was filtered off and dried under vacuum.

Caution! Heating must be avoided, as occasional explosions took place. Cesium amidotellurium pentafluoride is very hygroscopic; no solvent was found for it. *Anal.* Calcd for $CsNHTeF_5$: Cs, 35.8; H, 0.27; N, 3.8; Te, 34.4; F, 26.0. Found: Cs, 35.8; H, 0.21; N, 2.8; Te, 34.2; F, 25.2.

Ir spectrum: 3360 (m), 3280 (m), 935 (m), 835 (s), 630 (vs), 478 (s), 330 cm^{-1} (vs). The salt exploded immediately when brought into the laser beam of the Raman instrument.

$[-HgN(TeF_5)-]_x$. A 1:2 molar mixture of HgF_2 and $R_3SiNHTeF_5$, diluted in methylene chloride, was stirred for several hours. R_3SiF and H_2NTeF_5 were identified by nmr. The mercuric fluoride remained undissolved but reacted probably at its surface. The white solid was treated as the cesium salt. In contrast to it, the mercury compound may be dried at 100° under vacuum. Heating to nearly 300° caused a slight yellow-brown color. *Anal.* Calcd for $HgNTeF_5$: Hg, 46.0; N, 3.2; Te, 29.0; F, 21.7. Found: Hg, 46.3; N, 3.2; Te, 29.6; F, 21.2. Hydrogen was found less than 0.1% (as a test for purity).

Ir spectrum: 829 (vs), 772 (s), 690 (vs), 668 (vs), 650 (s), 619 (s), 592 (s), 339 (s), 330 cm^{-1} (s). Raman spectrum: 829 (m), 762 (m), 694 (m), 656 (vs) (TeF_4 symmetric stretch), 621 (s), 605 (m), 563 (m), 337 cm^{-1} (s).

Mass spectrum (at 300°): TeF_5^+, TeF_4^+, Hg^+, TeF_3^+, TeF_2^+, TeF^+, Te^+, N_2^+. All peaks appeared twice ionized (at half mass number) with remarkable intensity.

Results and Discussion

H_2NTeF_5 and $R_3SiNHTeF_5$ are easily prepared by the two reactions

$$(R_3Si)_2NH + TeF_6 \rightarrow R_3SiF + R_3SiNHTeF_5$$

$$R_3SiNHTeF_5 + HF \rightarrow R_3SiF + H_2NTeF_5$$

The nmr data of both new compounds are in agreement with the structure; especially the typical ab_4 patterns of the TeF_5 group are found. Characteristic frequencies in the vibrational spectra can well be assigned (see Experimental Section). The high and sharp N-H stretching modes in the infrared spectrum show that N-H-F bridge bonds do not exist in these compounds.

They both have unexpected high thermal stability; rapid decomposition does not occur below 150°. There seems to be an inhibition of the HF or R_3SiF elimination reaction, because a change of the normal octahedral environment of the tellurium is unfavorable.

Although $H_2NSF_5 \cdot BF_3$ is stable at room temperature,[5] $H_2NTeF_5 \cdot BF_3$ decomposes even at −60°.

$$H_2NTeF_5 + BF_3 \xrightarrow{-60^\circ} H_2NTeF_5 \cdot BF_3$$

$$H_2NTeF_5 + AsF_5 \rightarrow H_2NTeF_5 \cdot AsF_5$$

The conclusion is drawn that H_2NTeF_5 is a weaker base than its sulfur analog. The lower basity of the nitrogen in H_2NTeF_5 compared with H_2NSF_5 may be a further reason for the greater stability of the tellurium compounds.

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With arsenic pentafluoride, however, a stable adduct is formed.

Of interest was whether H_2NTeF_5 might behave as an acid. With nitrogen bases (triethylamine, pyridine) reaction was observed, but no definite products were obtained; reactions with CsF or HgF_2 are similar. However, definite derivatives were made by reaction of $R_3SiNHTeF_5$

$$R_3SiNHTeF_5 + CsF \rightarrow R_3SiF + Cs^+NHTeF_5^-$$

$$2R_3SiNHTeF_5 + HgF_2 \rightarrow 2R_3SiF + H_2NTeF_5 + (1/x)[\text{-HgN(TeF}_5)\text{-}]_x$$

The structure of the mercury compound calls for a comment. Although it is not definitely proven, because of the nonvolatility and insolubility of this compound, its structure is assumed to be a chain -Hg-N-Hg-N-. In contrast with the tetrahedral environment of nitrogen in the long known polymer[6] $[\text{-HgNH}_2^+(\text{Cl}^-)\text{-}]_x$ we have three-coordinated nitrogen in $[\text{-HgN(TeF}_5)\text{-}]_x$. This may be due to the so-called p_π-d_π back-donation between nitrogen and tellurium. The loss of basity in H_2NTeF_5 may be caused by the same effect.

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Registry No. $Me_3SiNHTeF_5$, 42005-82-3; $(Me_3Si)_2NH$, 999-97-3; TeF_6, 7783-80-4; H_2NTeF_5, 42005-83-4; AsF_5, 7784-36-3; $H_2NTeF_5 \cdot AsF_5$, 42005-84-5; $Cs^+NHTeF_5^-$, 42081-47-0; CsF, 13400-13-0; $[\text{-HgN(TeF}_5)\text{-}]_x$, 42005-81-2; HgF_2, 7783-39-3.

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Iron(II) and Iron(III) in the Tetrahedral Sulfide Environment of a Gallium Sulfide Host Crystal

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Iron is incorporated into crystals of Ga_2S_3 by chemical transport with hydrogen chloride. Two product phases are formed, and these are separated by careful control of the temperature profile in the crystallization zone. The material deposited at higher temperatures generally contains 5-10% iron by weight and has the γ-Ga_2S_3 structure. The material deposited at lower temperatures has the α-Ga_2S_3 structure and contains 0.1-0.5% iron. In both products the iron content varies with the temperature at which the material is deposited. The iron centers are characterized by means of Mossbauer, epr, and visible and near-infrared reflectance spectra. Most of the iron is in a high-spin iron(II) state and occupies distorted tetrahedral sites in the crystal lattice. The remainder of the iron is in a high-spin iron(III) state and exhibits, in the low-iron material, a rhombic epr signal with apparent g values in the region of 4.3. The visible spectrum of this Fe^{3+} arises from charge-transfer transitions and is consistent with a distorted tetrahedral field. Low-temperature magnetic susceptibility measurements indicate that there is no significant interaction between pairs of adjacent Fe^{2+} centers in the sulfide crystal.

Introduction

In the study of the coordination chemistry of iron, relatively little attention has been directed toward the properties of its ions in a tetrahedral sulfide environment. A tetrahedral coordination geometry has been inferred from spectral data[1-3] and recently established by an X-ray diffraction study[4] for certain iron-sulfur enzymes. The only magnetically and optically dilute, inorganic tetrahedral iron-sulfide system satisfactorily understood to date is that of iron-substituted zinc sulfide.[5-9] In view of the possibility that iron sites of this kind might be intimately involved in such phenomena as the biocatalysis of oxidation-reduction reactions[10] or the electrooptical properties of crystalline sulfide compounds,[11] it appears worthwhile to delineate, in a somewhat more extended scope, the peculiarities of tetrahedral iron-sulfide coordination. In particular, it is of interest to examine the effects of distortions from exact tetrahedral symmetry on the ligand field parameters of iron, the preference of iron for a given oxidation state in this ligand field environment, and the possible existence of metal-metal interaction between iron centers bridged by sulfide ligands. A strong iron-iron interaction, in the form of antiferromagnetic coupling, has been observed in the iron-sulfur enzyme spinach ferredoxin,[12] and its effects are apparent in the characteristic oxidation-reduction properties of this enzyme.

In this study iron ions were incorporated into a host crystal of gallium(III) sulfide since its cation sites, unlike the sites in zinc sulfide, are significantly distorted from tetrahedral symmetry. As with ZnS, the various crystal modifications of gallium(III) sulfide[13] consist of closest packed arrangements

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