facts can be explained in part by assuming that in the hexacyanide ions, the strong perturbation of the metal ion by the ligands results in the mixing of the T_{1u} charge transfer configuration and the promoted configuration $nd^5(n + 1)p^1$. As a result of the mixing, the transition moment will depend in part on the integral

$$\int \psi(nd^6) \sum_i er_i\psi(nd^5(n + 1)p^1)d\tau$$

which integral increases with n. However, the predicted increase is only 20% of that observed, and it would appear that such a mechanism, if operative at all, is not the only one of importance. Nevertheless, as regards the above mechanism in the dyes, integrals of the above kind appear with only a very small weight since not only do the electrons involved in the mixing integral have a much smaller overlap, but ΔW is much larger.

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Chemistry of the Difluorides of Germanium and Tin

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The difluorides of germanium and tin have been prepared in good yield by the reaction of the metals with hydrogen fluoride. Complexes of the difluorides with fluoride ion and with organic bases are described. The fluorocomplexes have the composition MF_3^-. The hydrolytic stability of GeF_3^- is greater than that of SnF_3^-; solutions of SnF_3^- slowly deposit crystalline SnO. All of the germanium and tin complexes, in solution, are oxidized by oxygen.

Germanium difluoride first was prepared by the reaction of Ge and GeF_4 above 100°.[1,2] Recently, we reported that germanium metal and hydrogen fluoride in a sealed vessel at 225° yield a mixture of GeF_2 and GeF_4.[3] By using stoichiometric amounts of reactants, this latter method serves as a simple, high-yield synthesis of GeF_2. In a similar fashion, stannous fluoride is quantitatively prepared at 200°; here excess hydrogen fluoride may be employed since this difluoride is not oxidized by hydrogen fluoride.

Germanium difluoride reacts exothermally with concentrated aqueous solutions of alkali metal fluorides, and crystalline trifluogermanites have been isolated from these solutions, *e.g.*, $CsGeF_3$ and $KGeF_3$. These complexes do not have the perovskite structure and this probably reflects the stereochemical significance of the non-bonding pair of electrons in GeF_3^-.[4]

Although GeF_3^- is hydrolytically stable, it does undergo very rapid exchange with fluoride ion. Aqueous solutions of $CsGeF_3$ and CsF show single F^{19} n.m.r. resonances which are between the GeF_3^- and the F^- resonances; the exact position is a function of the GeF_3^- and F^- concentrations. The fluostannite ion, described below, also was found to undergo fast exchange with fluoride ion.

Neutral aqueous solutions of $CsGeF_3$ absorb oxygen at a measurable rate at 25°, and in the presence of excess fluoride ion the final state of the germanium is the hexafluogermanate anion. Oxidation of the crystalline salt does not take place in the absence of moisture. In moist air or oxygen, oxygen absorption occurs and an orange color rapidly develops on the surfaces of the crystals. Oxidation of GeF_3^- takes a different course in strongly acid solutions in that hydrogen ion rather than oxygen is reduced. A solution of $CsGeF_3$ in 48% hydrofluoric acid rapidly evolves hydrogen and complete oxidation of GeF_3^- to $GeF_6^=$ takes only a few hours at 25°. Under acid conditions, oxidation may proceed through interaction of the proton with the non-bonding pair of electrons to give $HGeF_3$, which ultimately would yield hydrogen and $GeF_6^=$.

There have been several reports of fluoride

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(1) L. M. Dennis and A. W. Laubengayer, *Z. physik. Chem.*, **130**, 530 (1927).

(2) G. N. Bartlett and K. C. Yu, *Can. J. Chem.*, **39**, 80 (1961).

(3) E. L. Muetterties and J. E. Castle, *J. Inorg. & Nuclear Chem.*, **18**, 148 (1961).

(4) G. N. Bartlett and K. C. Yu, ref. 2, have shown that GeF_2 does not possess either of the two typical difluoride lattices (rutile and low quartz) but apparently is related to the SeO_2 structure. They suggest a pseudotetrahedral coördination for the germanium atom with three fluorine atoms and a non-bonding pair of electrons and a sharing of tetrahedra through fluorine atoms to give chains.

complexes of Sn^{+2}. Two of the reports[5,6] refer to $SnF_4^{=}$ complexes; however, in the only definitive work, Schaap, Davis, and Nebergall[7] concluded from a polarographic study that SnF_3^- is the only important anionic species in dilute aqueous solutions of SnF_2 and KF and that SnF_3^- has considerable stability, with an over-all dissociation constant of 1.2×10^{-10}. With low tin concentrations ($\sim 10^{-3}$ *M*), they found the half-wave potentials to be relatively insensitive to *p*H in the range 5.6 to 7.1 and to tin concentration. Accordingly they concluded that polynuclear or basic tin complexes are not important in neutral solutions containing excess fluoride ion.

Consistent with the work of Schaap, Davis, and Nebergall, we obtained from aqueous solution only complexes of the type $MSnF_3$, where M is NH_4,[8] K, and Cs. Crystalline salts were obtained by simply dissolving SnF_2 in concentrated solutions of MF and were recrystallized from water. In some recrystallizations, fine metallic suspensions were detected. This first was thought to be metallic tin from some disproportionation of Sn^{+2}; however, analysis of the metallic phase indicated it to be tin(II) oxide. X-Ray analysis demonstrated a tetragonal phase with cell parameters identical to the literature values for tin(II) oxide. Interestingly, fairly large crystals of the monoxide can be grown directly from hot aqueous solutions of $CsSnF_3$. High fluoride ion concentration does not inhibit the rate of oxide formation. The oxide also forms at room temperature from concentrated solutions of $CsSnF_3$. Oxide formation does require a minimal SnF_3^- concentration. At 80°, the minimal $CsSnF_3$ concentration is ~ 1 *M* and 0.1 *M* in water and in saturated aqueous cesium fluoride, respectively.

A number of texts[9] report that alkaline stannite solutions on standing deposit metallic tin. Our re-investigation of this system established the metallic phase as tin(II) oxide. However, we also found that these solutions do slowly form β-tin at 70–100°. Moreover, the oxide phase formed at room temperature dissolves rapidly in excess hot KOH solution, leaving behind a very small amount of β-tin. Thus, there would appear to be the possibility that the oxide phase formed at room temperature is oxygen-deficient. This behavior was not observed with the oxide phase obtained from the fluoride complexes. Tin(II) oxide also was found to be formed in aqueous solutions of $SnCl_2$ and excess KCN. Chlorostannite ($SnCl_3^-$) solutions, however, yielded only the white, amorphous hydroxide (or hydrous oxide) of Sn^{+2}. From solutions of $SnCl_2$ and KSCN heated to $\sim 70°$, a black metallic phase separated; this was not the oxide but the sulfide.

It has been reported[6,7] that aqueous fluostannite solutions undergo oxidation on contact with the atmosphere. We observed uptake of oxygen by solutions of $CsSnF_3$ in water, in saturated aqueous CsF, and in 48% HF; this indicates that the trifluostannite ion initially forms a complex with the oxygen molecule. Surprisingly, the thermodynamically favored process

$$SnF_3^- + 2H^+ + 3F^- \longrightarrow SnF_6^= + H_2$$

does not take place in solutions of $CsSnF_3$ in 48% hydrofluoric acid at 80°. This is in contrast to the fast oxidation of GeF_3^- by H^+.

Germanium and tin(II) fluorides are relatively weak acceptor molecules toward neutral donor molecules. They dissolve in most organic bases,[10] and in some cases crystalline adducts are isolable although the dissociation pressure of most adducts is significant at 25°. The most stable adducts of those investigated were derived from dimethyl sulfoxide. These complexes have the composition MF_2·donor, and thus GeF_2 and SnF_2 appear to behave primarily as monofunctional acceptor molecules whether the donor ligand is charged or neutral. The consistency here suggests a pyramidal model for the complexes. A recent crystal structure study[11] of "stannous chloride dihydrate" established that this is actually dichloroaquotin(II) hydrate, $Sn(OH_2)Cl_2 \cdot H_2O$, and that the aquo-complex $Sn(OH_2)Cl_2$ is pyramidal, which suggests that the non-bonding pair of electrons is in a directed orbital.

Experimental

1. Synthesis of GeF_2.—A Hastelloy-C-lined pressure vessel was charged with 38 g. of germanium metal powder (Eagle–Picher—first reduction grade) and evacuated.

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[5] R. Wagner, *Ber.*, **19**, 896 (1886), reported $(NH_4)_2SnF_4$ and K_2SnF_4.

[6] W. Pugh, *J. Chem. Soc.*, 1934 (1953), described $N_2H_6SnF_4$ and stated that aqueous solutions of this compound are rapidly oxidized by air.

[7] W. B. Schaap, J. A. Davis, and W. H. Nebergall, *J. Am. Chem. Soc.*, **76**, 5226 (1954).

[8] NH_4SnF_3 and $Zn(SnF_3)_2 \cdot 7H_2O$ are commercially available from Ozark Mahoning Company.

[9] *Cf.* N. V. Sidgwick, "Chemical Elements and Their Compounds," Oxford Press, 1950, Vol. 1, p. 621.

[10] G. N. Bartlett and K. C. Yu, ref. 2, have reported GeF_2 to be soluble in ethanol and in diethyl ether.

[11] B. Kamenar and D. Grdenic, *J. Chem. Soc.*, 3954 (1961).

Twenty g. of hydrogen fluoride was condensed in the vessel and then the closed vessel was heated to 225° for 16 hr. The vessel was opened and then evacuated for 0.5 hr. with a vacuum pump. The weight of the crude germanium difluoride averaged 54 g. for six runs, an average yield of 93%. Purification was effected by sublimation at 110–130° (10^{-3} mm.). Yields of sublimed product averaged about 70%; the major loss was due to disproportionation of GeF_2 to GeF_4 and GeF_x. The melting point of sublimed GeF_2 is 111–112°.

Anal. Calcd. for GeF_2: Ge, 65.6; F, 34.4. Found: Ge, 65.2; F, 34.2.

2. Synthesis of SnF_2.—A Hastelloy-C-lined pressure vessel was charged with 30 g. of mossy tin and then was evacuated. About 60 g. of hydrogen fluoride was condensed in the vessel which then was closed and heated to 200° for 8 hr. The vessel was vented while still hot, *ca.* 100°, and then evacuated for 1 hr. with a vacuum pump. The residual solid was dried further *in vacuo* for about 4 hr. at 80° to remove the last traces of hydrogen fluoride.

Anal. Calcd. for SnF_2: Sn, 75.7; F, 24.3. Found: Sn, 74.9; F, 25.0.

3. Fluogermanites.—Ten g. of germanium difluoride was added slowly to a stirred, saturated aqueous CsF solution. Heat was evolved and the hot slurry was filtered immediately. On cooling, colorless needles appeared. These were collected and vacuum dried at 25°. All of these operations were effected under a nitrogen atmosphere.

Anal. Calcd. for $CsGeF_3$: Ge, 27.7; F, 21.6. Found: Ge, 27.0; F, 21.9.

Single crystal X-ray analysis indicated an orthorhombic cell with $a = 8.085$, $b = 8.242$, and $c = 6.700$ with $z = 4$ and $d = 3.904$ g./cc.; the pycnometric density was 3.91 g./cc. This ternary fluoride begins to darken and decompose at 200–210°.

A potassium salt, colorless thin plates, was prepared in a similar fashion. (*Anal.* Calcd. for $KGeF_3$: F, 33.8. Found: F, 33.3.)

Dissolution of germanium difluoride in a solution of cesium fluoride in ~20% hydrofluoric acid led to rapid hydrogen evolution. Cubic, colorless crystals were isolated from the solution. These had the X-ray lines reported for cubic Cs_2GeF_6. (*Anal.* Calcd.: F, 25.2. Found: F, 25.9.)

4. Fluostannites.—Stannous fluoride was dissolved in a minimum amount of hot (~80°) saturated CsF solution. On cooling, colorless crystals of $CsSnF_3$ formed; these were recrystallized from warm water. Again, these operations were carried out under a nitrogen atmosphere.

Anal. Calcd. for $CsSnF_3$: Cs, 43.1; Sn, 38.4; F, 18.5. Found: Cs, 43.3; Sn, 36.3; F, 18.4.

On heating, $CsSnF_3$ begins to darken and decompose at about 230° and melts at 271–274° with decomposition and formation of metallic tin.

A solution of $CsSnF_3$ open to the atmosphere was heated for a day at 90°, filtered to remove tin(II) oxide, and on cooling yielded Cs_2SnF_6, which was recrystallized several times from hot water.

Anal. Calcd. for Cs_2SnF_6: Cs, 53.3; Sn, 23.8; F, 22.8. Found: Cs, 54.1; Sn, 22.8; F, 22.1.

This compound is not isomorphous with Cs_2GeF_6. The infrared spectrum of Cs_2SnF_6 always showed a very weak, sharp absorption at 3700 cm.$^{-1}$ and a very weak, broad absorption at 1020 cm.$^{-1}$ in addition to the major Sn–F band at 719 cm.$^{-1}$. The weak bands disappeared if the salt was recrystallized from aqueous hydrofluoric acid and then reappeared after repeated recrystallization from water. This behavior suggests that trace hydrolysis of $SnF_6^{=}$ may occur in water, since the bands at 3700 and 1020 cm.$^{-1}$ could be ascribed to OH and SnO, respectively. Analyses were not definitive with regard to this point. The tin and fluorine analyses, although low (~1%), always showed a F to Sn ratio of 6:1. Rubidium and potassium salts were prepared in similar fashion to further check the hydrolysis hypothesis.

Anal. Calcd. for Rb_2SnF_6: Sn, 29.0; F, 27.9. Found: Sn, 28.8; F, 27.7.

Anal. Calcd. for $K_2SnF_6 \cdot H_2O$: Sn, 36.0; F, 34.7. Found: Sn, 35.8; F, 34.7.

The rubidium salt showed the same behavior as the cesium salt with respect to the infrared spectrum, *i.e.*, O–H and Sn–O absorption when recrystallized from water and none when recrystallized from aqueous hydrofluoric acid. The infrared spectrum of the potassium salt showed little dependence on recrystallization media. Since this salt separates as a hydrate there are, of course, strong 3750 and 1630-cm.$^{-1}$ absorptions, but there was no evidence of a band at 1020 cm.$^{-1}$. All of these data may be rationalized if it is assumed that some $SnF_5OH^{=}$ is in equilibrium with $SnF_6^{=}$ in water and that M_2SnF_5OH salts have comparable solubilities to the M_2SnF_6 salts in the cesium and rubidium systems, but not in the potassium system.

The cesium and rubidium salts of $SnF_6^{=}$ are isomorphous. The rubidium compound was indexed as hexagonal with $a_0 = 6.038$ and $c_0 = 4.824$.

5. Decomposition of SnF_3^- and Related Complexes.—A saturated solution of $CsSnF_3$ in saturated aqueous CsF was sealed in an evacuated glass tube and then heated to 80°. A fine metallic suspension appeared within about 45 min. After 48 hr., large, gray-blue metallic crystals had appeared and the tube then was cooled and opened. The metallic crystals were thoroughly washed with hot water and then vacuum dried.

Anal. Calcd. for SnO: Sn, 88.2; F, 0. Found: Sn, 87.9; F, <0.2.

The X-ray pattern was identical to that reported in the literature for tetragonal SnO. Similar results were obtained with $CsSnF_3$ solutions at 25°, but in these cases the oxide phase was of very small particle size although still crystalline by X-ray analysis.

From a saturated solution of $SnCl_2$ in nearly saturated aqueous KOH (evacuated sealed tube) at room temperature, a metallic phase began to separate within about 5 min. This solid was recovered after 48 hr. and thoroughly washed with hot water.

Anal. Calcd. for SnO: Sn, 88.2; K, 0. Found: Sn, 87.6; K, 0.12.

The X-ray pattern was that of tetragonal SnO. About 25 g. of the solid was added to 300 cc. of warm (~50°) concentrated KOH solution. There was rapid dissolution, but about 0.3 g. of a shiny metallic phase remained undissolved; this proved to be β-tin by melting point and X-ray analysis. In 24 hr. at 80°, a saturated solution of $SnCl_2$ in nearly saturated aqueous KOH (evacuated sealed tube) yielded a single metallic phase (less than 1% of the total tin by weight) that was shown to be β-tin by melting point.

6. Base Adducts.—Stannous fluoride was dissolved in a minimum amount of dimethyl sulfoxide at 90°, and on cooling, colorless crystals formed; m.p. 85° with decomposition.

Anal. Calcd. for $SnF_2\cdot OS(CH_3)_2$: Sn, 50.6; S, 13.6. Found: Sn, 50.4; S, 13.7.

Germanium difluoride (5 g.) was dissolved in 15 ml. of dimethyl sulfoxide. Excess sulfoxide was removed under high vacuum to give an oil which, when ether washed and dried, gave a white solid which begins to decompose above 240°.

Anal. Calcd. for $GeF_2\cdot OS(CH_3)_2$: F, 20.3; S, 17.0. Found: F, 20.7; S, 17.3.

A referee correctly pointed out that the data initially presented did not preclude the possibility that oxygen is abstracted from dimethyl sulfoxide and that the isolated complexes might be $MF_2\cdot S(CH_3)_2$. The infrared data, which had not been included initially, clearly showed absorption in the region ($\sim$1020 cm.$^{-1}$) characteristic of S–O stretching vibration.

Germanium difluoride (5 g.) was dissolved in 25 ml. of dioxane and filtered. On cooling, colorless needles formed; m.p. 74–78° with decomposition. These needles, after a brief (0.5 hr.) vacuum drying, consistently analyzed for $GeF_2\cdot X$dioxane with X ranging from 0.92 to 0.95. Extended vacuum drying led to lower values of X, indicating dissociation of the complex at 25°.

All of the tin and germanium complexes, in solution, absorbed oxygen as shown by tensimetric measurements.

Analytical.—The compounds to be analyzed for Ge, Sn, or F were decomposed by peroxide fusion. Germanium was determined by a tannic acid procedure,[12] tin by a modified hydrolysis and ashing procedure,[13] and fluorine by distillation (Willard and Winter) and titration with standard thorium nitrate.

Acknowledgment.—The assistance of Mr. A. F. Biddle in the X-ray analyses is gratefully acknowledged.

[12] W. R. Schoeler and A. R. Powell, "Analysis of Minerals and Ores of the Rare Elements," Charles Griffin and Co. Limited, London, 1955, p. 170.

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The Hydrolysis of Lanthanum and Cerium Carbides[1]

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The hydrolysis of lanthanum and cerium carbides at various temperatures was investigated. The complex hydrocarbon mixtures resulting from the hydrolysis were analyzed by gas chromatography. The production of acetylene at room temperature was approximately 65 mole %, but no acetylene was produced at 200°.

Introduction

The hydrolytic reactions of rare earth dicarbides have been studied by Moissan,[2,3] by Damiens,[4] by Zambonini,[5] by Villelume,[6] and recently by Greenwood and Osborn.[7] Damiens and Moissan found the major product of the reactions to be acetylene, but differed markedly as to the constitution of the remainder of the gaseous products. The more recent work of Villelume conflicts with the earlier studies. Damiens also hydrolyzed a carbide, supposedly cerium tricarbide, which he reported to give 98% acetylene. The existence of this tricarbide and the products from the hydrolysis reaction have never been confirmed.

Greenwood and Osborn studied the reactions of lanthanum dicarbide and sesquicarbide with sulfuric, nitric, and chlorosulfonic acids and molten iodine. The reactions of the carbides with the above reagents are complicated by various side reactions which obscure the nature of the hydrolysis products. The present hydrolysis study was conducted under conditions which restrict the effect of the hydrolysis medium and the highly exothermic nature of the reaction in influencing the final products.

This study of the hydrolysis of lanthanum and cerium carbides was undertaken as part of a

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[2] H. Moissan and A. Etard, *Compt. rend.*, **122**, 576 (1896); *ibid.*, **123**, 148 (1896).

[3] H. Moissan, "The Electric Furnace," Chemical Publ. Co., Easton, Pa., 1920.

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[5] F. Zambonini, *Atti accad. naz. Lincei*, (v) **33**, 16 (1924).

[6] J. Villelume, Doctoral Thesis, University of Paris, 1952; *Compt. rend.*, **232**, 235 (1951); *Ann. chim.*, **7**, 265 (1952).

[7] N. N. Greenwood and A. J. Osborn, *J. Chem. Soc.*, 1775 (1961).