gardless of the method of preparation. The pattern is not that of a cubic substance.

Ebert and Woitinek prepared their material by treating massive copper with a mixture of chlorine and fluorine at 350°, assuming the layer adjacent to the copper to be copper(I) fluoride. No other experimental details or analyses of the preparations are given.

The copper(I) fluoride is given as having the zincblende structure, F$\bar{4}$3m, T_d^2, with $a_0 = 4.26$ Å.; the copper(II) fluoride, Fm3m, O_h^5, $a_0 = 5.41$ Å. The interplanar spacings for each of these structures have been calculated from these data and are shown in Table II. For comparison, the larger interplanar spacings found for copper(II) fluoride in this research are given, as are the values for copper(I) oxide and copper(I) chloride. The reported structure for copper(I) fluoride was apparently based on measurements of a red copper(I) oxide layer formed on the massive copper, possibly by contaminated gas or by air exposure on cooling. The structure of copper(II) fluoride was apparently based on measurements made with a white copper(I) chloride deposit.

TABLE II

INTERPLANAR SPACING COMPARISON

CuF_2 (this research), *d*, Å.	Relative intensity I/I_0	CuF_2 (Ebert and Woitinek) *d*, Å.	$CuCl^5$ *d*, Å.	CuF (Ebert and Woitinek) *d*, Å.	Cu_2O^5 *d*, Å.
3.22	100	3.12	3.12	2.46	2.45
2.82	25	2.70	2.70	2.13	2.12
2.66	35	1.91	1.91	1.51	1.51
2.53	8	1.63	1.63	1.28	1.28
2.39	15	1.56	..	1.22	1.23
2.28	8	1.35	1.35	1.06	1.07
2.21	8	1.24	1.24	0.98	0.98
2.04	3	1.21	..	.95	.95
1.82	18	1.10	1.10	.86	.87
1.77	15	1.04	1.04	.82	.82
1.69	18				
1.66	15				
1.64	13				
1.61	20				
1.51	3				
1.44	13				
1.42	8				
1.38	10				
1.32	8				

It has been possible to pick out of the solidified copper(II) fluoride melt small crystalline fragments of clear, colorless fluoride. Weissenberg photographs of these crystals have been taken and show the copper(II) fluoride to be monoclinic.

Experimental

The fluorination apparatus and techniques were the same as those used previously.[6] The copper metal used was heated at about 350° in hydrogen for two hours prior to fluorination. Stock C.P. copper oxides and bromide were used. Copper(I) chloride was freshly prepared by reduction of copper(II) chloride.[7] Anhydrous copper(II) chloride was prepared by dehydration of the dihydrate in the reactor furnace at 300° in nitrogen. Copper(I) sulfide was prepared by reduction of copper(II) sulfide with arsenic(III) oxide,[8] the treatment being repeated. Two forms of the sulfide have been reported, the formula often approaching Cu_9S_5.[9] Analysis showed a high sulfur content so the material was heated in nitrogen at 550°. The product gave a powder pattern similar to that for α-Cu_2S, the high chalcocite form of Buerger and Buerger.

Anal. Calcd. for Cu_2S: Cu, 79.85. Found: Cu, 80.11.

The copper(II) sulfide was prepared by precipitation with hydrogen sulfide from an acidified copper(II) sulfate solution.[8] The precipitated sulfide was extracted with carbon disulfide to remove free sulfur and stored under nitrogen.

Anal. Calcd. for CuS: Cu, 66.46. Found: Cu, 65.74, 65.78, 65.70.

C.P. anhydrous copper(II) sulfate was heated in the reactor furnace in nitrogen at 250° immediately prior to fluorination.

Copper was determined as anthranilate, after digestion with nitric or sulfuric acid, on samples from sulfide and sulfate fluorinations. All transfers involving fluoride were made in a dry-box; the anhydrous fluoride is extremely hygroscopic.

Anal. Calcd. for CuF_2: Cu, 62.58. Found: ($Cu_2S + F_2$)Cu, 63.08, 63.03. Found: ($CuSO_4 + F_2$)Cu, 62.91, 63.08, 62.91.

The melting point was determined by the technique used for cadmium and zinc fluorides, using, however, a horizontal 28 mm. diameter combustion tube wound with 22-gage nichrome wire. The samples were placed in a platinum boat and the calibrated chromel–alumel thermocouple placed directly above the sample. Nitrogen was purified by pyrogallol, dried with anhydrone and passed over copper turnings at 350°. Helium was used after traces of oxide were found in the fused samples.

The thermal analysis apparatus used was that described by Whitehead and Breger.[10]

Samples for powder photographs were sealed in Pyrex capillaries or coated on Pyrex fibers, followed by dipping in Formvar solution for protection against moisture. Copper radiation was used with a nickel filter.

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[5] X-Ray Diffraction Data Cards, American Society for Testing Materials, Philadelphia, Pennsylvania.

[6] H. M. Haendler, W. L. Patterson, Jr., and W. J. Bernard, THIS JOURNAL, **74**, 3167 (1952).

[7] W. C. Fernelius, Ed., "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 1.

[8] L. Vanino, "Handbuch der Präparativen Chemie," Vol. I, Enke Verlag, Stuttgart, 1925, p. 512.

[9] M. J. Buerger and N. W. Buerger, *Am. Mineral.* **29**, 55 (1944).

[10] W. L. Whitehead and I. A. Breger, *Science*, **111**, 279 (1950).

The Reaction of Fluorine with Tin, its Oxides and Sulfides[1]

BY H. M. HAENDLER, S. F. BARTRAM, W. J. BERNARD AND D. KIPPAX

RECEIVED NOVEMBER 10, 1953

A study has been made of the action of fluorine on tin, tin(II) oxide, tin(IV) oxide, tin(II) sulfide and tin(IV) sulfide similar to that reported with zinc and nickel.[2]

Mossy tin reacts completely with fluorine above 190°, forming the tetrafluoride. There is no visible reaction of fluorine with tin(II) oxide at 150°. Reaction occurs at 200°, with two distinct layers of product being formed over the black oxide substrate. The top layer is tin(IV) fluoride, the lower is tin(IV) oxide, as shown by X-ray powder pat-

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[1] Research supported by the Research Corporation and the Atomic Energy Commission.

[2] H. M. Haendler, W. L. Patterson, Jr., and W. J. Bernard, THIS JOURNAL, **74**, 3167 (1952).

terns. At 500° the sole product is tin(IV) fluoride, and conversion is complete. Tin(IV) oxide does not react with fluorine below 300°, at 400° conversion to tetrafluoride is about 80%, and at 500–550° conversion is complete.

The reaction with tin(II) oxide is thus similar to that with copper(I) oxide.[3] No evidence for an oxyfluoride was found.

Emeléus and Woolf[4] report a similar reaction between tin(II) oxide and bromine trifluoride, forming only tin(IV) oxide and fluoride.

Tin(II) sulfide reacts readily with fluorine, even at room temperature. At 400–500° reaction is so violent that much product is volatilized. Introduction of fluorine at room temperature, followed by gradual increase in temperature to 500°, gave complete conversion. X-Ray patterns of fluorination products from reactions at various temperatures showed only tin(IV) fluoride and unreacted sulfide. Tin(IV) sulfide does not react at 100° or below. Reaction is extensive at 200° and above. Fluorination over the range 25–300° gave complete conversion.

Experimental

The fluorinations were carried out as described previously.[5] All product transfers were made in the dry-box at a dewpoint of −25° or less. Stock C.P. tin and tin(IV) oxide were used. Tin(II) oxide was freshly prepared[6] to minimize possible contamination with tin(IV) oxide.

Anal. Calcd. for SnO: Sn, 88.12. Found: Sn, 88.07.

Tin(II) sulfide was prepared by precipitation from the chloride with hydrogen sulfide.[7] Tin(IV) sulfide was prepared by direct reaction between tin(II) chloride and sulfur.[8]

Anal. Calcd. for SnS: Sn, 78.73. Found: Sn, 78.54, 78.69. Calcd. for SnS_2: Sn, 64.93. Found: Sn, 64.73, 64.71.

Fluorination products of each run were also analyzed. Tin was determined as the oxide after treatment with nitric acid.

Anal. Calcd. for SnF_4: Sn, 60.96. Found: ($Sn + F_2$) Sn, 61.36, 61.18; ($SnO + F_2$, upper layer) Sn, 60.42, 60.88; ($SnO_2 + F_2$) Sn, 60.3, 61.5; ($SnS + F_2$) Sn, 61.27, 60.72; ($SnS_2 + F_2$) Sn, 61.09, 61.28.

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(3) H. M. Haendler, L. H. Towle, E. F. Bennett and W. L. Patterson, Jr., THIS JOURNAL, **76**, 2178 (1954).

(4) H. Emeléus and A. Woolf, *J. Chem. Soc.*, 164 (1950).

(5) H. M. Haendler and W. J. Bernard, THIS JOURNAL, **73**, 5218 (1951).

(6) W. Fraenkel and K. Snipischsky, *Z. anorg. Chem.*, **125**, 235 (1922).

(7) W. E. Henderson and W. C. Fernelius, "Inorganic Preparations," McGraw–Hill Book Co., Inc., New York, N. Y., 1935, p. 64.

(8) L. Vanino, "Handbuch der Präparativen Chemie," Vol. I, Enke Verlag, Stuttgart, 1925, p. 600.

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Non-exchange of Chlorine between Chloride and Hexachlorosmate(IV) Ions in Aqueous Solution[1]

BY LINDA L. LARSON AND CLIFFORD S. GARNER

RECEIVED NOVEMBER 30, 1953

The generally encountered slowness of substitution reactions of osmium(IV) complexes may be expected to result in low rates of exchange between ligands coördinated to osmium(IV) and the corresponding free ligand ion or molecule in solution. In favorable cases such slow exchanges may be accessible to kinetic studies. We have examined the chloride–hexachlorosmate(IV) system for chloride exchange in nitric and sulfuric acid solutions, as well as determining the absorption spectrum of potassium hexachlorosmate(IV) in 1.32 *f* and 0.10 *f* nitric acid solution.

Experimental

Radiochlorine Tracer.—Radiochlorine-36 (half-life, 4 × 10^5 years), produced by (n,γ) reaction on potassium chloride, was supplied in a radiochemically purified form as a hydrochloric acid solution by the Oak Ridge National Laboratory on allocation by the U. S. Atomic Energy Commission.

Potassium Hexachlorosmate(IV).—This substance was synthesized by heating a mixture of C.P. osmium(VIII) oxide, iron(II) chloride and concentrated hydrochloric acid in a pressure flask, followed by precipitation with potassium chloride, in a manner similar to that employed by Dwyer and Hogarth[2] for the preparation of the ammonium salt. The potassium salt was recrystallized from 3 *f* hydrochloric acid, cooled to 0°, filtered and washed with 1 *f* hydrochloric acid and finally with 95% ethanol. The crystals were dried over phosphorus(V) oxide in a vacuum desiccator. Weighed portions of the dried crystals were analyzed by reduction to metallic osmium in a stream of hydrogen at 400°, the hydrogen chloride formed being absorbed in an excess of standard silver nitrate solution which was later back-titrated with standardized potassium thiocyanate solution by the Volhard method. The residue, consisting of metallic osmium and an equivalent amount of potassium chloride, was transferred in a nitrogen atmosphere into a weighing vessel and weighed, then the potassium chloride leached out with water and this chloride determined as above.

Anal. Calcd. for K_2OsCl_6: Os, 39.5; Cl, 44.2. Found: Os, 39.8; Cl, 44.4.

Other reagents were C.P. or reagent grade and were used without further purification.

Separation Method.—The hexachlorosmate(IV) ion was separated from chloride ion by precipitation with excess ammonium nitrate. Experiments showed that precipitation from a solution 25 *f* in ammonium nitrate gave a rapid and quantitative separation. Two-gram portions of ammonium nitrate were added to the 1-ml. aliquots of the exchange mixtures, and the ammonium hexachlorosmate(IV) precipitates centrifuged and washed with saturated ammonium nitrate solution.

Exchange Runs.—Exchange mixtures (10-ml. volumes) were synthesized by weighing out potassium hexachlorosmate(IV) and dissolving in solutions volumetrically synthesized from standardized sodium chloride, sodium nitrate (used to adjust the ionic strength, μ), and nitric or sulfuric acid solutions. The mixtures were brought to the reaction temperature in a bath thermostated to ±0.2°, and exchange initiated by admixture with 50 μl. of radiochlorine tracer solution known to be in the form of chloride ion. One-ml. aliquots were removed at definite time intervals and subjected to the above separation procedure. All exchange runs were carried out in the absence of light.

Specific Activity Determinations.—In some cases the precipitated ammonium hexachlorosmate(IV) fraction was dissolved in 3 *f* sodium hydroxide and transferred to a cell used for radioassay with a dip-type Geiger–Mueller tube and associated scale-of-64 circuit. In other cases, the solution fractions were transferred directly to cells. These solutions were diluted in the cells to a volume of *ca.* 20 ml. and had essentially the same density so that self absorption and self-scattering corrections were unnecessary. Background corrections (*ca.* 30 c./min.) were applied, and the background with dip tube and cell determined just prior to each radioassay to check their decontamination.

Spectrophotometric Runs.—Certain exchange solutions were diluted 250-fold with solvent of the same composition as the exchange mixture except for the omission of the po-

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(1) These investigations were carried out under contract AT-(11-1)-34, Project 12, between the University of California and the U. S. Atomic Energy Commission.

(2) F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. N. S. Wales*, **84**, 194 (1951).