CONTRIBUTION FROM THE PARMA RESEARCH LABORATORY,
UNION CARBIDE CORPORATION, PARMA 30, OHIO

The Preparation and Properties of Niobium Tetrafluoride and Oxyfluorides

BY F. P. GORTSEMA AND R. DIDCHENKO

Received July 20, 1964

Niobium tetrafluoride has been prepared by the reduction of niobium pentafluoride with Si or Nb powder at 300–350°. X-Ray diffraction studies of the tetrafluoride show that it has a tetragonal unit cell with $a_0 = 4.081$ and $c_0 = 8.162$ Å. Reduction of NbF_5 in sealed quartz tubes with red phosphorus, arsenic, or silicon gave rise to a series of very stable niobium oxyfluorides having the same structure as NbF_3.

There is little information in the literature on the preparation and properties of the fluorides of niobium. The only fluorides that have been reported are the pentafluoride,[1-4] the trifluoride,[5] and recently the tetrafluoride.[6] The niobium(IV) halides, *viz.*, the tetrachloride,[7-10] tetrabromide,[10,11] and tetraiodide,[10,12] and the niobium(IV) halide pyridine adducts[10] are well known and their properties and structures have been described. Very little is known about niobium tetrafluoride.

Vanadium tetrafluoride had been prepared as early as 1911 by Ruff and Lickfett.[13] More recently, Cavell and Clark[14] have improved considerably the procedure for the preparation and more completely characterized the material. We have attempted to prepare the tetrafluoride of the next member of group VB, niobium, using Cavell and Clark's procedure. However, this method proved unsuccessful.

We have prepared niobium tetrafluoride both by the reduction of NbF_5 with Nb and also by reduction of NbF_5 with elements, such as Si, P, and B, that yield volatile fluorides. Since the completion of our work, a short note has appeared by Schäfer, *et al.*,[6] in which they mention the preparation of NbF_4 by the reduction of NbF_5 with Nb. However, they give no details on the conditions for preparation or properties of this new compound.

We have found that NbF_4 can be prepared easily and in high yields by Si reduction of NbF_5. This paper describes the details of the methods of preparation of NbF_4, the chemical, physical, and magnetic properties, and a proposed structure based on X-ray powder diffraction data.

Experimental

Niobium Pentafluoride.—NbF_5 was prepared by two methods: (a) fluorination of Nb powder in an all-nickel reactor at 300°[15]; (b) reaction of Nb powder with SnF_2. The latter is a convenient method for the preparation of NbF_5 (or TaF_5) since it involves only easy to handle chemicals. Powdered Nb (−200 mesh) and SnF_2 are thoroughly mixed and placed in a molybdenum crucible inside an Inconel reactor and a slow stream of purified argon is admitted. NbF_5 is produced at temperatures between 375 and 500° according to the equation

$$5SnF_2 + 2Nb = 5Sn + 2NbF_5\uparrow$$

The NbF_5 sublimes out of the reaction mixture and condenses on the water-cooled lid of the Inconel reactor. Less than 1% NbF_3 is also produced in this reaction. In addition, some NbF_5 was purchased from the Ozark-Mahoning Company, Tulsa, Okla. All NbF_5 was repurified by sublimation before use in reactions. The sublimation was carried out in a platinum crucible in an all-glass system under a few millimeters pressure at temperatures between 50 and 100°. All preparations and handling operations involving the use of NbF_5 were carried out in a glove box under an atmosphere of dry nitrogen.

Silicon.—Si was supplied by the Kemet Products Department of Linde Division, Union Carbide Corporation. The material was −200 mesh, semiconductor grade.

Tin(II) Fluoride.—The 40 mesh material was supplied by the City Chemical Corp., New York, N. Y.

Niobium.—The (−200 mesh) powder was obtained from the Fansteel Metallurgical Corp., North Chicago, Ill. The assay was 99.8+% Nb. Principal impurities were Ta, <500 p.p.m., and oxygen, <200 p.p.m.

Fluorine.—The 98% pure material was obtained from the General Chemical Division, Allied Chemical Co. The gas was passed through a heated NaF tower to absorb traces of HF.

All autoclave reductions of NbF_5 with silicon were carried out in a 100-ml. capacity nickel autoclave reactor custom built by Autoclave Engineers, Inc., Erie, Pa. The autoclave was of the A. E. patented, self-sealing design built to withstand 6000 p.s.i. at 300°. All valving connectors, Bourdon tube gauges, and auxiliary connections were constructed from Monel.

The reaction mixture of pentafluoride and silicon was thoroughly mixed in a copper crucible in a drybox and placed into the autoclave. After assembly, the autoclave was evacuated and flushed several times with argon by pressurizing to 2000 p.s.i. directly from an argon cylinder. The system was pressurized to keep the niobium pentafluoride in the liquid state and thus avoid the condensation of the volatile material in the cooler zones of the autoclave. The autoclave was then heated to 300° in a furnace or a heating mantle. In the early stages of the reaction, the autoclave was cooled to room temperature at 24-hr. intervals and the pressure released slowly, liberating large quantities of SiF_4. The system was then flushed with argon, repressurized, and reheated. This procedure was repeated 10 to 15 times, depending upon sample size and temperature. Near

---

(1) O. Ruff and E. Schiller, *Z. anorg. Chem.*, **72**, 329 (1911).
(2) F. Fairbrother and W. C. Frith, *J. Chem. Soc.*, 3051 (1951).
(3) H. C. Clark and H. J. Emeléus, *ibid.*, 190 (1958).
(4) H. J. Emeléus and V. Gutmann, *ibid.*, 2115 (1950).
(5) P. Ehrlich, F. Plöger, and G. Pietzka, *Z. anorg. allgem. Chem.*, **282**, 19 (1955).
(6) H. Schäfer, D. Bauer, W. Beckmann, R. Gerken, H.-G. Nieder-Vahrenholz, K.-J. Niehues, and H. Scholz, *Naturwissenschaften*, **51**, 241 (1964).
(7) H. Schäfer and K. D. Dohmann, *Z. anorg. allgem. Chem.*, **300**, 1 (1959).
(8) H. Schäfer, G. Göser, and L. Bayer, *ibid.*, **265**, 258 (1951).
(9) H. Schäfer, L. Bayer, and H. Lehmann, *ibid.*, **268**, 268 (1952).
(10) R. E. McCarley and B. A. Torp, *Inorg. Chem.*, **2**, 540 (1963).
(11) H. Schäfer and K. D. Dohmann, *Z. anorg. allgem. Chem.*, **311**, 134 (1961).
(12) J. D. Corbett and P. X. Seabaugh, *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).
(13) O. Ruff and H. Lickfett, *Ber.*, **44**, 2539 (1911).
(14) R. G. Cavell and H. C. Clark, *J. Chem. Soc.*, 2692 (1962).
(15) H. F. Priest, *Inorg. Syn.*, **3**, 179 (1950).

completion of the reaction, the venting procedure was carried out only once per 48 hr. When SiF_4 was no longer evolved, the autoclave was dismantled and the product removed in a drybox. Samples of NbF_4 from 10 to 50 g. can easily be prepared by this procedure. The material obtained was very finely divided, usually from 100 to 200 mesh. *Anal.* Calcd. for NbF_4: Nb, 55.0; F, 45.0. Found: Nb, 55.1; F, 44.3. Chemical analysis and X-ray diffraction results showed that their was no unreacted Si present in the sample. Smaller samples of NbF_4 and oxyfluorides were prepared in heavy-wall (3 mm.), 20-cm. long quartz tubes. These tubes were loaded in an inert dry atmosphere box, sealed off under vacuum, and heated for several days at 300°. This method is convenient for preparing sample sizes of 3 g. or less.

Density determinations were made pycnometrically using a 1-ml. Pyrex apparatus fitted with a thermometer. Water was used as the liquid for the determination of the densities of NbF_3 and the oxyfluorides. For NbF_4, the fluorocarbon liquid FC 43, produced by the 3M Company, was used.

X-Ray Diffraction Measurements.—X-Ray diffraction studies were carried out using the powder technique with the powder sealed in fine bore, thin-wall capillaries (0.3-mm. diameter, 0.01-mm. wall). Samples were loaded into the capillaries in a drybox under argon and mounted in a 114.6-mm. Debye–Scherrer camera. Measurements were made using Cu $K\alpha$ with a nickel filter or Ni radiation using a cobalt filter. The Straumanis film technique was employed. All films were corrected for film shrinkage.

Magnetic Susceptibility Measurements.—Magnetic measurements were made both by the Gouy and Faraday methods. The Gouy apparatus consisted of a Mettler semimicrobalance and a 10,000 gauss, variable magnet powered by a General Electric amplidyne. The samples were packed into 15-cm. thin-wall quartz tubes stoppered with tightly fitting Teflon plugs. For the Faraday measurements a quartz beam microbalance of the type described by Czanderna and Honig[16] was used with a 4-in. Varian magnet. The samples were contained in "tiny" glass ampoules suspended in the magnet on a Teflon thread. For both methods, corrections were applied for the diamagnetism of the container material.

Analytical Procedures.—The niobium and fluorine were determined by procedures developed by Mr. J. Dolesch of this laboratory. Careful analysis on several standard niobium fluoride samples showed that the procedures were capable of an accuracy of 0.3% for niobium and 0.8% for fluorine.

The samples were readied for analysis by KOH fusion in a platinum crucible to yield potassium niobate and KF. The melt was acidified with 10% sulfuric acid and the niobium precipitated from the cold solution with N-phenylbenzohydroxamic acid. The precipitate was separated and ignited at 800° to yield Nb_2O_5.

The fluorine content of the samples was determined by two different procedures which served as a check on each other. The solution containing the KOH-fusion products was transferred to a polyethylene beaker containing Dowex 50W-X4 ion-exchange resin (50–100 mesh) in the acid form and equilibrated overnight. The niobate attaches itself to the resin and the fluoride remains as HF. The resin and solution were transferred to a column previously charged with about 2 cm. of 200 mesh Dowex 50W-X12 resin which filters out any hydrolyzed niobate. The solution was allowed to drain through the resin until acid could no longer be detected in the effluent. The hydrofluoric acid was titrated potentiometrically with 0.1 *N* standard NaOH solution.

Another fluorine analysis was carried out on the same eluted solution after neutralization. To the solution (approximately 200 ml.), sulfuric acid was added to give a pH of 4–5. The solution was evaporated to a volume of 50 ml. to separate any dissolved niobate which was then filtered off. The pH of the filtrate was readjusted to 4, the filtrate was heated with an excess of standard Ca^{+2} solution, and CaF_2 precipitated. After standing overnight, the solution was back titrated with EDTA to determine the amount of excess Ca^{+2} present.

Oxygen analyses were made by the LECO combustion method.

Results and Discussion

Niobium pentafluoride can be reduced to the tetrafluoride at 300 to 350° according to the reaction

$$4NbF_5 + Si = 4NbF_4 + SiF_4$$

Other reducing agents have also been found to be effective. Among those studied were P, B, As, Sb, I_2, S, Nb, U, and Ti. The reduction of NbF_5 with Nb in a heavy-wall quartz tube at 250 to 300° for a period of 2 to 4 days is a simple method for the preparation of small amounts of NbF_4.

$$4NbF_5 + Nb = 5NbF_4$$

A similar method has been applied previously for the preparation of the tetrachloride[8] and tetrabromide.[11] The reduction of niobium pentafluoride with Si appears to proceed in the most straightforward manner and gives the highest purity product of all the nonmetallic reducing agents tried. Reduction with Ti sponge or U filings gave particularly fast reduction (about 24 hr.), but no simple method was found for separating the products.

Pure NbF_4 is a black, nonvolatile, very hygroscopic solid. It can be handled only under a dry atmosphere. In the presence of traces of water, it reacts with glass containers. The material can be stored for long periods of time in an inert atmosphere in a copper vial fitted with a Teflon stopper. When NbF_4 is left in the air, it hydrolyzes completely to white NbO_2F. NbF_4 reacts vigorously with water, forming a brown solution from which a brown precipitate soon settles. This material contains niobium, fluorine, and oxygen, but has not been completely characterized.

Niobium tetrafluoride appears to be thermally more stable than VF_4. Whereas VF_4 begins to disproportionate at 100–120° under vacuum,[14] NbF_4 is stable to approximately 275–325° under vacuum. At temperatures greater than 350°, disproportionation takes place rapidly. Determination of the weight loss due to the escape of volatile NbF_5, as well as X-ray and chemical analysis of the residue, shows that the reaction appears to proceed according to the equation

$$2NbF_4 = NbF_5 + NbF_3$$

However, the black to blue-black "NbF_3" product could never be prepared completely free of oxygen. Also the freshly prepared "NbF_3" was pyrophoric, but if subjected to oxygen slowly in dilute concentrations it then became very stable to air or water. It has not been possible to sublime NbF_4 at low temperatures. Thus NbF_4 does not resemble VF_4,[13,14] TiF_4,[17] or CrF_4,[18] which have been observed to sublime under vacuum between 100 and 200°, or ZrF_4,[19] and HfF_4,[19] which sub-

---

[16] A. W. Czanderna and J. M. Honig, *Anal. Chem.*, **29**, 1206 (1957).

[17] H. M. Haendler, S. F. Bartram, R. S. Becker, W. J. Bernard, and S. W. Bukada, *J. Am. Chem. Soc.*, **76**, 2177 (1954).

[18] H. von Wartenberg, *Z. anorg. allgem. Chem.*, **247**, 135 (1941).

[19] K. A. Sense, M. J. Snyder, and R. B. Filbert, *J. Phys. Chem.*, **58**, 995 (1954).

lime only at temperatures exceeding 700°. It also differs from $NbCl_4$, which has been observed to sublime at about 350°.[8,9]

The crystal structure of NbF_4 also differs from that of other known tetrafluorides, and also from that of niobium tetrachloride and tetrabromide. Measurements made on X-ray diffraction powder patterns from many different samples indicate a tetragonal unit cell with the cell dimensions: $a_0 = 4.081$, $c_0 = 8.162$ Å. ($c/a = 2.000$, $V = 135.9$ Å.^{3}). This corresponds to a unit cell containing two formula units, space group D_{4h}^{17}-I4/mmm. For I4/mmm the two niobiums in the unit cell occupy one set of 2-fold special positions: 2a of point symmetry 4/mmm, while the eight fluorides are in two sets of 4-fold special positions of point symmetry mmm and 4 mm, respectively. The sets and coordinates for the equivalent positions for the niobium and fluoride atoms are[20]

2Nb	2a	$0, 0, 0;\ ^1/_2, ^1/_2, ^1/_2$
4F	4c	$0, ^1/_2, 0;\ ^1/_2, 0, 0;\ ^1/_2, 0, ^1/_2;\ 0, ^1/_2, ^1/_2$
4F	4e	$0, 0, z;\ 0, 0, \bar{z};\ ^1/_2, ^1/_2, ^1/_2 + z;\ ^1/_2, ^1/_2, ^1/_2 - z$

where z was found to be $^1/_4$. For $c_0 = 2a_0$ the site symmetry about each niobium is of highest cubic point symmetry corresponding to a regular octahedron of six fluorides about each niobium. The structure consists of a body-centered tetragonal niobium lattice and a face-centered cubic closest packed fluoride lattice (see Figure 1).

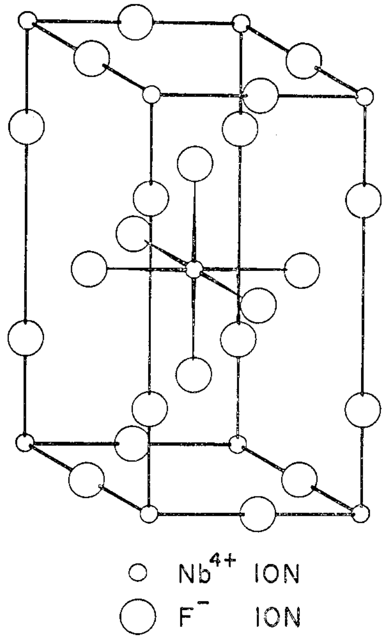

Figure 1.—Unit cell for niobium tetrafluoride.

The observed pycnometric density of 4.01 g./cc. agrees well with the calculated X-ray density of 4.13 g./cc. If the volume of the Nb^{+4} ion is neglected, the volume of the unit cell corresponds to a volume of 17.0 Å.^{3} for each fluoride ion. This value is in good agreement with values obtained for other fluoride structures.[14,21] The structure also leads to a value of 0.71 Å. for the radius of the Nb^{+4} ion, in fair agreement with the value of 0.67 Å. previously given.[22] Octahedral coordination of metal with fluorine ions also has been suggested for VF_4[14] and TiF_4.[23]

The positions of the fluoride and niobium atoms have been verified by comparison of the observed and calculated intensities assuming the previously described structure. The relative intensities were calculated according to the formula[24]

$$U \propto \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}\, \rho F^2$$

where θ is the Bragg angle, ρ the multiplicity factor, and $|F|$ the structure factor. The structure factor included the scattering power contribution of both F^- and niobium atoms. Scattering factors as a function of $\sin \theta/\lambda$, where λ is the wave length of radiation used, were obtained from International Tables.[25] In the calculation of the relative intensities, it was assumed that the contributions of the absorption factor and temperature factor would tend to cancel each other and therefore these factors were omitted.[24] A comparison of the observed and calculated relative intensities along with the observed and calculated d spacings is given in Table I. The observed intensities reported in the table are average diffractometer readings from patterns of ten different NbF_4 samples. The agreement between observed and calculated intensities is remarkably good.

As can be seen from the diagram of the proposed structure (Figure 1), there are two planes perpendicular to the c axis occurring at $^1/_4c_0$ and $^3/_4c_0$ that contain a high concentration of fluoride ions. Presumably, this condition is responsible for the instability of NbF_4 and the ease with which the compound can disproportionate into NbF_5 and NbF_3 at higher temperatures. Niobium pentafluoride also is believed to have an octahedral configuration in the liquid state[26] and possibly also in the crystalline state.[27]

The NbF_4 crystal structure is unusual in that the c/a ratio appears to be identically equal to 2, within experimental accuracy. Nowhere on the photographic film, even at high values of θ near 80°, was there evidence of line splitting expected from any departure of the c/a ratio from 2, which would become particularly significant in case of lines whose indices contain a high value of h and k and low value of l, such as the two pairs 400, 008 or 330, 118. These lines are sharp

---

(20) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, pp. 241, 242.

(21) R. W. M. D'Eye and E. Wait, "X-Ray Powder Photography in Inorganic Chemistry," Butterworth's Scientific Publication, London, 1960, p. 186.

(22) R. W. G. Wykoff, "The Structure of Crystals," Chemical Catalog Co., New York, N. Y., 1924.

(23) R. D. Euler and E. F. Westrum, *J. Phys. Chem.*, **65**, 132 (1961).

(24) N. F. M. Henry, H. Lipson, and W. A. Wooster, "The Interpretation of X-Ray Diffraction Photographs," Macmillan and Co., Ltd., London, 1960.

(25) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1952, pp. 202–207.

(26) F. Fairbrother, W. C. Frith, and A. A. Woolf, *J. Chem. Soc.*, 1031 (1954).

(27) A. J. Edwards, R. D. Peacock, and R. W. H. Small, *ibid.*, 4486 (1962).

TABLE I

X-RAY POWDER DIFFRACTION PATTERN FOR NIOBIUM TETRAFLUORIDE

$a_0 = 4.081$ Å.; $c_0 = 2a_0$ Cu Kα radiation

hkl	d_{obsd}	d_{calcd}	$(I/I_0)_{\text{obsd}}$	$(I/I_0)_{\text{calcd}}$
002	4.081	4.081	29	32
101	3.644	3.650	100	100
110	2.879	2.886	25	27
112	2.353	2.356	vw	0.7
103	2.260	2.263	21	26
200 004	2.039	2.041	39	48
202	1.823	1.825	15	13
211	1.778	1.781	24	25
114	1.665	1.666	10	10
105 213	1.514	1.515	20	21
220 204	1.441	1.443	22	25
006 222	1.358	1.360	7	6
301	1.340	1.342	5	5
310	1.290	1.291	4	4
312 116	1.228	1.230		2
303 215	1.215	1.217	10	10
224	1.176	1.178	7	8
206	1.130	1.132		3
321 107	1.122	1.121	5	8
314	1.089	1.091	3	5
323 305	1.045	1.045	5	7
400 008	1.019	1.020		4
226 402	0.9895	0.9898		4
217 411	0.9828	0.9827		8
330 118	0.9597	0.9618		4
332 316	0.9352	0.9362		1
413 325	0.9297	0.9300		8
404 208 420	0.9111	0.9126		15
422	0.8905	0.8905		4
307 309	0.8837	0.8853		5
334	0.8705	0.8702		5
415	0.8463	0.8463		5
424 228	0.8334	0.8330		19
00,10 406	0.8162	0.8162		4

and have no detectable splitting. The pattern has been indexed, therefore, on the basis of $c/a \equiv 2$.

The crystal structure of niobium tetrachloride recently has been determined by Schnering and Wöhrle.[28] They concluded from single crystal studies that $NbCl_4$ possesses a monoclinic unit cell. McCarley and Torp[10] have indexed the powder pattern of $NbCl_4$ and $NbBr_4$ on the basis of an orthorhombic unit cell containing four molecules. Niobium tetraiodide is also orthorhombic but contains eight molecules in a much larger unit cell.[29] The difference in crystal structure between the tetrafluoride and the other tetrahalides is undoubtedly due to the large difference in the radius ratio $\rho = r_c/r_a$ for these compounds ($\rho_{NbF_4} = 0.53$, $\rho_{NbCl_4} = 039,.$ $\rho_{NbBr_4} = 0.36$).

Magnetic measurements could provide information on the oxidation state of the niobium in these compounds. Our results on "NbF_3" were in good agreement with those of Ehrlich, *et al.*,[5] but the amount of ferromagnetic impurities, which are also mentioned by these authors, was large enough to make the results obtained from Honda–Owen extrapolation very unreliable. The ferromagnetic phase was present in all the lower valency fluorides and oxyfluorides studied, independent of the method of preparation, container material, etc.

Niobium pentafluoride used on the starting material in these preparations was always diamagnetic with a molar susceptibility $\chi_M^{296} = -2.4 \times 10^{-6}$ e.m.u. Measurements on NbF_4 by the Gouy method did not give any meaningful results, except to show that there was very little temperature dependence between 77 and 400°K., with a slight but reproducible hump around 195°K. which may be indicative of a Neél point, obscured by the ferromagnetic contribution. Measurements by the Faraday method gave considerably lower values for the molar susceptibility which could be easily extrapolated to 98×10^{-6} e.m.u. at 297°K. and 115×10^{-6} e.m.u. at 80°K., *i.e.*, considerably smaller than the values of $\chi_M^{298} = 143 \times 10^{-6}$ and $\chi_M^{90} = 250 \times 10^{-6}$ e.m.u. for NbF_3.[5] Despite repeated attempts, it was not possible to obtain any values at 195°K. because of unusually bad scatter of data developing in that temperature range. In conclusion, it may be said that magnetic measurements lend support to the existence of the Nb^{+4} ion, but also reveal a complex magnetic behavior for the entire class of lower valency niobium fluorides.

If an excess of silicon over that needed for reduction of the pentafluoride to the tetrafluoride is used, a lower oxidation state than +4 can be obtained. Evidence from X-ray diffraction indicates that the material is NbF_3.[5] Generally, the yield of NbF_3 is small, but can be improved somewhat by increasing the temperature and reaction times. The NbF_4 can be separated from the NbF_3 easily by washing the mixture with acetone or water and quickly decanting the wash liquid. The material left behind is dark blue to black NbF_3. In this case, as with the disproportionation of NbF_4, the "NbF_3" always contained a small amount of oxygen, usually less than 1.5%.

Very crystalline deposits of a material that appeared to be NbF_3 were obtained by the reduction of NbF_5 with silicon or red phosphorus in heavy-wall evacuated quartz tubes at temperatures greater than 325°. However, chemical analysis showed that, identical X-ray pattern notwithstanding, this material was not pure NbF_3. Reduction of NbF_5 carried out in quartz tubes at 300–350° with such materials as silicon, phosphorus,

---

(28) H. G. Schnering and H. Wöhrle, *Angew. Chem.*, **75**, 684 (1963).

(29) L. F. Dahl and D. L. Wampler, *Acta Cryst.*, **15**, 903 (1962).

Table II

Composition of Niobium Oxyfluorides

	Oxidation–reduction agent	% Nb	% F	% O[a]	Composition	a_0	ρ_{obsd}
9-1	P, red	61.3	28.2	10.5	$NbO_{0.99}F_{2.25}$	3.889	
9-2	As	59.7	26.4	13.8	$NbO_{1.34}F_{2.16}$	3.889	
9-7	P, red	63.7	20.6	15.7	$NbO_{1.43}F_{1.58}$	3.915	3.98
9-10	P, red	63.7	18.1	18.2	$NbO_{1.65}F_{1.39}$	3.906	
9-20	P, red	62.3	18.4	19.3	$NbO_{1.80}F_{1.44}$	3.908	4.01
9-27	Si	65.2	15.0	19.8	$NbO_{1.76}F_{1.12}$		4.10
8-73	Si	61.5	23.0	15.5	$NbO_{1.46}F_{1.83}$	3.917	

[a] Nb and F determined chemically, oxygen by difference.

arsenic, and antimony led to formation of a series of oxyfluorides, the oxygen being derived from the walls of the container. Mass spectroscopic analysis identified SiF_4 as one of the products. After a reaction time varying from 2 to 10 days, reduction was complete as evidenced by the absence of unreacted NbF_5 upon cooling the quartz tube. Heavy deposits of large crystals, dark gray to black, 0.1 to 1 mm., had built up along the entire length of the tube. These crystals were perfect cubes, many of them twinned. X-Ray diffraction studies showed these materials to have the ReO_3 type structure identical with that of NbF_3.[5] Chemical analysis of these materials showed the presence of only niobium, fluorine, and oxygen. Apparently oxygen can substitute for fluorine in the crystal to give a wide range of composition from NbO_xF_y to NbO_2F. Schäfer, *et al.*,[6] also reported the existence of a $Nb(O,F)_3$ phase with a ReO_3 structure and believe that NbF_3 completely free of oxygen is apparently not stable. We have observed that in the niobium oxyfluorides the sum of the number of anions per cation varies significantly from 3 in some cases. Tentatively, we interpret these results as indicating the presence of metal-deficient structures. A summary of the composition, density, and cell constant of these materials appears in Table II. The oxyfluoride materials are refractory and very resistant to attack by acids. No noticeable dissolution of the oxyfluoride occurred upon boiling a sample in a solution of concentrated H_2SO_4, HNO_3, and H_2O_2 for a 24-hr. period. The materials can be dissolved in molten alkali hydroxides.

Acknowledgment.—We are indebted to Mr. J. Dolesch for chemical analysis and to Mrs. M. Alley for technical assistance in the X-ray diffraction measurements. Special thanks are due to Dr. C. S. Smith for help in the structure determination and to Mr. C. Nezbeda for carrying out the Faraday magnetic susceptibility measurements.

Contribution from The Chemistry Department,
University of Canterbury, Christchurch, New Zealand

The Crystal and Molecular Structure of Diphosphorus Hexathiodibromide

By FREDERICK W. B. EINSTEIN, BRUCE R. PENFOLD, and QUENTIN T. TAPSELL

Received July 30, 1964

Crystal structure analysis of diphosphorus hexathiodibromide has established that the molecules contain a new type of six-membered ring of composition P_2S_4 in which there are two S–S linkages. The tetrahedral environment of each phosphorus is completed by a bromine atom and a double-bonded sulfur atom attached externally to the ring. There is complete disorder involving the external atoms. Molecules possess a crystallographic twofold symmetry axis normal to the ring and are related by the fourfold inversion axes of the tetragonal space group $P\bar{4}2_1c$. The ring has the *skew boat* conformation on account of the steric preference for large angles of torsion about S–S bonds. Three-dimensional least-squares refinement of parameters led to the mean interatomic distances P—Br = 2.07, P=S = 1.98, P—S = 2.10, and S—S = 2.03 Å.

Introduction

The known thiohalides of phosphorus[1] may be considered to belong to three classes: (I) the thiophosphoryl trihalides PSX_3, where X = F, Cl, or Br; (II) $P_4S_3I_2$, the only thioiodide; and (III) the thiobromides $P_2S_5Br_4$ and $P_2S_6Br_2$. The only molecular structures hitherto reported are for class I by electron diffraction[2] and for class II by X-ray diffraction.[3] The two compounds of class III were characterized in these laboratories by Andrews, Fergusson, and Wilkins,[1] who pointed out that S–S bonds must be present if the coordination of phosphorus with respect to sulfur is limited to four as would be expected. The high probability of the existence of this structural feature, not present in any other known crystalline compound of phosphorus and sulfur, led us to the structure analysis of $P_2S_6Br_2$, the more accessible of the two compounds in suitably crystalline form.

Experimental

Large opaque yellow needle-shaped crystals were prepared under dry carbon dioxide, following the method of Andrews, Fergusson, and Wilkins,[1] and were manipulated in a drybox.

Crystal Data.—$P_2S_6Br_2$, molecular weight 414.2, tetragonal, space group $P\bar{4}2_1c$ from systematic absences of X-ray reflections, $a = b = 9.79$ Å. ($\sigma = 0.01$ Å.), $c = 11.51$ Å. ($\sigma = 0.01$ Å.) ($\lambda = 1.5418$ Å. for Cu Kα radiation), $U = 1104$ Å.^{3}, $D_m = 2.53$

---

[1] See, *e.g.*, J. M. Andrews, J. E. Fergusson, and C. J. Wilkins, *J. Inorg. Nucl. Chem.*, **25**, 829 (1963).

[2] "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

[3] D. A. Wright and B. R. Penfold, *Acta Cryst.*, **12**, 455 (1959).