the values initially reported for $KPuO_2CO_3$. Unit cell dimensions are given in Table I.

A listing of portions of the observed and calculated X-ray powder diffraction patterns for $KNpO_2CO_3$ and $KAmO_2CO_3$ is given in Table II. The corresponding data for $KPuO_2CO_3$ are given in ref. 3.

Table II

		$KNpO_2CO_3$		$KAmO_2CO_3$	
hkl	*I* obsd.	*d* calcd., Å.	*d* obsd., Å.	*d* calcd., Å.	*d* obsd., Å.
002	s	4.99	5.01	4.87	4.87
100	m	4.43	4.44	4.43	4.43
101	vs	4.05	4.06	4.03	4.03
102	s	3.31	3.31	3.28	3.28
103	m	2.66	2.66	2.62	2.62
110	s	2.56	2.56	2.56	2.56
004	m	2.49	2.49	2.44	2.44
112	m	2.28	2.28	2.26	2.26
200	w	2.22	2.22	2.21	2.21
201	s	2.16	2.16	2.16	2.16
104		2.17		2.13	2.13 w
202	m	2.03	2.02	2.02	2.01
203	mw	1.844	1.846	1.829	1.828
105	mw	1.819	1.821	1.783	1.785
114	m	1.786	1.787	1.763	1.764
211		1.653		1.649	1.649
204	ms	1.657	1.653	1.638	...
006		1.662		1.623	1.618
212	w	1.589	1.588	1.582	1.584
105	vw	1.556	1.557	1.524	1.525
213	w	1.496	1.496	1.487	1.488
300	w	1.478	1.480	1.476	1.476 w
205		1.483		1.462	1.463 w

Discussion

As pointed out by Ellinger and Zachariasen,[3] the structure of these complexes consists of $[MO_2CO_3]^-$ layers held together by the K^+ cations. In addition, the MO_2^+ portion is linear and is parallel to the c_0 axis. The anticipated actinide contraction is evidenced by the decrease in the c_0 axis length. A lack of decrease in the a_0 dimension is not surprising since the carbonate oxygens are loosely coordinated to the actinide(V) central atom at 2.55 Å. as opposed to the 1.94 Å. bond length estimated for the Pu–O bond in the PuO_2^+ species.[3] Assuming the change in the c_0 axis length is due to change in the M–O bond length, Np–O would be *ca.* 1.98 Å. and Am–O would be *ca.* 1.92 Å. The observed difference in the c_0 dimension is four times that in the M–O bond distance, since each unit cell contains two MO_2^+ groups or four M–O bonds.

Contribution from the Institute for Atomic Research and
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The Preparation and Reactions of Some Tungsten(II) and Tungsten(IV) Halides[1-3]

By R. E. McCarley and T. M. Brown

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A method for the preparation of the tungsten(IV) halides WCl_4 and WBr_4 by aluminum reduction of WCl_6 and WBr_5, respectively, has been developed. The reactions are carried out in sealed, evacuated tubes under a controlled temperature gradient and afford virtually quantitative yields of the crystalline tetrahalides, which are deposited from the vapor phase. The solids WCl_4, WBr_4, and the corresponding chlorides and bromides of tantalum(IV) and niobium(IV) form an isomorphous series. A convenient synthesis of WCl_2 and WBr_2 in high purity results from the disproportionation of WCl_4 and WBr_4, respectively, at 450 to 500°. It is shown that the reactions of WCl_6 and WBr_5 lead to the dipyridine adducts of the respective tungsten(IV) halides also obtained by direct reaction between the tetrahalides and pyridine.

Introduction

The following methods for the preparation of WCl_4 have been reported: (1) reduction of WCl_6 with hydrogen,[4,5] (2) chlorination of WO_2 with CCl_4 in a sealed tube,[6] and (3) reduction of WCl_6 with red phosphorus.[7] Because each of these methods suffers at least one serious disadvantage (*e.g.*, high pressure reaction for (1) and (2) and difficulty in purification of product for (1) and (3), a more convenient method for the synthesis of the compound was sought.

Although a method for the preparation of WBr_4 by reduction of WBr_5 with tungsten had been previously reported by us,[8] the reaction gave low yields and was very slow. Substitution of aluminum for the tungsten has resulted in a much more rapid reaction and very good yields; the method has been applied to the preparation of WCl_4 with equal success.

Hydrogen reduction[9] of the higher halides has also

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(2) Presented in part before the Division of Inorganic Chemistry, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(3) A portion of a thesis presented by T. M. Brown to Iowa State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(5) W. Blitz and C. Fendius, *ibid.*, **172**, 385 (1928).

(6) A. Michael and A. Murphy, *Am. Chem. J.*, **44**, 365 (1910).

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(8) R. E. McCarley and T. M. Brown, *J. Am. Chem. Soc.*, **84**, 3216 (1962).

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been used for the preparation of WCl_2 and WBr_2; WCl_2 has also been obtained by the disproportionation of WCl_4.[9] The methods described herein for the preparation of WCl_4 and WBr_4 may be readily adapted for the preparation of pure WCl_2 and WBr_2.

Because previous studies[10-12] in this laboratory have shown that the halides of niobium(IV) and (V) and tantalum(IV) and (V) undergo some interesting reactions with pyridine, it was of interest to investigate the corresponding reactions of the tungsten(IV), (V), and (VI) halides with pyridine. Unlike the reaction between tantalum(V) halides and pyridine, where no reduction was obtained, the tungsten(V) and (VI) halides underwent reduction in pyridine to tungsten(IV) derivatives. These reactions are thus similar to the reactions between niobium(V) halides and pyridine. The synthesis and properties of the pure dipyridine adducts of WCl_4 and WBr_4 also are described herein.

Experimental

Materials.—The higher halides WCl_6 and WBr_5 were prepared by direct combination of the elements at elevated temperatures. However, the reaction of tungsten with bromine afforded a mixture containing both WBr_6 and WBr_5. The former was removed by sublimation of the mixture under a working vacuum at 250–300°. At these temperatures the WBr_6 decomposed with evolution of bromine and gave pure WBr_5. Storage and handling of these materials was effected in a drybox under an argon atmosphere, which was maintained at a dew point of *ca.* −75°.

Anal. Calcd. for WCl_6: W, 46.36; Cl, 53.64. Found: W, 46.28; Cl, 53.59. Calcd. for WBr_5: W, 31.51; Br, 68.49. Found: W, 31.34; Br, 68.40.

Tungsten metal powder obtained from General Electric was used in all preparations. The metal was freed of oxygen contamination by heating in a stream of hydrogen at 1000°.

Chlorine was obtained from the Matheson Company in lecture size cylinders. The chlorine was distilled into the apparatus from the cylinder and outgassed on the vacuum line at −196° before beginning a reaction.

Bromine was dried under vacuum over well-outgassed phosphorus(V) oxide. It was then vacuum distilled into a clean, evacuated flask for use in experiments as needed.

Spectro grade pyridine was dried over outgassed molecular sieves and then vacuum distilled onto freshly outgassed calcium hydride.

Preparation of Tungsten(IV) Chloride.—In a typical preparation 20–25 g. of WCl_6 and aluminum foil in an amount calculated to give a 1–2 g. excess of WCl_6 at completion of reaction 1 were placed in a straight 30-mm. o.d. Pyrex tube. This tube was subsequently evacuated, sealed, and placed in a double furnace so that one end (containing the Al) was maintained at 475° and the other end (containing the WCl_6) was maintained at 225°. Approximately 48 hr. was required for the reaction to be completed. During the reaction the product WCl_4 diffused to the cooler end of the tube and condensed as a coarse crystalline deposit. In order to free the product of excess WCl_6 and $AlCl_3$, the end of the tube containing the crystalline deposit was heated to 225° while the opposite end was held at room temperature. The tube was then opened in the drybox and the WCl_4 was removed for analysis or subsequent experiments. Based on the weight of aluminum used a 100% yield of WCl_4 was obtained.

$$3WCl_6 + 2Al = 3WCl_4 + 2AlCl_3 \qquad (1)$$

Anal. Calcd. for WCl_4: W, 56.45; Cl, 43.55. Found: W, 56.45; Cl, 43.10.

Tungsten(IV) Bromide.—This compound was prepared by two methods: (1) reduction of WBr_5 with tungsten metal and (2) reduction of WBr_5 with aluminum metal. In the case of the reduction of WBr_5 with tungsten metal, the starting materials were placed in opposite ends of a Vycor tube along which a uniform temperature gradient was maintained: 630° at the tungsten end and 340° at the WBr_5 end. The reaction was allowed to proceed for approximately 10 days. The WBr_4 deposited near the center of the tube while the excess WBr_5 collected in the cool end. Starting with 20–25 g. of WBr_5, a 10% yield of WBr_4 was obtained; most of the tungsten metal remained unconverted.

Anal. Calcd. for WBr_4: W, 36.52; Br, 63.48. Found: W, 36.36; Br, 63.45.

For the preparation of WBr_4 by the aluminum reduction of WBr_5, the experimental procedure was the same as that given for the preparation of WCl_4. For this reaction, however, the end of the tube containing WBr_5 was maintained at a temperature of 240° to give an appreciable vapor pressure of WBr_5, while the aluminum end was maintained at 475°. In this case WBr_5 was used in 1–2-g. excess of the amount needed for the reaction 2. A black crystalline deposit of WBr_4 was found near the cool end of the reaction tube. Excess WBr_5 and product $AlBr_3$ were removed by sublimation at 240°. Based on the quantity of aluminum used and starting with 20–25 g. of WBr_5, a 60–80% yield of WBr_4 was obtained.

$$3WBr_5 + Al = 3WBr_4 + AlBr_3 \qquad (2)$$

Anal. Found: W, 36.21; Br, 62.77.

Tungsten(II) Chloride and Tungsten(II) Bromide.—Each of these compounds was prepared in a high state of purity by disproportionation of the appropriate tungsten(IV) halide according to reaction 3.

$$3WX_4(s) = WX_2(s) + 2WX_5(g) \qquad (3)$$

The reactions were performed in sealed evacuated Pyrex tubes. The end of the tube containing the tungsten(IV) halide was heated to 450–500° while the opposite end was maintained at room temperature. As the reaction progressed the higher halide product condensed near the cool end of the tube. Finally, in the case of WBr_2, the product was placed in a straight Vycor tube and the sample heated for a few minutes at 600° to remove any additional volatile impurities. The products were light gray and yellow-green, respectively, for WCl_2 and WBr_2.

Anal. Calcd. for WCl_2: W, 72.17; Cl, 27.83. Found: W, 72.11; Cl, 27.67. Calcd. for WBr_2: W, 53.50; Br, 46.50. Found: W, 53.22; Br, 46.43.

X-Ray diffraction data for the two tungsten(II) halides are given in Table I.

Table I

X-Ray Diffraction Data of Tungsten(II) Halides

WCl_2		WBr_2	
d_{obsd},[a] Å.	d_{obsd},[a] Å.	d_{obsd},[a] Å.	d_{obsd},[a] Å.
6.94 vvs	2.05 w	7.31 vvs	2.15 s
5.63 vvs	2.00 vvw	5.91 s	2.09 w
3.47 w	1.92 vvw	3.63 vw	2.05 w
2.88 s	1.78 vw	2.72 s	2.02 w
2.61 s	1.75 vvw	2.64 w	2.00 w
2.52 vvw	1.47 w	2.48 vw	1.89 vvw
2.37 vvw		2.46 vw	1.86 w
2.32 vvw		2.42 vw	1.85 vw
2.20 s		2.30 s	1.82 w
2.09 vvw		2.18 vw	1.54 s

[a] The terms used for intensity are: v, very; w, weak; s, strong.

Analytical.—The composition of the tungsten(IV) and tungsten(II) halides was determined by hydrogen reduction at 650°. Tungsten was converted to the metal and weighed as such,

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(10) R. E. McCarley, B. G. Hughes, J. C. Boatman, and B. A. Torp, in "Reactions of Coordinated Ligands and Homogeneous Catalysis," Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, pp. 243–255.

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(12) R. E. McCarley and J. C. Boatman, *ibid.*, **2**, 547 (1963).

while the halogen was converted to hydrogen halide which was collected in a known amount of standard sodium hydroxide solution. This method gave excellent results, especially for the tungsten(II) halides which were resistant to attack by other methods. The halides of tungsten(V) and (VI) could not be analyzed by this method because they sublimed out of the reaction zone before complete reduction could occur. Hence they were hydrolyzed in NaOH solution and subsequently analyzed gravimetrically for tungsten as WO_3 and volumetrically for halogen.

Reaction of Tungsten(IV) Halides with Pyridine.—Known amounts of tungsten(IV) chloride and bromide were transferred to separate flasks equipped with a stopcock and ball joint for attachment to the vacuum manifold. The flask and contents then were evacuated and weighed, and 60 to 70 ml. of pyridine was subsequently vacuum distilled into the vessel. After the reaction mixture was stirred for several days at room temperature, the solvent pyridine was removed by vacuum distillation and the product dried to constant weight on the vacuum line. (Found: 2.576 g. of WCl_4 gained 1.214 g. of pyridine by weight, pyridine/WCl_4 1.94; 1.735 g. of WBr_4 gained 0.584 g. of pyridine by weight, pyridine/WBr_4 2.10). The products were obtained as light tan and green, powdery solids, respectively, for WCl_4 and WBr_4.

Anal. Calcd. for $WCl_4(py)_2$: W, 38.00; Cl, 29.31; py, 32.69. Found: W, 37.63; Cl, 29.13; py, 32.43. Calcd. for $WBr_4(py)_2$: W, 27.79; Br, 48.31; py, 23.90. Found: W, 27.52, Br, 47.83; py, 23.82.

X-Ray diffraction data for the two tungsten(IV) halide–pyridine complexes are given in Table II.

TABLE II

X-RAY POWDER DIFFRACTION DATA OF PYRIDINE COMPLEXES OF THE TUNGSTEN(IV) HALIDES

$WCl_4(py)_2$		$WBr_4(py)_2$	
d_{obsd},[a] Å.	d_{obsd},[a] Å.	d_{obsd},[a] Å.	d_{obsd},[a] Å.
6.43 vvs	2.42 vw	6.59 vvs	2.47 w
6.10 vvs	2.33 s	6.29 vs	2.40 vs
5.14 vs	2.29 vs	5.27 vs	2.36 vvvw
4.13 w	2.15 vvw	4.20 w	2.20 vvw
3.91 vw	2.11 vvw	4.03 vw	2.16 vvw
3.82 vs	2.09 vvw	3.84 vvs	2.11 vw
3.69 vw		3.78 vw	2.03 s
3.64 vw		3.69 vw	2.01 s
3.26 vvw		3.20 vs	1.93 w
3.20 vw		2.84 vw	1.89 s
3.12 vs		2.70 vvw	1.84 vvw
2.79 vw		2.62 vvs	1.80 s
2.67 vvw		2.52 s	1.75 s
2.55 s			1.68 w
2.49 w			

[a] The terms used for intensity are: v, very; w, weak; s, strong.

Magnetic Susceptibilities.—Magnetic susceptibilities were obtained from measurements on a Faraday balance. Powdered samples were contained in evacuated cylindrical Pyrex bulbs 1 cm. long and 0.5 cm. in diameter. Corrections for the diamagnetism of the Pyrex bulbs were applied in all cases.

X-Ray Data.—All X-ray data were obtained using a Debye–Scherrer 114.59-mm. powder camera. The samples were powdered, passed through a 200-mesh sieve, and packed in 0.2-mm. glass capillaries under an inert atmosphere. The samples were then exposed to nickel-filtered Cu Kα radiation for 16–20 hr. depending on the sample.

Analytical.—Tungsten was determined as WO_3 by treating the sample with hot, concentrated HNO_3 and digesting the solution until conversion to WO_3 was complete.

The method of Jonassen, Cantor, and Tarsey[13] was used to determine the chloride content. In this procedure, a known amount of sample was heated in concentrated sulfuric acid for about 3 hr. The HCl evolved during decomposition was transported in a stream of nitrogen to a 10% NaOH solution. A saturated aqueous solution of $K_2Cr_2O_7$ then was added to the sulfuric acid solution and heating was continued for several more hours to ensure complete removal of the chloride. The chloride was determined by the usual Volhard titration. In the case of samples containing bromide, the procedure was essentially the same as for the chloride except for the addition of sodium formate to the NaOH solution.[14] Any bromine resulting from the oxidizing action of the sulfuric acid was reduced to bromide by this solution.

In the analysis of pyridine, samples were digested with concentrated H_2SO_4 which resulted in complete solution of the samples along with the formation of pyridinium sulfate. The solutions were fumed almost to dryness. Concentrated NaOH was added and the pyridine was distilled[12] into glacial acetic acid and titrated potentiometrically with perchloric acid in acetic acid.

Reaction of Tungsten(V) and Tungsten(VI) Halides with Pyridine.—In order to check the possible reduction of WCl_6 and WBr_5 with pyridine, as reported previously for the niobium(V) halides,[10] reactions between liquid pyridine and the tungsten halides WCl_6 and WBr_5 were performed according to the procedure described above for the reaction between the tetrahalides and pyridine. After approximately 1 week at room temperature excess pyridine was removed by distillation and the product dried on a vacuum line. From weight gain data, mole ratios of pyridine/WCl_6 varying from 4.64 to 4.69 and pyridine/WBr_5 varying from 3.25 to 3.35 were indicated. For example, 2.3395 g. of WCl_6 gave 4.5005 g. of product, pyridine/WCl_6 of 4.64; 2.5350 g. of WBr_5 gave 3.6863 g. of product, pyridine/WBr_5 of 3.35. The crude products were washed with acetonitrile,[10] which removed all reaction products except the pyridine complexes, $WCl_4(py)_2$ and $WBr_4(py)_2$.

Anal. Calcd. for $WCl_4(py)_2$: W, 38.00; Cl, 29.31; py, 32.69. Found: W, 37.56; Cl, 28.85; py, 32.59. Calcd. for $WBr_4(py)_2$: W, 27.79; Br, 48.31; py, 23.90. Found: W, 27.40; Br, 47.51; py, 23.60.

The presence of 1-(4-pyridyl)pyridinium ion in the reaction mixture was identified from its chemical behavior and ultraviolet spectrum in aqueous sodium hydroxide solution.[10] The presence of pyridinium bromide in the bromide reaction mixture was verified from X-ray diffraction patterns. The X-ray data obtained on the tungsten(VI) chloride and pyridine reaction product were very poor and a positive identification of pyridinium chloride could not be made.

Results and Discussion

Tungsten(IV) Halides.—The solids WCl_4 and WBr_4 were produced as thin black needles and were found to be isomorphous with the corresponding tetrahalides of niobium[11] and tantalum.[12] X-Ray diffraction patterns of the solids were indexed on an orthorhombic unit cell of dimensions $a = 8.07$, $b = 8.89$, $c = 6.85$ Å. for WCl_4 and $a = 8.49$, $b = 9.29$, $c = 7.25$ Å. for WBr_4. A comparison of the observed and calculated d-spacings is shown in Table III.

Magnetic susceptibility data of the tetrahalides of tungsten showed the solids to be diamagnetic. The susceptibilities (e.m.u./mole) were -58×10^{-6} at 30° and -75×10^{-6} at 24° for the tetrachloride and tetrabromide, respectively. Diamagnetism has also been found for the niobium(IV) and tantalum(IV) halides.[11,12] Although a metal ion having a d^2 electron configuration may be diamagnetic as a result of low ligand field symmetry, diamagnetism also may result

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(13) H. B. Jonassen, S. Cantor, and A. R. Tarsey, *J. Am. Chem. Soc.*, **78**, 271 (1956).

(14) L. Spitzer, *Ind. Eng. Chem., Anal. Ed.*, **8**, 465 (1936).

TABLE III

OBSERVED AND CALCULATED d-SPACINGS FOR WCl_4 AND WBr_4[a]

hkl	d_{calcd}, Å.	d_{obsd},[b] Å.	d_{calcd}, Å.	d_{obsd},[b] Å.
110	5.97	5.97 vvs	6.27	6.32 vvs
020	4.45	4.45 vvs	4.65	4.69 vs
200	4.03	4.02 vvs	4.24	4.24 vs
211	3.24	3.23 vs	3.41	3.42 vvw
030	...	...	3.09	3.08 w
112	2.99	3.03 vvw	3.14	2.99 vw
220	2.97		3.13	
...	...	2.85 vw	...	...
130	2.78	2.77 w	2.91	2.89 vw
221	2.74		2.88	
202	2.61	2.62 vs	2.76	2.75 vvs
310	2.58	2.58 s	2.70	2.68 s
131	2.58		2.70	
301	2.51	2.54 w	...	...
040	2.22	2.23 s	2.32	2.35 vs
013	2.21		2.34	
032	2.24		2.35	
321	2.18	2.18 vvw	2.29	2.29 vvw
140	2.14	2.13 vw	2.24	2.25 vw
113	2.13		2.25	
041	2.11	2.10 w	2.21	2.21 w
400	2.02	2.02 s	2.13	2.13 s
023	2.03		2.14	
203	1.99	2.00 w	...	...
330	1.99		...	...
410	1.97	1.98 vvw	...	...
123	1.97		...	...
213	1.94	1.93 vvw	2.05	2.05 vvw
401	1.94		2.04	
240	1.95		2.04	
322	...	...	2.01	1.99 vw
331	...	...	2.01	
042	1.86	1.86 vvw	1.96	1.97 vw
241	1.87		1.96	
420	1.84	1.84 vvw	1.93	1.93 vvw
033	1.81	1.81 vvw	1.90	1.90 vvw
142	1.82		1.90	
223	1.81		1.90	
303	1.74	1.76 vvw	1.84	1.85 vvw
050	1.78		1.86	
133	1.77		1.86	

[a] Complete data up to $d = 1.54$ are available from the authors. [b] The terms used for intensity are: v, very; w, weak; and s, strong.

from direct metal–metal bonding. The latter possibility seems most probable because of the isomorphism of the tungsten(IV) halides with the corresponding halides of niobium(IV) and tantalum(IV). In the case of NbI_4 a prominent feature of the structure[15] is the pairing of adjacent niobium atoms by metal–metal bond formation; it is, of course, diamagnetic.

Tetrahalodi(pyridine)tungsten(IV) Complexes.—By further analogy with the compounds of niobium(IV) and tantalum(IV), it was anticipated that WCl_4 and WBr_4 should form complexes with pyridine of the formula $WCl_4(py)_2$ and $WBr_4(py)_2$, respectively. This was found to be the case and a light tan chloride adduct and green bromide adduct were obtained. Recently, Kennedy and Peacock[16] reported the preparation of these two adducts using another method. These workers obtained crystalline compounds by allowing pyridine to react with the corresponding hexahalotungstate(IV) salts. Reflectance spectra of the solids prepared by our method agreed with those reported by these workers. However, in addition to the bands reported by Kennedy and Peacock, we found an additional band, of lower intensity than the others, occurring at 4880 and 4950 Å. for the chloride and bromide adducts, respectively. Additional work on the spectra and magnetic susceptibility of these compounds has been done and will be reported at a later date.

The reactions of WCl_6 and WBr_5 with pyridine are interesting since they provide alternative paths to the preparation of the pyridine adducts of WCl_4 and WBr_4. The reduction of tungsten in this case is understandable since reduction of the tungsten halides is generally easier than reduction of niobium(V) halides, for which reduction in pyridine had been observed previously.[10] The greater tendency toward reduction exhibited by the tungsten halides is also reflected in the fact that the oxidation state of tungsten was reduced by two units in the case of WCl_6, whereas that of niobium was reduced by only one unit. Thus it was expected that WCl_5 would also undergo reduction in pyridine. From the weight gain data and the reaction products, eq. 4 and 5 are proposed as probable reactions by which the reduction of WCl_6 and WBr_5 occurs; in these equations $(py)_2{}^+X^-$ indicates the halide salts of the 1-(4-pyridyl)pyridinium ion. Equations 4 and 5 require over-all mole ratios of pyridine/WCl_6 and pyridine/WBr_5 of 5 and 3.5, respectively. These values are in fair agreement with the experimental values, where mole ratios of pyridine/WCl_6 varying from 4.64 to 4.69 and pyridine/WBr_5 varying from 3.25 to 3.35 were obtained.

$$WCl_6 + 5py = WCl_4(py)_2 + (py)_2{}^+Cl^- + pyH^+Cl^- \quad (4)$$

$$2WBr_5 + 7py = 2WBr_4(py)_2 + (py)_2{}^+Br^- + pyH^+Br^- \quad (5)$$

The reaction between tungsten(VI) chloride and pyridine in carbon tetrachloride as an inert solvent was also investigated. Prasad and Krishnaiah[17] reported that pyridine reacted with the hexachloride in carbon tetrachloride to give a dark brown pyridine adduct of the hexachloride, $WCl_6(py)_2$. Attempts to duplicate their work were not successful and some reduction was always observed. Cooper and Wardlow[18] obtained a green insoluble $(pyH)_2WOCl_5 \cdot H_2O$ complex in carbon tetrachloride even when water was excluded as much as possible. The formation of a green product in carbon tetrachloride was observed, but attempts to separate the resulting product from the oxidation products were unsuccessful. In addition, it was found that tungsten(IV) was also present in the reaction mixture. Extraction with acetonitrile separated the insoluble tungsten(IV) complex from the green material and other soluble products. Equivalent weight determinations on the soluble fraction after extraction with acetonitrile indicated the presence of a tungsten-

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(16) C. D. Kennedy and R. D. Peacock, *J. Chem. Soc.*, 3392 (1963).

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(V) compound. Additional work designed to establish the composition of the tungsten(V) derivative was unsuccessful because of the difficulty of separation from the associated oxidation products. It is interesting to note, however, that the reduction was slowed in carbon tetrachloride and provided some evidence for one of the intermediates in the reduction of the hexachloride. The available evidence thus indicates that the reaction of WCl_6 with pyridine proceeds stepwise: W(VI) → W(V) → W(IV), or that W(V) is formed after initial reduction to W(IV) by the reaction W(IV) + W(VI) = 2W(V). Evidence from the corresponding reactions of the niobium(V) halides[10] indicated that pyridine behaved as a two-electron reducing agent, hence the latter path seems more likely.[19]

(19) Note Added in Proof.—Although the X-ray powder pattern data[11,12] for the halides MX_4 (M = Nb, Ta, W; X = Cl, Br) have been indexed on the basis of an orthorhombic unit cell, more recent evidence from single crystal work indicates the true unit cell is monoclinic. According to a recent note [H. G. Schnering and H. Wöhrle, *Angew. Chem.*, **75**, 684 (1963)], it was found from single crystal data that $NbCl_4$ is monoclinic with a = 12.32, b = 6.82, c = 8.21 Å., and β = 134°.

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Structural Studies of Zirconium Trihalides and Hafnium Triiodide[1]

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Structural studies of $ZrCl_3$, $ZrBr_3$, ZrI_3, and HfI_3 have been carried out from X-ray powder diffraction patterns. The isomorphous compounds contain two formula units in a hexagonal unit cell and have the following dimensions in Å. (all with e.s.d. ±0.01 Å.) and densities in g./cc. at 25°: $ZrCl_3$, $a = 6.36$, $c = 6.14$, $d_{\text{exptl}} = 2.95$, $d_{\text{calcd}} = 3.05$; $ZrBr_3$, $a = 6.75$, $c = 6.31_5$, $d_{\text{exptl}} = 4.52$, $d_{\text{calcd}} = 4.42$; ZrI_3, $a = 7.25$, $c = 6.64$, $d_{\text{exptl}} = 5.13$, $d_{\text{calcd}} = 5.20$; HfI_3, $a = 7.22_5$, $c = 6.59$, $d_{\text{exptl}} = 6.17$, $d_{\text{calcd}} = 6.25$. Systematic absences of l odd for $h0l$ reflections indicate as probable space groups, D^3_{6h}-$P6_3/mcm$, C^3_{6v}-$P6_3cm$, and D^2_{3h}-$P\bar{6}c2$. From space group assignment (D^3_{6h}-$P6_3/mcm$), intensity calculations, and stereochemical considerations (with the assumption of no order–disorder phenomenon) a structure based on a distorted hexagonal close-packing of the halogen atoms can be proposed which consists of infinite chains along the c axis formed by MX_6 octahedra joined at opposite faces with the metal atoms regularly spaced midway between the halogen atoms; the resulting metal–metal distance is equal to one-half the c lattice constant. Evidence is presented to show that previous powder work (made on relatively impure samples) by Holze[3] including another space group assignment (D^3_{3h}-$P\bar{6}2m$) and a formulated structure of linear chains of $(Zr_2X_6)_n$ units is not substantiated by our powder data. A qualitative MO theory of bonding is proposed from which direct metal–metal interactions can be postulated for a chain configuration.

Introduction

Preliminary X-ray powder diffraction studies of zirconium and hafnium trihalides were carried out first by Leddy[4] and later more thoroughly by Holze[3] on the zirconium trihalides alone. Holze[3] concluded that the zirconium trihalides are isostructural with TiI_3[3,5] and the β-form (designated by Holze[3] as the N-form) of $TiBr_3$ and $TiCl_3$.[3,6] On the basis of indexed powder lines obtained from samples highly contaminated with metal, Holze[3] assigned a space group (D^3_{3h}-$P\bar{6}2m$) and carried out a limited structural analysis which indicated that these solid zirconium trihalides consist of linear chains of $(Zr_2X_6)_n$ units (X = Cl, Br, I) in a hexagonal close-packed lattice of halogen atoms.[7]

The present investigation was virtually completed before Holze's Ph.D. thesis[3] was made available to us. This paper presents evidence that Holze's space group assignment and proposed structure for the zirconium trihalides are not substantiated by our powder patterns of these compounds. X-Ray powder diffraction data for HfI_3 which show this compound to be isomorphous with the zirconium trihalides are presented for the first time, and experimental densities and lattice constants are reported for the four compounds.

Several synthetic investigations of these compounds recently have been published which also are pertinent to this work. The preparation of pure, anhydrous zirconium trihalides by reduction of the corresponding zirconium tetrahalides with hydrogen under a glow discharge was described by Newnham and Watts,[8] but no characterization of the resulting products by X-ray analysis was given. The synthesis of ZrI_3 by the reduction of ZrI_4 with Al was carried out by Watt and Baker,[9] who state that their X-ray powder data attributable to only ZrI_3 are in good agreement with the unpublished data (presented here) obtained by Larsen and Chiang.[10] The preparation of pure $ZrBr_3$ from the reduction of $ZrBr_4$ with Zr metal was

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(2) Fellow of the Alfred P. Sloan Foundation.

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