J. Chem. Soc. (A), 1968

Preparation, Crystallographic Properties, and Infrared Spectra of Quadrivalent Oxyhalides of Thorium, Protactinium, Uranium, and Neptunium

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Actinide(IV) oxydihalides of the type MOX₂ (M = Th, Pa, U, and Np; X = CI, Br, and I) have been prepared by reaction of the appropriate tetrahalide with antimony sesquioxide, Sb₂O₃, at 400° in a vacuum. Unit cell parameters are reported for the isostructural series of oxydichlorides which possess orthorhombic symmetry, space-group Pbam. Infrared spectra have been recorded for all the compounds and the results are compared with previous assignments for UOCI2. Metal-oxygen vibrations occur in the region 600-225 cm.-1.

THORIUM(IV) and uranium(IV) oxydihalides, MOX₂ (M = Th and U; X = Cl and Br), and thorium oxydiiodide have previously been prepared, for example, by interaction of the appropriate dioxide and tetrahalide 1-4 or, less satisfactorily, by thermal decomposition ⁵ of the hydrated tetrahalides. We recently reported ⁶ the preparation of protactinium(IV) oxydichloride and oxydibromide by reaction of antimony sesquioxide with the tetrahalides

$$3PaX_4 + Sb_2O_3 \longrightarrow 3PaOX_2 + 2SbX_3$$

Since the infrared spectra of these protactinium(IV) oxyhalides were inconsistent with the assignments of Selbin and Schober 7 for UOCl₂, we have studied the preparation of other quadrivalent actinide oxydihalides using both the antimony sesquioxide-metal tetrahalide and metal dioxide-metal tetrahalide methods and have recorded infrared spectra for a series of oxydichlorides, oxydibromides, and oxydi-iodides. The preparation and properties of neptunium(IV) oxydichloride and oxydibromide were of particular interest since the former had previously been observed 8 only in microgram amounts as a residue from the sublimation of neptunium tetrachloride and no preparative details were available⁹ for NpOBr₂. In addition, unit-cell parameters are reported for the isostructural series of oxydichlorides $MOCl_2$ (M = Th—Np inclusive).

All the known actinide tetrachlorides and tetrabromides MX_4 (M = Th-Np inclusive; X = Cl and Br), and thorium tetraiodide, react with antimony sesquioxide at about 150° in a vacuum. The antimony trihalides so produced sublime out of the reaction zone at this temperature but in order to obtain reasonably crystalline oxyhalides it is necessary to heat the product for several hours at 450° in vacuo. Neptunium(IV) oxydichloride was also obtained during attempts to prepare neptunium pentachloride or neptunium(v) oxychlorides by reaction of neptunium(v) hydroxide with thionyl chloride below 200° in an apparatus similar to that

- C. A. Kraus, U.S. Reports CC-342, 1942 and CC-1717, 1944.
 N. W. Gregory, U.S. Report TID-5290, 1958, 498.
 D. E. Scaife, A. G. Turnbull, and A. W. Wylie, *J. Chem. Soc.*,

- 1965, 1432. ⁴ M. V. Smirnov and L. E. Ivanovskii, Zhur. neorg. Khim., 1956, 1, 1843.
 - E. Chauvenet, Ann. Chim. Phys., 1911, 23, 425.
 - ⁶ D. Brown and P. J. Jones, J. Chem. Soc. (A), 1967, 719.

described ¹⁰ for the preparation of protactinium pentachloride. However, this reaction is less satisfactory for the preparation of NpOCl_2 because at higher temperatures further chlorination occurs and neptunium tetrachloride is the major product. The quadrivalent oxydichlorides and oxydibromides form two isostructural series of compounds; the partial X-ray powder diffraction pattern for ThOCl₂ is given in Table 1 which lists observed and calculated values of $\sin^2 \theta$ and visually estimated intensities. Following the recent determination¹¹ of the structure of PaOCl₂ our X-ray powder diffraction results have been interpreted on the basis of the reported orthorhombic unit cell, space-group Pbam, and the resulting cell parameters are listed in Table 2. The effect of the actinide contraction is illustrated by the decreasing cell parameters with increasing atomic number of the metal atoms. The partial X-ray powder diffraction pattern of NpOBr, (Table 3) can be compared with data⁶ for PaOBr₂. The oxydibromides possess low symmetry and the results have not been interpreted.

Although the reaction between a particular metal dioxide and the corresponding tetrahalide constitutes an excellent preparative method for the quadrivalent oxydihalides the antimony sesquioxide-metal tetrahalide method described here provides an attractive alternative. In particular it obviates the necessity of preparing ' reactive ' dioxide samples and this is of particular importance in the case of protactinium because the only satisfactory preparation of PaO₂ presently available consists of hydrogen reduction of the pentoxide at 1600°. Not unnaturally, the dioxide so obtained is not sufficiently reactive to yield pure oxydihalides.⁶

Few investigations of the infrared spectra of quadrivalent actinide oxyhalides have been reported. Scaife et $al.^3$ state that no band is observed in the spectrum of ThOI₂ above 600 cm.⁻¹ whilst Prigent ¹² has reported two bands, 500s,b and 546sh. cm.⁻¹ for UOBr₂. Selbin and Schober ⁷ have reported a detailed study of the spectra of various hydrated uranium(IV) hydroxychlorides such as

- ¹⁰ D. Brown and P. J. Jones, J. Chem. Soc. (A), 1966, 874.
- ¹¹ G. Smith, personal communication.
- ¹² J. Prigent, Ann. Chim., 1960, 5, 65.

[†] Present address: Department of Chemistry, Manchester University, Manchester 13.

⁷ J. Selbin and M. Schober, J. Inorg. Nuclear Chem., 1966, 28,

^{817.} ⁸ S. Fried and N. Davidson, J. Amer. Chem. Soc., 1948, 70,

⁹ W. H. Zachariasen, in 'The Transuranium Elements,' National Nuclear Energy Series IV-14B, p. 1473, ed. G. T. Seaborg, J. J. Katz, and W. H. Manning, McGraw-Hill, New York, 1949.

 $U(OH)Cl_3, xH_2O$ (x = 1.5 and 3.0) and of samples of composition $UO_{1.15}Cl_{2.1}$, the last obtained by thermal decomposition of the hydrates. The last compound,

TABLE 1

Partial X-ray powder diffraction results for thorium oxydichloride

$\sin^2 \theta$	$\sin^2 \theta$			$\sin^2 \theta$	$\sin^2 \theta$		
(obs)	(calc.)	h,k,l	I(est.)	(obs.)	(calc.)	h,k,l	I(est.)
0.0072	0.0073	0,2,0	w+	0.1107	(0·1111	3,7,0	
0.0097	0.0097	1,2,0	s	0.1107	10.1109	2, 6, 1	w —
0.0100	0.0099	2,0,0	s	0.1139	0.1138	5, 3, 1	vw-
0.0172	0.0172	2,2,0	w	0.1168	0.1161	0,8,0	vw-
0.0188	0.0188	1,3,0	w +	0.1187	0.1185	1,8,0	w
0.0262	0.0262	2,3,0	w	0.1204	0.1206	4,5,1	w —
0.0288	0.0290	0,4,0	w+	0.1939	∫0.1232	3, 6, 1	w
0.0357	0.0357	0,0,1	w+	0 1252	0.1230	7,1,0	
0.0387	0.0386	3,3,0	w+	0.1265	{0.1265	6,1,1	vw-
0.0390	0.0389	2,4,0	w	0 1200	0.1265	5,4,1	• ••
0.0397	0.0396	4,0,0	vw-	0.1320	0.1320	6,2,1	vw-
0.0431	0.0430	0,2,1	w	0.1345	<i>{</i> 0·1344	6,5,0	vw-
0.0455	0.0455	1,2,1	w	0 1010	0.1344	2,7,1	
0.0468	0.0458	2,0,1	w	0.1402	0.1405	4,6,1	w+
0.0474	{0.0469	4,2,0	S	0.1427	$\{0.1428$	5,5,1	m
0 0 1 1 1	0.0474	2, 1, 1	5	01120	(0.1428)	0,0,2	
0.0527	0.0528	2, 2, 1	vw-		0.1536	6,4,1	
0.0545	0.0545	1, 3, 1	W	0.1538	$\{0.1542$	6,6,0	w-
0.0553	0.0553	2,5,0	$\mathbf{w}+$		(0.1542)	1,8,1	
0.0596	0.0598	3, 1, 1	w	0.1565	0.1568	2,9,0	w-
0.0645	0.0648	0, 4, 1	m	0.1583	$\{0.1583$	8,0,0	w —
	0.0676	3,5,0		0 1000	(0.1587)	7,1,1	
0.0673	$\{0.0672$	1, 4, 1	m	0.1616	<i>{</i> 0·1615	1,3,2	w
	0.0678	1,6,0		0 1010	(0.1616)	2,8,1	
0.0691	∫0.0685	4,4,0	w	0.1643	$\{0.1641$	7,2,1	w —
	(0.0690)	5,2,0	••	0 2020	(0.1641)	4,7,1	
0.0746	0.0746	2, 4, 1	m	0.1690	10.1690	2,3,2	w
0.0770	0.0771	4,1,1	m	0 2000	10.1691	3,9,0	
0.0780	0.0781	5,3,0	w	0.1732	0.1732	7,3,1	w
0.0828	0.0825	4, 2, 1	w+		0.1813	3,3,2	
0.0838	0.0836	1,5,1	w-	0.1813	$\{0.1813$	0,10,0	w +
0.0848	0.0849	4,5,0	w+		(0.1816)	2,4,2	
0.0876	10.0871	3,4,1	w	0.1901	0.1895	4,2,2	w+
	(0.0876	3,6,0		0 1001	0.1005	6,6,1	•
0.0890	0.0890	6,0,0	w	0.1921	0.1925	2,9,1	w
0.0908	10.0908	6,1,0	w	0.1960	0.1957	8,1,1	w-
	10.0908	5,4,0		0.1987	0.1986	4,3,2	w
0.0970	0.0968	6,2,0	w+	0.0100	0.2102	8,3,1	
0.0989	∫0.0994	5,1,1	w+	0.2106	$\frac{1}{10000000000000000000000000000000000$	3,5,2	w-
0 1011	10.0988	2,7,0		0 0111	(0.2105	1,6,2	
0.1011	0.1010	0,6,1	w+	0.2111	0.2113	4,4,Z	w-
0.1034	10.1033	3,5,1	w+	0.2193	0.2194	1,10,1	
	(0.1035	1,6,1		0.2224	0.2221	4,9,1	w —
0 1040	0.1043	4,4,1		0.0004	0.2229	8,4,1	
0.1046	10.1048	4,0,0	w+	0.2304	0.2302	3,0,2 e 1 e	vw
	10.1048	5 Z L		0.2329	0.2335	$0 \mid \mathbf{Z}$	W

s, Strong; m, medium; w, weak.

TABLE 2

Crystallographic properties * of the actinide oxydichlorides

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	Lattice parameters (Å)		
	a_0	b_0	c _o
ThOCl,	15.494	18.095	4.078
PaOCl,	15.332	17.903	4.012
UOCI,	15.255	17.828	3.992
NpOČl,	15.209	17.670	3.948
Standard deviations	± 0.008	± 0.008	± 0.002
* All possess orthorhombic sy	ymmetry,	space-grou	up Pbam

which contained traces of residual OH⁻ and H_2O , gave medium-intensity bands at 736 and 719 cm.⁻¹ (assigned to O-U-O modes) and strong bands at 555 and 515 cm.⁻¹ which were assigned to U-O stretching vibrations.

Bands in similar positions to the last two were also recorded in the spectra of the various hydrated hydroxytrichlorides and assigned $\nu(U-O)_{OH}$. Although it is not clear from their discussion whether the 555 and 515 cm.⁻¹ bands for $UO_{1\cdot15}Cl_{2\cdot1}$ are also considered to be $(U-O)_{OH}$ vibrations Selbin and Schober state that a sample of $UOCl_2$ prepared by heating together uranium tetrachloride and dioxide at 700° gave a strong band at 730 cm.⁻¹.

Our results show that the infrared spectra of anhydrous $UOCl_2$ and other actinide(IV) oxydihalides, including $ThOF_2$,¹³ exhibit no absorption band in the region of 730 cm.⁻¹. In fact there is no band above 600 cm.⁻¹ in the spectra of $UOCl_2$ and $NpOCl_2$ prepared either by the antimony sesquioxide method or by interaction of the appropriate tetrachlorides and dioxides. The spectra of the oxydichlorides and oxydibromides of thorium to neptunium inclusive are very similar between 600 and 225 cm.⁻¹, the only differences being the appearance of

TABLE 3

Partial X-ray powder diffraction results for neptunium oxydibromide

$\sin^2 \theta$ (obs.)	I(est.)	$\sin^2 \theta$ (obs.)	I(est.)
0.0094	s+	0.0858	m
0.0178	w	0.0910	m
0.0247	w	0.0930	m
0.0273	w	0.0971	w
0.0366	s	0.0985	w +
0.0443	w+	0.1010	w
0.0462	w	0.1025	w+
0.0482	m+	0.1049	w
0.0521	w	0.1116	w+
0.0546	w+	0.1172	w
0.0600	w	0.1274	w —
0.0614	w —	0.1307	w
0.0642	w	0.1361	w
0.0665	m+	0.1421	w
0.0737	m+-	0.1482	s
0.0762	m +	0.1572	w
0.0802	m+	0.1675	w
0.0813	m +		

two weak bands in the spectra of certain of the oxydichlorides and a shift of band positions to longer wavelengths with increasing atomic number of both actinide element and halogen (Table 4). We have tentatively assigned the two weak bands around 290 and 280 cm.⁻¹ to metal-chlorine stretching vibrations; the strong, broad band which is common to all the oxydichloride spectra is centred around 300 cm.⁻¹ for UOCl₂ and this may account for the absence of the two weak bands from the spectrum of this compound. Certain of the spectra are illustrated in the Figure. In view of the close similarity in the positions of the remaining bands in the spectra of the oxydichlorides and oxydibromides we have assigned all of these to metal-oxygen vibrations. The large difference in the position of M-Cl and M-Br vibrational frequencies (ca. 260 and 180 cm.⁻¹, respectively) of the quadrivalent actinide hexahalogenocomplexes ¹⁴ suggests that it is unlikely that any of the bands we have observed, apart from, possibly, the two

- ¹³ D. Brown and J. F. Easey, to be published.
- ¹⁴ D. Brown and P. J. Jones, J. Chem. Soc. (A), 1967, 243.

weak ones discussed above, can be associated with metal-halogen vibrations. In addition, metal-iodide vibrations are not likely to be observed above 225 cm.⁻¹ and therefore all four bands in the spectra of ThOI, and PaOI₂ are also assigned to metal-oxygen vibrational modes.

The spectra show that actinide compounds of the type MOX₂ do not contain discrete MO²⁺ groups. Protactinium-oxygen stretching vibrations are also observed below 600 cm.⁻¹ for the quinquevalent oxychlorides,¹⁰ oxybromides,^{15,16} and oxyiodides,¹⁶ and recent structure



Infrared spectra of, from top to bottom, ThOCl₂, ThOBr₂, and PaOI₂

determinations have shown that both PaOBr₃¹⁷ and PaOCl₂¹¹ possess extensively oxygen-bridged structures with certain oxygen atoms co-ordinated to three or four protactinium atoms. Structural data are not available for actinide(IV) oxydibromides but the above infrared results suggest that they also possess oxygen-bridged, polymeric structures.

It is difficult to reconcile the observations of Selbin and Schober,⁷ namely that anhydrous UOCl₂ prepared from

 ¹⁵ D. Brown and P. J. Jones, J. Chem. Soc. (A), 1966, 262.
 ¹⁶ D. Brown, J. F. Easey, and P. J. Jones, J. Chem. Soc. (A), 1967, 1698.

D. Brown, T. J. Petcher, and A. J. Smith, *Nature*, in press.
 H. W. Dunn, U.S. Report ORNL-2092, 1956.
 S. A. Shchukarev, I. V. Vasil'kova, N. S. Martynova, and

Yu. G. Mal'tsev, Zhur. neorg. Khim., 1958, 3, 2647.

the tetrachloride and dioxide possesses a strong band at 730 cm.⁻¹, with our results for quadrivalent actinide oxydihalides. Unfortunately they do not report crystallographic data for their compound nor do they state whether the bands around 500 cm.⁻¹ occurred in the

TABLE 4

Metal-oxygen and metal-halogen stretching vibrations in the infrared spectra of quadrivalent actinide oxydihalides

Compound	Colour	$\nu_{\rm M-O}~({\rm cm.^{-1}})$	ν_{M-X} (cm. ⁻¹)
ThOCl ₂	White	571sh, 540s, 481s, 344s,b,	298w, 282w
PaOCl ₂	Yellow-green	555sh, 523s, 471s, 327s, 256sh, 243m	290w, 278w
UOCl ₂	Green	555sh, 521s, 455m, 300s, 259m, 242m	b,
NpOCl ₂	Light brown	555s, 529s, 460m, 335s,b, 255m, 240m	306w
ThOBr_2	White	543s, 529s, 495s, 463s, 223s b 256m 242yuu	
$PaOBr_2$	Orange	546sh, 518s, 495s, 446s, 319s b 259m 240yw	
UOBr ₂	Pale green	538sh, 505s, 429s, 294s,b, 253w	
$NpOBr_2$	Orange	540sh, 500s, 424s,b, 315s b 258w	
${ m ThOI}_2$ ${ m PaOI}_2$	White Burgundy	500m, 444m, 325s,b 459m, 434m, 303s,b	

spectrum of this compound. Our preparations of UOCl, all gave identical X-ray powder patterns and these were the same as that recorded by Dunn.¹⁸ Possibly their uranium dioxide contained U_3O_8 so that some uranium(v) oxytrichloride, UOCl₃, was obtained. This is usually obtained by heating together uranyl chloride and uranium tetrachloride ¹⁹ and we have in fact observed a strong band around 730 cm.⁻¹ in the spectrum of an impure sample of UOCl₃ so prepared. Further, all the compounds discussed here were perfectly anhydrous, no band being observed around 3400 cm.⁻¹ (OH stretching vibration) or 1600 cm.⁻¹ (H₂O wagging mode) so the strong bands in the 500 cm. $^{-1}$ region of the spectra are certainly not associated with (U-O)_{OH} modes.

EXPERIMENTAL

Work with protactinium and neptunium was carried out in glove-boxes on account of the radioactive hazards associated with weighable amounts of protactinium-231 and neptunium-237, the isotopes used. Following preparation all compounds were handled in an argon atmosphere box (oxygen content < 50 p.p.m.; water content < 60 p.p.m.) in which samples were prepared for X-ray powder diffraction, infrared studies, and analysis.

Materials .--- Tetrachlorides 6, 20, 21 (thorium to neptunium inclusive), tetrabromides 6,22 (thorium to uranium inclusive), and thorium tetraiodide ²³ were prepared by published methods. Neptunium tetrabromide was prepared ²⁴ by

²⁰ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, J. Chem. Soc. (A), 1966, 737.
 ²¹ K. W. Bagnall and J. B. Laidler, J. Chem. Soc. (A), 1966,

516. ²² K. W. Bagnall, D. Brown, and P. J. Jones, J. Chem. Soc.

(A), 1966, 1763.
 ²³ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, J. Chem. Soc., 1965, 350.
 ²⁴ D. Brown and J. F. Easey, unpublished observations.

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direct union of the elements at 600°. Protactinium(IV) oxydihalides were already available.⁶ Commercial antimony trioxide and bromine were used and neptunium metal was kindly provided by Mr. J. A. C. Marples (Ceramics Division, A.E.R.E., Harwell). Individual preparations were carried out with 20-200 mg. of actinide element.

Oxydihalides.—These were prepared by reaction of the appropriate tetrahalide with antimony trioxide in sealed, evacuated vessels as described ⁶ for the protactinium compounds. In certain instances (UOCl₂, NpOCl₂, and NpOBr₂) they were also prepared by reaction of the actinide tetrahalide with the stoicheiometric amount of the actinide dioxide at 500° in a vacuum. Analyses are in Table 5.

Analysis.—Thorium, uranium, and protactinium were weighed as ThO₂, U₃O₈, and Pa₂O₅, respectively, after ignition of the hydrous oxides obtained by hydrolysis of the oxydihalides with aqueous ammonia. Neptunium-237 was determined by α -assay (specific activity of ²³⁷Np = $1.562 \times 10^{6} \alpha$ -disintegrations min.⁻¹ mg.⁻¹) and halides were determined either by titration against standard silver nitrate solution or weighed as the silver salt.

Physical Measurements.—X-Ray powder diffraction photographs were obtained with both a Debye-Scherrer 19 cm. camera and a Guinier focusing camera with filtered Cu- K_{α} radiation ($\lambda_{\alpha 1} = 1.54051$ Å). Scales were contactprinted on the Guinier films before development to counteract film shrinkage during processing. Thoria was used as an internal standard for Guinier work to allow an accurate camera constant to be determined for each sample. The specimens were mounted between strips of Sellotape which were sealed with Bostikote to contain the α -activity. Protactinium(IV) oxydichloride slowly decomposed under such conditions but the remaining oxydichlorides were relatively stable. Cell constants for the orthorhombic oxydihalides were obtained by refining Guinier film results using a computer programme based on the Cohen-Hess method to obtain the best least-squares fit between observed and calculated sin² θ . Between 70 and 90 independent reflections were refined for each compound and the agreement between observed and calculated values of sin² θ for ThOCl₂ is shown in Table 1 which lists part of the recorded powder pattern. Infrared spectra were recorded with an Infrascan spectrometer (4000-600 cm.⁻¹) and a Grubb-Parsons DM-4 spectrometer (660-225 cm.⁻¹). Samples were mounted either as Nujol mulls or in wax discs as described ²⁵ elsewhere; the absence of OH and H₂O vibrations from the Infrascan region confirmed that the compounds remained anhydrous during spectral studies.

Та	BLE	5
ΊA	BLE	- 5

Analyses of actinide oxydihalides

	Found (%)		Required (%)	
Compound	\mathbf{M}	x	\mathbf{M}	\mathbf{X}
ThOCl ₂	72.61	$22 \cdot 25$	72.75	22.23
PaOCl ₂	72.15	22.07	72.66	22.30
UOCl,	73.38	21.71	$73 \cdot 25$	21.82
NpOCl,	72.96	21.62	73.17	21.88
ThOBr,	56.81	38.89	56.86	39.22
PaOBr	56.81	39.21	56.76	39.31
UOBr,	57.18	38.67	57.49	38.65
NpOBr,	56·81	38.69	57.38	38.74
ThOI,	46.41	50.41	46.21	50.60
X = Cl, B	r, or I;	M = actin	ide elemer	nt.

We thank Mr. A. M. Deane for infrared facilities, and Mr. R. Street for Guinier Camera facilities.

[7/849 Received, July 11th, 1967]

²⁵ A. M. Deane, J. Inorg. Nuclear Chem., 1965, 27, 751.