

## 950. Some Oxychloro-complexes of Quinquevalent Elements.

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X-Ray diffraction, magnetic susceptibility, and infrared studies are reported for caesium oxychloro-complexes of the type  $\text{Cs}_2\text{M}^{\text{V}}\text{OCl}_5$  ( $\text{M}^{\text{V}} = \text{Nb}, \text{Cr}, \text{Mo}, \text{and W}$ ).

QUINQUEVALENT niobium,<sup>1</sup> chromium,<sup>2</sup> molybdenum,<sup>3</sup> and tungsten<sup>4</sup> oxychloro-complexes of the types  $\text{M}_2^{\text{I}}(\text{M}^{\text{V}}\text{OCl}_5)$  and  $\text{M}_1^{\text{I}}(\text{M}^{\text{V}}\text{OCl}_4)$  were first characterised several years ago, but their properties were little investigated until recently. In fact, as pointed out by Kanzlemeyer *et al.*,<sup>5</sup> the information available on the niobium compound did not differentiate between  $\text{Cs}_2\text{NbOCl}_5$  and  $\text{Cs}_2\text{Nb}(\text{OH})_2\text{Cl}_5$ , although by analogy with the more fully characterised molybdenum and tungsten complexes the compound was probably the former. Recently, the spectral properties<sup>5-9</sup> of  $[\text{M}^{\text{V}}\text{OCl}_5]^{2-}$  ions have been examined in the visible- and ultraviolet regions, but no far infrared or X-ray powder diffraction studies have been reported and, although some magnetic susceptibility measurements<sup>8-11</sup> are available, the majority were made at one temperature only.

It was accordingly of interest to attempt to fill some of the existing gaps in the chemistry of these compounds, and some X-ray powder diffraction results, far infrared data, and magnetic susceptibility measurements (group VI A only) are now reported for the caesium oxypentachloro complexes of niobium, chromium, molybdenum, and tungsten. As this work was being completed, Fowles and his co-workers published<sup>9</sup> a detailed study of the spectral and magnetic properties of both types of molybdenum(v) and tungsten(v) complexes as well as a method of preparation of caesium oxypentachloromolybdate(v),  $\text{Cs}_2\text{MoOCl}_5$ , and magnetic data, similar to those observed here, for the tungsten analogue.

The caesium oxypentachloro-complexes have the  $\text{K}_2\text{PtCl}_6$  structure. Unit-cell dimensions, determined from Guinier X-ray powder photographs, are shown in Table I and the

TABLE I.  
Unit-cell dimensions (Å).

$\text{Cs}_2\text{NbOCl}_5$	Cubic	$10.24 \pm 0.01$	—	—
$\text{Cs}_2\text{CrOCl}_5$	Cubic	$10.19 \pm 0.01$	—	—
$\text{Cs}_2\text{MoOCl}_5$	Cubic	$10.24 \pm 0.01$	* $\text{Cs}_2\text{MoCl}_6$	Cubic $10.27 \pm 0.01$
$\text{Cs}_2\text{WOCl}_5$	Cubic	$10.24 \pm 0.01$	† $\text{Cs}_2\text{WCl}_6$	Cubic $10.27 \pm 0.01$

\* Ref. 12. † Ref. 13.

observed and calculated  $\sin^2\theta$  values are listed in Tables 2 and 3. We have assumed the anions to be statistically disordered (see Experimental section), and the structure of  $\text{Cs}_2\text{NbOCl}_5$  has been determined more fully in order to obtain a value for the covalent octahedral radius of the niobium atom and some idea of the niobium-chlorine bond length. By using a weighted mean scattering factor for the one oxygen and five chlorine atoms,

<sup>1</sup> Weinland and Storz, *Ber.*, 1906, **39**, 3057; *Z. anorg. Chem.*, 1907, **54**, 223.

<sup>2</sup> (a) Weinland and Fridrich, *Ber.*, 1905, **38**, 3784. (b) Weinland and Friederer, *Ber.*, 1906, **39**, 4042; 1907, **40**, 2090.

<sup>3</sup> (a) Klasen, *Ber.*, 1901, **34**, 148. (b) Foerster and Fricke, *Z. anorg. Chem.*, 1923, **36**, 458. (c) James and Wardlaw, *J.*, 1927, 2145.

<sup>4</sup> (a) Collenberg, *Z. anorg. Chem.*, 1918, **102**, 259; (b) Collenberg and Guthe, *Z. anorg. Chem.*, 1924, **134**, 317.

<sup>5</sup> Kanzlemeyer, Ryan, and Freund, *J. Amer. Chem. Soc.*, 1956, **78**, 3020.

<sup>6</sup> Jorgensen, *Acta Chem. Scand.*, 1957, **11**, 73.

<sup>7</sup> Gray and Hare, *Inorg. Chem.*, 1962, **1**, 363.

<sup>8</sup> Kon, *J. Inorg. Nuclear Chem.*, 1963, **25**, 933.

<sup>9</sup> Allen, Brisden, Edwards, Fowles, and Williams, *J.*, 1963, 4649.

<sup>10</sup> Hare, Bernal, and Gray, *Inorg. Chem.*, 1962, **1**, 831.

<sup>11</sup> "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Pub. Inc., New York, 1960.

<sup>12</sup> Edwards, Peacock, and Said, *J.*, 1962, 4643.

<sup>13</sup> Kennedy and Peacock, *J.*, 1963, 3392.

TABLE 2.

X-Ray diffraction data for  $\text{Cs}_2\text{NbOCl}_5$ .

$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$	$h, k, l$	$I_{\text{obs.}}$	$I_{\text{calc.}}$	$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$	$h, k, l$	$I_{\text{obs.}}$	$I_{\text{calc.}}$	
0168	0169	1,1,1	48.4	50.9	2716	2714	4,4,4	9.3	7.4	
0226	0226	2,0,0	10.1	6.1	2883	2883	5,5,1	3.5	5.1	
0451	0452	2,2,0	90.2	100			7,1,1		5.06	
0620	0622	3,1,1	11.3	11.4	2940	2940	6,4,0	v.w.	0.51	
0679	0678	2,2,2	55.3	48.0	3166	3165	6,4,2	18.8	19.2	
0902	0904	4,0,0	61.8	58.0	3333	3335	5,5,3	v.w.	2.45	
1074	1074	3,3,1	v.w.	0.3			7,3,1		0.001	
1128	1131	4,2,0	7.7	7.7	3621	3618	8,0,0	3.3	4.0	
1355	1357	4,2,2	34.0	31.0	—	3787	7,3,3	—	0.27	
1527	1526	{ 3,3,3 5,1,1	6.6	12.1	{ 0.19 11.90	3844	3844	{ 8,2,0 6,4,4	2.7	3.1
1811	1809	4,4,0	33.0	29.8	4072	4070	6,6,0	5.5	8.9	
1979	1978	5,3,1	4.8	6.6			8,2,2		5.8	
2034	2035	{ 6,0,0 4,4,2	3.9	4.7	{ 0.07 4.6	—	4239	{ 5,5,5 7,5,1	—	3.7
2262	2261	6,2,0	16.3	20.0	4296	4296	6,6,2	5.0	5.5	
—	2431	5,3,3	—	0.60	4521	4522	8,4,0	12.4	11.3	
2488	2487	6,2,2	14.4	10.3						

TABLE 3.

X-Ray diffraction data.

$\text{Cs}_2\text{CrOCl}_5$			$\text{Cs}_2\text{MoOCl}_5$			$\text{Cs}_2\text{WOCl}_5$			$h, k, l$
$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$	$I_{\text{obs.}}$	$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$	$I_{\text{obs.}}$	$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$	$I_{\text{obs.}}$	
0169	0171	40	0169	0169	50	0170	0170	50	1,1,1
0229	0229	5	0226	0226	5	0226	0226	1	2,0,0
0455	0457	100	0451	0452	100	0455	0453	100	2,2,0
0629	0629	10	0621	0621	10	0623	0623	30	3,1,1
0685	0686	50	0677	0678	50	0680	0680	50	2,2,2
0916	0915	60	0904	0904	60	0908	0906	60	4,0,0
1088	1087	1	1074	1074	1	1075	1076	10	3,3,1
1144	1143	5	1130	1130	5	1132	1133	1	4,2,0
1375	1372	30	1357	1356	30	1360	1359	30	4,2,2
1540	1543	5	1527	1526	5	1531	1529	5	{ 3,3,3 5,1,1
1827	1829	40	1808	1808	40	1815	1812	40	4,4,0
2003	2001	5	1980	1978	5	1984	1982	5	5,3,1
2062	2058	5	2034	2034	5	2039	2039	1	{ 6,0,0 4,4,2
2290	2286	20	2261	2260	20	2262	2265	20	6,2,0
—	—	—	—	—	—	2435	2435	1	5,3,3
2515	2515	20	2487	2486	20	2495	2492	20	6,2,2
2746	2744	10	2713	2712	10	2721	2718	10	4,4,4
2911	2915	5	2880	2882	5	2899	2888	5	{ 5,5,1 7,1,1
2973	2972	1	2936	2938	1	—	—	—	6,4,0
3200	3201	10	3166	3164	20	3172	3171	20	6,4,2
—	—	—	3334	3334	1	3339	3341	1	{ 5,5,3 7,3,1
—	—	—	3618	3616	5	3619	3623	5	8,0,0
3890	3887	1	3842	3842	1	—	—	—	7,3,3
4104	4105	5	4066	4068	5	4074	4075	5	{ 6,6,0 8,2,2
—	—	—	—	—	—	4246	4247	1	{ 5,5,5 7,5,1
4342	4344	5	4295	4295	5	4301	4303	5	6,6,2
4576	4573	10	4523	4521	10	4532	4530	10	8,4,0
4804	4802	5	4691	4690	5	—	—	—	{ 9,1,1 7,5,3
—	—	—	4747	4747	5	—	—	—	8,4,2

and assuming the space group to be  $Fm\bar{3}m(O_h^5, \text{No. } 225)$  the distances Nb-Cl,  $2.15 \pm 0.05$ , Nb-Cs,  $4.43 \pm 0.01 \text{ \AA}$  and Cs-Cl  $3.64 \pm 0.01 \text{ \AA}$  were obtained. Owing to the small number of reflections observed, no attempt was made to differentiate the Nb=O and Nb-Cl bond lengths although the former will obviously be somewhat shorter than the Nb-Cl distance

obtained by assuming a random distribution. Taking the covalent radius of chlorine as 0.99 Å, the octahedral radius of niobium in  $\text{Cs}_2\text{NbOCl}_5$  is 1.16 Å. The unit-cells of the molybdenum(v) and tungsten(v) complexes are very similar in size to those of the caesium hexachloromolybdate(IV) and hexachlorotungstate(IV) (Table 1), which have been assumed to have the same space group.<sup>12,13</sup>

The magnetic susceptibilities of the chromium, molybdenum, and tungsten salts were measured between 89 and 300°K and in each case the Curie-Weiss relation was obeyed with a small value of  $\theta$ , the Weiss constant (Table 4). The discrepancy between the magnetic moment of  $\text{Cs}_2\text{WOCl}_5$  reported here (1.56 B.M.) and that reported earlier<sup>9</sup> (1.49 B.M.) is probably due to the different Weiss constants obtained (−30 and −16°, respectively). The magnetic moments of the chromium and molybdenum compounds, 1.80 and 1.65 B.M., respectively, are close to the spin-only value, but that of the tungsten compound, 1.56 B.M., is appreciably less, presumably because of a larger spin-orbit coupling contribution. This behaviour may be contrasted with that of the hexachlorotungstate(v) complexes,<sup>14</sup> which exhibit antiferromagnetism.

All the complexes show a very strong metal-oxygen stretching vibration around 900–1000  $\text{cm}^{-1}$  (Table 5) as previously observed for analogous compounds,<sup>9,15</sup> thus confirming the presence of the  $\text{Nb}=\text{O}$  group in the niobium compound and precluding the possibility of it being  $\text{Cs}_2\text{Nb}(\text{OH})_2\text{Cl}_5$ . In contrast, niobium oxytrichloride,  $\text{NbOCl}_3$ , which has been shown<sup>16</sup> to have oxygen bridges between the niobium atoms, has a very sharp intense

TABLE 4.

## Magnetic susceptibilities.

(Temperatures are in °K; susceptibilities in  $10^{-6}$  c.g.s./mole.)

$\text{Cs}_2\text{CrOCl}_5$ ; $\theta = -14^\circ$		$\text{Cs}_2\text{MoOCl}_5$ ; $\theta = -10^\circ$		$\text{Cs}_2\text{WOCl}_5$ ; $\theta = -30^\circ$	
Temp.	$\chi_m$	Temp.	$\chi_m$	Temp.	$\chi_m$
300	1278	297	1091	300	934
279	1364	268	1219	278	989
266	1420	248	1289	260	1044
240	1591	220	1466	233	1138
210	1806	189	1671	205	1266
204	1842	155	2062	178	1434
171	2198	116	2684	150	1667
133	2722	89	3298	119	2056
95	3566			89	2433

TABLE 5.

Infrared vibrational frequencies ( $\text{cm}^{-1}$ ).

	M=O	M-O-M	M-Cl		M=O	M-O-M	M-Cl
$\text{Cs}_2\text{CrOCl}_5$ .....	925	—	336	$\text{Cs}_2\text{NbOCl}_5$ .....	922	—	319
$\text{Cs}_2\text{MoOCl}_5$ .....	950	—	324	$\text{NbOCl}_3$ .....	—	767	—
$\text{Cs}_2\text{WOCl}_5$ .....	954	—	306				

peak at 767  $\text{cm}^{-1}$ . Metal-chlorine vibrations in the far infrared are very broad, strong bands (Table 5) for the oxypentachloro-complexes. The tungsten-chlorine and molybdenum-chlorine stretching vibrations, 306 and 324  $\text{cm}^{-1}$ , respectively, are very close to those observed<sup>17</sup> in the hexachlorotungstate(IV)  $\text{Cs}_2\text{WCl}_6$  (308  $\text{cm}^{-1}$ ) and hexachloromolybdate(IV)  $\text{Cs}_2\text{MoCl}_6$  (325  $\text{cm}^{-1}$ ) as might be expected from the crystallographic similarities (Table 1).

## EXPERIMENTAL

*Preparation of  $\text{Cs}_2(\text{MVOCl}_5)$  salts* (M<sup>V</sup> = Nb, Cr, Mo, and W).—Niobium pentachloride was dissolved in concentrated hydrochloric acid and an excess of caesium chloride in a similar solution was added. The resulting solution was cooled to 0° and saturated with hydrogen chloride gas;

<sup>14</sup> Bagnall, Brown, and du Preeze, *J.*, 1964, 2603.<sup>15</sup> Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.<sup>16</sup> Sands, Zalkin, and Elson, *Acta Cryst.*, 1959, 12, 21.<sup>17</sup> Adams, Gebbie, and Peacock, *Nature*, 1963, 199, 278.

the precipitate was collected, washed with ether containing 10% of thionyl chloride (v/v) and vacuum dried at room temperature. Chromium,<sup>2</sup> molybdenum,<sup>18</sup> and tungsten<sup>4</sup> salts were prepared according to published methods. Care was necessary in the preparation of the caesium oxychlorochromate(v) in order to avoid contamination of the product with the oxychlorochromate(vi) compound, CsCrO<sub>3</sub>Cl or, if the reduction had proceeded too far, chloro complexes of chromium(III). The presence of the latter was inferred from the high magnetic susceptibilities observed for some preparations. We obtained the pure product in small yield by dissolving chromic oxide (0.5 g.) in glacial acetic acid (20 ml.) previously saturated with hydrogen chloride gas and precipitating the salt by the addition of caesium chloride (1.0 g.), dissolved in a similar solution, after passing hydrogen chloride gas for 15 min. *Niobium oxytrichloride* was prepared by the reaction between niobium pentachloride and dry oxygen.<sup>19</sup>

*Magnetic Susceptibilities.*—A Gouy balance described elsewhere<sup>20</sup> was used. Previously calibrated tubes were filled in a dry-box and sealed with polythene bungs to exclude atmospheric moisture during measurements.

*Infrared Spectra.*—A Hilger H.800 spectrometer was used over the range 2—38  $\mu$ ; samples were mounted as mulls in Nujol between silver chloride or polythene plates.

*X-Ray Diffraction.*—Powder photographs were obtained with a Guinier focussing camera with filtered Cu-K $\alpha$  radiation ( $\lambda = 1.54051$ ). Scales were contact printed on to the films before development, in order to counteract film shrinkage during processing. For the structure determination, intensities were measured with a Joyce-Loebl Double-Beam recording microdensitometer reading directly in film density, and values of the intensities in arbitrary units were obtained by measuring the areas under the plotted photometer curves. For intensity calculations, the structure factors were calculated for each reflection by using individual scattering factors<sup>21</sup> for the niobium atom and the caesium atom, and a weighted mean for the oxygen atom and the five chlorine atoms. A single temperature factor,  $B$ , was obtained from the relationship,  $|F_{\text{obs.}}|^2 = |F_{\text{calc.}}|^2 e^{-2B \sin^2 \theta / \lambda^2}$ ; the Lorentz-polarisation correction factors were calculated<sup>22</sup> and the appropriate values of the multiplicity factor were those quoted<sup>23</sup> in the "International Tables for X-Ray Crystallography." The space group was assumed to be  $Fm\bar{3}m$  and agreement between observed and calculated intensities was obtained by placing 4 molecules in the unit cell with atoms in the following special positions: 4 Nb in (a) at 0, 0, 0; 8 Cs in (c) at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ;  $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ ; 20 Cl and 4 O in (e) at  $\pm x, 0, 0$ ; 0,  $x, 0$ ; 0, 0,  $x$  when

TABLE 6.

Analyses of caesium oxychloro-compounds.

Compound	Colour	Found (%)		Requires (%)	
		MV	Cl	MV	Cl
Cs <sub>2</sub> NbOCl <sub>5</sub> .....	Pale yellow	16.79	32.26	16.84	32.13
Cs <sub>2</sub> CrOCl <sub>5</sub> .....	Dark red	10.31	34.51	10.17	34.70
Cs <sub>2</sub> MoOCl <sub>5</sub> .....	Green	17.35	31.99	17.28	31.95
Cs <sub>2</sub> WOCl <sub>5</sub> .....	Green-blue	28.51	27.42	28.60	27.60
NbOCl <sub>3</sub> .....	White	43.01	49.32	43.17	49.40

$x = 0.21 \pm 0.005$ . The observed and calculated intensities are shown in Table 2 and some idea of the agreement is obtained from the expression  $\Sigma |I_o - I_c| / \Sigma I_o = 0.12$ . The discrepancy factor  $R = \Sigma (|F_o - |F_c|) / \Sigma |F_o|$  cannot be used because of the overlapping powder lines.

*Analysis.*—Chlorine was determined potentiometrically against standard silver nitrate solution, whilst niobium(v)<sup>24</sup> and tungsten(v)<sup>14</sup> were determined as described previously.

<sup>18</sup> Simon and Souchay, *Bull. Soc. chim. France*, 1956, 1402.

<sup>19</sup> Fairbrother, Cowley, and Scott, *J. Less Common Metals*, 1959, 1, 206.

<sup>20</sup> Brown and Colton, *J.*, 1964, 714.

<sup>21</sup> "The International Tables for X-Ray Crystallography," Kynock Press, Birmingham, Vol. III, 1959, p. 201.

<sup>22</sup> D'Eye and Wait, "X-Ray Powder Photography," Butterworths Scientific Pub., London, 1960, p. 64.

<sup>23</sup> "The International Tables for X-Ray Crystallography," Kynock Press, Birmingham, Vol. I, 1959, p. 31.

<sup>24</sup> Bagnall and Brown, *J.*, 1964, 4434.

Molybdenum(v) was determined exactly as tungsten(v) and chromium(v) by oxidation with persulphate<sup>25</sup> to dichromate, which was estimated against ferrous ammonium sulphate.

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<sup>25</sup> Vogel, "A Text-book of Quantitative Inorganic Analysis," Longmans, Green & Co., London, 2nd edn., 1951, p. 297.

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