**629.** *Complex Chlorides and Bromides of Quadrivalent Tungsten.*

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Interaction of tungsten hexachloride and alkali-metal halides under dry conditions at 130° yields the complex chlorides $M_2W^{IV}Cl_6$ (M = K, Rb, Cs, Tl, or $\frac{1}{2}Ba$). Similar reactions involving tungsten hexabromide lead to the complex bromides $M_2W^{IV}Br_6$ (M = K, Rb, or Cs). The alkali-metal salts have unit cells related to that of K_2PtCl_6. Magnetic and chemical properties have also been studied.

Recently [1] a series of complex halides of quadrivalent molybdenum has been prepared, and we now report the synthesis of the corresponding halogenotungstates. Much of the earlier preparative work on complex tungsten halides has involved aqueous media which are not suitable for the study of the simpler complex anions of the quadrivalent element with six equivalent ligands. Consequently the only complex halide of quadrivalent tungsten reported in the literature before the start of the current researches was the compound $K_2W(OH)Cl_5$, prepared by the reduction of tungsten trioxide in concentrated hydrochloric acid in the presence of potassium chloride.[2] Very recently, however, it has been shown [3] that aliphatic amines react with tungsten hexachloride in the absence of moisture, to give complexes of the type $(NH_2R_2)_2WCl_6$ and $(NHR_3)_2WCl_6$.

In preliminary experiments, potassium chloride was allowed to react with an excess of tungsten hexachloride in a sealed tube at 200°. Chlorine was evolved and some potassium hexachlorotungstate(IV) was formed, but Debye X-ray photographs indicated that even over a period of several days the reaction was not complete and some potassium chloride remained. The dry reaction of potassium iodide with tungsten hexachloride at 130° leads to a pure product in three days, so that it is evident that the removal of any chlorine formed is essential:

$$WCl_6 + 2KCl \longrightarrow Cl_2 + K_2WCl_6$$
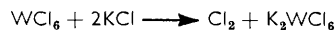
Replacement of the potassium iodide in the starting materials by other alkali-metal iodides or by barium or thallous iodide leads to corresponding hexachlorotungstates(IV), but with sodium iodide a pure product is not isolable.

The alkali-metal hexachlorotungstates(IV) are red crystalline salts, but the thallous and the barium compound are green. They decompose in moist air, but the cæsium salt is less sensitive to moisture than the potassium salt and much less sensitive than the barium and thallium salts. They dissolve in water to give blue solutions apparently containing tungsten(V), but on treatment with concentrated hydrochloric acid deep red solutions are formed [cf.[2] $K_2WCl_5(OH)$]. With alkali the hexachlorotungstates(IV) give hydrogen.

At −33° potassium hexachlorotungstate(IV) dissolves in liquid ammonia to give a pale green solution from which much of the starting material can be recovered unchanged. At 20°, however, this solution soon becomes red, and after a few days becomes colourless above brown and white residues. The white solid is a mixture of ammonium and potassium chloride, but the brown solid appears to be an aminotungsten chloride $W(NH_2)_3Cl$.

With pyridine, potassium chlorotungstate(IV) yields ultimately orange, crystalline tetrachlorobispyridinetungsten(IV). The reaction evidently goes through an intermediate stage, as a little of a reactive red solid, perhaps the salt $K[WCl_5py]$, has been isolated. The behaviour of aniline and of ethylenediamine towards potassium chlorotungstate is more complicated, and analytical data suggest replacement as well as addition.

It is interesting that the initial colour of solutions of chlorotungstate in liquid ammonia and in aniline is green, in contrast with the red solutions in aqueous hydrochloric acid.

[1] Edwards, Peacock, and Said, *J.*, 1962, 4643.
[2] Klemm and Steinberg, *Z. anorg. Chem.*, 1936, **227**, 193.
[3] Brisdon, Fowles, and Osborne, *J.*, 1962, 1330.

Since potassium chlorotungstate can be recovered unchanged from the green solution in liquid ammonia, it appears that this is the true colour of WCl_6^{2-} ion in solution. Solid chlorotungstates vary markedly in colour; besides the green and red salts reported here, Fowles and his colleagues describe others, with large organic cations, as being brown, yellowish, or even white.[3] It is tempting to associate such colours with shifts and intensity changes in charge-transfer absorption bands. In the visible spectrum of solid rubidium chlorotungstate a peak occurs at about 5500 Å (Table 5), and a small change in wavelength or intensity would certainly affect the colour. The red solutions of the salt $K_2WCl_5(OH)$ in hydrochloric acid absorb at 5100—5200 Å.[4]

Other reactions involving tungsten hexachloride and potassium hexachlorotungstate(IV) are given in the Experimental section.

Three hexabromotungstates(IV), K_2WBr_6, Rb_2WBr_6, and Cs_2WBr_6, have been made by treating the alkali-metal iodide with an excess of tungsten hexabromide in a sealed tube at 130° for four days, and then pumping off the volatile materials while raising the temperature gradually to 290°. They are green crystalline solids with chemical properties similar to those of the chlorine analogues. They dissolve in hydrobromic acid to give green solutions. In alkaline and probably in neutral solution hydrogen is evolved and blue or brown precipitates are formed. Potassium bromotungstate(IV) dissolved in pyridine, to give an amino-compound of composition WBr_4py_2, which Debye X-ray photographs have shown to have a structure resembling that of WCl_4py_2.

It is clear that the hexahalogenotungstates(IV) are more easily formed than the corresponding molybdenum compounds, as shown by the existence of barium hexachlorotungstate(IV) and potassium hexabromotungstate(IV) and the absence of the corresponding halogenomolybdates.[1] The tendency of molybdenum(IV) to disproportionate to molybdenum(III) and molybdenum(V) is not followed by tungsten, so that no tervalent derivative $K_2W_2Cl_9$, for example, is formed by the action of liquid ammonia on potassium hexachlorotungstate(IV), and the evidence suggests that a large body of quadrivalent tungsten–halogen chemistry remains to be investigated.

With the exception of the salts of $BaWCl_6$ and of K_2WBr_6, these hexahalogenotungstates have the K_2PtCl_6 structure. Unit cell sizes are shown in Table 1, together with

TABLE 1.

Unit cell sizes (Å).

		Hexachloro-tungstates	Hexachloro-molybdates *			Hexabromo-tungstates	Hexabromo-molybdates *
K_2WCl_6	Cubic	$a_0 = 9\cdot875 \pm 0\cdot01$	$9\cdot85 \pm 0\cdot01$	K_2WBr_6	Tetragonal	$a_0 = 7\cdot22$, $c_0 = 10\cdot64$	—
Rb_2WCl_6	Cubic	$10\cdot00$	$9\cdot99$	Rb_2WBr_6	Cubic	$a_0 = 10\cdot50$	$10\cdot50$
Cs_2WCl_6	Cubic	$10\cdot27$	$10\cdot27$	Cs_2WBr_6	Cubic	$10\cdot70$	$10\cdot70$
Tl_2WCl_6	Cubic	$9\cdot87$	$9\cdot84$				
$BaWCl_6$	Cubic	$9\cdot35$	—			* Ref. 1.	

those of the corresponding halogenomolybdates. Barium hexachlorotungstate has a primitive cubic unit cell containing 4 formula units, and the structure of potassium hexabromotungstate is probably a tetragonal distortion of the K_2PtCl_6 type.

Magnetic data reported for quadrivalent tungsten are confined to the hydroxy-complex $K_2WCl_5(OH)$[2] and to spin-paired types such as $K_4W(CN)_8$.[5] Details of the magnetic susceptibilities and of the magnetic moments of our compounds are given in Tables 2 and 3. Values of the magnetic moment at 25°, as expected, are much below the " spin only " value of 2·88 B.M. They deviate further from Kotani theory [6] than do the chloromolybdates, and in none of the hexahalogenotungstates would the value of μ_{eff} extrapolated to

[4] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 83.
[5] Bhar and Ray, *J. Indian Chem. Soc.*, 1928, **5**, 497.
[6] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293; Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 173; *Trans. Faraday Soc.*, 1958, **54**, 1009.

TABLE 2.

Magnetic susceptibilities and magnetic moments. (Temperatures are in °K, corrected molar susceptibilities are in 10^{-6} c.g.s./mole, and moments are in Bohr magnetons).

Temp.	χ_A	μ_{eff}	Temp.	χ_A	μ_{eff}	Temp.	χ_A	μ_{eff}	Temp.	χ_A	μ_{eff}
K_2WCl_6			Rb_2WCl_6			Cs_2WCl_6			Tl_2WCl_6		
292°	863·9	1·43	292°	927·5	1·47	294°	915·5	1·47	293°	1306	1·76
280	890·5	1·42	280	945·1	1·46	280	933·1	1·45	280	1318	1·72
263	915·3	1·39	263	977·8	1·44	263·5	966·0	1·43	263	1352	1·69
250	947·1	1·38	250	1000	1·42	250	944·5	1·42	250	1390	1·67
242	956·0	1·37	242	1023	1·41	242	1016	1·41	242	1415	1·66
227	991·6	1·35	227	1058	1·39	227	1056	1·39	227	1450	1·63
212	1032	1·33	212	1096	1·37	212	1104	1·37	212	1482	1·59
190	1094	1·29	190	1169	1·34	190	1183	1·35	191	1539	1·54
170	1165	1·26	170	1241	1·30	170	1266	1·32	170	1591	1·48
151	1218	1·22	152	1317	1·27	152	1354	1·29	152	1648	1·42
131	1342	1·11	114	1490	1·17	114	1558	1·20	132	1711	1·35
99	1370	1·05	99	1563	1·12	99	1674	1·16	114	1783	1·28
90	1379	1·00	90	1608	1·08	90	1740	1·12	99	1838	1·21
									90	1861	1·16
$BaWCl_6$			K_2WBr_6			Rb_2WBr_6			Cs_2WBr_6		
293	337·2	0·89	288	991	1·50	289	866	1·42	292	958	1·72
282	342·4	0·88	280	986	1·49	280	878	1·41	280	985	1·70
262	344·3	0·85	263	1028	1·48	263	909	1·39	263	1025	1·68
250	349·0	0·84	250	1056	1·46	250	936	1·37	250	1058	1·66
241	351·4	0·83	241	1079	1·45	242	948	1·36	242	1084	1·64
227	358·4	0·81	229	1108	1·43	227	984	1·34	227	1125	1·61
212	365·5	0·79	212	1157	1·41	212	1028	1·33	212	1197	1·60
190	379·7	0·76	191	1227	1·37	191	1095	1·30	190	1285	1·56
169	391·5	0·73	170	1291	1·33	170	1169	1·27	170	1385	1·52
151	408·1	0·70	152	1363	1·29	151	1252	1·23	151	1491	1·48
132	422·2	0·67	132	1435	1·24	132	1338	1·20	132	1619	1·43
113	438·8	0·63	114	1518	1·18	114	1446	1·15	113	1775	1·37
99	457·7	0·60	99	1588	1·13	99	1539	1·11	99	1926	1·34
90	469·5	0·58	90	1611	1·08	90	1590	1·07	90	2023	1·30
$WCl_4(C_5H_5N)_2$			$WCl_4(C_5H_5N)_2$			$WBr_4(C_5H_5N)_2$			$WBr(C_5H_5N)_2$		
291	1824	2·06	191	2173	1·83	288	1769	2·03	188	2250	1·85
279	1869	2·05	170	2240	1·35	276·5	1798	2·00	168	2382	1·80
263	1921	2·02	152	2303	1·68	265·5	1838	1·98	158	2500	1·78
250	1945	1·98	133	2354	1·59	248·5	1911	1·96	130	2657	1·67
242	1965	1·96	114	2384	1·48	237	1930	1·94	112	2799	1·59
227	2023	1·92	100	2393	1·39	227·5	2029	1·93	99	2936	1·53
212	2091	1·89	91	2371	1·29	205·5	2152	1·89	87	3035	1·46

TABLE 3.

Curie temperatures (°K).

Compound	K_2WCl_6	Rb_2WCl_6	Cs_2WCl_6	Tl_2WCl_6	$BaWCl_6$	K_2WBr_6
	180°	160°	122°	375°	400°	200°

Compound	Rb_2WBr_6	Cs_2WBr_6	$WCl_4(C_5H_5N)_2$	$WBr_4(C_5H_5N)_2$
	137°	148°	(Antiferromagnetic)	180°

0°K approach 1·22 B.M., the limiting minimum for the $d\varepsilon^2$ configuration. The observed Curie temperatures are sufficiently high to indicate the possibility of antiferromagnetism (Table 3) and for the compounds K_2WCl_6 and WCl_4py_2 Néel minima are just observable at about 80°K and 100°K, respectively. It has been shown that in potassium chloro-iridate(IV) antiferromagnetic interaction occurs through neighbouring chlorine atoms,[7] and the same phenomenon might be expected in the hexahalogenotungstates which have similar structures to the hexachloroiridates(IV).

The stretching frequencies of the hexahalogenotungstates(IV) lie, as expected, in the far infrared region, between 324 and 214 cm.$^{-1}$ (Table 4). The data presented for the pyridine complexes, which have been measured only with sodium chloride optics, show slight shifts in absorption maxima of a few wave-numbers from values for uncombined pyridine.

[7] Griffith, Owen, Park, and Partridge, *Proc. Roy. Soc.*, 1959, *A*, **250**, 84.

TABLE 4.

Infrared absorption frequencies (in cm.$^{-1}$).

WCl(NH$_2$)$_3$ 3150(s); 1630(m); 1300(w); 1160(w); 1070sh(w); 1040(s); 720(m)
WCl$_4$py$_2$ ... 3412b(w); 2959(w); 1622(w); 1487(m); 1452(s); 1213(m); 1160(w); 1063(ms); 1048(w); 1014(mw); 761(s); 686(s)
WBr$_4$py$_2$ ... 3410b(w); 2970(w); 1615(m); 1487(m); 1451(s); 1215(m); 1160(w); 1064(s); 1047(w); 1011(m); 965(w); 942(w); 859(vw); 759(s); 685(s)

K$_2$WCl$_6$	324	Cs$_2$WCl$_6$	308	Rb$_2$WBr$_6$	220
Rb$_2$WCl$_6$	306	K$_2$WBr$_6$	229	Cs$_2$WBr$_6$	214

TABLE 5.

Visible- and ultraviolet-light absorption maxima (in Å).

Rb$_2$WCl$_6$	5500, 3220, 2850, 2600, 2350
Cs$_2$WBr$_6$	4980, 3950, 3020
WCl$_4$py$_2$	3800, 3270, 2600
WBr$_4$py$_2$	4500, 4100, 3320, 3100

EXPERIMENTAL

Hexachlorotungstates.—(1) *Reaction between tungsten hexachloride and potassium iodide.* Finely ground, dry potassium iodide, and an excess of tungsten hexachloride were heated together in a sealed Carius tube in the absence of air for three days at 130°. The excess of tungsten hexachloride and the iodine formed during the reaction were removed in a high vacuum, the temperature being raised meanwhile to 280°. The red residue was *potassium hexachlorotungstate*(IV) (Found: K, 16·5; W, 38·4; Cl, 44·7. K$_2$WCl$_6$ requires K, 16·4; W, 38·8; Cl, 44·8%). Debye X-ray photographs confirmed that only a single phase was present.

(2) *Rubidium, cæsium, thallium, and barium hexachlorotungstate*(IV). These *salts* were prepared by a procedure similar to that outlined under (1) (Found: W, 32·7; Cl, 37·9. Rb$_2$WCl$_6$ requires W, 32·4; Cl, 37·5. Found: W, 28·3; Cl, 31·9. Cs$_2$WCl$_6$ requires W, 27·7; Cl, 32·1. Found: Tl, 51·1; W, 23·2; Cl, 26·9. Tl$_2$WCl$_6$ requires Tl, 50·8; W, 22·8; Cl, 26·4. Found: W, 35·4; Cl, 39·8. BaWCl$_6$ requires W, 34·5; Cl, 39·8%). The purity of the samples was checked by Debye X-ray powder photographs, which showed only single phases to be present.

(3) *Reaction between tungsten hexachloride and sodium iodide.* Under similar conditions to those outlined above under (1), a dark residue remained after iodine and the excess of tungsten hexachloride had been pumped off. Debye X-ray photographs indicated that the principal crystalline phase present in the residue was sodium chloride. The residue dissolved in water to give a red solution (Found: W, 31·7; Cl, 58·6. Calc. for WCl$_4$: W, 56·4; Cl, 43·6. Calc. for NaCl: Cl, 60·7%).

(4) *Reaction between tungsten hexachloride and ammonium iodide.* Under similar conditions to those outlined above, *i.e.*, with an excess of tungsten hexachloride, iodine and hydrogen chloride were formed. A black solid, which contained no iodine, remained in the Carius tube after all the volatile materials had been pumped off [Found: N, 4·6; W, 75·2; Cl, 17·8. Calc. for (W$_4$Cl$_5$)(NH$_2$)$_3$,NH$_3$: N, 5·7; W, 75·4; Cl, 18·1. Calc. for (W$_3$Cl$_4$)(NH$_2$),NH$_3$: N, 5·8; W, 74·3; Cl, 19·1%]. The black solid dissolved in water, with a smell of hydrogen chloride, to give a brown solution. When it was treated with alkali, ammonia was evolved. The solid was insoluble in methanol, chloroform, and tetahydrofuran, but dissolved slightly in dimethyl-formamide. It was slightly paramagnetic [μ_{eff} (292°K) = 0·36 B.M.]. Clearly a pure compound was not formed under these conditions, but the magnetic evidence points to presence of a complex chloro-cation of bivalent tungsten.

This reaction was repeated with an excess of ammonium iodide, and again iodine was evolved. The volatile materials, including the excess of ammonium iodide, were pumped off. Part of the residue dissolved in methanol to give a brown solution containing nitrogen, tungsten, and iodine. This solution deposited a brown precipitate after a few minutes (Found: I, 23·9%), and a pure compound was not isolated. The remainder of the residue, which did not dissolve in methanol, was a red crystalline solid. The Debye X-ray photographs indicated a face-centred cubic phase, and the unit cell size (a_0 = 9·98 Å) was close to that of (NH$_4$)$_2$ReCl$_6$ (a_0 = 10·07 Å).[8]

[8] Burovaya, *Kristallografiya*, 1957, **1**, 365; *Chem. Abs.*, 1957, **51**, 1686.

However, it was not possible to separate this phase from small quantities of other methanol-insoluble contaminants [Found: W, 48·0; Cl, 45·2. Calc. for $(NH_4)_2WCl_6$: W, 42·5; Cl, 49·2%].

(5) *Reaction between tungsten hexachloride and alkali chloride in the presence of iodine mono-chloride.* Under similar conditions to those described above, the potassium, rubidium, and cæsium compounds were formed. Debye X-ray photographs indicated that only single phases, identical with those obtained from (1) and (2), were formed.

(6) *Reaction of potassium hexachlorotungstate with liquid ammonia at* $-33°$. A large excess of dry ammonia was condensed on finely ground potassium hexachlorotungstate at $-180°$. When the apparatus was allowed to warm, the salt dissolved in the liquid ammonia to give a pale green solution which became brownish and turbid when most of the solvent had distilled away. A red solid and a very small quantity of brown material remained when all the ammonia was gone. Debye X-ray photographs showed the red solid to be unchanged potassium hexachlorotungstate. Rubidium hexachlorotungstate scarcely dissolved in liquid ammonia at $-33°$.

(7) *Reaction of potassium hexachlorotungstate with liquid ammonia at* $25°$. Liquid ammonia develops a pressure of about 10 atm. at $25°$, so the reaction was carried out in a gauze-wrapped Carius tube. When reaction was complete the Carius tube was cooled to $-180°$ and opened under dry conditions, and the ammonia was allowed to evaporate. The residue was washed 4 times with separate portions of liquid ammonia through a filter disc (No. 3 porosity). The brown insoluble residue (Found: K, 6·2; W, 59·3; Cl, 18·3; N, 12·9%) was amorphous, but Debye X-ray powder photographs showed that some potassium chloride remained. After allowance for this in the analytical figures the composition of the brown residue approached $WCl(NH_2)_3$ [Found: W, 69·4; Cl, 13·4; N, 15·0. Calc. for $WCl(NH_2)_3$: W, 68·8; Cl, 13·3; N, 15·7%]. This material gave an infrared spectrum with broad absorption peaks (Table 4).

(8) *Reaction of potassium hexachlorotungstate with pyridine.* The salt was treated with a large excess of water-free pyridine under nitrogen. No reaction occurred at $25°$, but on refluxing for a few minutes all the salt dissolved to give a deep red solution, which in the cold deposited orange crystals. The crystals were washed with several portions of pyridine, and later, after it had been shown that they were stable to moisture, with water and acetone. Debye X-ray photographs of the crude and washed preparations showed the former to contain potassium chloride. The complex phase could not be indexed. The orange solid was tetrachlorobispyridinetungsten(IV) [Found: W, 38·8; Cl, 28·0; C_5H_5N, 34·3. Calc. for $WCl_4(C_5H_5N)_2$: W, 38·0; Cl, 29·3; C_5H_5N, 32·7%]. The analytical results indicate the presence of a substituted tungsten chloride as impurity. Infrared absorption frequencies are given in Table 4.

The coloured pyridine filtrate remaining after the original deposition of orange crystals deposited a further crop on storage. Evaporation to dryness, under a vacuum, of the second filtrate yielded a small quantity of a reactive deep red solid which became blue on exposure to the atmosphere and contained tungsten : chlorine ratio of 1·0 : 4·8.

(9) *Reactions of rubidium chlorotungstates with aniline.* The salt was treated with a large excess of water-free aniline. No reaction occurred in the cold, but, on warming, the salt dissolved to give a green solution which after a few seconds changed to deep red. The addition of dry ether precipitated ribudium chloride and an orange solid. The orange solid, after being washed with water and acetone, contained no chlorine [Found: W, 60·4; C, 14·0; N, 2·9; H, 1·6%), but the figures indicate an approximate ratio of tungsten to aniline of 1 : 1 and suggest that decomposition had occurred during the separation from alkali-metal chloride.

(10) *Reaction of potassium chlorotungstate with ethylenediamine.* At $25°$ the salt dissolved to give a deep brown solution and a brown precipitate. Addition of dry ether to the solution gave the coloured material as an oily precipitate, which became less oily when shaken with ethanol. The brown precipitate was shown by Debye X-ray powder photography to contain potassium chloride as the only crystalline phase. It dissolved in water and in ethylenediamine, and a complete analysis (Found: W, 32·4; Cl, 21·9 C, 9·63; H, 2·55; N, 9·0; K, 19·0%); suggested that most of the chlorine originally combined with the tungsten had been replaced. It was not possible to separate the complex from alkali chloride.

(11) *Reaction of potassium chlorotungstate with acetylacetone.* A green, benzene-soluble sticky solid was formed and hydrogen chloride was evolved. No pure phase could be isolated.

Hexabromotungstates.—(1) *Potassium, rubidium, and cæsium hexabromotungstates*(IV). The iodine and the slight excess of tungsten bromides (some of the hexabromide had decomposed to lower bromides) were pumped off while the temperature was raised gradually to 290°. The

green residues were pure *hexabromotungstates*(IV) (Found: K, 10·4; W, 25·5; Br, 67·0. K_2WBr_6 requires K, 10·6; W, 24·8; Br, 64·7. Found: Rb, 20·3; W, 22·1; Br, 57·7. Rb_2WBr_6 requires Rb, 20·5; W, 22·1; Br, 57·4. Found: Cs, 29·6; W, 19·8; Br, 52·0. Cs_2WBr_6 requires Cs, 28·6; W, 19·8; Br, 51·6%). The slightly high results for tungsten and bromine in the potassium salt probably indicate decomposition.

(2) *Reaction of potassium bromotungstate with pyridine.* At 25° the salt dissolved slowly to give a red solution which became darker on warming. After all the salt had dissolved a greenish suspension appeared. Similar treatment to that described above for the chloro-tungstate yielded mixed green and red precipitates. The red component was washed out with acetone, and the remaining yellow-green solid was washed with water and dried in a vacuum-desiccator [Found: W, 28·1; Br, 48·2; C_5H_5N, 21·7. $WBr_4(C_5C_5N)_2$ requires W, 27·8; Br, 48·3; C_5H_5N, 23·9%]. Infrared data for the *complex* are presented in Table 4. Debye X-ray photographs indicate a close similarity between the unit cells of the chloro- and the bromo-complexes. The pyridine filtrate deposited a fresh crop of green crystals on storage, and addition of diethyl ether to the second filtrate precipitated a small quantity of a red material. Neither of these materials occurred in sufficient quantity to justify analysis.

Analysis.—Alkali metals were estimated as the tetraphenylborates, and thallium as thallous iodide. Tungsten was determined by precipitating the WO_3–cinchonine–tannin complex and igniting this to tungstic oxide at 800°. Halogens were determined by the Volhard procedure. Ammonia and amines were distilled from sodium hydroxide solution into known volumes of standard acid.

X-*Ray Measurements.*—Powder samples for X-ray examination were sealed in thin-walled capillaries. Photographs were taken with 19 cm. or with 12 cm. cylindrical powder cameras and filtered Cu-K_α radiation.

Magnetic Measurements.—These were made over the temperature range 80—300°K by the Gouy method. The apparatus was similar to that described by Figgis and Nyholm.[9] Since some of the salts are unstable in moist air, the powdered specimens were introduced into Pyrex magnetic tubes (whose diamagnetism had been previously determined) in a dry box.

Ultraviolet and Visible Spectra.—These (see Table 5) were measured on a Cary direct recording instrument from 7500 Å to 2000 Å. Specimens were made up in Nujol mulls, and the concentration of halogenotungstate between the plates was estimated by halogen analysis.

Infrared Spectra.—These were measured on a Perkin-Elmer instrument with sodium chloride optics. Specimens were made up in Nujol mulls.

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⁹ Figgis and Nyholm, *J.*, 1959, 331.