894. *Complex Chlorides and Bromides of Quadrivalent Molybdenum.*

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Interaction of molybdenum pentachloride and an alkali-metal halide in the presence of iodine monochloride yields the complex chlorides $M_2Mo^{IV}Cl_6$ (M = K, Rb, Cs, or Tl). Similar reactions involving molybdenum tribromide, MBr, and iodine monobromide yield the complex bromides $M_2Mo^{IV}Br_6$ (M = Rb or Cs). Potassium hexachloromolybdate has the K_2PtCl_6 structure, with Mo–Cl = 2·31 Å, and the unit-cell sizes of the other complex halides have been determined. Magnetic and chemical properties have also been studied.

Halogen compounds of quadrivalent molybdenum are not easily isolated from aqueous solution, and not much is known about the complex halides of the element in this oxidation state. The available information about dry reactions suggests that the tervalent complex K_3MoCl_6 is attacked by bromine at room temperature to give potassium bromide and a complex halide, probably K_2MoCl_6.[1] The compound Na_2MoF_6 has been isolated.[2]

We here report the preparation by non-aqueous methods of a series of complex chlorides and bromides of quadrivalent molybdenum; under similar experimental conditions complex iodides are not formed.

In preliminary experiments, potassium chloride was allowed to react with an excess of molybdenum pentachloride in a sealed tube at 200°. Chlorine was evolved and potassium hexachloromolybdate(IV) was formed, but this solid product was contaminated with traces of involatile lower molybdenum chlorides. However, in the presence of iodine monochloride the reaction is satisfactory at 150°, and the only solid material which remains after volatile materials have been pumped off or washed out is the chloromolybdate. When prepared in this way the compound is pure and, moreover, is more highly crystalline than the product from the dry method. Replacement of the potassium chloride in the starting materials by rubidium or cæsium chloride or by thallium iodide leads to the corresponding complex salts, but with sodium or barium chloride a pure product is not isolable. The results of experiments involving molybdenum pentachloride and other alkali halides are given in the Experimental section.

The hexachloromolybdates(IV) are dark green or olive-green crystalline salts. They are sensitive to moisture and dissolve in water or aqueous acids with decomposition. Potassium hexachloromolybdate(IV) reacts readily with, and is partially soluble in, liquid ammonia: the solid residue is the tervalent binuclear complex $K_3Mo_2Cl_9$, which has recently been prepared by other methods,[3] and the solution presumably contains ammines of quinquevalent molybdenum.[4] In other non-aqueous solvents the hexachloromolybdates are either completely insoluble or, if slightly soluble, undergo reaction. The behaviour towards iodine monochloride is probably exceptional, and the dissolved species in this solvent have not been identified.

Two hexabromomolybdates(IV), Rb_2MoBr_6 and Cs_2MoBr_6, have been prepared from molybdenum tribromide, alkali bromide, and iodine monobromide at 300°; attempts to obtain sodium, potassium, and thallous salts have not been successful. The properties of the hexabromomolybdates are similar to those of the chloro-analogues, *e.g.*, they are olive-green and sensitive to moisture, and the rubidium salt gives a compound $Rb_3Mo_2Br_9$ on treatment with liquid ammonia.

These halogenomolybdates have the K_2PtCl_6 structure. Unit-cell sizes, determined from Debye X-ray powder photographs, are shown in Table 1, together with those of the

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[1] Young and Laudige, *J. Amer. Chem. Soc.*, 1956, **78**, 4861.
[2] Edwards and Peacock, *Chem. and Ind.*, 1960, 1441.
[3] Lewis, personal communication, 1962.
[4] Edwards and Fowles, *J. Less-Common Metals*, 1961, **3**, 181.

TABLE 1.

Unit-cell sizes (Å).

		Hexachloro-molybdates	Hexachloro-platinates *			Hexachloro-molybdates	Hexachloro platinates *
K_2MoCl_6 ...	Cubic	9·85 ± 0·01	9·775	Tl_2MoCl_6 ...	Cubic	9·84 ± 0·01	9·755
Rb_2MoCl_6 ...	,,	9·99 ± 0·01	9·883	Rb_2MoBr_6...	,,	10·50 ± 0·01	10·41
Cs_2MoCl_6 ...	,,	10·27 ± 0·01	10·192	Cs_2MoBr_6 ...	,,	10·70 ± 0·01	10·63

* Wyckoff, " Crystal Structures," Interscience Publ., Inc., New York, 1953, Vol. III, tables IXc, 2 and IXc, 2a.

TABLE 2.

Dimensions (Å) of K_2MoCl_6

Unit cell size a_0	9·85 ± 0·01	Mo–K	4·26 ± 0·01
Mo–Cl	2·31 ± 0·05	K–Cl	3·48 ± 0·01

TABLE 3.

Relative intensities for K_2MoCl_6.

Plane	I_c	I_o	Plane	I_c	I_o	Plane	I_c	I_o	Plane	I_c	I_o
111	147	149	331	32	36	531	90	86	444	75	81
200	51	54	420	44	50	442	33	30	551	62	60
220	86	65	422	61	69	600			711		
311	91	80	433	92	90	620	40	26	642	47	52
222	115	119	511			533	26	21	553	43	52
400	266	295	440	210	220	622	34	38	731		

TABLE 4.

Magnetic susceptibilities.

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

K_2MoCl_6		Rb_2MoCl_6		Cs_2MoCl_6		Tl_2MoCl_6		Rb_2MoBr_6		Cs_2MoBr_6	
Temp.	χ_A	Temp.	χ_A	Temp.	χ_A	Temp.	χ_A	Temp.	χ_A	Temp.	χ_A
289·9°	2222	290·8°	2105	291·7°	2138	296·1°	2782	291·6°	2013	293°	1825
277·3	2339	277·1	2288	277·3	2222	277·2	2921	277	2087	277·1	1901
245·6	2499	246·5	2373	246·1	2326	246·5	3030	246·1	2182	241·3	1982
218·9	2772	219·6	2523	218·9	2520	219·1	3235	219·6	2356	219·1	2119
186·5	3183	187·3	2729	186·9	2738	186·8	3494	187·1	2594	186·8	2319
166·1	3480	167·3	2881	166·9	2943	166·9	3660	167·1	2753	166·9	2452
158·1	3618	158·9	2968	158·5	3006	157·3	3742	158·5	2875	157·3	2542
131·7	4114	132·7	3209	132·5	3345	132·5	4045	133·3	3150	131·7	2823
110·5	4627	110·9	3614	110·6	3743	110·9	4364	110·9	3356	110·5	3108
93·3	5197	94·1	3888	93·6	4105	93·9	4655	94·1	3689	93·5	3473
76·3	5389	86	4067	86	4273	86	4786	86·3	3800	85·6	3583

TABLE 5.

Curie temperatures, and effective magnetic moments at 300°K.

Compound	K_2MoCl_6	Rb_2MoCl_6	Cs_2MoCl_6	Tl_2MoCl_6	Rb_2MoBr_6	Cs_2MoBr_6
θ (K)..................	54°	176°	160°	200°	140°	160°
μ_{eff} (B.M.)	2·28	2·24	2·24	2·58	2·18	2·08

corresponding halogenoplatinates. To obtain a value for the covalent octahedral radius of the molybdenum atom the structure of K_2MoCl_6 has been determined more fully; essential parameters are given in Tables 2 and 3. If the covalent radius of chlorine is taken as 0·99 Å, the octahedral radius of molybdenum in K_2MoCl_6 is 1·32 Å, which is shorter than the value (1·37 Å) calculated by Pauling[5] for six co-ordinate molybdenum in the MoS_2 structure.

Quadrivalent molybdenum forms few spin-free compounds, and data are available only for the binary halides $MoCl_4$ and $MoBr_4$,[6] which are probably not magnetically dilute.

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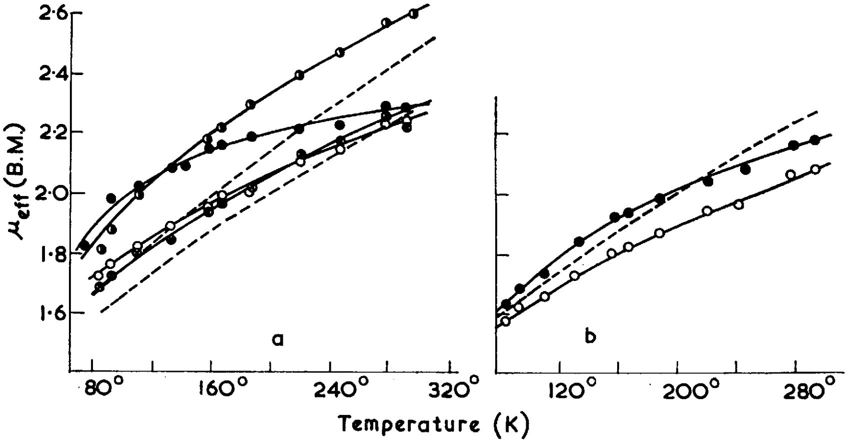
[5] Pauling, " The Nature of the Chemical Bond," Oxford Univ. Press, 1960, p. 253.

[6] Klemm and Steinberg, *Z. anorg. Chem.*, 1936, **227**, 193.

Details of the magnetic susceptibilities and of the magnetic moments of our compounds are given in Tables 4 and 5, and in the Figure. In these halogenomolybdates the molybdenum atom is surrounded by a regular octahedron of halogen atoms, and is acted on by a cubic or nearly cubic ligand field. For a $4d\varepsilon^2$-compound under these conditions Kotani's theory [7] predicts that in the ground state the magnetic moment should vary with temperature according to the equation:

$$\mu^2_{\text{eff}} = 3/2 + 9kT/\zeta_{4d},$$

where k is the Boltzmann constant and ζ_{4d} is the spin–orbit coupling constant. At 0°K μ_{eff} is 1·22 B.M. and, if the spin-orbit coupling constant is sufficiently large, μ_{eff} should vary approximately linearly with temperature.



Plots of μ_{eff} against temperature: (a) ◑ Tl_2MoCl_6; ● K_2MoCl_6; ○ Cs_2MoCl_6; ⊗ Rb_2MoCl_6; (b) ● Rb_2MoBr_6; ○ Cs_2MoBr_6. Broken lines are theoretical curves: (a) upper curve, ζ_{4d} = 400 cm.$^{-1}$; lower curve, ζ_{4d} = 500 cm.$^{-1}$; (b) ζ_{4d} = 500 cm.$^{-1}$.

Reference to the Figure shows that for rubidium and cæsium hexachloromolybdates(IV) the experimental results are in fair agreement with the theory, but the moments of the potassium and of thallium salts are generally higher than expected. It is not possible at this stage to be sure if these high results are real, or if they are due to the presence of small proportions of other paramagnetic impurities, *e.g.*, molybdenum(III), but it is significant that the corresponding hexachlorotungstates(IV) [8] follow a similar pattern of behaviour. Best values of the spin–orbit coupling constants (from the Kotani equation) are 450 cm.$^{-1}$ for the hexachloromolybdates, and 500 cm.$^{-1}$ for the hexabromomolybdates. These are lower than expected from the values for neighbouring elements.[9] It is possible, without theoretical justification, to make a better fit to the experimental curves by increasing the temperature-independent term in the equation.

Table 6 shows the positions of the absorption bands in the ultraviolet and visible regions

TABLE 6.

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

$MoCl_6^{2-}$	4150	3600	3150	2800	2450
$MoBr_6^{2-}$	6200	5100	4150	3570	2400

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[7] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293; Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 173; *Trans. Faraday Soc.*, 1958, **54**, 1009.

[8] Kennedy and Peacock, unpublished work.

[9] Figgis and Lewis, "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, p. 428.

of the spectrum. In the absence of a reflection attachment to the instrument the absorption was measured in a Nujol mull, so that the positions of the peaks are probably not accurate. A rough calculation of the amount of light absorbed indicates the spectra to be of the electron-transfer type (ε = 1500—2500).

EXPERIMENTAL

Hexachloromolybdates.—(1) *Reaction between molybdenum pentachloride and potassium chloride.* Finely ground, dry potassium chloride and an excess of molybdenum chloride were heated in a sealed tube (Carius) in the absence of air; after 3 days at 120°, no reaction had occurred, so the temperature was raised to 200° for a further 24 hr. Chlorine was then evolved and a dark crystalline product appeared. The tube was opened in a dry-box and the product separated from remaining pentachloride by leaching the latter out with dry chloroform. The bluish-black residue was impure potassium chloromolybdate(IV) (Found: Mo, 25·5; K, 19·9; Cl, 53·1. Calc. for K_2MoCl_6: Mo, 24·8; K, 20·2; Cl, 55·0%):

$$2KCl + MoCl_5 \longrightarrow K_2MoCl_6 + \tfrac{1}{2}Cl_2.$$

(2) *Reaction between molybdenum pentachloride, potassium chloride, and iodine monochloride.* A five-fold excess of iodine monochloride over the other reactants was used, but otherwise the procedure was similar to that outlined above. Reaction was complete after 3 days at 150°, and the remaining iodine monochloride and molybdenum pentachloride were washed out with chloroform. The green residue had a low chlorine content, probably owing to surface decomposition (Found: Cl, 52·4%), so in subsequent experiments the excess of reagents was removed under a high vacuum at 200°. Pure *potassium hexachloromolybdate*(IV) remained (Found: Mo, 24·8; K, 20·3; Cl, 54·8%). The purity of the sample was confirmed by Debye *X*-ray powder photographs, which showed the presence of only a single phase.

(3) *Rubidium and cæsium hexachloromolybdate*(IV). These *salts* were prepared by a procedure similar to that outlined under (2) (Found: Mo, 20·1; Rb, 35·3; Cl, 44·4. Rb_2MoCl_6 requires Mo, 20·0; Rb, 35·6; Cl, 44·4%. Found: Mo, 16·9; Cs, 45·3; Cl, 38·2, Cs_2MoCl_6 requires Mo, 16·7; Cs, 46·3; Cl, 37·6%). The purity of the compounds was checked by Debye *X*-ray powder photographs.

(4) *Thallous hexachloromolybdate*(IV). The technique used was similar to that outlined above, but thallous iodide replaced the alkali chloride and, after evacuation, traces of lower molybdenum chlorides were removed by washing the *salt* with chloroform (Found: Mo, 13·6; Tl, 57·1; Cl, 27·9. Tl_2MoCl_6 requires Mo, 13·4; Tl, 57·0; Cl, 29·6%). Debye *X*-ray powder photographs showed only one phase to be present.

(5) *Reaction between potassium bromide, molybdenum pentachloride, and iodine monobromide.* At 200° and after 3 days impure potassium hexachloromolybdate(IV) was formed. The product was probably contaminated with a small proportion of an involatile molybdenum bromide (Found: Mo, 20·1; K, 17·7; Cl, 54·5. Calc. for K_2MoCl_6: Mo, 24·8; K, 20·2; Cl, 55·0%).

(6) *Reaction between potassium iodide and molybdenum pentachloride.* When an excess of the chloride was used the product was identified from a Debye *X*-ray powder photograph as mainly potassium hexachloromolybdate but a second phase was also present. However, when a 2 : 1 mixture KI–$MoCl_5$ was kept at 200° for 3 days a red product of the approximate composition K_2MoCl_5 was formed: $2KI + MoCl_5 \longrightarrow K_2MoCl_5 + I_2$ (Found: Mo, 24·5; K, 20·4; Cl, 45·2. Calc. for K_2MoCl_5: Mo, 27·3; K, 22·2; Cl, 50·5%). A Debye *X*-ray powder photograph showed only faint lines which did not correspond to K_2MoCl_6 or to KCl.

(7) *Reaction of potassium hexachloromolybdate with liquid ammonia.* Dry, boiling liquid ammonia attacked potassium hexachloromolybdate and yielded a pink residue and a yellow solution. The residue was washed with liquid ammonia until the washings became colourless and was then allowed to dry in a desiccator (Found: Mo, 31·6; K, 19·6; Cl, 51·5. Calc. for $K_3Mo_2Cl_9$: Mo, 30·6; K, 18·6; Cl, 50·8%). The yellow filtrate and washings were allowed to evaporate to dryness and the solid residue was shown to contain molybdenum. A Debye *X*-ray photograph of the residue showed the presence of lines due to ammonium and potassium chloride.

Hexabromomolybdates.—(1) *Rubidium and cæsium salts.*—An accurately weighed 2 : 1 mixture of dry rubidium bromide and freshly prepared molybdenum tribromide was treated with an excess of iodine bromide (about five-fold, by volume) in a Carius tube. The tube was cooled, evacuated, sealed, and then kept at 300° for 6 days. After the iodine bromides had been pumped off, pure *rubidium hexabromomolybdate*(IV) remained (Found: Mo, 13·2; Rb, 23·8; Br, 64·2. Rb_2MoBr_6 requires Mo, 12·9; Rb, 22·9; Br, 64·2%). A Debye *X*-ray photograph showed the presence of one phase only.

Cæsium hexabromomolybdate(IV) was prepared similarly (Found: Mo, 12·1; Cs, 32·0; Br, 56·8. Cs_2MoBr_6 requires Mo, 11·4; Cs, 31·6; Br, 57·0%), the analysis being confirmed by a Debye *X*-ray powder photograph.

(2) *Reaction between potassium bromide, molybdenum tribromide, and iodine monobromide.* A procedure similar to that outlined above was used, but the product was always deficient in bromine, and its composition corresponded to $K_4Mo_2Br_{11}$ (Found: Mo, 15·8; K, 11·9; Br, 71·7. Calc. for $K_4Mo_2Br_{11}$: Mo, 15·6; K, 12·7; Br, 71·7%). Debye *X*-ray photographs showed no lines corresponding to the cubic Rb_2MoBr_6 pattern, but the possibility of the material's being impure K_2MoBr_6 is not ruled out.

(3) *Reaction of rubidium hexabromomolybdate*(IV) *with liquid ammonia.* The procedure outlined above for the liquid-ammonia reaction was followed. A red-violet solution and a greyish-brown residue were formed. The residue was the nearly pure salt $Rb_3Mo_2Br_9$ (Found: Mo, 17·4; Rb, 22·5; Br, 61·4. Calc. for $Rb_3Mo_2Br_9$: Mo, 16·4; Rb, 22·0; Br, 61·6%).

Attempted Preparation of Iodomolybdates.—Potassium iodide, molybdenum, and iodine in a sealed tube at 300° showed no signs of reaction, and use of molybdenum iodide under similar conditions did not yield an iodomolybdate. Further attempts involving cæsium iodide in the latter reactions did not lead to a complex salt.

Analysis.—Molybdenum was determined as oxine derivative or as silver molybdate. Potassium, rubidium, and cæsium were determined as the tetraphenylboron salts $MBPh_4$. Thallium was determined as thallous chromate or as thallous iodide. Chlorine, bromine, and iodine were determined as silver halides.

Structure of Potassium Hexachloromolybdate(IV).—Powder samples for *X*-ray examination were sealed in thin-walled capillaries. Photographs were taken with a 19 cm. cylindrical camera, and crystal-reflected Cu-K_α radiation from a pentaerythritol monochromator. The multiple-film technique was used to obtain graded intensities, and duplicate films were examined with a Hilger microphotometer (type 451). Values of the integrated intensities in arbitrary units were obtained by measuring areas under the plotted photometer curves.

For any line on a powder photograph the intensity is given by:

$$I = \text{Constant}\ \frac{1 + \cos^2 2\alpha \cos^2 2\theta p''}{\sin^2\theta \cos\theta} \cdot A .\ F^2{}_{hkl},$$

where α is the angle of reflection in the monochromator and the other symbols have their usual meaning.[10] For calculating intensities the absorption correction was obtained from Bradley's values [11] (absorption coefficient 340 cm.$^{-1}$). For the scattering factors the values of Thomas and Umeda [12] were used for molybdenum, and those of Freeman [13] for potassium and chlorine, quantities being taken for un-ionised atoms (cf. Gutmann and Jack [14]).

Observed *X*-ray reflections were indexed on a face-centred cubic unit cell, with side $a_0 = 9{\cdot}85 \pm 0{\cdot}01$ Å. The space group was assumed to be *Fm3m* ($0_h{}^5$, No. 225), and agreement between observed and calculated intensities was obtained by placing four molecules in the unit cell with atoms in the following positions: 4 Mo in (*a*) at 0, 0, 0; 8 K in (*b*) at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{3}{4}, \frac{3}{4}, \frac{3}{4}$; 24 Cl in (*c*) at $\pm x, 0, 0;\ 0, x, 0;\ 0, 0, x$; when $x = 0{\cdot}235 \pm 0{\cdot}005$. The individual temperature factors, found by trial and error, were: $B_{Mo} = 2{\cdot}0$; $B_K = 4{\cdot}0$; $B_{Cl} = 4{\cdot}0$ Å^2. Observed and calculated intensities are listed in Table 3.

Some idea of agreement between observed and calculated intensities can be obtained from the expression $\Sigma|I_o - I_c|/\Sigma I_o = 0{\cdot}092$. The discrepancy factor $R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$ cannot be used because of the overlapping of the powder lines. The accuracy of the determination was limited by the difficulty of obtaining sufficiently crystalline material, and it was not possible to measure or determine the intensities of high-angle lines.

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[10] "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, Vol. II, 1959, p. 237.

[11] Bradley, *Proc. Phys. Soc.*, 1935, **47**, 879.

[12] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

[13] Freeman, *Acta Cryst.*, 1959, **12**, 261.

[14] Gutmann and Jack, *Acta Cryst.*, 1951, **4**, 244.

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.[15] Since some of the salts are unstable in moist air, the powdered specimens were introduced into Pyrex magnetic tubes (whose diamagnetism had previously been determined) in a dry-box.

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[15] Figgis and Nyholm, *J.*, 1959, 331.