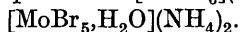


CCVII.—*Compounds of Tervalent Molybdenum. Part IV. Bromides.*

By WILLIAM WARDLAW and ARTHUR JACOB IMMINS HARDING.

By electrolytic reduction of molybdenum trioxide dissolved in hydrochloric acid, solutions of trivalent molybdenum are obtained which, on addition of alkali chlorides, yield complex salts of the types  $[\text{MoCl}_6]\text{R}_3$  and  $[\text{MoCl}_5, \text{H}_2\text{O}]\text{R}_2$ . Although the trichloride has not yet been isolated from such solutions, when the concentration of molybdenum is high, the oxychloride,  $\text{MoOCl}_4, 4\text{H}_2\text{O}$ , can be obtained (J., 1924, 125, 2370). From the reduced bromide solutions, Rosenheim and Braun (*Z. anorg. Chem.*, 1905, 46, 311) have prepared two complex salts  $[\text{MoBr}_6](\text{C}_5\text{H}_6\text{N})_3$  and



In all these cases, the co-ordination number is 6. Moreover, the different halogen complexes containing molybdenum in other stages of oxidation exhibit this co-ordination number, for in such compounds an oxygen atom occupies only one co-ordination position: e.g.,  $[\text{MoO}_2\text{Cl}_4]\text{R}_2$ ,  $[\text{MoO}_2\text{Br}_4](\text{C}_5\text{H}_6\text{N})_3$ ,  $[\text{MoOX}_5]\text{R}_2$  where X = Cl, Br, or F.

On the Bohr theory of atomic structure, molybdenum, like chromium, iron, cobalt, nickel, rhodium, osmium and platinum, which all form well-defined compounds of co-ordination number 6, is a member of one of the groups of elements the planetary electrons of which are undergoing reorganisation. It shows, therefore, variable valency and marked colour in its compounds. The *maximum* co-ordination number of molybdenum is not, however, 6. A co-ordination number of 8 is seen in the complex salt  $\text{R}_4\text{Mo}(\text{CN})_8$ . This is in accordance with Sidgwick's rule that the maximum co-valency number or co-ordination number is that of the maximum sub-group next to the largest completed group in the atom. Molybdenum, atomic number 42, has its 3-quanta orbits completed and the numbers of electrons in the 4-quanta sub-groups are 2, 2, 4, 4, 6, 6, 8. So far, 6 represents the maximum co-ordination number for trivalent molybdenum and further evidence for this is afforded by the results of the present investigation, whereby, from a reduced solution of molybdenum trioxide in hydrobromic acid, a fawn-coloured oxybromide  $[\text{MoOBr}_4, 4\text{H}_2\text{O}]$  and red salts of the general formulæ  $\text{R}_3[\text{MoBr}_6]$  and  $\text{R}_2[\text{MoBr}_5, \text{H}_2\text{O}]$  have been isolated.

## EXPERIMENTAL.

*Molybdenyl Monobromide.*—The most satisfactory method for the preparation of constant-boiling hydrobromic acid is that outlined

by Scott (J., 1900, **77**, 648), in which bromine is covered with water and reduced by sulphur dioxide and the resulting homogeneous liquid is distilled, the fraction boiling at 124—126° being collected and re-distilled.

In preparing his electrolyte, Rosenheim (*loc. cit.*) dissolved the dihydrate of molybdenum trioxide in the hydrobromic acid. However, the trioxide itself will dissolve in the hot acid. 25 G. of molybdenum trioxide and 350 c.c. of the hydrobromic acid were heated under reflux for 3 to 6 hours, the final solution being golden-brown in colour. The filtered solution was electrolysed in a diaphragm cell with smooth platinum electrodes (J., 1923, **123**, 169), a current of 3.5 amps. being used, until the cathode solution was reddish-brown. This solution was transferred to an air-free flask and concentrated at 70° under diminished pressure to 80—100 c.c. The liquid was then transferred to a small cell and re-electrolysed to ensure that the molybdenum was tervalent. The electrolysis was continued until a sample of the liquid added to air-free acetone gave a flocculent fawn precipitate of molybdenyl bromide. (If the electrolysis is continued beyond this stage, the product is hydrolysed and much darker than the true compound.) The cathode solution was now forced by pressure of carbon dioxide into air-free acetone, and the solid which separated was filtered off and washed with acetone. All these operations were performed in an atmosphere of carbon dioxide, air being rigidly excluded. The solid was transferred to a desiccator which was then evacuated.

*Valency of the Compound.*—This was determined as for the oxychloride (*loc. cit.*). Direct titration with standard permanganate required, for 1 g. of solid, 118.90 c.c. After oxidation and passage through the reductor a solution containing 1 g. of the substance required 118.40 c.c. The molybdenum is therefore tervalent, for the latter titration represents the oxidation of the tervalent molybdenum, produced by reduction, to the hexavalent condition.

*Analysis.*—The molybdenum was precipitated as sulphide and ignited to trioxide (J., 1924, **125**, 1911). The bromide in the filtrate and washings was weighed as silver bromide (Found: Mo, 37.5, 37.7; Br, 31.1, 31.3; Mo : Br = 1 : 1; 1 : 1.  $\text{MoOBr}_3 \cdot 3.5\text{H}_2\text{O}$  requires Mo, 37.7; Br, 31.35%). In all probability the normal hydrate is  $\text{MoOBr}_3 \cdot 4\text{H}_2\text{O}$ .

#### *Properties and Reactions of Molybdenyl Monobromide.*

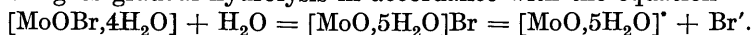
The dried solid is light fawn in colour and does not deliquesce in the air, although it gradually undergoes atmospheric oxidation. It is readily soluble in water or hydrobromic acid, its solubility in water being greater than that of the oxychloride. It is insoluble

in acetone or dry ether, slightly soluble in cold absolute alcohol and more soluble on warming. The substance has pronounced reducing properties. Silver nitrate is reduced to the metal, whilst with lead acetate acidified with acetic acid no precipitate of lead bromide is obtained. This test seems to indicate that molybdenyl bromide is not a binary electrolyte.

*Molecular Weight Determinations.*—The molecular weight was determined by depression of the freezing point of air-free water.

G. of MoOBr,4H <sub>2</sub> O per 10 g. of water ...	0.1235	0.0640	0.0698
“ Apparent ” mol. wt. ....	218.8	218.2	220.1

If the salt has the formula [MoOBr,4H<sub>2</sub>O], the molecular weight is 263.9, whereas if it is formulated as [MoO]Br,4H<sub>2</sub>O in dilute aqueous solution, if ionisation is complete, its “ apparent ” molecular weight should be 131.9. The above results furnish strong evidence in favour of its formulation as the co-ordination compound [MoOBr,4H<sub>2</sub>O], although they also indicate that the substance undergoes gradual hydrolysis in accordance with the equation



This view receives support from the fact that the molecular weights determined with solutions of the solid, after standing some hours in ice-cold water, were considerably less than those quoted above, whilst after longer periods the hydroxide of molybdenum gradually separated.

Conductivity measurements at 1° showed this continuous hydrolysis, which was accelerated by the presence of the electrodes (compare Duff, J., 1923, **123**, 572). For  $v = 24$  litres per mole

$\mu$ .....	66.8	68.2	75.2	76.1	76.9	77.6	77.8	78.2	78.2
Time (mins.) ...	2	3	4	5	6	7	8	9	10

In more dilute solutions, the rate of hydrolysis was increased. The fact that the conductivity alters with time and that it approaches the value for a binary electrolyte like potassium chloride, for which the data at 1° are

$v$ (litres per mole) .....	8	16	32
$\mu$ .....	72.2	75.2	77.3

supports the formula [MoOBr,4H<sub>2</sub>O] for the new compound. Many cases could be cited to show that ionisation of co-ordination compounds occurs with replacement of the co-ordinated halogen atom by a molecule of the solvent.

*Salts of the Types R<sub>3</sub>[MoBr<sub>6</sub>] and R<sub>2</sub>[MoBr<sub>5</sub>,H<sub>2</sub>O].*

By the addition of alkali bromide to a reduced bromide solution containing trivalent molybdenum, two salts have so far been pre-

pared conforming to the above types. The isolation of the oxy-bromide from a reduced molybdenum solution shows that a further possibility of complex salt formation may arise, namely, salts of the type  $\text{MoOBr}_x\text{KBr}$ . Although such a salt has not been isolated, the corresponding chlorine derivative  $[\text{MoOCl}_2, 3\text{H}_2\text{O}]\text{K}$  has been obtained (unpublished research). The preparation of these three classes of salts depends on the following factors: (a) Molybdenum concentration, (b) relative amount of alkali bromide present, (c) amount of "free" acid. By suitable adjustment of these factors we have isolated  $\text{K}_3\text{MoBr}_6$ ,  $\text{K}_2\text{MoBr}_5$ ,  $\text{Cs}_2\text{MoBr}_5, \text{H}_2\text{O}$ , and an impure rubidium salt of the last type.

*Preparation of Tripotassium Molybdenum Hexabromide.*—200 C.c. of the bromide solution containing trivalent molybdenum, to which was added a saturated aqueous solution of 10 g. of potassium bromide, were concentrated at 65–70° under diminished pressure to about 100 c.c. Air-free alcohol was then admitted to the flask, and the excess of potassium bromide precipitated. After filtration in an atmosphere of carbon dioxide, the filtrate was concentrated to 40 c.c. On addition of absolute alcohol a crystalline, light red solid was obtained which was filtered off and dried (Found: Mo, 13.9; Br, 69.0; K, 16.9.  $\text{K}_3\text{MoBr}_6$  requires Mo, 13.9; Br, 69.2; K, 16.9%). A valency determination showed the molybdenum in this salt to be trivalent.

*Preparation of Dipotassium Molybdenum Pentabromide.*—100 C.c. of the solution containing trivalent molybdenum and 20 c.c. of potassium bromide solution (containing 1.5 g.) were placed in an air-free flask and concentrated at 65–70° under diminished pressure until nearly dry. At this stage, air-free alcohol was admitted and a crystalline, brick-red salt separated which, after filtration and drying in an evacuated desiccator, was shown to contain trivalent molybdenum (Found: Mo, 16.7; Br, 69.5; K, 13.8.  $\text{K}_2\text{MoBr}_5$  requires Mo, 16.7; Br, 69.6; K, 13.6%).

This salt is obviously of the same type as the ammonium salt first obtained by Rosenheim and Braun (*loc. cit.*) and later by Foerster and Fricke (*Z. angew. Chem.*, 1921, **36**, 2, 458). The former investigators formulated the dark garnet-red crystals as  $(\text{NH}_4)_2\text{MoBr}_5, 2\text{H}_2\text{O}$ , whilst Foerster and Fricke considered them to be  $(\text{NH}_4)_2[\text{MoBr}_5, \text{H}_2\text{O}]$ . By double decomposition with caesium bromide a solution of the potassium salt yielded the very insoluble  $\text{Cs}_2\text{MoBr}_5, \text{H}_2\text{O}$  (Found: Mo, 12.3; Mo : Br = 1 : 5. Calc.: Mo, 12.3%).

A rubidium salt was prepared by a similar method to that used for the potassium derivative, but it could not be obtained pure.

*Properties of the Complex Salts.*

All these soluble complex salts give deep red solutions with water, in which both potassium salts are very soluble, the rubidium salt is sparingly soluble, and the caesium compound insoluble. The aqueous solutions gradually turn brown, then turbid, and finally yield a dark brown precipitate. This decomposition is accelerated by warming. The salts reduce copper sulphate solution to cuprous bromide, whilst silver nitrate solution is reduced to the metal.

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