CXLVI.—*Molybdenyl Salts and the Co-ordination Number of Oxygen.*

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ACCORDING to the acid concentration, red or green solutions containing tervalent molybdenum are produced by the electrolytic reduction of molybdenum trioxide in hydrochloric acid. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 173) suggested that the appearance of the green colour might be due to the formation of small masses of molybdenum dichloride which had not been detected chemically, and that in the red solutions bivalent molybdenum was not produced. The existence of two differently coloured solutions of chromic chloride is well known. Peligot (*Compt. rend.*, 1844, **19**, 783; *Ann. Chim. Phys.*, 1844, **12**, 537) first succeeded in obtaining green crystals of chromium trichloride, $[Cr(H_2O)_4Cl_2]Cl,2H_2O$, by treating the insoluble violet anhydrous trichloride with water in the presence of a small quantity of chromium dichloride. Attempts to isolate isomeric trichlorides of molybdenum have so far been unsuccessful, however.

Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458) conclude from their measurements of potential, that the existence of bivalent molybdenum in the green solutions is highly improbable. In view of the isolation of the complex salts R_3MoCl_6 and R_2MoCl_5,H_2O by the addition of alkali chlorides to solutions of tervalent molybdenum, these authors consider that the colours and properties of the green and red solutions may be due to the varying concentrations of the ions as determined by the equilibria :

$$[MoCl_6]''' \rightleftharpoons Mo^{\cdots} + 6Cl'; \quad [MoCl_5,H_2O]'' \rightleftharpoons Mo^{\cdots} + 5Cl' + H_2O;$$
$$[Mo,6H_2O]^{\cdots} \rightleftharpoons Mo^{\cdots} + 6H_2O.$$

Nevertheless it is possible to obtain from a green solution of tervalent molybdenum the green oxychloride, $MoOCl,4H_2O$, and from the red solution the brown isomeride, $MoOCl,4H_2O$ (this vol., p. 130). These facts, together with the isolation of the salt $KMoOCl_2,3H_2O$ (this vol., p. 512), furnish strong evidence in favour of the presence of the molybdenyl radical in all solutions of tervalent molybdenum, in accordance with the scheme

$$MoCl_3,xH_2O \rightleftharpoons [MoOCl,4H_2O] + 2HCl + (x - 5)H_2O;$$
$$[MoOCl,4H_2O] + H_2O \rightleftharpoons [MoO,5H_2O]^{\cdot} + Cl'.$$

Further proof of the existence of the molybdenyl radical is now received from the preparation of a series of its salts. In addition, the occurrence of a trichloride in the red solution, as postulated by Chilesotti, is confirmed by the isolation of the first *hydrated molybdenum trichloride*, the dark red crystalline substance $MoCl_3,3H_2O$. Previously, the only known trichloride was the insoluble solid prepared by dry methods.

EXPERIMENTAL.

Preparation of Hydrated Molybdenum Trichloride.—A solution of molybdenum trioxide (10 g.) in 400 c.c. of hydrochloric acid (*d* 1·16) was heated on a water-bath for some hours, made up to 600 c.c., and electrolysed in a diaphragm cell with smooth platinum electrodes (J., 1923, **123**, 969) until the cathode solution was red. This solution was then evaporated to dryness at 70—80° under diminished pressure in an air-free flask. The residue was a copper-coloured, crystalline substance, which undoubtedly contained portions of hydrolysed material, and on analysis gave values of the order 1 : 2·5 for the ratio Mo : Cl. 400 C.c. of pure ether, cooled in a freezing mixture of ice and salt, and saturated with dry hydrogen chloride, were drawn into the flask by releasing the vacuum, and the red solution obtained was evaporated to dryness under diminished pressure, whereupon a dark red, crystalline substance separated. In order to ensure the complete conversion of any hydrolysed salt into the normal chloride, this operation was repeated. The substance finally obtained was quickly transferred in an atmosphere of dry carbon dioxide to a desiccator containing phosphoric oxide. The product was extremely hygroscopic, and exceptional precautions had to be taken to exclude moisture.

Analysis.—The molybdenum was precipitated as sulphide and ignited to trioxide (J., 1924, **125**, 1911). The chloride in the filtrate and washings was estimated as silver chloride (Found : Mo, 36·44, 36·48; Cl, 40·77, 41·15; Mo : Cl = 1 : 3·03; 1 : 3·05. $MoCl_3,3H_2O$ requires Mo, 37·44; Cl, 41·49%).

Valency of the Compound.—This was determined as for the oxychloride (*loc. cit.*). One g. of the solid, on direct titration with standard permanganate, required 127·2 c.c. A similar solution, oxidised and passed through the reductor, required 130·2 c.c. The molybdenum is therefore tervalent.

Properties and Reactions of Molybdenum Trichloride.—The substance separates in dark, copper-coloured crystals, very soluble in water, acetone, or cold absolute alcohol, giving intensely red solutions. It rapidly reduces solutions of copper, silver, or mercuric salts. Sodium and ammonium hydroxides give black precipitates, soluble in acids; these are probably the trihydroxide. If potassium chloride is added to a solution of the substance in alcohol, the pink complex chloride, K_2MoCl_5,H_2O, is deposited on warming.

Salts containing the Molybdenyl Radical.—Molybdenyl bromide, like the chloride, has been obtained from a concentrated solution containing tervalent molybdenum by precipitation in acetone (J., 1926, 1592). Practical difficulties precluded the isolation of the corresponding fluoride in a similar way, but it has now been obtained by double decomposition of the oxychloride with ammonium fluoride in an air-free aqueous solution. *Molybdenyl fluoride* was deposited as a buff-coloured, insoluble precipitate the analysis of which agreed with the formula $MoOF,3{\cdot}5H_2O$. The properties of three out of the four possible molybdenyl halides of the general formula $[MoOR,4H_2O]$ can now be compared, and a close resemblance to the alkaline-earth halides is indicated inasmuch as the solubility of the molybdenyl halides increases with increase in the atomic weight of the halogen atom. Ease of hydrolysis accords with a similar generalisation.

Analysis of Molybdenyl Monofluoride.—The oxyfluoride, suspended in water, was brought into solution by the addition of sodium peroxide. In order to exclude ammonium salts, which have a solvent action on calcium fluoride, the alkaline solution was saturated with hydrogen sulphide, ruby-red thiomolybdate being formed. This was decomposed with dilute hydrochloric acid, and the precipitated sulphide was filtered off, ignited, and weighed as trioxide. The fluoride in the filtrate and washings was estimated as calcium fluoride (Found: Mo, 49·98, 49·60; F, 9·62, 9·45; Mo : F = 1 : 0·97, 1 : 0·96. $MoOF,3\cdot5H_2O$ requires Mo, 49·49%).

The univalent molybdenyl radical, MoO, appears to persist in aqueous solution. The oxygen atom seems to be firmly attached to the molybdenum nucleus and the whole behaves like a univalent metal. This conception is supported by the existence of other insoluble molybdenyl salts, such as the benzoate, phosphate, salicylate (this vol., p. 130), and tartrate.

Preparation of Molybdenyl Derivatives.—By double decomposition of the theoretical amounts of molybdenyl monochloride and the alkali salts of benzoic, tartaric, and phosphoric acids, respectively, in air-free aqueous solution, reactions occur in accordance with the equations :

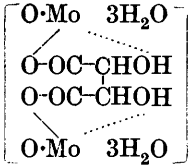
(1) $MoOCl + C_6H_5\cdot CO_2Na = C_6H_5\cdot CO_2\cdot MoO + NaCl.$
(2) $2MoOCl + NaKC_4H_4O_6 = (MoO)_2C_4H_4O_6 + NaCl + KCl.$
(3) $3MoOCl + Na_2HPO_4 = (MoO)_3PO_4 + 2NaCl + HCl.$

These insoluble molybdenyl salts are all buff-coloured and undergo gradual hydrolysis in contact with water. They are best purified by washing with dilute solutions of the corresponding acids. Solutions of sodium oxalate and normal sodium citrate also give well-defined, buff precipitates when they are added to a solution of molybdenyl chloride. These precipitates are probably the corresponding molybdenyl salts.

Analysis. In the following analyses, the phosphate was estimated both as magnesium pyrophosphate and as ammonium phosphomolybdate. The percentages of water correspond to the whole of the hydrogen in the compound and not merely to that in the water of crystallisation. The benzoate was found to be tervalent by titration with permanganate solution. Found for $(MoO)_3PO_4,12H_2O$: Mo, 44·45; PO_4, 14·92. Calc. : Mo, 44·51; PO_4, 14·68%. Found for $C_6H_5\cdot CO_2\cdot MoO, 2\cdot5H_2O$: Mo, 33·97; C, 29·95; H_2O, 31·75. Calc. : Mo, 34·53; C, 30·21; $5H_2O$, 32·39%. Found for

$(MoO)_2C_4H_4O_6,6H_2O$: Mo, 40·04; C, 9·96; H_2O, 29·65. Calc.: Mo, 40·00; C, 10·00; $8H_2O$, 30·00%.

These molybdenyl salts can be conveniently symbolised as co-ordination compounds in which the co-ordination number of tervalent molybdenum is six. On using such a formulation for the molybdenyl tartrate, it is seen that the tartrate grouping occupies four co-ordination positions :



The Co-ordination Number of Oxygen.

In dealing with the co-ordination number of multivalent atoms, Werner laid it down that oxygen and other bivalent atoms occupy only one position in the co-ordination sphere. Many examples could be quoted to support this view, but in other cases its acceptance involves assigning to an element an odd co-ordination number in circumstances which appear unlikely. Chromium, well known for the stability of its six-point system, forms salts of the type $[CrOCl_4]R$, in which, on Werner's view, the co-ordination number of chromium must be five. The same co-ordination number would be assigned to the central atom in the compounds $WOCl_4$, $MoOF_4$, $[VOF_4]K_2$, and $[NbOCl_4]C_5H_6N$. Nevertheless, the possibility that oxygen may occupy two positions, and thereby give rise to a co-ordination number of six, should not be overlooked. Electronic theories of valency have clearly demonstrated the essential difference between oxygen atoms occupying one or two positions in the co-ordination sphere. When an oxygen atom is attached to the central atom by a semipolar double bond, it occupies one co-ordination position, and when attached by a double bond, two. The resolution of the amine and phosphine oxides with the configuration $[R_1R_2R_3N \Rightarrow O]$ is explained most readily by supposing that the four units are tetrahedrally distributed round the central nitrogen or phosphorus atom, and that the oxygen bound to the central atom by a semipolar double bond occupies one position. Again, the optical activity associated with the sulphinates and sulphoxides (Phillips, J., 1925, **127**, 2552; Harrison, Kenyon, and Phillips, J., 1926, 2079) is satisfactorily explained by assigning to these substances a configuration $[O \Leftarrow SR_1R_2]$ in which the oxygen occupies one position in the tetrahedral structure.

Whilst the double link (two co-ordination positions) is required to avoid improbable co-ordination numbers in many compounds, such as those previously mentioned, it is especially necessary to explain the behaviour of carbon. If the carbonyl group were $C \overset{\rightarrow}{=} O$, the carbon would be tri-co-ordinated or tervalent. The results of Sugden and his colleagues (J., 1925, **127**, 1525) show, however, that carbon never forms a semipolar link with oxygen. This view is also supported by the conclusion from *X*-ray analysis, that the three oxygen atoms in the CO_3'' ion lie in the same plane with the carbon (W. L. Bragg, *Proc. Roy. Soc.*, 1914, *A*, **89**, 468), because with the tetrahedral model for carbon, the three atoms in $O{=}C{<}^{O}_{O}$ would lie in a plane with the carbon, whereas in $O \overset{\leftarrow}{=} C{<}^{O}_{O}$ they would lie out of a plane as they do in $O \overset{\leftarrow}{=} S{<}^{O}_{O}$. On the basis of the *X*-ray result that the angle between the valencies to any two oxygen atoms in the CO_3'' and NO_3' ions is 120°, whereas that between the two singly-linked atoms might be expected to be 109° 28′, Lowry has assigned (*Chemistry and Industry*, 1927, 78) a trigonal orientation to the oxygen atoms around the central atom of the anion and concludes " that it is clear that van 't Hoff's tetrahedral model of the carbon atom now has a rival." It must, however, be borne in mind that " the tetrahedron representing a carbon atom is approximately regular only when the carbon atom is attached to four atoms of a similar kind " (Ingold, J., 1921, **119**, 306). Thus the tetrahedral angle must be modified in every case where the four linkings are not exactly equivalent, and on the Thorpe–Ingold theory this angle must be increased by the double link to the third oxygen. Moreover, since the two singly-linked oxygen atoms are negatively charged, they must repel each other and give rise to a greater value for the angle between them. It seems doubtful, therefore, whether any modification of van 't Hoff's conception is necessary or justified.

A suitable interpretation of the structure of those molybdenyl salts, such as $[MoOR,3{\cdot}5H_2O]$, whose water content is less than would be anticipated from a co-ordination number of six for the molybdenum, would be to consider these compounds to be the result of the equilibrium

$$H_2O + [MoOR,3H_2O] = [MoOR,4H_2O]$$

where, in one case, the oxygen occupies one position, and in the other, two positions in the co-ordination sphere.

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