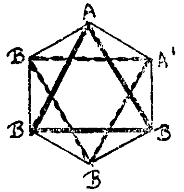
XXII.—*The Isomerism of Molybdenyl Monochloride.*

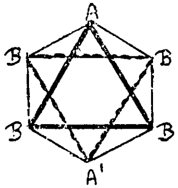
By William Wardlaw and Robert Louis Wormell.

The results of conductivity measurements have shown that a wide range of chemical compounds has a co-ordination number of six. In the cases of cobalt, iron, chromium, rhodium, and iridium, of which the derivatives exhibit geometrical isomerism and are capable of resolution into optically active components, it has been proved that the six associating units have an octahedral distribution round the central metallic atom.

Determinations of the ionisation of a number of compounds of tervalent molybdenum have indicated a co-ordination number of six, but so far there is no evidence as to the spatial distribution of the associating units. Three arrangements must be considered—the hexagon, the triangular prism, and the regular octahedron. Either of the first two configurations demands three isomeric forms for the complex $[MAA'B_4]$, but if the units are situated at the vertices of a regular octahedron then only two stereoisomerides are possible, *viz.*, *cis-* and *trans-* :



Cis-.



Trans-.

This important test has been applied to the co-ordination compound $[MoOCl,4H_2O]$, and two isomeric forms have been isolated to which *cis-* and *trans*-configurations have been assigned. This has furnished the first indication that molybdenum can give rise to co-ordination compounds in accordance with Werner's view of their sixfold structure.

EXPERIMENTAL.

Brown Molybdenyl Monochloride.—In a previous communication (J., 1924, **125**, 2370), it was shown that when a solution of molybdenum trioxide in hydrochloric acid is reduced electrolytically to the tervalent condition, concentrated to small bulk, re-electrolysed, and the resulting reddish-brown liquid poured into air-free acetone, a buff-coloured solid separates, the analysis of which corresponds to MoOCl with approximately $4H_2O$. It was later found that, on precipitating the oxychloride from a solution with a molybdenum content only one-fourth of that indicated in our paper (*loc. cit.*), the dried product gave an analysis in close accordance with that demanded by $MoOCl,4H_2O$ (Found: Mo, 44·1; Cl, 16·3; Mo : Cl = 1 : 1. $MoOCl,4H_2O$ requires Mo, 43·7; Cl, 16·2%).

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

G. of $MoOCl,4H_2O$ per 10 g. of water	0·2531	0·1669	0·1682
"Apparent" mol. wt.	191·3	185·6	186·1

The molecular weight for the non-ionised substance $[MoOCl,4H_2O]$ is 219·5. Here, as in the case of many co-ordination compounds, the substance has apparently undergone hydrolysis whereby the

$$[MoOCl,4H_2O] + H_2O = [MoO,5H_2O]Cl = [MoO,5H_2O]^{\cdot} + Cl'.$$

co-ordinated chlorine atom is replaced by a molecule of solvent; this hydrolysis produces a binary electrolyte, the existence of which would influence the molecular-weight determinations in the foregoing manner. This progressive hydrolysis is also shown by the results of conductivity measurements at 1°.

For $v = 4$ litres per mole :

μ	33·7	38·1	39·9	40·8	44·8	46·8	50·8
Time (mins.)	4	8	12	15	43	80	220

For $v = 25$ litres per mole :

μ	33·0	38·9	42·9	45·7	48·2	49·7	51·1	52·3	53·3	65·2
Time (mins.)	2	3	4	5	6	7	8	9	10	40

In more dilute solutions, the rate of hydrolysis increased.

Now, for a binary electrolyte, *e.g.*, potassium chloride, the data at 1° are :

v (litres per mole)	8	16	32
μ	72·2	75·2	77·3

and the fact that the above conductivities alter with time and approach the value for a binary electrolyte, combined with the molecular-weight determinations, indicates that the brown oxychloride is not a binary electrolyte and that it is correctly formulated as the co-ordination compound $[MoOCl,4H_2O]$.

On the assumption that the six associating units are octahedrally distributed round the molybdenum atom, two isomeric oxychlorides should exist corresponding to *cis*- and *trans*-isomerism. The existence of this second molybdenyl chloride seems to be indicated from the fact that a solution of tervalent molybdenum in hydrochloric acid may be either reddish-brown or green, depending on the acid concentration. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 146, 173) prepared the former solution by electrolytic reduction of molybdenum trioxide dissolved in $9N$-hydrochloric acid, and the green solution was obtained when the acid used was 4—$2{\cdot}7N$. Whilst the red solutions, having a content of 3·67% of molybdenum trioxide in the original solution and after complete reduction to the Mo^{III} stage, never exceed a static potential of $E_h = +0{\cdot}12$ volt at 24—26°, and are stable even in air, the green solutions under similar conditions attain potentials of $-0{\cdot}18$ volt and are readily oxidised by air and water—especially in contact with platinum—with evolution of hydrogen. A further difference between the two solutions was found by Bredig and Michel (*Z. physikal. Chem.*, 1922, **100**, 136), *viz.*, that the green solution reduces perchloric acid 2000 times as quickly as the red. It was anticipated, therefore, that a green molybdenyl chloride would be isolated from the green solution of tervalent molybdenum and that it would be characterised by much greater reactivity than its brown isomeride. Such an oxychloride was obtained as follows.

Green Molybdenyl Monochloride.—A solution of molybdenum trioxide (60 g.) in 390 c.c. of hydrochloric acid (*d* 1·16) was diluted to 500 c.c., electrolysed for 4 hours in a diaphragm cell and concentrated at 50° under diminished pressure to 250 c.c. This concentrated solution, in which the molybdenum was quinquevalent, was then re-electrolysed. On prolonged electrolysis, the solution became green and the concentration of "free" acid diminished. At this stage, a portion of the solution, on being poured into acetone, gave a bluish-green precipitate, a typical hydrolysed product. The cell was now cooled in ice, and the cathode liquid forced by pressure of carbon dioxide into an equal volume of ice-cold 10*N*-hydrochloric acid. The olive-green solution thus produced was poured into air-free acetone and a green solid then separated in excellent yield. It was filtered off, washed with acetone, and dried in a vacuum desiccator. All these operations were performed in an atmosphere of carbon dioxide, air being rigidly excluded.

The valency of the molybdenum in this compound was determined as in the case of the brown oxychloride, and was found to be three.

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, 46·2, 45·8; Cl, 17·2, 17·0; Mo : Cl = 1 : 1·01, 1 : 1·01. $MoOCl,3H_2O$ requires Mo, 47·6; $MoOCl,4H_2O$ requires Mo, 43·7%). As the solid had been dried in an evacuated desiccator, it is probable that its normal composition is $MoOCl,4H_2O$. These results show a close resemblance to those recorded (J., 1924, **125**, 2370) for the brown oxychloride isolated under similar conditions.

Properties and Reactions of Green Molybdenyl Chloride.—The freshly-precipitated solid is green, but on drying it becomes greyish-green. On exposure to the air, it darkens in colour and hydrolyses. It is more readily soluble in water and in concentrated hydrochloric acid than its brown isomeride, but is insoluble in alcohol. It has similar reducing properties to the brown oxychloride, but is much more reactive.

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

G. of $MoOCl,4H_2O$ per 10 g. of water ...	0·9774	1·0146	0·2302
"Apparent" mol. wt.	191·4	196·5	161·7

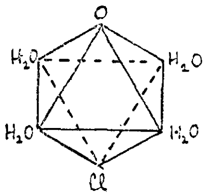
If the green solid were an ionisation isomeride of the brown oxychloride, it would be formulated as $[MoO]Cl,4H_2O$, in which case its apparent molecular weight would be 109·75 for complete ionisation. The above results indicate that green molybdenyl chloride should be formulated as $[MoOCl,4H_2O]$ and that it is much more rapidly hydrolysed than its isomeride. The results of conductivity measurements are open to the objection that during their determination the green solution undergoes slow oxidation by decomposition of the water, in the presence of the electrodes, with evolution of hydrogen. Nevertheless, in spite of the possibility of this side-reaction, the results obtained afford confirmatory evidence that the green solid has the co-ordination formula $[MoOCl,4H_2O]$:

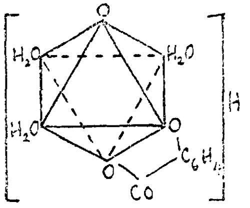
At 1° for $v = 5·7$ litres per mole :

μ	42·77	48·9	50·6	51·9	53·1	53·6
Time (mins.)	1	3	4	5	6	7

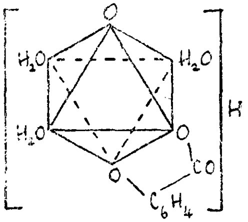
On the other hand, with concentrated solutions such as $v = 0·5$ litre per mole, the value of μ after one hour was only 19·7. These and other determinations indicated that by continuous hydrolysis a binary electrolyte was being formed, but that initially the compound was a non-electrolyte.

The Stereoisomerism of the Oxychlorides.—The existence of two isomeric co-ordination compounds, $MoOCl,4H_2O$, having been established, it is necessary now to assign to them *cis*- and *trans*-configurations. This has been made possible by a study of reactions in which the salicylate group has functioned as an unsymmetrical chelate group. Theoretical considerations indicate that by the interaction of monosodium salicylate, $NaH[O·C_6H_4·CO_2]$, and the *trans*-molybdenyl chloride, two products may be produced :



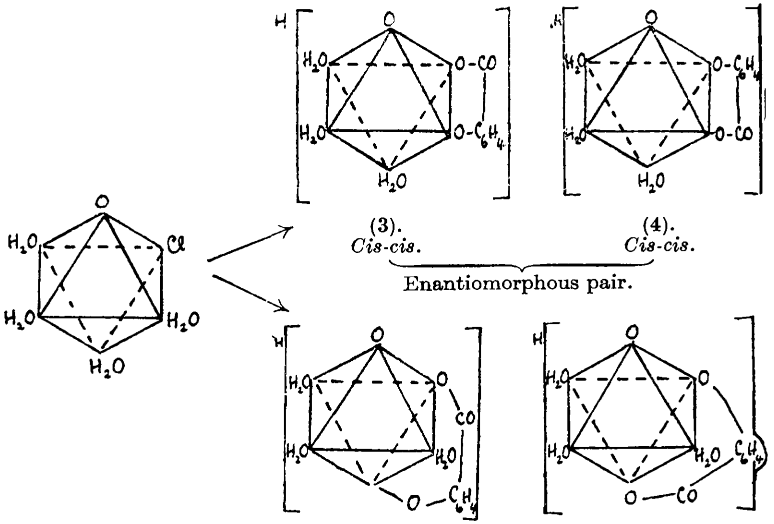


(1).
Trans-cis.



(2).
Cis-trans.

By interaction of monosodium salicylate and *cis*-molybdenyl chloride, on the other hand, four products are theoretically possible, of which two (Nos. 3 and 4) are enantiomorphs :



(3).
Cis-cis.

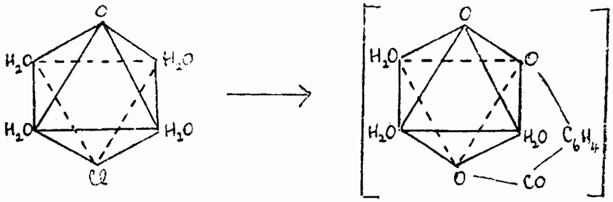
(4).
Cis-cis.

Enantiomorphous pair.

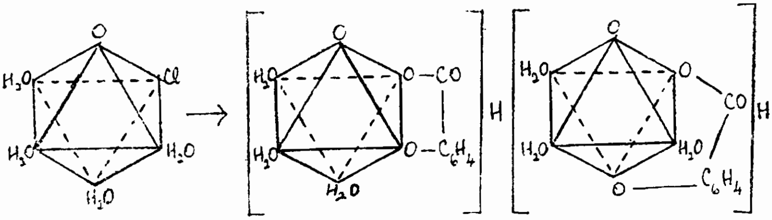
(5).
Cis-trans.

(6).
Trans-cis.

However, these different isomerides would be produced only on the assumption that the oxygen of the phenolic hydroxyl group and that of the carboxyl group equally well replace the chlorine unit in the co-ordination sphere. Experiment shows that this is not so. When the green oxychloride reacts with monosodium salicylate a precipitation of green molybdenyl salicylate takes place. This should theoretically be a mixture of isomerides (1) and (2). The interaction of the brown oxychloride and monosodium salicylate results in the formation of an insoluble brick-red substance, together with an intensely red-coloured liquid, which continuously deposits the insoluble product on keeping. Since (1) and (2) are identical with (5) and (6), it would be expected that the insoluble products from the green and brown oxychlorides would be identical, provided that products (1) and (2) as well as (5) and (6) were precipitated in equal proportions. The fact that these insoluble substances are clearly different in colour indicates a predominating replacement of the chlorine atom by either the carboxylic oxygen or the phenolic oxygen. To determine which was the more probable alternative, reactions were carried out with aqueous solutions of brown molybdenyl chloride and sodium phenoxide and sodium benzoate, respectively. In the case of the sodium phenoxide, molybdenum hydroxide was precipitated, whereas with the benzoate a well-characterised, insoluble derivative was obtained whose analysis corresponds to molybdenyl benzoate. These results indicate that in the case of reactions with sodium salicylate and compounds of tervalent molybdenum the carboxylic oxygen replaces the co-ordinated chlorine atom and that the reaction itself is dependent on the presence of the carboxyl group. Whether this conclusion be accepted or not, there is no doubt, from the nature of the colours of the products, that the chlorine atom is replaced almost exclusively by either the phenolic or the carboxylic oxygen, and so the proof of *cis-* and *trans*-isomerism reduces itself to demonstrating that one isomeride, the *trans-*, should yield one product by reaction with monosodium salicylate, and that the other isomeride, the *cis-*, should give rise to two products, neither identical with the foregoing. On the assumption that the carboxylic oxygen replaces the chlorine atom, the following scheme will obtain :



(a) *Trans-cis.*



(b) *Cis-cis.* (c) *Cis-trans.*

By reaction of the green molybdenyl chloride and monosodium salicylate, one insoluble green molybdenyl salicylate has been obtained, the configuration of which must be in accordance with (a). From the brown molybdenyl chloride there is evidence of one soluble isomeride (b) and one brick-red insoluble isomeride (c), which is actually distinct from (a), as anticipated on theoretical grounds. A *cis*-configuration has therefore been assigned to the brown oxychloride, and a *trans-* to the green oxychloride.

Reaction between Monosodium Salicylate and Brown Molybdenyl Chloride.—Equimolecular aqueous solutions of monosodium salicylate and molybdenyl chloride were mixed together. With highly concentrated solutions, a brick-red molybdenyl salicylate separated in a few minutes and an intensely red supernatant liquid was produced. From more dilute solutions, the solid was precipitated only after a longer period. In every case, however, the supernatant liquid was intensely red. On keeping, the red liquid continuously deposited the insoluble product, a process which was accelerated by warming. Undoubtedly two salicylates had been produced. One was insoluble in water whilst the other was readily soluble, producing a red solution. By intramolecular changes the soluble product was continuously changing to the insoluble isomeride.

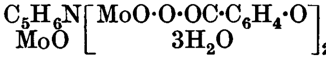
Insoluble Molybdenyl Salicylate.—This solid was obtained as above, and, after filtration and washing free from the red, supernatant liquid by means of air-free water, it was dried in a desiccator over calcium chloride. The behaviour of the compound during the drying process is noteworthy. When the brick-red solid is dried out of contact with air, it darkens and ultimately yields the brown compound $[MoO\cdot O\cdot C_6H_4\cdot CO\cdot O,2H_2O]H$. It is impossible to isolate the brick-red substance in a dry condition because of these changes, but it seems reasonable to assume that they are associated with a decreasing content of water. The brown solid is practically insoluble in water, but when freshly prepared it is soluble in alcohol and in acetone.

The acidic nature of the compound is indicated by its ready solubility in ammonia and in dilute solutions of sodium or potassium hydroxide. After a time, the solid loses its ability to dissolve in organic solvents and becomes less soluble in ammonia.

Analysis.—The molybdenum was determined both by ignition of the compound to molybdenum trioxide and by precipitation as sulphide and ignition to the trioxide. Combustion of the solid gave water derived from both the hydrogen and the water of constitution (Found: Mo, 33·45; C, 29·2; H_2O, 28·3.

$$[MoO\cdot O\cdot C_6H_4\cdot CO\cdot O,2H_2O]H$$

requires Mo, 33·7; C, 29·5; $4\cdot5H_2O$ [from 9H], 28·4%). Analyses of other samples have indicated that the water content may vary between 2—$2\cdot5H_2O$.

Soluble Molybdenyl Salicylate.—Numerous attempts have been made to isolate a solid substance from the red, supernatant liquid formed in the interaction of the brown chloride and the sodium salicylate. Concentration of the liquid resulted in the formation of large quantities of the brown, insoluble isomeride, and the use of organic liquids neither precipitated nor extracted any product. The addition of pyridine, however, caused an immediate precipitation of a reddish-brown substance which, after washing and drying, proved to have the formula  $\begin{matrix}C_5H_6N\\MoO\end{matrix}\left[\begin{matrix}MoO\cdot O\cdot OC\cdot C_6H_4\cdot O\\3H_2O\end{matrix}\right]_2 H_2O$, which requires Mo, 35·4; C, 28·0; N, 1·7; $14H_2O$ (from 28H), 31·0 (Found: Mo, 35·2; C, 28·3; N, 1·6; H_2O, 30·0%).

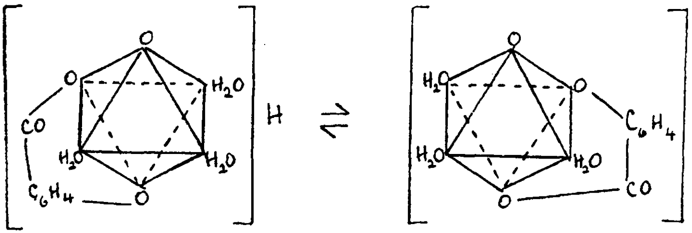
The isolation of this substance indicates the existence of the following equilibrium in the solution :

$$2[MoO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O]H \rightleftharpoons MoO[MoO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O] + OH{\cdot}C_6H_4{\cdot}CO_2H.$$

The addition of the pyridine disturbs the reaction in such a way as to form an increasing amount of $MoO[MoO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O]$, which is precipitated simultaneously with the pyridine salt of the soluble molybdenyl salicylate. Thus, although the molybdenyl salicylate has not been isolated, the results of the reaction with pyridine are strong evidence in favour of its existence and of its acidic character.

Reaction between Monosodium Salicylate and Green Molybdenyl Chloride.—On mixing an aqueous solution of sodium salicylate with a freshly-prepared, aqueous solution of green molybdenyl chloride, air being rigidly excluded, a pale green product was precipitated whilst the supernatant liquor was nearly colourless. The solid was separated and dried; a colour change from pale green to brown resulted, and the final product was almost identical in colour and properties with the dried insoluble molybdenyl salicylate prepared from the brown isomeric oxychloride. Analysis showed that the water content of the solid varied from 2—2·5H_2O (Found: Mo, 32·4; C, 28·2; H_2O, 29·55. $[O{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}MoO,2{\cdot}5H_2O]H$ requires Mo, 32·65; C, 28·6; $5H_2O$ [from 10H], 30·6%).

A point of interest in connexion with the oxychlorides is that both the insoluble green molybdenyl salicylate and the insoluble brick-red isomeride give the same brown product on drying. Two explanations may be suggested. (1) This change of colour might be due to an intramolecular reaction whereby the same mixture of the isomerides (a) and (c) would result in both cases; there is the possibility that a brown product would result from a mixture of red and green substances. (2) An alternative view is that, by the loss of one molecule of water, the oxygen can occupy two positions in the co-ordination sphere—the analysis of the brown product indicates a water-content of 2—2·5H_2O—and it can readily be shown that by such a rearrangement the structures (c) and (a) become identical.



(c) *Cis-trans* (red).

(a) *Trans-cis* (green).

This question of the co-ordination number of oxygen will be dealt with in a later communication.

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