CCCXLVI.—*Complex Bromides of Quinquevalent Molybdenum.*

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In previous communications it has been shown that one of the most satisfactory methods for the preparation of co-ordination compounds of molybdenum with valencies of 3, 4, or 5 is to utilise the important observation first made by Chilesotti (*Z. Elektrochem.*, 1906, **12**, 173), that by electrolytic reduction of molybdenum trioxide dissolved in hydrochloric or sulphuric acid of appropriate concentration, a solution of quinquevalent molybdenum results if a platinised platinum cathode is employed; whereas with a cathode of polished platinum, reduction to the tervalent state is obtained.

Therefore, one might anticipate that the best method for the preparation of salts of the type $R_2[MoOBr_5]$ and $R[MoOBr_4]$ would be electrolytic reduction of a solution of molybdenum trioxide in hydrobromic acid employing a platinised platinum cathode, followed by the addition of the appropriate bromide to the resulting solution of quinquevalent molybdenum. Reference to the literature discloses that this method has never been employed, but that owing to the use of inferior and untrustworthy methods, data relating to the colour of the complex salts and to their stabilities are conflicting.

The complex bromides are important, in that they form one of the series of co-ordination compounds of the general formula $R_2[MoOX_5]$. The chlorides are green crystalline substances, stable when dry but undergoing hydrolysis and extensive ionisation in aqueous solution; by treatment with thiocyanic acid, they yield the black salts $R_2[MoO(CNS)_5]$, which are almost insoluble in water but readily soluble in alcohol. It is now shown that equally remarkable changes in colour and stability occur when bromine atoms are substituted for chlorine atoms. The pentabromides produced are brown to yellow hygroscopic salts, more sensitive to oxidation than the chlorides, and rapidly hydrolysed by water. Physicochemical examination of solutions of the bromides shows that the scheme of ionisation and hydrolysis previously outlined (J., 1927, 2151) for the complex chlorides seems equally applicable to the bromides.

The possibility that the chlorides and bromides are double salts $2RX,MoOX_3$, rather than co-ordination compounds $R_2[MoOX_5]$, has also been considered. The complex bromides (where $R = C_5H_6N$, C_9H_8N, or NH_4) in absolute alcohol, like the chlorides [$R = C_9H_8N$, $(C_2H_5)_2NH_2$], give an osmotic factor of *ca.* 3. In all cases, the alcoholic solutions retain the characteristic colours of the salts themselves, but in aqueous solution quite different colours are obtained. This fact seems to indicate that in alcohol decomposition does not take place. If the substances are double salts of the type indicated above, the osmotic factor should be *ca.* 1; but if they are ionised co-ordination compounds of the formulæ $R_2[MoOX_5]$ an osmotic factor of 3 should result. Although results in alcoholic solution require cautious interpretation (compare Turner, J., 1914, **105**, 1751, 1777, 1786), the experimental data here obtained suggest that the co-ordination formulæ proposed are fully justified.

It is interesting to note that whereas chlorides of the type $R[MoOCl_4]$ are green, like the pentachlorides, the corresponding tetrabromides $R[MoOBr_4]$ are red, quite unlike the pentabromides. In the case of the thiocyanates this type of complex is at present unknown, the only known class, apart from the pentathiocyanates, being the insoluble salts $R_2[MoO_2(CNS)_3]$.

EXPERIMENTAL.

Weinland and Knoll (*Z. anorg. Chem.*, 1905, **44**, 81) first prepared bromides of quinquevalent molybdenum by passing hydrogen bromide over molybdic acid at 200—300°. The product was dissolved in hydrobromic acid (40%), and the dark brown liquid diluted, and warmed; it became dark yellow, and, it was claimed, contained molybdenum exclusively in the quinquevalent condition. Following the successful method of electrolytic reduction used for the preparation of the corresponding chlorides (J., 1927, 2146), molybdenum trioxide (50 g.) was refluxed with hydrobromic acid (300 c.c.; *d* 1·5) for about two hours until completely dissolved. Some reduction of the molybdenum occurred and the yellow solution obtained was utilised in the following preparations.

Salts of the Type $R_2[MoOBr_5]$.

In the literature the isolation of a number of pentabromides is recorded, and by use of the new electrolytic reduction method, the existence of salts $R_2[MoOBr_5]$, where $R = K$, Rb, NH_4, C_5H_6N, C_9H_8N, has been confirmed. On the other hand, it is doubtful whether the olive-green magnesium salt, $Mg[MoOBr_5],7H_2O$, previously recorded is a pure substance: it seems highly probable that the green colour is due to oxidation, for in other cases the initially red salts rapidly become green on exposure to the atmosphere.

In a number of cases it is possible to isolate either the penta- or the tetra-bromide. Weinland and Knoll demonstrated that the use of a high concentration of pyridinium or quinolinium bromide yields pentabromides $R_2[MoOBr_5]$, whilst lower concentrations favour the formation of the tetrabromides $R[MoOBr_4]$. Although this principle is applicable in the case of the salts mentioned above, and has been utilised in the preparations which follow, it is not of general application. Other factors, such as solubility in the hydrobromic acid itself, appear to determine the type of salt formed in other cases.

Diammonium Molybdenyl Pentabromide.—200 C.c. of the prepared molybdenum trioxide solution were reduced electrolytically in a diaphragm cell with a platinised platinum cathode, 5 cm. square, and a polished platinum anode. The anode chamber contained a small amount of molybdenum trioxide solution mixed with hydrobromic acid (*d* 1·5), and a current of 2·5 amp. was employed for about 50 minutes. Reduction to the quinquevalent condition was indicated when the cathode solution gave an emerald-green colour with concentrated hydrochloric acid. At this stage the reduced cathode solution was transferred in a current of nitrogen to an air-free flask (fitted with ground-glass joints) which contained ammonium bromide (11 g.), and was concentrated under diminished pressure to 50 c.c. The light brown crystals which separated were collected on a sintered-glass filter in a nitrogen atmosphere, washed with hydrobromic acid (*d* 1·7), and allowed to drain. The crystals were dried in a vacuum over potassium hydroxide and phosphoric oxide. By the addition of ammonium bromide (3 g.) to the filtrate, a further crop of crystals was obtained on concentration to 30 c.c., giving a combined yield of 21 g.

To exclude air during the preparation of the complex salts, the special precautions described above were taken throughout the experimental work, otherwise oxidised products resulted.

Analysis. The molybdenum was precipitated as sulphide, ignited, and weighed as trioxide (J., 1924, **125**, 1911), the bromide in the filtrate and washings being estimated as silver bromide. The ammonia was determined by the distillation method, the ammoniacal distillate being titrated continuously against a standard acid and bromophenol-blue being used as indicator. To obtain satisfactory results, these complex bromides must be rapidly transferred from the vacuum desiccator (opened in a current of nitrogen) to a stoppered weighing bottle. To avoid loss of hydrogen bromide, the solid was rapidly dissolved in water made slightly ammoniacal {Found: Mo, 17·3; Br, 72·6; NH_4, 6·4. Calc. for $(NH_4)_2[MoOBr_5]$: Mo, 17·5; Br, 73·0; NH_4, 6·6%}. In all probability a trace of moisture was present in this very hygroscopic salt.

Dipotassium Molybdenyl Pentabromide.—When 100 c.c. of the reduced molybdenum solution containing potassium bromide (5·5 g.) were concentrated to 40 c.c. under diminished pressure with the usual precautions, dark brown needles separated which were washed with hydrobromic acid (*d* 1·7) and dried in a vacuum over sodium hydroxide and phosphoric oxide. They proved to be a mixture of the required salt and potassium bromide, and the latter was removed by prolonged washing with hydrobromic acid (*d* 1·7). The complex bromide remaining was a pale yellow solid (Found: Mo, 15·2; Br, 63·5; K, 12·4. Calc. for $K_2[MoOBr_5],2H_2O$: Mo, 15·3; Br, 63·9; K, 12·5%). The molybdenum content of the salt was unaltered after keeping in a vacuum desiccator for one week.

Dirubidium Molybdenyl Pentabromide.—For the preparation of this salt 50 c.c. of the reduced molybdenum solution, to which rubidium bromide (2·75 g.) had been added, were concentrated to 20 c.c. and the flask was cooled in ice. The yellow solid which separated was freed from alkali bromide and dried as before (Found: Mo, 14·0; Br, 58·6; Rb, 25·1. Calc. for $Rb_2[MoOBr_5]$: Mo, 14·1; Br, 58·6; Rb, 25·0%). The rubidium salt previously prepared by Weinland and Knoll (*loc. cit.*) varied in colour, some samples being red and others yellowish-green, and their analytical figures showed appreciable variations.

Dipyridinium Molybdenyl Pentabromide.—The preparation of this compound in a pure state is difficult, owing to the ease with which it reverts to the red tetrabromide, even in the presence of concentrated hydrobromic acid. It was isolated from the mother-liquor obtained in the preparation of the tetrabromide. On standing over-night, there was deposited from this liquor a mass of yellowish-green crystals, which were filtered off in a nitrogen atmosphere and drained well without being washed. After drying in a vacuum over sodium hydroxide and phosphoric oxide, the product gave Br : Mo = 4·90 : 1, indicating that a small amount of tetrabromide was present as impurity. The pure pentabromide was only isolated by carefully readjusting the proportion of pyridinium bromide to molybdenum. This was attained by dissolving the impure bromide (24 g.) in the smallest volume of boiling hydrobromic acid (*d* 1·5), and finally adding 400 c.c. of a reduced solution of molybdenum trioxide (22·5 g.) in acid of the same concentration. From this solution, on boiling, yellowish-green needles separated, which were filtered off and drained well without being washed, and dried in a vacuum in the usual way (Found : Mo, 14·3; Br, 59·4; N, 4·2; C, 17·8; H, 2·1. Calc. for $(C_5H_6N)_2[MoOBr_5]$: Mo, 14·3; Br, 59·5; N, 4·2; C, 17·9; H, 1·8%); they were rapidly oxidised to a green material on exposure to the air. Both Weinland and Knoll (*loc. cit.*) and Rosenheim and Koss (*Z. anorg. Chem.*, 1906, **49**, 148) describe the preparation of a green pyridinium salt. The latter investigators consider their product to be the hydrated compound $(C_5H_5N)_2[H_2Mo(OH)_2Br_5,2H_2O]$, but their analytical figures are unsatisfactory. Weinland and Knoll quote widely differing analytical figures for various samples of the pyridinium salt which they obtained as flat green needles. The difference in colour between the product now described and that of previous workers may be due either to the presence of water of crystallisation or to oxidation.

Diquinolinium Molybdenyl Pentabromide.—150 C.c. of the solution containing quinquevalent molybdenum were concentrated under reduced pressure to 80 c.c. This hot solution was added to a boiling solution of quinoline (40 g.) in 100 c.c. of hydrobromic acid (*d* 1·5). Golden-brown crystals separated which were thoroughly drained by suction and dried as previously described. The compound was fairly stable in the air {Found : Mo, 12·4; Br, 51·5; N, 3·6; C, 27·9; H, 2·1. Calc. for $(C_9H_8N)_2[MoOBr_5]$: Mo, 12·4; Br, 51·8; N, 3·6; C, 28·0; H, 2·1%}. Weinland and Knoll (*loc. cit.*) first isolated this pentabromide in the form of olive-green needles, and their analyses indicated that the salt was a monohydrate. Rosenheim and Koss (*loc. cit.*), however, prepared the bromide as reddish-brown needles, although the analytical figures were almost identical with those of Weinland and Knoll. It appears highly probable that the green colour was the result of oxidation.

Salts of the Type $R[MoOBr_4]$.

Although a number of salts of the type $R[MoOBr_4]$ have been isolated, only two examples of the corresponding chlorides are known, *viz.*, $R[MoOCl_4,H_2O]$, where $R = (CH_3)_3NH$ and $(CH_3)_4N$. The degree of hydration of the tetrabromides is variously described. The existence of the red $Li[MoOBr_4,H_2O],3H_2O$ and the red $C_5H_6N[MoOBr_4]$ has been confirmed, and a red $C_9H_8N[MoOBr_4]$ has been isolated in the anhydrous condition. This salt in the hydrated condition is also described as red. The literature contains references to the existence of a red calcium salt $Ca[MoOBr_4]_2,7H_2O$, but numerous experiments have failed to give a product free from excess of calcium bromide. The existence of so many red salts, in both the anhydrous and the hydrated condition, made it questionable whether the potassium salt $K[MoOBr_4],2H_2O$ was correctly described as olive-green prisms. Many experiments indicated that a salt of this approximate composition can be isolated, although it is difficult to separate it completely from associated potassium bromide. In no case was an olive-green product obtained, but always a brown substance. The green colour reported in the case of the potassium salt is probably due to oxidation.

Monolithium Molybdenyl Tetrabromide.—A solution of quinquevalent molybdenum (7·7 g.) containing lithium bromide (3·5 g.) was concentrated under diminished pressure to 35 c.c., the flask cooled in ice, and the separated solid washed with hydrobromic acid (*d* 1·7). After drying over sodium hydroxide and phosphoric oxide in a vacuum, a red, moderately hygroscopic substance resulted (Found: Mo, 18·9; Br, 62·5; Li, 1·4. Calc. for $Li[MoOBr_4,H_2O],3H_2O$: Mo, 18·8; Br, 62·6; Li, 1·4%).

Monopyridinium Molybdenyl Tetrabromide.—200 C.c. of a solution of quinquevalent molybdenum (22 g.) in hydrobromic acid was concentrated to 50 c.c., and to the hot solution was added pyridine (35 g.) previously dissolved in a slight excess of hydrobromic acid. The copious yellowish-green precipitate which separated consisted of a mixture of the tetra- and the penta-bromide, the mother-liquor being utilised for the preparation of the latter. The precipitate was twice recrystallised from hydrobromic acid (*d* 1·5), washed with similar acid, and dried in a vacuum as usual. Red, somewhat hygroscopic needles resulted (Found: Mo, 18·7; Br, 62·4; N, 2·7; C, 11·7; H, 1·2. Calc. for $C_5H_6N[MoOBr_4]$:

Mo, 18·8; Br, 62·5; N, 2·7; C, 11·7; H, 1·2%). This salt sublimes with decomposition.

Monoquinolinium Molybdenyl Tetrabromide.—Quinoline (18 g.) in a slight excess of boiling hydrobromic acid was added drop by drop with continuous stirring to a concentrated solution (80 c.c.) of quinquevalent molybdenum, obtained from 200 c.c. of the original solution. The orange needles which separated were washed with hydrobromic acid (*d* 1·5) and recrystallised from the same acid; on being dried in the usual way they changed from orange to bright pink, and were then very hygroscopic (Found : Mo, 17·1; Br, 56·9; N, 2·5; C, 19·1; H, 1·5. Calc. for $C_9H_8N[MoOBr_4]$: Mo, 17·1; Br, 56·9; N, 2·5; C, 19·2; H, 1·4%).

Physico-chemical Measurements.

In a previous communication (J., 1927, 2149) it was shown that aqueous solutions of the complex chlorides $R_2[MoOCl_5]$ varied in colour from brown to yellow and it was impossible from such solutions to obtain the original salt satisfactorily by recrystallisation. A similar observation applies to the complex bromides, for they also give similarly coloured acid solutions from which the original salt cannot be recovered satisfactorily. This behaviour, in the case of the chlorides, was attributed to progressive ionisation and hydrolysis giving rise to the following compounds in succession : $R[MoOX_4,H_2O]$, $[MoOX_3,2H_2O]$, $[MoO(OH)X_2,2H_2O]$, $[MoO(OH)_2X,2H_2O]$, $[MoO_2X,3H_2O]$, $[MoO_2(OH),3H_2O]$; whence, at infinite dilution,

$$R_2[MoOX_5] + 5H_2O \rightleftharpoons [MoO_2(OH),3H_2O] + 2RX + 3HX.$$

The results of the molecular-weight determinations and molecular conductivities in air-free water gave strong support to the above hypothesis, whilst the isolation of intermediate substances further confirmed it. The physico-chemical measurements in the case of the bromides show a close analogy to those for the chlorides, and are therefore interpreted in a similar way. Moreover, by suitable adjustment of the composition of the solution of quinquevalent molybdenum, it has been possible to isolate a lithium derivative, $Li[MoO_2Br_2,2H_2O],4H_2O$, the existence of which accords with the above scheme.

The extensive hydrolysis which takes place in aqueous solution can be obviated by employing anhydrous alcohol as a solvent in the case of certain of the complex chlorides and bromides. It may be noted that this solvent is not always suitable, for in the case of the dipyridinium molybdenyl pentachloride, a reaction occurs and the insoluble salt $(C_5H_6N)[MoO_2Cl_2,2H_2O]$ separates.

Again, in the case of such salts as $K_2[MoOX_5]$, decomposition occurs with the separation of alkali halide. In suitable examples, however, an osmotic factor of *ca.* 3 has been obtained in determinations of molecular weight by the ebullioscopic method. Such results strongly support the formulation of the salts as co-ordination compounds rather than as double salts.

Molecular-weight Determinations—The molecular weight was determined by the depression of the freezing point of air-free water, and the results are appended in Table I. On the basis of the scheme outlined on p. 2584 the salt $R_2[MoOBr_5]$ should yield at

TABLE I.

Dipyridinium molybdenyl pentabromide (*M*, calc. = 671·7).

v	284	98·8	46·6	27·8
i	10·7	10·0	9·2	9·1
M_i	62·9	67·3	72·9	73·2

Diquinolinium molybdenyl pentabromide (*M*, calc. = 771·8).

v	129	77·5	54·1	32·0
i	10·7	9·7	9·5	8·8
M_i	71·7	79·9	81·5	87·7

Diammonium molybdenyl pentabromide (*M*, calc. = 547·7).

v	121	86·0	51·4	16·3
i	10·5	10·4	9·4	9·0
M_i	51·5	52·0	57·1	60·1

Dipotassium molybdenyl pentabromide (*M*, calc. for dihydrate = 625·8).

v	314	90·2	34·3	22·2
i	10·1	9·9	9·3	9·1
M_i	61·9	62·9	67·0	68·3

Dirubidium molybdenyl pentabromide (*M*, calc. = 682·5).

v = 42·8 i = 9·6 M_i = 71·0

Monopyridinium molybdenyl tetrabromide (*M*, calc. = 511·7).

v	191	88·3	42·1	28·4	23·1
i	8·9	8·1	7·9	7·6	7·6
M_i	57·3	63·4	64·6	67·7	67·6

Monoquinolinium molybdenyl tetrabromide (*M*, calc. = 561·8).

v	163	65·4	63·5	38·5	27·3	22·7
i	9·5	8·0	8·0	7·7	7·3	7·2
M_i	58·8	70·4	70·4	73·1	77·2	78·1

Monolithium molybdenyl tetrabromide (*M*, calc. for trihydrate = 510·7).

v	86·7	80·0	27·3
i	9·0	8·8	7·7
M_i	56·5	57·9	66·5

infinite dilution, 2 metal (or ammonium), 3 hydrogen, and 5 bromine ions, giving an osmotic factor of 11; experimental data support this conclusion, the factor varying from 9 in the reddish-brown solutions to 10—11 in the pale yellow solutions obtained by further dilution. Similarly, the limiting value of the osmotic factor for aqueous solutions of the tetrabromides will be 9, for 1 metal (or ammonium), 3 hydrogen, and 4 bromine ions can be set free.

Further evidence for these conclusions is forthcoming from the high values of the molecular conductivity of such solutions, measured at 0°, the results being summarised in Table II.

In the tables, v is the dilution (in litres/g.-mol.), i the osmotic factor, and M_i the apparent molecular weight.

TABLE II.

$(C_5H_6N)_2[MoOBr_5]$.

v	38·1	76·2	152·4	304·9	609·8	1219
μ	532·3	583·5	635·0	678·0	756·0	882·8

$(C_9H_8N)_2[MoOBr_5]$.

v	27·3	54·7	109·4	218·8	437·6	875
μ	548·9	565·6	596·0	624·8	688·4	766·5

$(NH_4)_2[MoOBr_5]$.

v	14·3	28·5	57·0	114·0	228·1	456·3
μ	561·0	598·8	613·0	655·0	689·3	757·0

$K_2[MoOBr_5],2H_2O$.

v	19·7	39·4	78·9	157·8	315·5	631·0
μ	450·1	487·1	515·2	526·8	566·1	660·4

$C_5H_6N[MoOBr_4]$.

v	24·7	49·4	98·9	197·8	395·5	791·0
μ	516·5	537·1	553·1	640·4	705·5	807·8

$C_9H_8N[MoOBr_4]$.

v	29·6	59·1	118·3	236·6	473·3	946·6
μ	520·2	537·4	568·4	608·6	678·8	805·0

On account of the catalytic effect of the platinised platinum electrodes in promoting oxidation to molybdenum blue, conductivities could not be determined for the solutions of the salts $Rb_2[MoOBr_5]$ and $Li[MoOBr_4,H_2O],3H_2O$.

Molecular-weight Determinations in Alcoholic Solution.—McCoy's modification of Beckmann's original apparatus was used; the alcohol employed was refluxed and distilled twice over barium oxide and twice over metallic calcium. Table III summarises the results obtained, and the osmotic factors are seen to be of the orders expected for both the penta- and the tetra-bromides.

TABLE III.

Dipyridinium molybdenyl pentabromide (M, calc. = 671·7).

v	28·2	26·5	19·1
i	3·07	3·08	3·14
M_i	219	218	214

Diquinolinium molybdenyl pentabromide (M, calc. = 771·8).

v	27·6	19·5	16·8	16·1
i	4·31	3·68	2·85	2·92
M_i	179	210	271	264

Diammonium molybdenyl pentabromide (M, calc. = 547·7).

v	29·4	25·0	19·5
i	3·84	4·16	4·12
M_i	143	131	132

Monopyridinium molybdenyl tetrabromide (M, calc. = 511·7).

v	16·6	15·6	9·61	9·33	8·37	8·14	8·10
i	2·67	2·68	2·23	2·24	2·08	2·11	2·07
M_i	191	190	229	228	246	243	247

Monoquinolinium molybdenyl tetrabromide (M, calc. = 561·8).

v	23·2	16·5	12·9	10·2	10·1
i	2·45	2·38	2·35	2·19	2·19
M_i	229	236	239	255	256

The figures obtained for the corresponding chlorides are given for comparison :

Diquinolinium molybdenyl pentachloride (M, calc. for monohydrate = 567·3).

v	58·8	28·2	17·5	15·3	10·4	7·5
i	2·69	2·69	2·25	2·24	2·26	2·25
M_i	215	215	252	254	249	252

Bisdiethylammonium molybdenyl pentachloride (M, calc. = 417·5).

v	13·3	8·85	7·43	5·67	5·64
i	2·84	2·88	2·88	2·63	2·74
M_i	146	144	144	157	151

Salts of the Type $R[MoO_2Br_2,2H_2O]$.

The isolation of such an intermediate substance would furnish valuable evidence in favour of the decomposition previously outlined. Attempts to decompose quinolinium molybdenyl tetrabromide in absolute alcohol by prolonged boiling gave, on cooling, products intermediate between $R[MoOBr_4]$ and $R_2[MoOBr_5]$. This indicated that by prolonged boiling the equilibrium

$$2R[MoOBr_4] \rightleftharpoons R_2[MoOBr_5] + MoOBr_3$$

was set up in alcohol.

It may be noted that, just as in the case of the chlorides, the complex bromides on boiling with oxalic acid and barium chloride in aqueous solution yield the insoluble oxalate,

$$Ba[MoO_2C_2O_4,2H_2O]_2,H_2O.$$

Lithium Molybdenyl Dioxydibromide.—This *salt* was isolated as a red solid, very hygroscopic and extremely sensitive to aerial oxidation. 100 C.c. of a solution of molybdenum trioxide (16·5 g.) in hydrobromic acid (*d* 1·5) were reduced electrolytically for 30 minutes, lithium bromide (5 g.) was added, and the whole concentrated under diminished pressure to 15 c.c. On prolonged cooling in ice, a solid separated which was washed with hydrobromic acid (*d* 1·7) and dried in the usual way (Found : Mo, 23·6; Br, 39·4; Li, 1·6. $Li[MoO_2Br_2,2H_2O],4H_2O$ requires Mo, 23·8; Br, 39·7; Li, 1·7%).

Conclusion.

In recent communications (J., 1927, 2145; 1928, 2726) it has been shown that all salts of the type $R_2[MoOX_5]$ are unstable in aqueous solutions, the order of decreasing stability being X = CNS, Cl, Br. It has been suggested that the instability of the complex ion $[MoOX_5]''$ may be due, amongst other factors, to the low effective atomic number of the molybdenum atom, which, as the oxygen is associated by means of a co-ordinate link, is seen to be 49, appreciably less than the atomic number of the next inert gas. Although there appears to be no doubt that the relative stability of co-ordination compounds does bear some relationship to the total effective atomic number of the central atom and the inert-gas numbers, yet, except when there is a valency group of eight, this matter is still very obscure. Examples of complex salts may be quoted which show that even when the effective atomic number of the central atom has an excess or deficit of electrons when compared with the atomic number of the nearest inert gas, the compounds still display marked stability. This is seen, for example, in the case of the complex salts recently discussed by Mann (this vol., p. 651), and in the chromammines, where chromium has an effective atomic number of 33; yet the salts have a stability comparable with that of the cobaltammines, in which cobalt has an effective atomic number of 36. It appears that, in addition to the effective atomic number of the central atom, the spatial configuration of the associated units and their nature are important factors influencing stability. In an interesting communication on " Valence Variable " to the Troisième Conseil de Chimie, Sidgwick has suggested (" Rapports et Discussions sur des Questions d'Actualité," 1928, pp. 309 *et seq.*) that one must also consider (*a*) the size of the atomic core, (*b*) the size of the valency group, and (*c*) the influence of the latter on the stability of different cores (as in $Co^{\cdot\cdot}$ versus $Co^{\cdot\cdot\cdot}$).

The behaviour of oxygen in different types of compound is a matter of some interest. The ease with which oxygen is removed from bismuth and antimony oxychlorides by the action of acids is in marked contrast to the difficulty experienced in displacing this atom from salts of the type dealt with in this communication. In all probability this ease of replacement of the oxygen atom in the oxy-salts mentioned is connected with the fact that here the oxygen is united by a double non-polar bond, whereas in the molybdenyl salts it is associated by a co-ordinate link. Although, in general, such a link is a less stable type of union than an ordinary covalency, yet oxygen is an exception to this rule. The complex salts discussed in this paper illustrate this fact. The co-ordinate link between the oxygen and molybdenum atoms is unaffected even by the action of concentrated acid, although under these conditions the atoms bound by covalencies are readily reactive, as illustrated by the reversible reaction

$$R_2[MoOCl_5] + 5HCNS \rightleftharpoons R_2[MoO(CNS)_5] + 5HCl.$$

An explanation of the fact that salts of the type $R[MoOBr_4]$ are more hygroscopic than those of the type $R_2[MoOBr_5]$ is possibly connected with the circumstance that in the former salts the oxygen occupies two positions. By association with water, however, the oxygen can revert to its normal stable state, in which it is connected by means of a co-ordinate link and retains only one position in the co-ordination sphere.

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