76. *Bromo- and Iodo-molybdenum*(II) *Compounds.*

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Molybdenum(II) chloride is converted by fused lithium bromide or iodide into molybdenum(II) bromide or iodide and these have yielded the following derivatives: $[(Mo_6Br_8)X_6]^{2-}$ (X = Cl, Br, I, or OH), $[(Mo_6I_8)X_6]^{2-}$ (X = Cl, Br, or OH), and $[(Mo_6Br_8)X_4]$ and $[(Mo_6I_8)X_4]$ (X = Cl, Br, I, or OH). Although the characterisation of bromo- and iodo-molybdenum(II) compounds is restricted by their insoluble nature, physical measurements show that these compounds are similar to those of the chloromolybdenum(II) series.[1] The (Mo_6I_8) group is the first iodo-hexanuclear group to be described and is attacked by hydroxide giving substituted groups of the type $[Mo_6I_{8-n}(OH)_n]$.

THE chemistry of molybdenum(II) chloride and its derivatives is readily understood on the basis that these compounds all contain the octa-μ_3-chlorohexamolybdenum(II) group [*i.e.*, (Mo_6Cl_8) and referred to in short as chloromolybdenum(II)] which normally acquires octahedral co-ordination to give $[(Mo_6Cl_8)X_6]$ complexes or polymeric $[(Mo_6Cl_8)X_4]$ compounds.[1] Nothing has been reported previously on the constitution of molybdenum(II) iodide, and although certain molybdenum(II) bromide compounds are reported with

[1] Sheldon, *J.*, 1960, 1007.

compositions analogous to chloromolybdenum(II) compounds,[2] no attempt has been made to support the suggested structural analogy by simple physical techniques. Therefore the present work has been a chemical and physical comparison of molybdenum(II) bromide and iodide with the chloride to establish whether these have similar polynuclear structures. The investigation has been rather limited by the insolubility of the bromide and iodide in useful solvents.

Substitution of the Chloromolybdenum(II) *Group by Halide Ions.*—It is known that the chloromolybdenum(II) group is inert to attack by halide ion in aqueous media [3] and moreover the present work has shown that it is even unaffected by boiling lithium iodide trihydrate (*ca.* 200°), although fused lithium bromide (m. p. 540°) or iodide (m. p. 450°) converts molybdenum(II) chloride into molybdenum(II) bromide or iodide. These observations are consistent with the view that halide ions are weak nucleophiles in aqueous media and frequently only cause substitution in a metal complex after a preliminary aquation step

$$[MX_n] \xrightarrow[\text{slow}]{H_2O} [MX_{n-1}H_2O] \xrightarrow[\text{fast}]{X'} [MX_{n-1}X']$$

for such an aquation of the chloromolybdenum(II) group is unlikely because it requires that an aquo-group bridges three molybdenum atoms simultaneously. However, the elevated temperatures and anhydrous conditions of fused lithium halides would be well suited to the direct attack of chloromolybdenum(II) by halide ions. It is notable that whereas fused lithium chloride (m. p. 610°) decomposes molybdenum(II) chloride slowly, fused potassium chloride (m. p. 770°) causes rapid disproportionation of molybdenum(II) chloride to molybdenum metal (identified by *X*-ray powder photograph) and $K_3[Mo^{III}Cl_6]$ (identified by aqueous absorbtion spectrum). No mononuclear chloromolybdenum(II) complex is in fact observed and it may be supposed that such complexes have, at the most, a transient existence at high temperatures yielding the observed products of molybdenum(III) and molybdenum metal. It is our view that the halide substitution of the chloromolybdenum(II) group is unlikely to involve dissociation into, and recombination of, unstable mononuclear molybdenum(II) species, and so the covalent Mo_6 octahedron, which is thought to confer high thermal stability on the chloromolybdenum(II) group,[4] is probably preserved during halide attack below 600°. This suggests that molybdenum(II) bromide and iodide may well contain bromo- and iodo-molybdenum(II) groups closely related structurally to chloromolybdenum(II).

Bromo- and Iodo-molybdenum(II) *Tetrahydroxides.*—Molybdenum(II) bromide and iodide are fairly inert once heated to high temperatures and thereafter can be dissolved in only a few solvents, *e.g.*, boiling dimethyl sulphoxide or hot concentrated sulphuric acid. Hot dilute alkali dissolves these halides although with considerable simultaneous decomposition to molybdenum(III) hydroxide. Addition of excess of acid to these alkaline solutions yields yellow gelatinous precipitates, but rendering the solutions faintly alkaline (addition of ammonium nitrate) gives dense, easily handled, precipitates of bromo- and iodo-molybdenum(II) tetrahydroxides. These are difficult materials to dry since they contain loosely bound water which is easily lost on being heated or on evacuation. The tetrahydroxides obtained from fresh alkaline solutions possess a halogen : molybdenum ratio close to 1·33 as required by $(Mo_6X_8)(OH)_4,nH_2O$. Only the bromomolybdenum(II) tetrahydroxide hydrate has been previously described, and formulated as $(Mo_6Br_8)(OH)_4,16H_2O$.[2a] However, the *X*-ray powder patterns in the present work show that this compound is isomorphous with $[(Mo_6Cl_8)(OH)_4(H_2O)_2],12H_2O$ whose structure is known.[5] This establishes that the bromomolybdenum(II) tetrahydroxide

[2] (*a*) Blomstrand, *J. prakt. Chem.*, 1859, **77**, 88; (*b*) Atterberg, *Bull. Soc. chim. France*, 1872, **18**, 21; (*c*) Lindner and Helwig, *Z. anorg. Chem.*, 1925, **142**, 180.
[3] Sheldon, *J.*, 1960, 3106.
[4] Sheldon, *Nature*, 1959, **184**, 1210.
[5] Brosset, *Arkiv Kemi, Min. Geol.*, 1946, **20**, *A*, No. 7.

hydrate contains 14 H_2O and that the (Mo_6Br_8) group is isostructural with (Mo_6Cl_8). It has not been possible to obtain an iodomolybdenum(II) tetrahydroxide hydrate of definite character, as all samples proved to be nearly amorphous, although yielding anhydrous tetrahydroxides on being dried. The bromo- and iodo-molybdenum(II) tetrahydroxides prepared in this work are listed below with their conditions of preparation, along with the previously reported chloromolybdenum(II) compounds.[1]

Preparation and appearance			
Yellow crystals from alkaline solution	$[(Mo_6Cl_8)(OH)_4(H_2O)_2],12H_2O$	$[Mo_6Br_8)(OH)_4(H_2O)_2],12H_2O$	
Red amorphous powders from above compds., dried *in vacuo* at 25°	$[(Mo_6Cl_8)(OH)_4(H_2O)_2]$	$[(Mo_6Br_8)(OH)_4(H_2O)_2]$	
Dark brown amorphous powders from above compds., dried *in vacuo* at 200°	$(Mo_6Cl_8)(OH)_4$	$(Mo_6Br_8)(OH)_4$	$(Mo_6I_8)(OH)_4$

Alkaline solutions of molybdenum(II) iodide darken and sometimes slowly give a brown sediment. These changes are not the complete decomposition to molybdenum(III) hydroxide as this is readily precipitated and is black. The hydroxides precipitated from these aged solutions have iodine : molybdenum ratios significantly lower than 1·33 and might be formulated as $[Mo_6I_{8-n}(OH)_n](OH)_4,mH_2O$. These compounds are being studied further.

Hexahydroxobromo(or iodo)molybdate(II) Ion.—Solutions of bromo- and iodo-molybdenum(II) tetrahydroxides in 0·1N-alkali can be titrated with 0·1N-acid, precipitating the tetrahydroxides, and giving a pH titration curve similar to that reported for $[(Mo_6Cl_8)(OH)_6]^{2-}$ in solution.[4] The number of hydroxo-groups per ion can be calculated from such a curve, *i.e.*,

$$[(Mo_6X_8)(OH)_{(4+x)}]^{x-} + xH^+ \longrightarrow (Mo_6X_8)(OH)_4,nH_2O$$

It is found that 0·492 g. of anhydrous bromomolybdenum(II) tetrahydroxide (*i.e.*, $3{\cdot}83 \times 10^{-4}$ moles) required 7·60 ml. of 0·1N-acid. Therefore x is 2·0 for bromomolybdenum(II). Iodomolybdenum(II) alkaline solutions give somewhat less satisfactory values of x, probably as a result of slow alkaline attack on this group. 0·554 g. of anhydrous iodomolybdenum(II) tetrahydroxide (*i.e.*, $3{\cdot}33 \times 10^{-4}$ moles) required 7·3 ml. of 0·1N-acid, giving 2·2 for x. Bromo- and iodo-molybdenum(II) are therefore present in alkaline solution as $[(Mo_6X_8)(OH)_6]^{2-}$ ions. The existence of the hexa-aquobromomolybdenum(II) ion has been demonstrated [6] by the alkaline titration of bromomolybdenum(II) tetranitrate in aqueous ethanol. The following equation appears to hold:

$$[(Mo_6Br_8)(H_2O)_6]^{4+} + 4OH^- \longrightarrow (Mo_6Br_8)(OH)_4,nH_2O$$

Bromo- and Iodo-molybdenum(II) Tetrahalides.—Addition of excess of hydrohalogeno-acids to alkaline chloromolybdenum(II) solutions gives, after concentration, crystalline, and unstable hexahalogeno-acids, $H_2[(Mo_6Cl_8)X_6],8H_2O$.[1,7] Similar treatment of bromo- and iodo-molybdenum(II) solutions gives insoluble and finely divided precipitates which can only be freed from excess of aqueous acid by such treatment that would be certain to decompose hexahalogeno-acids, if these existed in the bromo- and iodo-molybdenum(II) series and had stabilities comparable to the chloromolybdenum(II) acids. Bromomolybdenum(II) precipitates from hydrochloric acid solution possess a bromine : chlorine ratio of 1·7 after being dried in air, whereas the corresponding iodomolybdenum(II) precipitates have an iodine : chlorine ratio of 2·0 {cf., $H_2[(Mo_6X_8)Cl_6]$ requires X : Cl, 1·33 and $(Mo_6X_8)Cl_4$ requires X : Cl, 2·0}. These precipitates can be heated *in vacuo* at 200° to give the anhydrous bromo- and iodo-molybdenum(II) tetrahalides of which $(Mo_6Br_8)Cl_4$, $(Mo_6Br_8)I_4$, $(Mo_6I_8)Cl_4$, and $(Mo_6I_8)Br_4$ are new. If these tetrahalides were similar

[6] Durand, Schaal, and Souchay, *Compt. rend.*, 1959, **248**, 979.
[7] Rosenheim and Kohn, *Z. anorg. Chem.*, 1910, **66**, 1.

to the chloromolybdenum(II) analogues they should give "octahedral" complexes $[(Mo_6X_8)X'_4Don_2]$ with electron-pair donors (Don). The insoluble nature of these tetrahalides renders the achievement of pure products difficult, and the most satisfactory preparation has been the treatment of the suspended tetrahalides with refluxing pyridine for several hours, followed by removal of excess of pyridine *in vacuo* at 100°. In this way were prepared the new addition compounds $[(Mo_6I_8)Cl_4(C_5H_5N)_2]$ and $[(Mo_6I_8)Br_4(C_5H_5N)_2]$ and the previously reported $[(Mo_6Br_8)Br_4(C_5H_5N)_2]$[2c].

Hexahalogenobromo(or iodo)molybdate(II) *Salts.*—Tetraethylammonium and pyridinium salts of the unknown hexahalogenobromo(or iodo)molybdic(II) acids have been obtained in the present study possessing the anions $[(Mo_6Br_8)X_6]^{2-}$ (X = Cl, Br, or I) and $[(Mo_6I_8)X_6]^{2-}$ (X = Cl, or Br). The salts $[C_5H_5NH]_2$ $[(Mo_6Br_8)X_6]$ (X = Cl or Br) have been described [2c] but only molybdenum contents were given in characterisation. The tetraethylammonium salts were obtained by the addition of excess of hot hydrohalogeno-acid and tetraethylammonium halide to an alkaline bromo- or iodo-molybdenum(II) solution and digestion to coagulate the finely divided precipitate. These stable and sparingly soluble salts can be dried *in vacuo* at 100°. This method, however, gave only the iodomolybdenum(II) tetrabromide or tetraiodide instead of the hexabromo- or hexaiodo-salts presumably owing to the exceptionally low solubility of the two tetrahalides (or their undried precursors) in hydrobromic or hydriodic acids. The undried tetrahalides are all soluble in hot pyridine from which can be precipitated crystalline pyridinium hexa-halogeno-salts on the addition of the appropriate hydrohalogeno-acid. The salts can be washed free from pyridinium halide with ethanol and dried *in vacuo* at 100°, and prove slightly soluble (up to 10^{-3}M) in polar solvents.

Physical Properties.—Although the present and previous preparative studies indicate a close similarity between chloro-, bromo-, and iodo-molybdenum(II) compounds, physical data are desirable to confirm the apparent structural analogies. A large number of bromo- and iodo-molybdenum(II) compounds prepared in this work were studied semi-quantitatively by the Gouy method; all possess small negative magnetic susceptibilities. Thus it is significant that compounds of all three series are diamagnetic and this supports strong Mo–Mo interaction within the Mo_6 octahedron. Molybdenum(II) bromide has been previously reported as diamagnetic.[8]

The absorption spectra of chloro-,[1] bromo-, and iodo-molybdenum(II) in 0·01—0·1N-sodium hydroxide and in 2—5M-sulphuric acid solutions display bands in the region 300—400 mμ. These bands observed in alkaline and acid solutions {believed to be due to the complex ions $[(Mo_6X_8)(OH)_6]^{2-}$ and $[(Mo_6X_8)(H_2O)_6]^{4+}$ respectively} are shown in Figs. 1 and 2. The comparison of the ions $[(Mo_6X_8)Y_6]^{2-}$ (Y = Cl, Br, or I) was frustrated by the insolubility of bromo- and iodo-molybdenum(II) compounds in aqueous hydrohalogeno-acids necessary to suppress hydrolysis.

The spectrum of $[(Mo_6I_8)(OH)_6]^{2-}$ slowly changed and a new band at 304 mμ appeared which is tentatively correlated with the formation of $[Mo_6I_{8-n}(OH)_n]$ species by alkaline attack on iodomolybdenum(II). Sulphuric acid solutions of iodomolybdenum(II) [prepared by dissolving an iodomolybdenum(II) compound in hot concentrated sulphuric acid, cooling, and diluting] consistently displayed a sharp band at 290 mμ, *i.e.*, band (III) in the Table, which has no analogy in the chloro- and bromo-molybdenum(II) spectra. It is suggested that this band is due to species of the type $\{[Mo_6I_{8-n}(HSO_4)_n](H_2O)_6\}^{4+}$ introduced by the attack of bisulphate ion on iodomolybdenum(II), a feature which is at present under further study. Apart from this one band there is a marked resemblance between the spectra of the three series, analogous bands usually appearing at longer wavelengths and higher extinctions in the sequence chloro-, bromo-, and iodo-molybdenum(II).

The limited solubilities of bromo- and particularly iodo-molybdenum(II) compounds have prevented molecular weights, being determined cryoscopically, although a number

[8] Tjabbes, *Proc. Acad. Sci. Amsterdam*, 1932, **35**, 693.

of tetraethylammonium and pyridinium hexahalogeno-salts are sufficiently soluble in acetonitrile, nitromethane, and nitrobenzene to allow isopiestic molecular-weight determinations and conductivity measurements. These data are tabulated below:

Compound	Solvent	Concn. (10^{-3}M)	Λ_m, 25°	
$[C_5H_5NH]_2[(Mo_6Br_8)Cl_6]$	Nitrobenzene	0·91	55	
,, ...	Nitromethane	1·16	140	
$[(C_2H_5)_4N]_2[(Mo_6Br_8)I_6]$	Nitrobenzene	0·43	62	
$[C_5H_5NH]_2[(Mo_6Br_8)I_6]$	Nitromethane	0·73	149	
$[(C_2H_5)_4N]_2[(Mo_6I_8)Cl_6]$	Nitrobenzene	0·59	50	
,, ...	Nitromethane	0·76	140	
			M	Formula wt./*M*
$[C_5H_5NH]_2[(Mo_6Br_8)Cl_6]$	Nitromethane	1·16	500 (70°)	3·2
$[C_5H_5NH]_2[(Mo_6Br_8)I_6]$	Acetonitrile	0·65	770 (25°)	2·8

The molar conductances generally conform with those expected of 2 : 1 electrolytes in these solvents and the apparent molecular weights found for the two bromomolybdenum(II) salts are consistent with their formulation as 2 : 1 electrolytes.

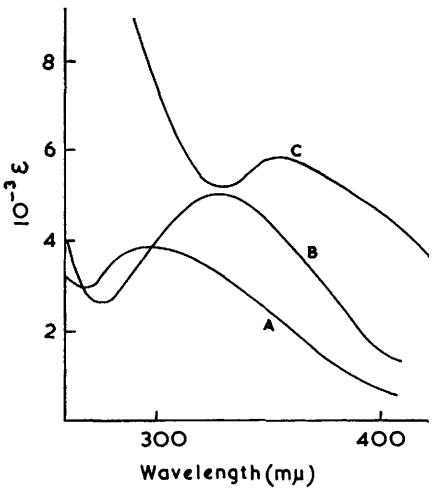

FIG. 1. Absorption spectra of: A, chloromolybdenum(II); B, bromomolybdenum(II); and C, iodomolybdenum(II) in solution in 0·01—0·1N-sodium hydroxide.

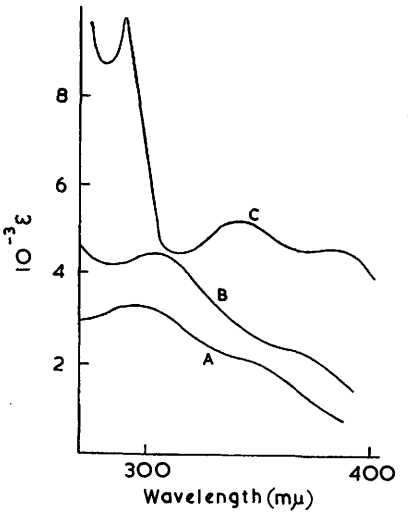

FIG. 2. Absorption spectra of: A, chloromolybdenum(II); B, bromomolybdenum(II); and C, iodomolybdenum(II) in solution in 2—5M-sulphuric acid.

Conclusion.—On the basis of compounds of analogous composition and the similar physical properties in the chloro-, bromo-, and iodo-molybdenum(II) series, it is concluded that bromo- and iodo-molybdenum(II) compounds are likely to contain the polynuclear groups (Mo_6Br_8) and (Mo_6I_8) structurally similar to (Mo_6Cl_8).

EXPERIMENTAL

Reaction of Molybdenum(II) *Chloride with Fused Lithium Halides.*—The chloride, mixed with a large excess of lithium bromide or iodide, was placed in a silica tube which was subsequently evacuated. The mixture was dried by gentle heating, followed by sufficient heating to maintain it molten for a few minutes. The cold mixture was leached with water, yielding the insoluble molybdenum(II) bromide or iodide, which was then purified by dissolving it in warm dilute alkali and reprecipitation with strong hydrobromic or hydriodic acid, respectively. The molybdenum(II) halides were dried *in vacuo* at 200°, giving molybdenum(II) bromide (yield 50%) (Found: Br, 61·0; Cl, 0·9; Mo, 37·5. Calc. for Br_2Mo: Br, 62·5; Mo, 37·5%) and iodide (yield 82%) (Found: I, 72·0; Mo, 28·3. Calc. for I_2Mo; I, 72·5; Mo, 27·5%).

Preparation of Molybdenum(II) *Bromide and Iodide.*—The bromide was obtained by the decomposition of molybdenum(III) bromide (prepared *in situ* from heated molybdenum powder and bromine vapour) at red heat in a nitrogen atmosphere. The iodide was obtained by the method of Nyholm *et al.*[9] involving the action of iodine at 300—400° on molybdenum powder for several days in sealed glass tubes.

Preparation of Bromo- and Iodo-molybdenum(II) *Compounds.*—The following compounds were prepared as described in the earlier sections: octa-μ_3-bromohexamolybdenum(II) tetrahydroxide 14-water (Found: H, 2·2; Br, 40·1; Mo, 37·4. Calc. for $H_{32}Br_8Mo_6O_{18}$: H, 2·1; Br, 41·6; Mo, 37·5%); *octa-*μ_3*-bromohexamolybdenum*(II) *tetrahydroxide 2-water* (Found: Br, 48·4; Mo, 44·5. $H_8Br_8Mo_6O_6$ requires Br, 48·5; Mo, 43·6%); *octa-*μ_3*-bromohexamolybdenum*(II) *tetrahydroxide* (Found: Br, 49·5. $H_4Br_8Mo_6O_4$ requires Br, 49·8%); *octa-*μ_3*-iodohexamolybdenum*(II) *tetrahydroxide* (Found: I, 60·4; Mo, 34·4. $H_4I_8Mo_6O_4$ requires I, 61·1; Mo, 34·7%), *octa-*μ_3*-bromohexamolybdenum*(II) *tetrachloride* (Found: Br, 46·5; Cl, 10·7. $Br_8Cl_4Mo_6$ requires Br, 47·1; Cl, 10·45%); *octa-*μ_3*-bromohexamolybdenum*(II) *tetraiodide* (Found: Br, 36·1; I, 29·6. $Br_8I_4Mo_6$ requires Br, 37·1; I, 29·4%; *octa-*μ_3*-iodohexamolybdenum*(II) *tetrachloride* (Found: Cl, 8·4; I, 57·4; Mo, 33·6. $Cl_4I_8Mo_6$ requires Cl, 8·2; I, 58·5; Mo, 33·2%); *octa-*μ_3*-iodohexamolybdenum*(II) *tetrabromide* (Found: Br, 16·4; I, 51·6. $Br_4I_8Mo_6$ requires Br, 16·7; I, 53·1%); *dipyridinetetrachloro-octa-*μ_3*-iodohexamolybdenum*(II) (Found: Cl, 7·3; I, 53·8; Mo, 29·9. $C_{10}H_{10}Cl_4I_8Mo_6N_2$ requires Cl, 7·5; I, 53·6; Mo, 30·4); *dipyridinetetrabromo-octa-*μ_3*-iodohexamolybdenum*(II) (Found: Br, 15·3; I, 48·0. $C_{10}H_{10}Br_4I_8Mo_6N_2$ requires Br, 15·45; I, 49·0%); bispyridinium hexachloro-octa-μ_3-bromohexamolybdate(II) (Found: Br, 39·5; Cl, 13·6. Calc. for $C_{10}H_{12}Br_8Cl_6Mo_6N_2$: Br, 40·3; Cl, 13·4%); *ditetraethylammonium hexabromo-octa-*μ_3*-bromohexamolybdate*(II) (Found: Br, 57·0; Mo, 29·5. $C_{16}H_{40}Br_{14}Mo_6N_2$ requires Br, 57·3; Mo, 29·5%); *bistetraethylammonium hexaiodo-octa-*μ_3*-bromohexamolybdate*(II) (Found: Br, 28·2; I, 33·1. $C_{16}H_{40}Br_8I_6Mo_6N_2$ requires Br, 28·6; I, 34·1%); *dipyridinium hexaiodo-octa-*μ_3*-bromohexamolybdate*(II) (Found: Br, 30·4; I, 33·6; Mo, 26·0. $C_{10}H_{12}Br_8I_6Mo_6N_2$ requires Br, 30·0; I, 35·7; Mo, 27·0%); *bistetraethylammonium hexachloro-octa-*μ_3*-iodohexamolybdate*(II) (Found: Cl, 10·2; I, 49·8; Mo, 28·6. $C_{16}H_{40}Cl_6I_8Mo_6N_2$ requires Cl, 10·3; I, 49·1; Mo, 27·9%); *dipyridinium hexachloro-octa-*μ_3*-iodohexamolybdate*(II) (Found: Cl, 10·8; I, 51·3; Mo, 29·6. $C_{10}H_{12}Cl_6I_8Mo_6N_2$ requires Cl, 10·8; I, 51·6; Mo, 29·4%); and *dipyridinium hexabromo-octa-*μ_3*-iodohexamolybdate*(II) (Found: Br, 22·8; I, 45·5; Mo, 25·0. $C_{10}H_{12}Br_6I_8Mo_6N_2$ requires Br, 21·5; I, 45·5; Mo, 25·8%).

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[9] Lewis, Machin, Nyholm, Pauling, and Smith, *Chem. and Ind.*, 1960, 259.