208. *Chloromolybdenum*(II) *Compounds.*

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X-Ray diffraction studies have shown that molybdenum(II) chloride derivatives contain the octachlorohexamolybdenum(II) group, $(Mo_6Cl_8)^{4+}$, which acts as a centre for octahedral complexes analogously to a single-atom ion.[1,2] Preparative work, cryoscopy, molecular conductivity, ultraviolet spectroscopy, and magnetic susceptibility support the octahedral co-ordination of this group. The existence of $[(Mo_6Cl_8)X_6]^{2-}$ (X = Cl, Br, I, or OH) ions in solution have been demonstrated. These complexes are starting materials in the preparation of compounds $(Mo_6Cl_8)X_4$ which are considered to be polymeric. Evidence is given for the existence of octahedral complexes $[(Mo_6Cl_8)Cl_4,2C_5H_5N]$, $[(Mo_6Cl_8)Cl_4,2NEt_3]$, $[(Mo_6Cl_8)(OH)_4,2H_2O]$, and $[(Mo_6Cl_8)Cl_3 \cdot OH,2H_2O]$. The stability, ultraviolet spectra, and diamagnetism of Mo_6Cl_8 compounds, and the co-ordination number nine for each molybdenum atom,[1,2] can be explained by regarding molybdenum as sexivalent in chloromolybdenum(II).

DERIVATIVES of molybdenum(II) chloride are best regarded as a novel type of octahedral co-ordination complex containing the octa-μ_3-chlorohexamolybdenum(II) group, $(Mo_6Cl_8)^{4+}$, centre.[3] The absence of typical transition-metal properties in octachlorohexamolybdenum-(II) compounds has been explained by the formation of molybdenum–molybdenum bonds. Although the established oxidation number is two, it has been suggested that the presence of such bonds requires that molybdenum should be considered as effectively sexivalent in these compounds. The established co-ordination number of molybdenum in octachloro-hexamolybdenum(II) is nine,[1,2] and this supports the view that molybdenum is sexivalent. A prominent member of the octachlorohexamolybdenum(II) complex series is the crystalline acid, $(H_3O)_2[(Mo_6Cl_8)Cl_6],6H_2O$. This paper is concerned with a physical and chemical study of this compound, and those conveniently prepared from it, and justifies regarding octachlorohexamolybdenum(II) compounds as octahedral complexes of the type $[(Mo_6Cl_8)X_6]$. Much of the chemistry of these compounds which has hitherto appeared unusual and unsystematic then appears simple.

Molecular Conductivity and Cryoscopy.—The empirical formula for the chloro-acid was established as early as 1910.[4] That work also indicated that the oxidation number of molybdenum was two and that only six of the fourteen chlorine atoms were easily removed by alkali. The importance of this acid is two-fold. First, it is easily obtained pure by dissolving crude molybdenum(II) chloride in hydrochloric acid from which the chloro-acid crystallises on cooling. Secondly, heating the chloro-acid *in vacuo* gives pure molybdenum-(II) chloride, *i.e.*, $[(Mo_6Cl_8)Cl_4]$, an observation not recorded by previous workers. The related bromo- and iodo-acids are conveniently prepared by dissolving the chloro-acid in hydrobromic or hydriodic acid respectively. Crystals of the other halogeno-acids readily

[1] Brosset, *Arkiv Kemi, Min., Geol.*, 1946, **20**, *A*, No. 7.
[2] Brosset, *Arkiv Kemi, Min., Geol.*, 1947, **22**, *A*, No. 11.
[3] Sheldon, *Nature*, 1959, **184**, 1210.
[4] Rosenheim and Kohn, *Z. anorg. Chem.*, 1910, **66**, 1.

appear and decompose, when heated *in vacuo*, to octachlorohexamolybdenum(II) tetrabromide and tetraiodide.

Though it is easy to formulate the halogeno-acids as octahedral complexes, which should be 2 : 1 electrolytes, these halides can only be octahedral complexes if they are polymeric with respect to (Mo_6Cl_8), some of the ligand groups acting as bridges between octachlorohexamolybdenum(II) groups. Conductivity and cryoscopic measurements for these compounds in nitrobenzene solution are summarised in Table 1.

TABLE 1.

	Molar conductivity at 25°		Cryoscopy		
	Condy.[a]	Concn. (10⁻³M)	$-\Delta T$	Concn. (10⁻²M)	M
$(H_3O)_2[(Mo_6Cl_8)Cl_6],6H_2O$ ...	49	1·03	0·320°	1·94	420
	51	0·665			
$(H_3O)_2[(Mo_6Cl_8)Br_6],6H_2O$	56	0·862	0·133	0·905	575
	53	0·590			
$(H_3O)_2[(Mo_6Cl_8)I_6],6H_2O$ ...	59	0·566	0·260	1·56	600
	59	0·378			
$(Mo_6Cl_8)Br_4$ [b]	9	3·34	~0·002	0·56	$\gg10^3$
$(Mo_6Cl_8)I_4$	23[c]	0·935	~0·02	0·35	~10^3
	22[c]	0·54			

[a] Molar conductivity in nitrobenzene at 25°: 1 : 1, ~25 mho; 2 : 1, ~50 mho.[5]   [b] $(Mo_6Cl_8)Cl_4$ is insoluble.   [c] After standing.

The conductivity data establish that the halogeno-acids are 2 : 1 electrolytes. The ratios of the theoretical to experimental molecular weights for the hexachloro-, hexabromo-,
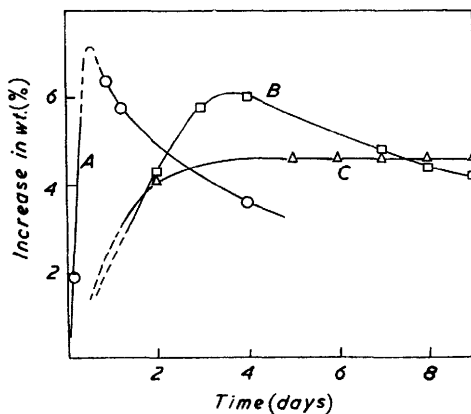

FIG. 1.   *Increase in weight on storage in air.*
A, $(Mo_6Cl_8)Cl_4$. B, $(Mo_6Cl_8)Br_4$. C, $(Mo_6Cl_8)I_4$.

and hexaiodo-acids are 2·9, 2·6, and 2·9 respectively, indicating the production of three ions per molecule. Thus the existence of $[(Mo_6Cl_8)Cl_6]^{2-}$, $[(Mo_6Cl_8)Br_6]^{2-}$, and $[(Mo_6Cl_8)I_6]^{2-}$ ions in nitrobenzene solution is certain. As the difference between the theoretical and the experimental molecular weights is best explained by electrolytic dissociation, the molecules of water shown in Table 1 must be bound to the ions. The halogeno-acids may be recovered from nitrobenzene solution by the addition of excess of light petroleum, and the crystalline precipitates give X-ray powder photographs identical with those of the original materials.

No simple deductions can be made from the results in Table 1 concerning the constitution of these halides. The insolubility of octachlorohexamolybdenum(II) tetrachloride in nitrobenzene may be attributable to the chloride's polymeric nature. The molecular weights found for the bromide and iodide indicate that the degree of polymerisation decreases from the bromide to the iodide. The molar conductivity of the iodide

[5] Harris and Nyholm, *J.*, 1956, 4375; Harris, Ph.D. Thesis, New South Wales, 1955; Phillips, Ph.D. Thesis, London, 1958.

increases for some time after the solution's preparation. The final value is close to that expected for a 1 : 1 electrolyte and it cannot be ruled out that the tetraiodide exists predominantly as $[(Mo_6Cl_8)I_3(Ph\cdot NO_2)_n]^+I^-$ in nitrobenzene solution.

Hygroscopic Nature of the Halides.—A typical consequence of the tendency of octa-chlorohexamolybdenum(II) to complete an octahedral arrangement of ligands is the formation of hydrates by the halides. The freshly prepared halides are amorphous but gradually acquire X-ray powder patterns in moist air. Simultaneously, the weights increase, eventually corresponding to the gain of several water molecules per halide molecule. The chloride and bromide, but not the iodide, then lose weight, indicating the evolution of hydrogen halide, and another characteristic X-ray powder pattern appears, indicating partial hydrolysis. Fig. 1 shows typical plots of weight increase against time. The maxima suggest that the chloride and bromide may give tetrahydrates $(Mo_6Cl_8)X_4,4H_2O$ before significant hydrolysis occurs. The iodide gives a stable 3·5-hydrate. It is possible that owing to incomplete reaction the number of water molecules given above does not correspond to maximum hydration. The hydrates, like the halogeno-acids, yield the anhydrous tetrahalides when heated *in vacuo.* It is noteworthy that the lowest reported hydrates of the chloride and bromide are the dihydrates,[4,6] which can conveniently be formulated as octahedral complexes. The anhydrous halides become paler in damp air, which is additional evidence of chemical change. Octachlorohexa-molydenum(II) compounds are thermochroic and darken reversibly with increase of temperature. The approximate colours of the halides under different conditions are given in Table 2.

TABLE 2.

	In moist air	Room temperature Freshly prepared *in vacuo*	200° *In vacuo*
$(Mo_6Cl_8)Cl_4$	Pale yellow	Deep yellow	Medium brown
$(Mo_6Cl_8)Br_4$	Medium yellow	Yellow-brown	Dark brown
$(Mo_6Cl_8)I_4$	Medium brown	Dark brown	Almost black

Molecular Addition Compounds.—Although the halides possess low solubilities in weak electron-donors, *e.g.,* nitrobenzene and methyl cyanide, they are freely soluble in strong donor solvents, *e.g.,* ethanol and pyridine. This is consistent with their tendency to complete an octahedral arrangement of ligands. The solvates may be isolated from strong donor solvents by addition of excess of diethyl ether or light petroleum ether. *E.g.,* $[(Mo_6Cl_8)Cl_4,2EtOH]$ was isolated earlier,[6] and $[(Mo_6Cl_8)Cl_4,2C_5H_5N]$ and $[(Mo_6Cl_8)Cl_4,2NEt_3]$ in the present work. The halides are insoluble in water, undoubtedly owing to the insolubility of the hydrates immediately formed; nevertheless, no definite hydrate has been characterised owing to the incomplete reaction with water and concurrent hydrolysis.

Hydrolysis of the Halogeno-acids.—In keeping with their ionic character, the halogeno-acids and their salts are somewhat soluble in many polar solvents, including water. However, the initially clear aqueous solutions rapidly give precipitates. Such a precipitate from the chloro-acid, and the amount of chloride liberated on its formation, have been reported by others,[4,6] but its nature has remained obscure. It was supposed that several chlorine atoms were successively lost, first by the soluble acid, then by the suspended precipitate, yielding octachlorohexamolydenum(II) tetrahydroxide as an end-product. We confirm that the extent of hydrolysis increases with temperature and length of digestion; however, the precipitate cannot be homogeneous if obtained under the more extreme conditions, since the dark colour of some of the samples suggests the formation of Mo(V) hydroxide. The freshly formed and dried precipitate is amorphous (X-rays). When heated to 250° *in vacuo* the precipitate yields octachlorohexamolybdenum(II) tetra-chloride. The amount of chloride that is found in solution after the precipitation always indicates that at least two chloride groups are hydrolysed per $[(Mo_6Cl_8)Cl_6]^{2-}$ ion. Thus the initial precipitate is $(Mo_6Cl_8)Cl_4,nH_2O$, which on further digestion gives a

[6] Lindner, Haller, and Helwig, *Z. anorg. Chem.,* 1923, **130**, 209.

material possessing an X-ray powder pattern characteristic of partially hydrolysed chlorohexamolybdenum(II) tetrachloride. One of the secondary products may be $[(Mo_6Cl_8)Cl_3 \cdot OH, 2H_2O]$ (after drying at 130°), for which there is some analytical evidence.

Octachlorohexamolybdenum(II) *Tetrahydroxide.*—In dilute alkaline solution the $[(Mo_6Cl_8)Cl_6]^{2-}$ ion is completely hydrolysed to the soluble $[(Mo_6Cl_8)(OH)_6]^{2-}$ complex. If the pH of the solution is adjusted below 8·5, a yellow gelatinous precipitate, probably $(Mo_6Cl_8)(OH)_4, nH_2O$, appears. A crystalline form of the hydroxide is prepared by the action of dilute ammonia buffer on the original chloro-acid. The exact water content of the crystalline hydroxide cannot be settled by analytical means as it loses water very easily and cannot be safely dried. Lindner and his co-workers favoured a composition corresponding to $(Mo_6Cl_8)(OH)_4, 16H_2O$,[6] and yet in summarising Lindner's and his own analyses, Brosset gave four molybdenum and five chlorine determinations, the mean of which agreed favourably with $(Mo_6Cl_8)(OH)_4, 14H_2O$.[1] The present work indicates a composition $(Mo_6Cl_8)(OH)_4, 15H_2O$, although it must be regarded approximate, like those given above. A decision in favour of the 14-water composition was made by Brosset on the grounds of crystal symmetry and some confirmation was obtained by the agreement of the experimental X-ray diffraction intensities with those calculated for this composition.[1]

The crystalline hydroxide gives two interesting products, $(Mo_6Cl_8)(OH)_4, 2H_2O$ and $(Mo_6Cl_8)(OH)_4$, on dehydration. The conditions of preparation and analyses are given below. Experiments A refer to the present work, and experiments B to those of Lindner and his co-workers,[6] who formulated these hydroxides as $(Mo_6Cl_8)(OH)_4, 4H_2O$ and $(Mo_6Cl_8)(OH)_4, 2H_2O$ respectively. It is significant that $(Mo_6Cl_8)(OH)_4, 2H_2O$ can be

Proposed product	Conditions of prep.	Found (%)	Calc. (%)
$(Mo_6Cl_8)(OH)_4, 2H_2O$	(A) $(Mo_6Cl_8)(OH)_4, 14H_2O$ *in vacuo* at 25°, ~10 hr.	Cl, 29·2	29·5
Orange, amorphous	(B) Heating $(Mo_6Cl_8)(OH)_4, 14H_2O$ at 67—100°	Wt. loss, 18·2	18·3
$(Mo_6Cl_8)(OH)_4$	(A) $(Mo_6Cl_8)(OH)_4, 14H_2O$ *in vacuo* at 200°	Cl, 30·8	30·6
Brown, amorphous	(B) Heating $(Mo_6Cl_8)(OH)_4, 14H_2O$ at 200—300°	Wt. loss, 21·0	21·4

regarded as an octahedral complex. The compound $(Mo_6Cl_8)(OH)_4$ is probably polymerised with respect to (Mo_6Cl_8) in the manner proposed for the halides, and is in fact hygroscopic and becomes paler on hydration.

Hexahydroxo-octachlorohexamolybdenate(II) *Ion.*—The existence of the $[(Mo_6Cl_8)(OH)_6]^{2-}$ ion has been shown by the pH titration of a known alkaline octachlorohexamolybdenum(II) solution by standard acid.[3] The typical curve shows a rapid decrease of pH in the region of 9, after the neutralisation of the excess of alkali, with a cusp at pH 8·5. At this point precipitation of the tetrahydroxo-compound commences and the pH remains constant for most of the remainder of the precipitation. At the equivalence point, corresponding to complete precipitation, the curve passes through the usual wave, with half-wave pH 5·5. Five such titrations are summarised in Table 3. The solutions were prepared from weighed

TABLE 3

| Compound	A 10⁴ mols.	B 10⁴ equivs.	C 10⁴ equivs.	B/A	C/A
$(H_3O)_2[(Mo_6Cl_8)Cl_6], 6H_2O$	3·29	26·0	6·60	7·9	2·0
	3·74	29·2	6·75	7·8	1·8
	1·00	7·8	1·85	7·8	1·85
$(Mo_6Cl_8)(OH)_4, 14H_2O$	1·61	3·11		1·95	
	0·43	0·85		1·95	

quantities of the chloro-acid or the crystalline tetrahydroxo-compound (given in moles in column A) dissolved in known volumes of 0·1n-sodium hydroxide and titrated with 0·1n-nitric acid. Column B gives the equivalents of hydroxide consumed by dissolving the octachlorohexamolybdenum(II) compound in the known alkali. This is given by the difference of the number of equivalents originally taken and the number neutralised up to the cusp at pH 8·5. Column C gives the equivalents of neutralisable hydroxo-groups in the hydroxo-complex and is found from the equivalents of acid added between the cusp

and the half-wave point at pH 5·5.   Quantities B and C are identical for the crystalline hydroxo-compound but not for the chloro-acid.   The ratio B/A is eight for the chloro-acid, in agreement with the reaction of two hydroxonium and six chloride groups with alkali.   The ratio C/A for both starting compounds is close to two, confirming the view that the hydroxo-complex is $[(Mo_6Cl_8)(OH)_6]^{2-}$.

The reaction of the hexahydroxo-complex might have been expected to proceed in two steps to the tetrahydroxide, $[(Mo_6Cl_8)(OH)_5H_2O]^-$ being the intermediate.   The large size of the octachlorohexamolybdenum(II) group renders such a stepwise reaction unlikely, for the *trans*-hydroxo-groups (the most likely to be protonated successively) are separated by several molybdenum atoms.   The protonation of one hydroxo-group will have little effect on the basicity of the *trans*-group, and the titration curves establish that the two hydroxo-groups react with indistinguishable basicity.

Ultraviolet Absorption Spectra.—Absorption spectra have been published [3] for the range 250—400 mμ of octachlorohexamolybdenum(II) solutions in 5N-hydrochloric and -hydro-

FIG. 2.   *Absorption spectra of* Mo_6Cl_8 *compounds in* (A) 2M-H$_2$SO$_4$ *and* (B) 2M-HClO$_4$.
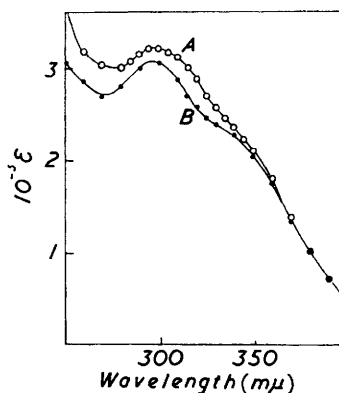
bromic acid and in 0·01N-sodium hydroxide.   The spectra for 2M-perchloric and -sulphuric acid solutions are given in Fig. 2 and Table 4.   At wavelengths shorter than 300 mμ the solvents and the solutions are intensely absorbing, and beyond 400 mμ the solutions possess no

TABLE 4.

Solvent	Band I λ (mμ)	10^{-3} ε	Band II λ (mμ)	10^{-3} ε	Solvent	Band I λ (mμ)	10^{-3} ε	Band II λ (mμ)	10^{-3} ε
5N-HCl	307·5	2·93	345 (sh)	2·68	2N-HClO$_4$ ...	298	3·2	~330 (sh)	2·4
5N-HBr	305 (sh)	3·8	352·5	3·4	2M-H$_2$SO$_4$ ...	298	3·05	~330 (sh)	2·4
0·01N-NaOH	300	3·8	~330 (sh) [a]						

sh = shoulder.   [a] Very weakly defined.

absorption bands.   The intensities of these bands indicate that they are not ligand field transitions, and the failure to observe them supports the view that molybdenum(II) is sexivalent in these complexes.   It is consistent with the chemistry of octachlorohexa-molybdenum(II) that aqueous solutions of this group in the presence of excess of chloride, bromide, hydroxide, or perchloric acid should contain $[(Mo_6Cl_8)X_6]$ complexes.   It is perhaps unexpected that the spectra assigned to these different complexes are similar. The bands may be assigned to charge transfer associated mainly with the octachlorohexa-molybdenum(II) group.   The intense absorption of the chloro-ion at 250 mμ appears at progressively longer wavelength for the bromo- and iodo-ions, and masks bands I and II almost completely in the last case.

Magnetic Susceptibility.—The molar susceptibilities of the chloride, hexachloro-acid, and diammonium salt have been found to be —230, —360, and —240 × 10^{-6} c.g.s. units

at 25°. In addition, the bromide and iodide, and the bromo- and iodo-acid are found to be diamagnetic.

The diamagnetism and effective co-ordination number nine of molybdenum are strong evidence that molybdenum is formally sexivalent in octachlorohexamolybdenum(II). Ultraviolet spectra and the stability of the compounds towards oxidation support this. The thesis that molybdenum exists in a lower effective valency, and thus possesses non-bonding d-electrons and empty d-orbitals, is more difficult to rationalise with the observed properties of octachlorohexamolybdenum(II) compounds.

EXPERIMENTAL

Preparation of Octachlorohexamolybdenum(II) *Compounds.—Octachlorohexamolybdenum*(II) *tetrachloride.* (a) A thick-walled Pyrex tube was constricted at two points to give three compartments. In the first two were placed equal quantities of molybdenum powder. Moisture and oxygen were removed by heating the whole with passage of nitrogen. The molybdenum in compartment 1 was heated in chlorine, and the resulting molybdenum(v) chloride condensed before reaching compartment 2. The chloride was gently warmed in a nitrogen stream, and the vapour passed over the molybdenum in compartment 2 at red heat. The molybdenum(III) chloride produced sublimed into compartment 3 and there disproportionated to octachlorohexamolybdenum(II) and molybdenum(v) chloride when heated to the softening point of Pyrex glass, the former product remaining as a residue, the latter distilling from the tube. The tetrachloride in compartment 3 is tolerably pure (Found: Cl, 42·3; Mo, 57·3; Mo_6Cl_8, 85·8. Calc. for $Cl_{12}Mo_6$: Cl, 42·5; Mo, 57·5; Mo_6Cl_8, 85·9%), but is frequently paramagnetic and leaves a dark residue on dissolution in hydrochloric acid. The main impurity is molybdenum(III) chloride owing to the incomplete disproportionation. Excessive heating is to be avoided, however, as the tetrachloride itself disproportionates to metal and higher halide at very high temperatures.

(b) The crude tetrachloride was dissolved in hot 17% hydrochloric acid, and any residue filtered off. The solution was concentrated, refiltered, and cooled in ice. A good yield of the chloro-acid, as bright yellow needles, was obtained on stirring. The crystals were filtered off and were heated *in vacuo*, appearing to decompose stepwise with vigorous decomposition at 200°. The residue was octachlorohexamolybdenum(II) tetrachloride. It was diamagnetic and soluble in hydrochloric acid without residue. The *compound* should be stored in anhydrous conditions (Found: Cl, 42·6; Mo, 57·2; Mo_6Cl_8, 85·2%).

Dihydroxonium hexachloro[octachlorohexamolybdate(II)*] 6-Water (Chloro-acid)* $(H_3O)_2[(Mo_6Cl_8)Cl_6],6H_2O$.—The solubility of the acid (cf. *b* above) depends on the temperature: 1% in 1 : 1 hydrochloric acid at 25°, <0·1% at 0°, though supersaturation is frequently observed. The *acid* rapidly loses water and hydrogen chloride if exposed and must be stored in a stoppered vessel after gentle drying in air (Found: Cl, 40·8; Mo, 47·6. $H_{18}Cl_{14}Mo_6O_8$ requires Cl, 40·8; Mo, 47·2%).

Dihydroxonium Hexabromo[octachlorohexamolybdate(II)*] 6-Water and Dihydroxonium Hexaiodo[octachlorohexamolybdate*(II)*] 6-Water (Bromo- and Iodo-acid).*—These were prepared analogously to the chloro-acid. The tetrachloride (or chloro-acid) was dissolved in hot ~5N-hydrobromic or -hydriodic acid; the corresponding halogeno-acid separated. Recrystallisation is difficult owing to the low solubility of these complex acids, and it is best to use pure tetrachloride. The bromo-acid separates as plates which pack together and so do not dry satisfactorily. These complex *acids* are unstable and should be stored in closed vessels [Found: (a) equivs. of halogen per g., 0·00943; Mo_6Cl_8, 58·8%. $H_{18}Br_6Cl_8Mo_6O_8$ requires equivs. of halogen per g., 0·00943; (Mo_6Cl_8), 57·9%. (b) Found: Cl, 15·8; I, 43·1; Mo_6Cl_8, 49·9. $H_{18}Cl_8I_6Mo_6O_8$ requires Cl, 16·0; I, 43·1; Mo_6Cl_8, 48·6%].

Octachlorohexamolybdenum(II) *Tetrabromide and Tetraiodide.*—These *compounds* are obtained as residues by heating the appropriate halogeno-acid to 200° *in vacuo*, and should be stored in anhydrous conditions [(a) Found: Br, 27·8; Cl, 23·2; Mo_6Cl_8, 74·1. $Br_4Cl_8Mo_6$ requires Br, 27·2; Cl, 24·0; Mo_6Cl_8, 72·9. (b) Found: Cl, 21·0; I, 37·1; Mo_6Cl_8, 63·0. $Cl_8I_4Mo_6$ requires Cl, 20·8; I, 37·2; Mo_6Cl_8, 63·0%].

Diammonium Hexachloro[octachlorohexamolybdate(II)*] 1-Water.*—This sparingly soluble crystalline *salt* separates from a concentrated ammonium chloride solution on the addition of

the chloro-acid. It appears to be stable in air and, though evolving ammonium chloride when strongly heated, does not give the tetrachloride with the same ease as the chloro-acid does (Found: Cl, 44·4; Mo, 50·9. $H_{10}Cl_{14}Mo_6O$ requires Cl, 44·2; Mo, 51·1%).

Bistriethylaminetetrachloro[*octachlorohexamolybdenum*(II)] *and Bispyridinetetrachloro*[*octa-chlorohexamolybdenum*(II)].—Mixing ethanol solutions of triethylamine or pyridine and of the tetrachloride, followed by addition of light petroleum, gives a pale yellow finely divided precipitate which may be dried *in vacuo*. Both addition *compounds* are amorphous to *X*-rays and when strongly heated *in vacuo* give the tetrachloride [(*a*) Found: C, 11·0; H, 2·6; Cl, 35·6; Mo_6Cl_8, 71·8. $C_{12}H_{30}Cl_{12}Mo_6N_2$ requires C, 11·9; H, 2·5; Cl, 35·4; Mo_6Cl_8, 71·5. (*b*) Found: C, 10·1; H, 1·0; Cl, 36·8; Mo_6Cl_8, 73·6; N, 2·6. $C_{10}H_{10}Cl_{12}Mo_6N_2$ requires C, 10·35; H, 0·85; Cl, 36·8; Mo_6Cl_8, 74·1; N, 2·4%].

Octachlorohexamolybdenum(II) *Tetrahydroxide* 14-*Water*.—The tetrahalides, and the halogeno-acids and their soluble salts, dissolved in a minimum of aqueous ammonia–ammonium nitrate buffer solution, gave a precipitate of the *tetrahydroxide* which was filtered off and dried carefully in air (Found: Cl, 23·9; Mo, 48·0; Mo_6Cl_8, 71·7. $H_{32}Cl_8Mo_6O_{18}$ requires Cl, 24·0; Mo, 48·8; Mo_6Cl_8, 72·9%).

Analytical Techniques.—Carbon, hydrogen, and nitrogen analyses were done by standard micro-procedures. Determination of halogens and molybdenum required hydrolysis to molybdenum(V) hydroxide and its conversion into molybdate by hydrogen peroxide. Halogens were determined potentiometrically, by titrating the acidified hydrolysis solution with standard silver nitrate.

Molybdenum was determined as lead molybdate. This procedure was particularly time-consuming and a rapid, though less accurate, spectrophotometric estimation of octachlorohexa-molybdenum(II) was adopted. A weighed quantity of compound was dissolved in hot 5N-hydrochloric acid and converted into a hexachloro[octachlorohexamolybdenum(II)] solution. The optical densities of the solution, determined from 300 to 400 mμ, were converted into molarities by the extinction coefficients listed in the Table for the hexachloro-anion. If this ion is the only absorbing species, the molarities should be substantially independent of wavelength and the mean was taken as that of the octachlorohexamolybdenum(II) in the prepared solution.

λ (mμ)	300	310	320	330	340	350	360	370	380	390	400
$10^{-3} \varepsilon$	2·87	2·92	2·82	2·70	2·68	2·66	2·48	2·14	1·67	1·23	0·86

Product of the Hydrolysis of the Chloro-acid.—The precipitate from a solution of the acid in warm water was rapidly filtered off and dried *in vacuo* at 200° (Found: Cl, 42·5; Mo_6Cl_8, 85·5%). A large number of analyses on the digested precipitates indicates the product of moderate hydrolysis of the precipitated hydrated tetrachloride to be $(Mo_6Cl_8)Cl_3 \cdot OH, nH_2O$, which dries at 130° to give $(Mo_6Cl_8)Cl_3 \cdot OH, 2H_2O$. A typical experiment is given. 0·8021 g. of chloro-acid, when boiled in water for 5 min., gave quantitatively a precipitate which after drying at 130° weighed 0·6648 g. The filtered solution contained $2·03 \times 10^{-3}$ mole of chloride and the precipitate $7·21 \times 10^{-3}$ mole. Thus 3·07 mol. of chloride are liberated and the molecular weight of the dried product determined by the yield is 1010 (theor., 1018) (Found: Cl, 38·5. Calc. for $H_5Cl_{11}Mo_6O_3$: Cl, 38·3%).

Cryoscopic Determination of Molecular Weights.—The freezing points of air-jacketed and stirred samples of " AnalaR " nitrobenzene were determined at least in duplicate by the warming-curve technique. Temperatures were read by a thermometer calibrated to 0·01° and K_f for nitrobenzene was taken as 6·9.

Molecular Conductivity.—Approx. 0·05 g. of the compound was made up to 25 ml. with " AnalaR " nitrobenzene. The conductivity cell, having shiny platinum electrodes and a constant 0·235, was kept at 25° and conductance readings were taken by a Wayne Kerr Universal B221 bridge.

Ultraviolet Absorption Spectra.—It was demonstrated that only one absorbing molybdenum species, presumably the $[(Mo_6Cl_8)Cl_6]^{2-}$ ion, was present in an octachlorohexamolybdenum(II) solution in 2—5N-aqueous chloride. A number of compounds, namely, the tetrachloride, the chloro-acid, the diammonium chloro-salt, and the crystalline hydroxide, gave the same spectrum in 2—5N-hydrochloric acid and 2—5N-sodium chloride. In view of the purity with which the chloro-acid and its ammonium salt could be prepared, these were taken as standards, and the molar extinction coefficients for the chloro-anion determined from optical density–molarity

plots at various wavelengths. These coefficients are listed in the preceding Table. A similar survey of octachlorohexamolybdenum(II) compounds in concentrated perchloric or sulphuric acid, diluted to 2M-acid, showed that the spectra were reproducible in the particular acid, indicating a common absorbing species in these solutions and plausibly this is the $[(Mo_6Cl_8)(H_2O)_6]^{4+}$ ion, but a small divergence between spectra in the two acids. Spectra reported for $[(Mo_6Cl_8)Br_6]^{2-}$ and $[(Mo_6Cl_8)(OH)_6]^{2-}$ are the mean of a few concordant spectra of various octachlorohexamolybdenum(II) compounds in 5N-hydrobromic acid or 4N-sodium bromide, and in 0·1—0·01N-sodium hydroxide. It was possible to obtain only a rough spectrum of octachlorohexamolybdenum(II) in aqueous iodide. Potassium iodide solution gives a precipitate of the potassium chloro-salt, and hydriodic acid is too rapidly oxidised for reliable results.

Magnetic Susceptibility.—This was determined at ∼25° by the Gouy method, employing a permanent magnet and Pyrex glass tubes calibrated with powdered copper(II) sulphate 5-water.

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