621. *Chloride Exchange and Bromide Substitution of the Hexachloro-octa-μ_3-chlorohexamolybdate*(II) *Ion.*

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A study of the chloride exchange and bromide substitution of the hexachloro-octa-μ_3-chlorohexamolybdate(II) ion, $[(Mo_6Cl_8)Cl_6]^{2-}$, in aqueous and moist ethanolic solutions has established that (i) the bonding within the complex ion is covalent, (ii) only the six peripheral chloride groups are capable of replacement, (iii) the rate of exchange or substitution is independent of halide-ion concentration and both processes have a similar rate constant. It is concluded that these reactions proceed through a common rate-determining aquation step.

THE crystal-structure determinations of certain molybdenum(II) chloride derivatives, namely, $[(Mo_6Cl_8)Cl_4,2H_2O],6H_2O$ [1] and $[(Mo_6Cl_8)(OH)_4,2H_2O],12H_2O$,[2] have established the existence of the $(Mo_6Cl_8)^{4+}$ group [given the short name " chloromolybdenum(II) "] and its ability to form co-ordination complexes of the type $[(Mo_6Cl_8)X_6]$. The present work is a quantitative study of the chlorine-36 exchange and bromide substitution of the hexachloro-octa-μ_3-chlorohexamolybdate(II) ion, $[(Mo_6Cl_8)Cl_6]^{2-}$, in aqueous hydrochloric acid or moist ethanol and attempts to establish the nature of bonding and relative labilities of the chlorine atoms within this complex.

EXPERIMENTAL

Counting Equipment.—A Twentieth Century Electronics Ltd. liquid counter type M6 (vol. 10 ml.) was used in conjunction with an Ekco Electronics Ltd. scaler type N529. Counting rates varied from 70 to 2000 counts min.$^{-1}$ with a background of 8—15 counts min.$^{-1}$.

Materials.—Dihydroxonium hexachloro-octa-μ_3-chlorohexamolybdate(II) *Hexahydrate,* $(H_3O)_2[(Mo_6Cl_8)Cl_6],6H_2O$. This was prepared as previously described;[3] 1% stock solutions were prepared by weighing out the almost dry *acid* (to avoid decomposition) and dissolving it

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[1] Brosset, *Arkiv Kemi, Min., Geol.*, 1947, **22**, *A*, No. 11.
[2] Brosset, *Arkiv Kemi, Min., Geol.*, 1946, **20**, *A*, No. 7.
[3] Sheldon, *Nature*, 1959, **184**, 1210.

in the desired solvent (*i.e.*, 5·6N-hydrochloric acid or "commercial" absolute ethanol). The concentrations of the hexachloro-acid solutions were checked by spectrophotometry,[3] and the solutions diluted as required.

Chlorine-36. This was obtained from the Radiochemical Centre, Amersham, in the form of $\sim$2N-hydrochloric acid, activity 116 μc g.$^{-1}$ of chlorine. Stock solutions were prepared by adding 1—2 ml. of this to 500 ml. of 5·6N-hydrochloric acid or ethanol. The chloride concentration of these solutions was determined by titration with silver nitrate. The chloride activity of the ethanol solutions was determined by counting a sample diluted in 1 : 1 water–ethanol, and of the aqueous solutions by precipitation of the chloride as silver chloride and counting a dried and weighed sample dissolved in ammonia solution.

Bromide solutions. Ethanolic bromide solutions were prepared from weighed quantities of lithium bromide and the concentrations checked by titration with silver nitrate.

Experimental Procedure.—Equal quantities of hexachloro-acid and chlorine-36 or bromide solutions (in a common solvent) were mixed within a thermostat, and aliquot parts withdrawn at known times for assay. The hexachloro-acid was quantitatively separated from 5·6N-hydrochloric acid solution as the triphenylphosphonium salt by the addition of a 25% solution of triphenylphosphine in concentrated hydrochloric acid. This salt was filtered off, washed with water, and decomposed in hot alkaline peroxide solution, and the chloride precipitated as silver chloride. A weighed quantity of the dried silver chloride was dissolved in ammonia solution and counted. Alternatively, a slow separation of the hexachloro-acid could be effected by crystallisation from the hydrochloric acid solution at 0°. The exchanged or substituted hexachloro-acid was separated from ethanol solutions as the tetraethylammonium salt by the addition of 2—5 vol. of 1% tetraethylammonium chloride solution [in 1 : 4 ethanol–light petroleum (b. p. 40—60°)]. The precipitated ammonium salt was filtered off, washed with ethanol–light petroleum, and dried at 110°. A weighed quantity of the salt was decomposed by hot alkaline peroxide solution and assayed for chlorine-36 (after adjustment of the solution to known volume and to the composition 1 : 1 water–ethanol) or analysed for bromide and chloride by titration.

Bistetraethylammonium and Bistriphenylphosphonium Hexachloro-octa-μ_3-chlorohexamolybdate-(II).—The existence of these compounds has been recorded[4] but without details. They can be prepared as described above. These salts are pale yellow powders which are, in common with other insoluble chloromolybdenum(II) salts, amorphous under the microscope but crystalline to *X*-rays. Chloromolybdenum(II) complexes which are non-electrolytes, on the other hand, are usually amorphous even to *X*-rays. The two hexachloro-salts are stable to moist air at 25° and *in vacuo* at 250°, and are insoluble in water though somewhat soluble in polar organic solvents. The triphenylphosphonium salt is converted into a triphenylphosphine oxide–chloromolybdenum(II) addition compound in air at 200°, or loses triphenylphosphine at 500° *in vacuo* to give molybdenum(II) chloride [Found (for tetraethylammonium salt): C, 14·6; H, 3·1; Cl, 37·2; N, 2·5. Calc. for $C_{16}H_{40}Cl_{14}Mo_6N_2$: C, 14·4; H, 3·0; Cl, 37·2; N, 2·1. Found (for triphenylphosphonium salt): C, 27·1; H, 2·1; Cl, 31·4. Calc. for $C_{36}H_{32}Cl_{14}Mo_6P_2$: C, 27·4; H, 1·9; Cl, 31·1%].

RESULTS AND DISCUSSION

Exchange in 5·6N-*Hydrochloric Acid at* 25°.—The hexachloro-acid, $(H_3O)_2[(Mo_6Cl_8)Cl_6],6H_2O$, was chosen for study on account of its solubility in hydrochloric acid and ethanol. Water attacks a soluble hexachloro-complex and precipitation of the hydrolysis product, $(Mo_6Cl_8)Cl_4,nH_2O$, commences within seconds and is complete in a few minutes. The hexachloro-complex appears to be indefinitely stable in 5N-hydrochloric acid or ethanol and thus these solvents are suitable for this investigation. Typical results of the chloride exchange of $\sim10^{-3}$M-hexachloro-acid with labelled 5·6N-hydrochloric acid are given in the following Table. The number of chlorine atoms exchanged per hexa-

Time (min.)	0·13	0·25	2	10	$\sim$30 [a]	3·9 × 10³	$\sim$100 [b]
Atoms of Cl exchanged per mole of complex	2·9	2·5	6·5	6·0	6·3	6·0	5·9

[a] Hexachloro-acid separated by crystallisation at 0°. [b] Exchange at boiling point of solution.

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

chloro-complex never significantly exceeds 6 even in boiling solution. The number exchanged is less than 6 for times of the order of seconds, but such experiments are inaccurate, as the times of mixing and separation are comparable with that of exchange. These observations indicate that only the peripheral (non-bridging) chlorine atoms are capable of exchange and do so at a rate comparable with the rate of hydrolysis. The exchange may therefore proceed by an aquation mechanism

$$[(Mo_6Cl_8)Cl_6]^{2-} + H_2O \rightleftharpoons [(Mo_6Cl_8)Cl_5,H_2O]^{-} + Cl^{-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

in which the slow forward reaction is followed by a fast reverse one involving labelled chloride ions leading to a net exchange. This mechanism requires first-order kinetic dependence for the hexachloro-complex and zero-order for chloride. It is difficult to test these requirements by measurements in aqueous solutions as there are major difficulties in adopting conditions in which the exchange is sufficiently slow.

Exchange in Ethanol at 25°.—The ethanol solutions used in this work have a 0·1—1·0M-water content, by virtue of their preparation from materials containing bound and free water, which is greatly in excess of the complex and chloride (or bromide) concentrations. Thus the reaction mechanism in these ethanol solutions will most likely be that corresponding to aqueous solutions. The hexachloro-complex exchanges with 10^{-2}M-chloride in ethanol with a half-life of the order of 0·5 hr. and so kinetic investigation is possible. It is not easy to establish the number of chlorine atoms exchanging per hexachloro-complex at concentrations of 10^{-2}M owing to isotopic dilution. The difference between the theoretical activity gained (S_∞, 10^4 counts min.$^{-1}$ g.$^{-1}$ of tetraethylammonium salt) for the exchange of 6 or 14 chlorine atoms is usually of the order of the experimental error, but is sufficiently great in Expts. 1 and 2 for useful comparison:

	Expt. 1	Expt. 2
S_∞, found	7·1	9·05
S_∞, calc. for 6 atoms exchanged	6·65	7·8
S_∞ ,, 14 ,,	9·75	12·7

The experimental values are closer to those expected for the exchange of 6 atoms than for 14, and in view of the results given above for experiments in hydrochloric acid, it is reasonable to conclude that only 6 chlorine atoms exchange per complex ion in moist ethanol.

The exchange data give a linear relation of ln (1 — F) (where F is the exchange fraction, *i.e.*, S_t/S_∞) against time (t) up to about 90% exchange and this establishes the kinetic equivalence of the 6 peripheral chlorine atoms. The rate constant (k) given in the Table below has been obtained from the gradients of the ln (1 — F) versus t plots by McKay's method [5] on the assumptions that (i) only 6 chlorine atoms exchange per complex, (ii) the rate of exchange is independent of chloride-ion concentration and is of first order in complex concentration.

Expt. no.	Concn. (mole l.$^{-1}$) $[(Mo_6Cl_8)Cl_6]^{2-}$	Concn. (mole l.$^{-1}$) Cl^-	10^4k (sec.$^{-1}$)
1	0·0016	0·0123	3·8
2	0·00195	0·0230	3·5
3	0·0157	0·0123	3·5
4	0·00195	0·00123	3·7
5	0·00080	0·0123	4·1

The acceptable consistency of the first-order rate constant justifies the above assumptions and also suggests that the rate is independent of the water concentration although water may play a part in the exchange (or substitution) reaction (see eqn. 1). The hexachloro-complex may be completely solvated by water in these ethanol solutions and the rate of aquation of the complex is thus insensitive to moderate variations of water content of the solvent.

Bromide Substitution in Ethanol at 22°.—The substitution of hexachloro-octa-μ_3-chloro-hexamolybdate(II) by bromide is rapid and complete in aqueous 5N-bromide solution,

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[5] McKay, *Nature*, 1938, **142**, 997.

yielding hexabromo-octa-μ_3-chlorohexamolybdate(II). A similar but slow substitution occurs in 4M-ethanolic lithium bromide solution, although only partial replacement of the 6 chlorine atoms occurs in the 0·04—2·0M-bromide range employed for kinetic investigation. It is plausible that the rates of forward and reverse substitution $[(Mo_6Cl_8)Cl_6]^{2-} + Br^- \rightleftharpoons [(Mo_6Cl_8)Cl_5Br]^{2-} + Cl^-$ are independent of halide-ion concentration in view of the results of the exchange experiments. Furthermore, it is likely that the rates of forward or reverse substitution of an intermediate complex $[(Mo_6Cl_8)Cl_nBr_{6-n}]^{2-}$ are independent of n as the peripheral halogen atoms are separated from each other by 2 or 3 molybdenum atoms. These ideas are confirmed by the linear relationship found between ln $(1 - R)$ (where R is the ratio of the amount of substitution at time t to that at infinite time) and t. It is therefore possible to treat the bromide-substitution reaction kinetically in the same manner as the chloride exchange, except that the first-order rate constant is now $(k_1 + k_2)$, where k_1 and k_2 are the constants for the forward and the reverse reaction, respectively. In the following Table are given the fractions of peripheral chloride groups replaced at equilibrium (R_∞), the equilibrium constant (K) for the system $[(Mo_6Cl_8)Cl_6]^{2-} + 6Br^- \rightleftharpoons [(Mo_6Cl_8)Br_6]^{2-} + 6Cl^-$, and $(k_1 + k_2)$ for three experiments.

	Concn. (mole l.$^{-1}$)				
Expt. no.	$[(Mo_6Cl_8)Cl_6]^{2-}$	Br^-	R_∞	K	$10^4(k_1 + k_2)$ (sec.$^{-1}$)
1	0·0126	0·0414	0·33	0·78	4·0
2	0·0126	0·414	0·685	0·31	3·0
3	0·0126	2·06	0·915	0·35	2·0

There is reasonable agreement between the values of $(k_1 + k_2)$, for these only decrease by a factor 2 over a 50-fold bromide concentration change. The most satisfactory values of K and $(k_1 + k_2)$ are likely to be given by Expt. 1 which used the most dilute solutions, and these give k_1 and k_2 (at 22°) as 1·8 and 2·2 × 10^{-4} sec.$^{-1}$, respectively. It can then be seen that the substitution-rate constants are similar to the chloride-exchange rate constant (3·7 × 10^{-4} sec.$^{-1}$ at 25°) and this lends further support to the idea that exchange and substitution of the hexachloro-complex proceed by similar mechanisms.

Conclusion.—The bonding within the hexachloro-octa-μ_3-chlorohexamolybdate(II) ion is covalent (in the sense that there is little ionic dissociation) in view of the measurable rate of replacement of the peripheral chlorine atoms, and the inertness of the bridging atoms. The independence of the exchange and substitution rates on the nature of the halide ion reacting or on its concentration supports the view that these reactions involve preliminary dissociation of a Mo–Cl bond, probably by nucleophilic attack of water, as a rate-determining step. It might appear that the bridging chlorine atoms are very strongly bound within the chloromolybdenum(II) group, but their lack of reactivity may well be due to the inability of water to occupy a bridging position between three molybdenum atoms as a prelude to halide-ion attack giving a substitution of the chloromolybdenum(II) group.

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