

Reaction Mechanisms of Binuclear Complexes Containing a Quadruple Metal–Metal Bond. The Reaction of Acetic Acid with Potassium Octachlorodimolybdate(II)¹

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The reaction of acetic acid with equilibrated solutions of tetrapotassium octachlorodimolybdate(II) in hydrochloric acid, p-toluenesulphonic acid (HPTS) and mixtures of these two acids has been studied. In HPTS the final product is tetrakisacetato-dimolybdenate(II), but in chloride-containing media mixed chloroacetato complexes are obtained. The reaction proceeds in two observable stages in all reaction media, and the kinetics of these two reactions have been measured. Both reactions are first order in complex, and the observed rate laws are of the form

$$k_{obs,1} = \left\{ \frac{[CH_3CO_2H]}{1 + [CH_3CO_2H]} \right\} \left\{ \frac{A_1 + A_0 [H^+]}{[H^+]} \right\}$$
$$k_{obs,2} = \left\{ \frac{[CH_3CO_2H]}{1 + \beta [CH_3CO_2H]} \right\} \{A'_1 [Cl^-]^2 + A'_0\}^{-1}$$

These two reactions are ascribed to the introduction of the first and third acetate ligands, respectively. A dissociative mechanism bearing considerable similarity to that for substitution reactions of octahedral cobalt(III) systems, is suggested.

Introduction

The chemistry of binuclear complexes containing a metal–metal quadruple bond has grown rapidly [2], since the synthesis [3] and structure elucidation [4] of the first compound of this type, $Mo_2(O_2CCH_3)_4$. The striking features of these compounds are the eclipsed square prismatic structure and the high formal order of the bond between the two metal atoms. This bond is evidently a structural unit of considerable robustness, as many substitution reactions of complexes of the type $M_2X_8^{4-}$ are known in which the quadruple bond is retained [2, 5–12]. Substitution reactions have been employed extensively for synthetic purposes in the preparation of new binuclear species of Mo^{II} [5, 7, 8, 12] and Re^{III} [6, 9–11].

Despite the extensive use of substitution reactions in the study of these compounds, there appear to have been only two reports concerning the kinetics

and mechanisms of these reactions [13, 14]. Hynes [13] measured the kinetics of the reactions of $Re_2X_8^{2-}$ ($X = Cl, Br$) with tri(*n*-butyl)phosphine and thiourea, and of $Re_2Cl_8^{2-}$ with Br^- . He proposed a two-path mechanism involving in one path a dissociative intermediate $Re_2X_7^-$, and in the other an associative intermediate $Re_2X_8Y^{2-}$. The results reported by Webb and Espenson [14] are relevant to Hyne's study only indirectly in that they also studied the kinetics of a reaction involving species containing a quadruple metal–metal bond. Noting the complications introduced by the possibility of substitution of all eight ligands in $Re_2X_8^{2-}$, Webb and Espenson sought to study the substitution of ligands in the axial positions of the related compounds $Re_2X_8Y_2$, where $X = O_2CC_2H_5/2$ was chosen such that the eight ligand positions of the square prism are inert to substitution.

Since the bulk of the reactions that have been employed synthetically involve substitution of ligands coordinated in the square prism, we sought to study the kinetics and mechanism of such a reaction. This paper reports the first of a series of mechanistic investigations of the substitution reactions of binuclear molybdenum complexes possessing square-prismatic geometry.

Experimental

Tetrapotassium octachlorodimolybdate(II) was prepared by the method of Brencic and Cotton [15]. All other materials were reagent grade and were used without further purification. Triply distilled water was used throughout.

Solutions of complex for spectral and kinetic measurements were prepared under a nitrogen atmosphere by dissolving weighed amounts of $K_4Mo_2Cl_8$ in previously deoxygenated solutions of the appropriate composition. Ligand solutions were also vigorously deoxygenated. Spectra were recorded on a Cary 14 spectrophotometer or a Perkin Elmer 402 spectrophotometer. A Durrum stopped-flow spectrophotometer, equipped with a thermostatted flow system that enabled the temperature to be controlled

to $\pm 0.2K$, was used for the kinetic measurements. Measurements were made at 512 nm, where a solution of $K_4Mo_2Cl_8$ in hydrochloric acid (2.0 mol dm^{-3}) shows an absorbance maximum. Some reactions were also measured at 528 nm, but no significant differences between the two sets of data were noted. Reactions were always conducted in a large excess of acetic acid to ensure pseudo-first-order conditions with respect to the complex.

Spectra of intermediate stages of the kinetic run were obtained by measuring the absorbance at various wavelengths at fixed times after initiation of the reaction between the molybdenum species and acetic acid.

The oxidation state of the reaction product was determined by titration with potassium permanganate [8].

Results and Discussion

Spectroscopic Measurements

The spectra of solutions of $K_4Mo_2Cl_8$ in HCl (2 mol dm^{-3}) (Fig. 1), in *p*-toluenesulphonic acid (HPTS) (2 mol dm^{-3}) and in 2 mol dm^{-3} mixtures of these acids are extremely similar. All possess peaks in the visible region at 510 nm, but the intensities vary with the chloride concentration (HPTS, $\epsilon = 330$; HCl, $\epsilon = 358$). In more concentrated HCl solutions, the spectrum is qualitatively unchanged, but the peak position shifts to longer wavelengths and there are small intensity changes (6 mol dm^{-3} HCl, $\lambda_{\text{max}} = 518 \text{ nm}$, $\epsilon = 375$; 11 mol dm^{-3} HCl, $\lambda_{\text{max}} = 522 \text{ nm}$, $\epsilon = 340$).

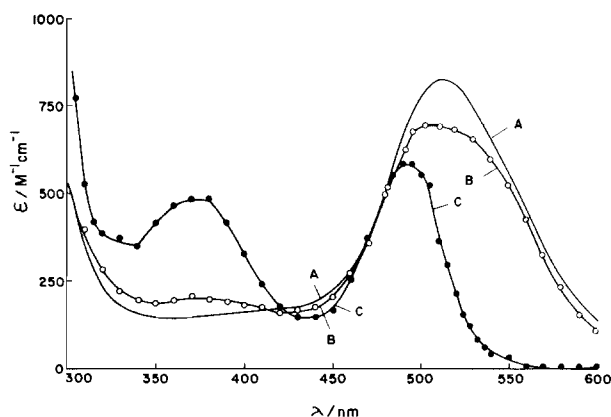


Figure 1. A. Spectrum of $K_4Mo_2Cl_8$ in HCl (1.95 mol dm^{-3}). B. Stopped-flow determination of spectrum of reaction of $K_4Mo_2Cl_8$ with acetic acid in HCl (1.95 mol dm^{-3}) at one-fifth half-life of first reaction (10 msec). C. Stopped-flow determination of spectrum of reaction of $K_4Mo_2Cl_8$ with acetic acid in HCl (1.95 mol dm^{-3}) at completion of first reaction (500 msec).

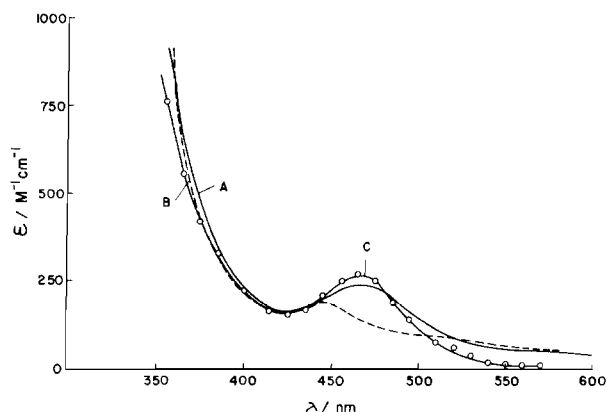


Figure 2. A. Spectrum after complete reaction between $K_4Mo_2Cl_8$ and acetic acid in HCl (1.95 mol dm^{-3}) (total time to completion of reaction after initiation of reaction, ca. 15 min). B. Spectrum after complete reaction between $K_4Mo_2Cl_8$ and acetic acid in HPTS (1.95 mol dm^{-3}). C. Stopped-flow determination of spectrum after complete reaction between $K_4Mo_2Cl_8$ and acetic acid in HCl (1.95 mol dm^{-3}), 25 sec after initiation of reaction.

When solutions in 2 mol dm^{-3} acid are treated with a solution of acetic acid in the same medium, the peak at 510 nm disappears and is replaced by an absorption band in the 440–465 nm region (Figure 2). The peak position is shifted within this range to longer wavelengths by increased chloride concentration. The spectrum in HPTS ($\lambda_{\text{max}} = 443 \text{ nm}$; $\epsilon = 190 \text{ M}^{-1} \text{ cm}^{-1}$) is in good agreement with that reported for $Mo_2(O_2CCH_3)_4$ in the solid state and in ethanol solution [16]. On standing, $Mo_2(O_2CCH_3)_4$ precipitates from HPTS solution but not from any of the chloride-containing solutions. The oxidation state of the final molybdenum species was determined to be +II. The spectra are stable with time only if oxygen is rigorously excluded. If this is not done then the peak at 440–465 nm slowly disappears, and molybdenum(VI) is the final product, as established by oxidation state determination and comparison with the spectrum of sodium molybdate in the same medium. The oxidation which occurs in at least two stages subsequent to the substitution reactions discussed here was not investigated, and we shall confine ourselves to the processes taking place when air is excluded.

When the mixing is monitored at 512 nm in the stopped-flow spectrophotometer, the absorbance is observed to fall in two stages, the half-life of the first processes being 6–60 times faster than that of the second. From the kinetic data (discussed below) it is possible to choose values of time such that both processes are essentially complete, and to construct a spectrum of the reaction solution at this time. The spectrum for the reaction in 1.95 mol dm^{-3} HCl is shown in Figure 2. The spectrum observed on the conventional spectrophotometer corresponds almost

exactly and certainly with respect to peak position, to that obtained at completion of the two kinetic events (differences are probably due to a small extent of oxidation that may have taken place in the time between mixing and the end of the determination of the spectrum on the conventional spectrophotometer: under most favourable conditions this is *ca.* 10 min; 10 half-lives of the second reaction can be as little as 15 sec.)

Similarly spectra were obtained at times corresponding to completion of the first reaction, but essentially before the second reaction had begun. Figure 2 shows the spectrum for the reaction in 1.95 mol dm⁻³ HCl. Peak position and intensity ($\lambda_{\text{max}} = 492 \text{ nm}$; $\epsilon = 575 \text{ M}^{-1} \text{ cm}^{-1}$) are intermediate between the initial and final spectra. A second peak at 375 nm is also observed, which has no counterpart in either the starting material or the final product. Spectra obtained at times corresponding to *ca.* one-fifth of the half-life of the first process are considerably less well defined. The intensity of the peak at 512 nm falls and the peak broadens, and incipient growth of the peak at 375 nm is evident. However, the spectrum shows no definite evidence for other species occurring in the time range before stopped-flow kinetic measurements can be reliably begun (*ca.* 5 msec).

Kinetic Measurements

Rate constants were obtained from the stopped-flow absorbance data by plotting $\log(A_t - A_\infty)$ against time. The resulting curves are linear at long times, and were stripped [17] into two components corresponding to the two reactions described above. The first reaction accounts for by far the greater part of the absorbance change monitored.

Values of rate constants obtained under various conditions are listed in Tables I–III. As can be seen from Table I, both reactions are first order in complex. Rate constants obtained at constant hydrogen

TABLE I. First-order Rate constants for the Reaction of $\text{K}_4\text{Mo}_2\text{Cl}_8$ with Acetic Acid: Complex Concentration Dependence.^a

$10^3 [\text{K}_4\text{Mo}_2\text{Cl}_8] / \text{mol dm}^{-3}$	First Reaction $k_{\text{obs},1} / \text{sec}^{-1}$	Second Reaction $k_{\text{obs},2} / \text{sec}^{-1}$
0.38	12.88	0.198
0.86	12.83	0.203
1.56*	11.75	0.195
1.56	12.46	0.202
1.58**	11.75	0.200
3.30	11.21	0.197
Mean	12.15 ± 0.7	0.199 ± 0.004

^aValues quoted are means of at least two determinations. $[\text{HCl}] = 1.95 \text{ mol dm}^{-3}$; $[\text{CH}_3\text{CO}_2\text{H}] = 0.492 \text{ mol dm}^{-3}$; $T = 298 \text{ K}$; $\lambda = 512 \text{ nm}$. (* $\lambda = 528 \text{ nm}$; ** 500 nm).

ion concentration are listed in Table II and the results of experiments at constant chloride ion concentration in Table III. In all cases, under a given set of conditions, the rate dependence on concentration of acetic acid could be expressed by equation (1)

$$\frac{1}{k_{\text{obs},1}} = \frac{a_1}{[\text{CH}_3\text{CO}_2\text{H}]} + a_0 \quad (1a)$$

$$\frac{1}{k_{\text{obs},2}} = \frac{a'_1}{[\text{CH}_3\text{CO}_2\text{H}]} + a'_0 \quad (1b)$$

Values of the parameters a_1 , a_0 , a'_1 and a'_0 for the two reactions derived from least-squares treatment of the raw data are listed in Table IV. The main reason for the higher error levels associated with the second reaction is probably, as mentioned above, the small extent of absorbance change associated with this reaction. In addition, diffusion of oxygen into the purged solutions contained in the stopped-flow apparatus cannot be totally avoided. Any oxidation

TABLE II. First-order Rate Constant for the Reaction of $\text{K}_4\text{Mo}_2\text{Cl}_8$ with Acetic Acid at Various Chloride Ion Concentrations.^a

$[\text{Cl}^-] / \text{mol dm}^{-3}$ $[\text{CH}_3\text{CO}_2\text{H}] / \text{mol dm}^{-3}$	First Reaction $k_{\text{obs},1} / \text{sec}^{-1}$						Second Reaction $k_{\text{obs},2} / \text{sec}^{-1}$					
	1.95	1.365	0.975	0.702	0.351	0.012 ^b	1.95	1.365	0.975	0.702	0.351	0.012 ^b
0.492	12.15	12.83	13.00	12.85	13.28	11.36	0.199	0.435	0.680	0.878	1.599	1.623
0.393	10.16	10.05	11.36	11.27	11.33	10.64	0.177	0.342	0.495	0.699	1.260	1.190
0.295	7.79	8.29	7.80	7.91	8.61	8.33	0.138	0.288	0.349	0.534	1.097	1.162
0.197	5.45	5.44	5.56	5.23	4.26	5.71	0.127	0.192	0.275	0.494	0.827	0.816
0.098	3.15	3.05	2.73	2.79	2.57	3.23	0.082	0.141	0.205	0.306	0.464	0.488
0.049	1.60	1.58	1.59	1.47			0.069	0.111	0.142	0.218		
0.025	0.87						0.040					

^aValues quoted are means of several determinations: $[\text{K}_4\text{Mo}_2\text{Cl}_8] = 1.56 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 1.95 \text{ mol dm}^{-3}$; $\mu = 1.95$ (HPTS). ^b Reaction conducted in 1.95 M HPTS. $[\text{Cl}^-]$ calculated on assumption of total aquation of molybdenum species.

TABLE III. First-order Rate Constant for the Reaction of $K_4Mo_2Cl_8$ with Acetic Acid at Various Hydrogen Ion Concentrations.^a

[HCl]/mol dm ⁻³ [CH ₃ CO ₂ H]/mol dm ⁻³	First Reaction						Second Reaction					
	$k_{obs,1}/sec^{-1}$						$k_{obs,2}/sec^{-1}$					
	1.95	0.80	0.40	0.20	0.10	0.05	1.95	0.80	0.40	0.20	0.10	0.05
0.492	12.15	14.33	16.20	21.40	33.70	49.30	0.199	0.185	0.200	0.136	0.161	0.133
0.393	10.16	11.65	13.70	18.35	26.11	39.60	0.177	0.142	0.153	0.123	0.119	0.116
0.295	7.79	9.93	11.48	15.15	21.06	31.30	0.137	0.123	0.117	0.082	0.081	0.084
0.197	5.45	7.00	8.00	10.70	14.48	20.55	0.127	0.090	0.060	0.049	0.054	0.055
0.098	3.15	3.87	4.53	5.92	7.79	11.10	0.081	0.039	0.036	0.024	0.023	0.029
0.049	1.60	2.02	2.24	3.05	4.40	6.19	0.044	0.015	0.021	0.014	0.012	0.012
0.025	0.87						0.026					

^aValues quoted are means of several determinations: $[K_4Mo_2Cl_8] = 1.56 \times 10^{-3} \text{ mol dm}^{-3}$; $[Cl^-] = 1.95 \text{ mol. dm}^{-3}$; $\mu = 1.95$ (NaCl); $T = 298 \text{ K}$; $\lambda = 512 \text{ nm}$ (some runs at 528 nm).

TABLE IV. Values of Equation (1) Parameters.^a

	First Reaction			Second Reaction		
	$10^3 a_1 / (\text{mol dm}^{-3} \text{ sec})$	$10 a_0 / (\text{sec})$	$\alpha (= a_0/a_1) / (\text{mol}^{-1} \text{ dm}^3)$	$a_1 / (\text{mol dm}^{-3} \text{ sec})$	$a_0' / (\text{sec})$	$\beta (= a_0'/a_1') / (\text{mol}^{-1} \text{ dm}^3)$
[HCl]/mol dm ⁻³				[Cl ⁻] = 1.95 mol dm ⁻³		
1.95	57.0 ± 1.7	30.6 ± 12.1	0.537	1.82 ± 0.16	3.39 ± 0.53	1.86
0.80	45.5 ± 2.5	25.5 ± 6.9	0.560	4.86 ± 0.58	0.13 ± 1.61	0.027
0.40	41.7 ± 1.4	17.3 ± 6.9	0.415	5.63 ± 0.65	negative	–
0.20	30.5 ± 0.7	15.1 ± 2.7	0.496	7.32 ± 0.38	0.12 ± 1.48	0.016
0.10	22.3 ± 0.7	10.3 ± 3.5	0.462	8.36 ± 0.26	negative	–
0.05	15.3 ± 0.5	6.6 ± 2.3	0.433	6.76 ± 0.29	0.52 ± 0.81	0.077
[Cl ⁻]/mol dm ⁻³				[H ⁺] = 1.95 mol dm ⁻³		
1.95	57.0 ± 1.7	30.6 ± 12.1	0.537	1.82 ± 0.16	3.39 ± 0.53	1.86
1.365	60.0 ± 2.5	22.2 ± 12.1	0.370	1.11 ± 0.22	1.60 ± 0.58	1.44
0.975	60.4 ± 4.1	24.5 ± 31.5	0.405	0.80 ± 0.20	1.01 ± 0.59	1.26
0.702	66.1 ± 1.8	15.2 ± 7.6	0.231	0.48 ± 0.08	0.83 ± 0.23	1.73
0.351	64.7 ± 9.2	16.6 ± 16.2	0.256	0.37 ± 0.03	0.28 ± 0.07	0.77
0.012	56.6 ± 4.3	25.2 ± 11.3	0.445	0.33 ± 0.06	0.37 ± 0.10	1.12

^aError limits are 95% confidence levels.

thus occurring is likely to interfere with the observed rate constants for the second reaction more than with those for the first, as qualitative tests on solutions of $K_4Mo_2Cl_8$ to which acetic acid was added reveal that acetate-containing molybdenum species are considerably more vulnerable to oxidation than the chlorocomplexes. The early stages of the oxidation process(es) involve an increase in absorbance at 510 nm, which would cause the measured $k_{obs,2}$ to be greater than its true value. For both reactions the error level at 95% confidence limits is considerably larger for the intercept term, a_0 or a_0' , than for the gradient term. The values presented in Table IV are, however, based on between 15 and 30 independent experimental values, and the error limits are borne in mind in interpreting the data.

For the first reaction, the values of a_1 and a_0 are essentially independent of chloride ion concentration but are dependent on the hydrogen concentration. The latter functional dependence can be expressed as

$$\frac{1}{a_1} = \frac{A_1}{[H^+]} + A_0 \quad (2a)$$

$$\frac{1}{a_0} = \frac{B_1}{[H^+]} + B_0 \quad (2b)$$

where the values of the constants A_1 , A_0 , B_1 and B_0 are given in Table V. As can be seen in Table IV, $\alpha = a_0/a_1$ is constant within experimental error. Equations (1a) and (2) can therefore be combined to give the overall rate equation (3) for the first reaction

TABLE V. Values of Rate Equation Parameters and Rate Constants.

First Reaction	Second Reaction
$A_1 = 2.56 \pm 0.3 \text{ sec}^{-1}$	$A_1' = 0.42 \pm 0.08 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}$
$A_0 = 17.5 \pm 2.0 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$	$A_0' = 0.32 \pm 0.11 \text{ mol dm}^{-3} \text{ sec}$
$B_1 = 5.85 \pm 0.8 \text{ mol dm}^{-3} \text{ sec}^{-1}$	$B_1' = 0.72 \pm 0.12 \text{ mol}^{-2} \text{ dm}^6 \text{ sec}$
$B_0 = 35.5 \pm 7.4 \text{ sec}^{-1}$	$B_0' = 0.42 \pm 0.15 \text{ sec}$
$k_2/k_{-1} = 0.419 \pm 0.08 \text{ mol}^{-1} \text{ dm}^3$	$k_4/k_{-3} = 1.36 \pm 0.5 \text{ mol}^{-1} \text{ dm}^3$
$k_1 = 41.8 \pm 6.0 \text{ sec}^{-1}$	$k_3 = 2.3 \pm 0.5 \text{ sec}^{-1}$
$k'K_H = 6.11 \pm 0.9 \text{ mol dm}^{-3} \text{ sec}^{-1}$	$K_{Cl} = 0.76 \pm 0.32 \text{ mol}^2 \text{ dm}^{-6}$

$$k_{\text{obs},1} = \left\{ \frac{[\text{CH}_3\text{CO}_2\text{H}]}{1 + \alpha[\text{CH}_3\text{CO}_2\text{H}]} \right\} \left\{ \frac{A_1 + A_0 [\text{H}^+]}{[\text{H}^+]} \right\} \quad (3)$$

For the second reaction, the observed chloride ion dependence is expressed in equation (4)

$$\frac{1}{a_1'} = A_1' [\text{Cl}^-]^2 + A_0' \quad (4a)$$

$$\frac{1}{a_0'} = B_1' [\text{Cl}^-]^2 + B_0' \quad (4b)$$

Values of the constants A_1' , A_0' , B_1' and B_0' are listed in Table V. The experimental values for the rate constants of the second reaction do not enable definite conclusions to be drawn about its hydrogen ion dependence. The negative values obtained in some cases for a_0' probably reflect the influence of the oxidation reaction discussed above (if a_0' is zero, simple linear dependence of $k_{\text{obs},2}$ on $[\text{CH}_3\text{CO}_2\text{H}]$ is expected; however, in all cases equation (1b) best describes the experimental results). In order to investigate more directly the hydrogen ion dependence of the second reaction, a series of experiments was conducted at the same concentration of acetic acid, but at four times the complex concentration. Under these condition the first reaction is essentially not "seen" as the absorbance of the reactant solution is too great, but the absorbance change associated with the second reaction is magnified. The results given in Table VI indicate that there is no hydrogen ion dependence, and we shall therefore conclude that the relevant figures in Tables III and IV simply reflect the large experimental error. Similar treatment to that described above for the first reaction enables the rate equation (5) for the second reaction to be expressed as

$$k_{\text{obs},2} = \left\{ \frac{[\text{CH}_3\text{CO}_2\text{H}]}{1 + \beta[\text{CH}_3\text{CO}_2\text{H}]} \right\} \{ A_1' [\text{Cl}^-]^2 + A_0' \}^{-1} \quad (5)$$

where β is the mean value of the ratio a_0'/a_1' .

The molybdenum(II)-chloride system in acid solution is described by nine rapid stepwise equilibria between the various members of the series $[\text{Mo}_2-$

TABLE VI. Rate Constants for the Second Reaction at Different Hydrogen Ion Concentrations.^a

$[\text{H}^+]/$ (mol dm^{-3})	$k_{\text{obs},2}$ (sec^{-1})
1.95	0.199
1.56	0.177
1.17	0.195
0.78	0.184
0.39	0.186
0.195	0.175
0.098	0.177

^a $[\text{K}_4\text{Mo}_2\text{Cl}_8] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{CH}_3\text{CO}_2\text{H}] = 0.492 \text{ mol dm}^{-3}$; $[\text{Cl}^-] = 1.95 \text{ mol dm}^{-3}$; $\mu = 1.95$ (NaCl); $\lambda = 528 \text{ nm}$; $T = 298 \text{ K}$.

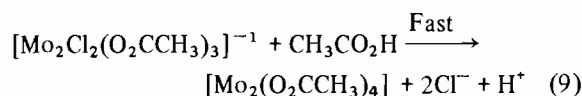
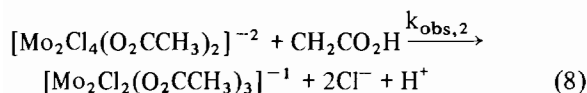
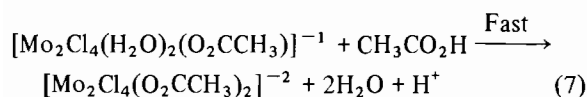
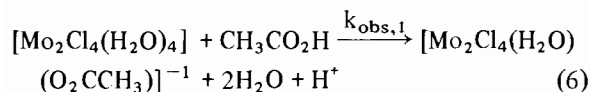
$\text{Cl}_{(8-x)}(\text{H}_2\text{O})_x]^{-4+x}$. The spectral results described above show that as the chloride concentration is increased, x falls till in concentrated HCl, the peak position agrees with that observed [18, 19] for solid $\text{K}_4\text{Mo}_2\text{Cl}_8$. However, the absorbance differences are too small to enable calculation of various equilibrium constants. Similarly, in a range of low chloride concentrations, where the lower members of the series should predominate, the absorbance changes were too small to enable calculation of the first equilibrium constant by the method of Newton and Arcand [20]. The nature of the species obtained upon solution of $\text{K}_4\text{Mo}_2\text{Cl}_8$ in HPTS has been previously investigated. Data reported by Bowen and Taube [18] suggest the dissociation of six chlorides per $\text{Mo}_2\text{Cl}_8^{4-}$ group while Pernick [19] has demonstrated the cationic nature of the species obtained. In the HCl concentration range of the kinetic experiments, the spectra more closely resemble that obtained for HPTS solution, than those where the $\text{Mo}_2\text{Cl}_8^{4-}$ group is present (as in solid $\text{K}_4\text{Mo}_2\text{Cl}_8$ or concentrated HCl solutions). Thus, although the reacting species cannot be more precisely defined because of the complexity of the system, within the HCl concentration range of the kinetic experiments, considerations of average ligand environment suggest that the molybdenum moiety can be represented as a mixed chloro-aquo complex

with $[\text{Mo}_2\text{Cl}_{(8-x)}(\text{H}_2\text{O})_x]^{-4+x}$ where $2 \leq x \leq 7$ accounts for the above observations. Despite the limitations imposed upon the interpretation of the kinetic results, it is possible to draw certain definite conclusions about the mechanism of substitution operating in these complexes, as discussed below, and in fact to use the kinetic results to redefine the possible values of n for $0 < [\text{HCl}] \leq 2 \text{ mol dm}^{-3}$.

When the reaction is conducted in HPTS, the final product is $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. Four substitution processes, in all, take place, in each of which one acetate group replaces two chloride ligands. However, the final spectrum obtained when the reaction is carried out in the presence of chloride differs from that of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ in being considerably more intense with peak position shifted to higher wavelengths. The final product is therefore a species of lower molecular symmetry than that of the tetraacetate, and is probably a mixed chloro-acetato complex similar to the mixed chloro-glycinato species reported by Cotton and Webb [12]. Since, regardless of reaction medium, only two substitution processes are observed, the second observed reaction cannot correspond to the introduction of the fourth acetate group. Therefore, one of the first three substitution processes is not observed kinetically. Spectra obtained 10 msec after initiation of the reaction were found to be adequately described as the appropriately weighted combinations of the spectra of the starting product and the product of the first reaction, thus eliminating the possibility of a reaction faster than the first measured process. We conclude therefore that the first observed reaction is, in fact, the first substitution process.

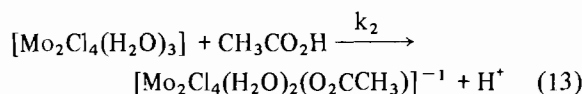
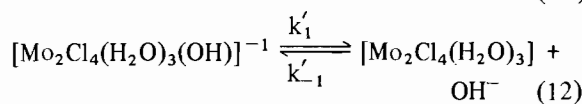
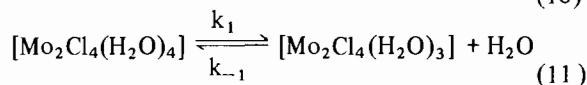
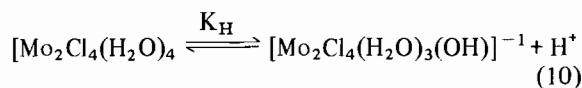
The second observed reaction may correspond to the introduction of the second or third acetate. However, because the second reaction is clearly observed even at very low chloride concentrations, where x is probably high, and since some chloride remains in the final product, it seems most logical to assign the second observed step to the substitution of the third acetate.

The measured kinetics can best be explained in terms of the following reaction sequence, in which, for simplicity as discussed below, the value of x is taken to be 4.



This reaction scheme resembles that for substitution reactions of square-planar MX_4 species giving MY_4 , in which only the first and third of the four possible substitution steps are measurable [21]. In view of the geometric relationship between the square-planar and the binuclear square prism, such a reaction pattern is reasonable. The decision as to whether the second or third step is the fast stage is made on the basis of the chloride dependence of the second observed reaction and on the reasonable assumption (in view of the kinetics discussed below) that coordinated water is more labile than coordinated chloride. This reaction pattern points to the possible existence of strong trans effects in square-prismatic systems in analogy with the well-documented trans effect in the square-planar case. In chloride media, the equilibrium position of (9) is such that only the tris(acetato) complex is obtained.

The dominant kinetic feature is that the functional dependence of both measured reactions on the incoming ligand are identical in form. The nature of the dependence is reminiscent of that observed in octahedral substitution reactions not complicated by ion-pair pre-equilibria [22] and suggests the following dissociative mechanism:



Application of the steady-state approximation to the seven-coordinate intermediate yields

$$k_{\text{obs},1} = \left\{ \frac{k_2 [\text{CH}_3\text{CO}_2\text{H}]}{k_{-1} + k'_{-1} [\text{OH}^-] + k_2 [\text{CH}_3\text{CO}_2\text{H}]} \right\} \left\{ k_1 + k'_1 \frac{K_{\text{H}}}{[\text{H}^+]} \right\} \left\{ \frac{1}{\frac{K_{\text{H}}}{[\text{H}^+]} + 1} \right\} \quad (14)$$

Spectral measurements at constant chloride concentration but varying hydrogen ion concentration reveal that the hydrolysis reaction (10) occurs, but the spectral changes are too small to measure K_{H} . Since all our present work was in strongly acid solution, we can assume that $(K_{\text{H}}/[\text{H}^+]) \ll 1$, and $k'_{-1} [\text{OH}^-] \ll$

k_{-1} . Equation (15) then reduces to equation (3), with

$$\alpha = \frac{k_2}{k_{-1}} \quad (15a)$$

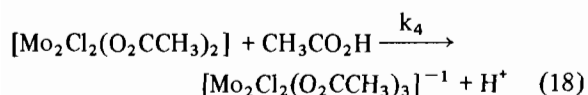
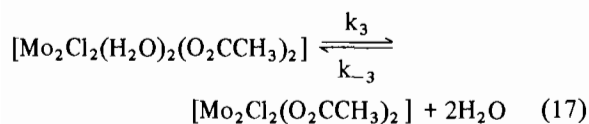
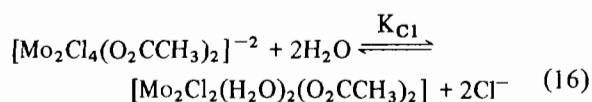
$$A_1 = \frac{k_1 k_2}{k_{-1}} \quad (15b)$$

$$A_0 = \frac{k'k_2}{k_{-1}} K_H \quad (15c)$$

It should be noted that if the hydrogen ion dependence is assumed to derive from dissociation of acetic acid, a rate law of the form (3) cannot be derived. Acetic acid is such a weak acid that in the range of the hydrogen ion concentrations used (5×10^{-2} to 2.0 mol dm^{-3}) there is essentially no dissociation. Furthermore, there are numerous precedents for the mechanistic activity of hydroxo-complexes in strongly acidic solution [23, 24].

The actual nature of the intermediate must, at this stage, be speculative. Whatever its precise form, however, the requirement for two conjugate-base species equivalent to those of (10) to undergo dissociative reaction *via* the same intermediate must be satisfied. Values of k_2/k_{-1} , k_1 and $k'K_H$ are presented in Table V. The ratio k_2/k_{-1} represents the relative reactivity of the intermediate for the two possible ligands available to it, water and acetate. Multiplication by the nominal molarity of water shows that attack by acetate on the intermediate is *ca.* 23 times more likely than re-aquation – a quantitative statement of the by now well known readiness of formation of dimeric carboxylato-molybdenum(II) complexes.

Equation (5) describing the second reaction can be explained on the basis of the following reaction mechanism:



Steady-state approximation for the intermediate yields

$$k_{\text{obs},2} = \left\{ \frac{k_3 k_4 [\text{CH}_3\text{CO}_2\text{H}]}{k_{-3} + k_4 [\text{CH}_3\text{CO}_2\text{H}]} \right\} \left\{ 1 + \frac{[\text{Cl}^-]^2}{K_{\text{Cl}}} \right\}^{-1} \quad (19)$$

This corresponds to equation (5) with

$$\beta = \frac{k_4}{k_{-3}} \quad (20a)$$

$$A'_1 = \frac{k_{-3}}{k_3 k_4 K_{\text{Cl}}} \quad (20b)$$

$$A'_0 = \frac{k_{-3}}{k_3 k_4} \quad (20c)$$

Values of k_4/k_{-3} , k_3 and K_{Cl} are listed in Table V. In principle, it should be possible to check K_{Cl} independently from the spectra at various conditions after completion of the first reaction. This was not done because the experimental error involved in such a procedure did not justify the effort. The ratio, k_4/k_{-3} , here again represents the relative reactivity of the intermediate towards the aquation or attack by acetate.

It should be noted that the rate equation requires prior hydrolysis of two chloride ligands. Assumption of an intermediate formed by loss of two chloride ligands in a step analogous to (10) does not enable derivation of a rate equation of the correct form. Prior aquation is a characteristic feature of substitution reactions in octahedral cobalt(III) complexes: to date direct substitution does not appear to have been substantiated.

The two mechanisms discussed here limit the possible values of x in the formula $[\text{Mo}_2\text{Cl}_{(8-n-x)}(\text{H}_2\text{O})_x]^{-4+x}$ mentioned above. At least one chloride must remain at the end of the second observed process, *i.e.*, the third substitution reaction, and two chlorides must be aquated in equation (16). This redefines the limits as $3 \leq x \leq 5$, all of which values are consistent with the proposed mechanism. The value of 4 chosen above represents the average between these extreme values.

It is of interest to compare our results with the only other kinetic study on a related complex. Hynes [13] found rate equations of different types to hold for the successive substitution steps of the reaction of thiourea with $\text{Re}_2\text{X}_8^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$), and different functional dependences again for the reactions of $\text{Re}_2\text{X}_8^{2-}$ with $\text{P}(\text{n-Pr})_3$. He suggested an overall mechanism involving two parallel reactions with intermediates formed both associatively $\text{Re}_2\text{X}_8\text{L}^{2-}$ and dissociatively Re_2X_7^- . For a given reactant and different conditions, one of the two paths was suggested to dominate. In the present study all the kinetics are adequately explained by a mechanism involving consistent use of only a dissociative pathway. We are currently investigating other systems that should enable a decision as to whether this dissociative behaviour is typical for reactions of the Mo_2^4 core.

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