A Study of the Ligand Exchange Reaction of Tetrakis(μ-trifluoroacetato)-dimolybdenum(II) in Acetonitrile by ^{19}F NMR Spectroscopy

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The dimeric molybdenum(II) complex, $Mo_2(CF_3COO)_4$, forms $Mo_2(CF_3COO)_4\cdot(CH_3CN)_2$ in acetonitrile, where solvent molecules are attached to positions trans to the metal–metal bond (apical positions). The rate of ligand exchange between $Mo_2(CF_3COO)_4$ ((1.31—8.28) × 10^{-2} M; M=mol dm^{-3}) and CF_3COONa ((1.31—4.56) × 10^{-1} M) was measured in acetonitrile by the use of ^{19}F NMR spectroscopy. The rate is independent of the total concentration of CF_3COONa and is linearly dependent on that of $Mo_2(CF_3COO)_4$. The first-order rate constant (k_{ex}) is $(1.1\pm0.2)\times10^4$ s^{-1} (25 °C), and the activation parameters are $\Delta H^{\neq}=(8.2\pm0.8)$ kcal mol^{-1} and $\Delta S^{\neq}=(-15\pm3)$ cal K^{-1} mol^{-1}. Under the given conditions the complex seems to exist as $Mo_2(CF_3COO)_4\cdot\underline{CF_3COO^-}$, where the underlined ligand occupies one of the apical positions, and the following mechanism is proposed (solvent molecules are omitted; asterisks indicate the molecule substituting for the coordinated ligand).

$$Mo_2(CF_3COO)_4\cdot\underline{CF_3COO^-} + {}^*CF_3COO^- \overset{\text{fast}}{\rightleftharpoons} Mo_2(CF_3COO)_4\cdot\underline{{}^*CF_3COO^-} + CF_3COO^-$$

$$Mo_2(CF_3COO)_4\cdot\underline{{}^*CF_3COO^-} \xrightarrow{k_8} Mo_2(CF_3COO)_3({}^*CF_3COO)\cdot\underline{CF_3COO^-}$$

The k_{ex} corresponds to k_8.

Bivalent molybdenum forms diamagnetic compounds having strong metal–metal bonds such as $Mo_2(RCOO)_4$ (R=CH_3, CF_3, *etc.*), $Mo_2X_8^{4-}$ (X^-=Cl^- and Br^-), and $Mo_2(SO_4)_4^{4-}$, with bond distances of about 2.1 Å.[1–5] Their structures in the crystalline state[1,2,4] and their spectroscopic properties[2,5] have been widely studied, but little attention has been drawn to their reactivities in solution.[6,7] The first and only report on the kinetics of the substitution reaction describes the substitution of acetate ions for the chloride ligands of $Mo_2Cl_8^{4-}$ to give $Mo_2(CH_3COO)_4$, and a dissociative mechanism was suggested.[7]

We have examined the solubility and stability of several dimeric molybdenum(II) complexes in various solvents in search of a simple system suitable for elucidating the substitution properties still further. Tetrakis(μ-trifluoroacetato)dimolybdenum(II), $Mo_2(CF_3COO)_4$ [I] (Fig. 1), in acetonitrile seemed suitable for our purpose. The Mo–Mo bond length of this compound is 2.090 Å, and the four trifluoroacetate ligands are equivalent in the crystalline state.[8] This paper reports on the results of a kinetic study of its ligand exchange reaction with sodium trifluoroacetate in acetonitrile by the use of ^{19}F NMR spectroscopy.

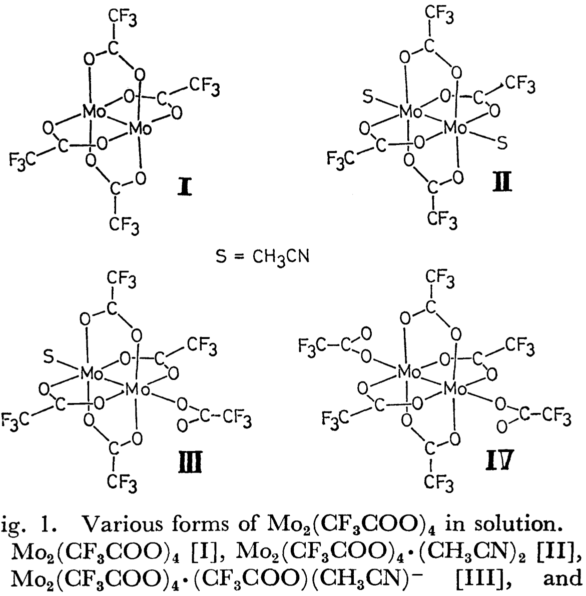

Fig. 1. Various forms of $Mo_2(CF_3COO)_4$ in solution. $Mo_2(CF_3COO)_4$ [I], $Mo_2(CF_3COO)_4\cdot(CH_3CN)_2$ [II], $Mo_2(CF_3COO)_4\cdot(CF_3COO)(CH_3CN)^-$ [III], and $Mo_2(CF_3COO)_4\cdot(CF_3COO)_2^{2-}$ [IV].

Experimental

Materials. Tetrakis(μ-trifluoroacetato)dimolybdenum(II) was prepared by the known method,[8] and sublimed before measurement of the ^{19}F NMR and electronic absorption spectra. Sodium trifluoroacetate (special grade reagent) was used without further purification. Acetonitrile was distilled twice over diphosphorus pentaoxide. Dichloromethane was distilled twice. Methanol (special grade reagent) was used without distillation. Each solvent was stored *in vacuo* over Linde 4a molecular sieves. The water content in each solvent was estimated to be as low as 5×10^{-3} M (M=mol dm^{-3}) using a Karl-Fischer titration.

Measurements. Electronic absorption spectra were measured using a Hitachi 323 Recording Spectrophotometer. The ^{19}F NMR spectra were recorded with a JEOL JNM-PM-100 high resolution NMR spectrometer operating at 94 MHz, with a variable temperature probe. Chemical shifts are recorded with respect to the internal standard CF_2Cl_2 (Freon 12).

Sample Preparation. Weighed samples of the complex and sodium trifluoroacetate were placed in an NMR tube, into which the solvent was introduced through a vacuum line. The molar concentration of each component was calculated from the volume of the prepared sample solution at room temperature, and expressed as $[Mo_2(CF_3COO)_4]_T$ and $[CF_3COO^-]_T$. Sample solutions were stored in liquid nitrogen for as long as a month without deterioration.

Evaluation of the Mean Life Time of the Coordinated and Free Ligands. A general method for studying a system involving two exchange sites[9] was applied to the present system. In the slow exchange region where two separate peaks are observed, the following equations were used:

$$\tau_c^{-1} = (W_c - W_c^{\circ}), \qquad (1)$$

$$\tau_f^{-1} = (W_f - W_f), \qquad (2)$$

where τ_c and τ_f are the mean life times of the coordinated and free ligands, and W_c and W_c° (or W_f and W_f°) are the half line widths in Hz at half-height of the signal of the coordinated (or free) ligand of the sample solution and of the solution without free (or coordinated) ligand, respectively. In the fast exchange region where the two peaks coalesce completely, the following equation was used:

$$\tau_c^{-1} = \frac{4\pi p_c p_f^2 (\Delta\nu)^2}{W_{cf} - p_c W_c^\circ - p_f W_f^\circ}, \qquad (3)$$

where p_c and p_f are the mole fractions of two exchanging species, W_{cf} is the half line width in Hz at half-height of the signal of the coalesced peak, and $\Delta\nu$ is the chemical shift difference in Hz between the signals of the coordinated and the free ligand (ν_c and ν_f) both measured in the absence of each other. The following equation should hold.

$$p_c/\tau_c = p_f/\tau_f \qquad (4)$$

In the region of intermediate exchange, τ_c^{-1} was obtained by comparison of the observed spectra with the calculated spectra.[10] A Nihon-minicon NOVA-01 was used for the calculation.

The W_c° and W_f° values showed small temperature dependence. The values at any temperature between −40 and 70 °C were estimated from the calibration curves for the temperature dependence. The ν_c and ν_f gave no appreciable temperature dependence over the temperature range from −40 to 70 °C. The $\Delta\nu$ value was 306 Hz at all temperatures.

Results and Discussion

Structure of the Complex in Acetonitrile. Various compounds are known which have the general formula: $\mathrm{Mo_2(CF_3COO)_4 \cdot L_n^{m-}}$ (n=1, m=0, L=$(\mathrm{C_6H_5})_3\mathrm{P}$;[11] n=2, m=0, L=pyridine (py)[12] and $\mathrm{CH_3OH}$;[11] n=1, m=1, $\mathrm{L^-}$=$\mathrm{Cl^-}$, $\mathrm{CF_3COO^-}$ *etc.*; n=2, m=2, $\mathrm{L^-}$=$\mathrm{Br^-}$ and $\mathrm{Cl^-}$[13]). X-Ray crystallography disclosed that $\mathrm{Mo_2(CF_3COO)_4 \cdot (py)_2}$ has two weakly coordinated pyridine molecules at both positions trans to the metal–metal bond (hereafter called apical positions).[12] The other L's are believed to coordinate similarly to the molybdenum ion.[11,13]

The ν(Mo–Mo) stretching frequency observed by Raman spectroscopy is sensitive to the apical ligand. The ν(Mo–Mo) value of solid $\mathrm{Mo_2(CF_3COO)_4}$ is 397 $\mathrm{cm^{-1}}$,[8] while those of the compounds containing apical ligands are between 386 (n=2, L=$\mathrm{CH_3OH}$) and 368 $\mathrm{cm^{-1}}$ (n=2, L=py) in the solid state.[11–13] The value for the solid $\mathrm{Mo_2(CF_3COO)_4 \cdot (CH_3OH)_2}$ is 386 $\mathrm{cm^{-1}}$.[13] On the other hand $\mathrm{Mo_2(CF_3COO)_4}$ has ν(Mo–Mo) values of 397 and 383 $\mathrm{cm^{-1}}$ in dichloromethane and methanol respectively.[12] The two apical positions must be occupied by solvent molecules in methanol and remain vacant in dichloromethane. The ν(Mo–Mo) values in acetone and diethylether are 385 and 383 $\mathrm{cm^{-1}}$ respectively,[12] and these solvent molecules are also likely to occupy the apical positions. Acetonitrile solution could not be used in similar studies because the solvent itself gives strong Raman bands in the region of interest. On the other hand, Cotton and Norman found that the energy of the electronic transition of $\mathrm{Mo_2(CF_3COO)_4}$ at *ca.* 430 nm in various solvents decreases as the ν(Mo–Mo) decreases.[12] Thus the coordination of solvent molecules at the apical positions lowers the energy of electronic transition. The electronic absorption spectra of $\mathrm{Mo_2(CF_3COO)_4}$ in dichloromethane, methanol and acetonitrile are shown in Fig. 2. The peak positions are at 428 (ε, 95 $\mathrm{cm^{-1}\,M^{-1}}$), 434 (118), and 434 nm (112), respectively. From these spectra it is concluded that $\mathrm{Mo_2(CF_3COO)_4}$ is present as $\mathrm{Mo_2(CF_3COO)_4 \cdot (CH_3CN)_2}$ (II) (Fig. 1) in acetonitrile.

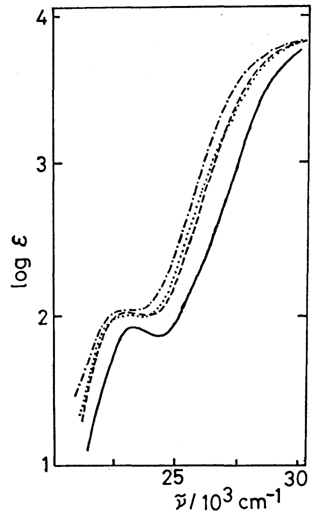

Fig. 2. The electronic absorption spectra of $\mathrm{Mo_2(CF_3COO)_4}$ in $\mathrm{CH_2Cl_2}$ (——), methanol (– – – –), acetonitrile (······) and in acetonitrile containing 4.6×10^{-2} M of $\mathrm{CF_3COONa}$ (-·-·-).

The Species in the Presence of the Free Ligand. A complex, $[(\mathrm{C_2H_5})_4\mathrm{N}][\mathrm{Mo_2(CF_3COO)_4 \cdot (CF_3COO)}]$, has been isolated from an equimolar mixture of $\mathrm{Mo_2(CF_3COO)_4}$ and $[(\mathrm{C_2H_5})_4\mathrm{N}][\mathrm{CF_3COO}]$ in dichloromethane.[12] On addition of sodium trifluoroacetate to an acetonitrile solution of $\mathrm{Mo_2(CF_3COO)_4}$, the peak position at 434 nm shifts to slightly longer wavelengths with an increase in strength (Fig. 2). This change may be caused by the substitution of trifluoroacetate ion(s) for acetonitrile in apical position(s). The following reactions are believed to be involved,

$$[\mathrm{Mo_2(CF_3COO)_4}\cdot\underline{(\mathrm{CH_3CN})_2}] + \mathrm{CF_3COO^-} \overset{K_1}{\rightleftarrows}$$
$$\text{(II)}$$
$$[\mathrm{Mo_2(CF_3COO)_4}\cdot\underline{(\mathrm{CF_3COO})}\underline{(\mathrm{CH_3CN})}]^- + \mathrm{CH_3CN}, \qquad (5)$$
$$\text{(III)}$$

$$[\mathrm{Mo_2(CF_3COO)_4}\cdot\underline{(\mathrm{CF_3COO})}\underline{(\mathrm{CH_3CN})}]^- + \mathrm{CF_3COO^-}$$
$$\text{(III)}$$
$$\overset{K_2}{\rightleftarrows} [\mathrm{Mo_2(CF_3COO)_4}\cdot\underline{(\mathrm{CF_3COO})_2}]^{2-} + \mathrm{CH_3CN}. \qquad (6)$$
$$\text{(IV)}$$

The underlined ligands denote the ligand at the apical positions. The change in electronic absorption spectra is too small to enable the evaluation of K_1 and K_2. However, as Fig. 3 shows, appreciable amounts of III and/or IV (Fig. 1), must be present when the free ligand concentration is $\geqq$0.01 M in the *ca.* 5×10^{-3} M complex solution.

^{19}F NMR Spectra in Acetonitrile. The ^{19}F NMR spectrum of the complex in acetonitrile (*ca.* 4×10^{-2} M)

Table 1. ^{19}F NMR chemical shifts (with respect to CF_2Cl_2 as an internal standard) of acetonitrile solutions of $Mo_2(CF_3COO)_4$ and CF_3COONa, and reciprocals of mean life time of the complexed ligand and activation energies for the ligand exchange reaction

Run	$[Mo_2(CF_3COO)_4]_T$ / 10^{-2} M	$[CF_3COO^-]_T$ / 10^{-1} M	Chemical shift/ppm[b)] at −40 °C	Chemical shift/ppm[b)] at 70 °C	τ_c^{-1}(25 °C)[c)] / 10^3 s^{-1}	E_a[d)] / kcal mol^{-1}
1	4.85	1.31	67.2, 70.5	68.9	3.2	9.6
2	5.26	1.46	67.4, 70.8	69.1	2.8	8.2
3	5.81	4.56	67.2, 70.8	70.7	2.5	9.1
4	1.51	2.10	67.4, 70.9	70.5	2.6	8.0
5	2.82	2.68	67.4, 70.9	69.8	2.5	8.4
6	8.28	1.71	67.5, 70.9	68.8	2.4	9.1
7[a)]	5.46	2.67	67.2, 70.0	69.2	3.7	9.0
8	4.90	8.68	67.5, 70.8	70.8	—	—
9	3.41	10.40	67.6[e)] 67.7, 71.1	70.6	—	—

a) $(C_2H_5)_4NClO_4$=0.7 M. b) Error, ±0.3. c) Error, ±0.3. d) Error, ±0.5. e) Doublet.

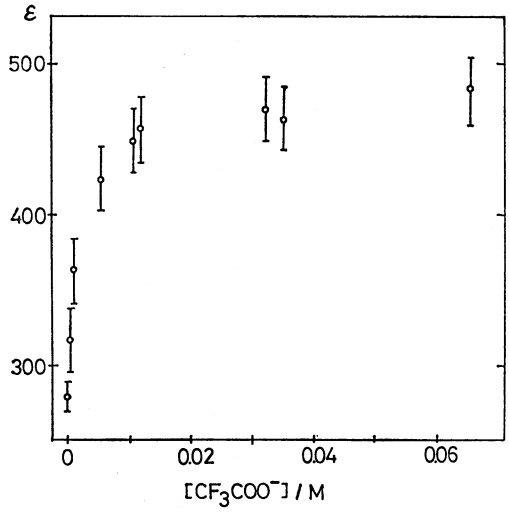

Fig. 3. The change in apparent molar absorption coefficient (ε) at 390 nm of $Mo_2(CF_3COO)_4$ in acetonitrile with a change in concentration of added CF_3COONa.

shows one sharp peak upfield from the reference peak at 67.6 ppm over a temperature range of −40 to 70 °C, suggesting that the four trifluoroacetate ligands are magnetically equivalent. Hence, no significant change in the basic structure of I occurs, except for coordination of the solvent molecules at the apical positions. Sodium trifluoroacetate (*ca.* 0.58 M) has one sharp band at 71.0 ppm in acetonitrile.

The temperature dependence over the temperature range from −40 to 70 °C of the ^{19}F NMR spectra of the solutions (Table 1) containing both the complex and the free ligand is exemplified in Fig. 4 (run 2 in Table 1). A similar dependence was observed for runs 1 and 3—7. The following observations were made for these solutions: (a) the positions of the two peaks (67.2—67.5 and 70.8—70.9 ppm) at a low temperature (−40 °C in Fig. 4) coincide with those of the complex and of the free ligand; (b) the p_c and p_f values obtained from the ratio of the integral strengths of the two peaks can be expressed by

$$p_c/p_f = 4[Mo_4(CF_3COO)_4]_T/[CF_3COO^-]_T; \qquad (7)$$

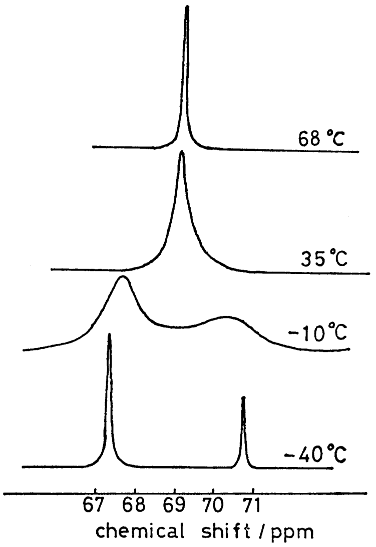

Fig. 4. An example of the temperature dependence of the ^{19}F NMR spectra of an acetonitrile solution of $Mo_2(CF_3COO)_4$ and CF_3COONa ($[Mo_2(CF_3COO)_4]$= 5.26×10^{-2} M and $[CF_3COONa]$=0.146 M). Chemical shifts are shown with respect to CF_2Cl_2 as an internal reference.

(c) the chemical shift of the coalesced peak at a high temperature (68 °C in Fig. 4) is close to the value determined from the expression, $67.6\times p_c+71.0\times p_f$; (d) the τ_c^{-1} values estimated from each of the two separate peaks (Eqs. 1 and 2) are in reasonable agreement with each other; (e) plots of log (τ_c^{-1}) against T^{-1} give straight lines (Fig. 5). All of these observations support the conclusion that the temperature dependence of the ^{19}F NMR spectra can be interpreted by chemical exchange of the bridging trifluoroacetate with "free" CF_3COO^- ("free" includes both the apical and the free ligands).

The values of τ_c^{-1} at 25 °C and the activation energy (E_a) were calculated from the best fit lines of Arrhenius plots, and are summarized in Table 1. In order to see the kinetic salt effect, $(C_2H_5)_4NClO_4$ was added to the reaction mixture (run 7). Addition of 0.7 M $(C_2H_5)_4NClO_4$ did not change the pattern of the temperature

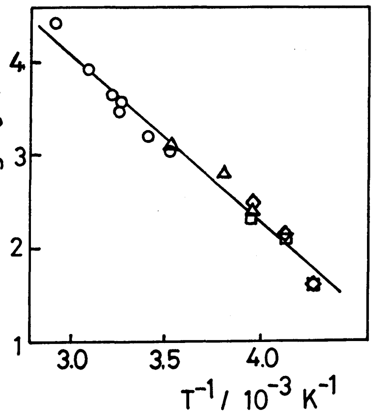

Fig. 5. An example of a plot of log (τ_c^{-1}) *vs*. T^{-1}. τ_c^{-1} values were obtained from Eq. 5 from the coalesced peak (○), by spectral simulation (△), from Eq. 1 from the peak in the coordinated ligand region (□), or from Eqs. 2 and 3 from the peak in the free ligand region (◇) ([$Mo_2(CF_3COO)_4$]=5.81×10^{-2} M and [CF_3COONa]=0.456 M). The solvent is acetonitrile.

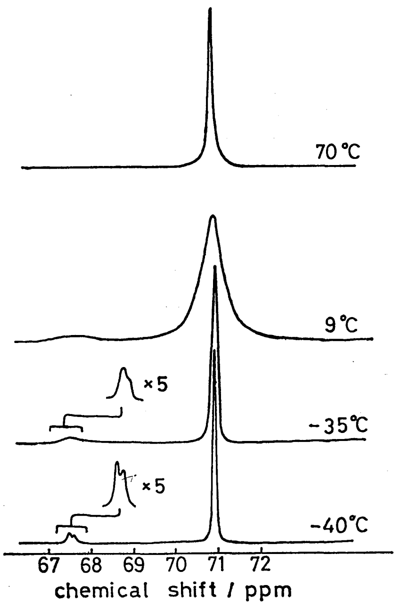

Fig. 6. Temperature dependence of the ^{19}F NMR spectra of an acetonitrile solution of $Mo_2(CF_3COO)_4$ (3.41×10^{-2} M) and CF_3COONa (1.04 M) (run 9 in Table 1).

dependence of the signals, but gave a slight increase in τ_c^{-1}.

The Arrhenius plot for run 8 gave a concave curve. In run 9, the signal peak in the coordinated ligand region splits at a low temperature (Fig. 6). Thus, the ^{19}F NMR spectra of the solutions containing more than 0.8 M sodium trifluoroacetate cannot be interpreted by simple chemical exchange.

Rate Law for the Exchange Reaction. The result of run 7 indicates that the kinetic salt effect is not significant over the range of concentrations of reactants in runs 1—6. Sodium trifluoroacetate is almost completely dissociated into sodium and trifluoroacetate ions in acetonitrile (dielectric constant: 35.95 at 25 °C).[13]

The τ_c^{-1} values in Table 1 are almost equal to one another, and seem to be independent of both $[CF_3COO^-]_T$ and $[Mo_2(CF_3COO)_4]_T$. The τ_f^{-1} value depends linearly on the ratio p_c/p_f, as is expected from Eq. 4. This was confirmed from the τ_f^{-1} values obtained from the peak in the free ligand region by Eq. 2. Thus the rate (R) of the exchange reaction is independent of $[CF_3COO^-]_T$ and is linearly dependent on $[Mo_2(CF_3COO)_4]_T$,

$$\begin{aligned} R &= 4\tau_c^{-1}[Mo(CF_3COO)_4]_T \\ &= k_{ex}[Mo_2(CF_3COO)_4]_T, \qquad (8) \end{aligned}$$

where R and k_{ex} are the rate and the first order rate constant of the exchange, respectively, of one of the four coordinated ligands. The rate constant and activation parameters were determined to be $k_{ex}=(1.1\pm0.2)\times10^4\ s^{-1}$ (25 °C), $\Delta H^{\ne}=(8.2\pm0.8)$ kcal mol^{-1} and $\Delta S^{\ne}=(-15\pm3)$ cal K^{-1} mol^{-1}.

Mechanism of Ligand Exchange. The electronic absorption spectra showed that an appreciable amount of III and/or IV is present in the solutions of runs 1—7. Therefore, more than three non-equivalent circumstances are involved for the trifluoroacetate. Only two ^{19}F NMR signals were observed at −40 °C, however, for runs 1—7. The ratios of the integral strengths of the two signals (Eq. 7) suggest that the signal due to the apical ligand must be included in the peak in the free ligand region.

The solution of run 9 which contained a larger amount of the "free" ligand, gives two peaks in the complex region. The two peaks are most likely due to the bridging ligands of III and IV, and the single peak of runs 1—7 in this region to the bridging ligand of III.[14]

Equation 9 can be applied to the runs 1—7.

$$\begin{aligned} [CF_3COO^-]_T &= [CF_3COO^-]_F + [CF_3COO^-]_A \\ &= [CF_3COO^-]_F + [Mo_2(CF_3COO)_4]_T, \qquad (9) \end{aligned}$$

where the suffices A and F denote the apical ligand of III and uncoordinated free ligand, respectively. An appreciable amount of added trifluoroacetate exists as the apical ligand (48.4% for run 6). The peak position of the apical ligand is very close to that of the free ligand, since, at −40 °C, no shift of the "free" ligand peak (coalesced peak of the free and the apical ligand) is observed upon addition of the complex (Table 1). This suggests very weak coordination at the apical positions.

The following mechanism is proposed for runs 1—7.

$$\begin{aligned} &[Mo_2(CF_3COO)_4\cdot\underline{CF_3COO}]^- + {}^*CF_3COO^- \overset{\text{fast}}{\rightleftarrows} \\ &\qquad [Mo_2(CF_3COO)_4\cdot{}^*\underline{CF_3COO}]^- + CF_3COO^-, \qquad (10) \\ &[Mo_2(CF_3COO)_4\cdot{}^*\underline{CF_3COO}]^- \xrightarrow{k_8} \\ &\qquad [Mo_2(CF_3COO)_3({}^*CF_3COO)\cdot\underline{CF_3COO}]^-, \qquad (11) \end{aligned}$$

where the asterisks indicate the molecule substituting for the coordinated ligand. The first process is proposed to be fast, and the exchange rate is expressed by

$$\begin{aligned} R &= k_8[Mo_2(CF_3COO)_4\cdot CF_3COO^-] \\ &= k_8[Mo_2(CF_3COO)_4]_T\,. \qquad (12) \end{aligned}$$

This equation is of the same form as the experimentally obtained equation (Eq. 8). The observed rate constant, k_{ex}, is equal to k_S.

An alternative assignment for the ^{19}F NMR spectra of runs 1—7 could be proposed by considering that both II and III are present in the solutions and that their interconversion (Eq. 5) was fast with respect to the ^{19}F NMR time scale (so that the signals of coordinated CF_3COO^- of II and III coalesced completely). However, such a consideration does not account for the rate law (Eq. 8), unless II and III give identical exchange rates.

Comparison with Other Reactions. Few kinetic studies are reported on the substitution reactions of the compounds containing strong metal–metal bond such as Mo^{II}–Mo^{II} or Re^{III}–Re^{III}. Mureinik studied the reaction of acetate ions with $[Mo_2Cl_{8-n}(H_2O)_n]^{(4-n)-}$ (partially aquated form of $Mo_2Cl_8{}^{4-}$) to give $Mo_2(CH_3COO)_4$ in aqueous acid solutions ($[H^+]=0.05$—1.95 M with HCl or *p*-toluenesulfonic acid) at 25 °C by the stopped-flow method.7) The entry of the first and the third acetate ions was kinetically analyzed. At a constant $[H^+]$, the following rate law (Eq. 13) was obtained for the first step.

$$k_{obsd} = \frac{b[CH_3COOH][Mo_2Cl_{8-n}(H_2O)_n{}^{(4-n)-}]}{1+a[CH_3COOH]} \tag{13}$$

The rate law was explained by the following dissociative mechanism.

$$[Mo_2Cl_{8-n}(H_2O)_n]^{(4-n)-} \rightleftarrows [Mo_2Cl_{8-n}(H_2O)_{n-1}]^{(4-n)-} + H_2O$$

$$[Mo_2Cl_{8-n}(H_2O)_{n-1}]^{(4-n)-} + CH_3COOH \longrightarrow [Mo_2Cl_{8-n}(H_2O)_{n-2}(CH_3COO)]^{(5-n)-} + H_3O^+ \tag{14}$$

A similar proposal was also put forth for the third step. We suggest that the rate law (Eq. 13) may also be explained by the following mechanism, which is similar to that proposed for our reaction.

$$[Mo_2Cl_{8-n}(H_2O)_n]^{(4-n)-} + CH_3COOH \overset{\text{fast}}{\rightleftarrows} [Mo_2Cl_{8-n}(H_2O)_n\cdot\underline{CH_3COO}]^{(5-n)-} + H^+$$

$$[Mo_2Cl_{8-n}(H_2O)_n\cdot\underline{CH_3COO}]^{(5-n)-} \longrightarrow [Mo_2Cl_{8-n}(H_2O)_{n-2}(CH_3COO)]^{(5-n)-} + 2H_2O \tag{15}$$

Further information, such as activation parameters, would be necessary to make a more definitive conclusion about the mechanism of this reaction.

The kinetics of the substitution of tributylphosphine or thiourea for the halide ligands of $Re_2X_8{}^{2-}$ ($X^-=Cl^-$ or Br^-), and of chloride ions for the bromide ligands of $Re_2Br_8{}^{2-}$ in methanol at 25 °C, have been studied by the stopped-flow method.16) The following general rate law was given:

$$k_{obsd} = \frac{k_s+k_LK[L]}{1+K[L]}, \tag{16}$$

where L is the incoming ligand. The following mechanism was proposed (the charges are omitted, and S denotes methanol).

$$\begin{tikzcd}
Re_2X_8(S) \arrow[r, "k_s"] \arrow[d, shift left, "+L"] & Re_2X_7(S) + X^- \arrow[d, "+L"', "\text{fast}"] \\
Re_2X_8L \arrow[u, shift left, "K"] \arrow[r, "k_L"] & \text{product}
\end{tikzcd}$$

Although the detailed structure of the species Re_2X_8L was not given, L coordinates most likely at the apical position. Thus, we suggest that the rate-determining-step is the intramolecular rearrangement between X and either S or L, for the k_S or k_L path, respectively. Such a mechanism is similar to that proposed for our reaction.

Mono-oxo metal ions, such as Mo^VO^{3+} and $V^{IV}O^{2+}$ have strong metal–oxygen bonds comparable to the metal–metal bond Mo–Mo, and their trans (apical) sites are vacant or weakly coordinated. The substitution of Cl^- for $OP(C_6H_5)_3$ in $Mo^VOCl_3\{OP(C_6H_5)_3\}_2$ and for $OP\{N(CH_3)_2\}_3$ in $Mo^VOCl_3[OP\{N(CH_3)_2\}_3]_2$ was claimed to occur first at the apical position followed by an intramolecular rearrangement to the basal position.17) This process is similar to that of our ligand exchange. A similar mechanism is also proposed for the substitution reactions of oxovanadium(IV) complexes at the basal site.18) The activation parameters for these reactions are close to those of our reaction. A substitution mechanism involving initial attack at the apical position, followed by rearrangement to the basal position would be a common feature of complexes containing strong metal–metal and metal–oxo bonds.

The rate of halide substitution at the apical positions of $Re_2(C_2H_5COO)_4\cdot X_2$ ($X^-=Cl^-$ or Br^-) in acetonitrile was reported to be *ca.* 10^{-3} s^{-1} at 25 °C.19) On the other hand, the rate of process (10) for our Mo(II) complex is fast ($>10^4$ s^{-1}). It is difficult to explain such a big difference at the present stage. The difference in the oxidation state of metal ions, the electronic charge of the $M_2(RCOO)_4$ unit, and/or the d-orbitals involved (3d or 4d) may be important.

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15) The assignment means that W_f°, W_c°, ν_f and ν_c are not appropriate to evaluate τ_f^{-1} and τ_c^{-1} (Eqs. 1—3), and the corresponding values of the coalesced peak of the free and apical ligands and of the bridging ligand of III should be used instead. However since the latter values are not estimated (even at −40 °C the chemical exchange is not frozen), the former values were used without any correction. The τ_f^{-1} and τ_c^{-1} values obtained do not appear to be unreasonable.

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