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Kinetic and Equilibrium Studies on Substitution Reactions of the Chlorobis(β-diketonato)manganese(III) Complexes with Other β-Diketones

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The MnCl(β-dik)$_2$ complexes, where β-dik stands for an anion of acetylacetone, benzoylacetone, and dibenzoylmethane, were confirmed to have the five-coordinate structure in dichloromethane and their adduct formation constants with various donor solvents were measured. Equilibria and kinetics of substitution reactions of MnCl(β-dik)$_2$ with other β-diketones were determined by the spectrophotometric method and the mechanism for these reaction is proposed.

The bis(acetylacetonato)halogenomanganese(III) complexes, MnX(acac)$_2$ (X=Cl, Br, and I), were prepared by the reactions of tris(acetylacetonato)-manganese(III) with an equimolar amount of hydrogen halide in organic solvents.[1] They were characterized by measurements of magnetic susceptibility, electronic and infrared spectra, molecular weight, and electric conductivity and were concluded to exist as five-coordinate molecules in noncoordinating solvents but behave as a uni-uni valent electrolyte in methanol. An analogous iron(III) complex, FeCl(acac)$_2$, was confirmed by X-ray analysis to have a square pyramid structure with the chloride anion at the apical position.[2] Although the pseudohalogenomanganese(III) complexes, MnX(acac)$_2$ (X=N$_3$ and NCS), were reported to have a polynuclear chain structure in crystals in which each manganese(III) ion assumes a tetragonally elongated octahedron with the trans-coordinated pseudohalides as the end-to-end bridging ligand,[3,4] they may be five coordinate in solutions of poorly coordinating solvents.[3]

Stults, et al.[5] showed that the MnX(acac)$_2$ complexes are useful in preparing the biologically important Mn(III)-porphyrin[6] in high purity and yield, although the mechanism of the ligand substitution reaction has not been clarified. Kinetic studies on the ligand substitution reactions of five-coordinate complexes have been rather few and to our knowledge, no reports on the reactions of five-coordinate manganese(III) complexes have appeared as yet. This paper is concerned with the substitution reactions of chlorobis(dibenzoylmethanato and benzoylacetonato)-mangangese(III) with acetylacetone, and kinetic and equilibrium data as well as mechanistic discussion are presented.

Experimental

Materials. Acetylacetone (acacH) of the extra-pure grade was distilled twice before use. Benzoylacetone (bzacH) and dibenzoylmethane (dbmH) were recrystallized twice from methanol and dried over silica gel in an evacuated desiccator. Dichloromethane was washed with a 10% aqueous solution of sodium carbonate followed by pure water, dried by means of Linde molecular sieves (Type 3A), and was then distilled through a fractionating column filled with Widmer spirals. Dichloromethane was used immediately after distillation as the solvent for kinetic studies. Diethyl ether was treated with metallic sodium and distilled. Pyridine of the highest grade for spectroscopy was used without further treatment. Methanol was dried by Linde molecular sieves (Type 3A) and distilled. Other organic solvents such as *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), benzonitrile (PhCN), and acetonitrile (MeCN) were similarly dried and distilled under reduced pressure of nitrogen. Deuterium oxide of 99.75% purity (Merck) was used for the deuteration studies.

Synthesis of Complexes. Bis(acetylacetonato)chloromanganese(III): The complex was prepared by Isobe's method[1] and recrystallized twice from a mixture of dichloromethane and diethyl ether (1:1 by volume) in a dry box under dry nitrogen atmosphere. Found: C, 41.16; H, 4.84%. Calcd for MnCl(acac)$_2$=C$_{10}$H$_{14}$O$_4$ClMn: C, 41.16; H, 4.89%.

Chlorobis(dibenzoylmethanato)manganese(III), MnCl(dbm)$_2$ and Bis(benzoylacetonato)chloromanganese(III), MnCl(bzac)$_2$: Isobe's method was modified a little. Dibenzoylmethane (5.2 g, 23.2 mmol) was added to a solution of MnCl(acac)$_2$ (0.5 g, 1.7 mmol) in dichloromethane (20 cm^3), and the mixture was allowed to stand for about 2 h to deposit the product (0.31 g) in a 33% yield. Recrystallization was performed in an atmosphere of dry nitrogen from an equivolume mixture of dichloromethane and diethyl ether containing six times as many moles of dibenzoylmethane as compared with the complex. Found: C, 66.18; H, 4.15%. Calcd for MnCl(dbm)$_2$=C$_{30}$H$_{22}$O$_4$ClMn: C, 67.11; H, 4.13%. Bis(benzoylacetonato)chloromanganese(III) was also prepared and recrystallized in a similar manner as above. The yield of a crude product was 0.20 g (28.0%). Found: C, 57.89; H, 4.41%. Calcd for MnCl(bzac)$_2$=C$_{20}$H$_{18}$O$_4$ClMn: C, 58.20; H, 4.40%.

Acetylacetonato(dibenzoylmethanato)- and Acetylacetonato(benzoylacetonato)-chloromanganese(III): In an atmosphere of dry nitrogen MnCl(acac)$_2$ (1.0 g, 3.7 mmol) was dissolved in dichloromethane (20 cm^3), and to this solution was added slowly a dichloromethane solution (100 cm^3) of dibenzoylmethane (1.7 g, 7.5 mmol) followed by diethyl ether (100 cm^3). After the reaction for 1 h, a precipitate was filtered and washed with diethyl ether. The yield was 0.60 g (42%). Found: C, 59.54; H, 3.96%. Calcd for MnCl(acac)(dbm)=C$_{20}$H$_{18}$O$_4$ClMn: C, 58.20; H, 4.40%. Acetylacetonato(benzoylacetonato)chloromanganese(III) was also prepared in a similar manner as above to obtain a crude product in a 38% yield. Found: C, 52.38; H, 4.42%. Calcd for MnCl(acac)(bzac)=C$_{15}$H$_{16}$O$_4$ClMn: C, 51.38; H, 4.60%.

Both of the mixed β-diketonato complexes were not recrystallized, since they are not stable in solution, but undergo disproportionation reactions. Thus the results of elemental analysis are not satisfactory.

*Preparation of Acetylacetone-methylene-*d$_2$. A mixture of acetylacetone (10 cm^3, 0.0975 mol) and D_2O (30 cm^3, 1.66 mol) was heated under reflux for 4—5 h, and allowed to stand overnight at room temperature. The mixture was extracted three times with 20 cm^3 portions of dichloromethane. The combined extract was subjected to distillation under reduced pressure to leave the deuterated acetylacetone. The ^{1}H NMR assay of the neat liquid indicates that the deuterium content of the methylene group is 90.2%. When potassium acetylacetonate was added to make the reaction medium basic, the methyl groups of acetylacetone were also deuterated. This product was not used in the following studies.

Measurements. Water contents of organic solvents were determined by means of an MCI digital water microanalyzer CA-O1. Absorption spectra were measured with a Hitachi EPS-3T recording spectrophotometer, and infrared spectra in Nujol with a JASCO DS 701G spectrophotometer. A JEOL JNM MH-100 spectrometer was used to obtain ^{1}H NMR spectra in CD_2Cl_2 with tetramethylsilane as internal reference.

The ligand substitution reactions were followed spectrophotometrically by means of a Union Stopped-Flow Rapid Scan Spectrophotometer RA-1300. The solution reservoir was covered with a polyethylene bag equipped with gloves and filled with dry nitrogen in order to prevent the stock solution from contacting with air.

Results

Addition Reactions of Donor Molecules to the Chlorobis(β-diketonato)manganese(III) Complexes, MnCl(β-dik)$_2$, in Solution. Based on the molecular-weight and other data, MnCl(acac)$_2$ has been considered to exist as five-coordinate molecules in noncoordinating solvents.[1] Now the following spectroscopic studies assure that the sixth coordination site of manganese(III) is really left vacant.

The complex is not so stable in dichloromethane solution, but some kind of decomposition proceeds as evidenced by the change of its spectrum with time. However the spectrum shows no change in the coexistence of an excess (*e.g.* ten times molar) amount of free acacH. Under such circumstances, coordination of an acacH molecule to manganese(III) might happen. To a solution of MnCl(acac)$_2$ in dichloromethane (4.00×10^{-4} mol dm^{-3}) containing water at a constant concentration (5.2×10^{-3} mol dm^{-3}) was added acacH to attain various concentrations in the range of (3.28—21.84)$\times10^{-3}$ mol dm^{-3}, but no change in spectrum was observed. Alternatively, the concentration of acacH was kept constant at 9.61×10^{-3} mol dm^{-3} and that of water was varied in the range of (4.87—49.8)$\times10^{-3}$ mol dm^{-3}. The spectrum showed no change, either. These results may be rationalized if the sixth coordination site of MnCl(acac)$_2$ is occupied preferentially by a molecule of either acacH or water at the given concentrations, or alternatively if the complex retains the five-coordinate structure even in the presence of more than fifty times molar excess of acacH and water. In order to find out which of the three possibilities is the case, the following experiments have been performed.

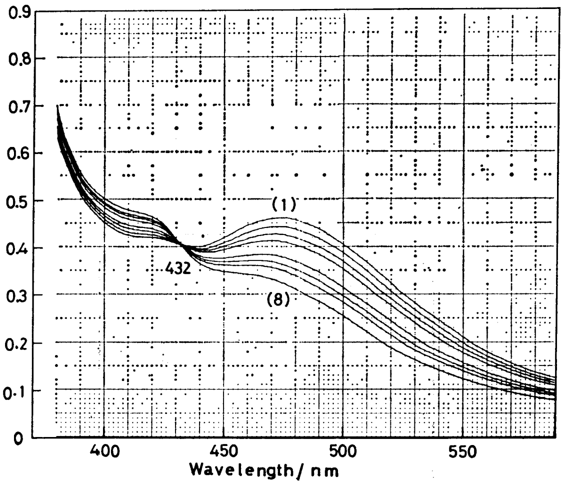


Fig. 1. Absorption spectra of MnCl(acac)$_2$ in dichloromethane at 25.0 °C containing 4.83×10^{-4} mol dm^{-3} complex, 9.80×10^{-3} mol dm^{-3} acacH, and 1.51×10^{-2} mol dm^{-3} H_2O in the absence (curve 1) and presence of DMF at various concentrations: 8.87×10^{-3} (2), 1.77×10^{-2} (3). 2.66×10^{-2} (4), 5.32×10^{-2} (5), 7.10×10^{-2} (6), 8.87×10^{-2} (7), and 1.33×10^{-1} (8) mol dm^{-3}.

When an increasing amount of DMF was added to a dichloromethane solution of MnCl(acac)$_2$ containing excess amounts of acacH and water, the absorption spectrum varied successively as is seen in Fig. 1, exhibiting a distinct isosbestic point. Thus the coordination of DMF to manganese as is expressed by Eq. 1 is conceivable.

$$\mathrm{MnCl(acac)_2X} + \mathrm{D} \rightleftharpoons \mathrm{MnCl(acac)_2D} + \mathrm{X}, \quad K_{ad}' \qquad (1)$$

The equilibrium quotient K_{ad}' is defined by $K_{ad}'=[\mathrm{MD}][\mathrm{X}]/[\mathrm{MX}][\mathrm{D}]$, where M and D represent the MnCl(acac)$_2$ moiety and a molecule of donor solvent such as DMF, respectively, and X is either acacH, H_2O, or nil. The observed absorbance per unit path length, A, of the solution is related to the concentration of D by Eq. 2.

$$\frac{1}{\varepsilon_{MX}c_M - A} = \frac{1}{(\varepsilon_{MX}-\varepsilon_{MD})c_M} + \frac{[X]}{(\varepsilon_{MX}-\varepsilon_{MD})c_M K_{ad}'[D]} \qquad (2)$$

Here each ε stands for the molar extinction coefficient of the species shown by a subscript, and c_M for the total concentration of the complex. The concentrations of uncoordinated X and D can be approximated by their total concentrations, c, since c_{acacH}, c_{H_2O}, $c_D \gg c_M$. The absorbance at 480 nm was used to calculate the left-hand term of Eq. 2, which was plotted against 1/[D] to result in a good straight line. The slope and intercept of the straight line gave $\varepsilon_{MD}=$ 416 dm^3 mol^{-1} cm^{-1} at 480 nm and $[X]/K_{ad}'=0.0994$ mol dm^{-3}.

If a water molecule is coordinated to manganese(III) as X, $K_{ad}'(H_2O)$ will be 0.152 since $c_{H_2O}=1.51\times10^{-2}$ mol dm^{-3}. On the other hand, K_{ad}'(acacH) is calculated to be 0.0986 from $c_{acacH}=9.80\times10^{-3}$ mol dm^{-3}. By virtue of these values for the equilibrium quotient of Reaction 1, the absorbance A at various concentrations of X can be calculated from Eq. 3.

$$A = \frac{(\varepsilon_{MX}-\varepsilon_{MD})c_M}{1+K_{ad}'[D]/[X]} + \varepsilon_{MD}c_M \qquad (3)$$

The curves in Fig. 2 display the expected change of A at 480 nm with concentrations of H_2O and acacH as X at a fixed [DMF]. As shown by circles in Fig. 2, the spectra in the 340—700 nm region showed no change under these circumstances, indicating that the coordinated DMF is not replaced at all by H_2O and acacH.

Thus the spectral change depicted in Fig. 1 can not be rationalized by substitution of the H_2O or acacH ligand by DMF, but should be considered to correspond to ligation of DMF at the sixth vacant coordination site according to Eq. 4. Other β-diketonato complexes, $MnCl(bzac)_2$ and $MnCl(dbm)_2$ showed similar behaviors in dichloromethane, indicating that they also reserve the five-coordinate structure in solution.

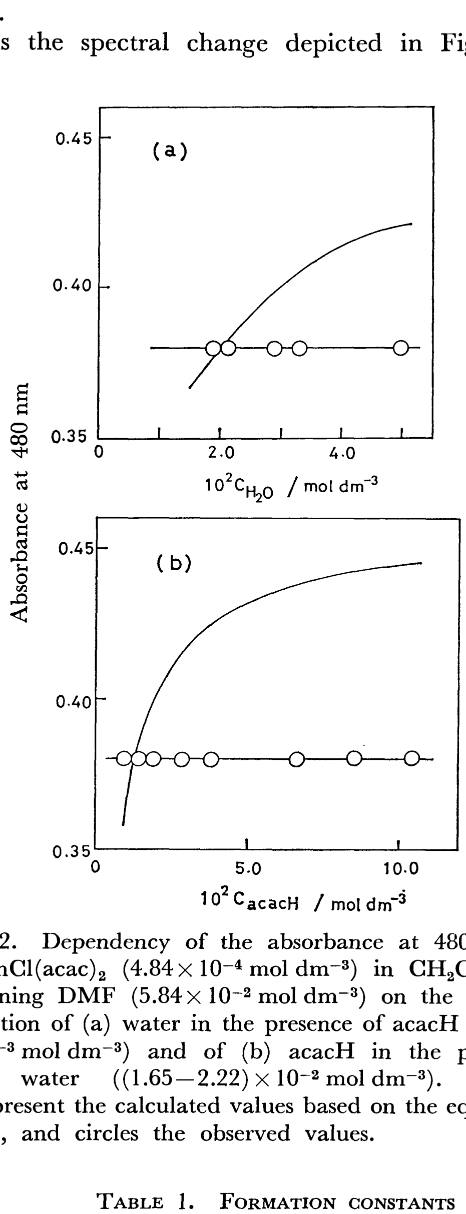


Fig. 2. Dependency of the absorbance at 480 nm of $MnCl(acac)_2$ (4.84×10^{-4} mol dm^{-3}) in CH_2Cl_2 containing DMF (5.84×10^{-2} mol dm^{-3}) on the concentration of (a) water in the presence of acacH (9.62×10^{-3} mol dm^{-3}) and of (b) acacH in the presence of water (($1.65-2.22)\times10^{-2}$ mol dm^{-3}). Curves represent the calculated values based on the equilibria (1), and circles the observed values.

$$MnCl(\beta\text{-dik})_2 + D \rightleftharpoons MnCl(\beta\text{-dik})_2D \quad (4)$$

$$K_{ad} = [MnCl(\beta\text{-dik})_2D]/[MnCl(\beta\text{-dik})_2][D] \quad (5)$$

Other donor solvents such as pyridine (py), DMSO, methanol (MeOH), MeCN, and PhCN also react with $MnCl(\beta\text{-dik})_2$. The formation constants K_{ad} of these adducts (Eq. 5) were determined in a similar manner as above and are collected in Table 1 together with the molar extinction coefficient of each adduct. The plots of log K_{ad} against the donor number[7] of each solvent gave straight lines (Fig. 3).

When increasing amounts of donor solvents were added to solution of $MnCl(acac)_2$ in dichloromethane, isosbestic points were observed at 434 (py), 431 (DMSO), 432 (DMF), 438 (MeOH), 450 (MeCN), and 447 (PhCN) nm. The reactions of $MnCl(bzac)_2$ with MeOH (432 and 452 nm) and MeCN (426 and 468 nm) also showed two isosbestic points, respectively, while the other donor solvents showed no isosbestic points in the 410—700 nm region. In the case of $MnCl(dbm)_2$, no solvents except MeCN (483 nm) exhibited isosbestic points. These adduct formation reactions are very rapid and could not be followed by the stopped-flow method.

As is exemplified by Fig. 1, a large excess of donor solvents were employed in these experiments, and it was supposed that β-diketone itself might add to $MnCl(\beta\text{-dik})_2$ if a large excess amount was used. Figure 4 shows it is the case in fact. When an increasing amount of acacH was added to a solution of $MnCl(acac)_2$ in dichloromethane, spectral change was observed accompanying an isosbestic point at 443 nm. The resulting spectrum is different from that of $Mn(acac)_3$ and seems to be ascribed to the adduct formed by Reaction 6, although it is not certain whether the acetylacetone molecule is added as a keto or an enol

Table 1. Formation constants (K_{ad}) in dm^3 mol^{-1} and molar extinction coefficients (ε_{ad}) of adducts in dichloromethane at 25.0 °C
$MnCl(\beta\text{-dik})_2 + D \rightleftharpoons MnCl(\beta\text{-dik})_2D$.

D	DN[a]	$MnCl(acac)_2D$			$MnCl(bzac)_2D$			$MnCl(dbm)_2D$		
		K_{ad}	ε_{ad}	(λ/nm)	K_{ad}	ε_{ad}	(λ/nm)	K_{ad}	ε_{ad}	(λ/nm)
py	33.1	102±1	460±13	(480)	310±2	374±1	(500)	374±1	459±1	(530)
DMSO	29.8	28.0±0.6	410±12	(480)	31.4±0.2	366±1	(500)	30.4±0.1	322±2	(530)
DMF	26.6	10.0±0.1	416±5	(480)	11.4±0.1	426±5	(500)	11.4±0.1	390±2	(530)
MeOH	19.0	1.34±0.01	57.4±0.2	(480)	1.12±0.01	144±15	(500)	1.29±0.31	16±6	(530)
MeCN	14.1	0.2444±0.015	569±42	(480)	0.200±0.016	220±24	(520)	0.234±0.005	316±8	(540)
PhCN	11.9	0.258±0.020	594±51	(480)	0.276±0.066	384±115	(500)	0.192±0.060	278±82	(530)
acacH	15.6[b]	0.516±0.008	541±10	(480)	0.46_8[c]			0.44_6[c]		
bzacH	16·4[b]	0.64_8[c]			0.614±0.033	262±18	(540)	0.58_4[c]		
dbmH	17.4[b]	0.86_4[c]			0.84_4[c]			0.822±0.010	164±3	(550)

a) Donor number as defined by Gutmann.[7] b) Determined in this study. c) Calculated. See the text.

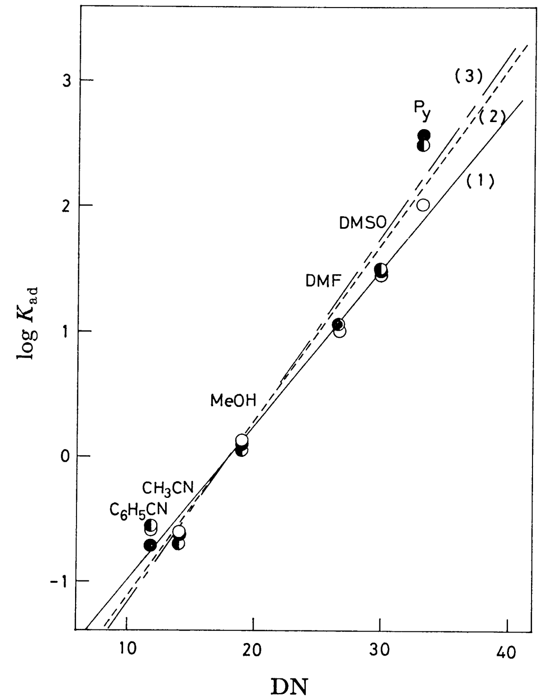


Fig. 3. Formation constants of adducts $MnCl(\beta\text{-dik})_2D$ related to the donor number of addendum D, β-dik being acac (line 1), bzac (2), and dbm (3).

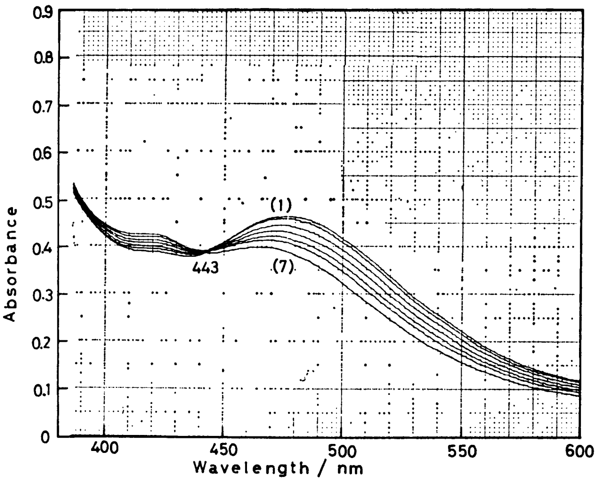


Fig. 4. Absorption spectra of $MnCl(acac)_2$ in dichloromethane at 25.0 °C containing 4.62×10^{-4} mol dm^{-3} complex in the presence of acacH at various concentrations: 9.35×10^{-3} (curve 1), 9.35×10^{-2} (2), 2.23×10^{-1} (3), 4.05×10^{-1} (4), 5.91×10^{-1} (5), 7.97×10^{-1} (6), and 1.17 (7) mol dm^{-3}.

tautomer.

$$MnCl(acac)_2 + acacH \rightleftharpoons MnCl(acac)_2(acacH) \qquad (6)$$

The $MnCl(bzac)_2$–(bzacH) and $MnCl(dbm)_2$–(dbmH) systems were also studied in a similar manner. The formation constants of the three kinds of adduct $MnCl(\beta\text{-dik})_2(\beta\text{-dikH})$ were thus determined and listed in Table 1 together with their extinction coefficients at the given wavelengths. The donor number of each β-diketone was estimated by interpolation of the log K_{ad} *vs.* DN plots in Fig. 3, and was in turn utilized to calculate the prospective formation constants of the adducts according to Eq. 7, which are included in Table 1.

$$MnCl(\beta\text{-dik})_2 + \beta\text{-dik'H} \rightleftharpoons MnCl(\beta\text{-dik})_2(\beta\text{-dik'H}) \qquad (7)$$

Equilibria for the β-Diketone Substitution Reactions of $MnCl(acac)_2$. Figure 5 shows the absorption spectra of the $MnCl(\beta\text{-dik})_2$ complexes in dichloromethane. When an increasing amount of bzacH or dbmH is added to a $MnCl(acac)_2$ solution containing uncoordinated acetylacetone to stabilize the complex solution, the spectrum changes successively to approach that of $MnCl(bzac)_2$ or $MnCl(dbm)_2$, respectively. The points plotted in Fig. 6 show the observed absorbances at 450 nm as a function of the dbmH concentration added to the solution of $MnCl(acac)_2$ in dichloromethane. These results conform with the following equilibria.

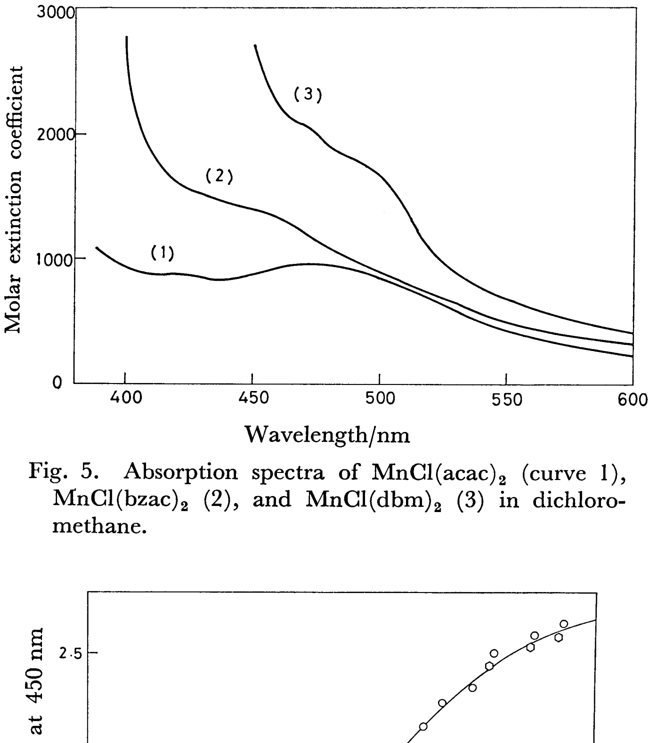


Fig. 5. Absorption spectra of $MnCl(acac)_2$ (curve 1), $MnCl(bzac)_2$ (2), and $MnCl(dbm)_2$ (3) in dichloromethane.

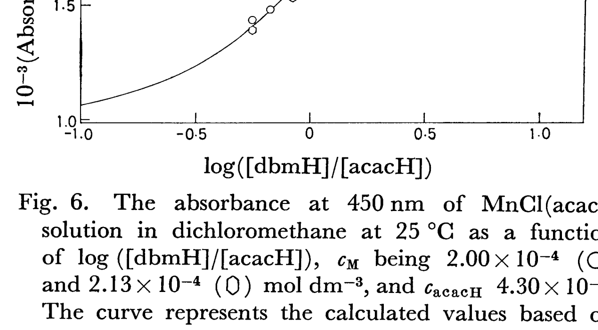


Fig. 6. The absorbance at 450 nm of $MnCl(acac)_2$ solution in dichloromethane at 25 °C as a function of log ([dbmH]/[acacH]), c_M being 2.00×10^{-4} (○) and 2.13×10^{-4} (○) mol dm^{-3}, and c_{acacH} 4.30×10^{-3}. The curve represents the calculated values based on $K_1=0.847$, $K_2=0.401$, and ε for MnCl(acac)(dbm) = 1980 cm^{-1} mol^{-1} dm^3 at 450 nm.

$$\mathrm{MnCl(acac)_2} + \beta\text{-dikH} \rightleftharpoons \mathrm{MnCl(acac)}(\beta\text{-dik}) + \mathrm{acacH},\ K_1 \tag{8}$$

$$\mathrm{MnCl(acac)}(\beta\text{-dik}) + \beta\text{-dikH} \rightleftharpoons \mathrm{MnCl}(\beta\text{-dik})_2 + \mathrm{acacH},\ K_2 \tag{9}$$

The observed absorbance of the reaction mixture is expressed by Eq. 10,

$$A = \varepsilon_{\mathrm{Ma_2}}[\mathrm{Ma_2}] + \varepsilon_{\mathrm{Mab}}[\mathrm{Mab}] + \varepsilon_{\mathrm{Mb_2}}[\mathrm{Mb_2}] = \bar{\varepsilon}c_{\mathrm{M}}, \tag{10}$$

where $\mathrm{Ma_2}$, Mab, and $\mathrm{Mb_2}$ represent $\mathrm{MnCl(acac)_2}$, $\mathrm{MnCl(acac)}(\beta\text{-dik})$, and $\mathrm{MnCl}(\beta\text{-dik})_2$, respectively. The mean molar absorptivity $\bar{\varepsilon}$ can be calculated by

$$\bar{\varepsilon}_{\mathrm{calcd}} = \frac{\varepsilon_{\mathrm{Ma_2}} + \varepsilon_{\mathrm{Mab}}K_1([\beta\text{-dikH}]/[\mathrm{acacH}]) + \varepsilon_{\mathrm{Mb_2}}K_1K_2([\beta\text{-dikH}]/[\mathrm{acacH}])^2}{1 + K_1([\beta\text{-dikH}]/[\mathrm{acacH}]) + K_1K_2([\beta\text{-dikH}]/[\mathrm{acacH}])^2}, \tag{11}$$

where K_1 and K_2 are the equilibrium constants for the stepwise substitution Reactions 8 and 9.

$$K_1 = \frac{[\mathrm{Mab}][\mathrm{acacH}]}{[\mathrm{Ma_2}][\beta\text{-dikH}]},\quad K_2 = \frac{[\mathrm{Mb_2}][\mathrm{acacH}]}{[\mathrm{Mab}][\beta\text{-dikH}]}. \tag{12}$$

Since acacH and β-dikH were used in more than twenty times molar excess than c_{M}, [acacH] and [β-dikH] may be approximated by the total concentrations c_{acacH} and $c_{\beta\text{-dikH}}$, respectively. A generalized least squares method was applied in order to minimize the error square sum $\sum(\bar{\varepsilon}_{\mathrm{obsd}} - \bar{\varepsilon}_{\mathrm{calcd}})^2$ for the set of constants K_1, K_2, and $\varepsilon_{\mathrm{Mab}}$. The constants thus obtained for both the $\mathrm{MnCl(acac)_2}$–bzacH and $\mathrm{MnCl(acac)_2}$–dbmH systems are listed in Table 2. The solid curve in Fig. 6 representing absorbance calculated for the $\mathrm{MnCl(acac)_2}$–dbmH system conforms satisfactorily with the experimental data, supporting presumed participation of the mixed-ligand complex. In fact MnCl(acac)(bzac) and MnCl(acac)(dbm) were prepared and isolated as described in the Experimental section.

TABLE 2. THE EQUILIBRIUM CONSTANTS IN DICHLOROMETHANE AT 25.0 °C FOR THE SUBSTITUTION REACTIONS OF $\mathrm{MnCl(acac)_2}$ WITH BENZOYLACETONE AND DIBENZOYLMETHANE ACCORDING TO EQS. 8 AND 9

β-Diketone	K_1	K_2	ε(At λ/nm)[a]
bzacH	1.09±0.01	0.43±0.02	1184±10 (434)
dbmH	0.85±0.01	0.40±0.02	1980±20 (450)

a) For the mixed ligand complex MnCl(acac)(β-dik).

Kinetics of the β-Diketone Substitution Reactions of MnCl(β-dik)₂. As is shown in Table 2, the equilibria for the β-diketone substitution reactions of $\mathrm{MnCl(acac)_2}$ are rather favorable to the acetylacetonato complex. Thus reactions (13) were studied under the pseudo first order conditions employing excess amounts of acacH.

$$\mathrm{MnCl}(\beta\text{-dik})_2 + 2\,\mathrm{acacH} \longrightarrow \mathrm{MnCl(acac)_2} + 2\beta\text{-dikH} \tag{13}$$

The spectral change during reactions was recorded over the 405—495 nm region by means of a rapid scan instrument. As was anticipated from the spectra in Fig. 5, no isosbestic point was observed, but the absorbance of the reaction mixture decreased monotonously with time in either case. The progress of reaction was followed spectrophotometrically at an appropriate wavelength by the stopped-flow method.

Figure 7(a) exemplifies a plot of $\ln(A-A_\infty)$ against time for the reaction of $\mathrm{MnCl(dbm)_2}$ with acacH in dichloromethane at 25.0 °C which was followed at 450 nm. The observed points in the later stage of reaction fall on a straight line, but those in the earlier stage deviate appreciably from it. This behavior may be rationalized on the assumption that the overall reaction is composed of two consecutive steps (14) and (15), since the existence of the metastable mixed ligand complex was revealed by the foregoing equilibrium studies.

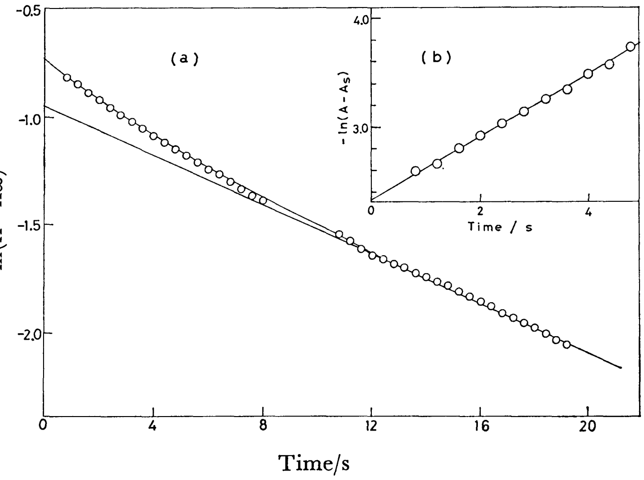


Fig. 7. (a) Pseudo first order plot for the reaction of $\mathrm{MnCl(dbm)_2}$ with acetylacetone in dichloromethane at 25.0 °C, c_{M}, c_{dbmH}, c_{acacH} and $c_{\mathrm{H_2O}}$ being 2.47×10^{-4}, 2.47×10^{-3}, 9.74×10^{-2}, and 7.42×10^{-3} mol dm^{-3}, respectively. (b) Linear plot for the earlier part of the above reaction.

$$\mathrm{MnCl}(\beta\text{-dik})_2 + \mathrm{acacH} \longrightarrow \mathrm{MnCl(acac)}(\beta\text{-dik}) + \beta\text{-dikH},\ k_1 \tag{14}$$

$$\mathrm{MnCl(acac)}(\beta\text{-dik}) + \mathrm{acacH} \longrightarrow \mathrm{MnCl(acac)_2} + \beta\text{-dikH},\ k_2 \tag{15}$$

Under the pseudo first order conditions, the absorbance of a reaction mixture at time t is related to k_1 and k_2 by

$$A - A_\infty = a_1\exp(-k_1t) + a_2\exp(-k_2t), \tag{16}$$

since A is expressed by Eq. 10 and $A_\infty = \varepsilon_{\mathrm{Ma_2}}c_{\mathrm{M}}$, a_1, and a_2 in Eq. 16 being given by

$$a_1 = \frac{(\varepsilon_{\mathrm{Mb_2}} - \varepsilon_{\mathrm{Mab}})k_1 + (\varepsilon_{\mathrm{Ma_2}} - \varepsilon_{\mathrm{Mb_2}})k_2}{k_1 - k_2}c_{\mathrm{M}} \tag{17}$$

$$a_2 = \frac{(\varepsilon_{\mathrm{Mab}} - \varepsilon_{\mathrm{Ma_2}})k_1}{k_1 - k_2}c_{\mathrm{M}}. \tag{18}$$

The later linear part of the $\ln(A-A_\infty)$ *vs.* t plot in Fig. 7(a) gives the slower one of the two rate constants, $k_{\mathrm{S}} = 0.0573\ \mathrm{s^{-1}}$, and the ordinate intercept, ln

$a_S = \ln(A_S - A_\infty) = \ln(9.85 \times 10^{-2})$. Then the values $A - A_S$ were calculated for the absorbance data in the earlier part of reaction and $\ln(A - A_S)$ was plotted against time to result in a straight line in Fig. 7(b). The slope and intercept of this straight line gave the faster rate constant $k_F = 0.293\ s^{-1}$ and $\ln a_F = \ln(A_0 - A_S) = \ln(3.83 \times 10^{-1})$. The solid curve in Fig. 7(a) reproduces the calculated values of $\ln(A - A_\infty)$ based on k_S, k_F, a_S, and a_F.

Equation 19 was derived from Eqs. 17 and 18 and utilized to assign k_S and k_F correctly to k_1 and k_2 in Eq. 16.

$$\frac{k_2}{k_1} = \frac{\varepsilon_{Mab} - \varepsilon_{Ma_2}}{\varepsilon_{Ma_2} - \varepsilon_{Mb_2}}\left(\frac{a_1}{a_2} - \frac{\varepsilon_{Mb_2} - \varepsilon_{Mab}}{\varepsilon_{Mab} - \varepsilon_{Ma_2}}\right) \qquad (19)$$

If it is assumed that $k_S = k_1$ and $k_F = k_2$, the left-hand side of Eq. 19 becomes 5.1, whereas the right-hand side is −1.7. On the other hand, the reverse assignment that $k_S = k_2$ and $k_F = k_1$ results in fair coincidence between the two values: the left-hand side=0.20 and the right-hand side=0.29. Therefore the latter assignment is reasonable and the pseudo first order rate constants thus obtained will be referred to k_1(obsd) and k_2(obsd) in the following discussion.

The pseudo first order rate constants obtained in dichloromethane at 25.0 °C containing various concentrations of acetylacetone and water are listed in Table 3. When c_{acacH} is maintained constant, k_1(obsd) and k_2(obsd) do not show appreciable change beyond the experimental error even if c_{H_2O} is varried in the $5.87-16.83 \times 10^{-3}$ mol dm^{-3} region for $MnCl(bzac)_2$ and in the $1.22-8.16 \times 10^{-3}$ mol dm^{-3} region for $MnCl(dbm)_2$. On the other hand both k_1(obsd) and k_2(obsd) increase with c_{acacH} and the slopes of each two straight lines in Figs. 8(a) and (b) give the second order rate constants k_1 and k_2 for the reactions of $MnCl(bzac)_2$ and $MnCl(dbm)_2$ with acacH, respectively. By combining these values with the equilibrium constants listed in Table 2, the second order rate constants for the forward reactions of (8) and (9) were obtained. Table 4 summarizes these rate data.

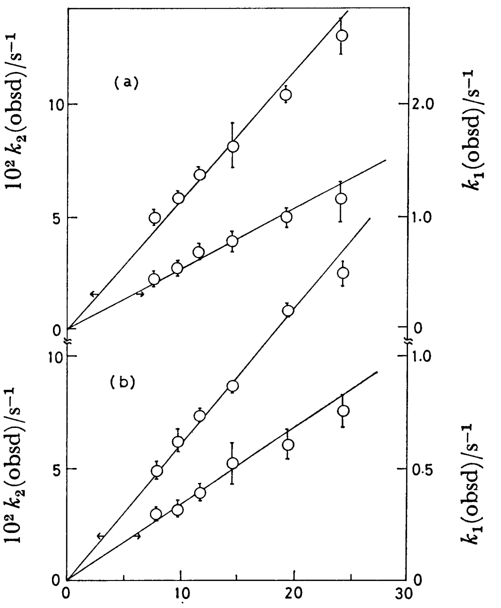


Fig. 8. Dependences on c_{acacH} of k_1(obsd) and k_2(obsd) for the reactions of $MnCl(bzac)_2$ (a) and $MnCl(dbm)_2$ (b) with acacH in dichloromethane at 25.0 °C.

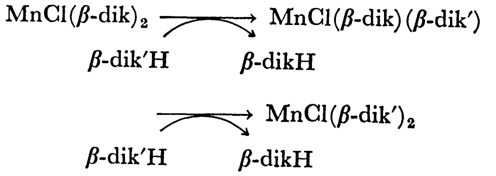
The plots of k_1(obsd) and k_2(obsd) for the reaction of $MnCl(dbm)_2$ with acetylacetone-d_2 (Table 3) against c_{acacH} resulted in straight lines passing through the origin, of which slopes gave $k_1(D) = 11.4 \pm 0.05\ s^{-1}$ and $k_2(D) = 0.281 \pm 0.031\ s^{-1}$. Thus the apparent rate ratios are $k_1(H)/k_1(D) = 2.96$ and $k_2(H)/k_2(D) = 2.16$. Taking into account the fact that the isotopic purity of the acetylacetone-d_2 used is 90.2%, the kinetic isotope effect is calculated as $k_1(H)/k_1(D) = 3.76$ and $k_2(H)/k_2(D) = 2.47$. The calculation is based on the assumption that the isotope exchange between acetylacetone-d_2 and water is so slow under the given conditions that the deuterium content of the acetylacetone-d_2 is unaltered during the rate measurements.

TABLE 3. PSEUDO FIRST ORDER RATE CONSTANTS IN DICHLOROMETHANE AT 25.0 °C OF THE SUBSTITUTION REACTIONS OF $MnCl(\beta\text{-dik})_2$ WITH ACETYLACETONE ACCORDING TO EQS. 14 AND 15

$10^2 c_{acacH}$ mol dm^{-3}	$10^3 c_{H_2O}$ mol dm^{-3}	$10^2 k_1$(obsd) s^{-1}	$10^2 k_2$(obsd) s^{-1}
	$MnCl(bzac)_2$[a]		
7.726	8.88	45.4±6.7	4.96±0.31
9.657	9.52	54.2±4.8	5.87±0.21
11.58	9.69	68.5±5.3	6.90±0.22
14.48	9.46	77.9±9.0	8.16±0.98
19.31	8.90	98.0±7.0	10.4±0.5
24.14	8.60	120±23	13.1±0.8
9.730	6.18	55.4±8.8	6.19±0.13
9.730	5.87	65±12	5.73±0.22
9.730	9.17	54±13	5.98±0.35
9.730	12.74	50.2±9.3	6.38±0.50
9.730	16.83	52.6±1.7	5.31±0.27
	$MnCl(dbm)_2$[b]		
7.795	7.90	30.0±2.6	4.91±0.36
9.744	7.42	32.1±3.8	6.19±0.50
11.69	8.88	39.6±3.4	7.29±0.30
14.62	8.14	51.7±9.1	8.60±0.23
19.48	7.92	60.6±6.1	11.99±0.36
24.36	7.94	75.3±7.1	13.64±0.53
9.952	1.22	45.7±0.4	6.00±0.71
9.952	1.48	38.5±8.8	5.85±0.14
9·952	1.42	45.9±1.6	6.26±0.73
9.952	1.47	37.6±3.4	6.1 ±1.3
9.952	4.14	39.2±2.3	6.28±0.19
9.952	8.16	36.6±0.8	6.80±0.28
9.820[c]	5.70	11.6±2.9	3.01±0.72
14.73[c]	5.43	16.2±1.0	3.99±0.27
19.64[c]	5.07	22.2±2.8	5.04±0.43

a) $c_M = 2.47 \times 10^{-4}$ mol dm^{-3} and $c_{bzacH} = 3.067 \times 10^{-3}$ mol dm^{-3} for the former six experiments, and $c_M = 2.46 \times 10^{-4}$ mol dm^{-3} and $c_{bzacH} = 3.110 \times 10^{-3}$ mol dm^{-3} for the latter five experiments. b) $c_M = 2.46 \times 10^{-4}$ mol dm^{-3} and $c_{dbmH} = 2.474 \times 10^{-3}$ mol dm^{-3}. c) Acetylacetone-d_2 was used and $c_{dbmH} = 2.472 \times 10^{-3}$ mol dm^{-3}.

TABLE 4. SECOND ORDER RATE CONSTANTS ($dm^3\ mol^{-1}\ s^{-1}$) IN DICHLOROMETHANE AT 25.0 °C FOR THE SUBSTITUTION REACTIONS OF $MnCl(\beta\text{-dik})_2$ WITH OTHER β-DIKETONE



$MnCl(\beta\text{-dik})_2$	β-dik′H		
	acacH	bzacH	dbmH
$MnCl(acac)_2$		0.634[a]	0.516[a]
$MnCl(bzac)_2$	5.47 ± 0.40		
$MnCl(dbm)_2$	3.38 ± 0.28		
MnCl(acac)(bzac)	0.582 ± 0.041	2.34[a]	
MnCl(acac)(dbm)	0.608 ± 0.029		1.36[a]

a) Calculated value (see text).

Discussion

Addition Equilibria of Donor Molecules to $MnCl(\beta\text{-dik})_2$. As is seen in Figs. 1 and 4, the reaction of $MnCl(\beta\text{-dik})_2$ with a donor slovent in large excess is accompanied by an appreciable change in the absorption spectrum, which suggests some alteration in the coordination sphere. It seems reasonable to suppose that a donor molecule added to $MnCl(\beta\text{-dik})_2$ attains six coordination (Eq. 4). In fact adducts such as $MnCl(acac)_2$(pyridine *N*-oxide),[1] $MnBr(acac)_2$(4-Me-py),[1] $MnBr(acac)_2(dioxane)\cdot H_2O$,[1] and $MnNCS(acac)_2(py)$[8] have been prepared and characterized, supporting the existence of addition equilibria represented by Eq. 4 in solution.

The formation constant of adducts, K_{ad}, increases with the donor number of addendum (Table 1), and the $\log K_{ad}$ *vs.* DN plots afford straight lines (Fig. 3) which are reproduced by the following equations based on the least squares treatment, r giving the correlation coeffecient in each case.

$$MnCl(acac)_2:\ \log K_{ad} = 0.125DN - 2.24 \quad (r=0.994) \qquad (20\text{-}1)$$

$$MnCl(bzac)_2:\ \log K_{ad} = 0.142DN - 2.54 \quad (r=0.981) \qquad (20\text{-}2)$$

$$MnCl(dbm)_2:\ \log K_{ad} = 0.146DN - 2.63 \quad (r=0.984) \qquad (20\text{-}3)$$

Such a linear relationship between the adduct formation constant and the donor number of addendum has seldom been noted for five-coordinate complexes. Gutmann found that adduct formation constants of antimony(V) chloride with various donor solvents increase with the donor number.[7] The linear relation is expressed by $\log K_{DSbCl_5}=0.580\ DN-5.44$ ($r=0.984$). Carlin and Walker studied the adduct formation of $VO(acac)_2$ with a variety of N- and O-donors in nitrobenzene by the calorimetric and spectroscopic methods, and determined the equilibrium constants as well as thermodynamic functions.[9] Of their data, those for pyridine, piperidine, methanol, and hexamethylphosphoric triamide of which DN values are available satisfy the linear relation: $\log K_{ad}=0.101\ DN-1.94$ ($r=0.979$). It is very interesting that both of the slope and intercept show a close resemblance to those in the present system (Eqs. 20) in spite of the difference in the nature of complex and the solvent used. Both of these slopes are much gentle compared with that for $DSbCl_5$, revealing that $VO(acac)_2$ and $MnCl(\beta\text{-dik})_2$ are less sensitive than $SbCl_5$ as the indicator of relative base strength.

Equations 20 were utilized to obtain the DN values of β-diketones based on the observed K_{ad} for $MnCl(\beta\text{-dik})_2(\beta\text{-dikH})$. The DN values were used in turn to calculate K_{ad} for the $MnCl(\beta\text{-dik})_2(\beta\text{-dik'H})$ adducts which can not be determined experimentally since the ligand substitution occurs. As is seen in Table 1, DN of β-diketone increases in the sequence of acacH< bzacH<dbmH and K_{ad} for a given $MnCl(\beta\text{-dik})_2$ also shows the same sequence. The infrared study on $Cu(\beta\text{-dik})_2$[10] and ^1H NMR study on β-diketones[11] show the ability of the aromatic substitutents to supply electron density to the chelate or enolic ring by resonance, and the pK_a values determined in aqueous dioxane (50% by volume) at 25 °C increase in the sequence of acacH(10.28) < bzacH(10.43) < dbmH (11.26).[12] The observed trend of K_{ad} also reflects the electron relasing effect of the phenyl substitutent in bzacH and dbmH. On the other hand, the K_{ad} values for the three $MnCl(\beta\text{-dik})_2$ complexes with a particular β-dikH show a slight decrease in the sequence of $MnCl(acac)_2>MnCl(bzac)_2>MnCl(dbm)_2$. Better β-diketonate ligands seem to suppress the acidity of $MnCl(\beta\text{-dik})_2$.

Water exists as a discrete molecule in benzene,[13] toluene,[14] and cyclohexane[14] solutions, but partially forms a dimer in chlorinated solvents such as chloroform,[13a] 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane.[14] Although the behavior of water in dichloromethane has not yet been reported, the dimerization constants determined in chloroform (0.47) and 1,2-dichloroethane (0.54) at 25 °C[13a] may be used to estimate the degree of dimerization of water in dichloromethane. In the present investigation, the concentration of water has been kept around 10^{-3} mol dm^{-3} and was 5×10^{-2} mol dm^{-3} at most. Under these conditions, the estimated fraction of dimer is less than 2%, and most part of water molecules exist as monomer in dichloromethane. The DN value (18.0) of water was obtained by Gutmann in 1,2-dichloroethane and refers to the monomeric species. Substituting this value into Eqs. 20, we can estimate the adduct formation constants of water with the $MnCl(\beta\text{-dik})_2$ complexes to be 1.02, 1.04, and 0.995 for β-dik=acac, bzac, and dbm, respectively. These figures rationalize the failure of water in affecting the absorption spectrum of $MnCl(acac)_2$ in dichloromethane.

Substitution Equilibria. Most of the equilibrium constants K_1 and K_2 for the substitution reactions of $MnCl(acac)_2$ with benzoylacetone and dibenzoylmethane according to Eqs. 8 and 9 are smaller than 1. This fact might look to contradict the above-mentioned basicity sequence of the β-diketonate anions: $acac^- < bzac^- > dbm^-$. However it should be noted that Equilibria 8 and 9 involve the β-diketone molecules instead of the β-diketonate anions. The equilibrium constant K_1' for the reaction

$$MnCl(acac)_2 + \beta\text{-dik}^- \rightleftharpoons MnCl(acac)(\beta\text{-dik}) + acac^- \quad (21)$$

will be certainly larger than 1 for $\beta\text{-dik}^- = bzac^-$ and dbm^-, but K_1 is related by K_1' by

$$\log K_1 = \log K_1' - (pK_a \text{ of } \beta\text{-dikH} - pK_a \text{ of acacH}). \quad (22)$$

Since the pK_a values of bzacH and dbmH are larger than that of acacH, log K_1 becomes smaller than log K_1' by the pK_a difference between the β-diketones.

Mechanism of the Substitution Reactions. Based on the information obtained from the equilibrium and kinetic studies described above, the scheme depicted in Fig. 9 is proposed as a mechanism of substitution reaction of $MnCl(\beta\text{-dik})_2$ with another β-diketone such as acacH. The first step, coordination of an acacH molecule to manganese at the sixth vacant site is evidenced by the equilibrium measurements. Although dbmH exists solely as enol molecules, bzacH and acacH are composed of two tautomers, neat liquids containing 98 and 79% enol, respectively, at 38 °C.[15] The enol content is further increased in inert solvents, and that of acacH was reported to be 87% in chloroform and 96% in carbon tetrachloride at 33 °C.[16] In the present study, acacH and bzacH in dichloromethane at 23 °C were found to contain 83.4 and 97.9% enol, respectively.

The enol tautomer of acetylacetone reacts with the copper(II) ion much faster than the keto form in water and methanol.[17] In the case of thenoyltrifluoroacetone only the enol tautomer was reported to react with nickel(II), cobalt(II), copper(II), and iron(II) in aqueous solution.[18] Although the tautomerization rate is estimated as low as 10^{-5} s^{-1} in aprotic solvents by extrapolation from data in mixed aqueous media,[19] it is difficult to distinguish the contribution of both tautomers in the present case. However mainly the enol tautomer seems to contribute to the overall rate because of its predominant abundance and higher deprotonation rate[20] as compared with the keto tautomer. In recent years many kinds of metal complexes containing β-dicarbonyl compounds as a neutral ligand have been prepared.[21] Most of them contain the keto tautomer,[22] but $UO_2(acac)_2(acacH)$,[23] $MnBr_2(acacH)_2$,[24] $[ReCl(CO)_3(bzacH)]_2$,[25] and $PtCl(acac)(acacH)$[26] involve the enol tautomer.

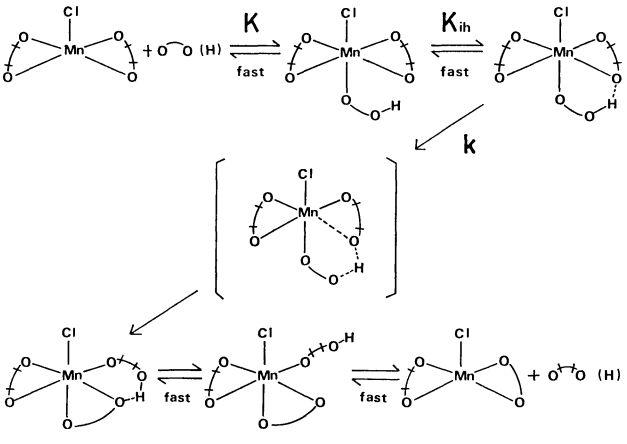


Fig. 9. Proposed mechanism for the ligand substitution reaction of $MnCl(\beta\text{-dik})_2$ with another β-diketone molecule.

As the second step of the reaction scheme, hydrogen-bonding interaction between the coordinated acacH and a neighboring β-diketonate ligand is presumed. Both ^1H NMR spectra[16] and cryoscopic measurements[27] of acacH in cyclohexane were consistent with intermolecular association. Hydrogen-bonding interaction between the coordinated β-diketonate ligand and various proton donors has also been evidenced by infrared[28] and electronic[29] absorption spectroscopy. X-Ray analysis of $VO(acac)_2(p\text{-}NO_2C_6H_4OH)$ revealed that a *p*-nitrophenol molecule is linked with one oxygen atom of an acac ligand *via* hydrogen bonding with the OH···O distance of 2.68 Å.[30] Thus the interligand hydrogen bonding presumed in the scheme seems reasonable.

Succeeding intramolecular dissociative interchange, that is, proton transfer from acacH to a leaving β-dik ligand, chelate-ring opening of the β-dik ligand, and chelation of the acac ligand in a synchronous fashion is presumed as the rate-determining step. The observed deuterium isotope effect may be caused by the hydrogen-bonding preequilibrium (K_{ih}) and proton transfer *via* this linkage (k). Thompson and Allred[27] compared the keto-enol equilibria in acetylacetone and acetylacetone-d_2 at various temperatures and concluded that protium forms a stronger hydrogen bond in this system than does deuterium, but the difference is not substantial at ambient temperature. Long and Watson[31] measured the rates of bromination of γ-methylacetylacetone and its γ-deuterio analogue in aqueous solution at 25 °C. The k_H/k_D ratios for the proton transfer from the keto molecule to water and acetate anion were 3.5 and 5.5, respectively, and those for the proton transfer from the enol molecule were also calculated to be 3.4 and 5, respectively. The observed values of k_H/k_D, 3.76 and 2.47 for k_1 and k_2, respectively, for the present system seem to accord with the proposed reaction scheme.

Recently Nishizawa and Saito studied the ligand exchange reaction between $VO(acac)_2$ and acacH-^{14}C in 1,2-dichloroethane.[32] They estimated the donor number of acacH to be 20 by a spectroscopic method, which is a little larger than the value (15.6) obtained in the present study. They also proposed a mechanism which involves the unidentate coordination of acacH to $VO(acac)_2$ ($K_{ad} = 0.14$ dm^3 mol^{-1}) as the first step and its chelation associated with the proton transfer to a leaving acac ligand as the rate-determining step, since the observed k_H/k_D value of 1.3 is not so large as to rationalize the assumption of a proton-transfer step as an independent rate-determining step.[32]

Based on the proposed scheme in Fig. 9, the overall rate of reaction is given by Eq. 23.

$$\text{rate} = \frac{kKK_{ih}[\text{acacH}]}{1+(1+K_{ih})K[\text{acacH}]}[MnCl(\beta\text{-dik})_2] \quad (23)$$

Here $(1+K_{ih})K$ corresponds to K_{ad} of which values are given in Table 1, and $1 \gg (1+K_{ih})K[\text{acacH}]$ under most of the experimental conditions listed in Table 3. Then Eq. 23 is reduced to

$$k_{obsd} = kKK_{ih}[\text{acacH}]. \tag{24}$$

Thus the second order rate constants in Table 4 are composite in reality. The value of K will be large for an entering ligand whose DN is large, while K_{ih} and k will be larger for a more acidic entering ligand. Table 4 indicates that the rate of reaction of MnCl(acac)$_2$ with bzacH is larger than that with dbmH, although K_{ad} for bzacH is smaller than that for dbmH (Table 1). More acidic bzacH seems to have large K_{ih} and k overcompensating for disadvantage in K as compared with dbmH.

On the other hand, the rate of reaction of acacH with MnCl(bzac)$_2$ is a little faster than that with MnCl(dbm)$_2$ at 25.0 °C (Table 4). Since the K_{ad} values are estimated to be comparable for the two systems (Table 1) and K_{ih} seems favorable to more basic dbm ligand, lower rate for MnCl(dbm)$_2$ may stem from the k factor, cleavage of the Mn–O(dbm) bond being a little more difficult as compared with the Mn–O(bzac) bond.

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