Some Mixed-Ligand Manganese(III) Complexes Produced by the Reactions of Tris(acetylacetonato)manganese(III) with Hydrogen Halides in Organic Solvents

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Although tris(acetylacetonato)manganese(III) is reduced by hydrogen halides in organic solvents, ultimately resulting in manganese(II) chloride, bromide or bis(acetylacetonato)manganese(II), the equimolar reactions afforded the intermediary manganese(III) products $MnX(acac)_2$, where X is Cl, Br, or I. These mixed-ligand complexes were characterized by measurements of electronic and infrared spectra, molecular weight, electric conductivity and magnetic susceptibility, and concluded to exist as a five-coordinate molecule in non-coordinating solvents, but behave as a uni-uni valent electrolyte in methanol. Six-coordinate complexes $[Mn(acac)_2(H_2O)_2]Br \cdot 2H_2O$ and $MnX(acac)_2B$ were also derived therefrom, where B is 4-methylpyridine, pyridine oxide or dioxane. Further reaction of $MnCl(acac)_2$ with equimolar hydrogen chloride in methylene chloride at −78 °C produced $MnCl_2(acac)(O\text{-}py)_2$ or $MnCl_2(acac)H_2O$ in the presence or absence of pyridine oxide (O-py), respectively, but the corresponding dibromo and diiodo complexes could not be obtained in similar reactions with hydrogen bromide or iodide.

The reactions of various metal acetylacetonates with bromine or hydrogen bromide in organic solvents have been investigated so far, and several intermediary products were isolated and characterized.[1] The behavior of tris(acetylacetonato)cobalt(III) against bromine was particularly interesting. The tervalent state of cobalt was maintained in the reaction of the chelate with equimolar bromine in methylene chloride at 0 °C, but warming of the reaction mixture to room temperature or addition of another mole of bromine at 0 °C caused the reduction of cobalt(III), precipitating dibromo(acetylacetone)cobalt(II), $CoBr_2(acacH)$.[2]

Tris(acetylacetonato)manganese(III) has been known as a powerful chain initiator in the vinyl polymerization especially in the presence of amine and other additives.[3] Manganese(III) is readily reduced by primary amines (L) and converted quantitatively into $Mn(acac)_2L_2$.[4] The present paper reports some mixed-ligand manganese(III) complexes which were isolated and characterized as intermediary products in the redox reactions between tris(acetylacetonato)manganese(III) and hydrogen halides in organic solvents.[5]

Experimental

Materials. Tris(acetylacetonato)manganese(III) was prepared by the permanganate oxidation of bis(acetylacetonato)manganese(II) according to Charles.[6] Found: Mn, 15.82; C, 50.91; H, 6.04%. Hydrogen chloride was generated by the reaction of hydrochloric acid with sulfuric acid, dried over calcium chloride, and dissolved in methylene chloride (*ca.* 0.20 mol/l). Hydrogen bromide was produced by the reaction between tetralin and bromine, dried over calcium bromide, and dissolved in methylene chloride (*ca.* 0.28 mol/l). Hydrogen iodide was evolved by treatment of hydroiodic acid with phosphorus pentaoxide, dried over the same compound, and lead directly as a gas into a reaction flask. Methylene chloride was distilled twice over phosphorus pentaoxide. Diethyl ether, benzene and petroleum ether were distilled over metallic sodium, and the fraction of petroleum ether boiling at 40—50 °C was used. Acetylacetone supplied by Daicel Co. Ltd was also distilled before use.

The Reactions of Tris(acetylacetonato)manganese(III) with Hydrogen Halides. A solution of $Mn(acac)_3$ in an adequate mixture of diethyl ether and benzene was placed in a three-necked flask equipped with a burette, a glass tube containing calcium chloride, and another outlet tube. A solution (*ca.* 0.1 mol/l) of hydrogen chloride or bromide in methylene chloride was added dropwise from the burette to the above solution with magnetic stirring. When hydrogen iodide was used as a reactant, the burette was replaced by a glass tube, through which the gas was bubbled into a solution of $Mn(acac)_3$ in a mixture of petroleum ether and benzene. In either case the usual precautions were taken for preventing moisture during filtration of the reaction product.

Isolation of Chlorobis(acetylacetonato)manganese(III): To a solution of $Mn(acac)_3$ (3.5 g, 10 mmol) in 300 ml of a mixture of diethyl ether and benzene (5: 1 by volume) was added a solution of an equimolar amount of hydrogen chloride in methylene chloride from the burette. Soon after the beginning of addition of hydrogen chloride, a sepia-colored precipitate began to separate out and increased its amount with the progress of reaction. The precipitate was filtered, washed with ether and dried *in vacuo*. Yield: 1.8 g, 62%. Found: Mn, 18.76; Cl, 12.22; C, 41.39; H, 4.91%. Calcd for $MnCl(acac)_2 = C_{10}H_{14}O_4ClMn$: Mn, 19.04; Cl, 12.28; C, 41.16; H, 4.89%.

Isolation of Bromobis(acetylacetonato)manganese(III): $Mn(acac)_3$ (2.5 g, 7.2 mmol) was dissolved in 220 ml of diethyl ether–benzene (10: 1 by volume), and allowed to react with an equimolar amount of hydrogen bromide in methylene chloride. Sepia-colored crystals were obtained in a 48% yield (1.2 g). Found: Mn, 16.98; Br, 23.18; C, 35.59; H, 4.22%. Calcd for $MnBr(acac)_2 = C_{10}H_{14}O_4BrMn$: Mn, 16.49; Br, 23.99; C, 36.07; H, 4.24%.

Isolation of Iodobis(acetylacetonato)manganese(III): Three grams (8.5 mmol) of $Mn(acac)_3$ was dissolved in 180 ml of petroleum ether–benzene (2: 1 by volume). Into this solution was passed gaseous hydrogen iodide gently for five minutes. An ochreous precipitate was filtered, washed with petroleum ether and dried *in vacuo*. Yield: 1.2 g, 38%. Found: Mn, 14.45; C, 31.60; H, 3.71%. Calcd for $MnI(acac)_2 = C_{10}H_{14}O_4IMn$: Mn, 14.79; C, 31.53; H, 3.75%.

Further Reactions of Halogenobis(acetylacetonato)manganese(III) with Hydrogen Halides. Isolation of Dichloro(acetylacetonato)aquomanganese(III): One gram (3.5 mmol) of $MnCl(acac)_2$ was dissolved in 120 ml of methylene chloride and stirred at −78 °C. A methylene chloride solution of equimolar hydro-

gen chloride was added drop by drop to this solution. The initially dark brown solution turned greenish gradually up to moss green at the end. Petroleum ether (200 ml) was added slowly to the solution to separate out a moss green precipitate, of which filtration and vacuum-drying resulted in a very dark green powder. Yield: 0.4 g, 48%. Found: Mn, 23.14; Cl, 30.20; C, 24.06; H, 3.55%. Calcd for $MnCl_2(acac)H_2O$= $C_5H_9O_3Cl_2Mn$: Mn, 22.61; Cl, 29.18; C, 24.72; H, 3.73%. After standing at room temperature the color changed to dark brown.

Preparation of Dichloro(acetylacetonato)bis(pyridine oxide)manganese(III): Pyridine oxide, O-py (2.3 g, 23.9 mmol) was added to a solution of $Mn(acac)_3$ (2.1 g, 6.0 mmol) in methylene chloride (40 ml), and the solution was kept at −78 °C. A methylene chloride solution of hydrogen chloride (12.0 mmol) was added dropwise to this solution. After the reaction an ochreous powder was isolated by the addition of 200 ml of petroleum ether. Yield: 2.0 g, 81%. Found: Mn, 14.06; Cl, 17.69; C, 44.40; H, 4.47; N, 6.24%. Calcd for $MnCl_2(acac)(O\text{-}py)_2$=$C_{15}H_{17}O_4N_2Cl_2Mn$: Mn, 13.23; Cl, 17.08; C, 43.40; H, 4.13; N, 6.75%.

The Reactions of $MnBr(acac)_2$ and $MnI(acac)_2$ with Hydrogen Bromide or Iodide: When a solution of hydrogen bromide (6.8 mmol) in methylene chloride was added at room temperature to a solution of $MnBr(acac)_2$ (1.1 g, 3.4 mmol) in the same solvent, a white precipitate of manganese(II) bromide was produced in a 100% yield, leaving a colorless supernatant solution. Found: Mn, 24.26; Br, 72.69%. The equimolar reaction of $MnBr(acac)_2$ with hydrogen bromide at −78 °C was also examined, but a product of the composition $MnBr_2(acac)\cdot nH_2O$ was not obtained. The reaction of excess hydrogen iodide with $MnI(acac)_2$ in methylene chloride afforded bis(acetylacetonato)manganese(II). Found: C, 45.10; H, 5.26%.

Preparation of Dibromobis(acetylacetone)manganese(II): Tris(acetylacetonato)manganese(III) (1.4 g, 3.8 mmol) was dissolved in a mixture (20 ml) of methylene chloride and acetylacetone (1:1 by volume). A methylene chloride solution of hydrogen bromide (11.4 mmol) was added dropwise to this solution with vigorous stirring. White tiny crystals were carefully filtered, quickly washed with petroleum ether, and dried under vacuum. Yield 1.2 g, 77%. Found: Mn, 13.10; Br, 38.97; C, 28.20; H, 3.74%. Calcd for $MnBr_2(acacH)_2$= $C_{10}H_{16}O_4Br_2Mn$: Mn, 13.24; Br, 38.51; C, 28.93; H, 3.89%.

Preparation of the Base Adducts of Halogenobis(acetylacetonato)-manganese(III). $Mn(acac)_3$ was allowed to react with an equimolar amount of hydrogen halide in a mixture of diethyl ether, benzene and a base in a similar fashion as described above. Alternatively, $MnX(acac)_2$ was dissolved in acetylacetone containing excess base and heated to 60—70 °C. After filtration of the undissolved residue, the filtrate was kept in a desiccator for a long time to separate out the product.

Chlorobis(acetylacetonato)(pyridine oxide)manganese(III): Pyridine oxide (2.7 g, 28.5 mmol) was added to a solution of $Mn(acac)_3$ (2.5 g, 7.1 mmol) in a mixture of diethyl ether and benzene (4:1 by volume). A solution of hydrogen chloride (7.1 mmol) in methylene chloride was added drop by drop to this solution. Ochreous crystals (1.8 g) were obtained in a 65% yield. Found: Mn, 14.51; Cl, 8.82; C, 46.21; H, 4.94; N, 4.29%. Calcd for $MnCl(acac)_2$-(O-py)=$C_{15}H_{19}O_5NClMn$: Mn, 14.32; Cl, 9.24; C, 46.95; H, 4.99; N, 3.65%.

Bromobis(acetylacetonato)dioxanemanganese(III) Monohydrate: $Mn(acac)_3$ (2.1 g, 6.0 mmol) was dissolved in a mixture of diethyl ether and benzene (130 ml, 3:1 by volume) containing dioxane (40 ml). A solution of hydrogen bromide (6.0 mmol) in methylene chloride was added to this solution and allowed to react for 6—7 hr. Black-brown crystals of product (1.0 g) were obtained in a 38% yield. Found: Mn, 12.65; Br, 18.33; C, 38.33; H, 5.56%. Calcd for $MnBr(acac)_2(C_4H_8O_2)\cdot H_2O$=$C_{14}H_{24}O_7BrMn$: Mn, 12.51; Br, 18.19; C, 38.29; H, 5.51%.

Bromobis(acetylacetonato)(4-methylpyridine)manganese(III): $MnBr(acac)_2$ (1.1 g, 3.4 mmol) was dissolved in 50 ml of acetylacetone containing 4-methylpyridine, 4-Me-py (1.2 g, 12.9 mmol), and the mixture was warmed to 60 °C for a while and filtered. The filtrate was kept standing in a desiccator for two days to afford light red crystals. Yield: 0.3 g, 22%. Found: Mn, 13.14; Br, 17.67; C, 45.15; H, 5.02; N, 3.37%. Calcd for $MnBr(acac)_2(4\text{-}Me\text{-}py)$=$C_{16}H_{21}O_4NBrMn$: Mn, 12.89; Br, 18.75; C, 45.09; H, 4.97; N, 3.29%.

Bis(acetylacetonato)diaquomanganese(III) Bromide Dihydrate: $MnBr(acac)_2$ (1.0 g, 3.0 mmol) was dissolved in 40 ml of acetylacetone saturated with water on a hot water-bath. The solution was then kept standing at room temperature to deposit olive-green needles, which were washed with diethyl ether. Yield 0.36 g, 30%. Found: Mn, 13.63; Br, 19.95; C, 30.28; H, 5.46%. Calcd for $[Mn(acac)_2(H_2O)_2]Br\cdot 2H_2O$=$C_{10}H_{22}O_8BrMn$: Mn, 13.56; Br, 19.72; C, 29.65; H, 5.47%. The corresponding chloride $[Mn(acac)_2(H_2O)_2]Cl\cdot 2H_2O$ was also derived in a similar way from $MnCl(acac)_2$ in a 32% yield, and identified by the IR spectra.

The Ligand Substitution of Chlorobis(acetylacetonato)manganese-(III) with Dibenzoylmethane. A solution of dibenzoylmethane, dbmH (1.7 g, 7.5 mmol) in methylene chloride (10 ml) was added slowly to a solution of $MnCl(acac)_2$ (1.0 g, 3.7 mmol) in the same solvent (20 ml), and the mixture was kept standing for 1 hr at room temperature to separate out light red crystals of $MnCl(dbm)_2$. Yield: 0.55 g, 30%. Found: Mn, 10.11; Cl, 6.33; C, 66.05; H, 4.22%. Calcd for $MnCl(dbm)_2$=$C_{30}H_{22}O_4ClMn$: Mn, 10.23; Cl, 6.60; C, 67.11; H, 4.13%.

Analysis. Each specimen of compounds was dried *in vacuo* at room temperature before subjecting to elemental analysis. The content of manganese was determined gravimetrically as manganese(II) sulfate, and those of chlorine and bromine as the silver salts. The concentration of hydrogen chloride and bromide in methylene chloride was measured by the method reported previously.[1]

Measurements. The visible and ultraviolet absorption spectra were measured by means of a Hitachi EPS-3T autorecording spectrophotometer. The infrared spectra were taken in Nujol on JASCO IR-E (4000—700 cm^{-1}), Hitachi EPI-L (700—200 cm^{-1}) and FIS-3 (400—30 cm^{-1}) infrared spectrophotometers.

The magnetic susceptibility was measured at various temperatures down to 77 K by the Gouy method with an automatically recording magnetic balance MB-2 of Shimadzu Seisakusho Co., Ltd. Hexaamminechromium(III) chloride was prepared and used as a reference. Found: H, 6.97; N, 32.50%. Calcd for $[Cr(NH_3)_6]Cl_3$=$H_{18}N_6Cl_3Cr$: H, 6.96; N, 32.26%.

The molecular weight was determined by the vapor-pressure osmometry with an apparatus manufactured by Knauer, Germany. Methanol and methylene chloride were used as the solvent, and benzil as a reference. The electric conductivity was measured in methanol or nitromethane by means of an MY-SERIAL 814007 apparatus of Yanagimoto Seisakusho, Ltd. The thermogravimetric measurement was performed with a thermo-spring-balance C-282 of Hamada Denki Seisakusho, Ltd.

Table 1. Molecular weight, conductance and magnetic moment data of halogenobis(acetylacetonato)manganese(III)[a]

Complex	Molecular weight			Molar conductance at 25 °C/ohm^{-1}·cm^2·mol^{-1}		Magnetic moment at (temp.)/B.M.
	in CH_2Cl_2 at 37 °C	in CH_3OH at 45 °C	Calcd	in CH_3NO_2	in CH_3OH	
$MnCl(acac)_2$	283	154	289	16	102	4.88 (20 °C)
$MnBr(acac)_2$	312[b]	157	333	18	88	4.93 (21 °C)
$MnI(acac)_2$	346	198	380	28	85	4.72 (22 °C)

a) The molecular weight was measured at 1.5—4.5$\times 10^{-2}$ M, and the molar conductance at 5$\times 10^{-4}$ M.
b) Measured at 25 °C.

Results

Tris(acetylacetonato)manganese(III) readily reacts with excess hydrogen chloride, bromide or iodide in organic solvents to produce manganese(II) chloride, bromide or bis(acetylacetonato)manganese(II), respectively. These redox reactions seem to proceed successively *via* a few intermediates. In fact several halogenobis(acetylacetonato)- and dichloroacetylacetonato-manganese(III) complexes have been isolated as intermediary products under the controlled reaction conditions.

Characterization of Halogenobis(acetylacetonato)manganese(III). The primary intermediate was afforded by the equimolar reaction between $Mn(acac)_3$ and hydrogen halide. The composition was established by the elemental analysis to be $MnX(acac)_2$, where X is Cl, Br, or I. As shown in Table 1 the magnetic moment at room temperature lies in the range of 4.72—4.93 B.M., indicating that they are all high-spin Mn(III) complexes.

The molecular weight determined in methylene chloride is near to the calculated value, indicating that each of the $MnX(acac)_2$ complexes exists essentially as a discrete molecule in the non-coordinating solvent. The measurement was performed at several concentrations in the range of (1.5—4.5)$\times 10^{-2}$ M, and no appreciable dependence of the molecular weight on concentration was noticed. However, close examination of the figures in Table 1 discloses that the discrepancy between the observed and the calculated values becomes larger in the order of X=Cl<Br<I. The molar conductance in nitromethane at 25 °C also indicates that they are essentially nonelectrolytes in this solvent, but the observed values show a slight increase in the same order. These results might indicate that the $MnX(acac)_2$ complexes have some tendencies to ionize even in the non-coordinating solvent increasing in the order of X=Cl<Br<I.

In methanol they dissociate almost completely and the observed molecular weight nearly coincides with half of the formular weight. The molar conductance in the same solvent reveals that the halide ion is extensively dissociated although the value is smaller in comparison with 118 ohm^{-1}·cm^2·mol^{-1} of tetraethylammonium iodide in methanol (113 ohm^{-1}·cm^2·mol^{-1} in nitromethane). It may be presumed that the complex is solvolyzed in methanol and the manganese(III) atom is six-coordinated:

$$MnX(acac)_2 + 2CH_3OH \longrightarrow Mn(acac)_2(CH_3OH)_2^+ + X^-$$

The assumed compound $[Mn(acac)_2(CH_3OH)_2]X$ could not be isolated, but recrystallization of $MnCl(acac)_2$ from acetylacetone saturated with water afforded $[Mn(acac)_2(H_2O)_2]Cl\cdot 2H_2O$. The corresponding bromide $[Mn(acac)_2(H_2O)_2]Br\cdot 2H_2O$ was also obtained from $MnBr(acac)_2$ in a similar way. Bis(acetylacetonato)-diaquomanganese(III) chloride had previously been prepared by Cartledge[7] by the trituration of $Mn(acac)_3$ with 1F hydrochloric acid or by the following reaction.

$$4MnCl_2 + KMnO_4 + 10acacH + 6H_2O = 5[Mn(acac)_2(H_2O)_2]Cl + KCl + 2HCl$$

Funk and Kreis prepared $MnCl(acac)_2$ and $MnCl_2(acac)$ by the reaction of manganese(III) chloride with acetylacetone in diethyl ether at −40 °C, but reported nothing about their properties.[8] The complexes $MnBr(acac)_2$ and $MnI(acac)_2$ are new compounds. On the other hand, the Mn(III) Schiff base (SBH_2) complexes of the type MnX(SB) have been studied rather extensively[9,10] in connection with the biological interest,[11] and their behaviors in solution were investigated. Van den Bergen, *et al.*[12] recorded the molar conductance of $MnBr(sal\text{-}N\text{-}Pr^n)_2$ and $MnO\text{-}COCH_3(sal\text{-}N\text{-}Pr^n)_2$ in nitromethane to be 4.96 and 0.192 ohm^{-1}·cm^2·mol^{-1}, respectively, and that of MnBr(salen) and MnI(salen) in methanol to be 69 and 71 ohm^{-1}·cm^2·mol^{-1}, respectively. Here sal-N-Pr^n denotes salicylaldehyde-*n*-propylimine, and salen*N,N'*-bis(salicylidene)ethylenediamine. The conductance data reported by Prabhakaram and Patel also reveal that the MnX(salen) complexes (X=Cl, Br, or I) dissociate very little in acetonitrile, while to a considerable extent in methanol and water.[13]

Infrared Spectra: In order to obtain informations concerning the structure of the $MnX(acac)_2$ complexes, their infrared spectra were measured in Nujol mull. In Fig. 1 the spectrum of $MnCl(acac)_2$ is compared with that of $FeCl(acac)_2$ which was prepared by the reaction of $Fe(acac)_3$ with hydrogen chloride in methylene chloride.[5] The parent complex $Mn(acac)_3$ shows the ν_s(C=O) and ν_{as}(C=C=C) bands at 1585 and 1520 cm^{-1}, and $Fe(acac)_3$ at 1565 and 1525 cm^{-1}, respectively. The higher frequency bands are lost in both $MnCl(acac)_2$ and $FeCl(acac)_2$, and shoulders are observed at 1546 and 1549 cm^{-1}, respectively. The δ(C–H) band around 1200 cm^{-1} is very much weaker

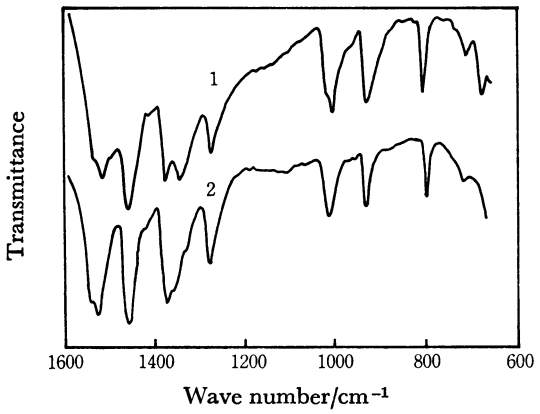

Fig. 1. Infrared spectra of $MnCl(acac)_2$ (curve 1) and $FeCl(acac)_2$ (curve 2).

in $MCl(acac)_2$ than in $M(acac)_3$, and the absorption assigned to $\nu_s(C{=}C{-}C)$ is shifted to the higher frequency 1280—1290 cm^{-1} region in the former mixed-ligand complex. Such a close resemblance in the IR spectra of $MnCl(acac)_2$ and $FeCl(acac)_2$ strongly suggests that both complexes have the same structure.

The molecular structure of $FeCl(acac)_2$ was determined by the X-ray analysis to be square-pyramidal with the chlorine atom located at the apical position,[14] and hence $MnCl(acac)_2$ can also be assumed to have the square-pyramidal structure, and not the trigonal-bipyramidal geometry. The IR spectra of $MnBr(acac)_2$ and $MnI(acac)_2$ are quite similar to that of the chloro complex, implying the structural analogy.

The infrared spectra in the 400—150 cm^{-1} region are shown in Fig. 2. The peak around 343 cm^{-1} is

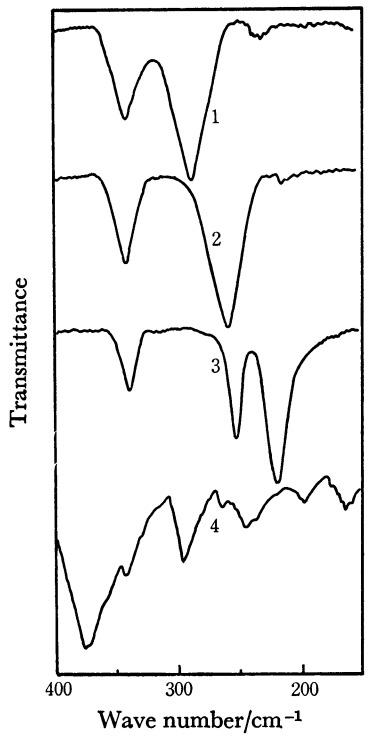

Fig. 2. Infrared spectra in the low-frequency region of $MnX(acac)_2$, where X=Cl (curve 1), Br (curve 2), or I (curve 3), and $MnCl_2(acac)\cdot H_2O$ (curve 4).

observed for each of the three $MnX(acac)_2$ complexes in common, and thus assigned to the ν(Mn–O) vibration. The corresponding absorption appears at 335 cm^{-1} in the parent complex $Mn(acac)_3$, and at 375 and 348 cm^{-1} in tris(salicylaldehydato)manganese(III).[12]

The stretching vibration of the terminal Mn(III)–Cl bond is observed in the 270—340 cm^{-1} region for the $MnCl_3L_3$ complexes where L is the oxide of pyridine, triphenylphosphine, or triphenylarsine,[15] and at 310 cm^{-1} for $MnCl(sal\text{-}N\text{-}Pr^n)_2$.[12] Thus the strong peak observed at 290 cm^{-1} for the present chloro complex $MnCl(acac)_2$ (Fig. 2) can reasonably be assigned to the ν(Mn–Cl) vibration. The corresponding strong absorption of $MnBr(acac)_2$ at 262 cm^{-1} is attributed to the ν(Mn–Br) vibration. Boucher[16] ascribed the most prominent absorption of the supposedly octahedral Mn(III) complex $MnX(H_2O)$ (protoporphyrin IX dimethyl ester) in the 650—160 cm^{-1} region to the manganese-halogen stretching vibration: 462 cm^{-1} for F^-, 262 cm^{-1} for Cl^-, 211 cm^{-1} for Br^-, and 190 cm^{-1} for I^-. These frequencies are rather low in comparison with the above-mentioned data, but show the expected decrease with the increasing mass of the halogen.

As is indicated in Fig. 2, $MnI(acac)_2$ exhibits two peaks in the ν(Mn–X) region. It can not be unequivocally concluded at the present stage of investigation which of the two bands at 254 and 219 cm^{-1} is related to the ν(Mn–I) vibration. Here we tentatively assign the 219 cm^{-1} peak to the ν(Mn–I) on a consideration of the mass effect. At any rate the fact that the frequencies of the ν(M–X) vibrations in the $MnX(acac)_2$ complexes lie in the region acceptable for the terminal Mn–X bonds is also compatible with the proposed five-coordinate structure.

Electronic Spectra: The $MnCl_5^{2-}$ ion was found to have a slightly elongated square-pyramidal structure in the bipyridinium[17] and phenanthrolinium[18] salts. Crystal polarized spectra of these Mn(III) compounds were recorded by Bellitto, *et al.*,[19] and it was concluded that three d-d transitions occur at $<20\times10^3$ cm^{-1}, and that the absorption present at *ca.* 24×10^3 cm^{-1} is due to

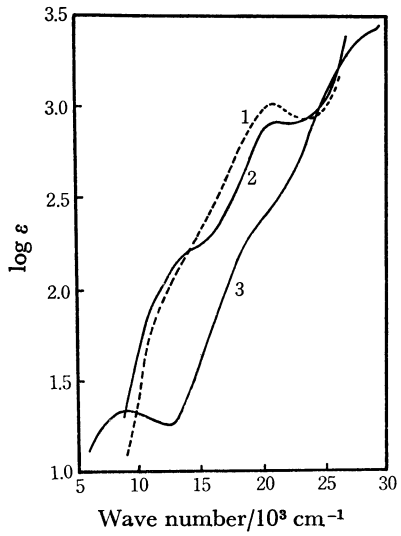

Fig. 3. Absorption spectra of $MnX(acac)_2$ in CH_2Cl_2, where X=Cl (curve 1), Br (curve 2), or I (curve 3).

a charge transfer transition. Boucher[20] also measured absorption spectra of several Schiff base complexes MnCl(SB), and assigned weak absorptions in the 12—21 $\times 10^3$ cm^{-1} region to the d-d transitions.

The observed visible absorption spectra of the present $MnX(acac)_2$ complexes in methylene chloride are reproduced in Fig. 3. The bromo complex shows a maximum at 20.8×10^3 cm^{-1} (ε=850) and two discernible shoulders at 14.3 and 11.8×10^3 cm^{-1}. The chloro complex also exhibits a more intense maximum at 20.8×10^3 cm^{-1} (ε=1070) and very broad indistinct shoulders in the 14.3—10×10^3 cm^{-1} region. On the other hand $MnI(acac)_2$ has shoulders at *ca.* 27.8 and 20×10^3 cm^{-1}, and a broad maximum at 9.1×10^3 cm^{-1} (ε=23). Low energy absorptions below 20×10^3 cm^{-1} may be assigned to the d-d transitions. The reason is not clear why only the iodo complex shows a distinct maximum in the 9×10^3 cm^{-1} region, while its spectrum in methanol (Fig. 4) is quite similar to those of chloro and bromo complexes.

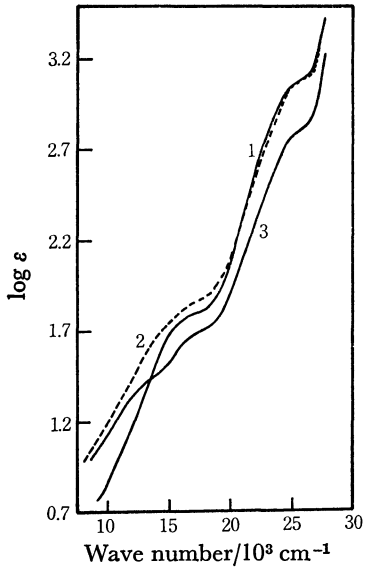

Fig. 4. Absorption spectra of $MnX(acac)_2$ in methanol, where X=Cl (curve 1), Br (curve 2), or I (curve 3).

The absorption bands at 20.8×10^3 cm^{-1} observed for methylene chloride solutions of both the chloro and bromo complexes and a shoulder at 27.8×10^3 cm^{-1} of the iodo complex seem to be ascribed to the same transition. In methanol all these absorptions appear equally as a shoulder at 25×10^3 cm^{-1}. It is difficult to conclude that they are assigned to the charge transfers, since they are supported by the general (background) absorption though their extinction coefficients are apparently high.

Magnetic Properties: The magnetic susceptibility of the $MnX(acac)_2$ complexes was determined at lower temperatures down to 77 K. The reciprocal of the molar susceptibility corrected for diamagnetism was plotted in Fig. 5 against the absolute temperature. All of these three compounds gave good straight lines, indicating to obey the Curie-Weiss law $\chi_M'=C/(T+\theta)$. The θ values were obtained from an extrapolation of the straight line to be 13, 11, and 68 K for the chloro, bromo, and iodo complexes, respectively.

Preparation of Dibromobis(acetylacetone)manganese (II).

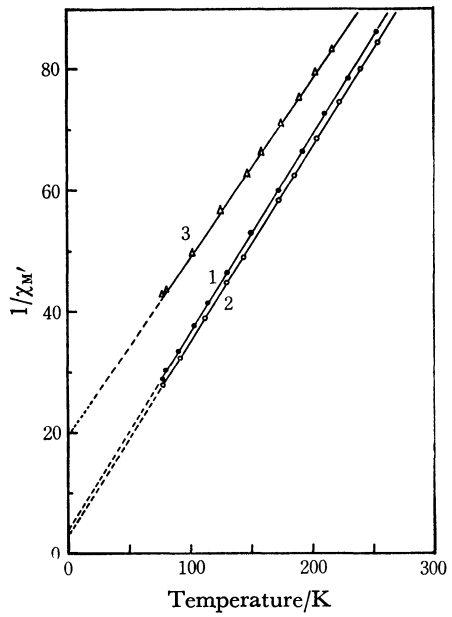

Fig. 5. Curie-Weiss plots for $MnCl(acac)_2$ (1), $MnBr(acac)_2$ (2) and $MnI(acac)_2$ (3).

As described already the reaction of excess hydrogen bromide with $Mn(acac)_3$ in methylene chloride afforded $MnBr_2$ quantitatively, but if acetylacetone had been added in advance to the solution, $MnBr_2(acacH)_2$ was produced in a good yield. This compound was previously prepared by the reaction of anhydrous $MnBr_2$ with acetylacetone,[21] but the present method offers a much more convenient route. Preparation of the corresponding chloro complex in a similar way was unsuccessful presumably because of instability of $MnCl_2(acacH)_2$.

The Six-coordinate Mixed Ligand Mn(III) Complexes. The five-coordinate complex $MnX(acac)_2$ is readily solvolyzed in methanol, producing the presumably six-coordinate cation $Mn(acac)_2(CH_3OH)_2^+$. Similarly the formula $[Mn(acac)_2(H_2O)_2]X\cdot2H_2O$ (X=Cl, Br) was assigned to the tetra-hydrate obtained by the recrystallization of $MnX(acac)_2$ from acetylacetone containing water. Non-existence of the ν(Mn–X) vibration in the IR spectrum of these salts indicates that the halide ion does not exist in the coordination sphere. As illustrated in Fig. 6 the thermogravimetric analysis of the bromide

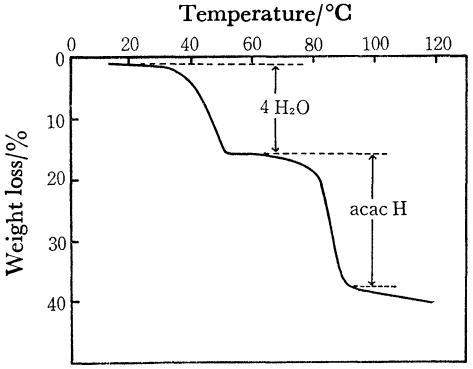

Fig. 6. Thermogravimetric analysis of $[Mn(acac)_2(H_2O)_2]Br\cdot2H_2O$ under vacuum at the heating rate of 10 °C/hr.

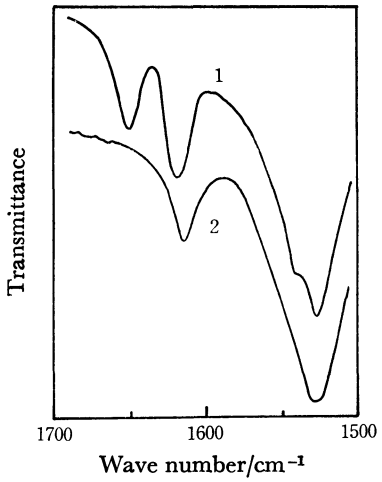

Fig. 7. The IR spectrum in the 1700—1500 cm^{-1} region of $[Mn(acac)_2(H_2O)_2]Cl \cdot 2H_2O$ (curve 1) and that after heating for a while at 50 °C (curve 2).

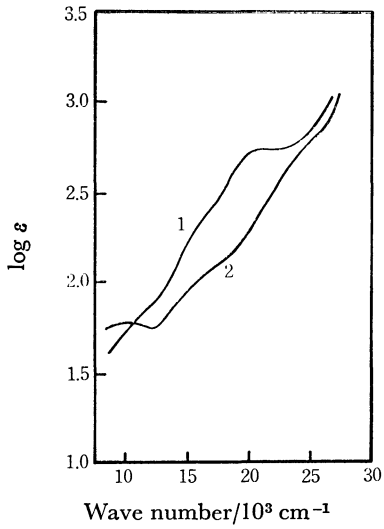

Fig. 8. Absorption spectra of $MnCl(acac)_2$(O-py) in CH_2Cl_2 in the absence (curve 1) and the presence (curve 2) of added pyridine oxide.

in vacuo could not discriminate the two types of water involved in this compound. Water begins to vaporize gradually at around 35 °C and is lost completely at 50 °C leaving $MnBr(acac)_2$, which was recovered and identified on interuption of thermolysis.

As shown in Fig. 7 the IR spectrum of $[Mn(acac)_2(H_2O)_2]Cl \cdot 2H_2O$ exhibits two bands in the region of HOH bending vibration, and the band at 1650 cm^{-1} disappears in preference to that at 1620 cm^{-1} on heating for a while at 50 °C. The higher frequency vibration may be ascribable to the lattice water.

After the loss of water, weight of the specimen still continued to decrease with temperature and became nearly constant at 90 °C (Fig. 6). The weight loss in the 75—90 °C region corresponds to one mole of acetylacetone, and in fact the volatile material trapped at −78 °C was identified to be acetylacetone by the IR and UV assays. Composition of the residue (Mn: 21.89, Br: 31.01, C: 27.90, H: 3.21%) is close to MnBr(acac), and its IR spectrum indicates the remaining of the acetylacetonate group. Very dark color might suggest the contamination with some Mn(III) species, but the detailed course of the thermal decomposition and the exact nature of the residue are not certain.

Several neutral six-coordinate complexes of the type $MnX(acac)_2B$ were prepared, where X is Cl or Br and B is dioxane, 4-methylpyridine or pyridine oxide. Figure 8 reveals that the absorption spectrum of $MnCl(acac)_2$(O-py) in methylene chloride resembles that of $MnCl(acac)_2$, but a spectrum in the presence of added pyridine oxide is quite similar to that of $Mn(acac)_3$. These results suggest that the base adduct is not so stable, but dissociates extensively in solution.

It is worth noting that 2,2′-bipyridine and 1,10-phenanthroline both react with MnBr(acac), reducing Mn(III) and resulting $MnBr_2(bipy)_2$ and $MnBr_2(phen)_2$, respectively. Another important finding is the lability of $MnX(acac)_2$. Although $Mn(acac)_3$ is substitution-inert and converted to $Mn(dbm)_3$ only under severe reaction conditions, the reaction of $MnX(acac)_2$ with dibenzoylmethane (dbmH) proceeds readily at room temperature, affording $MnX(dbm)_2$. The more detailed kinetic study of this interesting reaction is desirable.

Dichloro(acetylacetonato)manganese(III) Complexes. When $MnX(acac)_2$ (X=Cl or Br) was allowed to react with equimolar amount of HX in methylene chloride at room temperature, a precipitate of $MnCl_2$ or $MnBr_2$ was produced, but the solution still contained remaining $MnX(acac)_2$. Twice as many moles of hydrogen halide were necessary to complete the reaction resulting in a colorless solution. Then the manganese was quantitatively converted to MnX_2, and the freed acetylacetone in solution was determined spectrophotometrically to correspond to *ca.* 50% of acetylacetone contained in $MnX(acac)_2$. Thus the overall reaction is represented by the following reaction:

$MnX(acac)_2 + 2HX = MnX_2 + acacH +$ decomposition products. Here X is Cl or Br. In the case of $MnI(acac)_2$, a similar reaction did not produce MnI_2, but afforded $Mn(acac)_2$.

In contrast to $MnX(acac)_2$, the dihalogeno complex $MnX_2(acac)$ is not stable enough to allow isolation in the reaction at room temperature, but induces the reduction of Mn(III) to Mn(II). However, $MnCl_2(acac)H_2O$ and $MnCl_2(acac)(O\text{-py})_2$ could be obtained by reactions at −78 °C. The IR spectrum of $MnCl_2(acac)H_2O$ in the 4000—700 cm^{-1} region is quite similar to that of $MnCl(acac)_2$ except that the former has bands related to the coorinated water at 3440 and 1605 cm^{-1}, and that the band assignable to the ν_s(C=C=C) vibrations are split into two bands at 1280 and 1310 cm^{-1}.

On the other hand the spectrum in the lower frequency region is remarkably different from that of $MnCl(acac)_2$ (Fig. 2). The strong absorption at 377 cm^{-1} may be assigned to the ν(Mn–O) vibration, and the 294 cm^{-1} peak to ν(Mn–Cl). It is not certain at the present stage of investigation whether the 235 cm^{-1} or other minor bands could be ascribed to the bridging Mn–Cl stretch. It seems worth noting that frequency

of the ν(Mn–O) vibration increases in the order of $Mn(acac)_3$ (335 cm^{-1})<$MnCl(acac)_2$ (343 cm^{-1})<$MnCl_2(acac)H_2O$ (377 cm^{-1}), and that of the ν(C=O) vibration decreases in the same sequence from 1585 to 1520 and 1510 cm^{-1}, reflecting the strengthening of the Mn–O(acac) bond by the chloride substitution.

Discussion

Except the most stable divalent state manganese can exist in several higher oxidation states[9] and even the Mn(III) species functions as an oxidant for various substrates.[22] Tris(acetylacetonato)manganese(III) is especially useful for organic substrates because of its solubility in organic solvents, and has been shown, for example, to effect the oxidative coupling of phenols[23] and oxidative intramolecular cyclization of *p*-hydroxybenzyl ketoximes.[24]

Even by the reaction with hydrogen halide in non-coordinating solvent, $Mn(acac)_3$ is reduced to the Mn(II) species. The detailed mechanism of this redox reaction could not be established by the present investigation, but the preceding reaction steps seem to proceed in the following sequence (Eq. (i)).

$$Mn(acac)_3 \xrightarrow{+HX} \left[(acac)_2Mn\begin{matrix}X\\ \diagdown acacH\end{matrix}\right] \xrightarrow{-acacH}$$

Intermediate **1**

$$\begin{matrix}X\\ |\\ (acac)Mn(acac)\end{matrix} \xrightarrow{+HX} \left[\begin{matrix}X\\ |\\ (acac)Mn\\ \diagdown acacH\end{matrix}\right] \quad (i)$$

Intermediate **2**

The intermediates **1** and **2** have not been identified, but are just presumed here. In the reaction of $MnCl(acac)_2$ with hydrogen chloride at −78 °C, addition of petroleum ether to the methylene chloride solution precipitated $MnCl_2(acac)H_2O$, but warming of the reaction mixture to room temperature instead of adding petroleum ether resulted in a precipitate of $MnCl_2$, and the filtrate contained $MnCl(acac)_2$. Thus, such a reaction as represented by Eq. (ii) might have occurred in methylene chloride at room temperature.

$$2[MnCl_2(acac)(acacH)] \longrightarrow MnCl_2 + MnCl(acac)_2 + acacH + \text{decomposition products} \quad (ii)$$

Intermediate **2**

The decomposition products are not identified, but are assumed to be resulted by reactions involving acetylacetone radicals. Equation (ii) can explain why twice as many moles of hydrogen chloride were necessary to convert $MnCl(acac)_2$ to $MnCl_2$ completely.

Electron transfer in the reaction between $Mn(acac)_3$ and a primary amine such as ethylenediamine was concluded in a previous paper[4] to occur in the following step (iii).

$$(acac)_2Mn\begin{matrix}acac\\ \diagdown en\end{matrix} \longrightarrow (acac)_2Mnen + acac\cdot \quad (iii)$$

Similarly in the reaction (ii), an electron might be transferred from the acetylacetonate ligand to Mn(III):

$$MnCl_2(acac)(acacH) \longrightarrow MnCl_2 + acacH + acac\cdot \quad (iv)$$

followed by the attack of an acetylacetone radical on a chloride ligand in another molecule of $MnCl_2(acac)(acacH)$:

$$acac\cdot + MnCl_2(acac)(acacH) \longrightarrow MnCl(acac)_2 + (acac\cdot)HCl \longrightarrow \text{decomposition} \quad (v)$$

The reaction of $MnBr(acac)_2$ with HBr seems to follow a similar sequence, while $MnI(acac)_2$ reacts with HI affording $Mn(acac)_2$ instead of MnI_2. Although $MnI(acac)_2$ is stable at room temperature, it readily liberates iodine molecules on heating or by the reaction with acids. Thus an electron must be transfered from an iodide ligand to the manganese atom in the presumable intermediate $MnI_2(acac)(acacH)$.

$$MnI(acac)_2 + HI \longrightarrow [MnI_2(acac)(acacH)] \longrightarrow Mn(acac)_2 + HI + I\cdot \quad (vi)$$

These considerations lead to the conclusion that the tendency of a ligand to deliver an electron to manganese(III) increases in the following sequence: Cl^-<Br^-<$acac^-$<I^-. In order to clarify the detailed mechanism of these redox reactions, further kinetic studies are desired.

The magnetic susceptibility of apparently five-coordinate manganese(III) complexes has been studied hitherto in connection with their structures. Goodwin and Sylva[25] determined the magnetic susceptibilities of $(bipyH_2)[MnCl_5]$, $(phenH_2)[MnCl_5]$, $MnCl_3(H_2O)$(bipy), $MnCl_3(H_2O)$(phen), $MnF_3(H_2O)$(phen), $MnCl_3$(terpy), $MnCl_3$(bipy), and $MnCl_3$(phen) over the temperature range 100—300 K. All compounds obey the Curie-Weiss law, and the first six have small θ values (7 to 25 K), indicating that they are simple paramagnetics. On the other hand the last two compounds have very large θ values (154 and 183 K, respectively), and the antiferromagnetic behavior was presumed to be due to their chloro-bridged dimeric structures.

The Curie-Weiss behavior of MnBr(salen) and MnI(salen) was reported by van den Bergen, *et al.*[12] (θ=22 and 20 K, respectively), and explained in terms of very weak antiferromagnetic interactions. Earnshaw, *et al.*[26] also measured the magnetic susceptibility of MnOAc(salen) over the temperature range 85—300 K. This compound obeys the Curie-Weiss law with θ=22 K, and was considered to have the antiferromagnetic interactions possibly due to the polymeric structure. Recent X-ray study[27] of this compound really confirmed the linear polymeric chains of Mn(salen) moieties bridged by acetate groups.

The present complexes $MnCl(acac)_2$ and $MnBr(acac)_2$ have magnetic moments of 4.88 and 4.93 B.M. at 20 and 21 °C, respectively, which are close to the calculated spin-only value of 4.90 B.M. These complexes obey the Curie-Weiss law, but their θ values (13 and 11 K, respectively) are not so large as the indicate the intermolecular linkage in the solid state. On the other hand $MnI(acac)_2$ has a lower μ_{eff} value of 4.72 B.M. at 22 °C, and a rather large θ value of 68 K.

It may be appropriate to presume that the iodo complex has a strong intermolecular interaction, the iodide ligand bridging two manganese atoms just as the azide group in $MnN_3(acac)_2$.[28] Such a structural feature might be responsible for the IR pattern in the ν(Mn–I) region which is different from those of the chloro and bromo complexes. The exact structure must be determined by the X-ray analysis in future.

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