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Synthesis and Spectral Studies of Mixed Ligand Complexes of Mn (III) with 1,3-Diphenylpropane-1,3-Dione and Β-Diketones, Hydroxyl Aryl Ketones or Substituted Salicylaldehyde

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ABSTRACT

Mixed ligand complexes of the type [Mn (dbzm)$_2$L], (where dbzm = 1,3-diphenylpropane-1,3-dione and HL =pentane-2,4-dione, 1-phenylbutane-1,3-dione, 2-hydroxy- acetophenone, 2-hydroxypropio phenone, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde) have been synthesized by the reaction of metal salt with the corresponding carbonyl in 1:2:1 molar ratios. Resulting complexes have been characterized by elemental analysis, conductance, magnetic moments, IR, and FAB mass spectra. These complexes have octahedral structure.

Keywords: Mixed ligand complexes, [Mn (dbzm)$_2$L], magnetic moments, FAB mass spectra.

INTRODUCTION

Mn (II) complexes of the type MnL$_2$ with the aryl aldehyde and ketones have been widely studied. ML$_2$B$_2$ complexes [where M = Mn(II), Co(II), L = 2-pyridine aldoxime, B = neutral ligand (triazole, cabazole) have been synthesized by Nayak and co-workers[1]. A few mixed ligand complexes of Mn have also been reported. Singh and co-workers [2] have synthesized [Mn(L)(acac)], (where L = N-benzoyl-N-thiobnzhydrazide). Mixed ligand complexes of the type [M(AA)(BB)(L$_2$)] (where M = Mn or Fe, AA = diethyldithiocarbonate, BB = acetylacetonate, benzoylacetonate and L = picoline) have been reported by Baral et al[3]. Shu-feng and co-workers[4] have synthesized [Mn$^{(III)}$ (Salpn)(OH)]$_2$(CH$_3$COOH)(CH$_3$CN)$_2$, where Salpn = [N,N'- propanol bis(salicylic-dameiminato) dianion]. Ray and co-workers [5] have reported tris complexes such as Mn (acac)$_3$ and Mn (C$_2$O$_4$)$_3$. Ise and co-workers [6] synthesized [Mn (hafac)$_2$(hina)$_2$], (where, hafac = hexafluoroacetylacetone, hina = 4,4',5,5'-tetramethylimidazolin-1-oxyl). Bhattacharjee et al. [7] have synthesized mixed ligand complexes of Mn (III) with fluoro complexes of the type [MnF$_3$(L)$_2$].3H$_2$O, where L = Urea and [MnF$_3$(H$_2$O) L].3H$_2$O, Where, L = urea and [MnF$_3$ (H$_2$O) L].2H$_2$O, where L = phenanthroline-2,2'-bipyridine). However, the mixed ligand complexes of Mn(III) with β-diketones and other ligands have not been reported so far. In the present paper mixed ligand complexes of the type [MnL$_2$L'], where HL$_2$ = dibenzoylmethane and HL' = 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, pentane-2,4-dione, 1-phenylbutane-1,3-dione, 2-hydroxyacetophenone, 2-hydrxypropiophenone are described.

MATERIALS AND METHODS

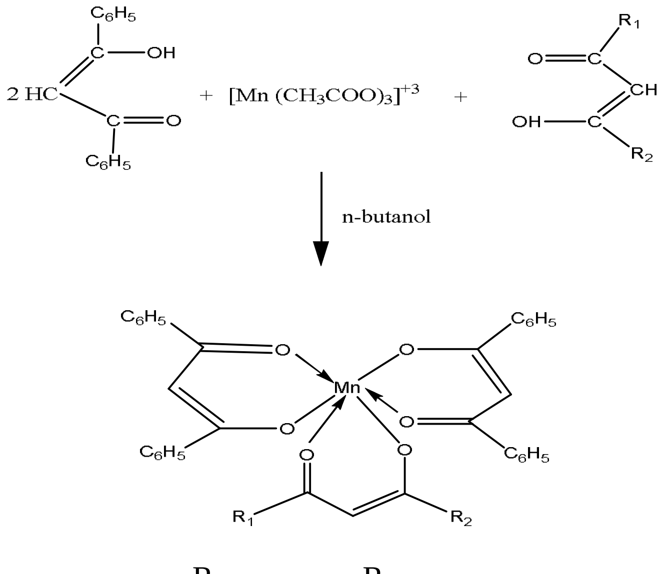
1,3-diphenylpropane-1,3-dione (sisco-chem), 1-phenylbutane-1,3-dione (fluka), 5-chloro- salicyl aldehyde (Aldrich), 5-bromosalicylaldehyde (Aldrich) were purified by recrystalization from ethanol. Pentane-2,4-dione (Aldrich), 2-hydroxyacetophenone (John Baker), 2-hydroxy- propiophenone (fluka) and butanol were purified by distillation.

Mn $(CH_3COO)_2$. 4 H_2O (FLUKA) was convert into $Mn(CH_3COO)_3.2H_2O$ by christention method. Mn $(CH_3COO)_3$. 2 H_2O was used as supplied. Manganese was determined by volumetrically by EDTA using Eriochrome black-T as an indicator [8]. Molar conductances were measured at room temperature in DMSO by a Chino make digital conductivity meter (model no-NDC-736) using a glass cell having a cell constant of 1.0 cm^{-1}. Magnetic measurements were carried out at room temperature (~300K) on a Guoy balance using Hg $[Co (NCS)_4]$ as a calibrant. IR spectra of the complex (KBr) were recorded in the region 400-4000 cm^{-1} on Nicolet Magma-550 FTIR spectrophotometer, FAB mass spectra was recorded on Jeol SX 102/DA-600 mass spectrometer/ Data System using Argon/Xenon (6kV, 10mA) as the FAB gas. The accelerating voltage was 10kV and spectra were recorded at room temperature. m-Nitrobenzylalcohol (NBA) was used as the matrix.

Synthesis of mixed ligand complexes: To a butanolic solution of Manganese (III) acetate (0.880 g in 10 mL. n-butanol), dibenzoylmethane (1.470 g in 5 mL. n-butanol) and Pentane-2,4-dione (0.532 g in 5 mL. n-butanol) were added after five minute with constant stirring at room temperature and a clear solution was obtained. The pH of the reaction mixture was raised up to ~8.5 by adding 5% aqueous sodium hydroxide solution drop wise with constant stirring. The pH was measured with the help of pH paper and stirring was continued for next 4-5 h. The solid complex was separated, filtered, washed with ether and dried under reduced pressure.

RESULTS AND DISCUSSION

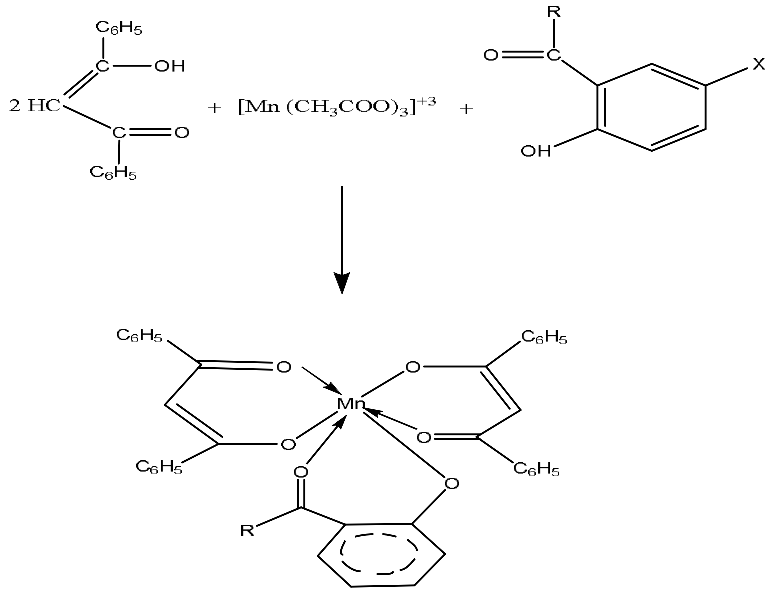
The reaction of Mn(III) acetate with 1,3-diphenylpropane-1,3-dione and Pentane-2,4-dione, or 1-phenylbutane-1,3-dione in 1:2:1 molar ratios result in the formation of mixed ligand complexes.



R_1	R_2
CH_3	CH_3
CH_3	C_6H_5

Scheme 1. Synthesis of mixed ligand complexes of Mn (III) with dbzm and β-diketones

Similarly the mixed ligand complexes of Mn $(CH_3COO)_3$ with 1,3-diphenylpropane-1,3-dione and 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, 2-hydroxyacetophenone, 2-hydroxy- propio phenone were synthesized.



R	X
CH_3	H
C_2H_5	H
H	Br
H	Cl

Scheme2. Synthesis of mixed ligand complexes of Mn (III) with dbzm and substituted salicylaldehydes

The resulting Mn(III) complexes are dark brown solid. They do not melt on heating but decompose at high temperature. They are insoluble in chloroform, carbon tetrachloride, benzene, nitrobenzene and methanol but soluble in DMF. The properties and analysis of the complexes are recorded in table-1.The molar conductance in DMF lies in the range 19-32 mho cm^2 mol^{-1} showing the non-electrolytic nature of the complexes [9].

Magnetic Moments: The observed magnetic moments of Mn(III) mixed ligand complexes lie in the range 4.33 -5.45 B.M. (Table-1) which are consistent with the high spin configuration of Mn(III) with four unpaired electrons. The values slightly higher than the spin only value (4.90 B.M.) for a d^4 system may be due to orbital contribution [10]. For Co^{III} complexes of the type CoL_2L' (where L = acetyl acetone, methylacetoacetate or ethyl acetoacetate and L' = ethylenediamine, propylenediamine or 8-hydroxyquinoline. Aly et al. [11] reported the magnetic moment values 4.18 and 4.21 B.M. for the mixed ligand complexes [CO $(acac)_2$ (btz)] and [Co $(acac)_2$ $(boz)_2$] respectively.

Table 1: Analyses and Characterization of Mixed Ligand Complexes of Mn (III)

S.No.	**Complex Molecular Formula Molecular Weight**	**Yield %**	**Decomp. Temp. (^oC)**	**Analysis % Found (calculated)**			**Molar Cond.(mho cm^2mol^{-1})**	**μ_{eff}/B.M)**
				Mn	**C**	**H**		
1.	[Mn$(dbzm)_2$(acac)] $C_{35}H_{29}O_6$ Mn 600.196 g/mol	92	208	9.15 (9.12)	69.59 (69.23)	4.86 (4.25)	26	4.65

2.	[Mn(dbzm)$_2$(bzac)] $C_{23}H_{18}O_6$ Br Fe 526.13 g/mol	68	220	8.29 (8.01)	72.48 (72.12)	4.71 (4.61)	22	4.83
3.	[Mn(dbzm)$_2$(2-hap)] $C_{23}H_{18}O_6$ Fe Cl 481.73 g/mol	39	270	8.64 (8.45)	71.68 (71.35)	4.59 (4.29)	19	5.45
4.	[Mn(dbzm)$_2$(2-hpp)] $C_{23}H_{18}O_8$ NFe 492.24 g/mol	68	218	8.45 (8.34)	71.98 (71.67)	4.80 (4.78)	32	5.12
5.	[Mn(dbzm)$_2$(5-chlorosal)] $C_{27}H_{21}O_6$Fe 497.30g/mol	75	220	8.37 (8.27)	67.62 (67.46)	3.99 (3.45)	19	4.33
6.	[Mn(dbzm)$_2$(5-bromosal)] $C_{21}H_{21}O_6$ Fe 362.39 g/mol	67	280	7.84 (6.95)	63.34 (63.01)	3.74 (3.65)	17	4.87

IR Spectra: The mixed ligand complexes exhibit strong absorption band in the region 1584-1696 cm^{-1} , which may be assigned to the coordinated ν(C=O) ,where as in free acetylacetone, benzoyl acetone, 2-hydroxyacetophenone, 2-hydroxypropiophenone, 5-chlorosalicylaldehyde bands at 1724, 1731, 1682, 1640, 1660 cm^{-1} respectively have been reported due to ν(C=O). Thus the shifting of ν(C=O) to lower wave number side in the mixed ligand complexes supports the chelation of these ligands to the metal atom. Patel et al. [12] have reported similar bands due to ν(C=O) at 1600 cm^{-1} in [Co(acphen)(sal)$_2$] and [Co(acphen)(5-bromosal)$_2$]. Bands in the region 1517-1546 cm^{-1} in the mixed ligand complexes may be due to ν(C=C) in the spectra of the mixed ligand complexes. Weak to medium intensity absorption bands in the region 458-556 which are not present in the free ligands may be attributed to ν(C=O) vibration. Similar bands in this region have been assigned to ν (M-O) vibration. In case of metal β-diketonates by nakamoto et al [13]. A broad band appears at 2598-2764 cm^{-1} which may be attributed to C-H* stretching in all aldehydes.

FAB Mass Spectra: All positive fragments have been denoted as positive ions irrespective of whether they are odd electron or even electron species.

The FAB mass spectra of two complexes [Mn(dbzm)$_2$(bzac)] and [Mn(dbzm)$_2$(5-chlorosal)] have been recorded and the spectrum of [Mn(dbzm)$_2$(bzac)] is reproduced in fig.1. The m/z values of the peaks along with their intensities relative to the base peak are given in table 2. Both the complexes exhibit molecular ion (M$^+$) peaks, (I complex m/z = 662, 5.2%) and for (II complex m/z = 656, 2.6%). Both the complexes peaks due to MnL_2^+ and MnL'^+ are also observed due to the formation of such species as a result of the loss of one or the other ligand moiety.

$$MnL_2L' \longrightarrow MnL_2^+ + L'^+$$

$$MnL_2^+ \longrightarrow MnL^+ + L^+$$

$$MnL_2L' \longrightarrow MnL'^+ + L_2^+$$

A peak at m/z 278 due to MnL$^+$ is observed in both complexes [73.68%(I) , 52.63% (II)] and the peak at m/z 501 due to MnL_2^+ is observed in both complexes also [100% (I) , 100% (II)]. Intense peaks corresponding to MnL'^+ which would have resulted by the loss of dbzm moiety are observed in both complexes.

In complex I peak at m/z 216 (5.26%) due to $Mn(bzac)^+$ and in complex II peak at m/z 211 (2.63%) due to $Mn(5\text{-chlorosal})^+$ have been observed.

In addition to the molecular ion peaks due to the mixed ligand complexes $MnL_2L'^+$ peaks due to the corresponding symmetrical tris-complexes MnL_3^+ and $MnL_3'^+$ are also observed as a result of the redistribution reaction.

$$2MnL_2L' \rightleftharpoons MnL_3 + MnLL_2'$$

Both the complexes exhibit MnL_3^+ peaks, [m/z 724,42.10% (I) and m/z 724,15.78% (II)]. A peak at m/z 599(2.63%) due to $[Mn(bzac)_2(dbzm)]$ and in complex II m/z 590 (2.63%) due to $[Mn(5\text{-chlorosal})_2(dbzm)]$ have been observed. Both the complexes exhibit less abundant peaks due to dimeric species $[Mn_2L_2L_2']^+$. Thus both complexes exhibit $[Mn_2L_2\ L_2']^+$ peaks, [m/z 878, 5.26% (I) and m/z 868, 2.63% (II)]. Peaks due to ions formally derived from the oligomeric species occur in the spectra of mixed ligand complexes $[MnL_2\ L']$. The spectra of both complexes exhibit peaks due to $Mn_2LL_2'^+$ and $MnL_2L'^+$ ions which might have been formed by the loss of either of the two ligand moieties from the dimeric species.

$$2MnLL' \longrightarrow Mn_2L_2L_2' \longrightarrow Mn_2LL_2'^+$$

$$Mn_2L_2L_2' \xrightarrow{-L'} Mn_2L_2L'^+$$

The peaks due to such polymeric ions a quite abundant, for example, in complex I the peak at m/z 655 (2.63%) due to $[Mn_2(dbzm)(bzac)_2]^+$ and in the II complex the peak at m/z 645(2.63%) due to $[Mn_2(dbzm)(5\text{-chlorosal})_2]^+$. Similarly both complexes exhibits peaks at [m/z 717, 5.26% (I) and for II 712(2.63%)]. In complex I the peak at m/z 1002 (26.31%) and in complex II the peak at m/z 1002(26.31%) due to $[Mn_2\ (dbzm)_4]^+$ are quite intense. Appearance of peaks due to these $Mn_2L_3^+$ ions can be explained with the help of the following reaction-

$$MnL_2 + MnL^+ \rightleftharpoons Mn_2L_3^+$$

The peaks due to such polymeric ions are quite abundant, in complex I the peak at m/z 779(21.05%) due to $[Mn_2(dbzm)_3]^+$ and in complex II the peak at m/z 779(26.31%) due to $[Mn_2(dbzm)_3]^+$. In the mas spectrum of calcium acetylacetonate peak at m/z 377 due to $[Ca_2\ (acac)_3]^+$ has been observed by Macklin and Dudek[14].

Thus the mass spectral studies support the formation of mixed ligand complexes and their proposed structures.

Table 2: Mass spectral data of mixed ligand complexes of Mn(III)
(m/z values and relative abundances)

Ions	**$[Mn(dbzm)_2(bzac)]^+$**	**$[Mn(dbzm)_2(5\text{-chlorosal})]^+$**
M^+	662 (5.26%)	656 (2.63%)
MnL^+	278 (73.68%)	278 (52.63%)
MnL'^+	216 (5.26%)	211 (2.63%)
$MnL_2'^+$	377 (2.63%)	367 (2.63%)
MnL_2^+	501 (100%)	501 (100%)
MnL_3^+	724 (42.10%)	724 (15.78%)
$MnL_2'L^+$	599 (2.63%)	590 (2.63%)

$Mn_2L_3^+$	779 (21.05%)	779 (26.31%)
$Mn_2L_2L_2$’	878 (5.26%)	888 (2.63%)
$Mn_2L_.L_2$’	655 (2.63%)	645 (2.63%)
Mn_2L_2L’	717 (5.26%)	712 (2.63%)
$Mn_2L_4^+$	1002 (26.31%)	1002 (26.31%)

HL= dibenzoylmethane, HL’=benzoylacetone, 5-chlorosalicylaldehyde

CONCLUSIONS

According to the above discussion, an octahedral environment around the metal has been proposed on the basis of magnetic moment data. Non-electrolytic behaviour has been assessed from their low conductance and high molecular weight data. All complexes are high spin paramagnetic in nature, is assessed from magnetic moment data. In the IR spectra of the complexes, shifting of ν(C=O) to lower wave number side supports the chelation of the ligand to the metal atom and also support the absence of coordinated water molecules in the complexes. Mass spectral study further confirms the proposed structure of the complexes. Further study of these complexes could lead to interesting results.

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