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Synthesis and Characterization of Some New Manganese(II) Complexes, Manganese(III) Heterochelates, and μ-Dioxo-dimanganese(IV) Complexes Involving Tetradentate Schiff Bases

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Synthesis and Characterization of Some New Manganese(II) Complexes, Manganese(III) Heterochelates, and μ-Dioxo-dimanganese(IV) Complexes Involving Tetradentate Schiff Bases

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ABSTRACT

Condensation of 1,3-diaminopropane-2-ol with diacetylmonoxime and acetylacetone yielded the tetradentate Schiff bases *N,N′*-(2-hydroxy) propylene-bis{(2-imino-3-oximino)butane} (H_2L^1) and *N,N′*-(2-hydroxy) propylene-*bis*(acetylacetoneimine) (H_2L^2), respectively. The ligands form mononuclear manganese(II) complexes of the type [Mn(II)(L^1)] (**1**) and [Mn(II)(L^2)] (**3**), which are used for the formation of the manganese(III) heterochelates of the type [Mn(III)(L)(L-L)] (where

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$H_2L = H_2L^1$ or H_2L^2; L-L = anion of acetylacetone or salicylaldehyde). Cationic heterochelates of the type $[Mn(L)(L\text{-}L)]ClO_4$ where $H_2L = H_2L^1$ or H_2L^2 and L-L = ethylenediamine and *N*,*N*′-propylene-*bis*(benzaldimine) (L^3) have been synthesized by the reactions of *bis*(acetylacetonato)manganese(II) or *bis*(salicylaldehydato)manganese(II) with the preformed Schiff bases or by the reactions of $[Mn(II)(L^1)]$ or $[Mn(II)(L^2)]$ with L-L in absolute alcohol under reflux. Some of the complexes, synthesized here, may be used as precursors in the synthesis of higher nuclearity manganese complexes. Air oxidation of $[Mn(II)(L^1)]$ (**1**) and $[Mn(II)(L^2)]$ (**3**) in DMF yielded the dark-brown μ-dioxo-*bis*-[*N*,*N*′-(2-hydroxy)propylene-*bis*{(2-imino-3-oximino)butane}]-dimangenese(IV) (**2**) and μ-dioxo-*bis*[*N*,*N*′-(2-hydroxy)propylene-*bis*{(acetylacetoneimine)}]dimangenese(IV) (**4**) complexes, respectively. All of the complexes have been characterized with the help of elemental analyses, molar conductance values, molecular weights, magnetic moments, and spectroscopic (IR, UV-VIS, ESR) data.

Key Words: Manganese(II) complexes; Manganese(III) heterochelates; μ-Dioxo-dimanganese(IV) complexes; Tetradentate Schiff bases.

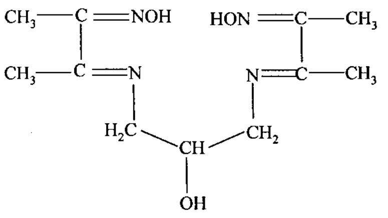
INTRODUCTION

The chemistry of the coordination compounds of manganese in its various oxidation states is gaining increasing attention due to their biological importance.[1–10] The three enzymes, viz., manganese superoxide dismutase, azide insensitive catalase, and photosynthetic oxygen evolving complex possibly involve manganese(III) in the catalytic cycles in such enzymatic reactions.[3] The enantioselective epoxidation of non-functionalized olefins catalyzed by manganese(III) complexes has also been reported.[11] N,O donor ligands are involved in such complexes, and such ligand systems have been used to synthesize new mononuclear complexes of manganese.[3,10,12–14] In addition, tetradentate Schiff base complexes of manganese(III) have been used for the oxidation of organic substrates[15,16] using oxygen-transfer agents such as PhIO, H_2O_2, or O_2. Multinuclear manganese(III) complexes having diverse structural features with Schiff bases are known.[17,18] A recent report has also demonstrated the synthesis of manganese(IV) complexes from manganese(III) precursors.[19] We report here the synthesis, characterization, and reactivity of manganese(II) complexes and manganese(III) heterochelates with tetradentate ligands and mixed tetradentate/bidentate imine ligands, and tetradentate/bidentate O,O or N,N donor ligands. The effects of aerial oxidation of manganese(II) complexes have also been studied leading to the isolation of μ-dioxo-dimanganese(IV) complexes and have been included in this paper.

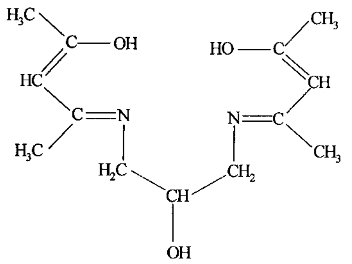
RESULTS AND DISCUSSION

Syntheses

The reactions of 1,3-diaminopropane-2-ol with diacetylmonoxime and acetylacetone yielded the tetradentate Schiff bases *N*,*N*′-(2-hydroxy) propylene-*bis*{(2-imino-3-oximino)butane} (H_2L^1) and *N*,*N*′-(2-hydroxy) propylene-*bis*(acetylacetoneimine) (H_2L^2), respectively as shown below:

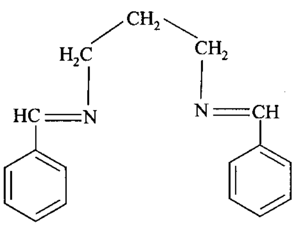


(H_2L^1)



(H_2L^2)

The neutral bidentate ligand *N*,*N*′-propylene-*bis*(benzaldimine) (L^3) was also used in this work.



(L^3)

The reaction of $[Mn(CH_3COO)_2] \cdot 4H_2O$ with H_2L^1 and H_2L^2 in oxygen-free ethanol (under N_2 atmosphere) gave the manganese(II) complexes $[Mn(II)(L^1)]$ (**1**) and $[Mn(II)(L^2)]$ (**3**) in high yield. These manganese(II) complexes are stable when dried, but in wet conditions the compounds darkened, possibly due to aerial oxidation. In fact, oxidation of (**1**) and (**3**) in DMF solution by dioxygen afforded dark-brown $[\{Mn(IV)(L^1)(O)\}_2]$ (**2**) and $[\{Mn(IV)(L^2)(O)\}_2]$ (**4**). The reaction of $[Mn(II)(L^1)]$ (**1**) or

[Mn(II)(L^2)] (**3**) with ethylenediamine (en) or the neutral bidentate Schiff base L^3 in air produced the cationic heterochelates, [Mn(L)(L-L)]ClO_4 where, $H_2L = H_2L^1$, L-L = en (**9**); $H_2L = H_2L^2$, L-L = en (**10**); $H_2L = H_2L^1$, L-L = L^3 (**11**) and $H_2L = H_2L^2$, L-L = L^3 (**12**). When $[Mn(II)(acac)_2] \cdot 2H_2O$ (where Hacac = acetylacetone) or $[Mn(II)(sal)_2] \cdot 2H_2O$ (where Hsal = salicylaldehyde) was allowed to react with the preformed Schiff bases H_2L^1 or H_2L^2 in absolute ethanol and in the presence of dioxygen, heterochelates (**5**)–(**8**) of the type [Mn(III)(L)(L-L)] (where L = dianions of the tetradentate Schiff bases H_2L^1 and H_2L^2; L-L = anion of acetylacetone or salicylaldehyde) were isolated. The formation of the complexes may be expressed by the following chemical equations:

$$H_2L^1 \text{ or } H_2L^2 + Mn(CH_3COO)_2 \cdot 4H_2O$$

$$\xrightarrow[\text{reflux, 2 hr}]{N_2\text{, Ethanol}} [Mn(II)(L^1)]\ (\mathbf{1}) \text{ or } [Mn(II)(L^2)]\ (\mathbf{3})$$

$$H_2L^1 \text{ or } H_2L^2 + Mn(acac)_2 \cdot 2H_2O$$

$$\xrightarrow[\text{reflux, 2 hr}]{O_2\text{, Ethanol}} [Mn(III)(L^1)(acac)]\ (\mathbf{5}) \text{ or } [Mn(III)(L^2)(acac)]\ (\mathbf{6})$$

$$H_2L^1 \text{ or } H_2L^2 + Mn(sal)_2 \cdot 2H_2O$$

$$\xrightarrow[\text{reflux, 2 hr}]{O_2\text{, Ethanol}} [Mn(III)(L^1)(sal)]\ (\mathbf{7}) \text{ or } [Mn(III)(L^2)(sal)]\ (\mathbf{8})$$

$$[Mn(II)(L^1)]\ (\mathbf{1}) \text{ or } [Mn(II)(L^2)]\ (\mathbf{3})$$

$$\xrightarrow[\text{reflux, 2 hr, } NaClO_4]{\text{en, } O_2\text{, Ethanol}} [Mn(III)(L^1)(en)]ClO_4\ (\mathbf{9})$$

$$\text{or } [Mn(III)(L^2)(en)]ClO_4\ (\mathbf{10})$$

$$[Mn(II)(L^1)]\ (\mathbf{1}) \text{ or } [Mn(II)\ (L^2)]\ (\mathbf{3})$$

$$\xrightarrow[\text{reflux, 2 hr, } NaClO_4]{L^3\text{, Ethanol}} [Mn(III)(L^1)(L^3)]ClO_4\ (\mathbf{11}) \text{ or}$$

$$[Mn(III)(L^2)(L^3)]ClO_4\ (\mathbf{12})$$

The characterization data of the manganese(II), manganese(III), and manganese(IV) complexes are summarized in Table 1, which support their formulations. The molecular weights (Table 1) of some of the compounds (measured by the Rast method) are also in good agreement with these formulations.

Table 1. Some characterization data of the complexes.

Compound	Colour	M.p. (°C)	Molecular weight found (calcd.)	Yield (%)	Analyses found (calcd.) (%)					μ_{eff} [a] (B.M.)	Λ_M [b] (Ω^{-1} cm^2 mol^{-1})
					C	H	N	C1/Br/I	M		
[Mn(II)(L^1)] (**1**), $C_{11}H_{18}MnN_4O_3$	Yellow-brown	242–247 (d)	298 (309.22)	80	42.48 (42.72)	5.68 (5.86)	18.01 (18.12)	—	17.9 (17.76)	5.9	11.2
[{Mn(IV)(L^1)(O)}$_2$] (**2**), $C_{22}H_{36}Mn_2N_8O_8$	Dark-brown	—	—	60	40.81 (40.62)	5.27 (5.58)	17.5 (17.21)	—	16.78 (16.89)	2.0	—
[Mn(II)(L^2)] (**3**), $C_{13}H_{20}MnN_2O_3$	Light-brown	247–250 (d)	292 (307.24)	80	50.68 (50.81)	6.26 (6.56)	9.0 (9.12)	—	17.69 (17.88)	5.89	15.0
[{Mn(IV)(L^2)(O)}$_2$] (**4**), $C_{26}H_{40}Mn_2N_4O_8$	Dark-brown	—	—	65	48.12 (48.3)	6.17 (6.24)	8.93 (8.66)	—	17.24 (17.0)	1.9	—
[Mn(III)(L^1)(acac)] (**5**), $C_{16}H_{25}MnN_4O_5$	Brown	278–281 (d)	396 (408.32)	60	47.5 (47.06)	6.42 (6.17)	13.92 (13.72)	—	13.68 (13.46)	4.8	9.8
[Mn(III)(L^2)(acac)] (**6**), $C_{18}H_{27}MnN_2O_5$	Brown	270–275 (d)	419 (406.36)	65	53.52 (53.2)	6.99 (6.7)	6.52 (6.89)	—	13.92 (13.52)	4.75	10.0

(*continued*)

Table 1. Continued.

Compound	Colour	M.p. (°C)	Molecular weight found (calcd.)	Yield (%)	Analyses found (calcd.) (%)					μ_{eff}[a] (B.M.)	Λ_M[b] (Ω^{-1} cm^2 mol^{-1})
					C	H	N	C1/ Br/I	M		
[Mn(III)(L^1)(sal)] (**7**), $C_{18}H_{24}MnN_4O_5$	Reddish-brown	300–305 (d)	460 (431.33)	65	50.44 (50.12)	5.88 (5.61)	13.04 (12.99)	—	12.88 (12.74)	4.85	6.0
[Mn(III)(L^2)(sal)] (**8**), $C_{20}H_{26}MnN_2O_5$	Reddish-brown	288–292 (d)	438 (429.37)	60	56.0 (55.94)	6.07 (6.1)	6.40 (6.53)	—	12.99 (12.79)	4.78	9.88
[Mn(III)(L^1)(en)]ClO$_4$ (**9**), $C_{13}H_{26}ClMnN_6O_7$	Brown	260–264 (d)	479 (468.79)	65	33.8 (33.31)	5.9 (5.59)	17.78 (17.93)	7.8 (7.56)	11.89 (11.72)	4.8	42.0
[Mn(III)(L^2)(en)]ClO$_4$ (**10**), $C_{15}H_{28}ClMnN_4O_7$	Brown	252–255 (d)	452 (466.82)	60	38.2 (38.59)	6.28 (6.05)	12.11 (12.0)	7.72 (7.6)	11.98 (11.77)	4.8	42.8
[Mn(III)(L^1)(L^3)]ClO$_4$ (**11**), $C_{28}H_{36}ClMnN_6O_7$	Brown	298–302 (d)	670 (658.98)	60	51.42 (51.03)	5.6 (5.51)	12.99 (12.75)	5.0 (5.38)	8.8 (8.34)	4.8	45.0
[Mn(III)(L^2)(L^3)]ClO$_4$ (**12**), $C_{30}H_{38}ClMnN_4O_7$	Brown	289–293 (d)	—	60	54.99 (54.84)	5.67 (5.83)	8.7 (8.53)	5.55 (5.4)	8.48 (8.36)	4.8	45.9

[a] Solid state at room temperature.

[b] 10^{-3} M solution in DMSO at room temperature.

Molar Conductance Data

The molar conductance values (Table 1) of the manganese(II) and manganese(III) complexes [except the complexes (**9**)–(**12**)] in DMSO and DMF solutions (found within the range 6–15 $\Omega^{-1}\,cm^2\,mol^{-1}$ for 10^{-3} M solutions), suggest their non-electrolytic nature.[20] The manganese(III) complexes (**9**)–(**12**), on the other hand, behaved as 1 : 1 electrolytes in DMSO solution (Table 1).

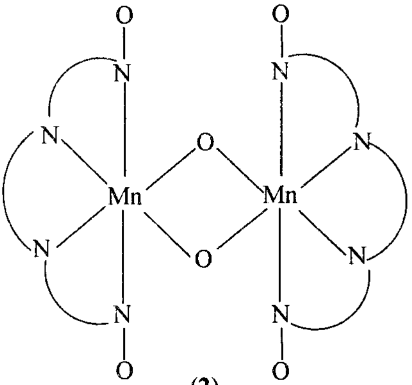
Magnetic Moments and ESR Spectra

The complexes (**1**) and (**3**) are soluble in $CHCl_3$, THF, pyridine, and other organic solvents, but rapidly darken on exposure to oxygen. The magnetic moment of *ca.* 5.92 B.M. is as expected for a high-spin manganese(II) complex, since an ^6S ground state persists in all symmetries of manganese(II) complexes. The manganese(II) complexes (**1**) and (**3**) exhibit magnetic moment 5.90 [for (**1**)] and 5.89 [for (**3**)], respectively, and are indicative of high-spin manganese(II). Complexes (**1**) and (**3**) exhibit strong, broad ESR signals centered at $g = 2$, consistent with manganese(II).[21] The passage of dioxygen (10 hr) through the yellow compounds (**1**) and (**3**) as slurries in DMF at room temperature causes a colour change to dark-brown. This brown solution yielded the dark-brown complexes $[\{Mn(IV)(L^1)(O)\}_2]$ (**2**) and $[\{Mn(IV)(L^2)(O)\}_2]$ (**4**), respectively. The room temperature magnetic moment values of 2.0 and 1.9 B.M. (per Mn atom), respectively, for (**2**) and (**4**) suggest the presence of manganese(IV) ion (a d^3 system). As these two dimeric complexes are ESR-active, the presence of antiferromagnetically coupled high-spin manganese(III) (a d^4 system) is less likely.[22] The solid-state ESR spectra at room temperature of the manganese(IV) complexes (**2**) and (**4**) are characterized by a strong broad signal at $g = 2$, which fits the proposed μ-dioxo structure[7] shown in Fig. 1.

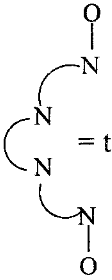
The manganese(III) heterochelates (**5**)–(**8**) are soluble in DMSO, DMF, and pyridine, while the heterochelates (**9**)–(**12**) are soluble in water, ethanol, DMSO, DMF, and pyridine. All these heterochelates are paramagnetic and show magnetic moment values in the range 4.75–4.85 B.M. at room temperature (Table 1) indicating the presence of trivalent manganese. These values show the absence of exchange or superexchange interactions.

UV-VIS Spectra

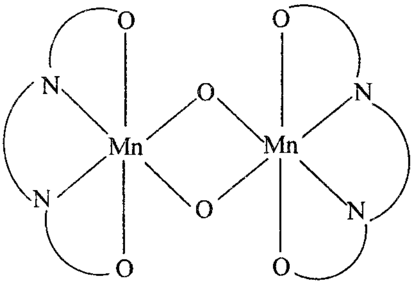
The electronic absorption spectra of the manganese(II) complexes (**1**) and (**3**) were obtained in DMF in an inert atmosphere, and are characterized



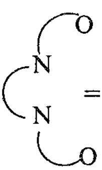
(2)



= the dianion of the tetradentate Schiff base H_2L^1



(4)



= the dianion of the tetradentate Schiff base H_2L^2

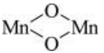
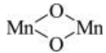
Figure 1. Proposed structure for $[\{Mn(IV)(L^1)(O)\}_2]$ (**2**) and $[\{Mn(IV)(L^2)(O)\}_2]$ (**4**).

by well-defined bands around 24,500 cm^{-1} (broad) and a well-defined shoulder at about 24,700 cm^{-1}. They probably originate from charge transfer phenomena and the findings are in accord with octahedral geometry (possibly solvent coordinated) of manganese(II) complexes.[15,16] However, the bands around 24,500 cm^{-1} diminished on passing dioxygen through the DMF solution, and shoulders appeared at the higher energy regions. In addition, a very weak band appeared around 20,000 cm^{-1} assignable to a d–d transition of manganese(IV).[23] Therefore, the dimanganese(IV) structure (Fig. 1) may be proposed for the complexes (**2**) and (**4**). The electronic spectra of the isolated dimeric manganese(IV) complexes $[\{Mn(IV)(L^1)(O)\}_2]$ (**2**) and $[\{Mn(IV)(L^2)(O)\}_2]$ (**4**) were also measured in chloroform and pyridine solutions. The absorption spectra of the dimers are difficult to analyse because of the lack of well-resolved bands; i.e., only broad, poorly resolved shoulders are seen. Nonetheless, the ligand $\pi \rightarrow \pi^*$ ($\sim$31,000 cm^{-1}) and $d\pi \rightarrow \pi^*$ ($\sim$24,000 and 28,000 cm^{-1}) bands can be identified if not accurately placed.

The fact that both infrared (see later discussion) and UV spectra of the other manganese(III) complexes, (**5**)–(**12**), of this study are qualitatively similar to those of the dimeric manganese(IV) complexes (**2**) and (**4**) supports the notion that the Schiff base ligands are not altered (i.e., oxidized) in the formation of the dimers.

The major difference between the spectra of the manganese(III) complexes and those of the dimeric complexes is the presence of a moderate-intensity band ($\varepsilon \sim 3800$) at $\sim$21,500 cm^{-1}. The intensity is such that the band cannot be assigned to a ligand field transition but is consistent with a charge-transfer transition. This band can most likely be associated with a charge-transfer from the bridging O^{2-} ligand to the metal $d\pi$ orbital. Similar assignments have been made for dimeric Mn(IV)[24] and dimeric Fe(III).[24] The question may arise at this point as to whether the electronic spectra of the dimer can be used to distinguish between the two possible oxidation states, Mn(III) or Mn(IV), and this aspect has been thoroughly discussed.[24]

The presence of a strong oxygen-to-metal charge-transfer transition in the visible region presents the possibility of photoactivated liberation of oxygen from this type of complex, as suggested by Calvin.[25] The chemical properties of the dimers are thus particularly relevant to the suggested role of manganese in green plant photosynthesis and, in particular, to the nature of the manganese photocatalyst that mediates the formation of oxygen from water in the chloroplast. It is interesting to note that the dimeric complexes are stable in solution, e.g., in pyridine and methanol. Comparable electronic spectra in the solid state and also in solution were observed in which the charge-transfer band was at around 21,500 cm^{-1}. The stability of the dimeric compounds may be related to the presence of strong $O^{2-}(p\pi) \rightarrow Mn(d\pi)$

mixing in the  unit. However, it is more probable that the electronic charge is being distributed in a localized molecular orbital, which encompasses the whole  unit. The main feature of the μ-dioxo-dimanganese(IV) structure of complexes (**2**) and (**4**) is possibly a planar, four-membered Mn_2O_2-ring, as reported recently by x-ray crystal structure analysis of an analogous complex,[26] $[Mn(C\text{-}X\text{-}salpn)(\mu{-}O)]_2 \cdot Me_2CO$, where Hsalpn = *N*,*N′*-*bis*(salicylidene)-1,3-diaminopropane and X = $-CH_2C({=}O)CH_3$.

The electronic absorption bands, with their log ε values, of manganese(III) heterochelates are given in Table 2. Usually, high-spin manganese(III) complexes with octahedral geometry are expected to give one charge-transfer band around 25,000 cm^{-1} (log ε = 3.5) and a spin-allowed d–d transition band, $^5E_g \rightarrow {}^5T_{2g}$, around 20,000 cm^{-1} (log ε = 2.5). The electronic absorption spectra of these manganese(III) heterochelates (**5**) to (**12**) measured in the region 41,000–26,000 cm^{-1}, consist of several intense bands and shoulders. The positions of the bands can be roughly divided into two areas, between 14,000–15,000 and 16,000–26,000 cm^{-1}. The bands at high wave numbers are seen as shoulders on intense charge-transfer absorptions. The absorptions in the visible region at 16,000–26,000 cm^{-1} can be assigned to the $^5E_g \rightarrow {}^5T_{2g}$ transition, though there is the possibility that the bands at around 25,000 cm^{-1} may be of charge-transfer in origin. The splitting of the bands is most likely due to the Jahn–Teller distortion as observed in many complexes of

Table 2. Electronic spectral data of some Mn(III) heterochelates and dimanganese(IV) complexes.

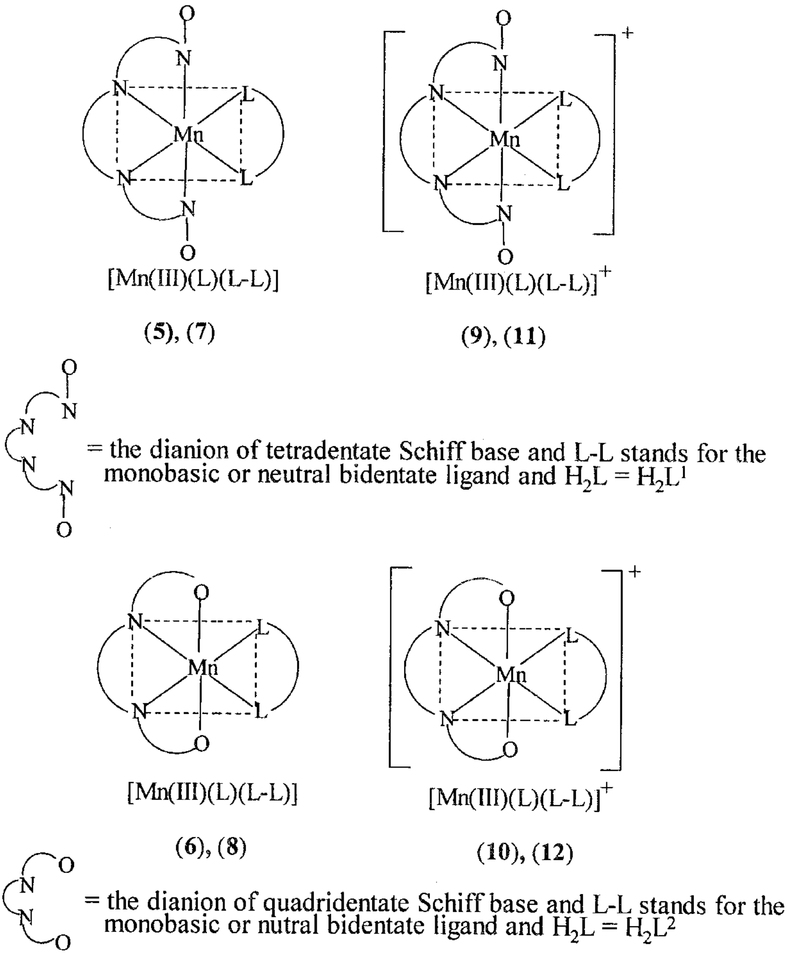
Compound	Solvent	ν_{max} in cm^{-1} (log ε)[a]
(**2**) $[\{Mn(IV)(L^1)(O)\}_2]$	$CHCl_3$	20,600; 24,000; 30,000
	Py	21,000; 23,600
(**4**) $[\{Mn(IV)(L^2)(O)\}_2]$	$CHCl_3$	20,980; 24,200; 31,000
	Py	21,000; 25,000; 30,000
(**5**) $[Mn\ (III)(L^1)(acac)]$	MeOH	40,000 (4.4); 35,700 (4.2); 24,800 (sh); 20,600 (sh); 16,500 (2.4)
(**8**) $[Mn(III)(L^2)(sal)]$	DMSO	25,500 (3.8); 15,600 (sh); 14,500 (sh)
(**9**) $[Mn(III)(L^1)(en)]ClO_4$	DMSO	41,666 (4.5); 40,450 (4.5); 36,000 (4.2); 32,500 (sh); 29,400 (sh); 27,000 (sh); 17,000 (sh); 14,500 (sh)
(**10**) $[Mn(III)(L^2)(en)]ClO_4$	EtOH	41,500 (4.1); 40,000 (4.4); 35,800 (4.0); 32,000 (sh); 27,800 (sh); 16,800 (sh); 15,000 (sh)

[a] log ε values are not quoted for shoulders and ill-defined bands.

manganese(III).[27–32] Despite much work on manganese(III) chelates,[27–30] difficulties have arisen in the assignments of the bands in the near-infrared region. High-spin manganese(III) complexes always show at least one absorption in the region 8,000–13,000 cm^{-1}. The relationship of this band to the structure of the complexes has not been clarified. We also observed a band in the region 14,000–15,000 cm^{-1}. Such a band has been assigned as a low-energy charge-transfer transition in such chelates.[31,32]

Infrared Spectra

The infrared spectra of the ligands show medium to strong bands in the range 3200–3300 cm^{-1} assignable to ν(OH) {=C(CH$_3$)OH} in the case of H_2L^2 and a band at 3000–3400 cm^{-1} assignable to ν(OH) (oxime) in the case of the ligand H_2L^1. The presence of the secondary alcoholic OH in these two ligands has been demonstrated by the appearance of a band around 3400 cm^{-1}. The broad nature of the bands suggests hydrogen bonding.[33–35] The ν(C=N) (azomethine) band in the ligands H_2L^1, H_2L^2, and L^3 appeared in the range 1610–1620 cm^{-1} as a very strong band. The ν(C=N) (oxime linkage) mode in the free ligand H_2L^1 is possibly submerged by an other strong band at around 1615 cm^{-1}. The ν(N–O) mode for the ligand H_2L^1 is observed as a strong band[36] at 940 cm^{-1}. The ν(C–O) band (secondary alcohol) appeared around 1350 cm^{-1} in the free ligands H_2L^1 and H_2L^2 and remains unchanged in the metal complexes demonstrating non-involvement of this group in these complexes.[36] The disappearance of bands around 3000–3300 cm^{-1} suggest deprotonation of oxime OH (of H_2L^1) and alcoholic OH {=C(CH$_3$)OH of H_2L^2} allowing these ligands to function in a dibasic tetradentate fashion. The presence of a broad band around 3400 cm^{-1} (secondary alcoholic group), however, complicates this interpretation. The bands due to C=N (both azomethine and oxime) shifted to lower frequencies by about 10–25 cm^{-1} compared with the free ligand values, indicating bonding through 4N atoms (involving ligand H_2L^1), 2N and 2O atoms (involving ligand H_2L^2) and 2N atoms (involving ligand L^3). For the complexes [Mn(III)(L^1)(acac)] (**5**) and [Mn(III)(L^2)(acac)] (**6**), the chelate oxygen-bonded acetylacetonate anion is shown in the vibrational spectral data[28–30] where we found ν(C–O) at 1555 and 1540 cm^{-1}, respectively, for complexes (**5**) and (**6**), while ν(C$\overset{\cdots}{-}$C) is observed at about 1500 cm^{-1} for both chelates. Infrared spectral data of the heterochelates of trivalent metal ions involving ligands of the present types have been discussed thoroughly elsewhere.[37] The infrared spectral data of complexes (**9**) to (**12**) show a strong and broad band in the range of 1070–1140 cm^{-1} assignable to the ν_3 mode of the ClO$_4$ ion vibration (in T_d system).[28–30] This band demonstrates the presence of ionic perchlorate in these chelates. The complexes (**5**) to (**12**) may attain pseudooctahedral structures where tetradentate Schiff bases have been rearranged from a planar to a twisted conformation by the displacement of only one oxygen atom from the equatorial plane of the planar isomer and the bidentate ligands are in cis-position (Fig. 2). The presence of Mn–O and Mn–N bonds in the complexes are demonstrated by the appearance of infrared absorption bands in the regions 400–430 cm^{-1} and 350–390 cm^{-1}, respectively.



[Mn(III)(L)(L-L)] [Mn(III)(L)(L-L)]$^+$

(5), (7) **(9), (11)**

= the dianion of tetradentate Schiff base and L-L stands for the monobasic or neutral bidentate ligand and $H_2L = H_2L^1$

[Mn(III)(L)(L-L)] [Mn(III)(L)(L-L)]$^+$

(6), (8) **(10), (12)**

= the dianion of quadridentate Schiff base and L-L stands for the monobasic or nutral bidentate ligand and $H_2L = H_2L^2$

Figure 2. Proposed structure for heterochelates (**5**) to (**12**).

The infrared spectra of the complexes (**2**) and (**4**) exhibit ligand bands essentially unchanged from those of their manganese(II) precursors (**1**) and (**3**), and in addition, there are some new, medium-intensity bands at about 635 and 600 cm^{-1}, which are predicted to be characteristic of a di-μ-oxobridged manganese system[22] (Fig. 1).

EXPERIMENTAL

Materials and Instruments

All the chemicals used were of AR grade. Solvents were purified and dried before use by the usual procedures. Infrared spectra were recorded in KBr, Nujol, or hexachlorobutadiene (more than one media were used for some compounds) on a Perkin–Elmer 1330 spectrophotometer. The electronic spectra were recorded on a Hitachi 200-20 spectrophotometer. Conductance measurements were made with a conductivity bridge (Elico Pvt. Ltd., model CM 80). Molecular weights were determined by the Rast method. The magnetic susceptibility was determined by the Guoy method at room temperature. The elemental analyses of the complexes were carried out at the Regional Sophisticated Instrumentation Centre, the Central Drug Research Institute, Lucknow, India. Some spectroscopic data were also collected from this centre.

Preparation of the Ligands and Starting Materials

bis(Acetylacetonato)manganese(II) dihydrate, $[Mn(II)(acac)_2] \cdot 2H_2O$, was prepared by a previously published method[38] as a pale yellow solid. The yellow *bis*(salicylaldehydato)manganese(II) dihydrate, $[Mn(II)(sal)_2] \cdot 2H_2O$, was also prepared following a previously published method.[38]

The Schiff bases H_2L^1, H_2L^2, and L^3 were prepared by our previously published methods[39–42] involving the condensation of 1,3-diaminopropane-2-ol with diacetylmonoxime, acetylacetone and 1,3 diaminopropane with benzaldehyde, respectively.

Preparation of Manganese(II) Complexes

Due to the instability of solutions of these manganese(II) complexes in air the complexes were prepared under nitrogen. The general methods of preparation was as follows.

$[Mn(II)(L^1)]$ (**1**)

To the stirred solution of H_2L^1 (2.56 g, 10 mmol) in dioxygen-free ethanol (60 mL) was added a solution of manganese(II) acetate tetrahydrate, $Mn(CH_3COO)_2 \cdot 4H_2O$ (2.45 g, 10 mmol) drop-wise in dioxygen-free ethanol (50 mL). The mixture was refluxed on a water bath for 2 hr and filtered while hot. The filtrate on concentration to 60 mL and cooling to about $\sim$10 °C gave a yellow-brown solid, which was filtered, washed with dioxygen-free ethanol and dried in *vacuo*. The complex was stored and handled under nitrogen. Yield, 2.47 g (80%).

$[\{Mn(IV)(L^1)(O)\}_2]$ (**2**)

A slurry of the yellow-brown complex $[Mn(II)(L^1)]$ (**1**) (0.77 g, 2.5 mmol) was made in DMF (50 mL) at room temperature, through which dioxygen was passed for 10 hr with occasional stirring. A dark-brown solution was obtained, which was filtered, concentrated to 30 mL, and on standing at room temperature the dark-brown complex (**2**) was obtained. It was filtered off, washed with dioxygen-free ethanol and dried in *vacuo*. Yield, 0.98 g (60%).

$[Mn(II)(L^2)]$ (**3**)

This light-brown compound was prepared following the method used for complex (**1**) using H_2L^2 in place of H_2L^1. Yield, 2.45 g (80%).

$[\{Mn(IV)(L^2)(O)\}_2]$ (**4**)

This dark-brown compound was prepared following the method used for complex (**2**) by oxidation of complex (**3**). Yield, 1.05 g (65 %).

Preparation of Manganese(III) Heterochelates

$[Mn(III)(L^1)(acac)]$ (**5**)

bis(Acetylacetonato)manganese(II) dihydrate, $[Mn(II)(acac)_2] \cdot 2H_2O$ (1.45 g, 5 mmol) was dissolved in dry ethanol (60 mL) and was added to the solution of the Schiff base H_2L^1 (1.28 g, 5 mmol) in dry ethanol (40 mL). Air was then drawn through the mixture for about 5 hr, followed by heating on a water bath under gentle reflux for 2 hr and then the mixture was filtered. The brown filtrate on concentration to 1/3 of the original volume and cooling to $\sim$10 °C afforded a brown gummy mass. It was washed several times with diethyl ether and then triturated with petroleum ether (40–60 °C) to yield a brown solid compound. Yield, 1.25 g (60%).

$[Mn(III)(L^2)(acac)]$ (**6**)

Following the method of (**5**) this brown compound was prepared by the reaction of H_2L^2 (1.25 g, 5 mmol) and $[Mn(II)(acac)_2] \cdot 2H_2O$ (1.45 g, 5 mmol). Yield, 1.3 g (65%).

$[Mn(III)(L^1)(sal)]$ (**7**)

To the solution of $[Mn(II)(sal)_2] \cdot 2H_2O$ (1.66 g, 5 mmol) in ethanol (50 mL) a solution of H_2L^1 (1.28 g, 5 mmol) in ethanol (50 mL) was added. Air was then bubbled through this mixture for about 6 hr followed by reflux on a water bath for an hour. The reddish-brown solid compound thus obtained was filtered, washed with a diethyl ether-alcohol mixture (50 : 50 v/v) and finally with diethyl ether. The compound was dried in a desiccator over fused $CaCl_2$. Yield, 1.4 g (65%).

$[Mn(III)(L^2)(sal)]$ (**8**)

Following the method of (**7**), this reddish-brown compound was prepared by the reaction of $[Mn(II)(sal)_2] \cdot 2H_2O$ (1.66 g, 5 mmol) and H_2L^2 (1.27 g, 5 mmol). Yield, 1.29 g (60%).

$[Mn(III)(L^1)(en)]ClO_4$ (**9**)

A mixture of $[Mn(II)(L^1)]$ (**1**) (1.54 g, 5 mmol) and ethylenediamine (0.3 g, 5 mmol) in ethanol (80 mL) was oxidized by drawing air through the solution (6 hr) followed by refluxing for 2 hr and then the mixture was filtered while hot. The brown filtrate was treated with the stoichiometric amount of a methanolic solution of $NaClO_4$ (0.7 g, 5 mmol) and then the volume was reduced to half. This, on standing at room temperature, yielded a brown solid compound, which was filtered, washed with a cold water–ethanol mixture (1 : 4, v/v) and then with methanol–diethyl ether mixture (1 : 1, v/v), and dried in a desiccator over fused $CaCl_2$. Yield, 1.52 g (65%).

$[Mn(III)(L^2)(en)]ClO_4$ (**10**)

This brown compound was prepared following the same procedure used for (**9**) by the reaction of $[Mn(II)(L^2)]$ (**3**) (1.53 g, 5 mmol) with ethylenediamine (0.3 g, 5 mmol). Yield, 1.4 g (60%).

$[Mn(III)(L^1)(L^3)]ClO_4$ (**11**)

Following the method of (**9**) this brown compound was prepared by the reaction of $[Mn(II)(L^1)]$ (**1**) (1.54 g, 5 mmol) and L^3 (1.25 g, 5 mmol). Yield, 1.98 g (60%).

$[Mn(III)(L^2)(L^3)]ClO_4$ (**12**)

Following the method of (**9**) this brown compound was prepared by the reaction of $[Mn(II)(L^2)]$ (**3**) (1.53 g, 5 mmol) and L^3 (1.25 g, 5 mmol). Yield, 1.97 g (60%).

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