Generation of manganese-(III) *versus* -(IV) complexes with a conjugated ONS donor set: controlling effect of ligand substituents †

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Manganese(IV) complexes, [MnL$_2$] [H$_2$L = MeC(OH)=CHCMe=NN=C(SH)SR (R = Me **1a** or CH$_2$Ph **1b**)] and manganese(III) complexes, [Mn(O$_2$CMe)L] **1c** or [Mn(acac)L] **1d** [acac = acetylacetonate; H$_2$L = PhCH(OH)CPh=NN=C(SH)SCH$_2$Ph] have been synthesized and characterized. The Schiff-base ligands which are derived from an aliphatic carbonyl function, favour the facile oxidation of manganese-(II) to -(IV) under ambient conditions. The structure determination of **1a** showed that the molecule is octahedral with the two equivalent tridentate ligands spanned meridionally. The EPR spectrum of **1a** with a strong but structured signal at $g \approx 4.0$ and a weak one at $g \approx 2.0$ implies a large zero-field splitting, but the spectral profile differed from an ideal axial form. All the complexes exhibited reversible or quasi-reversible Mn^{IV}–Mn^{III} redox couples in their cyclic voltammograms at potentials commensurate with the nature of the substituents in the appropriate ligands. A reasonable basis is suggested by which one may predict whether a particular ligand will stabilize manganese-(II), -(III) or -(IV) in an aerobic medium.

Tri- and tetra-valent manganese constitute the tetramanganese core (Mn$^{III}_3$Mn^{IV}) present in the charge-accumulation centre of the water-oxidizing system of photosystem II (PS II) in green plants.[1–3] Detailed studies of the prominent $g \approx 4$ signal, besides the multiline signal at $g \approx 2$, while implicating also a dimanganese (Mn^{III}Mn^{IV}) cluster[4] within the OEC (oxygen-evolving complex), cannot, however, exclude the existence of a mononuclear manganese(IV) centre in the S$_2$ state of PS II.[5] Furthermore, the uses of mononuclear manganese(IV) complexes in the stoichiometric and catalytic oxidation of organic compounds[6] make the investigation of mononuclear manganese(IV) chemistry still meaningful. Until ten years ago structurally characterized mononuclear manganese(IV) complexes for which the EPR spectra and redox properties had been reported were rather rare, but the last few years have witnessed a good amount of detailed work in this area.[7]

Manganese(III) occurs in superoxide dismutase, transferrin and catalase.[2] A sulfur function is implicated besides oxygen and/or nitrogen in the co-ordination sphere of manganese(III) in acid phosphatase.[8] Also, the recent discovery of the potential of some discrete mononuclear manganese(III) complexes in catalytic epoxidation of alkenes[9] dictates further research in this area, despite the ubiquity of such manganese(III) complexes in both inorganic[10] as well as organic[11] ligand environments. Notwithstanding all these, one very vital chemistry question concerning the situations under which a particular donor set is capable of stabilizing manganese-(II), -(III) or -(IV) still remains unclear.[12,13]

We reported earlier[14] that, in the presence of air, manganese(II) starting compounds reacted with primary hydroxamic acids producing hydroximato complexes of Mn^{III} or Mn^{IV} which invariably possess conjugated metal–ligand ring structure, but the secondary hydroxamic acids, which are incapable of forming such conjugation, produced only hydroxamato manganese(II) complexes.[15] We also recently reported that[12] in the conjugated metal–ligand framework exhibited by trifunctional and diprotic ONS donor ligands (*o*-OH)RC$_6$H$_3$CH=N-NHC(=S)R′ (H$_2$L), the R′ substituents (NH$_2$, NHPh, SMe or SCH$_2$Ph) played a vital role in controlling whether the ligand would stabilize manganese-(III) or -(IV). While the first two helped in isolating manganese(IV) products, the thioether substituents restrict the oxidation of manganese-(II) to -(III), leading to the isolation of manganese(III) complexes. This electronic effect has been given a more concrete shape in the present work which examines whether or not an aliphatic (against aromatic) carbonyl part (for instance Hacac = acetylacetone) in the ONS Schiff-base moiety with the same amine part as above and having R′ = same thioether substituents can generate manganese(IV) complexes. In fact, manganese(IV) complexes could be isolated, and herein we report the synthesis and spectroscopic characterization of such complexes and the X-ray crystallographic structural elucidation of a representative complex, [MnL$^a_2$] (H$_2$L^a = diprotic ONS Schiff base derived from acetylacetone and *S*-methyl dithiocarbazate). Also it is shown that a ONS Schiff base with an aromatic carbonyl part (benzoin) coupled with the same amine function as mentioned above with R′ = SCH$_2$Ph affords a manganese(III) complex. This electronic effect imposed by the ligands is also shown to have been reflected in the Mn^{IV}–Mn^{III} redox potentials of the isolated complexes.

Results and Discussion

(*a*) Ligands and their metal-binding sites

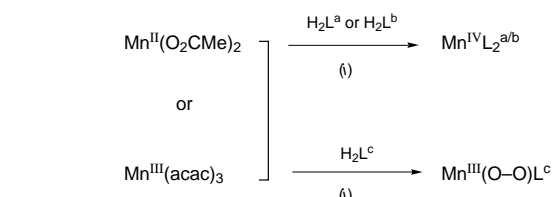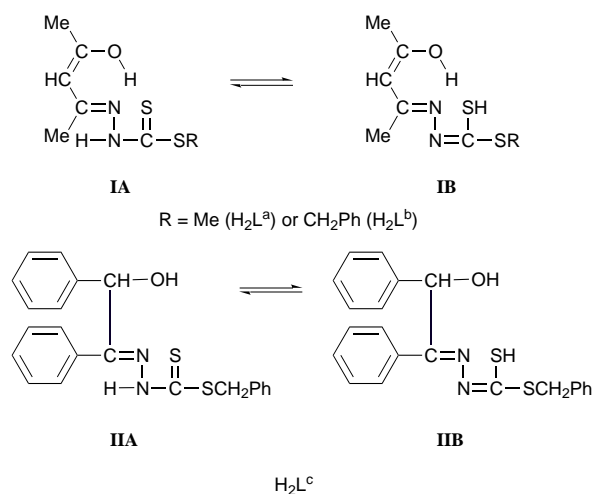The potentially tridentate diprotic Schiff-base ligands H$_2$L$^{a–c}$ are capable of existing as thione (**IA** and **IIA**) or thiol (**IB** and **IIB**) forms. Infrared scanning of the free H$_2$L$^{a–c}$ in the solid state revealed a ν(C=S) vibration[16] at $\approx$1025 cm^{-1}, indicating that they exist in the thione form **IA** or **IIA**. Metal coordination, however, occurs through the thiol form **IB** or **IIB** *via* deprotonation of the OH and SH groups. This is apparent from the disappearance of the ν(OH) (3200 cm^{-1} for H$_2$L^a and H$_2$L^b, and 3300 cm^{-1} for H$_2$L^c) and ν(NH) vibrations (3000 cm^{-1} for H$_2$L^a and H$_2$L^b, and 3100 cm^{-1} for H$_2$L^c) of the Schiff bases on complexation, as well as from the absence of any ν(SH) or ν(C=S) vibrations[17] for the resulting complexes. The

Table 1 Infrared,[a] magnetic, electronic spectral and electrochemical data

Complex	Selected IR bands (cm⁻¹)					μ_{eff}^{b}/μ_B	UV/VIS data λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹)[c]	Mn^{IV}–Mn^{III} [d] $E_{\frac{1}{2}}$/V (ΔE_p/mV)[e]
	ν(C=N)	ν(C–O)	ν(Mn–S)	ν(Mn–N)	ν(Mn–O)			
1a	1560	1060	360	440	500	3.84	804 (295), 546 (510), 502 (55), 470 (600)	−0.16 (80)
1b	1545	1050	340	450	510	3.86	812 (256), 548 (384), 494 (44), 468 (590)	−0.08 (80)
1c	1500	1090	350	440	490	4.82	796 (178), 588 (450), 528 (186), 436 (992)	−0.01 (100)
1d	1500	1090	350	440	485	4.78	790 (180), 592 (490), 525 (182), 432 (900)	+0.01 (100)

[a] As KBr disc. [b] In the solid state at 298 K. [c] In dichloromethane, intraligand transitions are not listed. [d] Solvent dichloromethane, supporting electrolyte NEt₄ClO₄ (0.1 mol dm⁻³), reference electrode SCE. [e] $E_{\frac{1}{2}}$ was calculated as the average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = E_{pa} - E_{pc}$.

R = Me (H₂Lᵃ) or CH₂Ph (H₂Lᵇ)

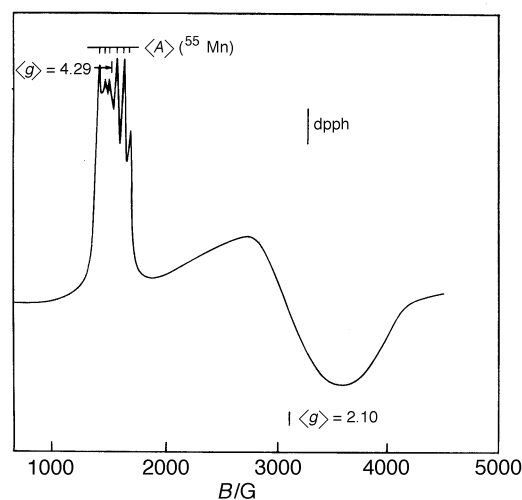**IA**   **IB**

IIA   **IIB**

H₂Lᶜ

Scheme 1 (*i*) Ethanol medium; O–O = O₂CMe or acac

Fig. 1 X-Band EPR spectrum of [MnLᵃ₂] in a dichloromethane–toluene glass (77 K). dpph = Diphenylpicrylhydrazyl

ONS mode of metal co-ordination, *i.e.* through hydroxyl oxygen, azomethine nitrogen and thiol sulfur of **IB** or **IIB** is ascertained from the red shifts of the ν(C–O) (20–35 cm⁻¹) and ν(C=N) vibrations (20–45 cm⁻¹)[18,19] of the appropriate parent Schiff bases on complexation. Further evidence in support of the co-ordination sites employed is provided by the ν(Mn–O),[20] ν(Mn–N)[21] and ν(Mn–S)[22] vibrations at *ca.* 490, 450 and 345 cm⁻¹ (Table 1), respectively,‡ for all the complexes. Besides the above-mentioned vibrations, the manganese(III) complexes exhibit bands at 1530 and 1450 cm⁻¹ for **1c**, and at 1580 and 1520 cm⁻¹ for **1d**, which may be attributed to the ν(CO) vibrations of chelated acetate[23] and acetylacetonate[24] anions, respectively. The co-ordination sites as well as meridional spanning[25] of the ONS ligand have been confirmed by structural characterization of [MnLᵃ₂] [see section (*d*)].

(*b*) Synthesis: ligand-controlled stabilization of Mn^{IV} or Mn^{III}

The compounds H₂Lᵃ and H₂Lᵇ separately react with Mn^{II}-(O₂CMe)₂·4H₂O or Mn^{III}(acac)₃ in ethanol producing the bis chelates [MnLᵃ₂] **1a** and [MnLᵇ₂] **1b**, respectively, thereby stabilizing manganese(IV). Under similar conditions H₂Lᶜ affords manganese(III) complexes, *viz.* [Mn(O₂CMe)Lᵃ] **1c** or [Mn(acac)Lᶜ] **1d**, depending on the manganese starting material used. Schiff bases generating ONS functionality and derived from an aromatic carbonyl function and dithiocarbazate derivatives as the amine part so far failed[12] to stabilize manganese(IV) as against manganese(III), because the non-co-ordinating sulfur in the dithiocarbazate framework constituted a rather electrophilic thioether centre which exerted an electron-attraction effect so that electron loss at the manganese centre

beyond Mn^{III} became impossible. In the present case the aliphatic framework containing the carbonyl function (*i.e.* in Hacac) of the Schiff bases H₂Lᵃ/ᵇ more than compensates the electron-attraction effect of the thioether residue. Once again, when benzoin is used to derive the ONS Schiff base H₂Lᶜ a manganese(III) complex is obtained. The above results are summarized in Scheme 1. There is a profound but predictable effect of ligand structure on the stabilization of Mn^{IV} *vis-à-vis* Mn^{III}.

(*c*) Magnetism and spectroscopy

Room-temperature magnetic moment values of *ca.* 3.8 μ_B for the manganese(IV) complexes **1a** and **1b** and *ca.* 4.8 μ_B for the manganese(III) complexes **1c** and **1d** (Table 1) correspond to the spin-only values for d³ and high-spin d⁴ systems, respectively. The EPR spectrum of **1a** in frozen (77 K) dichloromethane–toluene solution (Fig. 1) is not strictly typical of an axial form of a d³ configuration since a positive excursion from the baseline of the signal at $\langle g \rangle \approx 2$ is observed. This is due to the fact that the particular *mer* isomer formed conforms to a symmetry lower than axial [see also section (*d*)]. However, the spectrum of the above complex consists of weak (if the positive excursion is
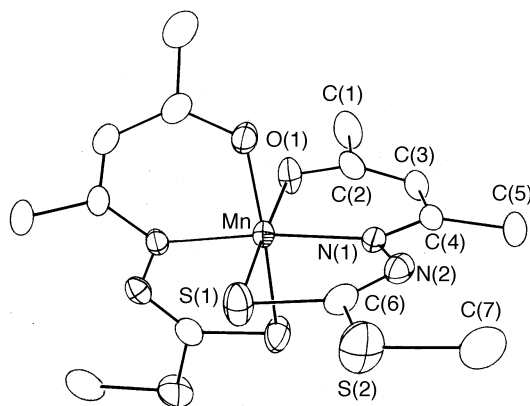
‡ In such complex systems these bands may also originate from vibrations of highly mixed character.

Fig. 2 An ORTEP view of [MnLᵃ₂] with the atom labelling scheme

III

Table 2 Selected bond lengths (Å) and angles (°) and their estimated standard deviations for [MnLᵃ₂]

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Mn–S(1)	2.292(2)	N(2)–C(6)	1.279(7)
Mn–N(1)	1.975(4)	C(2)–C(3)	1.370(7)
Mn–O(1)	1.923(4)	S(2)–C(6)	1.748(5)
S(1)–C(6)	1.736(6)	O(1)–C(2)	1.283(6)
N(1)–N(2)	1.391(5)	N(1)–C(4)	1.336(6)
C(3)–C(4)	1.400(6)		
S(1)–Mn–O(1)	173.9(1)	O(1)–Mn–S(1A)	90.4(1)
S(1)–Mn–N(1)	84.9(1)	O(1)–Mn–O(1A)	85.6(2)
S(1)–Mn–S(1A)	93.9(1)	O(1)–Mn–N(1A)	93.7(1)
S(1)–Mn–O(1A)	90.4(1)	N(1)–Mn–S(1A)	91.0(1)
S(1)–Mn–N(1A)	91.0(1)	N(1)–Mn–O(1A)	93.7(1)
O(1)–Mn–N(1)	93.7(1)	N(1)–Mn–N(1A)	172.7(2)

Symmetry operation: A $-x, y, \frac{1}{2} - z$.

ignored) and strong signals at $\langle g \rangle \approx 2.0$ and ≈ 4.0, respectively, implying reasonably large zero-field splitting commensurate with $|D| > h\nu \approx 0.31$ cm^{-1}.[26] A similar trend in zero-field splitting was observed for a number of manganese(IV) complexes, *viz.* manganese(IV) catecholate,[27] D-glucitolate,[28] hydroximate[14] and a few other cases[7b,26] and also in some actual manganese(IV)-containing enzymes.[2] However, a different trend in the spectra was observed for manganese(IV) thiohydroxamates,[29] dithio-carbamates[30] and manganese(IV) salicylaldehyde thiosemi-carbazonates,[12] where $|D| < h\nu$, which is characteristic of small zero-field splitting. Moreover, the strong signal at $\langle g \rangle \approx 4.0$ shows a well defined sextet which arises out of ^{55}Mn ($I = \frac{5}{2}$) hyperfines with $\langle A \rangle \approx 57$ G, the rather weak $g \approx 2$ signal being broad and single.

The manganese(IV) complexes **1a** and **1b** display four absorption maxima above 400 nm (Table 1), of which the bands at *ca.* 800, 550 and 500 nm represent three d–d transitions, *viz.* $^4A_{2g} \longrightarrow {}^4T_{2g}$, $^4A_{2g} \longrightarrow {}^4T_{1g}$ and $^4A_{2g} \longrightarrow {}^4T_{1g}$(P) as expected in the case of octahedral manganese(IV) (d³) complexes.[31] The high-intensity band at *ca.* 470 nm is assignable to the S(p$_\pi$) $\longrightarrow$ Mn(d$_\pi$) ligand-to-metal charge-transfer (l.m.c.t.) transition. Manganese(III) complexes **1c** and **1d** show four absorption maxima above 400 nm, of which three bands at *ca.* 790, 590 and 525 nm are assignable to $^5B_1 \longrightarrow {}^5B_2$, $^5B_1 \longrightarrow {}^5A_1$ and $^5B_1 \longrightarrow {}^5E$ transitions[32] in a ligand field created by a square-pyramidal structure which is an outcome of an orbital-doublet ground term of a Jahn–Teller sensitive d⁴ metal ion. The remaining intense band at *ca.* 435 nm (Table 1) is a similar l.m.c.t. transition to that observed in the manganese(IV) cases.

(*d*) Crystal and molecular structures

The crystal structure of complex **1a** consists of discrete molecules. An ORTEP[33] view of the compound with the atom labelling scheme is shown in Fig. 2. Bond angles and distances are shown in Table 2. The metal is bonded in the octahedral
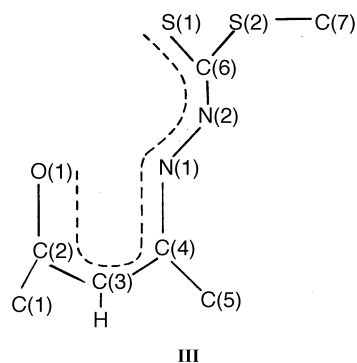
N₂O₂S₂ fashion. The angles described by the six co-ordinating atoms bound to manganese all deviate to some extent from either 180 or 90°. The ligand acts as tridentate meridional ONS donor. In [MnLᵃ₂] the two ligands are equivalent (metal located on the crystallographic C_2 axis). Hence, the said bis complex with both the tridentate ligands having O ··· N ··· S connectivity and meridional spanning can have only one structural option which conforms to that shown in Fig. 2. This clearly entails that O(1), N(1), S(1) (or their A analogues), and N(1A) [or N(1)] comprise the equatorial plane and O(1A) and S(1A) [or O(1) and S(1)] function as axial donors. The S(1) ··· S(1A) distance is 3.349 Å. The covalent radius of sulfur being higher than that of oxygen and nitrogen, the Mn–S distances are substantially greater than Mn–N and Mn–O (Table 2). Since the S atoms are situated *cis* to each other, the resulting structural distortion is expected to be greater than that for a tetragonally distorted octahedral geometry. This may be a reason for the noted departure of the EPR spectrum of this molecule from that of a typical axial spectrum [see section (*c*)].

The observed C(2)–O(1) distance is shorter than a C–O single-bond length.[34] At the same time C(2)–C(3) and C(3)–C(4) are intermediate between C–C [*viz.* C(2)–C(1) and C(4)–C(5)] and C=C bond lengths.[34] The C(4)–N(1) and N(2)–C(6) distances are also in between those of C–N and C=N,[34] but within this limit a significant difference in their lengths (Table 2) can be attributed to the fact that the nitrogen lone pair is intact in N(2) [but not in N(1)] enriching its electron density and facilitating a greater π overlap between the relevant orbitals. Again, the C(6)–S(1) distance is also in between C–S and C=S[34] distances. This observation, substantiates our contention that the metal–ligand ring involves a conjugated system as represented in structure **III**. Also the observed Mn–O, Mn–N and Mn–S distances in [MnLᵃ₂] are comparable to those observed in other structurally characterized manganese(IV) complexes.[7b,26,35–37] By analogy, a similar structure can be envisaged for complex **1b**. Complexes **1c** and **1d** on the other hand contain manganese(III) in its often encountered[2,8] five-co-ordinate (invariably square pyramidal[8,11]) state (see also Scheme 1 and ref. 12, p. 2802), the lone Mn–Lᶜ ring in both cases encompassing conjugation involving presumably only N and S donors, with a restriction imposed by the intervening sp³ carbon (**IIA**) for the same to be extended up to the O-donor.

(*e*) Electrochemistry

Cyclic voltammograms (Fig. 3) of the complexes have been recorded in CH₂Cl₂–NEt₄ClO₄ solution at a solute concentration of 10^{-3} mol dm^{-3}. The results are summarized in Table 1. In the potential range +0.2 to −0.3 V *vs.* saturated calomel electrode (SCE) a reversible or quasi-reversible Mn^{IV}–Mn^{III} couple is exhibited. This is evident from the magnitude of ΔE_p (Table 1) and ratio of the cathodic (i_c) and anodic (i_a) current heights (should ideally be 1:1) of **1a**–**1d** relative to a calibrant, *i.e.* [Fe(η⁵-C₅H₅)₂]; the response of ferrocene is $\Delta E_p = 75$ V under the same experimental conditions. The $i_c : i_a$ ratio in all the cases including ferrocene is *ca.* 0.96:1, but from the ΔE_p criterion the
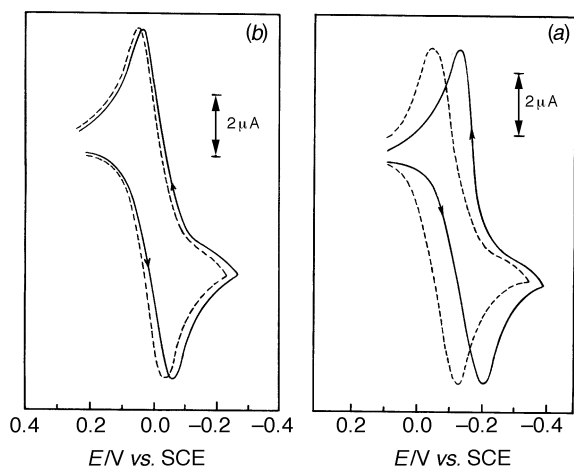
Fig. 3 Segmented cyclic voltammogram of (*a*) [MnL$^a_2$] (———), [MnL$^b_2$] (– – – –) and (*b*) [Mn(O$_2$CMe)L^c] (———), [Mn(acac)L^c] (– – – –) in CH$_2$Cl$_2$–NEt$_4$ClO$_4$ at a platinum electrode. Scan rate = 50 mV s^{-1}

responses of **1c** and **1d** should be termed as quasi-reversible. Constant-potential (at -0.35 V) coulometry of the typical manganese(IV) complex **1a** gives a coulomb count commensurate with a single electron transfer ($n = 0.96$)§ at the metal centre, and the electroreduced solution (Mn^{IV} $\longrightarrow$ Mn^{III}) is EPR silent. Exhaustive electrolysis (0.24 V) of **1c** shows a one-electron change ($n = 0.95$) but the manganese(IV) species furnished by electrooxidation is unstable as also reported for other manganese(III) complexes.[38] Interestingly, the E°_{298} values of the Mn^{IV}–Mn^{III} couple in [MnL$^a_2$] (where R′ = SMe) are found to be more cathodic than that of the corresponding [MnL$^b_2$] (where R = SCH$_2$Ph) (Table 1), which is in line with our previous observations on manganese(III) systems.[12] However, no Mn^{III}–Mn^{II} couple[7a,b] is found in the present cases.

Conclusion

A metal–ligand ring structure with a conjugated ligand framework facilitates ambient oxidation of manganese-(II) to -(III) or -(IV). Electron-releasing groups as ring substituents favour the facile synthesis of manganese(IV) complexes, and electron-withdrawing groups help in isolating manganese(III) products. The possibility of the interplay of a steric rather than electronic effect can be eliminated by noting that the reaction of Mn(O$_2$CMe)$_2$ with the Schiff base H$_2$L^d obtained by condensing dibenzoylmethane (in place of benzoin) with *S*-benzyl dithiocarbazate affords [Mn^{III}(O$_2$CMe)L^d]. A direct corollary of the above electronic effect is the obvious finding that the Mn^{IV}–Mn^{III} redox potential becomes more and more negative *vs.* SCE as the metal centre becomes more and more enriched with electrons. A well documented earlier work[7c] has also shown that in conjugated OON donors affording a MnO$_4$N$_2$ core the metal ion occurs as Mn^{III} when one of the O-donors in each ligand is a carboxylate oxygen (hence an unco-ordinated C=O group as electron attractor in each M–L ring), but if both the oxygens are phenolate oxygens, manganese(IV) complexes are formed.

The nature of the donor atoms is also very important. In the conjugated systems, highly electronegative donor atoms generating, for instance, a neutral [but not anionic, like tris(catecholato)manganese(IV)] MnO$_6$ functionality resist oxidation of manganese to the +IV state even in the presence of highly electron-donating substituents in the M–L ring, [Mn^{III}(acac)$_3$] being a typical example. This principle is also applicable in the case of inorganic ligands: for instance, [Mn^{IV}Cl$_6$]$^{2-}$ exists, whereas fluoride ligands stabilize the trivalent state of the metal.

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§ $n = Q/Q'$ where Q' is the calculated coulomb count for a one-electron transfer and Q the observed value after exhaustive electrolysis of 10^{-3} mol dm^{-3} solute.

However, quite a few complexes of Mn^{III} or Mn^{IV} are known where the M–L rings are essentially non-conjugated. The hitherto attempted generalization based on the negative charge density on the central manganese atom may also be applicable to those systems. However, a much more rigorous parametrization involving a great number and variety of structurally characterized manganese-(II), -(III) and -(IV) systems would be necessary to come to a definite conclusion.

Experimental

Materials

The compounds Mn(O$_2$CMe)$_2$·4H$_2$O (S. Merck Chemicals, India), acetylacetone (BDH, India) and benzoin (E. Merck, India) were used as such; [Mn(acac)$_3$], *S*-methyl dithiocarbazate[39] and *S*-benzyl dithiocarbazate[40] were prepared by literature methods. All solvents (AR or extrapure grade) used for spectroscopic and other physical methods of characterization were further purified by literature methods.[41] Commercial tetraethylammonium chloride was converted into pure tetraethylammonium perchlorate by a literature procedure.[42] All other chemicals used were of GR (E. Merck) grade unless specified.

Physical measurements

Infrared spectra were recorded as KBr discs on a Perkin-Elmer 597 spectrophotometer, electronic spectra using a Hitachi U-3400 UV/VIS/NIR spectrophotometer. X-Band EPR spectra were recorded on a Varian E-190C spectrometer fitted with a quartz Dewar for measurements at low temperatures. They were calibrated with diphenylpicrylhydrazyl ($g = 2.0036$). Voltammetric measurements were done with a PAR model 378-1 electrochemistry system, model 174 A polarographic analyser, model 175 universal programmer, model 173 potentiostat, model 179 digital coulometer and model 337 A cell system. All experiments were made at 298 K under a dinitrogen atmosphere in a three-electrode configuration using a stout platinum wire as working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. For coulometry, a platinum wire-gauze working electrode was used. The potentials reported are uncorrected for the junction contribution. The magnetic susceptibilities were obtained by the Gouy method using Hg[Co(NCS)$_4$] as a standard. The solution conductances were measured with a Systronics (India) model 304 digital conductivity meter. Elemental analyses were performed using a Perkin-Elmer 240C elemental analyser and manganese was estimated by the literature method.[43]

Preparations

Schiff bases. The compounds H$_2$L^a and H$_2$L^c were prepared by literature methods;[39,44] H$_2$L^b was obtained *via* a Schiff-base condensation reaction between *S*-benzyl dithiocarbazate (2.00 g, 10 mmol) and acetylacetone (1.00 g, 10 mmol) in ethanol with the usual work-up. Yield 2.48 g (80%) (Found: C, 55.9; H, 5.5; N, 9.8. Calc. for C$_{13}$H$_{16}$N$_2$OS$_2$: C, 55.7; H, 5.7; N, 10.0%).

[MnL$^a_2$] 1a and [MnL$^b_2$] 1b. The two complexes were prepared by the same general procedure, and details are given for [MnL$^a_2$]. To a filtered solution of H$_2$L^a (0.408 g, 2 mmol) in hot ethanol (60 cm^3) was added a hot ethanolic solution (15 cm^3) of Mn(O$_2$CMe)$_2$·4H$_2$O (0.24 g, 1 mmol) dropwise with stirring for 15 min until a crystalline deep brown product separated. It was filtered off, washed with cold ethanol and dried *in vacuo*. The compound was purified by crystallization from acetone–light petroleum (b.p. 40–60 °C) (1 : 1). Yield 0.42 g (65%) (Found: C, 36.7; H, 4.3; Mn, 12.1; N, 12.0. Calc. for C$_{14}$H$_{20}$MnN$_4$O$_2$S$_4$: C, 36.6; H, 4.3; Mn, 11.9; N, 12.2%). Compound **1a** was also prepared using an ethanolic solution of [Mn(acac)$_3$] (0.35 g, 1 mmol) instead of Mn(O$_2$CMe)$_2$·4H$_2$O. Yield 0.42 g (55%) (Found: C, 36.7; H, 4.3; Mn, 11.8; N, 12.1%).

Table 3 Details of crystal and refinement data for [MnL$^a_2$]

Formula	$C_{14}H_{20}MnN_4O_2S_4$
M	459.5
Crystal system	Monoclinic
Space group	$C2/c$
$a/Å$	15.886(7)
$b/Å$	8.867(4)
$c/Å$	14.893(6)
$\beta/°$	103.56(3)
$U/Å^3$	2039.4(15)
Z	4
$D_m, D_c/mg\ m^{-3}$	1.50, 1.497
$F(000)$	948
$\mu(Mo-K\alpha)/mm^{-1}$	1.072
Diffractometer	Siemens R 3m/v
Radiation $(\lambda/Å)$	Mo-Kα (0.710 73)
Monochromator	Graphite
Crystal size/mm	$0.30 \times 0.24 \times 0.46$
Orientation reflections	30
2θ Range/°	15–30
$T/°C$	22
Scan method, speed/° min^{-1}	ω, 7.32–29.30
h,k,l Ranges	-17 to 17, 0–9, 0–16
Measured 2θ range/°	3.0–47.0
Reflections collected	1678
Observed reflections $[I > 3.0\sigma(I)]$	1129
R^a	0.040
R'^b	0.048
Minimum/maximum transmission	0.5850, 0.6173
Goodness of fit^c	1.46
Largest and mean Δ/σ	0.002, 0.000
Largest difference peak, hole/e Å^{-3}	0.40, -0.32

$^a \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w^{-1} = \sigma^2(F) + 0.0001F^2$. $^c [w(|F_o| - |F_c|)^2/(n_o - n_v)]^{\frac{1}{2}}$, where n_o and n_v denote the numbers of data and variables, respectively.

Compound **1b** was prepared (yield 60%) by similar methods to those described above, using H_2L^b instead of H_2L^a (Found: C, 51.2; H, 4.6; Mn, 9.1; N, 9.0. Calc. for $C_{26}H_{28}MnN_4O_2S_4$: C, 51.0; H, 4.5; Mn, 9.0; N, 9.1%).

[Mn(O$_2$CMe)L^c] 1c. The compound $Mn(O_2CMe)_2\cdot 4H_2O$ (0.24 g, 1 mmol) in ethanol (15 cm^3) was added dropwise to a solution of H_2L^c (0.390 g, 1 mmol) in hot ethanol (50 cm^3). The resulting mixture was heated on a steam-bath for 5 min for the precipitated solid to settle. The product was filtered off, washed with ethanol and dried *in vacuo*. The crude material was purified by crystallization from acetone–light petroleum (40–60 °C) (1:1). Yield 0.35 g (55%) (Found: C, 57.2; H, 4.0; Mn, 10.8; N, 5.6. Calc. for $C_{24}H_{21}MnN_2O_3S_2$: C, 57.1; H, 4.1; Mn, 10.9; N, 5.5%).

[Mn(acac)L^c] 1d. The procedure applied for complex **1c** was followed using an ethanolic solution of $[Mn(acac)_3]$ (0.350 g, 1 mmol) and the crude product was crystallized from acetone–light petroleum (40–60 °C) (1:1). Yield 0.37 g (50%) (Found: C, 59.7; H, 4.5; Mn, 10.2; N, 5.0. Calc. for $C_{27}H_{25}MnN_2O_3S_2$: C, 59.5; H, 4.5; Mn, 10.1; N, 5.1%).

Crystallography

Well formed crystals of [MnL$^a_2$] were obtained by slow diffusion of light petroleum (b.p. 40–60 °C) into an acetone solution of the compound. The full crystallographic data and data collection parameters are listed in Table 3. Two check reflections, measured after every 98, did not show any significant change in intensity during 17 h of X-ray exposure. Data were corrected for Lorentz-polarization effects and absorption (azimuthal scan).[45]

The position of the metal was determined from a Patterson map and the rest of the molecule emerged from successive Fourier-difference syntheses. Of the 1678 reflections, 1518 were unique and 1129 with $I > 3\sigma(I)$ were used for structure solution. The structure was then refined by full-matrix least-squares procedures based on F. All the non-hydrogen atoms were made thermally anisotropic and hydrogen atoms were added at calculated positions with fixed U 0.08 Å^2 in the last cycle of refinement. All calculations were done on a Micro VAX II computer with the SHELXTL PLUS program.[46]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/501.

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