Ligand Control on the Synthesis and Redox Potency of Mononuclear Manganese-(III) and -(IV) Complexes with Tridentate ONS Co-ordination†

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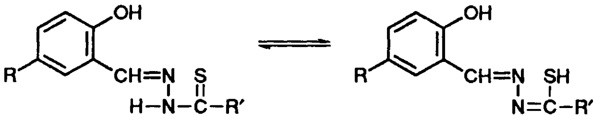
Trifunctional (ONS) Schiff bases H_2L^1 and H_2L^2 (H_2L^1 = 5-R-salicylaldehyde thiosemicarbazone; H_2L^2 = 5-R-salicylaldehyde 4-phenylthiosemicarbazone; R = H, Me or Br) furnished manganese(IV) complexes of the type $[MnL_2]$ (L = L^1 or L^2), whereas H_2L^3 and H_2L^4 {H_2L^3 = *S*-methyl 3-[(5-R-2-hydroxyphenyl)methylene]dithiocarbazate; H_2L^4 = *S*-benzyl 3-[(5-R-2-hydroxyphenyl)methylene]dithiocarbazate; R = H, Me or Br} afforded manganese(III) complexes of the type $[MnL(O_2CMe)]$ or $[MnL(acac)]$ (acac = acetylacetonate, L = L^3 or L^4), when treated with $Mn^{II}(O_2CMe)_2 \cdot 4H_2O$ or $[Mn^{III}(acac)_3]$ in alcoholic media in the air. The room-temperature magnetic moments confirm the corresponding oxidation states in the complexes. The EPR spectra of the manganese(IV) complexes in frozen dimethylformamide (dmf)–methanol solution show weak and strong signals at $\langle g \rangle \approx 4.0$ and ≈ 2.0, respectively, implying a small zero-field splitting. The $\langle g \rangle \approx 2.0$ signal shows hyperfine (due to ^{55}Mn) as well as forbidden lines. Cyclic voltammograms of all the complexes scanned in dmf showed reversible to quasi-reversible Mn^{IV}–Mn^{III} couples the E°_{298} values of which are significantly affected by the electronic effects of the R substituents in the salicyl phenyl ring and the R′ substituents attached to the carbon atom bound to the thiolate functionality of the ligands. The Hammett σ_p values of the R substituents are linearly correlated with the E°_{298} values.

One of the most outstanding traits of manganese is its ability to adopt the widest variety of oxidation states among the 3d elements, and explains its redox function in biological systems.[1] Though a tetranuclear cluster containing both manganese-(IV) and -(III) is widely believed to play a central role as the oxygen-evolving complex in photosystem II (PS II) in the photocatalytic four-electron oxidation of water to dioxygen in green plants,[2,3] a mononuclear manganese(IV) species in a non-porphyrinic but still unknown ligand environment is also implicated in the S_2 state of this complex. Different spectral and redox-based biomimetic studies have revealed a wide variety of ligand co-ordination spheres, *viz.* MnO_6, MnN_2O_4 or MnN_4O_2.[2] These have partial support from extended X-ray absorption fine structure (EXAFS) investigations of actual enzymes, but the option of at least one donor from the second short-period elements has not yet been revealed.[2,3] Until a few years ago, structurally characterized mononuclear manganese(IV) complexes with reported EPR spectra were rare.[4,5] However, a few such studies, involving MnN_6,[6] MnO_6,[5] MnN_2O_4[7] and MnN_4O_2[8] chromophores, have now been published.

Exclusively trivalent manganese is believed to be present[2,3] in the enzymes superoxide dismutase, phosphatase, transferrin and catalase. At least one sulfur function in the manganese(III) co-ordination is implicated in manganese(III)-acid phosphatase.[9] Mixed-ligand thiolate complexes having S_4N[10] and O_2N_2S[11] donors, thioacids possessing O_2S_2N[9] and a variety of Schiff bases in conjunction with a unidentate ligand providing O_2N_2X ($X = F^-, Cl^-, Br^-$ or I^-),[12–16] O_2N_2Y ($Y = OCN^-$, $MeCO_2^-$ or H_2O)[13–15] and O_2N_2Z ($Z = NCS^-$, N_3^-, NO_2^- or NCO^-)[13,15,16] donors have afforded five-co-ordinate square-pyramidal manganese(III) species.

Surveying the research work in this area it appears that a sound rationale as to whether a ligand will stabilize the tri- or tetra-valent state of manganese is not available. We have recently reported[17] that primary hydroxamic acids, RC_6H_4-CONHOH (R = H or NH_2‡) react with manganese(II) in the air producing either manganese-(IV) (R = H) or -(III) (R = NH_2‡) complexes. While details of the substituent effects as a function of the manganese oxidation states stabilized are being pursued by us separately, the present paper deals with manganese(III,IV) chemistry in a tridentate oxygen, nitrogen and sulfur environment.

The dianionic ONS Schiff-base compounds (H_2L) used here exist in the thione **A** and thiol **B** forms. It has been found that $Mn^{II}(O_2CMe)_2 \cdot 4H_2O$ or $[Mn^{III}(acac)_3]$ (acac = acetylacetonate) reacts with H_2L producing manganese-(IV) or -(III) complexes depending on the R′ group present.



A **B**

	R	R′
H_2L^{1a}	H	NH_2
H_2L^{1b}	Me	NH_2
H_2L^{1c}	Br	NH_2
H_2L^{2a}	H	NHPh
H_2L^{2b}	Me	NHPh
H_2L^{2c}	Br	NHPh
H_2L^{3a}	H	SMe
H_2L^{3b}	Me	SMe
H_2L^{3c}	Br	SMe
H_2L^{4a}	H	SCH_2Ph
H_2L^{4b}	Me	SCH_2Ph
H_2L^{4c}	Br	SCH_2Ph

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† *Non-SI units employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

‡ This group also participates in co-ordination.

Experimental

Physical Measurements.—The IR spectra were recorded using KBr discs on a Perkin-Elmer 597 IR spectrophotometer and electronic spectra on a Hitachi U-3400 UV/VIS-NIR spectrophotometer. X-Band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at low temperatures. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) (g = 2.0037). Voltammetric measurements were done with a PAR model 378-1 electrochemistry system with a model 174A polarographic analyser, model 175 universal programmer, model 173 potentiostat, model 179 digital coulometer and model 377A 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 (SCE). 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.[18]

Materials.—The compounds $Mn(O_2CMe)_2 \cdot 4H_2O$ (S. Merck Chemicals, India), thiosemicarbazide (Loba Chemie, India), salicylaldehyde (Central Chemicals, India) and *p*-cresol (S. D. Chemicals, India) were used as such; $[Mn(acac)_3]$,[19] 4-phenylthiosemicarbazide,[20] *S*-methyl dithiocarbazate[21] and *S*-benzyl dithiocarbazate[22] were prepared by literature methods. 5-Bromosalicylaldehyde was obtained from Aldrich (USA) and the corresponding 5-methyl derivative was prepared from *p*-cresol in good yields by using the Duff reaction, following the methods described in the literature.[23] The Schiff bases H_2L^{1a},[24] H_2L^{2a},[24] H_2L^{3a-3c} (ref. 25) and H_2L^{4a-4c} (ref. 25) were prepared according to the literature and further characterized by elemental analyses and by comparing the IR spectra of the isolated compounds with those of the reported ones. Dimethylformamide (dmf) used for electrochemical studies was dried by distillation over P_2O_5 *in vacuo*. All other solvents used were of analytical grade and distilled before use.

Preparations.—$H_2L^{1b,1c}$ *and* $H_2L^{2b,2c}$. These compounds were obtained by Schiff-base condensation of appropriate aldehydes (0.025 mol) with thiosemicarbazide or 4-phenylthiosemicarbazide (0.025 mol) in an ethanolic solution. Yield: *ca.* 70%. The analytical (C, H, N) data of the products obtained upon crystallization from ethanol are shown in Table 1.

The complexes. $[MnL_2]$ (L = L^{1a} **1a** *or* L^{2a} **2a**). To a hot ethanolic solution (*ca.* 15 cm^3) of $Mn(O_2CMe)_2 \cdot 4H_2O$ (0.24 g, 1 mmol) was added a hot ethanolic solution (*ca.* 50 cm^3) of the appropriate H_2L (2 mmol) dropwise with stirring for 10 min until a deep green solid separated. It was filtered off, washed with a small amount of ethanol and then with light petroleum (b.p. 40–60 °C) and dried *in vacuo*. Complex **2a** was purified by crystallization from chloroform–light petroleum (1 : 3). Yield: *ca.* 52%. Complexes **1a** and **2a** were also prepared using an ethanolic solution of $[Mn(acac)_3]$ (0.35 g, 1 mmol) instead of $Mn(O_2CMe)_2 \cdot 4H_2O$. Yield: *ca.* 55%.

$[MnL_2]$ (L = L^{1b} **1b**, L^{1c} **1c**, L^{2b} **2b** *or* L^{2c} **2c**). A hot methanolic solution (*ca.* 60 cm^3) of the respective H_2L (2 mmol) was added dropwise with stirring to a hot solution (*ca.* 15 cm^3) of $Mn(O_2CMe)_2 \cdot 4H_2O$ (0.24 g, 1 mmol) in the same solvent. The stirring was continued for 15 min and subsequently the volume of the solution was reduced (to *ca.* 15 cm^3) in a rotavaporator, when a deep green solid separated. It was filtered off, washed with a little methanol and then with light petroleum (b.p. 40–60 °C). The crude products were crystallized from chloroform–light petroleum (*ca.* 1:3) and dried *in vacuo*. Yield: *ca.* 50%. These compounds were also prepared using a methanolic solution of $[Mn(acac)_3]$ (0.35 g, 1 mmol) instead of $Mn(O_2CMe)_2 \cdot 4H_2O$. Yield: *ca.* 52%.

$[MnL(O_2CMe)]$ (L = L^{3a} **3a** *or* L^{4a} **4a**). These complexes were prepared from an ethanolic solution of $Mn(O_2CMe)_2 \cdot 4H_2O$ (0.24 g, 1 mmol) and the respective H_2L (1 mmol) by following the same method as described for **1a**. They were crystallized from chloroform–light petroleum (*ca.* 1:3). Yield: *ca.* 50%.

Complexes **3b**, **3c**, **4b** and **4c** were prepared by the procedure applied for **1b**, using appropriate starting materials and crystallized from chloroform–light petroleum (*ca.* 1:3). Yield: *ca.* 50%.

$[MnL(acac)]$ (L = L^{3a} **5a** *or* L^{4a} **6a**). The procedure applied for complex **1a** was followed using an ethanolic solution of $[Mn(acac)_3]$ (0.35 g, 1 mmol). Yield: *ca.* 52%.

Compounds **5b**, **5c**, **6b** and **6c** were prepared by following the procedure applied for **1b** using a methanolic solution of $[Mn(acac)_3]$ (0.35 g, 1 mmol) and the crude materials were crystallized from chloroform–light petroleum (*ca.* 1:3). Yield: *ca.* 52%.

Results and Discussion

(*a*) *Synthetic Aspects.*—The compound $MnCl_2 \cdot 4H_2O$ does not react with any of the above Schiff-base reagents even in the presence of sodium acetate, whereas $Mn(O_2CMe)_2 \cdot 4H_2O$ or $[Mn(acac)_3]$ reacts with each, producing manganese-(IV) or -(III) complexes, insofar as Cl^- is a weaker conjugate base than $MeCO_2^-$ or $acac^-$. It is also noted that, when the R′ substituent in the trifunctional (ONS) and dianionic reagent is NH_2 or NHPh, bis(chelates) are formed affording manganese(IV) complexes, but when R′ is a sulfur-containing residue, *viz.* SMe or SCH_2Ph, only one L^{2-} is co-ordinated and the other two sites are occupied by $MeCO_2^-$ or $acac^-$. This is not strictly due to steric effects since cobalt(III) is known[21,26] to form bis(chelates) of composition [CoL(HL)] with the same compounds. This entails that the neighbouring thioether (CSX where X = Me or CH_2Ph) group which is normally expected to be rather electrophilic (nucleophilicity of thioether groups known to be extremely low) will tend to oppose a further electron loss from the conjugated manganese(III)–ligand system.

(*b*) *Mode of Ligand Co-ordination.*—*Tridentate nature.* The infrared spectra of all the free H_2L^1–H_2L^4 show a ν(C=S) vibration[26] at *ca.* 1050 cm^{-1}, indicating that in the solid state they exist in the thione form **A**. On co-ordination they are found in the dianionic thiol form, involving deprotonation of the phenolic and SH group of **B**, commensurate with the disappearance of their ν(OH) (*ca.* 3400 cm^{-1}) and ν(NH) (*ca.* 3000 cm^{-1}), as well as the absence of any ν(SH) or ν(C=S), vibrations.[25,27] The ONS mode of co-ordination, *i.e.* through phenolic oxygen, azomethine nitrogen and thiol sulfur of **B**, in all cases is ascertained from the 10–30 cm^{-1} downward shift of the ν(C=N) vibrations and 10–20 cm^{-1} upward shift of the ν(C–O) vibrations of the free H_2L (*cf.* Table 1) after metal complexation. This mode is further supported by the presence of bands at *ca.* 340, 460 and 550 cm^{-1} due possibly to ν(Mn–S), ν(Mn–N) and ν(Mn–O) vibrations,* respectively.[28,29] It has been observed that H_2L where R′ = NHPh or NH_2 show one or two ν(NH) vibrations, respectively, around 3200 cm^{-1}, besides the ν(NH) vibrations mentioned above. In spectra of the corresponding metal complexes, however, the bands remain unaltered.

(*c*) *Complexes* $[MnL_2]$, $[MnL(O_2CMe)]$ *and* $[MnL(acac)]$.—All the complexes are non-electrolytes in dmf. The bulk magnetic susceptibility data (Table 2) show that the

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* In such complex systems these bands may also originate from vibrations of highly mixed character.

Table 1 Analytical[a] and IR[b] data for the isolated compounds

	Analysis (%)				Selected IR bands (cm^{-1})				
Complex	C	H	N	Mn	ν(C=N)	ν(C=O)	ν(Mn–S)	ν(Mn–N)	ν(Mn–O)
1a	43.8 (43.5)	3.1 (3.1)	18.5 (19.0)	12.3 (12.4)	1600	1550	340	458	550
1b	45.8 (46.0)	3.9 (3.8)	17.6 (17.9)	11.5 (11.7)	1610	1550	335	458	560
1c	31.6 (32.0)	2.0 (2.0)	13.9 (14.0)	9.0 (9.1)	1600	1550	350	462	560
2a	56.3 (56.6)	3.6 (3.7)	14.4 (14.1)	8.9 (9.2)	1600	1550	340	458	540
2b	57.6 (57.9)	4.0 (4.1)	13.2 (13.5)	9.0 (8.8)	1590	1550	358	450	550
2c	44.2 (44.7)	2.7 (2.6)	11.2 (11.1)	7.5 (7.3)	1600	1540	350	460	540
3a	39.0 (38.5)	3.2 (3.1)	8.2 (8.0)	16.2 (16.0)	1600	1540	340	450	560
3b	40.9 (41.2)	3.6 (3.5)	8.0 (8.1)	15.6 (15.8)	1610	1540	360	450	560
3c	31.9 (32.1)	2.5 (2.5)	5.5 (5.4)	13.1 (13.2)	1600	1530	340	460	570
4a	49.5 (49.2)	3.5 (3.6)	6.8 (6.7)	13.5 (13.2)	1600	1540	350	450	550
4b	51.9 (52.2)	3.9 (3.9)	6.6 (6.8)	12.8 (12.5)	1620	1540	360	440	560
4c	40.9 (41.3)	2.8 (2.8)	5.5 (5.6)	11.0 (11.1)	1600	1530	350	460	560
5a	44.1 (44.4)	4.0 (3.9)	7.3 (7.4)	14.2 (14.5)	1600	1540	340	450	560
5b	45.5 (45.9)	4.5 (4.3)	7.0 (7.1)	13.5 (14.0)	1610	1540	360	440	560
5c	36.5 (36.7)	3.2 (3.0)	5.9 (6.1)	11.7 (12.0)	1600	1530	350	460	550
6a	52.5 (52.8)	4.1 (4.1)	6.0 (6.1)	12.4 (12.1)	1600	1540	340	450	550
6b	53.6 (53.8)	4.6 (4.4)	5.7 (5.9)	11.6 (11.7)	1620	1540	360	440	560
6c	45.2 (45.0)	3.3 (3.3)	5.1 (5.2)	10.0 (10.3)	1600	1530	358	458	560
H_2L^{1b}	51.9 (51.6)	5.4 (5.2)	21.2 (20.0)	—	1620	1540	—	—	—
H_2L^{1c}	35.4 (35.0)	3.0 (2.9)	14.9 (15.3)	—	1620	1540	—	—	—
H_2L^{2b}	63.3 (63.1)	5.3 (5.2)	14.9 (14.7)	—	1600	1540	—	—	—
H_2L^{2c}	48.3 (48.0)	3.5 (3.4)	12.2 (12.0)	—	1630	1530	—	—	—

[a] Calculated values are given in parentheses. [b] As KBr discs; ν(O_2CMe) of **3a**–**3c** and **4a**–**4c** at 1415, 1380, 1385 and 1390, 1420, 1400 cm^{-1} respectively; ν(acac) of **5a**–**5c** and **6a**–**6c** appears as two bands each at 1570, 1530; 1560, 1530; 1570, 1520 and 1570, 1530; 1570, 1530; 1570, 1520 cm^{-1}, respectively.

Table 2 Electronic spectral[a] [λ nm (ε/dm^3 mol^{-1} cm^{-1})] and magnetic moment data[b] for the complexes

Complex	λ_{max} (ε)	μ_{eff}/μ_B
1a	723 (302), 574 (330), 535 (215), 447 (1130)[c]	3.80
1b	735 (275), 584 (220), 535 (100), 455 (985)[c]	3.86
1c	720 (230), 578 (200), 539 (165), 450 (1160)	3.70
2a	725 (145), 596 (300), 474 (1070)	3.80
2b	740 (105), 600 (140), 478 (915)	3.72
2c	730 (195), 600 (275), 480 (1180)	3.70
3a	723 (275), 600 (295), 530 (40), 453 (790)	4.90
3b	737 (370), 608 (350), 531 (65), 459 (765)	4.80
3c	723 (290), 608 (185), 533 (45), 463 (610)	4.72
4a	723 (268), 600 (305), 525 (40), 459 (695)	4.90
4b	725 (330), 616 (335), 535 (55), 465 (835)	4.72
4c	713 (210), 608 (220), 537 (55), 457 (810)	4.93
5a	714 (325), 600 (373), 523 (60), 455 (960)	4.87
5b	718 (340), 604 (375), 525 (60), 459 (705)	4.85
5c	721 (270), 600 (310), 525 (45), 462 (500)	4.80
6a	714 (270), 604 (305), 529 (50), 455 (780)	4.94
6b	718 (215), 602 (270), 529 (60), 459 (920)	4.83
6c	717 (215), 600 (270), 527 (40), 461 (850)	4.94

[a] In dichloromethane; intraligand transitions are not listed. [b] At 298 K. [c] In dimethylformamide.

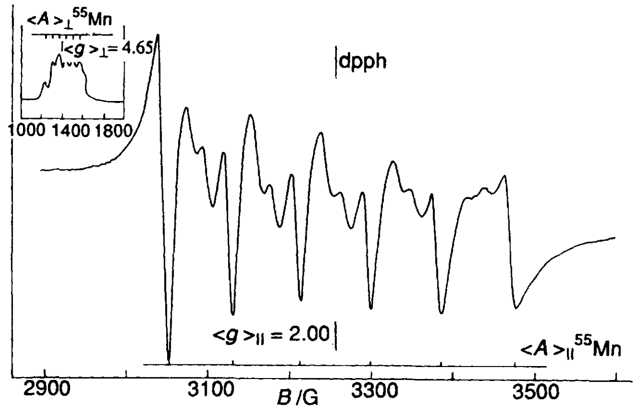

Fig. 1 X-Band EPR spectrum of $[MnL^{1a}_2]$ in dmf–methanol (1 : 1) at 77 K

manganese(IV) complexes of series **1** and **2** exhibit μ_{eff}^{298} values of 3.70–3.86 μ_B which corresponds to a d^3 configuration. For the trivalent complexes of series **3**–**6** the μ_{eff}^{298} values are in the range 4.72–4.94 μ_B which conforms to the high-spin d^4 configuration. As usual the complexes of Mn^{IV} are EPR sensitive and those of Mn^{III} are EPR silent.[7b] Complexes **1a** and **2a** display axial spectra in a dmf–methanol (1 : 1) glass with $\langle g\rangle_\perp = 4.65$, $\langle g\rangle_\parallel = 2.00$ for **1a** (Fig. 1) and $\langle g\rangle_\perp = 4.12$, $\langle g\rangle_\parallel = 2.01$ for **2a** (Fig. 2). For both complexes the signal at $g \approx 2$ is stronger than that at $g \approx 4$, which is indicative of a small zero-field splitting parameter,[30] $|D| < h\nu \approx 0.31$ cm^{-1}. This is due to the fact that the ligands provide a more symmetrical electronic environment around the metal. A similar trend in the EPR spectra was observed for manganese(IV) thiohydroxamates[30] and dithiocarbamates.[31] However, for manganese(IV) catecholate,[32] D-glucitolate,[33] hydroximate[17] and a few other complexes[7b,34] the trends are different, and the D values are characteristic of a large zero-field splitting. Interestingly, in the glass phase, both the signals ($g \approx 4$ and 2) for **1a** are further split into six hyperfine lines arising from ^{55}Mn $(I = \frac{5}{2})$ with $\langle A\rangle_\parallel^{Mn} \approx 85$ G and $\langle A\rangle_\perp^{Mn} \approx 66$ G. However, for **2a** only the $g \approx 2$ signal shows hyperfine lines with a coupling constant $\langle A\rangle_\parallel^{Mn} \approx 85$ G. In both cases forbidden ($\Delta M_S = \pm 1$, $\Delta M_I = \pm 1$) doublets[8,31] are also observed between the hyperfine sextet (Figs. 1 and 2) of the $\langle A\rangle_\parallel$ lines (*i.e.* corresponding to $g \approx 2$). The magnitudes of the D values calculated from the intensity ratios of the forbidden-to-allowed lines[8,31] are *ca.* 0.011 cm^{-1} in both cases.

The manganese(III) complexes **3a**–**3c**, **4a**–**4c**, **5a**–**5c** and **6a**–**6c** exhibit characteristic infrared bands corresponding to the chelated acetate and acetylacetonate anions. Complexes **3a**–**3c** and **4a**–**4c** exhibit a medium-intensity band at *ca.* 1400 cm^{-1} characteristic* of the co-ordinated acetate[35] and the bands at *ca.* 1560 and *ca.* 1520 cm^{-1} indicate the presence[36] of bidentate acetylacetonate in **5a**–**5c** and **6a**–**6c**. These bands

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* The band at *ca.* 1500 cm^{-1} appears to be hidden within the strong and broad band at *ca.* 1525 cm^{-1} due to the appropriate ONS donor ligand.

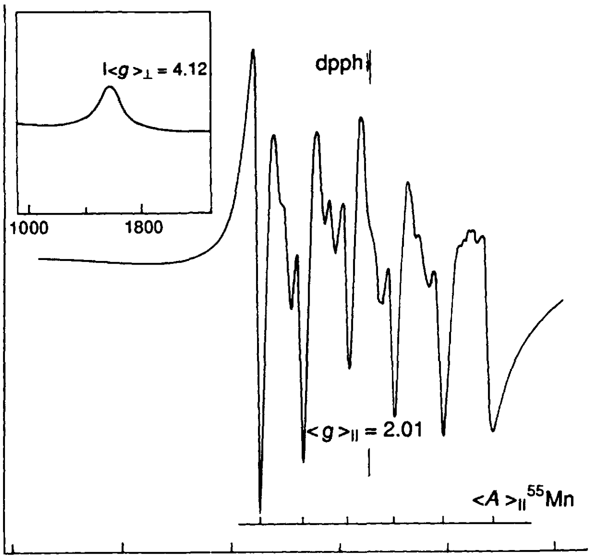

Fig. 2 X-Band EPR spectrum of $[MnL^{2a}{}_2]$ in dmf–methanol (1:1) at 77 K

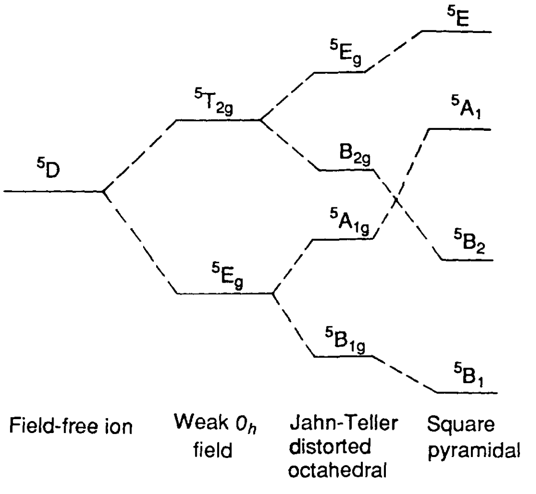

Fig. 3 Probable energy-level diagram of Mn^{III} in square-pyramidal co-ordination

are absent from the spectra of complexes **1a**–**1c** and **2a**–**2c**. Hence, a five-co-ordinate square-pyramidal structure, which has been noted in quite a few structurally characterized manganese(III) complexes,[9–11,15,37] may be postulated for the hitherto isolated manganese(III) complexes in which one of the ligands (H_2L^3 or H_2L^4) acts as a dinegatively charged tridentate and the other ($MeCO_2^-$ or $acac^-$) as a uninegatively charged bidentate chelating agent.

(*d*) *Electronic Spectra.*—Manganese(IV) complexes of series **1** give four-band spectra but series **2** give three-band spectra. Under the octahedral approximation, the bands at *ca.* 730, 580 and 530 nm (Table 2) of the $MnO_2N_2S_2$ core in **1a**–**1c** can be attributed to $^4A_{2g} \longrightarrow {}^4T_{2g}$, $^4A_{2g} \longrightarrow {}^4T_{1g}$ and $4A_{2g} \longrightarrow {}^4T_{1g}$ (P) transitions[1] and the intense band at *ca.* 450 nm to the $S(p_\pi) \rightarrow Mn(d_\pi)$ ligand-to-metal charge-transfer (l.m.c.t.) transition. However, the intense band of **2a**–**2c** at *ca.* 480 nm is assigned to the l.m.c.t. transition while those at *ca.* 730 and 600 nm are assigned to $^4A_{2g} \longrightarrow {}^4T_{2g}$ and $^4A_{2g} \longrightarrow {}^4T_{1g}$ (F) transitions, the $^4A_{2g} \longrightarrow {}^4T_{1g}$ (P) transition being missing as for octahedral and isoelectronic chromium(III) complexes.[7d]

The field-free ^5D term of manganese(III) in a weak O_h field splits into a ^5E_g ground and a $^5T_{2g}$ excited state. Since the ground state is an orbital doublet, Jahn–Teller distortion becomes pronounced giving rise to a five-co-ordinate square-pyramidal situation. To a reasonable approximation, the energy-level diagram is as in Fig. 3 which dictates the occurrence of three d–d transitions assignable to $^5B_1 \longrightarrow {}^5B_2$, $^5B_1 \longrightarrow {}^5A_1$ and $^5B_1 \longrightarrow {}^5E$.[13] Actually, all the manganese(III) complexes **3**–**6** exhibit three d–d bands at *ca.* 720, 600 and 530 nm (Table 2) besides an l.m.c.t. $[S(p_\pi) \rightarrow Mn(d_\pi)]$ band at *ca.* 460 nm. It may be concluded that conceptually and experimentally the manganese-(III) and -(IV) spectra are very much alike and hence, in the absence of magnetic susceptibility and EPR data, they cannot be used as a diagnostic tool. Admittedly, these three-band spectra are not necessarily characteristic of a square-pyramidal structure; highly distorted octahedral complexes* may also show such spectral behaviour. However, the assignments are, as pointed out earlier, based on the fact that a good number of mixed-ligand manganese(III) complexes are square-pyramidal,[9–11,15,37]

Table 3 Cyclic voltammetric[a] data for the complexes

Complex	$E^\circ_{298}/V(Mn^{III} \rightleftharpoons Mn^{IV})$[b]
1a	+0.01 (−0.03, +0.05)[c]
1b	−0.10 (−0.15, −0.06)[c]
1c	+0.13 (+0.08, +0.18)
2a	+0.03 (−0.01, +0.08)
2b	−0.02 (−0.07, +0.02)
2c	+0.14 (+0.09, +0.20)
3a	+0.17 (+0.12, +0.22)
3b	+0.09 (+0.06, +0.13)
3c	+0.27 (+0.23, +0.32)
4a	+0.28 (+0.24, +0.32)
4b	+0.17 (+0.14, +0.20)
4c	+0.38 (+0.35, +0.41)
5a	+0.23 (+0.20, +0.26)
5b	+0.12 (+0.08, +0.16)
5c	+0.29 (+0.26, +0.33)
6a	+0.27 (+0.24, +0.31)
6b	+0.17 (+0.13, +0.22)
6c	+0.37 (+0.34, +0.41)

[a] Solvent dmf, solute concentration *ca.* 10^{-3} mol dm^{-3}, reference electrode SCE. [b] Values in parentheses indicate E_{pc}/V and E_{pa}/V *vs.* SCE, respectively, where $E^\circ_{298} = \frac{1}{2}(E_{pc} + E_{pa})$. [c] Coulometry for complexes **1a** and **1b** was done at −0.23 and −0.35 V respectively.

(*e*) *Electrochemistry.*—Cyclic voltammetry of the isolated manganese-(IV) and -(III) complexes has been studied using a platinum working electrode and NEt_4ClO_4 as supporting electrolyte in dmf. All the complexes exhibit a reversible or quasi-reversible Mn^{IV}–Mn^{III} couple (Fig. 4) in their cyclic voltammograms in the range +0.40 to −0.20 V *vs.* SCE (Table 3). Constant-potential (*ca.* −0.25 V) coulometry of typical manganese(IV) complexes, **1a** and **1b**, indicates that the reduction involves a single electron transfer (n = 0.95)† and the electroreduced solutions are EPR silent as expected in the case of manganese(III) species. The electroreduced solutions show that the electronic band at *ca.* 447 nm of **1a** and **1b** shifts to *ca.* 420 nm, others remaining approximately unchanged. For **3a** also the constant-potential (+0.42 V) coulometry shows a one-electron change (n = 0.95),† but the electrooxidized solution is EPR silent, which may be due to decomposition of the resulting species. This type of instability of manganese(IV) formed upon electrooxidation was found for other related complexes.[38]

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* The possibility of bridging $MeCO_2^-$ or $acac^-$ ligands cannot be emphatically ruled out in the absence of structural data.

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

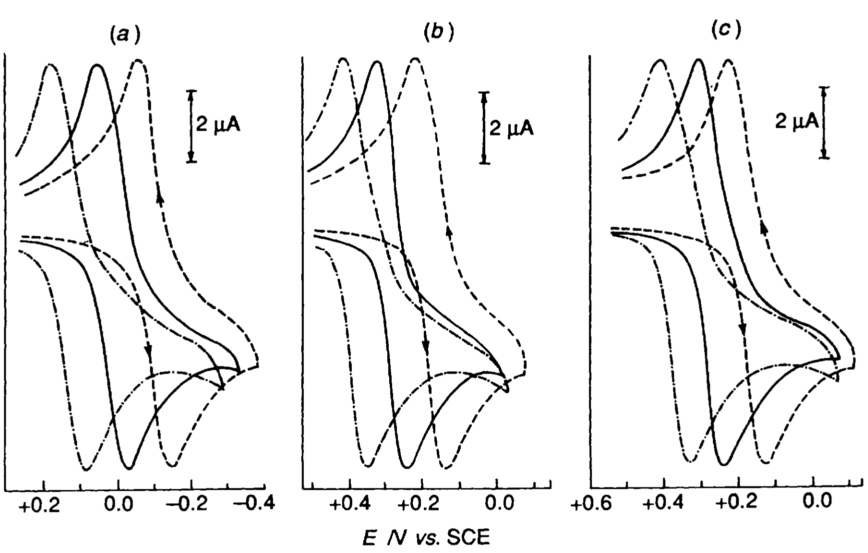

Fig. 4 Cyclic voltammograms for *ca.* 10^{-3} mol dm^{-3} solutions of the complexes in dmf (scan rate 50 mV s^{-1}): [MnL_2][L = L^{1a} (——), L^{1b} (– – – –) or L^{1c} (— · — · —)]; (*b*) [$MnL(O_2CMe)$] [L = L^{4a} (——), L^{4b} (– – – –) or L^{4c} (— · — · —)]; and (*c*) [MnL(acac)] [L as in (*b*)]

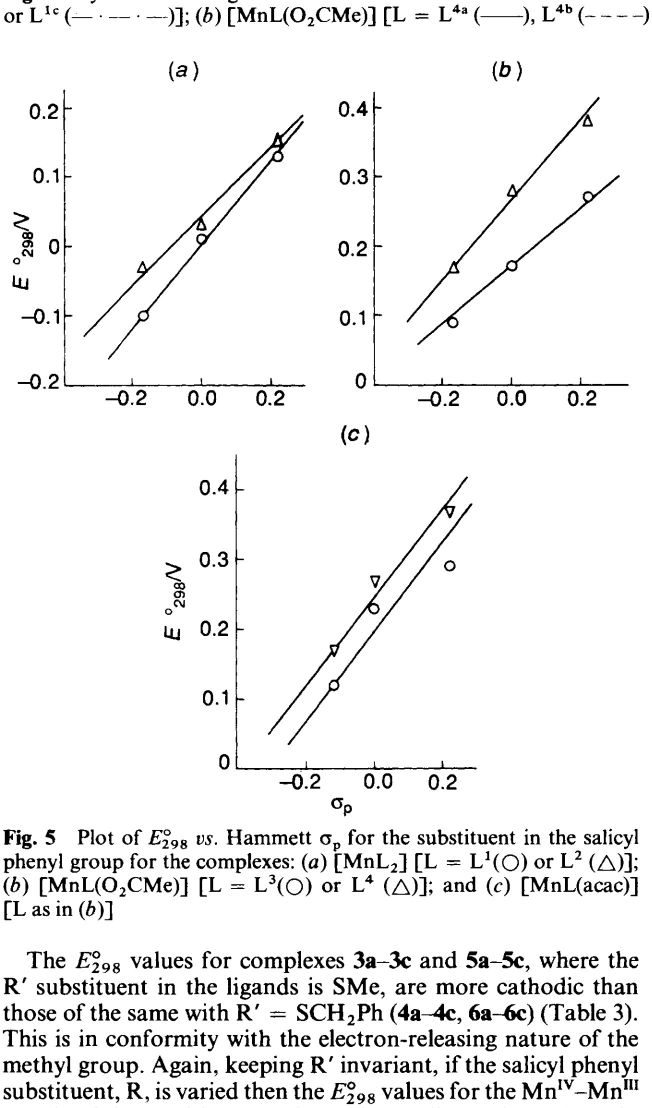

Fig. 5 Plot of E°_{298} *vs.* Hammett σ_p for the substituent in the salicyl phenyl group for the complexes: (*a*) [MnL_2] [L = L^1(○) or L^2 (△)]; (*b*) [$MnL(O_2CMe)$] [L = L^3(○) or L^4 (△)]; and (*c*) [MnL(acac)] [L as in (*b*)]

The E°_{298} values for complexes **3a**–**3c** and **5a**–**5c**, where the R′ substituent in the ligands is SMe, are more cathodic than those of the same with R′ = SCH_2Ph (**4a**–**4c**, **6a**–**6c**) (Table 3). This is in conformity with the electron-releasing nature of the methyl group. Again, keeping R′ invariant, if the salicyl phenyl substituent, R, is varied then the E°_{298} values for the Mn^{IV}–Mn^{III} couple of the resulting complexes show a linear dependence in the expected direction, on the Hammett σ_p parameter of the R substituents[1,39] (Fig. 5).

Conclusion

The dianionic ONS Schiff bases stabilize manganese(IV) as an $MnO_2N_2S_2$ chromophore. An additional thioether group adjacent to the above S-function of the ligand, when R′ is SMe or SCH_2Ph, controls the metal–ligand electron cloud so as to stabilize manganese(III) *via* a heterochelate Mn(ONS)(OO) moiety. The position of the Mn^{IV}–Mn^{III} couple is dependent on both substituents R and R′ of the ligand and a linear and predictable dependence of its potential on the Hammet σ_p parameters of the R substituents in the salicyl phenyl ring exists.

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