complex $Cu_2(bistrien)^{4+}$. The current/potential profile shows two consecutive peaks in reduction, followed, in the reverse scan, by two oxidation peaks. The separation between the peaks in the reduction scan is about 193 mV. The peaks do not shift on the potential axis as a function of scan rate. The intensity of each peak, compared with a monoelectronic standard,[8] would correspond to the addition of 1 e. It is worth noting that the two peaks in reduction are more separate ($\Delta E_{1/2}$ = 190 mV) than those in $Cu_2(bistrien)^{4+}$ ($\Delta E_{1/2}$ = 140 mV) (see Figure 1), indicating that in the $Cu_2(L_1)^{4+}$ complex the reduction of the first Cu(II) is easier than that in the corresponding $Cu_2(bistrien)^{4+}$ complex. The opposite is true for the second Cu(II) ion, which is more easily reduced in $Cu_2(bistrien)^{4+}$. These facts can be related to the overall minor stability of the dinuclear species $Cu_2(L_1)^{4+}$ when compared to that of $Cu_2(bistrien)^{4+}$ and to the possibility that the smaller macrocycle (L_1) forms stable mononuclear species. An anodic peak appears in the oxidation scan at ca. −140 mV whose intensity increases with the decreasing of the scan rate. This peak, which does not disappear even at high scan rate, can be ascribed to anodic stripping due to the oxidation of deposited copper metal.[9] Controlled-potential electrolysis at the potential of the first peak of reduction (−400 mV) causes deposition of copper metal, which plates the platinum electrode surface. This suggests that the $Cu^{II}Cu^{I}(L_1)^{3+}$ species is unstable with respect to the disproportionation by which copper metal is produced. In the case of $Cu_2(bistrien)^{4+}$ the anodic stripping peak appears only at low scan rate, and deposition of copper metal by controlled-potential electrolysis only occurs in correspondence with the second reduction peak when the $Cu^{I}Cu^{I}(bistrien)^{2+}$ species is present.

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Registry No. A, 111-40-0; B, 56187-04-3; C, 74461-29-3; D, 97783-00-1; E, 112-24-3; F, 55442-07-4; H, 52601-76-0; L_1, 296-85-5; $(L_1)\cdot 7HCl$, 56187-10-1; $Cu_2(L_1)Cl(ClO_4)_3$, 97783-02-3.

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Manganese(IV) in Discrete O_3S_3 Coordination

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Trivalent and tetravlent manganese are implicated in photosynthetic oxygen evolution.[1,2] The chemistry[3] of these oxidation states is therefore of particular interest. Surprisingly few well-characterized *discrete mononuclear* manganese(IV) species are known at present. Among these just two tris chelate types occur—$Mn^{IV}O_6$ in sorbitolato[4] and catecholato[5,6] species and $Mn^{IV}S_6$ in dithiocarbamates.[7-9] In the present work we describe the intermediate type, $Mn^{IV}O_3S_3$, furnished by thiohydroxamic acids. Because of the siderophoric role of such acids their transition-metal chemistry,[10,11] including that of manganese(II,III),[12,13] has received recent attention.

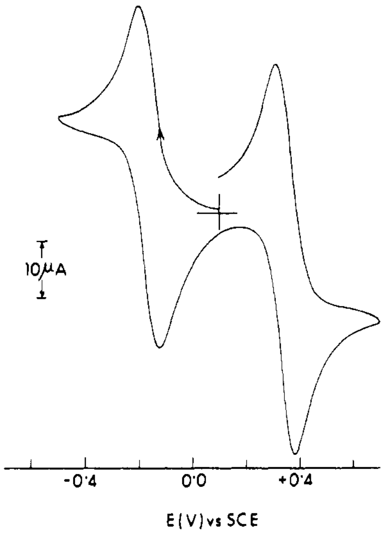
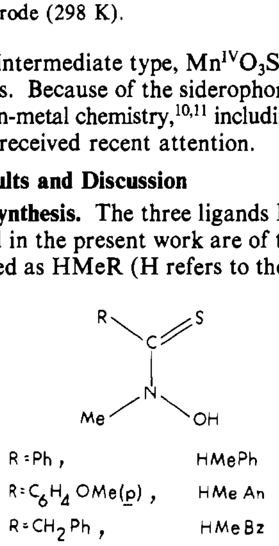


Figure 1. Cyclic voltammogram (scan rate 50 mV s^{-1}) of ~10^{-3} M solution of $Mn(MePh)_3$ in acetonitrile (0.1 M TEAP) at a platinum electrode (298 K).

Results and Discussion

Synthesis. The three ligands HMePh, HMeAn, and HMeBz used in the present work are of type **1** and are generally abbreviated as HMeR (H refers to the dissociable OH proton). The manganese(IV) complexes $Mn(MeR)_3^+$ are furnished in high yield by dichlorine oxidation of $Mn(MeR)_3$ in acetonitrile solution and are isolated as dark-colored hexafluorophosphates. The manganese(III) precursor is synthesized either as reported[12,13] or by the essentially quantitative displacement reaction (1) carried out in ethanol at room temperature (Hacac = acetylacetone).



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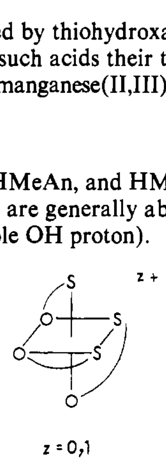

2

$$Mn(acac)_3 + 3HMeR \rightarrow Mn(MeR)_3 + 3Hacac \qquad (1)$$

In solution $[Mn(MeR)_3]PF_6$ behaves as a 1:1 electrolyte and its magnetic moment conforms to the d^3 configuration. Selected

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Table I. The Complexes and Their Physical Data

R in $[Mn(MeR)_3]PF_6$	molar conductivity[a] Λ_M, Ω^{-1} cm^2 M^{-1}	bulk susceptibility (298 K) μ_{eff}, μ_B	UV-vis data[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})
Ph	140	4.08	575 (2370), 410[b] (4800), 285[b] (16 940), 255 (20 770)
An	123	4.02	580[b] (3520), 410 (8980), 348 (45 370)
Bz	112	4.09	570 (1250), 460[b] (1100), 312[b] (6850), 260 (16 140)

[a] The solvent is acetonitrile. [b] Shoulder.

Table II. Manganese(IV)–Manganese(III) and Manganese(III)–Manganese(II) Formal Potentials[a] and Manganese(IV) EPR Data for $[Mn(MeR)_3]PF_6$

R	$E°_{298}$,[b] V (n[c])	g values
Ph	0.31 (0.95),[d] −0.21 (0.96)[e]	2.013, 4.441;[h] 1.991, 4.386;[i] 1.983, 4.330[j]
An	0.21 (1.01),[f] −0.29 (1.02)[g]	2.007, 4.361;[h] 2.009, 4.400;[i] 1.986, 4.226[j]
Bz	0.21 (0.97),[f] −0.32 (0.94)[g]	2.009, 4.226;[h] 2.016, 4.236;[i] 2.009, 4.324[j]

[a] Collected in acetonitrile solutions of $Mn(MeR)_3$ with use of a platinum working electrode at 298 K; supporting electrolyte TEAP (0.1 M), sandard SCE. [b] Cyclic voltammetric data at scan rate of 50 mV s^{-1}; solute concentration ~10^{-3} M. $E°_{298}$ is calculated as the average of anodic and cathodic peak potentials. [c] $n = Q/Q'$ where Q' is the calculated coulomb count for 1e transfer and Q is the observed coulomb count after exhaustive electrolysis of 0.01 mmol of solute. [d] Coulometry was done at +0.51 V. [e] Coulometry at −0.41 V. [f] Coulometry at 0.41 V. [g] Coulometry at −0.52 V. [h] Powder at 298 K. [i] Powder at 77 K. [j] In acetonitrile solution at 77 K.

data including absorption spectra are in Table I. Since ligand **1** is unsymmetrical, the tris chelates can in principle occur in facial and meridional forms. From X-ray work $Mn^{III}(MePh)_3$ is known[13] to have the facial structure (**2**, $z = 0$). Significantly, the IR spectrum (4000–400 cm^{-1}) of $[Mn^{IV}(MePh)_3]PF_6$ is superposable on those of facial[13] $M^{III}(MePh)_3$ (M = Cr, Mn, Co) except for small shifts of frequencies and appearance of a strong band at 840 cm^{-1} assignable to the PF_6^- anion. This may indicate that the manganese(IV) complex has the same stereochemistry as that of the trivalent counterpart.

Redox Behavior and Stereochemistry. Both manganese(IV)–manganese(III) and manganese(III)–manganese(II) couples are observable by cyclic voltammetry in acetonitrile solution at a platinum working electrode (Figure 1). Coulometric data confirm the one-electron character of couples 2 and 3 (Table II). The

$$Mn^{IV}(MeR)_3^+ + e^- \rightleftharpoons Mn^{III}(MeR)_3 \quad (2)$$

$$Mn^{III}(MeR)_3 + e^- \rightleftharpoons Mn^{II}(MeR)_3^- \quad (3)$$

yellow solution of $Mn^{II}(MeR)_3^-$ is unstable, and it has not been isolated as a pure salt. The $E°_{298}$ values of R = An species are lower than those of R = Ph, reflecting the electron-releasing nature of the methoxy group.

Couple 2 is ideally reversible with peak-to-peak separation (ΔE_p) of 60 mV while couple 3 is somewhat less reversible (ΔE_p = 80–120 mV). This suggests that all three species may have the same gross stereochemistry in solution.

EPR Spectra. The formal symmetry of **2** can be C_3 or lower. The X-band EPR spectrum of $Mn(MeR)_3^+$, however, reveals that the effective electronic environment of manganese(IV) lies close to the ideally octahedral situation. Spectra were run in powder form (298, 77 K) as well as in dilute frozen solutions (77 K). The major feature is the same in all cases: a strong signal at $g \approx 2$ and a weak broad signal at lower field ($g \approx 4$) (Figure 2; Table II). The $g \approx 2$ signal displays well-resolved ^{55}Mn hyperfine structure ($A \approx 100$ G; compare $A \approx 95$ G for $Mn^{IV}S_6$ in dithiocarbamates[9]) in frozen solution.

The nature and complexity of powder and frozen-solution EPR spectra of d^3 ions depend on the zero-field splitting parameters.[14-16]

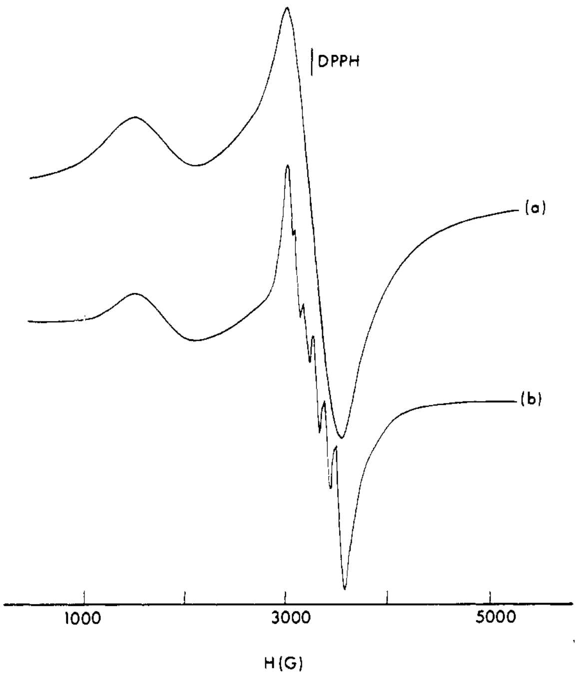

Figure 2. EPR spectra of $[Mn(MePh)_3]PF_6$: (a) in powder form at 77 K; (b) in acetonitrile solution at 77 K.

Particular simplification occurs when the axial parameter D takes the limiting forms $2D >> h\nu$ or $2D << h\nu$ ($h\nu = 0.31$ cm^{-1} at X-band). In the former case two signals occur: $g \approx 2$ (weak) and $g \approx 4$ (strong). In the latter case[16,17] the dominating signal is at $g \approx 2$ attended by one or more weak broad signal(s) at low fields (1000–1500 G). In the extreme limit of $D = 0$ (perfect octahedron), the spectrum becomes isotropic with a single signal at $g \approx 2$ (e.g. K_2MnCl_6[4]). The observed spectrum of $Mn(MeR)_3^+$ is thus in accord with small zero-field splitting.

Concluding Remarks. The tris(thiohydroxamato)manganese(IV) cation[18] is readily obtained by dichlorine or electrochemical oxidation of the manganese(III) congener. Its similarity to the tris(dithiocarbamato)manganese(IV) cation is indeed striking. First, metal-centered redox potentials[7] of the two groups are comparable. Second, both species have small zero-field splitting.[9] In contrast, the sorbitolato and catecholato complexes of manganese conform to the $2D >> h\nu$ situation (strong EPR signal

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(18) A reviewer noted that $Mn(MeR)_3^+$ may actually be a manganese(II) complex of ligand radicals—i.e., $Mn^{II}(MeR)(MeR\cdot)_2^+$—the unpaired electron of each MeR· being assumed to be paired with a manganese(II) spin, affording the $S = {}^3/_2$ ground state. This description is unrealistic. First, $Mn(MeR)_3$ is certainly[13] a manganese(III) complex and *not* $Mn^{II}(MeR)_2(MeR\cdot)$ as it would be in the reviewer's frame of description. Taking $Mn(MeR)_3$ as a manganese(III) complex and $Mn(MeR)_3^+$ as a manganese(II) complex would mean that, on oxidation of the former, the metal is actually reduced and both oxidation equivalents get concentrated on the ligands. This is chemically unacceptable. Second, free thiohydroxamic acids display an irreversible cyclic voltammetric oxidation at ~1.3 V (vs. SCE), and $Zn(MeR)_2$ behaves similarly.[19] Thus ligand oxidation occurs at much higher (by ≥1 V) potential than those used to achieve the oxidations corresponding to couples 2 and 3. We also note that the responses due to these couples remain unaffected on addition of free ligand (even in excess) to the voltammetric solution of Figure 1. Last, we stress that thiohydroxamates are well suited for stabilizing higher oxidation states as in the case of ruthenium[11] and other transition-metal ions.[19]

(19) Ray, D.; Pal, S.; Chakravorty, A., unpublished results.

at $g \approx 4$).[4-6] A soft ligand core (S_6 and S_3O_3 vs. O_6) appears to favor an effectively more symmetrical electronic environment around manganese(IV).

Experimental Section

Starting Materials. Thiohydroxamic acids (HMePh, HMeAn, HMeBz) were prepared[20] from appropriate dithiocarboxy methyl esters[21] and *N*-methylhydroxylamine. Tris(acetylacetonato)manganese(III) was made as reported.[22] Electrochemically pure acetonitrile and tetraethylammonium perchlorate were obtained as before.[23] All other solvents and chemicals used were of analytical grade available commercially.

Physical Measurements. Solution electrical conductivity and electronic and infrared spectra were recorded with a Philips PR9500 bridge and Hitachi 330 and Perkin-Elmer 783 spectrophotometers, respectively. Magnetic susceptibility was measured in a Princeton Applied Research (PAR) Model 155 vibrating-sample magnetometer. Electrochemical measurements were made with the help of a PAR Model 370-4 electrochemistry system incorporating the following components: 174A, polarographic analyzer; 175, universal programmer; RE0074, X-Y recorder; 173, potentiostat; 179, digital coulometer; 377A, cell system. Measurements were carried out under a dry and purified dinitrogen atmosphere. A planar Beckman Model 39273 platinum-inlay working electrode, platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in the three-electrode measurements. A platinum wire-gauge working electrode was used in coulometric experiments. All electrochemical data were obtained at 298 K and are uncorrected for junction potentials. X-band EPR spectra were recorded with a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). The spectra were calibrated with the help of DPPH ($g = 2.0037$). The microwave power level was maintained at around 0.2 mW.

Preparation of Complexes. The utility of reaction 1 is illustrated below with a specific example.

Tris(*N*-methyl-*p*-methoxybenzothiohydroxamato)manganese(III), Mn(MeAn)$_3$. To an ethanolic solution (20 mL) of HMeAn (0.6 g, 0.003 mol) was added an ethanolic solution (20 mL) of tris(acetylacetonato)manganese(III) (0.36 g, 0.001 mol), and the mixture was stirred at room temperature for $^1/_2$ h. The green solution was then evaporated, and a residue obtained was dissolved in benzene followed by slow addition of petroleum spirit (60-80 °C) with stirring. The green precipitate formed was collected by filtration. The process of dissolution in benzene and precipitation by petroleum spirit was repeated for another three times to obtain pure compound: yield 0.59 g (90%). Anal. Calcd for $MnC_{27}H_{30}N_3O_6S_3$: Mn, 8.55; C, 50.39; H, 4.67; N, 6.53. Found: Mn, 8.61; C, 50.60; H, 4.90; N, 6.20.

Tris(*N*-methyl-*p*-methoxybenzothiohydroxamato)manganese(IV) Hexafluorophosphate, [Mn(MeAn)$_3$]PF$_6$. Through an acetonitrile solution (25 mL) of Mn(MeAn)$_3$ (0.2 g, 0.31 mmol) was passed pure dry, Cl_2 gas until the green color changed to red-brown. To this solution was added excess NH_4PF_6, and the solution was allowed to evaporate at room temperature. The dark precipitated complex was collected by filtration, washed thoroughly with water, and dried under vacuum over P_4O_{10}. It was recrystallized from acetonitrile: yield 0.19 g (80%). Anal. Calcd for $MnC_{27}H_{30}N_3O_6S_3PF_6$: Mn, 6.97; C, 41.12; H, 3.81; N, 5.33. Found: Mn, 7.02; C, 41.33; H, 3.93; N, 5.54. The complexes [Mn(MePh)$_3$]PF$_6$ (yield 83%) and [Mn(MeBz)$_3$]PF$_6$ (yield 72%) were prepared by the same procedure as described above with use of the ligands HMePh and HMeBz, respectively, in place of HMeAn. Anal. Calcd for [Mn(MePh)$_3$]PF$_6$, $MnC_{24}H_{24}N_3O_3S_3PF_6$: Mn, 7.87; C, 41.27; H, 3.44; N, 6.02. Found: Mn, 7.83; C, 41.40; H, 3.50; N, 5.84. Anal. Calcd for [Mn(MeBz)$_3$]PF$_6$, $MnC_{27}H_{30}N_3O_3S_3PF_6$: Mn, 7.43; C, 43.79; H, 4.06; N, 5.68. Found: Mn, 7.48; C, 43.44; H, 4.17; N, 5.80.

Acknowledgment. We thank the Department of Science and Technology, Government of India, New Delhi, India, for financial support.

Registry No. Mn(MeAn)$_3$, 97825-97-3; [Mn(MeAn)$_3$]PF$_6$, 97825-99-5; [Mn(MePh)$_3$]PF$_6$, 97826-01-2; [Mn(MeBz)$_3$]PF$_6$, 97826-03-4; Mn(MePh)$_3$, 97826-04-5; Mn(MeBz)$_3$, 97826-05-6; Mn(acac)$_3$, 14284-89-0.

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Magnetic Properties of (2,3-Pyrazinedicarboxylato)copper(II) Hydrochloride: Another Look, at Lower Temperatures

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Received November 9, 1984

The *prediction* by O'Connor et al.[1] that CuL·HCl, where H_2L = 2,3-pyrazinedicarboxylic acid, is a ferromagnetic linear chain was based on the observation that the Curie-Weiss fit of magnetic susceptibility data (6-300 K) gave a positive Weiss constant ($\Theta = +1.4$ K) and that an X-ray crystal structure determination showed the molecule to crystallize in linear chains. A fit of the data to the Bonner-Fisher model was diagnostically inconclusive since the lack of data in the important low-temperature range precluded a definitive assignment of magnetic dimensionality.

In order to determine with greater precision the magnetic model that best describes the behavior of this complex, the magnetic susceptibility has now been measured to lower temperatures. We find no evidence for linear-chain behavior but, contrarily, that the substance undergoes three-dimensional magnetic ordering.

Experimental Section

The polycrystalline sample used was prepared as earlier.[1] It appeared clear, without decomposition. Measurements in the ^{4}He region were made in a glass cryostat in which each data point was calibrated against CMN. Measurements at lower temperatures were made in a dilution refrigerator. Our procedures have been described previously.[2,3]

Results and Discussion

The data above 3 K may be fit by the Curie-Weiss law for $S = {}^1/_2$ with $\langle g \rangle = 2.17 \pm 0.02$ and $\Theta = 1.17 \pm 0.02$ K, but this may be an unreliable analysis because the temperatures of measurement are of the same order as Θ.

The data (1.1-4.2 K) are displayed together with the later low-temperature measurements in Figure 1 along with several calculated fits. It has been found to be impossible to fit the data to a Heisenberg linear-chain model, $S = {}^1/_2$, with ferromagnetic interaction. Beyond the calculation illustrated in the figure, one knows[4] that χT must diverge as $T^{-2/3}$ for such a magnetic model; the measured values have a much stronger divergence at low temperature.

Several other linear-chain models were examined, such as with the introduction of some spin anisotropy as well as a lattice anisotropy. Even in the limit of the completely anisotropic linear chain (the Ising case), with an exponential divergence at low temperatures, values smaller than the experimental ones are found. Furthermore, copper(II) is well-known to exhibit very small spin anisotropy. None of these calculations were found to improve the fit. We were surprised however by the result that the data can be fitted perfectly in the limit of Heisenberg linear-chain calculation with a molecular field correction of the same magnitude. In other words, contrary to the earlier suggestion,[1] the data may be fit with the three-dimensional, $S = {}^1/_2$ Heisenberg magnetic model.

In view of the above results, measurements were then carried out to lower temperatures. Two rather sharp peaks are observed at temperatures below 1 K, as shown in Figure 2. The first is at 0.770 ± 0.015 K, and the second is at 0.470 ± 0.005 K. Large values of the susceptibility are found at each maximum, 21.9 and 23.3 emu/mol, respectively. These peaks correspond to long-range ordering and occur at what will be referred to, respectively, as

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[‡] University of New Orleans.
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