Notes

First Examples of Carboxyl-Bonded Low-Spin Manganese(III) Complexes

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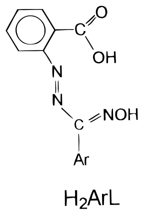
Introduction

We have been interested in realizing uncommon spin-configurations of 3d ions with the help of suitably designed ligands.[1−4] The ion of specific concern here, manganese(III), is generally high-spin ($s = 2$; $3d^4$) but for a few exceptions.[2,5,6] In particular, *all members* in the large family of complexes incorporating $Mn^{III}-O$(carboxylate) binding are high-spin.[7] Herein we describe the first group of carboxyl-coordinated low-spin manganese(III) complexes.

Results and Discussion

Synthesis and Characterization. The three ligands used are of the general type H_2ArL, **1**. The 1:2 reaction of $Mn(MeCO_2)_2\cdot 4H_2O$ with H_2ArL in methanol containing Et_4NCl furnished dark-colored $Et_4N[Mn^{III}(ArL)_2]$ in excellent yields. The bivalent complex $[Mn^{II}(ArL)_2]^{2-}$ is first formed in solution and is then oxidized by aerial oxygen (*vide infra*). Selected characterization data of the complexes are given in Table 1. These are low-spin, behave as 1:1 electrolytes ($\Lambda = 70-90$ Ω^{-1} cm^2 M^{-1} in dimethylformamide), and display moderately intense charge transfer absorptions in the visible region.



Ar	H_2ArL
phenyl	H_2PhL
p-tolyl	H_2ToL
α-naphthyl	H_2NpL

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Crystal and Molecular Structure. The X-ray structure of $Et_4N[Mn(PhL)_2]$ has been determined. A view of the complex is shown in Figure 1 and selected bond parameters are collected in Table 2. The metal lies on a crystallographic 2-fold axis and the tridentate ligand binds meridionally via oximato-*N*, azo-*N*, and carboxyl-*O* atoms. The two carboxyl C−O lengths are unequal, C−OMn being ∼0.07 Å longer than C═O. The *cis*-MnN_4O_2 coordination sphere is severely distorted from octahedral geometry. The five-membered chelate ring is satisfactorily planar (mean deviation 0.04 Å) and makes a dihedral angle of 16.9° with the pendent phenyl ring. The six-membered chelate ring is puckered (inset in Figure 1).[8]

The Mn−N(oxime) length 1.950(7) Å is marginally longer than Mn−N(azo) length 1.929(6) Å, the shortest metal−ligand bond being Mn−O(carboxylate) 1.906(7) Å. Thus all the Mn−ligand bond lengths are <2 Å. In high-spin manganese(III) complexes, Mn−N and Mn−O(carboxylate) bond lengths generally exceed 2 Å.[7e,9] Evidently the metal radius has significantly contracted upon spin-pairing.[10]

Spin and Oxidation States: Dual Control by Coordinating Functions. The paramagnetic moment of $Et_4N[Mn(ArL)_2]$ (2.9 u_B, Table 1) corresponds to $s = 1$ (idealized $^3T_1$ ground state). The variable temperature moment of $Et_4N[Mn(PhL)_2]$ displayed in Figure 2 reveals a steep decrease at low temperature due to mutual cancellation of orbital and spin moments.[5a,11] The complexes are EPR-silent which is normal for the $t_2{}^4$ configuration.[2]

Carboxyl coordination alone cannot lead to low-spin manganese(III) because of the high spin-pairing energy of the metal[12] and the weak-field nature of the carboxyl group.[13] On the other hand the azo-oxime function strongly promotes spin-pairing as demonstrated for trischelated manganese(II)—such chelation, however, fails to stabilize manganese(III).[3b,c] In H_2ArL the azo−oxime and carboxylate functions together produce the desired effects—the former promotes spin-pairing and the latter stabilizes manganese(III) by lowering reduction potentials. We have recently shown that the H_2ArL ligands are also effective in inducing low-spin character in iron(III).[4]

Metal Redox: Status of $[Mn^{II}(ArL_2)]^{2-}$. Dimethylformamide solutions of $Et_4N[Mn(ArL)_2]$ display a nearly reversible

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(8) The ligand frame (the pendent phenyl ring excluded) is nonplanar as a whole but has three planar segments: plane A, five-membered chelate ring; plane B, the benzene ring; and plane C, the carboxyl function. The dihedral angles between A and B and between B and C are respectively 17.6 and 10.0°.

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Table 1. Electrochemical Data,[a–f] Electronic Spectral Data,[a,g] and Magnetic Moments[h] at 298 K

compounds	$E_{1/2}$,[c] V (ΔE_p,[d] mV); n[e,f]	UV−vis data: λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)	μ_{eff}, μ_B
$Et_4N[Mn(PhL)_2]$	−0.065 (70); 1.01	840 (2560), 675[g] (2390), 550[g] (4620), 480 (5680)	2.83
$Et_4N[Mn(NpL)_2]$	−0.090 (100); 0.98	850 (2100), 675[g] (1950), 550[g] (3810), 480 (4760)	2.92
$Et_4N[Mn(ToL)_2]$	−0.125 (90); 1.02	850 (2390), 675[g] (2450), 550[g] (4450), 480 (5830)	2.90

[a] In dimethylformamide. [b] At a platinum disk electrode; supporting electrolyte tetraethylammonium perchlorate (TEAP, 0.1 M); scan rate 50 mV s^{-1}; reference electrode SCE; solute concentration ~10^{-3} M. [c] $E_{1/2}$ is calculated as the average of anodic (E_{p_a}) and cathodic (E_{p_c}) peak potentials. [d] $\Delta E_p = E_{p_a} - E_{p_c}$. [e] $n = Q/Q'$, where Q is the observed coulomb count and Q' is the calculated count for 1e transfer. [f] Constant potential electrolysis performed at 200 mV below E_{p_c} for reduction and 200 mV above E_{p_a} for oxidation. [g] Shoulder. [h] In solid state.

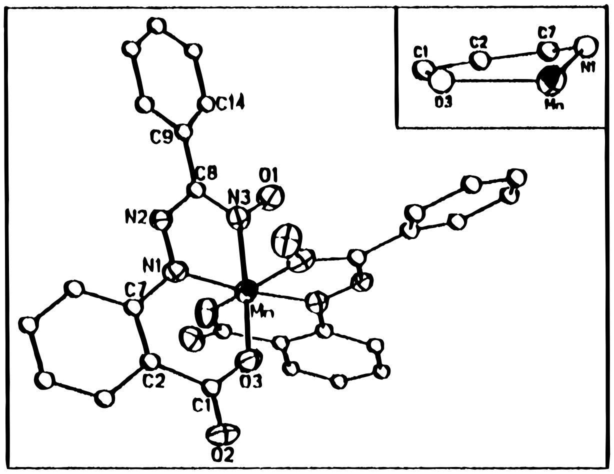

Figure 1. Perspective view and atom-labeling scheme for the anion of $Et_4N[Mn(PhL)_2]$ with atoms other than carbon represented by their 30% probability ellipsoids. The MnC_3NO chelate ring is shown in the inset.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Et_4N[Mn(PhL)_2]$

Distances			
Mn−N(1)	1.929(6)	N(2)−C(8)	1.338(11)
Mn−N(3)	1.950(7)	N(3)−C(8)	1.365(11)
Mn−O(3)	1.906(7)	O(1)−N(3)	1.265(10)
N(1)−N(2)	1.302(10)	O(2)−C(1)	1.218(11)
N(1)−C(7)	1.410(10)	O(3)−C(1)	1.290(11)

Angles			
N(1)−Mn−N(1A)	173.4(5)	N(3)−Mn−O(3A)	91.3(3)
N(1)−Mn−N(3)	79.1(3)	O(3)−Mn−N(1)	91.7(3)
N(1)−Mn−O(3A)	92.7(3)	O(3)−Mn−N(3)	168.4(3)
N(3)−Mn−N(1A)	95.9(3)	O(3)−Mn−O(3A)	96.2(4)
N(3)−Mn−N(3A)	82.7(4)	O(3A)−Mn−N(3A)	168.4(3)

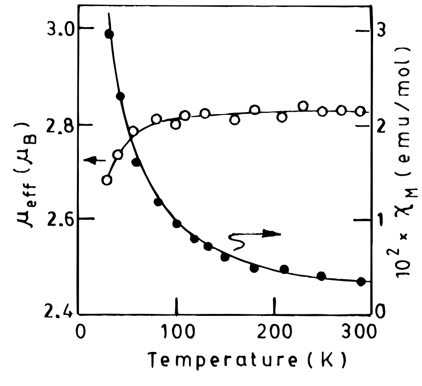

Figure 2. Plots of the magnetic moment μ_{eff} (μ_B) and the magnetic susceptibility χ_M (emu/mol) against temperature T (K) for $Et_4N[Mn(PhL)_2]$.

cyclic voltammetric response (Table 1) corresponding to eq 1.

$$[Mn^{III}(ArL)_2]^- + e^- \rightleftharpoons [Mn^{II}(ArL)_2]^{2-} \qquad (1)$$

Exhaustive electrolysis at −0.3 V afforded a brown solution of $[Mn(ArL)_2]^{2-}$ which showed the same voltammogram (initial scan anodic) as that of $[Mn(ArL)_2]^-$ (initial scan cathodic). Coulometric reoxidation of the brown solution at 0.1 V quantitatively regenerated $[Mn(ArL)_2]^-$. The same result is obtained upon exposing the reduced solution to air. This is consistent with the low $E_{1/2}$ value (~−0.1 V) of the couple of eq 1. The formation of $[Mn^{III}(ArL)_2]^-$ from the reaction of H_2ArL with Mn^{II} salts in air is thus understandable.

Solutions of $[Mn(ArL)_2]^{2-}$ can also be generated by reducing $[Mn(ArL)_2]^-$ with hydrazine hydrate. We have not succeeded in isolating it as solid salts but solution EPR results (X-band) suggest the rare[3] low-spin configuration (t_2^5). The $[Mn(ToL)_2]^{2-}$ is representative. In dimethylformamide solution its isotropic (298 K) spectrum consists of six hyperfine lines ($g_{iso} = 2.028$, $A_{iso} = 100$ G). When the sample is frozen (77 K), a well-resolved anisotropic spectrum results: $g_1 = 2.038$, $A_1 = 130$ G; $g_2 = 2.035$, $A_2 = 140$ G; $g_3 = 2.011$, $A_3 \leqslant 20$ G ($g_{av} = 2.028$, $A_{av} \sim 100$ G). In contrast to this, polycrystalline anisotropic spectra of rhombic high-spin manganese(II) complexes are generally quite broad and complex with g values spreading over a very wide region.[14]

Concluding Remarks. The first family of low-spin ($s = 1$) carboxyl-bonded manganese(III) complexes $Et_4N[Mn^{III}(ArL)_2]$ has been synthesized. The contraction of metal radius upon spin-pairing is clearly revealed in Mn−N and Mn−O bond length data. The ligand plays a dual role: it creates high ligand-field strength via azo−oxime chelation and it stabilizes manganese(III) by carboxyl coordination. The $[Mn^{III}(ArL)_2]^-/[Mn^{II}(ArL)_2]^{2-}$ reduction potential is ~−0.1 V. The EPR parameters of $[Mn(ArL)_2]^{2-}$, generated in solution, suggest low-spin character ($s = {}^1/_2$).

Experimental Section

Physical Measurements. A Hitachi 330 spectrophotometer was used to record UV−vis spectra. EPR spectra were studied with a Varian E-109C spectrometer fitted with a quartz dewar, and a flat cell was used to record solution EPR spectra in dimethylformamide solution at 298 K. Frozen glass (77 K) spectra were taken with a normal quartz tube. Room temperature magnetic susceptibilities were measured with Model 155 PAR vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Variable temperature (30−300 K) data were collected with a George Associates Model 300 Lewis coil force magnetometer. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (CHN). Electrochemical measurements were performed under nitrogen atmosphere on a PAR 370-4 electrochemistry system using solvents and supporting electrolyte purified/prepared as before.[1a,15] The reference electrode was saturated calomel electrode (SCE). Solution electrical conductivities were measured with the help of a Philips PR 9500 bridge, the solute concentration being ~10^{-3} M.

Synthesis of Ligands and Complexes. The ligands were synthesized as previously described.[4] The complexes were synthesized by a general method. Details for one representative case are given below.

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Table 3. Crystallographic Data for $Et_4N[Mn(PhL)_2]$

chem formula	$C_{36}H_{38}N_7O_6Mn$	T, °C	23
fw	719.7	λ, Å	0.710 73
space group (No.)	*Pbcn* (60)	ϱ_{obsd}, g cm^{-3}	1.378
a, Å	12.618(4)	ϱ_{calcd}, g cm^{-3}	1.384
b, Å	20.033(8)	μ, cm^{-1}	4.39
c, Å	13.665(8)	R^a %	5.95
V, Å^3	3454(3)	R$_w$,^{b} %	6.33
Z	4		

^{a} $R = \sum||F_o - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0001$ for $Et_4N[Mn(PhL)_2]$.

Tetraethylammonium Bis[((2-carboxylatophenyl)azo)benzaldoximato]manganese(III), $Et_4N[Mn(PhL)_2]$. The complex was prepared by adding a methanolic solution (10 mL) of H_2PhL (0.11 g, 0.40 mmol) containing Et_4NCl (0.04 g, 0.25 mmol) to a solution containing manganese(II) acetate tetrahydrate (0.05 g, 0.20 mmol). The mixture was stirred at room temperature for 1 h. The deposited dark crystalline solid (solution color:pink-brown) was filtered off, washed several times with aqueous methanol (1:1), and dried in vacuo over $CaCl_2$. Yield: 0.11 g (75%). Anal. Calcd for $Et_4N[Mn(PhL)_2]$, $C_{36}H_{38}N_7O_6Mn$: C, 60.08; H, 5.28; N, 13.63. Found: C, 60.14; H, 5.17; N, 13.72.

Anal. Calcd for $Et_4N[Mn(ToL)_2]$, $C_{38}H_{42}N_7O_6Mn$: C, 61.05; H, 5.62; N, 13.12. Found: C, 61.09; H, 5.54; N, 13.04. Anal. Calcd for $Et_4N[Mn(NpL)_2]$, $C_{44}H_{42}N_7O_6Mn$: C, 64.47; H, 5.13; N, 11.97. Found: C, 64.41; H, 5.22; N, 11.89.

X-ray Structure Determination. A crystal of $Et_4N[Mn(PhL)_2]$ (0.40 × 0.35 × 0.24 mm^3) grown by slow diffusion of methanol into dimethylformamide solution was used. The unit cell parameters were determined by the least-squares fit of 30 machine centered reflections having 2θ values in the range 15−25°. Data were collected at 296 K by the ω-scan method over the 2θ range 3−52° on a Nicolet R3m/V diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The upper 2θ limit was subsequently lowered to 45° because of the paucity of observed reflections at higher angles. Two check reflections measured after every 98 reflections showed no significant intensity reduction during 26.5 h of exposure to X-rays. All data were corrected for Lorentz−polarization effects. Absorption coefficient is small (4.39 cm^{-1}) and no absorption correction was made. Of 2750 unique reflections 1069 satisfying $I > 3.0\sigma(I)$ were used for structure solution by direct methods. The Mn, O, and N atoms were made anisotropic (data-to-parameter ratio, 7.37). Hydrogen atoms were added at calculated positions with $U = 0.08$ Å^2 in the last cycle of refinement. Significant crystal data are listed in Table 3. Computations were carried out on a MicroVAX II computer using the SHELXTL-PLUS program package[16] and crystal structure plots were drawn using ORTEP.[17]

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Supporting Information Available: Tables of crystallographic data (Table S1), complete atomic coordinates (Table S2), bond distances (Table S3) and angles (Table S4), anisotropic thermal parameters (Table S5), and hydrogen atom positional parameters (Table S6) for $Et_4N[Mn(PhL)_2]$ (5 pages). Ordering information is given on any current masthead page.

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