nomers and oligomers in metal vapor reactions surveying a thermal gradient varying from 12 to 300 K. In the context of the M_n/DC 510 work, a series of control experiments were performed which demonstrated that metal atoms are unreactive toward substituents (ether linkages, Si–O, C–H, etc.) other than the arene. In addition an experiment was designed which demonstrated that molybdenum atoms can be used to quantitatively titrate $(arene)_2Mo$ dissolved in an unreactive liquid polymer, exemplified by poly(dimethylsiloxane), DC 200. The product in DC 200 absorbed at 418 nm, identical in position with the Mo/DC 510 concentration-dependent absorption, thereby providing further credence for the binuclear formulation $(arene)_nMo_2$.

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Registry No. $HO(CH_2CH_2O)_6H$, 2615-15-8; $HO(CH_2CH_2O)_2H$, 111-46-6; $BrCH_2CH_2OCH_2CH_2Br$, 5414-19-7; $TsO(CH_2CH_2O)_6Ts$, 42749-27-9; TsCl, 98-59-9; $C_6H_5O(CH_2CH_2O)_6C_6H_5$, 20740-88-9; C_6H_5OH, 108-95-2; $C_6H_5O(CH_2CH_2O)_4C_6H_5$, 20768-77-8; $C_6H_5O(CH_2CH_2O)_5C_6H_5$, 20612-83-3; $CH_3C_6H_4O(CH_2CH_2O)_7C_6H_4CH_3$, 102073-92-7; $C_6H_5O(CH_2CH_2O)_7C_6H_5$, 20740-89-0; CH_3-*p*-C_6H_4-$(CH_2)_{10}C_6H_4$-*p*-CH_3, 102073-91-6; *p*-$BrC_6H_4CH_3$, 106-38-7; $Br(CH_2)_{10}Br$, 4101-68-2; $CH_3O(CH_2CH_2O)_4Ts$, 62921-76-0; $CH_3O(CH_2CH_2O)_4C_6H_5$, 80392-31-0; V, 7440-62-2; Cr, 7440-47-3; Mo, 7439-98-7; $CH_3O(CH_2CH_2O)_4H$, 23783-42-8; $CH_3O(CH_2CH_2O)_4CH_3$, 143-24-8; $C_{10}H_{21}OCH_3$, 7289-52-3; Santovac-5, 2455-71-2; 1,3-diphenylbutane, 1083-56-3; phenyldecane, 104-72-3; benzene, 71-43-2; toluene, 108-88-3.

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Bis(nitroxyl) Adducts of Bis(hexafluoroacetylacetonato)manganese(II). Preparation, Structures, and Magnetic Properties

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Adducts of bis(hexafluoroacetylacetonato)manganese(II) with the cyclic nitroxyl radicals 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) and 2,2,5,5-tetramethylpyrrolidinyl-1-oxy (proxyl) have been prepared. Both products are bis adducts, $Mn(F_6acac)_2L_2$ (L = tempo, proxyl), and have been shown by crystal structure analyses to have centrosymmetric trans octahedral structures. In each case, the metal ion is bound to two chelating F_6acac ligands and two monodentate nitroxyls, with Mn–O distances ranging from 2.12 to 2.16 Å. The configurations of the metal-bound nitroxyls closely resemble those of analogous uncoordinated radicals. Magnetic susceptibility measurements (6–300 K) are consistent with an $S = {}^3/_2$ ground state for both complexes, with a significant population at higher temperatures of one or more states of greater multiplicity. The susceptibility data are well-represented by a spin-only $({}^1/_2-{}^5/_2-{}^1/_2)$ interaction model, with J(Mn–nitroxyl) values of −79 (tempo adduct) and −105 cm^{-1} (proxyl adduct). Both adducts crystallize in the monoclinic space group $P2_1/c$ with $Z = 2$. For the tempo adduct $[Mn(C_5HF_6O_2)_2(C_9H_{18}NO)_2]$, $a = 10.698$ (5) Å, $b = 14.715$ (6) Å, $c = 12.378$ (5) Å, and $\beta = 113.48$ (3)°. For the proxyl adduct $[Mn(C_5HF_6O_2)_2(C_8H_{16}NO)_2]$, $a = 10.472$ (2) Å, $b = 14.488$ (4) Å, $c = 12.090$ (2) Å, and $\beta = 111.08$ (2)°.

Introduction

Complexes in which a transition metal center is coordinated to a nitroxyl radical function have been the subjects of considerable recent interest in our laboratory and elsewhere.[1-14] One of the motivations for the study of these compounds is the potential they give for the investigation of interactions between the free spins on the nitroxyl radical and on a paramagnetic metal center. Compounds prepared and characterized to date have shown interactions spanning a wide range of magnitudes. Strong interactions, characterized by room-temperature diamagnetism, have been found in a series of five-coordinate copper(II) complexes with short metal–nitroxyl distances.[4,8,12,15] Very weak couplings, with no measurable effect on magnetic behavior at ordinary temperatures, have also been observed.[3,5,10,13,14] The intermediate coupling regime, in which room-temperature magnetic susceptibility is determined by a distribution over more than one spin state, has had the fewest well-characterized examples. A series of cobalt(II) halide complexes of di-*tert*-butyl nitroxide appear to fall into this category, but quantitative interpretation of their magnetic properties has been hampered by instability.[7,11]

We now wish to report the preparation, crystal structures, and magnetic properties of a pair of bis(nitroxyl) adducts of Mn(II), which, in addition to providing the best characterized cases of metal–nitroxyl coupling in the intermediate range, are the first reported systems in which two nitroxyl radicals are coordinated to a single metal ion.

Experimental Section

Synthesis. $Mn(F_6acac)_2$ was prepared from the metal acetate by a standard procedure.[16] The 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) ligand was used as purchased from Aldrich Chemicals. The ligand 2,2,5,5-tetramethylpyrrolidinyl-1-oxy (proxyl) was synthesized from the corresponding crude hydroxylamine[17-19] by air oxidation in aqueous

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Table I. Crystal Data and Experimental Parameters for $Mn(F_6acac)_2L_2$

	L = tempo	L = proxyl
	A. Crystal Data	
formula	$MnC_{28}H_{38}F_{12}N_2O_6$	$MnC_{26}N_{34}F_{12}N_2O_6$
fw	781.54	753.49
a, Å	10.698 (5)	10.472 (2)
b, Å	14.715 (6)	14.488 (4)
c, Å	12.378 (5)	12.090 (2)
β, deg	113.48 (3)	111.08 (2)
vol, Å^3	1787.3 (13)	1711.6 (7)
Z	2	2
d(calcd), g cm^{-3}	1.45	1.46
space group	$P2_1/c$	$P2_1/c$
μ(Mo Kα), cm^{-1}	5.0	5.2
	B. Experimental Parameters	
radiation	Mo Kα[a]	Mo Kα[a]
temp, °C	22	22
receiving aperture	circular[b]	circular[b]
scan rate, deg min^{-1}	3–20	2–12
scan range, deg	−1.1 from Kα_1 to +1.2 from Kα_2	−1.1 from Kα_1 to +1.2 from Kα_2
bkgd counting	c	c
2θ(max), deg	55	50
no. of data collcd	4133 ($h,k,\pm l$)	3032 ($h,k,\pm l$)
no. of data with $F_o^2 > 3\sigma(F_o^2)$	2588	1646

[a] λ(Kα) = 0.71073 Å; graphite monochromator. [b] 4-mm diameter, 20 cm from the crystal. [c] Evaluated from 96-step peak profile.

Table II. Positional Parameters for Non-Hydrogen Atoms of $Mn(F_6acac)_2(tempo)_2$

atom	x	y	z
Mn	0.0000	0.0000	0.0000
F(1)	0.3044 (5)	0.0107 (5)	0.3983 (4)
F(2)	0.4439 (5)	−0.0845 (4)	0.3932 (4)
F(3)	0.4431 (5)	0.0441 (4)	0.3235 (4)
F(4)	0.2565 (9)	−0.2508 (4)	−0.0646 (7)
F(5)	0.3224 (7)	−0.3013 (4)	0.0989 (6)
F(6)	0.1251 (6)	−0.3132 (3)	−0.0085 (7)
O(1)	0.1136 (7)	0.0643 (4)	−0.0857 (5)
O(2)	0.1724 (4)	0.0116 (3)	0.1616 (3)
O(3)	0.0862 (3)	−0.1299 (2)	−0.0140 (3)
N	0.1631 (4)	0.0930 (3)	−0.1564 (4)
C(1)	0.2257 (6)	0.1856 (4)	−0.1294 (5)
C(2)	0.2551 (9)	0.2199 (6)	−0.2335 (9)
C(3)	0.3201 (7)	0.1514 (6)	−0.2809 (7)
C(4)	0.2223 (7)	0.0723 (5)	−0.3274 (5)
C(5)	0.1917 (6)	0.0257 (4)	−0.2327 (5)
C(6)	0.1237 (8)	0.2473 (5)	−0.1066 (8)
C(7)	0.3574 (7)	0.1757 (6)	−0.0154 (7)
C(8)	0.3124 (8)	−0.0338 (5)	−0.1529 (7)
C(9)	0.0643 (8)	−0.0324 (7)	−0.2883 (8)
C(10)	0.2591 (5)	−0.0480 (4)	0.2109 (4)
C(11)	0.2751 (5)	−0.1331 (4)	0.1717 (5)
C(12)	0.1891 (5)	−0.1655 (4)	0.0602 (5)
C(13)	0.3617 (7)	−0.0179 (6)	0.3344 (6)
C(14)	0.2238 (6)	−0.2576 (4)	0.0235 (6)

methanol using a copper(II) acetate catalyst.[20] The crude nitroxyl was purified by column chromatography (silica gel, dichloromethane eluent) and subsequent fractional distillation (bp 54 °C (30 mm)). To prepare the adducts, a mixture of 0.5 g of the appropriate nitroxyl radical and 0.5 g of $Mn(F_6acac)_2$ was placed in a 75-mL round-bottom flask fitted with a reflux condenser, and 25 mL of heptane was added. The mixture was then heated to reflux. After 5 min, the heat was removed and the resulting deep red solution was decanted from any water in the bottom of the flask. The solution was then stoppered and set aside to cool at room temperature. Crystals suitable for X-ray analysis were usually deposited overnight. The dark red prismatic crystals were filtered off, washed with heptane, and allowed to dry. Both $Mn(F_6acac)_2L_2$ complexes [L = tempo (I), proxyl (II)] could be stored for months in a closed vial with no visible signs of decomposition. No attempt was made to recrystallize the isolated solids. Approximate yield for both compounds was 0.5 g (70%). Anal. Calcd for I, $MnC_{28}H_{38}F_{12}N_2O_6$: C, 43.03; H, 4.90; F, 29.17; Mn, 7.03. Found: C, 43.18; H, 4.95; F, 29.19; Mn, 6.94. Calcd for II, $MnC_{26}H_{34}F_{12}N_2O_6$: C, 41.44; H, 4.55; F, 30.26; Mn, 7.29. Found: C, 41.49; H, 4.65; F, 29.65; Mn, 7.13. M points (uncorrected): I, 123–124 °C; II, 123–125 °C.

Collection and Reduction of X-ray Data. Crystallographic studies of both adducts were carried out on a Syntex P2$_1$ diffractometer. Crystals were mounted on glass fibers and coated with a thin layer of spray lacquer to retard decomposition. Initial centering, generation of possible unit cell vectors, and assignment of indices were carried out by procedures that have been described elsewhere.[21,22] Refined unit cell parameters were obtained from least-squares refinement based upon the setting angles of 15 reflections with $30° \leq 2\theta \leq 35°$. Intensities of four standard reflections were measured after every 50 data. Reflections whose intensities exceeded the valid range of the coincidence correction were remeasured at a lower filament current. The p factor in the expression[23] for the standard deviations of the observed intensities was assigned a value of 0.05. The data were corrected for standard decay and Lorentz and polarization effects. No absorption corrections were made. All computations were carried out with a locally modified version of the UCLA crystallographic computing package.[24] Crystal data and experimental parameters for both compounds are tabulated in Table I.

Interaxial angles and axial rotation photographs indicated that both compounds crystallize in the monoclinic system. Systematic absences ($h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$) uniquely define the space group $P2_1/c$, and a reasonable calculated density is obtained for $Z = 2$ molecules per unit cell. This implies a centrosymmetric molecular structure with the metal atom at the cell origin.

Intensity data for I were obtained from an irregularly shaped crystal of approximate dimensions 0.3 × 0.5 × 0.5 mm. The standard reflections declined in intensity by an average of about 6% during data collection; a correction was applied for this decay. The crystal of II, also irregularly shaped, had dimensions 0.3 × 0.4 × 0.4 mm. The decline of the intensities of the standard reflections was less than 2%, and no decay correction was applied.

Structure Solution and Refinement. Both structures were solved by heavy-atom methods with the metal atom placed at the cell origin. The final refinement model included anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at fixed, idealized positions but were not refined. Calculated positions of methyl hydrogen atoms were based on peaks observed on a difference Fourier map. In all refinements, the function minimized was $\sum w(|F_o| - |F_c|)^2$ and atomic scattering factors were taken from ref 25.

Final refinement for the proxyl adduct converged to conventional R factors $R_1 = 0.057$ and $R_2 = 0.073$. The final esd of an observation of unit weight was 1.98, and the largest peak height on a final difference Fourier map was 0.98 e/Å^3. For the tempo adduct, the final R factors were 0.070 and 0.116 and the esd of an observation of unit weight was 3.35. The top five peaks on a final difference Fourier map, ranging in height from 1.48 to 0.84 e/Å^3, were in the vicinity of the CF_3 groups. The somewhat larger R factor for this adduct is undoubtedly a consequence of the larger thermal motion and/or partial disorder of the CF_3 groups. This problem did not seriously affect the precision of the structural results.

Magnetic Susceptibility Measurements. Magnetic susceptibility data were obtained for T = 6–300 K at 10 T by use of an SHE Corp. SQUID magnetometer located at the University of Southern California. Data were corrected for magnetization of the sample holder and for ligand diamagnetism, estimated from Pascal's constants. The susceptibility values were converted to effective magnetic moments by the expression $\mu_{eff} = 2.828(\chi_m T)^{1/2}$. The observed susceptibilities were fit by least-squares methods to eq 1, the spin-only expression for a symmetrical

$$\chi_m = \frac{Ng^2\beta^2}{kT}\left[\frac{5x^{-7} + \frac{35}{2}(x^{-2} + x'^{-2}) + 42x^5}{4x^{-7} + 6(x^{-2} + x'^{-2}) + 8x^5}\right] \qquad (1)$$

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Table III. Positional Parameters for Non-Hydrogen Atoms of $Mn(F_6acac)_2(proxyl)_2$

atom	x	y	z
Mn	0.0000	0.0000	0.0000
F(1)	−0.3448 (5)	0.2939 (3)	−0.0969 (5)
F(2)	−0.1443 (5)	0.3174 (3)	−0.0002 (6)
F(3)	−0.2617 (8)	0.2471 (4)	0.0732 (5)
F(4)	−0.2874 (4)	0.0003 (4)	−0.4107 (3)
F(5)	−0.4473 (4)	0.0751 (3)	−0.3891 (3)
F(6)	−0.4087 (5)	−0.0599 (4)	−0.3283 (4)
O(1)	0.1600 (4)	0.0563 (3)	−0.0519 (4)
O(2)	−0.0863 (3)	0.1327 (2)	0.0095 (3)
O(3)	−0.1509 (4)	−0.0048 (3)	−0.1728 (3)
N	0.1881 (5)	0.0955 (3)	−0.1351 (4)
C(1)	0.2261 (7)	0.1935 (4)	−0.1274 (6)
C(2)	0.2818 (11)	0.2016 (6)	−0.2249 (8)
C(3)	0.2540 (12)	0.1183 (7)	−0.2916 (9)
C(4)	0.2164 (6)	0.0433 (5)	−0.2286 (6)
C(5)	0.1059 (10)	0.2534 (6)	−0.1401 (11)
C(6)	0.3394 (9)	0.2106 (7)	−0.0074 (8)
C(7)	0.3302 (10)	−0.0234 (6)	−0.1718 (9)
C(8)	0.0878 (9)	−0.0096 (8)	−0.3006 (8)
C(9)	−0.1949 (5)	0.1650 (4)	−0.0627 (5)
C(10)	−0.2787 (5)	0.1297 (4)	−0.1705 (5)
C(11)	−0.2495 (5)	0.0488 (4)	−0.2165 (5)
C(12)	−0.2377 (7)	0.2551 (5)	−0.0221 (7)
C(13)	−0.3495 (6)	0.0167 (5)	−0.3372 (6)

Table IV. Bond Distances (Å) in $Mn(F_6acac)_2(tempo)_2$

	(a) Mn Coordination Sphere		
Mn–O(1)	2.127 (4)	Mn–O(3)	2.160 (3)
Mn–O(2)	2.120 (4)		
	(b) F_6acac Ligand		
O(2)–C(10)	1.246 (6)	C(11)–C(12)	1.402 (7)
C(10)–C(11)	1.378 (8)	C(12)–C(14)	1.521 (8)
C(10)–C(13)	1.549 (8)	C(12)–O(3)	1.235 (6)
	(c) Nitroxyl Ligand		
O(1)–N(1)	1.262 (6)	C(2)–C(3)	1.472 (11)
N(1)–C(1)	1.498 (7)	C(3)–C(4)	1.517 (10)
N(1)–C(5)	1.481 (7)	C(4)–C(5)	1.502 (8)
C(1)–C(2)	1.529 (10)	C(5)–C(8)	1.547 (10)
C(1)–C(6)	1.529 (9)	C(5)–C(9)	1.522 (9)
C(1)–C(7)	1.554 (9)		

Table V. Bond Distances (Å) in $Mn(F_6acac)_2(proxyl)_2$

	(a) Mn Coordination Sphere		
Mn–O(1)	2.150 (4)	Mn–O(3)	2.120 (3)
Mn–O(2)	2.145 (4)		
	(b) F_6acac Ligand		
O(2)–C(9)	1.250 (6)	C(10)–C(11)	1.378 (8)
C(9)–C(10)	1.381 (7)	C(11)–C(13)	1.531 (7)
C(9)–C(12)	1.518 (8)	C(11)–O(3)	1.247 (6)
	(c) Nitroxyl Ligand		
O(1)–N(1)	1.278 (5)	C(1)–C(6)	1.529 (10)
N(1)–C(1)	1.469 (7)	C(2)–C(3)	1.422 (11)
N(1)–C(4)	1.475 (7)	C(3)–C(4)	1.460 (10)
C(1)–C(2)	1.495 (10)	C(4)–C(7)	1.495 (10)
C(1)–C(5)	1.491 (11)	C(4)–C(8)	1.521 (10)

three-spin ($^1/_2$–$^5/_2$–$^1/_2$) system.[26,27] In eq 1, $\chi = \exp(J/kT)$ and $\chi' = \exp(J'/kT)$, where J = the Mn–nitroxyl coupling constant and J' = the nitroxyl–nitroxyl coupling constant. Susceptibility data with $T < 20$ K were not included in the fitting process for the proxyl adduct; all data were used for the tempo adduct.

Results

Crystal Structure. Final positional parameters for the non-hydrogen atoms of the two adducts are tabulated in Tables II and III. Bond distances and angles are listed in Tables IV–VII.

Table VI. Bond Angles (deg) in $Mn(F_6acac)_2(tempo)_2$

	(a) Mn Coordination Sphere		
O(1)–Mn–O(2)	88.8 (2)	O(2)–Mn–O(3)	84.8 (1)
O(1)–Mn–O(3)	90.4 (2)		
	(b) F_6acac Ligand		
Mn–O(2)–C(10)	127.1 (4)	C(10)–C(11)–C(12)	122.1 (5)
Mn–O(3)–C(12)	126.8 (3)	O(3)–C(12)–C(11)	128.9 (5)
O(2)–C(10)–C(11)	129.8 (5)	O(13)–C(12)–C(14)	114.0 (5)
O(2)–C(10)–C(13)	112.2 (5)	C(11)–C(12)–C(14)	117.0 (5)
C(11)–C(10)–C(13)	118.0 (5)		
	(c) Nitroxyl Ligand		
Mn–O(1)–N(1)	167.2 (5)	C(1)–C(2)–C(3)	113.5 (6)
O(1)–N(1)–C(1)	115.1 (4)	C(2)–C(3)–C(4)	108.2 (6)
O(1)–N(1)–C(5)	118.0 (5)	C(3)–C(4)–C(5)	112.7 (5)
C(1)–N(1)–C(5)	124.2 (4)	N(1)–C(5)–C(4)	111.0 (5)
N(1)–C(1)–C(2)	109.6 (5)	N(1)–C(5)–C(8)	107.6 (5)
N(1)–C(1)–C(6)	107.0 (4)	N(1)–C(5)–C(9)	106.8 (5)
N(1)–C(1)–C(7)	106.3 (5)	C(4)–C(5)–C(8)	111.7 (5)
C(2)–C(1)–C(6)	111.2 (6)	C(4)–C(5)–C(9)	109.7 (6)
C(2)–C(1)–C(7)	112.4 (6)	C(8)–C(5)–C(9)	109.9 (6)
C(6)–C(1)–C(7)	110.1 (5)		

Table VII. Bond Angles (deg) in $Mn(F_6acac)_2(proxyl)_2$

	(a) Mn Coordination Sphere		
O(1)–Mn–O(2)	93.6 (2)	O(2)–Mn–O(3)	84.4 (1)
O(1)–Mn–O(3)	96.2 (2)		
	(b) F_6acac Ligand		
Mn–O(2)–C(9)	126.4 (3)	C(9)–C(10)–C(11)	122.6 (5)
Mn–O(3)–C(11)	127.4 (4)	O(3)–C(11)–C(10)	128.9 (5)
O(2)–C(9)–C(10)	129.1 (5)	O(3)–C(11)–C(13)	113.1 (5)
O(2)–C(9)–C(12)	113.3 (5)	C(10)–C(11)–C(13)	118.0 (5)
C(10)–C(9)–C(12)	117.6 (5)		
	(c) Nitroxyl Ligand		
Mn–O(1)–N(1)	145.3 (4)	C(1)–C(2)–C(3)	108.8 (6)
O(1)–N(1)–C(1)	120.9 (5)	C(2)–C(3)–C(4)	112.0 (7)
O(1)–N(1)–C(4)	122.8 (5)	N(1)–C(4)–C(3)	100.6 (6)
C(1)–N(1)–C(4)	114.8 (5)	N(1)–C(4)–C(7)	109.0 (6)
N(1)–C(1)–C(2)	101.5 (6)	N(1)–C(4)–C(8)	108.4 (5)
N(1)–C(1)–C(5)	110.9 (6)	C(3)–C(4)–C(7)	113.6 (7)
N(1)–C(1)–C(6)	108.4 (6)	C(3)–C(4)–C(8)	115.2 (8)
C(5)–C(1)–C(6)	110.0 (7)	C(7)–C(4)–C(8)	109.4 (7)

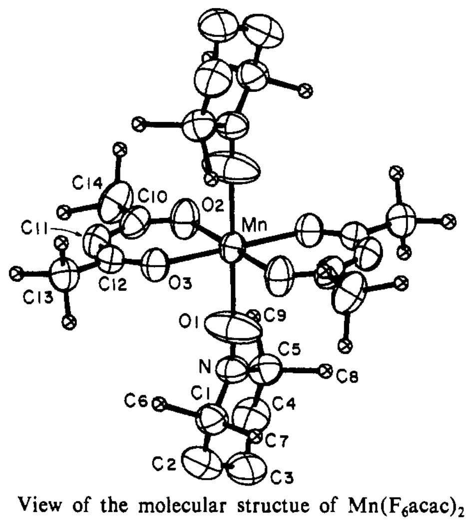

Figure 1. View of the molecular structue of $Mn(F_6acac)_2(tempo)_2$. Hydrogen atoms have been omitted for the sake of clarity. Thermal ellipsoids are drawn at the 50% level, with the exception that the thermal parameters of the methyl carbon atoms and the fluorines have been arbitrarily set at 1.0 Å^2.

Available supplementary material includes tables of observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom positional parameters, distances and angles within the CF_3 groups, and least-squares planes.

Description of the Structures. The crystal structures of both adducts are comprised of discrete centrosymmetric *trans*-Mn-

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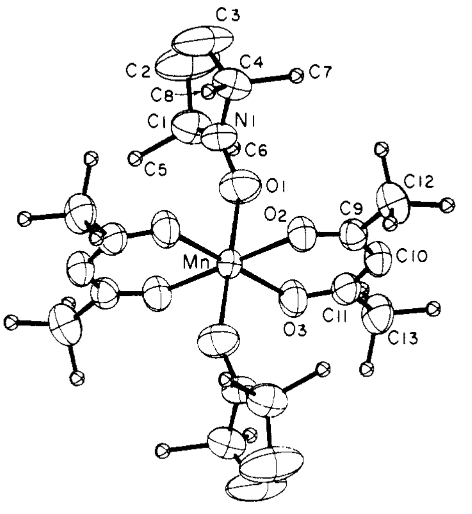

Figure 2. View of the molecular structure of $Mn(F_6acac)_2(proxyl)_2$. Hydrogen atoms have been omitted for clarity. Thermal parameters of the fluorine and methyl carbon atoms have been artificially set at 1.0 Å^2; all other thermal ellipsoids are drawn at the 50% level.

$(F_6acac)_2L_2$ molecules. The metal atoms are bound to two chelating F_6acac ligands and two monodentate nitroxyls in a distored octahedral configuration. Views of the molecular structures of the two adducts are shown in Figures 1 and 2. The distortions from regular octahedral geometry about Mn are rather small, with no bond angle deviating by more than about 6° from its ideal value. The largest distortions involve the "bite" angles of ca. 85° for the chelating F_6acac ligand. The Mn–O bond distances in both complexes lie within the relatively narrow range of 2.120 (3)–2.160 (3) Å. These are typical values for Mn^{2+} complexes of acac and related ligands.[28-32]

In the proxyl adduct, the OCCCO grouping of the F_6acac ligand is planar (maximum deviation = 0.004 Å), with the CF_3 carbon atoms in the chelate plane. Deviations from planarity are a bit greater ($\leq$0.026 Å) in the tempo complex, and one of the CF_3 carbons is displaced from the OCCCO plane by 0.121 Å. The metal atoms of both adducts are out of this plane, with the larger deviation (0.24 vs. 0.15 Å) in the proxyl adduct. Such "tilted" chelate rings are not uncommon in metal complexes of β-diketonate ligands. Other structural details of the F_6acac ligands are unexceptional.

Both adducts contain monodentate, O-bonded nitroxyls, as have been found in a series of Cu^{2+} complexes.[3-6,12,14] The most significant structural difference between the two manganese complexes involves the Mn–O–N bond angle, which has a value of 167.2 (5)° in the tempo adduct and 145.3 (4)° in the proxyl adduct. Both of these angles are substantially larger than the values of 124–134° found for the Cu–O–N angles in copper(II) nitroxyl complexes with short Cu–O(nitroxyl) distances.[4,6,12] The nitroxyl ligands themselves have structures essentially identical with those found in uncoordinated nitroxyls[32,34] and in other metal–nitroxyl complexes.[3-6,9,12,14,15,35] The most pertinent structural parameters are the N–O distances (1.262 (6) Å for the proxyl ligand and 1.278 (5) Å for the coordinated tempo) and the displacement of the nitrogen atom from the plane defined by its three bonded atoms (0.100 Å for proxyl and 0.135 Å for tempo).

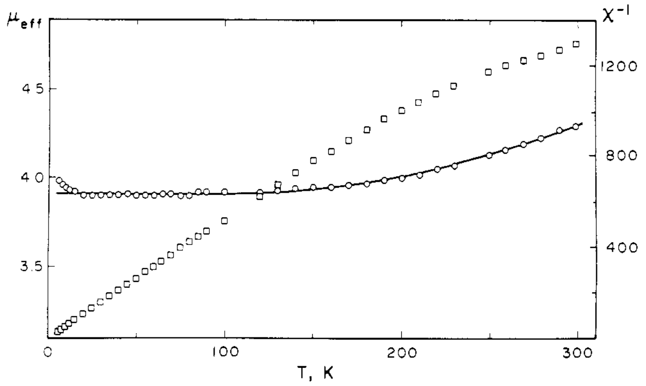

Figure 3. Plots of the reciprocal paramagnetic susceptibility (squares) and effective magnetic moment (circles) vs. *T* for $Mn(F_6acac)_2(proxyl)_2$. The solid line represents magnetic moment values based on susceptibilities calculated from eq 1 with the best-fit parameters $g = 2.02$ and $J = -105$ cm^{-1}.

Magnetic Results. The proxyl and tempo adducts show qualitatively similar magnetic behavior. Owing to the greater stability of the proxyl adduct, its magnetic susceptibilities are more precisely known and will serve as the primary basis for discussion. Full magnetic data for both complexes are included with the supplementary material. Plots of the temperature dependence of the reciprocal molar paramagnetic susceptibility and of the effective magnetic moment for $Mn(F_6acac)_2(proxyl)_2$ are shown in Figure 3. The inverse susceptibility plot is linear at low temperatures (15–120 K), with corresponding constant μ_{eff} values of 3.91 ± .01 μ_B. There is a small increase in μ_{eff} below 15 K, probably owing to the presence of a minor amount of higher spin impurity. Above 120 K, the χ^{-1} plot deviates from linearity and μ_{eff} increases to 4.29 μ_B at 299 K.

The observed susceptibility data for both complexes were closely reproduced by eq 1, the spin-only expression for a symmetrical three-spin ($^1/_2$–$^5/_2$–$^1/_2$) system. This expression includes three variable parameters—the average *g* factor, the coupling constant *J* for the Mn–nitroxyl interaction, and the nitroxyl–nitroxyl coupling constant *J'*. Early in the fitting process, it became clear that the experimental data did not support a nonzero value for *J'* and so this parameter was set to zero. For the proxyl complex, the best fit was obtained for $g = 2.020$ and $J = -105$ cm^{-1}. These values produced calculated susceptibility values deviating from the observed data by an average of 0.46%, with a maximum deviation of 1.0%. The corresponding best-fit values for the tempo adduct are $g = 1.95$, $J = -79$ cm^{-1}, mean deviation = 1.15%, and maximum deviation = 2.3%. The calculated μ_{eff} vs. *T* curves for the two adducts are shown as solid lines in the plots of magnetic data.

Discussion

The two manganese complexes reported herein, together with some closely related systems prepared in our laboratory,[15,35] represent the first documented examples of metal complexes in which two nitroxyl functions are bound to a single metal ion. All previously reported bis(nitroxyl) complexes have been binuclear, with one radical coordinated to each metal.[1,6,8,9,12,15]

Although the structure found for the two adducts was not unanticipated, the only previous structurally characterized example of a comparable manganese(II) complex is the diaquo adduct of manganese(II) acetylacetonate.[28,29] That material has the same centrosymmetric trans octahedral structure as the nitroxyl adducts, but with two significant differences. In the aquo complex, the metal ion is displaced by 0.56 Å from the acac plane, a value much larger than those in the two nitroxyl adducts. Also, the Mn–O(water) distance of 2.26 Å is significantly longer than the Mn–O(nitroxyl) distance we observe.

The structural results are consistent with the formulation of both complexes as manganese(II) adducts of neutral nitroxyl

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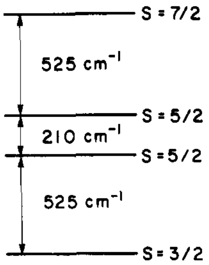

Figure 4. Spin energy levels derived from eq 1 with $g = 2.02$ and $J = -105$ cm^{-1}.

radicals, rather than as products of an internal redox reaction. Metal-coordinated reduced nitroxyls are known, but all structurally characterized examples to date are bound in an η^2 fashion, with a longer N–O distance and a more pyramidal N atom than are observed in the present case.[36,37] The stereochemistry about Mn is consistent with expectations for a high-spin Mn(II) complex. Trivalent manganese, the only viable alternative, would be expected to show shorter Mn–O distances and a Jahn–Teller distortion of the octahedral coordination sphere.[38]

Steric factors are known to play a significant role in the coordination chemistry of nitroxyl radicals. The methyl groups, necessary for stabilization of the radical function, are sterically demanding and play a significant role in determining the nature and structures of products that may be formed. For example, steric factors are probably the reason for the adoption of a novel copper coordination geometry in a series of dimeric nitroxyl adducts of the copper(II) trihaloacetates.[39] In the present case, the larger Mn–O–N angle is observed for the more demanding (because of its larger C–N–C angle) tempo ligand.

The qualitative features of the magnetic susceptibility curves for both adducts are the same. At low temperatures, μ_{eff} is constant at a value close to that expected for a system with $S = {}^3/_2$. At higher temperatures, μ_{eff} increases gradually, reaching a room-temperature value intermediate between those corresponding to $S = {}^3/_2$ and $S = 2$. These results are most simply interpreted by assuming an $S = {}^3/_2$ ground state, with population at higher temperatures of one or more excited states of greater multiplicity.

The expected insignificance of spin–orbit coupling in the ^{6}S ground state of high-spin Mn^{2+} made these systems likely candidates for the appliction of a spin-only magnetic susceptibility expression, and in fact the experimental data are well represented by eq 1. Three variable parameters were employed in the fitting process, but one of them, the nitroxyl–nitroxyl coupling constant J', proved to be indistinguishable from zero. The variable parameters, then, were the manganese–nitroxyl coupling constant J and the average g factor. As expected, the best fits were obtained for g values close to 2 (1.95 for L = tempo and 2.02 for L = proxyl). The best-fit J values were -79 cm^{-1} for the tempo adduct and -105 cm^{-1} for the proxyl adduct. The quality of both fits was very good and highly sensitive to the value of J. Consequently, we believe that these J values are precise to within a few percent.

The energy level pattern corresponding to the fitting model employed includes an $S = {}^3/_2$ ground state (for which E is taken as zero), two $S = {}^5/_2$ excited states with $E = -5J$ and $E = -7J$, and a $S = {}^7/_2$ state with $E = -12J$. This pattern is illustrated in Figure 4 for the specific case of the proxyl adduct. The observed magnetic behavior is hence a consequence of thermal population of the ground state and one or more of the higher spin excited states. Solid-state EPR experiments designed to provide independent characterization of the populated spin states of these systems have been carried out at the University of Florence and will be reported separately.[40]

Among metal–nitroxyl complexes, these adducts are the first structurally characterized examples in which metal–ligand magnetic coupling yields a room-temperature distribution over two or more states of different spin multiplicity. Other fully characterized metal–nitroxyl complexes, excluding those in which the radical ligand has been reduced, may be grouped into three categories: (1) copper(II)–nitroxyl complexes with short (ca. 1.95 Å) metal–nitroxyl bonds, where all known examples are five-coordinate and diamagnetic;[4,6,12,39] (2) copper(II)–nitroxyl complexes with long (>2.2 Å) metal–nitroxyl bonds, which are typically six coordinate and show no effects of magnetic interaction at room temperature.[3,5,14] (One such system, however, exhibits very interesting magnetic behavior at low (<4 K) temperatures.[10,13]); (3) binuclear bis(nitroxyl) complexes of rhodium(II) and molybdenum(II) carboxylates,[2,9] where nitroxyl–nitroxyl interactions are transmitted through the $M_2(O_2CR)_4$ framework.

It is noteworthy that the less negative J value occurs for the complex (the tempo adduct) with the larger Mn–O–N angle. This behavior is consistent with the expected variation with bond angle of the overlap of the N–O π^* ligand orbital and the metal d_{z^2} orbital, one of the two metal d orbitals whose symmetry is appropriate for antiferromagnetic metal–ligand interaction.[41] The π^* and d_{z^2} orbitals would be orthogonal for a 180° M–O–N bond angle but would have nonzero overlap for smaller angles. In the diamagnetic copper(II) nitroxyl complexes, the Cu–O–N angles are typically near 125°. The manganese systems are potentially more complicated than the copper adducts, and more work will be needed to define the nature of the interactions in these molecules.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, distances and angles within the CF_3 groups, least-squares planes, and magnetic susceptibility data and plots of the reciprocal paramagnetic susceptibility and effective magnetic moment vs. T (11 pages). Ordering information is given on any current masthead page.

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