was similar to that of sulfuranes 1 and 11. The reaction of 111a with primary amine also gave the corresponding S,S-bis(trifluoromethyl)-N-alkyl- (aryl-) sulfimides.

Support for structure 111a came from the spectral data. When the mass spectral data were measured at 100 °C and 17 eV, no molecular ion was found; however, other fragment peaks such as m/e 209 ($M^+ - CF_3$), 170 (C_2SF_6), 151 (C_2SF_5), 132 (C_2SF_4), 108 ($C_6H_4O_2$), 101 (CSF_3), 92 (C_6H_4O), and 69 (CF_3) appeared appropriately. The ^{19}F NMR spectrum showed only one singlet signal at ϕ 58.6. The ^1H NMR spectrum (CDCl₃) had a resonance at τ 1.88–1.97 (Ar–H). The infrared spectrum has absorption bonds at 3001 (w), 1598 (m), 1490 (m), 1251 (vs), 1186 (ms), 1113 (s), 1065 (ms), 746 (m) cm⁻¹. Anal. Calcd for $C_8H_4O_2SF_6$: C, 34.54; H, 1.45. Found: C, 34.45; H, 1.42.

111b (R = 3-CH₃): mp 169–170.5 °C; 41% yield; ^1H NMR (CDCl₃) τ 1.64–1.97 (Ar–H), and 7.97 (CH₃); ^{19}F NMR ϕ 57.6; IR 3002 (w), 2988 (w), 1599 (m), 1496 (m), 1381 (w), 1271 (vs), 1183 (s), 1126 (s), 1083 (s), 747 (m) cm⁻¹; mass spectrum m/e 223 ($M^+ - CF_3$), 122 ($C_7H_6O_2$). Anal. Calcd for $C_9H_6O_2SF_6$: C, 37.00; H, 2.07. Found: C, 36.75; H, 2.02.

111c (R = 3,5-di-t-C₄H₉): mp 191.5–192.5 °C; 26% yield; ^1H NMR (CDCl₃) τ 1.59–1.81 (Ar–H) and 8.69–9.02 (t-Bu); ^{19}F NMR ϕ 58.1; IR 3001 (w), 2987 (w), 1601 (m), 1486 (m), 1391 (m), 1387 (m), 1276 (vs), 1218 (s), 1186 (s), 1118 (s), 1079 (ms), 748 (m) cm⁻¹; mass spectrum m/e 321 ($M^+ - CF_3$), 220 ($C_{14}H_{20}O_2$). Anal. Calcd for $C_{16}H_{20}O_2SF_6$: C, 49.23; H, 5.16. Found: C, 48.96; H, 5.15.

Both electronegativity and apicophilicity effects must be considered in determining the conformation of the compound 111. Although a few sulfuranes are known in which rings occupy the diequatorial positions on sulfur,[28–31] compound 111 may instead have a zwitterionic structure which could account for its solubility in several solvents and its ^{19}F NMR spectrum and would be in agreement with electronegativity rules. Further structural studies will be reported.

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Spectroscopic and Magnetic Properties of an Exchange Coupled Copper(II)–Manganese(II) Dimer

Sir:

When crystals of dichloroaquo(pyridine N-oxide)copper(II) are doped with manganese(II), measurable quantities of an exchange coupled copper(II)–manganese(II) dimer are produced. Although hundreds of investigations of the magnetic and spectroscopic properties of dimeric complexes have appeared in the literature, relatively few studies have involved dimeric systems containing two different metal ions. This communication presents the results of an EPR study of the copper(II)–manganese(II) dimer.

The host material, $Cu(pyO)Cl_2 \cdot H_2O$, is one of a series of dimeric complexes which can be formed by reacting copper(II) halides ($CuCl_2$ and $CuBr_2$) with aromatic amine N-oxides.[1,2] In these dimeric complexes, a pair of copper(II) ions is bridged by oxygen atoms from two N-oxide ligands. The halide ions are bound terminally so that each copper(II) ion is surrounded by an approximately square-planar arrangement of two oxygen atoms and two halide ions. Each copper(II) ion adds an axial ligand (water in the case of $Cu(pyO)Cl_2 \cdot H_2O$) in a manner which retains a centrosymmetric structure for the dimer. Although the acutal crystal structure of $Cu(pyO)Cl_2 \cdot H_2O$ has not been determined, the close resemblance of the spectroscopic and magnetic properties of this complex to those of several similar complexes which have been structurally characterized leaves little doubt as to its basic structure. Kokoska and coworkers found that $Cu(pyO)Cl_2 \cdot H_2O$ exhibits the temperature-dependent EPR spectrum characteristic of an antiferromagnetically coupled pair of copper(II) ions.[3] They estimated the singlet–triplet separation to be approximately 885 cm⁻¹ which is typical of the N-oxide bridged dimer of copper(II) chloride. Our preliminary x-ray studies show $Cu(pyO)Cl_2 \cdot H_2O$ to be triclinic with one dimeric molecule per unit cell.

When crystals of this type of complex are doped with another divalent metal ion it appears that one of the two copper(II) ions in a small fraction of the dimeric molecules is replaced by the new metal ion. This results in small but measurable concentrations of mixed metal dimers. Kokoska and coworkers observed this phenomenon and were able to characterize copper(II)–zinc(II) and copper(II)–nickel(II) pairs.[4] Clearly, copper(II)–manganese(II) dimers also can be formed in this fashion. From the standpoint of magnetic interactions the copper(II)–manganese(II) dimer is a particularly interesting system since the two ions contribute different numbers of unpaired electrons and both metals have nuclear spins. If the magnitude of the exchange interaction is large compared to the other magnetic interactions, the copper(II) ions ($S = \frac{1}{2}$) will couple with the manganese(II) ion ($S = \frac{5}{2}$) to produce a two-state system. One state is characterized by a total spin
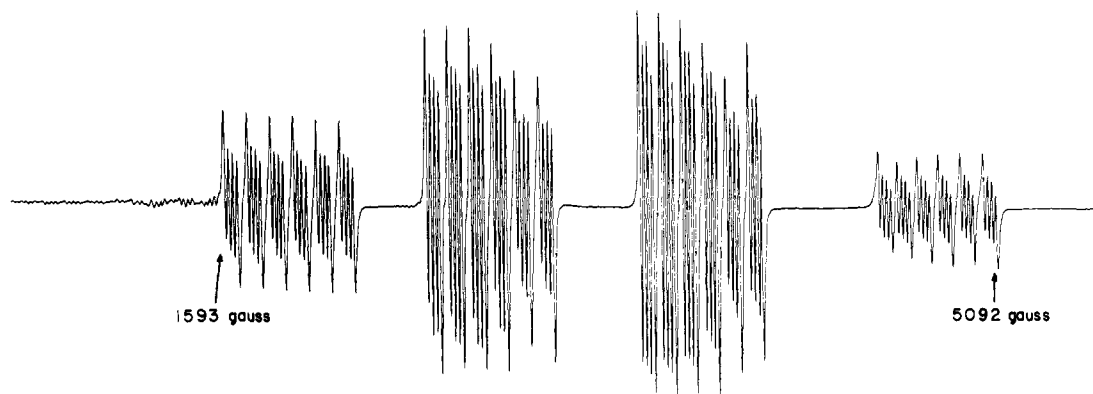
Figure 1. EPR spectrum of a manganese(II) doped crystal of Cu(pyO)Cl·H₂O at X-band frequency. The spectrum was recorded at 77 K with the magnetic field directed along the *x* axis of the zero-field splitting tensor.
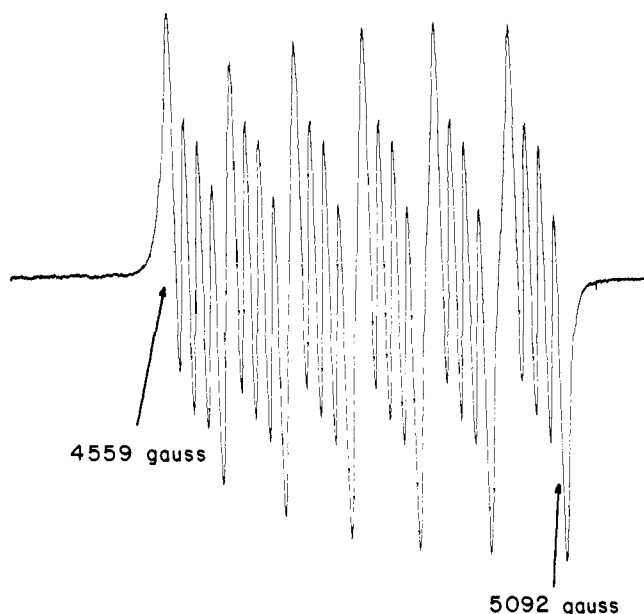

Figure 2. Expanded view of the high field component of the copper(II)-manganese(II) spectrum showing the manganese and copper hyperfine structure.

Table I. Spin Hamiltonian Parameters for the Copper(II)-Manganese(II) Dimer in Cu(pyO)Cl₂·H₂O[a]

$g_{x'} = 1.991$	$\|A(Cu)_{x'}\| < 0.0005$
$g_{y'} = 1.986$	$\|A(Cu)_{y'}\| < 0.0005$
$g_{z'} = 1.952$	$\|A(Cu)_{z'}\| = 0.0023$
$D = \pm 0.051$	$\|A(Mn)_x\| = 0.0091$
$E = \pm 0.013$	$\|A(Mn)_y\| = 0.0091$
	$\|A(Mn)_z\| = 0.0090$

[a] The *x*, *y*, and *z* axes refer to the principal directions of the zero-field splitting tensor while *x'*, *y'*, and *z'* refer to the principal directions of copper hyperfine and *g* tensors. The hyperfine and zero-field constants are given in cm⁻¹.

of two while the second state possesses a total spin of three. The relative energies of the two states is determined by the sign and magnitude of the exchange interaction. Since both states are paramagnetic one would expect to observe an EPR resonance irrespective of the nature of the exchange.

At liquid nitrogen temperature pure Cu(pyO)Cl₂·H₂O is essentially diamagnetic becasue of the strong antiferromagnetic interactions between copper(II) ions. Under these conditions crystals of the complex behave as a diamagnetic host lattice. The EPR spectra of paramagnetic impurities can be observed without interference from the copper(II)-copper(II) dimers. The EPR spectrum of a Cu(pyO)Cl₂·H₂O crystal doped with manganese(II) is shown in Figure 1. The beauti-

fully resolved spectrum leaves little doubt that the resonance arises from a magnetically coupled copper(II)-manganese(II) dimer. The four groups of lines correspond to the fine structure expected of a system having a total spin of two. Superimposed on this fine structure is the hyperfine structure from the manganese and copper nuclei. Each fine structure component is split into six lines by the interaction with the ⁵⁵Mn nucleus ($I = 5/2$). Each of these lines is then split into four by the ⁶⁵Cu or ⁶³Cu nucleus ($I = 3/2$) to produce the characteristic 24-line pattern (see Figure 2). The spectrum can be described by a spin Hamiltonian of the following form:

$$\mathcal{H} = \beta(\vec{H} \cdot \bar{g} \cdot \hat{S}) + D(\hat{S}_z{}^2 - 2) + E(\hat{S}_x{}^2 - \hat{S}_y{}^2) + \hat{I}_{Mn} \cdot \bar{A}_{Mn} \cdot \hat{S} + \hat{I}_{Cu} \cdot \bar{A}_{Cu} \cdot \hat{S}$$

The first term represents the electron Zeeman interaction, the next two terms describe the zero-field splitting, and the final two terms account for the hyperfine interactions with the copper and manganese nuclei. The spin Hamiltonian parameters for the copper(II)-manganese(II) dimer are given in Table 1. The angular dependence of the spectrum shows that the principal directions of the *g*, zero-field, and hyperfine tensors are not coincident. The fact that no resonances are observed which can be attributed to a system with a total spin of three suggests that the *S* = 3 state of the copper(II)-manganese(II) dimer is significantly higher in energy than the *S* = 2 state. We estimate that the *S* = 3 state must be at least 250 cm⁻¹ higher than the *S* = 2 state. This clearly indicates that the exchange is antiferromagnetic.

The principal *g* values which are all measurably lower than the free electron value represent the most unusual feature of the copper(II)-manganese(II) dimer. To our knowledge *g* values of this sort are without precedent for either copper(II) or manganese(II) containing systems. It appears that the spin-orbit interaction associated with the copper(II) ion produces a negative rather than positive contribution to the *g* tensor. The spin Hamiltonian parameters are qualitatively consistent with the view that the copper(II)-manganese(II) dimer is a six-electron system in which each electron spends one-sixth of the time on the copper(II) ion and five-sixths of the time on the manganese(II) ion. The absolute magnitudes of the *g* shifts ($g - 2.0023$) and copper hyperfine constant ($A(Cu)_{z'}$) are approximately one-sixth as large as those of the analogous copper(II)-zinc(II) system.[4] (The copper(II)-zinc(II) dimer which has the same structure as the copper(II)-manganese(II) system behaves as a monomeric copper(II) complex.) In contrast, the manganese hyperfine constants are about as large as those observed in monomeric manganese(II) complexes.

It is clear that the copper(II)-manganese(II) dimer is a unique and interesting system which deserves further theoretical as well as experimental characterization.

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Reversible Binding of Dioxygen by Tris(3,5-di-*tert*-butylcatecholato)manganese(III) in Dimethyl Sulfoxide

Sir:

For several years the redox chemistry of manganese complexes has been of interest to our group,[1,2] especially systems that involve polyhydroxy ligands.[3] We report here that an oxidation product of the tris(3,5-di-*tert*-butylcatecholato)-manganese(III) complex (1) reversibly binds molecular oxygen in dimethyl sulfoxide solutions. Figure 1 illustrates spectra for 1 in the absence and presence of O_2. When the latter solutions are deaerated with argon the dominant peak at 450 nm is eliminated; this change is reversible upon addition of O_2.

The results for a series of spectrophotometric experiments that further illustrate the formation of a reversible O_2 adduct with the oxidation product of 1 are summarized in Table I. The variability in the data is characteristic of the system and undoubtedly is due to the chemical oxidation of the catechol ligands of 1. The extent of such reactions is affected by concentration, solution acidity, O_2 partial pressure, moisture, and possibly light. In addition, the reaction products probably undergo exchange reactions, disproportionation, and further redox reactions. However, under dilute conditions the major process is the reversible formation of the O_2 adduct. Additional studies are in progress to find the optimum conditions for the stable formation of the adduct.

The redox chemistry of 1 is illustrated by the cyclic voltammogram of Figure 2a. Curve b is for O_2 at 1 atm in the absence of 1 and curve c is for 1 plus O_2 at 1 atm. The anodic
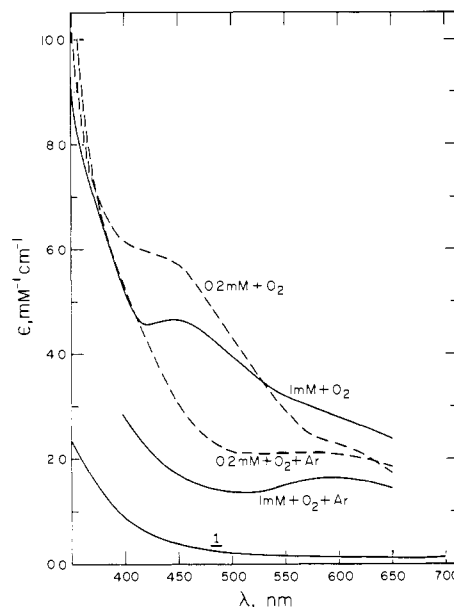

Figure 1. Absorption spectra for the tris(3,5-di-*tert*-butylcatecholato)-manganese(III) complex (1) in dimethyl sulfoxide in the absence and presence of molecular oxygen. The complex was formed in situ by combining $Mn^{III}(OAc)_3$, 3,5-di-*tert*-butylcatechol, and tetraethylammonium hydroxide in a mole ratio of 1:3:6. Oxygen was added to the complex solution by bubbling with O_2 at 1 atm for 5 min, and removed by bubbling with argon for 20 min. Molar absorptivity values, ϵ, are based on the formal concentrations of 1 in the solutions.

peak at −0.5 V vs. SCE represents the reduction product of the reversible O_2 adduct. Deaeration of the latter solution with argon results in the cyclic voltammogram of curve d; addition of O_2 reverses the change and results in a voltammogram identical with curve c.

Analysis of the spectrophotometric and electrochemical data indicates that for low metal-to-oxygen ratios a 1:1 O_2 adduct is formed. When the ratio is increased and with higher concentrations of 1, the extent of the irreversible chemical oxidation of the coordinated catechol ligands by O_2 increases (indicated by the absorption band at 580 nm for the spectra in Figure 1 and by the initial reduction peak at −0.5 V, curve c, Figure 2). The reduction peak at −0.5 V is due to the re-

Table I. Visible Spectrophotometric Data for 1, the O_2 Adduct (450-nm Band), and the Oxidation Products of 1 (580-nm band) in Dimethyl Sulfoxide[a]

Expt	Solution conditions	450 nm, ϵ (mM^{-1} cm^{-1})	580 nm, ϵ (mM^{-1} cm^{-1})
a	1 (0.1 mM → 20 mM)	0.35	0.15
b	1.0 mM 1 + O_2, 1 atm (5 min)	4.65	2.95
c	b + Ar (20 min)	1.70	1.65
d	1.0 mM + O_2, 1 atm (3 min)	3.60	1.90
e	d + Ar (20 min)	1.90	2.80
f	e + O_2, 1 atm (3 min)	3.60	1.90
g	f + Ar (20 min)	1.65	2.75
h	g + Ar (10 h)	1.53	2.30
i	h + O_2, 1 atm (25 min)	3.25	1.55
j	0.1 mM 1 + O_2, 1 atm (3 min)	3.25	0.93
k	j + Ar (20 min)	1.55	1.00
l	0.2 mM 1 + O_2, 1 atm (3 min)	3.45	1.10
m	l + Ar (20 min)	1.65	1.45
n	5 mM 1 + O_2, 1 atm (3 min)	4.30	3.65
o	n + Ar (20 min)	2.76	5.04
p	1.0 mM 1 + O_2, 1 atm (5 min)	4.65	2.95
q	1.0 mM 1 + air (5 min)	3.65	3.50
r	10 mM 1 + O_2, 1 atm (5 min)	6.20	5.30
s	10 mM 1 + air (5 min)	5.15	6.55

[a] Solutions of 1 were prepared in situ by combining $Mn^{III}(OAc)_3$, 3,5-di-*tert*-butylcatechol, and tetramethylammonium hydroxide in a mole ratio of 1:3:6. The apparent molar absorptivities, ϵ, are based on the formal concentrations of 1 in the solutions.