

Metal-nitroxyl interactions. 55: Manganese (III) – nitroxyl electron-electron spin-spin interaction

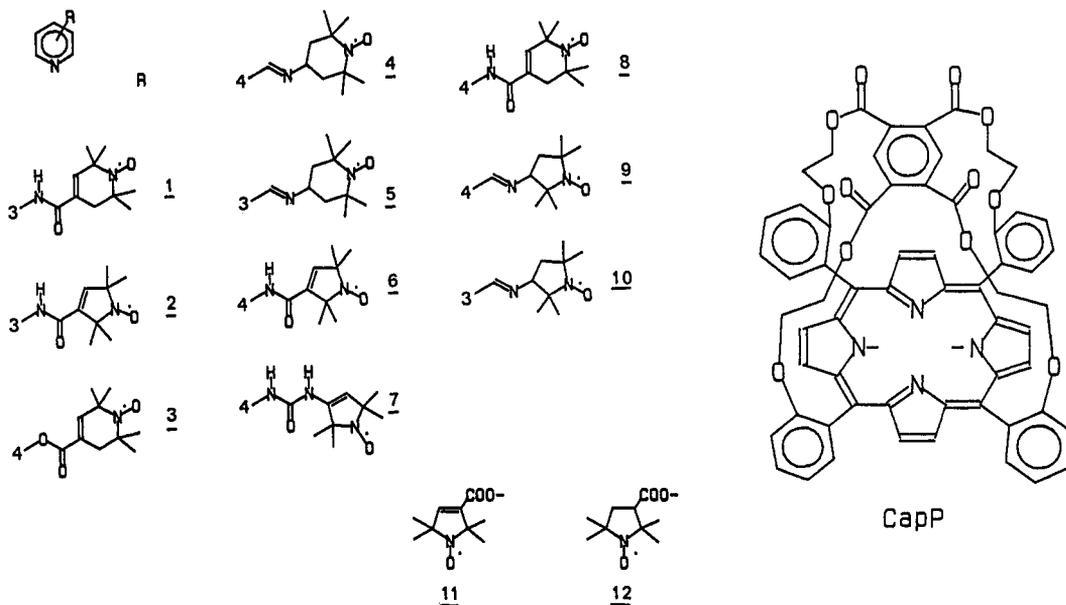
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Abstract - When a nitroxyl oxygen binds to the Mn(III) complex of a capped tetraphenylporphyrin there is strong antiferromagnetic coupling of the Mn $S = 2$ and the nitroxyl $S = 1/2$ to give an $S = 3/2$ ground state with a characteristic EPR signal at $g \sim 4$. When a spin-labeled pyridine coordinates to the Mn(III) porphyrin via the pyridine nitrogen, the electron-electron spin-spin interaction causes broadening and splitting of the nitroxyl EPR signal. Small splittings were partially collapsed at 100 K and resolved at 5 K. The Mn-nitroxyl spin-spin coupling constants were 0.3 to 0.5 times the values for copper bis(hexafluoroacetylacetonate) adducts of the same ligands. Stronger electron-electron exchange interaction was observed for two Mn(III) complexes with nitroxyl carboxylates as the axial ligands than for the spin-labeled pyridine complexes. This series of compounds demonstrates the effects on the nitroxyl EPR spectra of Mn-nitroxyl interaction ranging from less than the nitrogen hyperfine splitting to $|J| \sim 0.08 \text{ cm}^{-1}$ and highlights the long-range nature of electron-electron exchange interaction.

INTRODUCTION

Resolved electron-electron spin-spin coupling has been observed in the EPR spectra of nitroxide spin-labeled complexes of vanadyl ion, Cr(III), Mn(II), low spin (l.s.) and high spin (h.s.) Fe(III), l.s. Co(II), Ni(II), Cu(II), and Ag(II) (ref. 1,2). In this paper we extend this series to include h. s. Mn(III). Spin-labeled ligands were selected to permit comparison of the manganese-nitroxyl interaction with results reported previously for other metals (ref. 1,2).



EXPERIMENTAL METHODS

Nitroxyl spin-labeled pyridines 1 - 10 were prepared as previously reported (ref. 3,4). Meso-5,10,15,20-tetra(2-(2-propionyxyethoxy)phenyl)porphyrin (CapP) was prepared as reported in ref. 5. It was converted to the Mn(III) perchlorate complex by the method reported in ref. 6 for preparation of Mn(III) tetraphenylporphyrin perchlorate (MnTPPClO₄). MnTPP.11 and MnTPP.12 were prepared by reaction of (MnTTP)₂O (ref. 7) with the corresponding nitroxyl acid for about 2 hours at room temperature in 1:1 toluene:CH₂Cl₂ solution.

EPR spectra were recorded on a IBM/Bruker ER200 interfaced to an IBM CS9000 laboratory computer. Spectra at 100 K were obtained by cooling the sample in a stream of cold nitrogen gas. Spectra at 5 - 6 K were obtained with an Oxford liquid helium cryostat. Modulation amplitudes (100 kHz) were less than one-fifth of the line widths and microwave powers were below the values that caused saturation of the signals. Quantitation of the first-derivative EPR signals was done by comparison of double integrals of the spectra with double integrals of spectra of nitroxyl radicals at known concentration. Throughout the text, integral means the second integral of the first-derivative EPR spectra.

Simulated spectra were calculated with a computer program (METNO) that employs Belford's fourth-order frequency shift perturbation method (ref. 8). The Hamiltonian included the Zeeman interaction for Mn(III) and nitroxyl, dipolar interaction between the two paramagnetic centers, and an isotropic exchange interaction (ref. 9). A negative sign of *J* indicates an antiferromagnetic interaction. The manganese zero-field splitting was estimated to be -1.5 cm⁻¹ (ref. 10). The calculation does not include the nitroxyl nitrogen hyperfine splitting so it was applied only to spectra in which the spin-spin interaction was larger than the nitrogen hyperfine splitting. The superposition of the spectra for coordinated and free nitroxyl obscured part of the spectrum for the complex, which resulted in substantial uncertainties in the values of the electron-electron coupling constants, *J*. Although the simulated spectra were sensitive to the sign of *J*, the experimental spectra did not contain sufficient detail to permit determination of the sign of *J*.

COORDINATION OF NITROXYL OXYGEN

It is important to distinguish between the spin-spin coupling that occurs when the nitroxyl oxygen coordinates to a paramagnetic metal and the coupling that occurs when a spin-labeled ligand coordinates via a donor atom other than the nitroxyl oxygen (ref. 1). It has been shown that when a nitroxyl oxygen binds to MnTPPClO₄ there is strong antiferromagnetic coupling between the *S* = 2 Mn(III) and the *S* = 1/2 nitroxyl to give an *S* = 3/2 ground state. In frozen solution the EPR spectrum of the manganese-nitroxyl complex has a characteristic signal at *g*_⊥ = 4 (ref. 11). Coordination of a second mole of nitroxyl results in an *S* = 1 ground state for which EPR spectra were not detected.

Analysis of the equilibria for coordination of nitroxyl to MnTPPClO₄ was complicated by the presence of the mono- and bis-nitroxyl adducts. We have therefore prepared the Mn(III) complex of capped porphyrin, CapP, in which it was anticipated that bis-nitroxyl adducts could not form because these large ligands would have access to only one side of the porphyrin plane.

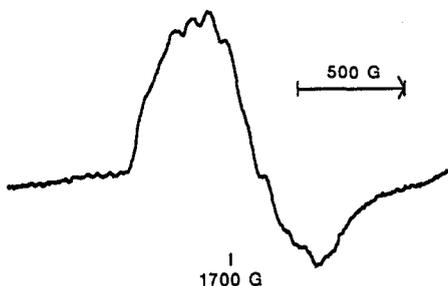


Fig. 1. 2000 G EPR spectrum of the *g* ~ 4 signal for Mn(CapP)ClO₄.TEMPO in 1:1 toluene:CH₂Cl₂ solution at 100 K.

When TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) was added to a solution of $\text{Mn}(\text{CapP})\text{ClO}_4$, an EPR signal was observed at $g \sim 4$ in frozen solution (Fig. 1). The partially resolved manganese hyperfine splitting of about 75 G was similar to that observed previously for nitroxyl radicals coordinated to MnTPPClO_4 (ref. 11). As the ratio of TEMPO to $\text{Mn}(\text{CapP})\text{ClO}_4$ was increased, the intensity of the signal at $g \sim 4$ increased and reached a plateau. The intensity of the $g \sim 4$ signal remained constant at high nitroxyl concentration, which indicated that the cap prevented coordination of a second mole of TEMPO. The concentration of TEMPO that was not coordinated was calculated by double integration of the nitroxyl signal. The concentration of $\text{Mn}(\text{CapP})\cdot\text{TEMPO}$ was calculated from the difference between the initial concentration of TEMPO and the concentration of TEMPO that was not coordinated. These values were consistent with the relative amplitudes of the $g \sim 4$ EPR signal. The concentration of $\text{Mn}(\text{CapP})\text{ClO}_4$ that was not coordinated was the difference between the initial concentration of $\text{Mn}(\text{CapP})\text{ClO}_4$ and the concentration of $\text{Mn}(\text{CapP})\cdot\text{TEMPO}$. The equilibrium constant for coordination of the nitroxyl oxygen was $(8 \pm 2) \times 10^3$ M.

COORDINATION OF SPIN-LABELED PYRIDINES VIA THE PYRIDINE NITROGEN

In solutions containing $\text{Mn}(\text{CapP})\text{ClO}_4$ and a spin-labeled pyridine there was competition between coordination of the nitroxyl oxygen and the pyridine nitrogen. When the concentration of spin-labeled pyridine exceeded the concentration of $\text{Mn}(\text{CapP})\text{ClO}_4$ the EPR signal at $g \sim 4$ was barely detectable, which indicated that coordination of the pyridine nitrogen was strongly favored over coordination of the nitroxyl oxygen. When the concentration of $\text{Mn}(\text{CapP})\text{ClO}_4$ was about twice as great as the concentration of the spin-labeled pyridine, there was a strong signal at $g \sim 4$. This signal is assigned to a dimer in which the pyridine nitrogen of a spin-labeled pyridine was coordinated to one manganese porphyrin and the nitroxyl oxygen of the same molecule was coordinated to a second manganese porphyrin. Analogous bridged species have been observed for copper (II), vanadyl, and l.s. cobalt(II) complexes of spin-labeled pyridines (ref. 1,2).

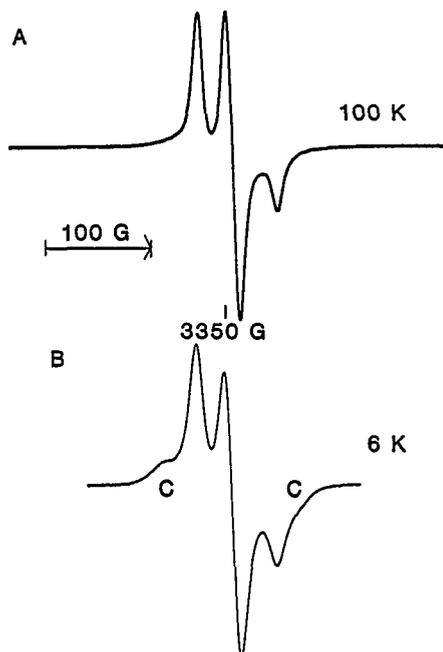


Fig. 2. EPR spectra of $\text{Mn}(\text{CapP})\text{ClO}_4 \cdot 2$ in 1:1 toluene: CH_2Cl_2 solution. A) 400 G spectrum obtained at 100 K. B) 250 G spectrum obtained at 6 K.

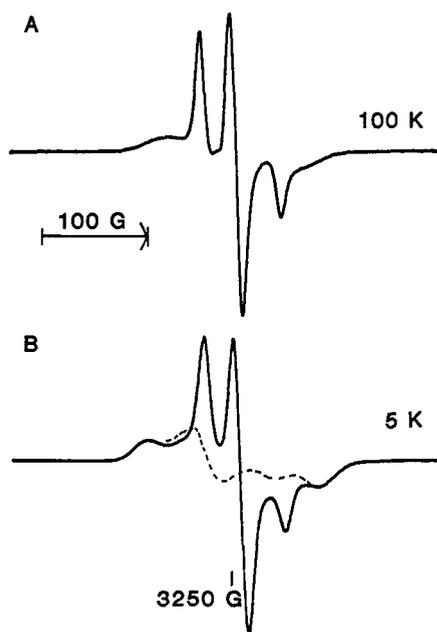


Fig. 3. 400 Gauss EPR spectra of $\text{Mn}(\text{CapP})\text{ClO}_4 \cdot 4$ in 1:1 toluene: CH_2Cl_2 solution at 100 K (A) and 5 K (B). The dashed line in (B) indicates a simulated spectrum in regions where it does not overlay the experimental data.

EPR spectra of a solution containing 1.0 mM Mn(CapP)ClO₄ and 1.0 mM 2 are shown in Fig. 2. At 100 K the nitroxyl signal for Mn(CapP)ClO₄.2 was broad and difficult to distinguish from the signal for 2 that was not coordinated ("free" ligand). When the sample was cooled to 6 K, peaks for the Mn(III)-nitroxyl complex were observed at higher and lower field than the signal for "free" ligand. The resolved peaks for the complex are designated with a C in Fig. 2B. The splitting between the two peaks designated C was about 125 G. This splitting is too small to permit simulation of the spectra without including the nitroxyl nitrogen hyperfine coupling.

EPR spectra of a solution containing 1.0 mM Mn(CapP)ClO₄ and 1.2 mM 4 are shown in Fig. 3. At 100 K the peaks for the Mn(III)-nitroxyl complex were partially resolved to low-field and high-field of the signals for "free" nitroxyl (Fig. 3A). At 5 K the peaks for the complex were sharper and more clearly resolved from the peaks for "free" nitroxyl (Fig. 3B) and the extrema were further apart than at 100 K. The simulated spectrum indicated by the dashed line in Fig. 3B was obtained with $J = 0.0040 \text{ cm}^{-1}$ and an interspin distance of 12 Å. Due to the overlap of the spectrum of the complex with that for "free" nitroxyl, there is a range of parameters that gave comparable agreement with the resolved portion of the spectrum. $|J|$ was estimated to be $0.004 \pm 0.001 \text{ cm}^{-1}$.

The EPR spectrum of a solution containing 1.0 mM Mn(CapP)ClO₄ and 1.2 mM 10 showed a broad signal for the coordinated nitroxyl (Fig. 4) that was not strongly temperature dependent. The simulated spectrum indicated by the dashed line in Fig. 4B was obtained with $J = 0.018 \text{ cm}^{-1}$ and an interspin distance of 8 Å. Comparison of simulations calculated for a range of parameters indicated $|J| = 0.018 \pm 0.003 \text{ cm}^{-1}$.

TEMPERATURE DEPENDENCE OF RESOLVED SPLITTING

It is proposed that the rate of relaxation of the manganese unpaired electrons at 100 K was sufficiently fast that the electron-electron spin-spin splitting was partially collapsed for splittings less than a few hundred gauss. At 6 K the slower relaxation of the Mn(III) permitted resolution of these spin-spin splitting. A similar collapse of electron-electron spin-spin splitting with increasing temperature has been observed for spin-labeled complexes of h.s. Fe(III) (ref. 12). Partial collapse of splittings of a few hundred gauss indicates that T_1 at 100 K for the Mn(III) in these complexes is of the order of $2 \times 10^{-10} \text{ s/rad}$ (ref. 12). Thus the manganese-nitroxyl interaction provided information about the Mn(III) despite the fact that the Mn(III) zero-field splitting was larger than the X-band EPR quantum and most of the Mn(III) EPR transitions were not observable.

DEPENDENCE OF EXCHANGE ON THE METAL-NITROXYL LINKAGE

Simulations of the spectra for several of the complexes confirmed that increasing splitting between the outermost turning points of the spectra of the manganese-nitroxyl complexes reflected increasing values of J for this series of spin-labeled complexes. This is true primarily because the interspin distances were relatively long for the complexes of 1 - 10, which caused the exchange interaction to have a greater impact on the spectra than the dipolar interaction (ref. 2). Comparison of the splittings between the outermost peaks in the spectra at 5 - 6 K gave the following order of increasing exchange interaction: 1 ~ 2 ~ 3 < 4 < 5 ~ 6 < 7 ~ 8 < 9 ~ 10. H.s. Mn(III) has an unpaired electron in the d_{z^2} orbital, which has σ symmetry with respect to the coordinated pyridine. If this unpaired electron dominates the spin-spin interaction, the dependence of J on the metal-nitroxyl linkage would be expected to be similar to that observed for Cu(II) complexes in which the unpaired electron also has σ symmetry with respect to the coordinated pyridine. The order of increasing exchange interaction observed for Cu(II) bis (hexafluoroacetylacetonate) complexes of the spin-labeled pyridines is: 1 < 3 < 2 ~ 4 ~ 5 < 6 ~ 8 < 7 < 10 < 9 (ref. 1). There is substantial similarity in the dependence of the electron-electron exchange interaction on the metal-nitroxyl linkage for the two series of compounds, which emphasizes the generality of long-range electron-electron exchange interaction.

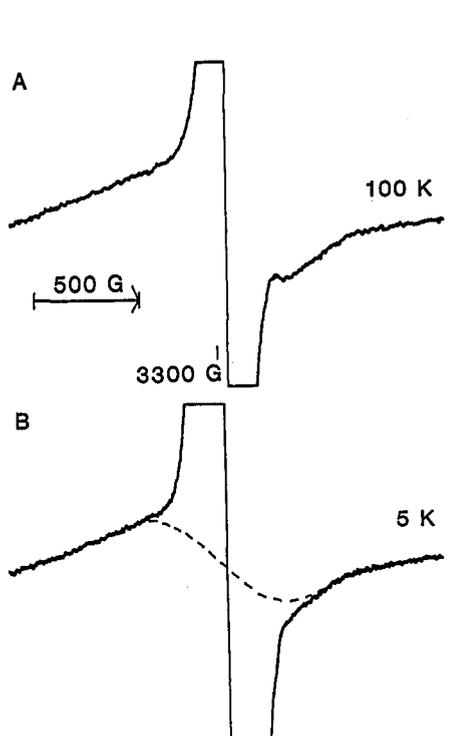


Fig. 4. 2000 Gauss EPR spectra of $\text{Mn}(\text{CapP})\text{ClO}_4 \cdot 10$ in 1:1 toluene: CH_2Cl_2 solution at 100 K (A) and 5 K (B). The dashed line in (B) indicates a simulated spectrum in regions where it does not overlay the experimental data.

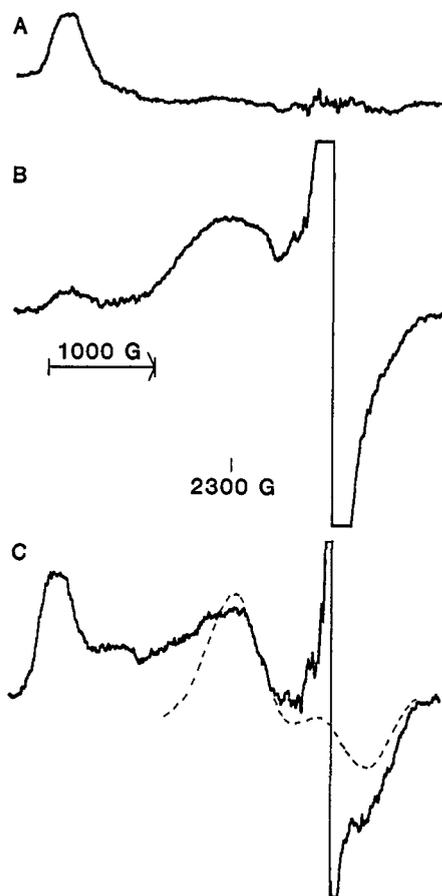


Fig. 5. 4000 G EPR spectra obtained at 100 K for 1:1 toluene: CH_2Cl_2 solutions of A) 10 mM $(\text{MnTPP})_2\text{O}$, B) 1 mM MnTPP.11 and 1 mM $(\text{MnTPP})_2\text{O}$, and C) 2 mM MnTPP.12 and 8 mM $(\text{MnTPP})_2\text{O}$. The dashed line in (C) indicates a simulated spectrum.

DEPENDENCE OF EXCHANGE ON THE NUMBER OF UNPAIRED ELECTRONS

If a single unpaired electron on the metal dominates the metal-nitroxyl interaction, the magnitude of J is expected to be inversely proportional to the number of metal unpaired electrons (ref. 13), which predicts that the values of J for $\text{Mn}(\text{III})$ would be $1/4$ the values of J for the corresponding $\text{Cu}(\text{II})$ complexes. The ratios of the values of J for the $\text{Mn}(\text{III})$ and $\text{Cu}(\text{II})$ complexes were about: 0.5, ligand 4; 0.3, ligand 7; and 0.4, ligand 10. These ratios are all higher than the 0.25 expected, which may be due to participation of more than one of the manganese unpaired electrons in the metal-nitroxyl spin-spin interaction. Comparison of values of J for $S = 3/2$ $\text{Cr}(\text{III})$ with values for $S = 1/2$ complexes gave ratios of $1/2$ to $2/3$. These ratios also are greater than the $1/3$ that was expected (ref. 9). Nevertheless, the general pattern is smaller values of J for increasing numbers of unpaired electrons on the metal.

NITROXYL CARBOXYLATES AS AXIAL LIGANDS

The EPR spectrum of $(\text{MnTPP})_2\text{O}$ gave a signal at $g = 8.1$ (Fig. 5A). The intensity and position of this signal are similar to those of the $g = 7.8$ signal reported for MnTPPCl (ref. 11). $(\text{MnTPP})_2\text{O}$ is readily hydrolyzed to MnTPPOH , which may be the source of this signal. Reaction of $(\text{MnTPP})_2\text{O}$ with nitroxyl acids 11 or 12 resulted in formation of a complex in which the carboxylate is the axial ligand. Excess $(\text{MnTPP})_2\text{O}$ was used to shift the equilibrium toward complex formation. The EPR spectra of frozen solutions of these complexes had peaks at $g = 8.1$ and 2.0 due to excess $(\text{MnTPP})_2\text{O}$ (or MnTPPOH) and unreacted nitroxyl. The spectrum of the complex was a broad signal extending from $g \sim 2.8$ to 1.8 (Fig. 5B, 5C). The simulated spectrum shown in Fig. 5C was obtained with $J = -0.08 \text{ cm}^{-1}$. Thus the manganese-nitroxyl exchange interaction was stronger for the axial nitroxyl acids than for the spin-labeled pyridines examined in this study. In frozen solutions of h.s. Fe(III) porphyrins with nitroxyl carboxylates 11 and 12 as the axial ligands the iron-nitroxyl exchange coupling constant was $0.15 \pm 0.03 \text{ cm}^{-1}$ (ref. 14), which is similar to the magnitude of the interaction observed for the analogous Mn(III) complex.

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REFERENCES

1. S. S. Eaton and G. R. Eaton, Coord. Chem. Rev., **83**, 29-72 (1988).
2. G. R. Eaton and S. S. Eaton, Biol. Magn. Reson., **8**, in press.
3. B. M. Sawant, A. L. W. Shroyer, G. R. Eaton, and S. S. Eaton, Inorg. Chem., **21**, 1093-1101 (1982).
4. J. K. More, K. M. More, G. R. Eaton, and S. S. Eaton, Inorg. Chem., **21**, 2455-2460 (1982).
5. J. Almog, J. E. Baldwin, M. J. Crossley, J. F. Debernardis, R. L. Dyer, J. R. Huff, and M. K. Peters, Tetrahedron, **37**, 3589-3601 (1981).
6. J. T. Landrum, K. Hatano, W. R. Scheidt, and C. A. Reed, J. Am. Chem. Soc., **102**, 6729-6735 (1980).
7. E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, J. Am. Chem. Soc., **93**, 3162-3167 (1971).
8. R. L. Belford, P. H. Davis, G. G. Belford, and T. M. Lenhardt, ACS Symp. Ser., **5**, 40-50 (1974).
9. K. M. More, G. R. Eaton, S. S. Eaton, and K. Hideg, Inorg. Chem., **25**, 3865-3869 (1986).
10. B. J. Kennedy and K. S. Murray, Inorg. Chem., **24**, 1557-1560 (1985).
11. K. M. More, G. R. Eaton, and S. S. Eaton, Inorg. Chem., **26**, 2618-2620 (1987).
12. L. Fielding, K. M. More, G. R. Eaton, and S. S. Eaton, J. Am. Chem. Soc., **108**, 8194-8196 (1986).
13. P. J. Hay, J. C. Thibeault, and R. Hoffmann, J. Am. Chem. Soc., **97**, 4884-4899 (1975).
14. L. Fielding, K. M. More, G. R. Eaton, and S. S. Eaton, Inorg. Chem., in press.