

An Eight-Coordinate Vanadium Thiolate Complex with Charge Delocalization between V(V)–Thiolate and V(IV)–Thiyl Radical Forms

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 Supporting Information

ABSTRACT: A six-coordinate oxovanadium(V) thiolate complex and an eight-coordinate non-oxovanadium thiolate complex, $[\text{PPh}_4][\text{VO}(\text{PS}3'')(\text{OCH}_3)]$ (**1**) and $[\text{NEt}_4][\text{V}(\text{PS}3'')_2]$ (**2**) ($\text{PS}3'' = \text{P}(\text{C}_6\text{H}_3-3\text{-Me}_3\text{Si-2-S})_3^{3-}$), respectively, have been isolated and structurally characterized. The former belongs to a limited collection of oxovanadium(V) thiolate complexes. The latter has an unusual coordination number of eight. More importantly, its consensus electronic structure derived from its spectroscopic data should be considered as the resonance forms of V^{V} –thiolate and V^{IV} –thiyl radical species. This implies that V^{IV} –thiyl radical can maintain a stable presence in biological systems.

Cysteine–thiyl radicals have been identified in several enzymes and have been suggested to play roles in their functions,¹ such as in ribonucleotide reductase (RNR).² In addition, a thiyl radical species is proposed as a key intermediate in the biological radical sulfur insertion reaction.³ Furthermore, a formal “Ni(III)Fe(II)” state containing cysteine–thiyl radical character has been recognized in the active site of NiFe hydrogenase according to spectroscopic and theoretical studies.⁴ Due to this biological significance, there is an increasing interest in studying (thiyl)metal complexes.⁵ Examples are $[\text{Co}^{\text{III}}\text{L}]^+$,⁶ $(t\text{-BuS}^\bullet)[\text{Cr}(\text{CO})_5]_2$,⁷ and $[\text{Ru}^{\text{III}}(\text{DPPBT})_2(\text{DPBT}^\bullet)]^{+8}$ generated from one-electron oxidation of their corresponding forms, respectively, where L is a TACN-trithiolato ligand and DPBT is 2-(diphenylphosphino)thiaphenolate. A bis(μ -thiolato)dinickel(II) complex can be oxidized by one electron and yield a dinickel species with the charge delocalization between the $[\text{Ni}^{\text{III}}(\text{RS}^-)]$ and $[\text{Ni}^{\text{II}}-(\text{RS}^\bullet)]$ redox extremes.⁹ A dithiosalicylidenediamine Ni^{II} complex can be oxidized by one electron and generate a complex with Ni^{II} –thiyl radical character.¹⁰

The broad relevance of vanadium thiolate chemistry to biological systems has garnered increasing attention from researchers.¹¹ The chemistry of high-valent vanadium ions interacting with cysteine and glutathione has several biomedical aspects, such as the protein tyrosine phosphatase (PTP) inhibition by vanadate,¹² the anti-diabetic behavior of vanadium compounds,¹³ the redox conversion of vanadium in ascidians,¹⁴ the function of amavadin isolated from *Amanita* mushrooms,¹⁵ and the toxicity of vanadium in biological systems.¹⁶ Based on these backgrounds, we and others have made efforts to investigate the reactions of high-valent vanadium ions with thiol-containing ligands.¹⁷ Examples have shown that the reaction of

V^{V} with thiolate might lead to the formation of a V^{V} thiolate complex.^{17d,f} Recently, studies have indicated that V^{V} –thiol complexes indeed form. Redox chemistry was also evident during the reaction of vanadate with 2-mercaptoethanol as well as dithiothreitol under biological conditions.^{17c,18}

In our previous studies, the redox conversion of $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$ coupled with $\text{RS}^-/\text{RS}^\bullet$ was demonstrated in the reactions of $\text{V}^{\text{V}}\text{O}(\text{O-}i\text{-Pr})_3$ with tris(benzenethiolato)phosphine derivatives, $\text{P}(\text{C}_6\text{H}_3-5\text{-Me-2-S})_3^{3-}$ ($\text{PS}3'$) and $\text{P}(\text{C}_6\text{H}_4-2\text{-S})_3^{3-}$ ($\text{PS}3$).^{17b} The pathway likely involves a thiyl radical-bound vanadium complex as an intermediate. To observe or trap intermediates of this transformation, $\text{PS}3''$ ligand, which has the sterically hindered substituent $\text{Si}(\text{CH}_3)_3$, in phenylthiolates was employed to react with $\text{V}^{\text{V}}\text{O}(\text{O-}i\text{-Pr})_3$. As a result, two species, $[\text{PPh}_4][\text{VO}(\text{PS}3'')(\text{OCH}_3)]$ (**1**) and $[\text{NEt}_4][\text{V}(\text{PS}3'')_2]$ (**2**), were isolated and characterized (Chart 1). Complex **1** is a $\text{V}^{\text{V}}=\text{O}$ species, whereas complex **2** is a formal V^{V} species. However, the electronic structure of **2** is best described as resonance forms between V^{V} –thiolate and V^{IV} –thiyl radical states. It is also worth noting that **2** represents a new set of eight-coordinate non-oxovanadium complexes (bare system) that has the same coordination number as amavadin, a natural V^{IV} product in *Amanita* mushrooms. Reports on synthetic vanadium complexes with a coordination number of eight are still scarce in the literature.¹⁹

An *i*-PrOH solution of $\text{VO}(i\text{-PrO})_3$ was added to a methanol solution of $\text{Na}_3[\text{PS}3'']$ to generate a deep green solution. By adding different counterions, $[\text{PPh}_4]\text{Br}$ and $[\text{NEt}_4]\text{Br}$, complexes **1** and **2** were precipitated as green and brick red crystalline solids, respectively. The structural data for **1** and **2** were obtained by X-ray crystallography, and their ORTEP diagrams are shown in Figures 1 and 2, respectively. Complex **1** belongs to a small class of V^{V} –thiolate complex.^{17d,f,k,20} The X-ray structure of **1** reveals a six-coordinate complex of V(V) through binding with an oxo group, a methoxide ion, and a tetradentate $\text{PS}3''$ ligand. The vanadium center adopts a highly distorted octahedral geometry with the oxo group *trans* to the thiolate and the methoxide *trans* to the phosphine donor. The three *trans* angles are 151.0° (S1-V-S2), 160.0° (O1-V-P1), and 168.6° (O2-V-S3) away from 180° for an ideal octahedron. The distance of the $\text{V}=\text{O}$ bond is $1.603 \text{ \AA}$, comparable to those in reported oxovanadium(V) thiolate complexes ($1.57\text{--}1.60 \text{ \AA}$). The V-S bond distance ($2.662 \text{ \AA}$) *trans* to the oxo group is much

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Chart 1

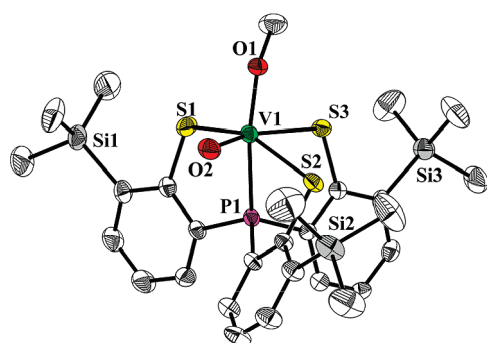
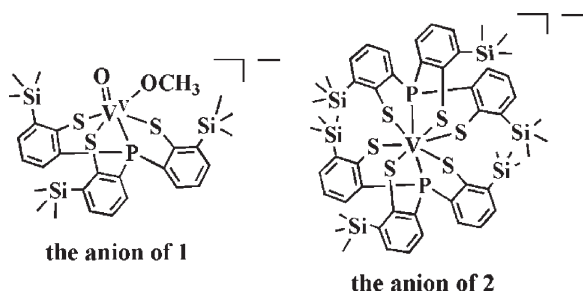


Figure 1. Molecular structure of **1** shown with 35% thermal ellipsoids. The counteranion and H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V–S1 2.3957(10), V–S2 2.4276(10), V–S3 2.6615(9), V–O1 1.790(2), V–O2 1.603(2), V–P1 2.3880(9), S1–V–S2 151.04(4), S1–V–S3 89.18(4), S2–V–S3 82.59(3), P1–V–S1 79.15(3), P1–V–S2 71.93(3), P1–V–S3 76.19(3), O1–V–S1 93.70(7), O1–V–S2 113.01(7), O1–V–S3 84.87(7), O1–V–P1 159.76(7), O2–V–S1 94.83(9), O2–V–S2 88.79(9), O2–V–S3 168.55(9), O2–V–P1 94.00(8), O1–V–O2 105.52(11).

longer than the other two (2.428 and 2.396 Å); the latter are much longer than those in the reported oxovanadium(V) thiolate complexes (2.24–2.31 Å) due to the difference in their coordination numbers.

Complex **2** consists of a dodecahedral vanadium center bound to two phosphorus and six sulfur atoms of two PS₃'' ligands. S1, S3, S6, and P1 atoms form the same plane, with a mean plane deviation of 0.0083 Å. This plane is nearly perpendicular to the plane generated by S2, S4, S5, and P2 atoms, with a mean plane deviation of 0.0425 Å. The dihedral angle of 89.8° between these two planes is close to the ideal value of 90° found in a regular dodecahedron.²¹ The vanadium center has a dodecahedral geometry which could be considered as one elongated tetrahedron formed with P1, P2, S3, and S4 atoms and a collapsed tetrahedron arising from S1, S2, S5, and S6 atoms.^{21a} In the elongated tetrahedron, the average length of the V–S bonds is 2.634 Å, 0.184 Å longer than in the collapsed one (2.450 Å).

Complex **1** has a V=O stretching band of 941 cm^{−1}. The electronic spectrum of **1** displays an intense shoulder around 390 nm which is associated with a ligand-to-metal charge-transfer band (Figure 3). The ⁵¹V NMR spectrum exhibits a single peak at −276 ppm (relative to VOCl₃), indicating a single V^V species in solution. The value is closer to the only reported six-coordinate oxovanadium(V) thiolate complex (−186 ppm) but more upfield shifted compared to other five-coordinate oxovanadium(V) thiolate complexes (338, 557, and 191 ppm).^{17d,f,20}

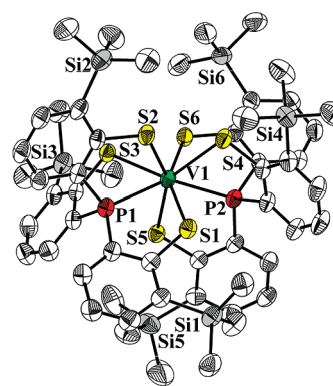


Figure 2. Molecular structure of **2** shown with 35% thermal ellipsoids. The counteranion and H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V–S1 2.4486(13), V–S2 2.4065(13), V–S3 2.6108(12), V–S4 2.6564(15), V–S5 2.4545(14), V–S6 2.4410(14), V–P1 2.4828(14), V–P2 2.4561(13), S1–V–S2 93.88(5), S1–V–S3 142.01(5), S1–V–S4 82.74(5), S1–V–S5 85.05(5), S1–V–S6 148.57(5), S2–V–S3 82.79(4), S2–V–S4 65.16(4), S2–V–S5 151.07(5), S2–V–S6 103.75(5), S3–V–S4 127.96(5), S3–V–S5 80.56(4), S3–V–S6 67.12(4), S4–V–S5 142.68(5), S4–V–S6 81.45(5), S5–V–S6 91.32(5), P1–V–S1 76.44(4), P1–V–S2 76.45(5), P1–V–S3 65.96(4), P1–V–S4 134.62(5), P1–V–S5 75.21(4), P1–V–S6 132.65(5), P2–V–S1 72.89(4), P2–V–S2 129.75(5), P2–V–S3 136.12(4), P2–V–S4 65.17(4), P2–V–S5 77.54(4), P2–V–S6 75.84(4), P1–V–P2 140.27(4).

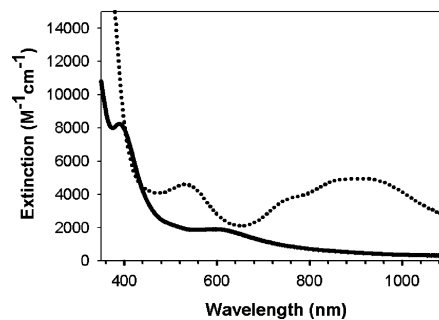


Figure 3. Electronic spectra of **1** (0.10 mM, solid line) and **2** (0.15 mM, dotted line) in CH₃CN.

Interestingly, the electronic spectrum of **2** exhibits very different absorption bands compared to **1**, one at 533 nm ($\epsilon = 4.61 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and the other at 908 nm ($\epsilon = 4.96 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) with a shoulder at 740 nm (Figure 3). The pattern is relatively similar to that for an electrochemically generated (thiyl)Co^{III} complex, [Co^{III}L^{•+}]⁺, where L is a TACN-trithiolato ligand.⁶ This implies that **2** might consist of a thiyl radical-bound vanadium species. The ⁵¹V and ¹H NMR spectra, as shown in Figure 4, further suggest that the electronic structure of **2** can be better understood as resonance forms $[\text{V}^{\text{V}}(\text{PS}_3'')_2]^- \leftrightarrow [\text{V}^{\text{IV}}(\text{PS}_3'')(\text{PS}_3'')^-]$. The ⁵¹V NMR spectrum shows a single peak at $\delta = 483 \text{ ppm}$, indicating a +5 oxidation state for the vanadium center. However, the ¹H NMR spectrum displays some characteristic peaks at 20.24, 19.02, 11.70, 9.61, and −3.20 ppm, suggesting a paramagnetic character of the metal center. Notably, the reported ⁵¹V NMR data for eight-coordinate non-oxovanadium complexes are very few. Compound **2** has a chemical shift at $\delta = 483 \text{ ppm}$ is more downfield shifted compared to oxidized

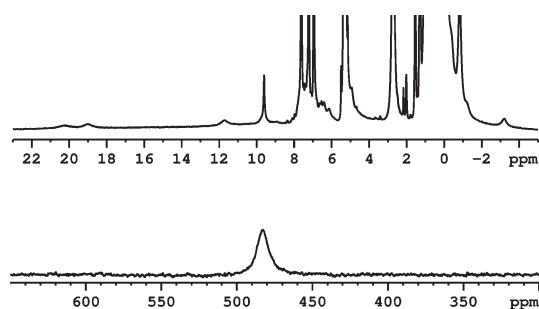


Figure 4. ^1H (top) and ^{51}V (bottom) NMR spectra of **2** in CD_2Cl_2 .

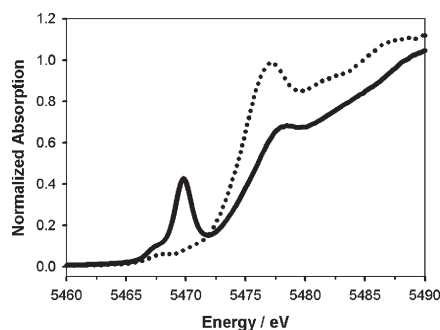


Figure 5. Vanadium K-edge X-ray absorption spectra of **1** (solid line) and **2** (dotted line).

amavadin and its related analogues (approximately -200 to -300 ppm),^{19c,22} likely attributed to S ligands for the former versus N/O ligands for the latter cases.²³

The V K-edge X-ray absorption spectrum (XAS) is informative for the oxidation state and coordination environment of metal complexes and has been applied in studying the charge distribution of vanadium complex with catecholate and dithiolene ligands.²⁴ The V K-edge XAS of **1** and **2** were measured, and the normalized spectra are shown in Figure 5. The edge energy, determined from the inflection point of the rising edge, is 5476.0 ± 0.2 eV for **1**, slightly higher than that for **2**, 5475.4 ± 0.2 eV (Figure 5). This implies that **1** has a higher oxidation state for the vanadium center than **2**. The spectra of **1** and **2** also display very different pre-edge peaks. The intensity of the pre-edge absorbance is sensitive to the ligation environment and geometry of the metal center.²⁵ As a result, **1** has a less-symmetrical ligation environment and a highly distorted geometry away from an ideal octahedron, giving a strong pre-edge peak. In contrast, the geometry of **2** is almost an ideal dodecahedron with inversion symmetry, leading to the relatively weak intensity of the pre-edge peak.

In summary, a six-coordinate oxovanadium(V) thiolate complex and an eight-coordinate non-oxovanadium thiolate complex have been isolated and structurally characterized. The former belongs to a limited collection of oxovanadium(V) thiolate complexes. The latter has an unusual coordination number with geometry similar to that of amavadin. Importantly, the consensus electronic structure for the latter, derived from spectroscopic data, should be considered as the resonance forms of $\text{V}^{\text{V}}\text{--thiolate}$ and $\text{V}^{\text{IV}}\text{--thiyl radical}$ species. Taken together, these results provide new insights into the chemistry of vanadate interacting with biological molecules containing sulfur ligands such as cysteine and glutathione. The electronic structure of the

vanadium–sulfur bond requires a more sophisticated examination; one that considers the presence of different resonance forms. This implies that $\text{V}^{\text{IV}}\text{--thiyl radical}$ can maintain a stable presence in biological systems. Furthermore, the reactivity of a vanadium-bound thiyl radical is also likely responsible for inhibiting PTP as well as being involved in the mechanism of vanadium-containing biomedical systems. The details of this chemistry and theoretical work are currently under investigation in our laboratories.

■ ASSOCIATED CONTENT

S Supporting Information. Synthetic details and additional characterization and crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) Giles, N. M.; Giles, G. I.; Jacob, C. *Biochem. Biophys. Res. Commun.* **2003**, *300*, 1.
- (2) Licht, S.; Gerfen, G. J.; Stubbe, J. *Science* **1996**, *271*, 477.
- (3) Fontecave, M.; Ollagnier-de-Choudens, S.; Mulliez, E. *Chem. Rev.* **2003**, *103*, 2149.
- (4) Marr, A. C.; Spencer, D. J. E.; Schröder, M. *Coord. Chem. Rev.* **2001**, *1055*.
- (5) Ray, K.; Petrenko, T.; Wieghardt, K.; Neese, F. *Dalton Trans.* **2007**, 1552.
- (6) Kimura, S.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 6025.
- (7) Springs, J.; Janzen, C. P.; Daresbourg, M. Y.; Calabrese, J. C.; Krusic, P. J.; Verpeaux, J. N.; Amatore, C. *J. Am. Chem. Soc.* **1990**, *112*, 5789.
- (8) Grapperhaus, C. A.; Poturovic, S. *Inorg. Chem.* **2004**, *43*, 3292.
- (9) Branscombe, N. D.; Atkins, A. J.; Martin-Becerra, A.; McInnes, E. J. L.; Mabbs, F. E.; McMaster, J.; Schröder, M. *Chem. Commun.* **2003**, 1098.
- (10) Stenson, P. A.; Board, A.; Marin-Becerra, A.; Blake, A. J.; Davies, E. S.; Wilson, C.; McMaster, J.; Schröder, M. *Chem.—Eur. J.* **2008**, *14*, 2564.
- (11) (a) Rehder, D. *Bioinorganic Vanadium Chemistry*; John Wiley & Sons: New York, 2008. (b) Crans, D. C.; Smeeth, J. J.; Gaidamaskas, E.; Yang, L. *Chem. Rev.* **2004**, *104*, 849.
- (12) Huyer, G.; Liu, S.; Kelly, J.; Moffat, J.; Payette, P.; Kennedy, B.; Tsapralis, G.; Gresser, M. J.; Ramachandran, C. *J. Biol. Chem.* **1997**, *272*, 843.
- (13) (a) Benabe, J. E.; Echegoyen, L. A.; Pastrana, B.; Martinez-Maldonado, M. *J. Biol. Chem.* **1987**, *262*, 9555. (b) Rehder, D. *Inorg. Chem. Commun.* **2003**, *6*, 604.
- (14) (a) Taylor, S. W.; Kammerer, B.; Bayer, E. *Chem. Rev.* **1997**, *97*, 333. (b) Michibata, H.; Yamaguchi, N.; Uyama, T.; Ueki, T. *Coord. Chem. Rev.* **2003**, *237*, 41.

- (15) (a) Garner, C. D.; Armstrong, E. M.; Berry, R. E.; Beddoes, R. L.; Collison, D.; Cooney, J. J. A.; Ertok, S. N.; Helliwell, M. J. *Inorg. Biochem.* **2000**, *80*, 17. (b) Berry, R. E.; Armstrong, E. M.; Beddoes, R. L.; Collison, D.; Ertok, S. N.; Helliwell, M.; Garner, C. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 795.
- (16) Bruech, M.; Quintanilla, M. E.; Legrum, W.; Koch, J.; Netter, K. J.; Fuhrmann, G. F. *Toxicology* **1984**, *31*, 283.
- (17) (a) Cooney, J. J. A.; Carducci, M. D.; McElhaney, A. E.; Selby, H. D.; Enemark, J. H. *Inorg. Chem.* **2002**, *41*, 7086. (b) Hsu, H.-F.; Su, C.-L.; Gopal, N. O.; Wu, C.-C.; Chu, W.-C.; Tsai, Y.-F.; Chang, Y.-H.; Liu, Y.-H.; Kuo, T.-S.; Ke, S.-C. *Eur. J. Inorg. Chem.* **2006**, 1161. (c) Crans, D. C.; Zhang, B.; Gaidamauskas, E.; Keramidas, A. D.; Willsky, G. R.; Roberts, C. R. *Inorg. Chem.* **2010**, *49*, 4245. (d) Cornman, C. R.; Stauffer, T. C.; Boyle, P. D. *J. Am. Chem. Soc.* **1997**, *119*, 5986. (e) Money, J. K.; Nicholson, J. R.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4072. (f) Nanda, K. K.; Sinn, E.; Addison, A. W. *Inorg. Chem.* **1996**, *35*, 1. (g) Tsagkalidis, W.; Rodewald, D.; Rehder, D. *Inorg. Chem.* **1995**, *34*, 1943. (h) Wang, D.; Ebel, M.; Schulzke, C.; Grüning, C.; Hazari, S. S.; Rehder, D. *Eur. J. Inorg. Chem.* **2001**, 935. (i) Wang, D.; Behrens, A.; Farahbakhsh, M.; Gätjens, J.; Rehder, D. *Chem.—Eur. J.* **2003**, *9*, 1805. (j) Tsagkalidis, W.; Rehder, D. *J. Biol. Inorg. Chem.* **1996**, *1*, 507. (k) Nekola, H.; Wang, D.; Grüning, C.; Gätjens, J.; Behrens, A.; Rehder, D. *Inorg. Chem.* **2002**, *41*, 2379.
- (18) Paul, P. C.; Tracey, A. S. *J. Biol. Inorg. Chem.* **1997**, *2*, 644.
- (19) (a) Bonamico, M.; Dessy, G.; Fares, V.; Scaramuzza, L. *J. Chem. Soc., Dalton Trans.* 1974, 1258. (b) Sutradhar, M.; Mukherjee, G.; Drew, M. G. B.; Ghosh, S. *Inorg. Chem.* **2007**, *46*, 5069. (c) Smith, P. D.; Berry, R. E.; Harben, S. M.; Beddoes, R. L.; Helliwell, M.; Collison, D.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1997**, 4509.
- (20) Davies, S. C.; Hughes, D. L.; Janes, Z.; Jerzykiewicz, L. B.; Richards, R. L.; Sanders, J. R.; Silverstone, J. E.; Sobota, P. *Inorg. Chem.* **2000**, *39*, 3485.
- (21) (a) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235. (b) Lippard, S. J.; Russ, B. J. *Inorg. Chem.* **1968**, *7*, 1686.
- (22) Ooms, K. J.; Bolte, S. E.; Baruah, B.; Choudhary, M. A.; Crans, D. C.; Polenova, T. *Dalton Trans.* **2009**, 3262.
- (23) Sendlinger, S. C.; Nicholson, J. R.; Lobkovsky, E. B.; Huffman, J. C.; Rehder, D.; Christou, G. *Inorg. Chem.* **1993**, *32*, 204.
- (24) (a) Milsmann, C.; Levina, A.; Harris, H. H.; Foran, G. J.; Turner, P.; Lay, P. A. *Inorg. Chem.* **2006**, *45*, 4743. (b) Sproules, S.; Weyhermüller, T.; DeBeer, S.; Wieghardt, K. *Inorg. Chem.* **2010**, *49*, 5241.
- (25) Shulman, R. G.; Yafet, Y.; Eisenberger, P.; Blumberg, W. E. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 1384.