Inorganic Chemistry

Article

The First Oxidation of a Cr_2^{4+} Paddlewheel Complex to an Isostructural Stable Product

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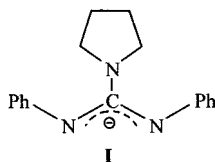
The first cation containing a Cr_2 core surrounded by a paddlewheel arrangement of four bridging ligands has been prepared and characterized. The bridging ligands are the guanidinate anions $[(PhN)_2CN(CH_2)_4]^-$. In the neutral Cr_2^{4+} compound the average Cr–Cr distance is 1.904[1] Å, and in the cation (which is accompanied by a PF_6^- anion) the Cr–Cr distance is 1.9249(9) Å. The cation has one unpaired electron, but the EPR spectrum is devoid of hyperfine structure and has $g \approx 2.00$. We proposed that the oxidation is essentially delocalized on the ligands.

Introduction

In the long history[1] of the many compounds containing the Cr_2^{4+} core (which dates back to the discovery of $Cr_2(O_2\text{-}CCH_3)_4(H_2O)_2$ in 1844), there has been no report of the oxidation of such a compound being accomplished with retention of the paddlewheel structure. A number of (unpublished) attempts have been made in this laboratory, but without success. Presumably, the removal of one electron from the Cr_2^{4+} core tends to result in the localized oxidation of one of the two chromium atoms, which, in turn, destroys the Cr−Cr bond, and complete decomposition follows.

We report here the first example of such an oxidation, wherein both the Cr_2^{4+} starting compound and the resulting cationic product, with a PF_6^- counterion, have been structurally characterized. The bridging ligand used is the guanidinate anion $[(PhN)_2CN(CH_2)_4]^-$, **I**.

Experimental Section

General. $CrCl_2$ was purchased from Strem Chemicals, Inc.; pyrrolidine, phenyl isocyanate, and $AgPF_6$ from Aldrich; $MgSO_4$

from EM Science and $W(CO)_6$ from Pressure Chemical Company. All were used without further purification. Diphenylcarbodiimide (DPC) was synthesized following a literature procedure[2] using $W(CO)_6$ as catalyst (2 wt %) and was stored in a freezer. All solvents were freshly distilled before use. Dry THF and ether were obtained by distillation from Na/K, and CH_2Cl_2 from P_2O_5. Reactions were carried out under a N_2 atmosphere. IR spectra were recorded on a Perkin Elmer 16PC FT-IR spectrometer; UV−vis spectra were recorded on a Cary-17D spectrometer; NMR spectra were recorded on a Varian 300 spectrometer; elemental analyses were carried out by Canadian Microanalytical Service, Ltd.; mass spectra were recorded on a mass spectrometer from VG Analytical using the +FAB/DP method; CV measurements were carried out on an electrochemical analyzer from CH Instruments (model CH1620A); the supporting electrolyte was Bu_4NPF_6 (0.1 M), the concentrations of compounds under study were 1 mM, and the solvents were THF and CH_2Cl_2, for **2** and **3**, respectively; magnetic susceptibility measurements were made on polycrystalline samples (the cocrystallizing solvents were removed under vacuum before measurements) with the use of a Quantum Design, model MPM-SR-2 SQUID susceptometer (the magnetic field used was 1000 G, and the temperature varied from 2 to 300 K); the EPR spectrum of a frozen glass of $[Cr_2(DPPC)_4]PF_6$ was recorded on a Bruker ESP 300 spectrometer.

Syntheses. *N,N*′-**Diphenyl-1-pyrrolidine Carbodiimide (HDPPC), 1.** In a 500 mL flask, pyrrolidine (4.32 g, 60.7 mmol) in 50 mL of THF was deprotonated by addition of 38 mL of 1.6 M (60.8 mmol) butyllithium in hexanes at 0 °C. Then diphenylcarbodiimide (11.8 g, 60.7 mmol) was transferred to the chilled mixture via cannula. The reaction was exothermic, and a red solution was obtained. After stirring at room temperature for 3 h, the solvents

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(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, 1993; Chapter 4.

(2) Ulrich, H.; Tucker, B.; Sayigh, A. A. R. *Tetrahedron Lett.* **1967**, 1731.

were removed under vacuum, and 10 mL of distilled water was slowly added. The addition of water resulted in a brown suspension. Chloroform (3 × 30 mL) was used to extract this suspension. The pale yellow solution was dried over $MgSO_4$ for 4 h, and the solvent was pumped off to give a yellow brown gel-like material. Further purification was carried out by recrystallization twice from dry ether to produce a colorless solid. Yield: 71%. Mp: 87.5−88.5 °C. MS: +FAB/DP, 266.17. ^{1}H NMR (CD_2Cl_2): δ 7.19 (4H, multiplet), 6.93 (6H, multiplet), 5.55 (1H, vbr), 3.97 (4H, triplet), 1.85 (4H, triplet). IR (cm^{-1}, KBr): 3153 (m), 2966 (s), 2872 (m), 2344 (w), 1612 (s), 1579 (s), 1510 (m), 1491 (s), 1450 (m), 1425 (s), 1347 (m), 1305 (m), 1259 (s), 1182 (m), 1069 (w), 1021 (w), 881 (w), 748 (s), 696 (s). Anal. Calcd for $C_{17}H_{19}N_3$: C, 76.95; H, 7.22; N, 15.84. Found: C, 77.12; H, 7.29; N, 15.66.

$Cr_2(DPPC)_4$, 2. Compound **1** (0.431 g, 1.63 mmol) dissolved in 20 mL of THF was deprotonated by addition of 1.1 mL of 1.6 M (1.76 mmol) BuLi in hexanes at −78 °C. After the mixture had warmed to room temperature, the resulting orange solution was transferred via cannula to a flask containing anhydrous $CrCl_2$ (0.100 g, 0.813 mmol) suspended in 5 mL of THF. After refluxing for 2 h, a yellowish brown solution containing a small amount of suspended solid was obtained. The solvent was removed under vacuum. Dichloromethane (20 mL) was then used to extract the yellowish brown solid. After filtration through a column of 2 cm of Celite, a clear orange solution was obtained. The remaining dark brown solid residue was discarded. The dichloromethane was pumped off, leaving a yellow solid, which was further washed by ether (3 × 20 mL). Yield 48%. Mp: >200 °C with decomposition. ^{1}H NMR (CD_2Cl_2): δ 7.09 (br), 6.74 (br), 4.66 (br), 2.78 (br), 2.29 (br), 1.50 (br), 1.26 (br). MS: +FAB/DP, 1162.22. IR (cm^{-1}, KBr): 3422 (s, br), 3056 (w), 2966 (m), 2870 (m), 1636 (w), 1593 (m), 1482 (s), 1435 (s), 1352 (m), 1294 (m), 1222 (m), 1167 (w), 1115 (w), 1069 (w), 1027 (w), 1001 (w), 931 (w), 859 (w), 784 (w), 728 (w), 697 (m). UV−vis (CH_2Cl_2): 454 nm, $\epsilon = 980$ L mol^{-1} cm^{-1}. Anal. Calcd for $Cr_2(DPPC)_4 \cdot 0.5Et_2O$ ($C_{70}H_{77}N_{12}Cr_2O_{0.5}$): C, 70.16; H, 6.48; N, 14.02. Found: C, 69.69; H, 6.57; N, 13.73.

$[Cr_2(DPPC)_4]PF_6$, 3. Compound **2** (0.200 g, 0.172 mmol) and $AgPF_6$ (0.044 g, 0.172 mmol) were mixed together and dissolved in 20 mL of CH_2Cl_2. The mixture became dark blue immediately and was stirred for 2 h. After filtration of the intensely dark blue solution, the solvent was pumped off, and a dark powder was obtained. Yield: 86%. UV−vis (CH_2Cl_2): 435 nm ($\epsilon = 2200$ L mol^{-1} cm^{-1}), 580 nm ($\epsilon = 3200$ L mol^{-1} cm^{-1}), 752 nm ($\epsilon = 6800$ L mol^{-1} cm^{-1}). IR (cm^{-1}, KBr): 3059 (w), 2972 (m), 2877 (m), 2343 (w), 1591 (m), 1485 (s), 1440 (s), 1378 (s), 1349 (m), 1285 (w), 1208 (m), 1104 (m), 1025 (w), 933 (m), 842 (s), 782 (m), 732 (m), 697 (m), 601 (w). Anal. Calcd for $[Cr_2(DPPC)_4]PF_6$ ($C_{68}H_{72}N_{12}Cr_2PF_6$): C, 62.52; H, 5.56; N, 12.87. Found: C, 62.21; H, 5.48; N, 12.63.

X-ray Determinations. Single crystals of **2**·0.5Et$_2$O and **3**·4CH$_2$Cl$_2$ for X-ray analysis were grown by layering the corresponding CH_2Cl_2 solutions with diethyl ether. Crystal data were measured at 213 K on a Bruker SMART diffractometer. A scan strategy was used to gather approximately one complete hemisphere of data from each crystal. Data from the collected frames were integrated with the Bruker SAINT program.[3] For both structures, the majority of the atomic positions were given by direct methods (SHELXS[4]) and the remainder found in subsequent difference Fourier maps.[5]

(3) *SAINTPLUS V5.05 Software for the CCD Detector System*; Bruker Analytical X-Ray System, Inc.; Madison, WI, 1998.
(4) Sheldrick, G. M. *SHELXS93. Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1993.
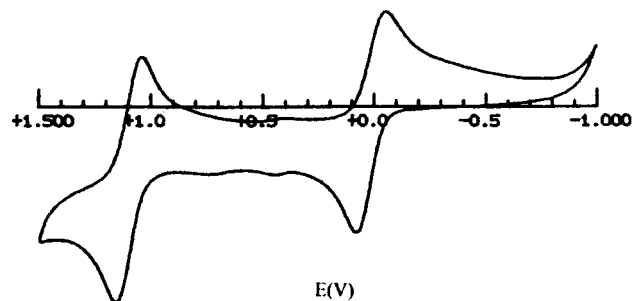
Figure 1. The cyclic voltammogram of **2**.

Results and Discussion

Syntheses. Although a method for the preparation of **1** has apparently been described in the patent literature,[6] we used a different method. A minor disadvantage of our method is that it employs the intermediate diphenylcarbodiimide, which must be kept below 0 °C. However, the guanidine complex **1** is stable and was obtained in high purity in 71% yield as follows:
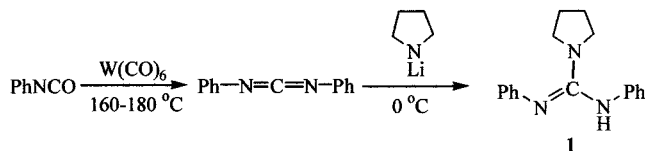
Compound **1** is readily soluble in THF, CH_2Cl_2, CHCl$_3$, and acetone. It is essential to meticulously dry the ligand **1** for the synthesis of **2**. The neutral complex, **2**, is soluble in CH_2Cl_2, but only slightly soluble in acetone and THF. A CH_2Cl_2 solution of **2** is quite stable, even when exposed to air, for 2 days. The one-electron oxidation of **2** was carried out with $AgPF_6$, but can be achieved also by $[FeCp_2]PF_6$ or $(NO)PF_6$. The product, **3**, is soluble in CH_2Cl_2 and acetone. It is stable both in the solid state and in solution. Further oxidation by another equivalent of $(NO)PF_6$ resulted in a dark red solid which was only slightly soluble in DMSO; no crystals are available yet.

CV Measurements. The ligand, **1**, can be oxidized irreversibly at about 0.8 V (relative to Ag/AgCl). The neutral complex, **2**, can be oxidized quasi-reversibly in two one-electron processes having $E_{1/2}$ of 0.02 and 1.10 V as shown in Figure 1.

Crystal Structures. In **2**·0.5Et$_2$O, the asymmetric unit contains two independent molecules of the complexes, each on a general position, and one slightly disordered molecule of diethyl ether. The two Cr_2^{4+} complexes are identical within reasonable error, having only slight differences in the conformations of the pyrrolidine rings. In **3**·4CH$_2$Cl$_2$, both the cationic complex and the PF_6^- anion lie on 2-fold axes

(5) Sheldrick, G. M. *SHELXL93. Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.
(6) (a) Ives, J. L. US Patents 4281004 and 4404219. (b) Bhat, L.; Georg, G. I. US Patent 6100428.

Table 1. Crystal and Structure Refinement Data for Compound **2**·0.5Et₂O and **3**·4CH₂Cl₂

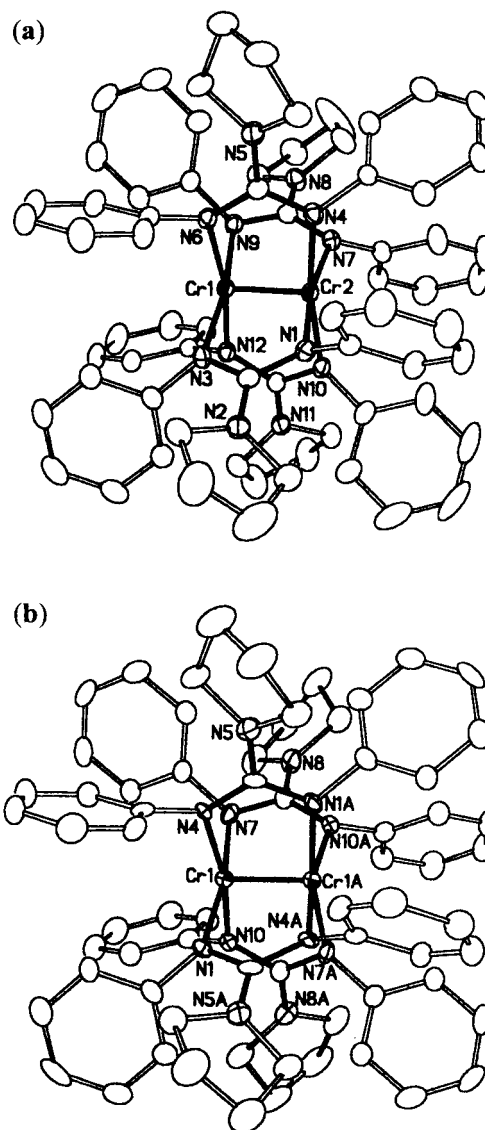|	**2**·0.5Et₂O	**3**·4CH₂Cl₂
chemical formula	C₇₀H₇₇Cr₂N₁₂O₀.₅₀	C₇₂H₈₀Cl₈Cr₂F₆N₁₂P
fw	1198.44	1646.05
space group	*P*2₁/*c* (No. 14)	*C*2/*c* (No. 15)
a, Å	26.944(3)	22.832(1)
b, Å	21.305(3)	15.7262(9)
c, Å	23.537(3)	23.816(1)
β, deg	112.545(3)	116.298(1)
V, Å³	12479(3)	7666.1(8)
Z	8	4
T, K	213(2)	213(2)
λ, Å	0.71073	0.71073
ρ₍calcd₎, g cm⁻³	1.276	1.426
μ, mm⁻¹	0.402	0.648
R1,[a] wR2[b] (all data)	0.109, 0.158	0.075, 0.157

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, where $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**·0.5Et₂O and **3**·4CH₂Cl₂[a]

2·0.5Et₂O
Molecule 1

Cr(1)−Cr(2)	1.9049(7)	Cr(1)−N(12)	2.056(2)
Cr(2)−N(1)	2.051(3)	Cr(2)−N(4)	2.063(2)
Cr(1)−N(3)	2.070(3)	Cr(2)−N(7)	2.064(3)
Cr(1)−N(6)	2.055(2)	Cr(2)−N(10)	2.065(2)
Cr(1)−N(9)	2.067(3)		
Cr(1)−Cr(2)−N(1)	95.53(7)	Cr(1)−Cr(2)−N(4)	94.68(7)
Cr(1)−Cr(2)−N(7)	95.50(7)	Cr(1)−Cr(2)−N(10)	94.71(7)
Cr(2)−Cr(1)−N(3)	94.49(7)	Cr(2)−Cr(1)−N(6)	95.28(7)
Cr(2)−Cr(1)−N(9)	94.48(7)	Cr(2)−Cr(1)−N(12)	95.25(7)
N(6)−Cr(1)−N(3)	90.2(1)	N(9)−Cr(1)−N(3)	171.0(1)
N(12)−Cr(1)−N(3)	89.6(1)	N(6)−Cr(1)−N(9)	89.2(1)
N(12)−Cr(1)−N(6)	169.5(1)	N(12)−Cr(1)−N(9)	89.3(1)
N(1)−Cr(2)−N(4)	89.8(1)	N(1)−Cr(2)−N(7)	169.0(1)
N(1)−Cr(2)−N(10)	89.6(1)	N(4)−Cr(2)−N(7)	89.7(1)
N(4)−Cr(2)−N(10)	170.6(1)	N(7)−Cr(2)−N(10)	89.2(1)

Molecule 2

Cr(3)−Cr(4)	1.9025(7)	Cr(4)−N(13)	2.056(2)
Cr(3)−N(24)	2.062(2)	Cr(4)−N(19)	2.063(2)
Cr(3)−N(15)	2.063(2)	Cr(4)−N(16)	2.070(2)
Cr(3)−N(18)	2.064(2)	Cr(4)−N(22)	2.071(2)
Cr(3)−N(21)	2.068(2)		
Cr(4)−Cr(3)−N(24)	95.22(7)	Cr(4)−Cr(3)−N(15)	95.45(8)
Cr(4)−Cr(3)−N(18)	95.08(8)	Cr(4)−Cr(3)−N(21)	94.70(7)
Cr(3)−Cr(4)−N(13)	94.51(7)	Cr(3)−Cr(4)−N(19)	95.28(8)
Cr(3)−Cr(4)−N(16)	95.02(7)	Cr(3)−Cr(4)−N(22)	94.76(7)
N(24)−Cr(3)−N(15)	90.1(1)	N(24)−Cr(3)−N(18)	169.7(1)
N(15)−Cr(3)−N(18)	89.8(1)	N(24)−Cr(3)−N(21)	89.6(1)
N(15)−Cr(3)−N(21)	169.8(1)	N(18)−Cr(3)−N(21)	88.66(9)
N(13)−Cr(4)−N(19)	170.2(1)	N(13)−Cr(4)−N(16)	90.2(1)
N(19)−Cr(4)−N(16)	88.6(1)	N(13)−Cr(4)−N(22)	90.3(1)
N(19)−Cr(4)−N(22)	89.3(1)	N(16)−Cr(4)−N(22)	170.2(1)

3·4CH₂Cl₂

Cr(1)−Cr(1)#1	1.9249(9)	Cr(1)−N(7)	2.014(3)
Cr(1)−N(1)	2.017(2)	Cr(1)−N(10)	2.021(2)
Cr(1)−N(4)	2.020(3)		
Cr(1)#1−Cr(1)−N(1)	94.99(7)	N(4)−Cr(1)−N(1)	89.3(1)
Cr(1)#1−Cr(1)−N(4)	95.11(7)	N(4)−Cr(1)−N(10)	170.1(1)
Cr(1)#1−Cr(1)−N(7)	94.91(7)	N(7)−Cr(1)−N(1)	170.1(1)
Cr(1)#1−Cr(1)−N(10)	94.88(7)	N(7)−Cr(1)−N(4)	89.7(1)
N(1)−Cr(1)−N(10)	88.9(1)	N(7)−Cr(1)−N(10)	90.4(1)

[a] Symmetry transformation used to generate equivalent atoms: #1 −*x*, *y*, −*z* + ¹/₂.

in *C*2/*c*. The crystal data and refinement parameters for **2**·0.5Et₂O and **3**·4CH₂Cl₂ are listed in Table 1. The selected bond lengths and angles are listed in Table 2. In the neutral

(a)

(b)

Figure 2. Drawings of (a) one of the molecules in **2**·0.5Et₂O and (b) the cation in **3**·4CH₂Cl₂, shown with 40% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

compound **2** the average Cr−Cr distance is 1.904[1] Å. This is slightly longer (ca. 0.05 Å) than those of the chemically related formamidinates.[1] In the cation in **3** (which is accompanied by a PF₆⁻ anion), the Cr−Cr distance is 1.9249-(9) Å. Drawings of **2** and the cation in **3** are shown in Figure 2.

Magnetic Measurements. Compound **2** exhibited weak paramagnetism that increased with temperature. Presumably this results from thermal population of a low-lying triplet state, as has been seen before for other Cr₂⁴⁺ species.[7] This would account for the unusual character of the ¹H NMR spectrum, in which all the lines are broad and displaced from their expected positions.

Compound **3** is paramagnetic and its magnetic susceptibility behavior closely follows the Curie law with $\chi_M T$ equal to 0.375 ± 0.008 cm³ K mol⁻¹ from 2 to 300 K, where χ_M

(7) Cotton, F. A.; Chen, H.; Daniels, L. M.; Feng, X. *J. Am. Chem. Soc.* **1992**, *114*, 8980.

has been corrected for diamagnetism using Pascal's constants (779×10^{-6} cm^3 mol^{-1}). This corresponds to a g value of 2.000 ± 0.015 and to $\mu_{eff} = 1.733$ μ_B.

The EPR spectrum of **3** consisted of one structureless line regardless of sample concentration (from 0.4 to 1 mM), power (from 2 to 40 dB), or modulation amplitude (from 0.132 to 1.05 G), centered at $g = 1.973$. This is the same, within experimental error ($<2\sigma$) as the value derived from the bulk susceptibility measurement. The peak-to-peak line width was 12.27 G.

With an essentially free-electron g value and a structureless EPR signal, we are led to conclude that oxidation of **2** to give **3** is essentially a ligand oxidation. In other words, the molecular orbital from which the electron has been removed is mainly spread over the ligands and has very little contribution from the chromium atomic orbitals. The fact that the oxidation leads to only a small change in the Cr–Cr distance (0.018 Å) is also consistent with this conclusion. Thus, even though we have, for the first time, obtained a stable, isostructural product by oxidizing a paddlewheel molecule with a Cr$_2^{4+}$ core, we have not really obtained a product with a Cr$_2^{5+}$ core.

The literature contains many prior examples of ligand-based oxidation. The one that is most closely related to the present case is Pd$_2$(DTolF)$_4$ going to the Pd$_2$(DTolF)$_4^+$ ion (DTolF = N,N'-di-p-tolylformamidinate anion).[8] In this case the oxidation produced practically no structural change and the g value (2.014) of the cation was very close to the free-electron value. Other examples of essentially ligand-based unpaired electrons occur widely in several classes of biologically important metal complexes.[9,10] Two specific examples are the oxidation of a Ni^{II} porphyrin to a π cation radical (not to a Ni^{III} complex)[11] and the oxidation of a Cu^{II} porphyrin which shows both one- and two-electron oxidations

in which the electrons are removed from the ligand, not from the copper ion.[12] In the present case (and in the case of the palladium compound just mentioned) the ligand-based MO from which the electron is removed is not distributed over a π system confined to one macrocyclic ligand, but over four π systems which are all connected by the metal atom orbitals even though there is very little contribution by metal atom orbitals to the MO. This situation finds precedent in the photoexcited state of Ru(bpy)$_3^{2+}$, where an electron is moved from the metal atom to a MO that is delocalized over all three of the ligands equally.[13]

Supporting Information Available: X-ray crystallographic files, in CIF format, containing data for structures **2**·0.5Et$_2$O and **3**·4CH$_2$Cl$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010925V

(8) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144.

(9) See: Kadish, K. M., Smith, K. M., Guilard, R., Eds. *The Porphyrin Handbook*; Academic Press: New York, 2000. (a) Kadish, K. M.; Van Caemelbecke, E.; Royal, G., Vol. 8, p 1. (b) Scheidt, W. R., Vol. 3, p 49. (c) Walker, F. A., Vol. 5, p 81. (d) Weiss, R.; Gold, A.; Trautwein, A. X.; Terner, J., Vol. 4, p 65.

(10) (a) Fajer, J.; Davis, M. S. In *The Porphyrin*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 4, p 197. (b) Lubitz, W. In *Chlorophylls*; Scheer, H., Ed.; CRC Press: Boca Raton, FL, 1991; p 903.

(11) Barkigia, K. M.; Renner, M. W.; Fajer, J. *J. Phys. Chem. B* **1997**, *101*, 8398.

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(13) Krausz, E. *Comments Inorg. Chem.* **1988**, *7*, 139.