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Magnetic Excitations in Metalloporphyrins by Inelastic Neutron Scattering: Determination of Zero-Field Splittings in Iron, Manganese, and Chromium Complexes

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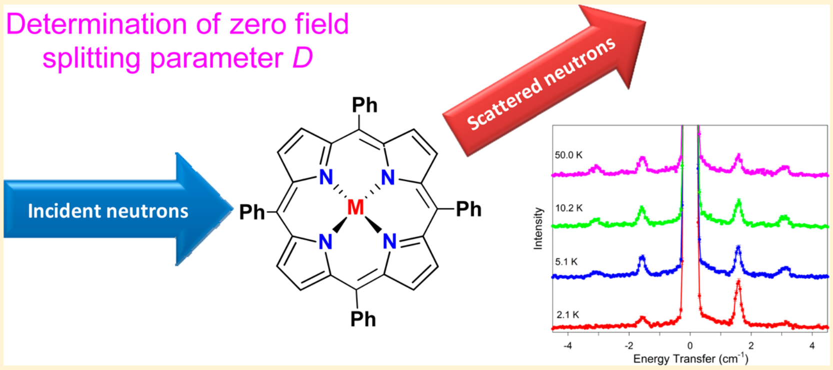
S Supporting Information



ABSTRACT: Zero field splitting (ZFS) parameters of several nondeuterated metalloporphyrins [M(TPP)Cl] and [Mn(TPP)] (H_2TPP = tetraphenylporphyrin) have been directly determined by inelastic neutron scattering (INS). The ZFS values are the following: D = 6.33(8) cm^{-1} for [Fe(TPP)Cl], −2.24(3) cm^{-1} for [Mn(TPP)Cl], 0.79(2) cm^{-1} for [Mn(TPP)], and $|D|$= 0.234(12) cm^{-1} for [Cr(TPP)Cl]. The work shows that compounds with magnetic excitations below ~30 cm^{-1} could be determined using nondeuterated samples.

■ INTRODUCTION

Metalloporphyrins are an important class of compounds, and they are found in both biological and geological systems.[1−3] Magnetic properties of paramagnetic metalloporphyrins, those with unpaired electrons, have been actively studied.[1c] One intrinsic magnetic property is the zero-field splitting (ZFS). For paramagnetic compounds with spin $S \geq 1$, there lies a splitting of the spin states of otherwise degenerate states as a result of the interaction of the electron spins mediated by the spin−orbital coupling.[4−6] The spin-Hamiltonian is given in eq 1

$$\hat{H}_s = D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + E[\hat{S}_x^2 - \hat{S}_y^2] \tag{1}$$

where D and E are the axial and rhombic ZFS parameters, respectively.

ZFS appears as small differences (usually a few cm^{-1}) among energy levels in the absence of an external magnetic field, and it is represented by the D and E parameters (eq 1). ZFS of single molecular magnets (SMMs) has been actively studied, as the D values are critical for their potential applications for, e.g., as new data storage materials.[7] ZFS, including that of metalloporphyrins, has been investigated using electron paramagnetic resonance (EPR), magnetic susceptibility, NMR, far-IR, Mössbauer, magnetic circular dichroism (MCD), and inelastic neutron scattering (INS).[1c,6−8] Among these techniques, INS is one of few that directly give both the magnitude of the D parameter and often its sign.

When a sample is placed in an incident neutron beam, neutrons may scatter by the sample elastically and inelastically. When neutrons are scattered inelastically, they transfer energy to molecules in the sample, leading to transitions between molecular energy levels. INS has been used to study dynamics of molecules such as rotational motion of H_2 ligands.[9] It has also been used to probe the magnetic properties of metal complexes, especially excitations among low-lying energy levels. In such a process, incident neutrons transfer energy to the molecules, leading to the magnetic excitations that are observed in an INS spectrum.[4g] For example, the low-lying energy levels of magnetic clusters have been characterized by INS.[4g,10] Güdel and co-workers have determined D for single-molecule magnets $[Mn_4O_3X(OAc)_3(dbm)_3]$ (X = Br^-, Cl^-, OAc^-, and F^-) and studied how the D values change with the axial X^- ligands.[11a] Chaboussant, Christou, and Lechner have found out that reduction of the Mn_{12} cluster $[Mn_{12}O_{12}(O_2CC_6F_5)_{16}(H_2O)_4]$ suppresses the axial ZFS parameter D.[11b]

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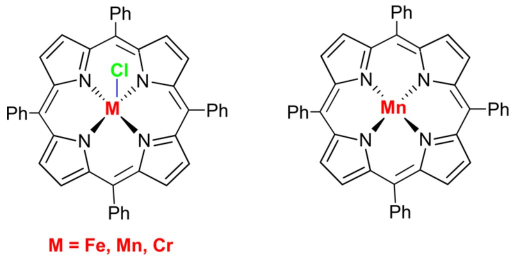
To our knowledge, few bioinorganic complexes have been studied by inelastic neutron scattering (INS). Traditionally neutron scattering studies have been conducted using deuterated samples, as D atoms have smaller incoherent scattering of neutrons than H atoms, reducing the background noise.[12] The Spallation Neutron Source (SNS) recently constructed at Oak Ridge National Laboratory (ORNL) in the United States provides the most intense pulsed neutron beams in the world for scientific research. State-of-the-art experimental stations at SNS have made it possible to probe magnetic properties of nondeuterated metal complexes in detail.[11h] We have used the cold neutron chopper spectrometer (CNCS)[13] at SNS to determine the *D* parameters for the nondeuterated metalloporphyrins [M(TPP)Cl] (H_2TPP = *meso*-tetraphenylporphyrin, M = Fe^{III}, Mn^{III}, and Cr^{III}) and [Mn(TPP)]. Our results are reported here.

Molecules of the complexes in the current studies have 4-fold symmetry (Scheme 1). If their crystals have a 4-fold symmetry as well in, e.g., a tetragonal space group, the spin-Hamiltonian in eq 1 is simplified into eq 2.

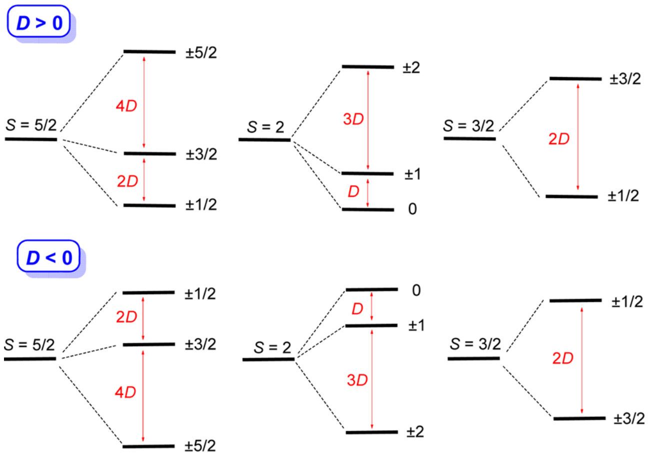
Scheme 1. Structures of Metalloporpyrins in the Current Studies



$$\hat{H}_s = D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] \tag{2}$$

In the absence of a magnetic field, electronic ground states of complexes with spins $S = {}^5/_2$, 2, ${}^3/_2$, and 1 are split (Scheme 2), as a result of ZFS by the combined effect of the spin–orbital coupling and the axial ligand field.[6]

Scheme 2. Zero-Field Splittings (ZFS) in Compounds with $S = {}^5/_2$, 2, and ${}^3/_2$ (Top $D > 0$; Bottom $D < 0$)



EXPERIMENTAL SECTION

[Fe(TPP)Cl] (Strem Chemicals, Lot 19089600), [Mn(TPP)Cl] (Sigma Aldrich, Lot 01909MEV), and [Cr(TPP)Cl] (Strem Chemicals; Lot 21803900) were used as received. [Mn(TPP)] was prepared through the reduction of [Mn(TPP)Cl] by $NaBH_4$ by the literature methods.[14] The identities and purities of the samples were confirmed by UV–vis spectroscopy.[6,14,15]

The solid samples were characterized by powder X-ray diffraction. Suitable polycrystalline samples of the air-stable complexes [Fe(TPP)-Cl], [Mn(TPP)Cl], and [Cr(TPP)Cl] were placed on a zero-background plate sample holder. Air-sensitive [Mn(TPP)] was placed on an air-sensitive sample holder with a zero background plate. The sample was covered with a 14 gauge DuPont Mylar C film.

Powder diffraction patterns were obtained on the PANalytical Empyrean diffractometer using Cu K*α* radiation (*λ* = 1.5418 Å). Analysis and unit cell determination were performed using the PANalytical HighScore Plus analysis software and the McMaille method.[16] Diffraction patterns of [Fe(TPP)Cl][17] and [Mn(TPP)Cl][18] were matched to simulated diffraction patterns from their single crystal X-ray diffraction data.

The INS measurements were carried out on the CNCS at the SNS, Oak Ridge National Laboratory. The CNCS is a direct geometry, time-of-flight spectrometer that receives a beam from a coupled cryogenic H_2 moderator. For energy selection, the CNCS employs four chopper assemblies. The speeds and slit widths of the choppers can be varied, allowing adjustments in the instrumental resolution and intensity of the incident beam. Approximately 500 mg of each sample was loaded into ${}^1/_2$ in. thick aluminum tubes and sealed under a helium atmosphere. The sample was mounted in a standard liquid helium cryostat with a base temperature of *T* = 1.5 K. An oscillating radial collimator was used to reduce background scattering from the tail of the cryostat. Vanadium was used as a standard for the detector efficiency correction.

The incident neutron energy for every measurement was chosen to cover the anticipated region of interest in both the energy *E* and scattering-vector *Q* space. The small incident energy is especially important to observe excitations near the elastic peak (at energy transfer = 0 cm^{-1}) as the full-width-at-half-maximum (fwhm) of the elastic peak, which is typically 1.5–2% of the incident energy, would be narrow, giving better energy resolution. As discussed below, the larger scattering angles reveal the change in the peak intensities versus |*Q*| and confirm whether a peak is magnetic or phonon in nature.

For [Fe(TPP)Cl], measurements were performed at 1.5 and 20 K with incident neutron beam energies of 24.20, 80.66, and 201.64 cm^{-1} and resolutions at the elastic peak of 0.59, 3.1, and 10 cm^{-1}, respectively. For [Mn(TPP)Cl], measurements were performed at 2.08, 5.1, 10.2, and 50.0 K with incident neutron beam energies of 12.58, 24.20, and 96.79 cm^{-1} and resolutions at the elastic peak of 1.9, 0.46, and 3.1 cm^{-1}, respectively. For [Mn(TPP)], measurements were performed at 2.08, 5.1, 10.2, and 50.0 K with incident neutron beam energies of 12.58, 24.20, and 96.79 cm^{-1} and resolutions at the elastic peak of 0.18, 0.43, and 3.0 cm^{-1}, respectively. For [Cr(TPP)Cl], the measurements were performed at 2.08, 10.2, and 50 K using incident neutron beam energies of 8.06 and 24.20 cm^{-1} and resolutions at the elastic peak of 0.097 and 0.43 cm^{-1}, respectively. It took approximately 24 h to run one sample at various temperatures and incident neutron energies. Data were then reduced and analyzed using the DAVE (Data Analysis and Visualization Environment) program package.[19]

The INS spectra were simulated by calculating the energies E_n and corresponding wave functions $|n\rangle$ via exact diagonalization of spin-Hamiltonian in eq 1. These can be used to get the INS intensity for a transition $i \rightarrow f$, which is proportional to the scattering function $S^{\alpha\beta}(\mathbf{Q},\omega)$:[20]

$$S^{\alpha\beta}(\mathbf{Q},\omega) = \sum_{j}^{j'} \exp\{i\mathbf{Q}(r_j - r_{j'})\} \times \sum_{i}^{f} p_i \langle i|\hat{S}_{j,\alpha}|f\rangle\langle f|\hat{S}_{j',\beta}|i\rangle \times \delta(E_i - E_f) \tag{3}$$

$S_{j,\alpha}$ is the α component of the spin operator S_j at position r_j where α, β stand for Cartesian coordinates x, y, z. The initial and final states of a transition with energy E_n are $|i\rangle$ and $|f\rangle$, respectively. $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ is the scattering vector of the momentum transfer where $\mathbf{k}_i$ and $\mathbf{k}_f$ refer to the wavevector of the incoming and outgoing neutrons, respectively, and p_i is the Boltzmann population factor of state $|i\rangle$. For powder samples eq 2 has to be averaged in $\mathbf{Q}$ space using known equations.[21] The values of D and, if necessary, E were systematically scanned in order to find the best fit to the experimental spectra. The linewidths of the INS peaks lie within experimental accuracy determined by the instrumental resolution. The effective resolution function $R(Q,E)$ of CNCS is nearly Gaussian in energy.[13] Therefore, the INS intensities were fit assuming Gaussian line shapes with fwhm of the energy resolution for the CNCS spectrometer. The detailed analyses, using the plots with smaller stepsize points, and calculations of errors in the D values, are given in the Supporting Information.[22]

■ RESULTS AND DISCUSSION

[Fe(TPP)Cl]. Powder X-ray diffraction of the sample at 296 K[22] is consistent with the simulated pattern predicted from the single crystal X-ray diffraction data at 20(2), 143(2), and 293(2) K, indicating that the solid sample is in the tetragonal crystal system (with the 4-fold symmetry).[17,23] Indexing of the powder X-ray diffraction data from the sample by the McMaille method also yielded the same tetragonal unit cell. Our earlier studies of the X-ray diffraction of a single crystal of [Fe(TPP)Cl] revealed that the crystal remains in the tetragonal system between 296(2) and 20(2) K.[17] Although the X-ray diffraction studies were not conducted at 1.5 K, the INS studies discussed below suggest that the sample remained in the tetragonal crystal system between 1.5 and 20 K.

In [Fe(TPP)Cl], the Fe(III) ion has a high spin ($S = {}^5/_2$) configuration, and its electronic ground state is split into three Kramers doublets: $M_S = \pm{}^1/_2, \pm{}^3/_2$, and $\pm{}^5/_2$. The spacings among the three doublets are $2D$ and $4D$, respectively (Scheme 2). The ZFS in [Fe(TPP)Cl] has been the subject of several studies. Its D values have been determined by, e.g., magnetic susceptibility measurements,[24] far-IR,[25] NMR,[26] and Mössbauer,[27] MCD,[6] and EPR[28] spectroscopies. The D values obtained, ranging from 3.2 to 11.9 cm^{-1}, are summarized in Table 1.

Table 1. ZFS Values for [Fe(TPP)Cl]

D, cm^{-1}	sample form	technique
11.9	powder	magnetic susceptibility[24a]
8.0(5)	powder	magnetic susceptibility[24b]
6.0(1)	single crystal	magnetic susceptibility[24c,d]
6.5	powder	far-IR[25]
11.3	solution	NMR[26]
7.0(1.0)	powder	Mössbauer[27]
6.9	polystyrene film	MCD[6]
3.2	doped in H_2TPP	EPR[28]
6.33(8)	powder	INS (this work)

In the INS spectra of [Fe(TPP)Cl], a peak at 12.65(8) cm^{-1} was observed (Figure 1, left) at both 1.5 and 20 K. This corresponds to the $\pm{}^1/_2 \rightarrow \pm{}^3/_2$ excitation (Scheme 1). At 20 K, a peak at −12.65(8) cm^{-1} is observed, indicating that the incident neutrons *gain* energy from the sample in the process. In other words, at 20 K, the excited $\pm{}^3/_2$ states in Scheme 1 are partially populated. During the scattering process, those molecules return to the ground $\pm{}^1/_2$ states, transferring the energy to the neutrons.

INS is unique in that it is capable of distinguishing peaks of magnetic excitations from those of vibrations.[12] Peaks of magnetic excitations *decrease* in intensity with increased $|Q|$, while those from vibrations *increase* in intensity with increased $|Q|$.[12] The decrease in magnetic excitations follows the square of the magnetic form factor $F(Q)$. Changes in peak intensities versus $|Q|$ are given in Figure 1, right. The intensity of the 12.65(8) cm^{-1} peak indeed decreases with increased $|Q|$, confirming that it is magnetic in nature. The intensities of the peaks >16 cm^{-1} increase with increased $|Q|$, indicating that they are vibrational peaks.

Earlier studies of [Fe(TPP)Cl] have given positive D values, as summarized in Table 1. INS, however, can be used to confirm the sign of the D parameter. If $D > 0$, the lowest energy level is $\pm{}^1/_2$, and the first excitation is from this level to $\pm{}^3/_2$ level with a peak at $2D$, as shown in Scheme 1, top. When the temperature is raised, the $\pm{}^3/_2$ is populated, and one expects to see the $\pm{}^3/_2$ to $\pm{}^5/_2$ transition with a peak at $4D$ at a higher energy. If $D < 0$, the lowest energy level is $\pm{}^5/_2$, and the first excitation is from this level to $\pm{}^3/_2$ level with a peak at $4D$, as shown in Scheme 1, bottom. When the temperature is raised, the $\pm{}^3/_2$ is populated, and one expects to see the $\pm{}^3/_2$ to $\pm{}^1/_2$ transition with a peak at $2D$ at a lower energy. Figure 2, left, shows the measured INS spectra with incident neutron energies of 80.66 cm^{-1}. Although there is considerable phonon scattering at both temperatures, a new peak is visible at around 25.60 cm^{-1} in the 20 K spectrum. This peak matches nicely with the theoretical INS spectra (Figure 2, right).

Our earlier single crystal diffraction studies of [Fe(TPP)Cl] at 20(2) K indicate that the crystal is in a tetragonal system at this temperature.[17] A comparison of the INS spectra at 1.5 and 20 K in Figure 1, left, shows no observable rhombic splitting(s) at 1.5 K, suggesting that the solid samples remained in the tetragonal crystal system at this temperature. Thus, the INS studies here give $2D$ = 12.65(8) cm^{-1}, D = 6.33(8) cm^{-1} for [Fe(TPP)Cl].[22]

The D value of 6.33(8) cm^{-1} for [Fe(TPP)Cl] is close to 6.95(14) cm^{-1} for protoporphyrin IX dimethyl ester Fe(III) chloride (Scheme 3) that Brackett and co-workers measured using far-IR spectroscopy.[29] The protoporphyrin complex in Scheme 3 does not have 4-fold symmetry, and its $E/D \approx 0$, indicating there is nearly no rhombic splitting in this complex.

[Mn(TPP)Cl]. Single crystals of [Mn(TPP)Cl] and [Fe(TPP)Cl] are isomorphous.[17,18,23] Powder X-ray diffraction of the sample at 296 K[22] is consistent with the simulated pattern predicted from the single crystal X-ray diffraction data at 293(2) K, indicating that the solid sample is in the tetragonal crystal system (with the 4-fold symmetry).[18] Indexing of powder X-ray diffraction data from the sample by the McMaille method also yielded the same tetragonal unit cell. As in [Fe(TPP)Cl], powders of [Mn(TPP)Cl] likely remain in the tetragonal crystal system at 2.1 and 5.1 K used to conduct INS studies. The INS data discussed below are also consistent with the solid sample with the 4-fold symmetry.

[Mn(TPP)Cl] is a d^4 complex with $S = 2$. Its integer spin electronic ground state is split into three levels: $M_S = 0, \pm1$, and ±2. The ZFS parameter for [Mn(TPP)Cl] was first obtained by Behere and co-workers through magnetic susceptibility measurements.[30] Using a single crystal they obtained D = −2.3(2) cm^{-1}. When a powder sample was used, the D value obtained is −1.9 cm^{-1}.[30] [Mn(TPP)Cl] is an “EPR silent” integer spin system, and it was not until the use of high-field, high-frequency EPR (HFEPR) by Hoffman and co-workers

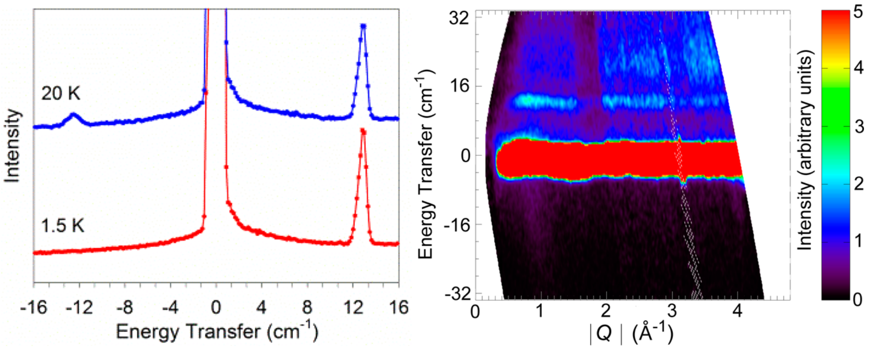


Figure 1. (Left) INS spectra of [Fe(TPP)Cl] using a 24.20 cm^{-1} incident neutron beam. (Right) Change in the peak intensities vs |Q| at 1.5 K. Incident neutron energy: 80.66 cm^{-1}.

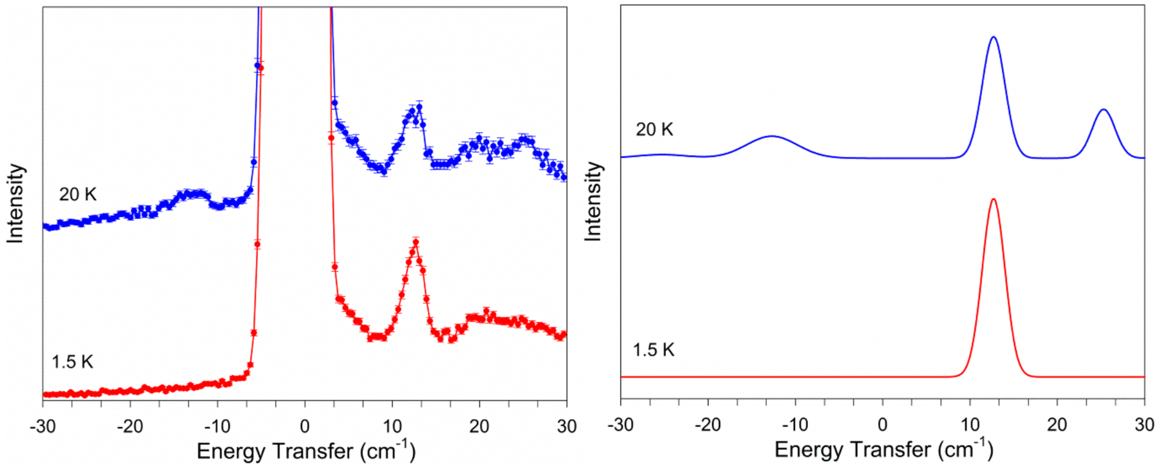
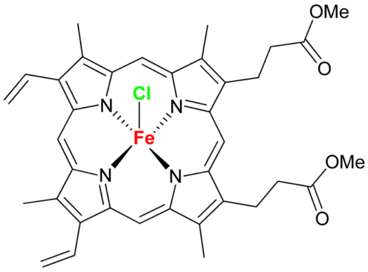


Figure 2. (Left) INS spectra of [Fe(TPP)Cl] using a 80.66 cm^{-1} incident neutron energy. (Right) Theoretical INS spectra of an $S = {}^{5}/_{2}$ spin system with $D = 6.33$ cm^{-1}.

Scheme 3. Protoporphyrin IX Dimethyl Ester Fe(III) Chloride



that the ZFS of the complex could be probed to give the $D \approx -2.3$ cm^{-1}.[31]

The measured and theoretical INS spectra of [Mn(TPP)Cl] are shown in Figure 3. The small neutron incident energy (12.58 cm^{-1}) excludes vibrational peaks. At 2.1 K there is only one large peak at 6.70(3) cm^{-1}. When the temperature is increased to 5.1 K, a second peak becomes visible at 2.24(3) cm^{-1}. As in the INS spectra of [Fe(TPP)Cl], the sign of D can be determined directly using INS for complexes with $S > {}^{3}/_{2}$. If its D value is positive ($D > 0$), the ZFS would take the spacings among the three levels as illustrated in Scheme 2, top. At 2.1 K, the peak at 6.698(15) cm^{-1} would correspond to the $0 \rightarrow \pm1$ transition and equal to D. As the temperature is increased to 5.1 K, the ±1 level is populated, and a peak at $3D = 20.09$ cm^{-1} corresponding to the $\pm1 \rightarrow \pm2$ transition would be expected. If the D value is negative ($D < 0$), the ZFS would take the spacings among the three levels as illustrated in Scheme 2, bottom. At 2.1 K, the peak at 6.698(15) cm^{-1} would correspond to the $\pm2 \rightarrow \pm1$ transition and equal $-3D$. As the temperature is increased to 5.1 K, the ±1 level is populated, and a peak at 2.23(3) cm^{-1} (= $-D$) corresponding to the $\pm1 \rightarrow 0$ transition would be expected. The fact that only the larger $\pm2 \rightarrow \pm1$ transition is populated at the low temperature of 2.1 K in Figure 3 indicates that the D value is negative. Thus, for [Mn(TPP)Cl], the INS study gives $D = -2.24(3)$ cm^{-1}. This value is similar to $D = -2.3(2)$ cm^{-1} and $D \approx -2.3$ cm^{-1} that Behere et al.[30] and Hoffman et al.[31] reported, respectively. This D value for [Mn(TPP)Cl] is also close to $D = -2.48(7)$ cm^{-1} for [Mn(TPP)(O_2)] that does not have the C_{4v} symmetry.[32]

[Mn(TPP)]. [Mn(TPP)] is an air-sensitive, d^5 complex. Unlike its chloride derivative [Mn(TPP)Cl], there is no ligand in the axial position. Both [Mn(TPP)] and its adducts [Mn(TPP)L] (L = THF, pyridine) and [Mn(TPP)L_2] (L = toluene, pyridine) have been actively studied.[24,32] ESR studies of [Mn(TPP)(py)] by Hoffman and co-workers gave $D^{Mn} = \sim 0.55$ cm^{-1}.[32]

Powder X-ray diffraction of the sample was conducted using an air-sensitive sample holder with a zero background plate. After removing the peak of the Mylar film at $2\theta = 26.52°$, the peaks by [Mn(TPP)] were indexed by the McMaille method to give a tetragonal unit cell. The results are given in the Supporting Information.[22]

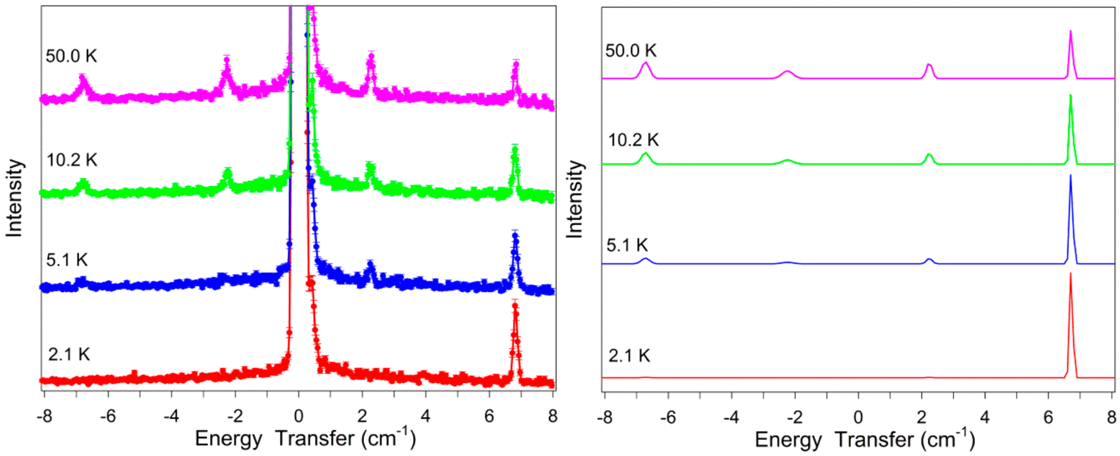


Figure 3. (Left) INS spectra of [Mn(TPP)Cl] using a 12.58 cm^{-1} incident neutron beam. (Right) Theoretical INS spectra of an $S = 2$ spin system with $D = -2.24$ cm^{-1}.

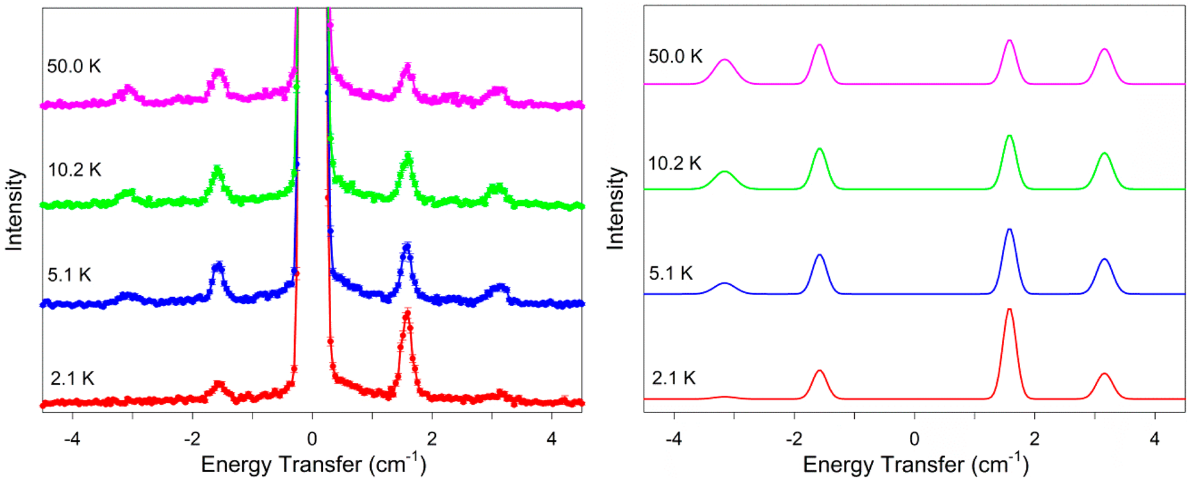


Figure 4. (Left) INS spectra of [Mn(TPP)] using a 12.58 cm^{-1} incident neutron beam. (Right) Theoretical INS spectra of an $S = {}^5/_2$ spin system with $D = 0.79$ cm^{-1}.

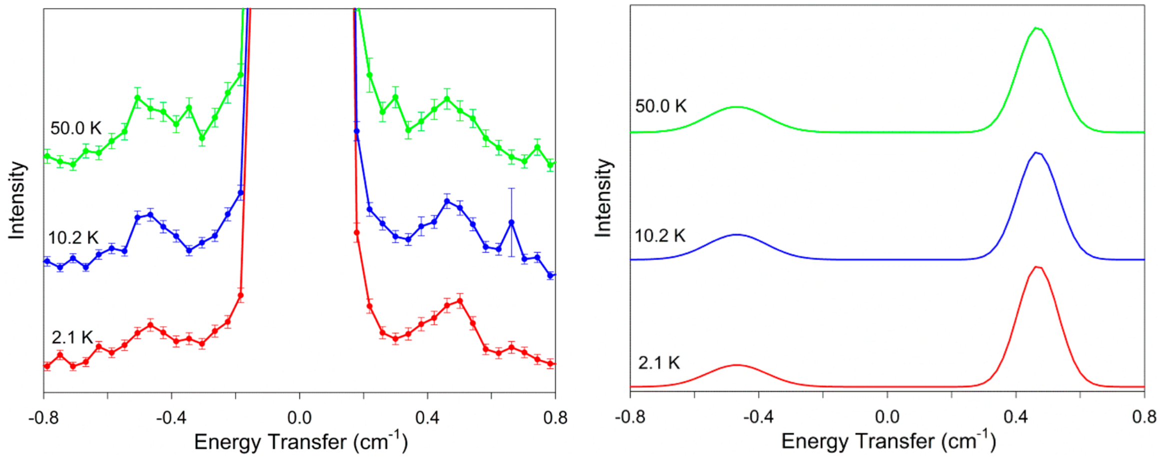


Figure 5. (Left) INS spectra: [Cr(TPP)Cl]. Incident neutron energy: 8.06 cm^{-1}. (Right) Theoretical INS spectra of an $S = {}^3/_2$ spin system with $D = 0.234$ cm^{-1} and $E = 0$.

The electronic ground state of [Mn(TPP)] is split into three Kramers doublets: $M_S = \pm{}^1/_2, \pm{}^3/_2$, and $\pm{}^5/_2$. If its D value is positive ($D > 0$), the ZFS would take the spacings among the three doublets as illustrated in Scheme 2. To our knowledge, ZFS of adduct-free [Mn(TPP)] has not been reported. The measured and theoretical INS spectra for [Mn(TPP)] are shown in Figure 4. It is assumed that the solid sample remained in the tetragonal crystal system at 2.1−50 K, as no observable rhombic splitting(s) was observed. At 2.1 K, the peak for the $\pm{}^1/_2 \to \pm{}^3/_2$ excitation is very prominent at 1.57(2) cm^{-1}. At

5.1 K a second excitation peak is already visible at 3.14(2) cm^{-1} which corresponds to the $\pm{}^3/_2 \rightarrow \pm{}^5/_2$ excitation. For [Mn(TPP)], the INS measurements are consistent with a positive D value and they give $2D$ = 1.57(2) cm^{-1} and thus D = 0.79(2) cm^{-1}.

[Cr(TPP)Cl]. A single crystal structure of [Cr(TPP)Cl] or its powder X-ray diffraction pattern has not been reported. We have collected the powder X-ray diffraction[22] of the sample at 296 K, and the results are given in the Supporting Information. Indexing of the powder X-ray diffraction data from the sample by the McMaille method yielded an orthorhombic unit cell (10.6576 Å, 8.5982 Å, 13.3577 Å). In phase transformation of crystals, the trend is that, at a lower temperature, crystals usually go to a lower symmetry phase.[33] Thus, it is unlikely that the sample solids transformed to the tetragonal crystal system at 2.1–50 K, temperatures at which INS data were collected.

[Cr(TPP)Cl] has a d^3 configuration ($S = {}^3/_2$). If the solids of the sample have 4-fold symmetry, the four states split into two Kramers doublets as shown in Scheme 2. To our knowledge, the ZFS for [Cr(TPP)Cl] has not been studied. However, using EPR spectroscopy, Hoffman and co-workers studied [CrTPP(Cl)(L)] (L = N, S, or O donors), a series of its adducts.[34] $|D|$ is ca. 0.156 cm^{-1} for N-donor ligands and 0.232 cm^{-1} for O- and S- donor ligands. The small D values are typical of other Cr(III) octahedral complexes, and this is mainly due to the small spin–orbital coupling of octahedral Cr(III) complexes. For an octahedral d^3 complex with a $t_{2g}{}^3$ configuration, the electron distribution is essentially spherical, making its D value near zero.[35] The largest D value recorded for a Cr(III) complex is the pseudo-octahedral complex $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}]^+$ [dmpe = 1,2-bis(dimethylphosphino)ethane], $|D|$ = 2.30 cm^{-1}, that Long and co-workers reported.[35]

Figure 5 shows the experimental and theoretical INS spectra for [Cr(TPP)Cl]. The zero-field splitting for [Cr(TPP)Cl] is very small and almost at the limits for detection by CNCS.[13] A peak is clearly shown at 0.468(12) cm^{-1} which corresponds to the transition between the $\pm{}^3/_2 \rightarrow \pm{}^1/_2$ levels. The value was calculated using the peaks at 10.2 and 50.0 K. As mentioned earlier and shown in Scheme 2, the sign of D for complexes with $S = {}^3/_2$ cannot be determined directly using INS. *If the solids of the sample had a 4-fold symmetry*, $|2D|$ would equal 0.468(12) cm^{-1}, and $|D|$ would be 0.234(12) cm^{-1}. Since the solids of the sample are in an orthorhombic crystal system, the peak at 0.468(12) cm^{-1} includes both the axial (D) and rhombic (E) ZFS parameters, as shown in eq 1. As 0.468(12) cm^{-1} is small and normally it is assumed that the ZFS parameters obey the relationship $|D| \geq 3E \geq 0$,[4a,29] the E value is likely very small as well. The fitting procedure of the observed excitation as described in the Experimental Section yields the range $|D|$ = 0.234(12)–0.203(12) cm^{-1} and the corresponding range E = 0.000–0.068(8) cm^{-1}. These data indicate small zero-field splittings for this square pyramidal complex with a $d_{xy}{}^1$ ($b_2{}^1$) and $d_{xz}{}^1$,$d_{yz}{}^1$ (e^1) configuration. If a sample of [Cr(TPP)Cl] in the tetragonal crystal system is available, it is expected that INS studies using this sample will give the $|D|$ value. Then using the results from the current work, the E value may be calculated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

XRD analyses of the samples, additional INS spectra, and error analyses. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000–2003. (b) *Handbook of Porphyrin Science with Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific: Singapore, 2010. (c) Walker, F. A. *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978–1979; Vol. *5*, Chapter 36, pp 81–183. La Mar, G. N.; Satterlee, J. D.; De Ropp, J. S. *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978–1979; Vol. *5*, Chapter 37, pp 185–298. Cheek, J.; Dawson, J. H. *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978–1979; Vol. *7*, Chapter 53, pp 339–369.

(2) For geochemistry of porphyrins, see, e.g.: Callot, H. J.; Ocampo, R. *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. *1*, Chapter 7, pp 349–398.

(3) (a) Collman, J. P.; Boulatov, R.; Sunderland, C. J.; Fu, L. *Chem. Rev.* **2004**, *104*, 561. (b) Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3575. (c) Yang, F.; Shokhireva, T. K.; Walker, F. A. *Inorg. Chem.* **2011**, *50*, 1176. (d) Scheidt, W. R.; Barabanschikov, A.; Pavlik, J. W.; Silvernail, N. J.; Sage, J. T. *Inorg. Chem.* **2010**, *49*, 6240. (e) Decker, A.; Solomon, E. I. *Angew. Chem., Int. Ed.* **2005**, *44*, 2252. (f) de Visser, S. P.; Valentine, J. S.. V.; Humphreys, K. J. *Pure Appl. Chem.* **1998**, *70*, 855. (g) Brand, H.; Arnold, J. *Coord. Chem. Rev.* **1995**, *140*, 137. (h) Fujii, H. *Coord. Chem. Rev.* **2002**, *226*, 51. (i) Richter-Addo, G. B. *Acc. Chem. Res.* **1999**, *32*, 529. (j) Zhang, P.; Wang, M.; Li, X.; Qiang, C.; Hong, G.; Dong, J. F.; Sun, L. C. *Sci. China: Chem.* **2012**, *55*, 1274.

(4) (a) Boca, R. *Coord. Chem. Rev.* **2004**, *248*, 757. (b) Neese, F.; Solomon, E. I. In *Magnetism*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: New York, 2003; Vol. *IV*, pp 345–466. (c) Long, J. R. In *Chemistry of Nanostructured Materials*; Yang, P., Ed.; World Scientific: Hong Kong, 2003; pp 291–315. (d) Misra, S. K. In *Multifrequency Electron Paramagnetic Resonance*; Wiley-VCH: New York, 2011; pp 589–597. (e) McInnes, E. L. In *Single-Molecule Magnets and Related Phenomena*; Winpenny, R., Ed.; Springer: New York, 2006; Vol. *122*, pp 69–102. (f) Krzystek, J.; Ozarowski, A.; Telser, J. *Coord. Chem. Rev.* **2006**, *250*, 2308. (g) Gatteschi, D. *J. Phys. Chem. B* **2000**, *104*, 9780. (h) Reiff, W. M. *ACS Symp. Ser.* **1996**, *644*, 115.

(5) (a) Yoon, J.; Mirica, L. M.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **2004**, *126*, 12586. (b) Her, J.-H.; Stephens, P. W.; Kennon, B. S.; Liu, C.; Miller, J. S. *Inorg. Chim. Acta* **2010**, *364*, 172. (c) Reisner, E.; Telser, J.; Lippard, S. J. *Inorg. Chem.* **2007**, *46*, 10754. (d) Krzystek, J.; Telser, J.; Pardi, L. A.; Goldberg, D. P.; Hoffman, B. M.; Brunel, L.-C. *Inorg. Chem.* **1999**, *38*, 6121. (e) Godwin, H. A.; Collman, J. P.; Marchon, J.-C.; Maldivi, P.; Yee, G. T.; Conklin, B. J. *Inorg. Chem.* **1997**, *36*, 3499. (f) Holman, T. R.; Juarez-Garcia, C.;

Hendrich, M. P.; Que, L., Jr.; Münck, E. *J. Am. Chem. Soc.* **1990**, *112*, 7611. (g) Schulz, C. E.; Song, H.; Mislankar, A.; Orosz, R. D.; Reed, C. A.; Debrunner, P. G.; Scheidt, W. R. *Inorg. Chem.* **1997**, *36*, 406. (h) Miyasaka, H.; Clérac, R.; Campos-Fernández, C. S.; Dunbar, K. R. *J. Chem. Soc., Dalton Trans.* **2001**, 858. (i) Ma, L.-H.; Liu, Y.; Zhang, X.; Yoshida, T.; Langry, K. C.; Smith, K. M.; La Mar, G. N. *J. Am. Chem. Soc.* **2006**, *128*, 6391. (j) Reynolds, P. A.; Moubaraki, B.; Murray, K. S.; Cable, J. W.; Engelhardt, L. M.; Figgis, B. N. *J. Chem. Soc., Dalton Trans.* **1997**, 263.

(6) Browett, W. R.; Fucaloro, A. F.; Morgan, T. V.; Stephens, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 1868.

(7) Yang, E. C.; Wernsdorfer, W.; Hill, S.; Edwards, R. S.; Nakano, M.; Maccagnano, S.; Zakharov, L. N.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Polyhedron* **2003**, *22*, 1727−1733.

(8) (a) *Magnetism: Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: New York, 2002. (b) Larese, J. Z. *Applications of Physical Methods to Inorganic and Bioinorganic Chemistry*; Scott, R. A., Lukehart, C. M., Eds.; Wiley: New York, 2007; pp 291−313.

(9) (a) Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324. (b) Van der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831. (c) Mojet, B. L.; Eckert, J.; van Santen, R. A.; Albinati, A.; Lechner, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 8147. (d) Rowsell, J. L. C.; Eckert, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 14904. (e) Ma, S.; Eckert, J.; Forster, P. M.; Yoon, J. W.; Hwang, Y. K.; Chang, J.-S.; Collier, C. D.; Parise, J. B.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 15896. (f) Sumida, K.; Horike, S.; Kaye, S. S.; Herm, Z. R.; Queen, W. L.; Brown, C. M.; Grandjean, F.; Long, G. J.; Dailly, A.; Long, J. R. *Chem. Sci.* **2010**, *1*, 184.

(10) Clemente-Juan, J. M.; Andres, H.; Borrás-Almenar, J. J.; Coronado, E.; Güdel, H. U.; Aebersold, M.; Kearly, G.; Büttner, H.; Zolliker, M. *J. Am. Chem. Soc.* **1999**, *121*, 10021.

(11) (a) Andres, H.; Basler, R.; Güdel, H.-U.; Aromi, G.; Christou, G.; Buettner, H.; Ruffle, B. *J. Am. Chem. Soc.* **2000**, *122*, 12469. (b) Basler, R.; Sieber, A.; Chaboussant, G.; Güdel, H. U.; Chakov, N. E.; Soler, M.; Christou, G.; Desmedt, A.; Lechner, R. *Inorg. Chem.* **2005**, *44*, 649. (c) Piligkos, S.; Rajaraman, G.; Soler, M.; Kirchner, N.; van Slageren, J.; Bircher, R.; Parsons, S.; Güdel, H.-U.; Kortus, J.; Wernsdorfer, W.; Christou, G.; Brechin, E. K. *J. Am. Chem. Soc.* **2005**, *127*, 5572. (d) Clemente-Juan, J. M.; Coronado, E. *Coord. Chem. Rev.* **1999**, *193−195*, 361. (e) Dreiser, J.; Waldmann, O.; Carver, G.; Dobe, C.; Güdel, H.-U.; Weihe, H.; Barra, A.-L. *Inorg. Chem.* **2010**, *49*, 8729. (f) Kittilstved, K. R.; Hauser, A. *Coord. Chem. Rev.* **2010**, *254*, 2663. (g) Blake, A. B.; Anson, C. E.; arapKoske, S. K.; Cannon, R. D.; Jayasooriya, U. A.; Saad, K.; White, R. P.; Summerfield, D. *J. Chem. Soc., Dalton Trans.* **1997**, 2039. (h) Wang, C. H.; Lumsden, M. D.; Fishman, R. S.; Ehlers, G.; Hong, T.; Tian, W.; Cao, H.; Podlesnyak, A.; Dunmars, C.; Schlueter, J. A.; Manson, J. L.; Christianson, A. D. *Phys. Rev. B* **2012**, *86*, 064439/1.

(12) (a) Bacon, G. E. *Neutron Scattering in Chemistry*; Butterworth: London, 1977. (b) Squires, G. L. *Introduction to the Theory of Thermal Neutron Scattering*; Cambridge University Press: Cambridge, U.K., 2012.

(13) Ehlers, G.; Podlesnyak, A.; Niedziela, J. L.; Iverson, E. B.; Sokol, P. E. *Rev. Sci. Instrum.* **2011**, *82*, 085108.

(14) Jones, R. D.; Summerville, D. A.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 4416.

(15) (a) Hill, C. L.; Williamson, M. W. *Inorg. Chem.* **1985**, *24*, 3024. (b) Liston, D. J.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1568.

(16) Le Bell, A. *Powder Diffr.* **2004**, *19*, 249.

(17) Dougan, B. A. Ph.D. Dissertation, The University of Tennessee, Knoxville, TN, December 2009, Chapter 5.

(18) Cheng, B.; Scheidt, W. R. *Acta Crystallogr., Sect. C* **1996**, *52*, 361.

(19) Azuah, R. T.; Kneller, L. R.; Qiu, Y.; Tregenna-Piggott, P. L. W.; Brown, C. M.; Copley, J. R. D.; Dimeo, R. M. *J. Res. Natl. Inst. Stand. Technol.* **2009**, *114*, 341.

(20) Basler, R.; Boskovic, C.; Chaboussant, G.; Güdel, H. U.; Murrie, M.; Ochsenbein, S. T.; Sieber, A. *ChemPhysChem* **2003**, *4*, 910.

(21) Waldmann, O.; Güdel, H. U. *Phys. Rev. B* **2005**, *72*, 094422/1.

(22) See Supporting Information for details.

(23) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992.

(24) (a) Maricondi, C.; Swift, W.; Straub, D. K. *J. Am. Chem. Soc.* **1969**, *91*, 5205. (b) Behere, D. V.; Mitra, S. *Indian J. Chem.* **1980**, *19A*, 505. (c) Behere, D. V.; Mitra, S. *Inorg. Chem.* **1979**, *18*, 1723. (d) Behere, D. V.; Marathe, V. R.; Mitra, S. *J. Am. Chem. Soc.* **1977**, *99*, 4149.

(25) Uenoyama, H. *Biochim. Biophys. Acta* **1971**, *230*, 479.

(26) La Mar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63.

(27) Dolphin, D. H.; Sams, J. R.; Tsin, T. B.; Wong, K. L. *J. Am. Chem. Soc.* **1978**, *100*, 1711.

(28) Sato, M.; Rispin, A. S.; Kon, H. *Chem. Phys.* **1976**, *18*, 211.

(29) Brackett, G. C.; Richards, P. L.; Caughey, W. S. *J. Chem. Phys.* **1971**, *54*, 4383.

(30) (a) Behere, D. V.; Mitra, S. *Inorg. Chem.* **1980**, *19*, 992. (b) Behere, D. V.; Marathe, V. R.; Mitra, S. *Chem. Phys. Lett.* **1981**, *81*, 57.

(31) (a) Goldberg, D. P.; Telser, J.; Krzystek, J.; Montalban, A. G.; Brunel, L.-C.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 8722. (b) Krzystek, J.; Telser, J.; Pardi, L. A.; Goldberg, D. P.; Hoffman, B. M.; Brunel, L.-C. *Inorg. Chem.* **1999**, *38*, 6121. (c) Krzystek, J.; Pardi, L. A.; Brunel, L.-C.; Goldberg, D. P.; Hoffman, B. M.; Licoccia, S.; Telser, J. *Spectrochim. Acta, Part A* **2002**, *58*, 1113.

(32) Hoffman, B. M.; Weschler, C. J.; Basolo, F. *J. Am. Chem. Soc.* **1976**, *98*, 5473.

(33) White, R. M.; Geballe, T. H. *Long Range Order in Solids*; Solid State Physics, Supplement 15; Academic Press: New York, 1979.

(34) Summerville, D. A.; Jones, R. D.; Hoffman, B. M.; Basolo, F. *J. Am. Chem. Soc.* **1977**, *99*, 8195.

(35) Karunadasa, H. I.; Arquero, K. D.; Berben, L. A.; Long, J. R. *Inorg. Chem.* **2010**, *49*, 4738.