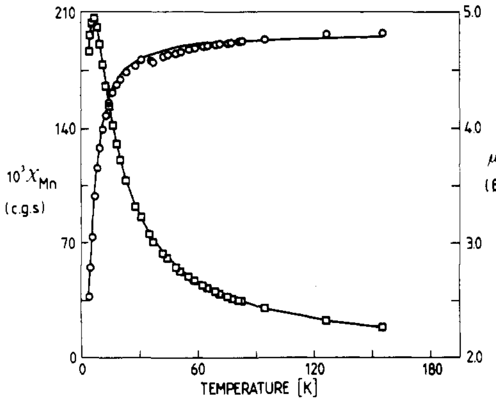

Figure 5. Temperature dependence of the magnetic moment (○) and molecular susceptibility (□) for a polycrystalline sample of [Mn(salen)SCN] (field 10 kG). Solid line is for $J = -0.44$ cm^{-1}, $D = -3.8$ cm^{-1}, and $g = 1.97$.

structure of either of these complexes, the exact molecular geometry is uncertain; however, it is probable that in both complexes Mn exists in an octahedral coordination with the anion and a phenolic oxygen of a neighboring [Mn(salen)] moiety making up the octahedron, as is observed in [Fe(salen)Cl]$_2$[29] and postulated in [Fe(salen)SCN].[20]

The infrared spectrum of [Mn(salen)SCN] shows bands attributable to the thiocyanate group at 2050 and 775 cm^{-1}, suggesting[31] coordination to the metal via nitrogen rather than the sulfur atoms. The preference of the Mn center for the nitrogen donor was also observed in the precursor molecule [Mn(acac)$_2$SCN]$_m$, which exists[11] as an infinite chain, where the Mn–S bond distance of 2.880 Å is very much longer than the corresponding Mn–N distance, 2.189 Å, even allowing for the larger covalent radius of sulfur. The presence of a second good donor atom, the phenolic oxygen, then results in the sulfur atom remaining uncoordinated.

The magnetic moment of [Mn(salen)NCS] drops slowly from 4.88 μ_B at 295 K to 4.80 μ_B at 120 K, and then more rapidly to 2.52 μ_B at 4.2 K (Figure 5). The susceptibility gradually increases as the temperature is lowered to 7 K, where it shows a sharp maximum. We initially attempted to fit the data to the simple $S = 2$ dimer coupled model.[3] The best fits obtained with this model placed the maximum in susceptibility at temperatures slightly greater than that observed, and χ_{calcd} was always greater than the observed value in the temperature region below 10 K, suggesting the need to include a ZFS term. Use of the more complete spin Hamiltonian model (eq 2) for a symmetrical dimer led to satisfactory fits over the entire temperature range, although it was not possible to distinguish the sign of D. As the complexes [Mn(sal-N-R)$_3$] (R = Benz, Ph) and [Mn(salen)OAc] have negative D values, it is probable that a similar ground state will be present here. Careful variation of D and J then gave a best fit with $D = -3.8 \pm 0.2$ cm^{-1} and $J = -0.44 + 0.02$ cm^{-1} shown in Figure 5.

The magnetic moment of [Mn(salen)Br] shows a similar temperature dependence to the thiocyanate complex, dropping slowly from 4.7 μ_B at 300 K to 4.46 μ_B at 120 K and finally reaching 1.47 μ_B at 4.2 K. At all temperatures the susceptibility for this complex is less than that observed for the thiocyanate complex, implying a stronger exchange interaction. Fitting of the data to eq 2, with D assumed to be negative, confirmed this, and a best fit J value of -1.84 ± 0.10 cm^{-1} was deduced. As a result of the stronger coupling, the susceptibilities were found to be relatively insensitive to the size of the ZFS on the Mn(III) center with values between -0.6 and -1.3 cm^{-1} providing equally good fits.

The surprising difference in the strength of the coupling observed for the two binuclear complexes, which presumably have similar pathways for exchange, is thought to be a result of a greater delocalization of electrons about the anion in the thiocyanate complex, resulting in weaker exchange. This may also explain the larger zero-field splitting observed for this complex.

Conclusion

Powder susceptibility and magnetization measurements have shown that the zero-field splitting parameter, D, is negative in a series of monomeric Mn(III) Schiff-base complexes. Polycrystalline sample tend to act as oriented single crystals in the presence of magnetic fields unless the sample is mulled into a diamagnetic Vaseline paste. Magnetization measurements on these pastes show that D falls within the range -1.5 to -2.6 cm^{-1}, although the presence of weak magnetic exchange can result in a marked overestimation of the size of the ZFS if it is not taken into account.

Polymeric Mn(III) Schiff-base complexes are less susceptibile to such orientation effects, although complex magnetic behavior at low temperatures can result from the $M_S = \pm 2$ doublet lying lowest. The exact nature and strength of magnetic exchange in these complexes depend on both the anion and the in-plane Schiff base.

Acknowledgment. This work was supported by grants from the Australian Research Grants Scheme and Monash University Special Research Fund.

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Magnetic Properties and Zero-Field Splitting in High-Spin Manganese(III) Complexes.

2. Axially Ligated Manganese(III) Porphyrin Complexes

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Received June 11, 1984

Magnetization data in the temperature range 4.2–300 K and field range 5–50 kG for some five- and six-coordinate high-spin manganese(III) tetraaryl- and octaethylporphyrin complexes are reported. The results have been interpreted by means of spin Hamiltonian formalism that includes zero-field splitting and exchange terms. D values in the range -1 to -2.3 cm^{-1} and in some cases J values of less than -0.17 cm^{-1} were obtained. A brief discussion on the origin of the small, negative zero-field splitting in these and related complexes is given.

Introduction

This detailed study of the magnetic susceptibility and magnetization of Mn(III) porphyrin complexes complements a similar study on Mn(III) Schiff-base chelates described in part 1.[1] It also forms part of a wider study of paramagnetic susceptibilities in d-block metalloporphyrins,[2,3] a subject that until recently had been neglected in comparison to other physico-

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Table I. Elemental Analyses of Mn(porph)X·L Complexes

complex	% found C	% found H	% found N	% found halide	% calcd C	% calcd H	% calcd N	% calcd halide
Mn(OEP)Cl·H_2O ($C_{36}H_{36}ClMnN_4O$)	67.72	6.99	8.66	5.70	67.44	7.23	8.74	5.53
Mn(OEP)Br·H_2O ($C_{36}H_{36}BrMnN_4O$)	63.35	6.62	8.09	11.6	63.07	6.76	8.17	11.65
Mn(OEP)OAc·H_2O ($C_{38}H_{49}MnN_4O_3$)	68.32	7.23	8.52		68.66	7.43	8.43	0.00
Mn(OEP)ClO_4·H_2O ($C_{36}H_{46}ClMnN_4O_5$)	61.55	6.25	8.09	4.90	61.32	6.57	7.95	5.03
Mn(TPP)ClO_4·$2H_2O$ ($C_{44}H_{32}ClMnN_4O_6$)	65.72	4.46	6.74		65.80	4.01	6.97	4.41
Mn(TTP)Cl·C_6H_6 ($C_{54}H_{42}ClMnN_4$)	77.25	5.18	6.69	4.03	77.46	5.06	6.60	4.23
Mn(TTP)Cl·H_2O ($C_{48}H_{38}ClMnN_4O$)	73.74	4.85	6.79		74.18	4.93	7.21	4.56

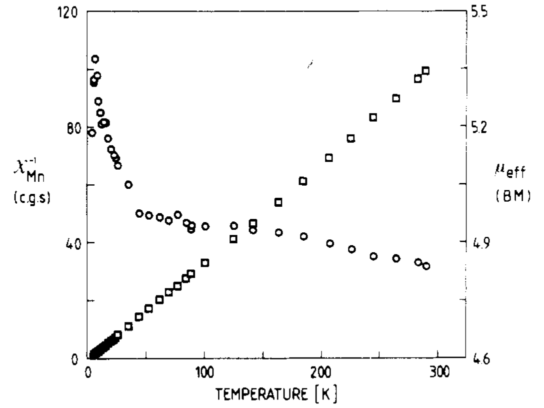

Figure 1. Average magnetic moments (○) and reciprocal susceptibilities (□) of a powdered sample of Mn(TTP)Cl·C_6H_6 under a magnetic field of 10 000 G. (NB: The Faraday balance operates from 4.2 K to higher temperatures.)

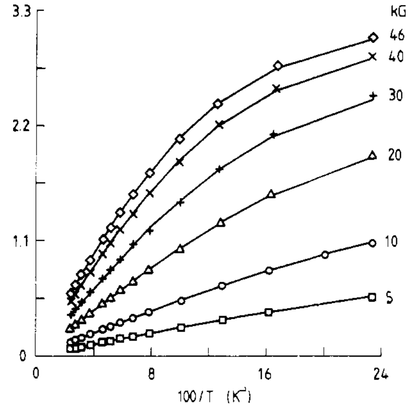

Figure 2. Magnetization ⟨μ⟩ vs. reciprocal temperature for a Vaseline mull of Mn(TTP)Cl·C_6H_6 with values of the applied field shown. The solid lines are those calculated from the parameters of Table II.

chemical investigations of this class of macrocycles.[4] It is particularly important that a good understanding of the electronic structures of Mn(III) porphyrins is achieved since these compounds are being used widely as precursors to the formation of Mn(IV) and Mn(V) species, some of which are capable of activating hydrocarbons and water under suitable conditions.[5-7] Mitra and co-workers have made related studies on other Mn(III) porphyrins concurrent with our own, and these results are compared with the present where appropriate.[8,9]

The compounds investigated are of general type Mn(porph)X·L where L may be H_2O, CH_3OH, or nothing, X = Cl, Br, CH_3CO_2, or ClO_4, and porph = TPP, TTP, or OEP. It will be seen that the zero-field splitting (ZFS) of the $^5B_1$ ground state in these complexes is small in comparison to related Fe(III) derivatives. In many cases it has been necessary to include a small antiferromagnetic exchange term between neighboring Mn(III) centers to fully reproduce the magnetic data.

Experimental Section

Synthesis. Mn(TTP)Cl·C_6H_6. Manganese(II) acetate (0.5 g) and *meso*-tetratolylporphyrin (0.5 g) were refluxed in 100 mL of dimethylformamide for 30 min. Addition of 100 mL of saturated sodium chloride solution yielded a fine green product, which was collected, dissolved in methanol, filtered, and reprecipitated by careful addition of concentrated hydrochloric acid. The solid was recrystallized from benzene, and the analytical data (Table I) indicated the presence of 1 mol of solvated benzene. The latter could be removed by heating in vacuo at 150 °C to yield the anhydrous material that appears to readily absorb a molecule of water from the atmosphere (Table I).

All the other manganese(III) complexes were prepared in a manner similar to that described above, except that the perchlorate salts were dried at room temperature in order to minimize risks of explosions. **Magnetic measurements** were carried out as described in part 1.[1] The variable-temperature susceptibility measurements were generally made under a field of 10 kG.

Results and Discussion

The temperature dependence of μ_{Mn} and χ_{Mn} for a neat polycrystalline sample of Mn(TTP)Cl·C_6H_6 obtained at 10 kG is shown in Figure 1. The unusually rapid increase in the moment at low temperatures is similar to that observed in some monomeric Mn(III) Schiff-base complexes[1] and is reminiscent of the behavior expected for μ in single-crystal samples with a negative value of the zero-field parameter, *D*, i.e. M_S ±2 ground level. Orientation or alignment effects of this kind appear to be particularly prevalent in Mn(III) compounds in which the M_S ±2 level lies lowest.[1,9,10] A polycrystalline sample of Mn(OEP)Cl·H_2O showed similar behavior. In order to overcome these alignment problems, all of the samples were finely dispersed in Vaseline mulls and the subsequent data refer to measurements made on these mulls.

The μ_{Mn} vs. *T* behavior for Mn(TTP)Cl·C_6H_6 is typical of that expected for a zero-field split *S* = 2 system.[8,9,11] The moment remains constant in value (4.95 μ_B) between 300 and 40 K and then decreases to 4.53 μ_B at 4.2 K. The data were fitted to a simple axial spin Hamiltonian of the type

$$\mathcal{H} = g\beta\hat{H}\cdot\hat{S} + D[\hat{S}_z^2 + \tfrac{1}{3}(S+1)] \qquad (1)$$

to yield best fit parameter values of $g = 2.01 \pm 0.01$ and $D = -2.2 \pm 0.2$ cm^{-1}. The sign of *D* was assumed to be negative by analogy to the single-crystal susceptibility data for the related compound Mn(TPP)Cl·$2C_6H_6$.[8]

Removal of the molecule of benzene and subsequent exposure to the atmosphere yields the hydrated species Mn(TTP)Cl·H_2O, which displays very similar magnetic behavior to the benzene

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Table II. Best Fit Magnetic Parameters[a]

complex	D, cm^{-1}	J, cm^{-1}	g	ref
$Mn(OEP)Cl·H_2O$	−1.6	−0.03	2.02	*b*
$Mn(OEP)Br·H_2O$	−1.0	−0.04	2.02	*b*
$Mn(OEP)(OAc)·H_2O$	−1.9	0.00	1.97	*b*
$Mn(OEP)ClO_4·H_2O$	−2.3	−0.17	1.96	*b*
	+3.0	−0.19	1.96	*b*
$Mn(TPP)ClO_4·2H_2O$	−2.3	−0.07	2.00	*b*
$Mn(TTP)Cl·C_6H_6$	−1.8	−0.02	2.01	*b*
$Mn(TTP)Cl·H_2O$	−1.8	−0.04	2.00	*b*
$Mn(TPP)Cl·2C_6H_6$	−1.9	−0.025 (ZJ)	2.00	*c*
$Mn(TPP)Cl(py)·C_6H_6$	−3.0	0	2.00	*c*

[a] Estimated errors: D, ±0.10; J, ±0.01; g, ±0.02. [b] This work. [c] Reference 9.

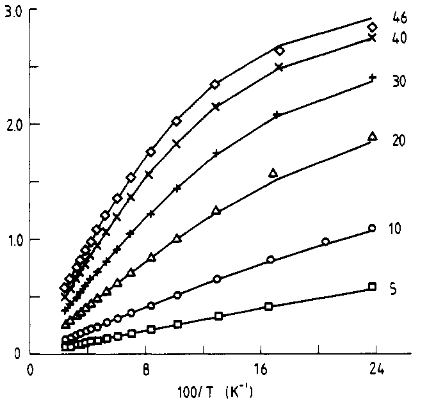

Figure 3. Magnetization ⟨μ⟩ vs. reciprocal temperature for a Vaseline mull of $Mn(OEP)OAc·H_2O$ with values of the applied field shown. The solid lines are those calculated from the parameters of Table II.

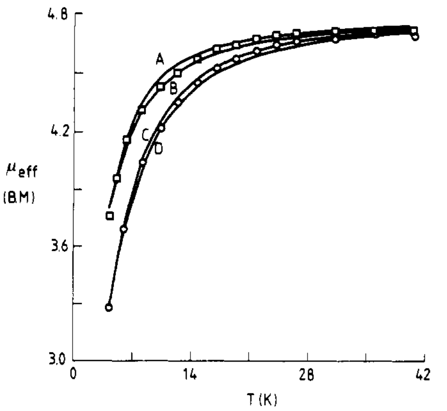

Figure 4. Average magnetic moment vs. temperature for a Vaseline mull of $Mn(OEP)ClO_4·H_2O$ under fields of 10 000 G (□) and 46 000 G (○). Solid lines are calculated from the following parameter values: (A and C) $g = 1.96$, $D = -2.3$ cm^{-1}, $J = -0.17$ cm^{-1}; (B and D) $g = 1.96$, $D = +3.0$ cm^{-1}, $J = -0.19$ cm^{-1}.

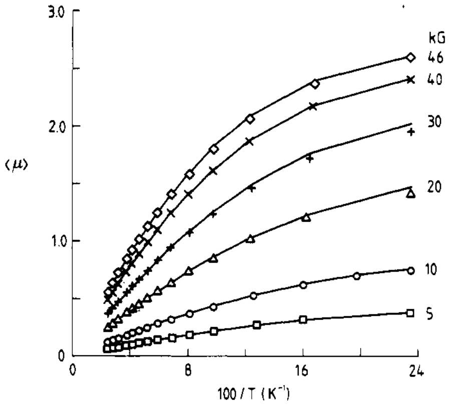

Figure 5. Magnetization ⟨μ⟩ vs. reciprocal temperature for a Vaseline mull of $Mn(OEP)ClO_4·H_2O$ with values of the applied field shown. The solid lines are those calculated from the parameters given in Table II.

solvate. The best fit parameters to (1) in this case were $g = 2.00 \pm 0.01$ and $D = -2.3 \pm 0.2$ cm^{-1}. Magnetization measurements were then carried out in order to confirm the sign of D and to investigate the nature of any exchange interactions that might be present. It soon became evident from field-dependent measurements that the axial Hamiltonian (1) could not adequately fit the data nor could the sign of D be unambiguously distinguished. A spin Hamiltonian applicable to exchange-coupled pairs of Mn(III) ions was then employed, as discussed in part 1. Least-squares fitting of the magnetization data for the two Mn(TTP)Cl complexes showed that significantly better fits were obtained with negative values of D rather than positive values. A very small J value was also required (Figure 2). The best fit parameter values are given in Table II. The D and J values found here are very similar to those reported by Mitra et al.[8,9] for the related tetraphenylporphyrin derivative $Mn(TPP)Cl·2C_6H_6$. In view of the similarity of the zero-field splitting for the two different solvates of Mn(TTP)Cl, together with the observation that Mn(TPP)Cl solvates are known to be five-coordinate,[12,13] it appears likely that the benzene and water molecules in the present TTP complexes are not coordinated to the metal center. Further indirect evidence for this comes from the observation that the ZFS in the six-coordinate complex Mn(TPP)Cl·py is noticeably larger than that found in the five-coordinate complex $Mn(TPP)Cl·2C_6H_6$.[8]

The octaethylporphyrin complex $Mn(OEP)Cl·H_2O$ displays very similar D and J values (Table II), which suggests that the in-plane macrocycle has a minimal effect on the size of the ZFS in these $S = 2$ species. $Mn(OEP)Br·H_2O$ produces a smaller D value than the corresponding chloride, which is opposite to the anion dependence of D displayed by the iron(III) porphyrin species Fe(TPP)X.[14] We had hoped to extend the Mn^{III}OEP series to include the fluoride and the iodide, but although analytically and spectroscopically pure samples could be prepared, they unfortunately did not give field-independent susceptibilities at 300 K.

Average susceptibility and magnetization data for $Mn(OEP)(CH_3CO_2)·H_2O$ showed no evidence for magnetic exchange interactions, and a value for D similar to that found in the chloride complex was obtained. The results are displayed in Figure 3. Since it is possible to detect small rhombic contributions to the ZFS in related (acetato)iron(III) porphyrins by means of ESR and Mössbauer measurements,[15] an E term was included in the analysis of the magnetic data for $Mn(OEP)(CH_3CO_2)·H_2O$. This did not improve the fits over the axial models, which is perhaps not surprising in view of the insensitivity toward rhombic contributions when D is very small and negative.[11]

Two perchlorate complexes were investigated. These were of particular interest in view of the change of spin state induced by O-bonded perchlorate ligation in analogous Fe(III) complexes ($S = {}^5/_2$–${}^3/_2$ admixed) compared to the halide derivatives ($S = {}^5/_2$).[14,16] However, the susceptibility and magnetization data for both $Mn(OEP)ClO_4·H_2O$ and $Mn(TPP)ClO_4·2H_2O$ clearly indicate a pure high-spin ground state. In the OEP derivative the μ_{eff} value decreases to 3.76 μ_B at 4.2 K (Figure 4), which is lower than that observed in the halide and acetate complexes and symptomatic of a larger ZFS and/or exchange coupling. Careful variation of D and J during the fitting procedure showed acceptable fits could be obtained for D positive (+3.0 cm^{-1}) or negative (−2.3 cm^{-1}) with a relatively large J value, viz. −0.18 cm^{-1} (Table II; Figures 4 and 5). The relationships between the sign

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of D and magnitude of J have been described in more detail in part 1. Somewhat similar behavior was observed for Mn(TPP)$ClO_4 \cdot 2H_2O$, but with a smaller J value of -0.07 cm^{-1}. Since completion of the present work a similar study has been reported on two other perchlorate derivatives of Mn^{III}TPP, viz. the anhydrous complex Mn(TPP)ClO_4 and a bis(base) adduct [Mn(TPP)(*N*-MeImd)$_2$](ClO_4).[17] The μ_{eff} values at 4.2 K for these two complexes were similar to each other but noticeably higher than in the present complexes (ca. 4.4 μ_B). A contribution from exchange effects was apparently not required to interpret the susceptibility and limited magnetization data.[17] The reported D values were very similar to those deduced here for the hydrated species.

X-ray crystallographic details on Mn(III) porphyrin perchlorate complexes are somewhat sketchy. The structure of anhydrous Mn(TPP)ClO_4 has not been reported, but presumably it is monomeric and five-coordinate with O-bonded perchlorate similar to that found in the analogous Fe(TPP)ClO_4 complex.[16] In contrast, the details recently given for a methanol solvate, Mn(TPP)$ClO_4 \cdot 3CH_3OH$, show a structure involving pairs of [Mn(TPP)(CH_3OH)$_2$]$^+$ groups bridged by a ClO_4^- ion.[18] In the absence of crystallographic data on the present complexes, the exact structures of Mn(TPP)$ClO_4 \cdot 2H_2O$ and Mn(OEP)$ClO_4 \cdot H_2O$ remain uncertain; each could conceivably be six-coordinate, the former with two bonded water molecules and the latter with one. The larger D values found in the perchlorate complexes may indicate six-coordination, for the reason indicated earlier, or may reflect the axial ligand field of a single O-bonded perchlorate. Unfortunately the infrared spectra are not sufficiently well resolved to help determine the coordination mode of the perchlorate anion.

The origin of the larger J values in the present perchlorate complexes may be a result of a bridging ClO_4^- moiety similar to that observed in the methanolate.[18] The weaker antiferromagnetic exchange observed in the halide complexes is similar to that recently detected in a variety of five-coordinate Fe(III)[14] and Mn(III) porphyrin[9] and other chelate complexes[1,19] of general formula [M(chelate)$_n$X] where $n = 1$ or 2. While it is not always possible to identify obvious metal–metal or super-exchange pathways in the solid-state molecular structures, M–X···X–M seem to be the preferred interactions.

Summary

The present work, and that of others using magnetic or far-infrared spectroscopic methods,[8,9,17,20] has shown that axially ligated Mn(III) porphyrin complexes display zero-field splitting of the $^5B_1$ ground state with D values in the range -1 to -3 cm^{-1}. For a constant porphyrin the order of D is Br < Cl < CH_3CO_2 $\sim$ ClO_4. Experimentally it has been shown that these polycrystalline compounds generally need to be dispersed in uniform Vaseline mulls in order to obtain meaningful magnetic data, especially when using low temperatures and high magnetic fields. Many of the complexes display weak antiferromagnetic exchange interactions between neighboring Mn centers, the perchlorate being more strongly coupled than the halide or acetate analogues.

The above observations hold true for a number of other Mn(III) chelate compounds including five- and six-coordinate Schiff-base complexes.[1] From the somewhat limited amount of information now known about the nature of ZFS in Mn(III) compounds it appears that unlike the analogous high-spin Fe(III) systems that display an unusually large range of values of D and E, both positive and negative,[14] ZFS in Mn(III) complexes appears to be much smaller and surprisingly insensitive to the coordination geometry around the metal center. Presumably, the sense of the distortion, i.e. axial elongation, overcomes differences in coordinate number etc. With these comments in mind, considerable care is therefore needed to obtain meaningful estimates of such splittings in Mn(III) compounds.

It is pertinent to comment further on the origin of small negative values of D in Mn(III) complexes even though the magnitude of zero-field splittings can be influenced by a variety of subtle structural and ligand field effects. ZFS essentially arises through the coupling of low-lying excited states by spin–orbit coupling with the ground state. The energies of these excited states, which themselves are split by the low-symmetry ligand field, can in favorable cases be measured by optical spectroscopy and used to determine the magnitude of ZFS.[10] Unfortunately, intense metal–ligand based transitions (e.g., in porphyrins and Schiff bases) often obscure the d–d transitions. The relationship between D and the energy difference between the ground $^5B_1$ and excited states ^5E, $^5B_2$, and ^3E shows that a small negative value of D is much more likely than a positive value.[10,11] Mitra et al. have recently proposed that the main variations in D values for a series of type [Mn(porph)X] would be due to the position of the ^3E spin triplet, the energy of which is a function of both the interelectronic repulsion (Racah) and ligand field parameters.[17] The energy of the ^3E is lowered when small tetragonal distortions occur. Confirmation of this proposal will require more systematic studies of both the crystal structures and magnetic properties in compounds with different X groups, as well as in other six-coordinate Mn(III) complexes.

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