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Low-Temperature Magnetic Properties of Three Vanadium(III) and Manganese(III) β-Diketonate Complexes

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The low-temperature (2–100 K) polycrystalline magnetic properties of V(acac)$_3$, Mn(acac)$_3$, and Mn(trop)$_3$ are reported [Hacac = 2,4-pentanedione and Htrop = tropolone]. For V(acac)$_3$ the zero-field splitting (D) is 7.7 cm^{-1}, $g_\parallel = 1.96$ and $g_\perp = 1.78$, all compatible with the reinterpreted optical spectrum. The magnetic data for Mn(acac)$_3$ have been interpreted with $D = 3.1$ cm^{-1} and $g = 2.00$ and are also compatible with ligand field calculations based on the reinterpreted optical spectrum. In Mn(trop)$_3$ there appears to be a very weak intermolecular coupling through the tropolonate ligands, the magnetic parameters being $D = -2.6$ cm^{-1}, $g = 2.00$, and $J = -0.18$ cm^{-1}.

Introduction

Recent work on the ^{1}H and ^{13}C isotropic shifts and nuclear and electron spin relaxation times of a series of transition-metal acetylacetonates has shown that the interpretation of the data depends intimately on the detailed magnetic properties of the metal ion in question.[2-5] The isotropic shifts depend on the anisotropy in the susceptibility tensor (pseudocontact) and $\langle S_z \rangle$ (contact). For ions with $S > {}^1/_2$, the relaxation times have been correlated with the zero-field splitting parameter. However, we have recently shown that other mechanisms for relaxation in paramagnetic materials are possible.[2,4,5] In all cases, a detailed knowledge and description of the magnetic susceptibility tensor is necessary. This information is available for the chromium(III),[6] iron(III),[7,8] ruthenium(III),[9] and copper(II)[10] acetylacetonates. The experimental data for Ti(acac)$_3$ is available,[11,12] although the interpretation is, as yet, unsatisfactory.

In this paper we give an account of the low-temperature magnetic behavior of V(acac)$_3$, Mn(acac)$_3$, and also Mn(trop)$_3$ (Htrop = tropolone). The magnetic behavior of Mo(acac)$_3$ and Mo(trop)$_3$ is more complicated and will be treated separately. In a subsequent publication we will apply all of this information to the temperature-dependent isotropic shifts we have accumulated over the last couple of years.

Experimental Section

The compounds studied were prepared by standard literature methods: V(acac)$_3$,[13] Mn(acac)$_3$,[14] Mn(trop)$_3$.[15]

The magnetic properties were measured by a SQUID magnetometer manufactured by Superconducting Technology Inc. (ScT). The digital readout of magnetization is calibrated internally in terms of a flux quantum $h/2e$ ($\psi_0 = 2.07 \times 10^{-15}$ Wb). An optional inductance switch extending the dynamic range by a factor of 643 is also incorporated. The temperature is measured using a silicon diode and controlled with a Lakeshore Model DTC-500 temperature controller. The magnet (0–0.7 T) is energized by an Electronic Measurements Model SCR10 power supply. The magnet current constant has been calculated from the known winding geometry of the coil to better than 0.1%, 50 A produces 2.0154 T, so an accurate measure of the current allows an accurate determination of the magnetic field strength. However, we have found in practice that it is more convenient to measure the magnetization of a known material and calculate the magnetic field strength. Often the calculated (from the current) field was not completely trapped inside the superconducting shield or the current could not be read precisely enough, especially at very low fields (up to ~0.05 T). Both MnCl$_2$·4H$_2$O and CuSO$_4$·5H$_2$O were employed as calibrants. The former is more convenient as it is isotropic, powders well, and the diamagnetic correction for the quartz sample tube is relatively unimportant. If the magnetization of a sample of MnCl$_2$·4H$_2$O (freshly recrystallized) over a temperature range is compared with[16] $\bar{\chi} = C/(T + \Delta)$ where $C = 4.3770$ and $\Delta = 2.0$ K, an average value of H is easily obtained. The same value for H is obtained if CuSO$_4$·5H$_2$O is used with[17] $\bar{\chi} = C/(T - \Theta)$ where $C = 0.4580$ and $\Theta = 0.7$ K.

All the theoretical magnetic moments were calculated with $H = 0.1$ T (the experimental value) using the program VVLECH.[18] Although there was very little dependence of μ_{eff} on H in the field strength region available to us, there can be significant changes when the field strength of a typical NMR experiment (2.1 T) is used.

Table I. Magnetic Parameters for Several Compounds Containing the V(III) Ion

Compound	$g_\parallel$	$g_\perp$	D/cm^{-1}	Ref
Cs$_3$VCl$_6$·3H$_2$O	1.93	1.74	8.05	19
V$^{\text{III}}$ in Al$_2$O$_3$	1.92	1.74	8.25	20
[C(NH$_2$)$_3$]V(SO$_4$)$_2$·6H$_2$O	1.94	1.66	3.74	21
(NH$_4$)V(SO$_4$)$_2$·12H$_2$O			4.9	22
V(urea)$_6$Br$_3$·3H$_2$O			5.9	23

Results and Discussion

(1) V(acac)$_3$. The electronic structure of the V(III) ion is of interest because the results of the few low-temperature studies on pure compounds show that all have unusually large zero-field splittings of up to between 3.74 and 8 cm^{-1}. The ^{3}A$_2$ ground state in an axial field is described by the usual spin Hamiltonian for $S = 1$

$$\mathcal{H} = g_\parallel \beta H S_z + g_\perp \beta [H_x S_x + H_y S_y] + D[S_z^2 - {}^1/_3 S(S + 1)] \qquad (1)$$

The data including the g values are collected in Table I. In each case the g values are rather lower than 2.00 and anisotropic.

In our preliminary report[2a] on the nuclear magnetic resonance of V(acac)$_3$, the unusually narrow and easily observable proton and ^{13}C spectra suggested that the zero-field splitting be large and/or the g values be anisotropic.

The low-temperature magnetic moment of a powdered sample is shown in Figure 1. The agreement between the present data and that of Machin and Murray[24] is quite good around 100 K. For this particular experiment it was not feasible to go higher in temperature because the sensitivity was too low with the particular mass of sample and the inductance switch setting.

Preliminary fitting of the data to the spin Hamiltonian (eq 1) showed that with an average g value of 2.00, $D \simeq 8$ cm^{-1}. This represented the temperature variation moderately well although the magnitude at $T > 20$ K was too large by 0.15 μ_{B} due to $g_\parallel$ and $g_\perp$ being too large (see below). It is also possible to demonstrate that D is positive. Plots of $\bar{\mu}_{\text{eff}}$ vs. T with each sign of D showed that very much larger values of D (<−20 cm^{-1}) are required if D is negative. Moreover all previous values of D for the V(III) ion have been shown to be positive.[19] This is not difficult to understand when calculations based on the formal ^{3}T$_1$ ground state are considered. Perturbation theory shows[25] that $D \simeq (1.25\lambda)^2/v$ where λ is the spin–orbit coupling constant and v is the trigonal field splitting of the ^{3}T$_1$ state into ^{3}A$_2$ and ^{3}E. When ^{3}A$_2$ is the ground state v is positive and so D is always positive. This theory also predicts that deviations from 2.00 occur in first

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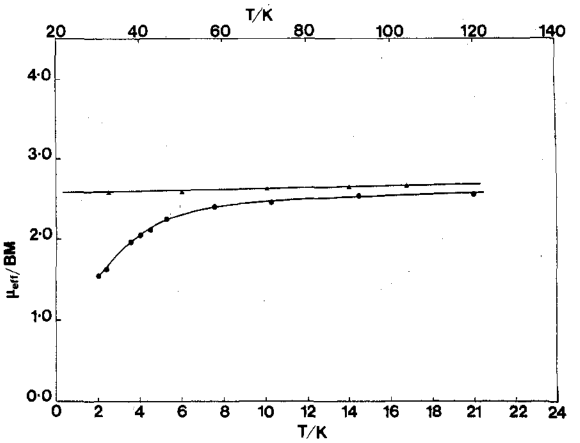

Figure 1. Average magnetic moment of V(acac)$_3$: ●, 0–20 K; ▲, 20–120 K; —, calculated (see text).

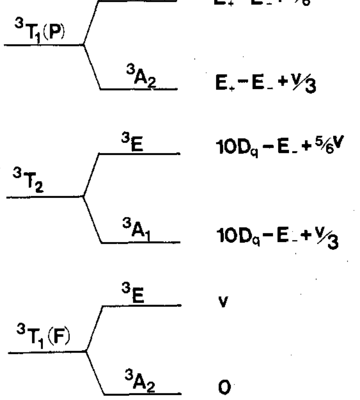

Figure 2. A simplified energy level diagram for the V(III) ion. $E_\pm$ is given by the expression $E_\pm = {}^1/_2[(15B + 10Dq) \pm (225B^2 + 18B{\cdot}10Dq + (10Dq)^2)^{1/2}]$.

order for $g_\perp$ but only in second order for $g_\parallel$, in agreement with experiment.

It is of interest to use the full $^3T_1$ ground state with a trigonal splitting in order to assess the applicability of the spin Hamiltonian formalism and also to calculate the values of D, $g_\parallel$, and $g_\perp$ as a function of λ and v. This assumes that D, $g_\parallel$, and $g_\perp$ are only affected by the ground-state $^3T_1$ manifold, a reasonable approximation in this situation. The unknown parameters in the Figgis[26] matrices are A (the amount of configurational mixing into the ground $^3T_1(F)$ state from the excited $^3T_1(P)$ state), λ, and v, assumed positive when the orbital singlet lies lowest.

The parameter A can be calculated from a knowledge of $10Dq$ and the Racah parameter B. The available optical absorption spectral data on V(acac)$_3$ are limited. Both solution[24] and diluted single-crystal spectra[27] show two shoulders, one at 18180 cm^{-1} and another at 21740 cm^{-1} with several maxima at higher energies. Unfortunately the crystal spectrum does not improve the resolution nor the assignment. It is generally agreed that the first shoulder corresponds to the transition from $^3T_1(F) \rightarrow {}^3T_2$ although the second is still open to question. The assignment[24] $^3T_1(F) \rightarrow {}^3T_1(P)$ is obviously incorrect[28] because it leads to B = 285 cm^{-1}, far too small when the free-ion value is 860 cm^{-1}. A simplified energy level diagram (Figure 2) helps to rationalize the observed spectra. The energies of each level have been taken from Pryce and Runciman,[25] neglecting the off-diagonal trigonal field term in v'. This could be important but the quality of the available spectra does not warrant the extra refinement. A possible explanation for the two observed shoulders could then be transitions to the two components of the $^3T_2$ state but this would lead to v = 7120 cm^{-1}, rather high and unreasonable. A more likely explanation is that they are due to $^3A_2[^3T_1(F)] \rightarrow {}^3E[^3T_2]$ and $^3A_2[^3T_1(F)] \rightarrow {}^3A_2[^3T_1(P)]$, respectively. This leads to the relation

$$10Dq - 15B + (4/3)\nu = 14620 \qquad (2)$$

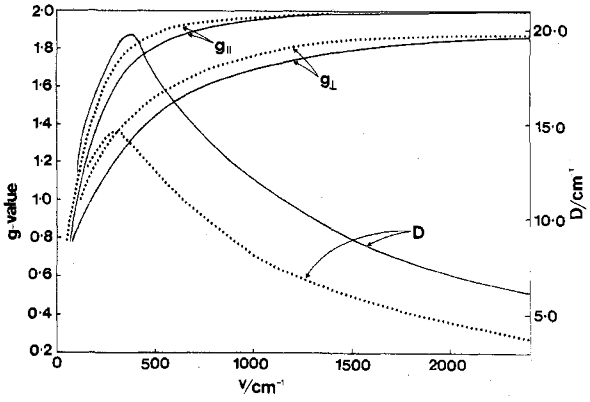

Figure 3. Variation of D, $g_\parallel$, and $g_\perp$ as a function of v for the $^3T_1$ ground state: —, calculated with λ = 100 cm^{-1}, - - -, calculated with λ = 80 cm^{-1}.

It is interesting to note that the $^3A_2 \rightarrow {}^3A_1[^3T_2]$ transition is not allowed in C_{3v} symmetry, lending some support to this assignment. The Racah parameter B for the V(III) ion ranges from 644 cm^{-1} [V(H$_2$O)$^{3+}$] to 536 cm^{-1} [VCl$_6$$^{3-}$][29] so a value of 600 cm^{-1} for the acac$^-$ ligand would be reasonable. It is also known that $10Dq$ for V(H$_2$O)$_6$$^{3+}$ is ~19 000 cm^{-1} [29] and also that $10Dq$(acac)/$10Dq$(H$_2$O) ≃ 1.2[30] so a reasonable estimate for $10Dq$(acac) would be 22 250 cm^{-1}. This leads to v ≃ 1000 cm^{-1} consistent with other V(III) compounds[24] and leads to the correct order of magnitude for D (see below). With B = 600 and Dq = 2225 cm^{-1} A is calculated to be 1.23. The spin–orbit coupling constant is assumed to be 80 cm^{-1}, an average (reasonable) value for V(III) compounds. Machin and Murray[24] deduce λ values of between 75 and 100 cm^{-1}, Rahman[31] uses 88 cm^{-1} in [V(urea)$_6$]$^{3+}$ while Chakravarty[32] and McFarlane[33] use ~60 cm^{-1} in their work on V(KC$_2$O$_4$)$_3$·3H$_2$O and V(III) in vanadium alum, respectively.

The eigenvalues of the 9 × 9 matrices describing the $^3T_1$ ground state were determined and the three lowest were fitted to the spin Hamiltonian (eq 1) with D, $g_\parallel$, and $g_\perp$ as a function of v, shown in Figure 3. This is carried out as follows. If $E_1{}^\parallel$, $E_2{}^\parallel$, and $E_3{}^\parallel$ are the three lowest eigenvalues, $E_1{}^\parallel$ being the lowest and calculated with the magnetic field in the z or (||) direction, then

$$g_\parallel = (E_3{}^\parallel - E_2{}^\parallel)/2\beta H$$

$$D = (E_3{}^\parallel - E_1{}^\parallel) - g_\parallel \beta H$$

$$g_\perp = [\{\frac{E_3{}^\perp - E_1{}^\perp}{2}\}^2 - \frac{D^2}{4}]^{1/2}/\beta H \qquad (3)$$

where $E_i{}^\perp$ are the eigenvalues calculated with H in the x or (⊥) direction.

The variation in D is particularly sensitive to λ, as expected. Figure 3 explains the relative magnitudes of $g_\parallel$, $g_\perp$, and D for all the compounds in Table I, except for [C(NH$_2$)$_3$V(SO$_4$)$_2$·6H$_2$O] where the small value of D and the relatively low $g_\perp$ are hard to understand.

The magnetic moment of V(acac)$_3$ can be fitted quite well to the $^3T_1$ ground state with λ = 80 cm^{-1} and v = 1100 cm^{-1}. The data between 20 and 120 K are also compatible with these parameters, that of Machin and Murray being high. However, even at room temperature, we predict an average magnetic moment of 2.83 μ_B which is only 0.04 μ_B lower than the

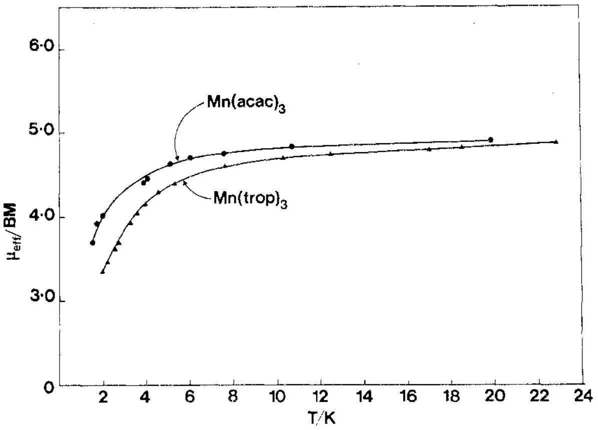

Figure 4. Average magnetic moment of $Mn(acac)_3$ (●) and $Mn(trop)_3$ (▲). The theoretical curve for $Mn(acac)_3$ has been calculated with $D = 3.1$ cm^{-1} and $g = 2.00$ and for $Mn(trop)_3$ the solid line is compatible with both $D = +5.9$ cm^{-1} and $D = -2.6$ and $J = -0.18$ cm^{-1}, each with $g = 2.00$ (see text).

"unexplainably" high measured value.[24] We conclude that with the help of low-temperature data the average magnetic moment over the whole range of temperature can be satisfactorily explained within the framework of the $^3T_1$ ground state. These parameters can then be used in conjunction with Figure 3 to give $D = 7.7 \pm 0.1$ cm^{-1}, $g_\parallel = 1.96$, and $g_\perp = 1.78$ and substitution of these values in the spin Hamiltonian (eq 1) gives an excellent representation of the data. The main effect of using the anisotropic g values is to reduce the absolute magnitude of $\bar{\mu}_{\mathrm{eff}}$ from the spin-only value of 2.83 μ_B to about 2.60 μ_B at 20 K.

Two further points need to be made. The first is the applicability of averaging $\chi_\parallel$ and $\chi_\perp$ via

$$\bar{\chi} = {}^1/_3(\chi_\parallel + 2\chi_\perp) \qquad (4)$$

Marathe and Mitra[34] and Vermaas and Groeneveld[35] have shown that this simple relation may not hold in the low-temperature/large-D/high-field regions. However, we have used the relationships given by Mitra[34] and find no variation between the two averaging procedures even though D is quite large. The low-magnetic field (~0.1 T) appears to ensure the validity of eq 4. Secondly the molecular structure[36] of $V(acac)_3$ is quite distorted so the presence of an E term in the spin Hamiltonian is probably justifiable but in the present situation was not considered worthwhile because the effect of E on $\bar{\mu}_{\mathrm{eff}}$ is not very pronounced.

(2) $Mn(acac)_3$. The magnetic properties of manganese(III) materials are normally uncomplicated except at very low temperatures where the effects of zero-field splitting and high magnetic fields may become important. In the high-temperature region (100–300 K) most studies[37] show that the average magnetic moment is at about 4.8–4.9 μ_B and close to the spin-only value of 4.89 μ_B.

The only low-temperature data on $Mn(acac)_3$ is the early work of Jackson[38] who measured the average magnetic susceptibility down to 16.95 K. The present data (Figure 4) agree quite well with the earlier work, even to reproducing the slight rise in magnetic moment between 10 and 50 K. Below 10 K the $\bar{\mu}_{\mathrm{eff}}$ begins to fall until at 1.5 K it is only 3.8 μ_B, presumably due to the sizable zero-field splitting of the orbitally nondegenerate ^5E ground state. A slight TIP reduction from the spin-only value is expected from the interaction via spin–orbit coupling of the excited $^5T_{2g}$ term at $10Dq$. By use of the formula[39] $\bar{\mu}_{\mathrm{eff}} = 4.90[1 - 2\lambda/10Dq]$ $\bar{\mu}_{\mathrm{eff}}$ is then about 4.84 μ_B. Another source of lowering in the magnetic moment is the possible influence of an excited $^3T_{1g}$ term which was postulated[40] to cause a small degree of spin mixing. However, later work by Figgis and Toogood[41] on $Mn(Et_2dtc)_3$ has discounted this so we deduce that these complicating factors are not present in $Mn(acac)_3$.

The simplest interpretation would be to use the spin Hamiltonian (eq 1) with $S = 2$. We find that a good account of the data in Figure 4 can be given with $D = +3.1 \pm 0.1$ cm^{-1} and $g = 2.00$. The sign of D has been assumed to be positive. Theoretical plots of $\bar{\mu}_{\mathrm{eff}}$ vs. T for negative D give quite the wrong temperature variation for $\bar{\mu}_{\mathrm{eff}}$ when compared with the experimental results, except for very large unreasonable values of D. This appears to be only the third detailed account of the low-temperature magnetic properties of a Mn(III) ion where a value can be placed on the zero-field splitting parameter. In the first Mathe et al.[42] found $D = -3.5$ cm^{-1}, $g_\parallel = 1.963$, and $g_\perp = 1.993$ for the tartrate complex $Na_5[(C_4H_4O_6)_2]\cdot 9H_2O$. The Mn(III) ion doped into rutile was shown from ESR measurements[43] to have $D = -3.4$ cm^{-1}, $g_\parallel = 1.99$, and $g_\perp = 2.00$ while in $Mn(Et_2dtc)_3$ the value of D appears to be much smaller as little evidence of a falling moment is observed down to ~5 K.[41] These derived values are consistent with the theoretical expressions for g and D. The g-value expressions are similar to those for the Cu(II) ion although the relatively low value of the Mn(III) spin–orbit coupling constant guarantees that both g values are very close to 2.00. Expressions for D have been derived using perturbation theory[43]

$$D = \pm 3\left(\frac{\lambda^2}{10Dq} + \frac{4}{3}\frac{\lambda^2}{E}\right) \qquad (5)$$

E is the energy between the ground state and the low lying $^3T_1(H)$ state. The positive sign applies when the ground state is $^5A_{1g}$ (compression of the octahedron) and the negative sign applies when the ground state is $^5B_{1g}$ (elongation of the octahedron). Calculations show that $|D|$ can have values from near zero to at least 6 cm^{-1} but we return to more precise estimates of D using direct diagonalization techniques after a consideration of the structure and optical spectrum of $Mn(acac)_3$.

The average M–O bond distances in the MO_6 chromophore of $Mn(acac)_3$ indicate that the structure is a tetragonally compressed octahedron and so compatible with the predicted Jahn–Teller effect of this molecule.[44] This corresponds to a $^5A_{1g}$ ground state and a positive zero-field splitting which agrees with experiment. An attempt to confirm this was not successful. For positive D we expect $K_\perp > K_\parallel$ (susceptibilities perpendicular and parallel to the symmetry axis). Crystals of $Mn(acac)_3$ grow very easily as large plates but reproducible or internally consistent magnetic anisotropy results could never be obtained, presumably because of crystal twinning.[45]

The optical spectrum of $Mn(acac)_3$ becomes interesting in the light of the more recent crystal structure[44] because in the past the three d–d spin-allowed transitions (9520, 17 900, and 21 500 cm^{-1}) have been assigned on the basis of an elongated octahedron.[46] With the revised ground state the three transitions correspond to $^5A_{1g} \rightarrow {}^5B_{1g}$, $^5A_{1g} \rightarrow {}^5E$, and $^5A_{1g} \rightarrow {}^5B_{2g}$, respectively, with $Dq = 1198$, $Ds = -1875$, and $Dt = -405$ cm^{-1}. These values are to be compared with those based on the earlier assignment (1790, 1875, and 405 cm^{-1}, respectively) and appear to be reasonable. The sign in Ds and Dt corresponds to the sign change in the axial perturbation and the lower Dq is compatible with the four longer in-plane bonds in the compressed structure.

It is now possible to calculate a value for D using the matrices of interelectronic repulsion and spin-orbit coupling for the d^4 electronic configuration in D_{4h} symmetry.[47] We have added the diagonal ligand field matrix elements (in terms of Dq, Ds, and Dt) to all the triplet and quintet states[48] and obtained the eigenvalues. The five lowest can be easily fitted to the spin Hamiltonian (eq 1) with $S = 2$. The ligand field parameters are fixed from the optical spectra so the only unknowns are the Racah parameters B and C and the one-electron spin–orbit coupling constant ξ. If we choose B and C to be 0.85 their free-ion values[49] (970 and 3124 cm^{-1}, respectively) and ξ to be 250 cm^{-1}, we calculate D to be +3.1 cm^{-1}, in excellent agreement with experiment. D is sensitive to B, C, and ξ as shown by expression 5 but reasonable values of these parameters do give a very satisfactory account of the magnitude and sign of the zero-field splitting.

(3) Mn(trop)$_3$. The structure of Mn(trop)$_3$ (crystals grown from a chloroform/toluene solution) is interesting for two reasons.[50] First there are two quite separate molecular geometries in the unit cell. One type of molecule is tetragonally elongated while the other possesses an orthorhombic distortion. Secondly the axial distortion (elongation) in Mn(trop)$_3$ is just the opposite to that in Mn(acac)$_3$ (compression). Ligand field theory would then predict the ground state in Mn(trop)$_3$ to be $^5B_{1g}$ and D to be negative.

At first sight the magnetic data (Figure 4) are only compatible with $D = 5.9 \pm 0.1$ cm^{-1} or an unacceptably large (>20 cm^{-1}) value if D is negative. However the structure is such that a weak intermolecular coupling through the tropolonate ligands may be possible[50] so the effect of a pairwise interaction between two $S = 2$ ions with zero-field splitting was investigated. This is easily accomplished using the Hamiltonian

$$\mathcal{H} = -JS_1S_2 + D_1[S_{1z}^2 - {}^1/_3S(S+1)] + D_2[S_{2z}^2 - {}^1/_3S(S+1)] \qquad (6)$$

and the 25 basis functions $|M_{S^1}M_{S^2}>$ where each M_S value can take the values 2, 1, 0, −1, or −2. Only very small values of J are required to affect the magnetic moment below about 10 K and a negative value has the effect of introducing the quite large drop in moment as $T \rightarrow 2$, even with a negative value of D which is required by the structure.

The reflectance spectra of Mn(trop) has been interpreted with $Dq = 1670$, $Ds = 2100$, and $Dt = 440$ cm^{-1}.[46] These ligand field parameters, and the same B, C, and ξ as used for Mn(acac)$_3$ above, lead to a calculated zero-field splitting of −2.6 cm^{-1}. Using this value for D_1 and D_2 in (eq 6) the value of J refines to -0.18 ± 0.01 cm^{-1}. It is interesting to note that when both D ($=D_1 = D_2$) and J are allowed to refine together, $D = -2.5 \pm 0.1$ and $J = -0.18 \pm 0.01$ cm^{-1} so both methods of determining these parameters appear to be fairly consistent. If the published structural characteristics were present in our sample of Mn(trop)$_3$ (recrystallized from CHCl$_3$), then the value of −2.6 cm^{-1} for D would certainly only be an effective average over the two different molecules in the unit cell. Further, the orthorhombic molecules would probably impose a nonzero E term in the usual spin Hamiltonian (eq 1).

Conclusions

Low-temperature magnetic measurements have been used to characterize the zero-field splitting parameter in V(acac)$_3$, Mn(acac)$_3$, and Mn(trop)$_3$. In each case ligand field calculations, utilizing the reinterpreted optical spectra of V(acac)$_3$ and Mn(acac)$_3$, have been able to account quantitatively for the magnitude and sign of D. A small intermolecular interaction is present in Mn(trop)$_3$.

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Registry No. V(acac)$_3$, 13476-99-8; Mn(acac)$_3$, 14284-89-0; Mn(trop)$_3$, 21757-62-0.

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