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Low-temperature Magnetic Susceptibility and Zero-field Splitting in some High-spin Manganese(III) Compounds

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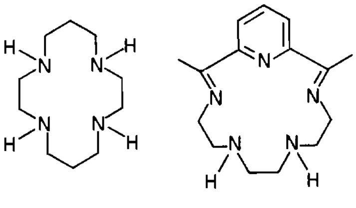
Abstract

We have determined the value of the ground-state zero-field splitting parameter D for several high-spin d^4 Mn(III) compounds from average susceptibility measurements down to 5 K with a SQUID magnetometer. We determined $g_\parallel = 1.96$, $g_\perp = 1.98$, $D = -2.96$ cm^{-1} for [Mn(III)([14]aneN$_4$)Cl$_2$]Cl·3H$_2$O; $g_\parallel = 1.95$, $g_\perp = 1.98$, $D = -2.11$ cm^{-1} for [Mn(III)([15]pydieneN$_5$)Cl$_2$]PF$_6$; and $g_\parallel = 1.95$, $g_\perp = 1.98$, $D = -2.59$ cm^{-1} for [Mn(III)([15]pydieneN$_5$)Br$_2$]PF$_6$ by least-squares fitting of the low-temperature magnetic-moment data. The zero-field splittings in these compounds are similar to some results reported for Mn(III) porphyrins and are insensitive to ligand structure and axial halide binding, in contrast to what has been reported for the analogous Fe(III) compounds.

Introduction

The combined effects of spin–orbit coupling and axial ligand fields can partially remove the spin degeneracy of high-spin ($S = 2$) manganese(III) compounds. Average magnetic susceptibility measurements made at low temperature (<20 K) can sometimes be used to determine the magnitude of the zero-field splitting parameter D by which the energy separations between the $M_s = \pm 2$, $M_s = \pm 1$, $M_s = 0$ sublevels of the spin-quintet ground state are characterized. Some values for Mn(III) zero-field splitting in Mn(III) porphyrins and a few other compounds have been determined in this way [1–5]. However, few Mn(III) compounds are available for further studies and comparisons.

The synthesis and characterization of manganese(III) compounds with *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**I**, [14]aneN$_4$) and 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-(12,3,1)-octadeca-1(18),2,12,14,16-pentaene (**II**, [15]pydieneN$_5$) were reported previously as a part of a study to examine the chemistry of manganese macrocyclic systems as a function of ligand structure (Fig. 1) [6, 7].



I **II**

Fig. 1. Structures of the macrocyclic ligands [14]aneN$_4$ (I) and [15]pydieneN$_5$ (II).

We have now measured the average magnetic susceptibility on some of these compounds down to 5 K with a SQUID magnetometer. The measurements have allowed us to determine the value of the zero-field splitting parameter D for [Mn([14]aneN$_4$)Cl$_2$]Cl·3H$_2$O and [Mn([15]pydieneN$_5$)X$_2$PF$_6$ (X = Br, Cl). The importance of the porphyrins in biological processes is well known, and the role of Mn(III) porphyrins is of much interest [8–10]. The similarities of coordination environment between Mn(III) porphyrins and Mn(III) complexes with ligands **I** and **II** make a comparison between the values of the zero-field splitting in the compounds of this study and those of Mn(III) porphyrins of interest. In addition, it is of interest to determine the magnitude of the zero-field splitting in [Mn([15]pydieneN$_5$)X$_2$PF$_6$ (X = Cl or Br) because the analogous [Fe(III)([15]pydieneN$_5$)X$_2$]ClO$_4$ (X = I or SCN) compounds have a zero-field splitting that is very sensitive to axially coordinated halide ions [11, 12].

Experimental

The syntheses, room-temperature magnetic moments, electronic spectra, and elemental analyses of [Mn([14]aneN$_4$)X$_2$]Y (X = Cl, Br, SCN; Y = Cl·3H$_2$O, PF$_6$, BF$_4$, NCS) and [Mn([15]pydieneN$_5$)X$_2$]PF$_6$ (X = Cl, Br) have been reported [13].

Magnetic measurements were obtained with a superconducting magnetometer (SHE VTS-10) at 5–300 K in applied fields ranging from 10.0 to 200.0

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TABLE I. Curie–Weiss Parameters for some Mn(III) Compounds

Compound[a]	C (emu-K mol^{-1})	θ (K)	μ_{eff} (μ_β)	Temperature (K)
$[Mn([14]aneN_4)Cl_2]Cl \cdot 3H_2O$	2.984	−0.72	4.89	5–75
$[Mn([14]aneN_4)Br_2]PF_6$	2.773	−2.99	4.71	5–300
$[Mn([14]aneN_4)Cl_2] \cdot PF_6$	2.977	−4.44	4.88	10–100
$[Mn([14]aneN_4)SCN_2]SCN$	2.647	+1.58	4.60	10–75
$[Mn([15]pydieneN_5)Cl_2]PF_6$	2.954	−0.49	4.86	5–75
$[Mn([15]pydieneN_5)Br_2]PF_6$	2.947	−0.61	4.86	5–75

[a] $[14]aneN_4$ = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; $[15]pydieneN_5$ = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo(12,3,1)-octadeca-1(18),2,12,14,16-pentaene.

mT (1 mT = 10 gauss). The magnetometer was factory calibrated with NBS standards, and the calibration was checked at various temperatures and fields in the range indicated against the susceptibility of both $HgCo(SCN)_4$ and cubic Gd_2O_3. Agreement between measured and accepted magnetic properties of these materials was within 0.2% [14].

The experimental data were corrected for the ligand diamagnetism of $[14]aneN_4$ by using the value -264×10^{-6} emu mol^{-1}, which was previously determined via the Faraday method [6]. The diamagnetism of the other constituents was estimated by using Pascal's constants [15]. The diamagnetism of $[15]pydieneN_5$ was assumed to be equal to that of $[14]aneN_4$ because ligand diamagnetism is insignificant at the low temperatures of this study. The magnetism of the empty sample holders was determined for each temperature reported and subtracted from the data. The sample holders were tightly packed with fine powders. The data were reproducible to better than 0.3% on the same sample and to 0.5% on different samples of the same material. The data were fitted using the least-squares technique to equations by using statistical weighting, as discussed in the text.

Results and Discussion

The experimental data $\bar{\chi}_m^{-1}$ *vs.* temperature were fitted by linear least-squares to obtain the Curie constant, *C*, and the Curie–Weiss temperature, θ, as reported in Table I. Figure 2 shows a plot of $\bar{\chi}_m^{-1}$ and $\bar{\mu}_{eff}$ *vs.* temperature for $[Mn([14]aneN_4)Br_2]PF_6$; the other compounds gave similar plots with only slight differences as noted in the text. The magnetic moments at high temperature are not very different from the spin-only value of 4.89 μ_B and show only a slight variation with temperature down to about 20 K (Fig. 2).

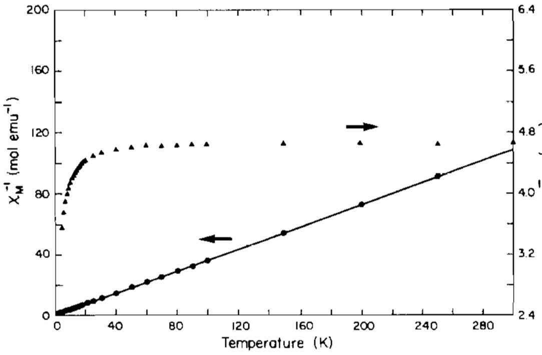

Fig. 2. $\bar{\chi}_m^{-1}$ and $\bar{\mu}_{eff}$ for $[Mn[14]aneN_4Br_2]PF_6$. Solid line is the least-squares fit to the Curie–Weiss law $\chi_m = C/T - \theta$ with $C = 2.773$ emu-K mol^{-1} and $\theta = -2.99$ K. (●) $\bar{\chi}_m^{-1}$, (▲) $\bar{\mu}_{eff}$.

$[Mn([14]aneN_4)(NCS)_2]NCS$ shows evidence of ferromagnetic exchange and low-temperature susceptibility behavior reminiscent of that reported for $Mn(acac)_2NCS$ and $Mn(acac)N_3$ [16]. The magnetic susceptibility data of $Mn(acac)_2NCS$ and $Mn(acac)_2N_3$ have been interpreted according to a Heisenberg linear chain model with ferromagnetic exchange because the crystal structures of these compounds show nearly square-planar $Mn(acac)_2^+$ units with NCS^- and N_3^- bridges forming the one-dimensional network [16]. No information is available about the structure of $[Mn([14]aneN_4)(NCS)_2]NCS$ to permit such detailed interpretation of its magnetic parameters.

Several of these compounds have significantly large negative values of θ, which suggests antiferromagnetic ordering at low temperature. It is not easy to deconvolute the effects of exchange in decreasing the low-temperature magnetic moment from effects due to the zero-field splitting, especially if no structural data are available to suggest an appropriate model to make such analyses meaningful. For further analyses we concentrate only on those compounds with little evidence of magnetic interactions at low temperature.

Zero-field splitting is an important property of ions with $S \geqslant 1$. The Curie–Weiss law is not general enough to give any information about this ground-state parameter, because it is a high-temperature approximation. Typical zero-field splitting energies are only a few cm^{-1}, and magnetic properties will be sensitive to zero-field splitting with this magnitude only at very low temperature.

If the excited-state energy is much greater than the zero-field splitting in the ground state, the spin-Hamiltonian formalism can be used to obtain the susceptibility expressions from the thermodynamic equation for molar susceptibility [17].

$$\chi_m = -\frac{N}{H}\,\frac{\sum\limits_i \frac{dE_i}{dH}\exp(-E_i/kT)}{\sum\limits_i \exp(-E_i/kT)} \tag{1}$$

In this equation H is the applied magnetic field, and the E_i are energy eigenvalues calculated from the Hamiltonian

$$\mathcal{H} = g\beta\vec{H}\vec{S} + DS_z^2 \tag{2}$$

where D is the zero-field splitting parameter that characterizes the effect of the spin–orbit interaction and the axially symmetric ligand field in removing the ground-state spin dependency of the $^5B_{1g}$ ground term.

The X-ray crystal structure of $[Mn([14]aneN_4)Cl_2]Cl{\cdot}3H_2O$ shows that the coordination environment about the Mn(III) ion is close to axially distorted D_4h symmetry [18]. The optical and circular dichroism spectra have been interpreted to indicate that the ground level is $^5B_{1g}$ and that excited levels occur at energies $>10\,000$ cm^{-1} [6]. The excited-state energies in the seven-coordinate complexes are not expected to differ much from those of the six-coordinate compounds, so that the spin-Hamiltonian approach is well justified.

The equations for the magnetic moment when the H field is applied parallel and perpendicular to the symmetry axis are given by

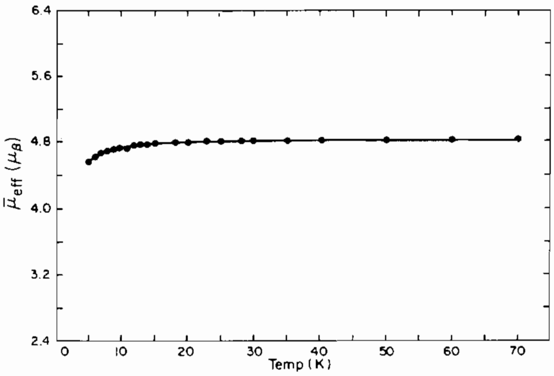

Fig. 3. $[Mn([14]aneN_4)Cl_2]Cl{\cdot}3H_2O$. (●) experimental data $\bar{\mu}_{eff} = 2.828\sqrt{\chi_m^{corr}\,T}$. Solid line is best least-squares fit using eqns. (3) and (4) with $g_\parallel = 1.96$, $g_\perp = 1.98$, $D = -2.96$.

$$\mu_\parallel^2 = \frac{6g_\parallel^2(e^{-(D/kT)} + 4e^{-(4D/kT)})}{1 + 2e^{-(D/kT)} + 2e^{-(4D/kT)}} \tag{3}$$

$$\mu_\perp^2 = \frac{g_\perp^2 kT}{D}\left\{\frac{18 - 14e^{-(D/kT)} - 4e^{-(4D/kT)}}{1 + 2e^{-(D/kT)} + 2e^{-(4D/kT)}}\right\} \tag{4}$$

The parameters $g_\parallel$, $g_\perp$, and D were fitted by least-squares to the experimental data for magnetic moment by averaging the magnetic-moment eqns. (3) and (4).

The average magnetization represented in this manner is not always valid for magnetically anisotropic compounds that are near to saturation [19, 20]. To minimize saturation, we obtained our low-temperature data in a 100.0 mT applied field. The fit we obtain for $[Mn([14]aneN_4)Cl_2]Cl{\cdot}3H_2O$ is shown in Fig. 3. The data for $[Mn([15]pydieneN_5)Cl_2]PF_6$ and $[Mn([15]pydieneN_5)Br_2]PF_6$ were fitted to a similar degree of accuracy; the parameters are listed in Table II. The negative sign for D is chosen because the crystal structure of $[Mn([14]aneN_4)Cl_2]Cl{\cdot}3H_2O$ shows that the Mn(III) coordination

TABLE II. Zero-field Splitting Parameters in High-spin Mn(III) Compounds

Compound	$g_\parallel$	$g_\perp$	D (cm^{-1})	Reference
$[Mn([14]aneN_4)Cl_2]Cl{\cdot}3H_2O$	1.96	1.98	−2.96	this work
$[Mn([15]pydieneN_5)Br_2]PF_6$	1.95	1.98	−2.59	this work
$[Mn([15]pydieneN_5)Cl_2]PF_6$	1.95	1.98	−2.11	this work
Mn(TPP)Cl[a]	2.0	2.0	−2.3	3
Mn(TPP)(Py)Cl[a]	2.0	2.0	−3.0	3
$Mn(TPP)ClO_4$[a]	2.0	2.0	−2.0	4
$Mn(TPP)(1\text{-}MeIm)_2ClO_4{\cdot}THF$[a]	2.0	2.0	−2.5	4
$Mn(acac)_3$[a]	2.0	2.0	−3.1	2
$Mn(trop)_3$[a]	2.0	2.0	−2.6	2
$Na_5[Mn(C_4H_2O_6)_2(H_2O)_2]{\cdot}9H_2O$	1.96	1.99	−3.5	1

[a] Only parameter fitted was D; $g_\parallel$ and $g_\perp$ chosen as equal to 2.0.

is tetragonally elongated [18]. A negative value for *D* is reported for all other cases in which the zero-field splitting of high-spin Mn(III) has been determined (Table II). Negative *D* means that the $M_s = \pm 2$ levels are lowest in energy. There is good agreement between the values for *D* determined in this study and the values reported for high-spin Mn(III) compounds from other studies (Table II).

In the seven-coordinate [Mn([15]pydieneN$_5$)X$_2$]PF$_6$ (X = Br, Cl) we find $|D_{\mathrm{Cl}}| < |D_{\mathrm{Br}}|$. This is in agreement with $D_{\mathrm{SCN}} < D_{\mathrm{I}}$ as determined for [Fe([15]pydieneN$_5$)X$_2$]ClO$_4$ (X = SCN, I), although the magnitude of the zero-field splittings varies more dramatically in the Fe(III) compounds and is of opposite sign [5]. The zero-field splittings in Fe(III) porphyrins are similarly more affected by different axial halide ions than those of Mn(III) porphyrins [4, 21].

The compounds investigated here are somewhat similar to the porphyrins with respect to the in-plane coordination environment of the central Mn(III) ion. The zero-field splitting in these compounds is comparable in magnitude to values determined for the Mn(III) porphyrins. The significance of the results reported here is that the zero-field splittings in Mn(III) compounds are not very sensitive to ligand structure of axial halide ions, in contrast to the dramatic effects seen in corresponding Fe(III) compounds. It has been suggested that the Fe(III) compounds may be more sensitive because the ground states of these species are near the crossover region between high-, low-, and intermediate-spin states [5]. Spin-state crossover phenomena are well documented for Fe(III) compounds, but there is only one report of similar phenomena for Mn(III) [22]. Thus spin-state crossover is not expected to be important in understanding Mn(III) porphyrins.

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