Single-Crystal Studies of the Zero-Field Splitting and Magnetic Exchange Interactions in the Magnetic Susceptibility Calibrant $HgCo(NCS)_4$

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Powder and single-crystal magnetic susceptibility data are reported for $HgCo(NCS)_4$ in the temperature range 1.7–300 K. Confusion concerning various previously reported magnetic parameters is rectified by developing an understanding of the magnetic behavior throughout the temperature range examined. Curie–Weiss analysis of the data is valid only in the temperature interval of 40–300 K, where the best-fit parameters $C = 2.305$ ($g = 2.218$) and $\Theta = -0.32$ K allow the experimental values to be calculated to better than 0.02% when the diamagnetic correction is taken as -190×10^{-6} emu/mol and the temperature independent paramagnetic correction is taken to be the spectroscopically determined value of $+428 \times 10^{-6}$ emu/mol. Between 1.7 and 40 K, a "best-fit" Curie–Weiss model simply does not represent the data well enough for it to be used as a parametric equation for a calibrant. The low-temperature data are best understood in terms of a model that accounts for zero-field splitting ($D = +10.6$ cm^{-1}) of the ^4A ground state and for antiferromagnetic exchange interactions ($zJ = -0.095$ cm^{-1}) between the Co(II) ions. The exchange is XY in character because of the positive D value ($S = |\pm^1/_2\rangle$ ground state). Since there are two possible types of NCS–Hg–SCN bridge geometries between nearest neighbors, the magnetic lattice is of mixed dimensionality and additional studies will be needed to further clarify the magnetic structure at lower temperatures.

Introduction

$HgCo(NCS)_4$ has been widely used as a calibrant for magnetic susceptibility apparatuses ever since the early work by Figgis and Nyholm.[1] Driven in part by the confusion surrounding the early work, but also by the development of improved instrumentation, other groups have since reported new or revised sets of magnetic parameters (Table I). Figgis and Nyholm[1] were the first to report the experimentally observed, uncorrected gram magnetic susceptibility (16.44×10^{-6} emu/mol) for $HgCo(NCS)_4$ at 293 K. Later, the same authors[2] reported Faraday balance data in the temperature range 80–300 K. This second paper led to the ambiguity that was first pointed out by Cotton et al.[3] Rade[4] subsequently reported Faraday balance data in the temperature range 6–300 K, but the data were oddly different and were retracted at a later date after Hatfield and co-workers[5] reported the first low-temperature VSM data (1.7–50 K). Although Hatfield provided an estimate of the zero-field splitting, they found no evidence for exchange interactions (although they did report that the best-fit was not excellent). O'Connor et al.[6] reported the first SQUID-based data (2–100 K) and confirmed that the data of Figgis, Cotton, and Hatfield were all in qualitative agreement. They too considered zero-field splitting, but only on a qualitative basis, and as a result suggested that antiferromagnetic exchange interactions were a possibility. Bunzli[7] attempted to reconcile the confusion and lack of quantitative agreement by pointing out the dissimilar use of diamagnetic corrections. However, he did not report any new data, nor did he consider temperature independent paramagnetism, zero-field splitting, or magnetic exchange in his reanalysis. As a widely used calibrant, $HgCo(NCS)_4$ confronts anyone interested in the proper operation of a magnetometer, and it ought to be better characterized. Equally important, having rather unique lattice in which anisotropic spins are exchange coupled, its structure and properties ought to be better understood.

We set out to develop an understanding of why and how the different parameter sets were obtained when, during our recent attempt to use $HgCo(NCS)_4$ as a calibrant, we became intrigued by this confusion and the lack of understanding that still remained concerning the magnetic properties of $HgCo(NCS)_4$. Two sets of crucial experiments were clearly lacking. First, a determination of the powder magnetic susceptibility of $HgCo(NCS)_4$ on a single magnetometer throughout the temperature range 1.7–300 K had never been reported. The advantage of such data would have been the requirement that the magnetic susceptibility be understood in terms of both temperature-*dependent* and temperature-*independent* contributions. Second, single-crystal susceptibility measurements provide a more rigorous understanding of magnetic behavior if a material has the potential of exhibiting zero-field splitting and magnetic exchange interactions. In this paper, we report the first single-crystal magnetic susceptibility data (rf-SQUID based) to be measured for $HgCo(NCS)_4$. The measurements were carried out in the temperature range 1.7–300 K and are utilized in conjunction with powder data; data were also collected for the first time on a single magnetometer and throughout the temperature range 1.7–300 K. We demonstrate that temperature-independent paramagnetism, zero-field splitting, and magnetic exchange are all required in order to account for the observed magnetic behavior.

Experimental Section

Synthesis. $HgCo(NCS)_4$ was prepared as a microcrystalline powder according to methods previously reported in the literature.[1,2] All reagents (Aldrich) were used as received. Single crystals suitable for SQUID-based magnetic susceptibility measurements were grown using soxhlet extraction techniques. In all cases, doubly distilled water was used. Elemental analysis confirmed the chemical composition. Powder X-ray diffraction patterns, and single-crystal X-ray diffraction photographs confirmed the structure as that reported by Jeffery.[8] Faces of well-formed crystals were indexed to facilitate the mounting of single crystals on rigid rod sample holders.

Magnetic Measurements. Magnetic susceptibility data were collected in the temperature range 1.7–300 K for a variety of powder and single-crystal samples using a Quantum Design SQUID-based magnetometer.

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Table I. Summary of Literature Data That Describe the Magnetic Behavior of $HgCo(NCS)_4$

ΔT (K)	method	$10^6\chi_g$ (emu/g ⟨at 293 K⟩)	$10^6\chi_{dia}$ (emu/mol)	$10^6\chi_{TIP}$ (emu/mol)	C	Θ (K)	g (from C)	D (cm^{-1})	μ_{eff} (μ_B)	ref
292.5–293.5	Gouy	16.44 (0.08)								1
80–300	Gouy	15.88^{b}	−137			−10^{a}			4.33 (300 K)	2
									4.18 (90 K)	
80–300	Gouy	16.44^{c}	−137	+428^{e}		−4^{c,d}			4.32^{d}	3
6–300	Faraday	16.45				+2^{f}				4
						−1.8				ref 13 in 5
			−189^{k}		2.43 (0.04)^{f}	2.4 ± 2.3^{j}				7
1.7–50	VSM	16.20^{g}	−190	+400	2.351^{h} (0.002)	−1.86^{h} (0.01)	2.24^{g}	+19 (3)		5
							2.21^{i}			
1.3–100	SQUID	16.50^{g}	−141.8		2.41	−0.62	2.26^{g}		4.37 (0.05) (30–100 K)	6
		16.34^{j}	−189^{k}		2.42 (0.01)^{j}	−1.1 (0.2)^{j}				7
no new data		16.43	−189		2.433	−1.1				7
1.7–300	SQUID	16.47	−190	+428	2.305	−0.32	2.218^{g}	10.6^{n}	4.36^{l} (293 K)	this work
							2.220^{j}		4.29^{m} (293 K)	
							2.251^{i} (⊥)	10.8^{n}		
							2.168^{i} (∥)	10.2^{o}		

[a] Apparently determined from corrected inverse-molar susceptibility plots, but was prematurely referred to in ref 1 using a Curie–Weiss formalism based on uncorrected gram-susceptibility data; this would not have been proper usage. [b] No value was specified in the reference itself, but this is the value hypothesized in ref 3 on the basis of a back-calculation; it was argued to be incorrect. [c] The value considered to be the correct one according to ref 3, after a new analysis of the data presented in ref 1. [d] Calculated according to a molar susceptibility that was corrected for both diamagnetism and TIP, but the authors also used the unconventional "corrected temperature", $T - \Theta$, instead of a straightforward T. [e] Determined on the basis of spectral data; this is the value which is most reliable and should be used in calculating the total TIM. [f] According to Curie–Weiss formalism based on gram-susceptibility data; not a proper usage. No mention was made as to whether or not any type of corrections were applied. [g] Calculated value on the basis of the reported molar Curie–Weiss parameters. [h] Best-fit molar Curie–Weiss parameters that were deliberately obtained without corrections for diamagnetism or TIP. [i] Best-fit value obtained from a zero-field splitting analysis; corrections for diamagnetism and TIP were included. [j] Proposed value according to the new analysis provided in ref 7. [k] Value used in ref 7 in a new analysis of the data. [l] Value when using uncorrected molar susceptibility data, i.e., the observed magnetic moment of a sample of $HgCo(NCS)_4$. [m] Value when molar susceptibility has been corrected for diamagnetism and TIP, i.e. the magnetic moment of Co(II) in $HgCo(NCS)_4$. [n] Best-fit parameter obtained with the use of a molecular-field correction for antiferromagnetic exchange interactions (see text). [o] No molecular field correction for antiferromagnetic exchange interactions was required.

[The superconducting magnet was generally operated at field strengths ranging from 0.01 to 10kG. The data specifically reported in the figures of this manuscript were collected at 5000 Oe. The absolute accuracy of the magnetometer was calibrated at 298 K (not 293 K) with a National Bureau of Standards Pd sample ($\chi_g = 5.25 \times 10^{-6}$) and with a saturated Ni sphere. Temperatures were measured using calibrated platinum and germanium thermometers. A Lake Shore Ga/As diode was used to confirm the temperature calibration in the precise location of the sample scan length (typically 6 cm) throughout the temperature range of study. Conforming to ITPS standards,[9] the low-temperature calibration and operation was also confirmed by measuring the superconducting T_c (diamagnetic Meissner effect) for a series of pure superconductors (In, Pb, Nb, Hg). In all cases, the measured transition temperatures agreed with literature values[9] to better than 0.5%. During all data collection sequences, thermal equilibrium of the sample was assumed to have been obtained when temperature stability was observed to be better than 0.2% for $T < 10$ K, down to 0.02% at $T = 300$ K, for an amount of time ranging from at least 120 s ($T < 10$ K) to 1200 s ($T = 300$ K). At each temperature, the sample's magnetic moment was determined in the following manner: the sample was microstepped (0.01 mm resolution) through the double gradiometer detector (a four-loop array), allowing the SQUID response to be measured as an accurate function of voltage vs distance by conducting a series of voltage measurements (typically 60) over a predetermined scan length (typically 6 cm); each such scan resulted in a response curve from which a "machine moment" (emu) was calulated; a minimum of three such scans, or machine moments, were recorded at each temperature and field value; if the deviation between three such scans was greater than 0.01% of the average or if three such scans showed a systematic drift in the value of the moment (e.g., due to a lag in thermal equilibrium), an additional series of scans were recorded. The average value of at least three such scans was used as the observed magnetization of the sample (and the holder) at a given magnetic field; this value was subsequently corrected for the diamagnetism of the sample holder and converted to the gram susceptibility, χ_g, of the compound. The experimentally determined χ_g values were converted to *observed* molar susceptibilities, χ_M, by using a molecular weight of 491.86 g/mol. Up to this point, no other corrections of any type were employed.

Results and Discussion

The gram susceptibility of $HgCo(NCS)_4$ was measured at 293 K for several samples and found to average 16.47 (5) × 10^{-6} emu/g, a value in excellent agreement with the well-accepted, uncorrected experimental value of 16.44 (8) × 10^{-6} initially reported by Figgis.[1] In the interest of verifying data collection methods and differential sensitivity, powder data were collected from 1.7 to 300 K on three different sample preparations; sample sizes ranged from 75 to 125 mg. As in previous studies, we also observed that $HgCo(NCS)_4$ is an excellent calibrant material from the vantage point of easy sample preparation, consistent batch-to-batch characteristics and sample shelf-life. Yet, when the data were plotted against "theoretical" curves that were calculated using any of the parameters in Table I, none of the curves were particularly descriptive throughout the entire temperature range. Discrepancies were most noticeable when plotting χT or μ_{eff} against temperature. Since incorrect temperature and magnetic field measurements can easily lead to erroneous conclusions, the magnetometer's calibration and temperature control (stability) were repeatedly verified, and only then did it seem appropriate to reexamine $HgCo(NCS)_4$.

The objective was to elucidate the best magnetic description of $HgCo(NCS)_4$ and to determine why so many different parameters had been reported. We began with the hypothesis that the various "best-fit" parameters reflected an unintentional bias due to data-fitting procedures being limited to experimentally predetermined temperature ranges. Measurements in the temperature range of 1.7 to 300 K should, in principle, allow one to mimic the previous results by selecting appropriate temperature windows for data analysis. Because of the nature of a paper which describes a calibrant, we feel compelled to emphasize some details. It is important to note that the data points plotted in the graphs of χ_M, χ_M^{-1} and μ_{eff} (defined as $2.828(\chi_M T)^{1/2}$) are based on the experimentally observed molar susceptibilities for $HgCo(NCS)_4$. The data points themselves are *not* corrected for diamagnetism or temperature-independent paramagnetism (as explained below, the only exception is Figure 1). Throughout

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(9) White, G. K. *Experimental Techniques in Low Temperature Physics*; Clarendon Press: Oxford, England, 1987.

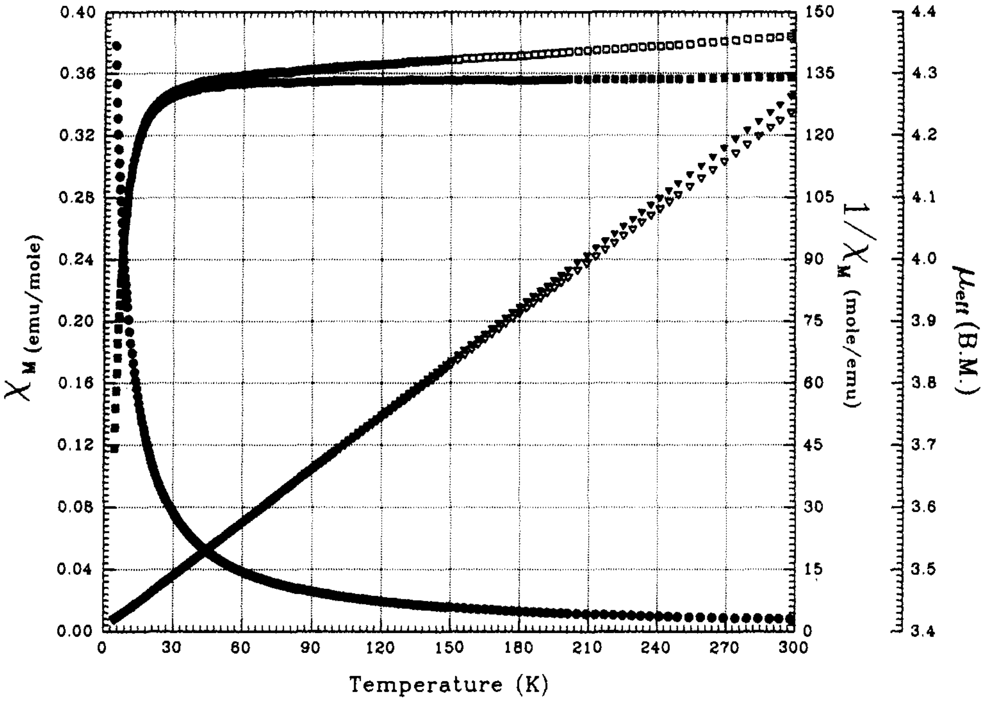

Figure 1. Uncorrected (hollow points) and corrected (filled points) molar-based magnetic data for a typical $HgCo(NCS)_4$ powder sample at 5000 Oe: χ_M (circles); χ_M^{-1} (inverted triangles); μ_{eff} (squares). The magnitude of the correction that resulted in the filled points is the total value of all of the temperature independent contributions to the magnetism, $+240 \times 10^{-6}$ emu/mol.

this paper, χ_M is the observed molar susceptibility of the compound $HgCo(NCS)_4$, χ_{Co} is the temperature-dependent paramagnetic susceptibility of the Co(II) ion, χ_{TIP} is the temperature-independent paramagnetism of the Co(II) ion, and χ_{dia} is the diamagnetic correction according to the data that have been tabulated[10] as Pascal's constants and constituent corrections. This procedure preserves that data points as *experimentally observed* values, values from which the temperature dependent calibration of a magnetic susceptibility apparatus can be readily ascertained.

Temperature-Independent Magnetism. Temperature-independent magnetism (TIM) in a material such as $HgCo(NCS)_4$ has two sources: the diamagnetism of the paired electrons in the atoms and molecules of the compound and the temperature independent paramagnetism (TIP) of metal ions such as tetrahedral Co(II) where the mixing of excited states into the ground state is facilitated by spin–orbit coupling.[11] These "corrections" are considered as part of the data analysis by the generalized molar susceptibility expression

$$\chi_M = \chi_{Co} + \chi_{TIP} + \chi_{dia} \qquad (1)$$

Since both terms are temperature-independent, the origin of any experimentally observed TIM can not be distinguished on the basis of susceptibility measurements alone, i.e., the expression in eq 1 can just as well be written as

$$\chi_M = \chi_{Co} + \chi_{TIM} \qquad (2)$$

where $\chi_{TIM} = \chi_{TIP} + \chi_{dia}$. For the diamagnetic correction, it should be obvious from Table I that different values are often calculated for the same material. *In the case of high-temperature data (>100 K) or paramagnetically dilute compounds, it is important that one report the value used.* We calculate the molar diamagnetic correction for $HgCo(NCS)_4$ to be -190×10^{-6}. This value is in agreement with Hatfield and Bunzli.

The TIP in a compound such as $HgCo(NCS)_4$ will be reflected in a χ_{TIM} fitting parameter that is statistically different from that of the diamagnetic correction; i.e., χ_{TIM} should correspond to the sum $\chi_{TIP} + \chi_{dia}$. The experimental data for a representative powder sample of $HgCo(NCS)_4$ are plotted in Figure 1. The two sets of data points correspond to the two ways in which one can plot magnetic data: "corrected" and "uncorrected" for TIM. The hollow data points represent the experimentally observed molar data without having applied any TIM corrections; as mentioned above, it is these "uncorrected" data which are also plotted in the other figures. To obtain the data represented by the filled symbols, an additive molar TIM correction was allowed to vary until μ_{eff} became independent of temperature for temperatures greater than 100 K (thereby reflecting the effective magnetic moment of a Curie paramagnet). The value of χ_{TIM} which yielded the filled symbols in such a manner was $+240 \times 10^{-6}$ emu/mol. Using a diamagnetic correction of -190×10^{-6} emu/mol, the experimentally determined TIP value for the Co(II) ion in $HgCo(NCS)_4$ can be readily calculated to be $+430 \times 10^{-6}$ emu/mol. This is identical to the value which was spectroscopically determined (Table I) by Cotton.[3] Note that the magnitude of the TIP is 5.7% of the observed molar susceptibility at 293 K.

Curie–Weiss Analysis. After establishing that the proper value of the TIM term is $+240 \times 10^{-6}$ emu/mol the temperature-dependent χ_{Co} can be fit to a number of theoretical expressions. The first of these is the so-called Curie–Weiss law which can be written as

$$\chi_{Co} = C/(T - \Theta) \qquad (3)$$

where the Curie constant, C, can be used to calculate an electronic g value according to

$$C = N_A\beta^2 g^2/3k_B \cdot S(S + 1) \qquad (4)$$

in which all symbols have their usual meaning. χ_{Co} corresponds to the filled data points (corrected molar susceptibilities) in Figure 1. It should be obvious that if TIM were not properly accounted

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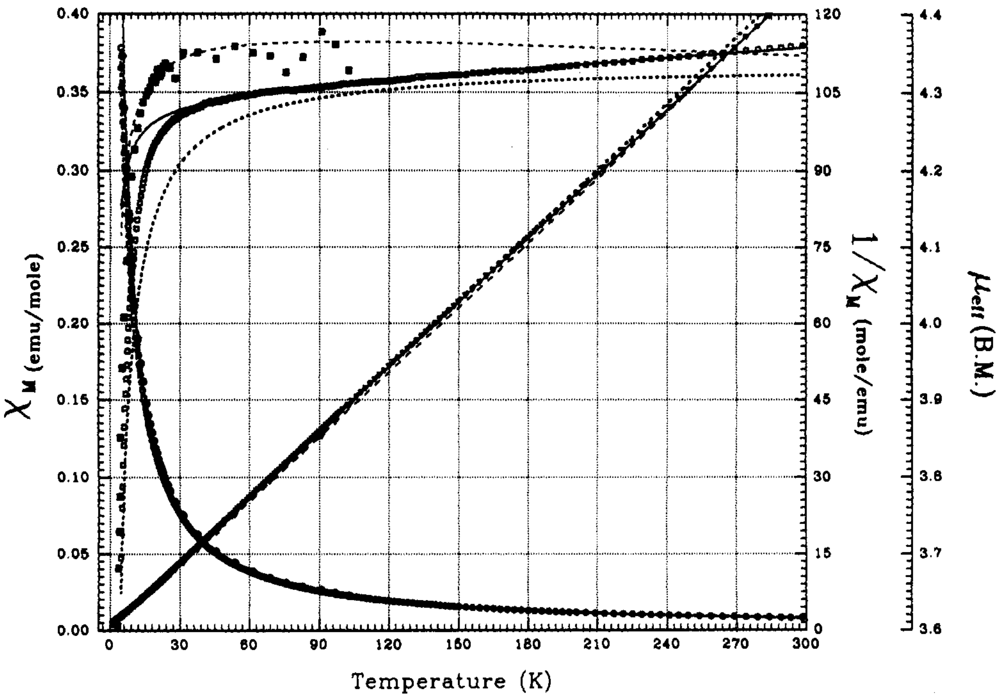

Figure 2. Uncorrected data of Figure 1 are again plotted as hollow points: χ_M (circles); χ_M^{-1} (inverted triangles); μ_{eff} (squares). The solid points correspond to the uncorrected data as tabulated in ref 6. All curves are calculated using the appropriate Curie–Weiss parameters and TIM values listed in Table 1: (—) this work; (- - -) ref 5; and (– –) ref 6.

for as part of the data analysis, the Curie constant and the Weiss temperature would be profoundly and incorrectly influenced; they are equivalent to the slope and x intercept of the χ_{Co}^{-1} vs T plot, *not* the plot of χ_M^{-1} vs T (as we have defined χ_M). *For a compound such as $HgCo(NSC)_4$ where the TIP is quite large, applying diamagnetic corrections (opposite in sign) without simultaneously applying TIP corrections results in a greater error than if no corrections were made at all.* For these reasons, our results (Table I) for the Curie constant are in better agreement with the parameters of Hatfield than any others.

The validity of the Curie–Weiss expression is bound by a minimum temperature because the Weiss constant can only approximate so much "correction" for phenomena such as zero-field splittings and magnetic exchange interactions. Nonlinear curve fitting procedures in temperature regions which are bound by progressively lower minimum temperatures will establish such a value. As shown in Figure 2, the Curie–Weiss law can accommodate the $HgCo(NCS)_4$ data down to approximately 40 K; best-fit parameters are C = 2.305, Θ = −0.32 K and χ_{TIM} = +235 × 10^{-6} emu/mol. Note that χ_{TIM} was not held constant; it was allowed to function as a fitting parameter and its best-fit value is in excellent agreement with the value determined above. In contrast, when the minimum temperature was extended to values below 40 K, the quality of the fit progressively decayed and the best-fit parameters defined curves which were not at all good representations of the data. *Curie–Weiss parameters determined in such a manner are not valid if the objective is to define a parametric equation for a material which is intended to be used as a calibrant.* Using our best-fit parameters, the typical agreement between experimental and calculated values is better than 0.02% for temperatures greater than 40 K. From the relationship in eq 4, the average electronic g value can be calculated to be 2.218, a reasonable value for Co(II).

Also plotted in Figures 2 and 3 are the SQUID-based data tabulated in ref 6 by O'Connor. The curves are based on the recommended Curie–Weiss parameters (Table I). The third set of curves are calculated according to Hatfield's Curie–Weiss parameters. Since their corresponding data were not tabulated, it is presumed that the curves approximate the data in the range 1.7–50 K. Since our data are in-between the limits of these two data sets, and since our best fit Curie–Weiss parameters describe the powder data to better than 0.02% for all temperatures greater than 40 K, we recommend these new values be considered the Curie–Weiss parameters of $HgCo(NCS)_4$.

Zero-Field Splitting and Exchange Interactions. The crystal structure of $HgCo(NCS)_4$ has been previously determined and the environment of the Co(II) is that of an axially distorted tetrahedron.[8] The ^4A ground state can therefore exhibit a zero-field splitting which arises as a second-order effect from spin-orbit coupling and can be described by the Hamiltonian

$$H = D\left[S_z^2 = \frac{1}{3}S(S + 1)\right] + g\beta\mathbf{H}\cdot S \qquad (5)$$

where $S = {}^3/_2$ and D corresponds to the energy separation between the two resulting doublets, $|\pm1/2\rangle$ and $|\pm3/2\rangle$. When D is positive in sign, the $|\pm1/2\rangle$ doublet lies lowest in energy; for negative D, the ground state corresponds to the $|\pm3/2\rangle$ doublet. O'Connor and Hatfield both recognized that the magnetic susceptibility expressions originally reported by Figgis[12] were incorrect. The correct expressions for the susceptibilities parallel and perpendicular to the axial crystal field distortion can be obtained by direct application of the Van Vleck expression.[11] Following the formalism of Hatfield, the correct expressions are

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4k_BT}\left[\frac{\frac{\sinh(y/2)}{y/2} + 9e^{-x}\frac{\sinh(3y/2)}{3y/2}}{\cosh(y/2) + e^{-x}\cosh(3y/2)}\right] \qquad (6)$$

and

$$\chi_{\perp} = \frac{Ng^2\beta^2}{k_BT}\left[\frac{\frac{\sinh(y)}{y} + \frac{3}{2x}\cosh(y)\,e^{z} - \frac{3}{2x}e^{-z}e^{-x}}{e^{z}\cosh(y) + e^{-z}e^{-x}}\right] \qquad (7)$$

where $x = D/kT$, $y = g\beta H/kT$ and $z = 2x/3y$. The powder susceptibility is then given by

$$\chi_{Co} = (\chi_{\parallel} + 2\chi_{\perp})/3 \qquad (8)$$

which demonstrates that isofield powder measurements will give

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(12) Figgis, B. N. *Trans. Faraday Soc.* **1960**, *56*, 1553.

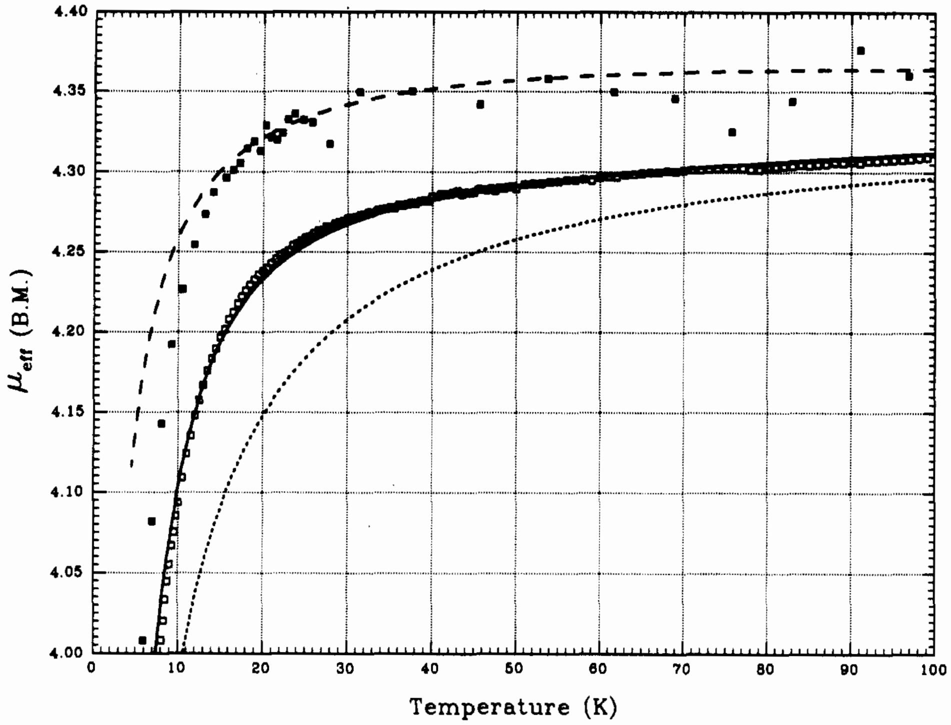

Figure 3. Expanded plot of the powder data in terms of uncorrected μ_{eff} (squares). As in Figure 2, the data tabulated in ref 6 are plotted as solid points. Note that in the analysis of their data, the authors only employed the data in the temperature interval 20–100 K. Curves calculated using the Curie–Weiss parameters and TIM values listed in Table 1 are for reference 5 (- - -) and reference 6 (– –); the curve corresponding to this work (—) is calculated according to the parameters $g = 2.220$, $D = +10.6$ cm^{-1}, $zJ = -0.095$ cm^{-1} and $\chi_{TIP} = +410 \times 10^{-6}$ emu/mol.

the magnitude of D but not the sign (or the ground state). The sign of D can only be determined by field dependent studies or single crystal orientation studies.

When the proper substitutions are carried out and eq 8 is substituted into eq 2, the best-fit of the χ_M expression to the powder data is obtained for the parameters $g = 2.220$, $D = +10.6$ cm^{-1}, and $\chi_{TIP} = +410 \times 10^{-6}$ emu/mol. Note that the g value and the χ_{TIP} value were both allowed to be fitting parameters and that the best-fit values are consistent with the best-fit values obtained from the Curie–Weiss analysis above. Hatfield estimated the zero-field parameter $D = +19$ (3) cm^{-1} on the basis of magnetization measurements, but they also noted that their fit was not excellent and that the main conclusion was that the sign of D was clearly positive. O'Connor made no attempt to quantify D, and Figgis estimated the magnitude of D to be 10 cm^{-1}. Using our best-fit parameters, the calculated curve is an excellent fit above 10 K where the typical percent difference between experimental and calculated is better that 0.05% (and again, no single error is greater than 0.02% for temperatures above 40 K). Below 8 K, the average deviation between experimental and calculated values increases too rapidly for zero-field splitting alone to be responsible for the deviation from Curie–Weiss magnetism. The observation that μ_{eff} decreases more rapidly than that predicted suggests that a plausible explanation is antiferromagnetic exchange interactions between the Co(II) ions.

The $HgCo(NCS)_4$ lattice is tetragonal and is the result of a unique combination of two tetrahedrally coordinated atoms, Hg(II) and Co(II). They are alternately interlinked by a network bonding arrangement in which the Hg(II) and Co(II) atoms are held apart by four spirals, each spiral containing four NCS^- bridges, and each NCS^- bridge belonging to eight such spirals. Each Co(II) ion is bridged by four NCS^- groups to four different Hg(II) ions, with each of those Hg(II) ions being bridged to three other Co(II) ions. Such a magnetic lattice geometry is complex and no specific theoretical models are available. Since the exchange interaction is clearly quite small compared to the zero-field splitting, a reasonable approach is to apply a molecular field correction[13] as defined by

$$\chi_M = \chi_{Co}/[1 - (2zJ\chi_{Co}/N\beta^2 g^2)] \qquad (9)$$

where χ_M is now a function of the isolated single-ion magnetism, and the numbers z (number of nearest neighbors) and J (exchange interaction) are taken together as a single fitting parameter, zJ. The low-temperature fit improved substantially, yielding best-fit parameters $g = 2.220$, $D = +10.6$ cm^{-1}, $zJ = -0.095$ cm^{-1}, and $\chi_{TIP} - +410 \times 10^{-6}$ emu/mol. The curve calculated with these parameters is shown in Figure 3. Care should be taken to note the expanded scale of the y axis.

The sign of D is established by examining single-crystal susceptibility data. Single-crystal measurements were repeated on two separate crystals by orienting the axis of tetragonal distortion (collinear with the crystal c axis) parallel and perpendicular to the magnetic field. The susceptibility measured with the magnetic field parallel to the axis of distortion is shown in Figure 4; the magnetic field perpendicular to the axis of distortion (either the a- or b-axes) is shown in Figure 5. Data were collected up to 300 K, but are only displayed up to 50 K because at higher temperatures the data are equally well described by Curie–Weiss magnetism. The curves in Figures 4 and 5 are calculated and drawn according to the best-fit parameters $g(\|) = 2.168$, $D = +10.2$ cm^{-1}, and $zJ = 0.00$ cm^{-1} (eq 6) and $g(\perp) = 2.251$, $D = +10.8$ cm^{-1}, and $zJ = -0.19$ cm^{-1} (eq 7). The quality of the fits is excellent for both orientations and in all three manners of plotting magnetic data. The sign of D is unequivocably positive.

Figure 4 clearly demonstrates that the magnetic moment approaches the low temperature value of 1.8 μ_B in the parallel direction. This is expected for a positive D, i.e. an effective $S = {}^1/_2$ ion. Similarly, the slope of the line in the reciprocal susceptibility plot clearly switches from that of an $S = {}^3/_2$ ion ($T > 20$ K) to the steeper slope of an $S = {}^1/_2$ ion ($T < 5$ K). In Figure 5 it is readily observed that effective magnetic moment

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[13] Smart, J. S. *Effective Field Theories of Magnetism*; Saunders: Philadelphia, PA, 1966.

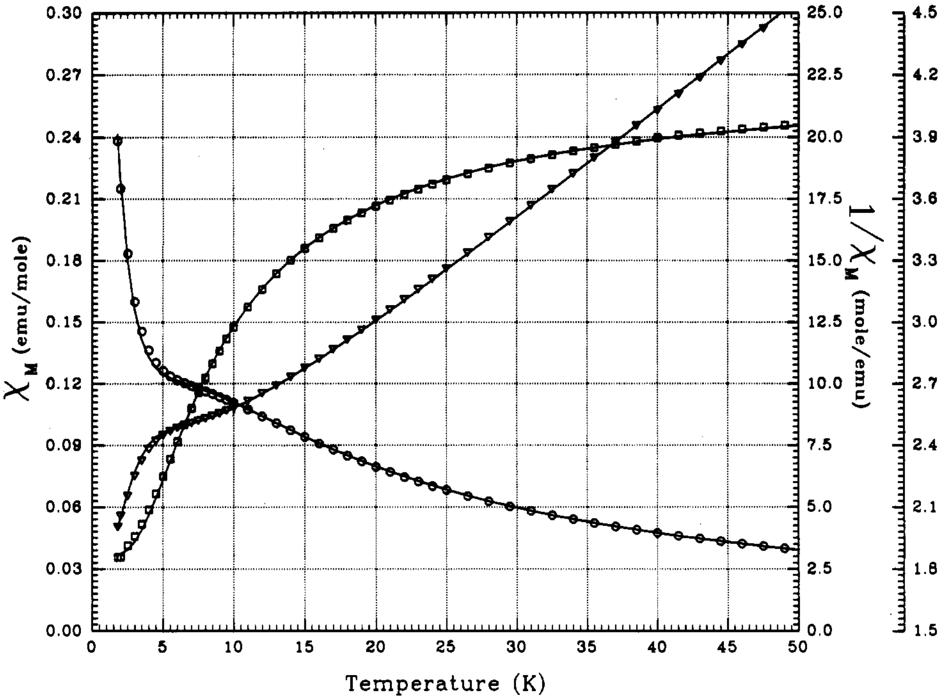

Figure 4. Magnetic data for $HgCo(NCS)_4$ when the magnetic field is parallel to the axis of tetragonal distortion in the Co(II) tetrahedron: χ_M (circles); χ_M^{-1} (inverted triangles); μ_{eff} (squares). Curves are drawn using $g = 2.168$, $D = +10.2\ cm^{-1}$, and $zJ = 0.0\ cm^{-1}$.

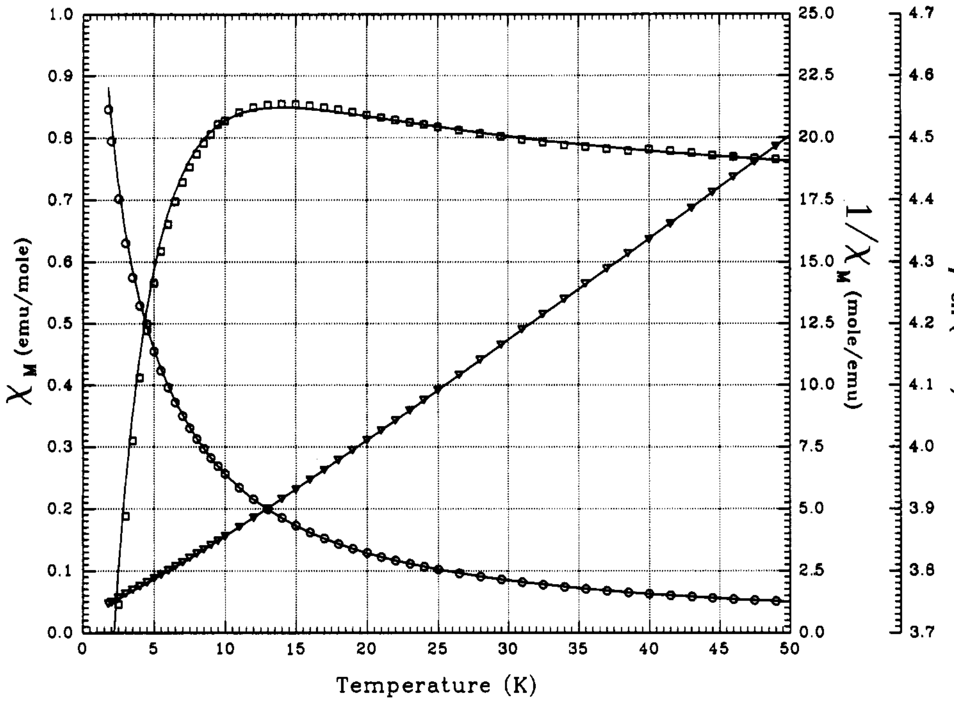

Figure 5. Magnetic data for $HgCo(NCS)_4$ when the magnetic field is perpendicular to the axis of tetragonal distortion in the Co(II) tetrahedron: χ_M (circles); χ_M^{-1} (inverted triangles); μ_{eff} (squares); curves are drawn using $g = 2.251$, $D = +10.8\ cm^{-1}$, and $zJ = -0.19\ cm^{-1}$.

exhibits a maximum at approximately 14.5 K, in excellent agreement with the best-fit value of D. Finally, the positive D value results in reciprocal susceptibility plots which would correctly yield negative (Figure 4) and positive (Figure 5) Θ values, should Curie–Weiss extrapolations be done from higher temperature ($T > 40$).

These results provide the first-ever complete picture of the magnetic properties of $HgCo(NCS)_4$. The slightly anisotropic g values are not uncommon[14] for tetrahedral Co(II), and their average values are in excellent agreement with the powder-based values obtained from both the Curie–Weiss and the zero-field splitting models. Although the best fit D values should nearly be identical, the values $+10.2$ and $+10.8\ cm^{-1}$ are interchangeable in terms of representing the data and are in excellent agreement with the magnitude of the D value obtained from the analysis of the powder data, $10.6\ cm^{-1}$.

The direction perpendicular to the axial distortion is the one for which a zJ is required; without it, a proper fit simply could not be obtained at the lower temperatures. The perpendicular direction also exhibits a D value which is closer in magnitude to that obtained from the analysis of the powder data. Similarly, the zJ value is larger than that found in the powder analysis. For

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[14] Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Oxford University Press: Oxford, England, 1970.

the parallel direction, the zJ parameter consistently tended towards zero; it simply was not required to explain the data and was in fact rejected when attempts were made to include it in the best-fit. These results confirm that the ground state of the Co(II) ion in $HgCo(NCS)_4$ is the $|\pm 1/2\rangle$ doublet and that as an effective $S = {}^1/_2$ ion, the Co(II) ions are most likely antiferromagnetically exchange coupled through NCS–Hg–SCN bridges to eight possible nearest neighbors.

The Co(II) ions are exchange coupled in such a manner that the susceptibility measured in the plane normal to the axis of distortion reflects the main deviation with respect to single-ion magnetism. This is not surprising since the structure of $HgCo(NCS)_4$ exhibits a significant amount of lattice anisotropy. Although its structure does not lend itself to being classified as any specific type of low-dimensional lattice (chains or layers), the NCS–Hg–NCS exchange pathways can be observed to preferentially propagate the lattice within the *ab* plane, producing a quadratic-like layer. Since the layers are linked together at the Hg(II) ions, the strength of the interlayer interactions could in principle be comparable to the intralayer interactions resulting in a lattice which is of mixed dimensionality. What is clear, is that because of the bimetallic tetrahedral lattice, there are two types of nearest neighbor exchange paths for each Co(II) ion. It is the relative sizes of these exchange interactions which will ultimately determine the dimensionality of the magnetic lattice.

The spin dimensionality (spin anisotropy) that results from large zero-field splittings in Co(II) provides for one of the most convenient methods of exploring *XY* and Ising magnetic models; be they chains, layers or other novel network lattices. In the case of positive D, the $|\pm 1/2\rangle$ ground state leads to *XY*-like behavior instead of Ising behavior because the effective g value in the perpendicular direction is twice the real g and therefore larger than the parallel value.[15] What makes $HgCo(NCS)_4$ interesting in this respect, is that experimental examples of *XY* models (for any type of lattice dimensionality) continue to be relatively rare. In addition, the analyses of the data demonstrate quite clearly that the exchange energies are much less than the zero-field splitting—a desirable situation if a compound is to be of further utility for studies concerning *XY* magnetic model systems. A particularly interesting experiment would be to determine whether $HgCo(NCS)_4$ undergoes a transition to long-range order or whether the remaining entropy is further removed through short-range ordering. In this respect, lower temperature ($T < 1.7$ K) magnetic studies and specific heat measurements could be of additional use in correlating the structural lattice to the magnetic behavior.

Conclusions

The magnetic behavior of $HgCo(NCS)_4$ in the temperature range 1.7–300 K is described by the equation $\chi_M = \chi_{Co} + \chi_{TIP} + \chi_{dia}$. χ_{dia} can be calculated from Pascal's constants to be -190×10^{-6} emu/mol. χ_{TIP} can be taken from spectroscopic parameters to be $+428 \times 10^{-6}$, a value which is in agreement with our static measurement. χ_{Co} represents the temperature-dependent paramagnetism of the Co(II) ion and it should be calculated at low temperatures ($T < 40$ K) according to a model which accomodates zero-field splitting and spin–spin exchange interactions (eqs 6 through 9). Above 40 K, the Curie–Weiss law is better than 0.02% when using the parameters $C = 2.305$ ($g = 2.218$) and $\Theta = -0.32$ K. Since the $HgCo(NCS)_4$ structure presents a novel lattice arrangement of two tetrahedral atoms with a bidentate three atom bridge, more may be learned about XY magnetic model systems by studying $HgCo(NCS)_4$ at lower temperatures. Other interesting bimetallic magnetic lattices may also be possible by replacing the Hg(II) with other magnetic ions. Experiments along these lines are in progress and indicate some new areas of research.

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(15) Carlin, R. L. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; D. Reidel Publishing: Dordrecht, The Netherlands, 1985.