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Single-Crystal Magnetic Properties of Sodium Bis(carbonato)cuprate(II): A Three-Dimensional Antiferromagnet

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Magnetic measurements on crystals of the layer compound sodium bis(carbonato)cuprate(II) have confirmed that the material orders antiferromagnetically at 5.6 K with the spins aligned along the crystallographic *a* axis. The copper ions within each layer are coupled ferromagnetically with an exchange coupling constant of 4.1 cm^{-1}. The antiferromagnetic interlayer exchange field is calculated to be 0.65 T, and the ratio of the interlayer to intralayer exchange constants is estimated to be ~0.076.

Introduction

Materials with strictly chain or layered structures are interesting because no cooperative ordering can be sustained in one or two dimensions.[1] However examples of magnetically ordered compounds with just these structural characteristics are quite common because the anisotropy field and/or interchain or interlayer interaction is said to trigger order in three dimensions. Compounds of copper are well suited to studies in this area because none of the complications of $S > {}^1/_2$ are present. Particular systems relevant to the present study are the layered materials K_2CuF_4,[2] which possesses two-dimensional ferromagnetic intralayer interactions as well as ferromagnetic interlayer interactions, and the $[CuCl_4]^{2-}$ derivatives[3,4] where layers of ferromagnetically coupled copper atoms can be coupled ferromagnetically or antiferromagnetically. For those which form three-dimensional antiferromagnets the interlayer coupling energy is often quite small. Further, the anisotropy field in these copper compounds can also be quite small so the spin–flop field can be exceeded by rather smaller applied magnetic fields than is otherwise possible in normal three-dimensional antiferromagnets.[3]

Many different compounds can be isolated from aqueous solutions containing the copper(II) and carbonate ions, depending on the conditions and the other cations present. For example $Na_2Cu(CO_3)_2{\cdot}3H_2O$ has a discrete chainlike structure,[5] and $Cu(NH_3)_2CO_3$ possesses a complicated intertwined chain structure[6] whereas $K_2Cu(CO_3)_2$ has a three-dimensional structure of bridging carbonate groups.[7] $Na_2Cu(CO_3)_2$ is best described[8] (Figure 1) as a two-dimensional polymeric network of $[Cu(CO_3)_2{}^{2-}]_\infty$ with each copper in an approximately square-planar environment coordinated by four symmetry-related binuclear bridging carbonate groups. Successive layers of $[Cu(CO_3)_2{}^{2-}]_\infty$ are bound ionically by the sodium ions.

Average susceptibility measurements on $Na_2Cu(CO_3)_2$ as a function of temperature and applied magnetic field[9] suggested the presence of ferromagnetic intralayer exchange with a weak antiferromagnetic interlayer coupling. The field dependence of the average susceptibility below the transition temperature indicated that spin–flop behavior was being observed in applied magnetic fields greater than ~10 mT. These observations were important for two reasons. First, the ferromagnetic interaction is unusual and is, as far as is known, the first example of a bridging carbonate sustaining a ferromagnetic coupling between paramagnetic centers. Second, $Na_2Cu(CO_3)_2$ provides another example of the few well-characterized layered materials where the antiferromagnetic interlayer interactions are weak enough for the spin–flop field to be studied in low and easily accessible applied magnetic fields. Single-crystal measurements reported here now confirm that $Na_2Cu(CO_3)_2$ is a three-dimensional antiferomagnet below 5.6 K.

Experimental Section

Crystals of $Na_2Cu(CO_3)_2$ large enough for the magnetic measurements were difficult to prepare although a variation of the method used by Healy and White[8] was eventually successful. The hydrated salt $Na_2Cu(CO_3)_2{\cdot}3H_2O$ was prepared, dissolved in an aqueous sodium carbonate/bicarbonate solution, and refluxed gently at 70 °C. A few suitable crystals (2 × 1 × 1 mm) formed after about 1 week. The royal blue elongated crystals are monoclinic and were identified by using X-rays. The axes were defined according to ref 8: $a = 6.18$ Å, $b = 8.19$ Å, $c = 5.64$ Å, and $\beta = 116.2°$, in the space group $P2_1/a$.

The magnetization data on two different crystals were collected by using the SQUID susceptometer described recently.[10] For these crystal measurements the quartz sample tube used for powders was replaced with a quartz rod ground with vertical and horizontal faces, so allowing easy crystal alignment. No corrections for demagnetizing effects were made as they were found to be insignificant for each of the crystalline susceptibilities around the critical temperature. No corrections for the diamagnetism of the substituent atoms were made either; below 70 K they are negligible. Unfortunately our SQUID only operates to an applied magnetic field of ~0.35 T, so no high-field magnetization measurements could be performed.

The EPR spectra were obtained from a Varian E-3 X-band spectrometer. The free radical DPPH ($g = 2.0036$) was used as a field marker.

Results and Discussion

Previous work on the average powder susceptibility ($\bar{\chi}$)[9] of $Na_2Cu(CO_3)_2$ had shown that the Curie–Weiss expression $\bar{\chi} = C/(T - \Theta)$, where $C = Ng^2\beta^2/4k$ with $\Theta = +9.2$ K and $g = 2.23$, represented the data above 15 K quite well. The positive value of Θ confirmed the presence of ferromagnetic interactions. Further, the data between 15 and 70 K could be fitted to the 11-term series expansion for a two-dimensional Heisenberg system[11] with $J = 4.1$ cm^{-1} and $g = 2.24$. Below 5.6 K and in the lowest applied magnetic field (1.7 mT), $\bar{\chi}$ extrapolated to $\sim{}^2/_3\chi_{max}(T_c)$ at $T = 0$. This is the behavior expected for a three-dimensional antiferromagnet. However in applied fields of between 10 mT and 0.1 T $\bar{\chi}$ was field dependent and rose with H until $\bar{\chi} \simeq \chi_{max}(T_c)$ in 0.1 T. This suggested that a spin–flop transition had taken place.

The present single-crystal measurements were performed along the a^*, b, and c axes of the monoclinic crystal in 0.2227 T and 2.22 mT (Figures 2–4). The susceptibility along each

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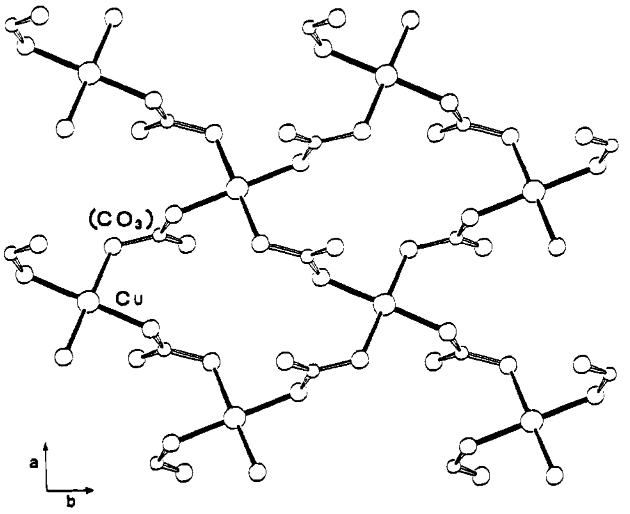

Figure 1. Unit cell of $Na_2Cu(CO_3)_2$ viewed perpendicular to the *ab* plane.

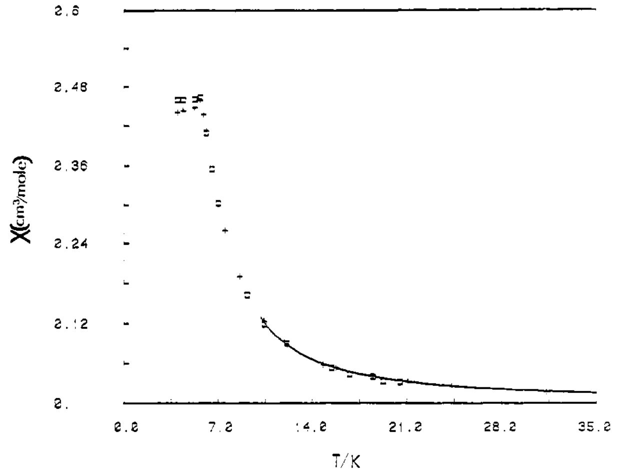

Figure 2. Magnetic susceptibilities along the *b* axis of $Na_2Cu(CO_3)_2$ in two different applied magnetic fields: □, 0.2227 T; +, 2.23 mT. The solid line represents the best fit to the Baker series expansion for $kT/J > 1.67$.

direction passes through a transition at 5.6 K. Above the critical temperature each susceptibility is nearly independent of the applied magnetic field and was fitted to the Baker series expansion[11] by using a nonlinear least-squares computer program. In each case $J = 4.1\ \mathrm{cm}^{-1}$ with $g_{a^*} = g_b = 2.045$ and $g_c = 2.25$. These derived *g* values are very similar to the experimental values described below and are compatible with the structure; i.e. the layers of $[Cu(CO_3)_2{}^{2-}]$ lie nearly parallel to the *a*b* plane, and so this plane is expected to be nearly magnetically isotropic.

Below 5.6 K the three susceptibilities behave differently. χ_b (Figure 2) in both 0.2227 T and 2.22 mT is relatively constant, i.e., independent of the applied magnetic field. This direction must then be $\chi_\perp$ of the antiferromagnetically ordered state, i.e., perpendicular to the spin direction. Therefore $\chi_\parallel$ of the antiferromagnetically ordered state must lie in the *ac* plane. The data in Figure 4 show clearly that in the lower field χ_{a^*} drops rapidly toward zero, and so $\chi_\parallel$ must lie along or near this direction. The susceptibility along the crystallographic *c* direction in 2.23 mT (Figure 3) drops rather more with decreasing temperature than would be expected if $\chi_\perp$ lay in the *bc* plane. However in this monoclinic cell $\beta = 116.2°$, and so $\chi_\perp$ probably lies in the *bc** plane. This was confirmed by making several measurements along the *c** direction where χ_{c^*} was found to be nearly constant below 5.6 K and of a magnitude at 5.6 K equal to that expected with use of g_{c^*}.

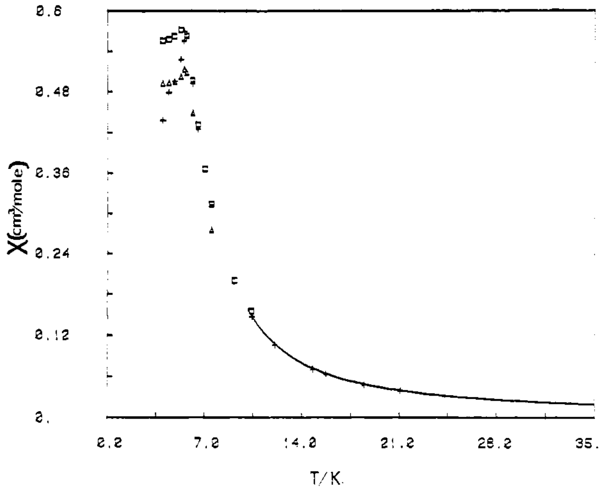

Figure 3. Magnetic susceptibilities along the *c* and *c** axes of $Na_2Cu(CO_3)_2$ in different applied magnetic fields. *c* axis: □, 0.2227 T; +, 2.23 mT. *c** axis: △, 3.2 mT. The solid line represents the best fit to the Baker series expansion for $kT/J > 1.67$.

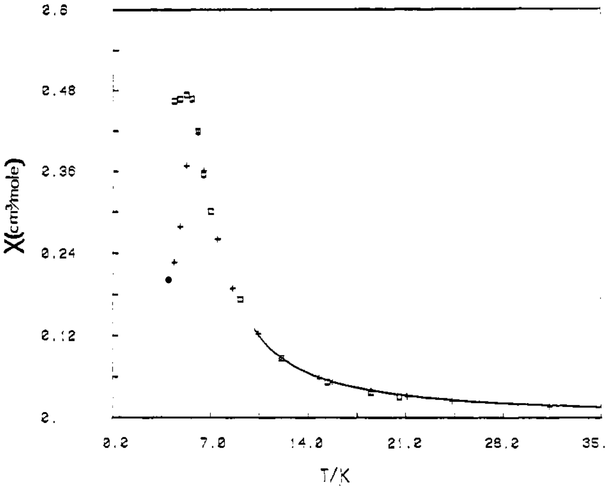

Figure 4. Magnetic susceptibility along the *a** axis of $Na_2Cu(CO_3)_2$ in two different applied magnetic fields: □, 0.2227 T; +, 2.23 mT. The solid line represents the best fit to the Baker series expansion for $kT/J > 1.67$.

Thus $\chi_\parallel$, and so the preferred spin direction, actually lies perpendicular to the *bc** plane and so parallel to the crystallographic *a* axis.

The EPR spectrum of a crystal of $Na_2Cu(CO_3)_2$ was recorded at X band at room temperature. Two rotations were made. In the *a*b* plane the *g* value was, within experimental error, isotropic and equal to 2.04. This corresponds to the intralayer *g* value. In the *bc* plane the minimum and maximum *g* values were 2.04 (g_b) and 2.27 (g_c), g_b corresponding to the isotropic intralayer *g* value and g_c the *g* value perpendicular to the layer. It was also easy to show experimentally that $\chi_\parallel$ of the antiferromagnetically ordered state is associated with one of the smaller intralayer *g* values at and above the critical temperature because one of the two *smaller* susceptibilities (χ_{a^*}) above T_c becomes $\chi_\parallel$ below T_c (on the assumption that $\chi_a \simeq \chi_{a^*}$). This has important implications in determining the reason for the spin direction (see below).

The new single-crystal susceptibility and EPR data now allow a more precise determination of some of the exchange and anisotropy fields.[9] The effective intralayer exchange field can be calculated from expression 1. Using the magnetic

$$H_e = 2zJS/g\beta \qquad (1)$$

parameters derived above the $z = 4$, we find that the intralayer

Table I. Exchange Parameters for Some Quasi-Two-Dimensional Heisenberg Ferromagnets[a]

	T_c, K	J, K	kT_c/J	$R = J'/J$	d_1, Å	d_2, Å
$Na_2Cu(CO_3)_2$	5.6	5.9	0.95	-7.6×10^{-2}	4.89	5.64
$Rb_2CuCl_2Br_2$	17.2	16.3	1.06	-2.6×10^{-2}	5.130	8.9
K_2CuF_4	6.28	11.2	0.561	$+2.1 \times 10^{-4}$	4.155	6.98
$(C_2H_5NH_3)_2$-$CuCl_4$	10.20	18.6	0.548	-8×10^{-4}	5.240	11.21
$(C_{10}H_{21}NH_3)_2$-$CuCl_4$	7.92	17.9	0.442	-3×10^{-6}	5.239	25.78

[a] The intra- and interlayer interactions are denoted by J and J', respectively. d_1 and d_2 are the intra- and interlayer copper–copper distances, respectively.

exchange field is 17.2 T. The interlayer exchange field, H_{af}, for these antiferromagnetically coupled layer-type materials can be estimated from the value of $\chi_\perp$ at the critical temperature[3] (eq 2). H_A is the anisotropy field and for copper

$$\chi_\perp(T_c) = Ng\beta S/(2H_{af} + H_A) \qquad (2)$$

compounds is expected to be small. With $\chi_\perp(T_c) = \chi_b(T_c) = 0.44$ cm^3 mol^{-1} and $g_b = 2.04$ we find that $2H_{af} + H_A = 1.3$ T, and so $H_{af} \simeq 0.65$ T. We have observed previously from the applied magnetic field dependent nature of $\bar{\chi}$[9] that the spin–flop field must be 10.0 mT $< H_{SF} <$ 0.1 T. This quantity is given by eq 3. When this is solved simultaneously with $2H_{af}$

$$H_{SF} = (2H_{af}H_A - H_A{}^2)^{1/2} \qquad (3)$$

$+ H_A = 1.3$ T, limiting values of 0.650 and 0.646 T are obtained for H_{af}, and 0.1 and 7.8 mT are obtained for H_A when H_{SF} = 10.0 mT and 0.1 T, respectively. Average values for H_{af} and H_A would then be 0.648 T and ~4 mT, respectively. The ratio of the effective interlayer to intralayer exchange constants ($H_{af}/H_e = 0.038$ and so $|J'|/|J| = 0.076$ with $z' = 2$) is much larger than for other layered compounds of this type (see Table I). This reflects the much shorter interlayer interaction in $Na_2Cu(CO_3)_2$ (5.64 Å) than is observed in the layered $[CuCl_4]^{2-}$ derivatives. The critical field needed for the transition from the flopped to the paramagnetic phases (H_c) is given by eq 4. Unfortunately the 1–1.3 T predicted

$$H_c = 2H_e - H_A \qquad (4)$$

for H_c is well outside our experimental range of applied magnetic fields. Also it is known that these critical fields are temperature dependent, so precise values as $T \rightarrow 0$ K will have to await detailed single-crystal magnetization experiments as a function of temperature and applied magnetic field.

One of the current interests in cooperative phenomena is how the real lattice and spin dimensionality influence the behavior around the critical temperature. De Jongh[12] has shown how both these quantities depend on the value of R, the ratio of the interlayer to intralayer coupling. We have already seen that R is much larger in $Na_2Cu(CO_3)_2$ than it is in most of the structurally related two-dimensional $[CuCl_4]^{2-}$ derivatives, and this is best illustrated in a $\chi T/C$ vs. kT/J plot, shown in Figure 5. De Jongh[12] has shown that for very weak interlayer interactions, i.e., as near an ideal two-dimensional ferromagnet as possible, as for example in $(C_{10}H_{21}NH_3)_2CuCl_4$ where $R = -3 \times 10^{-6}$, the 11-term Baker series expansion works well down to kT/J values approaching 1.0. In fact for compounds with $R < 10^{-3}$ the experimental data lie on a smooth curve which extrapolates to kT/J values even lower than this. However as the interlayer coupling becomes stronger, deviations occur at larger values of kT/J, upward for ferromagnetic and downward for antiferromagnetic interlayer interactions. For example in $(C_2H_5NH_3)_2CuCl_4$ where $R = -8 \times 10^{-4}$ there is a peak in the $\chi T/C$ vs. kT/J plot at

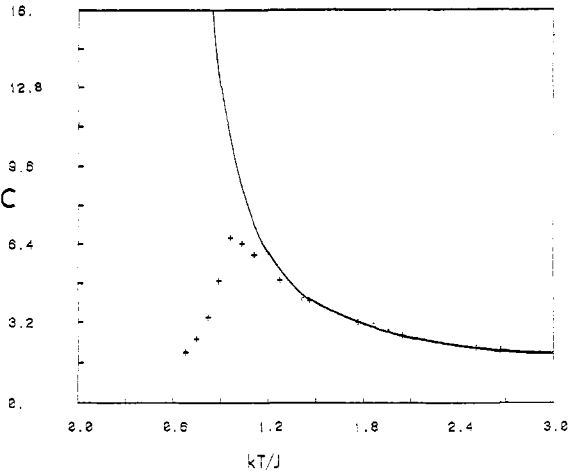

Figure 5. Near zero-field susceptibility behavior of $Na_2Cu(CO_3)_2$: + is the experimental data along the a^* axis; the curve is the best fit to the Baker series expansion for $kT/J > 1.67$.

$kT/J \simeq 0.55$. This is obviously a less ideal two-dimensional planar ferromagnet than the C_{10} derivative where no maximum nor deviations are seen down to a kT/C of 0.4. $Na_2Cu(CO_3)_2$ is an even worse example because deviations from the ideal curve in Figure 5 begin at $kT/J \simeq 1.5$ with a maximum near $kT/J = 1.0$. This illustrates in a quantitative manner the effect of a much larger interlayer coupling resulting from the smaller interlayer separation.

Most of the layered materials studied so far order with the spins lying parallel to the layer. The spin direction is determined by a combination of anisotropy fields which depend on the g values, dipolar interactions, anisotropy in the exchange interaction, etc. In each of the layered $[CuCl_4]^{2-}$ derivatives studied in detail so far, the spin direction lies in the plane parallel to the largest crystalline g value. However the structure of these materials is such that the layer actually contains the largest and smallest molecular g values, $g_\parallel$ and $g_\perp$, respectively, so the in-plane crystalline g value $[(g_\parallel + g_\perp)/2]$ is larger than the crystalline g value perpendicular to this ($g_\perp$) and so the spins are expected to lie in the plane. In $Na_2Cu(CO_3)_2$ the situation appears to be different because, although the spins lie in the plane of the layer, the largest molecular and crystalline g value ($g_\parallel$) lies at right angles to this, being a consequence of the simpler molecular structure of $Na_2Cu(CO_3)_2$. There is no doubt about this because as mentioned above it is easy to show experimentally that $\chi_\parallel$ is associated with the smaller of the two g values. With the smaller interlayer separation in $Na_2Cu(CO_3)_2$ the dipole–dipole interactions are probably responsible for this unusual spin configuration.

The closest approach of the intralayer copper atoms is 4.89 Å, so no significant direct overlap of the metal ion d orbitals is expected. Superexchange via the intervening binuclear carbonate group must be responsible for the observed interaction and so appears to be the first well-documented case of ferromagnetic coupling by a bridging carbonate group. There are potentially two superexchange pathways connecting the unpaired electrons in the $d_{x^2-y^2}$ orbitals on copper. One of these involves the orthogonal σ orbitals of the $CO_3{}^{2-}$ group while the second pathway involves the π-electron system of the bridging ligand. The structural data on $Na_2Cu(CO_3)_2$ emphasize the low symmetry of the carbonate group. For example the intralayer Cu–O distances are slightly different: Cu–O(1) = 1.947 Å and Cu–O(2) = 1.934 Å[8] which may affect the σ mechanism whereas the deviations of the copper atoms from the carbonate plane may influence the π mechanism. On the other hand the magnetic interaction in polymeric $K_2Cu(CO_3)_2$[7] is also ferromagnetic[13] (T_c = 6.6 K) although

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the symmetry of the $[Cu(CO_3)_2]^{2-}$ unit is much higher.[7] A consideration of the possible exchange pathways using orbital symmetry relationships and the carbonate molecular orbitals indicates that both antiferromagnetic and ferromagnetic pathways are possible. Obviously the latter dominate in this case. This will be considered in more detail in due course.[13] Apart from $K_2Cu(CO_3)_2$ copper(II) oxydiacetate is the only other system where superexchange via a similar bridging unit results in ferromagnetic intralayer exchange ($J = 4.66$ cm^{-1}).[14] Here the CO_2^- group bridges adjacent coppers in a rather puckered fashion and the σ mechanism was thought to be mainly responsible for the observed interaction.

One of the more difficult problems in these layered materials is the question of exactly why some order ferromagnetically and others order antiferromagnetically. For example the layers in K_2CuF_4 and $[CH_3NH_3]_2CuCl_4$ couple ferromagnetically whereas in the other $CuCl_4^{2-}$ derivatives they couple antiferromagnetically. Hatfield and co-workers have tried to identify some of the features which determine the type of three-dimensional ordering which results in these types of compounds.[14] In $Na_2Cu(CO_3)_2$ this feature is probably easier to understand because of the detailed nature of the structure. Each copper ion in a layer has an identical copper ion as its immediate neighbor in the layers above and below. This may then encourage some sort of direct exchange between the copper ions in adjacent layers or even a superexchange via the interleaved sodium ions and so an antiferromagnetic interlayer coupling.

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Registry No. $Na_2Cu(CO_3)_2$, 37224-64-9; $Na_2Cu(CO_3)_2$ (salt), 37224-64-9.

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Quantitative Description of the Magnetic Properties and Proton Isotropic Shifts of Hemichrome Salts (Derivatives of Iron(III) Octaethylporphyrin Complexes): The Presence of a Spin Equilibrium

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A quantitative interpretation of the temperature-dependent magnetic and NMR properties of a series of $Fe(OEP)X_2ClO_4$ derivatives is given by using the quantum mechanical spin-mixed model (OEP = octaethylporphyrin, X = heterocyclic base). A small temperature variation in the ligand-field parameters (~1%) is necessary to account for both the magnetic and NMR data. In the quantum mechanical spin-mixed model limiting high-temperature magnetic moments of between 4.0 and 4.5 μ_B are not necessarily an indication of a spin quartet state.

Introduction

In view of the recent articles on the possibility of quantum mechanical spin-mixed ground states for several iron-containing proteins[1] and even (octaethylporphyrinato)iron(III) perchlorate, $Fe(OEP)ClO_4$,[2] we are prompted to report in detail some calculations made several years ago[3] on the rather unusual magnetic and NMR properties of the series $Fe(OEP)X_2ClO_4$ (X = substituted heterocyclic base (Figure 1)). Our description is tentative and probably not unique although it does offer a tenable phenomenological *quantitative* explanation which is consistent with most of the available experimental data.

The magnetic properties of the $Fe(OEP)X_2ClO_4$ derivatives[3b,4] (summarized in Figure 2) are unlike those of typical high-spin ($S = {}^5/_2$) or low-spin ($S = {}^1/_2$) ferric heme proteins. In some respects they resemble more the properties of several of the ferricytochromes *c′* where a quantum mechanical admixture of the intermediate-spin state ($S = {}^3/_2$) with the $S = {}^5/_2$ state was able to reproduce the experimental data to a very good approximation.[1] The data shown in Figure 2 are different from the ferricytochromes *c′* in that there appears to be an apparent (see later) equilibrium between the intermediate $S = {}^3/_2$ state and the low-spin $S = {}^1/_2$ state.

The very large changes in magnetic moment over such a small temperature range (4.22–2.7 μ_B over 120 K in the extreme case) are most unusual and probably indicate a changing spin state and/or some type of spin-equilibrium situation. This can be looked at in several ways. The first considers the equilibrium to consist of simple thermal mixtures over noninteracting $S = {}^5/_2$, ${}^3/_2$, and ${}^1/_2$ levels on one molecule; the second would be a similar equilibrium but over different molecules. A combination of these was the first to be proposed and can be often account for the magnetic data of iron(III) materials possessing spin-equilibrium properties.[5] The third possibility involves a quantum mechanical mixture, first introduced by Harris,[6] which allows spin–orbit coupling to mix all the levels to give a thermal average over a single molecule.[1] The real situation may even be different quantum mechanical mixtures over different molecules although this would be too difficult for a quantitative description. The observed magnetic properties of the first two models would be similar except if the populations of different molecules with different ground states did not follow a Boltzmann distribution. These cooperative spin transitions are known[7] but probably do not exist in this case because the solution (from NMR measurements) and solid-state magnetic data are very similar.[3b] This latter observation also eliminates two further situations: (i) an equilibrium between chemically different species in solution

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