Notes

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Low-Temperature Paramagnetic Anisotropy and Zero-Field Splitting in High-Spin (Tetraphenylporphyrinato)iron(III) Chloride

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(Tetraphenylporphyrinato)iron(III) chloride ((TPP)FeCl) is a synthetic iron porphyrin which closely resembles chlorohemin. The ferric ion in (TPP)FeCl is high spin ($S = {}^5/_2$) with an ${}^6S_{5/2}$ electronic ground state. The degeneracy of the sextet is partly removed by the combined effect of spin–orbit coupling and axial ligand field, to give three Kramers doublets, namely, $M_s = \pm{}^1/_2, \pm{}^3/_2$, and $\pm{}^5/_2$. A spin Hamiltonian of the form

$$\mathcal{H} = DS_z^2 + g\beta HS \qquad (1)$$

gives the energy separation between the Kramers doublets, where D is the zero-field splitting (ZFS) parameter.[2,3]

The ZFS in (TPP)FeCl has recently been the subject of several studies. It was originally deduced from the temperature dependence of the average magnetic susceptibility[4] that D in (TPP)FeCl is 11.8 cm^{-1}. A similar value of D was indicated from the analysis of the temperature-dependent isotropic proton-shift studies[5] and also accepted in the analysis of very low temperature (<1 K) susceptibility studies.[6] However, this value of D for (TPP)FeCl is much larger than the value deduced from far-infrared studies on (TPP)FeCl (D = 6.5 cm^{-1} [7]) and analogous chlorohemin (D = 6.95 cm^{-1} [8]). It was later shown from the measurement of paramagnetic anisotropy[9] that D = 5.9 cm^{-1} in (TPP)FeCl. A value of D in the range 4–6 cm^{-1} was also indicated from an electron spin resonance study[10] of (TPP)FeCl doped in TPPH$_2$.

The above measurement of paramagnetic anisotropy was done in the liquid nitrogen temperature range (80–300 K). Although the experimental data were useful in giving both the magnitude and sign of D, the ZFS parameter can be more accurately and reliably determined if the measurements are done at lower temperatures, especially in the liquid helium temperature range. In this temperature range the anisotropy is very large and thus can be determined more accurately. Further, any uncertainty involved in the diamagnetic correction (by using the value of Ni(TPP)) becomes insignificant in view of the expected large paramagnetic anisotropy of the Fe^{3+} ion. We have therefore measured the magnetic anisotropy of (TPP)FeCl down to 5 K to determine a more reliable and accurate value of D in this molecule. The present paper also forms a part of our magnetic studies on metalloporphyrins at low temperatures, since such experimental studies, especially on the single crystals of this important series of molecules, are very scarce.

(TPP)FeCl was prepared by the literature method.[11] It was purified and characterized as described earlier.[9] Large well-developed single crystals were grown from methylene chloride solution. The crystals of (TPP)FeCl belong to the tetragonal system, with the mean plane of all the porphyrin molecules lying in the *ab* plane and the Fe–Cl bond along the *c* axis of the crystal.[12] The crystal anisotropy is thus the same as its molecular anisotropy. The crystal anisotropy over the temperature range 83–5 K was measured by Krishnan's angle flip method,[13] using an instrument described elsewhere.[14] The quartz fibers used in the measurement were calibrated using triphenylbenzene as the secondary standard.[15,16] Measurements were made at external magnetic field strengths ranging from 800 to 4000 Oe; magnetic fields in the 800–1000 Oe range were employed in the measurements below 15 K. The experimental results were corrected for diagmagnetic anisotropy by using the value of Ni(TPP),[9,17] though such corrections were not in fact essential in view of the large paramagnetic anisotropies, especially at lower temperatures.

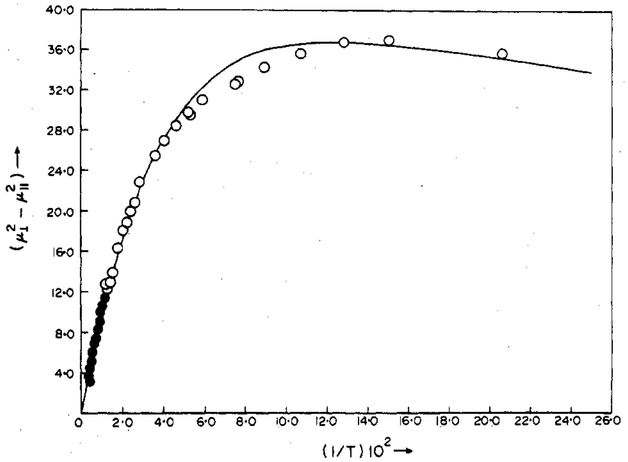

Figure 1. Temperature dependence of $\mu_\perp^2 - \mu_\parallel^2$ of (TPP)FeCl. The open circles are the experimental data of the present work and the solid circles are those of ref 9.

The present experimental data between 80 and 5 K are summarized in Figure 1. The results are plotted in terms of $\mu_\perp^2 - \mu_\parallel^2$ vs. $1/T$, where $\mu_\perp^2 - \mu_\parallel^2 = 7.997(K_\perp - K_\parallel^2)T$. $K_\perp - K_\parallel$ is the corrected molecular paramagnetic anisotropy; the parallel and perpendicular subscripts refer to the quantities parallel and perpendicular to the c axis of the crystal. Throughout the temperature range, $K_\perp > K_\parallel$ implying that D remains positive.[3] The Hamiltonian in eq 1 has been used to deduce[9] eq 2 for $\mu_\perp^2 - \mu_\parallel^2$. Here we have taken[9,18] $g_\parallel$ =

$$\mu_\perp^2 - \mu_\parallel^2 = \frac{3}{1 + e^{-2x} + e^{-6x}}\left[8\left(1 + \frac{1}{x}\right) - \left(\frac{11}{2x} + 9\right)e^{-2x} - \left(\frac{5}{2x} + 25\right)e^{-6x}\right] \qquad (2)$$

$$x = D/kT$$

$g_\perp$ = 2. The experimental data over the entire temperature range (see below) can be satisfactorily fitted to eq 2, which gives D = 6.0 cm^{-1}. A slight discrepancy exists in the fit between 20 and 10 K, the maximum being about 5% which is outside the estimated experimental uncertainty of ±2%. Any slight change in the value of D does not improve the situation.

A possible explanation of the above misfit in the 20–10 K region may be the neglect of the fourth-order terms in eq 1.[19] The effect of these higher order terms is to mix the $M_s = \pm{}^5/_2$ and $\pm{}^3/_2$ spin states, which is expected to affect the anisotropy. The small magnitude of the discrepancy ensures that these terms, as expected in a recent theoretical study,[20] must be very small.

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The paramagnetic anisotropy of (TPP)FeCl in the 77–5 K temperature range is thus in agreement with the deduction from the high-temperature anisotropy data that the ZFS parameter D in this case is 6.0 cm^{-1}. In this respect (TPP)FeCl appears to resemble closely chlorohemin and other structurally similar iron(III) porphyrins.[8] A very recent Mössbauer study[21] also gives $D = 7.0 \pm 1.0$ cm^{-1} for (TPP)FeCl.

Registry No. (TPP)FeCl, 16456-81-8.

References and Notes

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(18) The observation in Figure 1 that the $\mu_\perp^2 - \mu_\parallel^2$ vs. $1/T$ plot passes through the origin ensures that there is no g anisotropy in (TPP)FeCl.[8] Hence the assumption $g_\parallel = g_\perp = 2$ seems reasonable.
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Chloro- and Methyltris[(hexamethyldisilyl)amido]zirconium(IV) and -hafnium(IV)

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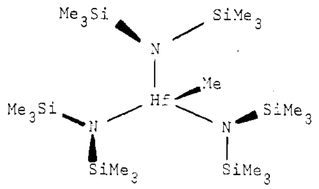
In contrast to the large number of compounds with the (hexamethyldisilyl)amido ligand which have been described for the first-row transition series,[1,2] only one is known for a second- or third-row transition element, $[(Me_3Si)_2N]_2Zr(NMe_2)_2$.[3]

Reaction of lithium or sodium (hexamethyldisilyl)amide with zirconium or hafnium tetrachloride yields the hydrocarbon-soluble $ClM[N(SiMe_3)_2]_3$. Physical properties are shown in Table I. The chloro amides are surprisingly substitutionally inert. They are air- and water-stable, and they are not hydrolyzed by dilute mineral acid. A suspension of the compounds in dilute nitric acid does not yield a precipitate of silver chloride upon addition of aqueous silver nitrate. The amides do not react with (trimethylsilyl)methyllithium, lithium tetrahydroborate, nor with sodium (hexamethylsilyl)amide, the last in refluxing toluene.

Both amides do, however, react with methyllithium, yielding $MeM[N(SiMe_3)_2]_3$. These alkyl amides are also stable toward molecular oxygen and water. They are recovered unchanged from methanol, tetrafluoroboric acid, or carbon dioxide. However, they are hydrolyzed by dilute hydrochloric acid, yielding $ClM[N(SiMe_3)_2]_3$.

The surprising lack of reactivity toward a variety of reagents is doubtless due to kinetic stability. The sterically voluminous silylamide ligands effectively prevent potential reactants from getting close enough to the metal atom for reaction to occur. Only the sterically small nucleophile methyllithium is able to react with the chloro amides.

X-ray crystallographic studies on tris(silylamides), $M[N(SiMe_3)_2]_3$, show them to have a propeller conformation (D_3) in the solid state.[4] The only tetravalent silylamide which has been examined crystallographically is $BH_4Th[N(SiMe_3)_2]_3$.[5] The Me_3Si groups also exist in the propeller conformation in which all three $(Me_3Si)_2N$ groups are twisted in the same sense with respect to a reference plane defined by the three nitrogen atoms bonded to the thorium atom. The compound is chiral and may exist in two enantiomeric forms which differ in their sense of twist.[6] The low-temperature-limiting ^{1}H NMR spectrum should show two equal-area resonances due to the trimethylsilyl groups. However, only a single resonance due to this group was observed at −65 °C for the tetrahydroborate or methylthorium derivatives. In contrast, the methylhafnium compound, $MeHf[N(SiMe_3)_2]_3$, shows two equal-area resonances at δ 0.66 and 0.56 at −40 °C due to the trimethylsilyl groups which coalesce due to a single resonance at ca. −25 °C. This is consistent with two enantiomeric forms, one form being shown in I. The failure to resolve the line shapes for the thorium compounds is presumably related to the larger ionic radius of thorium relative to that of hafnium.



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Experimental Section

Analyses were by the microanalytical laboratory of this department. The proton nuclear magnetic resonance spectra were recorded on a modified Bruker WH-1180 machine operating at 180 MHz. Proton-decoupled carbon nuclear magnetic resonance spectra were re-

Table I. Physical Properties of $XM[N(SiMe_3)_2]_3$

		^{1}H NMR[a]		^{13}C{^{1}H} NMR[b]		infrared[c]	
compd	mp, °C	Me-M	$(Me_3Si)_2N$-M	Me-M	$(Me_3Si)_2N$-M	M-Cl	M-N
$ClZr[N(SiMe_3)_2]_3$	182–183		0.67		6.15	348 s	408 s, 400 s
$ClHf[N(SiMe_3)_2]_3$	180–181		0.62		6.38	338 s	404 s, 388 m
$MeZr[N(SiMe_3)_2]_3$	176–177	1.18	0.62	31.4	6.16		404 s, 390 s
$MeHf[N(SiMe_3)_2]_3$	188–190	1.01	0.61	65.4	6.32		400 s, 395 m

[a] Benzene solution relative to Me_4Si (δ units) at 37 °C. [b] Benzene solution relative to Me_4Si (δ units) at 37 °C. [c] Nujol mull.

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