packing in materials such as $Fe(phen)_2(NCS)_2$, famous as the first example of a highly cooperative, thermally induced intersystem crossing chelate,[11] has not been reported. Were the packing to be analogous to that of the parent $Fe(phen)_3^{2+}$ cations discussed here, a simple chemical basis for the cooperativity would exist: the electron density rearrangement within a chelate that experiences the singlet–quintet intersystem crossing would be communicated to both nearest-neighbor chelates. More quantitatively, the finding that ΔH is positive and is on the order of 4 kJ/mol[1b] for the local reaction singlet···singlet → singlet···quintet finds a logical explanation in the frontier orbital interaction described here.

It is important to note further that the phen π HOMO and π LUMO are mixed with the metal $d\pi$ AOS, themselves directly involved in the orbital occupation change ($d\pi^6d\sigma^0$–$d\pi^4d\sigma^2$) accompanying the singlet–quintet conversion. Other ramifications, such as the possibilities for thermal, chemical, and photoinduced conductivities in solids analogous to those discussed here, are under consideration in our laboratory.

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Registry No. $Fe(phen)_3I_2 \cdot 2H_2O$, 42992-96-1.

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Comment on the Measurement and Interpretation of Susceptibility Data

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The aim of this paper is to draw the chemists attention to some aspects of experimental magnetochemistry. For magnetic investigations, Faraday balances, SQUID magnetometers, etc., equipped with superconducting solenoids and low-temperature accessories are quite common nowadays. Since they are working at high magnetic fields and temperatures even below 4 K, substantial complications in the measurement and interpretation are expected for many magnetic compounds. We therefore discuss two important aspects: (i) "orientation effect" in magnetically anisotropic, loosely packed powder samples (see also ref 2 and 3); (ii) nonlinear field effects at low temperatures and in high fields.[1]

(i) Any magnetically anisotropic particle is subject to a torque if placed in a homogeneous magnetic field. This torque tends to align crystallites with the magnetic axis of maximum magnetization parallel to the field (see i.e., ref 3). The effect is opposed by mechanical friction forces between the particles of the sample and hence can be avoided by increasing this force. Since the torque is proportional to the anisotropy of magnetization and to the square of the field strength, pronounced effects are expected at low temperature and in high fields. Figure 1 shows that even in the case of a magnetically diluted sample, a partial orientation of crystallites can take place. Curve a represents the data from a mechanically fixed powder, whereas curve b was obtained from a loosely packed sample, slightly shaken at 4 K and 6.2 T before measurement.

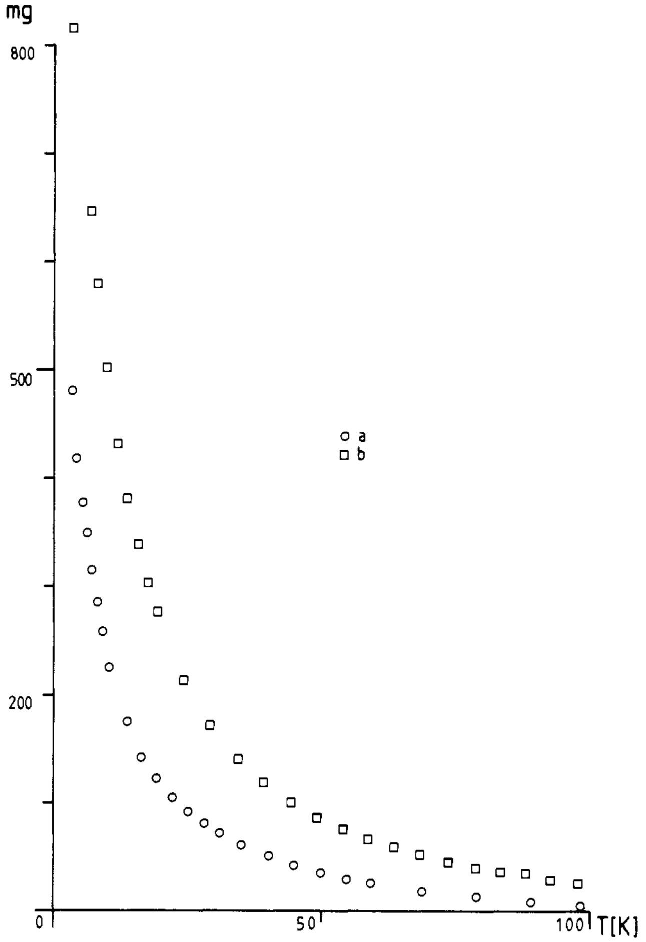

Figure 1. Measured effect on the microbalance of a Faraday setup calibrated to 1 g of a powder sample of 5% decamethylmanganocene in decamethylruthenocene at 6.19 T and 0.7 T cm^{-1}: (a) mechanically fixed; (b) oriented in high magnetic field (see text).

The same behavior has been observed for the well-known calibration standard $HgCo(NCS)_4$ (MTC). The measured effect on a Faraday balance for this compound increased about 10% even at 200 K when a loosely packed powder was treated as described above. This might explain the quite different low-temperature results reported for MTC.[4] A magnetically anisotropic compound should therefore be mechanically fixed, when used as a calibrant in modern susceptibility setups. Throughout our investigations we performed this mechanical fixation with the simple tool shown in Figure 2.

A cylindrical sample holder made from aluminum foil[5] (common household foil), put into the cavity (O), is filled with the powdered material. The screw (M8) and the plug (ST) press the sample to the bottom. This augments the mechanical friction forces within the sample. The pressed sample and the sample holder can then be removed by means of screw (M3). Finally, the sampleholder is shut by pressing together the open top of the aluminum cylinder.

On the other hand, the orientation effect may also favor an investigation if an almost perfect alignment can be achieved.

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[5] Compared with a usual sample holder made of quartz glass with similar dimensions, our sample holder is much lighter (about 10 times) and therefore its effect on the measured susceptibility is much smaller.

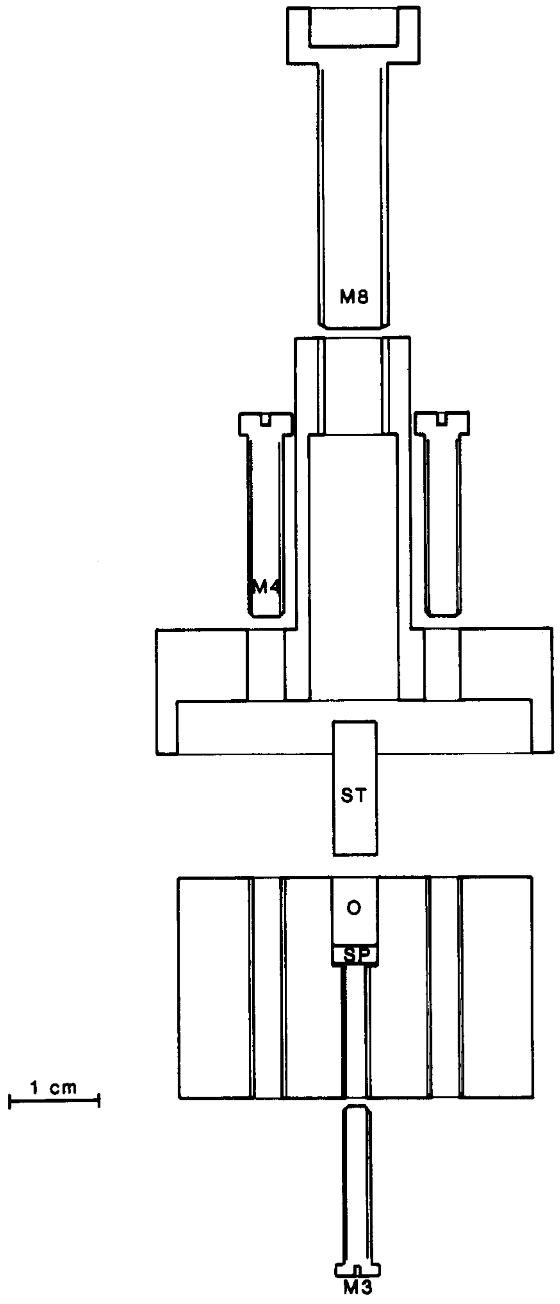

Figure 2. Sample pressing setup. For description, see text.

Powder measurements of oriented powders will then lead to a principal axis value of magnetization M or at least along a distinguished direction in the crystal. We have successfully used this technique in the reinvestigation of the magnetic properties of nickelocene.[6]

(ii) As pointed out earlier by several authors,[1] the interpretation of powder magnetization in terms of the average along three orthogonal axes (eq 1) is an approximation and

$$M_{\text{iso}}(\text{av}) = \tfrac{1}{3}(M_x + M_y + M_z) \tag{1}$$

can lead to erroneous results. In addition to the reported calculation on systems having spin greater than 1 we found a similar situation for a Kramers doublet with anisotropic **g** tensor (see Figure 3).

For experiments in high magnetic fields and at low temperatures, eq 1 should be replaced by an integration over all possible orientations of the field vector with respect to the molecular axes:

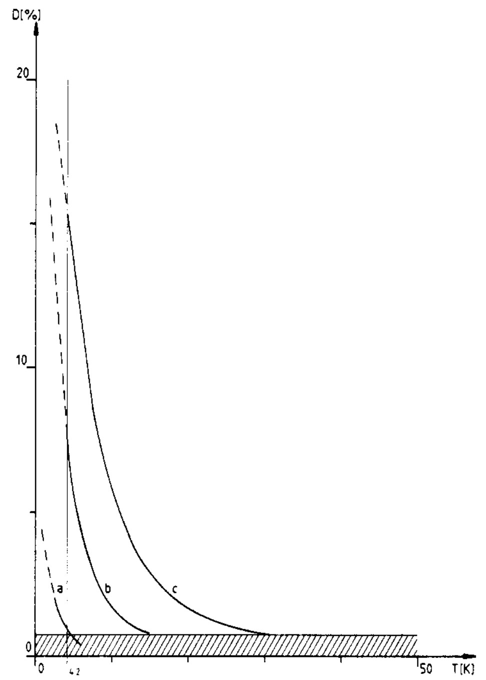

Figure 3. Calculated difference between magnetization after eq 1 and 2 for decamethylmanganocene in decamethylruthenocene ($g_{\parallel}$ = 3.466, $g_{\perp}$ = 0.74[6a]) for different field strengths: a = 1 T; b = 3.5 T; c = 7 T. $D = 100[(M_{\text{iso}}(\text{int}) - M_{\text{iso}}(\text{av}))/M_{\text{iso}}(\text{int})]$; shaded area, estimated accuracy of routine susceptibility measurements.

$$M_{\text{iso}}(\text{int}) = \frac{1}{4\pi}\int_{\theta=0}^{\pi}\int_{\Phi=0}^{2\pi} M(|\vec{H}|,\theta,\Phi,T)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\Phi \tag{2}$$

$$M(|\vec{H}|,\theta,\Phi,T) = -N\left\{\left[\sum_i \frac{\partial E}{\partial H}i \exp[-E_i(|\vec{H}|,\theta,\Phi)/kT]\right]\Big/ [\sum_i \exp[-E_i(|\vec{H}|,\theta,\Phi)/kT]]\right\}$$

In contrast to common approximations such as eq 1 or the Van Vleck formula, a more complicated procedure is needed in order to get spin Hamiltonian parameters (i.e., g or D values or exchange constants J) from eq 2. In figure 3 the results obtained from eq 1 and 2 for a Kramers doublet with an axial **g** tensor are compared.

Therefore, our conclusions are as follows:

Powder samples for experiments in high magnetic fields and at low temperatures should always be mechanically fixed, if accidental orientation of crystallites has to be avoided. Assuming the investigated material undergoes no chemical or structural changes on pressing, this may be realized as discussed above.

If one is working with high magnetic fields and at low temperatures, one has to be aware of the nonvalidity of most common approximations for simulating experimental data measured under such conditions. Since an interpretation in terms of an exact description may be rather complicated, an iterative procedure is recommended, evaluating initial magnetic parameters from common approximations and refining them by numerical integration according to eq 2 above. It must be pointed out that all sources of errors mentioned here can also be present when dealing with common electromagnet systems. They may be less substantial, however.

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Registry No. Decamethylmanganocene, 67506-86-9; decamethylruthenocene, 84821-53-4.

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(6) (a) Baltzer, P. Ph.D. Thesis, University of Zürich, 1984. (b) Baltzer, P.; Hulliger, J.; Stebler, A. to be submitted for publication.