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Magnetic Properties of a Dysprosium(III) Complex with a Nitronyl Nitroxide

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We are currently investigating the magnetic properties of metal complexes with nitronyl nitroxides, 2-*R*-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide (NITR), which are stable organic radicals capable of binding to metal ions through their oxygen atoms [1]. The magnetic interaction between the radicals and the metal ions is of the direct type and it can be either ferro- or antiferromagnetic depending on the overlap of the magnetic orbitals. We have studied systems in which the NITR radicals are bound to either the transition metal or the lanthanide ions [2, 3].

Lanthanide ions are present in many magnetic materials, to which they often provide highly anisotropic properties [4]. Establishing structural–magnetic correlations of the type which are now rather well understood for transition metal ions would be helpful for being able to control the magnetic anisotropy; complexes of the lanthanides with NITR radicals are in principle very well suited to provide first hand informations on the involvement of the f orbitals in magnetic interactions.

We previously reported [3, 5] the crystal structure and the magnetic properties of complexes of formula $Ln(hfac)_3(NITR)_2$ (Ln = Gd, Eu; hfac = hexafluoroacetylacetonate) and we wish to report here the magnetic properties of $Dy(hfac)_3(NITPh)_2$, which are expected to be highly anisotropic, in contrast to the isotropic properties of the isomorphous $Gd(hfac)_3(NITPh)_2$.

$Dy(hfac)_3(NITPh)_2$, which was prepared as previously described for the gadolinium analogue [3], has been found to be isomorphous to that by determining the unit cell with a single crystal X-ray diffractometer. The cell is triclinic, $P\bar{1}$, $a = 1166.4(2)$, $b = 1264.7(4)$, $c = 1910.6(3)$ pm, $\alpha = 83.7(4)$, $\beta = 73.31(1)$, $\gamma = 87.2(7)^\circ$. We assume that the two compounds are isostructural. The coordination polyhedron around the metal ion is a distorted dodecahedron [3].

We measured the magnetic susceptibility of $Dy(hfac)_3(NITPh)_2$ in a Faraday susceptometer, with the usual technique of putting a polycrystalline powder in a sample holder, obtaining results which are field dependent. In particular, we found that the value of χT increases on increasing the field, with much more dramatic effects observed at low temperatures. We attribute these results to the selective orientation of the microcrystallites in the external magnetic field, due to the presence of a large anisotropy in the susceptibility tensor. This is confirmed by the fact that the field dependence decreases if the sample is pressed in its holder, making reorientation of the crystals in the field more difficult. In Fig. 1 we show the temperature dependence of one of such samples, together with the corresponding data for the same sample which has not been pressed. It is apparent that the two sets of values are different at all temperatures, and while χT goes up to a value of 28.3 emu mol^{-1} K at 25 K for the unpressed powder, for the other sample it stays at a value of 14.5 emu mol^{-1} K. The two lower sets of points shown in Fig. 1 correspond to measurements performed on cooling and heating, respectively. The small difference between the two sets of points indicates that some orientation effects are still present.

The χT curve for $Dy(hfac)_3(NITPh)_2$ is substantially constant from room temperature down to *c.* 30 K. The constant value, 14.5 emu mol^{-1} K, corresponds well to that expected for uncoupled Dy^{3+} and two radicals. Below 30 K a decrease in the χT value down to 10 emu mol^{-1} K is observed. The data obtained at low field with a SQUID susceptometer provided practically identical results.

The magnetic data alone do not provide much information on the coupling between radicals and

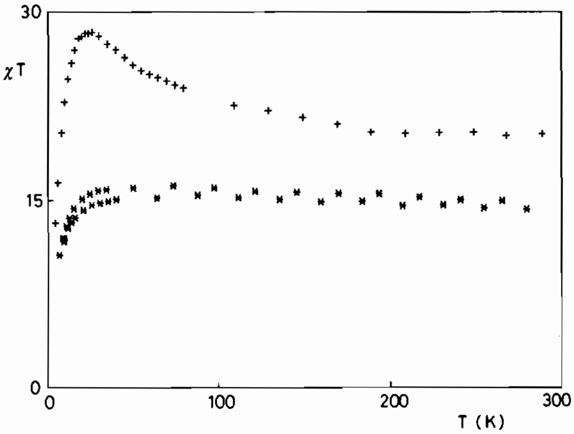

Fig. 1. Temperature dependence of the χT product of $Dy(hfac)_3(NITPh)_2$ in the range 4.2–300 K. The two curves refer to: (*) the sample pressed in its holder; (+) the unpressed sample (see text).

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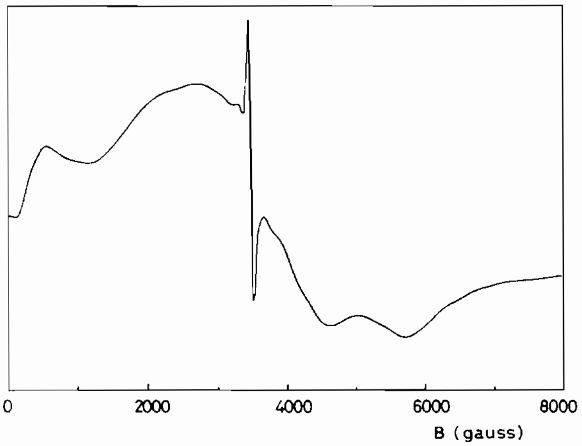

Fig. 2. Polycrystalline powder EPR spectrum of Dy(hfac)$_3$-(NITPh)$_2$ recorded at 4.2 K and X band frequency.

dysprosium, because the observed decrease of χT at low temperature may be due to the large zero-field splitting of the $^6H_{15/2}$ ground state of dysprosium. Sample calculations on an isolated dysprosium using the Angular Overlap Model show that indeed χT must decrease on decreasing the temperature. The ground state is a Kramer's doublet, which can be considered as an effective $S = 1/2$ state, which can couple to the $S = 0$ and $S = 1$ states obtained by coupling the spins of the two radicals. The other Kramer's doublets of the $^6H_{15/2}$ manifold are expected not to be populated at 4.2 K.

The EPR spectra provide a clear indication that the radicals and the metal ion are indeed coupled in such a way that we do not observe the separate signals of the two different spins. In Fig. 2 is shown the polycrystalline powder spectrum of Dy(hfac)$_3$-(NITPh)$_2$ recorded at 4.2 K. We observe a feature at low field, a broad absorption at $g \approx 2$, and a weak absorption at $g \approx 1.1$. An increase of a few degrees K broadens the signal beyond detection. Further, we observe a sharp signal at $g \approx 2$, which is much less intense than the others, which we attribute to free radical impurities.

Single crystal EPR spectra showed that the low field and high field features correspond to a Kramer's doublet. Accurate g values could not be obtained, because in many crystal orientations the signal is obscured by another broad absorption, which presumably is responsible for the feature seen at $g \approx 2$. The signals are in every case very broad, however, an approximate analysis provides $g_\parallel = 1.1(2)$ and $g_\perp = 11(2)$ with estimated errors in parentheses. These values correspond well to those expected for a Kramer's doublet which can be loosely described as $M_S = 1/2$ belonging to $^6H_{15/2}$ ($g_\parallel = 1.3$, $g_\perp = 8g_\parallel = 10.4$), suggesting that the observed Kramer's doublet corresponds to the $M_S = \pm 1/2$ of dysprosium coupled to $S = 0$ of the two radicals.

The other feature seen in the EPR spectra could not be identified positively, because it gives broad absorptions also in single crystals which cannot be followed in the different orientations. Tentatively we assign it to a transition between the states originating from $M_S = \pm 1/2$ of dysprosium(III) and $S = 1$ of the two radicals. Sample calculations, using the g values obtained for dysprosium, show that indeed this assignment is feasible. The extent of the coupling between metal and radicals cannot be determined, but it appears to be small. Low temperature measurements are needed in order to obtain a quantitative estimate.

The observed anisotropy of the ground state is very large, thus justifying the dramatic orientation effects seen in the magnetic susceptibility measurements. Furthermore, it is of the XY type, while generally it has been reported to be of the Ising type in simple dysprosium compounds [6]. Therefore the interaction with NITR can effectively modulate the magnetic anisotropy of dysprosium derivatives, thus opening interesting perspectives for the synthesis of molecular magnetic materials.

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