

On the Magnetic Properties of $\text{Pr}_2(\text{DPM})_6$ and $\text{Eu}_2(\text{DPM})_6$

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Among the various, currently used NMR shift reagents (*cf.*, *e.g.*, Ref. 1), the lanthanide chelate type reagents introduced by Hinckley² play an important role. Typical representatives for this class of complexes are tris-dipivalomethanato-praseodymium ($\text{Pr}(\text{DPM})_3$) and -europium ($\text{Eu}(\text{DPM})_3$). As a link in a protracted research programme^{3,4} on the effects of these reagents, a thorough examination of the physical properties of the reagents themselves and a few suitable model adducts is being carried out in order to obtain further insight in the NMR shift mechanism. The present communication gives an account of the magnetic properties of the dimers $\text{Pr}_2(\text{DPM})_6$ and $\text{Eu}_2(\text{DPM})_6$, which prevail in the solid state, advertisement for such data being submitted by, *e.g.*, Weissman.⁵

Experimental. Samples of $\text{Pr}_2(\text{DPM})_6$ and $\text{Eu}_2(\text{DPM})_6$ were prepared and purified according to the procedure of Eisentraut and Sievers,⁶ analysed, and identified as the dimeric⁷ compounds on the basis of X-ray diffraction (Guinier) data.

Magnetic susceptibilities were measured between 80 and 500 K by the Faraday method

(maximum field ~ 8 kO) using 20–30 mg samples. In the low temperature range (15–293 K), additional measurements on 50–80 mg samples were performed at field strengths up to 16 kO in a Princeton Applied Research Model FM-1 vibrating sample magnetometer.

Results. The reciprocal magnetic susceptibility *versus* temperature curves for $\text{Pr}_2(\text{DPM})_6$ and $\text{Eu}_2(\text{DPM})_6$ are shown in Fig. 1. Field strength dependent susceptibilities were not observed and the experimental points represent mean values at different field strengths without correcting for induced diamagnetism. The points refer to four samples and two different measuring techniques for each compound, thus demonstrating an excellent reproducibility of the characteristics.

The thermomagnetic curves of $\text{Pr}_2(\text{DPM})_6$ and $\text{Eu}_2(\text{DPM})_6$ obey the Curie-Weiss Law $\chi^{-1} = C^{-1}(T - \theta)$ over the approximate ranges 100 to 500 K and 50 to 500 K, respectively. (The upper temperature limits are imposed by the melting/decomposition points of the compounds in the sealed, evacuated measuring capsules.) Least squares fits of the experimental data over the linear sections of the curves give $\theta = 30 \pm 20$ K and $\mu_{\text{P}} = \sqrt{8C_{\text{mol}}} = 3.4 \pm 0.1 \mu_{\text{B}}$ for $\text{Pr}_2(\text{DPM})_6$ and $\theta = -140 \pm 20$ K and $\mu_{\text{P}} = 3.8 \pm 0.1 \mu_{\text{B}}$ for $\text{Eu}_2(\text{DPM})_6$. The μ_{P} values are accordingly in line with those commonly found in the literature (3.4 to 3.6 μ_{B} ; *cf.*, *e.g.*, Ref. 8) for compounds of Eu^{3+} and Pr^{3+} . The minimum in $\chi^{-1}(T)$ at $T_{\text{crit.}} = 50 \pm 10$ and 100 ± 10 K

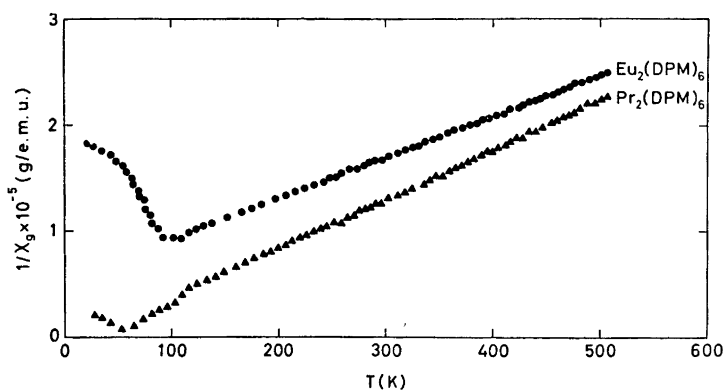


Fig. 1. Inverse magnetic susceptibility as a function of temperature for $\text{Pr}_2(\text{DPM})_6$ and $\text{Eu}_2(\text{DPM})_6$.

for $\text{Pr}_2(\text{DPM})_6$ and $\text{Eu}_2(\text{DPM})_6$, respectively, very strongly suggests that there is magnetic coupling between the lanthanide ions of the binuclear clusters. The fact that $T_{\text{crit.}} \approx |\theta|$ shows that essentially one exchange interaction is operative in both cases.

The above results are fully consistent with the recent theory of Bleaney⁹ for NMR shifts in solutions containing lanthanide chelate reagents. It should be emphasized, however, that this theory is based on the anisotropy in the susceptibility of the *mononuclear*, paramagnetic complex which prevails in solution. Hence, the present study (which was started before Bleaney's paper came to hand) does not provide a critical test of the theory. Experimental confirmation of some of the more fundamental predictions of Bleaney's theory has, very recently, been published by Grotens *et al.*¹⁰

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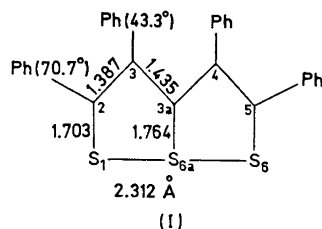
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The Structure of 2,3,4,5-Tetraphenyl-6a-thiathiophthene

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So far structure studies on 2-phenyl-, 2,4- and 3,4-diphenyl-, and 2,3,4-triphenyl-6a-thiathiophthene have been reported.¹⁻⁴



The present structure study of 2,3,4,5-tetraphenyl-6a-thiathiophthene (I) has been carried out in order to obtain further information about the degree to which phenyl substituents affect the S-S bonding in 6a-thiathiophthenes; the preliminary results are presented here.

The S(6a)-C(3a) bond in I lies along a crystallographic two-fold axis, and the two halves of the molecule are therefore exactly equal. The bond lengths in the 6a-thiathiophthene system of I are, S(1)-S(6a) = 2.312(2) Å, S(1)-C(2) = 1.703(7) Å, S(6a)-C(3a) = 1.764(10) Å, C(2)-C(3) = 1.387(10) Å, and C(3)-C(3a) = 1.435(8) Å. The phenyl groups in 2 and 3 positions are twisted 70.7° and 43.3° about the respective connecting bonds.

A sample of I was generously supplied by M. Stavaux.⁵ The crystals are dark purple and belong to the monoclinic space group $Ic/2$. The cell dimensions are, $a = 20.6370(20)$ Å, $b = 9.7541(8)$ Å, $c = 11.3520(22)$ Å, and $\beta = 92.90(2)^\circ$. There are four molecules per unit cell; density, calculated 1.352 g/cm³, found 1.36 g/cm³.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using $\text{MoK}\alpha$ radiation. 1952 reflections were observed within $\theta = 28^\circ$.