Crystal and Molecular Structure of a Nuclear Magnetic Resonance Shift Reagent, the Dipyridine Adduct of Tris-[(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III), $Eu(dpm)_3(py)_2$]

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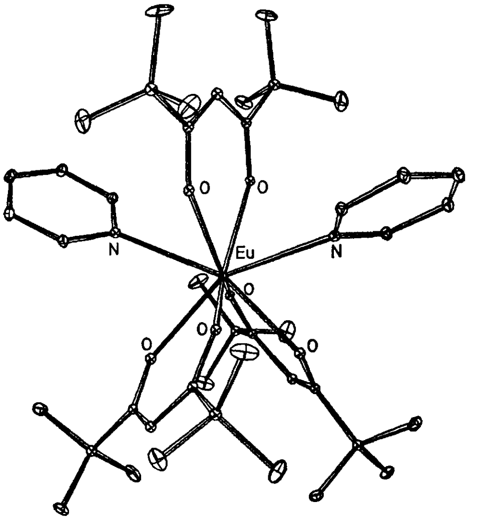
Summary The molecular symmetry of the n.m.r. shift reagent, $Eu(dpm)_3(py)_2$, has been found to be C_2 by X-ray crystallography.

SINCE the original discovery of europium n.m.r. shift reagents by Hinckley,[1] many studies have used paramagnetic lanthanide shift reagents. Several authors have attempted to correlate the paramagnetically induced shifts with the so-called geometric factors, usually given as $(3\cos^2\theta - 1)/r^3$. A geometric factor of this form is only valid for complexes with axial (n-fold, $n \geqslant 3$) symmetry,[2] and Horrocks[3] has recently reported that $Ho(dpm)_3(4\text{-pic})_2$ is not axially symmetric in the solid state. Hinckley[4] determined the space groups of a number of lanthanide complexes of composition $Ln(dpm)_3(py)_2$ and $Ln(dpm)_3(py)$ and found that both $Pr(dpm)_3(py)_2$ and $Eu(dpm)_3(py)_2$ crystallize in the triclinic space group $P\bar{1}$, so that these widely used shift reagents are not necessarily isostructural with $Ho(dpm)_3(4\text{-pic})_2$, which crystallizes in the orthorhombic space group *Pbcn*. Accordingly, we have determined the crystal and molecular structure of $Eu(dpm)_3(py)_2$.

Nearly regular parallelopipedons form from pyridine solution: $a = 13{\cdot}611(5)$, $b = 17{\cdot}306(4)$, $c = 10{\cdot}493(7)$ Å, $\alpha = 98{\cdot}33(3)°$, $\beta = 105{\cdot}20(5)°$, $\gamma = 94{,}75(4)°$, $U = 2333$ (2) Å^3, $Z = 2$, $D_c = 1{\cdot}224$ g cm^{-3}.

Diffraction intensities were collected using a Syntex computer-controlled diffractometer with Mo-K_α radiation. A total of 8311 reflections ($2\theta < 50°$) were measured, of which 6841 with $I \geqslant 3\sigma(I)$ were included in the structure solution. The structure was solved using Patterson and Fourier methods and was refined by least-squares techniques using anisotropic temperature factors for the Eu ion and the pyridine and methyl carbon atoms but not for the remaining 23 atoms. At present, $R_1 = 0{\cdot}050$ and $R_2 = 0{\cdot}048$.

The structure (see Figure) closely resembles that of $Ho(dpm)_3(4\text{-pic})_2$; the co-ordination sphere is best described as a square antiprism. The pyridine molecules occupy apices of opposite square faces so that they are as far apart as possible. The Eu–O bond distances range from 2·315(4) to 2·371(4) Å (average 2·35 Å), compared to the Ho–O bond distances of 2·24(2)–2·30(2) Å (average 2·27 Å). The average Eu–N distance [2·651(4) Å] is longer than the corresponding distance [2·53(3) Å] in the Ho complex. The average Eu–N bond is 0·305 Å longer than the Eu–O bonds, and this difference is greater than that found in the Ho complex (0·26 Å). These results are consistent with the lesser stability of the Eu complex noted by other workers.[4] The Eu atom lies in the plane of the chelate which bridges the two square faces, but is 0·332 and 0·330 Å from the planes of the other two chelate rings. The Eu atom lies out of the planes defined by the pyridine rings, the displacements being 0·386 and 0·337 Å, owing to steric interaction between the t-butyl groups and the pyridine rings, which shows that this complex is quite crowded.



FIGURE

The $Eu(dpm)_3(py)_2$ molecule shows barely significant departures from 2-fold symmetry, probably owing to crystal packing forces. This molecule, then, should be considered to have a C_2 axis, making it isomorphous with $Ho(dpm)_3$-$(4\text{-pic})_2$ which is crystallographically required to have C_2 symmetry.

Any study which attempts to correlate dipolar-shifted n.m.r. spectra with molecular structure must consider the configuration and relevant magnetic properties of the complex.[5] Moreover, since this molecule is not axially symmetric, the use of the $(3\cos^2\theta - 1)/r^3$ geometric factor in the calculation of such shifts, as is commonly done, is inappropriate, and conclusions based upon it must be regarded with suspicion.

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