symmetry[7] and only two dipolar couplings are available, no structural information is possible for this ion.

The mechanism which allows ordering in this phase and that described by Flautt and Lawson[2] is quite different from that in thermotropic nematic phases. The small ions or molecules are located in the interstitial aqueous region of the middle soap phase and have available a very large surface area of the relatively static component of an electrical double layer. The small ions form a mobile component of the double layer and are free to exchange between the highly ordered surface of the cylindrical superstructure and the interstitial water. On the average over these motions the ions are ordered by the surface forces. For the case of sodium ion 2–5% of the ions are at the interface of the double layer region at any one time.[9]

Acknowledgment. The support of the following organizations in providing equipment, operating and personal expenses, and a student scholarship is gratefully acknowledged: the Conselho Nacional de Pesquisas do Brasil (CNPq), Fundação de Amparo á Pesquisa do Estado de São Paulo (FAPESP), Banco Nacional de Desenvolvemento Economico (BNDE), the Ford Foundation, the National Research Council of Canada, and The Defence Research Board of Canada.

(9) D. M. Chen and L. W. Reeves, *J. Amer. Chem. Soc.*, **94**, 4384 (1972).

(10) Visiting professor, 1967–present.

L. W. Reeves,*[10] A. S. Tracey, M. M. Tracey
Instituto de Quimica, Universidade de São Paulo
São Paulo, Brazil

Received April 2, 1973

Implications of the Low-Temperature Nuclear Magnetic Resonance Spectrum of the 3-Picoline Diadduct of Tris[2,2,6,6-tetramethylheptane-3,5-dionato]europium

Sir:

Numerous authors[1–14] have suggested that lanthanide-induced shifts (LIS) can be rationalized on the basis of an equation of the type

$$\frac{\Delta\nu_i}{\nu_0} = K\left\langle\frac{3\cos^2\theta_i - 1}{r_i^3}\right\rangle \qquad (1)$$

where $\Delta\nu_i$ is the induced shift, ν_0 is the probe frequency, r_i is the length of a vector joining the metal with the ith proton, and θ_i is the angle that this vector makes with the unique magnetic axis, when axial symmetry of the complex is assumed. Furthermore it is commonly assumed[1–14] that this magnetic axis passes through the lanthanide ion and the donor atom of the substrate. Were this true, then the low-temperature spectrum in the slow or nonexchange region for the system $Eu(dpm)_3(3\text{-pic})_2$ would exhibit a single peak for the ortho protons since both θ_i and r_i would be identical for all ortho protons. For the same reason a single meta, a single methyl, and a single para peak would be observed.

Some authors, while assuming axial symmetry for the complex, have carried out a systematic search for the location of the magnetic axis which yields the best fit of the observed data, and have found that the axis does not pass through the donor atom.[15,16] If such a model were true, and if the 3-picoline ring were not free to rotate, then two ortho, two meta, two methyl, and a single para peak would be observed in the nonexchange region.

The recently reported crystal structures of $Ho(dpm)_3(4\text{-pic})_2$[17] and $Eu(dpm)_3(py)_2$[18,19] show that these complexes, far from having axial symmetry, possess only a C_2 axis passing through the lanthanide ion and the methine carbon of a chelating dpm^- [20] moiety. Furthermore, each pyridine ring in $Eu(dpm)_3(py)_2$ experiences 11 close intramolecular contacts[18,19] so that free rotation about the Eu–N bond cannot occur. The principal axis of symmetry of such a complex does not lie along the lanthanide–substrate line but is near the C_2 axis. The structural results thus suggest that two ortho, two meta, and two methyl peaks, and a single para peak should be observed.

Evans[21] has recently reported that exchange between free and complexed Me_2SO can be stopped at −80° for the system $Eu(fod)_3(Me_2SO)_2$. In an attempt to obtain experimental evidence which could indicate which of the above models is correct, we have carried out low-temperature studies of the $Eu(dpm)_3(3\text{-pic})_2$ system in CS_2. Upon lowering the temperature of a sample which is 0.0240 *M* in $Eu(dpm)_3$ and 0.1120 *M* in 3-picoline in CS_2, the signals begin broadening and resolve into peaks due to free and complexed substrate at approximately −110°. This lower coalescence temperature confirms Evan's hypothesis[21] that the chemical exchange within the $Eu(dpm)_3(\text{substrate})_n$ (n = 1, 2) system would be faster due to the weaker acceptor properties of the $Eu(dpm)_3$ shift reagent. The low-temperature spectrum reveals *two* ortho, *two* meta, and *two* methyl resonances. The chemical shifts of the resulting complexed peaks are given in Table I. We have also carried out similar

(1) W. DeW. Horrocks, Jr., and J. P. Sipe III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

(2) O. A. Gansow, M. R. Willcott, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **93**, 4296 (1971).

(3) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

(4) S. Farid, A. Ateya, and M. Maggio, *Chem. Commun.*, 1285 (1971).

(5) J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, 1506 (1970).

(6) J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem., Commun.*, 364 (1971).

(7) B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 3282 (1971).

(8) C. C. Hinckley, M. R. Klotz, and F. Patil, *J. Amer. Chem. Soc.*, **93**, 2417 (1971).

(9) C. Beauté, Z. W. Wolkowski, and N. Thoai, *Tetrahedron Lett.*, 817 (1971).

(10) Z. W. Wolkowski, *Tetrahedron Lett.*, 821 (1971).

(11) Z. W. Wolkowski, *Tetrahedron Lett.*, 825 (1971).

(12) J. Goodisman and R. S. Matthews, *J. Chem. Soc., Chem. Commun.*, 127 (1972).

(13) E. Wenkert, D. W. Cochran, E. W. Hagaman, R. B. Lewis, and F. M. Schell, *J. Amer. Chem. Soc.*, **93**, 6271 (1971).

(14) J. Reuben and J. S. Leigh, Jr., *J. Amer. Chem. Soc.*, **94**, 2788 (1972).

(15) C. D. Barry, A. C. T. North, J. A. Glasel, R. J. P. Williams, and A. V. Xavier, *Nature (London)*, **232**, 236 (1971).

(16) M. R. Willcott, R. E. Lenkenski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1744 (1972).

(17) W. DeW. Horrocks, Jr., J. P. Sipe III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

(18) R. E. Cramer and K. Seff, *J. Chem. Soc., Chem. Commun.*, 400 (1972).

(19) R. E. Cramer, and K. Seff, *Acta Crystallogr., Sect. B*, **28**, 3281 (1972).

(20) 2,2,6,6-Tetramethylheptane-3,5-dionate = dpm^-.

(21) D. F. Evans and M. Wyatt, *J. Chem. Soc., Chem. Commun.*, 312 (1972).

Table I. Chemical Shifts, Isotropic Shifts, Geometric Factors, and Calculated Isotropic Shifts for Eu(dpm)$_3$(3-pic)$_2$ at −115°

Assignment	$\frac{3\cos^2\theta - 1}{r^3}$	$\frac{\sin^2\theta\cos 2\Omega}{r^3}$	Chem shift, ppm	$\left(\frac{\Delta\nu}{\nu_0}\right)_{\text{obsd}^a}$	$\left(\frac{\Delta\nu}{\nu_0}\right)_{\text{calcd}^d}$	$\left(\frac{\Delta\nu}{\nu_0}\right)_{\text{calcd}^e}$
Methine	+0.0090	−0.0028	+29.2	+35.0[b]	+37.6	37.5
tert-Butyl	+0.0030	−0.0005	+10.1	+11.3[b]	+10.8	12.5
Methyl (1)	−0.0009	+0.0022	−15.7	−13.4	−11.3	−3.8
Methyl (2)	−0.0037	+0.0008	−18.5	−16.2	−14.1	−15.4
Meta (1)	−0.0017	+0.0038	−28.1	−20.9	−20.0	−7.1
Meta (2)	−0.0047	+0.0024	−29.4	−22.2	−23.3	−19.6
Ortho (1)	−0.0089	+0.0089	−69.5	−61.1	−61.2	−37.0
Ortho (2)	−0.0246	+0.0014	−87.2	−78.8	−78.1	−102.4
Para	−0.0015	+0.0029	*c*	*c*	−15.4	−4.52
					R = 0.038	R = 0.337

[a] The diamagnetic references for the 3-picoline protons were taken from free 3-picoline and for the dpm$^-$ chelate they were taken as CH$_3$ = −116 Hz and CH = −575 Hz as found for Lu(dpm)$_3$.[22] [b] Both the *tert*-butyl and methine peaks of the dpm$^-$ chelate are found upfield of Me$_4$Si and can be assigned by their relative areas, 18:1, respectively. [c] Unobserved, see text. [d] Calculated using eq 2. [e] Calculated using eq 1.

experiments with pyridine and 4-methylpyridine and similar low-temperature results are obtained. These results show that for a system of this type *the lanthanide-induced shifts cannot be explained by eq 1 where the magnetic axis passes through the nitrogen atom of the substrate.*

For complexes of twofold symmetry the LIS should be governed by an equation of the form

$$\frac{\Delta\nu_i}{\nu_0} = D_1\left\langle\frac{3\cos^2\theta_i - 1}{r_i^3}\right\rangle + D_2 \times \left\langle\frac{\sin^2\theta_i\cos 2\Omega_i}{r_i^3}\right\rangle \quad (2)$$

where $\Delta\nu_i$, ν_0, θ_i, and r_i have been previously defined, Ω_i is the angle which the projection of the ith vector into the x–y plane makes with the x magnetic axis, and the parameters D_1 and D_2 are related to magnetic anisotropy.[23]

The results of the X-ray crystal structure of Eu(dpm)$_3$(py)$_2$[18,19] were used to calculate the two geometric factors in eq 2 and these are listed in Table I. The magnetic z axis was defined as the C$_2$ axis passing through the methine carbon of the unique dpm$^-$ chelate. The x magnetic axis was refined by rotation about the z magnetic axis and the best fit was obtained when the x axis was rotated 8°, in the direction away from the center of the square face of the coordination polyhedron,[18,19] from a line which passes through the Eu ion and is parallel to the internitrogen vector. The methyl coordinates on the 3-picoline were calculated assuming tetrahedral angles and the methyl group was considered to be freely rotating. A better fit was obtained when the *tert*-butyl groups were considered to be nonrotating. A least-squares fit of the data using eq 2 yielded D_1 = 2950 ± 25 VVk/mol and D_2 = −3930 ± 180 VVk/mol (1 VVk = 10^{-6} cgsu). A comparison of calculated and observed isotropic shifts ($\Delta\nu/\nu_0$), using both eq 1 and 2, is given in Table I, along with the agreement factor R[24] defined by Willcott. While the para proton was not located, its calculated chemical shift using the results from eq 2 is −23.0 ppm, which would place it under the first downfield side band of the *tert*-butyl protons thus rendering it unobservable. The single peak for the para position is confirmed in experiments with 4-picoline which shows only a single coordinated 4-methyl peak at −9.48 ppm at −115°.

In conclusion we feel that this represents conclusive experimental evidence that the principal axis of symmetry does not lie along the line defined by the metal ion and the donor nitrogen, as has been assumed,[1–14] at least for complexes of this type. Finally, the much better fit, found by using eq 2 rather than eq 1 for calculating isotropic shifts, indicates that the single term equation often assumed[1–14] is too simple and that lanthanide shifts can be reproduced using the theoretically correct equation.[25]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

---

(22) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, 87, 5254 (1965).

(23) W. DeW. Horrocks, Jr., and E. S. Greenberg, *Inorg. Chem.*, 10, 2190 (1971).

(24) M. R. Willcott, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, 94, 1744 (1972).

(25) NOTE ADDED IN PROOF. W. DeW. Horrocks, Jr., and J. P. Sipe III, *Science*, 177, 994 (1972), has reported the single-crystal magnetic anisotropies for the entire series of Ln(dpm)$_3$(4-pic)$_2$ complexes. Those results show large values for both D_1 and D_2 and that the location of the magnetic axes is in agreement with our results.

Roger E. Cramer,* Ronald Dubois
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

Received September 21, 1972

Stereochemistry of Octadecacarbonylhexaosmium(0). A Novel Hexanuclear Complex Based on a Bicapped Tetrahedron of Metal Atoms

Sir:

The pyrolysis of dodecacarbonyltriosmium(0) provides[1] polynuclear complexes based on four, five, six, seven, and eight osmium atoms. The infrared spectra of Os$_4$(CO)$_{13}$, Os$_5$(CO)$_{16}$, Os$_6$(CO)$_{18}$, Os$_7$(CO)$_{21}$, Os$_8$(CO)$_{23}$, and Os$_5$(CO)$_{15}$C are similar in that no bands assignable to bridging carbonyl groups are observed. It is reasonable to assign an octahedral arrangement of metal atoms in Os$_6$(CO)$_{18}$ with three terminal carbonyl groups per osmium, since such a stereochemistry would reflect an effective "rare-gas" electronic configuration about each metal. An X-ray analysis of Os$_6$(CO)$_{18}$, summarized here, fails to support this prediction.

The crystals (toluene–hexane) are triclinic with a =

---

(1) C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organometal. Chem.*, 37, C39 (1972).