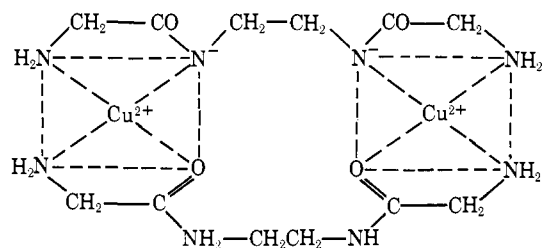


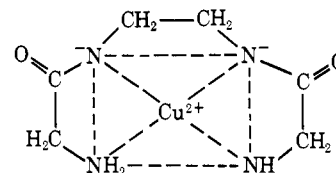
copper(II) chelates has been discussed by Bai and Martell<sup>7</sup> and some of the possibilities are shown by structures IIIa, IIIb, and IIIc. Previously structure IIIa



IIIc Binuclear Cu(II)-DGEM Chelate,  $\text{CuL}(\text{H}_2\text{L})^{2+}$   
(open, or ethylene-bridged, form)

was the preferred possibility, involving bridging of the two copper(II) ions by the strongly binding  $\text{N}^-$  groups. Since this gives a Cu(II)-Cu(II) distance that is considerably shorter than the experimental distance determined by esr, this arrangement may now be ruled out as a possible structure. Structures IIIb and IIIc on

the other hand lead to separations of the copper(II) ions which would be comparable with the experimental distance. The data, of course, do not allow any further distinction to be made but one can speculate that structure IIIb is the stronger proposition since it provides equal distribution of the strongly coordinated negative deprotonated, amidic nitrogens between the two Cu(II) ions, and since the completely deprotonated ligand,  $\text{H}_2\text{L}^{2-}$ , indicated in IIIc has been found<sup>7</sup> to form a very stable 1:1 chelate, IV, which does not react further



IV Cu(II)-DGEM Chelate,  $\text{Cu}(\text{H}_2\text{L})$

with additional ligand.

## Dipolar Shifts and Structure in Aqueous Solutions of 3:1 Lanthanide Complexes of 2,6-Dipicolinate<sup>1</sup>

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**Abstract:** Tris tridentate chelate complexes of 2,6-dipicolinate (dpa) and tripositive lanthanides yield isotropic proton magnetic resonance shifts that increase upfield for  $\text{Eu} < \text{Yb} < \text{Er} < \text{Tm}$  and downfield for  $\text{Sm} < \text{Nd} < \text{Pr} < \text{Ho} < \text{Tb} < \text{Dy}$ . Shifts in the last half of the lanthanide series are all greater than any of those in the first half. For the last three complexes in each list the para and meta hydrogens are sufficiently shifted so that their resonances appear separately. The pair of meta hydrogens is always shifted more than the para, and for the last half of the lanthanide series, the ratio of chemical shifts is  $1.14 \pm 0.02$ . This ratio may be accommodated by an exclusively dipolar origin for the isotropic shift consistent with a proposed structure. The tris tridentate complexes possess  $D_3$  symmetry with the three nitrogen donors in a plane normal to the  $C_3$  axis. Each planar ligand makes an angle of about  $49^\circ$  with the plane containing the three nitrogen donors. The nine donor atoms describe the surface of a prolate ellipsoid of revolution with the long axis the  $C_3$  axis. For the Eu and Pr complexes a small upfield contact contribution is required if the structure and the dipolar shift ratio of 1.14 are to be retained. Excess dpa and other ligands undergo shifts in the opposite directions from the first three more strongly bound dpa ligands.

Most of the numerous applications of lanthanide shift reagents have been made on adducts of neutral complexes in nonaqueous solvents. Despite widespread interest in the use of  $\text{Eu}^{3+}$ ,  $\text{Pr}^{3+}$ , and other paramagnetic lanthanide complexes as shift reagents in structural analysis, few studies have been conducted on the chemical shifts occurring in more strongly bound ligands. When the extent of complex formation is known more definite statements may be made about the origin of isotropic shifts in the proton magnetic resonance spectrum. In this paper we report chemical shifts experienced by water-soluble tris complexes of the tridentate ligand 2,6-dipicolinate (dpa).

For an investigation of proton magnetic resonance (pmr) spectra of lanthanide complexes in aqueous

solutions 2,6-dipicolinate offers the advantages of a chelatable ligand with two meta for each para hydrogen so that pmr peaks for the two kinds of protons are readily identifiable. Formation constants and thermodynamic properties of lanthanide complexes indicate that relatively strong complexes are formed with 3 mol of ligand for one lanthanide.<sup>2</sup> The rigid geometry of the aromatic ligand with two coplanar oxygen donors offers an excellent opportunity for assessing the relative importance of contact and dipolar (pseudocontact) interactions induced by paramagnetic lanthanides. Contact interactions are weak in lanthanide complexes, and dpa should provide a favorable case for their observation if they do occur.

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## Results

In the presence of about 0.1 *M* paramagnetic lanthanide in basic solutions the pmr peaks of dpa undergo marked upfield or downfield shifts until the dpa to Ln<sup>3+</sup> ratio exceeds three when peaks characteristic of excess ligand also appear. Thus three molecules of dpa are strongly bound to each metal ion to give Ln(dpa)<sub>3</sub><sup>3-</sup>. Any additional ligand exchanges slowly with bound ligand. The existence of a predominantly 3:1 complex in the presence of excess ligand was verified by potentiometric titration. A solution containing a 3:1 molar ratio of dpa to Tb<sup>3+</sup> gives a sharp end point by pH 4 while the last equivalent of base added to a solution containing a 4:1 ratio titrates a group with p*K*<sub>a</sub> = 4.5, identical with the p*K*<sub>2</sub> found for the free ligand in absence of lanthanide. All further results refer to 3:1 complexes, Ln(dpa)<sub>3</sub><sup>3-</sup>.

The isotropic proton resonance shifts for the lanthanide complexes of dpa are listed in Table I. There

**Table I.** Isotropic Shifts of Tris Chelates of 2,6-Dipicolinate Complexes of Tripositive Lanthanides

Ln(dpa) <sub>3</sub> <sup>3-</sup>	Shift, ppm	
	meta	para
La		0.0
Pr		-3.9
Nd		-2.3
Sm		-0.4
Eu	+4.1	(+3.1)
Tb	-29.2	-26.4
Dy	-32.2	-28.3
Ho	-16.5	-14.4
Er	+9.9	+8.6
Tm	+20.6	+18.0
Yb	+7.3	+6.5

is little shift from the pmr peak positions of free dpa upon formation of La(dpa)<sub>3</sub><sup>3-</sup>. All isotropic shifts are calculated by reference to this diamagnetic complex. Table I shows that the first four paramagnetic lanthanides give modest shifts upfield or downfield while the last six yield large, even huge, shifts. Contrary to results from many other studies, these shifts are fully developed as they refer to completely complexed ligand that is not undergoing exchange with unbound ligand. All the results in Table I were obtained in solutions containing a 4:1 molar ratio of dpa to lanthanide. For all paramagnetic complexes of Table I peaks of bound and excess unbound ligand appear separately. The first three paramagnetic complexes of Table I did not shift enough to give a separation of meta and para resonances. The position of the para peak for the Eu complex is uncertain as it probably resides under the residual water peak.

Of the complexes of Table I that yield separate peak positions for meta and para protons, the line width of the Eu complex is about average and that of the Yb complex is the narrowest. Only in the last case was the dipolar shift great enough and the line width sufficiently narrow so that a five-line spectrum appeared allowing determination of *J* = 6.9 cps for coupling between meta and para hydrogens in dpa. Lowering the temperature sharpens the peaks in several of the complexes.

Each solution in Table I was internally referenced to *tert*-butyl alcohol which gave no evidence of complexing. The shift of internal *tert*-butyl alcohol from external TMS varies linearly with the paramagnetic ion concentration, permitting calculation of accurate magnetic susceptibilities.<sup>3</sup> Tetramethylammonium ion (TMAC) interacts with Ln(dpa)<sub>3</sub><sup>3-</sup>. Increasing the complex to TMAC ratio caused the peaks of the ligand and TMAC to shift in opposite directions for both Ho and Yb complexes. In contrast Yb(NTA)<sub>2</sub><sup>3-</sup> gave no shifts with TMAC. For the Tb, Ho, Dy, and Tm complexes of Table I, the meta peaks of excess ligand are sufficiently shifted so that they are separate from the relatively unshifted para peaks. The separations of meta from para peaks for 1 mol of excess ligand are as follows: Tb (0.56 ppm), Dy (0.35), Ho (0.25), and Tm (0.37). These shifts are opposite in direction to those of the three strongly bound ligands in each complex.

The nature of the isotropic shifts in the lanthanide complexes of dpa may be compared with those observed for octahedral Ni(dpa)<sub>2</sub><sup>2-</sup>. The peak due to bound meta hydrogen is shifted 54.7-ppm downfield and that due to the para hydrogen 13.5-ppm downfield from excess unbound dianionic ligand. The ratio of shifts in this Ni(II) complex is markedly different from those of the lanthanide complexes and is similar to those reported for other pyridine type ligands coordinated to Ni(II), where only contact interactions are operative.<sup>4</sup> For the analogous octahedral Co(II) complex, the downfield shifts of the meta and para hydrogens are 82.2 and 20.7 ppm, respectively. For both octahedral metal ion complexes, the ratio of meta to para isotropic shifts is 4.0, and only a small dipolar contribution to the isotropic shift in the Co(II) complex is indicated.<sup>5</sup>

## Discussion

Whether to upfield or downfield the pair of meta protons of 2,6-dipicolinate is always shifted more than the para proton. Though the variation in observed ratios of chemical shifts of meta to para protons for the last six complexes in Table I seems to be beyond experimental error, we utilize the average value of 1.14 ± 0.02 as representative of the last half of the lanthanide series. Since we are not dealing with chemical shifts of loosely bound adducts, which do not bind with axial symmetry in a solid,<sup>6</sup> but rather with three tightly bound ligand molecules, an excellent complex is available for testing whether the isotropic shift is predominantly dipolar in origin. A tris chelate complex of like ligands is expected to possess axial symmetry so that the equation describing the ratio of dipolar shifts of meta to para hydrogens is given by<sup>7</sup>

$$R = \frac{\Delta H_m}{\Delta H_p} = \left(\frac{r_p}{r_m}\right)^3 \frac{(3 \cos^2 \chi_m - 1)}{(3 \cos^2 \chi_p - 1)} \quad (1)$$

The distance term in eq 1 is dependent upon the geometry of a single ligand bound to Ln while the angular

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term also depends upon the disposition of the three ligands about the Ln. These two terms are considered in order.

Intraligand distances derived from accurate bond lengths and angles reported for pyridine<sup>8</sup> and utilized in the subsequent calculations are as follows: from N to H<sub>p</sub>, 3.887 Å; from H<sub>m</sub> perpendicular to line joining N and H<sub>p</sub>, 2.152 Å; and from N to previous right angle intersection, 2.600 Å. The distance from Ln to H<sub>p</sub>,  $r_p = d + 3.887$ , where  $d$  is the Ln-N distance. The distance from Ln to H<sub>m</sub>,  $r_m$ , is found from a right triangle by  $r_m^2 = (2.152)^2 + (d + 2.600)^2$ . These geometrical relations may be used to show that the distance term in eq 1 is relatively unaffected by the exact placement of Ln; for  $d = 2.5$ – $2.7$  Å,  $(r_p/r_m)^3 = 1.53$ .

Consideration of the angular part of eq 1 permits deduction of the details of the arrangement of the ligands about Ln. A likely arrangement of three dpa ligands about a single lanthanide is as in mononuclear octahedral tris acetylacetonate complexes. The three dpa ligands can be similarly disposed to give a nine-coordinate complex with  $D_3$  symmetry. The three nitrogen atoms lie in a plane normal to the  $C_3$  axis and the angle  $\chi_p$ , between the  $C_3$  axis and the Ln to H<sub>p</sub> line is 90°. The angle  $\chi_m$  between the  $C_3$  axis and the Ln to H<sub>m</sub> line may be found by substituting the average value of  $R$  along with the other values indicated in eq 1 to obtain  $\cos^2 \chi_m = 0.085$  and  $\chi_m = 73.0^\circ$ .

The experimentally inferred value of  $\chi_m$  may be related to  $\alpha$ , the angle that the plane of the aromatic dpa ring forms with the plane normal to the  $C_3$  axis containing the three nitrogen donor atoms. It may be shown that  $\sin \alpha = (r_m \cos \chi_m)/2.152$  and hence that  $\sin^2 \alpha = [1 + (d + 2.600)^2/(2.152)^2] \cos^2 \chi_m$ . This equation shows that  $\alpha$  is sensitive to the choice of  $d$ . Utilizing for  $d$  the value 2.53 Å found<sup>6</sup> for the Ho-N distance in the bis 4-picoline adduct of Ho(dpm)<sub>3</sub> yields  $\alpha = 49.0^\circ$ . For each increase of 0.01 Å in  $d$ ,  $\alpha$  increases by 0.1°. Further calculation shows that reducing the chemical shift ratio  $R = 1.14$  by 0.01 at constant  $d$  increases  $\alpha$  by 0.8°.

That the deduced value of  $\alpha$  near 49° exceeds that at 45° is probably due at least in part to the geometrical requirements of a tridentate dpa ligand. For Ln-N bond lengths shorter than 2.8 Å, the Ln-O bond lengths are of necessity longer. As a consequence repulsion between carboxylate groups from different ligands in the complex is minimized with a small increase in the value of  $\alpha$  above 45°. Thus the nine donor atoms in the tris tridentate complex describe the surface of a prolate ellipsoid of revolution with the long axis the same as the  $C_3$  axis of the complex. Thus the chemical shift ratio of meta to para protons in a ligand strongly bound to lanthanides in the last half of the

series is adequately accounted for by a dipolar mechanism.

At least two meta to para chemical shift ratios in the first half of the lanthanide series do not correspond to the 1.14 value. For Eu the ratio is about 1.3 and for Pr a value near unity is indicated as no additional peak appears at the position required if the ratio were 1.14. The structure of the complex might differ from that considered above or there may be a small contact contribution to the isotropic shift. A dipolar shift ratio of 1.14 is accommodated for Eu and Pr by including an upfield contact contribution of +0.2 and +0.8 ppm for the para and meta protons, respectively, for both metal ions. However, the contact shift of Eu is expected to be greater in magnitude and opposite in sign to that of Pr. In the absence of other information the contact shift ratio was taken as 4.0 for the two kinds of protons. Thus the contribution to the isotropic shift of the commonly employed Eu<sup>3+</sup> and Pr<sup>3+</sup> may not be exclusively dipolar in origin, and some caution seems indicated before deriving geometric information from a wholly dipolar analysis of complexes with aromatic ligands exhibiting small isotropic shifts.

The signs of dipolar shifts of bound dpa in the Ln-(dpa)<sub>3</sub><sup>3-</sup> complexes correlate with the anisotropy of the magnetic susceptibility arising in less than cubic ligand fields.<sup>7,9</sup> Weakly interacting adducts exhibit, for a given lanthanide, dipolar shifts in the direction opposite to those of dpa, indicating that they approach the complex within the 55° cone of the  $C_3$  axis. Signs observed in most applications of shift reagents to organic systems correspond to those observed for weakly interacting adducts in this paper and are opposite to those of three strongly bound dpa ligands.

## Experimental Section

Lanthanides were obtained as oxides from the Michigan Chemical Corp. and Research Organic/Inorganic Chemical Corp. (Roc/Ric). Stock solutions were prepared by dissolving the oxides in DCl. Complexes with dipicolinic acid (Aldrich Chemical Co.) were prepared by mixing a solution of dpa which had been neutralized with 2 equiv of base with a stock solution of the appropriate lanthanide ion and adjusting the pH to within the 8–11 range. The pH of the mixtures was monitored with a Beckman Model GS pH meter with a Sargent pH combination electrode (5-30070-10). A typical solution 0.10 M in lanthanide and 0.40 M in dpa would at low pH contain solid protonated dpa, which is insoluble. As the pH of the mixture is raised solid dpa dissolves by pH 4, after which the solution remains clear until pH 11.5 when hydroxide starts to precipitate. When 0.10 M solutions of the dpa complex are left standing a complex crystallized out over a period of hours and could be redissolved by heating. It was not possible to obtain a solution of the complex more concentrated than 0.15 M. Pmr measurements were made on Hitachi Perkin-Elmer R-20 and Varian HA-100 spectrometers. The latter was operated in HR mode and a standard sample of CCl<sub>4</sub>-TMS was used to calibrate the spectra. Probe temperature was 35°.

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