A:B:M:X = 1.0:4.4:1.1:1.0. J_{AB} = 148.0 Hz; J_{BM} = 9.7 Hz; J_{BX} = 21.5 Hz; J_{MX} = 7.1 Hz.

Anal. Calcd for $C_2CsF_7O_3S_2$: C, 5.97; Cs, 33.06; F, 33.1; S, 15.95. Found: C, 6.00; Cs, 33.13; F, 33.6; S, 15.95.

Reaction of 5 and CsF. Finely ground cesium fluoride (2.80 g, 18 4 mmol) was dried (3 days, 115 °C, high vacuum) in a 20-mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve. Then 0.19 g of **5** (0.76 mmol) was added by vacuum transfer (−196 °C); the vessel was maintained at 40 °C (19 h). The weight gain of the vessel was 0.16 g, after the volatile material had been removed by vacuum transfer. An infrared spectrum of the solid showed vibrational bands that were attributable to the complex $Cs^+[F_5SC(SO_2F)COF]^-$. A ^{19}F NMR spectrum of the acetone extract, which was obtained as described below, was also consistent with only the presence of the cesium compound.

The reaction mixture was rinsed several times with acetone (4 × 3 mL), the acetone extract was filtered, the filter residue was washed with several small portions of acetone, and the solution was brought to dryness, leaving 0.15 g of the cesium salt, **6**. Yield: 49.1%.

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Metal Complexes with Tetrapyrrole Ligands. 53.[1] ^1H NMR Spectrum of Dicerium(III) Tris(octaethylporphyrinate), $Ce_2(OEP)_3$: Evidence for Alkyl Group Steric Interaction

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The synthesis and single-crystal, solid-state structure of a novel dilanthanide tris(porphyrinate), $Ce_2(OEP)_3$, was previously reported.[3] In this triple decker each cerium atom is sandwiched between two octaethylporphyrin rings as illustrated in Figure 1. Two salient structural features are the strong C_{4v} doming of the outer OEP rings and the 24.5° staggering of adjacent OEP rings, both effects undoubtedly to relieve inter-ring alkyl crowding. This paper is concerned with the ^1H NMR spectrum of $Ce_2(OEP)_3$ in CCl_4, the analysis of the isotropic shifts of this paramagnetic binuclear metalloporphyrin, and the structural information that can be deduced regarding the extent of alkyl congestion and doming in solution. We also report the ^1H NMR spectra of the previously described homologues of Pr,[4] Nd,[5] Sm,[5] and Eu.[6]

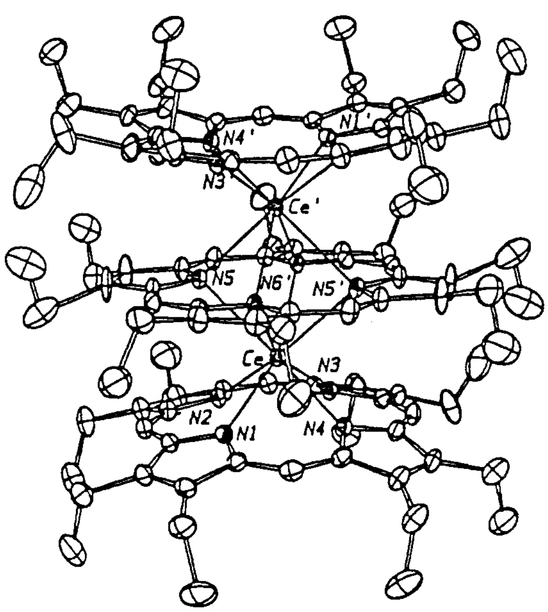

Figure 1. ORTEP plot of $Ce_2(OEP)_3$ (taken from ref 1 with permission).

Table I. $Ln_2(OEP)_3$ ^1H NMR Isotropic Shifts[a]

	CH_3		CH_2		meso	
	outer	inner	outer	inner	outer	inner
Ce	1.19	−7.59	−3.69 −2.82	−9.42	−4.72	−16.25
Pr	0.95	−5.93	−2.76 −2.04	−6.80	−7.28	−12.90
Nd	0.45	−2.79	−1.24 −0.72	−3.01	−3.53	−7.31
Sm	0	−0.63	−0.28 −0.32	−0.89	−0.39	−1.54
Eu	−0.61	2.16	−0.57 1.42	1.48	4.58	5.46

[a] Shifts are in ppm relative to $La_2(OEP)_3$ in CCl_4 at 293 K (see also ref 3).

The ^1H NMR spectrum of $Ce_2(OEP)_3$ was previously described.[3] The isotropic shifts relative to those of diamagnetic $La_2(OEP)_3$ are listed in Table I and are due to the presence of the paramagnetic Ce^{3+} ions. Two sets of OEP proton resonances are observed and attributed to the outer and inner OEP rings, respectively. Since the outer rings do not possess a symmetry plane, the outer ring α-CH_2 protons are diastereotopic and two resonances, separated by 0.87 ppm, result.

The observed isotropic shift ($\Delta H/H$) for any proton is the sum of two components: $\Delta H/H = (\Delta H/H)_{dip} + (\Delta H/H)_{con}$. The contact shift, $(\Delta H/H)_{con}$, is directly related to spin delocalization via covalency, whereas the dipolar shift, $(\Delta H/H)_{dip}$, results from a dipolar, through-space interaction and is a function of the magnetic anisotropy and geometry of the complex.[7] From numerous NMR studies of the interaction of organic substrates with lanthanide(III) chelates, commonly called "lanthanide shift reagents", it is accepted that ^1H NMR lanthanide-induced isotropic shifts are primarily dipolar in origin.[8,9] This seems especially certain for protons four or more bonds removed from the paramagnetic lanthanide ion.[10] We will proceed with this assumption for $Ce_2(OEP)_3$; hence, $\Delta H/H = (\Delta H/H)_{dip}$.

The dipolar shift for nuclei in complexes of axial symmetry is given by eq 1,[11] where $\chi_\parallel$ and $\chi_\perp$ represent the principal com-

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[1] Part 52: Buchler, J. W.; Kihn-Botulinski, M.; Scharbert, B. *Z. Naturforsch.* **1988**, *43B*, 1371.

[2] (a) Technische Hochschule Darmstadt. (b) Western Washington University.

[3] Buchler, J. W.; DeCian, A.; Fischer, J.; Kihn-Botulinski, M.; Paulus, H.; Weiss, R. *J. Am. Chem. Soc.* **1986**, *108*, 3652.

[4] Buchler, J. W.; Knoff, M. In *Optical Spectra and Structure of Tetrapyrroles*; Blauer, G., Sund, H., Eds.; de Gruyter: West Berlin, 1985.

[5] Kihn-Botulinski, M. Ph.D. Dissertation, Technische Hochschule Darmstadt, 1986.

[6] Buchler, J. W.; de Cian, A.; Fischer, J.; Kihn-Botulinski, M.; Weiss, R. *Inorg. Chem.* **1988**, *27*, 339.

[7] Bertini, I.; Luchinat, C. *NMR of Paramagnetic Molecules in Biological Systems*; Benjamin/Cummings: Menlo Park, NJ, 1986.

[8] Williams, R. J. P. In *Structure and Bonding*; Springer-Verlag: West Berlin, 1982; Vol. 50.

[9] Morrill, T. C. In *Lanthanide Shift Reagents in Stereochemical Analysis*; Morrill, T. C., Ed.; VCH: New York, 1986.

[10] Kemple, M. D.; Ray, B. D.; Lipkowitz, K. B.; Prendergast, F. G.; Rao, B. D. N. *J. Am. Chem. Soc.* **1988**, *110*, 8275.

[11] Bleaney, B. *J. Magn. Reson.* **1972**, *8*, 91.

0020-1669/89/1328-3770$01.50/0

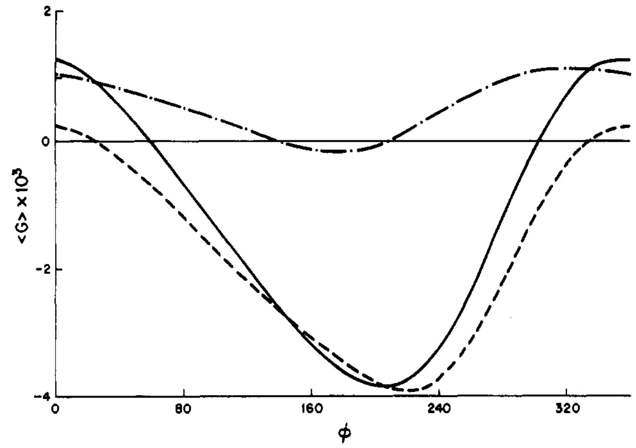


Figure 2. Variation of the geometric factor, G (—), of the β-CH_3 protons and its components, G_1 (- - -) and G_2 (-·-), as a function of the rotational angle, ϕ, shown in the Newman projection A.

ponents of the magnetic susceptibility, r is the proton–metal distance, θ is the angle that the vector **r** makes with the principal symmetry axis, and N is Avogadro's number. The term $(3\cos^2$

$$(\Delta H/H)_{\mathrm{dip}} = \frac{1}{3N}(\chi_\parallel - \chi_\perp)(3\cos^2\theta - 1)/r^3 \qquad (1)$$

$\theta - 1)/r^3$ is commonly called the geometric factor, G, and for any two protons, i and j, $(\Delta H/H)_{\mathrm{dip,i}}/(\Delta H/H)_{\mathrm{dip,j}} = G_i/G_j$. Since the interaction of electron spins of the two cerium(III) ions is negligible at ambient temperature,[12] the dipolar shifts for each OEP ring—inner and outer—are influenced independently by each cerium(III):

$$\text{outer ring} \quad \Delta H/H = (\Delta H/H)_{\mathrm{dip,Ce(1)}} + (\Delta H/H)_{\mathrm{dip,Ce(2)}}$$

$$\text{inner ring} \quad \Delta H/H = 2(\Delta H/H)_{\mathrm{dip,Ce(1)}}$$

In the above notation Ce(1) is proximal to and Ce(2) is distal to the outer OEP ring. Intuitively it is expected that the outer ring dipolar shifts will be influenced primarily by the proximal cerium, i.e., $(\Delta H/H)_{\mathrm{dip,Ce(1)}} > (\Delta H/H)_{\mathrm{dip,Ce(2)}}$, and, hence, the inner ring dipolar shifts will be substantially larger than those of the outer ring. This is indeed observed.

In the analysis of the dipolar shifts, we have attempted to find a solution geometry for $Ce_2(OEP)_3$ for which there is reasonable agreement between experimental dipolar shift ratios and calculated geometric factor ratios. As a geometrical model we used the structural parameters from the single-crystal diffraction results. Cerium was placed 2.50 Å from the outer OEP nitrogen atoms and 2.76 Å from the inner nitrogen atoms. The outer OEP was fashioned to replicate the doming found in the solid-state structure, while the inner OEP ring was kept planar. The degree of doming and the cerium position could be changed systematically, and geometric factors for each geometry were calculated by computer as reported previously.[13,14] Alkyl group bond rotation was also incorporated and evaluated at 1° intervals.

Outer OEP Ring. Four resonances are observed as follows: meso, 3.47 ppm; α-CH_2, 0.72 ppm and −0.15 ppm; β-CH_3, 2.08 ppm. The α-CH_2 protons are disastereotopic with *unequal* isotropic shifts of −2.82 and −3.69 ppm, *and most unexpectedly the* β-CH_3 *isotropic shift is opposite in sign from that of* α-CH_2. These data, assuming the absence of a contact contribution to the isotropic shift, suggest limited rotation of the alkyl groups. To test this properly, geometric factors were calculated for free rotation and various restricted-rotation schemes. With use of the solid-state geometry as an initial model (vide supra) free rotation can be dismissed readily, because the calculated geometric factors do not match the dipolar shifts.[15] Furthermore, there is no reasonable geometry with free rotation incorporated for which an upfield β-CH_3 dipolar shift (positive geometric factor) is predicted. The variation of G and its components G_1, which refers to the proximal Ce(1), and G_2, which refers to the distal Ce(2), was calculated as a function of rotation angle—rotation about the α-C to pyrrole-C bond—and is presented in Figure 2. The initial point, $\phi = 0°$, refers to the rotamer A (shown in a Newman type projection) in which β-CH_3 is above the outer OEP ring and the z projection of its α-C to β-C bond is parallel to the C_4 molecular rotation axis. As expected, G_1 is on the average substantially larger in magnitude than G_2, since Ce(2) is more distant from the outer OEP ring. For the most part, G_1 and G_2 are opposite in sign, but surprisingly there is a region of space, corresponding to $\phi = 0 \pm 60°$, where G_1 is small, G_2 dominates in effect, and consequently $G > 0$. This is precisely the region for which positive β-CH_3 dipolar shifts are predicted. Thus, the β-CH_3 groups should, on the average, be located above the outer OEP ring and away from the central OEP ring and its alkyl groups.[16]

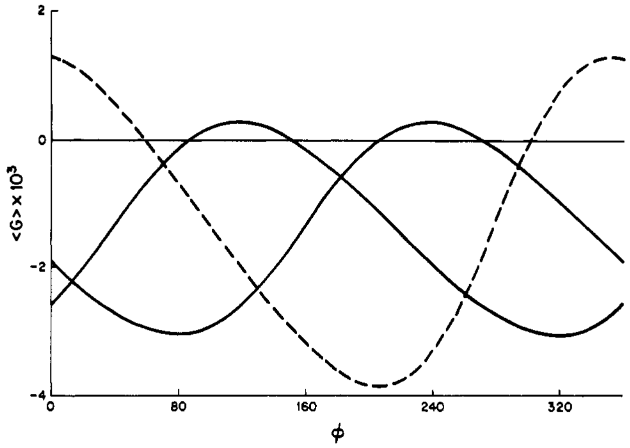
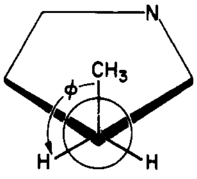


Figure 3. Variation of the geometric factors of the α-CH_2 (—) and β-CH_3 (- - -) protons as a function of the rotational angle ϕ.

Table II. Comparison of Relative Isotropic Shifts and Calculated Geometric Factors

proton[a]	$(\Delta H/H)_{\mathrm{dip}}$	$\langle G\rangle^{b,c}$	proton[a]	$(\Delta H/H)_{\mathrm{dip}}$	$\langle G\rangle^{b,c}$
meso (o)	1.28	1.39	meso (i)	4.40	4.34
α-CH_2 (o)	1	1	α-CH_2 (i)	2.55	2.62
	0.764	0.807	β-CH_3 (i)	2.06	2.05
β-CH_3 (o)	−0.322	−0.318			

[a] o = outer ring; i = inner ring. [b] Geometric factors are relative to the high-field, outer α-CH_2 resonance for which $G = -2.23 \times 10^{-3}$ Å^{-3} (inner OEP) and $G = -3.11 \times 10^{-3}$ Å^{-3} (outer OEP). [c] Calculated geometric factors are predicated upon limited rotation for the inner and outer ring alkyl groups (see text).



rotamer A

The variation of G with ϕ for the diastereotopic α-CH_2 protons is shown in Figure 3. While the best static-position fit of relative geometric factors and isotropic shifts for the three outer ring alkyl resonances—α-CH_2 and β-CH_3—is obtained for $\phi = 30°$ (defined for β-CH_3), there undoubtedly must be substantial rotational

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(12) The magnetic moment per cerium(III) is constant, 2.23 μ_B, from 20 to 298 K: Kihn-Botulinski, M. Ph.D. Dissertation, Technische Hochschule Darmstadt, 1986.

(13) Botulinski, A.; Buchler, J. W.; Tonn, B.; Wicholas, M. *Inorg. Chem.* **1985**, *24*, 3239.

(14) Botulinski, A.; Buchler, J. W.; Lee, Y. J.; Scheidt, W. R.; Wicholas, M. *Inorg. Chem.* **1988**, *27*, 927.

(15) The geometric factors for free rotation are as follows: meso, −0.003 11 Å^{-3}; α-CH_2, −0.001 39 Å^{-3}; β-CH_3, −0.001 29 Å^{-3}.

(16) Were free rotation to occur for both inner and outer OEP alkyl groups, the β-CH_3 carbons (inter-ring) would approach as closely as 1.43 Å.

motion of these alkyl groups. It should be clear, however, that a unique conformational model involving a statistical average of rotamers cannot be specified from only four NMR observables. Instead there are many closely related rotational models that appear reasonable, but all must have the β-CH_3 groups spending a great majority of the time above the outer OEP ring. One plausible model has the eight β-CH_3 groups centered above the outer OEP ring with $\phi = 0°$. The average geometric factors for an equally populated set of rotamers, $\phi = 0 \pm 60°$, are listed in Table II, and there is good agreement (within 10%) with the experimental dipolar shift ratios.[17] A better fit could, perhaps, be obtained by making minor adjustments in bond lengths and angles; however, such "fine tuning" is not warranted, considering the above limitations. The aforementioned model for reasons of simplicity has the eight β-CH_3 groups above the outer OEP ring at all times. It is also possible to include small excursions of β-CH_3 into the region near the inner OEP ring as long as the mathematical averaging over all rotamer contributions yields the proper geometric factor ratios.

Inner OEP Ring. Three resonances are observed for the meso, α-CH_2, and β-CH_3 protons at −8.12, −5.33, and −5.00 ppm, respectively. With the use of the solid-state geometry as an initial model (vide supra), the respective geometric factors were calculated by assuming equal interaction with both cerium ions. There are three rotational models that preserve the plane of symmetry of the inner OEP: (1) complete and free rotation; (2) restricted rotation centered about $\phi = 270°$ for β-CH_3 (see rotamer A); (3) restricted rotation centered about 90° for β-CH_3. The last model has poor agreement of geometric factors and isotropic shifts and can be discarded. At $\phi = 90°$, adjacent β-CH_3 carbon atoms approach most closely, 1.48 Å, and it seems unlikely that any model of restricted rotation would feature this as its central rotamer.[18] While free rotation of alkyl groups, model 1, offers acceptable mathematical agreement,[19] model 2 is preferable with adjacent β-CH_3 groups being most distant at $\phi = 270°$ and rotating about this position. The best fit is obtained for $\phi = 270 \pm 130°$ as listed in Table II, and this specifically excludes that region of space where the β-CH_3 groups would be in closest proximity.

We have prepared other members of the $Ln_2(OEP)_3$ series[5] by the synthetic procedure used for $Ce_2(OEP)_3$.[3] The compounds and their isotropic shifts are listed in Table I. The shifts for Ln = Pr, Nd, and Sm are qualitatively similar—positive β-CH_3 shift, for example—but are too small in magnitude for computer modeling of the geometry. The binuclear $Eu_2(OEP)_3$ complex also has relatively small isotropic shifts which are opposite in sign to that of $Ce_2(OEP)_3$ because of a change in sign of $\chi_{\parallel} - \chi_{\perp}$, a change that is anticipated theoretically[20] and is consistent with other experimental studies.[21,22]

In summary, it is apparent that the ^1H dipolar shifts provide compelling evidence for inter-ring steric crowding and subsequent limited rotation of the outer OEP alkyl groups such that the outer β-CH_3 groups stay far away from the inner OEP ring. It also appears likely that there is limited rotation of the inner OEP alkyl groups in order to minimize intra-ring steric crowding.

Experimental Section

All dilanthanide(III) tris(octaethylporphyrinates) were prepared by the reaction of octaethylporphyrin and the respective lanthanide(III) tris(acetylacetonate) in refluxing trichlorobenzene under a nitrogen atmosphere as described in detail elsewhere for $Ce_2(OEP)_3$[3] and $Eu_2(OEP)_3$.[6] Except for $Eu_2(OEP)_3$, the percent yield decreased with each successive lanthanide, and no product could be isolated for Ln = Gd–Lu.

The ^1H NMR spectra were obtained on a Bruker WM 300-MHz spectrometer as previously described.[3]

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(17) If rotation becomes more extensive, however, the agreement between relative values of G and $\Delta H/H$ progressively worsens.

(18) The adjacent β-CH_3 group in the symmetry-equivalent conformation has $\phi = 270°$.

(19) The geometric factors for free rotation are as follows: meso, −0.004 84 $Å^{-3}$; α-CH_2, −0.002 83 $Å^{-3}$; β-CH_3, −0.002 46 $Å^{-3}$.

(20) Golding, R. M.; Pyykkö, P. *Mol. Phys.* **1973**, *26*, 1389.

(21) Horrocks, W. D., Jr.; Sipe, J. P., III. *Science* **1972**, *177*, 994.

(22) Alsaadi, B. M.; Rossotti, F. J. C.; Williams, R. J. P. *J. Chem. Soc., Dalton Trans.* **1980**, 597.

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Preparation and Characterization of the Monomeric Copper(II) Siloxide Complex $Cu[OSi(OCMe_3)_3]_2(py)_2$

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Trialkoxysiloxy ligands, $-OSi(OR)_3$, have not been extensively employed in transition-metal chemistry. Our interest in these ligands stems from their potential to form new types of siloxy complexes with interesting chemical properties. For example, $M-OSi(OR)_3$ complexes may exhibit properties that resemble catalytic metal species supported on a silica surface.[1] Also, such compounds may serve as convenient molecular precursors to oxide and silicate materials via hydrolysis or thermolysis.[2,3] To our knowledge, the only transition-metal trialkoxysiloxy complexes that have been reported are the titanium derivatives $(RO)_3TiOSi(OR)_3$ (R = ^{n}Pr,[4] ^{t}Bu[5]), $[(^tBuO)_3SiO]_3Ti(O^iPr)$,[3] and $[(^tBuO)_3SiO]_2TiX_2$, (X = O^iPr, acac)[3] and the zirconium complexes $Zr[OSi(O^tBu)_3]_4$[6] and $[(^tBuO)_3SiO]_2ZrX_2$ (X = O^iPr, acac).[6]

Here we report the synthesis, characterization, and molecular structure of the copper(II) siloxide complex $Cu[OSi(O^tBu)_3]_2(py)_2$. This compound is unusual, since copper(II) alkoxides are generally highly associated and insoluble.[7] In addition, siloxy derivatives of copper are quite rare, and no well-characterized examples appear to have been reported for copper(II). An ill-defined siloxy complex, $(Ph_2SiO)_x(CuO)_y$, formed by addition of $Ph_2(ONa)SiOSi(ONa)Ph_2$ to $CuCl_2$, was reported to rapidly decompose to CuO and c-$Ph_8Si_4O_4$,[8] although $Cu[OSi(OH)_2Ph]_2$ and related polymeric derivatives have been claimed.[9] Schmidbaur has reported a series of copper(I) compounds, $[CuOSiMe_3]_4$ and $(Me_3P)_xCuOSiMe_3$ (x = 1–3), that are polymeric with bridging siloxide ligands.[10]

Results and Discussion

Addition of 2 equiv of $NaOSi(O^tBu)_3$ to $CuBr_2$ in tetrahydrofuran results in a yellow solution from which a mixture of green and yellow crystals can be isolated. Numerous attempts failed to separate these products by fractional crystallization or to drive the reaction to a single product by changing reaction conditions. These products have therefore not been characterized, but we know that neither contains solvent or bromide. This mixture therefore probably contains $\{CuOSi(O^tBu)_3\}_n$ and/or $\{Cu[OSi(O^tBu)_3]_2\}_n$ species.

A single copper(II) siloxide complex, $Cu[OSi(O^tBu)_3]_2(py)_2$, was isolated by addition of pyridine to the above reaction mixture. This paramagnetic ($\mu_{eff} = 1.16\ \mu_B$ at 34 °C in benzene solution; Evans method[11]) complex is pale green and soluble in saturated hydrocarbons. Because there is a great lack of structural data

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