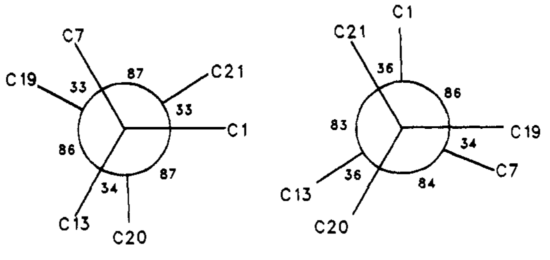

II I

**Figure 3.** Newman projections of I and II along the Ge–Sn bond.

of the isomeric Ge–Si compounds in exactly the same manner: $Me_3SiGePh_3$, 2.384 (1) Å; $Ph_3SiGeMe_3$, 2.394 (1) Å. When the heavier element is bonded to the electron-withdrawing Ph groups and the lighter element to the electron-releasing methyl groups, contraction of the higher energy valence orbitals, coupled with an increase in energy of the lower energy system, results in a better energy match, which in turn results in a clear contraction of the Ge–Sn and Si–Ge bonds. The effect is much greater for the Ge–Sn bond, 0.051 Å; cf. the Si–Ge bond length difference, which is 0.01 Å. The overall greater polarizability and higher energy of the valence orbitals of the larger Ge–Sn grouping are probably responsible for this result.

The conformations of I and II (Figure 3) are identical and are between the fully staggered and eclipsed forms. These conformations are also identical to those observed in the analogous compounds $Me_3SiSiPh_3$,[8e] $Me_3SiGePh_3$,[12a] and $Ph_3SiGeMe_3$,[12b] which possess a crystallographic 3-fold axis. Since molecules I and II have no crystallographic molecular symmetry, this conformation seems to be a characteristic feature of these molecules.

**Acknowledgment.** Support of this research by the National Science Foundation under Grant RII-88-02973 for the establishment of a Minority Research Center of Excellence in Materials Science and Grant CHE-91-16934 for USA/East European collaborative research is gratefully acknowledged.

**Supplementary Material Available:** For complexes I and II, complete listings of crystallographic data, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, and bond distances and angles (12 pages); listings of observed and calculated structure factors for I and II (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Western Washington University,
Bellingham, Washington 98225, and Institut
für Anorganische Chemie, Technische Hochschule Darmstadt,
D-6100 Darmstadt, Germany

# Metal Complexes with Tetrapyrrole Ligands. 62.[1] $^{13}C$ NMR Spectra of Dicerium(III) and Dipraseodymium(III) Tris(octaethylporphyrinate)

Johann W. Buchler,*[,2a] Jürgen Löffler,[2a] and Mark Wicholas*[,2b]

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With the recent synthesis of two new families of lanthanide porphyrins, the double-decker $LnP_2$ and the triple-decker $Ln_2P_3$ sandwich compounds,[3-6] opportunities are now present to study molecular properties as a function of lanthanide contraction and concomitant sandwich compression. Recent physical studies have involved cyclic voltammetry,[7] optical and resonance Raman spectroscopy,[8] and $^1H$ NMR spectroscopy.[9] This note discusses the $^{13}C$ NMR spectra of the paramagnetic "triple-decker" sandwiches $Ce_2(OEP)_3$ and $Pr_2(OEP)_3$, OEP = octaethylporphyrin, and presents further commentary on the $^1H$ NMR spectra of the series $Ln_2(OEP)_3$, Ln = Ce, Pr, Nd, Sm, Eu.[9]

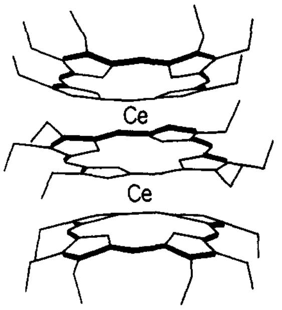

**Figure 1.** Line drawing of $Ce_2(OEP)_3$, showing doming of the outer OEP rings. Some $C_2H_5$ groups have been omitted for clarity.

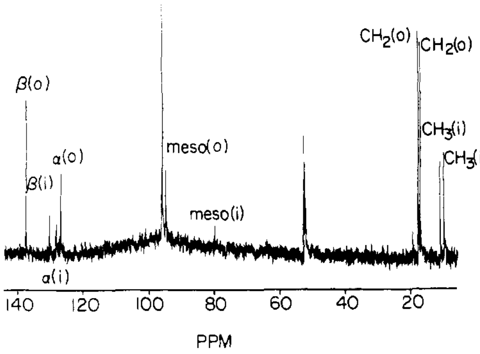

**Figure 2.** Broadband-decoupled $^{13}C$ NMR spectrum of $Ce_2(OEP)_3$ in $CCl_4/CD_2Cl_2$ at 125 MHz and 293 K.

In our previous work we examined in detail the $^1H$ NMR spectrum of $Ce_2(OEP)_3$ and showed that the observed isotropic shifts (*meso*-H, $CH_2$, and $CH_3$) were essentially dipolar in origin, a fact consistent with the literature on lanthanide complexes and shift reagents.[10-12] Also the $C_2H_5$ outer-ring protons exhibited isotropic shifts consistent only with a solution geometry in which the outer ethyl groups, on average, point upward, away from the inner porphyrin ring. This geometry is illustrated schematically in Figure 1. Although the proton resonances appear to result solely from a dipolar interaction between proton and unpaired electron spin, this does *not* preclude the existence of a covalent interaction between the spin containing cerium orbital and a low-lying ($\pi$ or $\pi^*$) porphyrin molecular orbital. Recent work by McGarvey,[13] for example, shows that uranocene, a $5f^2$ sandwich compound, has substantial $^1H$ and $^{13}C$ contact shift contributions. In $Ce_2(OEP)_3$, a lanthanide porphyrin sandwich, the protons in

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(1) Part 61: Buchler, J. W.; De Cian, A.; Elschner, S.; Fischer, J.; Hammerschmitt, P. *Chem. Ber.*, in press.

(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.

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(6) (a) Buchler, J. W.; Knoff, M. In *Optical Spectra and Structure of Tetrapyrroles*; Blauer, G., Sund, H., Eds.; de Gruyter: West Berlin, 1985. (b) Buchler, J. W.; Hammerschmitt, P.; Kaufeld, I.; Löffler, J. *Chem. Ber.* **1991**, *124*, 2151. (c) Buchler, J. W.; Kihn-Botulinski, M.; Löffler, J.; Scharbert, B. *New J. Chem.*, in press.

(7) Buchler, J. W.; Scharbert, B. *J. Am. Chem. Soc.* **1988**, *110*, 4272.

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(9) (a) Buchler, J. W.; Kihn-Botulinski, M.; Löffler, J.; Wicholas, M. *Inorg. Chem.* **1989**, *28*, 3770. (b) We have also measured proton $T_1$ relaxation times for $Ce_2(OEP)_3$, and these values, albeit less accurate than isotropic shifts, are consistent with the above geometry and a dipolar relaxation mechanism.

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**Table I.** $^{13}C$ Chemical Shifts[a]

| carbon | $Ce_2(OEP)_3$ | $Pr_2(OEP)_3$ | $La_2(OEP)_3$ |
|---|---|---|---|
| | Outer Ring | | |
| α | 126.1 | 122.7 | 144.8 |
| β | 137.0 | 149.4 | 136.4 |
| meso | 94.9 | 99.2 | 97.6 |
| $CH_2$ | 17.8 | 19.5 | 19.4 |
| $CH_3$ | 17.2 | 16.6 | 17.4 |
| | Inner Ring | | |
| α | 127.7 | 120.2 | 145.6 |
| β | 129.3 | 139.1 | 141.0 |
| meso | 79.1 | 80.6 | 96.8 |
| $CH_2$ | 9.9 | 11.4 | 20.2 |
| $CH_3$ | 11.0 | 13.8 | 18.6 |

[a] Chemical Shifts are in ppm relative to TMS in $CCl_4/C_6D_6$ at 293 K.

question are rather distant, four–six bonds removed from Ce, and thus $^1H$ NMR spectroscopy does not constitute an especially sensitive test for covalency.

In contrast, $^{13}C$ NMR spectroscopy is an apposite probe for metal–ligand covalency in paramagnetic lanthanide porphyrins because of the proximity of cerium to the pyrrole α- and β-carbon atoms of the porphyrin.[14] Hence as an alternative and complementary study, we report here the $^{13}C$ NMR spectra of $Ce_2(OEP)_3$ and $Pr_2(OEP)_3$. The $^{13}C$ NMR spectra were measured in the same solvent mixture, $CCl_4/C_6D_6$, used in our previous $^1H$ NMR report[9] and also in $CCl_4/CD_2Cl_2$. The latter mixture was useful because of partial overlap of the inner OEP ring α-C resonance of $Ce_2(OEP)_3$ with that of $C_6D_6$ in the standard solvent mixture. The broadband-decoupled $^{13}C$ NMR spectrum of $Ce_2(OEP)_3$ in $CCl_4/CD_2Cl_2$ is shown in Figure 2. Assignments were made with the aid of DEPT and off-resonance proton decoupling and are shown with the spectrum. The general and not unexpected pattern—observed also for $Pr_2(OEP)_3$—is that the outer-ring OEP $^{13}C$ resonances are more intense than the inner OEP resonances and that the α-carbon resonances are broader than the β-carbon resonances because of the closer proximity of the α-carbon atoms to lanthanide metal. The chemical shifts for $Ce_2(OEP)_3$, $Pr_2(OEP)_3$, and the diamagnetic $La_2(OEP)_3$ are listed in Table I. Using $Ce_2(OEP)_3$ as an illustration, the isotropic shift for any carbon nucleus is the sum of the shifts experienced independently by interaction with each cerium(III), since electron spin interactions are negligible between the two cerium(III) ions.[15]

$$\text{outer-ring } (\Delta H/H)_{\text{iso}} = (\Delta H/H)_{\text{Ce(1)}} + (\Delta H/H)_{\text{Ce(2)}}$$

$$\text{inner-ring } (\Delta H/H)_{\text{iso}} = 2(\Delta H/H)_{\text{Ce(1)}}$$

Furthermore in $^{13}C$ NMR spectroscopy of paramagnetic systems, the isotropic shift can have three separate components, as given by eq 1.[12] The first term, $(\Delta H/H)^{\text{MC}}_{\text{dip}}$, is the traditional dipolar

$$(\Delta H/H)_{\text{iso}} = (\Delta H/H)^{\text{MC}}_{\text{dip}} + (\Delta H/H)_{\text{con}} + (\Delta H/H)^{\text{LC}}_{\text{dip}} \qquad (1)$$

shift arising from the dipolar interaction of the metal-centered electron spin magnetic moment with the $^{13}C$ nuclear spin magnetic moment. The contact shift, $(\Delta H/H)_{\text{con}}$, while not apparently significant in the $^1H$ NMR spectrum, could be of consequence here especially for the pyrrole ring carbons (vide supra). If the latter is important, then an additional shift, $(\Delta H/H)^{\text{LC}}_{\text{dip}}$, the ligand-centered dipolar shift, must be considered. This would arise were significant spin density to reside on the porphyrin carbon atoms.

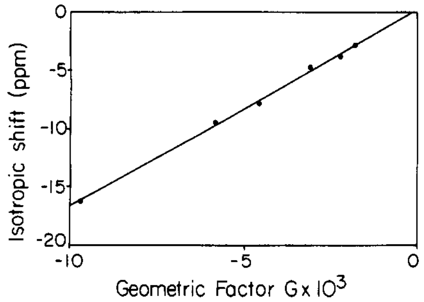

**Figure 3.** Plot of geometric factor vs isotropic shift (293 K) for $^1H$ nuclei in $Ce_2(OEP)_3$.

**Table II.** Isotropic Shifts: Experimental and Calculated[a]

| | $Ce_2(OEP)_3$ | | $Pr_2(OEP)_3$ |
|---|---|---|---|
| | exptl $(\Delta H/H)_{\text{iso}}$ | calcd[b] $(\Delta H/H)^{\text{MC}}_{\text{dip}}$ | exptl $(\Delta H/H)_{\text{iso}}$ |
| | | Outer Ring | |
| α | −18.7 | −4.3 | −22.1 |
| β | 0.6 | −3.3 | 13.0 |
| meso | −2.7 | −4.9 | 1.6 |
| $CH_2$ | −1.6 | −2.7 | 0.1 |
| $CH_3$ | −0.3 | −1.7 | −0.8 |
| | | Inner Ring | |
| α | −17.7 | −13.6 | −25.4 |
| β | −11.7 | −10.8 | −1.9 |
| meso | −17.7 | −17.1 | −16.2 |
| $CH_2$ | −10.3 | −10.9 | −8.8 |
| $CH_3$ | −7.6 | −8.1 | −4.8 |

[a] All shifts are in ppm relative to $Ln_2(OEP)_3$ in $CCl_4/C_6D_6$ at 293 K. [b] The dipolar shifts are calculated using the geometrical parameters from ref 9.

Of the three components it is easiest to estimate the metal-centered dipolar shifts, $(\Delta H/H)^{\text{MC}}_{\text{dip}}$. In axial metal-based symmetry, these shifts, whether for $^{13}C$ or $^1H$, are directly proportional to the magnetic anisotropy and geometry[16] (eq 2), where $\chi_\parallel$ and

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

$\chi_\perp$ represent the principal components of the magnetic susceptibility, $r$ is the proton–metal distance, $\theta$ is the angle that the vector $\vec{r}$ makes with the principal symmetry axis, and $N$ is Avogadro's number. With rapid rotation of the porphyrin rings about the Ce–Ce axis, the symmetry at each cerium is effectively axial. Since eq 2 is also valid for the $^1H$ dipolar shifts of $Ce_2(OEP)_3$, we use the *proton* isotropic shifts—assumed to be totally dipolar—and plot these against the respective geometric factors, $G = (3\cos^2\theta - 1)/r^3$. The essentially linear plot, shown in Figure 3, yields $(\chi_\parallel - \chi_\perp) = 2980 \times 10^{-6}$ cm$^3$/mol per cerium, which is then valid for the $^{13}C$ NMR shift analysis. This sizeable magnetic anisotropy should not be unexpected, since cerium is without direct equatorial ligands in $Ce_2(OEP)_3$. As reference points, the single-crystal magnetic anisotropy for $Ce(C_2H_5SO_4)_3{\cdot}9H_2O$,[17] a symmetric nine-coordinate $D_{3h}$ molecule, is 203 × $10^{-6}$ cm$^3$/mol whereas the less symmetrical cyclohexyl isocyanide adduct of tris($\eta^5$-cyclopentadienyl)cerium(IV) has a magnetic anisotropy of approximately 1000 × $10^{-6}$ cm$^3$/mol.[18] And although not directly comparable, uranocene, a $5f^2$ organometallic sandwich compound with a similarly weak equatorial field as $Ce_2(OEP)_3$, has a very large magnetic anisotropy of 6200 × $10^{-6}$ cm$^3$/mol.[19]

The $^{13}C$ metal-centered dipolar shifts can be calculated for the respective carbon nuclei of $Ce_2(OEP)_3$ from eq 2 using the above magnetic anisotropy of 2980 × $10^{-6}$ cm$^3$/mol and the solution geometry established previously.[9] The results are listed in Table

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(18) This value is calculated from the solution NMR plot of $(\Delta H/H)_{\text{iso}}$ vs $G$ for the cyclohexyl protons: Fischer, R. D. In *Organometallics of the f-elements*; Marks, T. J., Fischer, R. D., Eds.; D. Reidel: Boston, MA, 1979; p 352.

(19) McGarvey, B. R.; Nagy, S. *Inorg. Chem.* **1987**, *26*, 4198.

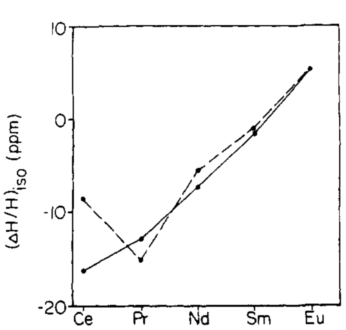

**Figure 4.** Plot of observed inner-ring meso $^1H$ isotropic shifts (293 K) for $Ln_2(OEP)_3$(- - -) and Bleaney's predicted dipolar shift values normalized for Eu (—) vs lanthanide.

II and compared to the observed $^{13}C$ isotropic shifts. As a general observation, there is very good agreement qualitatively, save for the $\alpha$-carbon nuclei, between the observed isotropic shifts and those calculated on the basis of a metal-centered dipolar shift model. This is further confirmation that the solution geometry, proposed on the basis of the $^1H$ shifts and used herein, is indeed correct. The discrepency at $\alpha$-carbon, the carbon atom closest to cerium, signals that some covalency must occur, whether from direct f orbital overlap or indirect spin polarization of the 6s or 6p orbitals. This is most manifest at the $\alpha$-carbon of the outer ring, the ring which is closest to cerium.[20] There is no direct way to measure $(\Delta H/H)_{con}$ for the outer-ring carbon atoms; instead one must rely on indirect method—solution of simultaneous equations with numerous assumptions about spin delocalization—for separating $(\Delta H/H)_{con}$ from $(\Delta H/H)^{LC}_{dip}$. In the only complete study following this line of analysis, Goff[21] calculated $(\Delta H/H)_{con}$, $(\Delta H/H)^{LC}_{dip}$, and spin densities for the low-spin bis(1-methylimidazole) adduct of Fe(TPP)Cl. In this case the isotropic shife were as large as 100 ppm. Our attempts to separate $^{13}C$ contact from ligand-centered dipolar shifts for the outer-ring carbon atoms produced only nonsensical numerical results. This undoubtedly is due to the small isotropic shifts in $Ce_2(OEP)_3$ and the numerous assumptions necessary for a successful calculation.[22]

There is substantially less covalency, perhaps none, involving the inner OEP ring, the large shifts resulting from the metal-centered dipolar interaction with *two* equally distant cerium(III) ions. At an average Ce–N distance of 2.76 Å, it appears that the 4f orbitals are too contracted to interact covalently with the inner porphyrin ring.

Analysis of the $^{13}C$ isotropic shifts for $Pr_2(OEP)_3$ is problematic.[23] Were the shifts entirely metal-centered dipolar and the geometry—including disposition of the alkyl groups—identical, then the same pattern of shifts as seen for $Ce_2(OEP)_3$ would be expected. This is not observed. Because the $^{13}C$ and $^1H$ isotropic shifts are small and the term $(3\cos^2\theta - 1)/r^3$ is quite sensitive to changes in geometry, we chose not to proceed further with calculations. In summary, the $^{13}C$ $Pr_2(OEP)_3$ isotropic shifts appear irregular, particularly at the $\alpha$- and $\beta$-positions, and may have sizeable contact and ligand-centered dipolar shift contributions.

Comparison of the isotropic shifts of $Ce_2(OEP)_3$ and $Pr_2(OEP)_3$, whether $^{13}C$ or $^1H$, signals another difficulty: the relative magnitudes are not consistant with theory. According to the calculations of Bleaney,[16] metal-based dipolar shifts of Ce complexes should be approximately 60% less than those for Pr. This clearly is not the case if judged by the inner-ring $CH_2$, $CH_3$, and *meso*-carbon shifts, those most likely to be dipolar. This observation is reinforced in the $^1H$ NMR spectra where, with one exception, the $Ce_2(OEP)_3$ shifts are 25–35% greater than those of $Pr_2(OEP)_3$, although with the same general pattern of shifts. This irregularity is clearly evident in plots of the inner-ring meso and $CH_2$ isotropic shifts (assumed to dipolar) for $^1H$ (Ce, Pr, Nd, Sm, Eu) shown in Figure 4 along with a plot of Bleany's prediction[16,24] for the lanthanide series. In contrast the $^1H$ shifts from Pr through Eu qualitatively follow the pattern proposed by Bleaney.[14]

At this point it is unclear why the above irregularity occurs.[25] One possible cause could be a significant structural change distinguishing $Pr_2(OEP)_3$ from $Ce_2(OEP)_3$, although it is not obvious which geometry, if any, would be preferable for the former.

## Experimental Section

The triple-decker $Ce_2(OEP)_3$ and $Pr_2(OEP)_3$ sandwich compounds were prepared as reported previously.[3,5] The $^{13}C$ NMR spectra were run on Bruker AC 300 and AM 500 spectrometers operating at 75 and 125 MHz, respectively. Because of the limited solubility of these complexes, as many as 40 000 transients (AC 300 spectrometer, 90° pulse) were needed to identify definitively the weakest resonance, that of the inner-ring *meso*-carbon.

**Acknowledgment.** Financial support from NATO (Grant 0034/85) is gratefully acknowledged. We also thank Drs. S. Braun and T. Pratum for their technical assistance.

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(20) The Ce–N distances taken from ref 3, are as follows: outer, 2.50 Å; inner, 2.76 Å.

(21) Goff, H. *J. Am. Chem. Soc.* **1981**, *103*, 3714.

(22) These calculations require four empirical polarization constants which are derived from ESR studies of simple $\pi$-radical systems. It is unclear whether these constants are meaningful for the nonplanar, saucer-shaped porphyrin rings of $Ce_2(OEP)_3$.

(23) The room-temperature magnetic moment of $Pr_2(OEP)_3$, 3.41 $\mu_B$ per Pr, is normal for a $4f^2$ system.

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

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Contribution from the Department of Chemistry,
University of New Brunswick, Bag Service No. 45222,
Fredericton, New Brunswick, Canada E3B 6E2

# A Linear Relationship between the Sulfur–Nitrogen Bond Enthalpy Term and Bond Length and an Assessment of the Reliability of Empirical Length–Strength Relationships in the Estimation of Thermochemical Properties of Sulfur–Nitrogen Compounds

Simon Parsons and Jack Passmore*

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Although the kinetic aspects of sulfur–nitrogen chemistry have received much recent attention,[1] the thermodynamics of these systems has been relatively neglected. Part of the reason for this is the paucity of experimental data.[2] However, we have recently shown that many properties of homopolyatomic cations[3] and chalcogen–iodine cations[4] can be rationalized by reference to simple thermochemical estimates utilizing lattice energies obtained by the method of Bartlett[5a,b] (see below). We apply a similar

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