

last authors assumed that the simple Steinberger-Westheimer mechanism accounts for all of the uv spectral changes, contrary to the results reported here.

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Lanthanide Porphyrin Complexes. A Potential New Class of Nuclear Magnetic Resonance Dipolar Probe

Sir:

The nuclear magnetic resonance (nmr) probe capability of low-spin d^5 iron(III) in heme or porphyrin environments is well established,¹⁻⁷ and a number of fruitful nmr studies of proteins containing this prosthetic group have been reported.^{8,9} The short electronic spin-lattice relaxation times and the sizable magnetic anisotropies in such systems combine to yield well-resolved nmr spectra which exhibit large dipolar resonance shifts. Complexes of trivalent lanthanide ions have potentially even greater magnetic anisotropies^{10,11} and certain of these (Pr, Eu, Yb) have extremely short electron spin-lattice relaxation times. The usefulness of lanthanide shift reagents,¹² for the study of functional organic molecules, and of lanthanide ions to probe the structures of proteins¹³ and molecules of biological interest^{14,15} is well documented. In an effort to develop a potent new dipolar nmr probe for use in biological systems, we have sought to combine the desirable qualities of the heme moiety (rigid, well-defined structure; specific, tight binding site in proteins; resistance to demetalation) with the propitious electronic and magnetic properties of trivalent lanthanide ions. As a start in this direction we have synthesized lanthanide complexes of *meso*-tetraphenylporphine

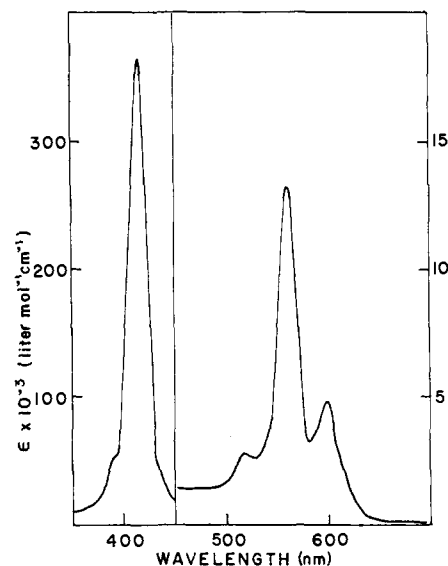


Figure 1. Electronic spectrum of 2,4-pentanedionato-*meso*-tetraphenylporphineeuropium(III) in dimethyl sulfoxide at room temperature.

(TPP) and some of its derivatives. Despite considerable current interest in metalloporphyrin chemistry,¹⁶ lanthanide complexes of this class of macrocycle have not previously been reported.¹⁷

The synthetic procedure employed was a modification of that employed by Treibs¹⁸ and by Buchler¹⁹ for the preparation of a variety of metallo derivatives of octaethylporphine. In a typical preparation hydrated *tris*(2,4-pentanedionato)europium(III) (2 mmol) and H₂TPP (1 mmol) were refluxed in 1,2,4-trichlorobenzene (214°) for 3-4 hr, after which the solvent was removed under reduced pressure and the product was purified by column chromatography. *Anal.*²⁰ Calcd for Eu(C₄₄H₂₈N₄)(C₅H₇O₂): C, 68.13; H, 4.06; N, 6.49; Eu, 17.6; TPP, 70.9. Found: C, 65.33; H, 4.53; N, 5.89; Eu, 16.3; TPP, 62.7. The uv-visible spectrum, shown in Figure 1, strongly resembles those of Sn^(II)TPP and Cd^(II)TPP.²¹ Spectroscopic evidence reveals that the reaction is a general one which proceeds for the entire lanthanide series. We have carried out the reaction with a variety of substituted TPP derivatives and with several different β -diketonate complexes of the lanthanides. The complexes are reasonably soluble to organic solvents and are stable to air and to water when the latter is added to an organic solvent with which it is miscible. When treated with hydrogen chloride gas in organic solvents the complexes are decomposed within seconds and quantitatively converted to the green dication,²² H₄TPP²⁺, which reaction forms

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the basis for a facile analysis of the porphyrin content of the complexes. Treatment of the complexes with hydroxide ion in water-organic solvent mixtures produces minor but definite spectral changes similar to those which occur upon μ -oxo dimer formation by octaethylporphyrin complexes of iron(III) and scandium(III).²³ We tentatively assign these changes to this cause.

The nmr spectra confirm the formation of paramagnetic metalloporphyrins with the metal ion considerably displaced from the porphyrin plane.^{5,24-26} The proton nmr spectrum of the tetra-*p*-tolyl derivative, Eu(*p*-CH₃)TPPacac, at -21° exhibits peaks (ppm from TMS) at -13.31 d (*ortho-endo*), -9.33 d (*meta-endo*), -8.30 (pyrrole), -8.13 (*ortho-* and *meta-exo*), -3.44 (*p*-CH₃), and 0.88 (acac-CH₃), with areas consistent with this assignment. These may be compared with diamagnetic free-base resonances at -9.22 (pyrrole), -8.43 d (*ortho*), -7.80 d (*meta*), and -2.82 (*p*-CH₃) (d signifies a doublet with 8 Hz splitting). The signals shift linearly with T^{-1} as expected for isotropically shifted resonances. Shift ratios for the phenyl protons (*ortho-endo*:*meta-endo*:*ortho-exo*:*meta-exo*:*p*-CH₃ = -10.00:-3.14:0.61:-0.68:-1.28) agree well with those calculated²⁷ assuming axial symmetry (-10.00:-3.09:0:80:-0.68, -1.23). The ratios agree best for a model with the europium atom 2.0 Å out of the porphyrin plane. This implies a Eu-N distance of 2.83 Å which is 0.18 Å larger than the pyridine nitrogen to europium distance in a shift reagent system.²⁸ No attempt was made to account for phenyl ring oscillation, porphyrin skeleton doming, or Fermi contact contributions, so the above estimate, which is extremely sensitive to the small *ortho-endo* and *meta-endo* shifts, must be considered highly uncertain and is probably too large. The same structural parameters predict a *relative* dipolar shift of -4.77 for the pyrrole protons, while this resonance is observed to shift *upfield* by 0.92 ppm at -21°. We attribute this to a sizeable Fermi contact interaction. It is for the pyrrole protons that contact shifts are particularly evident in both low- and high-spin iron(III) porphyrin systems.⁵ Preliminary nmr spectra of Pr(*p*-CH₃)TPPacac and Yb(*p*-CH₃)TPPacac show well-resolved signals with the *p*-CH₃ resonances shifted by +1.15 and -3.28 ppm, respectively, at -21°. These shifts may be compared with the -0.63 ppm shift for this resonance in the analogous europium complex. The observed sign changes are entirely consistent with the results in shift reagent systems.¹¹ The shift observed for the ytterbium complex implies that its dipolar shifting ability is about 2.4 times that of the low-spin, d⁵, iron(III) hemin moiety in metmyoglobin cyanide.⁶

These preliminary findings, and particularly the ob-

served stability of lanthanide porphyrin complexes toward water suggest that the analogous complexes of naturally occurring porphyrins may serve as potent and specific nmr shift and broadening probes in biological systems.²⁹ Lanthanide porphyrin complexes may find application as heavy-atom probes for electron microscopy and X-ray structure determination. Gadolinium derivatives are potential epr spin labels. Work on various aspects of this new area is in progress in these laboratories.

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(29) Spectroscopic evidence from preliminary experiments with the dimethyl esters of proto- and mesoporphyrin IX reveals that lanthanide complexes of these ligands have been synthesized.

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Mechanism of 1,4-Disilacyclohexa-2,5-diene Formation from Acetylenes and Silylenes

Sir:

One of the best known and most perplexing problems in organosilicon chemistry is the nature of the reaction of silylenes (R₂Si:) with acetylenes. In 1962 it was reported¹ that dimethylsilylene, generated either from pyrolysis of polysilane or from sodium and dimethyldichlorosilane, reacted with diphenylacetylene to produce silacyclopentene, **1**. Soon after this report a variety of methods² were employed to show that the product was actually the 1,4-disilacyclohexadiene, **2**. The mechanism for formation of **2** was suggested³ to involve π -dimerization of **1**. However, generation of dimethylsilylene in the presence of both diphenylacetylene and 2-butyne afforded none of the mixed disilacyclohexadiene (**3**) of the type demanded by such a mechanism.⁴ The possibility of **1** opening to a 1,3-diradical followed by a head-to-tail dimerization was excluded since even in the presence of a large excess of diphenylacetylene, no silacyclopentadiene (**4**) was formed. Thus it has been assumed that "the formation of the disilacyclohexadienes proceeds by a rather specific dimerization of silacyclopentene intermediates with rupture of the carbon-silicon ring bonds."⁴

We suggest here an alternative mechanism and present the results of initial experiments which are consistent with this suggestion. Our interest in molecules containing the silicon-carbon (p-p) π double bond produced the suggestion that disilacyclohexadiene formation might arise from the Diels-Alder reaction be-

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