was found to be the same as determined by X-ray crystallography,[14–16] although the X-ray data suggested a single orientation. The present deuteroHRP constitutes the first example where the reconstituted protein has essentially the completely reversed heme orientation from that of the native protein.

The different orientations of protohemin and deuterohemin in HRP dictate that a comparison of the two proteins must take into consideration not simply the replacement of vinyl groups by protons, but instead the more complex effects of replacing vinyl by methyl groups and methyl groups by protons in order to rationalize the characteristic differences in physicochemical properties.[2,4] It is now abundantly clear that not only must altered heme orientations be considered in comparing properties of reconstituted hemoproteins but also recognition must be given to the fact that the X-ray crystallographically defined orientation may reflect only one of several orientations adopted in solution.[11] As illustrated here and elsewhere,[5,6,11] proton NMR hyperfine shifts are particularly suited for establishing the presence of variable porphyrin orientations in solution.

The interpretations of the methyl shifts as well as those of other resonances assigned via isotope labeling will be presented elsewhere.

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(14) Takano, T. *J. Mol. Biol.* **1977**, *110*, 537–568.
(15) Steigemann, W.; Weber, E. *J. Mol. Biol.* **1979**, *127*, 309–338.
(16) Argos, P.; Mathews, F. S. *J. Biol. Chem.* **1975**, *250*, 747–751.

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Structure of Bis(phthalocyaninato)neodymium(III)

Sir:

Since the synthesis of lanthanide(III)-phthalocyanine complexes was established by Kirin and Moskalev,[1] many studies on their compositions and properties have been reported.[2] For instance, intense attention has been directed toward electrochromism of bis(phthalocyaninato)lanthanide(III) complexes, $\mathrm{Pc_2Ln^{III}H}$ (Pc and Ln denote a phthalocyanine dianion and a lanthanide cation, respectively). Their electrochromism was first reported by Moskalev and Kirin.[2e] Subsequently, Nicholson and Galiaridi attempted to make electrochromic displays with bis(phthalocyaninato)lutetium(III) and found that a full spectral change of color is generated by adjustment of the applied voltage (from −1.0 to 1.2 V).[3a] They proposed the structure illustrated in Figure 1 for this complex.

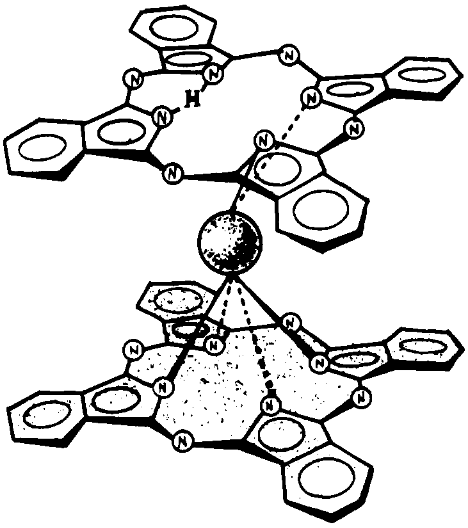

Figure 1. The proposed structure of bis(phthalocyaninato)lutetium(III).[3a]

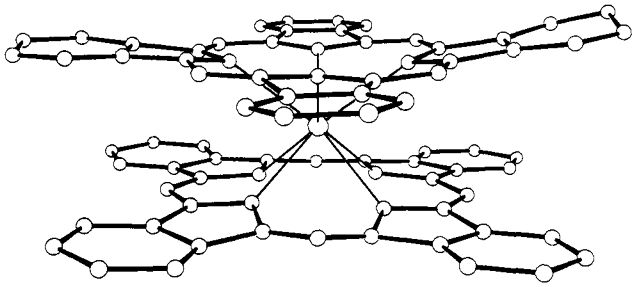

Figure 2. Molecular structure of bis(phthalocyaninato)neodymium(III).

With further developments, these electrochromic materials must become useful for full-color imaging and graphic displays, as well as alphanumerics. Recently, Corker et al. investigated the electrochromic behavior of bis(phthalocyaninato)lutetium(III) by using ESR and optical techniques.[4] The structural analysis of bis(phthalocyaninato)lanthanide(III) complexes would provide useful information to investigate their electrochromism and will also be useful to clarify the nature of the complexes. We report here the results of an X-ray diffraction analysis of bis(phthalocyaninato)neodymium(III). The synthesis and purification of the complex were described in a previous paper.[2d] A purple, single crystal of the monosolvated $\mathrm{Pc_2Nd^{III}H}$ complex prepared by recrystallization from dichloromethane was used for X-ray analysis. Anal. Calcd for $\mathrm{C_{64}H_{33}N_{16}NdCH_2Cl_2}$: Cl, 5.66. Found: Cl, 5.71. Crystal data: orthorhombic; $a = 8.030$ (4), $b = 22.925$ (7), $c = 28.315$ (7) Å; $V = 5212$ (3) Å^3; space group $P2_12_12_1$; ρ(calcd) = 1.60 g cm^{-3}; M_r 1255.2; $F(000) = 2524$ electrons; μ(Mo Kα) = 11.7 cm^{-1}.[5] The neodymium ion occupies a central position between two parallel but staggered (45°) phthalocyanine ligands (Figure 2).

The eight Nd–N bond distances vary from 2.39 to 2.49 Å. While one of the phthalocyanine macrocycles is slightly saucer shaped toward the neodymium atom, the other is planar; angles of tilt range from 2.5 to 7.0°. The pyrrole nitrogen atoms vary from the macrocylic planes by distances ranging from 0.04 to 0.21 Å. The tilted benzimidazole group is an equal distance of 1.47 (1) Å from each of the two least-squares planes containing the four pyrrole nitrogen atoms. An acidic hydrogen in this complex is known to play an important role in the electrochromic properties.[2e] Although an obvious distortion from macrocyclic planarity (13°) is manifest by one benzimidazole moiety, the elusive hydrogen is not directly revealed by the crystallographic results.

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(1) (a) Kirin, I. S.; Moskalev, P. N.; Makashev, Yu. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1965**, *10*, 1065–6. (b) Kirin, I. S.; Moskalev, P. N.; Ivannikova, N. V. *Ibid.* **1967**, *12*, 497–8.

(2) (a) Kirin, I. S.; Moskalev, P. N.; Makashev, Yu. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1967**, *12*, 369–72. (b) Kirin, I. S.; Shelekhin, Yu. L.; Moskalev, P. N. *Sov. Phys.-Solid State* (*Engl. Transl.*) **1967**, *9*, 1461–2. (c) Moskalev, P. N.; Kirin, I. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1971**, *16*, 57–60. (d) Misumi, S.; Kasuga, K. *Nippon Kagaku Zasshi* **1971**, *92*, 335–8. (e) Moskalev, P. N.; Kirin, I. S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1972**, *46*, 1019–22. (f) Lux, F. *Proc. Rare Earth Res. Conf.*, *10* **1973**, *2*, 871–80. (g) Mackay, A. G.; Boas, J. F.; Troup, G. J. *Aust. J. Chem.* **1974**, *27*, 955–64. (h) Kirin, I. S.; Moskalev, P. N. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1967**, *41*, 251.

(3) (a) Nicholson, M. M.; Galiardi, R. V. *U.S. NTIS, AD Rep.* **1977**, AD-A039596, 67 pp. (b) Yamana, M. *Ohyou Butsuri* **1979**, *48*, 441–2.

(4) Corker, G. A.; Grant, B.; Clecak, N. J. *J. Electrochem. Soc.* **1979**, *126*, 1339–43.

(5) Intensity data were collected by the Molecular Structure Corporation, College Station, TX 77840. Of the 4736 independent reflections measured, 3505 were classed as being significantly above the background. The structure was solved by the heavy atom method and refined by least-squares calculation to $R = 0.072$.

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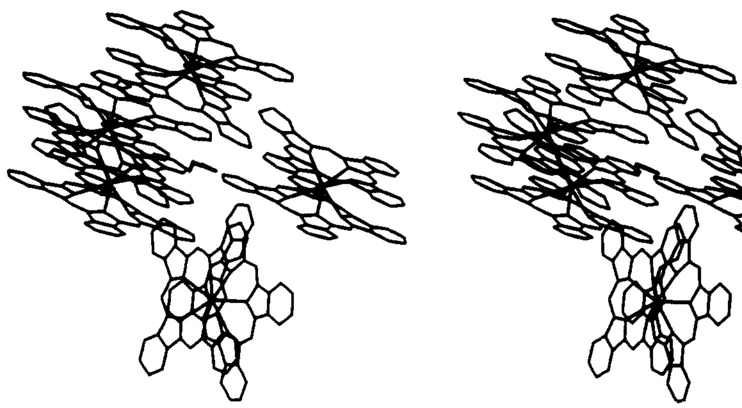

Figure 3. Stereoscopic view of molecular packing cell of the structure.

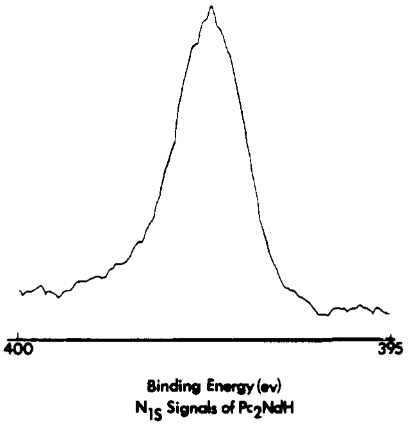

Figure 4. An N 1s X-ray photoelectron spectrum of bis(phthalocyaninato)neodymium(III).

However, the molecules are packed in a three-dimensional "herringbone" pattern (Figure 3) with the molecule of solvation, dichloromethane, on the pseudomirror plane and between the benzimidazole rings of translationally related molecules; it is these rings which show the greatest distortion from symmetry.

One may therefore conclude that the hydrogen occurs at this locus of asymmetry. In order to verify the location of the acidic hydrogen in the complex, we also obtained an N 1s X-ray photoelectron spectrum (Figure 4).[6] The spectrum shows a sharp, single peak (at 398.8 eV with the width of 1.1 eV) in analogy with the spectra of usual types of metallophthalocyanines.[7] The data imply that eight central nitrogen atoms are chemically equivalent to each other, and thereby the acidic hydrogen does not bind strongly to any of the nitrogen atoms in the complex, as opposed to the structure proposed by Nicholson and Galiaridi (Figure 1), though a possibility of a weak interaction between the hydrogen atom and the nitrogen atom(s) cannot be excluded. Recently, Moskalev et al. proposed a double-sandwich model of the neodymium(III) complex, $\mathrm{PcNd^{(III)}Pc(\mu\text{-}H)_2\,PcNd^{(III)}Pc}$, to explain electrochromism.[8] In their model, the acidic hydrogen has a weak intermolecular hydrogen bond, consistent with the result of the N 1s spectrum. Although the position of the acidic hydrogen of the complex could not be detected distinctly in this study, it is elucidated that the two phthalocyanine ring systems form the sandwich-type compound with the neodymium atom in the center and are oriented in the staggered configuration. We are studying electrochromism of bis(phthalocyaninato)neodymium(III) in further detail by using ESR and cyclic voltametry, and the results will be described in a forthcoming paper.

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(6) The X-ray photoelectron spectra were obtained with a Hewlett-Packard 5950 Å ESCA spectrometer with an Al X-ray anode. The detailed procedure was described in our previous paper: Tatsumi, K.; Kasuga, K.; Tsutsui, M. *J. Am. Chem. Soc.* **1979**, *101*, 484-6.

(7) Niwa, Y.; Kobayashi, H.; Tsuchiya, T. *J. Chem. Phys.* **1974**, *60*, 799-807.

(8) Moskalev, P. N.; Shapkin, G. N.; Darovskikh, A. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 188-92.

Importance of Solvation on the Gas-Phase Proton-Transfer Reaction between Cyclopentadienyl Anion and Alcohols

Sir:

The reactions of gas-phase ion-neutral clusters, $(IN)^{\pm}$, are of considerable interest since they may bridge the chemistry of these ions in gas- and condensed-phase processes. Most research in this area has involved studies of the association and clustering equilibria (eq (1-3)).[1] Recent reports by several investigators have demonstrated the mediating effect of solvent molecules on the intrinsic properties of gas-phase anions in proton-transfer equilibria[2] and nucleophilic reactivity.[3] We wish to report a "contrathermodynamic" protonation reaction which occurs at a moderate rate because of the role of the "solvent molecule" on the thermochemistry of the overall reaction. This result is directly related to the origin of different acidity scales for proton donors in solution (e.g., in H_2O) and in the gas phase.[4]

$$I^{\pm} + N \rightleftarrows (IN)^{\pm} \tag{1}$$

$$(IN_x)^{\pm} + N \rightleftarrows (IN_{x+1})^{\pm} \tag{2}$$

$$(IN_x)^{\pm} + M \rightleftarrows (IN_{x-1}M)^{\pm} + N \tag{3}$$

Cyclopentadienyl anion, $c\text{-}C_5H_5^-$, was prepared in our flowing afterglow apparatus ($\bar{v} = 80\ \mathrm{m\ s^{-1}}$, $P = 0.5$ torr) from the reaction of CH_3O^- with $c\text{-}C_5H_6$ ($\Delta H^\circ_{\mathrm{acid}} = 356.1 \pm 2\ \mathrm{kcal\ mol^{-1}}$)[4] (see eq 4 and 5). Various alcohols were then added downstream of

$$CH_3ONO + e^- \rightarrow CH_3O^- + NO \tag{4}$$

$$CH_3O^- + c\text{-}C_5H_6 \rightarrow CH_3OH + c\text{-}C_5H_5^- \tag{5}$$

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(1) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445 and references therein.

(2) Mackay, G. I.; Bohme, D. K. *J. Am. Chem. Soc.* **1978**, *100*, 327.

(3) (a) Bartmess, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 2483. (b) Fukuda, E. K.; McIver, R. T. *Ibid.* **1979**, *101*, 2498.

(4) Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York. Vol. 2, 1979.

0002-7863/80/1502-4836$01.00/0