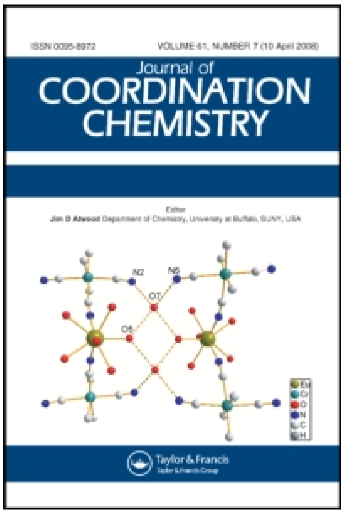

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# THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF BISPHTHALOCYANINATOLANTHANIDE(III)

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# THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF BISPHTHALOCYANINATOLANTHANIDE(III)

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The NMR spectra of bisphthalocyaninatolanthanide(III) complexes (La, Nd, Sm, and Eu) have been examined. An effect of a macrocyclic-ring current and an induced shift caused by lanthanide(III) ions were discussed.

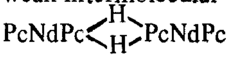
## INTRODUCTION

NMR studies of phthalocyanine compounds have been difficult for a long time because of their poor solubilities.[1] Recently, using Fourier transform techniques, Marks *et al.* reported some NMR results of lithium, zinc, and uranyl phthalocyanines.[2] Lanthanide complexes such as acethylacetonatolanthanide(III) and its derivatives are also known to be useful for NMR shift reagents.[3] We report here NMR results of bisphthalocyaninatolanthanide (La(III), Nd(III), Sm(III), and Eu(III) to study the effects of a macrocyclic ring current of phthalocyanine ligands and induced shifts caused by lanthanide(III) ions on peaks of benzene ring protons of the complexes.

## EXPERIMENTAL

Samples used for NMR measurements were prepared by the methods of Kirin *et al.* and Misumi *et al.*[4] The purity of samples was verified by elemental analyses and visible spectra. A deuteriodimethylsulfoxide ($DMSO_{d6}$) solution of the samples was refluxed for ca. 30 minutes under argon gas, and the filtrate was transferred into a NMR tube under argon atmosphere. A Varian FT-80 spectrometer was used to obtain spectra at 60°C.

## RESULTS AND DISCUSSION

Since the synthesis of bisphthalocyaninatolanthanide(III) complexes was published,[4] many studies on their properties have been reported.[5] For instance, the complexes show blue in polar solvents such as methanol, N,N-dimethylformamide, and dimethylsulfoxide, while they show green in dichloromethane and chloroform.[4] A few ideas have been reported to explain the color difference.[5 c,d,e] Previously, we reported that green bisphthalocyaninatoneodymium(II) recrystalized from dichloromethane is a radical species, $\mathrm{PcNd\dot{P}c}$ which is generated by abstracting imine hydrogen of a blue $Pc_2NdH$ complex (Pc = phthalocyanine dianion).[6] Furthermore, a molecular structure of the green bisphthalocyaninatoneodymium(III) complex was analyzed; a neodymium(III) ion occupies a central position between parallel, but staggered phthalocyanine ligands.[7] A N ls X-ray photoelectron spectrum was also obtained to verify the location of acidic hydrogen–imine hydrogen in bisphthalocyaninatoneodymium(III).[7] The data imply that eight central nitrogen atoms are chemically equivalent to each other, and thereby acidic hydrogen does not bind strongly to any of the nitrogen atom in the complex, consistent with Kirin's model which has a weak intermolecular hydrogen bond,  $\mathrm{PcNdPc}\!<^{\mathrm{H}}_{\mathrm{H}}>\!\mathrm{PcNdPc}$.[5 e] We studied a FT-NMR of bisphthalocyaninatolanthanide(III) to verify the behavior of acidic proton of the complex, but it could not be detected. Figure 1 shows the FT-NMR spectrum of bisphthalocyaminatone odymium(III). . On the basis of works of Lever and Marks, the lower-field multiplet is assigned to α proton of a benzene ring and the higher field one is assigned to β proton.[1,2] FT-NMR results of bisphthalocyaninatolanthanide(III) (La, Nd, Sm, and Eu) and lithium and zinc phthalocyanine complexes are shown in Table 1.

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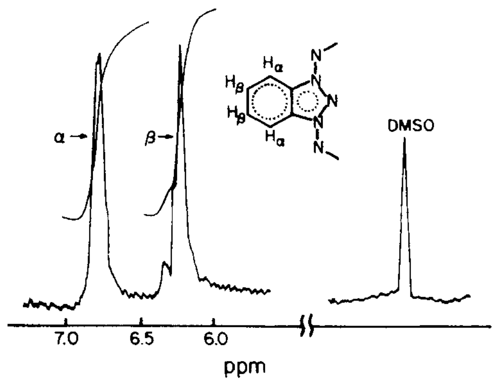

FIGURE 1. NMR spectrum of bisphthalocyaninatonedymium(III) in $DMSO_{d_6}$ at 60°C.

TABLE 1
$^1H$ NMR Data for Bisphthalocyaninatolanthanide(III) and Lithium and Zinc Phthalocyanine Complexes†,‡

| Compound | $^1H$ NMR |  |
|---|---|---|
|  | α proton | β proton |
| $Pc_2LaH$ | 8.75 (16H) | 8.10 (16H) |
| $Pc_2NdH$ | 6.90 (16H) | 6.30 (16H) |
| $Pc_2SmH$ | 18.67 (16H) | 18.34 (16H) |
| $Pc_2EuH$ | 10.84 (16H) | 9.03 (16H) |
| $PcLi_2$ §,[2] | 9.38 (8H) | 8.04 (8H) |
| PcZn¶,[2] | 9.50 (8H) | 7.94 (8H) |

†Ft data in δ (ppm). ‡All data in $DMSO_{d_6}$ at 60°C. §$C_6D_6$ added 2% $DMSO_{d_6}$. ¶$C_6D_6$. All peaks show multiplets

Comparing of sandwich-type bisphthalocyaninatolanthanum(III) complex with 1 : 1 type metallophthalocyanine complexes, it can be shown that the position of a β proton signal in the lanthanum(III) complex is almost the same as those of normal-type complexes, while the position of α proton of the lanthanum(III) complex shifts to the higher magnetic field (Table 1). This shift is the result of shielding of α protons belonging to one macrocycle by the benzene ring current associated with the other macrocycle. Since the two multiplets have the same general outline as in the 1 : 1 type compound, it is apparent that both α protons of the benzene ring are affected by equal shielding, consistent with the fact of the staggered arrangement of the two phthalocyanine ligands. The induced shifts of α and β protons of the complexes increase in the order Nd < Eu ≪ Sm (Figure 2).

It is interesting that the induced shift of bisphthalocyaninatosamarium(II) is much larger than those of acetylacetonatosanarium(III) and its derivatives.[3] Further studies on this point may be performed.

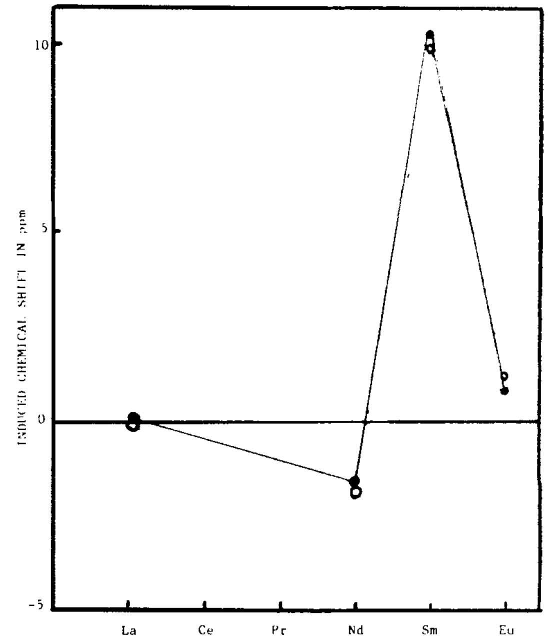

FIGURE 2. Induced chemical shifts of α and β protons ○, α proton; ● β proton.

## ACKNOWLEDGEMENTS

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