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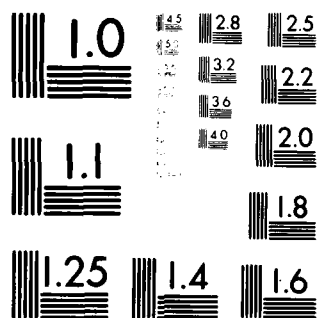
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The Structure of Bis(phthalocyaninato)neodymium(III)

by

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ABSTRACT:

△ Single crystal X-ray diffraction analysis and X-ray photoelectron spectroscopy have been employed to investigate a bis(phthalocyaninato)-neodymium(III) compound which exhibits electrochromism. A neodymium ion occupies a central position between two parallel but staggered phthalocyanine ligands. An acidic hydrogen may play an important role in electrochromism of the compound, but apparently does not bind strongly to any of the pyrrole nitrogen atoms, in opposition to the structure proposed by Nicholson and Galiaridi. However, a weak interaction between the hydrogen and nitrogen atom(s) cannot be excluded.

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A

The 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, $Pc_2Ln(III)H$ (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 (-1.0 - 1.2 V).^{3a} They proposed the following structure for this complex (Fig. 1).

Figure 1

With further developments, these electrochromic materials must become useful for full color imaging and graphic displays, as well as alpha-numerics. Recently, Corker et al. investigated the electrochromic behavior of bis(phthalocyaninato)lutetium(III) 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 would like to 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 mono-solvated $Pc_2Nd(III)H$ complex prepared by recrystallization from dichloromethane was used for the X-ray analysis. Anal.

Calcd. for $C_{64}H_{33}N_{16}Nd \cdot CH_2Cl_2$: Cl, 5.66%. Found: Cl, 5.71%.

Crystal data: orthorhombic; $a = 8.030(4)$, $b = 22.925(7)$, $c = 28.315(7)$

$\text{\AA}$; $V = 5212(3) \text{\AA}^3$; space group $P2_12_12_1$; $Z = 4$; $\rho_o = \text{g cm}^{-3}$;

$\rho_c = 1.60 \text{ g cm}^{-3}$; $M = 1255.2$; $F(000) = 2524$ electrons; $\mu(\text{MoK}\alpha) = 11.7$

cm^{-1} .⁵ The neodymium ion occupies a central position between two parallel, but staggered (45°) phthalocyanine ligands (Fig. 2).

Figure 2

The eight Nd-N bond distances vary from $\text{\AA}$ to $\text{\AA}$. While one of the phthalocyanine macrocycles is slightly saucer-shaped towards the neodymium atom, the other is planar; angles of tilt range from 2.5° to 7.0° . The pyrrole nitrogen atoms vary from the macrocyclic planes by distances ranging from 0.04 to $0.21 \text{\AA}$. The tilted benzimidazol group is an equal distance of $1.47(1) \text{\AA}$ 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. However, the molecules are packed in a three-dimensional "herring-bone" pattern (Fig. 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.

Figure 3

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 a N 1s X-ray photoelectron spectrum (Fig. 4).⁶

Figure 4

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 (Fig. 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, $\text{Pc} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{PcNd(III)Pc}$ to explain electrochromism.⁸ In their model, the acidic hydrogen have 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. In further detail, we are studying electrochromism of bis(phthalocyaninato)neodymium(III) using ESR and cyclic voltmeter, and the results will be described in a forthcoming paper.

FIGURE CAPTIONS

Figure 1. The proposed structure of bis(phthalocyaninato)lutetium(III).^{3a}

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

Figure 3. Stereoscopic view of one unit cell of the structure.

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

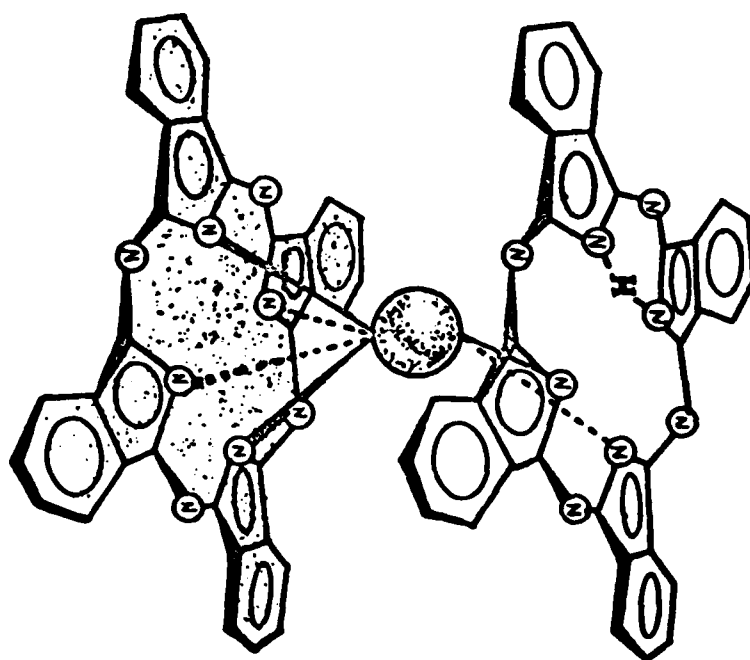


Figure 1. Kasuga, Tsutsui

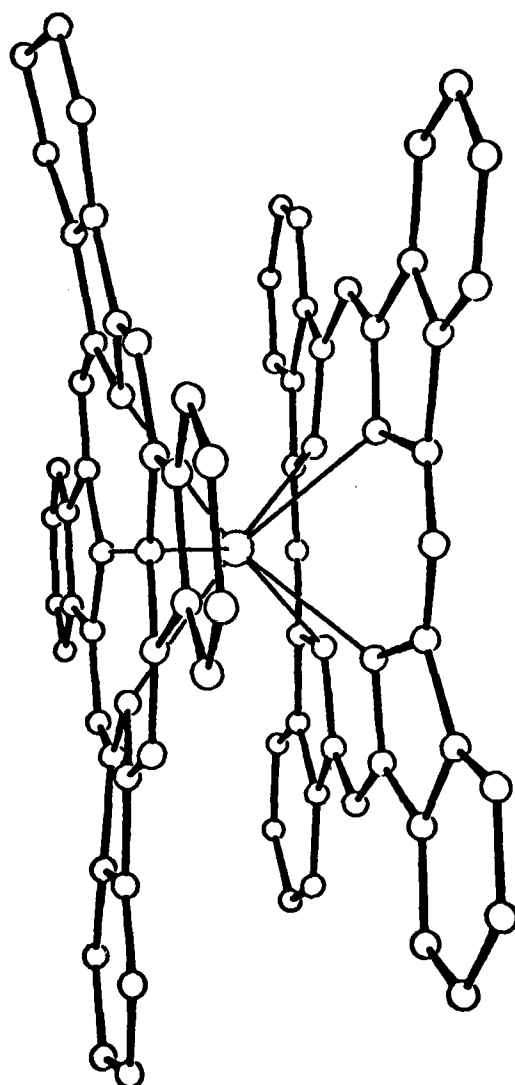


Figure 2. Kaeuga, Teutsul

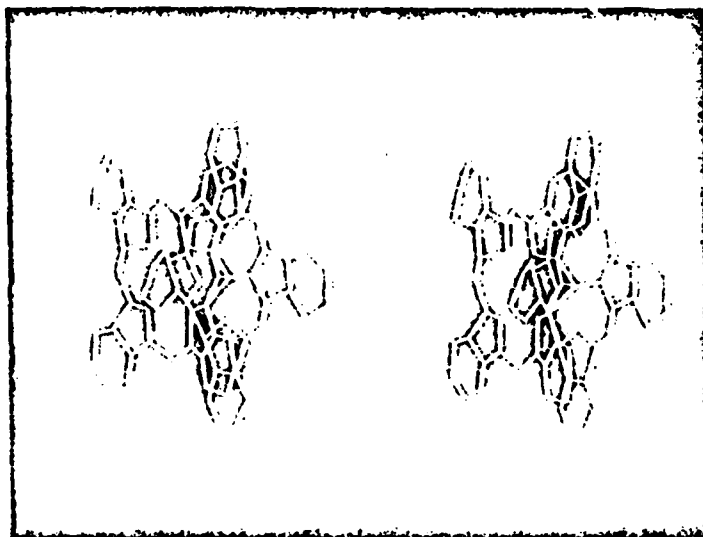


Figure 3. Kasuga, Teutsul

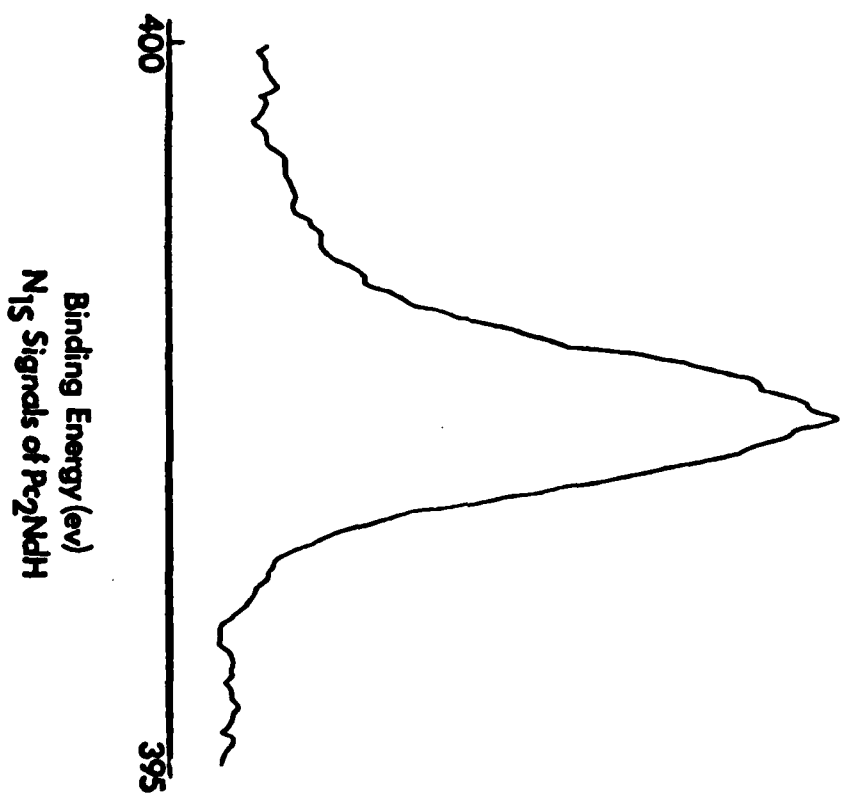


Figure 4. Kasuga, Teutsui

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