Volume 25
Number 13
June 18, 1986

Inorganic Chemistry

Communications

(Porphyrinato)bis(phthalocyaninato)dilanthanide(III) Complexes Presenting a Sandwich Triple-Decker-like Structure

Sir:

Bis(phthalocyaninato)lanthanide(III) derivatives presenting a sandwich-type structure have been known for many years.[1–6] These complexes are still intensively studied due to their semiconductor and electrochromic properties.[7–9] The synthesis and properties of bis(porphyrinato) and tris(porphyrinato)lanthanide(III) derivatives have also been reported.[10,11] X-ray structural studies have shown that bis(porphyrinato) complexes have geometries that are similar to those displayed by the $LnPc_2$ complexes (Ln = lanthanide; Pc = phthalocyanine) whereas the tris(porphyrinato) derivatives present structures in which two lanthanide(III) metal cations are sandwiched between three macrocyclic rings in a triple-decker-like geometry.[12]

Structural, magnetic, and spectroscopic properties of the green form of lutetium(III) bis(phthalocyanate) have shown that this complex is in a nonprotonated, one-electron-oxidized ligand form, Ln $(Pc^{2-})(Pc^{\bullet-})$.[5,6] In such a molecule, the unpaired spin could be either located on one phthalocyanine ring or delocalized over both rings. In order to force the localization of the unpaired spin on one ring, we have tried to synthesize a dissymmetric mixed-ligand, porphyrin (Por), phthalocyanine (Pc), lanthanide sandwich Ln(Por)(Pc). However, under the conditions used we obtained dilanthanide sandwich–triple-decker-like complexes. [Por(Ln)-Pc(Ln)Pc] in which the two metal cations are sandwiched between three macrocyclic rings. We report here the synthesis and spectral properties of such derivatives obtained with Ln = Nd(III), Eu(III), and Gd(III) and with *meso*-tetrakis(4-methoxyphenyl) porphyrin ($H_2T(4\text{-}OCH_3)PP$) and phthalocyanine (H_2Pc). The X-ray structure of the neodymium complex is also reported.

Table I. Visible Spectral Data for (Porphyrinato)bis(phthalocyaninato)dilanthanide(III) Derivatives in CH_2Cl_2

compd	λ_{max} nm (log ϵ)
Nd_2PorPc_2	338 (5.03), 418 (5.00), 515 sh, 550 sh, 620 (4.60), 704 (4.35)
Eu_2PorPc_2	340 (4.98), 418 (4.80), 518 sh, 545 sh, 617 (4.53), 724 (4.26)
Gd_2PorPc_2	340 (5.17), 417 (5.03), 520 sh, 538 sh, 618 (4.84), 730 (4.54)

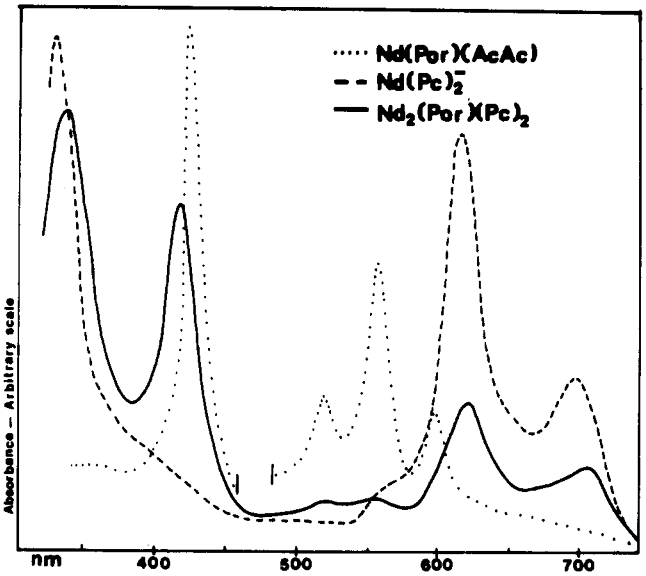

Figure 1. UV–visible spectra of $Nd_2Pc_2[T(4\text{-}OCH_3)PP]$, $(NdPc_2)^-(NBu_4)^+$, and $Nd(acac)[T(4\text{-}OCH_3)PP]$ in dichloromethane.

A 1,2,4-trichlorobenzene solution of $H_2T(4\text{-}OCH_3)PP$ and $Ln(acac)_3{\cdot}nH_2O$[13] (Ln = Nd, Eu, Gd) was refluxed during 4 h under a slow stream of argon to form the mono(porphyrinato)lanthanide.[15] To this solution was added, after cooling under argon, dilithium phthalocyaninate,[14] and the whole mixture was refluxed again for 2 h. Cooling, addition of hexane, redissolution of the precipitate in dichloromethane, chromatography on a basic alumina column with a 2% $MeOH/CH_2Cl_2$ mixture as eluent, concentration, and addition of hexane yielded green microcrystalline powders. All three compounds gave analytical and spectral data in agreement with a $Ln_2Pc_2[T(4\text{-}OCH_3)PP]$ formulation (Ln

---

(1) Kirin, I. S.; Moskalev, P. N.; Makashev, Yu. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1965**, *10*, 1065.
(2) Kasuga, K.; Tsutsui, M. *Coord. Chem. Rev.* **1980**, *32*, 67.
(3) Kasuga, K.; Tsutsui, M.; Petterson, R. C.; Tatsumi, K.; Van-Opdebosch, N.; Pepe, G.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4835.
(4) Darovskikh, A. N.; Tsytsenko, A. K.; Franf-Kamenetskaya, O. V.; Fundamenskii, V. S.; Moskalev, P. N. *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1984**, *29*, 273.
(5) De Cian, A.; Moussavi, M.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1985**, *24*, 3162.
(6) Chang, A. T.; Marchon, J. C. *Inorg. Chim. Acta* **1981**, *53*, L241.
(7) Corker, G. A.; Grant, B.; Clecak, N. J. *J. Electrochem. Soc.* **1979**, *126*, 1339.
(8) Collin, G. C. S.; Schiffrin, D. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *139*, 335.
(9) André, J. J.; Holczer, K.; Petit, P.; Riou, M. T.; Clarisse, C.; Even, R.; Fourmigue, M.; Simon, J. *Chem. Phys. Lett.* **1985**, *115*, 463.
(10) Buchler, J. W.; Kappellmann, H. G.; Knopff, M.; Lay, K. L.; Pfeifer, S. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1983**, *38B*, 1339.
(11) Buchler, J. W.; Knoff, M. In *Optical Properties and Structure of Tetrapyrroles*; Blauer, G., Sund, H., Eds.; De Gruyter: Berlin, 1985; pp 91–105.
(12) Buchler, J. W.; De Cian, A.; Fischer, J.; Kihn, M.; Paulus, H.; Weiss, R. *J. Am. Chem. Soc.*, in press.
(13) Stites, J. G.; Mc Carty, C. N.; Quill, L. *J. Am. Chem. Soc.* **1948**, *70*, 3142.
(14) Barret, R. A.; Frye, D. A.; Linstead, R. P. *J. Chem. Soc.* **1938**, 1157.
(15) Wong, C. P. *Inorg. Synth.* **1983**, *22*, 156.

0020-1669/86/1325-2107$01.50/0 © 1986 American Chemical Society

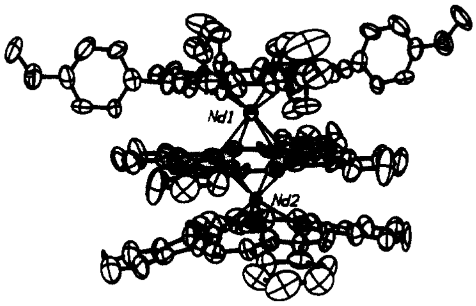

Figure 2. ORTEP plot of a $Nd_2Pc_2[T(4\text{-}OCH_3)PP]$ molecule. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

= Nd(III), Eu(III), Gd(III)).[16]

The UV-visible spectral data[17] obtained in dichloromethane are reported in Table I and Figure 1. In the 500–700-nm region these spectra are similar to those displayed by the blue bis(phthalocyaninato)lanthanide sandwich-type complexes[18] but in addition present a strong band near 418 nm, which is typically the Soret band region of porphyrin derivatives. Hence, these spectra are compatible with the presence of phthalocyanine and porphyrin ligands.

Single crystals of the neodymium derivative marginally suitable for X-ray studies were obtained by diffusion of pentane into trichloroethane solutions of the compound.[19] These crystals contain $[T(4\text{-}OCH_3)PP(Nd)Pc(Nd)Pc]$ molecules that lie on a fourfold symmetry axis of space group $P4/n$ and thus present C_4 point group symmetry. Such a symmetry implies that the mean planes of the three rings are precisely parallel and exactly perpendicular to the Nd1···Nd2 axis. Two $CHCl_2$–CH_2Cl solvent molecules are also present in the unit cell. They are also located on a C_4 symmetry axis and hence are severely disordered. The geometry of one $[T(4\text{-}OCH_3)PP(Nd)Pc(Nd)Pc]$ molecule is shown in Figure 2.

As shown by this figure, two neodymium atoms are sandwiched between two phthalocyanine macrocycle and one porphyrin macrocycle in a triple-decker-like structure. Thus, both metal atoms are eightfold coordinated to eight nitrogens, either to four porphyrinato and four phthalocyaninato nitrogen atoms (Nd1) or to eight phthalocyaninato nitrogens (Nd2). The coordination polyhedron of Nd1 is a distorded cube. This geometry minimizes the nonbonding interactions between the four *p*-methoxyphenyl groups of the tetraanisylporphyrin and the inner phthalocyanine ring Pc1. As a result, the four porphyrinato nitrogens are rotated with respect to the four isoindole nitrogens by 1.5° only and the four Nd1–Np(Por) bonds eclipse almost the four Nd1–N_{iso}(Pc1) bonds. The coordination polyhedron of Nd2 sandwiched between the two phthalocyanine rings is as usual a distorted square antiprism.[3-5] One Pc ring is rotated with respect to the other by 42.8°. The location of the neodymium atoms with respect to the 4Np and 4N_{iso} planes are respectively Nd1···4Np = 1.294 (3) Å, Nd1···4N_{iso}(Pc1) = 1.966 (3) Å, Nd2···4N_{iso}(Pc1) = 1.722 (2) Å, and Nd2···4N_{iso}(Pc2) = 1.364 (2) Å. Thus, the metal separation Nd1···Nd2 is 3.688 (9) Å. The Nd–N bond distances are Nd1–Np(Por) = 2.47 (2) Å, Nd1–Niso (Pc1) = 2.74 (2) Å, Nd2–N_{iso}(Pc1) = 2.57 (2) Å, and Nd2–N_{iso}(Pc2) = 2.43 (2) Å.

The inner phthalocyanine ring Pc1 is almost planar. The mean displacement of the carbon and nitrogen atoms with respect to their mean plane is only 0.01 Å, the largest deviation being 0.03 Å. The porphyrin ring is slightly domed. Whereas the 4Np plane lies at 1.294 (3) Å from Nd1, the corresponding distance of the 24-atom-core mean plane is 1.324 (3) Å. The outer phthalocyanine ring Pc2 is also convex; the largest displacement of the outermost carbon atoms of the phenyl groups with respect to the 4N_{iso} plane of Pc2 is 0.83 (4) Å away from Nd2.

In conclusion, despite the unfavorable cubic coordination geometry that is sterically imposed to one of the metal atoms, *meso*-tetraarylporphyrin–bis(phthalocyanine) complexes (Ln = Nd(III), Eu(III), Gd(III)) having a sandwich triple-decker-like structure can be isolated both in solution and in the solid state. Similar triple-decker-like structures with ligands allowing a more favorable coordination geometry for both metals are presently under study.

Supplementary Material Available: Listing of positional parameters for all non-hydrogen atoms (2 pages). Ordering information is given on any current masthead page.

Laboratoire de chimie des métaux de transition et
de catalyse associé au CNRS (UA 424)
Institut Le Bel
Université Louis Pasteur
67070 Strasbourg, France

M. Moussavi
A. De Cian
J. Fischer
R. Weiss*

Received January 2, 1986

---

(16) Anal. of $Ln_2C_{112}N_{20}O_4H_{68}$ (**1**, Ln = Eu; **2**, Ln = Nd; **3**, Ln; Gd). Calcd for **1**: C, 65.24; H, 3.30; N, 13.59. Found: C, 64.84; H, 3.34; N, 13.19. Calcd for **2**: C, 65.74; H, 3.32; N, 13.69. Found: C, 66.63; H, 3.36; N, 13.60. Calcd for **3**: C, 64.91; H, 3.28; N, 13.52. Found: C, 64.83; H, 3.21; N, 13.14.

(17) UV–visible spectra were recorded on a Cary 219 instrument.

(18) Blue $(LnPc_2)^-(NBu_4)^+$ (Ln = Nd, Gd, Lu) complexes have been isolated. They have similar spectra, and the structure of the Lu compound has been determined by x-ray diffraction: Weiss, R., to be submitted for publication.

(19) The deep green single crystals belong to the tetragonal system with $a = b = 20.248$ (6) Å, $c = 13.098$ (4) Å, space group $P4/n$, $C_{114}H_{71}N_{20}O_4Cl_3Nd_2$, $Z = 2$, and $d_{calcd} = 1.348$ g cm^{-1}. They were only marginally suitable for X-ray studies. Their largest dimensions were 0.04 × 0.10 × 0.10 mm; hence, their diffraction power was very low. A total of 2761 $+h,+k,+l$ unique data were collected at room temperature with graphite-monochromated copper Kα radiation (λ = 1.5405 Å) on a Philips PW1100/16 automatic diffractometer, in the $\theta/2\theta$ flying-step-scan mode with a scan speed of 0.024° s^{-1}, a step width of 0.05° deg and a scan angle of $\Delta\theta = 0.9° + 0.143 \tan \theta$. They were corrected for Lorentz, polarization, and absorption factors. The structure was solved and refined by using 1811 reflections having $I > 3\sigma(I)$. A final difference map showed residual electronic density near the C_4 axis. These residues arise from a highly disordered $CHCl_2$–CH_2Cl solvent molecule and were unresolvable. The presence of this unresolvable entity explains partly the high R values of $R_1 = 0.10$ and $R_2 = 0.14$.