

Synthesis and study of chemiochromic properties of highly soluble dysprosium octa-*tert*-butyldinaphthalocyaninate

V. N. Nemykin,* N. A. Kostromina, and S. V. Volkov

Institute of General and Inorganic Chemistry, National Academy of Sciences of the Ukraine,
32–34 prosp. Palladina, 252680 Kiev, Ukraine.
Fax: +7 (044) 444 3070

Chemiochromic properties of dysprosium octa-*tert*-butyldinaphthalocyaninate were studied by electron spectroscopy. An initial blue form is chemically oxidized and reduced in an inert atmosphere to form stable green and pale green forms that are reversibly transformed into one another.

Key words: dinaphthalocyanine, dysprosium, chemiochromism, electronic spectra.

Diphthalocyanine complexes of lanthanides (Pc_2Ln) have "sandwich" structures¹ and pronounced electro- and chemiochromic properties.^{2–4} For example, four color transitions (green, blue, red, and violet) are observed for the lutetium diphthalocyanine complex when the potential is varied within 1.5 V.⁵

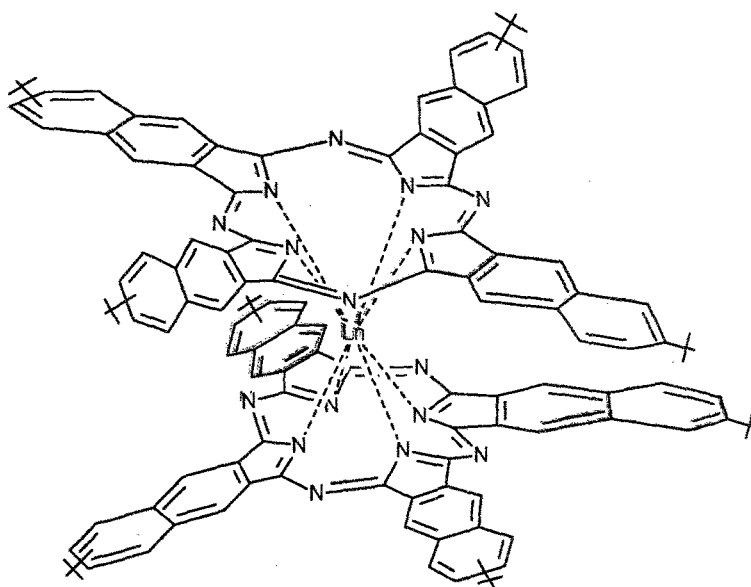
At the same time, diphthalocyanine complexes of lanthanides (Nc_2Ln) are scarcely studied. Only two lutetium complexes of this class have been described in the literature.⁶

In this work, highly soluble dysprosium bis(tetra-*tert*-butylnaphthalocyanine) was synthesized, and its redox properties in various organic solvents were studied.

Experimental

Electronic spectra were recorded on a Specord M-40 spectrophotometer in the 300–900 nm range.

Synthesis of octa-*tert*-butyldinaphthalocyaninedysprosium (Nc_2Dy). Anhydrous dysprosium acetate (0.339 g, $1 \cdot 10^{-3}$ mol L^{-1}) was added to a solution of 0.938 g ($1 \cdot 10^{-3}$ mol L^{-1}) of tetra-*tert*-butylnaphthalocyanine⁷ in 200 mL of DMSO. The mixture was refluxed for 30 min, filtered, and poured into 400 mL of water. The precipitate formed was filtered off and dried in air. The complex was dissolved in benzene and chromatographed on alumina (benzene as eluent). Yield 0.508 g (50 %). Calculated (%): C, 75.57; H, 5.54; N, 11.00. $\text{C}_{128}\text{H}_{112}\text{N}_{16}\text{Dy}$. Found (%): C, 75.71; H, 5.49; N, 10.87.



*Ln = Lu, Dy

Results and Discussion

The dysprosium complex is a deep-blue crystalline substance that is stable in air (m.p. > 250 °C), highly soluble in most organic solvents (benzene, methylene chloride, DMF, etc.), and, unlike tetra-*tert*-butyl-naphthalocyanines of transition metals,⁷ stable in solutions.

Three groups of bands in the regions of 700–780, 580–600, and 300–420 nm are observed in the electronic absorption spectrum of $\text{Nc}^{\text{I}}_2\text{Dy}$ (Table 1, Fig. 1). The first of them consists of a very intense Q-band (780 nm) with vibrational satellites. This band is more than 100 nm bathochromically shifted compared to spectra of previously studied phthalocyanine complexes^{5,8} due to an increase in the π -conjugated system of dinaphthalocyanine complexes. The band at 580–600 nm is also typical of lutetium dinaphthalocyanine complexes⁶ (see Table 1) and is not observed in the spectra of naphthalocyanine complexes of transition metals. Thus, this band is characteristic of "sandwich" naphthalocyanine complexes. A similar band at 450 nm is observed for the green form of dinaphthalocyanine complexes of lanthanides⁶ (see Table 1). Its considerable bathochromic shift (>100 nm) is caused by an increase in the conjugated system of the macrocycle due to linear annelation of four isoindole fragments. The bands in the 300–420 nm range observed in the spectra of naphthalocyanine complexes of transition metals⁷ correspond to the same transitions that have been found in phthalocyanine analogs.⁹

Table 1. Electronic absorption spectra of "sandwich" complexes of lanthanides

Compound	Solution	λ/nm (ratio of intensities of bands)
$[\text{Nc}^{\text{I}}_2\text{Dy}]'$ blue	Toluene	785, 742 sh, 694, 590, 420 sh, 356 sh, 329 (3.15:0.74:0.59:1:0.87:1.42:2.49)
$[\text{Nc}^{\text{I}}_2\text{Dy}]^-$ pale green	Toluene— Et_2NH	810, 741, 328 (1:4.18:3.46)
$[\text{Nc}^{\text{I}}_2\text{Dy}]^+$ green	Toluene— (Br_2)	825, 641, 323 (1:4.88:12)
$[\text{Nc}^{\text{I}}_2\text{Dy}]^+$ green	$\text{HOAc}(\text{O}_2)$	789, 687, 345, 323 (1:3.03:3.91:5.58)
$[\text{Nc}^{\text{I}}_2\text{Lu}]'^*$	<i>o</i> -DCB	758, 720 sh, 678, 582, 328 (3.68:0.73:1:1:2.56)
$[\text{Nc}^{\text{I}}_2\text{Lu}]'^*$	<i>o</i> -DCB	820, 704, 326 (1:2.97:2.72)
$[\text{Nc}^{\text{I}}_2\text{Lu}]^{+*}$	<i>o</i> -DCB	808, 616, 332 (1:1.49:1.76)
$[\text{Pc}^{\text{I}}_2\text{Dy}]'^{**}$ green	<i>o</i> -DCB	667, 454
$[\text{Pc}^{\text{I}}_2\text{Dy}]'^{**}$ blue	<i>o</i> -DCB	677, 607
$[\text{Pc}^{\text{I}}_2\text{Lu}]'^{**}$ blue	<i>o</i> -DCB	706, 622, 335 (1:1.94:2.48)

* From Ref. 6. ** From Ref. 11.

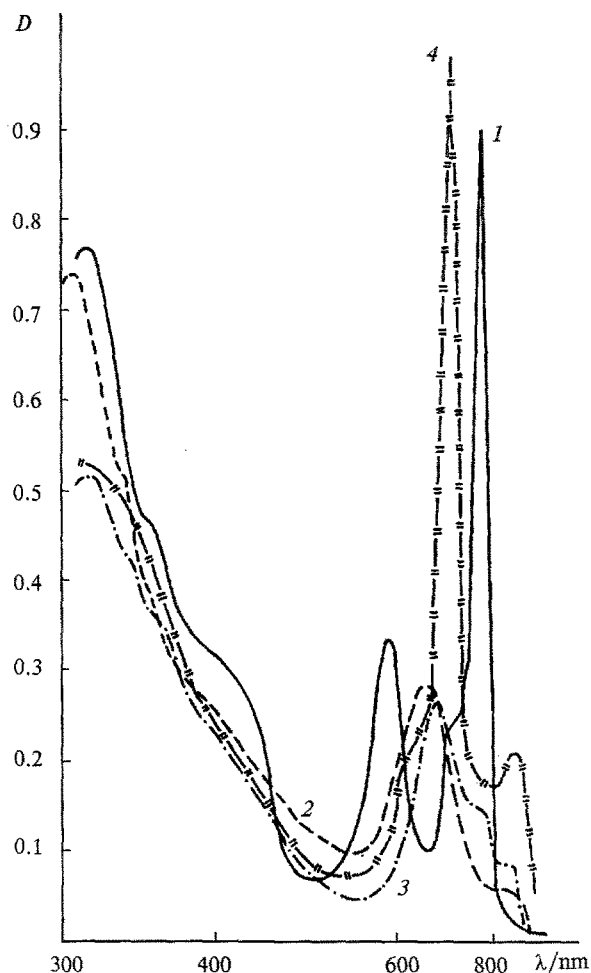
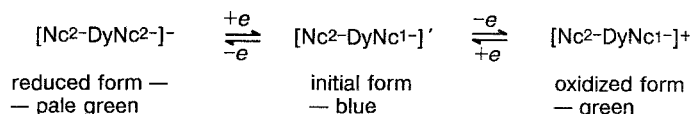


Fig. 1. Electronic absorption spectra of the complex $\text{Nc}^{\text{I}}_2\text{Dy}$ (1) and its forms: oxidized by bromine (2) and oxygen in the presence of AcOH (3), reduced (4); toluene as solvent.

As mentioned previously, for diphthalocyanine complexes of lanthanides an increase in the pH of solutions of the green form results in its transition to the blue form.¹⁰ The band at 450 nm disappears, and the Q-band is split into two components that are well resolved for late lanthanides and are almost fused into one band for early lanthanides (see Table 1). The addition of diethylamine to a solution of the dysprosium complex in *o*-dichlorobenzenes or toluene results in the transition of the initial blue form into the pale green one. The transition is characterized by isobestic points and is reversible. The band at 580–600 nm disappears, and two new bands appear at 740 and 810 nm instead of the Q-band (see Fig. 1). The pale green form is stable in an inert atmosphere and gradually disappears in air. The electronic absorption spectrum of this form is similar to that of the electrochemically one-electron reduced forms of lutetium dinaphthalocyanine complexes.⁶ The differences in splitting the bands of dysprosium and lutetium complexes are the same as those of their phthalocyanine analogs and can be due to an increase in the ionic radius

Scheme 1



of dysprosium compared to that of lutetium.¹¹ Thus, it is likely that the pale green dysprosium complex obtained is the one-electron reduced form similar to those of lutetium complexes. This transition occurs at lower concentrations of amine and is much faster in an *o*-DCB solution than in toluene.

Bromine titration of a solution of Nc^1_2Dy in *o*-DCB or toluene results in the formation of its oxidized form (see Fig. 1), to which the bands at 640 and 825 nm correspond. The transition is characterized by isobestic points, while the color of the solution changes from blue to green. The bands in the electronic absorption spectrum of this form are similar to those observed for the electrochemically generated one-electron oxidized form of the lutetium dinaphthalocyanine complex.⁶ A gradual increase in the concentration of acetic acid in an *o*-dichlorobenzene solution of the dysprosium complex results in the transition, which is similar to one-electron oxidation by elementary bromine (see Fig. 1). However, the most intense band in the electronic absorption spectrum is somewhat bathochromically shifted relative to that of the analog obtained by oxidation with bromine. It is likely that the same oxidation of "sandwich" complexes of hafnium and zirconium diphthalocyanines by organic acids, which has already been observed previously,¹² is related to oxygen traces. Bathochromic shift of the bands in the electronic absorption spectra during oxidation of the dysprosium complex in the presence of acetic acid can be caused by protonation of nitrogen meso-atoms, which is observed, as a rule, in phthalocyanine systems.¹³

Thus, the following scheme of transitions of the dysprosium dinaphthalocyanine complex seems to be the most probable (Scheme 1).

As in the case of diphthalocyanine complexes of lanthanides, the dysprosium complex synthesized exhib-

its chemiochromic properties, which, however, are less pronounced. On the other hand, the potentials of these transitions are considerably lower, making it possible to use dinaphthalocyanine complexes for selective sensors.

References

1. I. S. Kirin, P. N. Moskalev, and Yu. A. Mokashev, *Zh. Neorg. Khim.*, 1965, **10**, No. 8, 1951 [*J. Inorg. Chem. USSR*, 1965, **10**, No. 8 (Engl. Transl.)].
2. A. T. Chang and J. Marchon, *Inorg. Chim. Acta*, 1981, **53**, L241.
3. D. Walton, B. Ely, and G. Elliot, *J. Electrochem. Soc.*, 1981, **128**, 2479.
4. M. L'Her, Y. Cozien, and J. Courtot-Coupes, *J. Electroanal. Chem.*, **157**, 183.
5. M. M. Nicholson, *Ind. Eng. Chem. Res. Dev.*, 1982, **21**, 261.
6. M. G. Gal'pern, T. D. Talismanova, L. G. Tomilova, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1985, **55**, 1099 [*J. Gen. Chem. USSR*, 1985, **55** (Engl. Transl.)].
7. V. I. Kovshev and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1972, **42**, 696 [*J. Gen. Chem. USSR*, 1985, **42** (Engl. Transl.)].
8. P. N. Moskalev, *Koord. Khim.*, 1990, **16**, 147 [*Sov. J. Coord. Chem.*, 1990, **16** (Engl. Transl.)].
9. A. M. Schaffer, M. Goutermann, and E. R. Davidson, *Theoret. Chim. Acta*, 1973, **30**, 9.
10. K. Kasuga and M. Tsutsui, *J. Coord. Chem.*, 1981, **11**, 177.
11. E. I. Kapinus, L. I. Smykalova, and I. I. Dilung, *Zh. Neorg. Khim.*, 1980, **25**, 412 [*J. Inorg. Chem. USSR*, 1980, **25** (Engl. Transl.)].
12. N. A. Ovchinnikova, L. G. Tomilova, N. B. Seregina, V. V. Minin, G. M. Larin, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1992, **62**, 1631 [*J. Gen. Chem. USSR*, 1992, **62** (Engl. Transl.)].
13. B. D. Berezin, *Koordinatsionnye soedineniya porfirinov i ftalotsianinov* [Coordination Compounds of Porphyrins and Phthalocyanines], Nauka, Moscow, 1978 (in Russian).

Received December 21, 1994;
in revised form May 12, 1995