Inorg. Chem. **1985**, *24*, 3162–3167

Contribution from Institut Le Bel,[1]
Université Louis Pasteur, 67070 Strasbourg Cedex, France

Synthesis, Structure, and Spectroscopic and Magnetic Properties of Lutetium(III) Phthalocyanine Derivatives: $LuPc_2{\cdot}CH_2Cl_2$ and $[LuPc(OAc)(H_2O)_2]{\cdot}H_2O{\cdot}2CH_3OH$

ANDRÉ DE CIAN, MEHDI MOUSSAVI, JEAN FISCHER, and RAYMOND WEISS*

Received December 28, 1984

The bis(phthalocyaninato)lutetium(III) derivative $LuPc_2{\cdot}CH_2Cl_2$ (**1**, $LuC_{65}H_{34}N_{16}Cl_2$) and the (phthalocyaninato)lutetium(III) complex $[LuPc(OAc)(H_2O)_2]{\cdot}H_2O{\cdot}2CH_3OH$ (**2**, $LuC_{36}H_{33}N_8O_7$) were synthesized in boiling 1-hexanol with use of lutetium(III) acetate and 1,2-dicyanobenzene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene and purified by chromatography. The visible spectroscopic properties are reported for both complexes. **1** crystallizes in the orthorhombic system with a = 28.242 (9) Å, b = 22.877 (8) Å, c = 8.050 (4) Å, Z = 4, and space group *Pnma*. **2** belongs to the monoclinic system with a = 12.033 (3) Å, b = 20.807 (6) Å, c = 14.011 (3) Å, β = 95.34 (2)°, space group $P2_1/n$, and Z = 4. **1** is a sandwich type complex in which the lutetium atom is eightfold coordinated by the isoindole nitrogens (N_{iso}) of two staggered phthalocyanine rings. The mean value of the Lu–N_{iso} bond distances with one ring is 2.387 (4) Å whereas the average value for the four Lu–N_{iso} bond lengths with the other ring is 2.372 (3) Å. Both rings are convex. In **2**, the lutetium atom is also eightfold coordinated to the four isoindole nitrogens of one phthalocyanine ring, to two oxygens of one acetato anion, and to two water molecules. The mean value of the four Lu–N_{iso} bond distances with the nitrogens of the phthalocyanine ring is 2.345 (2) Å. The structure and the magnetic properties of **1** are consistent with a nonprotonated, ligand-oxidized $[LuPc_2]$ formulation.

Introduction

The bis(phthalocyaninato)lanthanide(III) complexes have generated a great deal of interest recently.[2-5] Some of these complexes present interesting electrochromic properties. Since they sublime in general unchanged, they can be deposited on optically transparent electrodes and used in electrochromic displays.[6] Several groups[3-8] have reported the synthesis of blue and green compounds by reaction of lutetium acetate with 1,2-dicyanobenzene in the solid state at high temperature and separation by chromatography. The nature of these compounds has been the subject of long debate.[4] Proposed structures for these blue and green compounds were respectively as follows: (i) ionized, $[LuPc_2]^-$, and protonated, $[LuPc_2H]$, forms of lutetium(III) diphthalocyanine;[2] (ii) protonated, $[LuPc_2H]$, and one-electron ligand-oxidized protonated, $[LuPcPc^{\cdot -}H]^+$, forms;[3] (iii) reduced, $[LuPc_2]^-$, and one-ligand-oxidized nonprotonated, $[LuPcPc^{\cdot -}]$, forms[8] (Pc = phthalocyanine dianion). To our knowledge, the molecular structures of these compounds have, so far, not been described. We have now, using a novel synthetic method, obtained single crystals of the green derivative suitable for X-ray studies. We report here the synthetic methods used and the structure and magnetic and spectral properties of the green lutetium(III) diphthalocyanine $LuPc_2{\cdot}CH_2Cl_2$ and of a blue monophthalocyanine derivative, $[LuPc(OAc)(H_2O)_2]{\cdot}H_2O{\cdot}2CH_3OH$, which represents presumably an intermediate in the formation of the green compound.

Experimental Section

The UV/visible spectra were recorded on either a Cary 210 or a Cary 219 spectrometer. The magnetic susceptibility measurements were carried out with a Faraday type magnetometer equipped with a continuous-flow cryostat in the range 100–290 K. The sample consisting of crushed single crystals weighed about 9 mg. The applied magnetic field was 0.7 T. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. EPR spectra were obtained on a solid sample at 77 K with a Bruker spectrometer. Magnetic field measurements were made by using an NMR proton probe.

$LuPc_2{\cdot}CH_2Cl_2$ (1) and $[LuPc(OAc)(H_2O)_2]{\cdot}H_2O{\cdot}2CH_3OH$ (2). 1,2-Dicyanobenzene and 1,8-diazabicyclo[5.4.0]undec-7-ene[9] (DBU) were obtained from EGA-Chimie, France, and lutetium acetate was purchased from Johnson-Mathey Co., Paris, France; all were used without further purification. **1** and **2** were prepared with use of the following procedures: a mixture of 1,2-dicyanobenzene (4.0 g, 31.2 mmol), $Lu(OAc)_3{\cdot}xH_2O$ (0.7 g, 2 mmol), and DBU (2.4 g, 16 mmol) in 100 mL of 1-hexanol was heated at reflux for 5 h. The solution was cooled to room temperature and then filtered. The resulting purple crystalline precipitate was washed rapidly with acetic anhydride, cold acetone, and pentane and then dried in air. A total of 2.6 g of crude product was obtained in this way. The solid was then extracted with several 100-mL portions of chloroform. The remaining violet solid was identified by visible spectroscopy as being free phthalocyanine, PcH_2. The green remaining solution was reduced in volume on a rotary evaporator and then chromatographed on a column of silica gel. A 2% CH_3OH/CH_2Cl_2 solution was first used as eluent. A green fraction was obtained in this way, which gave by concentration and addition of hexane 0.52 g of the microcrystalline lutetium diphthalocyanine $LuPc_2{\cdot}CH_2Cl_2$ (**1**). Anal. Calcd for $Lu(C_{32}H_{16}N_8)_2{\cdot}CH_2Cl_2$: C, 60.7; H, 2.6; N, 17.4. Found: C, 60.3; H, 2.5; N, 17.0. The visible spectrum (Figure 1) presents bands at λ_{max} (log ϵ) 456 (3.40), 572 (3.04), 595 (3.32), 629 (3.20), and 658 (4.16) nm. Deep green single crystals of **1** were obtained by slow evaporation of the 2% CH_3OH/CH_2Cl_2/hexane solutions.

After collection of the green diphthalocyanine, a 20% CH_3OH/80% CH_2Cl_2 solution was used as eluent. A blue solution was obtained in this way, which yielded after concentration and addition of hexane 0.32 g of a blue microcrystalline powder of the monophthalocyanine derivative $[LuPc(OAc)(H_2O)_2]{\cdot}H_2O{\cdot}2CH_2Cl_2$. Anal. Calcd for $Lu(C_{32}H_{16}N_8)(CH_3CO_2)(H_2O)_3(CH_2Cl_2)_2$: C, 44.5; H, 2.9; N, 11.5. Found: C, 43.8; H, 2.9; N, 10.8. Visible spectrum (Figure 1):[10] λ_{max} (log ϵ) 673 (5.14), 645 (sh), 608 (4.32), 342 (4.67) nm. Blue single crystals of a methanol solvate, $[LuPc(OAc)(H_2O)_2]{\cdot}H_2O{\cdot}2CH_3OH$ (**2**), were obtained by slow evaporation of a solution of the CH_2Cl_2 solvate in methanol at 4 °C.

During chromatography of the green compound, a blue color is also observed, which slowly transforms to green during migration on the column. The species responsible for this blue color is the one-electron-reduced form of the green complex[11] **1**. The crude product obtained by the synthetic method used is mostly in the blue reduced form. During extraction, a large part of this blue compound is oxidized by air in the green compound **1**. A minor part remains in the reduced blue form, and is slowly oxidized by air during migration on the chromatography column.

The yield for the monophthalocyanine complex can be slightly increased by increasing the proportion of lutetium acetate in the starting mixture or by reducing the duration of heating at reflux of the 1-hexanol solution.

---

(1) Laboratoire de Cristallochimie et de Chimie Structurale associé au CNRS (ERA 08).

(2) Moskalev, P. N.; Kirin, I. S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1972**, *46*, 1019.

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

(4) Kasuga, K.; Tsutsui, M. *Coord. Chem. Rev.* **1980**, *32*, 67–95.

(5) Collin, G. C. S.; Schiffrin, D. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *139*, 335–369.

(6) Automatics Strategic Systems Division Rockwell International Report; C82-268-281, No. AD-A 120483, 1982.

(7) These compounds were first reported by: Kirin, I. S.; Moskalev, P. N.; Makashev, Yu. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1965**, *10*, 1065.

(8) Chang, A. T.; Marchon, J. Cl. *Inorg. Chim. Acta* **1981**, *53*, L241–243.

(9) Diazabicyclo[5.4.0]undec-7-ene (DBU) has been used for the preparation of various metallophthalocyanines; see: Tomoda, H.; Saito, S.; Shiraishi, S. *Chem. Lett.* **1983**, 313–316.

(10) Sugimoto, H.; Higashi, T.; Maeda, A.; Mori, M.; Masuda, H.; Taga, T. *J. Chem. Soc., Chem. Commun.* **1983**, 1234 and references therein.

(11) De Cian, A.; Moussavi, M.; Weiss, R., to be submitted for publication.

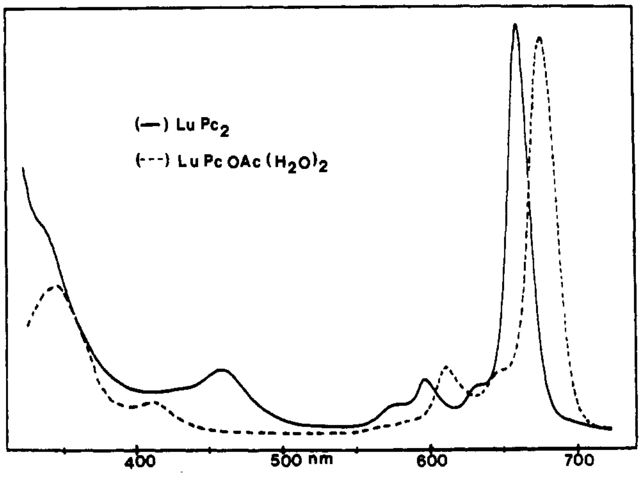


Figure 1. UV/vis spectra of $LuPc_2$ and $LuPc(OAc)(H_2O)_2$ (arbitrary scale).

Table I. Crystallographic Data

	1	2
formula	$LuC_{65}H_{34}N_{16}Cl$	$LuC_{36}H_{33}N_8O_7$
mol wt	1285	864
cryst syst	orthorhombic	monoclinic
a, Å	28.242 (9)	12.033 (3)
b, Å	22.877 (8)	20.807 (6)
c, Å	8.050 (4)	14.011 (3)
β, deg	90	95.34 (2)
U, Å^3	5201	3492
Z	4	4
D_{calcd}	1.64	1.64
μ, cm^{-1}	50.126	57.95
space group	*Pnma*	$P2_1/n$
radiation	Cu (graphite monochromator)	as for **1**
cryst size, mm	0.096 × 0.108 × 0.186	0.050 × 0.140 × 0.120
diffractometer	Philips PW 1100/16	as for **1**
temp, °C	20	−100
scan mode	$\theta/2\theta$ flying step scan	as for **1**
$\Delta\theta$, deg	$0.9 + 0.14 \tan \theta$	$1.0 + 0.14 \tan \theta$
step width, deg	0.04	0.05
scan speed, deg s^{-1}	0.016	0.024
θ limits, deg	5/57	4/57
no. of data measd	3948	5037
no. of data obsd ($I > 3\sigma(I)$)	2663	4044
Abs_{min}/Abs_{max}	35.72/67.97	0.80/1.42
R_1	0.044	0.027
R_2	0.059	0.048
ERRFIT	1.36	1.12

X-ray Crystallography. Diffraction data were collected at ~20 °C for **1** and −100 °C for **2** on a Philips PW 1100/16 automatic diffractometer equipped with a locally built low-temperature device.[12] The crystal used in the X-ray study of **1** was sealed in a Lindemann glass capillary whereas that used for the structure determination of **2** was glued at the end of a glass wire. Both crystals were mounted on a rotation-free goniometer head, and both had parallelepipedic habits. Data collection parameters and crystal data are displayed in Table I. Orientation matrices and unit cell parameters were obtained from 25 machine-centered reflections. For **1**, the octant $+h+k+l$ and, for **2**, the two octants $+h+k\pm l$ were measured. No equivalent reflections were recorded. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The data collection sets were transferred to a PDP 11/60 computer, and for computations the Enraf-Nonius SDP/V18[13] package was used, with the exception of a local data-reduction program. Three standard reflections measured every 1 h revealed no decay over the duration of data collection.

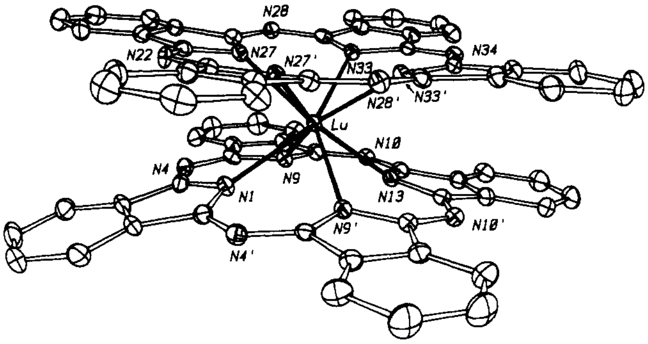


Figure 2. ORTEP plot of one $Lu(Pc)_2$ molecule with part of the atom-numbering scheme used. Ellipsoids are scaled to enclose 30% of the electron density. Hydrogen atoms are omitted.

The raw step-scan data were converted to intensities with use of the Lehmann–Larsen method[14] and corrected for Lorentz, polarization, and absorption factors, the last computed by the numerical integration method of Busing and Levy[15] for **1** and by the empirical method of Walker and Stuart[16] for **2**. No extinction corrections were applied. The centrosymmetric space group *Pnma* was assumed for **1** on the basis of a $N(Z)$ cumulative test on $|F_o|$.

The structures were solved with use of the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electron density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates for carbon-bonded hydrogens (C–H = 0.95 Å) and isotropic temperature factors such as $B(H) = 1 + B_{eqv}(C)$ Å^2. Water and OH hydrogen atoms were introduced by their difference-Fourier coordinates and the same form of isotropic temperature factors as the carbon hydrogens. The carbon hydrogen atoms of the MeOH moieties were not introduced. No hydrogen atom parameter was allowed to vary during full-matrix least-squares refinements minimizing $\sum w(|F_o| - |F_c|)^2$. The unit weight observations are for $p = 0.08$ in $w = 1/(\sigma_{counts}{}^2 + (pI)^2)$. The final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from ref 17 and 18.

Results and Discussion

The visible spectra of **1** and **2** are shown in Figure 1. The magnetic susceptibility measurements obtained between 100 and 290 K with use of a microcrystalline sample of **1** follow the Curie–Weiss law with $\mu_{eff} = 1.78 \pm 0.02\ \mu_B$ and $\Theta = 16°$. These results are in complete agreement with the susceptibility measurements reported by Marchon et al.[8] between 4.2 and 100 K on the green lutetium(III) diphthalocyanine prepared by following the method of Moskalev and Kirin.[7] They show that an unpaired electron is present in **1**. The EPR spectrum of **1**, which shows a strong signal at $g = 2.009$, confirms the presence of an unpaired spin and is consistent with the occurrence of a phthalocyanine radical. The presence of such a radical was already shown by Corker et al.,[3] who proposed for the green complex the one-electron ligand-oxidized, protonated form $[LuPcPc^{\cdot-}H]^+$. The mass spectrometric measurements made by Marchon et al. on their sample, which presents the same spectroscopic and magnetic characteristics as **1**, are not consistent with the presence of a proton. Furthermore, no anion is present in the structure of **1** (vide infra). Thus, the green lutetium(III) diphthalocyanine has a one-electron ligand-oxidized, nonprotonated structure, $[LuPcPc^{\cdot-}]$.

Structure of $LuPc_2 \cdot CH_2Cl_2$ (1). The asymmetric unit of the crystals contains a half-molecule of independent $LuPc_2$ and a half-molecule of crystallization both located in a crystallographic

---

(12) Ricard, L., to be submitted for publication.

(13) Frenz, B. A. In "Computing in Crystallography"; Schenk, M., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, C. G., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 64–71.

(14) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580–584.

(15) Busing, W. R.; Levy, M. A. *Acta Crystallogr.* **1957**, *10*, 180–182.

(16) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 159–166.

(17) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2b.

(18) Cromer, D. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

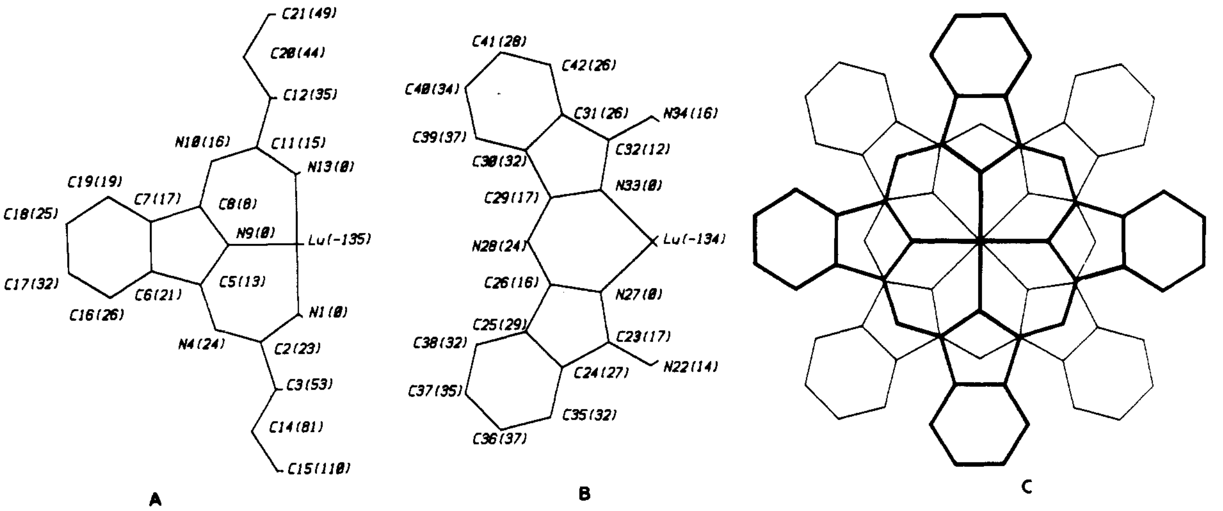


Figure 3. Stick bond models of rings A and B of $LuPc_2$ with the atom-numbering scheme used. The numbers enclosed in parentheses give the deviations in 0.01-Å units of the atoms with respect to the 4 N_{iso} mean planes. C is a projection of ring B on the 4 N_{iso} mean plane of ring A.

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Lu	0.36538 (1)	0.750	0.61057 (6)	2.144 (8)
N1	0.4499 (3)	0.750	0.617 (1)	3.2 (2)
C2	0.4766 (2)	0.7015 (3)	0.6494 (8)	3.1 (1)
C3	0.5222 (2)	0.7196 (3)	0.7183 (9)	3.4 (1)
N4	0.4660 (2)	0.6460 (2)	0.6218 (7)	3.2 (1)
C5	0.4272 (2)	0.6285 (3)	0.5404 (9)	3.0 (1)
C6	0.4171 (2)	0.5679 (3)	0.5029 (9)	3.5 (2)
C7	0.3763 (3)	0.5683 (3)	0.4055 (9)	3.6 (2)
C8	0.3628 (2)	0.6294 (3)	0.3843 (8)	3.2 (1)
N9	0.3927 (2)	0.6642 (2)	0.4735 (7)	2.9 (1)
N10	0.3279 (2)	0.6455 (2)	0.2843 (7)	3.2 (1)
C11	0.3170 (2)	0.7016 (3)	0.2583 (9)	3.3 (1)
C12	0.2811 (2)	0.7200 (3)	0.1378 (8)	3.6 (2)
N13	0.3366 (3)	0.750	0.331 (1)	2.9 (2)
C14	0.5614 (3)	0.6883 (3)	0.775 (1)	4.5 (2)
C15	0.6005 (3)	0.7191 (4)	0.829 (1)	5.3 (2)
C16	0.4391 (3)	0.5163 (3)	0.549 (1)	4.3 (2)
C17	0.4196 (3)	0.4648 (3)	0.492 (1)	5.4 (2)
C18	0.3784 (4)	0.4640 (4)	0.399 (1)	5.7 (2)
C19	0.3558 (3)	0.5163 (4)	0.351 (1)	4.8 (2)
C20	0.2490 (3)	0.6874 (3)	0.043 (1)	4.3 (2)
C21	0.2162 (3)	0.7193 (4)	-0.049 (1)	5.6 (2)
N22	0.4317 (2)	0.750	1.0040 (9)	2.6 (2)
C23	0.4135 (2)	0.6994 (3)	0.9574 (9)	2.9 (1)
C24	0.4308 (2)	0.6440 (3)	1.0218 (8)	3.0 (1)
C25	0.4022 (2)	0.6004 (3)	0.9529 (9)	2.9 (1)
C26	0.3682 (2)	0.6300 (3)	0.8469 (8)	2.8 (1)
N27	0.3773 (2)	0.6894 (2)	0.8455 (7)	2.7 (1)
N28	0.3330 (2)	0.6029 (2)	0.7712 (7)	2.8 (1)
C29	0.3006 (2)	0.6297 (3)	0.6791 (9)	2.8 (1)
C30	0.2606 (2)	0.6000 (3)	0.6012 (8)	3.2 (1)
C31	0.2337 (2)	0.6433 (3)	0.5248 (9)	3.2 (1)
C32	0.2566 (2)	0.6990 (3)	0.5606 (8)	2.5 (1)
N33	0.2979 (2)	0.6892 (2)	0.6459 (7)	2.5 (1)
N34	0.2375 (3)	0.750	0.518 (1)	2.9 (2)
C35	0.4685 (3)	0.6301 (3)	1.1238 (9)	4.0 (2)
C36	0.4775 (3)	0.5713 (3)	1.154 (1)	4.5 (2)
C37	0.4498 (3)	0.5287 (3)	1.082 (1)	4.3 (2)
C38	0.4120 (2)	0.5416 (3)	0.982 (1)	3.7 (2)
C39	0.2504 (3)	0.5414 (3)	0.582 (1)	3.9 (2)
C40	0.2117 (3)	0.5280 (3)	0.481 (1)	4.6 (2)
C41	0.1848 (3)	0.5703 (4)	0.404 (1)	4.7 (2)
C42	0.1951 (2)	0.6288 (3)	0.427 (1)	4.0 (2)
ClS	0.4131 (1)	0.1866 (2)	0.6885 (5)	11.2 (1)
CS	0.4466 (9)	0.250	0.729 (3)	13.2 (8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Selected Bond Lengths (Å), Angles (deg), and Averages with Their Esd's for $LuPc_2 \cdot CH_2Cl_2$

	Lu-N Distances		
Lu-N1	2.386 (6)	Lu-N27	2.369 (5)
Lu-N9	2.381 (5)	Lu-N33	2.375 (4)
Lu-N13	2.392 (7)	mean	2.380 (2)
	Isoindole Moieties (Averages)[a]		
N_{iso}-C_α	1.376 (3)	C_α-N_m	1.327 (2)
C_α-C_β	1.456 (2)	C_{phe}-C_{phe}	1.389 (3)
C_β-C_β	1.390 (4)		
C_α-N_{iso}-C_α	107.6 (2)	C_α-N_m-C_α	123.0 (4)
N_{iso}-C_α-C_β	109.6 (2)	C_β-C_β-C_{phe}	121.2 (2)
C_α-C_β-C_β	106.5 (2)	C_β-C_{phe}-C_{phe}	117.3 (3)
N_{iso}-C_α-N_m	127.5 (3)	C_{phe}-C_{phe}-C_{phe}	121.2 (5)
	CH_2Cl_2 Contacts <4 Å[b]		
CS···C3	3.77 (2×) (sm)	ClS···C17	3.81 (2×) (sm)
ClS···C3	3.82 (2×) (sm)	ClS···C42	3.84 (2×) (dm)
ClS···C14	3.80 (2×) (dm)		

[a] Legend: N_{iso} = nitrogen atom of the isoindole group; C_α = α carbon atom of the isoindole group with respect to N_{iso}; C_β = β carbon atom of the isoindole group with respect to N_{iso}; C_{phe} = phenyl carbon atom; N_m = methine nitrogen atom. [b] Legend: sm, same $LuPc_2$ molecule; dm, two different $LuPc_2$ molecules.

plane of symmetry. Figure 2 shows the geometry of one of these $LuPc_2$ molecules; Figure 3 displays the stick bond model projections on the corresponding four isoindole nitrogen mean planes of the two crystallographically independent half-phthalocyanine moieties A and B and a projection of ring B on the 4 N_{iso} mean plane of ring A.

Table II lists the coordinates of the non-hydrogen atoms. As shown by Figures 2 and 3, the lutetium atom occupies a central position between two macrocyclic ligands A and B. The metal atom, the two isoindole nitrogens N1 and N13 of ring A, and the two azomethine nitrogens N22 and N34 of ring B are located in the crystallographic symmetry plane. Thus, the metal is eightfold coordinated by the isoindole nitrogens of the two phthalocyanine rings A and B. One ring is rotated by 45° with respect to the other. Consequently, the coordination polyhedron of lutetium is a square antiprism and the molecular geometry of $LuPc_2$ is very similar to those of $SnPc_2$,[19] UPc_2,[20] β-$NdPc_2$,[21] and $NdPc_2$ in $NdPc_2 \cdot CH_2Cl_2$.[22,23] Selected bond distances and angles are given

---

(19) Bennett, W. E.; Broberg, D. E.; Baenziger, N. C. *Inorg. Chem.* **1973**, *12*, 930–936.

(20) Gieren, A.; Hoppe, W. *J. Chem. Soc., Chem. Commun.* **1971**, 413–414.

(21) Darovskikh, A. N.; Tsytsenko, A. K.; Franck-Kamenetskaya, O. V.; Fundamenskii, V. S.; Moskalev, P. N. *Sov. Phys.-Crystallogr. (Engl. Transl.)* **1984**, *29*, 273–276.

(22) Kasuga, K.; Tsutsui, M.; Petterson, R. C.; Tatsumi, K.; Van Opdenbosch, N.; Pepe, G.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4835–4836.

Table IV. Bond Lengths and Angles Found in Isoindole Moieties of Phthalocyanines[a]

	H_2Pc[24]	$(MnPc(py))_2O$[27]	MnPc[25]	CoPc[25]	SnPc[26]	$SnPc_2$[19]	UPc_2[20]	β-$NdPc_2$[21]	$LuPc_2$	$LuPc(OAc)(H_2O)_2$
N_{iso}–C_α	1.37	1.37	1.390	1.375	1.373	1.375	1.38	1.377	1.376	1.369
C_α–C_β	1.47	1.45	1.446	1.450	1.456	1.467	1.46	1.472	1.456	1.456
C_β–C_β	1.41	1.38	1.383	1.384	1.391	1.387	1.40	1.398	1.390	1.400
C_α–N_m	1.30	1.33	1.319	1.316	1.328	1.321	1.32	1.344	1.327	1.331
C_{phe}–C_{phe}	1.40		1.389	1.383	1.390	1.409	1.40	1.401	1.389	1.387
C_α–N_{iso}–C_α	108	108	107.5	106.7	108.2	108.1	107.9	107.5	107.6	107.8
N_{iso}–C_α–C_β	109	109	109.0	110.1	109.2	109.2	109.4	109.8	109.6	109.8
C_α–C_β–C_β	106	107	107.2	106.5	106.6	106.6	106.6	106.3	106.5	106.2
N_{iso}–C_α–N_m		127	127.3	127.6	128.1	128.7	127.6	127.4	127.5	127.8
C_α–N_m–C_α		124	122.7	121.4	122.4	121.8	123.9	123.2	123.0	123.3
C_β–C_β–C_{phe}	121		121.3	121.4	121.3	122.7	121.6	122.1	121.2	121.1
C_β–C_{phe}–C_{phe}	118	115	117.1	117.1	117.3	115.3	116.8	116.2	117.3	117.5
C_{phe}–C_{phe}–C_{phe}	120	123	121.4	121.5	121.3	121.8	121.5	121.7	121.2	121.3

[a] See Table II for definition of N_{iso}, C_α, C_β, C_{phe}, and N_m.

in Table III. The four isoindole nitrogens of both macrocycles are coplanar (Figure 3). These two planes are almost parallel, their dihedral angle being only 0.1°.

The lutetium atom lies 1.35 Å from the four-isoindole-nitrogen mean plane of ring A and 1.34 Å from the 4 N_{iso} mean plane of ring B. The separation between the two 4 N_{iso} mean planes of ring A and ring B is thus very close to 2.69 Å. The three independent bond distances Lu–N_{iso}(A) range from 2.381 (5) to 2.392 (7) Å. The two independent Lu–N_{iso}(B) bond lengths of 2.369 (5) and 2.375 (4) Å are slightly shorter. The mean values corresponding to these two sets of Lu–N_{iso} bond distances of 2.387 (4) (A) and 2.372 (3) (B) Å are however not significantly different at the 3σ level.

Both macrocyclic ligands are severely distorted from planarity, but ring A deviates more from planarity than ring B (Figure 3). Both rings are convex. The isoindole moieties of ring A except that containing N1 and all the isoindole groups of ring B show comparable displacements with respect to the corresponding 4 N_{iso} mean planes:

(i) The displacements of the outermost carbon atoms of each phenyl ring range from 0.25 to 0.49 Å (Figure 3).

(ii) The dihedral angles of the pyrrole rings range from 4.6 to 8.7°.

(iii) The dihedral angles of the phenyl rings range from 1.9 to 3.6°.

In contrast, the displacements of the outermost carbon atoms (C15, C15′; Figure 3) of the isoindole moiety containing N1 are now 1.10 Å with respect to the 4 N_{iso} mean plane of ring A. Relative to this 4 N_{iso} mean plane, the dihedral angle of the N1C2C3C2′C3′ pyrrole ring is 13.5° and that of the attached phenyl ring is 13.8°.

Despite the large distortion from planarity observed especially for ring A, the average bond distances and angles within the five independent isoindole moieties present in **1** are not significantly different from those known for H_2Pc[23] and other metallophthalocyanines[24-26] (Table IV).

The CH_2Cl_2 molecule of crystallization located in the crystallographic mirror plane is surrounded by four $LuPc_2$ molecules. The CCl_2 plane lies above the severely tilted isoindole moiety (N1...C15C15′) and is approximately parallel to the mean plane of this group. The shortest contact distances occur between the chlorine atoms of CH_2Cl_2 and the carbon atoms C3C3′, C14C14′, C17C17′, and C42C42′ (Table III).

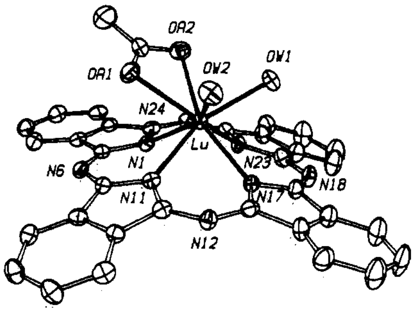


Figure 4. ORTEP plot of one $LuPc(OAc)(H_2O)_2$ molecule with part of the labeling scheme used. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted.

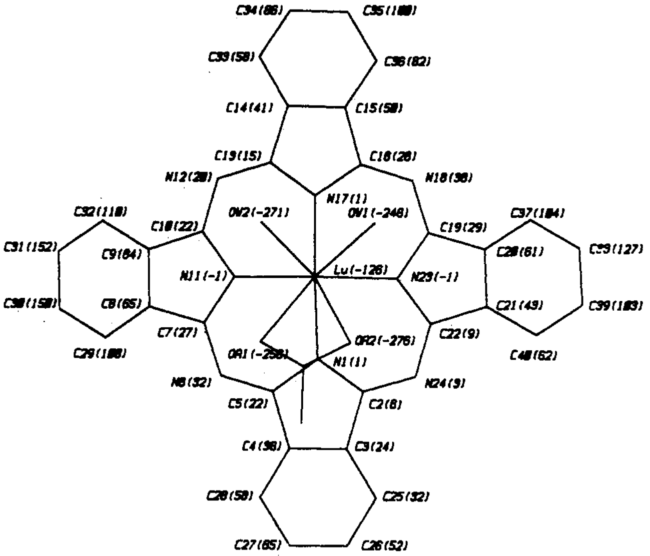


Figure 5. Stick bond model of $LuPc(OAc)(H_2O)_2$ with the atom-numbering scheme used. The numbers is parentheses give the deviations in 0.01-Å units of the atoms with respect to the 4 N_{iso} mean plane.

Structure of $[LuPc(OAc)(H_2O)_2]\cdot H_2O\cdot 2CH_3OH$ (2). Figure 4 displays the molecular geometry of $[LuPc(OAc)(H_2O)_2]$. Figure 5 shows a stick bond model projection of this molecule on the four-N_{iso} mean plane of the phthalocyanine ring. The coordinates for the non-hydrogen atoms are given in Table V. Selected bond distances and angles are given in Table VI.

In this monophthalocyanine derivative, the coordination geometry is again a slightly distorted square antiprism. The donor atoms consist of the four isoindole nitrogens of the phthalocyanine ring, two oxygen atoms of one acetate anion, and two oxygens of two water molecules. The four Lu–N_{iso} bond distances range from 2.333 (3) to 2.359 (3) Å with a mean value of 2.345 (2) Å. The Lu–N_{iso} bond distances are slightly shorter than those present in $LuPc_2\cdot CH_2Cl_2$ (mean value 2.380 (2) Å). The Lu–OA1,2 bond lengths are 2.366 (3) and 2.426 (3) Å whereas the Lu–OW1,2 separations equal 2.306 (3) and 2.356 (3) Å. While the two Lu–OW and the Lu–OA1 bonds adopt a staggered orientation

---

(23) The structure of $NdPc_2\cdot CH_2Cl_2$[22] has never been completely described so that a close comparison with that of $LuPc_2\cdot CH_2Cl_2$ is not possible presently. The crystal structure of $NdPc_2\cdot CH_2Cl_2$ (space group $P2_12_12_1$) is probably similar to that of $LuPc_2\cdot CH_2Cl_2$; the values of the lattice parameters are close, and space group $P2_12_12_1$ is a nonisomorphic subgroup of *Pnma*.

Table V. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Lu	0.82482 (2)	0.01340 (1)	0.13509 (1)	1.475 (5)
N1	0.6706 (3)	0.0218 (2)	0.0188 (3)	1.76 (7)
C2	0.6781 (4)	0.0046 (2)	−0.0745 (3)	1.82 (8)
C3	0.6020 (3)	0.0444 (2)	−0.1375 (3)	1.82 (8)
C4	0.5459 (3)	0.0844 (2)	−0.0768 (3)	1.68 (8)
C5	0.5904 (3)	0.0687 (2)	0.0203 (3)	1.63 (8)
N6	0.5535 (3)	0.0963 (2)	0.0967 (2)	1.76 (7)
C7	0.5883 (3)	0.0806 (2)	0.1872 (3)	1.60 (8)
C8	0.5297 (3)	0.1024 (2)	0.2669 (3)	1.87 (8)
C9	0.5787 (3)	0.0714 (2)	0.3480 (3)	1.79 (8)
C10	0.6683 (4)	0.0321 (2)	0.3160 (3)	1.80 (8)
N11	0.6728 (3)	0.0397 (2)	0.2194 (2)	1.74 (7)
N12	0.7279 (3)	−0.0086 (2)	0.3743 (3)	1.79 (7)
C13	0.7894 (3)	−0.0558 (2)	0.3421 (3)	1.88 (8)
C14	0.8362 (4)	−0.1083 (2)	0.4031 (3)	2.25 (9)
C15	0.8775 (4)	−0.1536 (2)	0.3409 (3)	2.39 (9)
C16	0.8575 (3)	−0.1269 (2)	0.2448 (3)	1.93 (8)
N17	0.8088 (3)	−0.0678 (2)	0.2489 (2)	1.74 (7)
N18	0.8791 (3)	−0.1599 (2)	0.1684 (2)	2.16 (7)
C19	0.8534 (3)	−0.1404 (2)	0.0784 (3)	2.10 (9)
C20	0.8658 (4)	−0.1825 (2)	−0.0022 (3)	2.34 (9)
C21	0.8306 (4)	−0.1470 (2)	−0.0842 (3)	2.15 (9)
C22	0.7913 (3)	−0.0855 (2)	−0.0504 (3)	1.73 (8)
N23	0.8090 (3)	−0.0826 (2)	0.0473 (2)	1.79 (7)
N24	0.7369 (3)	−0.0429 (2)	−0.1083 (2)	1.87 (7)
C25	0.5791 (4)	0.0473 (2)	−0.2364 (3)	2.07 (9)
C26	0.4997 (4)	0.0908 (2)	−0.2730 (3)	2.42 (9)
C27	0.4426 (4)	0.1305 (2)	−0.2127 (3)	2.39 (9)
C28	0.4642 (3)	0.1275 (2)	−0.1143 (3)	2.13 (9)
C29	0.4364 (4)	0.1414 (2)	0.2706 (3)	2.04 (9)
C30	0.3939 (4)	0.1487 (2)	0.3587 (3)	2.43 (9)
C31	0.4415 (4)	0.1164 (2)	0.4396 (3)	2.26 (9)
C32	0.5331 (4)	0.0775 (2)	0.4360 (3)	2.29 (9)
C33	0.8430 (4)	−0.1193 (2)	0.5016 (3)	2.8 (1)
C34	0.8905 (5)	−0.1769 (3)	0.5342 (4)	3.9 (1)
C35	0.9280 (5)	−0.2234 (3)	0.4719 (4)	4.0 (1)
C36	0.9222 (4)	−0.2122 (2)	0.3735 (3)	3.4 (1)
C37	0.9000 (5)	−0.2454 (2)	−0.0082 (3)	3.4 (1)
C38	0.9012 (5)	−0.2725 (3)	−0.0979 (4)	4.1 (1)
C39	0.8716 (5)	−0.2366 (3)	−0.1804 (3)	3.7 (1)
C40	0.8346 (4)	−0.1737 (2)	−0.1750 (3)	2.8 (1)
OA1	0.8118 (3)	0.1275 (2)	0.1002 (2)	2.61 (6)
OA2	0.9000 (3)	0.0655 (2)	0.0055 (2)	2.65 (6)
CA1	0.8534 (4)	0.1195 (2)	0.0217 (4)	2.7 (1)
CA2	0.8424 (5)	0.1697 (3)	−0.0555 (4)	4.5 (1)
OW1	1.0029 (2)	−0.0285 (2)	0.1463 (2)	2.26 (6)
OW2	0.9249 (3)	0.0643 (2)	0.2665 (2)	2.74 (7)
OW3	1.1526 (3)	0.0294 (2)	0.2791 (2)	2.85 (7)
CS1	0.8364 (7)	0.0939 (4)	0.5581 (6)	7.9 (2)
OS1	0.7730 (3)	0.0369 (2)	0.5651 (2)	3.71 (8)
CS2	0.7894 (5)	0.2072 (3)	0.3315 (5)	5.1 (1)
OS2	0.8764 (3)	0.1913 (2)	0.2721 (3)	5.1 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VI. Selected Bond Lengths (Å), Angles (deg), and Averages with Their Esd's for LuPc(OAc)$(H_2O)_2 \cdot H_2O \cdot 2MeOH$

	Lu–N Distances		
Lu–N1	2.359 (3)	Lu–N23	2.344 (3)
Lu–N11	2.333 (3)	mean	2.345 (2)
Lu–N17	2.344 (3)		
	Lu–O Distances		
Lu–OA1	2.426 (3)	Lu–OW1	2.306 (3)
Lu–OA2	2.366 (3)	Lu–OW2	2.356 (3)
	Isoindole Moieties (Averages)[a]		
N_{iso}–C_α	1.369 (2)	C_α–N_m	1.331 (2)
C_α–C_β	1.456 (2)	C_{phe}–C_{phe}	1.387 (2)
C_β–C_β	1.400 (3)		
C_α–N_{iso}–C_α	107.8 (2)	C_α–N_m–C_α	123.3 (2)
N_{iso}–C_α–C_β	109.8 (1)	C_β–C_β–C_{phe}	121.1 (1)
C_α–C_β–C_β	106.2 (1)	C_β–C_{phe}–C_{phe}	117.5 (1)
N_{iso}–C_α–N_m	127.8 (1)	C_{phe}–C_{phe}–C_{phe}	121.3 (1)

Contacts <3 Å

	dist	equiv code[b]		dist	equiv code[b]
OW1···OA2	2.63	75502	OW3···H22	1.98	55501
OW1···OW3	2.74	55501	CS1···H24	2.79	75602
OW2···OW3	2.82	55501	OS1···N12	2.84	55501
OW2···OS2	2.70	55501	OS1···H8	2.65	55501
OW3···N24	2.86	75502	OS1···H9	2.69	55501
OW3···OS1	2.66	75602	CS2···H23	2.51	55501
OW3···H1	2.96	75502	OS2···OA1	2.79	55501
OW3···H9	2.76	75602	OS2···H22	2.99	55501
OW3···H16	2.63	75502	OS2···H23	1.63	55501
OW3···H20	1.98	55501			

[a] See Table II for definitions of N_{iso}, C_α, C_β, C_{phe}, and N_m. [b] Equivalent codes are as defined in the program ORTEP.[28]

with respect to the Lu–N_{iso} bonds, the projection of the Lu–OA2 bond on the 4 N_{iso} mean plane makes an angle of 28° with Lu–N1 (Figure 5). The four isoindole nitrogen atoms of the phthalocyanine ring are coplanar (Figure 5). This is also approximately true for the four oxygen atoms bonded to lutetium. These two mean planes make a small dihedral angle of 1.9°. The lutetium atom lies only 1.26 Å away from the 4 N_{iso} mean plane. This distance is significantly shorter than those occurring in $LuPc_2 \cdot CH_2Cl_2$ (1.34 and 1.35 Å). The separation between lutetium and the four-oxygen mean plane is 1.36 Å (Figure 5).

The phthalocyanine deviates largely from planarity. It is again convex in shape (Figure 4). With respect to the 4 N_{iso} mean plane of the phthalocyanine ring, the following can be noted:

(i) The displacements of the four azomethine nitrogens range from 0.09 to 0.38 Å (mean value 0.25 Å).

(ii) The average displacements of the outermost carbon atoms of each phenyl ring range from 0.68 to 1.51 Å (mean value 1.07 Å). The pyrrole and phenyl rings are bent away from the 4 N_{iso} mean plane at angles that range from 8.4 to 17.4° for the pyrrole groups and 8.7 to 21.3° for the phenyl rings.

Again, despite the very large deviations from planarity, the average bond distances and angles found within the four crystallographically independent isoindole moieties are not significantly different from those present in H_2Pc[24] and other metallophthalocyanines[25-27] (Table IV). The acetate group bonded to lutetium shows the usual shape and dimensions. The shortest contact distances occurring between the [LuPc(OAc)$(H_2O)_2$] molecules and the water and the two MeOH molecules of crystallization are listed in Table VI. These moieties are linked to each other and to equivalent molecules by a network of van der Waals contacts and hydrogen bonds as seen from the values reported in Table VI.

In conclusion, the green lutetium(III) diphthalocyanine is in a nonprotonated, one-electron ligand-oxidized form. In such a molecule, the unpaired spin could be (i) located on one phthalocyanine ring or (ii) delocalized over both rings. Unfortunately, the geometry of the molecule does not allow us presently to discriminate between these two possibilities: the average value of the Lu–N_{iso} bond distances of 2.387 (5) Å with the isoindole nitrogens of one ring (A) appears to be slightly longer than the mean value of the Lu–N_{iso} bond lengths of 2.372 (3) Å with the isoindole nitrogens of ring B. However, this difference is small and not significant at the 3σ level. Thus, no firm conclusion can be derived from this result. Ring A deviates more from planarity than ring B, but larger distortions from planarity are present in the monophthalocyanine derivative [LuPc(OAc)$(H_2O)_2$]$\cdot H_2O \cdot 2CH_3OH$. Moreover, very large distortions from planarity are

---

(24) Hoskins, B. F.; Mason, S. A.; White, J. B. C. *J. Chem. Soc., Chem. Commun* **1969**, 554–555.

(25) Mason, R.; Williams, G. A.; Fielding, P. E. *J. Chem. Soc., Dalton Trans.* **1978**, 676–683.

(26) Friedel, M. K.; Hoskins, B. F.; Martin, R. L.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1970**, 400.

(27) Vogt, L. H.; Zalkins, A.; Templeton, D. H. *Inorg. Chem.* **1967**, *6*, 1725–1730.

(28) Johnson, C. K. *Oak Ridge Natl. Lab.*, [*Rep.*] *ORNL* (*U.S.*) **1965**, *ORNL-3794*.

also present in $SnPc_2$[19] and UPc_2,[20] where clearly no phthalocyanine ring is in an oxidized form.

Registry No. **1**, 97633-44-8; **2**, 97633-46-0; 1,2-dicyanobenzene, 91-15-6; 1,8-diazabicyclo[5.4.0]undec-7-ene, 6674-22-2.

Supplementary Material Available: Listings of thermal and positional parameters and esd's (Tables VII and VIII for $LuPc_2{\cdot}CH_2Cl_2$ (**1**) and Tables IX and X for $[LuPc(OAc)(H_2O)_2]{\cdot}H_2O{\cdot}2CH_3OH$ (**2**)), bond distances and angles (Tables XI and XII for **1** and Tables XIII and XIV for **2**), least-squares planes (Table XV for **1** and Table XVI for **2**), and observed and calculated structure factor amplitudes (Table XVII for **1** and Table XVIII for **2** (F_o and F_c, ×10)) and a stereopair of the surroundings of the CCl_2 moiety in $LuPc_2{\cdot}CH_2Cl_2$, showing one complete and three half $LuPc_2$ molecules (hydrogen atoms omitted) (63 pages). Ordering information is given on any current masthead page.

Contribution No. 3633 from the Central Research and Development Department,
E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

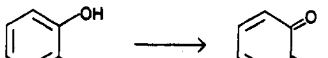
Synthesis, Spectroscopy, and Structures of Copper(II)-3,5-Di-*tert*-butyl-*o*-semiquinone Complexes

JEFFERY S. THOMPSON* and JOSEPH C. CALABRESE

Received December 14, 1984

The synthesis, spectroscopy, structures, and reactivity of a series of Cu(II)-di-*tert*-butyl-*o*-semiquinone (DTBSQ) complexes are presented. These compounds were prepared by reacting Cu(I)-ethylene complexes with the corresponding *o*-benzoquinone or by reacting Cu(II) dimers with the catechol. The oxidation states for the metal ion and ligand were assigned from analytical and spectroscopic data. In addition, the di-2-pyridylamine ($NH(py)_2$) complex $[Cu(NH(py)_2)(DTBSQ)]ClO_4{\cdot}0.5$tetrahydrofuran was characterized by X-ray diffraction techniques. The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$ in a unit cell of dimensions $a = 14.794$ (4) Å, $b = 19.513$ (4) Å, $c = 9.766$ (2) Å, $\alpha = 90.74$ (2)°, $\beta = 105.37$ (2)°, and $\gamma = 93.79$ (2)° at −100 °C. Least-squares refinement of 697 variables led to a value of the conventional R index (on F) of 0.050 and R_w of 0.044 for 4107 reflections having $I > 2\sigma(I)$. Each copper ion is coordinated to two pyridyl nitrogen atoms from $NH(py)_2$ and to two oxygen atoms from the DTBSQ ligand. There are two cations in the asymmetric unit with slightly different bond angles and distances about each copper ion. In addition to the $NH(py)_2$ and DTBSQ ligands, the perchlorate anions are coordinated in the axial positions to form distorted-octahedral geometries about each copper ion, with long and short Cu-O interactions. The C-O bond lengths of the coordinated DTBSQ ligand (1.284 (8)-1.304 (7) Å) are characteristic of DTBSQ complexes.

In this contribution, we present the synthesis, spectroscopy, structures and reactivities of a series of Cu(II)-3,5-di-*tert*-butyl-*o*-semiquinone (DTBSQ) complexes prepared by reacting bis(μ-methoxy)- or bis(μ-hydroxy)dicopper(II) compounds with the catechol or by reacting Cu(I)-ethylene complexes[1,2] with the corresponding *o*-benzoquinone. A series of bidentate nitrogen-donating ligands, with the type of coordinated nitrogen varying from tertiary amines to heterocyclic nitrogen donors, is used as the other ligands in the copper coordination sphere. These ligands allow isolation and complete characterization of the starting materials for both of these synthetic procedures.[1,2] The Cu(II)-dimer-catechol reaction has been suggested as a critical step in the copper-catalyzed oxidation of catechols to quinones (eq 1).[3,4]



(1)

Copper-catechol derivatives from this reaction have not been previously characterized, although several structures have been proposed.[3-5] Our preparative methods are similar to those of *o*-semiquinone complexes with other redox-active metals, including vanadium, chromium, manganese, iron, nickel, and zinc.[6] The metal ions are the electron acceptors for reactions with catechols or electron donors for reactions with quinones, yielding in both cases metal ion-semiquinone complexes. Our results are also consistent with a recent electrochemical study, which demonstrates the stability of Cu(II)-DTBSQ complexes.[7]

Experimental Section

General Methods. All chemicals were reagent grade and used as received unless otherwise noted. The Cu(I)-ethylene complexes were prepared as described elsewhere.[1,2] The solvents methanol, pyridine, diethyl ether, petroleum ether, and tetrahydrofuran (THF) were deaerated with prepurified nitrogen and stored over molecular sieves (4A), which were treated as described elsewhere.[1,2,8] Standard glovebox and Schlenkware techniques were used in the handling of air-sensitive compounds. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. NMR spectra were obtained in deuteriodichloromethane with a Perkin-Elmer EM-390 spectrometer. Electron paramagnetic resonance spectra were obtained on an Bruker ER 200B-SRC spectrometer at −110 °C. Absorption spectra were obtained with a Perkin-Elmer 330 spectrophotometer.

Preparation of (Di-2-pyridylamine)(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II) Perchlorate-0.5-Tetrahydrofuran, $[Cu(NH(py)_2)(DTBSQ)]ClO_4{\cdot}0.5THF$ (1). Method A. (Ethylene)(di-2-pyridylamine)copper(I) perchlorate, $[Cu(NH(py)_2)(C_2H_4)]ClO_4$, was dissolved in methanol. Dioxygen was bubbled through the flask at room temperature to yield a dark blue solution. Addition of diethyl ether yielded dark blue crystals of $[Cu_2(NH(py)_2)_2(OCH_3)_2](ClO_4)_2$. Anal. Calcd for $C_{22}H_{24}Cl_2Cu_2N_6O_{10}$: C, 36.18; H, 3.31; N, 11.50. Found: C, 36.20; H, 3.39; N, 11.32. To this Cu(II) dimer (0.50 g, 0.685 mmol) in approximately 15 mL of methanol was added 3,5-di-*tert*-butylcatechol, DTBC (0.152 g, 0.685 mmol). The resulting green solution was stirred for 0.5 h. A white precipitate formed and was removed by filtration. The solvent was removed from the filtrate under high vacuum to yield a green solid. Recrystallization from THF-petroleum ether yielded dark green crystals of **1**. Anal. Calcd for $C_{26}H_{33}ClCuN_3O_{6.5}$: C, 52.88; H, 5.63; N, 7.11. Found: C, 52.65; H, 5.55; N, 7.18. IR (cm^{-1}): 3340 m, 3270 w, 3230 w, 3165 w, 3130 w, 3100 w, 3040 w, 1650 s, 1620 w, 1595 s, 1580 m, 1535 s, 1340 w, 1305 w, 1245 w, 1240 m, 1210 w, 1165 m, 1125 s, 1095 s, 1060 s, 1030 w, 990 m, 965 w, 930 w, 915 m, 865 w, 860 m, 830 w, 810 w, 765 s, 750 w, 740 w, 725 w, 685 w, 670 w, 620 m.

---

(1) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813-2819.
(2) Thompson, J. S.; Swiatek, R. M. *Inorg. Chem.* **1985**, *24*, 110-113.
(3) (a) Rogic, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472-5487. (b) Willett, R. D.; Breneman, G. L. *Inorg. Chem.* **1983**, *22*, 326-329. (c) Speier, G.; Tyeklar, Z. *J. Mol. Catal.* **1980**, *9*, 233-235.
(4) (a) Rogic, M. M.; Swerdloff, M. D.; Demmin, T. R. In "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1983; pp 259-279. (b) Bulkowski, J. E.; Summers, W. E. *Ibid.* pp 445-456.
(5) (a) Demmin, T. R.; Swerdloff, M. D.; Rogic, M. M. *J. Am. Chem. Soc.* **1981**, *103*, 5795-5804. (b) Kida, S.; Okawa, H.; Nishida, Y. In "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1983; pp 425-444.
(6) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45-87.
(7) Harmalker, S.; Jones, S. E.; Sawyer, D. T. *Inorg. Chem.* **1983**, *22*, 2790-2794.
(8) Thompson, J. S.; Harlow, R. L.; Whitney, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 3522-3527.

0020-1669/85/1324-3167$01.50/0