Synthesis, Properties and Crystal Structure of Di(phthalocyaninato)lanthanum(III), a Partially Oxidized Semiconductor

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Di(phthalocyaninato)lanthanum. Crystal Structure, Cyclic Voltammetry, UV-VIS-NIR Spectra, Vibrational Spectra

[Introduction]

The electrochromic [1, 2] and semiconducting [3] properties of lanthanide diphthalocyanines (Ln(Pc)2) have attracted intensive research interest in the past two decades. Much of the work has been focussed, in particular, on the Lu derivatives, since this ion has the smallest ionic radius within the lanthanide series which leads to the most attractive interactions between the π electron systems of the two neighbouring Pc ligands. The unusual electrical properties of these compounds are closely correlated to the peculiar radical nature of one or both Pc ligand(s). There remains some uncertainty and debate about the composition of the "green compounds" [4]. Two structures have been proposed: (i) a protonated complex H[Ln(Pc2-)2] with a labile hydrogen and (ii) a half oxidized neutral compound Ln(Pc)2. A third structural proposal as a lanthanide monophthalocyanine, e.g. Ln(Cl)Pc2-, suggested by Kirin et al. [5], has been excluded by Boas et al. [6], who claimed an acid-base equilibrium (eq. (1)):

\[ H[Ln(Pc^2-)2] \rightleftharpoons [Ln(Pc^2-)2]^+ + H^+ \]  

(1)

Early lanthanides have been largely excluded from these investigations because of difficulties with the synthesis, particularly of the diphthalocyanines of La and Ce. These problems have been resolved recently [7], and the spectroscopic and structural properties of the whole series of the anionic complexes \([Ln(Pc^2-)2]^-(Ln = La--Lu)\) with different cations, including H+, have been investigated in detail [8–10]. We have now directed our interest towards oxidized diphthalocyanines of the early lanthanides, and report here on the preparation, spectroscopic properties and crystal structure of the half oxidized complex di(phthalocyaninato)lanthanum, \([La(Pc)2] \cdot CH_2Cl_2\). Diagnostic spectral differences with regard to \(H[La(Pc^2-)2]\) are pointed out and significant clarifications as to the nature of the "green compounds" are presented.

[Results and Discussion]

Preparation and properties

The oxidation potentials of lanthanide diphthalocyanines increase almost linearly with increasing ionic radius of the rare earth ion [11]. In the cyclic voltammogram shown in Fig. 1 of the very soluble \((^nBu_4N)[La(Pc^2-)2]\) the quasi-reversible first ring-centered oxidation (eq. (2))

\[ [La(Pc^2-)2]^- \rightarrow [La(Pc)2]^- + e^- \]  

(2)

occurs at \(E_{1/2}(1) = 0.34 \text{ V} \quad (\Delta E_{ca} \approx 78 \text{ mV})\), in good agreement with this linear relationship. Above 0.5 V, poorly resolved waves are detected at ~0.6 V and ~1.0 V on the anodic current sweep (not...
shown). The corresponding cathodic waves are missing, but a new wave at 0.08 V is observed instead. Such irreversible behaviour was documented for diphthalocyanines of other earlier lanthanides and has been attributed to chemical instability of the oxidized products. However, stable diphthalocyanines of Ce and Pr have been isolated in different oxidation states [12,13]. We therefore assume that this irreversibility is caused by the moderate solubility of the oxidation products which form an electrically conducting film on the surface of the electrode. This also applies to the half oxidized complex [La(Pc)2] which is insoluble in most common solvents. The stepwise reduction of the two Pc ligands yields complexes of the Pc3- radical anion at $E_{1/2}^{I/II} = -0.99$ V ($\Delta E_{ca} \approx 110$ mV) for the redox couple $[La(Pc^2-)_2]^{-}/[LaPc^2-]^{-2}$ and at $E_{1/2}^{I/II} = -1.17$ V ($\Delta E_{ca} \approx 130$ mV) for $[LaPc^2-]^{-2}/[LaPc^3-]^{-3}$.

In accordance with this electrochemical behaviour, [La(Pc)2] has been prepared, as the dichloromethane solvate, by the anodic oxidation of ($^n$Bu4N)[La(Pc2-)2]. After several days, black needles suitable for single crystal X-ray structure determination appeared at the Pt electrode. The bulk dark-green microcrystalline product has been shown to have the same composition as the single crystal by use of X-ray powder diffraction measurements.

Acidification of ($^n$Bu4N)[La(Pc2-)2] results in spontaneous demetallation, thus yielding H$_2$Pc$^2$-. This contrasts with the later lanthanide diphthalocyanines, in which oxidation competes with protonation and thus mixtures of [Ln(Pc)$_2$] and H[Ln(Pc$^2$-)$_2$], the so called “green compounds”, are precipitated. Therefore, blue-green hydrogen-(dipthalocyaninatolanthanate), H[La(Pc$^2$-)$_2$], was prepared by thermal decomposition of the corresponding tetrabutylammonium salt (eq. (3)) [7]:

$$\text{($^n$Bu}_4\text{N})[\text{La(Pc}^2-\text{)}_2] \rightarrow \text{H}[\text{La(Pc}^2-\text{)}_2] + ^n\text{Bu}_3\text{N} + \text{H}_2\text{C}=\text{CH}(\text{C}_2\text{H}_5).$$

This reaction, which was first used for the synthesis of H[LiPc$^2$-] [14] proceeds cleanly only for the early lanthanides. With decreasing Ln$^{III}$ radius, oxidation is favoured, and contaminations of H[Ln(Pc$^2$-)$_2$] with [Ln(Pc)$_2$] cannot be avoided.

Structure of di(phthalocyaninato)lanthanum(III) dichloromethane solvate, [La(Pc)$_2$]·CH$_2$Cl$_2$

[La(Pc)$_2$]·CH$_2$Cl$_2$ crystallizes in the orthorhombic space group $Pnma$ (No. 62). Crystal data and details of data collection and crystal structure solution are given in Table I. Atomic coordinates and equivalent isotropic displacement coefficients for the non-hydrogen atoms are given in Table II. Selected bond lengths and angles are given in Table III [15].

[La(Pc)$_2$]·CH$_2$Cl$_2$ is isomorphous with [Lu(Pc)$_2$]·CH$_2$Cl$_2$ [16], and the lanthanum and carbon atom of the solvate molecule are located

| Table I. Crystal data and structure refinement for [La(Pc)$_2$]·CH$_2$Cl$_2$. |
|-------------------------------|------------------|
| **Formula** | C$_{65}$H$_{34}$Cl$_2$LaN$_{16}$ |
| **Formula weight, g/mol** | 1248.9 |
| **Crystal system** | orthorhombic |
| **Space group** | $Pnma$ (No. 62) |
| **a [Å]** | 28.365(5) |
| **b [Å]** | 22.935(3) |
| **c [Å]** | 8.026(3) |
| **a; B; y; [deg]** | 90; 90; 90 |
| **V [Å$^3$]** | 5221(2) |
| **Z** | 4 |
| **$\theta$ max; [°]** | 1.589 |
| **$\mu$ (cm$^{-1}$)** | 98.4 |
| **Radiation** | MoK$\alpha$ |
| **Temperature, [°C]** | 30 |
| **Scan mode** | $\Omega/2\theta$ |
| **$\theta$ Limits, [°]** | 2.28 – 22.07 |
| **Index range** | 0 ≤ $h$ ≤ 29, 0 ≤ $k$ ≤ 24, 0 ≤ $l$ ≤ 8 |
| **Reflections collected** | 3290 |
| **Independent reflections** | 3290 |
| **Refinement method** | Full-matrix least-squares on F$^2$ |
| **$R_1$ [I > 2$\sigma$(I)]** | 0.038 |
| **wR$_2$ (all data)** | 0.114 |
Table II. Atomic coordinates (×10⁴) and equivalent isotropic displacement coefficients (Å²×10³) for \([\text{La}(\text{Pc})_2]CH_2Cl_2\). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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Table III. Selected (averaged) bond lengths (Å) and angles (deg).

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Niso = N1–N5; N = N6–N10; Cα = C1, C3, C6, C7, C9, C12, C13, C16; Cβ = C2, C4, C5, C8, C10, C11, C14, C15; Cα = C17, C19, C22, C23, C25, C28, C29, C32; Cβ = C18, C20, C21, C24, C26, C27, C30, C31.

Fig. 2. ORTEP plot of the [La(Pc)₂] molecule. H atoms omitted for clarity, ellipsoids plotted with 30% probability.

sequence of the large LaIII radius, the mean distance La–Niso of 2.513(1)Å is significantly longer than in the corresponding Lu complex (2.380(2)Å). The four Niso donor atoms of each macrocycle are coplanar forming quasi parallel planes, with a dihedral angle of ~1°. The La atom is considered equidistant to both planes (1.556 Å resp. 1.550 Å to A resp. B). The distance between the planes is much longer compared to the Lu analogue, and this allows a smaller distortion of both Pc rings. The Pc ligand B is approximately planar with dihedral angles between the (Niso)₄ plane (N4, N4', N5, N5') and the mean planes of the isoindole moieties of less than ~1°. Macrocycle A is distorted asymmetrically in a saucer shaped manner. In particular, one isoindole moiety containing N1 and C18 is displaced with respect to the (Niso)₄ plane (N1, N1', N2, N3). For the outermost car-
bon atoms (C18, C18′) the displacement amounts to 0.87(1) Å. With respect to the (N\text{iso})₄ plane the dihedral angle of this isoindole moiety is ~11°. The dihedral angle of the opposite isoindole ring is, in contrast, only ~1°. The same holds for the other two isoindole moieties which have dihedral angles of ~2°. Although the two macrocyclic ligands have distinctly different geometries, the average La–N\text{iso} bond lengths to both rings do not differ significantly. Nevertheless, it is known from α-[Pr(Pc)₂]Br₅ [12] and α₁-[Er(Pc)₂] [17] that the Pc ligand tends to become planar upon oxidation. In this orthorhombic (γ-)modification the rings keep their individuality, and we assign the more planar ring B to the oxidized Pc⁻ ligand. Despite the partial deviation from planarity, the inner ring bond distances and angles given in Table III closely resemble those of other metallophthalocyanines [16].

Fig. 3 shows the packing arrangement in [La(Pc)₂]·CH₂Cl₂. The unit cell contains four [La(Pc)₂]·CH₂Cl₂ formula units. The complexes are arranged in the well known “fish bone” pattern. The molecules of solvation (atoms designated CS and CIS in Table II) are located on the pseudomirror plane. The CCl₂ plane deviates by ~9° from being parallel with respect to the mean plane of the isoindole moiety which has the greatest distortion from planarity. Instead of the solvate molecules being located inside the unit cell, those of the neighbouring unit cells having the shortest distance (> 3.5 Å) to the diphthalocyanine units are shown. There is no interaction between the complex and the solvate.

**Electronic absorption spectra**

The electronic absorption spectra of [La(Pc)₂] (a) and H[La(Pc²⁻)₂] (b) (500–39000 cm⁻¹) are compared in Fig. 4. Due to their low solubility in common solvents, spectra have been measured on solid complexes dispersed in KBr pellets. Both spectra show strong τ-τ* transitions of the Pc²⁻ macrocycle at 14300/14600 cm⁻¹ and 30500/29000 cm⁻¹. These are assigned as B and Q band, respectively [18]. The considerably broadened B band for H[La(Pc²⁻)₂] has no pronounced fine structure. This is typical of the spectra of cofacial (Pc²⁻)₂ systems on account of strong exciton coupling and the shape is comparable to the B band in the spectrum of [La(Pc²⁻)₂]⁻ [7]. The shape of the B region in the spectrum of [La(Pc)₂] is more complicated, indicating the presence of two distinctly different Pc molecules in accordance with the molecular structure. The absorption at 16100 cm⁻¹ is too strong to be assigned to the vibronic structure found in typical “D₄h-spectra” of metallomonophthalocyanines (MPc²⁻) [4]. From a comparison with oxidized metallophthalocyanines (MPc⁻) [19], especially those of tervalent metal ions [20], this band should be attributed to the B band of the oxidized Pc⁻ moiety. The high energy of this B band may
be a consequence of exciton coupling between Pc− ligands of neighbouring [La(Pc)2] molecules. It is common in solids with MPc− units that do not have spacer ligands coordinated to the axial positions [19]. Because of this excitonic coupling, the B band is split into a dipole-forbidden lower and dipole-allowed higher energy band. The low energy band (often called “dimeric band”) is generally observed in the near infrared region (NIR) [19] and should be assigned to the bands at 8500, 9700 and 11200 cm−1, while the high energy band is at 16100 cm−1. Simon et al. [21] have found similar, but stronger NIR bands in the spectra of the later lanthanide diphthalocyanines, whose band shape and energy depend slightly on the LnIII radius. Thus an intramolecular charge transfer $\text{Pc}^2\text{LnPc}^- \rightleftharpoons \text{Pc}^{-}\text{LnPc}_2^-$ is assumed. The absorptions at 19400 and 21500 cm−1 are characteristic of the Pc− radical and may be assigned to Q bands if it is assumed, that the sequence of the $\pi, \pi^*$ orbitals of the macrocycle is shifted (at least partially) to lower energy, but not changed, upon oxidation.

As in other reported MPc− species, the energy of these Q bands is not much affected by different coordination geometries [20]. The extinction coefficients of the $\pi-\pi^*$ transitions of Pc− are 5 to 10 times lower than those of the Pc2− ligand due to the reduced electron density. This accounts for the small contribution of the Pc− moiety to the overall shape of the electronic absorption spectrum.

To our knowledge, no report has previously been given for the low energy band observed at 4600 cm−1 in [Ln(Pc)2] type complexes. Absorptions at comparable energy have been observed for oxidized compounds such as LiPcX (X = Cl, Br, I) [22] and [Pr(Pc)2]Br1.5 [12]. For the latter compounds, this band may arise from the “dimeric band” shifted to lower energy upon incorporation of dopant (in this case bromine) accompanied by an organization of the molecules into quasi one-dimensional columnar stacks with strongly interacting macrocycles. Conspicuously, all partially oxidized metallophthalocyanines exhibit unusual electrical conductivities (10−2 to 10−5 S cm−1) and this is valid for polycrystalline [La(Pc)2]·CH2Cl2, too, whose semiconducting behaviour (3·10−5 S cm−1) is comparable with that of [Lu(Pc)2]·CH2Cl2, while H[La(Pc2−)2] is an insulator. We therefore propose to assign this low energy band to electron-phonon coupling.

**Vibrational spectra**

The IR spectra of H[La(Pc2−)2] (a) and [La(Pc)2] (b) shown in Fig. 5 show the “signature” of the different Pc macrocycles from 400 to 1650 cm−1. In the far infrared (not shown) only a few weak bands are observed. In contrast to the electronic absorption spectrum, the vibrational spectra of [La(Pc)2] are dominated by vibrations essentially due to the Pc− component of the molecule. In the IR spectrum of [La(Pc)2] the strong band at 1312 cm−1 in combination with the absorptions at 1356 and 1439 cm−1 are known to be characteristic of the Pc− ligand [19]. These bands are assigned to C−N stretching vibrations of the inner (CN)8 ring and C−C stretching vibrations of the pyrrole moi-
eties of the macrocycle. They correspond to the metal sensitive bands at 1329, 1402 and 1474 cm\(^{-1}\) in the spectrum of \(\text{H}[\text{La}(\text{Pc}^2-)\_2]\), and shifts to lower wavenumbers are caused by the reduced electron density within the \(\pi\) electron system. Further characteristics of the ligand centered oxidation are the attenuated intensities of the band group around ~725 cm\(^{-1}\) and 1100 cm\(^{-1}\). Lanthanide diphthalocyanines containing more oxidized Pc ligands, e.g. \([\text{Pr}(\text{Pc})_2]\)Br\(_{1.5}\) [12], show similar IR spectra. Only the disappearance for these compounds of the band centred at 1107 cm\(^{-1}\) allows a distinction from the half oxidized [LnPc\(_2\)]-type complexes.

In Fig. 5c–e selected resonance Raman spectra of [La(Pc)\(_2\)] are shown. The shapes of the spectra depend strongly on the excitation wavelength, a common feature in the resonance Raman effect. Typical Pc\(^{-}\) spectra were observed when excitation wavelengths between 457.9 and 514.5 nm were used, with strongly enhanced Raman lines at 1593, 1170 and 1112 cm\(^{-1}\). None of these point to the presence of a Pc\(^{2-}\) ligand. In resonance with the B band absorptions (647.1 nm, Fig. 4e) the deformation vibrations at 400-900 cm\(^{-1}\) are selectively intensified and the spectrum closely resembles those reported by Aroca et al. for [Ln(Pc)\(_2\)] where Ln = Pr, Dy, Ho [23,24]. These B band enhanced spectra have almost the same signature for the Pc\(^{2-}\) and Pc\(^{-}\) ligands [20], and are less valuable for the diagnosis of the oxidation state of the macrocyclic ligand.

**Experimental Section**

\((^\text{t Bu}_4\text{N})[\text{La}(\text{Pc}^2-)\_2]\) and \(\text{H}[\text{La}(\text{Pc}^2-)\_2]\) were prepared following literature procedures [7].

**Synthesis of di(phthalocyaninato)lanthanum(III) dichloromethane solvate, \([\text{La}(\text{Pc})_2] \cdot \text{CH}_2\text{Cl}_2\)**

150 mg of \((^\text{t Bu}_4\text{N})[\text{La}(\text{Pc}^2-)\_2]\) is dissolved in 30 ml of dry dichloromethane and oxidized anodically using \((^\text{t Bu}_4\text{N})\text{ClO}_4\) as supporting electrolyte. After several days the deep blue solution turns green and black needles of \([\text{La}(\text{Pc})_2] \cdot \text{CH}_2\text{Cl}_2\) precipitate. The oxidation is stopped at this point, and the product filtered off, washed several times with dichloromethane, and dried.

**Analysis for \(C_{65}H_{52}Cl_2LaN_{16}\) (1248.9)**

Calcd. C 62.5 H 2.7 N 17.9%.

Found C 62.3 H 2.6 N 17.8%.

**Instrumentation**

**IR spectra**: FT-IR-Interferometer NIC 5 DXB (Nicolet), KBr pellet.

**Raman spectra**: multichannel spectrometer XY (Dilor); excitation with Kr\(^+\) and Ar\(^+\) lasers (Spectra Physics Model 171 and 2025). The sample was fixed on a rotating steel disk, and the spectra were measured at ~80 K.

**UV-VIS-NIR spectra**: Cary 5 (Varian), KBr pellets.

**Cyclic voltammetry**: Polarecord 626 and VA-Scanner 612 (Metrohm). Reference electrode: Ag/AgCl (0.1 M LiCl/C\(_2\)H\(_5\)OH), working and auxiliary electrode: Pt bead and Pt wire. Supporting electrolyte: 0.1 M (\(^{t}\text{Bu}_4\text{N})\text{ClO}_4\) in dry dichloromethane. All measurements were carried out at ~25 °C under a stream of nitrogen and with a scan speed of 30 mVs.

**Elemental analysis**: Combustion analysis (CHN-Rapid-Elementaranalysator, Heraeus)

**X-ray crystal structure determination**: D 500 diffractometer (Enraf-Nonius). A crystal of dimension 0.1 mm×0.2 mm×0.4 mm was fixed at the top of a glass capillary and measured in a N\(_2\) stream cooled to ~30 °C. Orientation matrices and unit cell parameters were obtained from 25 machine-centred reflections. Further details are given in Table I. The structure was solved by direct methods. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded \(R_1 = 0.037\), \(wR_2 = 0.114\). Hydrogen atoms were placed in idealized positions with isotropic thermal parameters. The maximum and minimum peaks of the Fourier difference map corresponded to +0.77 and ~1.15 e/Å\(^3\), respectively. Programs used: SHELXS-86 [25], SHELXL-93 [26], ORTEP [27], XANADU [28].

**Powder diffraction**: D 500 diffractometer (Siemens AG) with CuK\(_\alpha\) radiation.

**Conductivity**: Two-point-method with compressed powder.

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[15] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD 401799.