Syntheses and Properties of Cerium Diphthalocyanines in High Oxidation States; Crystal Structure of $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$

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Ring oxidized green Cerium(IV)diphthalocyanines, $[\text{Ce}(\text{Pc})_2]\text{X}$ ($\text{X} = (\text{poly})\text{halide}, \text{NO}_3^-$) are prepared by chemical oxidation of $(^n\text{Bu}_4\text{N})[\text{Ce}(\text{Pc}^{2-})_2]$ with the corresponding halogen in solution or of solid $[\text{Ce}(\text{Pc}^{2-})_2]$ with aqueous HNO_3 . Electrochemical oxidation of $(^n\text{Bu}_4\text{N})[\text{Ce}(\text{Pc}^{2-})_2]$ in solution in the presence of $(^n\text{Bu}_4\text{N})\text{BF}_4$ yields $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$, which crystallizes in the tetragonal space group P4/nnc ($a, b = 19.643(3) \text{ \AA}$, $c = 6.525(3) \text{ \AA}$, $Z = 2$). The Ce^{IV} ion is eightfold coordinated by the isoindole N atoms (N_{iso}) of the two staggered ($\text{ca. } 41^\circ$), slightly distorted Pc ligands. The “ $[\text{Ce}(\text{Pc})_2]^{0.33+}$ ” subunits are arranged in infinite columns along $[001]$ with the Ce atoms statistically disordered over two positions and Ce– N_{iso} bond lengths of 2.45(1) and 2.69(1) $\text{\AA}$, respectively. The UV-VIS spectrum is dominated by the transitions of the Pc^{2-} ligand at $\text{ca. } 15,000$ (B band), $30,000$ and $36,000 \text{ cm}^{-1}$ (Q, N region). A low energy (“metallic”) band at $\text{ca. } 2800 \text{ cm}^{-1}$ typical for partially oxidized systems is present. The UV-VIS-NIR spectrum of $[\text{Ce}(\text{Pc})_2]\text{NO}_3$ indicates a cofacial Pc^{2-} – Pc^- complex. In addition to the π – π^* transitions of the Pc^{2-} moiety at $\text{ca. } 14,000$, $30,000$ and $36,000 \text{ cm}^{-1}$, the Q_1 transition of the Pc^- ring is observed at $\text{ca. } 19,200 \text{ cm}^{-1}$ and the typical NIR band at 6380 cm^{-1} . Oxidation of a thin film of $(\text{PNP})[\text{Ce}(\text{Pc}^{2-})_2]$ with dry Br_2/N_2 gas yields purple $[\text{Ce}(\text{Pc}^-)_2]\text{Br}_x$, whose UV-VIS-NIR spectrum shows the diagnostic features of dimeric Pc^- radicals with intense bands at $\text{ca. } 14,000$ and $18,000 \text{ cm}^{-1}$ assigned as B and Q_1 bands, respectively. At $\text{ca. } 9000 \text{ cm}^{-1}$ the typical Q_D absorption is observed. The vibrational spectra are dominated by the transitions of the Pc^- ligand at $1305/1445 \text{ cm}^{-1}$ (IR) and $560/1120/1172/1591 \text{ cm}^{-1}$ (resonance Raman). Excitation with 1064 nm strongly enhances the sym. Ce–N stretch at 163 cm^{-1} .

Introduction

In the last twenty years metallodiphthalocyanines, especially those of the lanthanides ($[\text{Ln}(\text{Pc})_2]$), have been investigated intensively because of their (semi)conducting [1,2] and electrochromic [3,4] properties. Within the lanthanide series cerium keeps an exceptional position as there is a low lying redox couple $\text{Ce}^{3+}/\text{Ce}^{4+}$, and it has been shown that the one electron oxidation of $(^n\text{Bu}_4\text{N})[\text{Ce}^{\text{III}}(\text{Pc}^{2-})_2]$ ($(^n\text{Bu}_4\text{N})$: tetra-*n*-butylammonium) yields $[\text{Ce}^{\text{IV}}(\text{Pc}^{2-})_2]$ [5]. On the other hand small singlet-triplet splittings and a possible Kondo analogue behaviour is predicted for cerium diphthalocyanine [6,7]. This type of a partially oxidized radical species “ $[\text{Ln}^{\text{III}}(\text{Pc}^{2-})(\text{Pc}^-)]$ ” is typically formed by the one-electron oxidation of the

complex salts of the other lanthanides [8,9]. An analogous di(porphyrinato)cerium(IV) compound, containing the “ $[\text{Ce}^{\text{IV}}(\text{Por}^{2-})(\text{Por}^-)]^+$ ” radical ion, is well known [10–12]. No reports have so far been given to our knowledge on oxidized di(phthalocyaninato)cerium complexes. In the present paper we describe the preparation and properties of the complexes $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$, $[\text{Ce}(\text{Pc})_2](\text{NO}_3)$, $[\text{Ce}(\text{Pc})_2]\text{Cl}_{3.5}$ and $[\text{Ce}(\text{Pc})_2]\text{Br}_{2.7}$.

Experimental Section

$(^n\text{Bu}_4\text{N})[\text{Ce}(\text{Pc}^{2-})_2]$ ($^n\text{Bu}_4\text{N}$: Tetra-*n*-butylammonium), $(\text{PNP})[\text{Ce}(\text{Pc}^{2-})_2]$ (PNP: Bis(triphenylphosphine)iminium) and $[\text{Ce}(\text{Pc}^{2-})_2]$ were prepared as described previously [5,13].

Synthesis of $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$

A concentrated solution of $(^n\text{Bu}_4\text{N})[\text{Ce}(\text{Pc}^{2-})_2]$ in dichloromethane was oxidized electrochemi-

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cally in the presence of $(^n\text{Bu}_4\text{N})(\text{BF}_4)$ as supporting electrolyte. After several days black needles of $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ grew at the Pt anode. The solution was filtered off, and the precipitate washed several times with dichloromethane.

Synthesis of $[\text{Ce}(\text{Pc})_2](\text{NO}_3)$

Finely powdered $[\text{Ce}(\text{Pc})_2]$ was stirred in aqueous HNO_3 (20%) for 30 min at room temperature. With progressing reaction the colour of the solid changed from blue-purple to dark green. $[\text{Ce}(\text{Pc})_2](\text{NO}_3)$ was separated, washed with cold water, and dried *in vacuo*.

Synthesis of $[\text{Ce}(\text{Pc})_2]\text{Br}_{2.7}$ and $[\text{Ce}(\text{Pc})_2]\text{Cl}_{3.5}$

100 mg of $(^n\text{Bu}_4\text{N})[\text{Ce}(\text{Pc}^{2-})_2]$ was dissolved in 50 ml of dry dichloromethane and bromine or chlorine was added in excess. The mixture was stirred for 15 min to complete the oxidation. Black-green $[\text{Ce}(\text{Pc})_2]\text{Br}_{2.7}$ or $[\text{Ce}(\text{Pc})_2]\text{Cl}_{3.5}$ precipitated. The solid was collected, washed with dry dichloromethane and dried *in vacuo*. The composition of the complex salts is not reproducible due to variable amounts of halogen incorporated.

All complex-salts gave satisfactory elemental analysis [14].

Instrumentation

CHN analysis: Heraeus CHN-Rapid-Elementaranalysator.

Cl, Br analysis: After combustion potentiometrically with Ag^+ .

Difference pulse polarography and cyclic voltammetry: Polarecord 626 and VA-Scanner 612 (Metrohm). Reference electrode: Ag/AgCl (0.1 M $\text{LiCl}/\text{C}_2\text{H}_5\text{OH}$), working and auxiliary electrode: Pt bead and Pt wire. Supporting electrolyte: 0.1 M $(^n\text{Bu}_4\text{N})\text{ClO}_4$ in dry dichloromethane. All measurements were carried out at -25°C under a stream of nitrogen. Scan speed: 10 mV/s (DPP); 30 mV/s (CV).

UV-VIS-NIR spectra: Varian spectrophotometer Cary 5; KBr pellets or thin films on a CaF_2 disk; range: 200–3300 nm.

MIR spectra: ATI Mattson FT-IR interferometer model Genesis; KBr pellets.

FIR spectra: Bruker FT-IR interferometer IFS 66 CS; polyethylene pellets.

Raman spectra: Instruments SA spectrometer U 1000 or Dilor multichannel spectrometer XY; KBr pellets, 10 K or 80 K. Excitation with Ar^+ and Kr^+ lasers (Spectra Physics, model 2025 and 171).

FT-Raman spectra: Bruker interferometer IFS 66 with FRA 106 Raman equipment. Excitation with a NDYAG laser (Adlas).

Crystal structure determination: Details of data collection and crystal structure refinement of α - $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ are given in Table I. Cell parameters and space group were determined by Weissenberg and precession methods. Intensities were collected on an Enraf-Nonius CAD4 diffractometer at 293 K. No absorption correction was applied. The structure determination and refinement were performed with the programs SHELX86 and SHELXL92 [15,16]. The occupancy coefficients of the Ce and the boron atom were refined with fixed isotropic temperature factors. In a last step these isotropic temperature factors were refined with fixed occupancy coefficients. Only the C and N atoms were refined anisotropically. The hydrogen atoms were located at calculated positions. The $[\text{BF}_4]^-$ ion is rotationally disordered; therefore fluorine atoms could not be located. Atomic coordinates, equivalent isotropic temperature factors for non-hydrogen atoms, listings of anisotropic thermal parameters and a complete list of bond distances and angles have been deposited as supplementary material [17]. Figures 2 and 3 were drawn with an ORTEPII program [18].

Table I. Crystal data and structure refinement for $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$.

Formula	$\text{C}_{64}\text{H}_{32}\text{B}_{0.33}\text{CeF}_{1.32}\text{N}_{16}$
Formula Weight	1194.1
<i>a</i> (Å)	19.643(3)
<i>b</i> (Å)	19.643(3)
<i>c</i> (Å)	6.525(3)
<i>V</i> (Å ³)	2517(2)
<i>Z</i>	2
<i>D</i> _{cal} (g·cm ⁻³)	1.567
Crystal System	tetragonal
Space Group	P4/nnc (No. 126)
<i>h</i> , <i>k</i> , <i>l</i>	±23, ±23, -7
Radiation (Å)	$\text{MoK}\alpha$, $\lambda = 0.71069$
Scan Mode	$\omega/2\theta$
θ (min, max)	2.93, 24.98
Data collected	4268
Independent data	1117
Data obs. [(<i>I</i> > 4σ(<i>I</i>))]	642
Parameter	98
μ (cm ⁻¹)	0.98
<i>R</i> 1 [(<i>I</i> > 4σ(<i>I</i>))]	0.052
<i>wR</i> 2 (all data)	0.232
$\Delta\rho_{\text{max/min}}$ (e Å ⁻³)	0.77/-0.81

Results and Discussion

Synthesis and properties

The difference pulse polarogram (Fig. 1) of a solution of $(^n\text{Bu}_4\text{N})[\text{Ce}(\text{Pc}^{2-})_2]$ in dichloromethane shows five distinct current peaks representing quasi-reversible single electron electrode processes. The two current peaks in the cathodic range are related to the successive first one-electron reduction of the two Pc ligands ($E_{\text{red}}(\text{I}) = -1.10 \text{ V}$; $[\text{Ce}(\text{Pc}^{2-})_2]^-/[\text{CePc}^{2-}\text{Pc}^{3-}]^{2-}$; $E_{\text{red}}(\text{II}) = -1.32 \text{ V}$; $[\text{CePc}^{2-}\text{Pc}^{3-}]^{2-}/[\text{Ce}(\text{Pc}^{3-})_2]^{3-}$; for a better understanding all redox couples are given in the formalism of localized states). The first anodic current peak at $E_{\text{ox}} = 0.07 \text{ V}$ is metal centered: $[\text{Ce}^{\text{III}}(\text{Pc}^{2-})_2]^-/[\text{Ce}^{\text{IV}}(\text{Pc}^{2-})_2]$, while the second anodic current peak at $E_{\text{ox}}(\text{I}) = 0.60 \text{ V}$ is related to the oxidation of one of the Pc ligands ($[\text{Ce}(\text{Pc}^{2-})_2]/[\text{Ce}(\text{Pc}^{2-})(\text{Pc}^-)]^+$). Due to the presence of formally quadrivalent cerium, $E_{\text{ox}}(\text{I})$ is shifted to higher potential as compared with the neighbouring Ln^{III} diphthalocyanines and thus deviates distinctly from the linear relationship found within the series of Ln^{III} diphthalocyanines, by which $E_{\text{ox}}(\text{I})$ increases almost linearly with increasing Ln^{III} radius [19]. The shape of this current peak indicates that there is a further not resolved electrode process present, probably originating from $\text{H}[\text{Ce}(\text{Pc})_2]$. The oxidation of the second Pc ligand ($[\text{Ce}(\text{Pc}^{2-})(\text{Pc}^-)]^+/[\text{Ce}(\text{Pc}^-)_2]^{2+}$) is observed at $E_{\text{ox}}(\text{II}) = 1.07 \text{ V}$, formerly described as an irreversible electrode process in the cyclic voltammogram [5]. These high potentials are in good agreement with data observed for diphthalocyanines of the quadrivalent metal ions of zirconium and hafnium [20].

In accordance with the electrochemical data $[\text{Ce}(\text{Pc}^{2-})_2]$ is prepared by anodic oxidation of dis-

solved $(^n\text{Bu}_4\text{N})[\text{Ce}(\text{Pc}^{2-})_2]$ at low potential [5]. By electrocrystallization at higher voltage with $(^n\text{Bu}_4\text{N})\text{BF}_4$ as supporting electrolyte only the partially oxidized compound $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ is formed. Neither $[\text{Ce}(\text{Pc})_2](\text{BF}_4)$ nor even $[\text{Ce}(\text{Pc}^-)_2](\text{BF}_4)_2$ is obtained by this method. Comparable behaviour has been reported for diphthalocyanines of trivalent rare earth ions, recently [21]. Obviously, this seems to be intrinsic to the electrocrystallization technique favouring the less soluble and most electrical conducting compound to cover the surface of the anode. Independent of the oxidant used (Cl_2 , Br_2 or HNO_3), chemical oxidation yields salts of the half-oxidized green $[\text{Ce}^{\text{IV}}(\text{Pc})_2]^+$ ion. Contrary to the Ln^{III} diphthalocyanines the fully oxidized purple diradical $[\text{Ce}(\text{Pc}^-)_2]^{2+}$ is difficult to synthesize and isolate in this manner. On the other hand, treatment of a thin film of blue $(\text{PNP})[\text{Ce}(\text{Pc}^{2-})_2]$ on a CaF_2 disk with a dry Br_2/N_2 gas mixture leads to a purple film characterized by the typical absorption bands of dimeric co-facial phthalocyanine π -radicals (vide infra). Due to its high oxidation potential, $[\text{Ce}(\text{Pc}^-)_2]^{2+}$ is very sensitive against moisture. To our knowledge the same is true for other quadrivalent diphthalocyanines that have not been isolated as pure dications so far.

Structure of α -di(phthalocyaninato)cerium(IV)-tetrafluoroborate, α - $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$

The structure of the title compound closely resembles structures reported for partially ring oxidized diphthalocyanines of trivalent rare earth metal ions, e.g. α - $[\text{Pr}(\text{Pc})_2]\text{Br}_{1.5}$ [22], α - $[\text{Sm}(\text{Pc})_2]\text{Br}_{1.38}$ and α - $[\text{Sm}(\text{Pc})_2](\text{ClO}_4)_{0.63}$ [21]. Crystal data and details on data collection and structure solution are given in Table I. Atomic coordinates and (equivalent) isotropic displacement coefficients for the non-hydrogen atoms are given in Table II.

The crystal packing of $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ is illustrated in Fig. 2. Infinite columns of the sandwich-like $[\text{Ce}(\text{Pc})_2]^{0.33+}$ subunits along the tetragonal axis represent the quasi-one-dimensional character of the crystal structure. Voids formed by adjacent molecular stacks contain the $[\text{BF}_4]^-$ counter ions. A disordered disposition of the Ce atoms onto two special crystallographic positions ((2a) and (2b)) in the ratio of 1:6.2 is found com-

Fig. 1. Difference pulse polarogram of $(^n\text{Bu}_4\text{N})[\text{Ce}(\text{Pc}^{2-})_2]$ in $\text{CH}_2\text{Cl}_2/(^n\text{Bu}_4\text{N})\text{ClO}_4$; $-1.5 \text{ V} - 1.3 \text{ V}$, -25°C .

Table II. Atomic coordinates ($\times 10^4 \text{ \AA}$) and (equivalent) isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ce 1	2500	2500	2500	27(1)
Ce 2	2500	2500	7500	48(5)
N1	942(4)	1770(4)	58(16)	41(5)
N2	1561(4)	2835(4)	272(14)	40(5)
C1	1364(6)	3511(6)	115(16)	41(8)
C2	201(6)	4100(7)	-119(21)	61(7)
C3	-481(6)	3960(8)	-272(25)	84(7)
C4	-723(7)	3291(9)	-226(25)	84(8)
C5	-291(6)	2737(7)	-111(22)	69(6)
C6	984(4)	2444(8)	117(15)	39(4)
C7	627(5)	3549(6)	-61(18)	45(6)
C8	398(5)	2881(6)	-32(18)	46(6)
B	7500	2500	7500	75(44)

Fig. 2. View of the crystal packing of $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$. H atoms omitted for clarity.

parable to situation in the Pr and Sm compounds mentioned. The present structure differs by the ordered disposition of the anions. In accordance with the elementary analysis, the refinement of the occupancy coefficient for the boron atoms yields the stoichiometric composition $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$. Thus the Pc ligands are partially oxidized and in a localized view the solid phase can be described as $2 [\text{Ce}(\text{Pc}^{2-})_2]_2 \cdot [\text{Ce}(\text{Pc}^{2-})(\text{Pc}^-)](\text{BF}_4)$. In fact, all Pc ligands in this highly symmetrical structure are equal due to symmetry requirements; no distinction between the dianionic Pc^{2-} and the monoanionic radical Pc^- can be made. This is in agreement with the diamagnetism of the compound indicating strong spin-spin coupling within the columns. The Ce atom is coordinated by the eight isoindole nitrogen atoms ($\text{N2} = \text{N}_{\text{iso}}$) of the two staggered (41°) macrocycles forming a distorted square antiprism. The $(\text{N2})_4$ planes are separated by 2.908 and $3.616 \text{ \AA}$ intra- and interplane distances, alternatively. Correspondingly the Ce–N2 bond dis-

tance is $2.45(1)$ for Ce1 and $2.67(1) \text{ \AA}$ for Ce2. The Pc rings are significantly distorted from planarity. As evidenced by the vertical displacement of the outermost carbon atoms C3 ($0.365 \text{ \AA}$) and C4 ($0.312 \text{ \AA}$) from the $(\text{N2})_4$ plane, this distortion is smaller in $\alpha\text{-}[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ than in other diphthalocyanines of quadrivalent metals such as Sn ($1.09 \text{ \AA}$) [23], Zr ($1.47 \text{ \AA}$) [24] or Ti ($0.64 \text{ \AA}$) [25]. All inner bond length and angles (Fig. 3) of the macrocycle compare closely with other metallophthalocyanines.

Fig. 3. Atom labeling scheme, inner bond lengths and angles for the asymmetric unit.

Electronic absorption spectra

Selected absorption spectra are compiled in Fig. 4 and 5. The spectra of $[\text{Ce}(\text{Pc}^{2-})_2]$ (4a), $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ (4b) and $[\text{Ce}(\text{Pc})_2](\text{NO}_3)$ (4c) are dominated by the typical intense bands of the Pc^{2-} ligand at *ca.* $15,000 \text{ cm}^{-1}$ (B band), $30,000 \text{ cm}^{-1}$ (Q region) and $36,000 \text{ cm}^{-1}$ (N region). For di(phthalocyaninato)cerium(IV) and the tetrafluoroborate salt the B band absorption ($a_{1u} \rightarrow e_g$; designation following [26]) shows the considerably broadened and poorly structured shape as well as the band splitting characteristic for exciton coupling between dimeric co-facial Pc^{2-} complexes [27,28]. The low energy (“metallic”) band at *ca.*

Fig. 4. UV-VIS-NIR-MIR spectra (400–40,000 cm^{-1} , 293 K, KBr disks) of $[\text{Ce}(\text{Pc}^{2-})_2]$ (a), $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ (b) and $[\text{Ce}(\text{Pc})_2](\text{NO}_3)$ (c).

Fig. 5. VIS-NIR spectra (800–22,500 cm^{-1} , 293 K, thin film on CaF_2 disk) of $(\text{PNP})[\text{Ce}(\text{Pc}^{2-})_2]$ after oxidation with Br_2/N_2 gas: (a) 5 s, (b) 30 s, (c) 1 min.

2800 cm^{-1} in the spectrum of $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ is typical for partially oxidized phthalocyanines and has been reported for several other incompletely

oxidized lanthanide(III) [21,22], titanium(IV) and tin(IV) [25] diphthalocyanines and for lithium phthalocyanines [29], showing high electrical conductivities. Therefore it may be assigned to electron phonon coupling.

The B band of half oxidized $[\text{Ce}(\text{Pc})_2](\text{NO}_3)$ exhibits a significantly smaller bandwidth with a vibronic transition at 15,600 cm^{-1} comparable to the analogous complex $[\text{La}^{\text{III}}(\text{Pc})_2]$ [9]. The presence of the Pc^- radical is evident from the weak absorption at *ca.* 19,200 cm^{-1} , which is assigned to the Q_1 transition ($a_{2u} \rightarrow e_g$) of the oxidized macrocycle. Furthermore the NIR band established for “ $[\text{Pc}^{2-}\text{LnPc}^-]$ ” compounds [30], is observed at 6380 cm^{-1} . The spectra of $[\text{Ce}(\text{Pc})_2]\text{Cl}_{3.5}$ and $[\text{Ce}(\text{Pc})_2]\text{Br}_{2.7}$ are very similar to that of $[\text{Ce}(\text{Pc})_2](\text{NO}_3)$ and are not reproduced here. Fig. 5 shows the absorption spectra of purple $[\text{Ce}(\text{Pc}^{2-})_2]\text{Br}_x$. The oxidation of both Pc ligands is clearly indicated by the intense Q_1 and Q_D bands (designation following ref. 21) at *ca.* 18,000 cm^{-1} and 9000 cm^{-1} , respectively, and the low absorbance of the B band (*ca.* 14,000 cm^{-1}). Additional bands comparable to those observed in the NIR spectra of fully oxidized $[\text{Ln}^{\text{III}}(\text{Pc}^-)_2]\text{Br}_x$ occur in the low energy region at *ca.* 4500 cm^{-1} and 2000 cm^{-1} . With increasing Br_2 contact time (5a–5c) these bands shift to lower wavenumbers and an extreme decrease of intensity takes place. We suggest that these bands arise from very small amounts of less oxidized cerium diphthalocyanines. After still longer Br_2 contact the purple film slowly turns green showing a spectrum comparable to that in Fig. 4c. This reduction process is probably caused by traces of moisture.

Vibrational spectra

The MIR spectra of $[\text{Ce}(\text{Pc})_2]$ (6a), $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ (6b), $[\text{Ce}(\text{Pc})_2]\text{Br}_{2.7}$ (6c) and $[\text{Ce}(\text{Pc})_2](\text{NO}_3)$ (6d) are shown in Fig. 6. Fig. 6a has the characteristic “fingerprint” of the Pc^{2-} ligand, whereas Fig. 6c is dominated by features of the π radical Pc^- with the intense bands at *ca.* 1306 and 1445 cm^{-1} and weak absorptions between 1000 and 1200 cm^{-1} . In contrast to the electronic absorption spectra, the contribution of the π -radical Pc^- to the shape of the vibrational spectra is much greater. The band at 1384 cm^{-1} in the spectrum of $[\text{Ce}(\text{Pc})_2]\text{NO}_3$ (Fig. 6d) is due to the

asymmetric N–O stretching vibration ($\nu_{as}(\text{NO})$) of the nitrate ion. $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ exhibits strong $\nu_{as}(\text{BF})$ of the tetrafluoroborate at 1075 cm^{-1} . The oxidation of every sixth Pc ligand is verified by the presence of the typical “oxidation bands” mentioned above. The resonance Raman spectra (not shown) closely resemble those of $[\text{La}(\text{Pc})_2]$ [31] and are not discussed here in detail. Characteristic bands for the Pc^- moiety are centered at $\sim 560/1120/1172/1591\text{ cm}^{-1}$. It should be mentioned that for $[\text{Ce}(\text{Pc})_2\text{Br}_{2.5}]$ excitation between 457.9 and 476.5 nm strongly enhances the symmetric stretching vibrations of the polybromide chains at 150 cm^{-1} . In the FT-Raman spectra excited with 1064 nm the symmetric vibration ($\nu_s(\text{Ce}-\text{N}_{\text{iso}})$) at 163 cm^{-1} is selectively enhanced. For $[\text{La}(\text{Pc}^-)_2]\text{Br}_{2.2}$ and $[\text{Pr}(\text{Pc}^-)_2]\text{Br}_{2.1}$ $\nu_s(\text{Ln}-\text{N}_{\text{iso}})$ is found at 141 and 151 cm^{-1} , for $[\text{La}(\text{Pc})_2]$ and $[\text{Pr}(\text{Pc})_2]$ at 138 and 148 cm^{-1} , respectively. The significantly higher value of $\nu_s(\text{Ce}-\text{N}_{\text{iso}})$ is due to the higher formal oxidation state and the smaller Ce^{IV} ionic radius.

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Fig. 6. MIR spectra ($400\text{--}1650\text{ cm}^{-1}$, 293 K ; b-d baseline corrected) of $[\text{Ce}(\text{Pc}^{2-})_2]$ (a), $[\text{Ce}(\text{Pc})_2](\text{BF}_4)_{0.33}$ (b), $[\text{Ce}(\text{Pc})_2\text{Br}_{2.7}]$ (c) and $[\text{Ce}(\text{Pc})_2]\text{NO}_3$ (d).

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