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FULL PAPER

Synthesis and characterization of new mixed-ligand lanthanide–phthalocyanine cation radical complexes

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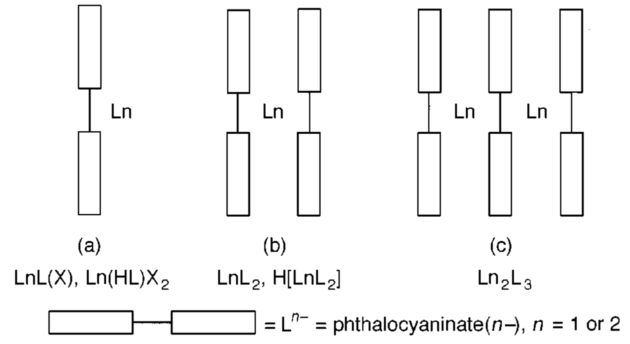
The mixed-ligand phthalocyanine lanthanide complexes [Ln(pc)X$_2$] [pc = phthalocyanine radical anion; Ln = Sm, Eu, Gd or Lu; X = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate (fod), 1,1,1-trifluoro-4-phenylbutane-2,4-dionate (btfa) or 3-heptafluorobutyryl-D-camphorate (hfbc)] have been synthesized and characterized by electronic, ESR and plasma desorption mass spectroscopy as well as elemental analysis. Bands in the electronic spectra at 820, 716, 500, 425 and 330 nm typical for phthalocyanine radical anions have been observed for the red initial [Ln(pc)X$_2$] complexes. The ESR spectra are also consistent with the radical nature of the phthalocyanine ligand in these complexes. The reversible chemical reduction of [Ln(pc)X$_2$] complexes has been studied.

The phthalocyanines are an interesting class of macrocyclic compounds used as dyes and pigments.[1] Relatively recently they have been used as catalysts,[2] semiconductors,[3] materials for sensor devices,[4] laser switches,[5] photosensitizers for photodynamic therapy of cancer cells,[6] near infrared (NIR) photoreceptors,[7] *etc*. In the case of phthalocyanine lanthanide complexes three general groups are known (Scheme 1). The sandwich-type diphthalocyanine subgroup (b) is the most investigated because these complexes are the best candidates for electrochromic display materials,[8] electro- and chemio-chromic sensor devices[9] and molecular semiconductors.[10] On the other hand, many aspects of the chemistry of mixed-ligand monophthalocyanine lanthanide complexes of subgroup (a) are still poorly understood.[11] Only three types of complexes from this subgroup, [LnL(O$_2$CMe)], [LnL(acac)] and Li[LnL(acac)] (H$_2$L = a phthalocyanine) have been systematically studied.[11a,d]

Recently[12] we briefly reported the synthesis of new mixed-ligand phthalocyanine lanthanide complexes with general formula [Ln(pc)X$_2$] (pc = phthalocyanine anion radical; Ln = Lu, Gd, Eu or Sm; X = anion of fluorine-containing β-diketones). In this paper we detail this synthesis and some properties of these compounds.



Scheme 1 Types of phthalocyanine lanthanide complexes

Experimental

Measurements

Electronic spectra were recorded on a Specord M-40 spectrometer in the concentration range 10^{-4}–10^{-6} mol dm^{-3} in the 280–900 nm region, ESR spectra on a RE-1301 spectrometer both in toluene solution and in the solid state at 298 or 77 K. Plasma desorption mass spectra (PDMS) were obtained on a BC MS 4 spectrometer with a ^{252}Cf source. Samples were prepared by evaporation of benzene solutions of the corresponding phthalocyanine complexes on a gold spectrometer holder.

Preparations

Initial tris(β-diketonato)lanthanide complexes[13] were synthesized as described previously. The [Ln(pc)X$_2$] complexes were synthesized as follows.

Bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)[phthalocyaninato(1−)]samarium(III), [Sm(pc)(fod)$_2$] 1a (typical procedure). Metal-free phthalocyanine (514 mg, 0.001 mol) and [Sm(fod)$_3$] (3.11 g, 0.003 mol) were added to anhydrous dmso (200 cm^3) in an argon atmosphere. The reaction mixture was refluxed for 20 min, cooled and filtered. The filtrate was poured into a saturated aqueous solution of KCl (300 cm^3). The precipitate was centrifuged, washed with water (10 × 50 cm^3) and dried in vacuum at 70 °C. The resulting solid was dissolved in hot benzene (30 cm^3) and chromatographed on silica (60 mesh). The first red-brown fraction was eluted by hexane–benzene (4:1 v/v), the solvent evaporated and drying in vacuum at room temperature gave red-brown *crystals* of [Sm(pc)(fod)$_2$] **1a** (0.075 g, 6%) (Found: C, 50.12; H, 3.04; N, 8.43. $C_{52}H_{36}F_{14}N_8O_4Sm$ requires C, 49.84; H, 2.89; N, 8.94%).

Bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)[phthalocyaninato(1−)]europium(III) 2a. Yield of red-brown *crystals* 0.044 g, 3.5% {Found: C, 49.42; H, 2.95; N, 8.53%; *m/z* 1253.9 ([*M* − *H*]$^+$). $C_{52}H_{36}EuF_{14}N_8O_4$ requires C, 49.77; H, 2.89; N, 8.93%; 1254.8 ([*M* − H]$^+$)}; *m/z* 1253.9 ([*M* − H]$^+$), 958.7 (*M* − fod − H) and 664.4 (*M* − 2fod).

Bis(3-heptafluorobutyryl-D-camphorato)[phthalocyaninato-(1−)]europium(III), [Eu(pc)(hfbc)$_2$] 2c. Yield of bluish-red *crystals* 0.027 g, 2% (Found: C, 52.80; H, 3.00; N, 8.29. $C_{60}H_{44}EuF_{14}N_8O_4$ requires C, 53.03; H, 3.26; N, 8.24%).

Bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)[phthalocyaninato(1−)]gadolinium(III) 3a. Yield of red-brown *crystals* 0.048 g, 3.7% (Found: C, 49.14; H, 3.33; N, 9.05. $C_{52}H_{36}F_{14}GdN_8O_4$ requires C, 49.56; H, 2.88; N, 8.89%).

[Phthalocyaninato(1−)] bis(1,1,1-trifluoro-4-phenylbutane-2,4-dionato)lutetium(III), [Lu(pc)(btfa)$_2$] 4b. Yield of red-brown

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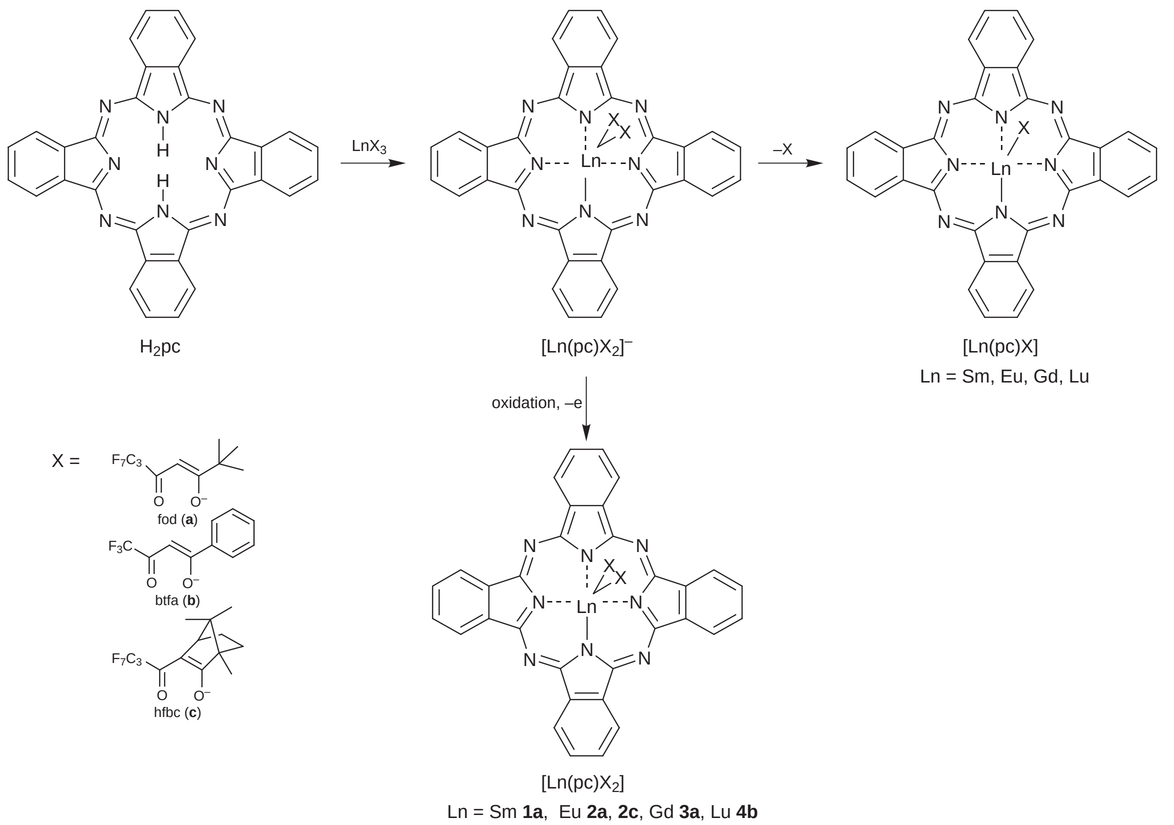

Scheme 2 Synthesis of complexes. Systematic names for ligands X are: 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate (fod); 4,4,4-trifluoro-1-phenylbutane-1,3-dionate (btfa); 3-heptafluorobutyryl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-onate (hfbc)

Table 1 Electronic spectra of $[Ln(pc)X_2]$ complexes and corresponding reduced forms in benzene

	Ln	Charge on pc	X	λ/nm (relative intensity)
1a	Sm	1−	fod	820 (1.05), 717 (0.36), 675,[a] 497 (1.0), 424 (0.89), 320 (sh), 292 (3.42)
2a	Eu	1−	fod	821 (1.08), 716 (0.45), 674,[a] 500 (1.0), 425 (0.9), 320 (sh), 292 (3.64)
2c	Eu	1−	hfbc	821 (0.92), 717 (0.41), 692 (0.55), 675,[a] 496 (1.0), 424 (0.95), 320 (sh), 292 (3.41)
3a	Gd	1−	fod	821 (1.1), 714 (0.2), 694 (0.17), 499 (1.0), 424 (0.88), 320 (sh), 292 (3.96)
4b	Lu	1−	btfa	821 (0.9), 717 (0.36), 675,[a] 609,[a] 501 (1.0), 424 (0.96), 320 (sh), 291 (4.47)
1a[b]	Sm	2−	fod	675 (1), 640 (sh), 608 (0.15), 337 (0.64), 293 (0.32)
2a[b]	Eu	2−	fod	674 (1), 643 (sh), 609 (0.2), 341 (0.67), 295 (0.36)
2c[b]	Eu	2−	hfbc	675 (1), 642 (sh), 611 (0.17), 335 (0.65), 309 (0.38)
3a[b]	Gd	2−	fod	676 (1), 641 (sh), 604 (0.16), 300 (0.72)
4b[b]	Lu	2−	btfa	675 (1), 645 (0.33), 609 (0.15), 328 (0.74), 292 (0.56)
	Mg[c]	1−	—	825,[d] 720, 670,[a] 505, 420, 320
	Mg[c]	2−	—	670,[d] 642, 605, 345

[a] Traces of reduced form. [b] Reduced form (solvent benzene–amine 1000 : 1). [c] Ref. 16. [d] Solvent CH_2Cl_2.

crystals 0.05 g, 4.5% {Found: C, 56.02; H, 2.82; N, 9.76%; *m*/*z* 1117.2 ($[M - H]^+$). $C_{52}H_{28}F_6LuN_8O_4$ requires C, 55.87; H, 2.52; N, 9.76%; 1117.8 ($[M - H]^+$); *m*/*z* 1117.2 $(M - H)^+$, 901.7 (M − fod − H) and 686.4 (M − 2fod).

Results and Discussion

Synthesis

Reaction of metal-free phthalocyanine or its lithium salt with LnX_3, where X = inorganic or carboxylate anion, in different solvents leads to formation of $[Ln(pc)X(solv)_n]$ complexes,[11a,14] equations (1) and (2). On the other hand, when X is the anion

$$H_2pc + LnX_3 \longrightarrow [Ln(pc)X] + 2HX \quad (1)$$

$$Li_2(pc) + LnX_3 \longrightarrow [Ln(pc)X] + 2LiX \quad (2)$$

of a β-diketone the formation of different types of complexes under the same conditions, [Ln(pc)X], $[Ln(Hpc)X_2]$, $[Ln_2(pc)X_4]$, *etc.* have been reported.[11c,14,15] We chose metal-free phthalocyanine as initial material because it is easily available and leads to high yields of mixed-ligand monophthalocyanine lanthanide complexes in boiling dmso.[11a] When the β-diketone contained an electron-withdrawing fragment, for example polyfluoroalkyl, clearly detected quantities of $[Ln(pc)X_2]$ complexes were observed unexpectedly (Table 1, Scheme 2).

Thus, chromatography of the crude reaction mixture leads to the separation of two main fractions. The first red fraction contains the $[Ln(pc)X_2]$ complex which can be eluted by non-polar solvents such as benzene, toluene, hexane, *etc.* in yields up to 6%. The second blue fraction (yield up to 86%), which can be eluted by ethanol, acetonitrile or ethyl acetate, contains the [Ln(pc)X] complex. Changing from dmso to 1,3,5-trichlorobenzene also leads to clearly detected quantities of $[Ln(pc)X_2]$ complexes. On the other hand, reaction in octan-1-ol, acetone or thf leads to formation of complexes only with the pc macrocyclic ligand. The mechanism of formation of the phthalocyanine anion radical in the above reaction is not clear and additional investigations are in progress. The present compounds are the first examples of uncharged 1 : 1 (pc : M) species

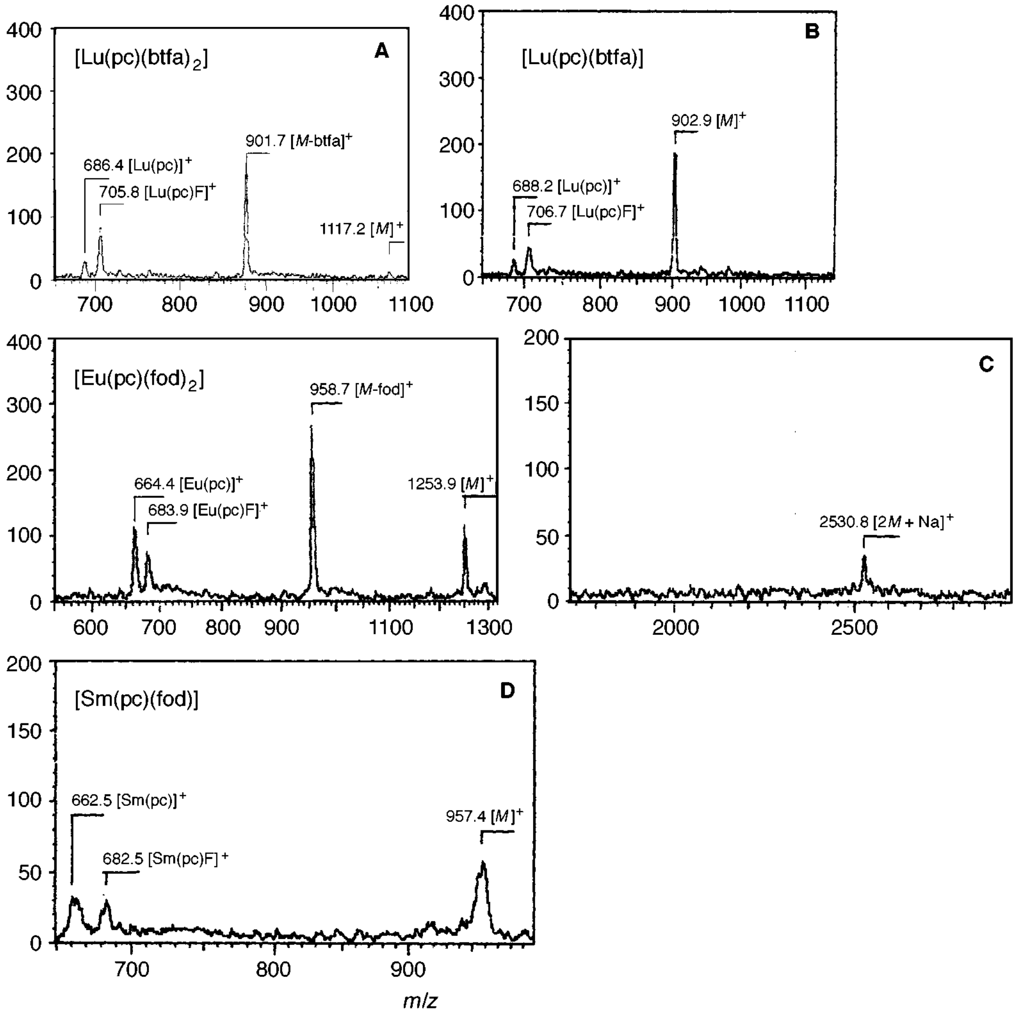

Fig. 1 Typical PD mass spectra of $[Ln(pc)X_2]$ and $[Ln(pc)X]$ complexes

stable under the usual conditions and which contain the phthalocyanine anion radical. All the complexes are stable in the solid state for at least a year. They are less stable in non-polar solutions, but the solutions are still red after at least a week. These red compounds have a unique (for unsubstituted phthalocyanines) high solubility in non-polar organic solvents (benzene, chloroform, hexane, *etc.*). On the other hand, they react with polar solvents or have low solubility in them.

Plasma desorption mass spectra

As was mentioned by many authors,[11c,14,15] reaction of metal-free phthalocyanine or its lithium salt with various tris(β-diketonato)lanthanide complexes leads to formation of several types of mono- and di-phthalocyanine complexes. To support the composition of the complexes obtained their PD mass spectra were recorded. Four typical examples are shown in Fig. 1. In all cases an intense peak of the expected molecular ion was detected with typical resolution.[17] Additionally, in one case, $[Eu(pc)(fod)_2]$, a peak due to the non-covalent dimeric cluster $[\{Eu(pc)(fod)_2\}_2 + Na]^+$ was observed [Fig. 1(C)]. The presence of clusters of type $[M(\text{fragment}) + Na(K)]^+$ are typical for PDMS and related to traces of Na^+ or K^+ ions from samples, solvents or the working surface of the spectrometer holder.[17] In all cases fragments $[M - nX]^+$ were observed (Fig. 1). For all complexes the smallest fragment containing a phthalocyanine ligand is $[Ln(pc)]^+$. The relatively intensive peak of the $[Ln(pc)F]^+$ fragment can be assigned to fragmentation of an axial ligand. Thus, all our assignments in PDMS shown in Fig. 1 are consistent with the proposed structures of the mixed-ligand complexes obtained.

Electronic and ESR spectra

A typical electronic spectrum of the $[Ln(pc)X_2]$ complexes is shown in Fig. 2 and band positions are presented in Table 1. The spectrum is typical of phthalocyanine complexes with macrocyclic radical anions.[18] For all $[Ln(pc)X_2]$ complexes bands at ≈820, 716, 500, 424, 320 and 290 nm have been observed (Table 1). These spectra are very similar to that of the chemically, electrochemically or photochemically generated complex $[Mg(pc)]^+$ which was studied by electronic, ESR and MCD spectroscopy by Stillman's group[16] and those of electrochemically generated $[Ln(pc)(O_2CMe)]^+$ complexes.[11a] Bands at 820 and 716 nm can be assigned to Q-bands of monomeric and non-covalent dimeric forms of $[Ln(pc)X_2]$.[16,18] The ratio of these two bands is sensitive to the solvent purity and sample history. Our attempts to synthesize pure monomeric or dimeric forms have been unsuccessful. In all cases the band of the monomeric complex at 820 nm is more intense than that of the dimer (Table 1). Our assumption that both monomeric and dimeric forms of $[Ln(pc)X_2]$ complexes are present in solution and in the solid state is consistent with PDMS (Fig. 1). Like pc^{2-}-containing complexes,[19] in all cases well resolved weak vibronic satellites have been observed on the Q-band of the monomeric $[Ln(pc)X_2]$ complexes at ≈820 nm (Fig. 2). All the electronic spectra are practically independent of not only the nature of the central ion but also of the type of axial ligand. Similar results were found also for $[Ln(pc)X]$ and $Li[Ln(pc)X_2]$ complexes.[11d,14a] This probably means that the pc–Ln bond in $[Ln(pc)X_2]$ complexes has a predominantly ionic character.

The radical nature of the $[Ln(pc)X_2]$ complexes is supported by their ESR spectra. Like the so-called 'green' radical form

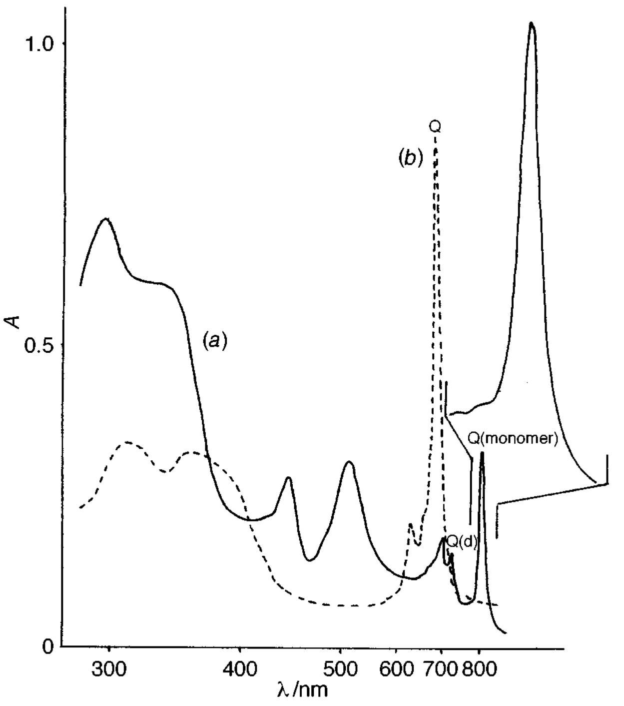

Fig. 2 Typical UV/VIS spectra of $[\mathrm{Ln(pc)X_2}]$ [**2a** (*a*)] and [Ln(pc)X] {[Lu(pc)(btfa)] (*b*)} complexes in benzene

of bis(phthalocyaninato)lanthanide(III) complexes,[18,19] $[\mathrm{Lu(pc)(btfa)_2}]$ showed a narrow ($\Delta_{\frac{1}{2}} = 4$ Hz) signal with $g \approx 2$ [Fig. 3(A)] while other complexes with paramagnetic central ions are ESR silent, probably because of spin–spin relaxation.

Sugimoto *et al.*[20] have published the synthesis and some properties of $[\mathrm{Ln(pc)(dpm)_2}]$ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate) complexes. However, the electronic spectra (680, 620, 500, 330 nm) differ significantly from those of $[\mathrm{Ln(pc)X_2}]$ complexes reported in this paper. Taking into account that the ESR spectra of $[\mathrm{Ln(pc^-)(pc^{2-})}]$ and $[\mathrm{Ln(pc)X_2}]$ complexes are similar and electronic spectra of $[\mathrm{Ln(pc^-)(pc^{2-})}]$ (680, 610, 470, 320 nm)[18,19] very similar to those of $[\mathrm{Ln(pc)(dpm)_2}]$, it can be concluded that the previous authors probably studied the so-called ‘green’ form of the diphthalocyanine lanthanide complexes instead of $[\mathrm{Ln(pc)(dpm)_2}]$.

Reduction of $[\mathrm{Ln(pc)X_2}]$ complexes

Reduction of the initial red-brown $[\mathrm{Ln(pc)X_2}]$ complexes leads to formation of blue $\mathrm{H[Ln(pc)X_2]}$ complexes (Figs. 3 and 4). Good isosbestic points have been observed in the region ≈700, 590, 390 nm in the electronic spectra of all complexes for this reduction (Fig. 4). It is interesting that the rate of reduction depends on the nature of the reducing agent. For example, in the case of alkylamines, reduction of $[\mathrm{Ln(pc)X_2}]$ complexes by *n*-butylamine was complete after a few minutes, while with dicyclohexylamine a few hours were required. In the first step of the reduction by alkylamines the formation of the radical cation of the corresponding amine has been detected by ESR spectroscopy (Fig. 3).

It is interesting that the solubility of the reduced species in non-polar solvents is lower than that of the initial $[\mathrm{Ln(pc)X_2}]$ complexes. This behavior can be assigned to the more ionic character of the reduced form. On the other hand, axial ligand dissociation which may lead to a reduction in solubility can also take place; equation (3). The reduction process is fully

$$[\mathrm{Ln(pc)X_2}] \longrightarrow \mathrm{A^+[Ln(pc)X_2]^-} \longleftrightarrow [\mathrm{Ln(pc)X}] + \mathrm{AX} \qquad (3)$$

reversible. Chemical oxidation of the reduced blue form leads to formation of the corresponding $[\mathrm{Ln(pc)X_2}]$ complexes.

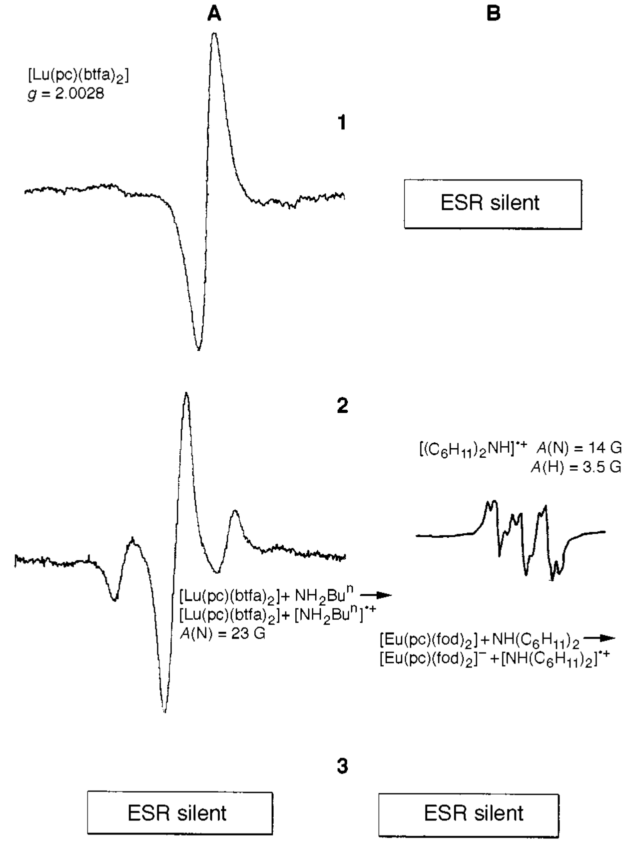

Fig. 3 The ESR spectra of complexes **4b** (**A**) and **2a** (**B**) before (**1**), 1 min after (**2**) and 2 h after (**3**) adding *n*-butylamine (**4b**) or dicyclohexylamine (**2a**); $\mathrm{G} = 10^{-4}$ T

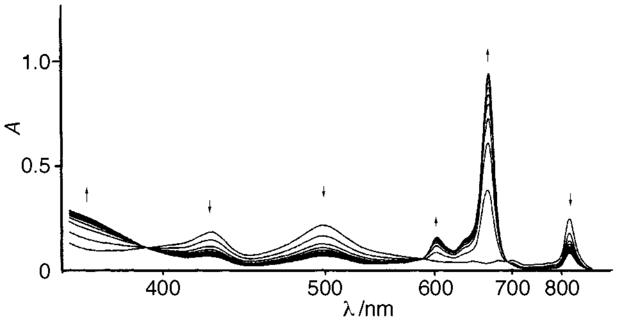

Fig. 4 Reduction of complex **3a** by dicyclohexylamine. Interval between spectra is 10 min

Study of other chemical, electrochemical and photochemical properties of the $[\mathrm{Ln(pc)X_2}]$ complexes is in progress.

Acknowledgements

We acknowledge Drs. T. I. Mironiuck and V. Y. Zub for assistance in recording ESR spectra and thank Professors E. A. Luk’yanets and O. L. Kaliya for valuable discussions.

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Received 20*th January* 1998; *Paper* 8/00542G