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Synthesis and Characterization of Rare Earth Monophthalocyanine Complexes*

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The rare earth phthalocyanine (Pc) complexes have attracted a great deal of interest recently. In particular, many studies on rare earth diphthalocyanine complexes $LnPc_2H$ (where $Pc = C_{32}H_{16}N_8$) have been published, because such compounds present interesting electrochromic properties and semiconductor behaviour. However, there have been very few publications concerning the synthesis of rare earth monophthalocyanine complexes. Kirin *et al.* [1] have synthesized a NdPcCl complex. Mackay *et al.* [2] have reported the synthesis of $Cl(Pc)YbCl\cdot 2H_2O$, but the charge on this compound is not in balance and there should be a monovalent anion in existence. More recently, De Cian *et al.* [3] have reported the single crystal structure of $LnPc(OAc)(H_2O)_2\cdot 2CH_3OH$.

This paper reports the synthesis of a new series of rare earth monophthalocyanine complexes $LnPc(OAc)_2H$, $LnPc(TTA)_2H$, LnPc(OH), LnPc(NPA) (where TTA = thenoyltrifluoroacetone, NPA = 4-nitrophthalic acid). The ^1H and ^{13}C NMR spectra of $LnPc(OAc)_2H$ were recorded. Cyclic voltammogram and half-wave potentials of these complexes have been determined. The total energy of LnPcCl and electronic configuration of Ln in LnPcCl were calculated by the INDO method.

Experimental

The lanthanide acetates were obtained by reaction of acetic acid with rare earth oxides of 99.9% purity. For ^1H NMR measurements 5 mg of rare earth monophthalocyanine complex were dissolved in 0.3 ml DMSO-d_6. A JEOL-100 FT spectrometer was used to obtain the spectra. Cyclic voltammetric measurements were carried out on a model FA-1 cyclic-voltammeter with a three electrode system. The working electrode was a platinum button, a platinum wire served as the counter electrode and a commercial saturated Calomel electrode was used as the reference electrode.

Synthesis of Rare Earth Monophthalocyanine Complexes

Synthesis of $LnPc(OAc)_2H$ was as follows. A mixture of anhydrous rare earth acetate and diiminoisoindoline was refluxed in dry DMF for 20–60 min under an argon or nitrogen atmosphere. The solution was cooled to room temperature and then filtered. The green precipitate obtained by addition of a large amount of hot water and some ammonium acetate to the filtrate was filtered, washed with water and dried *in vacuo*. The crude product obtained was redissolved in DMF and separated with centrifugal thin layer chromatography (CTLC), a 10% $CH_3OH/CHCl_3$ solution was used as eluent. A blue solution was collected and was subjected to further purification by CTLC. The blue powder of the monophthalocyanine complex $LnPc(OAc)_2H$ was obtained by evaporation of the solvent.

The same procedure was employed for the preparation of $LnPc(TTA)_2H$ and LnPc(NPA). However $Ln(TTA)_3$ and $Ln(NPA)_3$ were used as starting material instead of $Ln(OAc)_3$. All these monophthalocyanine complexes showed satisfactory elemental analysis results.

We have synthesized the LnPcCl compound according to Kirin's method [1]. It is interesting to note that when this compound was dissolved in DMF, a blue precipitate was obtained on addition of 1:10 NH_4OH to the solution. The precipitate was dried at 100 °C; elemental analysis results show that this product was $LnPc(OH)\cdot H_2O$.

Anal. Calc. for $LnPc(OH)H_2O$: Ln, 24.22; C, 53.19; H, 2.65; N, 15.80. Found: Ln, 24.53; C, 53.54; H, 3.14; N, 15.51%.

$$LnPcCl + NH_4OH \xrightarrow[H_2O]{DMF} LnPc(OH)H_2O + NH_4Cl$$

It is interesting to note that by heating $LnPc(OH)H_2O$ to 240 °C a compound $(LnPc)_2O$ can be obtained. We consider that this is due to the formation of a binuclear compound containing an oxygen bridge by loss of one molecule of H_2O upon heating.

Results and Discussion

NMR of Rare Earth Monophthalocyanine Complexes

For rare earth phthalocyanine complexes, only ^1H NMR spectra of four rare earth diphthalocyanine complexes $LnPc_2H$ (Ln = La, Nd, Sm, Eu) have been determined by Kasuga and Tsutsui [4]. But the NMR spectra of rare earth monophthalocyanine com-

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TABLE I. ^{1}H NMR Chemical Shifts of Monophthalocyaninato Lanthanide Compounds

Compounds	δ (ppm)			$\Delta\delta_\alpha/\Delta\delta_\beta$ [a]
	α	β	CH_3COO^-	
$SmPc(OAc)_2H$	9.08	7.49	1.47	
$EuPc(OAc)_2H$	10.30	8.48	−6.24	
$TbPc(OAc)_2H$	−36.24 (−22.13)[b]	−15.58 (−7.88)	0.77	1.92
$DyPc(OAc)_2H$	−18.63 (−11.34)	−6.43 (−2.45)	0.89	1.92
$HoPc(OAc)_2H$	4.27	5.24	−46.92	1.75[c]
$ErPc(OAc)_2H$	22.99 (18.85)	14.85 (12.57)	−21.65	2.04
$TmPc(OAc)_2H$	21.52 (15.30)	14.22 (10.93)	−38.09	2.01
$YbPc(OAc)_2H$	10.03	8.53	−15.59	1.90
$LuPc(OAc)_2H$	9.44	8.22	0.37	
ErPcCl	18.81	12.70		2.10
TmPcCl	15.50	11.17		2.07
YbPcCl	9.88	8.46		2.09
LuPcCl	9.44	8.25		

[a] $\Delta\delta = \delta_{Ln} - \delta_{Lu}$. [b] The number in parentheses is the chemical shift of another weaker line. [c] The shift is disturbed near the strong water peak.

Fig. 1. Variation of ^{1}H NMR shift of monophthalocyaninato lanthanide complexes: (1) α proton; (2) methyl proton of acetic acid group; (3) theoretical value of induced shift.

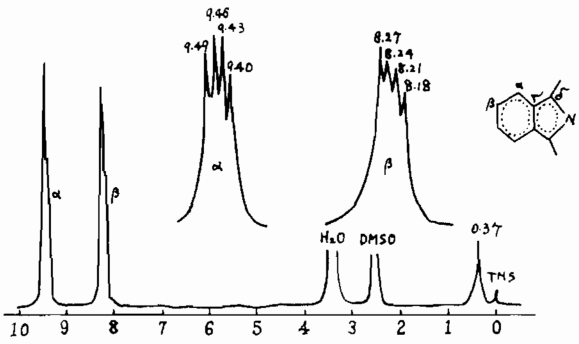

Fig. 2. ^{1}H NMR spectrum of $LuPc(OAc)_2H$.

pounds have not yet been reported. We investigated the ^{1}H NMR spectra of $LnPc(OAc)_2H$ (Ln = Sm–Lu) and LnPcCl (Ln = Er, Tm, Yb, Lu). The results are shown in Table I and Fig. 1.

From Fig. 1 it can be seen that a 'triad effect' appears for the variation of the induced chemical shifts of α and β protons in the benzene ring. This is in agreement with the result calculated by Bleaney's equation. At the same time, the $\Delta\delta_\alpha/\Delta\delta_\beta$ value remains almost constant, which means that the shifts determined are dominantly dipolar contribution. A quadruplet was observed for the lines of α and β protons in $LuPc(OAc)_2H$ with coupling constant $J = 2.95$ Hz (Fig. 2). Furthermore, from the results of Table I it can be seen that two sets of peaks of different intensities appear for Tb^{3+}, Dy^{3+}, Er^{3+} and Tm^{3+} complexes containing the acetic acid group. The ratio of their integrated intensity is about 3:1. It is possible that by coordination with the rare earth ion the plane of the phthalocyanine ring is somewhat twisted and thus leads to the inequality among the chemical environments for the protons of the benzene ring.

We have also determined the ^{13}C NMR spectra of these complexes (Table II) and assigned α, β, γ and δ carbons by several decoupling techniques (see Fig. 3).

Electrochemical Behaviour of Rare Earth Monophthalocyanine Complexes

The electrochemical behaviour of diphthalocyanine complexes of lanthanides has been the subject of many electrochromic display investigations during the last few years [5]. However, little has been published concerning the electrochemical behaviour of rare earth monophthalocyanine complexes. We have investigated the oxidation–reduction behaviour

TABLE II. ^{13}C NMR Shifts of Monophthalocyaninatolanthanides

Compounds	δ (ppm)					
	α	β	γ	δ	CH_3	$-COO^-$
$DyPc(OAc)_2H$	80.15	104.12	131.02	171.28	28.78	192.10
$HoPc(OAc)_2H$	106.30	121.20	134.80	87.80		182.00
$ErPc(OAc)_2H$	130.15	135.60	141.65	206.57		230.94
$LuPc(OAc)_2H$	122.35	129.37	138.14	155.10	22.93	180.83
ErPcCl	125.67	133.07	169.92	212.61		
TmPcCl	124.89	132.10	142.82	191.95		
YbPcCl	120.21	128.20	140.48	162.71		
LuPcCl	121.37	128.78	137.16	154.71		

Fig. 3. ^{13}C NMR spectrum of LuPcCl.

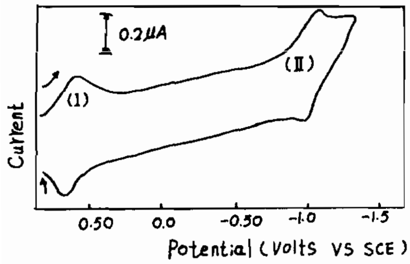

Fig. 4. Cyclic voltammogram for $LuPc(OAc)_2H$ in 0.1 M TBAP/o-$C_6H_4Cl_2$ solution (scan rate 0.2 V/s, conc. 2×10^{-4} M).

of these $Ln(OAc)_2H$ compounds in dichlorobenzene and their half-wave potential, cyclic voltammograms were measured. We have also observed the influence of different solvents and scan rates.

The cyclic voltammograms obtained by changing the initial potential and potential scan rate are shown in Figs. 4 and 5.

The electrochemical data for $LuPc(OAc)_2H$ in 0.1 M TBAP/o-$C_6H_4Cl_2$ are listed in Table III. $E_{1/2}$ and E_p in Table III are calculated according to ref. 6. From the results in Fig. 4 and Table III, and the criteria for the reversibility of oxidation–reduction reaction reported in ref. 6, it can be considered that the oxidation reaction (I) of $LuPc(OAc)_2H$ is a reversible one electron transfer and the reduction reaction (II) is a quasi-reversible one electron transfer process.

We have also investigated the half-wave potentials for $LuPc(OAc)_2H$ in several solvents. The results are listed in Table IV. The standard electron-transfer rate constant K_s was found by the method of Nicholson [7].

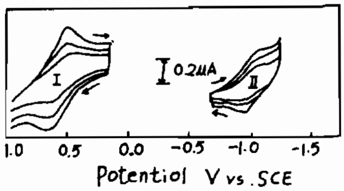

Fig. 5. Cyclic voltammogram for $LuPc(OAc)_2H$ at different scan rates (scan rates 0.1, 0.2, 0.3 V/s; conc. 2×10^{-4} M).

TABLE III. Electrochemical Data for $LuPc(OAc)_2H$ in 0.1 M TBAP/o-$C_6H_4Cl_2$ Solution

Parameter	Scan rate ν (V/s)	$LuPc(OAc)_2H$	
		Reaction (I)	Reaction (II)
$E_{1/2}$ (V)	0.1	0.65	−0.99
	0.2	0.64	−0.98
	0.3	0.64	−0.99
ΔE_p (mV)	0.1	60	80
	0.2	60	70
	0.3	60	70
$i_p/\nu^{1/2}$	0.1	0.19	0.28
(μ_A $V^{-1/2}$ $s^{1/2}$)	0.2	0.18	0.27
($i_p = i_{pa} = i_{pc}$)	0.3	0.18	0.27

TBAP = tetrabutylammonium perchlorate.

$$K_s = \frac{\phi}{\gamma^{\alpha}} \left(\frac{n\pi D_o F\nu}{RT}\right)^{1/2}$$

where K_s = electron-transfer rate constant (cm/s); D_o = diffusion coefficient (cm^2/s); ν = potential sweep rate (V/s); n = number of electrons transferred in each step. ϕ is related to ΔE, the potential difference between the cathodic and anodic peak potentials. K_s values are listed in Table V.

Since $i_{pa} \approx i_{pc}$, $D_{ox} = D_{red}$ and $r \approx 1$.

TABLE IV. The Half-wave Potentials of the Redox Reactions for LuPc(OAc)$_2$H in Several Solvents

Solvent (Donor number)	$E_{1/2}$ (V)	
	Reaction (I)	Reaction (II)
CH_2Cl_2 (0)	0.59	−1.05
$C_2H_4Cl_2$ (0)	0.58	−1.05
$PhNO_2$ (4.4)	0.61	
PhCN (11.9)	0.59	−1.09
DMF (26.6)	0.65	−1.03
Py (33.1)	0.62	−1.03
o-$C_6H_4Cl_2$ (−)	0.65	−0.99

TABLE V. The Electron Transfer Rate Constants for LuPc(OAc)$_2$H

Solvent (Viscosity)	$K_s \times 10^2$ (cm/s)	
	Reaction (I)	Reaction (II)
$C_2H_4Cl_2$ (0.73)	3.2	3.6
DMF (0.80)	2.5	2.9
Py (0.88)	2.8	2.4
PhCN (1.11)	1.1	0.9

During our investigation of the spectral electrochemical behaviour of LuPc(OAc)$_2$H, for the first time electrochromic phenomena were discovered for rare earth monophthalocyanine complexes; when the electrolytic potential changed from −1.2 V to +1.2 V, the colour changed from blue to brown.

Molecular Configuration Calculation for the LnPcCl Complexes

The possible geometric configurations of the LnPcCl complexes have been studied by using the INDO method. The results show that, for stable geometric configuration, Ln in LnPcCl is located at the central axis out of the phthalocyanine plane. The LnPcCl complex molecules belong to the symmetry point group C_{2v}. The distance from Ln to the phthalocyanine plane in LnPcCl gradually increases with decreasing atomic number and at the same time the total energies of the complexes increases (see Fig. 6), while the molecular energy differences caused by coordination reaction decreases, which indicates decreasing stability of the complexes. This is in agreement with the experimental results obtained in our laboratory. It has been found in our experiments that the LnPcCl complexes for heavy lanthanides can be synthesized, but desired products of LnPcCl for the light lanthanides could be obtained only with difficulty. The yield of LnPcCl complexes decreases obviously with increasing Ln ion radius. The electronic configuration has been calculated. The result shows that the main contribution to bonding is due to the 5d electrons of Ln, while 4f electrons are essentially localized.

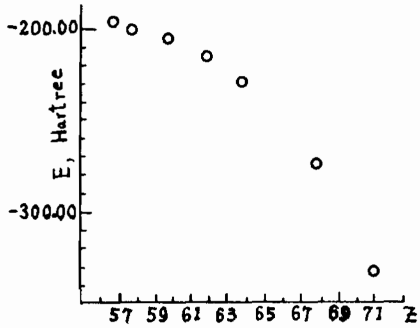

Fig. 6. The correlation between total energy of LnPcCl and atomic number (Z).

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TABLE VI. Distance (h_0) from Ln to the Phthalocyanine Plane in LnPcCl at Stable Configuration

Ln	La	Nd	Sm	Gd	Dy	Er	Lu
h_0 (Å)	2.30	2.00	1.9	1.83	1.78	1.70	1.50
$-E$ (a.u.)	195.033	205.931	216.021	230.948	250.758	276.531	335.426

a.u. = atomic unit.