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Investigación

## Direct Electrochemical Synthesis of Metal Complexes. Lanthanide Phthalocyanines: Optimization of the Synthesis

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**Abstract.** The phthalocyanine complexes of four lanthanides (lanthanum, neodymium, praseodymium, and samarium) have been synthesized by direct electrochemical dissolution of corresponding metal anodes in non-aqueous solutions. The products are characterized by elemental analysis and spectral data. The advantages of the electrochemical route in comparison with conventional chemical methods are shown.

**Resumen.** La vía de disolución electroquímica directa se ha utilizado para la preparación de complejos de ftalocianina y cuatro lantánidos (lantano, neodimio, praseodimio y samario). El proceso se llevó a efecto a partir de la oxidación anódica de los metales correspondientes en soluciones no acuosas. Los productos fueron caracterizados por diferentes métodos analíticos y espectrales. Se demuestran las ventajas de la vía electroquímica en comparación con los métodos tradicionales.

### Introduction

Starting from the discovery of phthalocyanine, this macrocycle and its numerous derivatives and metal complexes have been intensively studied. Among the systematic investigations, it is necessary to mention the first fundamental works of Linstead *et al.* [1-4], which are devoted to the synthesis of transition metal complexes with phthalocyanine from the different precursors (*o*-phthalonitrile, *o*-cyanobenzamide, phthalimide) and to study their stability, the patent [5] on the preparation of metal-free phthalocyanines, the paper of Baumann *et al.* [6] on the properties of the 1,3-diiminoisoindoline as intermediate product in the phthalocyanine synthesis and the excellent recent monographs [7, 8], where all the required information on phthalocyanines is generalized. The detail mechanisms of this macrocycle formation are contained in several papers [6, 9-12].

The metal phthalocyanines can be obtained both starting from metal salts and bulk (elemental) metals [2-4, 7, 8] or their alloys [13 and references therein]. The second reaction type belongs to the area of the *direct synthesis* of coordination compounds starting from metals in the liquid phase [14-16], which includes the *direct electrochemical synthesis* [14-20]. The last technique has been also used in order to obtain free phthalocyanines or their complexes with transition and *p*-metals [21-26]. However, the only examples of electrosynthesis of lanthanide phthalocyanines are those of uranium [27] and dysprosium  $\beta$ -diketonates [28, 29] and, for this reason, in our opinion, this area should be developed.

The lanthanide phthalocyanines complexes, obtained by conventional methods starting from metal salts at 170-290°C, contain one or two macrocycles for each metal atom [7, 8, 30-43]. Thus, according to the papers [7, 32, 33], the complexes having the compositions  $\text{LnPc}_2\text{H}$ ,  $\text{XLnPc}$  ( $\text{X}^-$  is halide anion), and  $\text{Ln}_2\text{Pc}_3$  (a "super-complex") were prepared from phthalonitrile as a precursor; the ratio of the reaction products depends on the synthesis conditions and the metal nature. The ionic structure  $\text{Nd}(\text{Pc})^+\text{Nd}(\text{Pc})_2^-$  was suggested [33] and refuted [32] for the neodymium super complex  $\text{Nd}_2\text{Pc}_3$ ; the covalent character of the donor-acceptor bonds in this compound and other lanthanide triple-decker phthalocyanines was proved by the study of dissociation conditions of these compounds [32].

The lanthanide phthalocyanines can be also obtained from the corresponding metal salts and metal-free phthalocyanine or 1,3-diiminoisoindoline [7]. It has been established [7, 34] that "whereas a diphtalocyanine complex  $\text{Pc}_2\text{LnH}$  is mainly obtained for the heaviest lanthanides (Dy-Lu), a super complex  $\text{Pc}_3\text{Ln}_2$  is progressively formed with the lighter lanthanides, and predominates for La and Nd". However, it is impossible to avoid, using all the precursors of the phthalocyanine, the possibility of the mixed salts ( $\text{XLnPc}$ ) formation [7].

This work is devoted to the synthesis and characterization of the phthalocyanine complexes with four lanthanides (lanthanum, praseodimium, neodimium and samarium) by direct electrochemical dissolution of zero-valent compact metals as sacrificial anodes in the conditions of the simultaneous ultrasonic treatment of the reaction system.

## Experimental

**Materials.** Solvents were dried according standard procedures. *o*-Phthalonitrile, standard PCH<sub>2</sub>, and CH<sub>3</sub>ONa (*Aldrich*) were used as supplied. *n*-Bu<sub>4</sub>NBr (*Aldrich*) was dried at 80-90°C before use. The metal surface was polished before process in order to remove oxidation products and to plane the surface.

**Electrochemical synthesis.** The electrochemical cell was a 100-mL glass flask with reflux. The anode was a piece of metal and the cathode was a platinum foil. A stream of dry nitrogen served to stir the solution during all the time of electrolysis. The solution phase containing *i*-BuOH (100 mL), CH<sub>3</sub>ONa (in CH<sub>3</sub>OH, 25% solution, 1 mL), phthalonitrile (3 g), and previously dried *n*-Bu<sub>4</sub>NBr (0.1g) as supporting electrolyte, was heated to 100°C with agitation, and then the electrolysis begun (power supply PS 500-1 *Sigma-Aldrich*). The time of electrolysis was 2 h (Table 1). After finishing the experiment, the solution was cooled and the metal phthalocyanine complex was filtered and purified in a Soxhlet equipment (absolute ethanol was used as solvent).

**Simultaneous ultrasonic treatment.** A simultaneous ultrasonic treatment of the reaction phase (from ultrasonic cleaner *Bransonic 12*) was carried out in all experiments using a weak source of ultrasound in order to eliminate formed products out of metal surface and, thus, to stabilize the current in the process. Stronger sources of ultrasound have not been used to avoid turbulent processes and the uncontrolled superheating of the reaction zone.

We have not applied higher concentrations of the supporting electrolyte, in spite of the fact that the generated voltage is 55-63 V, to avoid collateral reactions, in particular, the formation of free Br<sub>2</sub> on the anode and its further interaction with the macrocycle molecules or the metal anode.

**Analysis and spectroscopy.** The metal content was determined by atomic absorption spectroscopy; organic microanalysis was carried out by standard methods (Table 2). The infrared spectra were recorded on a *Perkin-Elmer* spectrophotometer (Table 3). The <sup>1</sup>H NMR spectra were recorded on *Bruker DPX 400* equipment (125 MHz, 298 K, Me<sub>4</sub>Si as internal reference and CDCl<sub>3</sub> as a solvent). The UV-visible spectra were recorded on a *Lambda 12, Perkin Elmer* spectrophotometer (in cyclohexane).

**Table 1.** Conditions of the electrosynthesis of lanthanide phthalocyanines.

Metal	Initial voltage, V	Current, mA	Yield, %
La	60	30	97
Sm	55	30	95
Nd	63	30	92
Pr	58	30	95

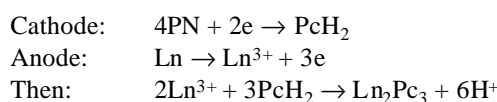
**Table 2.** Analytical data of phthalocyanines obtained.

Metal	Content (found/calculated, %)			
	M	C	H	N
La	15.11/15.32	62.91/63.50	2.46/2.65	17.89/18.53
Sm	16.03/16.37	61.98/62.72	2.42/2.62	17.76/18.29
Nd	15.47/15.81	62.42/63.14	2.44/2.64	17.81/18.41
Pr	14.98/15.51	62.63/63.36	2.44/2.65	17.80/18.48

## Results and discussion

All synthesized products are blue powders, insoluble in water and ethanol.

The electrodic reactions could be represented as follows:



According to Sokolova *et al.* [32], the maximum yield (80-90%) of the Ln<sub>2</sub>Pc<sub>3</sub> compounds (in comparison with XLnPc and LnPc<sub>2</sub>H) is obtained when, in the chemical way, the molar ratio "*o*-phthalonitrile: rare earth element salt" was 6:1 (La, Sm, Gd, Tm, Lu initial metal salt is LnCl<sub>3</sub>). The use of the electrochemical dissolution of the lanthanides allows to obtain Ln<sub>2</sub>Pc<sub>3</sub> complexes with almost 100% yields on *o*-phthalonitrile conversion, according to the elemental analysis and spectral data.

According to our previous research [44], there is no formation of free phthalocyanine in the system "*i*-BuOH -

**Table 3.** IR spectra data of complexes obtained.

<i>n</i> , cm <sup>-1</sup>	Group	<i>n</i> , cm <sup>-1</sup>	Group
3500-3380v.s.,w	v(C-H)	1448m	v(C-C) of pyrrol rings
3280m		1385v.s.	Pyrrol nuclei-
3080sl			mesoatoms of N
2865* m		1365s	
2815m		1320m	γ(C-H)
2775sl		1150s	
2705*m		1000m	
2504m	v(C-C) of	887-865**m	v(M-N)
2300-2280s	benzene rings	850-835**m	
1730v.s.		720-735**m	
1607s		480-465**m	
1592m		435-330**m	
1570m		281-260**m	
1524m			
1496m			

\*These absorption bands are absent in the PCH<sub>2</sub> spectra.

\*\*The centers of absorption bands for the spectra of each metal phthalocyanine are very close; the difference is about 3-5 cm<sup>-1</sup>.

CH<sub>3</sub>ONa - *n*-Bu<sub>4</sub>NBr - *o*-phthalonitrile” without the application of electrolysis at about 100°C, unlike some other solvents where both chemical and electrochemical formation of phthalocyanine could take place. So, this solvent was chosen in order to synchronize metal anode dissolution with the formation of free phthalocyanine on the cathode surface and to avoid the obtention of the mixture “metal-free phthalocyanine - lanthanide phthalocyanine”. Unlike the conventional chemical methods of the preparation of rare-earth metal phthalocyanines [32-34], where the syntheses have been carried out at 170-290°C, it is possible to decrease reaction temperature to about 100°C.

The analysis of the IR spectra of the synthesized products (Table 3) [7, 8, 32, 45] permits to conclude that the typical “sandwich” metal-phthalocyanine super complexes M<sub>2</sub>Pc<sub>3</sub> are formed. Thus, the spectra of these products present more absorption bands than the free phthalocyanine in the range of 2500-3000 cm<sup>-1</sup>. According to [7, 8, 32, 35], such a result is a consequence of the presence of a third phthalocyanine ligand between two metal atoms and the formation of a “doble sandwich” (triple-decker) structure in which the metal is in the 3+ oxidation state in the obtained complex (Fig. 1). Such type of complexes is also typical of the metal-macrocycle compounds similar to the phthalocyanine one, for example, tristetrapyrroles M<sub>2</sub>P<sub>3</sub> [46] (no ions were observed in these porphyrin sandwiches). In this type of compound both central metal atoms are connected *covalently* with two macrocycles. Two external macrocycles are identical. According to data reported for similar structures (lanthanide phthalocyanines and porphyrines) [7, 32, 46], the internal macrocycle is plane and the external (terminal) phthalocyanines are severely distorted.

The <sup>1</sup>H NMR spectral data of all four complexes obtained are practically identical (they contain the peaks at δ 8.5, 7.6, 6.2, 4.8, and 3.6, corresponding to proton signals of methine groups [45]) and show the absence of the proton of NH group (8 ppm) [45] which could additionally confirm the formation of the Ln<sub>2</sub>Pc<sub>3</sub> complexes. The electronic spectra show a small band at 400-410 nm (*Soret* band), an intensive band in the area 670-650 (*Q* -band), and an extra band at 880-860 nm. A comparison of the above data with those reported earlier for phthalocyanine and porphyrine complexes [7-10, 30, 32-35, 46] allows to ascribe the Ln<sub>2</sub>Pc<sub>3</sub> structure to the isolated products.

The application of simultaneous ultrasonic treatment [47-50] with the electrochemical dissolution permits to increase their efficiency, since it is not necessary to stop periodically the electrolysis to remove mechanically the formed product



**Fig. 1.** Proposed structure of lanthanide-phthalocyanine sandwich.

out of the electrodic surface. As a consequence, it is possible to stabilize the voltage during the electrochemical process.

## Conclusions

The results show that it is possible to carry out the electrosynthesis of lanthanide phthalocyanine complexes with almost quantitative yields in the mild conditions.

The use of the system *i*-BuOH-CH<sub>3</sub>ONa-*n*-Bu<sub>4</sub>NBr-*o*-phthalonitrile-lanthanide avoids the formation of the mixture of free phthalocyanine and lanthanide phthalocyanine and, thus, leads to the pure products.

The electrochemical dissolution of the four lanthanides reported, in the presence of phthalonitrile under the established conditions led to the formation of only the Ln<sub>2</sub>Pc<sub>3</sub> type compounds, without admixtures of the LnPc<sub>2</sub>H or XLnPc. All the processes, unlike those by the conventional chemical way, were carried out at about 100°C temperature which it is a great advantage of this synthetic route.

According to the obtained results in this research, the application of simultaneous ultrasonic treatment with the electrochemical dissolution is strongly recommended in the processes with the use of elemental lanthanides to improve existing electrochemical techniques.

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