

1,10-Phenanthroline N-Oxide Complex with Europium(III)

A. C. M. de ANDRADE, M. A. de BRITO, A. L. COELHO
*Departamento de Química, UFCE, Cidade Universitária,
60.000 Fortaleza, Ceará, Brasil*
and G. F. de SÁ*

*Departamento de Física, UFPe, Cidade Universitária, 50.000
Recife, Pernambuco, Brasil*

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Coordination compounds of 1,10-phenanthroline mono-N-oxide (N-phenO) with 3d transition metal ions have been extensively studied.¹⁻⁵ Complexes of this ligand with lanthanide ions, by contrast, have not been reported in the literature. The present note deals with the synthesis and characterization of the complex formed between (N-phenO) and europium(III).

Experimental

Reagents

N-phenO was prepared by the method described by Corey *et al.*¹ The purified ligand was characterized by microanalyses, melting point¹ and i.r. spectrum.² All other chemicals were of reagent quality. The nitromethane was distilled prior to use and had a specific conductance of $2.5 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$.

Preparative Procedure

An ethanol solution containing 3.3 mmol of N-phenO was stirred and warmed slowly. To this solution was gradually added 5 ml of an ethanolic solution containing 1.0 mmol of hydrated europium (III) nitrate. The new lanthanide complex precipitated immediately. The precipitate was filtered, washed with alcohol and dried in a vacuum dessicator over P_2O_5 .

Analyses

The europium content was determined by titration with EDTA using xylenolorange as indicator; calculated for $[\text{EuL}_3\text{NO}_3](\text{NO}_3)_2$, 16.4%. Found 16.4%. Microanalyses for carbon, hydrogen, and nitrogen were done by PCR, Inc.; calculated for $\text{Eu C}_{36}\text{H}_{24}\text{N}_6\text{O}_{12}$: C, 46.7; H, 2.6; N, 13.6. Found: C, 47.0; H, 2.8; N, 13.9%.

Instrumentation

Conductance measurements were made with a Wiss-Mechn. Werkstätten D-812 conductivity meter.

I.R. spectra on KBr pellets were taken in the region 4000–400 cm^{-1} with a Carl-Zeiss UR-20. The emission spectra were measured on a Beckman Acta V Spectrophotometer equipped with the model 569384 Fluorescence Attachment. The excitation source was a 100-watt mercury lamp used in conjunction with Corning CS-7-39 and CS-7-54 filters. For measurements at 77 °K the solid compound was placed in a quartz tube of 3mm in diameter and immersed in a Dewar flask which had a quartz tail and was filled with liquid nitrogen.

Results and Discussion

The reaction between the hydrated nitrate of europium(III) and 1,10-phenanthroline N-oxide results in the formation of a solid crystalline yellow compound, melting point 245–247 °C. The compound could not be recrystallized since it is essentially insoluble in the common solvents. The analytical results are in good agreement with the formula $[\text{EuL}_3\text{NO}_3](\text{NO}_3)_2$.

The molar conductivity of a $10^{-3} M$ solution of the complex in nitromethane ($\Lambda_m = 155.9 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) may indicate the presence of 1:2 electrolyte,⁶ implying that one nitrate ion is coordinated to the metal.

The ligand N-phenO exhibits a rich i.r. spectrum in the 1660–400 cm^{-1} region and assignments were recently tabulated by Dega-Szafran.² In fact the i.r. spectra of the N-phenO–Eu(III) complex show shifts and splittings of several vibrational modes similar to that found for the corresponding complexes of 3d metal.^{4,5} This is considered to be indicative that N-phenO is coordinated as bidentate O,N-chelating agent. Finally, in the 1800–1700 cm^{-1} region, the

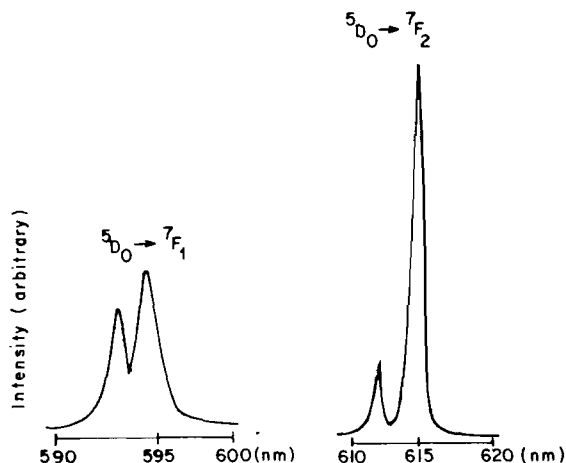


Fig. 1. Emission spectrum of $[\text{EuL}_3\text{NO}_3](\text{NO}_3)_2$ from solid at 77 °K.

*Author to whom inquiries should be directed.

complex shows three bands and exhibits a $\Delta(\nu_1 + \nu_4)$ value of 33 cm^{-1} , indicative of the presence of uncoordinated and bidentate nitrate groups.⁷ This is in agreement with conductivity values which favor formulation with one coordinated group.

The europium complex luminesces very strongly both at room temperature and at liquid nitrogen temperature when excited with near ultraviolet radiation.⁸ The emission spectrum of the complex at 77°K is given in Fig. 1. The most intense transition is $^5\text{D}_0 \rightarrow ^7\text{F}_2$ followed by $^5\text{D}_0 \rightarrow ^7\text{F}_1$. The former transition is split into two strong lines at 612.0 and 614.6 nm, and the latter is split into two weaker ones at 592.2 and 594.0 nm. No line was observed corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. According to the scheme of Blasse, Brill and Nieuwpoort,⁹ this corresponds to an absence of a center of inversion, consequent to a symmetry lowering from D_{3h} to D_3 .

Quite recently we have synthesized the analogous complexes of Nd(III) and Ho(III) and further work is in progress.

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