

2-Pyrazinecarboxylic Acid Complexes of Lanthanide Ions

G. F. DE SA, B. DE B. NETO and R. FERREIRA

Departamento de Física, Laboratório BS/TR1, Universidade Federal de Pernambuco, Cidade Universitária, 50.000 Recife, Pe., Brazil

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The complexes formed in the reaction between the lanthanide basic carbonates and 2-pyrazinecarboxylic acid (Hpya) have been prepared and characterized. The compounds, of formula $[Ln(pyra)_3 \cdot xH_2O]$, where $x = 2$ or 3 , are solid crystalline substances. The new complexes were characterized by means of chemical analyses, vibrational spectrum, and electronic absorption and emission spectra. The oscillator strengths of the hypersensitive transition ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ of the Nd(III) complex have been studied and the nephelauxetic effect has been evaluated. The emission spectrum of the Eu(III) complex at 77°K have been studied and the determination of the maximum observed splitting of the values of J indicates a very low site symmetry.

Introduction

Coordination compounds of 2-pyrazinecarboxylic acid (Hpya) with 3d transition metal ions have been studied [1]. Complexes of this ligand with lanthanide ions, on the other hand, have not been reported in the literature. In this paper we describe the preparation and characterization of lanthanide complexes of that ligand obtained from the basic carbonates. In order to expand our understanding of the interaction of pyrazine derivatives with the lanthanide ions, we have also studied (Hpya) and pyrazinamide complexes obtained from the lanthanide perchlorates, and these results will appear in a forthcoming publication [2 a,b].

It is well known that lanthanide complexes of pyridine-2,6-dicarboxylate [3] and of carboxylates in general [4] can be prepared as crystals large enough to have their structures determined by X-ray diffraction analysis. Because of the chemical analogies it was anticipated that the bidentate ligand 2-pyrazinecarboxylic acid would likewise form rare-earth complexes susceptible of X-ray structure determination. It is also known that complexes of that type with Eu(III) and Tb(III) are generally luminescent. The character of the luminescence spectrum is determined by selection rules arising from the symmetry

of the chemical environment. This anticipation was not fulfilled, the lanthanide complexes of Hpya being obtained only as powders. However, their emission spectra are remarkable, showing a very intense luminescence with characteristic sharp lines and allowing the symmetry of the chemical environment to be assigned.

Some of the results have been presented previously [2c].

Experimental

Reagents

The 2-pyrazinecarboxylic acid (Aldrich) was purified by recrystallization from ethanol–water solution. The ligand was characterized by microanalyses, melting point and i.r. spectrum. The lanthanide basic carbonates were prepared by the method described by Willard [5] from the freshly ignited oxides (99.9 per cent Sigma and Johnson–Matthey). All other chemicals were of reagent quality.

Preparative Procedure

An ethanol solution containing 3.2 mmol of the ligand was stirred and warmed. To this solution was gradually added an aqueous suspension containing 1 mmol of the lanthanide basic carbonate. The solution cleared and after reduction of the volume the compounds were obtained in microcrystalline form. The compounds were purified by recrystallization from an aqueous ethanolic solution.

Analyses

The lanthanide content was determined by titration with EDTA using xylenolorange as indicator. Microanalyses for carbon, hydrogen, and nitrogen were done by PCR, Inc. and by the Microanalytical Lab. of the University of Sao Paulo.

Instrumentation

Infrared spectra obtained on mulls (Nujol and Fluorolube) and on KBr pellets were taken in the

TABLE I. Analytical Data for $\text{Ln}(\text{pya})_3 \cdot \chi\text{H}_2\text{O}$

Compound	% Metal		Analysis % Carbon		% Hydrogen		% Nitrogen	
	Theor	Exptl	Theor	Exptl	Theor	Exptl	Theor	Exptl
$\text{La}(\text{pya})_3 \cdot 3\text{H}_2\text{O}$	24.71	24.6	32.04	32.25	2.69	2.58	14.95	14.81
$\text{Pr}(\text{pya})_3 \cdot 3\text{H}_2\text{O}$	24.97	24.6	31.93	31.68	2.69	2.69	14.89	14.50
$\text{Nd}(\text{pya})_3 \cdot 3\text{H}_2\text{O}$	25.41	25.3	31.74	31.38	2.64	2.68	14.81	14.61
$\text{Sm}(\text{pya})_3 \cdot 3\text{H}_2\text{O}$	26.21	25.9	31.40	31.80	2.61	2.20	14.64	14.86
$\text{Eu}(\text{pya})_3 \cdot 3\text{H}_2\text{O}$	26.42	26.5	31.32	31.14	2.63	2.79	14.61	14.42
$\text{Gd}(\text{pya})_3 \cdot 3\text{H}_2\text{O}$	27.09	26.8	31.03	30.85	2.58	2.20	14.47	14.02
$\text{Tb}(\text{pya})_3 \cdot 3\text{H}_2\text{O}$	27.30	27.5	30.94	31.22	2.60	2.48	14.44	14.30
$\text{Ho}(\text{pya})_3 \cdot 2\text{H}_2\text{O}$	28.92	29.0	31.59	31.72	2.30	2.41	14.74	14.58
$\text{Tm}(\text{pya})_3 \cdot 2\text{H}_2\text{O}$	29.42	29.2	31.37	31.02	2.29	2.12	14.64	14.34
$\text{Lu}(\text{pya})_3 \cdot 2\text{H}_2\text{O}$	30.15	29.6	31.04	30.71	2.24	2.01	14.48	14.01

region 4000–250 cm^{-1} with a Perkin–Elmer 457 as well as with a Beckman 4220 spectrophotometer.

The electronic absorption spectra of the neodymium compound in Fluorolube mull and aqueous solutions were recorded with a Beckman Acta V spectrophotometer equipped with a Temperature Module. Spectral measurements were made at $25.0 \pm 0.5^\circ$, $50.0 \pm 0.5^\circ$, $75.0 \pm 0.5^\circ$ and $90.0 \pm 0.5^\circ$ using fused quartz cells of 1.0 or 5.0 cm (nominal) path length. The emission spectra were measured with the same spectrophotometer equipped with the model 569384 Fluorescence Attachment. The 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 3 mm in diameter and immersed in a Dewar flask which had a quartz tail and was filled with liquid nitrogen. The wavelength scale for the spectrophotometer was calibrated with lines from a low-pressure mercury lamp.

Determination of Oscillator Strengths

The absorption intensities, presented as oscillator strengths were calculated from the expression [6]

$$P_{\text{exp}} = 4.32 \times 10^{-9} \int \epsilon_i(\sigma) d\sigma$$

where $\epsilon_i(\sigma)$ is the molar extinction coefficient at energy $\sigma(\text{cm}^{-1})$. In this paper these values were calculated using the method of numerical integration (Simpson's Rule). The independence of oscillator strength on concentration was shown to be valid for the neodymium complex solutions in the range 2×10^{-2} to $2 \times 10^{-3} M$.

Results and Discussion

The reaction between the lanthanide basic carbonates and 2-pyrazinecarboxylic acid (Hpya)

results in the formation of solid crystalline compounds. These complexes are finely divided powders which decompose at temperatures between 240–285 °C without melting. The results of the analyses of these compounds are presented in Table I. These analytical results are in good accord with the formulation as $[\text{Ln}(\text{pya})_3 \cdot \chi\text{H}_2\text{O}]$, in which the symbol pya refers to the loss of the carboxyl proton from the ligand Hpya, χ is 2 or 3 and Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Tm and Lu. Studies are under way on the synthesis of Hpya complexes of the remaining lanthanides.

Since Hpya probably functions as a bidentate ligand, it is likely that the water molecules are coordinated to the lanthanide ion; otherwise this would lead to the relatively rare coordination number six for the lanthanide ions [7]. An indirect indication of the coordination of water molecules to the metal was obtained by heating the compounds at 100 °C *in vacuo* over P_2O_5 . When the compounds were subjected to such treatment, no loss of water could be detected. This implies rather strongly that the water molecules in the compound are not simply part of the crystal lattice but are coordinated directly to the lanthanide ion.

All the complexes studied show very similar i.r. spectra. In the free ligand the relevant bands are a strong one at 1710 cm^{-1} and two broad ones of medium intensities at 2450 and 1900 cm^{-1} . The first band, generally assigned to the antisymmetric carbonyl stretch in the COOH group [8] is totally absent in the spectra of the complexes. This band is replaced by a very strong one centered at 1610–1620 cm^{-1} which is the antisymmetric stretching mode of the coordinated carboxylate [9]. The presence of the 2450 and 1900 cm^{-1} bands in the free ligand shows that it exists as a monomeric species [10]. The spectra are characteristic of chelate ring formation, with bonding of the ligands to the metal through the nitrogen atom and the carboxyl group [1].

TABLE II. Oscillator Strengths for Nd(III) in Aqueous Solutions ($P_{\text{exp}} \times 10^6$).

Transition (Assignment) ^a	Energy (cm^{-1})	[Nd(py _a ₃ ·3H ₂ O)]				Aquo Ion (25 °C) ^b
		(25.0 ± 0.5 °C)	50.0 ± 0.5 °C	75.0 ± 0.5 °C	90.0 ± 0.5 °C)	
⁴ I _{9/2} →	⁴ S _{3/2} 13000–	11.4	11.1	10.8	10.6	8.78
	⁴ F _{7/2} 14100					
⁴ I _{9/2} →	⁴ G _{5/2} 16600–	18.2	18.0	17.9	17.6	9.34
	² G _{7/2} 18200					
⁴ I _{9/2} →	² K _{13/2} 18600–	9.8	9.6	9.5	9.3	6.82
	⁴ G _{7/2} , ⁴ G _{9/2} 20200					

^aReference 14. ^bReference 15.

The i.r. spectra also show features that indicate coordinated water molecules, in agreement with our observations that no water is lost on heating at 100 °C *in vacuo* over P₂O₅.

It is well known that the use of electronic absorption spectroscopy in evaluating the nature of the bonds in complexes of the lanthanides is limited, since the transitions responsible for the observed bands occur in 4f orbitals which are well shielded from the influence of the ligands [11]. However, the nephelauxetic effect and the hypersensitivity of some bands can provide useful information.

The absorption spectra of the neodymium and praseodymium complexes in the visible and near i.r. show that the peaks are considerably displaced towards the red, with respect to the aquo ions [12]. In the case of the four peaks in the neodymium spectrum between 500 and 900nm this displacement averages 108 cm^{-1} . The nephelauxetic effect in this compound is thus fairly large, which is usually taken to mean that there is a reasonable degree of covalency in the bonds between the ligand and the lanthanide ion.

The solution spectra of lanthanide complexes often contain certain bands the intensity of which is markedly affected by the environment. These bands have been termed "hypersensitive" bands [13].

In order to see if such bands are present in the Hpya compounds, we measured the spectrum of the solid compound [Nd(py_a)₃·3H₂O] dissolved in water. It is sometimes argued that the integrity of the complexes in aqueous solution is questionable. However, their spectra in mulls are similar to the aqueous one, especially the hypersensitive band, and we take this as a good indication that there is no significant change in the structure. Unfortunately, the compounds are insoluble in all other usual solvents. The oscillator strengths for three bands are given in Table II.

It is evident that in the presence of the ligand the intensity of the second transition is noticeably increased when compared with that of the aquo ion, the ratio being 1.95. The other two bands have about the same intensities in the complex and the aquo ion.

The hypersensitivity effect is more intense with the Schiff base complexes [14] and work is underway in this group with analogous ligands, such as pyrazinamide [2].

Peacock [17, 18] has studied the variation of $f \leftrightarrow f$ hypersensitive transitions in Eu(III) and Ho(III) solid glasses with temperature. A positive (dP_{exp}/dT) would be considered as evidence for a vibronic mechanism, but Peacock's results show that this does not happen, indicating rather a static contribution. We have studied the temperature dependence of the oscillator strengths of Nd(III) complexes in aqueous solution in the range 25° to 90 °C (Table II). We have observed a slight decrease in P_{exp} with T. However, especially in the case of the hypersensitive transition ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2}, the observed variation is entirely compatible with the change in concentration due to the expansion coefficient of the solution (3% in the range 25 to 90 °C). The results should be considered with caution because the temperature range was not very large and reached the high temperature side, where the Boltzmann factor makes the measurements of dP_{exp}/dT less sensitive.

The europium and terbium strongly emit visible radiation both at room and at liquid nitrogen temperature, when excited with near ultraviolet radiation [19]. The emission spectrum of the europium complex at 77 °K is given in Fig. 1 and shows transitions that originate on the ⁵D manifold (mainly from the ⁵D₀ excited state) of europium(III) and terminate on the ⁷F₀, ⁷F₁ and ⁷F₂ components of the ground ⁷F term [20].

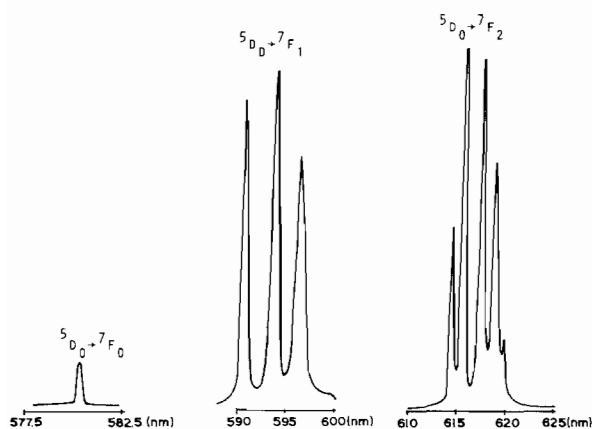


Fig. 1. Emission spectrum of $[\text{Eu}(\text{pya})_3 \cdot \text{H}_2\text{O}]$ from solid at 77°K .

The most intense transition is $^5\text{D}_0 \rightarrow ^7\text{F}_2$, followed by $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and by a very weak $^5\text{D}_0 \rightarrow ^7\text{F}_0$. The first transition is split into five lines at 620.2, 619.0, 617.5, 615.5 and 614.5 nm. Three lines at 596.0, 593.3 and 590.0 nm are observed, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. Since this is the maximum possible splitting, the symmetry around the europium ion must be quite low. A single line at 580.0 nm appears, corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_0$. This emission line is sharp and unsplit, indicating the existence of only one crystallographic site.

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References

- 1 A. Tenhunen, *Suomen Kemistilehti*, **B45**, 76 (1972).
- 2a M. A. Almeida, O. A. Serra and G. F. de Sá, *Ciência e Cultura, Proc. of the 28th Annual Meeting of the S.B.P.C.*, 146 (1976).
- 2b I. M. Xavier Jr., O. M. L. Malta, A. A. S. da Gama and G. F. de Sá, *Ciência e Cultura, Proc. of the 28th Annual Meeting of the S.B.P.C.*, 145 (1976).
- 2c G. F. de Sá and B. de B. Neto, *Proc. 12th Rare Research Conference, Vail, Colorado*, 1976.
- 3 J. Albertsson, *Acta Chem. Scand.*, **24**, 1213 (1970).
- 4 E. Hansson, *Acta Chem. Scand.*, **24**, 2969 (1970).
- 5 H. Willard, "Precipitation from Homogeneous Solutions", Wiley, New York (1959).
- 6 W. T. Carnall, P. R. Fields and B. G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).
- 7 T. Moeller, *MTP International Review of Science, Lanthanide and Actinides Series I*, Vol. VII (1972).
- 8 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York (1970).
- 9 K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Am. Chem. Soc.*, **84**, 2081 (1962).
- 10 S. Yoshida and M. Asai, *Chem. Pharm. Bull.*, **7**, 679 (1953).
- 11 T. Moeller, D. R. Martin, L. C. Thompson, R. Ferrús, G. R. Feistel and W. J. Randall, *Chem. Rev.*, **1**, 65 (1965).
- 12 C. K. Jørgensen, *Prog. Inorg. Chem.*, **4**, 73 (1962).
- 13 C. K. Jørgensen and B. R. Judd, *Mol. Phys.*, **8**, 281 (1964).
- 14 W. T. Carnall, P. R. Fields and K. Rajanak, *J. Chem. Phys.*, **49**, 4424 (1968).
- 15 W. T. Carnall, P. R. Fields and G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).
- 16 G. F. de Sá, E. Giesbrecht and L. C. Thompson, *J. Inorg. Nucl. Chem.*, **37**, 109 (1975).
- 17 R. D. Peacock, *Chem. Phys. Letters.*, **10**, 134 (1971).
- 18 R. D. Peacock, *J. Chem. Soc. Faraday*, **II**, **68**, 169 (1972).
- 19 G. A. Crosby, R. E. Whan and R. M. Aline, *J. Chem. Phys.*, **34**, 743 (1961).
- 20 L. G. Deshazer and G. H. Dieke, *J. Chem. Phys.*, **38**, 2190 (1963).