

## Synthesis and characterization of lanthanide trifluoroacetate complexes with 3-picoline-*N*-oxide

L. B. Zinner, C. A. Alves de Carvalho and K. Zinner

Instituto de Química, Universidade de São Paulo, C.P. 20.780, CEP 01498, São Paulo SP (Brazil)

### Abstract

Complexes with composition  $\text{Ln}(\text{F}_3\text{C}-\text{COO})_3 \cdot 2(3\text{-picNO}) \cdot x\text{H}_2\text{O}$  were synthesized. According to X-ray powder patterns and IR data five series of isomorphous compounds were detected: La–Nd; Sm–Eu; Gd > Tm, Y; Ho, Er, Tb; Dy, Yb, Lu. They behave as non-electrolytes in methanol. IR spectra show a shift of  $\nu\text{NO}$  to lower frequencies, as compared with the free ligand, as a result of coordination through the oxygen. The bands attributed to the anions indicate two modes of coordination. The neodymium spectrum at 77 K shows that the central ion is not involved in a cubic site. Electrostatic bonds between  $\text{Nd}^{3+}$  and ligands were evidenced by the nephelauxetic, Sinha's parameters and covalent factor from the room temperature spectrum. Using the electronic emission spectrum, at 77 K, it was possible to conclude that europium ions present two different symmetry sites, since a splitting of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  band was observed. The complex species are probably polymeric or at least dimeric, and europium ions are involved in two different sites, but with the same  $\text{C}_{3v}$  symmetry.

### 1. Introduction

Lanthanide trifluoroacetate complexes with 3-picoline-*N*-oxide (3-picNO) as ligand and of composition  $\text{Ln}(\text{F}_3\text{C}-\text{COO})_3 \cdot 2(3\text{-picNO}) \cdot x\text{H}_2\text{O}$  (the water content is close to unity, varying from 0.75 to 1.33) were prepared and characterized.

### 2. Experimental details

A mixture of the hydrated lanthanide trifluoroacetates and the ligand (molar ratio, 1:2) was gently warmed and the complexes were precipitated by addition of dry ethyl ether under vigorous stirring with a glass rod. The compounds were decanted, washed with ether and dried *in vacuo* over anhydrous calcium chloride.

Lanthanide ion content was determined by EDTA complexometric titration. Carbon, hydrogen and nitrogen were measured by the usual microanalytical procedures.

Conductance measurements were performed at  $25.00 \pm 0.02$  °C using a pointer galvanometer, a resistance box and a Leeds and Northrup cell

( $K_c = 0.10708 \text{ cm}^{-1}$ ). IR spectra were recorded in a Perkin–Elmer 1750 spectrophotometer using KBr pellets or Nujol mulls between KBr windows. X-ray powder patterns were obtained on a Rigaku RU-200B instrument using Cu  $K\alpha$  radiation. The absorption spectra of the neodymium compound were obtained on a Cary 2300 spectrophotometer. The fluorescence spectrum of the europium complex was recorded on an MPF-4 Perkin–Elmer spectrofluorometer with 394 nm excitation. Thermogravimetric (TG) studies employed Perkin–Elmer TGA-7 and DSC-7 systems using *ca.* 2 mg samples and several heating rates.

### 3. Results and discussion

Analytical results are in accordance with the proposed composition  $\text{Ln}(\text{F}_3\text{C}-\text{COO})_3 \cdot 2(3\text{-picNO}) \cdot x\text{H}_2\text{O}$  (Table 1). According to TG analysis water is eliminated in the 40–130 °C range. Differential scanning calorimetry curves for the lighter lanthanides reveal more than one peak in this range. The water content varied but was generally close to unity. Detailed studies related to the decomposition of the complexes are under investigation. The non-hygroscopic complexes are only sufficiently soluble in methanol where conductance data ( $\Delta_m \approx 60 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) are indicative of a non-electrolyte behaviour [1].

X-ray patterns, that in several cases indicate poor crystallinity, can be arranged, considering also IR data (Table 1), in five series as follows: (a) lanthanum–neodymium; (b) samarium–europium; (c) gadolinium, terbium, yttrium; (d) holmium, erbium, terbium; (e) dysprosium, ytterbium, lutetium.

All IR spectra exhibit water bands [2]. The  $\nu(\text{NO})$  stretching bands of the compounds cannot be clearly distinguished from the corresponding  $\beta\text{-CH}$  (ligand) and  $\nu_s(\text{CF}_3)$ ,  $\nu_{\text{as}}(\text{CF}_3)$  (trifluoroacetate) frequencies, as they occur in the same region (1210–1130  $\text{cm}^{-1}$ ) [3–5]. However, the general aspect of the bands exhibits a tendency towards lower frequencies, indicative of a  $\nu(\text{NO})$  shift as compared with the free ligand (1269  $\text{cm}^{-1}$ ) and interpreted as a ligand coordination to the  $\text{Ln}^{3+}$  ions through the oxygen atom of the NO group. Further evidence is provided by the shift of the  $\gamma\text{-CH}$  band (877–755  $\text{cm}^{-1}$ ) towards higher frequencies [6].

The  $\nu_{\text{as}}(\text{COO}^-)$  mode corresponding to the trifluoroacetate in the adducts appears resolved into several components (1730–1620  $\text{cm}^{-1}$ ) (Table 1). Since the  $\text{CF}_3\text{COO}^-$  ion possesses a low  $C_s$  symmetry [5] and since all its frequencies in this region are allowed, the former behaviour cannot be attributed to an ion symmetry decrease in the compounds [7, 8], a structural and chemical non-equivalence of trifluoroacetates being much more acceptable [8–11]. Evidence which favours this interpretation is further provided by compounds already characterized crystallographically [12–14]. It is suggested that the trifluoroacetate groups are bonded to the metal centre both as bridge and as bidentate ligands. This suggestion is also based on the comparison of the resolved  $\nu_{\text{as}}(\text{COO}^-)$  stretching mode frequencies with the 1688  $\text{cm}^{-1}$

TABLE 1

Summary of analytical and IR data for some representative compounds of formula  $\text{Ln}(\text{F}_3\text{C}-\text{COO})_3 \cdot 2(3\text{-picNO})_3 \cdot x\text{H}_2\text{O}$

Ln	Analysis (%)		C		N		H		H <sub>2</sub> O		$x$	$\nu_{\text{as}}(\text{COO}^-)^b$ ( $\text{cm}^{-1}$ )
	Theo- retical	Experi- mental <sup>a</sup>										
Nd	20.05	20.44	30.05	29.54	3.89	3.93	2.24	2.23	2.50	2.49	1.00	1702 (vs), 1682 (s)
Eu	21.02	20.85	29.91	29.86	3.87	3.53	2.16	2.17	1.87	1.89	0.75	1716 (vs), 1698 (s), 1671 (s)
Gd	21.47	21.30	29.51	29.50	3.82	3.84	2.20	2.18	2.46	2.56	1.00	1730 (vs), 1668 (m)
Er	22.39	22.49	28.94	28.93	3.75	3.85	2.23	2.23	3.01	3.00	1.25	1731 (s), 1699 (vs), 1673 (s)
Yb	22.94	22.98	28.66	28.69	3.71	3.55	2.23	2.24	3.18	3.22	1.33	1700 (vs), 1625 (m)

<sup>a</sup>The amount of water was estimated by TG.

<sup>b</sup>Nujol.

mode of sodium trifluoroacetate [5, 7, 15, 16]. However, as the distinction between the different trifluoroacetate coordination modes is not unambiguously clear, a monodentate coordination is not to be totally excluded [17]. Detailed X-ray single-crystal diffraction studies are clearly necessary in order to establish definitely a correlation between stretching frequency shifts and structural parameters.

Figure 1 shows the absorption spectra of the neodymium compound in the  ${}^2G_{7/2}$ ,  ${}^4G_{5/2} \leftarrow {}^4I_{9/2}$  and  ${}^2P_{1/2} \leftarrow {}^4I_{9/2}$  transition regions. The number of bands of the 77 K spectrum is indicative of an involvement of  $\text{Nd}^{3+}$  in a non-cubic symmetry. The spectroscopic parameters  $\beta = 0.989$ ,  $b^{1/2} = 0.0735$  [18] and  $\delta = 1.09$  [19] indicate an essentially electrostatic bond between  $\text{Nd}^{3+}$  and the ligands. The spectrum in methanol solution is different from the room temperature solid state spectrum owing to modifications around the central ion.

The 77 K emission spectrum of the europium compound is shown in Fig. 2. More than three or five lines are observed in the  ${}^5D_0 \rightarrow {}^5F_1$  and  ${}^5D_0 \rightarrow {}^7F_2$  transition regions respectively, suggesting different coordination modes around the metal centre, since all f-f transitions have a maximum of  $2J+1$  components [20]. The  ${}^5D_0 \rightarrow {}^7F_2$  hypersensitive transition is the most intense, indicating low symmetry sites without inversion centres. As both the  ${}^5D_0$  and  ${}^7F_0$  levels do not resolve under crystal field effects, the  ${}^5D_0 \rightarrow {}^7F_0$  transition can present multiple lines only when differently coordinated europium(III) species are present [21, 22]. The fact that they are resolved permits us to conclude that the complex species are possibly polymeric or, at least, dimeric, containing bridge trifluoroacetates, europium ions being involved in two different sites. The extent of the polymerization may be also

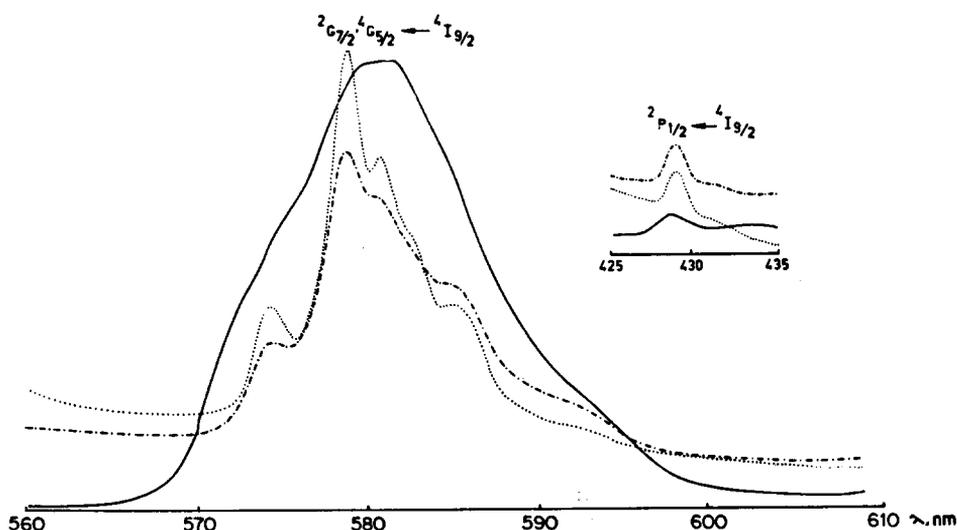


Fig. 1. Absorption spectra of neodymium complex: room temperature (---); 77 K (.....); methanolic solution (—).

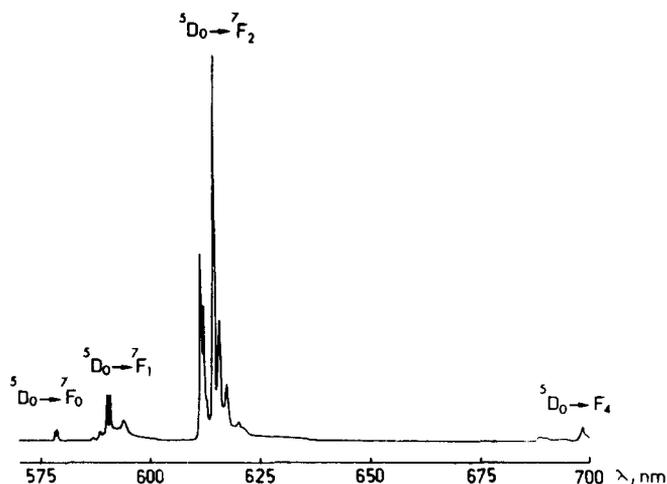


Fig. 2. Emission spectrum of the europium compound at liquid nitrogen temperature.

responsible for the different amount of water detected. The presence of the  ${}^5D_0 \rightarrow {}^7F_0$  band is suggestive of  $C_n$ ,  $C_s$  or  $C_{nv}$  symmetries [23]. On the basis of the number and intensity of bands we suggest europium ions involved in different sites but with the same  $C_{3v}$  symmetry [24].

## Acknowledgments

C.A.A.C. is deeply indebted to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and to Coordenação de Aperfeiçoamento de Pessoal do Ensino Superior (CAPES) for a Ph.D. fellowship and financial support.

## References

- 1 W. J. Geary, *Coord. Chem. Rev.*, **7** (1971) 81.
- 2 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1978, p. 226.
- 3 A. R. Katritzky, J. A. T. Beard and N. A. Coats, *J. Chem. Soc.*, (1959) 3680.
- 4 J. A. Faniran and K. S. Patel, *Spectrochim. Acta A*, **32** (1976) 1351.
- 5 K. O. Christie and D. Naumann, *Spectrochim. Acta A*, **29** (1973) 2017.
- 6 S. Kida, J. V. Quagliano, J. A. Walmsley and S. Y. Tyree, *Spectrochim. Acta*, **19** (1963) 189.
- 7 C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, **17** (1975) 1.
- 8 V. Ya. Kavun, V. I. Sergienko, V. I. Kostin, B. N. Chernyshov and N. I. Steblevskaya, *Russ. J. Inorg. Chem.*, **30** (1985) 190.
- 9 M. Singh and S. N. Misra, *J. Inorg. Nucl. Chem.*, **40** (1978) 1939.
- 10 V. Ya. Kavun, B. N. Chernyshov and N. S. Vasilyuk, *Russ. J. Inorg. Chem.*, **31** (1986) 358.
- 11 O. Velasquez, K. W. Bagnall, H. H. Alvarez, I. Berrio and L. Montalvo, *Rev. Colomb. Quim.*, **13** (1984) 37.

- 12 S. P. Bone, D. B. Sowerby and R. D. Verma, *J. Chem. Soc., Dalton Trans.*, 11 (1978) 1544.
- 13 E. E. Castellano, G. Oliva, L. B. Zinner and G. Vicentini, *Inorg. Chim. Acta*, 110 (1985) 77.
- 14 L. B. Zinner, W. Oliveira, J. L. Fejfar, E. E. Castellano and J. Zukerman-Schpector, *Eur. J. Solid State Inorg. Chem.*, 28 (1991) 283.
- 15 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 33 (1980) 327.
- 16 B. S. Manhas and A. K. Trikha, *J. Indian Chem. Soc.*, 59 (1982) 315.
- 17 S. N. Misra and M. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, 11 (1981) 157.
- 18 D. E. Henrie and G. R. Choppin, *J. Chem. Phys.*, 49 (1968) 477.
- 19 S. P. Sinha, *Spectrochim. Acta*, 22 (1966) 57.
- 20 G. Vicentini and A. B. Nascimento, *An. Acad. Bras. Ciênc.*, 58 (1986) 199.
- 21 J. C. Bünzli and A. Giorgetti, *Inorg. Chim. Acta*, 110 (1985) 225.
- 22 V. Balzani, N. Sabbatini and F. Scandola, *Chem. Rev.*, 86 (1986) 319.
- 23 P. Porcher and C. Caro, *Semin. Chim. Etat Solide*, 5 (1972) 141.
- 24 J. H. Forsberg, *Coord. Chem. Rev.*, 10 (1973) 195.