Journal of Alloys and Compounds, 207/208 (1994) 461–464
JALCOM 3068

Pyrazine-*N*-oxide (pyzNO) complexes of lanthanide(III) trifluoroacetates (TFA)

F.L. Alencar, J.R. Matos and L.B. Zinner*
Instituto de Química, Universidade São Paulo, Caixa Postal 20780, CEP 01498-970, São Paulo (Brazil)

Abstract

The reaction products of the interaction of lanthanide trifluoroacetates and pyzNO present the general formula $Ln(TFA)_3 \cdot 2pyzNO \cdot H_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb, Y). They were characterized by conductance measurements, IR spectra, X-ray powder patterns, absorption spectra of the neodymium and emission spectrum of the europium compounds as well as TG, DTG and DSC techniques.

1. Introduction

Complexes of lanthanide trifluoroacetates and the ligands: thioxane-oxide [1], dimethylformamide [2], crown ethers [3], tetramethylenesulfoxide [4], 2-picoline-*N*-oxide [5], triphenylphosphine-oxide [6], *N*,N,N′,N′-tetramethyladipamide [7], 4-picoline-*N*-oxide [8], *N*,*N*,*N*′,*N*′-tetramethylurea [9], 3-picoline-*N*-oxide [10] and pyridine-*N*-oxide [11] have already been published.The interest in the trifluoroacetate anion results from its potentially bidentate and/or bridging between two central ions behavior. It can also act as a monodentate and shows moderate donor strength and the steric hindrance is large due to the bulky trifluoromethyl group.

2. Experimental details

Pyrazine-*N*-oxide was prepared according to Koelsch and Gumprecht [12] by the reaction of pyrazine with hydrogen peroxide.

A solution of pyrazine-*N*-oxide (solvent anhydrous ethyl ether) was added dropwise to a solution of hydrated trifluoroacetate (2:1). The mixture was stirred in order to precipitate the adducts. They were separated, washed with ethyl ether and dried *in vacuo* over anhydrous calcium chloride.

Measurements were performed as described in ref. 11, but using a conductivity cell ($K_c = 0.10708$) cm^{-1} and an IR Nicolet 510 spectrophotometer. Thermogravimetric measurements were performed on a Mettler TA4000 system at a heating rate 5 °C min^{-1}. X-Ray diffraction patterns were obtained with a URD-6 instrument using Cu Kα radiation.

3. Results and discussion

Complexes with composition $Ln(TFA)_3 \cdot 2pyzNO \cdot H_2O$ were isolated, generally as polycrystalline powders. Analytical data were in good agreement with the proposed stoichiometry (Table 1). Conductance measurements of millimolar acetonitrile and nitromethane solutions ($\Lambda_m = \sim 33$ and $15\ \Omega^{-1}\ cm^2\ mol^{-1}$, respectively) indicate a non-electrolyte behavior [13].

TABLE 1. Summary of analytical data for the compounds of formula $Ln(TFA)_3 \cdot 2pyzNO \cdot H_2O$

Ln	Analysis (%)							
	Lanthanide[a]		Carbon[b]		Nitrogen[b]		Hydrogen[b]	
	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.
La	20.18	20.18	24.43	23.98	8.14	8.31	1.46	1.51
Pr	20.42	20.43	24.37	24.50	8.12	8.28	1.46	1.45
Nd	20.80	20.85	24.24	23.72	8.02	8.42	1.45	1.36
Sm	21.49	21.58	24.00	24.03	8.00	7.50	1.45	1.38
Eu	21.67	21.65	23.98	23.74	7.99	7.35	1.44	1.42
Gd	22.26	22.69	23.80	23.85	7.93	7.90	1.42	1.55
Tb	22.44	22.18	23.75	23.63	7.91	7.50	1.42	1.46
Dy	22.83	22.79	23.63	23.50	7.87	7.66	1.42	1.35
Er	23.34	23.43	23.67	23.03	7.82	7.40	1.40	1.40
Yb	23.96	23.94	23.28	23.02	7.76	7.16	1.40	1.40
Y	13.93	13.62	26.35	26.50	7.78	8.52	1.58	1.57

[a] Complexometric titration with EDTA.
[b] Microanalytical procedure.

---

*Author to whom correspondence should be addressed.

0925-8388/94/$07.00
SSDI 0925-8388(93)03068-T

IR spectra show water bands at 3400 and 1620 cm^{-1}. A shift of ν(NO) (1300 cm^{-1} for free pyzNO) to lower frequencies (1270 cm^{-1}) indicates a coordination through the oxygen. The local symmetry of the trifluoroacetate anion is low, at most C_s. The IR spectra are expected to display 15 bands arising from the anions. The distinction between different coordination modes is not clear cut and has not yet been unambiguously established [14]. However, the modes due to COO^- (ν_{as}, ν_s) and δCOO^- are expected to be more sensitive to coordination and the frequencies can be shifted on complexation [14]. The $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes corresponding to the trifluoroacetate in the adducts appear resolved into two components (ν_{as} ~1730–1670 cm^{-1} and ν_s 1470–1436 cm^{-1}) and since all its frequencies in this region are allowed, a structural and chemical non-equivalence of TFA is much more acceptable [15]. It is suggested that the trifluoroacetate groups are bonded to a metal centre both as bridge and as bidentate [16]. Evidence favouring this interpretation is further provided by compounds already characterized crystallographically [4a,9,17]. X-Ray single crystal diffraction studies are clearly necessary in order to establish definitively the type of coordination mode.

X-Ray powder diffractograms show that all patterns are very similar suggesting the existence of only one isomorphous series.

The absorption spectra of the neodymium compound in the solid state at room temperature and 77 K are presented in Fig. 1. The spectrum at room temperature is very similar to that at 77 K except that in the latter case the lines are well resolved and present different intensities. From the spectrum recorded at room temperature and using the transition $^2P_{1/2} \leftarrow {}^4I_{9/2}$ and $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$, the nephelauxetic parameter ($\beta = 0.991$) [18] and the covalent factor ($b^{1/2} = 0.067$) [19] and Sinha's parameters ($\delta = 0.91$) [20] were determined. All the parameters clearly indicate the electrostatic character of the bonds between Ln^{3+} and the ligands.

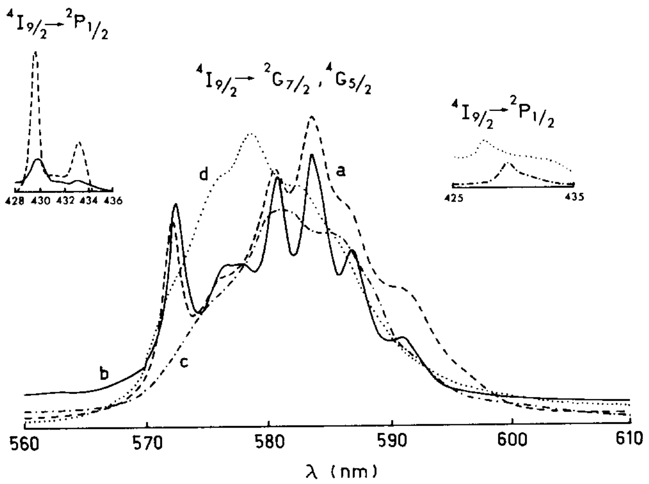

Fig. 1. Absorption spectra of neodymium compound; solid at room temperature (– – – –) and at 77 K (——); nitromethane (–·–·–) and acetonitrile (· · · · ·) solutions.

The number of peaks in the 77 K spectrum suggests that Nd^{3+} is not involved in a cubic site. The spectra in solutions (Fig. 1) are different from those of the solid, indicating an interaction with the solvents. The two different spectra present different oscillator strengths [21] ($P = 12.6$ in acetonitrile and 21.6 in nitromethane) and were calculated by applying Simpson's rule [22].

The emission spectrum of the europium compound (Fig. 2) at 77 K, presents an extremely weak $^5D_0 \to {}^7F_0$ transition that was interpreted as a possible distortion of the symmetry. The $^5D_0 \to {}^7F_1$ transition presents three peaks (one attributed to A_2' and two due to an E″ species) and the $^5D_0 \to {}^7F_2$ transition shows four peaks due to E′ and E″ species. The spectrum was interpreted in terms of a D_{3h} symmetry [23].

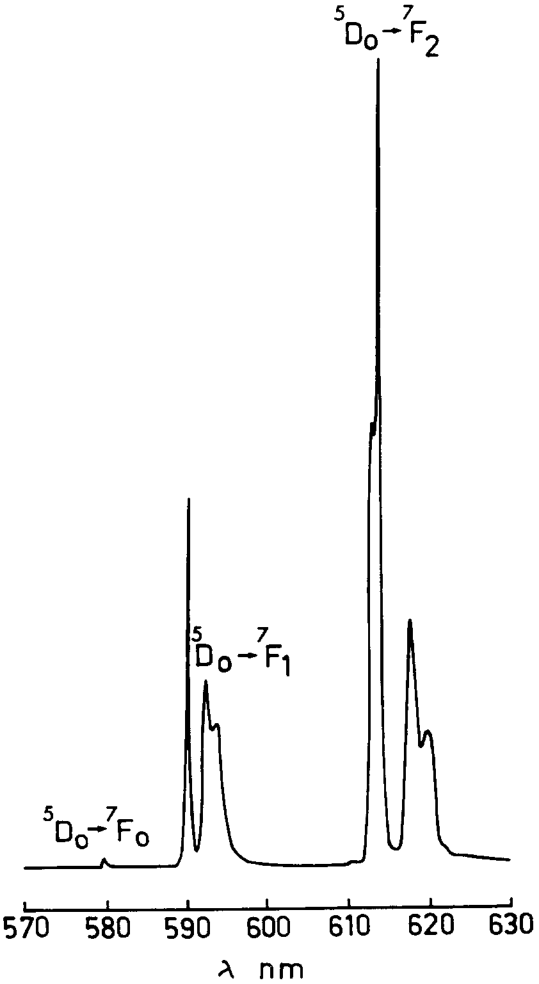

Fig. 2. Emission spectrum of the europium compound at 77 K.

TABLE 2. Some typical TG and DSC data of the compounds of formula Ln(F_3C–COO)$_3$·pyzNO·H_2O

Ln	TG				DSC	
	Temperature (°)	Attribution (residue)	Theory (%)	Exp. (%)	Peak (°C)	ΔH (kJ mol^{-1})
Sm	160–240	Sm(TFA)$_3$·pyzNO[a]	83.69	84.0	93	67.9
	350	SmF_3[a]	29.64	29.8	140	37.8
	700	SmOF[b]	26.49	25.8	305	−121.0 (3 peaks)
Tb	160–210	Tb(TFA)$_3$·pyzNO[a]	83.88	84.0	104	63.9
	350	TbF_3[a]	30.49	30.9	173	59.3
	700	TbOF[b]	27.38	27.0	293	51.5
					318	−112.4 (2 peaks)
Yb	155–190	Yb(TFA)$_3$·pyzNO[a]	84.20	85.0	110	102.3
	320	YbF_3[a]	31.85	32.5	183	53.6
	800	YbOF[b]	28.80	28.0	231	48.5
					305	−121.5 (3 peaks)

[a] Dynamic nitrogen.
[b] Dynamic air.

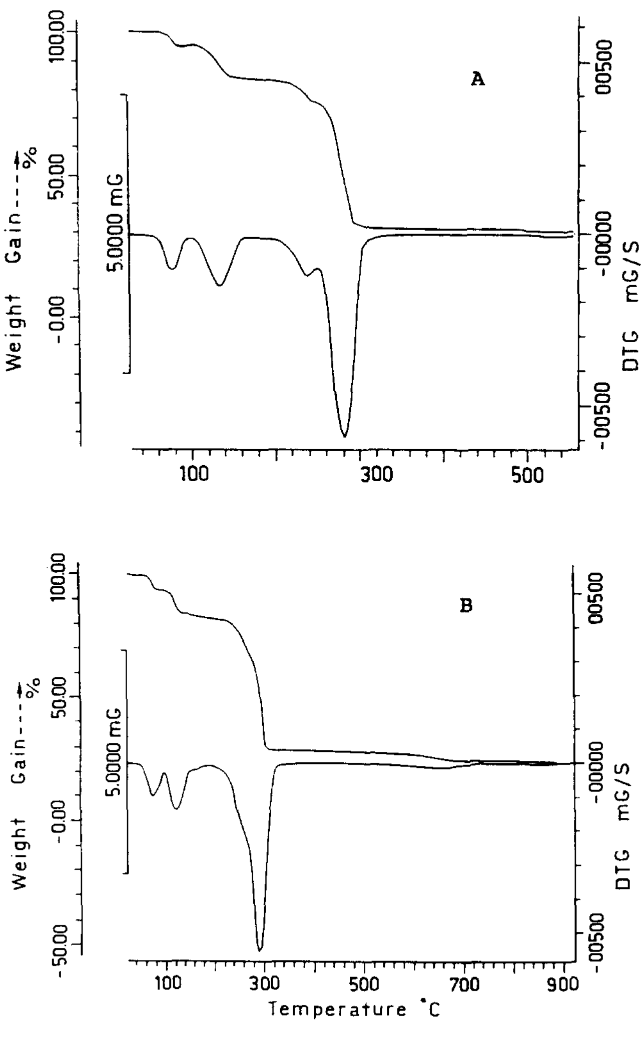

Fig. 3. TG and DTG curves of the gadolinium compound under dynamic (A) nitrogen and (B) air atmospheres.

TG data indicate that between 50 and 160 °C, the compounds loose water and one pyzNO in two or three steps giving Ln(F_3C–COO)$_3$·pyzNO. The existence of this product was determined by C, H, N microanalytical results, and by IR. At about 200–320 °C, decomposition occurs with liberation of pyrazine and other gaseous products such as CO, CO_2, COF_2, CF_3COF and $(CF_3CO)_2$ [8]. In some cases, small carbonization occurs. The residues are LnF_3 under a nitrogen atmosphere. In air, the final residues are lanthanide oxyfluorides, LnOF. DSC shows that the evolution of the ligands is endothermic and that the decomposition around 300 °C is exothermic. Table 2 presents some typical TG and DSC data. Figure 3 shows TG and DTG in N_2 and air dynamic atmospheres.

It is interesting to note that although the pyzNO and pyO [11] ligands are very similar, the experimental data of the prepared compounds show differences in stoichiometry, solubility and site symmetry around the central Eu^{3+} ion.

Acknowledgments

F.L.A. is much indebted to Conselho Nacional de Desenvolvimento Cientifíco e Tecnológico (CNPq) for a MS fellowship. The authors are deeply indebted to Micronal S.A. for the use of the Mettler System TA4000 and to Financiadora de Estudos e Projetos (FINEP), Fundação de Amparo à Pesquisa do estado de São Paulo (FAPESP) and Plano de Apoio ao Desenvolvimento Científco e Tecnológico (PADCT) for financial support.

References

1 (a) L.B. Zinner, Anais do VI-Simpósio Anual da Academia de Ciências do Estado de São Paulo (ACIESP), *Quím. Terras Raras, 36* (1982) 185. (b) P.O. Dunstan, G. Vicentini and L.B. Zinner, *Thermochim. Acta, 78* (1984) 449.

2 G. Vicentini and M.G. Silva. Anais do VII-Simpósio da Academiade Ciências do Estado de São Paulo (ACIESP), *Quím. Terras Raras, 14* (1984) 145.

3 (a) J.C. Bünzli and A. Giorgetti, *Inorg. Chim. Acta, 110* (1985) 225. (b) D. Harrison, A. Giorgetti and J.C. Bünzli, *J. Chem. Soc. Dalton Trans., 5* (1985) 885.

4 (a) E.E. Castellano, G. Oliva, L.B. Zinner and G. Vicentini, *Inorg. Chim. Acta, 110* (1985) 77. (b) L.B. Zinner, *An. Acad. Brasil. Ciênc., 57* (1985) 313.

5 (a) L.B. Zinner and H.F. Brito, *Inorg. Chim. Acta, 110* (1985) 175. (b) L.B. Zinner, G. Vicentini, H.F. Brito and P.O. Dunstan, Anais do X-Simpósio Anual da Academia de Ciências do Estado de São Paulo (ACIESP), *Quím. Lantanídeos Actinídeos, 50* (1986) 89.

6 G. Vicentini and L.R.F. Carvalho, *Lanthanide Actinide Res., 1* (1985) 49.

7 L.B. Zinner and G. Vicentini, *An. Acad. Brasil. Ciênc., 58* (1986) 375.

8 G. Vicentini, L.B. Zinner, R.P. Chaparro and P.O. Dunstan, *Thermochim. Acta, 177* (1991) 341.

9 L.B. Zinner, W. Oliveira, J.L. Fejfar, E.E. Castellano and J. Zukerman-Schpector, *Eur. J. Solid State Inorg. Chem., 28* (1991) 283.

10 L.B. Zinner, C.A. Alves de Carvalho and K. Zinner, *J. Alloys Comp., 180* (1992) 343.

11 L.B. Zinner and W. Carvalho Melo, *J. Alloys Comp., 192* (1993) 274.

12 C.F. Koelsch and W.H. Gumprecht, *J. Org. Chem., 23* (1958) 1603.

13 W.J. Geary, *Coord. Chem. Rev., 7* (1971) 81.

14 C.D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem., 17* (1975) 1.

15 G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev., 33* (1980) 227.

16 B.S. Manhas and A.K. Trikha, *J. Indian Chem. Soc., 59* (1982) 315.

17 S.P. Bone, D.B. Sowerby and R.D. Verma, *J. Chem. Soc., Dalton Trans., 11* (1978) 1544.

18 H.H. Caspers, H.E. Rast and R.D. Buchanan, *J. Chem. Phys., 42* (1965) 3214.

19 D.E. Henrie and G.R. Choppin, *J. Chem. Phys., 49* (1968) 477.

20 S.P. Sinha, *Spectrochim. Acta, 22* (1966) 57.

21 W.T. Carnall, P.R. Fields and B.G. Wybourne, *J. Chem. Phys., 42* (1965) 3797.

22 D.D. MacCracken and W.S. Dorn, *Numerical Methods and Fortran Programming*, Wiley, New York, 1966.

23 J.H. Forsberg, *Coord. Chem. Rev., 7* (1973) 81.