Thermochimica Acta, 177 (1991) 341–345
Elsevier Science Publishers B.V., Amsterdam

Note

SYNTHESIS, PROPERTIES AND THERMAL STUDY OF 4-PICOLINE-*N*-OXIDE (4-picNO) LANTHANOID TRIFLUOROACETATE COMPLEXES

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(Received 30 May 1990)

Complexes with general formula $[Ln(CF_3COO)_3(4\text{-picNO})_2]_2$ (Ln = La–Er) were synthesized and characterized by microanalytical procedures, conductance measurements, IR spectra, electronic absorption spectra of the neodymium and emission spectra of the europium complex, and a TG study of the praseodymium, neodymium, europium, holmium and erbium compounds.

EXPERIMENTAL

The complexes were prepared by reaction of the hydrated salts with 4-picNO in triethyl orthoformate and 2,2-dimethoxypropane. They were characterized by the usual carbon, hydrogen and nitrogen microanalytical procedures and complexometric titration of the lanthanoids with EDTA [1]. Conductance measurements were performed in a Leeds and Northrup apparatus composed of a resistance box, a needle galvanometer and a cell ($K_c = 0.10708$ cm^{-1}). IR spectra were recorded on a Perkin–Elmer IR-783 spectrophotometer, using Fluorolube and Nujol mulls between CsI plates. The absorption spectra of the neodymium compound were recorded in a Cary 17 spectrophotometer. The fluorescence spectrum was registered in a Zeiss ZFM-4 spectrofluorometer. TG curves were determined, under nitrogen atmosphere, in a Du Pont 1090 system at a heating rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

Analytical data were in good agreement with the stoichiometry proposed. Conductance measurements of millimolar solutions ($\Lambda m \approx 55$ Ω^{-1} cm^2 mol^{-1}) indicate a non-electrolyte behaviour in methanol [2].

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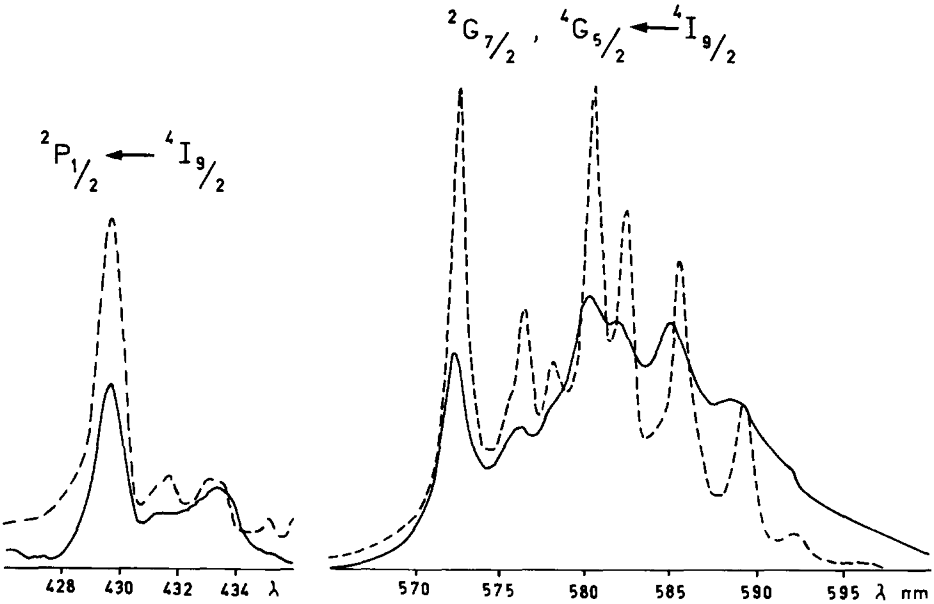

Fig. 1. Absorption spectra of the neodymium compound at room temperature (solid line) and at 77 K (dashed line).

From the IR spectra it is possible to observe that: (i) the υ_{as}COO splitting in the 1720–1660 cm^{-1} region may be indicative of the existence of two different types of trifluoroacetate coordinated to the central ion; (ii) evidence for the coordination of 4-picNO through the oxygen is obtained with the υNO shifts to lower frequencies ($\approx$ 1235s cm^{-1}) as compared to the free ligand (1250s cm^{-1}) and δNO at 830_{m-s} cm^{-1} and 850_s cm^{-1}, respectively.

Figure 1 contains the absorption spectra of the neodymium complex at room temperature and at 77 K, showing the hypersensitive $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ and $^2P_{1/2} \leftarrow {}^4I_{9/2}$ transitions. The following were concluded from the spectra: (i) the number of bands in the 77 K spectrum suggests the existence of a non-cubic symmetry around Nd^{3+}; (ii) the nephelauxetic parameter $\bar{\beta} = 0.992$, covalent factor, $b^{1/2} = 0.067$ [3], and Sinha's parameter, $\delta = 0.91$ [4] determined from the room temperature spectrum are indicative of an essentially electrostatic bonding between the ligands and the central ion.

Figure 2 presents the emission spectrum of the europium compound at 77 K. The transitions observed are: $^5D_0 \rightarrow {}^7F_0$ vw at 17300 cm^{-1}; $^5D_0 \rightarrow {}^7F_1$ with three peaks, 17020w, 16850sh and 16830w cm^{-1} and $^5D_0 \rightarrow {}^7F_2$ with three peaks, 16370s, 16300m and 16240sh cm^{-1}. The spectrum was interpreted in terms of a $C_{4\upsilon}$ symmetry around the central ion [5].

TG curves are presented in Fig. 3 and the corresponding data in Table 1. The process of decomposition corresponds to a stepwise 4-picNO evolution, but in some cases this occurs concomitantly, followed by evolution of gases like CO, CO_2, COF_2, CF_3COF and $(CF_3CO)_2O$ [6], leaving the correspond-

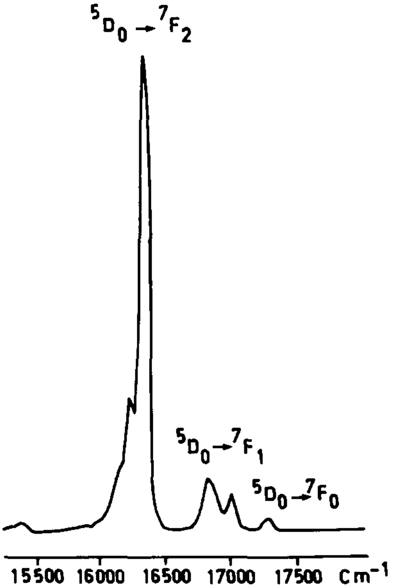

Fig. 2. Emission spectrum of the europium compound at 77 K.

ing lanthanoid trifluorides as residues. Similar results were obtained for the 2-picNO complexes [7]. The complexes were formulated as dimers based in the fact that, for example, the praseodymium salt is a dimer, formed by trifluoroacetate ions acting as bridges between two Pr^{3+} ions, two bidentate

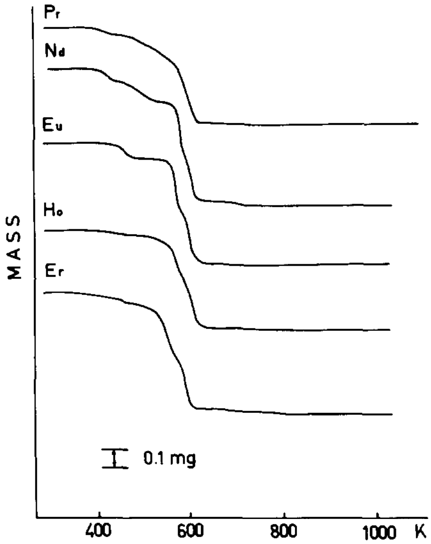

Fig. 3. TG curves.

TABLE 1

TG data for [Ln $(CF_3COO)_3(4\text{-picNO})_2]_2$ complexes

Element	Temperature (K)	Weight loss(%) and residue (%)		Attribution
		Exp.	Theor.	
Pr	313–453	5.5	7.83	−1(4-picNO)
	453–578	22.0	23.45	−3(4-picNO)
	578–613	44.9	40.39	−gaseous products
				$2PrF_3$
Residue	1073	27.6	28.34	
Nd	298–468	7.8	7.78	−1(4-picNO)
	468–523	9.2	7.78	−1(4-picNO)
	523–615	53.9	55.75	−1(4-picNO) −gaseous products
				$2NdF_3$
Residue	1073	29.1	28.69	
Eu	293–356	2.2	3.85	−0.5(4-picNO)
	366–576	7.7	7.70	−1(4-picNO)
	576–636	58.6	59.00	−2.5(4-picNO) −gaseous products
				$2EuF_3$
Residue	1073	31.5	29.45	
Ho	293–366	4.0	3.78	−0.5(4-picNO)
	366–576	19.2	18.89	−2.5(4-picNO)
	576–585	9.3	7.56	−0.5(4-picNO)
	585–616	36.2	39.05	−gaseous products
				$2HoF_3$
Residue	1073	31.3	30.73	
Er	328–348	3.0	3.77	−0.5(4-picNO)
	349–569	34.3	32.84	−3.5(4-picNO)
	569–609	33.7	32.44	−gaseous products
				$2ErF_3$
Residue	1073	29.0	30.95	

trifluoroacetate ions and water molecules coordinated to the cations [8], but in some complexes polymeric species were obtained [9].

ACKNOWLEDGEMENT

The authors are much indebted to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support.

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