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Synthesis and Properties of Complexes between Lanthanide Trifluoroacetates and 2-picoline-N-oxide (2-picNO)*

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Abstract

Complexes of lanthanide trifluoroacetates with 2-picoline-N-oxide (2-picNO), with composition Ln($CF_3COO)_3 \cdot 2$(2-picNO), are described. They were characterized by elemental analysis, electrolytic conductance measurements, X-ray powder patterns, IR and absorption (neodymium) and emission (europium) spectra. The compounds were grouped in three isomorphous series: (a) La, Pr; (b), Nd, Sm and (c) Eu–Lu, Y. They behave as non-electrolytes in acetonitrile. Two types of coordination of the anion and coordination of 2-picNO through the oxygen are suggested. Absorption spectra indicate an essentially electrostatic interaction between Ln^{3+} and ligands. The fluorescence spectrum was interpreted in terms of a C_{2v} symmetry for the europium complex.

Introduction

Lanthanide complexes containing inorganic anions have been actively investigated. Compounds with organic anions, especially those derived from strong acids, are now under systematic investigation in our laboratory, specially trifluoroacetates. Several lanthanide complexes containing 2-picNO as ligand and the anions Br^-, NO_3^-, ClO_4^-, Cl^-, I^-, NCS^-, PF_6^-, ReO_4^-, $CH_3SO_3^-$, $CF_3SO_3^-$ [1–14] have been described.

In this paper, the synthesis and properties of compounds of formula $Ln(CF_3COO)_3 \cdot 2$(2-picNO) (Ln = La–Lu, Y, except Ce and Pm) are presented. Techniques like electrolytic conductance measurements, IR spectra, X-ray powder patterns, electronic absorption and emission spectra were used for characterization.

Experimental

The hydrated trifluoroacetates were prepared by the reaction of an aqueous suspension of the respective basic carbonates with trifluoroacetic acid, using a small excess of the former. The solution obtained was filtered and evaporated in a water bath. The crystals were dried *in vacuo* over anhydrous calcium chloride.

The complexes were obtained by mixing the hydrated salts with 2picNO (molar ratio: ~1:3). The gently warmed mixture was stirred with a glass rod. The complexes were precipitated by addition of 2,2-dimethoxypropane. The compounds were collected, washed with the solvent and dried *in vacuo*, over $CaCl_2$.

Lanthanide ions were analysed by complexometric titration with EDTA [15]. Carbon, nitrogen and hydrogen were determined by microanalytical procedures. Electrolytic conductance measurements were made at 25.00 ± 0.02 °C, using a resistance box, a pointer galvanometer and a cell (Kc = 0.10708 cm^{-1}) from Leeds and Northrup. X-ray powder patterns were performed in Norelco Instruments, using CuKα radiation. IR spectra were registered in a Perkin-Elmer, model 283, using Nujol and Kel-F mulls between KBr plates. Absorption spectra of the neodymium compound at room temperature, at 77 K and in acetonitrile solution, at 298 K, were recorded in a Cary 17 spectrophotometer. The fluorescence spectrum of the europium compound at 77 K was registered in a Zeiss ZFM-4 spectrofluorimeter, using 394 nm excitation radiation. The refractive index of the acetonitrile solution was measured in an Abbe type, Bausch and Lomb refractometer. Melting ranges were measured in a Yotar apparatus.

Results and Discussion

The analytical results, melting ranges and conductance data are presented in Table I. The compounds are hygroscopic and behave as non-electro-

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TABLE I. Summary of Analytical Results, Melting Ranges and Conductance Data for the Compounds of Formula $Ln(CF_3COO)_3 \cdot 2(2\text{-picNO})$.

Ln	Analysis (%)								Melting range (°C)	Conductivity	
	Lanthanide		Carbon		Nitrogen		Hydrogen			conc. (mM)	Λ_m [a]
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.			
La	19.95	19.33	30.99	30.57	4.01	3.73	2.02	2.25	218–223	1.03	6.3
Pr	20.18	19.80	30.96	31.02	4.01	4.14	2.02	2.48	147–151	0.99	11.0
Nd	20.59	20.56	30.81	30.10	3.99	3.81	2.01	2.05	160–164	1.09	16.6
Sm	21.24	20.25	30.55	30.72	3.95	3.74	1.99	2.18	166–170	0.92	14.0
Eu	21.34	21.41	30.48	30.06	3.95	3.70	1.98	2.15	167–171	0.99	17.0
Gd	21.74	22.00	30.25	30.36	3.92	3.99	1.97	1.77	160–164	1.01	17.6
Tb	22.33	22.18	30.18	29.73	3.91	3.89	1.97	1.72	159–163	0.99	17.7
Dy	22.78	22.59	30.06	29.88	3.89	3.79	1.96	1.70	157–161	1.03	17.9
Ho	22.75	22.83	29.93	30.13	3.87	3.66	1.95	2.04	148–152	1.07	17.2
Er	23.08	23.10	29.83	30.03	3.86	3.99	1.94	2.26	147–151	1.02	18.6
Tm	23.35	23.26	29.77	29.85	3.86	3.99	1.94	1.80	133–137	1.00	17.3
Yb	23.75	23.69	29.60	29.87	3.83	3.85	1.93	1.83	126–130	1.00	16.5
Lu	24.19	23.92	29.56	29.25	3.83	3.83	1.93	1.83	118–122	1.00	16.6
Y	13.66	13.75	33.45	33.25	4.33	4.32	2.18	1.90	145–149	1.06	16.8

[a] $\Lambda_m = \Omega^{-1}\ cm^2\ mol^{-1}$.

TABLE II. IR Data (cm^{-1}) for the Compounds of Formula $Ln(CF_3COO)_3 \cdot 2(2\text{-picNO})$.

Ln	$\nu_{as}COO^-$	ν_sCOO^- [a]	$\Delta\nu_1$	$\Delta\nu_2$	δ_{COO^-}	ν_{NO}
La	1695sh 1685vs 1661sh[b]	1462m 1450sh	223	199	711s	1230sh
Pr	1708sh 1686vs 1650sh	1460m 1630vw	226	190	719s	1230sh
Nd	1720s 1668s	1465m 1458m 1447vw	255	203	721s	1239sh 1232s
Sm	1720s 1665s	1467sh 1460m 1448vw	260	205	720s	1239sh 1231s
Eu	1723s 1664m 1650sh	1462m 1452m 1445vw	261	202	731m 720s	1293sh 1229s
Gd	1730s 1651m	1466m 1430vw	264	185	735m 722s	1240s
Tb	1727s 1648m	1467m 1430vw	260	181	728m 712s	1230sh
Dy	1730s 1650m	1465m 1432vw	265	185	733m 721s	1240s
Ho	1730s 1652m	1465m 1430vw	265	187	732m 720s	1238s
Er	1732s 1651m	1465m 1432vw	267	186	731m 719s	1238s
Tm	1731s 1655m	1465m 1430vw	266	190	728m 719s	1230sh
Yb	1730s 1651m	1465m 1430vw	265	186	727m 712s	1230sh
Lu	1738s 1660m	1468m 1435vw	270	192	735m 725s	1240s
Y	1733s 1653m	1464m 1433vw	270	193	735m 722s	1241s

[a] Kel-F mull. [b] vs = very strong; s = strong; m = medium; vw = very weak; sh = shoulder.

lytes in acetonitrile. According to the X-ray patterns, three different isomorphous series were observed: (a) La, Pr; (b) Nd, Sm and (c) Eu–Lu, Y.

The coordination of 2-picNO through the N–O oxygen to the lanthanide ions results in a shift of the ν_{N-O} to lower frequencies as compared to the free ligand [16] (Table II). The δ_{NO} mode shows a small shift to higher frequencies (~5 cm^{-1}) and the CH out of plane deformation band is shifted towards higher frequencies (~20 cm^{-1}). These positive shifts are due to a decrease of the electron density of the ring, resulting from the coordination of the ligand to the metal ion [17]. The observed splittings are attributed to solid state effects.

The CF_3COO^- ion can behave as either a uni-, a bidentate group or bridge between two metal ions. All the fifteen vibrational modes are IR active, even in the free ion (C_{2v}) and a lowering of the symmetry upon coordination is not expected to increase the number of IR bands due to the CF_3COO^- group. However, the modes due to COO^- (ν_{asCOO^-}, ν_{sCOO^-} and δ_{COO^-}) are expected to be more sensitive to coordination and the frequencies due to them could be shifted on complexation [18]. The shift of the first two have indeed been observed and the magnitude of the separation ($\Delta = \nu_{as} - \nu_s$) was found to be affected by several factors (modes of coordination). The compounds which have unidentate CF_3COO^- present Δ values of very high order, while those of the chelating and/or bridging bidentate type have significantly lower Δ values than in the case of ionic trifluoroacetate [19]. From the analysis of the ν_{asCOO^-} and ν_{sCOO^-} values in the compounds whose crystal structures had already been determined, Manhas and Trikha [20] observed that the unidentate coordination removes the equivalence of the two oxygen atoms and the two CO bond orders are appreciably affected originating a pseudo esther configuration. In the case of the chelating and bridging bidentate type, there is little change in the CO bond orders and the movement of frequencies is less when compared to those of unidentate. The direction of the shifts in the ν_{asCOO^-} and ν_{sCOO^-}, when compared with ionic trifluoroacetate (1688 and 1444 cm^{-1} for the potassium salt) are: (a) unidentate: higher and lower; (b) unsymmetrical bridging: higher and almost the same; (c) symmetrical bridging: higher and higher; (d) unsymmetrical chelating bidentate: almost the same and higher; (e) symmetrical chelating bidentate: lower and higher.

In our lanthanide complexes two bands are attributed to ν_{asCOO^-} (~1720 and 1655 cm^{-1}) (Table II). The existence of this doublet suggests two types of coordination to the central ion. Using the above considerations and criteria and also taking into account that the shifts for ν_{asCOO^-} (~1720 cm^{-1}) and ν_{sCOO^-} (1465 cm^{-1}) are higher and higher respectively as compared to those of the potassium salt, and the other two (1655 and 1465 cm^{-1}) are lower and higher in relation to the same salt, it is possible to suggest that the trifluoroacetate groups behave as a symmetrical bridging and symmetrical chelating bidentate. Using the Δ criterion, $\Delta\nu_1$ is ~260 cm^{-1} and $\Delta\nu_2$ ~190 cm^{-1} (Table II) attributed to bridging and to bidentate modes, respectively.

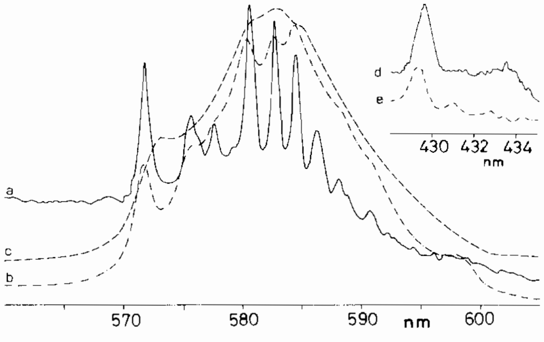

Fig. 1. Absorption spectra of the neodymium (III) complex: transitions $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$: (a) solid state, at 77 K; (b) solid state, at room temperature; (c) acetonitrile solution; transition $^2P_{1/2} \leftarrow {}^4I_{9/2}$: (d) solid state room temperature; (e) solid state 77 K.

The absorption spectra of the neodymium compound in the solid state at room temperature and at 77 K and in acetonitrile are presented in Fig. 1. From the spectrum at room temperature, using the transitions $^2P_{1/2} \leftarrow {}^4I_{9/2}$ and $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$, the wave numbers of the several peaks were determined (Table III). The nephelauxetic parameter, $\bar{\beta}$, was calculated from the spectroscopic data, by comparison with the corresponding values in the standard $Nd^{3+}:LaF_3$ [21], as follows:

TABLE III. Observed Transitions for the Neodymium Compound.

Room temperature			Liquid nitrogen temperature		
	nm	cm^{-1}		nm	cm^{-1}
a	571.60	17495	a	571.80	17489
b	575.50	17376	b	575.70	17370
c	–	–	c	577.65	17311
d	580.25	17234	d	580.70	17221
e	582.50	17167	e	582.80	17158
f	584.35	17113	f	584.60	17106
g	–	–	g	586.40	17053
h	–	–	h	588.13	17003
i	–	–	i	591.00	16920
j	429.50	23282	j	429.35	23291
l	–	–	l	431.00	23202
m	–	–	m	432.80	23105
n	433.40	23073	n	433.40	23073
o	–	–	o	434.25	23028

$$G(Nd^{3+}:LaF_3)_{^4G_{5/2},\,^2G_{7/2}}$$

$$= \frac{17089\ cm^{-1} + 17179\ cm^{-1}}{2} + 195\ cm^{-1}$$

$$= 17329\ cm^{-1}$$

(media of the center of gravity of the two bands, plus the crystal field stabilization energy)

$$\beta_{^4G_{5/2},\,^2G_{7/2}} = \frac{G(\text{complex})}{G(Nd^{3+}:LaF_3)} = \frac{17147\ cm^{-1}}{17329\ cm^{-1}} = 0.990$$

$$\beta_{^2P_{1/2}} = \frac{23282\ cm^{-1}}{23468\ cm^{-1}} = 0.992$$

The values for $^2P_1 \leftarrow {}^4I_{9/2}$ were determined from the higher energy peak of this transition.

From the data above we obtain $\bar{\beta} = 0.991$. The values of the covalency factor ($b^{1/2} = 0.0670$) [22] and Sinha's parameter ($\delta = 0.908$) [23] were determined from $\bar{\beta}$. All the parameters clearly indicate the electrostatic character of the bonds between Ln^{3+} and the ligands.

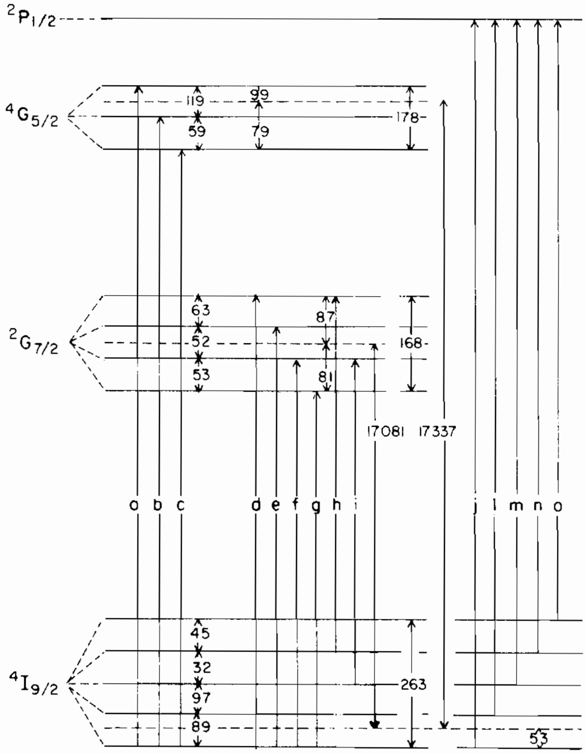

Fig. 2. Energy levels and transitions for neodymium(III) compound at 77 K.

The number of peaks in the 77 K spectrum suggests that Nd^{3+} is not involved in a cubic site. The energy levels and transitions in the neodymium compound at 77 K are represented in Fig. 2 and Table III.

The spectrum in acetonitrile solution is different from that of the solid at room temperature, indicating an interaction with the solvent. The oscillator strength was calculated ($P = 28.4 \times 10^{-6}$ cm^{-2} mol^{-1} l) [24], by applying Simpson's rule [25] (other related data are: refractive index of the solution, $\eta = 1.3430$; concentration, $c = 1.05 \times 10^{-2}$ mol l; optical path, 2.00 cm; area, A = 165.69).

The emission spectrum of the europium compound is presented in Fig. 3. According to Porcher and Caro [26], the existence of a $^5D_0 \rightarrow {}^7F_0$ band is indicative that only the C_n, C_s or $C_{n'v'}$ symmetries are possible. The bands due to $^5D_0 \rightarrow {}^7F_1$ are less intense than those due to $^5D_0 \rightarrow {}^7F_2$, suggesting that the complex is not centro-symmetric. Three peaks due to $^5D_0 \rightarrow {}^7F_1$ and four to $^5D_0 \rightarrow {}^7F_2$ were observed. From these considerations, together with conductance and IR data, we suggest the coordination number eight and a C_{2v} symmetry for the complex species [27]. The emission spectrum (Fig. 3) may be compared with that recently presented by Seminara and Musumeci [28].

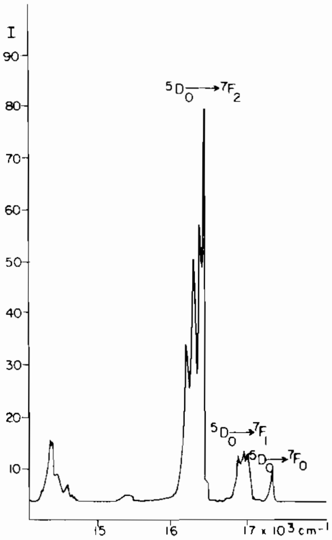

Fig. 3. Emission spectrum, from solid at 77 K of $Eu(TFA)_3 \cdot 2(2\text{-picNO})$.

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