

N,N-DIMETHYLFORMAMIDE (DMF) ADDUCTS
OF LANTHANIDE TRIFLUOROACETATES

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INTRODUCTION

Addition compounds of lanthanide iodides |1|, acetates |2|, nitrates |3|, perchlorates |4, 5|, chlorides |6|, per-rhenates |7, 8|, hexathiocyanates chromiates (III) |9|, isothiocyanates and hexafluorophosphates |11| with DMF have been described.

In this article the preparation and characterization of adducts with general formula $\text{Ln}(\text{CF}_3\text{COO})_3 \cdot 2\text{DMF}$ ($\text{Ln} = \text{La-Lu}$, Y) are reported.

EXPERIMENTAL

The hydrated trifluoroacetates were prepared by reaction of the lanthanide basic carbonate with trifluoroacetic acid in aqueous media, using a small excess of the basic carbonate. The solution was filtered and evaporated in a water bath to dryness. The crystals were maintained in a vacuum dessiccator, containing anhydrous calcium chloride. The adducts were obtained by treating the hydrated trifluoroacetates with an excess of DMF, evaporating the excess of the ligand in a vacuum dessiccator, over anhydrous calcium chloride. The compounds formed were dried to constant weight.

Analysis and measurements. Lanthanide ions were titrated with EDTA, according to the method described by Lyle and Rahman [12]. Carbon, hydrogen and nitrogen were determined by micro analytical procedures. Conductance measurements were performed at $25.00 \pm 0.02^\circ\text{C}$, using a Leeds and Northrup equipment, consisting of a resistance box, a pointer galvanometer and a cell with $K_c = 0.10708 \text{ cm}^{-1}$. X-ray powder patterns were recorded in a Norelco instrument, using Cu K α radiation. I.R. spectra were recorded in a Perkin-Elmer model 180 spectrophotometer. Absorption spectra of the neodymium compound were obtained in a Cary 17 and the emission spectra of the europium adduct in a Zeiss ZFM-4 spectrofluorometer. The refractive index of the neodymium solutions were determined in a Abbe model G refractometer.

RESULTS AND DISCUSSION

A summary of the analytical results and melting ranges is presented in Table 1. The adducts are hygroscopic, specially those from terbium to lutetium and yttrium. They are soluble in nitromethane, acetonitrile, ethanol, methanol and water; practically insoluble in benzene and chloroform.

Conductance measurements in acetonitrile and nitromethane (Table 2) indicate a behavior of non-electrolytes [13].

X-ray powder patterns show three types of isomorphous adducts: a) La-Eu; b) Gd and Tb and c) Dy-Lu, Y.

The frequency attributed to Ln-O in the I.R. spectra was observed in the region of 450 cm^{-1} . Two bands attributed to $\nu_{as} \text{ COO}$ (at 1730 and 1650 cm^{-1}) are due to coordinated non equivalent, probably monodentated and bridged acetate groups. The two bands in the region of 1650 due to $\nu \text{ CO}$ of the DMF and $\nu_{as} \text{ COO}$, can not be unequivocally attributed to such vibration modes. Anyway, a small shift of $\nu \text{ CO}$ in rela-

Table 1 - Summary of analytical data and melting ranges of the compounds of
formula $\text{Ln}(\text{CF}_3\text{COO})_3 \cdot 2\text{DMF}$

Ln	Analysis (%)								Melting range (9C \pm 109C)
	Lanthanide		Carbon		Hydrogen		Nitrogen		
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	
La	22.26	22.41	23.09	22.32	2.26	2.16	4.49	4.19	220
Ce	22.41	22.82	23.05	23.22	2.26	2.03	4.48	4.16	226
Pr	22.50	21.87	23.02	23.11	2.25	2.19	4.47	4.46	228
Nd	22.90	23.21	22.90	23.25	2.24	2.41	4.45	4.44	232
Sm	23.66	23.98	22.68	22.33	2.22	2.20	4.41	4.32	238
Eu	23.85	24.44	22.62	22.53	2.21	2.97	4.40	4.30	244
Gd	24.47	25.30	22.44	21.68	2.20	2.11	4.36	4.28	244
Tb	24.67	24.92	22.38	22.29	2.19	2.19	4.35	4.64	130
Dy	25.08	24.40	22.25	22.91	2.18	2.58	4.32	4.11	120
Ho	25.37	25.19	22.17	22.12	2.17	2.84	4.31	4.88	93
Er	25.62	24.82	22.09	21.84	2.16	2.73	4.29	4.46	85
Tm	25.83	25.70	22.03	22.00	2.16	3.08	4.28	4.83	90
Yb	26.28	26.16	21.90	22.65	2.14	2.87	4.25	4.58	85
Lu	26.50	26.55	21.83	21.21	2.14	2.63	4.24	3.96	72
Y	15.49	15.70	25.10	25.25	2.46	2.70	4.88	5.29	103

Table 2 - Summary of infrared frequencies (cm^{-1}) and conductance data

Ln	I.R.				Conductance			
	$\nu_{\text{as}} \text{COO}$	$\nu_{\text{as}} \text{COO}$ $\nu_{\text{s}} \text{CO}$	νCN	$\nu \text{M-O-L}$	Acetonitrile		Nitromethane	
					Conc., mM	Λ_{m}	Conc., mM	Λ_{m}
La	1745s	1670s-1650s	1500s	447w	0.98	8.5	1.01	2.3
Ce	1755s	1662s-1650s	1495s	442w	1.00	8.9	1.04	2.4
Pr	1755s	1660s-1645w	1498s	445w	1.01	9.9	1.04	2.7
Nd	1758s	1663s-1648w	1494m	445w	1.02	8.7	1.11	2.5
Sm	1763s	1660s-1645w	1495s	445w	1.03	8.1	1.13	2.7
Eu	1765s	1664w-1650w	1495m	-	1.00	7.9	1.00	3.0
Gd	1748w	1660w-1648w	1498s	-	1.00	7.8	1.02	3.1
Tb	1755s	1665s-1645s	1458m	-	0.98	7.6	0.96	3.3
Dy	1759s	1680s-1655s	1500s	439w	0.99	7.1	0.96	3.3
Ho	1740s	1655s-1650s	1496s	450w	0.98	6.7	0.99	3.5
Er	1740s	1660s-1640m	1498s	449w	1.00	7.2	1.07	3.7
Tm	-	1658s-1652m	1458s	-	1.09	6.9	1.05	4.0
Yb	1738	1655s-1649sh	1460s	453w	1.07	7.2	1.04	4.4
Lu	-	1660s-1650sh	1453s	-	0.98	6.2	1.05	4.3
Y	1730vw	1660s-1650sh	1498m	453w	1.04	7.3	1.08	3.2
DMF	-	1675vs	1501m	450w	-	-	-	-

Λ_{m} : $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; s: strong; w: weak; v: very; sh: shoulder

tion to the free DMF ($\sim 10 \text{ cm}^{-1}$) may be considered, indicating coordination through the carbonyl oxygen. The ν_{CN} frequency is observed, practically unchanged, in the region of $\sim 1500 \text{ cm}^{-1}$. Table 2 contains the IR data.

Figure 1 presents the absorption spectrum of the neodymium compound at room temperature, showing the transition ${}^2P_{1/2} \leftarrow {}^4I_{9/2}$ and ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$. From the spectrum the nephelauxetic parameter, was calculated for both transitions by comparison with the corresponding values of Nd^{3+} : LaF_3 [14]:

$${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2} = \frac{17193 \text{ cm}^{-1}}{17329 \text{ cm}^{-1}} = 0.992$$

$${}^2P_{1/2} \leftarrow {}^4I_{9/2} = \frac{23277 \text{ cm}^{-1}}{23467 \text{ cm}^{-1}} = 0.992$$

The $\bar{\beta} = 0.992$ value, very close to unit is indicative of an electrostatic interaction between Ln^{3+} and the ligands. The covalent factor ($b^{1/2} = 0.063$ [15]) and Sinha's parameter ($\delta = 0.806$ [16]) confirm the small covalent character of the bonds. The number of bands in the neodymium spectrum at 77K (Figure 2) shows that the Nd^{3+} ion is not involved in a cubic site. The spectra of the neodymium compound were also determined in nitromethane and acetonitrile solution. The shapes of the spectra are altered in relation to that of the solid at room temperature, specially in acetonitrile, indicating interaction with solvents. The oscillator strengths [17] were determined in both solvents and are given in Table 3.

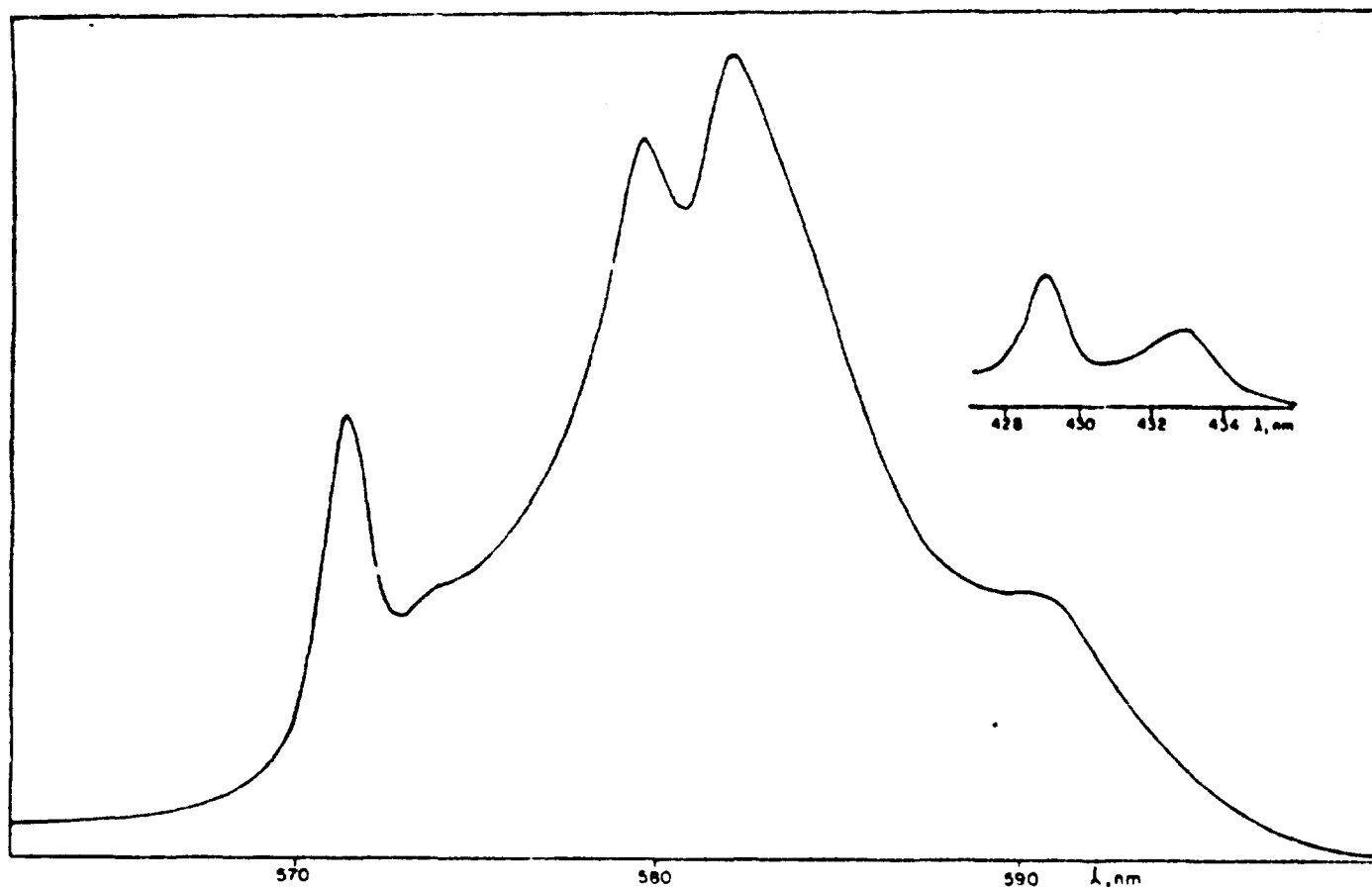


Fig. 1 - Absorption spectrum of the neodymium adduct at room temperature

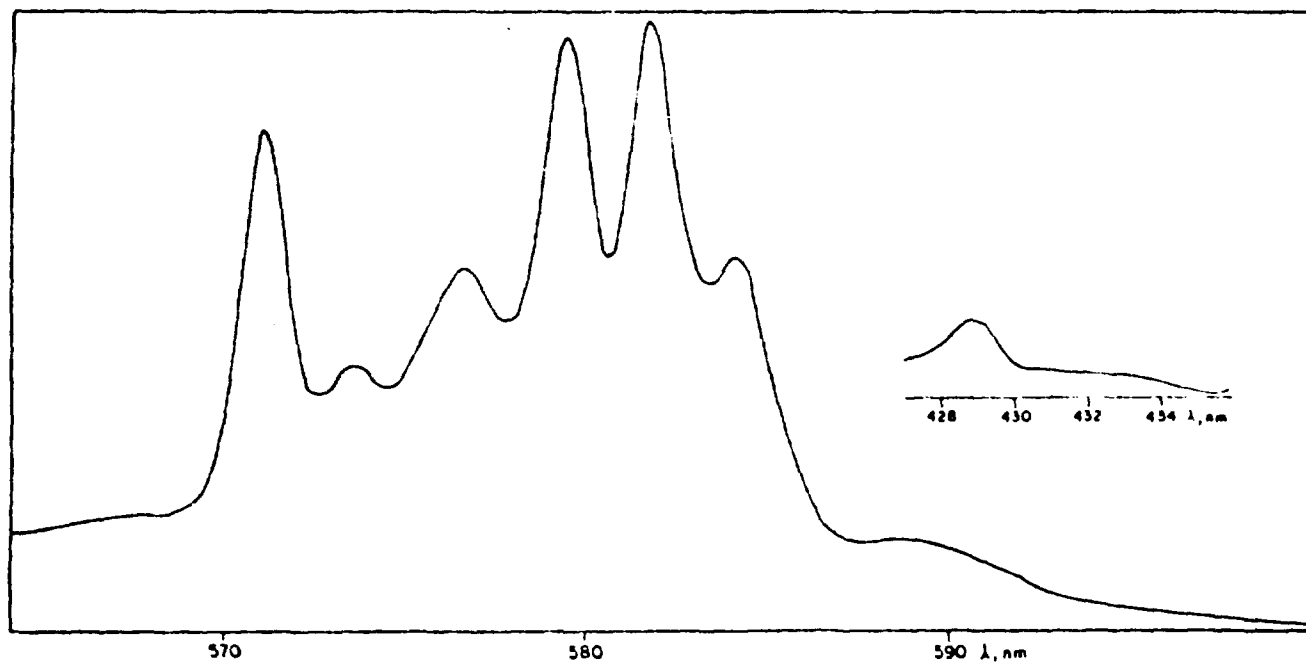


Fig. 2 - Absorption spectrum of the neodymium adduct at 77K.

Figure 3 contains the emission spectrum of the europium adduct. The existence of two peaks, one of which contains a shoulder, attributed to ${}^5D_0 \rightarrow {}^7F_1$ (~590 nm) transition and two peaks due to ${}^5D_0 \rightarrow {}^7F_1$ (~610 nm) transition and the the absence of a ${}^5D_0 \rightarrow {}^7F_0$ transition was interpreted in terms of a D_{2d} symmetry for the europium complex species[18].

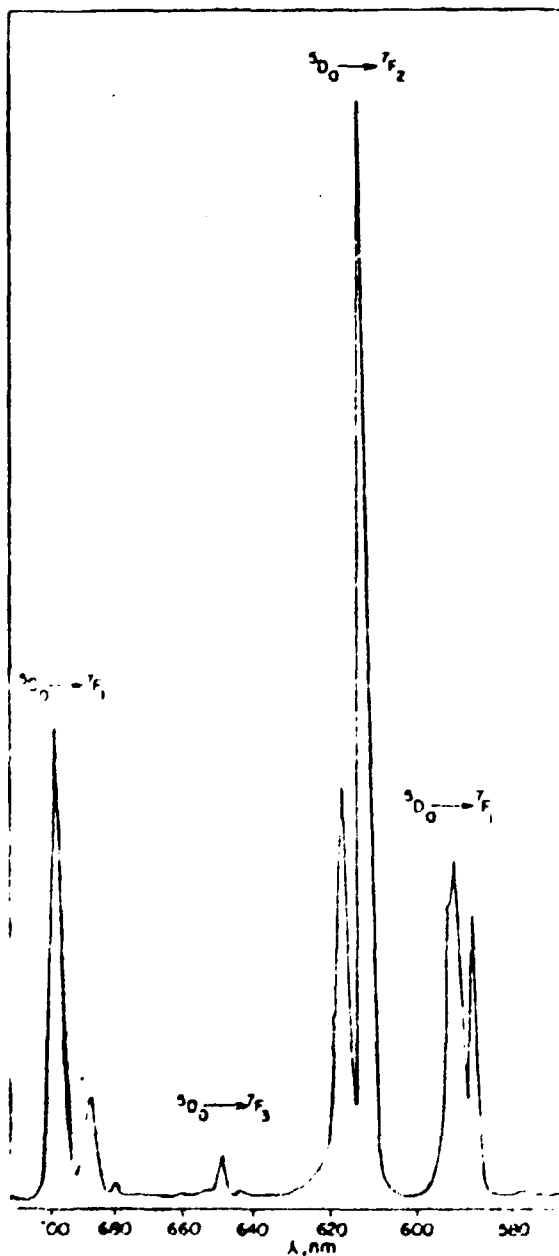


Fig. 3 - Emission spectrum of the compound of europium at 77K

Table 3. Oscillator strengths (P) of the neodymium adduct in acetonitrile and nitromethane

Solvent	Area	η	b(cm)	Conc. M	$P \times 10^6$ $\text{cm}^{-2} \text{mol}^{-1} \text{L}$
Acetonitrile	335.574	1.3443	2.00	0.0362	16.7
Nitromethane	360.949	1.3799	2.00	0.0361	17.6

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