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Note

Lanthanon picrate complexes with tetramethylenesulfoxide (TMSO)

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Abstract

Compounds with composition $Ln(pic)_3 \cdot 3TMSO$ (pic is picrate, Ln is La, Nd, Eu, Gd, Er, Yb and Y) were synthesized and characterized. A thermogravimetric study was performed in order to determine their decomposition products.

Keywords: Atmosphere; Decomposition; DTG; Lanthanon compound; Ligand; Picrate; TG; TMSO; XRD

1. Introduction

Hydrated lanthanide picrates [1,2] and complexes containing dimethylsulfoxide [3,4], 4-picoline-*N*-oxide [5] and 2-picoline-*N*-oxide [6] have been reported. This article describes the synthesis, characterization and thermogravimetric study of TMSO–picrate complexes.

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2. Experimental

The compounds were prepared by addition of TMSO in a 1:3 molar ratio to ethanolic solutions of the respective picrates. The resulting adducts were filtered, washed with ethanol, and dried in a vacuum over anhydrous calcium chloride.

The trivalent metal ions were analyzed by complexometric titration with EDTA. Carbon, hydrogen and nitrogen contents were measured by the usual microanalytical procedures, and sulfur was determined according to Schöriger [7].

Electrolytic conductance measurements were performed with a resistance box, a pointer galvanometer and a Leeds and Northrup cell ($K_c = 0.11597\,\mathrm{cm}^{-1}$), using acetonitrile and nitromethane as solvents. X-ray powder patterns were registered on a Rigaku RU-200 B using Cu Kα radiation. IR spectra were recorded on Perkin-Elmer 1750 and Bomem FTIR MB-102 spectrophotometers in Nujol and Fluorolube mulls between KBr plates. TG analyses were performed in a Perkin-Elmer, Delta Series TGA-7 instrument under dynamic nitrogen or air atmospheres with a 2 or 10 K min^{-1} heating rate, using small amounts of material (1.6–2.7 mg) to avoid possible explosion.

3. Results and discussion

Table 1 present a summary of the analytical results. The conductance measurements obtained with approx. 10^{-3} M nitromethane and acetonitrile solutions ($\Lambda_m \approx 5$ and $18\,\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$, respectively) are indicative of non-electrolyte behavior [8].

X-ray diffraction powder patterns allow us to group the compounds as one isomorphous series, the only exception being the lanthanum adduct.

The characteristic vibrational modes of water do not appear, which is evidence for anhydrous compounds. The typical picrate anion vibration modes, $\nu_{as}(NO_2)$ (1538 cm^{-1}) and $\nu_s(NO_2)$ (1330 cm^{-1}), remain essentially the same as those found in the hydrated salts [2]. The free ligand ($\nu(SO) = 1022$ cm^{-1}) vibrational mode is shifted to 980 cm^{-1} indicating ligand co-ordination through the sulfoxide oxygen.

Table 1
Summary of analytical results for compounds with the general formula Ln(pic)$_3$ · 3TMSO in %

Ln	Lanthanon		Carbon		Hydrogen		Nitrogen		Sulfur	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
La	12.33	12.81	31.73	31.35	2.66	2.42	11.10	10.60	8.47	8.26
Nd	12.64	12.93	31.58	31.37	2.65	2.37	11.05	10.78	8.43	8.22
Eu	13.23	13.46	31.37	30.92	2.63	2.51	10.97	10.44	8.37	8.12
Gd	13.63	13.92	31.22	31.31	2.62	2.55	10.92	10.64	8.33	8.52
Er	14.37	14.29	30.95	29.53	2.60	2.37	10.83	10.40	8.26	8.35
Yb	14.79	15.10	30.80	30.54	2.58	2.38	10.77	10.48	8.22	8.82
Y	8.19	8.14	33.19	32.70	2.78	2.58	11.61	11.27	8.82	8.56

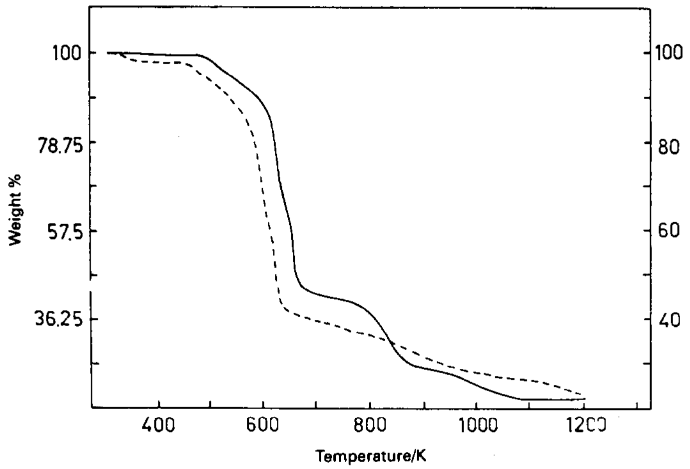

Fig. 1. TG curves of the neodymium compound in dynamic atmospheres: air (——, left scale), sample weight 2.094 mg; N_2 (– – –, right scale), sample weight 0.979 mg.

The complexes are stable up to 453 K in both nitrogen and air atmospheres (Fig. 1). After this temperature, TMSO elimination occurs in two steps. The first (1TMSO) is clearly defined by the DTG curves, with loss of approximately 9% mass.

After 533 K, a continuous mass loss is observed. The gray residues obtained at 1173 K liberate H_2S when treated with HCl, indicating the formation of sulfides from the thermodecomposition of the complexes under N_2 and the continued presence of carbon (Table 2).

Under dynamic air atmosphere, a sample isolated at 568 K was a yellow caramel color. The IR spectrum (Fig. 2, curve a) and the yellow colour of the water solution indicates that picrate ions remain unchanged. At about 580 K, the intermediates

Table 2
TG data, with residues in %

Nitrogen atmosphere			Air atmosphere			
	Theor.	Exp. [a]		Theor.	Exp. [b]	Exp. [c]
La_2S_3	16.47	22.5	La_2O_3	14.34	17.5	13.9
Nd_2S_3	16.92	24.1 [d]	Nd_2O_3	14.74	17.5	14.5
Eu_2S_3	17.42	19.7	Eu_2O_3	15.31	18.3	15.4
Gd_2S_3	17.79	31.8	Gd_2O_3	15.71	15.8	–
Er_2S_3	18.50	28.4	Er_2O_3	16.43	16.8	–
Yb_2S_3	18.90	29.8	Yb_2O_3	16.84	17.8	–
Y_2S_3	12.62	21.5	Y_2O_3	10.40	10.7	–

[a] Contains carbon at $T = 1183$ K. [b] $T = 1183$ K. [c] $T = 1423$ K. [d] At 2 K min^{-1}, 16.91% Nd.

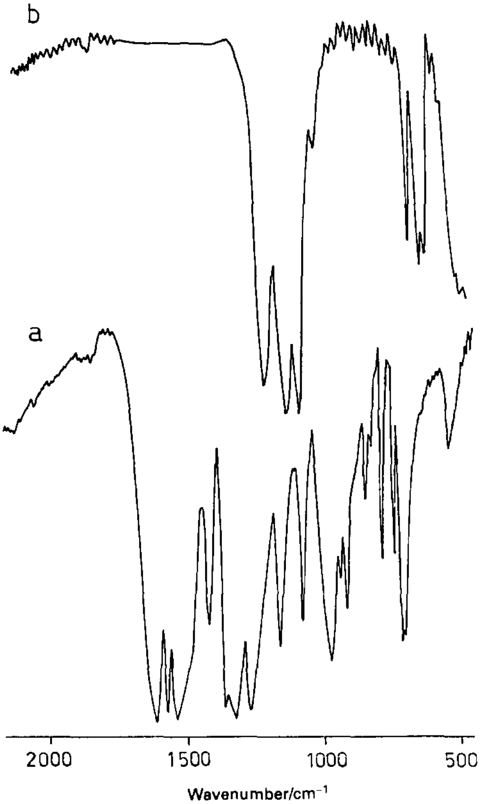

Fig. 2. Infrared spectra of the residues: curve a at 536 K; and curve b at 1073 K.

isolated are black due to partial carbonization. Treatment with water separates the carbon, and the remaining yellow solutions contain picrate and sulfate ions (tested with Ba^{2+}). The sample obtained at 633 K shows the same behavior (tests for SO_4^{2-} were again positive but negative for nitrate and sulfide). IR spectra show bands due to picrate and sulfate. At 793 K, the sample still contains picrate (microanalytical data: C, 17.52%; H, 1.88%; N, 8.50%). Qualitative tests indicate the presence of sulfate and the absence of both nitrate and sulfide. The gray residues isolated at 973 K contain sulfide and sulfate (tests with Ba^{2+} and HCl). The presence of sulfide is due to partial reduction of sulfate by carbon with evolution of CO_2. After 973 K, the TG curves show a small mass gain probably due to oxidation of sulfide to sulfate (in air atmosphere). The residues isolated at 1073 K contain sulfate ions, corroborated by the IR spectrum (Fig. 2, curve b) and practically no organic material (microanalytical data: C, 0.25%; H, 0.03%; N, 0.09%).

At 1173 K, the residues are oxides for the heavier lanthanides (Gd, Er, Yb, Y (Table 2)). For the lighter lanthanides (La, Nd, Eu) the corresponding oxides are formed only at 1423 K.

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References

[1] K. Nakagawa, K. Amita, H. Mizuno, Y. Inoue and T. Nakushi, Bull. Chem. Soc. Jpn., 60 (1987) 2037.
[2] T. Youngchi, L. Yingquiu and N. Jiazan, J. Mol. Sci. (China), 5 (1987) 82.
[3] G. Vicentini, L.B. Zinner and K. Zinner, Koord. Khim., 17 (1991) 422.
[4] J.R. Matos, L.B. Zinner and G. Vicentini, Thermochim. Acta, 214 (1993) 361.
[5] G. Vicentini, E.M. da Silva, J.R. Matos and K. Zinner, Thermochim. Acta, 195 (1992) 39.
[6] G. Vicentini and F.J.S. Lima, J. Alloys and Compounds, 192 (1993) 277.
[7] C. Ingram, Methods of Organic Elemental Microanalyses, Chapman and Hall, New York, 1962. S. Siggia and J.H. Stolten, An Introduction to Modern Organic Analysis, Interscience, New York, 1956.
[8] W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.