1.10 – PHENANTHROLINE COMPLEXES OF THE RARE EARTH NITRATE: SYNTHESIS AND CHARACTERIZATION.

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ABSTRACT

The interaction of lanthanide nitrates (Ln – Nd, Sm, Dy and Er) and 1.10 – phenantroline were studied and complexes of the general formulae $Ln(NO_3)_3(C_{12}H_8N_2)_2$ or $Ln(NO_3)_3.(o\text{-}fen)_2$

The complexes were characterized by elemental analyses (CHN), titration with EDTA, IR spectra and thermogravimetric analysis. X-ray powder patterns further indicated that the complexes are isomorphous having the same d -interplanar spacing.

Keywords: Lanthanides, Nitrates, 1.10 – Phenantroline

INTRODUCTION

The coordination chemistry of the lanthanides has become of great importance over the last few decades for its use in several applications. The compounds obtained by the reaction among lanthanides nitrates with organic ligands **[Sousa et al, 2000]**, (1.10 - phenanthroline) they have been studied in the last decades they constitute a family with physical and chemical properties extremely similar. The atomic and ionic rays decrease along the lanthanide series with the increase of the atomic number. This fact is known as "lanthanide contraction". With this the basicity of the elements decreases along the series. Ions lanthanides that have separated electrons are colored and paramagnetic **[Judd, 1972].** The coordination number happens between 3 and 9, but some are frequently high with small ligands, as for instance, nitrate and water **[Moeller, 1975; Ofelt, 1962; Najjar 1971].** In this article the complexes formed by reactions of hydrated lanthanide and 1.10 – Phenantroline $Ln(NO_3)_3(C_{12}H_8N_2)_2$ (Ln = Nd, Sm, Dy and Er) are described.

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DOI: 10.52571/PTQ.v2.n04.2005.AGOSTO/4_pgs_46_50.pdf

EXPERIMENTAL

The complexes were prepared by reaction of nitrate solution lanthanides $Ln(NO_3)_3$, (Ln = Nd, Sm, Dy and Er) with ligand 1.10 phenantroline in absolute ethanol (molar ratio 1:2), and dried in vacuum over.

Thermogravimetric curve were obtained on SHIMADZU TGA-50H instrument at a heating rate 10ºC/min in nitrogen (50 cm^3min^{-1} flow). The generated curves make possible obtaining of information with relationship to the thermal stability of the intermediate and final products **[Vicentini, 1971]**. Infrared spectroscopy using a Perkin Elmer FTIR-16 PC set-up. To that end, KBr pellets having 1 wt.% of the sample material were pressed under 5 t during 3 min. The range between 4000 and 400 cm-1 was studied **[Nakamoto, 1977]**. Carbon, hydrogen and nitrogen contents were determined using a CHN Perkin-Elmer model 240 instrument. The crystallographic structures present were determined from a Shimadzu diffraction equipment, model XRD-6000, using CuK_a radiation the range studied was 10^0 to 80^0.

RESULTS AND DISCUSSION

The reaction proposed for the lanthanides salts with the ligands 1.10 - phenanthroline is the following:

$$Ln(NO_3)_3xH_2O + 2C_{12}H_8N_2 \rightarrow Ln(NO_3)_3(C_{12}H_8N_2)_2$$

The estequiometer of the compositions were certain through the data of the titration with EDTA Table 01 and Table 02 presents a summary of the analytical results, which are in accordance with the general composition $Ln(NO_3)_3(C_{12}H_8N_2)_2$. The obtained data confirm the formation of compounds with 2 ligands evidencing her it formulates low $Ln(NO_3)_3(C_{12}H_8N_2)_2$. The curves TG Fig. 01 demonstrate that the compounds are stable up to 390ºC, being the first event of associated thermaldecomposition the loss of molecules of water. The second associated event the decomposition of the molecules of the salts that happens up to 800ºC.

The spectra in the area of the infrared of the compositions $Ln(NO_3)_3(C_{12}H_8N_2)_2$ they demonstrate a displacement νCN for the area of smaller frequency indicating the coordination of the ligands Table 03. The manners of stretching ν_1, ν_2 and ν_5 of NO_3 **[Nakamoto, 1977]**, indicate at least an anion NO_3 of form bidentate and they suggest her it formulates $Ln(NO_3)_3.\ 2C_{12}H_8N_2$.
The X-ray powder diffraction data are tabulated in Table 04. The solutions prepared are 1:1:2 and it seems that due to solubility products only one isomer crystallizes for ach of the rare earths used, the X-ray powder show isomorphism.

TABLE CAPTIONS

Table 01 – Titration Complexiometric with and without photocolorimetric nitrates and complexes.

Table 02 - Summary of analytical results of $Ln(NO_3)_3(C_{12}H_8N_2)_2$ (Ln = Sm, Dy, Er e Nd).

Table 03 – Infrared absorption spectra of the complexes.

Table 04 – X-ray powder diffraction patterns of $Ln(NO_3)_3(C_{12}H_8N_2)_2$ (Ln = Sm, Dy, Er e Nd).

Table 01 – Titration Complexiometric with and without photocolorimetric nitrates and complexes.

Complexes	T.C.P (N^0 de $C_{12}H_8N_2$)	T.C.P V_{EDTA} (mL)	T.C.W.P (N^0 de $C_{12}H_8N_2$)	T.C.W.P V_{EDTA} (mL)
$Nd(NO_3)_3(o\text{-}fen)_2$	2,1	1,40	1,9	1,48
$Sm(NO_3)_3(o\text{-}fen)_2$	2,3	1,34	1,9	1,46
$Dy(NO_3)_3(o\text{-}fen)_2$	2,0	1,40	1,8	1,48
$Er(NO_3)_3(o\text{-}fen)_2$	1,9	1,44	1,7	1,52

T.C.W.P = Titration complexometric without photocolorimetric, **T.C.P** Titration complexometric with photocolorimetric.

Table 02 – Summary of analytical results of $Ln(NO_3)_3.(o\text{-}fen)_2$ (Ln = Sm, Dy, Er, Nd).

Complexes	%C	%H	%N	
$Dy(NO_3)_3.(o\text{-}fen)_2$	40.14	2.56	13.55	Experimental
$Dy(NO_3)_3.(o\text{-}fen)_2$	40.66	2.25	13.82	Theoretical
$Sm(NO_3)_3.(o\text{-}fen)_2$	42.01	2.62	14.05	Experimental
$Sm(NO_3)_3.(o\text{-}fen)_2$	41.36	2.87	14.06	Theoretical
$Nd(NO_3)_3.(o\text{-}fen)_2$	38.33	2.79	12.95	Experimental
$Nd(NO_3)_3.(o\text{-}fen)_2$	37.80	2.62	12.85	Theoretical
$Er(NO_3)_3.(o\text{-}fen)_2$	40.55	2.54	13.58	Experimental
$Er(NO_3)_3.(o\text{-}fen)_2$	40.39	2.80	13.73	Theoretical

Table 03 – Infrared absorption spectra of the complexes.

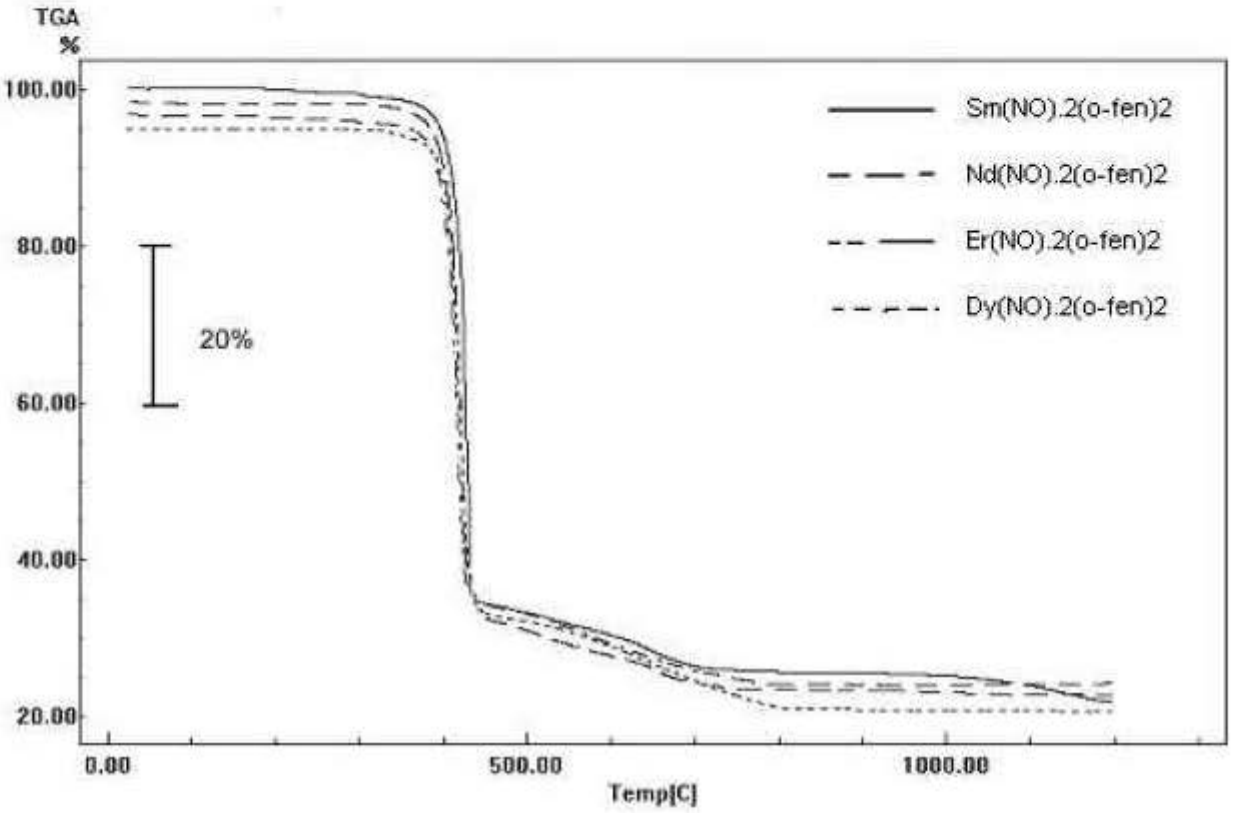
Complexes	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$Nd(NO_3)_3.(o\text{-}fen)_2$	1258	1081	723	1414	-	844
$Sm(NO_3)_3.(o\text{-}fen)_2$	1308	1034	724	-	-	843
$Dy(NO_3)_3.(o\text{-}fen)_2$	1307	1095	-	1494	628	845
$Er(NO_3)_3.(o\text{-}fen)_2$	1307	1027	726	1490	728	845

Table 04 – X-ray powder diffraction patterns of $Ln(NO_3)_3.(o\text{-}fen)_2$ (Ln = Sm, Dy, Er e Nd).

Nd		Sm		Dy		Er	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
8.95	100	8.51	42	8.82	100	8.84	100
7.02	17	6.99	100	6.96	38	6.99	3
6.39	7	-	-	6.34	23	6.35	2
5.71	8	5.71	41	5.65	22	-	-
5.24	9	-	-	5.19	21	5.21	2
4.64	9	4.75	22	4.60	22	4.61	2
4.50	53	4,58	39	-	-	4.44	48
4.24	35	4.33	49	-	-	4.20	7
4.12	10	4.03	33	4.09	27	3.85	2
-	-	3.75	48	3.65	21	3.73	2
3.58	11	3.51	31	3.56	28	3.56	2
3.42	27	-	-	3.44	30	-	-
3.35	29	3.35	27	3.38	56	3.38	8
3.12	10	3.15	43	3.10	29	3.11	2

FIGURE CAPTIONS

Figure 01 – Termogravimetric curve of complexes $Nd(NO_3)_3.(o\text{-}fen)_2$, $SM(NO_3)_3.(o\text{-}fen)_2$, $Dy(NO_3)_3.(o\text{-}fen)_2$ and $Er(NO_3)_3.(o\text{-}fen)_2$



REFERÊNCIAS

1 - Judd, B. R., ***Optical Absorption Intensities of Rare-Earth Ions***, Phys. Rev., 127, (1972) 750-61.

2 - Moeller, T., ***The Chemistry of Lanthanides - Comprehensive Inorganic Chemistry***, vol.4, Ch.44, Pergamon Press, (1975) 1-101

3 - Najjar, R., "***Compostos de Adição Entre Nitratos dos Elementos Lantanídeos e a Tetrametiluréia (TMU)***", Tese de Doutoramento - IQ-USP, São Paulo-SP (1971)

4 - Nakamoto, K., ***Infrared and Raman Spectra of Inorganic and Coordination Compounds***, 3ª Ed., John Wiley & Sons, New York, 1977.

5 - Ofelt, G. S.. ***Intensities of Crystal Spectra of Rare-Earth Ions*** - J. Chem. Phys., 37, (1962) 511.

6 - Souza, H. K., Melo, D. M. A., Fernandes, J. D. G., Zinner, K., Zinner, L. B., Zukerman-Schpector, J., Vicentini, G., ***Bis(pentamethylene)urea complexes of the lanthanide nitrates: synthesis, characterization, properties*** - *Journal Alloy Compounds*, 303 – 304 (2000) 168.

7 - Vicentini, G., ***"Adducts between some lanthanide nitrate and perchlorates and n, n, n', n' – Tetramethylmalonamide (TMMA)***, Journal of Inorganic Chemistry 34, (1971) 669.