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1,10-Phenanthroline-N-Oxide Chelates with Rare Earth Nitrates

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The interactions of 1,10-phenanthroline-N-oxide with the lanthanide nitrates were studied and complexes of the general formulae $Ln(PhenNO)_2(NO_3)_3$ were isolated from alcoholic solutions. The complexes were characterized by elemental analysis, conductivity measurements and ir spectra. X-ray powder patterns further indicated that the complexes are isomorphous having the same d-interplanar spacings.

Introduction

The mono-N-oxide of 1,10-phenanthroline (hereafter abbreviated as PhenNO) was prepared by Corey *et al.* [1] who also reported on its complexes with some of the 3d metal ions. Since then several related studies have appeared in the literature, concerning mainly the preparation and characterization of complexes with the 3d metal ions [2–5]. In this communication we report on the chelate complexes formed from the interaction of PhenNO with the rare earth nitrates in alcoholic solution. To our knowledge there

TABLE I. Analytical and Conductivity Data of the Complexes.

Compound	%C	%N	%M	$\Omega^{-1}\ \Lambda_M\ \mathrm{cm}^2\ M^{-1}$	Color
$La(PhenNO)_2(NO_3)_3$	40.57 (40.17)	13.34 (13.67)	19.80 (19.37)	68	Pale yellow
$Pr(PhenNO)_2(NO_3)_3$	40.43 (40.06)	13.88 (13.63)	20.01 (19.59)	61	Greenish
$Nd(PhenNO)_2(NO_3)_3$	39.24 (39.89)	13.74 (13.57)	20.40 (19.96)	60	White pink
$Sm(PhenNO)_2(NO_3)_3$	39.10 (39.54)	13.48 (13.46)	21.02 (20.63)	68	White
$Eu(PhenNO)_2(NO_3)_3$	39.03 (39.45)	13.53 (13.43)	21.48 (20.81)	65	White
$Gd(PhenNO)_2(NO_3)_3$	39.30 (39.17)	12.98 (13.33)	21.80 (21.38)	65	Pale Yellow
$Tb(PhenNO)_2(NO_3)_3$	39.60 (39.08)	13.48 (13.30)	22.02 (21.56)	65	White-pink
$Tb(PhenNO)_2(NO_3)_3$	39.25 (38.76)	12.85 (13.19)	22.60 (22.19)	68	White-pink
$Er(PhenNO)_2(NO_3)_3$	38.34 (38.66)	13.03 (13.15)	22.80 (22.43)	65	White-pink
$Tm(PhenNO)_2(NO_3)_3$	38.06 (38.55)	12.73 (13.12)	23.00 (22.61)	61	White
$Yb(PhenNO)_2(NO_3)_3$	38.64 (38.35)	13.00 (13.05)	23.50 (23.03)	70	White
$Lu(PhenNO)_2(NO_3)_3$	38.64 (38.25)	12.75 (13.02)	23.60 (23.22)	67	White-pink

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TABLE II. Characteristic IR Bands of the Complexes.

Compound	ν_{N-O}	δ_{N-O}	Ring stretchings	γ_{C-H}	$(\nu_1 + \nu_4)$	$\Delta(\nu_1 + \nu_4)$	Vibrational modes of the nitrate anion			
							ν_1	ν_2	ν_3	ν_4*
PhenNO	1269 1249	810	1615w, 1590m, 1560sh, 1550m, 1545sh	855s, 835s, 720s, 710s						
La(PhenNO)$_2$(NO$_3$)$_3$	1230 1215	820	1620w, 1594w, 1570m, 1562m	850s, 835s, 718s, 704s	1780w, 1742w, 1720w	38	995vw 980vw	838sh	1290ns, b	
Pr(PhenNO)$_2$(NO$_3$)$_3$	1225 1215	820	1627w, 1594w, 1578m, 1570m, 1562m	843s, 834s, 719s, 701s	1782w, 1745w, 1720w	37	995vw 980vw	840sh	1310vs, b	
Nd(PhenNO)$_2$(NO$_3$)$_3$	1230 1215	825	1625w, 1593w, 1575m, 1568m, 1560m	848s, 833s, 717s, 702s	1780w, 1740w, 1720w	40	995vw 980vw	837	1310vs, b	
Sm(PhenNO)$_2$(NO$_3$)$_3$	1230 1215	815 825	1628w, 1596w, 1575m, 1568m, 1558m	849s, 832s, 718s, 701s	1782w, 1745w, 1720w	37	995vw 980vw	838sh	1290vs, b	
Eu(PhenNO)$_2$(NO$_3$)$_3$	1220 1205	825	1620w, 1595w, 1575m, 1568m, 1558m	850s, 833s, 716s, 703s	1780w, 1742w, 1720w	38	995vw 980vw	840sh	1300vs, b	
Gd(PhenNO)$_2$(NO$_3$)$_3$	1225 1215	815 825	1622w, 1593w, 1575m, 1570m, 1560m	849s, 832s, 718s, 704s	1780w, 1740w, 1720w	40	995vw 980vw	839sh	1300vs, b	
Tb(PhenNO)$_2$(NO$_3$)$_3$	1225 1215	820	1625w, 1592m, 1577m, 1568m, 1558m	848s, 831s, 715s, 702s	1782w, 1745w, 1720w	37	995vw 980vw	838sh	1300vs, b	
Ho(PhenNO)$_2$(NO$_3$)$_3$	1225 1215	820	1623w, 1595m, 1578m, 1570m, 1560m	850s, 835s, 717s, 706s	1780w, 1742w, 1720w	38	995vw 980 vw	840sh	1300vs, b	
Er(PhenNO)$_2$(NO$_3$)$_3$	1230 1215	815 820	1620w, 1598m, 1575m, 1569m, 1560m	851s, 831s, 718s, 701s	1782w, 1742w, 1720w	40	995vw 980vw	838sh	1290vs, b	
Tm(PhenNO)$_2$(NO$_3$)$_3$	1230 1215	815 820	1625w, 1600m, 1577m, 1570m, 1560m	848s, 832s, 718s, 703s	1780w, 1742w, 1720w	38	995vw 980vw	840sh	1300vw, b	
Yb(PhenNO)$_2$(NO$_3$)$_3$	1230 1215	825	1626w, 1598m, 1578m, 1568m, 1560m	849s, 831s, 720s, 703s	1782w, 1745w, 1720w	37	995vw 980vw	838sh	1300ns, b	
Lu(PhenNO)$_2$(NO$_3$)$_3$	1225 1215	815 820	1622w, 1600m, 1580m, 1567w, 1560m	850s, 832s, 718s, 704s	1780w, 1742w, 1720w	38	995vw 980vw	838sh	1300vs, b	

*Strong ligand bands in the 750–700 cm^{-1} region prohibit the assignment of ν_4(NO$_3$).

TABLE III. Main Band in the X-ray Powder Diffraction Patterns.

θ	d(Å)	(LaL$_2$X$_3$)	(PrL$_2$X$_3$)	(NdL$_2$X$_2$)	(Sm$_2$L$_2$X$_3$)	(EuL$_2$X$_3$)	(GdL$_2$X$_3$)	(TbL$_2$X$_3$)	(DyL$_2$X$_3$)	(HoL$_2$X$_3$)	(ErL$_2$X$_3$)	(TmL$_2$X$_3$)	(YbL$_2$X$_3$)	(LuL$_2$X$_3$)
5.15	8.57	85	87	87	86	57	88	87	80	65	57	67	67	94
6.25	7.07	100	98	95	100	79	80	96	92	83	100	81	73	66
7.70	5.75	80	88	87	95	64	77	77	72	65	74	65	65	57
9.65	4.59	65	50	50	55	46	58	54	64	42	45	46	40	50
10.20	4.36	50	65	64	60	50	58	58	65	46	46	44	35	34
11.00	4.04	63	70	75	75	50	70	67	65	48	60	52	50	42
11.50	3.87	70	100	100	100	100	100	100	100	100	90	100	100	100
14.15	3.16	40	50	55	60	50	58	58	60	40	38	44	37	34

*L = PheNO; X = NO_3.

is only one reference in the literature concerning the interaction of PhenNO with the rare earths, and this refers to the preparation of the complex Eu(PhenNO$_3$)$_3$(NO$_3$)$_3$ [6].

Results and Discussion

The rare earth nitrates react with phenanthroline-N-oxide in alcoholic solution giving microcrystalline powdered complexes of the constant stoichiometry, Ln(PhenNO)$_2$(NO$_3$)$_3$, irrespective of the metal to ligand ratio. The prepared complexes, together with their analytical data and some physical properties, are listed in Table I.

The molar conductivities of 10^{-3} *M* solutions of the complexes in nitromethane may in all cases indicate the presence of 1:1 electrolytes [7], implying that two nitrate ions are coordinated to the metals.

The structures of the complexes were further deduced mainly from their ir spectra. The ligand PhenNO exhibits a rich ir spectrum in the 1660–440 cm^{-1} region and some of the characteristic bands are tabulated in Table II. It was found that positional changes of certain bands which occur upon metal complex formation can be ascribed to the pyridine and pyridine-N-oxide fragments of the molecule. In fact the ir spectra of phen–metal complexes exhibit shifts and splittings of several vibrational modes, similar to those found for metal complexes with pyridine and bipy [9]. Thus coordination of PhenNO to rare earth ions results in red shifts of the bands at 1269 and 1249 cm^{-1}, attributed to the νN–O, and to violet shifts of the bands at 810 cm^{-1}, attributed to the δN–O of the pyridine-N-oxide fragment of the ligand, implying that the oxygen atom of the N–O group is a ligation site. Shifts and/or splittings of the following bands attributable to both the pyridine and pyridine-N-oxide fragments were also found: ring stretching vibrations, 1615, 1590, 1560, 1550 and 1545 cm^{-1}; CH out-of-plane bending vibrations (γCH), 855, 835, 720, 710 cm^{-1} (see Table II). This further suggests that the pyridine nitrogen is also a ligation site in these complexes, and that PhenNO acts as a bidentate ligand [4].

The conductivity data of the complexes (see Table I) suggest the presence of two coordinated and one ionic nitrate group in all cases. This was further confirmed by the ir spectra of the complexes. The most reliable ir criterion for distinguishing the types of nitrate ions present is provided by the relative energies of various combination bands of the anion, especially the (ν_1 + ν_4) combination band in the 1800–1700 cm^{-1} region [9]. Compounds involving ionic nitrate exhibit a single band in this region, while compounds containing coordinated nitrate exhibit two bands due to a splitting of ν_4 into two components and their combination with ν_1 [10]. The degree of splitting of these two combination bands, ($\nu_1 + \nu_4$), is generally larger for bidentate than for monodentate nitrato groups, owing to a greater distortion from D_{3h} symmetry for bidentate coordination [9, 11]. In fact Lever *et al.* found that ($\nu_1 + \nu_4$) for monodentate nitrato groups lies in the range 5–26 cm^{-1}, while for bidentate groups the range is 20–66 cm^{-1} [9]. Finally, complexes containing both uncoordinated and monodentate or uncoordinated and bidentate nitrate groups exhibit three bands in the 1800–1700 cm^{-1} region [9] and, in many cases, bands corresponding to the fundamental vibrations of each type of nitrate present [11]. The various ir absorption bands for the nitrate ion in the new complexes are included in Table II. There are three bands in the 1800–1700 cm^{-1} region suggesting the presence of both coordinated and uncoordinated nitrate groups in all cases. Furthermore the separation ($\nu_1 + \nu_4$) (37–40 cm^{-1}) lies well in the range expected for bidentate nitrato groups.

In conclusion, the lanthanide ions in the new complexes may attain coordination number eight with four sites occupied by the two bidentate PhenNO molecules and the other four by the two bidentate nitrato groups.

The X-ray powder diffraction data are tabulated in Table III and a typical pattern is shown in Fig. 1.

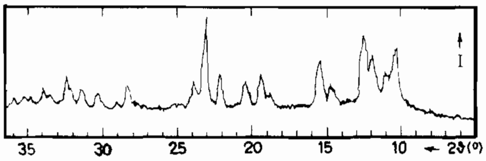

Fig. 1. X-ray powder diffraction pattern of the complex $\{Tm(PhenNO)_2(NO_3)_2\}NO_3$.

All patterns are very well resolved with all bands coinciding with respect to the position of the angles in which they appear. The complexes therefore are of crystalline nature and isomorphous with the same d-interplanar spacings [12]. The ligand PhenNO has no two-fold symmetry and there are three possible bis chelates, roughly speaking, O's of ligand *cis*, N's of ligand *cis*, and one of each. The statistical weights, other things being equal, in solution are 1:1:2 and it seems that due to solubility products only one isomer crystallizes (or the same mixture of isomers crystallizes) for each of the rare earths used, since the X-ray powder patterns show isomorphism.

Experimental

Materials

The rare earth nitrates were purchased from Merck A.G. 1,10-phenanthroline-N-oxide was prepared according to the literature [1]. All other chemicals were reagent grade and used without further purification.

Methods

The ir spectra were recorded on a JASCO-DS 701 G spectrophotometer. Conductivity data were taken with a Metrohm-Herisaw E 365 B Conduktoskop at room temperature. The X-ray powder diffraction patterns were obtained on a Philips X-ray powder diffractometer with Cu-Kα radiation and the range studied was from 20.5° to 80°. The microanalyses were performed at the microanalytical laboratories of Hellenic Nuclear Research Centre, Democritus.

Preparation of the Complexes

The following general procedure was applied for the preparation of the complexes. 1 mmol of the hydrated lanthanide nitrates was dissolved in 7 ml absolute ethanol, 3 ml of the dehydrating agent triethylorthoformate were added and the solution heated at 50 °C for 45 min. 3 mmol of 1,10-phenanthroline-N-oxide were dissolved in 10 ml absolute ethanol and this was added dropwise to the lanthanide solution and the heating at 50 °C was continued for 10 min. The mixture was then cooled in an ice bath and the precipitate formed was filtered, washed with ice-cold absolute methanol, ether, and dried at 100 °C under vacuum over phosphorus pentoxide. The yields were in the range 70 to 75%.

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