Inorganica Chimica Acta, 27 (1978) 67–68

Chelates of the Rare Earth Nitrates with 1,10-Phenanthroline-N,N′-Dioxide

C. CHASSAPIS and G. PNEUMATIKAKIS

Chemistry Department, Athens University, 13A Navarinou Str., Athens, Greece

Received July 4, 1977

The donor properties of 1,10-phenanthroline mono-N-oxide (N-phenO) towards the 3d transition metal ions and recently Eu(III) [1–6] *have been extensively studied. By contrast, the only complexes of the 1,10-phenanthroline-N,N′-dioxide (phenO$_2$) reported in the literature are those with VCl$_4$* [7]. *In this communication the donor properties of the phenO$_2$ towards the lanthanide ions have been studied and complexes of the general formula Ln(phenO$_2$)$_2$(NO$_3$)$_2$NO$_3$ were isolated and characterized by their elemental analysis, ir spectra and conductivity data.*

Experimental

Reagents

Rare earth nitrates were obtained from E. Merck A. G. 1,10-phenanthroline-N,N′-dioxide was prepared by the method described for 2,2′-bipyridine-N,N′-dioxide [8, 9]. All other chemicals were of analytical grade and used without further purification.

Preparation of the Complexes

In a typical experiment 1mmol of hydrated rare earth nitrate was dissolved in 10ml absolute ethanol, 3ml triethylorthoformate were added and heated to 60 °C for 30 min. 3mmol phenO$_2$ were dissolved, by heating, in 10ml absolute ethanol. The two solutions were mixed and refluxed for 1h. The complexes were generally isolated as fine crystalline powders, filtered, washed with absolute ethanol and ether and dried at 110 °C under vacuum.

In the table below the prepared complexes and some of their characteristic properties are given.

Results and Discussion

The rare earth(III) nitrates all react with 1,10-phenanthroline-N,N′-dioxide giving crystalline compounds and their analytical results are in good agreement with the general formula Ln(phenO$_2$)$_2$(NO$_3$)$_2$-NO$_3$. The molar conductances of $10^{-3}M$ solutions of the complexes in nitromethane (Λ_m) are all in the range of 70–110 ohm^{-1} cm^2 mol^{-1} and may indicate the presence of 1:1 electrolute [10], implying that two nitrato groups are coordinated to the metal. However, the molar conductances of the complexes in water are all in the range of 450–600 ohm^{-1} cm^2 mol^{-1} and may indicate the presence of 1:3 electrolyte [11], implying that the two labile nitrato groups in the inner coordination sphere of the complexes are substituted by water molecules according to the equation:

$$\mathrm{Ln(phenO_2)_2(NO_3)_2NO_3 + 2H_2O \longrightarrow Ln(phenO_2)_2(H_2O)_2^{3+} + 3NO_3^-}$$

The function of phenO$_2$ as a bidentate ligand in the new complexes was established by shifts and/or splittings of several characteristic vibrational modes of the ligand. The ir spectra of phenO$_2$ are rather complex, but the nitrogen–oxygen stretching frequency (νN–O) and bending frequency (δN–O) have been reasonably assigned on the basis of the respective spectra of bipyO$_2$ [12].

In the free ligand the ν(NO) and δ(NO) appear as doublets at 1282, 1312 cm^{-1} and 844, 880 cm^{-1} respectively. Upon complexation the ν(NO) is broadened and centered in the region 1280 to 1295 cm^{-1} *i.e.* 32 to 17 cm^{-1} lower than the upper part of the ν(NO) doublet of the free ligand. This lowering of the ν(NO) frequency is in accordance with OO complexation in all the new complexes [7].

In most of the complexes prepared the δ(NO) appears as a triplet in the region 835 to 860 cm^{-1} meaning that it is lowered by some 10 cm^{-1} from the lower and 20 cm^{-1} from the upper part of the ν(NO) doublet of the free ligand and this is further support of the OO chelation.

The intensity of the band at 1280 to 1295 cm^{-1} in the complexes is increased almost three times from the mean intensity of the ν(NO) doublet of the free ligand. This is attributed to the fact that the symmetric ν(NO$_3$) occurs in the same region and most probably coincides with the ν(NO) band in the complexes. The asymmetric ν(NO$_3$) band is found in the region 1405 to 1420 cm^{-1} in all complexes. This splitting of the free nitrate band together with the

TABLE . Physical and Other Data for the Complexes.[a]

Compounds	Color	M.p. (°C)	Λ_m, Ohm^{-1} cm^2 mol^{-1}		ν(N–O)	δ(N–O)	νNO_3^-	$\nu_{asym}NO_3$	$\nu_{sym}NO_3$
			$MeNO_2$	H_2O					
$PhenO_2$		167			1282, 1312	845, 880			
$\{La(PhenO_2)_2(NO_3)_2\}NO_3$	pale yellow	256	82	481	1295	844, 858	1365	1405	1295
$\{Pr(PhenO_2)_2(NO_3)_2\}NO_3$	greenish	298	107	523	1285	840, 850	1370	1410	1285
$\{Nd(PhenO_2)_2(NO_3)_2\}NO_3$	white-pink	273	100	506	1280	835, 847,858	1370	1410	1280
$\{Sm(PhenO_2)_2(NO_3)_2\}NO_3$	white	295	98	456	1290	840, 850, 860	1370	1405	1290
$\{Eu(PhenO_2)_2(NO_3)_2\}NO_3$	white	311	76	456	1290	840, 850, 860	1375	1410	1290
$\{Gd(PhenO_2)_2(NO_3)_2\}NO_3$	white	304	95	473	1290	840, 850, 860	1380	1415	1290
$\{Tb(PhenO_2)_2(NO_3)_2\}NO_3$	white-pink	298	70	539	1295	838, 850, 860	1380	1415	1295
$\{Dy(PhenO_2)_2(NO_3)_2\}NO_3$	yellow	261	76	523	1295	840, 860	1380	1420	1295
$\{Ho(PhenO_2)_2(NO_3)_2\}NO_3$	yellow	263	80	498	1285	840, 860	1380	1420	1285
$\{Er(PhenO_2)_2(NO_3)_2\}NO_3$	white-pink	262	76	531	1285	838, 860	1370	1410	1285
$\{Tm(PhenO_2)_2(NO_3)_2\}NO_3$	yellow	266	75	581	1295	844, 852, 860	1370	1415	1295
$\{Yb(PhenO_2)_2(NO_3)_2\}NO_3$	yellow	265	83	598	1295	843, 851, 860	1370	1408	1295
$\{Lu(PhenO_2)_2(NO_3)_2\}NO_3$	pale yellow	241	99	473	1295	843, 852, 860	1370	1412	1295

[a] Satisfactory analytical figures have been obtained for all these compounds.

appearance of the band at 1370 cm^{-1} assigned to the nitrate ion implies the existence of both coordinated and free nitrate groups in all the complexes [13].

This is in agreement with conductivity data which favor formulation with two coordinated and one free nitrate ions. The ir spectra of all the complexes definitely indicate the absence of water or ethanol and we tentatively assign the coordination number 6 to the lanthanide ions in all these complexes.

Acknowledgment

We thank Hellenic National Research Foundation for financial support.

References

1 N. M. Karayannis, S. D. Sonsino, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 2,* 439 (1968).

2 A. N. Speca, N. M. Karayannis and L. L. Pytlewski, *Inorg. Chim. Acta, 9,* 87 (1974).

3 A. N. Speca, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem., 36,* 1227 (1974).

4 A. N. Speca, L. L. Pytlewski, N. M. Karayannis and C. Owens, *J. Inorg. Nucl. Chem., 36,* 3751 (1974).

5 A. N. Speca, L. L. Pytlewski, C. Owens and N. M. Karayannis, *ibid., 38,* 1119 (1976).

6 A. C. M. de Andrade, M. A. de Brito, A. L. Coelho and G. F. de Sà, *Inorg. Chim. Acta, 19,* L19 (1976).

7 B. E. Bridgland and W. R. McGregor, *J. Inorg. Nucl. Chem., 31,* 43 (1969).

8 G. M. Badger and W. H. F. Sasse, *J. Chem. Soc.,* 617 (1956).

9 P. G. Simpson, A. Vinciguerra and J. V. Quagliano, *Inorg. Chem., 2,* 282 (1963).

10 W. J. Geary, *Coord. Chem. Reviews, 7,* 81 (1971).

11 M. Sneed, J. Maynard, "Gen. Inorg. Chemistry", Van Nostrand, New York (1942) p. 813.

12 A. Vinciguerra, P. G. Simpson, Y. Kakinti and J. V. Quagliano, *Inorg. Chem., 2,* 286 (1963).

13 G. Pneumatikakis, *Chem. and Ind., London,* 770 and 882 (1968) and references therein.