

Lanthanide Complexes with N-oxides. Synthesis and Fluorescence Spectra of Lanthanide Nitrate and Thiocyanate Complexes with Pyridine N-oxide

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Eight-coordination for lanthanide(III) complexes is prevalently encountered in systems containing chelating agents, while the number of octacoordinated complexes with equivalent unidentate ligands is relatively scanty. The N-oxide molecules behave as strongly basic ligands towards *a*-type acceptor cations and normally give rise to well-definite stoichiometry compounds.

Octacoordinated complexes of the type $\text{Ln}(\text{PyO})_8\text{-X}_3$ where PyO is the pyridine N-oxide and X is a weakly or non-coordinating anion (Cl, Br, I, ClO_4 , CF_3SO_3) are known [1–3], but only complexes containing three or four molecules of PyO have been reported when X is the coordinating nitrate group [4]; to our knowledge, no complex of lanthanide(III) thiocyanates with this ligand has been prepared. The synthesis and fluorescence spectra of the octakis (PyO) complexes of lanthanide(III) nitrates and of some complexes of lanthanide(III) thiocyanates with this ligand are reported here.

Experimental

Pyridine N-oxide (PyO), from Aldrich, was distilled at reduced pressure.

The complexes were obtained by mixing 1 mmol of the lanthanide(III) nitrate or thiocyanate hydrate in 10 ml of anhydrous ethanol with 8 and 5 mmol of PyO, respectively, in 10 ml of the same solvent. The solution obtained was refluxed for 30 min under dry nitrogen and slowly concentrated. Successively, 50 ml of anhydrous diethyl ether were added to the solution vigorously stirred. When necessary, the solution was further refluxed and concentrated. Abundant precipitates formed on cooling the solution; they were rapidly filtered off, washed with anhydrous ethanol–diethyl ether mixture (1:5) and dried *in vacuo* at room temperature over CaCl_2 .

Thermal analysis, electrolytic conductivity, vibrational and electronic (absorption and emission) spectra were performed as previously described [3].

Results and Discussion

Whereas octakis (PyO) complexes were obtained with the lanthanide(III) nitrates, only four or three PyO molecules we were able to attack to the lanthanide(III) thiocyanates. The complexes are highly hygroscopic and soluble in alcohols and acetonitrile. Molar conductivity data for the nitrate complexes in millimolar solutions in ethanol and acetonitrile indicate lower than 1:3 electrolytic behaviour. Since the three nitrate groups in the solid complexes exhibit undoubtedly ionic character (see spectra)

TABLE I. Selected Analytical Data, Molar Conductivity and Temperature of Thermal Decomposition of Lanthanide(III) Nitrate and Thiocyanate Complexes with Pyridine N-oxide (PyO). In Parentheses the Calcd. Values.

Complex	%C	%H	%N	%Ln	Λ_M^a		$t_i, ^\circ\text{C}$
					EtOH	CH_3CN	
$\text{La}(\text{PyO})_8(\text{NO}_3)_3$			13.92(14.19)	12.60(12.79)	105	338	190
$\text{Nd}(\text{PyO})_8(\text{NO}_3)_3$	44.61(44.03)	3.80(3.70)	14.05(14.12)	13.47(13.22)		315	195
$\text{Sm}(\text{PyO})_8(\text{NO}_3)_3$			13.88(14.04)	13.58(13.70)		293	195
$\text{Eu}(\text{PyO})_8(\text{NO}_3)_3$	43.57(43.72)	3.75(3.67)	13.81(14.02)	13.61(13.83)	112	287	190
$\text{Tb}(\text{PyO})_8(\text{NO}_3)_3$	42.95(43.45)	3.78(3.65)	13.96(13.93)	14.02(14.37)		301	180
$\text{Ho}(\text{PyO})_8(\text{NO}_3)_3$			13.67(13.86)	15.06(14.84)	98	290	180
$\text{La}(\text{PyO})_4(\text{NCS})_3 \cdot 2\text{H}_2\text{O}$			13.58(13.44)	18.72(19.04)		18	220
$\text{Nd}(\text{PyO})_4(\text{NCS})_3 \cdot 2\text{H}_2\text{O}$	37.19(37.59)	3.38(3.29)	13.21(13.34)	19.13(19.63)	25	16	220
$\text{Eu}(\text{PyO})_4(\text{NCS})_3 \cdot \text{H}_2\text{O}$			13.40(13.53)	21.35(20.97)		17	215
$\text{Er}(\text{PyO})_3(\text{NCS})_3 \cdot 2\text{H}_2\text{O}$	32.80(32.62)	3.00(2.89)	12.49(12.68)	24.75(25.23)	18	10	210

^a $\text{Ohm}^{-1} \text{cm}^2 \text{M}^{-1}$, at $25 \pm 0.1 ^\circ\text{C}$; $c = 0.8\text{--}1.1 \cdot 10^{-3} \text{M}$.

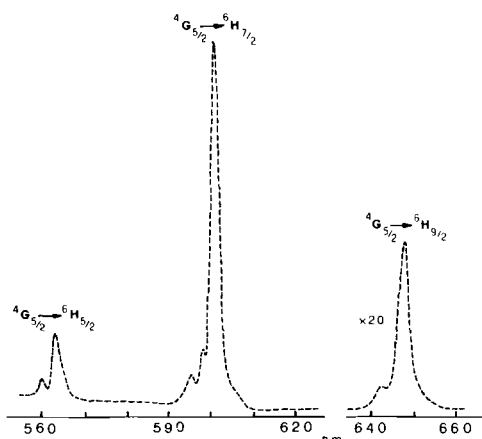


Fig. 1. Emission spectrum of $\text{Sm}(\text{PyO})_8(\text{NO}_3)_3$ from solid at 77 K, excitation with 365 nm radiation.

this trend arises from replacement of PyO inner-sphere molecules by nitrate groups. This phenomenon is not observed for the corresponding octakis (PyO) complexes of lanthanide(III) perchlorates and trifluoromethanesulphonates which show 1:3 electrolytic behaviour [3]. The thiocyanate complexes are non-electrolytes in ethanol and acetonitrile.

The IR spectra of the complexes show the shift of the NO stretching mode from 1265 cm^{-1} to $1230\text{--}1225\text{ cm}^{-1}$. The NO bending mode that appears at 842 cm^{-1} in the spectrum of the free ligand is slightly affected whereas the pyridine ring mode at 1460 cm^{-1} shifts to $1475\text{--}1470\text{ cm}^{-1}$ upon complexation. This spectral trend has been associated with the coordination of PyO to the cation through the oxygen atom [3]. In the regions of the nitrate vibrations the spectra of the solid complexes show a strong band at 1385 cm^{-1} and a weaker one at 832 cm^{-1} both assigned to the D_{3h} symmetry nitrate group. No band arising from coordinated nitrate appears in the spectra indicating that only ionic nitrate groups act in these complexes. The appearance in the spectra of the thiocyanate complexes of a slightly split band around 2050 cm^{-1} and of another band at $480\text{--}470\text{ cm}^{-1}$ assigned respectively to the CN stretching and NCS bending modes is consistent with the N-coordination of the three thiocyanate groups. The absorption and the emission f-f spectra of the nitrate complexes and the spectra of the corresponding octakis(PyO) perchlorate and trifluoromethanesulphonate complexes are practically superimposable on one another, but differ markedly from the thiocyanate complexes. Unfortunately, the nitrate complexes undergo solvolysis, even in acetonitrile, and the solution spectra are different from the reflectance ones. This is in line with conductivity data and is due to changes between coordinated PyO molecules and nitrate groups. Nevertheless, the intensity of the hyper-

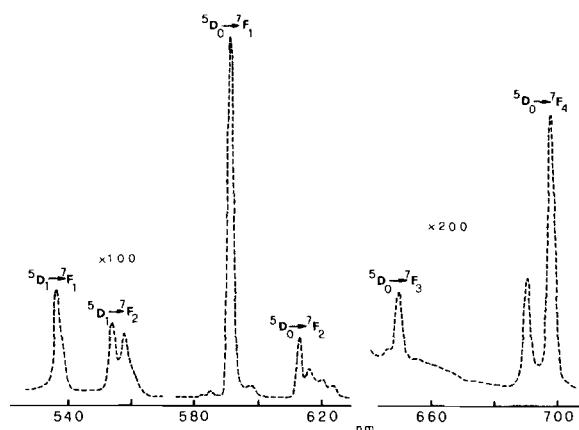


Fig. 2. Emission spectrum of $\text{Eu}(\text{PyO})_8(\text{NO}_3)_3$ from solid at 77 K, excitation with 365 nm radiation.

sensitive transitions measured for the neodymium and holmium complexes in acetonitrile increases about four and eight times, respectively, with respect to the aquo ions, while the barycentre of the band group shifts to lower frequencies. It is known that both these effects have been correlated with covalency.

There is little doubt both from synthetic and spectral data that the nitrate complexes consist of the octacoordinated ion $[\text{Ln}(\text{PyO})_8]^{3+}$ surrounded by the three nitrate groups, while three thiocyanate groups, four or three PyO molecules and one or two water molecules contribute to the formation of nona- or octacoordinated structures. Useful information concerning the nature of the chromophoric group and symmetry of the complex can be obtained by the study of the fluorescence spectra. The complex $\text{Sm}(\text{PyO})_8(\text{NO}_3)_3$ shows strong fluorescence originating almost totally at the $^4G_{5/2}$ level. Samarium(III) ion has several resonance and final states; these, however, can be manifoldly split under the field of the various symmetries and several lines associated with the various transition normally appear in the spectra. All the point groups other than cubic give rise for the half-integral values of J to $J + \frac{1}{2}$ levels whereas a cubic symmetry splits the state of $J = 5/2$ into two levels and the states of $J = 7/2$ and $9/2$ into three levels each. The emission spectrum of this complex shows the $^4G_{5/2} \rightarrow ^6H_{7/2}$ as the most populated transition; it consists, however, of a line at 600.6 nm and two much weaker lines at 594.2 and 598.0 nm . A very weak component at 559.8 nm and a more intense, though broad, one at 563.2 nm appear in the region of the $^4G_{5/2} \rightarrow ^6H_{5/2}$ while the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition consists of a unique, but weak and broad component at 647.8 nm accompanied by a much weaker side band at higher frequencies (Fig. 1). This emission spectrum exhibits a number of components associated with the various transitions

which is rather low and consistent with a high symmetry for the electrostatic field surrounding the samarium(III) ion. The octakis (PyO) lanthanum(III) and neodymium (III) perchlorate complexes have been described in terms of square antiprismatic geometry; however, a geometry intermediate between a cube and a square antiprism is stabilized in a second modification [5].

The emission spectrum of the complex $\text{Eu}(\text{PyO})_8(\text{NO}_3)_3$ obtained from solid excited with near ultraviolet radiations (365 nm) at 77 K, shows a line in the region of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition the intensity of which is, however, so low that it can be taken as forbidden. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition consists of an intense component at 592.1 nm and a very weak one at 598 nm (Fig. 2). Four weak components of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ appear at 613.5, 617.0, 621 and 624.5 nm; the most intense is, however, just a 15% the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition.

The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ transition consists of an unique very weak component at 650.5 nm accompanied by a much weaker side band at lower frequencies. Two weak and broad components of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition appear at 691.5 and 699.3 nm; both are just more intense than the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition. A single broad line at 536.8 nm and two broad lines at 554.9 and 558 nm can be associated with the ${}^5\text{D}_1 \rightarrow {}^7\text{F}_{1,2}$ transitions while the two weak lines at 583.5 and 586.0 nm arise from the ${}^5\text{D}_1 \rightarrow {}^7\text{F}_3$ transition. The spectrum is practically the same as observed for the octakis (PyO) europium(III) trifluoromethanesulphonate complex showing only small differences in the energy and relative intensity of the various transitions [3]. When the europium(III) ion is located at a site that is a centre of symmetry in the crystal lattice, the only purely electronic transitions which can occur are those for which the

magnetic dipole selection rule $\Delta J = 0, \pm 1$ (except $J = 0 \rightarrow J = 0$) is obeyed. If the ion is brought into the ${}^5\text{D}_0$ state, the only possible transition accompanied by emission of radiation is ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$. The ${}^5\text{D}_0$ level ($J = 0$) can never be split, while the ${}^7\text{F}_1$ level ($J = 1$) is triply degenerate and can be split under the field of the various symmetries. A field possessing a cubic symmetry, however, permits triple degeneration and does not cause splitting. The emission spectrum of this complex is essentially the same as observed for systems having ascertained cubic symmetry [6, 7]; however, the slight broadening of the band associated with the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition, the exhibition in this region of a second, though very weak, component and the appearance of discrete lines in the region of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition suggest deviation from the idealized polyhedron; most probably a geometry intermediate between the cube and the square antiprism, similar to that of $\text{La}(\text{PyO})_8(\text{ClO}_4)_3$, is stabilized in this case.

References

- 1 V. N. Krishnamurthy and S. Soundararajan, *Can. J. Chem.*, **45**, 189 (1967).
- 2 E. Butter and W. Seifert, *Z. Anorg. Allg. Chem.*, **368**, 133 (1969).
- 3 A. Seminara and E. Rizzarelli, *Inorg. Chim. Acta*, **40**, 249 (1980).
- 4 G. A. Pneumaticakis, *Chem. Ind. (London)*, 770 (1968).
- 5 A. R. Al-Karaghoulis and J. S. Wood, *Inorg. Chem.*, **18**, 1177 (1979).
- 6 G. Blasse, 'Handbook on the Physics and Chemistry of Rare Earths', Vol. 4, 237-274 (1979), North-Holland Publishing Company, edited by K. A. Gschneidner and L. Eyring.
- 7 O. A. Serra and L. C. Thompson, *Inorg. Chem.*, **15**, 504 (1976).