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Pyridine-1-Oxide Complexes of Lanthanide Iodides

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Pyridine-1-oxide complexes of lanthanide iodides of the formula $Ln(PyO)_8I_3$ where Ln = La, Pr, Nd, Tb, Dy, Er, and Yb have been prepared and characterised by analyses, molecular weight, conductance, infrared and proton NMR data. Proton NMR and IR data have shown the coordination of the ligand to the metal through the oxygen atom of the N—O group. NMR data have been interpreted in terms of a distorted square antiprismatic geometry in solution.

Introduction

Many complexes of lanthanides with the anions perchlorate, chloride and nitrate are known. Reports on complex salts of lanthanide iodides are very few[1–3] and they show a similarity to the corresponding complexes[3–5] of perchlorates as far as the stoichiometry is concerned. Since iodide is known to coordinate to the metal ions in metal complexes, we may expect a higher coordination number for the iodides of lanthanide complexes compared to the corresponding complex-perchlorates. Complex salts of lanthanide iodides where the iodides are coordinated to the metal ion have been prepared in this laboratory[6a, 6b]. In order to study the effect of iodide as the anion on the complex species we started the work on pyridine-1-oxide (*Py*O) complexes of lanthanide iodides as we could compare the results with the corresponding perchlorate-salts of the complexes prepared and characterised in this laboratory[7]. *Py*O complexes of transition and non-transition metals have been well studied[8–10]. *Py*O complexes of lanthanide perchlorates and nitrates[7, 11] are known, as are the complexes[12] with the anion $[Cr(SCN)_6]^{3-}$. $La(PyO)_8(ClO_4)_3$ has been shown to have a distorted square antiprismatic arrangement of ligands around the metal ion[13]. The fluorescence spectrum of $Eu(PyO)_8I_3$ has also been interpreted in terms of square antiprismatic arrangement of oxygen atoms around the metal ion[14]. In the present paper we report the preparation and characterisation of seven lanthanide iodide complexes of *Py*O with the general formula $Ln(PyO)_8I_3$. The preparative procedure is simple and different from that reported for $Eu(PyO)_8I_3$. For the sake of comparison we have also prepared and characterised the corresponding yttrium complex.

Experimental

Hydrated lanthanide iodides were prepared by dissolving the corresponding lanthanide oxide (obtained from American Potash and Chemicals Corporation, U.S.A.) in hydriodic acid and evaporating the solution on a water bath. The residue obtained was washed well with benzene till the washings were colourless and dried on a water bath.

Pyridine-1-oxide was prepared according to the method of *Ochiai*[15] and purified by vacuum distillation (129 °C/2 Torr).

All the solvents used were purified by standard methods before use.

Preparation of the Complex

0.5 g of the hydrated lanthanide iodide was dissolved in about 10 ml of acetone. To this solution was added 1.0 g *Py*O dissolved in about 10 ml of acetone with constant stirring. The complex separated out as fine crystalline solid. After standing for about 10 min., the precipitate was filtered off through a sintered crucible, washed well with ice cold acetone and dried over phosphorus(V) oxide in a vacuum desiccator.

Analyses

The metal content of the complexes was estimated by *EDTA* titrations using xylenol orange as indicator[16]. Iodide content was estimated by *Volhard's* method[17]. *Py*O was estimated polarographically using the calibration curve method[18]. A manual d.c. polarograph was used for the analyses. The complexes were decomposed in water before the estimation. The ionic strength of the solution was maintained at 0.45 using KCl at pH 2.15. The temperature and drop-time were adjusted to be 30 ± 0.1 °C and 5 sec/drop resp. The half-wave potential $E_{1/2}$ with respect to a standard Calomel electrode was found to be -0.98 V (Table 1).

Physical Methods

Conductivity measurements were carried out at 25 °C in a Siemens Conductivity bridge using an immersion cell (type LTA) previously calibrated with standard KCl solutions. The concentrations of the solutions used were of the order of $0.001M$.

Molecular weight of a few representative complexes was determined in water using the conventional cryoscopic method. The conductance and molecular weight data are given in table 2.

IR spectra of the ligand in CCl_4 and in CS_2 and of the complexes in nujol mulls were recorded in a Carl Zeiss UR-10 spectrophotometer. The principal IR bands and their assignments are given in table 3.

Proton NMR spectra were recorded in a Varian T 60 instrument using $CDCl_3$ as the solvent and *TMS* as the internal standard. The proton NMR data are given in table 4.

Table 1. *Analytical Data*

Compound	Colour	Found (%)			Calculated (%)		
		Metal	Iodide	*Py*O	Metal	Iodide	*Py*O
La(*Py*O)$_8$I$_3$	Pale yellow	10.90	29.64	58.61	10.85	29.75	59.40
Pr(*Py*O)$_8$I$_3$	Yellowish green	11.01	29.80	58.22	10.98	29.70	59.32
Nd(*Py*O)$_8$I$_3$	Pale orange	11.43	29.68	58.57	11.22	29.53	59.25
Tb(*Py*O)$_8$I$_3$	Pale yellow	12.42	29.17	58.09	12.23	29.29	58.48
Dy(*Py*O)$_8$I$_3$	Pale yellow	12.52	29.22	57.23	12.47	29.20	58.33
Er(*Py*O)$_8$I$_3$	Pale pink	12.89	29.03	58.92	12.79	29.12	58.09
Yb(*Py*O)$_8$I$_3$	Pale yellow	12.98	28.91	57.10	13.15	28.96	57.89
Y(*Py*O)$_8$I$_3$	Pale yellow	7.35	30.85	—	7.23	30.95	—

Table 2. *Conductance and Molecular Weight Data*

Compound	Molar conductance ohm^{-1} cm^2 mole^{-1}		Molecular weight in water	Number of species
	in CH_3CN *	in *DMF* **		
La(*Py*O)$_8$I$_3$	335.9	226.5	—	—
Pr(*Py*O)$_8$I$_3$	356.7	202.0	—	—
Nd(*Py*O)$_8$I$_3$	313.5	226.7	107.6	11.96
Tb(*Py*O)$_8$I$_3$	357.8	225.1	—	—
Dy(*Py*O)$_8$I$_3$	348.7	221.7	110.3	11.82
Er(*Py*O)$_8$I$_3$	344.9	217.8	—	—
Yb(*Py*O)$_8$I$_3$	345.7	207.0	110.5	11.91

* In acetonitrile, 1 : 3 electrolytes have a molar conductance in the range 340–420 ohm^{-1} cm^2 mole^{-1} (Ref. [19]).

** In *DMF*, 1 : 3 electrolytes have a molar conductance in the range 200–240 ohm^{-1} cm^2 mole^{-1} (Ref. [19]).

Results and Discussion

The analytical data for all the complexes conform to the general formula Ln(*Py*O)$_8$I$_3$. Molecular weight data in water for a few complexes also support this formula. As in the corresponding perchlorate-salts of the complexes there is no change in the stoichiometry on going from lanthanum to ytterbium. The complexes are all soluble in acetonitrile, dimethyl formamide, dimethyl sulphoxide and chloroform and sparingly soluble in nitromethane and nitrobenzene. All the complexes are hygroscopic unlike the corresponding perchlorate-salts. The colours of all the complexes are given in table 1. Preliminary

Table 3. *Some Important IR Bands and Their Assignments**

*Py*O	La	Pr	Nd	Tb	Dy	Er	Yb	Assignment
1610 m	1619 w	1618 w	1617 w	1619 w	1619 w	1619 w	1619 w	ring deformation
1265 vs	1232 vs	1233 vs	1232 vs	1230 vs	1233 vs	1230 vs	1230 vs	N—O stretching
1166 m	1157 m	1158 m	1158 m	1158 m	1158 m	1158 m	1157 m	C—H in-plane deformation
1014 s	1026 m	1025 m	1028 m	1028 m	1025 m	1028 m	1029 m	ring breathing
883 w	917 w	920 w	920 w	920 w	925 w	920 w	926 w	C—H out-of-plane vibration
841 m	842 vs	842 s	842 s	843 s	844 vs	843 vs	845 vs	N—O bending
759 vs	739 vs	738 m	739 m	739 m	740 vs	739 s	738 s	
	783 vs	783 vs	785 s	784 s	783 vs	784 vs	784 vs	C—H out-of-plane vibrations
	793 m	790 m	—	791 m	792 s	792 m	792 m	
669 s	673 s	671 m	673 m	673 m	675 vs	674 s	673 m	—

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* Spectrum of *Py*O was taken in CCl_4 and in CS_2. Spectra of the complexes were taken in nujol mulls. Abbreviations: vs = very strong, s = strong, m = medium, w = weak. The peak positions are given in wave-numbers (cm^{-1}).

differential thermal analyses of the complexes show that all the complexes melt around 200 °C. The complexes start decomposing around 250 °C with the evolution of iodine. The conductance data in acetonitrile and dimethyl formamide suggest a 1 : 3 electrolytic behaviour[19] of the complexes in these solvents. So a coordination number of eight can be postulated for these complexes in these solvents.

The IR spectra of all the complexes are similar exhibiting no significant dependence upon the metal ion. The N—O stretching vibration which occurs at 1,265 cm^{-1} in *Py*O (in CCl_4) is shifted to lower frequencies by about 30–35 cm^{-1} in the complexes, indicating the coordination through the oxygen of the N—O group. The shift observed in the N—O stretching frequency upon complexation is smaller than that observed in the corresponding perchlorate-salts. This may be an indication of a weaker metal—ligand bond in lanthanide complex iodides compared to the corresponding perchlorates. A similar trend has also been observed in the lanthanide dimethyl sulphoxide complexes[6b, 20].

Table 4. *Proton NMR Spectral Data* *

Signal	*Py*O	La	Pr	Nd	Tb	Dy	Er	Yb	Y
H_α	1.80	1.50	1.25	1.50	0.39	0.14	**	1.45	1.40
$H_\beta + H_\gamma$	2.75	2.57	2.30	2.37	1.67	1.22	2.73	2.67	2.52
H[a]	—	7.52	11.68	—	—	—	—	—	7.10

* Spectra were taken in $CDCl_3$ solutions using *TMS* as the internal reference. Chemical shift data are given in τ.

** Signal is very much broadened.

[a] High-field peak.

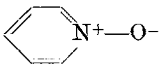
The CH out-of-plane vibration which appears at 759 cm^{-1} in the free ligand (in CS_2) is shifted to about 783 cm^{-1} in the complexes. The shift in the γ-CH vibration has been attributed to the decrease in the electron density of the ring which arises due to the coordination of the ligand to the metal through the oxygen of the N—O group[21]. As in the other *Py*O complexes, the N—O bending vibration does not undergo any shift upon coordination. The CH out-of-plane vibration of the free ligand occurring at 883 cm^{-1} (in CS_2) shifts to higher frequencies by about 40 cm^{-1}. This is in agreement with the observations mady by *Kakiuti* et al. on the *Py*O complexes of transition metal ions[22].

All the complexes are soluble in chloroform unlike the corresponding complex perchlorates. Proton NMR spectral data of all the complexes in $CDCl_3$ solutions are presented in table 4. Spectra of only

$La(PyO)_8I_3$ and $Y(PyO)_8I_3$ are sharp and resolved. Other complexes give broader spectral lines. The multiplet occurring at 1.8 τ in the free ligand is due to the α protons while that occurring at 2.75 τ is due to the β and γ protons. The assignments were made on the basis of the intensities of the signals and on the signals obtained for α, β, and γ-picoline-1-oxides in $CDCl_3$. Apart from the two multiplets occurring at about 1.5 τ and 2.57 τ, $La(PyO)_8I_3$ and $Y(PyO)_8I_3$ show a small peak at about 7.5 τ and 7.1 τ resp. The corresponding peak for $Pr(PyO)_8I_3$ is broadened and occurs at 11.68 τ. The high-field peak for other complexes could not be identified in the frequency region scanned.

The proton NMR spectra show a general downfield shift of H_α, H_β, and H_γ signals upon complexation. A significant shift in the signals of the ligand in $La(PyO)_8I_3$ and $Y(PyO)_8I_3$ (about 20 Hz) indicates a deshielding of the protons of the pyridine ring. In other complexes, which are paramagnetic, the contribution to the shift from the pseudocontact shift is also possible[23]. The presence of only a pure pseudocontact interaction in the paramagnetic complexes studied has been ruled out by comparing the ratios of shifts at different proton sites for various lanthanide complexes[24]. Even those metal ions like Pr^{3+}, Nd^{3+}, Tb^{3+}, and Dy^{3+} which usually give a positive shift[25, 26] give down-field shifts of the ring protons in the complexes studied. The deshielding of the ring protons in the complexes, as shown by $La(PyO)_8I_3$ and $Y(PyO)_8I_3$, may be explained as due to the migration of the electron spin from the ring to the metal due to the coordination of the ligand to the metal ion through oxygen.

Proton NMR data show that the shifts of the H_α signals are larger than those of the H_β and H_γ signals. The fact that the H_β and H_γ signals were not separated upon complexation[27] rules out the possibility of a conjugative mechanism of deshielding. If the deshielding occurs by a conjugative mechanism, the H_α and H_γ signals will be more affected than the H_β signal[28]. The deshielding at the α proton which is higher than that at β and γ protons may indicate an inductive deshielding effect originating from the nitrogen of the pyridine ring. We may expect such an effect if the contribution of the structure



is more than that of the other canonical forms of PyO in the complexes studied.

It is generally believed that the coordination geometry of a lanthanide complex cannot be predicted in solution due to the stereochemical non-rigidity of the coordination sphere in the lanthanide complexes[29]. But the assumption of a single geometry for the lanthanide complexes in solution has been proved to be valid in the calculation of pseudocontact shifts of proton NMR signals using lanthanide shift reagents[23]. Thus we can make a fairly valid assumption that the present complexes exhibit a single geometry in solution. So far only three geometries have been identified for the eight coordinated lanthanide complexes[30]. On the lines of the arguments of *Fay* and *Piper*[31] for the transition metal complexes, we may expect a single set of resonance signals for a square antiprismatic geometry, two for the dodecahedral geometry, and three for the bicapped trigonal prismatic geometry. Since all the complexes studied show only one set of resonance signals, we can expect a square antiprismatic geometry around the metal ion in solution. X-ray diffraction study and fluorescence spectral study of $La(PyO)_8(ClO_4)_3$[13] and $Eu(PyO)_8I_3$[14] resp. have shown a square antiprismatic arrangement of ligating oxygens around the metal ion. As a further proof of the above assumption we have observed two sets of signals for $Yb(\beta\text{-picoline-1-oxide})_8I_3 \cdot 2\,H_2O$ indicating a dodecahedral geometry around the metal ion.

The appearance of a signal at 7.52 τ in $La(PyO)_8I_3$ and at 7.10 τ in $Y(PyO)_8I_3$ may indicate a distortion in the regular geometry in such a way to bring one or two protons of the pyridine ring very near to the metal ion. That the protons responsible for this signal are very near the metal ion is evident from the shift of this signal in the complex $Pr(PyO)_8I_3$. Whereas the α, β, and γ proton signals show only slight shifts in the complex $Pr(PyO)_8I_3$, the signal corresponding to the 7.52 τ signal of $La(PyO)_8I_3$ appears at 11.68 τ in $Pr(PyO)_8I_3$. The disappearance of this signal in other paramagnetic complexes may be due to relaxation effects, or due to pseudocontact shifts which are too large to be observed in the available spectrometer.

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