

## 3-Picoline-N-Oxide Complexes of Rare-Earth Bromides

By

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3-Picoline-N-oxide (3-*PicNO*) complexes of rare-earth bromides of the formula  $MBr_3(3-PicNO)_{8-n} \cdot nH_2O$  where  $n = 0$  for  $M = La, Pr, Nd, Sm, Tb$  or  $Y$  and  $n = 2$  for  $M = Ho$  or  $Yb$  have been prepared. Infrared and proton NMR studies indicate that the coordination of the ligand is through oxygen. Conductance data in acetonitrile suggest that two bromide ions are coordinated to the metal ion. Proton NMR studies suggest a bicapped dodecahedral arrangement of the ligands around the metal ion in solution for Pr(III), Nd(III) and Tb(III) complexes.

### Introduction

In order to study the effect of the anion on the coordination chemistry of the rare-earth metal ions, complexes of dimethyl sulphoxide with various salts have been prepared and characterized in this laboratory<sup>1-4</sup>. We have found that in the presence of bromide ions, rare-earths attain a higher coordination number than in the presence of other halide ions<sup>3</sup>. We have now extended our studies on the complexes of rare-earth bromides with neutral donor ligands to aromatic amine N-oxides. Recently we have prepared and characterized pyridine-N-oxide (*PyO*) complexes of rare-earth bromides with two different stoichiometries by changing the method of preparation<sup>5</sup>. However, attempts to prepare 3-*PicNO* complexes with rare-earth bromides having two different stoichiometries as in the corresponding *PyO* complexes were unsuccessful. Proton NMR studies could be done on the present complexes as these are soluble in chloroform. These studies might be used to find the geometry of these complexes in solution<sup>6</sup>. In the present paper we report the results of the physico-chemical studies on the 3-*PicNO* complexes of rare-earth bromides.

## Experimental

### Materials

Hydrated rare-earth bromides were prepared by dissolving the corresponding oxides in dilute HBr and evaporating the solution on a water-bath.

3-*PicNO*, obtained from Aldrich Chemical Co., U.S.A., was purified by distillation under reduced pressure (146 °C/15 mm).

The solvents dimethylformamide (*DMF*) and acetonitrile, used for conductance studies, were purified by standard methods.

### Preparation of the Complexes

All the complexes reported were prepared by the same method. 0.5 g of the hydrated bromide was dissolved in 1.5 g of 3-*PicNO* by heating the mixture on a water bath. The contents were kept warmed for about 20 min. during which time the crystalline complex slowly separates out. The complex was treated with acetone, filtered through a sintered crucible and washed well with the same solvent to remove any free ligand present. In the case of Ho and Yb complexes it was found necessary to scratch the mixture to initiate the crystallization of the complexes. The complexes were dried in an evacuated desiccator over phosphorus(V) oxide.

### Analyses

The metal content of the complexes was estimated by *EDTA* titrations using xylenol orange as indicator. Bromide content was estimated by *Volhard's* method. 3-*PicNO* was estimated spectrophotometrically at 257 nm using the calibration curve method<sup>7</sup>.

### Physical Methods

IR spectra of the ligand (neat) and of the complexes in both nujol mulls and KBr pellets were recorded using a Carl Zeiss UR-10 spectrophotometer. The principal IR bands and their assignments are given in Table 1.

Conductance measurements were carried out 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 0.001*M* (Table 2).

Proton NMR spectra were recorded in Varian T 60 as well as in Varian HA 100 instruments using CDCl<sub>3</sub> as the solvent and *TMS* as the internal reference. Proton NMR spectra of the complexes are presented in Table 3.

### Properties of the Complexes

The complexes are hygroscopic and are soluble in water, *DMF* and *DMSO*. While the La(III), Pr(III), Nd(III), Sm(III), Tb(III) and Y(III) complexes are very soluble in CHCl<sub>3</sub>, the complexes of Ho(III) and Yb(III)

Table 1. Some Important IR Bands and Their Assignments\* (in  $\text{cm}^{-1}$ )

3-PicNO	La	Pr	Nd	Sm	Tb	Ho	Yb	Y	Assignment
—	—	—	—	—	—	3425 w, b	3408 w, b	—	O—H stretching
—	—	—	—	—	—	3260 w, b	3300 w, b	—	—
1290 vs	1268 vs	1268 vs	1262 vs	1264 vs	1268 vs	1273 vs	1273 vs	1270 vs	N—O stretching
1175 vs	1172 vs	1168 vs	1164 vs	1164 vs	1165 vs	1170 vs	1170 vs	1170 vs	C—H in-plane vibration
1100 w	1100 w	1100 w	1100 w	1100 w	1100 w	1100 w	1100 w	1100 w	C—H in-plane vibration
1021 s	1025 m	1030 m	1025 m	1030 m	1030 m	1028 m	1030 m	1028 m	Ring breathing
952 s	954 s	956 s	952 s	954 s	956 s	956 s	956 s	956 s	C—H out-of-plane vibration
883 m	884 w	886 w	884 w	885 w	884 w	892 w	884 w	884 w	C—H out-of-plane vibration
800 s	800 s	803 s	800 s	802 s	805 s	808 s	808 s	805 s	N—O bending
752 s	752 s	753 s	753 s	754 s	754 s	755 s	755 s	755 s	C—H out-of-plane vibration
675 vs	677 s	675 s	673 s	673 s	676 s	676 s	675 s	676 s	Ring bending

\* "Neat" spectrum of the ligand and mull spectra of the complexes are given. Abbreviations: vs = very strong; s = strong; m = medium; w = weak; b = broad.

are insoluble in this solvent. In acetonitrile also the solubility of the latter complexes is poor. All the complexes are insoluble in benzene and  $\text{CCl}_4$ . The colours of the complexes resemble closely those of the parent salts but are less in intensity.

Table 2. *Conductance Data*

Compound	Molar conductance ( $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ )	
	in $\text{CH}_3\text{CN}$ *	in $\text{DMF}$ **
$\text{La}(3\text{-PicNO})_8\text{Br}_3$	142.8	172.8
$\text{Pr}(3\text{-PicNO})_8\text{Br}_3$	148.8	177.1
$\text{Nd}(3\text{-PicNO})_8\text{Br}_3$	145.1	176.4
$\text{Sm}(3\text{-PicNO})_8\text{Br}_3$	147.7	180.3
$\text{Tb}(3\text{-PicNO})_8\text{Br}_3$	148.1	179.2
$\text{Y}(3\text{-PicNO})_8\text{Br}_3$	150.9	185.1
$\text{Ho}(3\text{-PicNO})_6\text{Br}_3 \cdot 2 \text{H}_2\text{O}$	112.1	161.7
$\text{Yb}(3\text{-PicNO})_6\text{Br}_3 \cdot 2 \text{H}_2\text{O}$	124.8	183.6

\* In acetonitrile, 1 : 1 electrolytes have a molar conductance in the range 120–160  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  (Ref. <sup>8</sup>).

\*\* In  $\text{DMF}$ , 1 : 2 electrolytes have a molar conductance in the range 130–170  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  (Ref. <sup>8</sup>).

Table 3. *Proton NMR Spectral Data* ( $\tau$  p.p.m.)

Compound	$\text{H}_\alpha$	$\text{H}_{\beta+\gamma}$	$\text{CH}_3$
$3\text{-PicNO}$	1.82	2.77	7.65
$\text{La}(3\text{-PicNO})_8\text{Br}_3$	1.40	2.69	7.64
$\text{Pr}(3\text{-PicNO})_8\text{Br}_3$	— 0.26	1.94	7.48
		0.30	2.16
$\text{Nd}(3\text{-PicNO})_8\text{Br}_3$	1.00	2.28	7.65
		2.56	
$\text{Sm}(3\text{-PicNO})_8\text{Br}_3$	—	2.60	7.60
$\text{Tb}(3\text{-PicNO})_8\text{Br}_3$	—	— 3.36	5.65
		— 2.13	
$\text{Y}(3\text{-PicNO})_8\text{Br}_3$	1.54	2.76	7.64

### Results and Discussion

The results of analyses of the complexes conform to the general formula  $M\text{Br}_3(3\text{-PicNO})_{8-n} \cdot n\text{H}_2\text{O}$  where  $n = 0$  for  $M = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Tb}$  or  $\text{Y}$  and  $n = 2$  for  $M = \text{Ho}$  or  $\text{Yb}$ . It is of interest to note that the  $\text{PyO}$  complexes of two different compositions with the metal to ligand ratio 1 : 8 or 1 : 6 could be prepared for all the lanthanide

bromides<sup>5</sup>. But in the present case only either composition is possible for a particular lanthanide.

The conductance data (Table 2) for the complexes in acetonitrile, a solvent of poor donor properties, show that the complexes behave as 1 : 1 electrolytes in this solvent<sup>8</sup>. This suggests that two of the bromide ions are coordinated to the metal ion while the third one is ionic. The conductance data in *DMF* show that the complexes behave as 1 : 2 electrolytes in this solvent<sup>9</sup>. Hence it may be suggested that the two bromide ions coordinated are not identically placed in the polyhedron around the metal ion.

The IR spectra of all the complexes in the 400–1,800  $\text{cm}^{-1}$  range are very similar. Only in the complexes of Ho and Yb, frequencies due to water stretching modes are obtained in the range 3,200–3,500  $\text{cm}^{-1}$ .

The N—O stretching vibration of the ligand occurring at 1,290  $\text{cm}^{-1}$  is shifted to about 1,270  $\text{cm}^{-1}$  in the complexes indicating the complexation of the ligand through 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 *PyO* complexes. This may be due to the fact that the peak at 1,290  $\text{cm}^{-1}$  usually assigned to N—O stretching vibration is not a pure one, but is coupled with  $\nu$  C—CH<sub>3</sub><sup>9</sup>. The N—O bending vibration of the ligand at 800  $\text{cm}^{-1}$  does not undergo any shift upon complexation. The C—H out-of-plane deformations of the ligand are shifted to higher frequencies in the complexes due to the decrease in the electron density of the ring on coordination.

The ligand proton NMR spectrum shows signals at 1.82  $\tau$ , 2.77  $\tau$  and 7.65  $\tau$  which are assignable respectively to  $\alpha$ ,  $\beta + \gamma$  and methyl protons. The La(III) and Y(III) complexes, being diamagnetic, gave sharp signals, while all other complexes, being paramagnetic, showed signals broadened to different extents.

The shift in the positions of the various proton signals in the diamagnetic La(III) and Y(III) complexes represents the deshielding of these protons resulting from the decrease in the electron density of the pyridine ring as a consequence of the coordination of the ligand to the metal ion. While the shifts of the  $\alpha$  and  $\beta + \gamma$  signals are significant, the shift of the methyl signal is negligible. This may be due to the fact that the ring currents do not influence the methyl protons appreciably.

A change in the sign of the isotropic shift on going from Ce(III) to Yb(III) was usually observed in the earlier studies<sup>10</sup>. This has been attributed to either the change in the sign of the  $g_L - 1$  or a change in the structure<sup>11, 12</sup>. But the present complexes show a general down-field shift of the resonances even in the case of Pr(III), Nd(III) and Tb(III) which usually show up-field shifts.

The isotropic shifts of the proton signals in the paramagnetic complexes studied may have contributions from both contact and pseudocontact (dipolar) interactions. Calculation of the value of  $\Delta H_i/g_L(g_L - 1)J(J + 1)$ , where  $\Delta H_i$  is the isotropic NMR shift [the La(III) complex has been taken as the diamagnetic standard] and the other symbols have their usual meaning, shows that the value for the same proton site in different complexes is not the same or nearly the same. Also the ratios of the shifts at different proton sites in different complexes are not the same. These two calculations suggest that both contact and pseudo contact interactions are contributing to the observed isotropic shifts, in the paramagnetic complexes studied.

Proton NMR data may be used in the elucidation of the structure of the lanthanide complexes in solution if we assume that there is no fast intramolecular ligand exchange (or intramolecular structural conversion) in solution. Studies on the complexes of naphthyridine with lanthanide perchlorates show that the intramolecular ligand exchange is slow in these complexes<sup>13</sup>. Studies on the temperature dependence of the NMR spectrum of  $\text{YbI}_3(3\text{-PicNO})_8 \cdot 2\text{H}_2\text{O}$  also show that the intra-molecular ligand exchange is slow in the lanthanide complexes<sup>14</sup>. Our observation of two sets of signals for most of the paramagnetic complexes studied also support this view.

The most probable species present in solution is a ten coordinated species with eight 3-*PicNO* ligands and two bromides in the coordination sphere as shown by the conductance data. Three geometries, a bicapped square antiprism and two polyhedra based on the dodecahedron (bicapped-dodecahedrons of  $D_2$  and  $C_{2v}$  symmetries) have been reported for a ten coordinated lanthanide species<sup>15-17</sup>. Since a different geometric factor,  $(3 \cos^2 \theta_i - 1)r_i^{-3}$  where the symbols  $r_i$  and  $\theta_i$  have their usual meaning, is expected for different geometries, the NMR data can be used in deciding the polyhedron as the isotropic shift has contribution from pseudocontact interaction in the present complexes.

The presence of a single set of resonance signals indicates a square antiprismatic geometry. But when two or more sets of signals are obtained, the geometry of the complex as well as the dispositions of the ligands in the polyhedron can be determined by considering their intensity ratios. In the present case, two sets of signals are obtained indicating either a bicapped-dodecahedron with the cap positions occupied by the two bromides or a bicapped square-antiprism where one or no cap position is occupied by the bromide. The choice between these three possibilities could be made on the basis of the intensity ratios of the signals. While the bicapped dodecahedron with the cap positions occupied by the bromides demands two signals of intensity

ratio 1 : 1, the bicapped square antiprism demands the intensity ratio of either 1 : 7 or 1 : 3 depending upon the position of the coordinated bromides in the polyhedron.

In the Pr(III), Nd(III) and Tb(III) complexes, two sets of signals of intensity ratio 1 : 1 are obtained for ( $\beta + \gamma$ ) protons. In the case of the Pr(III) complex two sets of signals of intensity ratio 1 : 1 are also obtained for the  $\alpha$  protons. In the case of the Nd(III) complex, a broadening of the signal for  $\alpha$  protons has been observed which may be due to the overlap of the two signals expected. However, in the case of the Tb(III) complex the signals due to  $\alpha$  protons could not be obtained in the frequency region scanned. The Sm(III) complex showed a broadened signal for the  $\beta + \gamma$  protons and the signal due to the  $\alpha$  protons could not be observed. However, as the methyl protons are far away from the metal ion, only one set of signals is obtained in all the complexes. The above discussed results indicate a bicapped-dodecahedral geometry with the two cap positions occupied by the bromides for the complexes of Pr(III), Nd(III) and Tb(III) in solution.

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