2, 6-DIMETHYLPYRIDINE-1-OXIDE COMPLEXES OF RARE-EARTH PERCHLORATES

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ABSTRACT

Complexes of rare-earth perchlorates with 2, 6-dimethylpyridine-1-oxide (2, 6-Lutidine-N-oxide, LutNO) of the general formulae, $Ln\ (LutNO)_4\ (ClO_4)_3\ 2H_2O$ *where Ln = La, Pr and Nd, and* $Ln\ (LutNO)_3\ (ClO_4)_3$ *where Ln = Sm, Ho, Er, Yb and Y have been prepared and characterised by chemical analysis, infrared and conductance data. Infrared and conductance data show that two perchlorate groups are coordinated to the metal in all the complexes. Conductance data show that in La, Pr and Nd complexes the two coordinated perchlorate groups are equivalent and in the rest the two are differently bound to the metal. The results have been interpreted in terms of an octahedral structure for La, Pr and Nd complexes and an octahedral bridge structure involving the oxygen atom of the N-O groups for the rest of the complexes.*

Keywords: Rare-earths, Lanthanides, 2, 6-Dimethylpyridine-1-oxide, 2, 6-Lutidine-*N*-oxide.

INTRODUCTION

Previous work on the rare-earth perchlorate complexes of pyridine-1-oxide, 4-, 3- and 2-methylpyridine-1-oxides [1, 2, 3] has shown that the presence of a methyl substituent at 4- and 3-positions in pyridine-1-oxide does not introduce any steric interference at the coordination site, but its presence in the 2-position introduces steric effects which results in a decrease in the coordination number. Thus it was expected that the presence of a methyl substituent at both 2-and 6-positions would further increase the steric hindrance. Hence the rare-earth perchlorate complexes of 2, 6-dimethylpyridine-1-oxide were prepared and characterised by chemical analyses, infrared and conductance data.

EXPERIMENTAL

Materials.—Hydrated rare-earth perchlorates were prepared by dissolving the corresponding rare-earth oxides (99·9 % purity, obtained from the

American Potash and Chemical Corporation, U.S.A.) in minimum amoun of aqueous perchloric acid and evaporating the clear solutions to drynes on a water-bath. 2, 6-Dimethylpyridine-1-oxide was obtained from th Aldrich Chemical Company, U.S.A. Acetone (Analar), acetonitrile an nitrobenzene (purified by standard methods) were used for the conductanc measurements.

Preparation of the Complexes.—The complexes were prepared by th following general method. The rare-earth perchlorate (0·2 gm oxide was mixed well with dimethylpyridine-1-oxide (0·8 gm). To this abou 10 ml of acetone was added followed by 10 ml of chloroform and the mixtur was kept on a water-bath for about 10 minutes with vigorous stirring. Th crystalline precipitate obtained was filtered through a sintered crucible an washed with chloroform. All the complexes were dried over anhydrou calcium chloride under reduced pressure. Since perchloric acid also give a precipitate with the ligand, care was taken to see that no traces of the aci were present along with the rare-earth perchlorate.

Analyses.—The metal content of the complexes was estimated by EDT titrations using xylenol orange as the indicator. The perchlorate conten in a few complexes was estimated by the Kurz method. The ligand wa estimated spectrophotometrically at 253 nm.

Physical Methods.—The infrared spectra of the ligand (neat) and o the complexes, in nujol mull, were recorded with a Carl-Zeiss UR-10 auto matic spectrophotometer. The spectra of the ligand and two of the complexe are given in Fig. 1.

Molar conductance data of the complexes in acetone, nitrobenzene an acetonitrile were obtained using a Siemens conductivity bridge with platinise platinum electrodes. The concentration of the solutions used for the conduc tance measurements were around 0·001 M in the case of acetone an acetonitrile and 0·0005 M in the case of nitrobenzene.

RESULTS AND DISCUSSION

Results of chemical analyses (Table I) of the complexes conform to th general formulae, $\mathrm{Ln\,(LutNO)_4\,(ClO_4)_3 \cdot 2H_2O}$ where Ln = La, Pr and N and $\mathrm{Ln\,(LutNO)_3\,(ClO_4)_3}$ where Ln = Sm, Ho, Er, Yb and Y. Th complexes are soluble in ethanol, methanol, acetone and acetonitrile, bu insoluble in benzene, chloroform and carbon tetrachloride.

The composition of the complexes shows that the presence of meth groups at both 2- and 6-positions introduces considerable steric hindranc and brings down the number of ligand molecules attached to the metal from seven in the 2-methylpyridine-1-oxide complexes [3] to four and three in the present complexes.

TABLE I

Analytical and conductance data

Complex		% Metal	% Perchlorate*	% Ligand	Molar Conductance (mho cm^2 mol^{-1})		
					$C_6H_5NO_2$	$(CH_3)_2CO$	CH_3CN
La $(LutNO)_4 (ClO_4)_3 \cdot 2H_2O$	Found	14·48	29·74	51·42	35·0	172·3	406·6
	Calc.	14·39	30·01	50·97			
Pr $(LutNO)_4 (ClO_4)_3 \cdot 2H_2O$	Found	14·40	..	51 38	36·2	165·8	403·4
	Calc.	14·56	..	50·87			
Nd $(LutNO)_4 (ClO_4)_3 \cdot 2H_2O$	Found	15·05	..	50·74	32·3	165·0	412·6
	Calc.	14·86	..	50·67			
Sm $(LutNO)_3 (ClO_4)_3$	Found	18·13	..	46·00	..	118·0	236·0
	Calc.	18·39	..	45·11			
Ho $(LutNO)_3 (ClO_4)_3$	Found	19·82	35·58	45·70	..	124·2	219·8
	Calc.	20·01	35·86	44·33			
Er $(LutNO)_3 (ClO_4)_3$	Found	20·20	..	44·00	..	126·9	220·7
	Calc.	20·03	..	44·20			
Yb $(LutNO)_3(ClO_4)_3$	Found	20·70	35·40	44·14	..	127·7	225·6
	Calc.	20·58	35·50	43·89			
Y $(LutNO)_3 (ClO_4)_3$	Found	11·94	..	48·08	..	125·0	227·7
	Calc.	11·76	..	48·78			

* Perchlorate was estimated only in a few complexes.

The infrared spectra of all the complexes are similar and do not show any appreciable dependence on the central metal ion. The N–O stretching frequency of the ligand occurring at 1258 cm^{-1} shifts to lower frequencies in the complexes, indicating the coordination of the ligand to the metal through the oxygen of the N–O group. The N-O stretching vibration of the La, Pr and Nd complexes shows a single band, but in the other complexes it shows appreciable splitting. This shows that all the ligand molecules in the former group of complexes are equivalently bound to the metal, but in the latter they are bound to the metal in two different ways.

The band due to the N-O bending mode occurring at 846 cm^{-1} in the ligand undergoes a slight shift to the higher frequencies in the complexes. This

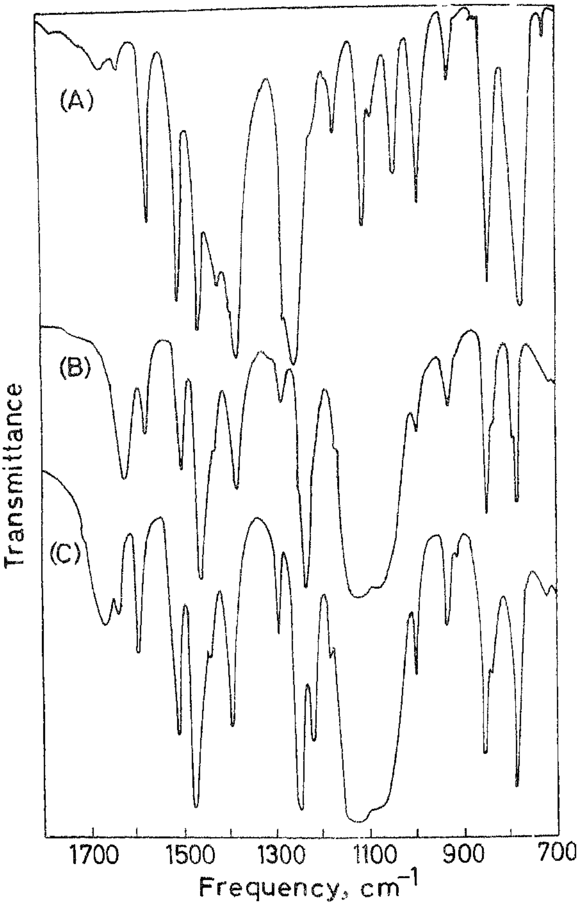

FIG. 1. Infrared spectra of (A) 2, 6-LutNO (Neat), (B) [Nd (LutNO)$_4$ (ClO$_4$)$_2$] ClO$_4$·2 and (C) [Ho (LutNO)$_3$ (ClO$_4$)$_2$] ClO$_4$.

shows that the effect of the bonded metal atom on the N–O group which would cause a vibrational shift to higher frequencies slightly outweighs the effect due to the decrease in the double bond character of the N–O bond arising from coordination which tends to lower the frequency [4].

The C–H out-of-plane bending vibration appearing at 780 cm^{-1} in the ligand also shows slight shifts to higher frequencies in the complexes due to the drainage of the electron density from the ring to the metal due to complex formation [4].

The complexes of La, Pr and Nd show a band around 3500 cm^{-1} which is attributed to the O–H stretching vibrations of the water molecules. The occurrence of this band at comparatively higher frequencies and the absence of any new band around 700 cm^{-1} in the spectra of these complexes suggests that the water molecules are not coordinated to the metal. These complexes also show a band in the region 1600–1650 cm^{-1} attributed to the bending mode of the water molecules. A similar band (weak to medium in intensity) also appears in the spectra of the rest of the complexes which do not contain any water molecules. This band is probably due to water which is absorbed during sampling.

The ionic perchlorate group having the T_d symmetry gives a strong and broad band around 1100 cm^{-1} (ν_3 mode) in the infrared spectrum. If the perchlorate group is coordinated and if the symmetry is lowered to C_{3v} the broad ν_3 band is split into two peaks. In the present complexes the ν_3 band due to ClO_4 is split into two peaks suggesting the presence of coordinated perchlorate groups in these complexes. The coordination of the perchlorate group to the rare-earth metal, although known in a few cases [5], is very rare.

The conductance data in acetone show that the complexes behave as 1 : 1 electrolytes in this solvent [6]. The conductance data in nitrobenzene were obtained only for the La, Pr and Nd complexes, since the other complexes were insoluble in this solvent. Even in this solvent the three complexes behave as 1 : 1 electrolytes [6]. This suggests that two of the perchlorate groups are coordinated and the third one is ionic. Thus the coordination number appears to be six for La, Pr and Nd, and five for the rest.

In acetonitrile, the La, Pr and the Nd complexes show 1 : 3 electrolytic behaviour [6], possibly due to the displacement of the coordinated perchlorate groups by the solvent molecules. The displacement of both the perchlorate groups suggests that they are bound to the metal in the same fashion. From the infrared and conductance data the possible polyhedron for these three complexes could be an octahedron with the four ligand molecules in one plane and the two perchlorate groups above and below the plane. With such a structure the equivalence of the four ligand molecules and also of the two perchlorate groups can be explained.

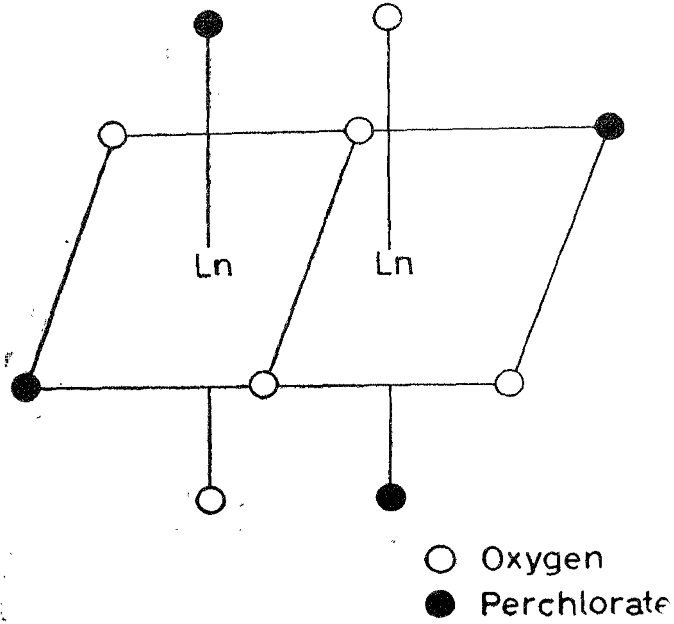

FIG. 2.

The complexes of Sm, Ho, Er, Yb and Y, however, show a 1 :2 electrolytic behaviour in acetonitrile. This shows that only one of the two perchlorate groups which were coordinated is displaced. This may be due to the fact that the two coordinated perchlorate groups are not equivalently bound to the metal. This conductance behaviour and the splitting of the N–O stretching band in the infrared spectra of these complexes can be explained on the basis of a square pyramidal or a trigonal bipyramidal structure with one perchlorate group in the horizontal plane and the other at the apex. But the lanthanide ions have a tendency to attain high coordination numbers and such five coordinated complexes are not known for the lanthanides. Hence the results could be better explained on the basis of an octahedral bridge structure involving the oxygen of the N–O groups as shown in Fig. 2. The two N–O stretching frequencies observed in the infrared spectra could be explained as arising from the bridged and the terminal ligand molecules. Bridge structures are known for a number of lanthanide β-diketonates [7] and also for a number of complexes of aromatic amine-N-oxides [8]. Such bridge structures have also been postulated for the dimethylpyridine-1-oxide complexes of lanthanide iodides [9]. Recalculation of the conductance data employing the dimeric structure shows 1 : 2 and 1 : 4 electrolytic nature of these complexes in acetone and acetonitrile, respectively.

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