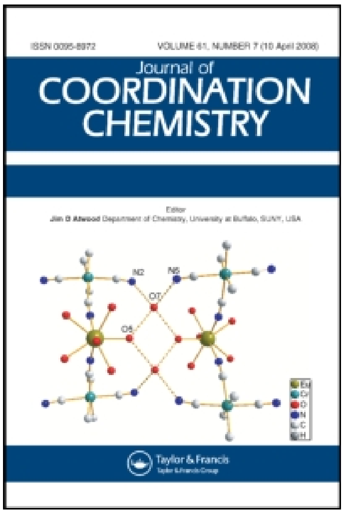

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COMPLEXES OF LANTHANIDE PERCHLORATES WITH N,N,N′,N′-TETRAMETHYL PYRIDINE DICARBOXAMIDE

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The synthesis and a study of the physical properties of lanthanide perchlorate complexes with N,N,N′,N′ Tetramethyl pyridine dicarboxamide of the general formula $Ln(ClO_4)_3$ (tmpd)$_3$ where Ln = La–Yb and Y and tmpd = N,N,N′,N′ Tetramethyl pyridine dicarboxamide have been made. Conductance and infra-red data show that all the perchlorates are ionic. Infra-red spectral data suggest that the co-ordination of the ligand occurs through the oxygen atoms of the two amide moieties and through the pyridine nitrogen. Proton NMR spectra of the diamagnetic Y and La complexes confirm bonding through the pyridine nitrogen. Electronic spectral data for the Pr, Nd, Ho and Er complexes are also reported. A co-ordination number of nine has been assigned for all the complexes.

INTRODUCTION

While a large number of complexes of lanthanides with neutral unidentate and bidentate ligands have been reported in the literature, complexes with tridentate ligands seem to be restricted to those of terpyridyl type of ligands.[1,2]

In this paper we report for the first time the preparation and characterization of lanthanide perchlorate complexes with N,N,N′,N′ Tetramethyl pyridine dicarboxamide (tmpd) a potentially tridentate ligand capable of bonding through two amide groups and the pyridine nitrogen, all the three donor centers being situated in a favourable position, for the ligand to function as a tridentate chelating ligand to a metal ion. The prepared complexes have been characterized by chemical analysis, melting point, conductance measurements, infrared and visible spectra and proton NMR data (for diamagnetic complexes only).

EXPERIMENTAL

Materials:

Lanthanide oxides (99·9% pure) were purchased from Indian rare-earths limited, Kerala State. Pyridine 2,6 dicarboxylic acid was a 1964 gift from the Midland Tar Distillers Ltd., England. All other chemicals used were reagent grade. Solvents were purified by standard methods.

Preparation of the Ligand:

Pyridine 2,6 dicarboxylic acid was refluxed with excess of thionylchloride in the presence of a few drops of N,N dimethylformamide catalyst for two hours. Excess thionyl chloride was removed azeotropically with benzene to obtain the crude acid chloride which was used as such in the next step. The pyridine 2,6 dicarbonyl chloride was taken in benzene and reacted with greater than four fold excess of dimethyl amine (99%) in benzene. After standing for 10–12 hours the amine hydrochloride was filtered off and the benzene concentrated to give the crude tetramethyl amide. Recrystallization from ethylacetate provided pure white crystals in 60% yield m.p. 149°C (lit[3] 144–6°C).

Preparation of Hydrated Lanthanide Perchlorates:

Hydrated lanthanide perchlorates were prepared by dissolving the corresponding oxide in less than minimum of 40% perchloric acid. The undissolved oxide was filtered off and the filtrate evaporated to dryness on a steam bath when the perchlorate salt crystallized.

Preparation of the Complexes

To the hydrated lanthanide perchlorate (1 m mole) dissolved in 20 ml ethyl acetate the ligand (4 m mole) in 30 ml hot ethylacetate was added dropwise with stirring. An immediate precipitation of a sticky mass was noticed. The mixture was refluxed on a steam bath for four to five hours. The precipitated complexes were filtered from the hot solution in a sintered crucible (G–3) and washed three times with 10 ml portions of hot ethylacetate and then with diethylether. The complexes were dried in vacuo over calcium chloride for 24 hours.

Analysis:

Metal content of the complexes was estimated by complexometric titration with EDTA using xylenol orange as indicator.[4] Perchlorate was estimated gravimetrically as nitron perchlorate. Ligand content was found spectrophotometrically in water using the calibration curve method (at 268 nm).

Physical Measurements:

Infra-red spectra were obtained in nujol mulls on a Carl-Zeiss UR–10 spectrophotometer in the region 4000–400 cm^{-1}. Electronic spectra in the region 360–750 nm were recorded on a Beckmann Model 25 Spectrophotometer and also on a Unicam SP 700 Spectrophotometer. Spectra in solution were run in acetonitrile and in the solid state in nujol mulls smeared on Whatman filter paper pieces. Conductivity measurements were performed using a Siemann's conductivity bridge with immersion (type LTA) cell previously calibrated with standard KCl solutions. Proton NMR spectra for the diamagnetic Y and La complexes were recorded on a Varian T–60 spectrometer (60 MHz) using CH_3CN as solvent and TMS as the internal standard.

RESULTS AND DISCUSSION

The analytical data and melting points of the complexes are summarized in Table I along with the electrolytic conductance values in acetonitrile. The analytical results show that all the complexes have the general formula $Ln(tmpd)_3\ (ClO_4)_3$. The complexes are all non-hygroscopic and soluble in methanol, ethanol, acetone, acetonitrile, dmf and dmso but insoluble in chloroform, carbontetrachloride and benzene.

Conductivity data for the complexes in acetonitrile, a solvent of poor donor property, are in the range expected for 1:3 electrolytes.[5] This indicates that all the perchlorate groups are ionic.

Infra-red spectra showed no absorptions attributable to lattice or co-ordinated water in line with the analytical data. Essentially there are three regions of importance in the infrared spectra of the present complexes. They are (a) perchlorate group vibrations, (b) amide group vibrations and (c) pyridine ring vibrations. The infra-red spectral data along with tentative assignments are presented in Table II.

The regions of perchlorate absorptions confirm the conductivity evidence of the ionic nature of the perchlorate group. A strong band at 625 cm^{-1} and a very strong band around 1095 cm^{-1} neither of which are split are indicative of perchlorate groups with Td symmetry and these bands are assignable to the

TABLE I

Melting points, analytical and conductance data for the complexes of the general formula $Ln\ (Tmpd)_3\ (ClO_4)_3$

Ln	Melting[a] point (°C)	% Metal Calcd.	Found	% Anion Calcd.	Found	% Ligand Calcd.	Found	Molar conductivity[b, c] Con cn.	Ohm^{-1}cm^{2}mole^{-1}
Y	274	8.47	8.41	28.42	28.27	63.11	62.63	0.981	370
La	275	12.63	12.50	27.12	26.85	60.24	59.26	1.023	379
Pr	282	12.78	12.60	27.07	26.73	60.13	59.28	1.043	376
Nd	290	13.06	12.86	27.00	26.82	59.96	59.29	1.056	372
Tb	284	14.20	14.16	26.64	27.03	59.17	59.00	0.964	411
Dy	274	14.46	14.40	26.56	26.25	58.99	59.55	1.148	374
Ho	287	14.64	14.69	26.50	26.94	58.84	58.32	1.039	381
Er	281	14.82	14.61	26.44	26.32	58.73	58.69	1.110	387
Yb	281	15.25	15.28	26.31	26.64	58.43	58.21	1.084	365

[a] Melting point with decomposition.

[b] Conductance in Acetonitrile solution at 23°C.

[c] In acetonitrile 1:3 electrolytes have a molar conductance in the range 340–420 ohm^{-1} cm^2 mole^{-1} (Ref. 5).

TABLE II
I.R. spectral data and tentative assignments

Y	La	Pr	Nd	Tb	Dy	Ho	Er	Yb	Ligand	Assignment
1632 vs	1638 vs	1638 vs	1625 vs	1630 vs	1630 vs	1630 vs	1630 vs	1632 vs	1640–1660	C = O stretching
1600 m	1610 m	1610 m	1595 m	1595 s	1595 m	1595 m	1595 m	1600 m	1595 m	Pyridine
									1580 sh	C = C and C′ = N stretching
1515 s	1520 s	1522 s	1512 s	1515 m	1515 m	1512 s	1515 s	1510 s	1520 s	Pyridine C = C and C = N stretching
1438 m	1420–1430	1418–1440	1410–1432	1415–1430	1430 s	1430 m	1430 m	1432 m	1430 w	C–N stretching and
1418 sh	1410 wsh				1412 sh	1415 sh	1415 wsh	1415 wsh	1415 m	CH_3 deformation
									1400 w	
1265 m	1270 m	1270 m	1265 m	1265 m	1265 m	1265 m	1265 m	1265 m	1270 m	N–CH_3 stretching
–	–	–	–	–	–	–	–	–	1288 w	
1190 m	1190 m	1192 m	1185 m	1190 m	1188 m	1190 m	1190 m	1190 m	–	
1155 m	1160 m	1158 m	1155 m	1155 m	1155 m	1155 m	1155 m	1155 m	1160 m	Ring CH deformations
1115 sh	1100 vsbr	1100 vsbr	1095 vsbr	1115 wsh	1115 sh	1100 sbr	1110 sh	1100 sbr	1090 s	ν_3ClO_4 and pyridine
1100 s				1095 sbr	1095 sbr		1095 sbr			CH deformation
–	–	–	–	–	–	–	–	–	1060 w	
1020 w	1022 w	1025 sw	1020 w	–	–	–	–	–	1010 w	CH_3 rock and ring
1015 m	1015 m	1015 m	1010 m	1015 m	1015 m	1015 m	1015 m	1015 m	995 m	breathing
–	–	–	–	–	–	–	–	–	915 w	CH out of plane bending
845 m	845 m	845 m	842 m	845 m	845 m	845 m	845 m	840 m	840 s	
									810 w	
772 m	772 m	772 m	770 m	772 m	772 m	775 m	775 m	772 m	775 s	CH out of plane bending
720 m	720 m	720 m	718 m	720 m	720 m	720 m	720 m	718 m	740 m	CH out of plane bending
690 sh	692 sh	692 sh	690 sh	–	–	–	–	–	–	
675 s	680 s	680 s	677 s	675 s	680 s	680 s	680 s	682 s	687 s	Ring bending
645 m	645 m	645 m	643 a	645 w	645 w	645 w	645 w	647 m	632 s	Pyridine ring in-plane deformation
625 s	627 s	627 s	625 s	625 s	625 s	625 s	625 s	625 s	–	ν_4ClO_4
522 w	522 wbr	522 wbr	525 wbr	527 wbr	530 w	532 w	532 w	532 wbr	500 m	
430 m	432 s	432 s	432 s	437 m	437 m	437 m	437 m	440 m	422 w	Pyridine ring out of plane deformation

Abbreviations: vs = very strong; s = strong; m = medium; w = weak; br = broad; sh = shoulder

ν_4 and ν_3 modes respectively. If perchlorate groups were co-ordinated the symmetry would be lowered from Td to C_{3v} and a splitting of the ν_3 band would be expected along with the activation of ν_1 mode.

Amide groups are capable of co-ordinating to a metal ion either via the oxygen atom or the nitrogen. From a study of the infra-red spectra it is easy to distinguish between either of the two modes of bonding.

Bonding via the oxygen atom of the amide group should result in a drainage of the electron density from the C = O group, hence a lowering of the force constant of the C = O bond and consequently a decrease in the infra-red stretching frequency of the C = O in the complexes compared to the ligand. In the present complexes a decrease of 12–20 cm^{-1} in the C = O stretching frequency confirms bonding of the amide group via the oxygen atom.

In general only small shifts in the vibrational frequencies of the pyridine rings are observed on complex formation.[6-9] In the complexes of tmpd, the pyridine ring vibrations of the ligand are not very much altered on co-ordination. However evidence of co-ordination of the pyridine ring nitrogen is manifested in the changes in the ring breathing, in-plane and out of plane ring deformation modes in going from the ligand to the complexes. The ring breathing mode at ca 995 cm^{-1} in the ligand disappears and a band at 1015 cm^{-1} appears in the complexes. The assignment is based on the general contour of the band. Also a similar shift of the corresponding band has been observed in the terpyridyl complexes.[10] The CH out of plane bending at 740 cm^{-1} in the ligand shifts to about 720 cm^{-1} in the complexes. The in-plane ring deformation at 632 cm^{-1} in the ligand is shifted to ca 645 cm^{-1} and the out of plane deformation at 422 cm^{-1}, to ca 435 cm^{-1} in the complexes. These bands have been found to be sensitive to metal ion co-ordination.[9]

Additional evidence for the bonding of the pyridine moiety is obtained from the nmr spectra of the diamagnetic complexes in acetonitrile. Due to interference by the solvent peak spectra were run upto 6τ only. The nmr spectrum of the ligand reveals a seven line AB_2 complex pattern the analysis of which gives the values τ_β 2·47, τ_γ 2·03, $J_{\beta\gamma}$ ± 7·67 and $J/\Delta\nu$ 0·295. In the La complex the τ_β and τ_γ are 1·90 and 1·65 respectively, $J_{\beta\gamma}$ is ± 8·33 and $J/\Delta\nu$ is 0·555, the seven line AB_2 pattern being maintained. In the Y complex τ_β and τ_γ are 1·94 and 1·73 respectively $J_{\beta\gamma}$ is ± 8·33 and $J/\Delta\nu$ is 0·667, the AB_2 pattern being retained again. A downfield shift of 34 Hz of the β and of 23 Hz of γ protons in the La complex and of 31·5 Hz and 18 Hz of the β and γ protons in the Y complex compared to the ligand amply demonstrate deshielding of the pyridine ring protons. This deshielding is attributable to the drainage of electron density from the pyridine ring due to bonding to the metal ion via the nitrogen atom.

That the co-ordination of the ligand in solution and solid state is similar is demonstrated by the shapes of the electronic spectra of the Pr, Nd, Er and Ho complexes in the visible region. The f-f electronic transitions of Ln (III) ions have been observed to be influenced by the nature of the surroundings.[11,12] Three types of changes are generally observed, (i) spectral shift, (ii) line splitting, (iii) change in intensity. Enhancement of intensity of certain "hypersensitive bands" ($\Delta J \leqslant \pm 2$) by factors of two to four compared to the aquo ion has been observed. This has been ascribed to quadrupolar effects due to an inhomogeneous electrostatic field and changes in symmetry around the In (III) ion.[13] Taking the aquo ion as the standard, all ligands except the fluoride ion have been found to cause a slight red shift of the bonds, due to alterations in the interelectronic repulsion parameters (F_k) in the complexes. It has been suggested by Jϕrgensen that the extent of shift of the spectral lines represents the nephelauxetic effect and could be used as a measure of Metal-ligand covalent bonding.[14] Sinha has proposed a δ scale to express the covalency of the M–L bond in the complexes of lanthanides.[12] The Sinha's parameter of covalency (δ) in percent is expressed as $\delta = 1 - \beta/_\beta$. 100 where β is the average value of the ratio $\nu_{complex}/\nu_{aquo}$. Positive values of δ have been taken as indicative of covalent bonding and negative of ionic bonding.

Electronic spectral data for the Pr(III), Nd(III), Ho(III) and Er(III) complexes along with ϵ values in acetonitrile solutions are presented in Table III. Since the spectra of the complexes in nujol mulls are similar in shape and position (± 5 nm) the calculations of β and δ have been made from the solution spectral data. The δ values are also given in Table III.

The values of the Sinha's covalency parameter (δ) for the Nd(III) ion in the tmpd complexes are less compared to the values in terpyridyl and bipyridyl complexes reported by Sinha.[11] A lower ligand field strength for the tmpd ligand compared to terpyridyl can be derived from this data. The enhanced intensity of the hypersensitive bands could also be explained as due to the greater basic character of the tmpd ligand compared to the aquo ion.

The shapes of hypersensitive bands have been

TABLE III
Electronic spectral data of Pr, Nd, Ho and Er complexes

	Pr			*Nd*			*Ho*			*Er*	
J level	Energy (KK)	ε	J level	Energy (KK)	ε	J level	Energy (KK)	ε	J level	Energy (KK)	ε
$^3P_2$	22.27	9.68	$^4G_{9/2}$	19.45	2.06	$^5G_6$	27.63	14.29	$^4G_{11/2}$	26.17	16.84
$^3P_1$	21.05	3.59	$^4G_{7/2}$	19.01	5.15	$^3K_6$	22.22	13.52	$^4F_{3/2}$	22.47	1.33
$^3P_0$	20.49	2.60	$^4G_{5/2}$	17.04	14.41	$^5F_1$ $^5G_6$	22.03	19.82	$^4F_{5/2}$	22.13	1.11
$^1D_2$	16.62	2.99	$^2G_{7/2}$	17.18	12.61	$^5S_2$ $^5F_4$	18.59	6.64	$^4F_{7/2}$	20.32	1.99
						$^5F_5$	15.52	7.38	$^2H_{11/2}$	19.04	7.09
									$^4F_{9/2}$	15.31	1.77
δ; 0.786			δ; 1.307			δ; 0.2			δ; 0.555		

related to the co-ordination number by Karraker.[15,16] The shapes of the hypersensitive bands in the present complexes are almost similar to the shapes of bands of Ln(III) ions in dilute aqueous solutions where the co-ordination number of Ln(III) ions is assumed to be nine.[17] Also the shapes of the hypersensitive $^4G_{5/2}, ^2G_{7/2} \leftarrow ^4I_{9/2}$ band in the Nd(III) tmpd complex resembles that of Nd(tso)$_9$(PF$_6$)$_3$ complex reported by Serra et al.[18]

CONCLUSIONS

The analytical, conductivity and ir spectral data for the tetramethyl pyridine dicarboxamide complexes of lanthanide perchlorates along with the nmr spectra of the dimagnetic complexes and the electronic spectra in solution and solid state of the Pr, Nd, Ho and Er complexes indicate that the three tmpd ligands are bound to the lanthanide ions in a tridentate fashion with a ONO donor sequence around the metal ion. A probable co-ordination number of nine for all the lanthanides is assigned in the complexes.

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