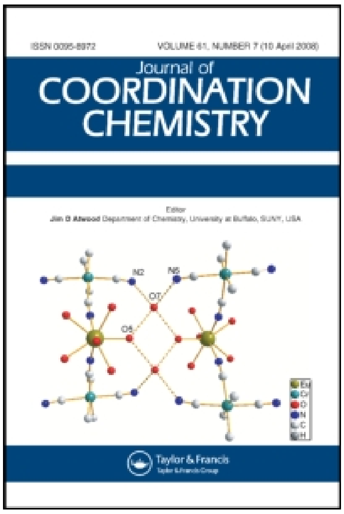

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NONAMETHYLIMIDODIPHOSPHORAMIDE ADDUCTS OF LANTHANIDE PERCHLORATES

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The preparation of compounds with the general formula $Ln(ClO_4)_3.3NIPA$ (where Ln=La–Lu, NIPA = nonamethylimidodiphosphoramide) is reported. The vibrational spectra support a Td symmetry for the perchlorate ion. Infrared spectra in the 1330 to 400 cm^{-1} range suggest that coordination takes place via both oxygen atoms. The x-ray powder diffraction patterns indicate the isomorphism of the lanthanide series and the conductance data in nitromethane and nitrobenzene agree with the 1:3 electrolyte type.

INTRODUCTION

The coordination chemistry of rare earths with potentially bidentate phosphoryl oxygen ligands has received attention only recently with octamethylpyrophosphoramide[1,2] bis(diisopropoxyphosphinil)methane,[3] and diphosphonates.[4] These publications report both oxygens bonding the metal simultaneously or bridging two metals.

Nonamethylimidodiphosphoramide (NIPA) resembles the structure of those ligands, presenting the $>N(CH_3)$ group between the PO bonds. The ability of the NIPA to form stable complexes with both transition and non-transition metals has been investigated extensively,[5–13] where both oxygens are bidentate to the metals.

In an attempt to obtain information about the nature of the complexes formed between NIPA and the lanthanide perchlorates, we have prepared a series of complexes, $Ln(ClO_4).3NIPA$ (Ln=La–Lu). Here we report some results on their synthesis and properties based on elemental analysis, x-ray patterns, vibrational spectra and molar conductances in nitromethane and nitrobenzene.

EXPERIMENTAL

The hydrated lanthanide perchlorates were prepared as described previously.[14] NIPA, $[(CH_3)_2N]_2P(O)N(CH_3)P(O)[N(CH_3)_2]_2$, was prepared following the literature methods,[6,15] and had a melting range of 58–59°C. The ligand was handled in a dry-box due to high hygroscopicity.

The solvents were purified and converted to an anhydrous form before using.

Preparation of the complexes

The hydrated metal salts were dissolved in ethanol and the solution was evaporated in vacuo at room temperature. The solid was then dissolved in acetone and heated. To this stirred solution was added dropwise an excess of the ligand (4:1) in acetone. The resulting solution was refluxed for two hours and cooled to room temperature.

After standing, the addition of dry ethyl ether forced crystals out of the solution. These were collected by filtration, washed twice with the same solvent and finally dried in a vacuum dessicator over phosphorus pentoxide for several hours.

Analytical Procedure

The lanthanide was determined by titration with Edta using xilenol orange as indicator. Phosphorus was determined colorimetrically using an established method.[16] Nitrogen was determined as described previously[14] or together with carbon and hydrogen by a microanalytical procedure performed in the Instituto de Química Universidade de São Paulo.

Measurements

All spectra or measurements were obtained under the same conditions used previously.[17]

TABLE I

Summary of analytical results for the compounds of formula $Ln(ClO_4)_3.3NIPA$

	Analysis (%)									
	Lanthanide		Phosphorus		Carbon		Hydrogen		Nitrogen	
Ln	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
La	10.40	10.15	13.92	13.97	24.29	24.07	6.12	6.31	15.73	15.96
Ce	10.48	10.46	13.90	14.04	24.27	24.48	6.11	6.20	15.72	15.65
Pr	10.54	10.32	13.90	14.02	24.25	23.97	6.11	5.90	15.71	15.81
Nd	10.76	10.38	13.87	13.97	24.19	24.37	6.09	6.00	15.67	15.50
Sm	11.16	11.01	13.80	13.84	24.08	23.83	6.06	6.13	15.60	15.45
Eu	11.27	11.17	13.78	13.95	24.05	24.23	6.06	6.25	15.58	15.69
Gd	11.62	11.49	13.73	13.74	23.96	23.94	6.03	6.31	15.52	15.49
Tb	11.73	11.55	13.71	13.77	23.92	23.91	6.02	6.24	15.50	15.48
Dy	11.96	12.09	13.67	13.56	23.87	23.78	6.01	5.94	15.46	15.68
Ho	12.12	11.97	13.65	13.55	23.82	23.80	6.00	6.08	15.44	15.71
Er	12.27	12.29	13.63	13.59	23.78	23.34	5.99	5.86	15.41	15.38
Tm	12.37	12.52	13.61	13.72	23.75	23.60	5.98	5.85	15.39	15.20
Yb	12.63	12.85	13.57	13.47	23.68	23.26	5.96	5.97	15.34	15.37
Lu	12.71	12.49	13.55	13.42	23.65	23.59	5.95	5.82	15.32	15.23

RESULTS AND DISCUSSION

The compounds are only slightly hygroscopic, with their melting or decomposition points higher than 230° C. In Table I the analytical results are listed for all the compounds considered in the present work. The X-ray diffraction patterns show the existence of only one isomorphic form.

The infrared spectral data of NIPA and its complexes in the 1330 to 400 cm^{-1} range are given in Table II, together with a tentative assignment. Four Raman active frequencies for the perchlorate ion are observed at 930, 458, 1100 and 630 cm^{-1} (Table III). They do not show the splitting of the ν_2, ν_3 and ν_4 bands which would be expected from Td symmetry lowering,[18] caused by the coordination of the metal-to-perchlorate as well as by the lattice effect.[19] The i.r. spectra confirm the existence of the ionic perchlorate with Td symmetry, with the two well defined active bands at 1095 and 625 cm^{-1}.

The PO and CN stretching vibrations coincide in a broad infrared absorption band found at 1205 cm^{-1} in the free ligand. It has been noted that after coordination via oxygen atoms this band splits into a strong one at ~1200 cm^{-1}, the CN stretching, followed by a medium intensities peak at ~1170 cm^{-1},

TABLE III

Vibrational frequencies of the perchlorate ion (cm^{-1})

	Raman				I.R.	
$Ln(ClO_4)_3 \cdot 3NIPA$	$\nu1$	$\nu2$	$\nu3$	$\nu4$	$\nu3$	$\nu4$
La	932vs	459w	1097vw	627vs	1095vs	625m
Ce	930vs	459w	1095vw	629vs	1092vs	627m
Pr	934vs	459w	1090vw	629vs	1094vs	624m
Nd	932vs	457w	–	629vs	1090vs	626m
Sm	930vs	457w	1099vw	629vs	1095vs	627m
Eu	930vs	457vw	–	630vs	1093vs	625m
Gd	930vs	458w	1100vw	630vs	1096vs	625m
Tb	931vs	455w	1100vw	630vs	1095vs	625m
Dy	930vs	460w	–	629vs	1093vs	625m
Ho	930vs	459w	1090vw	630vs	1095vs	622m
Er	930vs	457w	1098vw	630vs	1092vs	625m
Tm	930vs	460vw	–	634vs	1095vs	627m
Yb	930vs	458w	1100vw	630vs	1095vs	622m
Lu	930vs	458w	–	630vs	1094vs	625m

v = very, s = strong, m = medium, w = weak.

TABLE II
Infrared spectra of $Ln(ClO_4)_3.3NIPA$ complexes (cm^{-1})

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	NIPA	Assignment
1308s	1305s	1305s	1305s	1305s	1305s	1307s	1305s	1308s	1305s	1305s	1305s	1305s	1305vs	1308s	CH_3 rocking
1187sh	1185sh	1185sh	1183sh	1187sh	1187sh	1187sh	1187sh	1187sh	1187sh	1186sh	1188sh	1188sh	1186sh	1205s,b	CN stretching
1170sh	1170sh	1171sh	1170sh	1172sh	1170sh	1174sh	1173sh	1171sh	1170sh	1172sh	1170sh	1172sh	1170sh		PO stretching
1153vs	1152vs	1152vs	1152vs	1153vs	1155vs	1165vs	1160vs	1155vs	1155vs	1158vs	1158vs	1158vs	1158vs	1152shw	CH_3 rocking
1062sh	–	1062sh	1062sh	1062sh	–	1062sh	1062sh	1060sh	1060sh	1060sh	1060sh	1062sh	1062sh	1065m	CN stretching
1038w	1039w	–	1040w	1038w	–	1040w	1038w	–	1040w	1040w	1045sh	1047w	1045w	–	
1000vs	1000vs	999vs	1000vs	1002vs	1000vs	1002vs	1003vs	1000vs	1000vs	1000vs	1000vs	1000vs	1000vs	993vs	PN stretching
898s	899s	900s	897s	899s	898s	902s	900s	899s	900s	900s	905s	902s	905s	895s	PN stretching
764s	764s	763s	763s	764s	765s	765s	767s	764s	765s	764s	765s	7765s	765s	756s	PN stretching
738w	740w	738w	742w	738w	740w	740w	740w	738w	742w	740w	738w	740w	740w	740m	PN stretching
–	720w	–	–	718w	720w	718w	720w	720w	–	720w	–	–	720w	–	
669w	669w	666w	665w	669w	670w	670w	668w	667w	670w	670w	668w	668w	668w	663m	PN stretching
528m	530m	528m	529m	530m	530m	532m	532m	530m	530m	532m	535m	531m	534m	508m	PO bending
500m	500m	497m	498m	498m	498m	498m	498m	498m	495m	498m	500m	499m	497m	496m	CNP bending
455w	452w	450vw	455w	458vw	452vw	455vw	452vw	452w	452vw	455m	455vw	455vw	455vw	443m	CNP bending

v = very, s = strong, m = medium, w = weak, sh = shoulder, b = broad

which corresponds to the PO stretching.[9,10] The same characteristic bands have been observed for $La(NO_3)_3.2NIPA$ compounds.[20]

Our results however, show the presence of a lower frequency broad peak with shoulders in the complexes. Assuming the sequence of bands assigned in Table II we have attributed the first shoulder at 1187 cm^{-1} to CN stretching and the second one at 1170 cm^{-1} to PO stretching. The CH_3 rocking band overlaps with these shoulders, thus contributing to the broad peak.

The bond between oxygen and the metal ion tends to withdraw electron density from the PO bond and thus decrease its bond order, lowering the stretching frequency by 35 cm^{-1}. In this case the nitrogen lone pair can be delocalized into the available $d\pi$ orbitals on the phosphorus, increasing the PN bond order causing the stretching bands to shift to higher frequencies.[5,9,10] Although the maximum shift is only of the order of 11 cm^{-1}, the band at 740 cm^{-1} in the free ligand does not change its position in the complexes.

The phosphoryl bending shifts 25 cm^{-1} to higher frequency. This is an indication that coordination has occurred through both oxygen atoms of the ligand.[10,21] The CNP bending bands shift to higher frequencies and the NPN bending at 598 cm^{-1} in the free ligand is obscured by the ν_4 perchlorate band.

The solubility of the complexes in the relatively low donor capacity solvents, nitromethane and nitrobenzene, permitted the conductance measurements of these complexes (Table IV).

The observed values vary in the series, showing increases with increasing atomic number, for both solvents. The conductance data for the entire series in nitromethane show the behaviour of a 1:3 electrolyte type. Twenty values of Λ_M were measured in a concentration range between $(0.0241-2.038) \times 10^{-3}$ M for $[Gd(NIPA)_3](ClO_4)_3$ as a representative complex. They resulted in an average within the interval of 220–260 $\Omega^{-1}.cm^2.mole^{-1}$ suggesting the existance of a 1:3 electrolyte type in nitromethane.[22] In nitrobenzene the metals from La to Ho indicate a somewhat lower ratio whereas the metals with higher atomic number exhibit the same behaviour as in nitromethane.[22]

It has been reported that the decrease in 20% of the crystal radius from the La^{3+} to the Lu^{3+}, can affect the metal coordination number, by reducing the number of ligands or by modification of the anion coordination through the lanthanide series.[23] Our compounds present three bidentate ligands with all elements of the series and the perchlorate displays a

TABLE IV
Electrolityc conductance in nitromethane and nitrobenzene

$Ln(ClO_4)_3 \cdot 3NIPA$	Nitromethane		Nitrobenzene	
	Conc · (mmole · l^{-1})	Λm(ohm^{-1} · cm^2 · mole^{-1})	Conc · (mmole · l^{-1})	Λm(ohm^{-1} · cm^2 · mole^{-1})
La	1.04	220	1.00	59
Ce	1.03	220	0.99	61
Pr	1.03	220	0.96	69
Nd	0.99	233	1.06	69
Sm	1.03	235	0.99	64
Eu	1.00	224	1.05	67
Gd	1.02	226	1.01	62
Tb	1.00	237	1.05	69
Dy	1.01	240	1.00	66
Ho	1.02	259	1.02	64
Er	1.00	261	1.03	70
Tm	1.00	271	1.02	73
Yb	0.98	271	1.03	77
Lu	1.00	270	1.01	75

Td symmetry. This fact should be associated to the poor coordination ability of the anion and the hindrance of the bulky methyl groups. On the other hand the isomorphism of the complexes and the 1:3 electrolyte behaviour suggests a coordination number of six for Ln(NIPA)$_3^{3+}$ species. Of course, only a detailed X-ray analysis of the crystals would be conclusive about the real coordination number.

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