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Diphenylphosphinamide Adducts of the Lanthanide Hexafluorophosphates

L. B. ZINNER and G. VICENTINI
Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, Brazil
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Adducts of lanthanide hexafluorophosphates and diphenylphosphinamide (DPPA) were prepared and show a general formula $Ln(PF_6)_3 \cdot 6DPPA$ (Ln = La–Lu, Y). They were characterized by elemental analyses, infrared and visible spectra, conductance measurements, and X-ray powder patterns.

Evidences that the DPPA is coordinated through the phosphoryl oxygen and that the PF_6^- ions are not coordinated to the tripositive lanthanide were obtained. The compounds behave as 1:3 electrolytes in acetonitrile and nitromethane and present only one isomorphous series.

Introduction

Preparation and properties of adducts of lanthanide salts and DPPA have been described in the literature. Compounds with compositions: $Ln(ClO_4)_3 \cdot 6DPPA$[1] (Ln = La–Lu, Y), $LnCl_3 \cdot 5DPPA$ (Ln = La–Nd), $LnCl_3 \cdot 4DPPA$ (Ln = Sm–Lu, Y), $Ln(NO_3)_3 \cdot 3DPPA$ (Ln = La–Ho) $Ln(NO_3)_3 \cdot 4DPPA$ (Ln = Er–Lu, Y)[2] have been obtained.

In this paper we report the preparation and some properties of the addition compounds between lanthanide hexafluorophosphates and DPPA. The compounds obtained present the stoichiometry $Ln(PF_6)_3 \cdot 6DPPA$ (Ln = La–Lu, Y). The adducts were characterized by elemental analyses, melting ranges, infrared and visible spectra, conductance measurements in acetonitrile and nitromethane and X-ray powder patterns.

Experimental

The ligand was prepared by hydrolysis and oxidation of chlorodiphenylphosphine[3], followed by reaction with thionyl chloride[4] and finally by reaction with an excess of concentrated ammonia solution[5]. The solid obtained was purified by recrystallization from hot water (m.r. 164–166 °C).

TABLE I. Summary of Analytical Results and Melting Ranges of the Compounds of Formula $Ln(PF_6)_3 \cdot 6DPPA$.

Ln	Analysis %								Melting Range °C (dec.)
	Lanthanide		Carbon		Hydrogen		Nitrogen		
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	
La	7.40	7.09	46.07	45.75	3.87	3.96	4.48	4.52	156–158
Ce	7.46	7.15	–	–	–	–	4.47	4.38	151–152
Pr	7.50	7.31	–	–	–	–	4.47	4.78	155–156
Nd	7.66	7.37	45.94	45.92	3.86	4.05	4.46	4.24	145–146
Sm	7.96	7.76	–	–	–	–	4.45	4.72	143–146
Eu	8.04	7.87	–	–	–	–	4.45	4.42	155–156
Gd	8.30	8.28	–	–	–	–	4.43	4.37	145–147
Tb	8.38	7.78	45.59	45.45	3.83	3.99	4.43	4.39	154–155
Dy	8.55	8.09	–	–	–	–	4.42	4.40	155–158
Ho	8.67	8.24	–	–	–	–	4.42	4.29	157–159
Er	8.78	8.50	45.39	45.19	3.81	4.00	4.41	4.42	155–159
Tm	8.86	8.70	–	–	–	–	4.41	4.61	153–154
Yb	9.05	8.73	–	–	–	–	4.40	4.35	153–155
Lu	9.15	8.97	45.20	44.68	3.79	3.93	4.39	4.47	149–150
Y	4.87	4.73	47.33	47.01	3.97	4.09	4.60	4.52	155–157

Concentrated aqueous solutions of lanthanide hexafluorophosphates were obtained by reaction of dilute solutions of hexafluorphosphoric acid and the lanthanide basic carbonates[6].

The adducts were prepared by two ways: a) a large excess of an ethanolic solution of DPPA was added, with stirring, to a solution containing a very high concentration of lanthanide hexafluorophosphate. The precipitate was collected, washed with absolute ethanol and dried *in vacuo* over anhydrous calcium chloride; b) the concentrated aqueous solution of lanthanide hexafluorophosphate was treated with a sufficient amount of methanolic solution of DPPA and the adduct was precipitated by addition of 2,2-dimethoxypropane. The compounds were washed with 2,2-dimethoxypropane and dried as above.

Analysis and Measurements

The compounds were dissolved in methanol and the lanthanides titrated with EDTA[7]. Nitrogen was determined by micro-Kjeldahl method[8] and carbon and

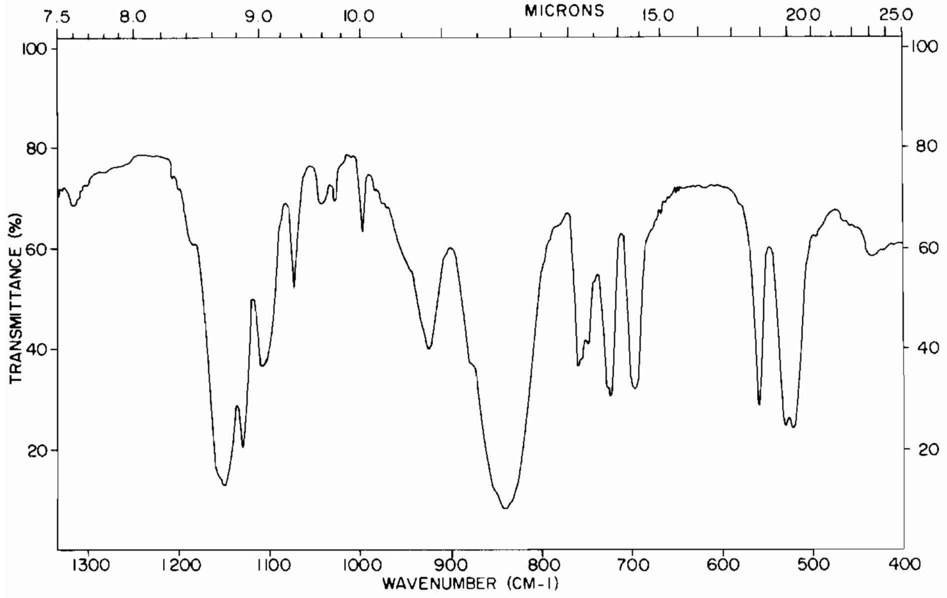

Figure 1. Infrared spectrum of the compounds of formula $La(PF_6)_3 \cdot 6DPPA$ in the region of 1333 to 400 cm^{-1}.

TABLE II. I.r. Data (cm^{-1}) of the Compounds of Formula $Ln(PF_6)_3 \cdot 6DPPA$.

Ln	$\nu_{as}NH_2$	ν_sNH_2	$\nu P{=}O$	$\nu P{-}N$	PF_6^-	
					ν_3	ν_4
La	3430	3370	1150–1130	935	840	560
Ce	3440	3350	1130–1110	930	840	560
Pr	3460–3430	3350	1140–1130	935	840	560
Nd	3470–3440	3380–3350	1140–1130	930	840	560
Sm	3470–3430	3380–3350	1138–1130	935–928	840	560
Eu	3460–3430	3350	1140–1130	940–925	840	560
Gd	3470–3430	3380–3350	1140–1130	935–928	840	560
Tb	3450–3420	3350	1140–1130	935–925	840	560
Dy	3460–3435	3360–3350	1145–1130	940–925	840	560
Ho	3460–3420	3370–3350	1140–1130	940–925	840	560
Er	3460–3420	3350	1145–1130	940–925	840	560
Tm	3460–3420	3355	1145–1130	940–925	840	560
Yb	3460–3420	3350	1145–1130	945–928	840	560
Lu	3460–3430	3355	1145–1128	940–922	840	560
Y	3460–3430	3350	1145–1130	940–925	840	560

TABLE III. Molar Absorptivities of the Compounds of Formula $Ln(PF_6)_3 \cdot 6DPPA$ in Acetonitrile and Nitromethane.

Ln	Acetonitrile		Nitromethane	
	λ, nm	ε	λ, nm	ε
Pr	441	10.50	440	1.33
	–	–	444	1.67
	468	3.50	468	0.99
	481	7.00	–	–
	587.5	2.05	–	–
Nd	512	2.00	511	0.94
	513	2.00	–	–
	523	3.50	523	1.30
	526	3.00	527	1.23
	528	3.00	–	–
	532	2.00	532	2.07
	–	–	535	0.76
	571.5	10.88	571	19.01
	573.5	9.75	–	–
	576	9.50	575.5	7.64
	583.5	17.88	583	11.82
	591	7.00	591	6.16
	597	2.75	598	1.63
	–	–	606	2.24
	737	9.38	737.5	3.45
	742	9.13	743	2.66
	–	–	798	2.51
	804	13.58	804	2.96
	875	3.00	877	0.91
Ho	446	20.53	445.5	19.66
	448	9.78	447.5	8.45
	453	5.43	452	4.59
	458.5	8.09	458	7.71
	461	4.59	460.5	4.11
	537	1.74	536	1.20
Er	518	9.31	518	9.27
	519	9.56	519.5	8.93
	521	10.05	521	9.54
	532	1.03	532.5	1.17

hydrogen by microanalytical procedure (Anorgan. Chem. Laboratorium Tech. Universität München).

Infrared, conductance measurements and X-ray powder patterns were determined as described in Ref. 6. Spectra in the visible region were recorded with a Cary Model 17 using a 2.000 cm cell.

Results and Discussion

The analytical results and melting ranges for the compounds obtained are summarized in Table I. The adducts are crystalline, non hygroscopic and colorless except those of praseodymium, neodymiun and erbium which present respectively a green, blue and pink hue.

TABLE IV. Electrolytic Conductance Data of the Compounds of Formula $Ln(PF_6)_3 \cdot 6DPPA$ in Acetonitrile and Nitromethane.

	Acetonitrile		Nitromethane	
	Conc. (mM)	Λ_m[a]	Conc. (mM)	Λ_m[a]
La	1.12	420	1.11	257
Ce	1.13	415	1.09	253
Pr	1.16	405	1.01	255
Nd	0.945	432	1.10	259
Sm	1.17	394	1.08	235
Eu	1.13	426	1.01	258
Gd	1.10	390	1.04	255
Tb	1.09	416	1.07	253
Dy	1.20	410	1.08	258
Ho	0.996	433	1.04	258
Er	1.12	429	1.06	257
Tm	1.08	428	1.04	253
Yb	1.16	420	1.06	259
Lu	1.01	434	1.06	255
Y	0.961	434	1.01	255

[a] Λ_m, mho cm^2 mol^{-1}.

They are very soluble in acetonitrile, nitromethane and methanol, soluble in nitrobenzene, ethylacetate, slightly soluble in ethanol and practically insoluble in chloroform, benzene and carbon tetrachloride.

Coordination through the phosphoryl oxygen is evidenced by shift of the P=O stretching mode to lower frequencies and of the νP–N to higher frequencies, in relation to the free ligand (DPPA νP=O, 1175; νP–N, 915 cm^{-1}). The splittings observed for these two bands are probably due to solid state effects. Shifts of the N–H stretching vibrations appeared in the spectra, as observed for the perchlorate adducts[1]. The octahedral symmetry of the PF_6^- is maintained, since only two bands were observed[9,10]. The spectra do not present water bands, indicating that anhydrous compounds were obtained. Table II contains the most important infrared frequencies and Figure 1 a typical spectrum obtained.

The number, intensities and the general shape of the bands in the visible spectra are different in acetonitrile and nitromethane, suggesting that interactions may occur between the solvent and the complex species in solution. Some molar absorptivities are shown in Table III.

According to molar electrolytic conductances in acetonitrile and nitromethane (Table IV) the compounds behave as 1:3 electrolytes in both solvents[11].

The X-ray powder patterns are very similar and consistent with the existence of only one isomorphous series.

The coordination number six may be attributed to all lanthanides in the compounds prepared. As observed for the perchlorate adducts, higher coordination numbers[12,13] are not achieved, due to the steric hindrance of the bulky DPPA.

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