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N,N-dimethyl-diphenylphosphinamide (DDPA) Adducts of Lanthanide Isothiocyanates

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The preparation of the adducts of lanthanide isothiocyanates and N,N-dimethyl-diphenylphosphinamide (DDPA) having the general formulas Ln $(NCS)_3 \cdot 4DDPA$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) and $Ln(NCS)_3 \cdot 3DDPA$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) is described.

Infrared spectra indicate coordination of the NCS^- ion through the nitrogen and of the DDPA through the phosphoryl oxygen.

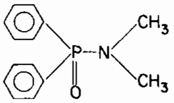
Electrolytic conductance data in acetonitrile and nitromethane show that the compounds are non-electrolytes in these solvents.

X-ray data indicate the existence of two isomorphous series of substances, corresponding to the compounds containing four and three DDPA respectively.

Introduction

Adducts between lanthanide salts and amides of phosphorus have been described in the literature. The complexes of octamethylpyrophosphoramide and lanthanide perchlorates have been described by Joester and Jacob.[1] Addition compounds of triphenylphosphine oxide with lanthanide nitrates, chlorides, and thiocyanates have been studied by Cousins and Hart.[2,3] Solid adducts of rare earth nitrates and chlorides with bis(diisopropoxyphosphinyl)methane have been prepared and characterized by Stewart and Siddall.[4] The same authors have prepared compounds of some nitrates and chlorides with diisopropyl-N,N-diethylcarbamyl phosphonate.[5] The hexamethylphosphoramide adducts with some rare earth salts have been studied by several authors.[6–10] Chloride and perchlorate lanthanide adducts of trimorpholinophosphine oxide have been prepared by Donoghue and Fernandez.[11,12] The preparation of anhydrous diphenylphosphinamide adducts of the lanthanide perchlorates nitrates and chlorides have been described by Vicentini *et al.*[13,14]

In recent papers we have described the adducts of some lanthanide nitrates[15] and perchlorates[16] with N,N-dimethyl-diphenylphosphinamide (DDPA). Compounds of general compositions $Ln(NO_3)_3 \cdot 3DDPA$ (Ln = Ce, Pr, Sm, Er, Y) and $Ln(ClO_4)_3 \cdot 4DDPA$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) have been isolated and characterized.



This paper reports the preparation of the addition compounds of lanthanide isothiocyanates with DDPA. The compounds of general formulas $Ln(NCS)_3 \cdot 4DDPA$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) and $Ln(NCS)_3 \cdot 3DDPA$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) were characterized by elemental analyses, melting ranges, infrared spectra, X-ray powder patterns, as well as conductance measurements in acetonitrile and nitromethane.

Experimental

Preparations

For the preparation of the DDPA, the diphenylphosphinic acid (m.p. 190–192° C) was first prepared from the chlorodiphenylphosphine (from K and K Laboratories, Inc.) by hydrolysis and oxidation, using an excess of 30% hydrogen peroxide.[17] The acid was transformed into the diphenylphosphoryl chloride by reaction with thionyl chloride.[18] The DDPA (m.p. 104–105° C) was finally obtained by the reaction of the diphenylphosphoryl chloride with dimethylamine in benzene solution.[19]

The hydrated lanthanide thiocyanates used for the preparation of the adducts were obtained by reaction of dilute solutions of thiocyanic acid and the respective lanthanide basic carbonate.[20]

To prepare the adducts, a stirred solution of the hydrated thiocyanates in absolute ethanol was treated with a sufficient amount of the DDPA in ethanolic solution. The solid adducts were collected, washed with absolute ethanol and dried *in vacuo,* over anhydrous calcium chloride.

Analysis and Measurements

The lanthanide analyses were determined by treating the samples with ammonia solution. After several hours of digestion the solution was filtered, the precipitates washed with dilute ammonia and dissolved with dilute hydrochloric acid. The excess acid was neutralized with ammonia, using Methyl Red as an indicator. The lanthanide oxalate was precipitated and ignited to the oxide. In the case of the compound of cerium, the cerium(IV) hydroxide was precipitated using ammonia and a solution of hydrogen peroxide, collected on filter paper, washed with dilute ammonia, and ignited to the oxide. Carbon and hydrogen were determined by microanalytical procedures.

Infrared spectra were recorded with Perkin–Elmer model 457–A spectrophotometer, using Nujol mulls between KBr plates. Acetonitrile and nitromethane solutions were measured in a 0.1 mm sodium chloride cell.

Conductance measurements were made at 25.00 ± 0.02° C with a conductivity bridge composed of a Leeds and Northrup 4760 resistance box and a 2370 A.C. pointer galvanometer, using a Leeds and Northrup cell ($K_c = 0.1070_8$ cm^{-1}).

X-ray powder patterns of the compounds were obtained with a Norelco instrument with a diffractometer from Philips Electronic Instruments, using CuK_α radiation.

TABLE I. Summary of Analytical Results and Melting Ranges of the Compounds of General Formula $Ln(NCS)_3 \cdot xDDPA$.

Compound	Analysis %						Melting Range °C
	Lanthanide		Carbon		Hydrogen		
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	
$Y(NCS)_3 \cdot 3DDPA$	8.90	9.07	54.11	53.75	4.84	4.85	256–258
$La(NCS)_3 \cdot 4DDPA$	10.73	10.88	54.76	53.96	4.98	4.98	215–217
$Ce(NCS)_3 \cdot 4DDPA$	10.82	11.16	54.70	54.71	4.98	4.99	221–223
$Pr(NCS)_3 \cdot 4DDPA$	10.87	10.51	54.61	54.76	4.98	5.02	209–211
$Nd(NCS)_3 \cdot 4DDPA$	11.10	11.03	54.53	54.67	4.96	4.96	203–205
$Sm(NCS)_3 \cdot 4DDPA$	11.52	11.58	54.28	54.23	4.94	4.94	199–200
$Eu(NCS)_3 \cdot 4DDPA$	11.62	11.73	54.21	53.95	4.93	5.00	197–199
$Gd(NCS)_3 \cdot 4DDPA$	11.98	12.06	53.99	53.63	4.91	4.95	187–190
$Tb(NCS)_3 \cdot 3DDPA$	14.87	14.83	50.56	50.24	4.53	4.57	225–227
$Dy(NCS)_3 \cdot 3DDPA$	15.15	15.09	50.39	50.10	4.51	4.75	233–235
$Ho(NCS)_3 \cdot 3DDPA$	15.34	15.19	50.28	50.02	4.50	4.63	242–245
$Er(NCS)_3 \cdot 3DDPA$	15.53	15.45	50.17	49.27	4.49	4.67	247–249
$Tm(NCS)_3 \cdot 3DDPA$	15.66	15.74	50.09	49.72	4.48	4.75	248–249
$Yb(NCS)_3 \cdot 3DDPA$	15.98	16.05	49.90	49.69	4.47	4.37	250–252
$Lu(NCS)_3 \cdot 3DDPA$	16.13	16.20	49.82	49.52	4.46	4.46	246–247

TABLE II. Infrared Data (cm^{-1}) of the Compounds of General Formula $Ln(NCS)_3 \cdot xDDPA$.

Compound	$\nu P{=}O$	$\nu P{-}N$	$\nu C{\equiv}N$	$\delta N{\equiv}C{-}S$
DDPA	1188	963	–	–
$Y(NCS)_3 \cdot 3DDPA$	1130–1122	988–980–976	2060–2040–2025	–
$La(NCS)_3 \cdot 4DDPA$	1148–1130–1120	982–970	2058	495
$Ce(NCS)_3 \cdot 4DDPA$	1145–1132–1120	982–970	2058	495
$Pr(NCS)_3 \cdot 4DDPA$	1148–1135–1122	982–975	2055	495
$Nd(NCS)_3 \cdot 4DDPA$	1150–1132–1122	988–973	2062	495
$Sm(NCS)_3 \cdot 4DDPA$	1150–1136–1122	995–978	2072–2056	490
$Eu(NCS)_3 \cdot 4DDPA$	1152–1135–1120	976–972	2065–2058	495
$Gd(NCS)_3 \cdot 4DDPA$	1150–1138–1120	978 –	2078–2058	488
$Tb(NCS)_3 \cdot 3DDPA$	– 1128–1122	995–988–975	2058–2030–2028	–
$Dy(NCS)_3 \cdot 3DDPA$	– 1132–1125	995–982–978	2060–2038–2030	–
$Ho(CNS)_3 \cdot 3DDPA$	– 1130–1122	988–980–975	2058–2038–2028	–
$Er(NCS)_3 \cdot 3DDPA$	– 1132–1122	990–982–978	2062–2040–2030	–
$Tm(NCS)_3 \cdot 3DDPA$	– 1132–1122	986–982–975	2062–2040–2030	–
$Yb(NCS)_3 \cdot 3DDPA$	– 1134–1122	995–990–982	2062–2040–2035	–
$Lu(NCS)_3 \cdot 3DDPA$	– 1132–1122	995–988–982	2064–2042–2035	–

Results and Discussion

In Table I the coordination compounds are listed together with analytical results and melting ranges. The complexes are crystalline, air stable and presented fainter colors than the rare earth ions. They are fairly soluble in chloroform, slightly soluble in acetonitrile and nitromethane and practically insoluble in acetone, benzene, ethanol and carbon tetrachloride.

Table II contains the most important infrared frequencies and Figure 1 shows a characteristic spectrum. The spectra do not show water bands, indicating that anhydrous compounds were obtained. In the free ligand the P=O and P–N stretching vibrations appear at 1188 and 963 cm^{-1} respectively. In the complexes these vibrations are shifted to lower and higher frequencies, respectively, indicating that coordination occurs through the phosphoryl oxygen. The splitting observed are attributed to solid state effects. The bands corresponding to C≡N stretching vibrations are observed at ~ 2060 cm^{-1}. In some cases a splitting, also attributed to solid state effects, appears. According to Mitchell and Williams[21] the frequence observed for the νC≡N may be interpreted in terms of coordination through the nitrogen. Sabatini and Bertini[22] studied the NCS deformation concluding that when coordination occurs through the nitrogen one or two bands appear around 480 cm^{-1}. In the compounds from lanthanum to gadolinium this vibration was observed at ~ 495 cm^{-1}. The band corresponding to the C–S stretching mode was not observed. Attempts to confirm N-coordination of the NCS groups by integrated absorption intensities of CN stretching bands using Ramsay's[23] method of direct integration in acetonitrile and nitromethane solutions were unsuccessful. The adducts, as mentioned, are slightly soluble in these solvents (only $\sim 10^{-3}$ molar solutions were obtained); the existence of weak solvent bands at 2070 cm^{-1} for acetonitrile and at 2035 cm^{-1} for nitromethane complicates the determination of the peak half-widths, specialy in dilute solutions. Also the complexes seems to be partially dissociated[24] in these solvents.

The molar conductance data (Table III) in acetonitrile and nitromethane solutions compared with those published by Geary[25] indicate that the compounds behave as non-electrolytes in these solvents. The values obtained for the $Ln(NCS)_3 \cdot 4DDPA$ compounds may be interpreted in terms of partial dissociation in both solvents or may be attributed to the existence of ionic thiocyanate in the solid state. If we consider that in the $Ln(NCS)_3 \cdot 4DDPA$ adducts all the NCS groups are coordinated to the tripositive lanthanide ions, the coordination number seven may be attributed to these compounds. In accordance with the infrared data and, also, with the conductance measurements, the coordination number six may be attributed to the compounds containing three DDPA. The lan-

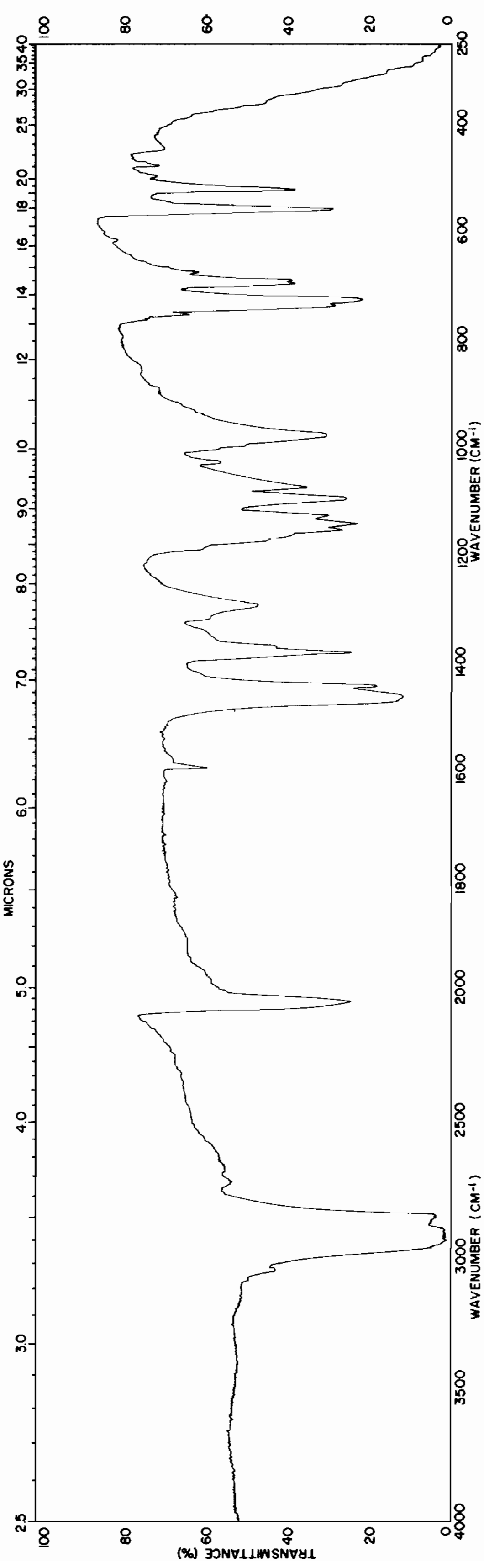


Figure 1. Infrared spectrum of the compound of formula $Pr(NCS)_3 \cdot 4DDPA$.

TABLE III. Electrolytic Conductance Data for the Compounds of General Formula $Ln(NCS)_3 \cdot xDDPA$ in Nitromethane and Acetonitrile.

Compound	Nitromethane		Acetonitrile	
	Conc. mM	Λ_m[a]	Conc. mM	Λ_m[a]
$Y(NCS)_3 \cdot 3DDPA$	1.07	7.39	1.00	15.9
$La(NCS)_3 \cdot 4DDPA$	1.01	25.7	1.00	49.5
$Ce(NCS)_3 \cdot 4DDPA$	0.988	26.9	1.01	50.0
$Pr(NCS)_3 \cdot 4DDPA$	1.00	27.6	0.996	47.6
$Nd(NCS)_3 \cdot 4DDPA$	1.01	29.8	1.00	45.8
$Sm(NCS)_3 \cdot 4DDPA$	0.997	35.5	1.01	45.3
$Eu(NCS)_3 \cdot 4DDPA$	0.994	33.8	0.998	43.1
$Gd(NCS)_3 \cdot 4DDPA$	0.987	39.6	0.997	48.9
$Tb(NCS)_3 \cdot 3DDPA$	1.03	9.17	0.993	21.3
$Dy(NCS)_3 \cdot 3DDPA$	0.974	8.36	0.995	18.3
$Ho(NCS)_3 \cdot 3DDPA$	1.02	8.11	0.987	15.9
$Er(NCS)_3 \cdot 3DDPA$	0.995	7.69	0.982	14.0
$Tm(NCS)_3 \cdot 3DDPA$	0.986	6.65	0.994	17.8
$Yb(NCS)_3 \cdot 3DDPA$	0.998	4.57	0.989	11.0
$Lu(NCS)_3 \cdot 3DDPA$	0.996	8.58	0.995	14.3

[a] Λ_m (mho cm^2 mol^{-1}).

thanide contraction may be responsible for the apparently different coordination numbers or for the different stoichiometries, assuming that the lighter lanthanides may accomodate a higher number of bulky ligands.

According to the X-ray powder patterns two series of isomorphous substances were obtained. The first series contains the compounds of formula $Ln(NCS)_3$ 4DDPA and the second, the adducts of composition $Ln(NCS)_3 \cdot 3DDPA$.

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