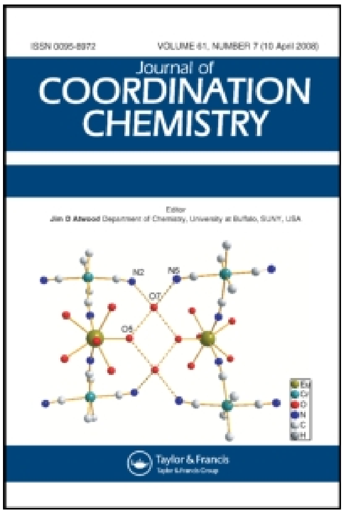

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SYNTHESIS AND PROPERTIES OF ADDITION COMPOUNDS BETWEEN TRIPHENYLPHOSPHINE-OXIDE(TPPO) AND LANTHANIDE TRIFLUOROMETHANESULFONATES

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SYNTHESIS AND PROPERTIES OF ADDITION COMPOUNDS BETWEEN TRIPHENYLPHOSPHINE-OXIDE(TPPO) AND LANTHANIDE TRIFLUOROMETHANESULFONATES

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Additon compounds between triphenylphosphine-oxide and trifluoromethanesulfonates are synthesized and characterized by microanalyses, electrolytic conductance, vibrational (infrared) spectra, absorption spectra in the visible region and thermogravimetric procedures. The results are in agreement with the formulas $La(CF_3SO_3)_3 \cdot 3TPPO \cdot 4H_2O$ and $Ln(CF_3SO_3)_3 \cdot 4TPPO$. The ligands (TPPO) coordinate through the phosphoryl oxygen. Complex interactions with solvents of different donating capacities are also found. Thermogravimetric studies result in lanthanide trifluoride products.

Keywords: Triphenylphosphine-oxide; lanthanide; complex; addition compound; weakly-coordinating anion

INTRODUCTION

Trifluoromethanesulfonic acid (CF_3SO_3H) (triflic acid) is known as one of the strongest acids, with several applications in organic and inorganic chemistry.[1] The anion, albeit possessing a low donating capacity, may act as mono, bi or tridentate ligand and also as a bridge.[2] Phosphine-oxides are

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known to coordinate to several metals. On coordination the stretching frequencies of the phosphoryl group become lower. The compound Eu(fod)$_3$·2TPPO was previously characterized by elemental analysis, melting point and emission spectroscopy.[3] Oxidation studies with Ce(III) nitrate and chloride with TPPO were made using IR spectroscopy and X-ray diffraction techniques, showing that the ligand coordinates to the metal center.[4] The influence of ligand coordination for compounds Eu(TTA)$_3$·3TPPO and Eu(TTA)$_3$·2TPPO was determined together with the decomposition kinetics.[5] The stability and dissociation constants and also distribution coefficients were determined for the complexes Ln(PMHFP)$_3$·2TPPO (Ln = La–Lu, Y; PMHFP = 1-phenyl-3-methyl-4-heptafluorobutyryl-pyrazolone-5).[6]

In this work the preparation and study of some properties of the compounds between hydrated lanthanide trifluoromethanesulfonates and TPPO are presented.

EXPERIMENTAL

The addition compounds were prepared from 0.5 g of Ln(CF$_3$SO$_3$)$_3$·9H$_2$O and 1.2 g of TPPO (molar ratio 1 : 4). The salt was dissolved in 10 mL absolute ethanol and TPPO in 10 mL triethyl-orthoformate. The solutions were mixed and heated for 30 min at 30°C under constant stirring. After cooling to room temperature the vial was closed and put in the freezer for *ca* 15 days. The compounds were filtered, washed with ethyl ether and dried on CaCl$_2$. Lanthanides were determined by complexometric titration with EDTA using xylenol orange as indicator.[7] C, H and N were determined on a Perkin-Elmer microanalyzer.

Electrolytic conductance was measured in 10^{-3} M acetonitrile and nitromethane solutions using Leeds and Northrup equipment and a cell of $K_c = 0.122231\ \text{cm}^{-1}$. Vibrational spectra of the salts, ligand and complexes were registered on a Perkin-Elmer 283 spectrometer. Absorption spectra of the Nd compounds at room temperature and 77 K were obtained in a Hitachi U3000 spectrophotometer. Thermogravimetric curves were obtained in a TGA-7, Delta Series Perkin-Elmer thermobalance under air dynamic atmosphere at 25 mL min^{-1} flow and 10°C min^{-1} heating rate.

RESULTS AND DISCUSSION

The same technical procedure was employed along the lanthanide series but as the ionic radius decreases crystal formation becomes more difficult and

TABLE I Analytical and molar conductance data of the lanthanide trifluoromethanesulfonate complexes with triphenylphosphine-oxide

	Analysis %						*Conductance*	
	Lanthanide		*Carbon*		*Hydrogen*		*Acetonitrile* $\Lambda_M(\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1})$	*Nitromethane* $\Lambda_M(\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1})$
Ln	*Theor.*	*Exp.*	*Theor.*	*Exp.*	*Theor.*	*Exp.*		
La*	9.42	9.30	46.41	46.90	3.35	3.52	154	81
Ce**	8.24	8.18	52.75	52.78	3.56	3.32	157	94
Pr**	8.28	8.24	52.95	52.84	3.55	3.60	157	95
Nd**	8.46	8.62	52.85	52.79	3.55	3.25	158	95
Sm**	8.79	8.66	52.66	52.34	3.54	3.48	157	95
Eu**	8.87	8.95	52.60	52.23	3.53	3.83	153	90
Gd**	9.16	9.23	52.45	52.12	3.52	3.61	154	88
Tb**	9.24	9.34	52.40	52.15	3.52	3.49	152	89
Dy**	9.43	9.30	52.29	51.95	3.51	3.75	157	87
Ho**	9.56	9.53	52.21	52.01	3.50	3.70	154	84
Er**	9.68	9.67	52.14	52.85	3.50	3.44	151	90
Tm**	9.69	9.59	52.09	51.73	3.50	3.51	160	89
Yb**	10.00	10.24	52.06	51.70	3.50	3.43	159	89
Lu**	10.08	10.28	51.91	51.68	3.48	3.39	160	93
Y**	5.99	5.62	54.62	54.30	3.67	3.66	160	86

*$La(CF_3SO_3)_3\cdot 3TPPO\cdot 4H_2O$.

**$Ln(CF_3SO_3)_3\cdot 4TPPO$.

time consuming. From Ln, C, H and N analysis, the general formula was deduced: $Ln(CF_3SO_3)_3 \cdot yTPPO \cdot xH_2O$ where Ln = La, $y = 3$, $x = 4$; Ln = Ce–Lu and Y, $y = 4$ and $x = 0$ (Table I). Electrolytic conductance measurements (Table I) are suggestive of 1 : 1 electrolyte behavior when compared to the Geary data.[8] Table II contains representative IR bands and their assignments. The La compound presents an intense band at 3400–3200 cm^{-1} due to water molecules. The free TPPO phosphoryl stretching frequency was shown at 1195 cm^{-1}. This was shifted toward lower frequencies (*ca* 56 cm^{-1}) in the compounds, indicating coordination through the phosphoryl oxygen. The $\nu_{as}SO_3$ stretching vibrations show minor shifts as compared to the hydrate salt but, except for the La compound, unfoldings also occur, evidence for distortion of the C_{3v} symmetry

TABLE II IR data for compounds of formula $La(CF_3SO_3) \cdot 3TPPO \cdot 4H_2O$ and $La(CF_3SO_3) \cdot 4TPPO$ (cm^{-1})

Compound/Ln	$\nu_{as}SO_3$	ν_{PO}	$\delta_{as}SO_3$
TPPO	—	1191	—
La	1232s	1143vs	636s
Ce	1241s 1219vs	1136vs	638vs 619m
Pr	1240s 1220s	1135s	637s
Nd	1241s 1220s	1135vs	638s
Sm	1240m 1220s	1134vs	637s
Eu	1239s 1221s	1133vs	637vs
Gd	1238s 1220s	1134vs	637vs
Tb	1238s 1221m	1134vs	637s
Dy	1238s 1222s	1134vs	637s
Ho	1237s 1221s	1134vs	637vs
Er	1238s 1222vs	1137vs	637vs 619m
Tm	1238s 1223s	1136vs	637vs
Yb	1238s 1223s	1137s	637s 618m
Lu	1238s 1223s	1134vs	637s
Y	1238s 1222s	1136vs	637vs 618m

Note: vs = very strong; s = strong and m = medium.

of the $CF_3SO_3^-$ ion and suggestive of coordination where the oxygen atoms are not equivalent.[9]

Figure 1 shows the absorption spectra of $Nd(CF_3SO_3)_3{\cdot}4TPPO$ (silicone dispersion) at the regions corresponding to the hypersensitive transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ and $^4I_{9/2} \rightarrow {}^2P_{1/2}$. The number of bands indicates that the Nd^{3+} ion is not of cubic symmetry. The parameters, nephelauxetic[10] ($\beta = 0.993$): covalence factor ($b^{1/2} = 0.59$) and Sinha's[11] ($\delta = 0.70$), show that the interactions are essentially electrostatic. Figure 1 also displays the spectra of the Nd compound in solution. The oscillator strengths[12] in nitromethane ($P \times 10^6 = 10\,cm^2/M$) and acetonitrile ($P \times 10^6 = 14\,cm^2/M$) show minor differences but large effects concerning the shape and the number of bands in relation to the solid state spectrum. This can be explained on the basis of interactions with solvents of different donating capacity.

Figure 2 shows the TG and DTG curves of representative compounds. They are thermally stable up to *ca* 350°C suffering decomposition with partial ligand liberation. In the case of lanthanum, four water molecules are lost in the first step from 97°C to 152°C. The anhydrous complex decomposes rapidly with TPPO, COF_2 and SO_2 evolution[13] resulting in a final LaF_3 product (Table III). Thermal decompositions of the Ce–Lu, and

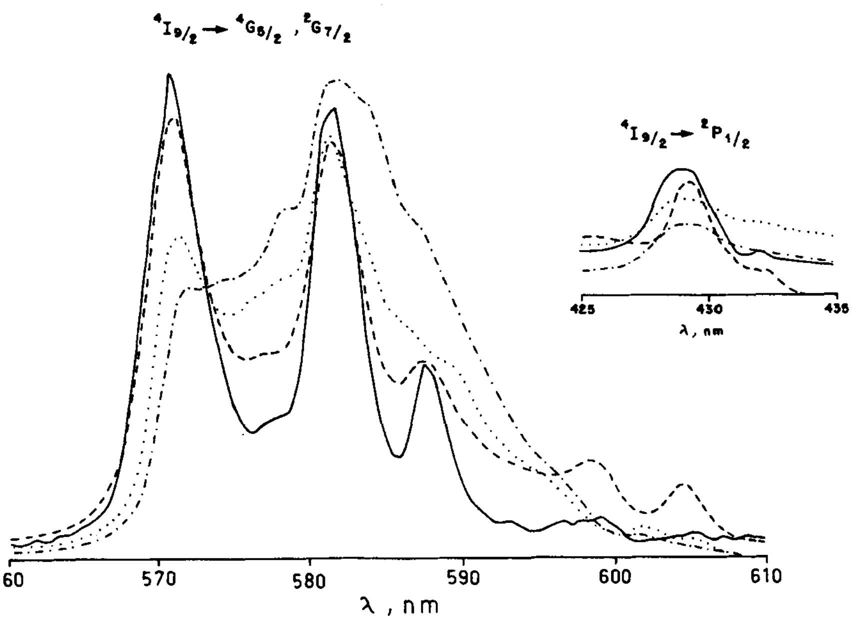

FIGURE 1 Absorption spectra of the neodymium compound: (a) solid state at room temperature (---); (b) solid state at 77 K (—); (c) acetonitrile solution (–·–·) and (d) nitromethane solution (...).

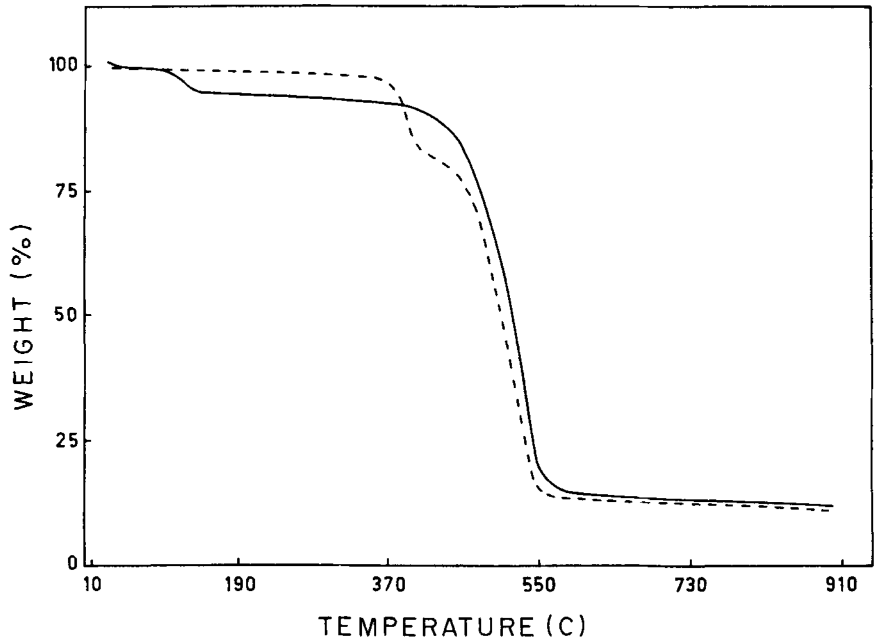

FIGURE 2 TG Curves: (a) $La(CF_3SO_3)_3 \cdot 3TPPO \cdot 4H_2O$ (—) and (b) $Lu(CF_3SO_3) \cdot 4TPPO$ (- - -).

TABLE III Thermoanalytical data and melting ranges

Ln	*Temperature range* (°C)	*Weight loss/res.* (%) *Theor.*	*Exp.*	*Attribution residue*	*Melting range* (°C)
La	97–152	4.79	5.10	$-4H_2O$	355
	302–640	82.05	81.27	–3TPPO	
	640–910	13.12	13.03	LaF_3	
Ce	332–440	11.78	11.65	–3/4TPPO	260–266
	440–568	76.63	77.00	–13/4TPPO	
	568–910	11.59	11.39	CeF_3	
Pr	345–360	9.02	9.02	–3/4TPPO	265–270
	460–580	79.30	79.10	–13/4TPPO	
	580–942	11.59	11.75	PrF_3	
Nd	329–437	18.94	19.09	–5/4TPPO	275–280
	437–512	25.30	25.38	–6/4TPPO	
	512–650	43.96	43.59	–5/4TPOO	
	650–910	11.80	11.97	NdF_3	
Sm	329–436	21.55	21.59	–4/3TPPO	285–287
	436–510	28.33	28.64	–5/4TPPO	
	510–602	37.79	36.86	–1TPPO	
	602–910	12.12	12.44	SmF_3	
Eu	337–441	16.18	15.56	–1TPPO	287–290
	441–600	71.54	71.69	–3TPPO	
	600–910	12.16	12.32	EuF_3	

TABLE III (*Continued*)

Ln	*Temperature range* (°C)	*Weight loss/res* (%).		*Attribution residue*	*Melting range* (°C)
		Theor.	*Exp.*		
Gd	337–441	17.96	17.18	–1TPPO	285–290
	441–571	69.54	69.64	–3TPPO	
	571–910	12.47	12.43	GdF_3	
Tb	368–460	19.41	19.20	–5/4TPPO	287–290
	460–513	16.72	16.59	–1TPPO	
	513–625	51.23	51.09	–7/4TPPO	
	625–910	12.56	12.89	TbF_3	
Dy	339–443	16.15	15.85	–1TPPO	290–294
	443–513	32.31	32.44	–2TPPO	
	513–650	38.78	38.16	–TPPO	
	650–910	12.74	13.00	DyF_3	
Ho	377–450	13.67	13.70	–4/5TPPO	290–294
	450–631	73.43	73.43	–16/5TPPO	
	631–943	12.86	12.53	HoF_3	
Er	325–441	12.89	12.46	–4/5TPPO	285–287
	441–620	73.04	73.23	–16/5TPPO	
	620–900	12.98	12.68	ErF_3	
Tm	356–450	14.64	14.32	–1TPPO	290–293
	450–600	72.45	72.81	–3TPPO	
	600–910	13.06	13.82	TmF_3	
Yb	340–440	19.87	19.89	–5/4TPPO	289–293
	440–561	66.73	66.57	–11/4TPPO	
	561–910	13.27	13.40	YbF_3	
Lu	343–441	19.26	19.23	–5/4TPPO	290–294
	441–513	35.20	34.53	–9/4TPPO	
	513–590	32.04	32.56	–2/4TPPO	
	590–910	13.37	13.47	LuF_3	
Y	381–500	15.40	15.43	–1TPPO	287–290
	500–595	74.11	75.90	–3TPPO	
	595–943	8.69	8.60	YF_3	

Y compounds are characterized by partial ligand liberation, beginning at *ca* 350°C until a stable product is obtained at 910°C. Mass loss and gaseous product liberation are in agreement with the theory.[13] Thermal decompostion steps were followed by IR. The IR of the 350°C residue present characteristic bands of both CF_3SO_3 and TPPO. The spectrum of the residue at 750°C does not show any band attributable to anion and ligand. Qualitative tests of the residue at 900°C were also performed with concentrated H_2SO_4 in lead crucibles to detect fluorine containing compounds.

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