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Hexafluorophosphate as a Non-coordinating Anion in Lanthanide Complexes. II*. Thioxane Oxide Complexes**

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Thioxane oxide (tso) complexes of the lanthanide hexafluorophosphates of the general composition Ln $(PF_6)_3 \cdot 8tso$, where Ln = La–Nd, Sm–Er, and Y, have been prepared and characterized as part of a systematic investigation of lanthanide complexes containing poorly-coordinated anions.

Vibrational spectral data for the complexes provide evidence for the ionic character of the hexafluorophosphate groups and the coordination of the ligand through the oxygen atom of the sulfinyl group. The molar conductance data in nitromethane solutions and X-ray powder patterns are also included. The results obtained from the measurements of the electronic absorption spectrum of $Nd(PF_6)_3 \cdot 8tso$ are discussed and compared with the corresponding data for $Nd(ClO_4)_3 \cdot 9tso$.

Introduction

A great accumulation of data on coordination compounds has led to the conclusion that the notion of the truly non-coordinating anion is a misconception and that almost any anion can be found to coordinate to metal ions under proper conditions.[1] However, large, mononegative anions have been frequently used to minimize anion coordination, thus achieving full ligand coordination. In order to obtain further insight into the influence of "non-coordinating" anions on the structure of lanthanide complexes we have initiated a systematic investigation of rare earth coordination compounds containing hexafluorophosphate as the anion. The ligands to be investigated are oxo-ligands, particularly those already employed in the coordination chemistry of rare earth perchlorates.

The preceding paper[2] in this series dealt with dimethylsulfoxide (dmso). Thioxane oxide (tso) is a sulfoxide similar to dmso in that it involves minimal steric interaction in the coordination sphere of metal ions.[3] For this reason it was chosen to continue our studies.

The use of tso as a ligand in the formation of lanthanide perchlorate complexes was first reported by Edwards *et al.*[3] who prepared the compounds $Ln(ClO_4)_3 \cdot 9tso$, in which Ln = Ce and Y, together with several other nontransition metal complexes, in an attempt to make complexes with high coordination numbers and to obtain information about the metal ion coordination numbers to oxygen.

Later, Vicentini and Perrier[4] obtained compounds corresponding to the compositions: $Ln(ClO_4)_3 \cdot 9tso$ (Ln = La–Nd), $Sm(ClO_4)_3 \cdot 8.5tso$, $Ln(ClO_4)_3 \cdot 8tso$ (Ln = Eu–Er) and $Ln(ClO_4)_3 \cdot 7tso$ (Ln = Tm–Lu, Y). The complex of yttrium showed a different composition from that described by Edwards *et al.*[3]

In the present work we wish to report our results on the complexes of tso with lanthanide hexafluorophosphates.

Experimental

Preparations

Thioxane oxide was prepared from 1,4-thioxane according to Dankleff *et al.*[5] using acetone as the solvent and was purified by distillation under reduced pressure. After cooling the product was obtained in crystalline form (m.p. 44–45° C; lit.m.p. 41–43° C[5]).

The complexes were obtained by the following procedure: the stoichiometric amounts of hydrated lanthanide chloride and ammonium hexafluorophosphate were dissolved in a minimum amount of methanol and the resulting solution was cooled. The precipitated ammonium chloride was filtered off and washed with a small volume of cold methanol. The filtrate was treated with a methanolic solution of an excess of the ligand tso. The precipitate which formed was collected, washed with cold methanol, and dried in a vacuum desiccator over anhydrous calcium chloride. The absence of chloride ions in the complexes was confirmed by qualitative tests with silver nitrate solution. The complexes of thulium, ytterbium and lutetium could not be obtained in a pure form, probably due to the coprecipitation of complexes containing chloride ions.

Analysis and Measurements

The metal content was estimated by complexometric titration.[6] Hexafluorophosphate ions were determined

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* Part I: See ref. 2.

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TABLE I. Physical Properties and Analytical Data of the Complexes.

Complex	Melting Range (°C)	Λ_m[a]	Lanthanide		Anion		Thioxane Oxide	
			% Calc.	% Fd.	% Calc.	% Fd.	% Calc.	% Fd.
$La(PF_6)_3 \cdot 8tso$	172–174	190	9.05	9.16	28.33	28.4	62.62	61.7
$Ce(PF_6)_3 \cdot 8tso$	175–177	190	9.12	9.36	28.31	28.2	62.57	61.6
$Pr(PF_6)_3 \cdot 8tso$	171–175	195	9.17	9.21	28.29	28.6	62.54	61.1
$Nd(PF_6)_3 \cdot 8tso$	~185	195	9.36	9.37	28.23	28.4	62.41	61.0
$Sm(PF_6)_3 \cdot 8tso$	174–176	195	9.72	9.59	28.12	28.2	62.16	61.4
$Eu(PF_6)_3 \cdot 8tso$	165–168	195	9.82	9.81	28.09	28.3	62.10	61.3
$Gd(PF_6)_3 \cdot 8tso$	168–170	200	10.12	10.07	27.99	28.0	61.88	61.2
$Tb(PF_6)_3 \cdot 8tso$	159–162	200	10.22	10.14	27.96	28.0	61.82	61.3
$Dy(PF_6)_3 \cdot 8tso$	160–163	195	10.42	10.39	27.90	28.0	61.68	61.2
$Ho(PF_6)_3 \cdot 8tso$	155–157	195	10.56	10.57	27.86	27.8	61.58	60.5
$Er(PF_6)_3 \cdot 8tso$	151–155	190	10.70	10.67	27.81	28.0	61.49	60.5
$Y(PF_6)_3 \cdot 8tso$	149–152	180	5.99	6.01	29.28	29.5	64.73	63.4

[a] Molar conductance in $ohm^{-1}\ cm^2\ mol^{-1}$ of 1.00×10^{-3} *M* nitromethane solutions, at 25 °C.

through an ion exchange procedure using a cationic resin (Amberlite IR-120 H^+). Thioxane oxide was determined by the method described by Wimer[7] and by the procedure suggested by Douglas.[8] The data presented in Table I are the averages of the results obtained by the two methods, which agree within 1–2 per cent.

The infrared spectra were recorded with a Perkin–Elmer model 180 spectrophotometer, using Nujol mulls for the complexes between CsI and polyethylene plates and a film for the ligand, between CsI plates.

The Raman spectra were recorded with a Jarrel–Ash model 25–300 Raman laser spectrometer, using an argon ion laser (488.0 and 514.5 nm) for excitation.

The electronic spectra of the complexes were obtained with a Cary 17 recording spectrophotometer. The Fluorolube mulls were enclosed in a Hellma 106-QI cell with a loose window plate and path length of 0.50 mm. Nitromethane solutions were measured in 5.0 mm semi-micro cells.

Conductance measurements were made at (25.0± 0.2) °C with an Industrial Instrument model RC-16B conductivity bridge.

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

Results and Discussion

In Table I the coordination compounds are listed together with the analytical results and melting ranges. The complexes are crystalline and air stable. A spot-test for fluoride ion was performed according to Godinho and Neto,[9] and no evolution of hydrogen fluoride from the sample was observed at room temperature, indicating that the compounds are more stable than the corresponding complexes with dmso.[2] However, prolonged heating of the sample or treatment with concentrated perchloric acid caused decomposition, and the evolved vapours gave a positive test for fluoride ion.

The complexes are soluble in acetone, nitromethane, and acetonitrile, slightly soluble in methanol and ethanol, and practically insoluble in less polar organic solvents.

The infrared and Raman spectra of all the complexes are very similar. Table II contains a tentative assignment of S=O and M–O stretching vibrations.

A detailed study of the vibrational spectra of thioxane oxide has not yet been reported. In the present work we are interested in the vibrations of the sulfinyl group and of the $CH_2–O–CH_2$ part of the ring because these are the two possible donor sites of the ligand in the complexes.

TABLE II. Infrared and Raman Spectral Data of the S=O and M–O Stretching Vibrations (cm^{-1}).

Compound	ν(S=O)		ν(M–O)	
	i.r.	R.	i.r.	R.
tso[a]	1019 vs	1010 m[b]	–	–
$La(PF_6)_3 \cdot 8tso$	973 vs	975 m	217 m	218 m
$Ce(PF_6)_3 \cdot 8tso$	973 vs	977 m	218 m	220 m
$Pr(PF_6)_3 \cdot 8tso$	975 vs	978 m	219 m	222 m
$Nd(PF_6)_3 \cdot 8tso$	974 vs	977 m	222 m	223 m
$Sm(PF_6)_3 \cdot 8tso$	975 vs	977 m	223 m	227 m
$Eu(PF_6)_3 \cdot 8tso$	976 vs	978 m	224 m	228 m
$Gd(PF_6)_3 \cdot 8tso$	976 vs	976 m	228 m	230 m
$Tb(PF_6)_3 \cdot 8tso$	977 vs	978 m	228 m	232 m
$Dy(PF_6)_3 \cdot 8tso$	978 vs	977 m	231 m	232 m
$Ho(PF_6)_3 \cdot 8tso$	978 vs	978 m	230 m	233 m
$Er(PF_6)_3 \cdot 8tso$	978 vs	976 m	232 m	233 m
$Y(PF_6)_3 \cdot 8tso$	979 vs	978 m	238 m	234 m

[a] Data from reference 11. [b] Raman spectral data of solid.

It has been stated that the coordination of a cyclic ether generally results in a significant shift in the bands attributed to asymmetric and symmetric COC stretching vibrations.[10] The infrared spectrum[11] of free tso shows bands at 1098 and 827 cm^{-1} and in the solid state Raman spectrum[11] at 1095 and 828 cm^{-1} which may be assigned to asymmetric and symmetric COC stretching vibrations, respectively. In the complexes, the bands at 1107 cm^{-1} in both the spectra and at 834 cm^{-1} in the Raman spectra are only slightly modified from those of the free ligand – an evidence that the ether oxygen atom of the ligand is not involved in coordination.

The strong band at 1019 cm^{-1} in the infrared spectrum of the free ligand was assigned to the S=O stretching vibration according to previous assignments in which the band was observed at 1020[3] and 1026[12] cm^{-1}. In the complexes the band at 1020 cm^{-1} has shifted to the lower frequency region as would be expected for metal–oxygen bonding. However, the assignment of the S=O stretching vibration in the complexes is difficult because of the occurrence of several bands in the 1100–900 cm^{-1} region and in general these modes are coupled with other vibrational modes. All the bands, in this region, except the one at $\cong$975 cm^{-1}, remain virtually unchanged for all the complexes. Comparing the spectral data of the free ligand with that of the 1,4-thioxane[13] the vibrational frequencies were tentatively assigned. The bands at 945 and 1056 cm^{-1} were assigned to the symmetric and asymmetric CC stretching vibrations, respectively, the bands at 1035, 1000 and 965 cm^{-1} to the CH_2 rocking vibrations, and the most intense band in the infrared and Raman spectra, of this region, at $\cong$975 cm^{-1}, was assigned to the S = O stretching vibration. The bands at 638 and 674 cm^{-1} are other characteristic ones, which can be assigned to symmetric and asymmetric CSC stretching vibrations, respectively. The occurrence of these bands in the complexes at higher frequencies than those of the free ligand and their weak intensities in the infrared spectra (the symmetric stretch was not observed) further confirm the coordination of the oxygen atom of the S = O group of tso to the metal ions.[14]

The metal–oxygen stretching vibration is also difficult to assign because of the occurrence of several bands of the free ligand in the low frequency region.[11] The infrared and Raman spectra show that all the bands remain virtually unchanged for the complexes, except the band at $\cong$230 cm^{-1}, which is slightly shifted to the high frequency region in the heavier lanthanide compounds. The magnitude of the shift increases as the ionic radius of the metal ion decreases. This band was tentatively assigned to the metal–oxygen stretching vibration.

The hexafluorophosphate ion of O_h symmetry has two infrared active vibrations, $\nu_3(F_{1u})$ and $\nu_4(F_{1u})$, three Raman active vibrations, $\nu_1(A_{1g})$, $\nu_2(E_g)$ and $\nu_5(F_{2g})$, and one vibration, $\nu_6(F_{2u})$, which is inactive both in the infrared and Raman spectra.[15] The bands at 840 and 557 cm^{-1} in the infrared spectra of the complexes were assigned to ν_3 and ν_4, respectively. The bands at 743, 578 and 470 cm^{-1} observed in the Raman spectra were assigned to the ν_1, ν_2 and ν_5 vibrational modes of the anion, respectively. The bands at 743 and 578 cm^{-1} were also observed in the infrared spectra of all the complexes. The last one is probably a ligand band which appears in the infrared and Raman spectra[11] at 570 cm^{-1} in the free ligand and occurs accidentally degenerate with the ν_2 in the complexes. The former one, although formally forbidden, is observed in the spectra of all the complexes and is the only apparent deviation from the rigorous selection rules for octahedral symmetry for the hexafluorophosphate ion.

In addition, the infrared spectra of some of the tso complexes of lanthanide perchlorates were re-examined and extended to the metal–ligand stretching region. The results confirm that the perchlorate anion is not coordinated.[4] The assignment of the bands in the metal–ligand region, however, is complicated by the appearance of two absorptions and also by the change in the number of coordinated ligands in the series. No definite trend in the frequencies of the bands is observed.

The molar conductance data of the hexafluorophosphate compounds (Table I) indicate that they behave as 1:2 electrolytes in nitromethane solutions,[16] as was also reported for the corresponding perchlorate complexes.[4] These observations are contrary to the expectation suggested by the above discussion on the ionic character of the hexafluorophosphate and perchlorate groups. The formation of ion pairs is probably responsible for the results.

X-ray powder patterns of the hexafluorophosphate compounds were obtained. According to the data, the complexes seem to be isostructural, with slight deviations in the patterns of the lanthanum, cerium and praseodymium compounds. In the case of the perchlorate compounds, three series of isomorphous substances have been observed.[4]

The results discussed above show that in spite of the ionic character of both perchlorate and hexafluorophosphate anions in tso complexes there is significant variation between these two series of compounds. All the hexafluorophosphate complexes have the same composition in contrast with the corresponding perchlorate complexes in which the number of coordinated molecules of tso was observed to decrease with the increase in the atomic number of the metal.[4] In this sense tso complexes behave differently from dmso complexes in which the decrease in the coordination number was observed for both the perchlorate and the hexafluorophosphate compounds.[2]

Recently, different experimental conditions have been employed for the preparation of tso complexes of the lanthanide hexafluorophosphates and the compounds obtained were formulated as $Ln(PF_6)_3 \cdot 7.5tso$.[17] The observation that the stoichiometry of the complexes shows no dependence on the nature of the central metal is in agreement with our results.

In order to obtain further information for the comparison between the perchlorate and hexafluorophosphate compounds, the electronic spectra of the neodymium complexes were recorded in the region of the hypersensitive transitions using solid samples as Fluorolube mulls (Figure 1) and nitromethane solutions. Observing the color of the compounds, it can be seen that the $Nd(PF_6)_3 \cdot 8tso$ is more blue (less red) than the $Nd(ClO_4)_3 \cdot 9tso$. Accordingly, in the mull spectra for the hexafluorophosphate compound, the $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ bands are shifted toward a higher wavelength, giving a more intense nephelauxetic effect than in the perchlorate compound. This effect is likely due to an increase of the Nd–tso bond interaction with shorter metal–ligand distance,[18] probably due to a lower coordination number. As already mentioned, the appearance of two bands in the metal–ligand stretching region (at 210 and 230 cm^{-1} for the $Nd(ClO_4)_3 \cdot 9tso$) makes the assignment of these bands difficult, precluding at this time a comparison of the metal–ligand vibration with the nephelauxetic behavior.

The electronic spectra of both complexes in nitromethane solutions ($10^{-2}M$) are identical to that of the $Nd(PF_6)_3 \cdot 8tso$ in the solid state. This information agrees with the same behavior of the solutions under conductivity measurements and also with the possibility of an equilibrium between compounds with a different environment. When precipitation occurs such an equilibrium could be responsible for the isolation of some compounds with non-integral number of ligands.[4,19] Likewise, such an equilibrium could account for the formation of different compounds upon changing the preparative conditions, as is observed in the cases of $Ln(ClO_4)_3 \cdot 6hmpa$[20] and $Ln(ClO_4)_3$ 4hmpa,[21] where the anion can be coordinated.

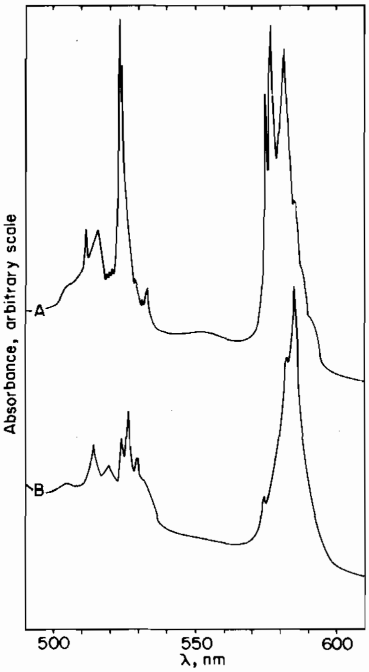

Figure 1. Electronic absorption spectra of $Nd(ClO_4)_3 \cdot 9tso$ (A) and $Nd(PF_6)_3 \cdot 8tso$ (B) in Fluorolube mull.

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