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HEXAFLUOROPHOSPHATE AS A NON-COORDINATING ANION IN LANTHANIDE COMPLEXES. III. TETRAMETHYLUREA (TMU) COMPLEXES

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The complexes $\text{Ln}(\text{TMU})_6(\text{PF}_6)_3$ ($\text{Ln} = \text{La, Pr-Gd, Dy, Er, Y}$ and TMU = tetramethylurea) have been prepared and characterized by conductance, infrared, absorption and emission spectra measurements. All the complexes have structures involving complex cation and non-coordinated anion, consistent with the extremely weak ligating ability for PF_6^- . Coordination number six with a rather high symmetry is proposed for these compounds. The crystal field parameter B_0^2 was calculated from the splitting in the 7F_1 level of the Eu^{3+} ion, without assuming a known molecular geometry; the value 107 cm^{-1} was obtained. Additional comparative study with the corresponding perchlorate and tetraphenylborate compounds is presented and the influence of poorly coordinating anions in the hypersensitivity behaviour is discussed.

INTRODUCTION

As part of the systematic investigation of rare earth coordination compounds containing neutral oxo-ligands and hexafluorophosphate as the counter-ion, the results obtained with TMU are reported. This study is being carried out in order to obtain structural information and to gain further insight into the influence of poorly coordinating anions on the nature of lanthanide complexes.

The preceding papers in this series dealt with the ligand dimethylsulfoxide¹ and thioxane oxide.² A comparative study with the corresponding perchlorate compounds was severely limited by the instability of the compounds and by the lack of isomorphous coordination. Moreover, the nature of the isolated species with the sulfoxide ligands seems to be very dependent on the conditions of preparation,³ such as molar ratios of ligand to cation, concentration, temperature of mixing, nature of solvent and identity of cation.

The ligand here chosen besides being a rather unique electrolytic solvent,⁴ works admirably well towards lanthanide ions, as has been proved by some previous studies with perchlorate⁵ and tetraphenylborate⁶ as the anions. Compounds of general composition $\text{Ln}(\text{TMU})_6\text{X}_3$ ($\text{Ln} = \text{a lanthanide ion}$

and $\text{X} = \text{ClO}_4^-$ or BO_4^-) have been described; hexa-coordination proposed by conductance and spectroscopic measurements was confirmed, by X-ray structural determination⁷ for the $\text{Er}(\text{TMU})_6(\text{ClO}_4)_3$ compound: erbium lies in a center of symmetry, the six O atoms of TMU forming an essentially regular octahedron. This is a rather unique geometry for a lanthanide complex involving six identical neutral ligands; the antipyrene yttrium iodide⁸ and hexamethylphosphoramide neodymium perchlorate⁹ complexes seem to be the only preceding cases.

The combination of this ligand and hexafluorophosphate as the counter-ion was chosen expecting that it would form similar compounds to the perchlorate and tetraphenylborate ones. In this case these systems of isomorphous character afford the opportunity of studying the influence of poorly coordinating anions on the properties of lanthanide complexes, mainly spectroscopic properties associated with f–f transitions localized on the rare earth ions.

EXPERIMENTAL

Preparations

TMU (K. & K. Laboratories Inc., New York) was dried over CaH_2 and distilled under reduced pressure. The intermediate fraction was used.

The complexes were obtained by adding 2.5 ml

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of TMU (*ca* 20 mmoles) to 15 ml of a methanolic solution containing rare earth hydrated chloride (2 mmoles) and ammonium hexafluorophosphate (6 mmoles). The fine precipitates that formed (immediately for the heavier lanthanides and only after cooling for the lighter ones), were filtered off and washed with 15 ml of cold absolute methanol; further they were dried *in vacuo* over CaCl_2 . Yields of preparation (based upon the lanthanide chloride used) increase with the atomic number of the lanthanide, varying from 15 to 80 percent as one proceeds from praseodymium to erbium. Lanthanum compound does not precipitate under the described conditions; attempts made to reduce the volume of methanol led to the separation of a few crystals of the complexes contaminated by NH_4Cl . However by employing different experimental conditions,¹⁰ the lanthanum compound could also be prepared. These compounds can be recrystallized from methanol or acetonitrile without change in the composition; well defined crystals of the neodymium compound were obtained by slow evaporation of the acetonitrile solution.

Analysis and Measurements

Lanthanide and hexafluorophosphate contents were estimated as previously described.¹ Nitrogen was determined by the Kjeldahl method.

Conductance, infrared and electronic absorption spectra were measured as previously described.² The hygroscopic neodymium perchlorate compound used in the comparative study of the electronic spectra was prepared as previously described⁵ and handled in a dry box.

The emission spectra were recorded at 77 K with a McPherson RS-10 Spectrophotometer equipped with the model 606 fluorescence attachment as previously described.¹¹ The exciting line of the 100-watt mercury lamp was isolated with both glass and interference filters. The slits were routinely set at 100 μ which gave an instrument resolution of 1 Å.

RESULTS AND DISCUSSION

Results of the analyses conform to the formulation of the compounds as $\text{Ln}(\text{PF}_6)_3 \cdot 6\text{TMU}$ ($\text{Ln} = \text{La}, \text{Pr-Gd}, \text{Dy}, \text{Er}$ and Y), as in the case of the perchlorates⁵ and tetraphenylborates.⁶ Satisfactory analytical data were obtained for all the isolated compounds. They are crystalline, more stable air than the corresponding perchlorate and tetraphenylborates soluble in nitromethane and acetonitrile, slightly

soluble in methanol and ethanol, and practically insoluble in less polar organic solvents.

Electrolytic conductance data at millimolar concentration in nitromethane and acetonitrile are consistent with the behavior of a 1:3 electrolyte type; the mean values of 244 and 392 $\text{ohm}^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$, with no definite trend in the series of compounds prepared, were observed respectively in these solvents.

The infrared spectra of the complexes were analysed in comparison with that one of the free ligand; the vibrational analysis of the ligand was undertaken independently by three authors.¹²⁻¹⁴ The following relevant aspects may be considered regarding this point:

- absence of water bands indicates that, in all cases anhydrous compounds were obtained;
- a considerable shift of the $\text{C}=\text{O}$ frequency to lower values in relation to that of the free ligand ($\Delta\nu \cong 70 \text{ cm}^{-1}$) indicates that coordination of amide occurs through the carbonyl oxygen; this conclusion is reinforced by the shift of the band primarily due to CN asymmetric stretching frequency to higher

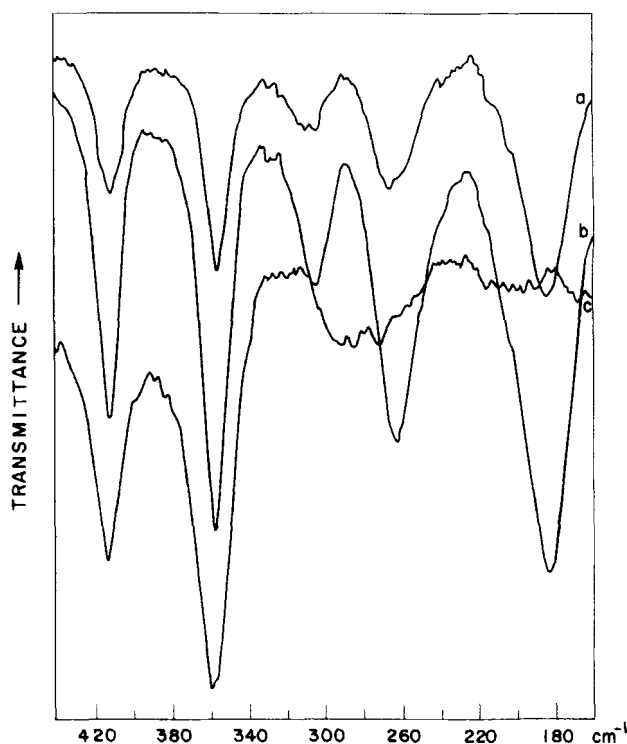


FIGURE 1 Infrared spectra.

- $\text{Er}(\text{TMU})_6(\text{ClO}_4)_3$
- $\text{Er}(\text{TMU})_6(\text{PF}_6)_3$
- TMU (liquid film)

values ($\Delta\nu \cong 45 \text{ cm}^{-1}$). The opposite shifts of these vibrations apparently originated the somewhat broad band in the region $1570\text{--}1545 \text{ cm}^{-1}$;

c) two strong bands at 837 and 560 cm^{-1} assigned respectively to ν_3 and ν_4 vibrations of PF_6^- group¹⁶ indicate the ionic character of this anion, in accordance with the criteria for non-coordinating anion described by Morrison and Thompson,¹⁶

d) the low frequency region was also examined in order to obtain some additional information concerning the frequency depending on the interaction between ligand and metal and analyzed in comparison with those ones of TMU¹³ and KPF_6 ¹⁵ previously reported.

It was observed (Figure 1) that in the complexes all the bands of the free ligand remain virtually unchanged; the most remarkable effect is the appearance of a medium intensity band at about 185 cm^{-1} in the spectra of the complexes. This band does not show definite trend in the series of the lanthanide complexes; however a pronounced shift to higher frequency (in 220 cm^{-1}) is observed in the yttrium compound. This band was tentatively assigned to a metal–oxygen depending vibration. Two other bands at about 303 and 260 cm^{-1} unchangeable throughout the lanthanide series may be also a vibration of this type; however the presence of several overlapping absorptions bands in this region, in the spectrum of free ligand, precludes some definite conclusion.

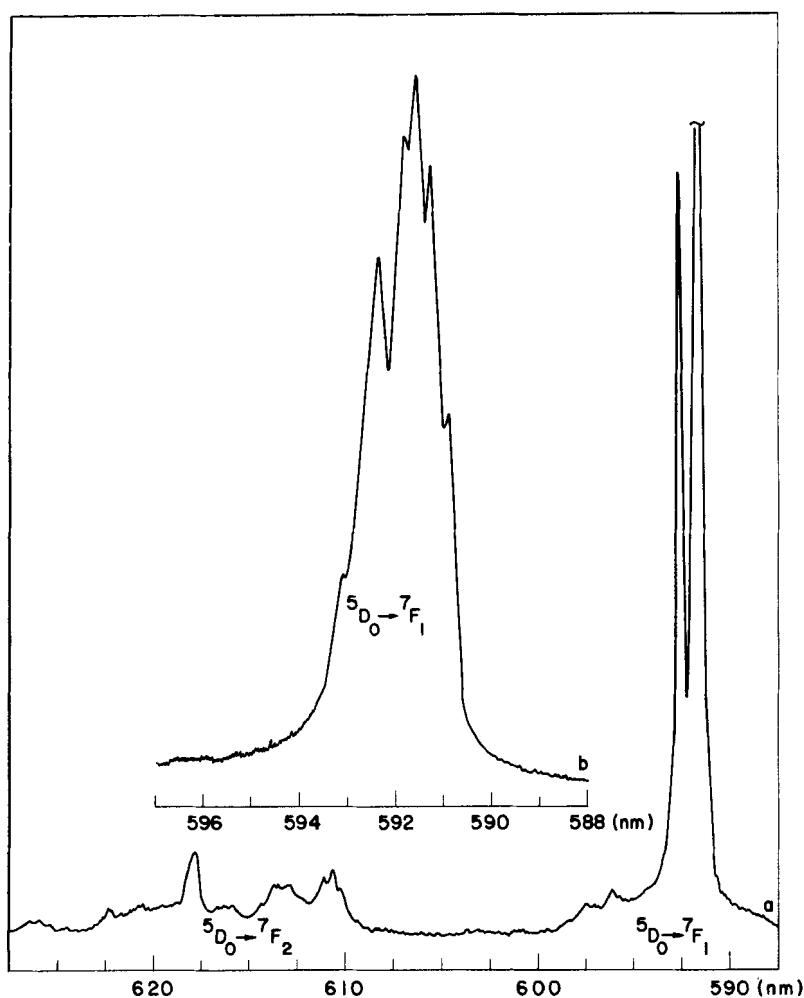


FIGURE 2 Fluorescence spectra of solid compounds at 77 K.

- a) $\text{Eu}(\text{TMU})_6(\text{PF}_6)_3$
 b) $\text{Eu}(\text{TMU})_6(\text{ClO}_4)_3$

In addition the low frequency region of the corresponding perchlorate erbium compound was examined and compared with that one of the hexafluorophosphate. The spectra of these isomorphous compounds are virtually superimposable in the region 450–180 cm^{-1} (Figure 1), indicating the presence of the same vibrationally active species.

Emission spectrum of the europium compound at 77 K (Figure 2) shows the following aspects:

a) the spectrum is dominated by the transition $^5D_0 \rightarrow ^7F_1$, splitted in two bands, respectively at 16873 and 16905 cm^{-1} ; this magnetically allowed transition is very sharp and approximately fourteen times more intense than any other transition;

b) the $^5D_0 \rightarrow ^7F_0$ transition was not observed even under increased sensitivity;

c) the $^5D_0 \rightarrow ^7F_2$ electric dipole transition occurs only as a relatively weak and somewhat large bands;

d) the emissions from the second excited state ($^5D_1 \rightarrow ^7F_{0-3}$), were not observed; additional weak bands are observed for $^5D_0 \rightarrow ^7F_3$, transition.

These features are consistent with a rather high symmetry for the electrostatic field surrounding the Eu^{3+} ion. The ill defined bands due to $^5D_0 \rightarrow ^7F_2$ transition, apparently vibronic in origin, and the low number of observed transitions, preclude the assignment of the real site symmetry. However, since only two $^5D_0 \rightarrow ^7F_1$ lines are observed one can conclude that only the crystal field parameter $B_0^{2,17}$ appears in the 7F_1 secular determinant. The resolution of the secular equations¹⁸⁻²⁰ leads to the value of 107 cm^{-1} for this parameter.

The fluorescence spectrum of the corresponding perchlorate compound was also recorded in the same conditions. The great number of bands observed for the $^5D_0 \rightarrow ^7F_1$ transition (Figure 2b) is not consistent with any symmetry; it can be explained by a decomposition of the compound originating species of more than one coordination geometry. This possibility is a likely one because of the hygroscopic nature of this compound.

The electronic absorption spectra of the neodymium compound was recorded in the region of hypersensitive transitions ($^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$) and compared to those ones of the corresponding perchlorate and tetraphenylborate. Because of their essentially isomorphous character it is interesting to see the hypersensitivity dependence with the nature of the counter-anion. The following observations can be made concerning this point;

a) the general features of hypersensitive transitions of the $\text{Nd}(\text{PF}_6)_3 \cdot 6\text{TMU}$ are essentially the same either in solid state (Fluorolube mull or single crystal spectra) or in nitromethane solution (Figure 3 and 4b); this means that the same environment around the neodymium ion is present in these conditions;

b) the five principal bands observed for these transitions (Figure 3) seem to be consistent with a cubic site symmetry. Moreover, the normal (non-hypersensitive) bands present molar absorptivity, in nitromethane solutions, of the same order of hexahalide compounds of neodymium;²¹ this

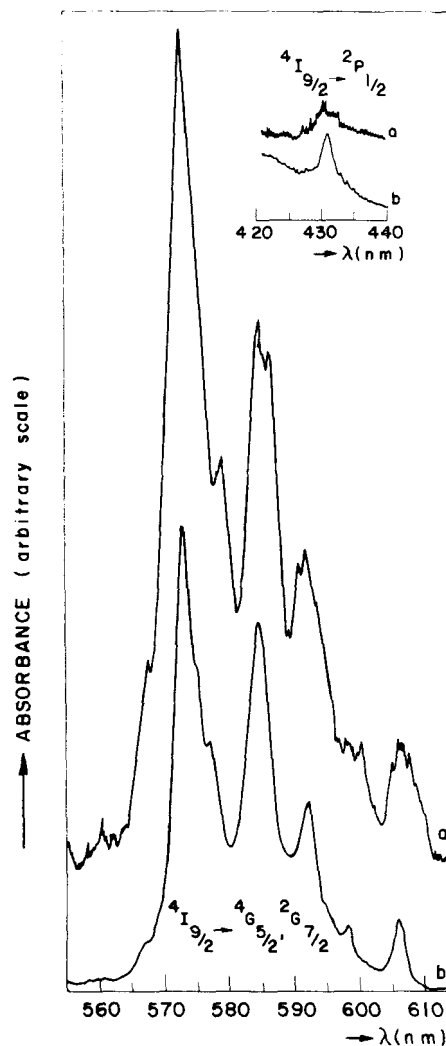


FIGURE 3 Electronic absorption spectrum of $\text{Nd}(\text{TMU})_6(\text{PF}_6)_3$
a) Single crystal
b) 0.1 M nitromethane solution

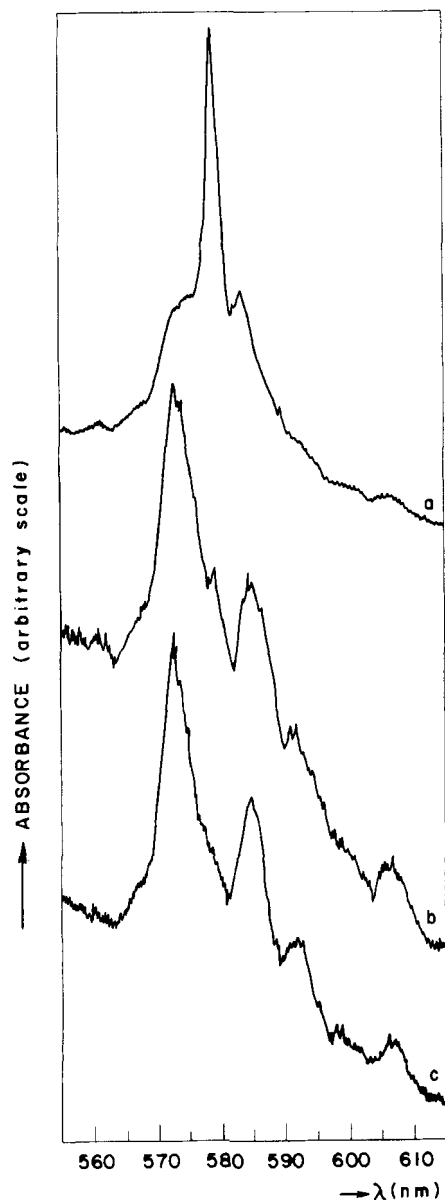


FIGURE 4 Electronic absorption spectra of solid complexes on Fluorolube mulls.

- a) $\text{Nd(TMU)}_6(\text{ClO}_4)_3$
 b) $\text{Nd(TMU)}_6(\text{PF}_6)_3$
 c) $\text{Nd(TMU)}_6(\text{BO}_3)_3$

indicates that the symmetry around the neodymium ion is octahedral or near to it; also a single band observed for the transition $^4I_{9/2} \rightarrow ^2P_{1/2}$ in the crystal and nitromethane solution spectra (Figure 3) is consistent with the presence of only one site symmetry;

- c) the great similarity (either in position, number

and shape of the bands) of the hexafluorophosphate and tetraphenylborate compounds indicates that the same environment around the neodymium ion is present in these compounds.

However the isomorphous perchlorate compound presents a completely different pattern for the hypersensitive transitions (Figure 4). Since there does not seem to be any reason to these isomorphous compounds to present such a behavior, it can be concluded that the nature of the compensating anion (even apparently not coordinated) is of significance in the nature of hypersensitive bands. Also the possibility of structural change, because of partial coordination of anion or water absorption [$\text{Nd(TMU)}_6(\text{ClO}_4)_3$ is highly hygroscopic] cannot be ruled out; in spite of the care used in the handling of the perchlorate compound, water bands were detected (by infrared measurements) in the Fluorolube mull used in the recording of the absorption spectrum.

In conclusion, as was expected, lanthanide complexes with coordination number six were obtained; this relatively rare number for the lanthanide ions seems to be a complicated compromise between steric factors, basicity of ligand and nature of the counter-ion; packing considerations³ may also be considered in the stabilization of this number. In the TMU complexes the characteristics of the geometry of the ligand may be responsible for this low coordination number. At this point, it is interesting to observe that the less bulky ligand, 1,3 dimethylurea can also form six coordinated complexes, as evidenced by conductance and infrared measurements however, this compound is easily hydrated leading to a seven coordinated complex, as evidenced by X-Ray structural determination.²² The participation of a water molecule may lead to a more favorable arrangement. Also it is observed that the concept of non-coordinating anion inferred mainly by infrared spectroscopy will be frequently misleading in lanthanide complexes; it is proved that differing degrees of coordination produce varying effects on the vibration spectrum.²³ "Semi-coordination", a term used to define this delicate balance between coordinated and uncoordinated anion²³ seems to play an important role in the stabilization of a particular geometry around a lanthanide ion. This fact is evidenced by a great number of lanthanide complexes containing specially nitrate and perchlorate as the anions: a smooth decrease or increase in the amount of ionic anion is observed as one proceeds from the lighter to the heavier lanthanides. In this sense hexafluorophosphate ion exhibits a weaker

coordinating ability; in no case conclusive evidence for coordination was detected in lanthanide complexes; only some evidence for semi-coordination to $3d$ metal has been claimed.¹⁶

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