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Synthesis and Optical Study of Ln(III)(tetramethylurea)$(AsF_6)_3$ (Ln = La–Lu, Y) and Crystal Structure for Ln = Eu [Eu(TMU)$_6$$(AsF_6)_3$]

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Abstract

The fluorescence spectrum of Eu^{3+} recorded at a temperature of 12 K between 14.000 and 20.000 cm^{-1} shows transitions from the excited state ^5D_O to the Stark components of the lowest ^7F_J. The optical analysis suggests an octahedral site symmetry for the rare earth ion which is confirmed by the three-dimensional crystal determination. The highly disordered crystal structure refined in space group *F*23 to an *R*-factor of 13.2%. Both the europium and the arsenic ions are located in special positions of point symmetry 23(T). The Eu–O bond distance is 2.28 Å. The value of the $B_q{}^k$ parameters was determined.

Introduction

Addition compounds between TMU and rare earth ions were first prepared by Seminara *et al.* [1]. Later studies using as precipitant agent the ions of perchlorates [2], chlorides [3], nitrates [4], perrhenates [5], isothiocyanates [6], bromides [7], tetraphenylborates [8], hexafluorophosphates [9] and trifluoromethanesulfonates [10], were reported. To extend these previous studies, we have now prepared adducts containing hexafluoroantimonate [11] and hexafluoroarsenate ions. Compounds with this non-coordinating anion have a high symmetry and a coordination number of six. The hexafluoroarsenate ion is a good precipitant and has non-coordinating properties.

Experimental

Synthesis

The hydrated lanthanide hexafluoroarsenates were obtained by reaction of the corresponding perchlorate salts with stoichiometric quantities of the potassium hexafluoroarsenates in an acetone medium. The solutions were filtered, the salts separated and treated with tetramethylurea. The compounds obtained were filtered, washed with cool anhydrous ethanol and stored in a desiccator. In order to obtain suitable crystalline forms, the powdered compounds were recrystallized from an ethanol–acetone mixture.

Analysis

The lanthanide ion content was determined by the standard EDTA compleximetric titration, nitrogen content by the semimicro Kjeldahl procedure and arsenic content by atomic absorption spectrometry. A microanalysis for C and H was made by Galbraith Laboratories, Inc.

Measurements

Conductance measurements were carried out on 10^{-3} M nitromethane solutions at 25.00 ± 0.02 °C with a bridge composed of a Leitfahingkeits messer BR resistance box and a cell previously calibrated with aqueous potassium chloride (H_c = 0.57964 cm^{-1}). The results are summarized in Table I. Infrared spectra were recorded with a Perkin-Elmer model 283B spectrophotometer using nujol mulls between KBr plates or with a Perkin-Elmer model 180 spectrophotometer using polyethylene plates. The emission spectra were recorded with both a Perkin-Elmer MPF-44B spectrofluorimeter using 396 nm excitation and with a SPEX 1451N double monochromator using an argon laser with excitation lines of 4880 and 5145 Å. The solid samples were placed in a quartz tube of 3 mm i.d. and inserted into a dewar with a quartz tail in the first case and into a crystal from Air Products and Chemicals Inc. Displex in the second case.

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TABLE I. Summary of Analytical Results.

Compound	Ln (%)		N (%)		C (%)		Λ_M[a]
	The.	Obs.	The.	Obs.	The.	Obs.	
$La(AsF_6)_3 \cdot 6TMU$	9.90	9.6	11.98	12.06	25.68	–	269
$Ce(AsF_6)_3 \cdot 6TMU$	9.98	9.9	11.97	11.97	25.66	25.62	263
$Pr(AsF_6)_3 \cdot 6TMU$	10.05	9.8	11.97	11.75	25.65	–	264
$Nd(AsF_6)_3 \cdot 6TMU$	10.25	10.2	11.93	12.19	25.59	25.58	269
$Sm(AsF_6)_3 \cdot 6TMU$	10.64	10.6	11.88	11.60	25.48	–	263
$Eu(AsF_6)_3 \cdot 6TMU$	10.74	10.8	11.87	12.08	25.45	25.44	263
$Gd(AsF_6)_3 \cdot 6TMU$	11.07	11.1	11.83	11.85	25.35	25.66	263
$Tb(AsF_6)_3 \cdot 6TMU$	11.17	11.2	11.81	11.73	25.32	–	263
$Dy(AsF_6)_3 \cdot 6TMU$	11.40	11.6	11.78	11.60	25.26	–	269
$Ho(AsF_6)_3 \cdot 6TMU$	11.53	11.4	11.76	12.02	25.22	–	257
$Er(AsF_6)_3 \cdot 6TMU$	11.68	11.5	11.74	11.92	25.17	–	263
$Tm(AsF_6)_3 \cdot 6TMU$	11.79	11.6	11.73	11.64	25.15	–	263
$Yb(AsF_6)_3 \cdot 6TMU$	12.05	12.2	11.70	11.65	25.07	–	269
$Lu(AsF_6)_3 \cdot 6TMU$	12.16	11.9	11.68	11.86	25.04	25.23	257
$Y(AsF_6)_3 \cdot 6TMU$	6.57	6.6	12.42	12.27	26.64	–	263

[a] Ohm^{-1} cm^2 mol^{-1} (10^{-3} M solutions in nitromethane).

Three-Dimensional X-Ray Analysis

A fragment of irregular shape of maximum and minimum linear dimensions of 0.30 and 0.25 mm respectively was mounted on a CAD-4 Enraf-Nonius diffractometer. Cell dimensions and the orientation matrix for data collection were calculated by least-squares from 25 centered reflections using graphite-monochromatized MoK_α radiation. Diffraction intensities for reflections having θ in the range 0–27° were measured by the ω–2θ scan technique at a speed between 5–20° min^{-1} determined by a fast prescan of 20° min^{-1}. The intensity of one standard reflection was essentially constant throughout the experiment. Of the 751 independent reflections measured, 277 having $I > 3\sigma(I)$ were used in the calculations. One octant of reciprocal space was measured and the Laue equivalents were averaged. The corresponding agreement R-factor [13] was 4%. Data were corrected for Lorentz and polarization effects but not for absorption or extinction. Relevant crystal data are: cubic, space group $F23$, $a = 18.000(3)$, $V = 5832(3)$ Å^3, $Z = 4$, $D_c = 1.603$ g cm^{-3}, MoK_α radiation $\lambda = 0.71073$ Å, μ (MoK_α) = 27.4 mm^{-1}, $F(000) = 2820$.

Diffraction symmetry indicated a cubic space group with an F-centered lattice except for a few small violations to the systematic absences expected for centering, which were later attributed to disorder. Since $Z = 4$ as determined from the observed density, the heavy atoms sites are fixed by the space group symmetry. A difference map phased on the europium and arsenic atoms placed on each of the four special positions of point symmetry 23, showed the only crystallographically independent oxygen atom in a special position of point symmetry 2, plus two more peaks corresponding to very disordered fluorine atoms which account for 55% of the total amount of fluorine in the unit cell. Alternate full matrix refinement of the isotropic temperature factors and occupation numbers of these atoms gave an R-factor of 13.2%. A subsequent difference map showed a few peaks of about 1e Å^{-3} that could not be interpreted as further atoms of the complex. This fact, together with the few small violations to the systematic absences and the poor diffracting power of the crystal, were indicative of a high positional disorder. No meaningful progress could be envisaged and the refinement was stopped at this point. The function minimized was $\Sigma(|F_o| - |F_c|)^2$; the R-factor was defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; the temperature factors of the independent As ions were treated as a common parameter. The coordinates of the fluorine and oxygen atoms were fixed at the values obtained from the difference map. Scattering form factors were taken from references [12] and [13]. Most calculations were performed on a VAX computer with the SHELX 76 system of programs [14]. Final parameters are given in Table II.

Results and Discussion

Analytical results for the compounds are presented in Table I. The analytical data for metal, nitrogen, carbon and hydrogen contents are in good agreement with the formulation $[Ln(TMU)_6](AsF_6)_3$, where Ln = La–Lu and Y.

The analysis and the IR spectra show that water is not present in the composition of the compounds.

TABLE II. Atomic Coordinates, Temperature Factors and Site Occupation Factors in the Partial Molecular Model.

Atom	x/a	y/b	z/c	BISO (A^2)	S.O.F.
Eu	0.000	0.000	0.000	1.9(1)	0.083
As(1)	0.250	0.250	0.250	7.4(2)	0.083
As(2)	0.500	0.500	0.500	7.4(2)	0.083
As(3)	0.750	0.750	0.750	7.4(2)	0.083
F(1)	0.250	0.345	0.250	14(1)	0.233
F(2)	0.013	0.007	0.419	15(1)	0.179
O	0.127	0.000	0.000	16(1)	0.500

Conductance data in nitromethane are close to that of 1:3 electrolytes and indicate that the hexafluoroarsenate ions are uncoordinated, as is also suggested by the IR spectrum. Electrolytic conductance data in nitromethane are included in Table I.

The infrared spectra of the complexes show the shift of the CO stretching mode from 1640 cm^{-1} to 1550–1560 cm^{-1}. It is interesting to note that the shift to lower wave numbers of 80 cm^{-1} is a little higher for similar complexes with other anions [1–10]. The considerable shifts of ν_{CO} to lower and the shifts of ν_{CN} to higher frequencies in the lanthanide complexes, as compared with the free ligand, confirm that the CO group is also bound to the lanthanide *via* oxygen, and suggest strong bonding of the ligand to these metal ions. Because of a small decrease in wave numbers upon complexation, we would expect ν_{MO} bands at lower energy for these complexes when compared with similar compounds. We observed that the MO stretching band occurs at 180–220 cm^{-1} in lanthanide complexes.

The AsF_6^- anions of the complexes are probably ionic in nature since ν_3 (690 cm^{-1}) does not split and ν_4 (395 cm^{-1}) appears as a single and sharp band. The O_h symmetry of the hexafluoroarsenate ion in these complexes confirms the non-coordinating character of the anion.

The fluorescence spectrum of $[Eu(TMU)_6](AsF_6)_3$ at 12 K obtained by argon laser excitation and the spectrum of this compound at 77 K recorded with a Perkin-Elmer spectrofluorimeter show an intense and sharp line at 592 nm as the most populated transition, and two very weak bands around 618 nm. This situation indicates that the europium(III) ion is located at a site that is a center of symmetry in the crystal lattice. This is consistent with the X-ray results because even though the special position of the lanthanide ion is not a center of symmetry, it behaves exactly as that with regard to its immediate environment of oxygen atoms sited at the special positions $x,0,0$; $0,x,0$; $0,0,x$; $\bar{x},0,0$; $0,\bar{x},0$ and $0,0,\bar{x}$. The emission spectrum obtained from a solid sample excited with laser radiation (5145 Å) at 12 K is essentially the same as that observed at 77 K (Fig. 1) and shows a similar relation between these transitions with the absence of lines in the $^5D_0 \rightarrow {}^7D_0$ region, but shows other weak bands not observed in the previous case.

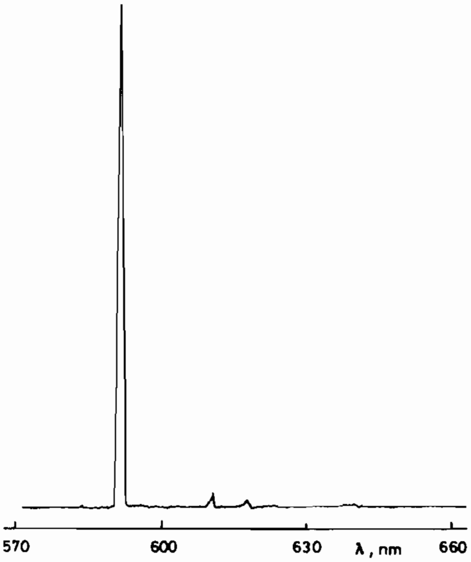

Fig. 1. Emission spectrum.

The analysis of this spectrum indicates the following attributions: the $^5D_0 \rightarrow {}^7F_0$ transition is not observed; the $^5D_0 \rightarrow {}^7F_1$ transition consists of an intense line at 592.2 nm; two weak bands that appear at 612.6 and 618.4 nm can be associated with the $^5D_0 \rightarrow {}^7F_2$ transition; one single line at 535.8 nm and another at 556.6 nm (both very weak when observed at room temperature) are consistent with the transitions $^5D_1 \rightarrow {}^7F_1$ and $^5D_1 \rightarrow {}^7F_2$; the transition $^5D_1 \rightarrow {}^7F_0$ is observed as a very weak line at 525.2 nm. This indicates a high site symmetry for Eu(III) and the main possibility is the O_h site. This hypothesis is consistent with the X-ray study. In fact, in spite of the high degree of disorder found in the crystal, the X-ray analysis shows unambiguously the crystallographically octahedral coordination of the Eu ion. On symmetry grounds, only electronic transitions for which the magnetic dipole selection rule $\Delta_J = 0, \pm 1$ (0 0 excluded) can occur. The $^5D_0 \rightarrow {}^7F_1$ is a pure magnetic dipole transition appearing as the most intense emission line and the ratio of the electric to magnetic intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ lines has been proposed as a measure of the deviation from inversion symmetry [15]. Since we have an octahedral system, it is not surprising that the $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ intensities relation is very low, consistent with the Eu(III) ion positioned exactly in the inversion center of the complex. Table III shows the energy levels

TABLE III. Observed Energy Levels for Eu^{3+} in $[Eu(TMU)_6](AsF_6)_3$.

Energy (cm^{-1})		Attributions
19041	A_{2g}——A_{1g}	$^5D_1$——$^7F_0$
18662	A_{2g}——T_{1g}	$^5D_1$——$^7F_1$
17964	A_{2g}——T_{2g}	$^5D_1$——$^7F_1$
16892	A_{1g}——A_{1g}	$^5D_0$——$^7F_1$
16324	A_{1g}——T_{1g}	$^5D_0$——$^7F_2$
16171	A_{1g}——T_{2g}	$^5D_0$——$^7F_2$

observed in the spectrum. The $^5D_0$ level cannot be measured directly since the O_h site symmetry forbids any optical activity for the $^5D_0 \rightarrow {}^7F_0$ transition, but we determined its value through the $^5D_1$ level.

Assuming O_h symmetry, we made the calculations of the crystal field parameters of polycrystalline $[Eu(TMU)_6](AsF_6)_3$ based on the fluorescence spectrum obtained at 12 K.

Two crystal-field parameters were determined through the secular determinant of the $^7F_2$ level, using the relationship $B_0^4/B_4^4 = \sqrt{14}/\sqrt{5}$ [15].

In the present case, we determined only the B_0^4 and B_4^4 parameters because we observed only four levels in the ^7F septuplet. The set of B_q^k parameters obtained without J-mixing effect was the following:

$B_0^4 = +995.4\ cm^{-1}$

$B_4^4 = +596.0\ cm^{-1}$

Conclusions

From analytical, conductometric, crystallographic and spectroscopic data there is little doubt that the lanthanide hexafluoroarsenate complexes consist of the hexacoordinated ion $[Ln(TMU)_6]$ with O_h symmetry, surrounded by three AsF_6^- anions with O_h symmetry as well. The hexafluoroarsenate ion behaves as a non-coordinating anion and confers high stability to the complexes. The parameter B_0^4 gives an indication that the crystal field is not significantly affected by the surrounding atoms.

In other two six-coordinated complexes of lanthanides with organic ligands ($Ln(ClO_4)_3 \cdot 6DPPA$, Ln = La, Eu, DPPA = $C_{12}H_{12}NOP$) recently studied in our Laboratory [16], we found a similar interesting situation in which the compound crystallizes in a cubic space group with the lanthanide atom in a special position of high point symmetry which forces the rest of the structure (or part of it) to be highly disordered. This seems to indicate that the energy of the lattice is dominated by the tri-positive lanthanide atom and its immediate surrounding, while the rest of the structure contributes to the minimization of the free energy by increasing its occupational entropy. The very high degree of disorder in the present case, however, does not prevent us from stating that the oxygen atoms of six TMU ligands are octahedrally coordinated to the europium atom with crystallographic point symmetry O_h.

The spectroscopic properties of similar complexes, $Ln(TMPO)_6 \cdot X_3$, have recently been studied [17]. Comparison of crystal field parameters shows that the effect of the crystal field is more significant in TMPO complexes ($B_0^4 = 1640\ cm^{-1}$) than in TMU complexes.

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