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Structural Studies of Addition Compounds of Lanthanides with Organic Ligands. I. Structures of Samarium and Erbium Hexafluorophosphates with N,N,N',N'-Tetramethylmalonamide

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Abstract

The crystal structures of the title compounds, $Ln(PF_6)_3 \cdot 4C_7H_{14}N_2O_2$ with Ln = Sm^{3+}, Er^{3+}, have been determined from diffractometric X-ray data and refined anisotropically to final R factors of 0·088 and 0·054, from 2184 and 3359 independent reflections above background, respectively. The space groups and cell dimensions are $C2/c$, $a = 24 \cdot 581$ (7), $b = 12 \cdot 264$ (1), $c = 16 \cdot 980$ (1) Å, $\beta = 110 \cdot 37$ (2)° for the Sm compound and $P2_1/c$, $a = 18 \cdot 555$ (1), $b = 17 \cdot 085$ (1), $c = 16 \cdot 372$ (3) Å, $\beta = 102 \cdot 1$ (2)° for the Er compound. The samarium structure has half a formula weight per asymmetric unit with the cation mounted on a twofold axis; in the erbium structure all atoms are in general positions with $Z = 4$. Both cations are eight-coordinated to the carbonyl oxygens of four N,N,N',N'-tetramethylmalonamide ligands which form an approximate Archimedean square antiprism of local point symmetry $\bar{8}2m$ (D_{4d}). The complexes are essentially different in that for the case of Sm the bites of the chelate ligands span only edges along the square faces of the antiprism while in the erbium structure the ligands also span lateral edges. Spectroscopic and structural evidence seems to indicate the possibility of $\bar{4}m2$ (D_{2d})–$\bar{8}m2$ (D_{4d}) dimorphism in the Sm complex.

In both structures the PF_6^- ions are slightly disordered as indicated by a rather high apparent thermal motion of the F atoms.

Introduction

Addition compounds of lanthanide hexafluorophosphates and N,N,N',N'-tetramethylmalonamide (TMMA), corresponding to the composition $Ln(PF_6)_3 \cdot x$TMMA, with $x = 5$ for Ln = La and $x = 4$ for Ln = Ce–Lu, Y, except Pm, have been prepared and extensively studied by several physicochemical methods (Vicentini & Becker, 1977). Infrared and Raman spectra seemed to indicate that the ligands are coordinated through the carbonyl O atoms and that the PF_6^- ions are not coordinated to the tripositive lanthanides. X-ray powder patterns showed that the complexes belong to one of three different series of isomorphous structures: the first corresponds to that of the lanthanum complex, the second includes the cerium to the erbium complexes and the third the dysprosium to the lutetium plus the yttrium complex. The hypersensitivity band of the neodymium, the fluorescence spectrum of the europium and the X-ray patterns suggest D_{2d} local symmetry for cations from cerium to

terbium. To interpret and to extend these results a three-dimensional X-ray analysis of several of these complexes was undertaken. We report here the crystal structures of the Sm and Er complexes, which belong to different isomorphous series and crystallize in different space groups, though they have identical stoichiometry.

Experimental

Both complexes were prepared as described by Vicentini & Becker (1977).

The compounds were dissolved in nitromethane; ethanol was then slowly added by the method of vapor diffusion, as described by Stout & Jensen (1968). After a few weeks, single crystals suitable for X-ray diffraction were obtained. A microanalysis of C, H and N performed on the crystals confirmed the stoichiometry of the compounds. Small irregularly shaped crystals, with maximum linear dimensions no greater than 0·3 mm in both cases, were mounted on a CAD-4 Enraf–Nonius diffractometer. 25 centered reflections using least-squares refinement produced the unit-cell dimensions and the orientation matrices for the data collection. Intensities were measured by the θ–2θ scan technique at a rate between 1·33 and 20·0° min^{-1} determined by a fast prescan of 20·0° min^{-1}. For both compounds reflections were collected in the range $0 < \theta < 50°$ using graphite-monochromated Cu $K\alpha$ radiation. Of the 3454 reflections measured for the Sm complex, 2184 had $I \geq 3\sigma(I)$, with $\sigma(I)$ estimated from counting statistics. For the Er complex, of the 5663 reflections measured, 3359 had $I \geq 3\sigma(I)$.

The intensity of one standard reflection was essentially constant over the duration of both experiments. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

Other relevant crystal data are as follows: $M_r = 1218·05$, $V = 4798·7$ Å^3, $D_m = 1·68$ (by flotation), $D_c = 1·686$ Mg m^{-3}, $\mu = 10·52$ mm^{-1} for the Sm structure and $M_r = 1234·96$, $V = 5074·7$ Å^3, $D_m = 1·62$ (by flotation), $D_c = 1·616$ Mg m^{-3}, $\mu = 5·08$ mm^{-1} for the Er structure.

Structure solution and refinement

(a) Samarium complex

From the observed density value the number of formula weights was found to be four. This indicated that the Sm atom and one or possibly three of the P atoms should be in the special position 4(e) of point symmetry 2 (C_2). The Sm atom was readily located from a Patterson map and all other non-hydrogen atoms were then found from alternate difference Fourier syntheses and full-matrix isotropic least

squares. One of the P atoms is sited in a general position and the other on the twofold axis. The F atoms, particularly those bonded to the P in a special position, were hard to locate and eventually refined to rather high isotropic temperature factors. The final isotropic R factor was 0·12. Anisotropic refinement was then carried out with the introduction of the weighting scheme $w = 1$ if $F_{obs} < C$, $w = 1/F_{obs}$ if $F_{obs} \geq C$ with $C = 30·00$ on an absolute scale. The final R terminated at 0·088 and R_w at 0·117. The 2184 reflections with intensities above $3\sigma(I)$ were included in the refinement; the maximum parameter shift was less than 0·02 of the standard deviation and refinement was considered complete.

(b) Erbium complex

In this case all atoms occupy general positions. A procedure similar to that described for the Sm structure was carried out. The final isotropic R factor was 0·10; the F atoms of all three PF$_6^-$ ions presented the same problems of location as in the Sm structure and they also refined to high isotropic temperature factors. In the

Table 1. *Final atomic parameters for the samarium structure*

	x	y	z	B_{eq} (Å^2)
Sm	0·0000	0·0388 (1)	0·2500	2·13
P(1)	0·2544 (2)	−0·0004 (5)	0·3601 (3)	3·87
P(2)	0·5000	0·0138 (9)	0·2500	5·10
F(11)	0·3180 (6)	0·023 (2)	0·3668 (12)	8·88
F(12)	0·1917 (6)	−0·028 (2)	0·3503 (11)	9·22
F(13)	0·2828 (10)	−0·037 (2)	0·4546 (9)	9·34
F(14)	0·2325 (9)	0·034 (2)	0·2656 (10)	10·15
F(15)	0·2643 (11)	−0·120 (2)	0·3340 (13)	11·17
F(16)	0·2472 (10)	0·114 (2)	0·3895 (18)	16·14
F(21)	0·4808 (9)	0·108 (2)	0·2968 (15)	12·07
F(22)	0·4400 (10)	0·017 (2)	0·1792 (23)	17·76
F(23)	0·4794 (11)	−0·076 (2)	0·2948 (13)	12·24
O(11)	0·0419 (5)	0·1050 (14)	0·1520 (6)	4·20
O(12)	0·0659 (5)	0·1864 (11)	0·3128 (7)	2·99
O(21)	−0·0589 (5)	−0·1068 (9)	0·2695 (6)	2·36
O(22)	−0·0625 (5)	−0·0297 (12)	0·1133 (6)	3·44
N(11)	0·0457 (6)	0·256 (2)	0·0753 (8)	3·59
N(12)	0·1424 (6)	0·299 (1)	0·3633 (9)	3·53
N(21)	−0·1285 (6)	−0·234 (1)	0·2507 (8)	3·26
N(22)	−0·1360 (6)	−0·103 (1)	0·0116 (8)	3·56
C(11)	0·0642 (6)	0·197 (2)	0·1468 (10)	2·66
C(12)	0·1059 (7)	0·236 (2)	0·3014 (10)	2·81
C(13)	0·1158 (8)	0·240 (2)	0·2180 (11)	4·34
C(111)	−0·0036 (9)	0·206 (3)	0·0047 (13)	6·02
C(112)	0·0679 (12)	0·363 (2)	0·0624 (14)	5·43
C(121)	0·1915 (8)	0·361 (2)	0·3565 (14)	5·06
C(122)	0·1344 (11)	0·297 (2)	0·4456 (12)	5·76
C(21)	−0·0909 (6)	−0·182 (1)	0·2258 (9)	2·12
C(22)	−0·0848 (8)	−0·210 (2)	0·1417 (10)	3·35
C(23)	−0·0939 (6)	−0·109 (2)	0·0893 (9)	2·73
C(211)	−0·1350 (9)	−0·205 (2)	0·3315 (11)	3·92
C(212)	−0·1667 (9)	−0·325 (2)	0·2031 (13)	4·35
C(221)	−0·1425 (11)	−0·004 (2)	−0·0380 (12)	5·01
C(222)	−0·1810 (9)	−0·190 (2)	−0·0213 (13)	5·25

Table 2. *Final atomic parameters for the erbium structure*

	x	y	z	B_{eq} (Å²)
Er	0·24032 (3)	0·04014 (4)	0·78600 (4)	2·59
P(1)	0·4484 (2)	0·2533 (3)	0·4703 (2)	4·99
P(2)	0·7425 (2)	0·4279 (2)	0·2190 (3)	4·26
P(3)	−0·0044 (2)	0·1944 (3)	0·3362 (3)	6·01
F(11)	0·4382 (10)	0·1728 (8)	0·5006 (11)	14·08
F(12)	0·4641 (8)	0·3321 (8)	0·4329 (11)	14·34
F(13)	0·4042 (7)	0·2825 (11)	0·5496 (7)	18·31
F(14)	0·4918 (9)	0·2214 (11)	0·3908 (9)	15·10
F(15)	0·3767 (5)	0·2564 (9)	0·4345 (6)	9·91
F(16)	0·5163 (6)	0·2554 (9)	0·5112 (8)	10·50
F(21)	0·7859 (5)	0·3749 (6)	0·2709 (7)	8·29
F(22)	0·7517 (6)	0·4980 (6)	0·2764 (6)	7·68
F(23)	0·8167 (5)	0·4504 (9)	0·1629 (7)	10·93
F(24)	0·7314 (6)	0·3553 (6)	0·1648 (7)	8·58
F(25)	0·6674 (5)	0·4067 (9)	0·2752 (6)	10·42
F(26)	0·7023 (5)	0·4788 (5)	0·1618 (5)	6·37
F(31)	−0·0626 (7)	0·2522 (9)	0·3293 (11)	13·77
F(32)	0·0184 (8)	0·2464 (11)	0·3921 (10)	21·49
F(33)	0·0586 (8)	0·1375 (12)	0·3337 (12)	17·35
F(34)	−0·0380 (9)	0·1316 (9)	0·2927 (11)	15·80
F(35)	0·0420 (11)	0·2258 (13)	0·2632 (13)	23·78
F(36)	−0·0540 (17)	0·1645 (13)	0·4059 (12)	25·02
O(11)	0·3349 (4)	0·0316 (5)	0·8598 (4)	3·56
O(12)	0·1915 (4)	0·0721 (5)	0·9233 (5)	3·43
N(11)	0·3833 (6)	−0·0328 (7)	0·9536 (7)	5·14
N(12)	0·1878 (6)	0·1582 (7)	1·0294 (6)	4·50
C(11)	0·3357 (6)	0·0180 (7)	0·9348 (7)	3·40
C(12)	0·2184 (6)	0·0988 (8)	0·9825 (7)	3·64
C(13)	0·2850 (6)	0·0609 (8)	1·0067 (7)	3·84
C(111)	0·3929 (9)	−0·0478 (11)	1·0410 (9)	7·52
C(112)	0·4352 (9)	−0·0719 (11)	0·8836 (10)	8·24
C(121)	0·2142 (9)	0·1871 (11)	1·1044 (9)	6·43
C(122)	0·1233 (8)	0·2011 (9)	1·0073 (10)	5·57
O(21)	0·2724 (4)	0·1685 (5)	0·7975 (5)	5·87
O(22)	0·3498 (4)	0·0596 (5)	0·6908 (5)	3·70
O(31)	0·1923 (5)	0·1065 (5)	0·6869 (5)	3·92
O(32)	0·1153 (4)	0·0114 (5)	0·8073 (5)	3·51
O(41)	0·2424 (5)	−0·0553 (4)	0·6836 (5)	3·55
O(42)	0·2354 (4)	−0·0831 (5)	0·8465 (5)	3·54
N(21)	0·3159 (6)	0·2882 (6)	0·7708 (6)	3·51
N(22)	0·4725 (6)	0·0676 (8)	0·6715 (7)	5·70
N(31)	0·1672 (9)	0·0747 (8)	0·5622 (8)	7·04
N(32)	−0·0053 (6)	0·0163 (7)	0·8217 (8)	5·32
N(41)	0·2816 (7)	−0·1591 (7)	0·6080 (7)	4·93
N(42)	0·1526 (6)	−0·1770 (6)	0·8966 (7)	4·73
C(21)	0·3259 (7)	0·2115 (7)	0·7674 (7)	3·21
C(22)	0·4056 (6)	0·1017 (9)	0·6974 (7)	3·88
C(23)	0·4010 (7)	0·1813 (8)	0·7311 (9)	3·98
C(211)	0·3760 (9)	0·3461 (9)	0·7475 (10)	5·75
C(212)	0·2407 (8)	0·3193 (9)	0·8122 (9)	5·26
C(221)	0·4792 (10)	−0·0124 (11)	0·6349 (12)	7·26
C(222)	0·5402 (8)	0·1163 (13)	0·6750 (12)	7·30
C(31)	0·1441 (9)	0·0834 (9)	0·6506 (9)	5·28
C(32)	0·0622 (7)	0·0318 (8)	0·7793 (8)	4·18
C(33)	0·0682 (8)	0·0711 (12)	0·6936 (11)	7·50
C(311)	0·1140 (14)	0·0483 (14)	0·5138 (12)	10·27
C(312)	0·2466 (12)	0·0925 (13)	0·5206 (12)	8·37
C(321)	−0·0127 (9)	−0·0333 (15)	0·8962 (11)	9·29
C(322)	−0·0744 (7)	0·0359 (13)	0·7899 (13)	7·98
C(41)	0·2452 (7)	−0·1254 (7)	0·6783 (8)	3·50
C(42)	0·1988 (6)	−0·1435 (7)	0·8322 (8)	3·36
C(43)	0·2065 (8)	−0·1787 (8)	0·7483 (8)	4·63
C(411)	0·2860 (12)	−0·2459 (10)	0·5928 (12)	8·39
C(412)	0·3209 (12)	−0·1099 (11)	0·5367 (10)	7·96
C(421)	0·1079 (9)	−0·2478 (9)	0·8856 (11)	6·53
C(422)	0·1419 (11)	−0·1399 (11)	0·9829 (10)	7·27

anisotropic refinement the weighting scheme $w = 1$ if $F_{obs} < C$, $w = 1/F_{obs}$ if $F_{obs} \geq C$ with $C = 80·00$ on an absolute scale was used, including the 3359 reflections with intensities greater than $3\sigma(I)$.

The final R factors were $R = 0·054$, $R_w = 0·068$ and the largest parameter shift was less than 0·04 of the standard deviation.

The atomic scattering factors used were those given by Cromer & Waber (1974) and the anomalous-dispersion correction coefficients those given by Cromer & Ibers (1974). The ionization states were considered to be 3+ for the Sm and Er atoms and neutral for all others. In both cases, the function minimized by least squares was $M = \sum w(|F_o| - |F_c|)^2$.

The final positional parameters for the Sm structure are given in Table 1, those for the Er structure in Table 2,* together with the equivalent isotropic temperature factors calculated following Hamilton (1959). The nomenclature system is shown in Fig. 1.

All calculations were performed on a PDP 11/45 computer with programs of the *Enraf–Nonius Structure Determination Package*.

Description of the structures

(a) Samarium complex

Fig. 2 is a stereoscopic view of the adduct along the c direction. The cation is sited on the twofold axis surrounded by four TMMA groups, only two of which are crystallographically independent. All eight oxygens of the organic ligands are coordinated to the cation at a mean distance of 2·409 Å, forming an approximate square antiprism around the Sm^{3+} ion. This configuration is better appreciated in Fig. 3 which shows a projection of the coordination polyhedron down the approximate 8 symmetry axis. The four O atoms of the approximate squares are no more than 0·13 Å from the best least-squares plane through them and the dihedral angle between the two planes is approximately 2°.
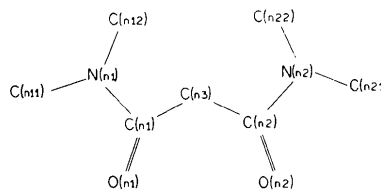
Fig. 1. Nomenclature system of N,N,N',N'-tetramethylmalonamide.
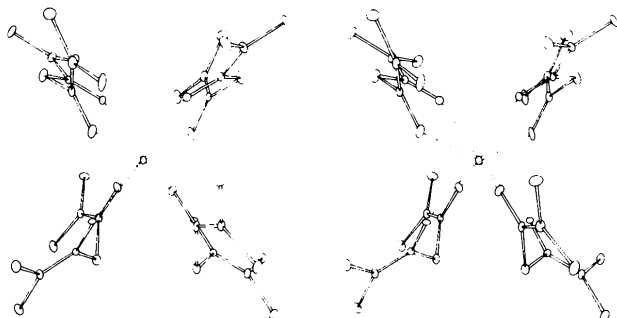
Fig. 2. Stereoview of the Sm complex.

Table 4. *Bond angles* (°) *in the samarium complex*

O(11)—C(11)—C(13)	121·3 (7)	O(21)—C(21)—C(23)	118·0 (6)
O(11)—C(11)—N(11)	121·3 (6)	O(21)—C(21)—N(21)	121·8 (6)
C(13)—C(11)—N(11)	117·2 (7)	C(23)—C(21)—N(21)	120·2 (6)
O(12)—C(12)—C(13)	124·1 (6)	C(21)—C(23)—C(22)	108·8 (6)
O(12)—C(12)—N(12)	120·5 (6)	O(22)—C(22)—C(23)	121·1 (6)
C(13)—C(12)—N(12)	115·3 (6)	O(22)—C(22)—N(22)	117·1 (7)
C(11)—C(13)—C(12)	111·9 (6)	C(23)—C(22)—N(22)	121·7 (6)
C(11)—N(11)—C(111)	115·2 (7)	C(21)—N(21)—C(211)	120·2 (6)
C(11)—N(11)—C(112)	126·0 (7)	C(21)—N(21)—C(212)	124·6 (6)
C(111)—N(11)—C(112)	118·7 (8)	C(211)—N(21)—C(212)	115·2 (6)
C(12)—N(12)—C(121)	124·9 (6)	C(22)—N(22)—C(221)	120·2 (6)
C(12)—N(12)—C(122)	117·2 (6)	C(22)—N(22)—C(222)	120·1 (7)
C(121)—N(12)—C(122)	117·7 (6)	C(221)—N(22)—C(222)	117·4 (6)

Fig. 3. Projection of the Sm complex down the approximate $\bar{8}$ axis, showing some interatomic distances (Å).

Table 3. *Interatomic distances* (Å) *in the samarium complex*

C(11)—O(11)	1·266 (8)	C(21)—O(21)	1·269 (7)
C(11)—C(13)	1·510 (9)	C(21)—C(23)	1·528 (9)
C(11)—N(11)	1·351 (9)	C(21)—N(21)	1·306 (8)
C(12)—O(12)	1·227 (7)	C(22)—O(22)	1·219 (8)
C(12)—C(13)	1·519 (9)	C(22)—C(23)	1·500 (11)
C(12)—N(12)	1·359 (8)	C(22)—N(22)	1·367 (8)
N(11)—C(111)	1·504 (10)	N(21)—C(211)	1·479 (9)
N(11)—C(112)	1·471 (12)	N(21)—C(212)	1·502 (9)
N(12)—C(121)	1·465 (9)	N(22)—C(221)	1·446 (10)
N(12)—C(122)	1·476 (10)	N(22)—C(222)	1·500 (10)

Interatomic distances and angles for the ligands are shown in Tables 3 and 4 respectively. Their values are all within the expected range with some minor exceptions, for example O(11)—C(11) and C(21)—O(21) which are rather too long. However, since no absorption corrections were applied, these differences are probably not significant. The groups C(*nm*), O(*nm*),

Table 5. *Dihedral angles between best least-squares planes through the groups* O(*nm*), C(*nm*), N(*nm*), C(*nm*1), C(*nm*2)

Samarium complex		Erbium complex			
n m	Angle (°)	*n m*	Angle (°)	*n m*	Angle (°)
1 1 1 2	45·1	1 1 1 2	34·0	3 1 3 2	44·4
2 1 2 2	59·0	2 1 2 2	25·7	4 1 4 2	34·8

N(*nm*), C(*nm*1), C(*nm*2), with $n = 1, 2, m = 1, 2$, are all approximately planar. The dihedral angle between two moieties of the same TMMA is different in the two crystallographically independent ligands. The relevant angular values are given in Table 5.

One of the PF_6^- ions is in a special position of point symmetry 2 (C_2) and the other is in a general position; both have an approximate O_h symmetry. The relevant interatomic distances are given in Table 6. The mean P—F distances for the groups are 1·543 and 1·551 Å respectively.

Table 6. P—F *distances* (Å)

(a) In the Sm structure

P(1)—F(11)	1·555 (6)	P(2)—F(21)	1·561 (8)
P(1)—F(12)	1·527 (6)	P(2)—F(22)	1·545 (8)
P(1)—F(13)	1·576 (6)	P(2)—F(23)	1·523 (9)
P(1)—F(14)	1·561 (6)		
P(1)—F(15)	1·572 (8)		
P(1)—F(16)	1·515 (8)		

(b) In the Er structure

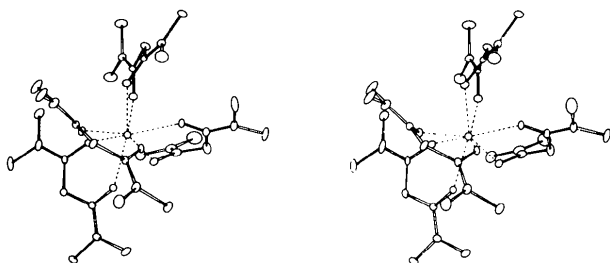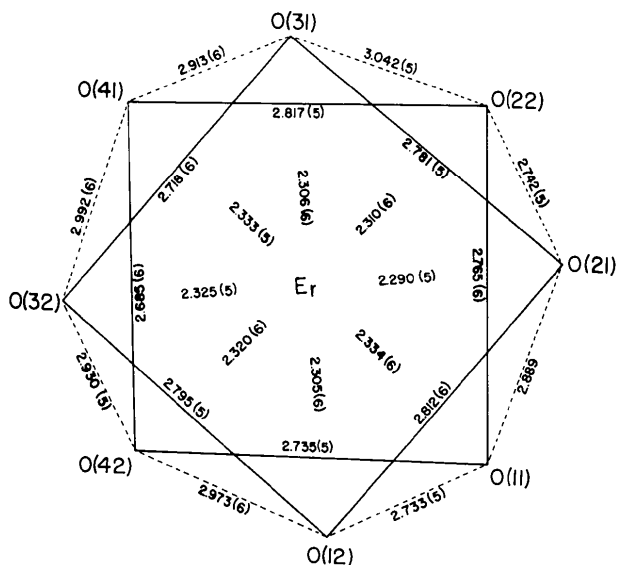|			
P(1)—F(11)	1·461 (7)	P(2)—F(24)	1·564 (5)
P(1)—F(12)	1·481 (7)	P(2)—F(25)	1·545 (5)
P(1)—F(13)	1·469 (6)	P(2)—F(26)	1·576 (4)
P(1)—F(14)	1·484 (7)	P(3)—F(31)	1·485 (7)
P(1)—F(15)	1·563 (5)	P(3)—F(32)	1·404 (7)
P(1)—F(16)	1·546 (5)	P(3)—F(33)	1·516 (8)
P(2)—F(21)	1·575 (5)	P(3)—F(34)	1·494 (7)
P(2)—F(22)	1·553 (5)	P(3)—F(35)	1·423 (9)
P(2)—F(23)	1·535 (5)	P(3)—F(36)	1·404 (10)

Fig. 4. Stereoview of the Er complex.

Fig. 5. Projection of the Er complex down the approximate $\bar{8}$ axis, showing some interatomic distances (Å).

(b) Erbium complex

Unlike the case of Sm, the Er atom is not sited on a special position; however, its coordination to the O atoms is in a similar square-antiprismatic configuration. The mean Er—O distance is 2·315 Å. Fig. 4 is a stereoscopic view of the adduct along the c direction and Fig. 5 shows a projection of the coordination polyhedron down the approximate $\bar{8}$ symmetry axis. The two (approximate) squares are in this case planar to within experimental accuracy, with a maximum deviation from the best least-squares plane through them of less than 0·03 Å; the dihedral angle between the planes is approximately 3°. Interatomic distances and angles for the ligands are shown in Tables 7 and 8 respectively. The groups O(nm), C(nm), N(nm), C(nm1), C(nm2), with $n = 1$, 4 and $m = 1$, 2, are also approximately planar. The dihedral angles between two moieties of the same TMMA ligand are given in Table 5. The P—F interatomic distances for the three independent anions are given in Table 6. The mean values of these distances for each group are 1·501, 1·558 and 1·454 Å respectively.

Table 7. *Interatomic distances* (Å) *in the erbium complex*

O(11)—C(11)	1·253 (7)	O(31)—C(31)	1·239 (8)
O(12)—C(12)	1·264 (7)	O(32)—C(32)	1·222 (6)
C(11)—C(13)	1·531 (8)	C(31)—C(33)	1·450 (11)
C(11)—N(11)	1·320 (7)	C(31)—N(31)	1·429 (10)
C(12)—C(13)	1·520 (8)	C(32)—C(33)	1·538 (10)
C(12)—N(12)	1·326 (8)	C(32)—N(32)	1·324 (8)
N(11)—C(111)	1·501 (9)	N(31)—C(311)	1·460 (11)
N(11)—C(112)	1·492 (9)	N(31)—C(312)	1·519 (11)
N(12)—C(121)	1·499 (9)	N(32)—C(321)	1·467 (10)
N(12)—C(122)	1·509 (9)	N(32)—C(322)	1·520 (9)
O(21)—C(21)	1·250 (6)	O(41)—C(41)	1·202 (6)
O(22)—C(22)	1·284 (7)	O(42)—C(42)	1·284 (6)
C(21)—C(23)	1·488 (8)	C(41)—C(43)	1·521 (8)
C(21)—N(21)	1·324 (7)	C(41)—N(41)	1·336 (7)
C(22)—C(23)	1·464 (8)	C(42)—C(43)	1·478 (8)
C(22)—N(22)	1·355 (7)	C(42)—N(42)	1·341 (7)
N(21)—C(211)	1·480 (8)	N(41)—C(411)	1·502 (9)
N(21)—C(212)	1·514 (8)	N(41)—C(412)	1·498 (9)
N(22)—C(221)	1·487 (10)	N(42)—C(421)	1·500 (9)
N(22)—C(222)	1·518 (9)	N(42)—C(422)	1·521 (9)

Table 8. *Bond angles* (°) *in the erbium complex*

O(11)—C(11)—C(13)	126·2 (6)	O(31)—C(31)—C(33)	122·6 (8)
O(11)—C(11)—N(11)	119·8 (6)	O(31)—C(31)—N(31)	115·1 (8)
C(13)—C(11)—N(11)	118·0 (6)	C(33)—C(31)—N(31)	122·1 (8)
O(12)—C(12)—C(13)	121·2 (6)	O(32)—C(32)—C(33)	123·8 (8)
O(12)—C(12)—N(12)	122·1 (6)	O(32)—C(32)—N(32)	119·6 (7)
C(13)—C(12)—N(12)	116·6 (6)	C(33)—C(32)—N(32)	116·5 (6)
C(11)—C(13)—C(12)	114·0 (5)	C(31)—C(33)—C(32)	112·6 (6)
C(11)—N(11)—C(111)	123·6 (6)	C(31)—N(31)—C(311)	119·2 (10)
C(11)—N(11)—C(112)	118·2 (6)	C(31)—N(31)—C(312)	119·4 (8)
C(111)—N(11)—C(112)	118·0 (6)	C(311)—N(31)—C(312)	121·4 (9)
C(12)—N(12)—C(121)	123·6 (6)	C(32)—N(32)—C(321)	117·7 (6)
C(12)—N(12)—C(122)	119·8 (6)	C(32)—N(32)—C(322)	123·3 (7)
C(121)—N(12)—C(122)	116·6 (6)	C(321)—N(32)—C(322)	118·2 (7)
O(21)—C(21)—C(23)	123·6 (6)	O(41)—C(41)—C(43)	122·3 (6)
O(21)—C(21)—N(21)	118·2 (6)	O(41)—C(41)—N(41)	119·9 (6)
C(23)—C(21)—N(21)	118·1 (6)	C(43)—C(41)—N(41)	117·7 (5)
O(22)—C(22)—C(23)	124·5 (6)	O(42)—C(42)—C(43)	123·1 (5)
O(22)—C(22)—N(22)	115·9 (6)	O(42)—C(42)—N(42)	118·3 (6)
C(23)—C(22)—N(22)	119·6 (6)	C(43)—C(42)—N(42)	118·6 (5)
C(21)—C(23)—C(22)	116·7 (5)	C(41)—C(43)—C(42)	113·3 (5)
C(21)—N(21)—C(211)	124·1 (6)	C(41)—N(41)—C(411)	124·6 (6)
C(21)—N(21)—C(212)	118·3 (5)	C(41)—N(41)—C(412)	120·3 (6)
C(211)—N(21)—C(212)	117·1 (6)	C(411)—N(41)—C(412)	115·1 (6)
C(22)—N(22)—C(221)	120·9 (6)	C(42)—N(42)—C(421)	121·9 (6)
C(22)—N(22)—C(222)	117·6 (7)	C(42)—N(42)—C(422)	119·4 (6)
C(221)—N(22)—C(222)	121·3 (6)	C(421)—N(42)—C(422)	118·7 (6)

Discussion

In both structures four TMMA molecules act as bidentate ligands with their carbonyl groups pointing to the tripositive ion and in both cases the coordination polyhedron has the shape of an approximate Archimedean square antiprism.

On comparison of the two adducts it is clear that the differences between them must be mainly a consequence of the different ionic radii of the central ions.

The effect of shrinkage of atomic radius with increasing atomic number (the lanthanide contraction) is clearly observed; the difference between the mean Sm—O distance and the mean Er—O distance of 0·09 Å is similar to the corresponding difference of the Pauling (1960) crystal radii of 0·08 Å.

In spite of having the same approximate local point symmetry $\bar{8}m2$ (D_{4d}), the complexes are essentially different in one important respect: in the case of Sm the bite of the chelate ligands spans only s-type edges [along the square faces of the antiprism (Lippard, 1967)] while in the case of Er two ligands span s edges and the other two span l-type [lateral, joining vertices of the different square faces (Lippard, 1967)] edges.

The shape of the square antiprism is determined by only two independent parameters: the ratio l/s and the angle θ between any central atom—ligand bond and the $\bar{8}$ axis. Table 9 compares the relevant experimental values with the corresponding theoretical ones for the 'hard-sphere model' (HSM) and the 'most favorable polyhedron' (MFP) as reported by Hoard & Silverton (1963). In the Sm complex, in which no chelate bite constrains directly the l-type edges, the θ closely approaches the theoretical value predicted by the MFP. In the Er complex the shortest l-type edges correspond to those spanned by the TMMA ligands; this indicates that the l-type bites of the chelate ligands force a shortening of the interplanar distance between the square faces of the antiprism thus enlarging the value of the θ angle.

In the Er complex the mean bite distance of all ligands, irrespective of whether they span s- or l-type edges, is 2·72 (2) Å, and all bite distances are shorter than any in the Sm structure [mean bite distance = 2·78 (1) Å]. Also, the four l-type edges spanned by the ligands are still shorter than the remaining four. This

seems to indicate that steric requirements impose a limit on the maximum bite-distance span by a ligand and that this limit is almost attained in the case of the Er complex; as a consequence the larger ionic radius of Sm prevents the TMMA ligands from spanning both s- and l-type edges which would produce the more rigid ion–ligand configuration adopted by the Er complex. So, a change in the ionic radius plus steric limitations for the ligands which arbitrarily increase their bite distances are responsible for the essentially different coordination arrangements of the two structures. The importance of ionic radius is even more dramatic in the adduct between TMMA and La^{3+}, the cation with the largest ionic radius of the series, which turns out to be coordinated to nine oxygens of five TMMA ligands (Becker & Castellano, to be published).

Spectroscopic considerations (Vicentini & Becker, 1977) indicated D_{2d} symmetry for the compounds from cerium to terbium. The spectroscopic analysis was based on the activities table given by Forsberg (1973) for complexes of lanthanide ions with nitrogen donor ligands. This table, which is based on group-theory considerations alone, lacks an entry corresponding to probably the most common point group for an eight-coordination configuration, namely D_{4d}; for completeness we give it in Table 10. The fluorescence spectrum, however, is not completely consistent with any of the splittings expected for the possible point groups associated with eight-coordination. The strongest spectroscopic evidence in favor of D_{2d} symmetry is the presence of two bands corresponding to the transition $^5D_0$–$^7F_2$, in agreement with the calculations by Forsberg. The most intense of these bands corresponds to the doubly degenerate E species and is expected for both D_{4d} and D_{2d} symmetries. The other band is nearly an order of magnitude less intense and, according to Forsberg, should correspond to an electric-dipole transition of the B_2 species in the D_{2d} symmetry.

The present X-ray analysis shows that neither D_{2d} nor D_{4d} symmetry is exactly realized in the Sm complex. Strictly speaking, the symmetry of the cation is that of the crystallographic special position in which the Sm ion is sited, namely C_2, although its approximate local symmetry is D_{4d}. It is then reasonable to suppose that

Table 9. *Coordination-polyhedra parameters for the Sm and Er complexes*

	HSM	MFP	Sm complex	Er complex
$\langle s\rangle$ (Å)			2·85	2·76
$\langle l\rangle$ (Å)			3·08	2·90
$\langle l\rangle/\langle s\rangle$	1·0	1·06	1·08	1·05
θ (°)	59·2	57·3	56·7	57·6

Table 10. *Splitting of ^7F_J levels and activity of $^5D_0$–^7F_J transitions in a crystal field of point symmetry D_{4d}*

	$J = 0$			$J = 1$			$J = 2$			$J = 3$			$J = 4$	
Γ	ED	MD	Γ	ED	MD	Γ	ED	MD	Γ	ED	MD	Γ	ED	MD
A_1	–	–	A_2	–	+	A_1	–	–	A_2	–	+	A_1	–	–
			E_1	+	–	E_1	+	–	E_1	+	–	B_1	–	–
						E_2	–	–	E_2	–	–	B_2	+	–
									E_3	–	+	E_1	+	–
												E_2	–	–
												E_3	–	+

Γ: irreducible representation. ED: electric-dipole allowed transition. MD: magnetic-dipole allowed transition.

the distortion of the antiprismatic configuration, which lowers the local symmetry to C_2, is responsible for the occurrence of the weakest band corresponding to the transition $^5D_0-^7F_2$.

A small splitting at liquid-nitrogen temperature of the strongest band corresponding to the transition $^5D_0-^7F_1$ is probably another consequence of the distorted D_{4d} symmetry, which partially removes the degeneracy of the E species (Vicentini & Becker, 1977).

A possible alternative to conciliate spectroscopic and crystallographic results is to postulate a $D_{4d}-D_{2d}$ dimorphism for the Sm complex.

The D_{2d} symmetry in eight-coordination can be realized by a triangular dodecahedron while the D_{4d} symmetry corresponds to that of a square antiprism (Lippard, 1967). It has been found theoretically that the energy difference between the two stereochemical forms is very small, amounting to about 4 kJ mol^{-1} (Parish & Perkins, 1967). As has been pointed out, it is conceivable that by slightly changing the conditions a given eight-coordinated complex could be converted from one form into another (Parish, Simms, Wells & Woodward, 1968). In our case, this hypothesis is made plausible by the following two facts: (a) neither the D_{2d} nor the D_{4d} symmetry is fully realized, as discussed above, which means that the potential barrier for the transition is even lower than for the ideal theoretical case; (b) the lack of ligand bites along l-type edges loosens the antiprism rigidity. In particular, the distorted square faces perpendicular to the 8 axis can easily be converted into the puckered faces of the dodecahedron, formed from two m- and two g-type edges (Lippard, 1967).

The hypothesis that the Sm complex may display dimorphism is presented here on a speculative basis and its eventual verification awaits further investigation.

All PF$_6^-$ ions in both structures have approximate O_h point symmetry. The F atoms all refined to rather high temperature factors and the mean P—F distance for each group varies quite a lot from one to another as can be seen in Table 6. The high values of the temperature factors may be interpreted as an apparent thermal motion due to some disorder of the groups.

It is interesting to note that the higher the mean temperature factor of a group the shorter is the mean P—F interatomic distance. This effect of apparent shortening of a bond distance with increasing thermal motion has been discussed by Busing & Levy (1964).

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