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Structural Studies of Addition Compounds of Lanthanides with Organic Ligands. II. Lanthanum Hexafluorophosphate and *N*,*N*,*N'*,*N'*-Tetramethylmalonamide

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Abstract

The crystal structure of the title compound, $La(PF_6)_3.5C_7H_{14}N_2O_2$, has been determined from X-ray diffractometric data and refined anisotropically to a final R factor of 0·073, from 5073 reflections above background. The space group is $P\bar{1}$, with M_r = 1354·7, Z = 2, a = 13·287 (1), b = 13·845 (1), c = 18·528 (4) Å and α = 71·46 (1), β = 80·19 (1), γ = 62·56 (1)°, V = 2866·8 Å^3, D_m = 1·56 (by flotation), D_c = 1·569 Mg m^{-3}, μ = 7·41 mm^{-1}. The cation is coordinated to nine carbonyl O atoms of the *N*,*N*,*N'*,*N'*-tetramethylmalonamide groups, located at the vertices of a distorted capped Archimedean square antiprism of point symmetry 4*mm*. 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 hexafluorophosphate and *N*,*N*,*N'*,*N'*-tetramethylmalonamide (TMMA), corresponding to the composition $Ln(PF_6)_3.x$TMMA, crystallize in three different series of isomorphous structures (Vicentini & Becker, 1977). In a previous paper (Castellano & Becker, 1981), the structures of two complexes belonging to each of two of these series, namely those corresponding to Ln = Sm, x = 4, and Ln = Er, x = 4, were reported.

The fact that these complexes crystallize in different space groups was explained in terms of the joint effect of changing ionic radii of the lanthanide atoms and maximum bite possibility of the chelate ligands.

We report here the structure corresponding to Ln = La, belonging to a third isomorphous series, which is formed just by itself. In the study by Vicentini & Becker (1977), it was assigned the value x = 5 in the general formula and the La atom was believed to be coordinated to the ten O atoms of five TMMA ligands.

Experimental

The complex was prepared as described by Vicentini & Becker (1977) and the crystals were obtained by the same method used for the Sm and Er complexes (Castellano & Becker, 1981). A prismatic crystal of linear dimensions 0·5 × 0·3 × 0·3 mm was mounted on a CAD-4 Enraf–Nonius diffractometer. 25 centered reflections using least-squares refinement produced the unit-cell dimensions and orientation matrix 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}. Reflections were collected in the range $0 < \theta < 50°$ using graphite-monochromated Cu $K\alpha$ radiation. Of the 5883 independent reflections collected, 5073 had $I \geq 3\sigma(I)$. The intensity of one standard reflection was essentially constant over the duration of the experiment. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

Structure solution and refinement

The La atom was readily located from a Patterson map and all other non-H atoms were then found from alternate difference Fourier syntheses and full-matrix isotropic least squares. The final isotropic R factor was 0·11. Anisotropic refinement was then carried out until the maximum parameter shift was less than 0·01 of the standard deviation, minimizing the quantity $M = \sum w(|F_o| - |F_c|)^2$ where w = 1. The final R terminated at 0·073 and a final difference synthesis was essentially featureless. Atomic scattering factors were those from *International Tables for X-ray Crystallography* (1974). The oxidation states were considered to be 3+ for the La atom and neutral for all others. The final positional parameters together with the equivalent isotropic temperature factors calculated following Hamilton

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Table 1. *Final coordinates and equivalent isotropic temperature factors calculated following Hamilton* (1959) *with e.s.d.'s in parentheses*

	x	y	z	B_{iso} (Å^2)
La	0·0905 (1)	0·4133 (1)	0·2285 (0)	2·31 (2)
P(1)	0·3037 (4)	0·8774 (4)	0·0171 (3)	5·0 (1)
F(11)	0·308 (2)	0·832 (2)	0·1010 (8)	20·0 (1)
F(12)	0·315 (2)	0·923 (1)	−0·0706 (8)	14·6 (7)
F(13)	0·268 (1)	0·793 (1)	0·010 (1)	14·3 (8)
F(14)	0·424 (1)	0·789 (2)	0·003 (1)	19·0 (1)
F(15)	0·188 (2)	0·962 (2)	0·026 (1)	22·3 (9)
F(16)	0·345 (3)	0·962 (2)	0·018 (1)	20·0 (1)
P(2)	0·3618 (4)	0·0362 (4)	0·6695 (3)	5·5 (1)
F(21)	0·4795 (9)	0·030 (1)	0·6861 (6)	9·5 (5)
F(22)	0·421 (1)	−0·091 (1)	0·669 (1)	12·2 (6)
F(23)	0·2478 (8)	0·0394 (9)	0·6507 (6)	7·9 (4)
F(24)	0·304 (2)	0·158 (1)	0·673 (1)	17·9 (9)
F(25)	0·337 (1)	−0·007 (2)	0·7567 (6)	13·9 (7)
F(26)	0·389 (1)	0·073 (2)	0·5841 (6)	14·3 (8)
P(3)	0·2425 (6)	0·7341 (5)	0·4325 (3)	7·5 (2)
F(31)	0·199 (2)	0·791 (2)	0·498 (1)	15·6 (9)
F(32)	0·131 (2)	0·823 (2)	0·395 (1)	24·0 (1)
F(33)	0·266 (2)	0·702 (2)	0·356 (1)	17·0 (1)
F(34)	0·194 (2)	0·652 (2)	0·466 (2)	20·0 (1)
F(35)	0·305 (2)	0·807 (2)	0·395 (1)	17·0 (1)
F(36)	0·347 (2)	0·653 (3)	0·472 (2)	32·0 (1)
O(11)	0·2338 (8)	0·2164 (6)	0·2256 (5)	3·7 (3)
C(11)	0·324 (1)	0·170 (1)	0·1885 (6)	3·1 (4)
N(11)	0·3480 (9)	0·0692 (9)	0·1828 (6)	3·7 (3)
C(111)	0·280 (1)	0·007 (1)	0·221 (1)	5·2 (5)
C(112)	0·455 (1)	0·005 (1)	0·143 (1)	5·4 (5)
C(13)	0·404 (1)	0·222 (1)	0·1589 (9)	3·7 (4)
O(12)	0·2492 (6)	0·4086 (6)	0·1295 (5)	3·4 (3)
C(12)	0·355 (1)	0·348 (1)	0·1409 (8)	3·2 (4)
N(12)	0·421 (1)	0·396 (1)	0·1327 (6)	4·0 (4)
C(121)	0·551 (1)	0·331 (2)	0·141 (1)	6·4 (6)
C(122)	0·377 (1)	0·522 (1)	0·112 (1)	5·8 (5)
O(21)	−0·0996 (8)	0·5627 (8)	0·1731 (6)	5·0 (3)
C(21)	−0·157 (1)	0·597 (1)	0·1170 (9)	4·0 (5)
N(21)	−0·237 (1)	0·706 (1)	0·1007 (8)	5·0 (4)
C(211)	−0·252 (2)	0·779 (1)	0·147 (1)	7·0 (6)
C(212)	−0·315 (2)	0·752 (2)	0·035 (1)	8·9 (7)
C(23)	−0·151 (1)	0·523 (1)	0·0724 (9)	4·7 (5)
O(22)	0·0462 (8)	0·4042 (8)	0·1016 (5)	4·1 (3)
C(22)	−0·043 (1)	0·408 (2)	0·0846 (8)	4·1 (5)
N(22)	−0·052 (1)	0·325 (1)	0·0738 (6)	4·8 (4)
C(221)	0·053 (2)	0·214 (2)	0·082 (1)	7·1 (7)
C(222)	−0·157 (2)	0·328 (2)	0·053 (1)	8·1 (8)
O(31)	0·2656 (8)	0·3799 (8)	0·2938 (6)	4·0 (3)
C(31)	0·319 (1)	0·314 (1)	0·3548 (8)	3·3 (4)
N(31)	0·3859 (9)	0·343 (1)	0·3788 (6)	3·9 (4)
C(311)	0·401 (1)	0·445 (1)	0·338 (1)	6·3 (6)
C(312)	0·457 (1)	0·269 (2)	0·4494 (9)	5·8 (6)
C(33)	0·314 (1)	0·204 (1)	0·3935 (8)	4·0 (4)
O(32)	0·1165 (6)	0·2887 (8)	0·3639 (5)	3·6 (3)
C(32)	0·204 (1)	0·200 (1)	0·3945 (8)	3·3 (4)
N(32)	0·194 (1)	0·108 (1)	0·4288 (6)	4·2 (4)
C(321)	0·296 (1)	−0·001 (1)	0·464 (1)	5·6 (5)
C(322)	0·086 (2)	0·100 (2)	0·436 (1)	7·2 (6)
O(41)	−0·0415 (8)	0·3207 (8)	0·2548 (5)	3·8 (3)
C(41)	−0·131 (1)	0·318 (1)	0·2876 (8)	3·6 (4)
N(41)	−0·154 (1)	0·229 (1)	0·3007 (6)	4·4 (4)
C(411)	−0·260 (1)	0·224 (2)	0·334 (1)	5·8 (6)
C(412)	−0·070 (2)	0·130 (2)	0·271 (1)	7·4 (7)
C(43)	−0·217 (1)	0·418 (1)	0·3156 (8)	3·8 (4)
O(42)	−0·3207 (9)	0·4638 (9)	0·2031 (6)	5·3 (4)
C(42)	−0·319 (1)	0·492 (1)	0·259 (1)	4·2 (5)
N(42)	−0·400 (1)	0·585 (1)	0·2792 (9)	5·4 (4)
C(421)	−0·396 (2)	0·622 (2)	0·345 (1)	7·8 (7)
C(422)	−0·497 (1)	0·660 (1)	0·225 (1)	6·6 (6)
O(51)	−0·0286 (8)	0·5272 (8)	0·3235 (5)	3·7 (3)
C(51)	−0·019 (1)	0·596 (1)	0·3483 (9)	4·1 (4)
N(51)	−0·078 (1)	0·615 (1)	0·4157 (6)	5·1 (4)
C(511)	−0·151 (2)	0·558 (2)	0·452 (1)	6·5 (6)
C(512)	−0·073 (2)	0·698 (2)	0·449 (1)	7·6 (7)
C(53)	0·058 (2)	0·650 (2)	0·312 (1)	6·2 (6)
O(52)	0·0924 (8)	0·5990 (8)	0·1976 (6)	4·0 (3)
C(52)	0·054 (1)	0·679 (1)	0·2248 (8)	3·8 (5)
N(52)	0·016 (1)	0·786 (1)	0·1846 (8)	5·0 (4)
C(521)	0·017 (2)	0·808 (2)	0·101 (1)	7·9 (7)
C(552)	−0·024 (2)	0·886 (1)	0·215 (1)	9·4 (8)

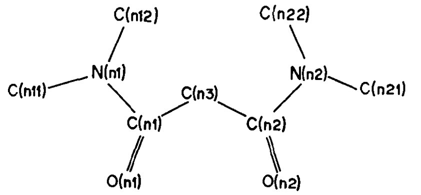

Fig. 1. System of nomenclature for the ligand atoms.

(1959) are given in Table 1. The system of nomenclature is shown in Fig. 1. All calculations were performed on a Digital PDP-10 computer with the *SHELX* 76 system of crystallographic programs (Sheldrick, 1976).*

Description of the structure

Fig. 2 is a stereoscopic view of the adduct along the normal to the *ab* plane. All O atoms of the TMMA ligands, except O(42), are coordinated to the cation at a mean distance of 2·54 Å, at the vertices of an approximate monocapped Archimedean square antiprism. This configuration is better appreciated in Fig. 3, showing a projection of the coordination polyhedron down the normal to the best least-squares plane through atoms O(11), O(31), O(51) and O(41), which define the capped face of the antiprism. The maximum distance of these atoms to the plane is 0·06 Å. The base of the antiprism is defined by atoms O(12), O(52), O(11) and O(22), with a maximum deviation from the best least-squares plane through them of 0·05 Å. The dihedral angle between the base and capped planes is 4·7°. All relevant interatomic bond distances of the coordination polyhedron are given in Table 2. Edges were labeled following Drew (1977).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36142 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

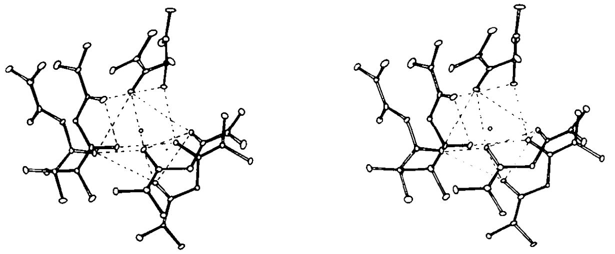

Fig. 2. Stereoscopic view of the adduct along the normal to the *ab* plane.

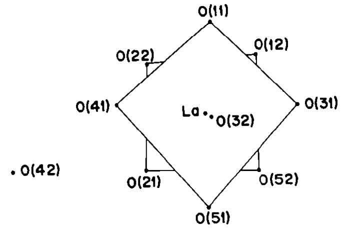

Fig. 3. The coordination polyhedron projected down the normal to the best least-squares plane through atoms O(11), O(31), O(51) and O(41).

Table 2. *Interatomic distances* (Å) *in the coordination polyhedron*

Edges are named following Drew (1977): *c* edges contain the capping atom; *s*1 are edges of the capped square face; *s*2 are edges of the uncapped square faces; *l* are the remaining lateral edges.

La—O distances

	O(11)	O(12)	O(21)	O(22)	O(31)
La	2·52 (1)	2·54 (1)	2·54 (1)	2·57 (1)	2·59 (1)

	O(32)	O(41)	O(51)	O(52)
La	2·53 (1)	2·52 (1)	2·57 (1)	2·46 (1)

c-type edges

	O(11)	O(31)	O(51)	O(41)
O(32)	2·97 (1)	2·75 (1)	2·87 (1)	2·95 (1)

*s*1-type edges

	O(31)	O(41)
O(11)	3·13 (1)	3·27 (1)
O(51)	3·52 (1)	3·50 (1)

*s*2-type edges

	O(22)	O(52)
O(12)	2·86 (1)	3·01 (1)
O(21)	2·72 (1)	2·95 (1)

l-type edges

	O(22)	O(12)
O(11)	3·23 (1)	2·77 (1)

	O(52)	O(21)
O(51)	2·78 (1)	2·92 (1)

	O(12)	O(52)
O(31)	2·97 (1)	3·03 (1)

	O(21)	O(22)
O(41)	2·98 (1)	2·96 (1)

Table 3. *Interatomic distances* (Å) *for the five* TMMA *groups*

	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
C(*n*1)–O(*n*1)	1·27 (2)	1·23 (2)	1·28 (2)	1·26 (2)	1·24 (2)
C(*n*1)–C(*n*3)	1·48 (2)	1·47 (3)	1·49 (2)	1·51 (2)	1·50 (3)
C(*n*1)–N(*n*1)	1·32 (2)	1·36 (2)	1·31 (3)	1·33 (3)	1·39 (2)
C(*n*2)–O(*n*2)	1·27 (2)	1·25 (2)	1·28 (1)	1·23 (3)	1·22 (2)
C(*n*2)–C(*n*3)	1·50 (2)	1·56 (2)	1·49 (3)	1·58 (2)	1·53 (2)
C(*n*2)–N(*n*2)	1·30 (3)	1·28 (3)	1·28 (2)	1·36 (2)	1·32 (2)
N(*n*1)–C(*n*11)	1·48 (2)	1·45 (3)	1·47 (2)	1·47 (2)	1·48 (3)
N(*n*1)–C(*n*12)	1·50 (2)	1·52 (3)	1·53 (2)	1·51 (2)	1·49 (3)
N(*n*2)–C(*n*21)	1·54 (2)	1·50 (2)	1·53 (2)	1·46 (3)	1·47 (3)
N(*n*2)–C(*n*22)	1·49 (2)	1·50 (3)	1·46 (3)	1·51 (2)	1·49 (3)

Table 4. *Bond angles* (°) *for the five* TMMA *groups*

	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
O(*n*1)–C(*n*1)–C(*n*3)	122 (2)	124 (1)	122 (2)	119 (2)	123 (2)
O(*n*1)–C(*n*1)–N(*n*1)	117 (2)	117 (2)	117 (1)	123 (1)	117 (2)
C(*n*3)–C(*n*1)–N(*n*1)	121 (1)	120 (2)	121 (1)	118 (1)	120 (2)
O(*n*2)–C(*n*2)–C(*n*3)	121 (2)	118 (2)	121 (2)	120 (1)	116 (1)
O(*n*2)–C(*n*2)–N(*n*2)	120 (1)	125 (1)	119 (2)	125 (1)	125 (2)
C(*n*3)–C(*n*2)–N(*n*2)	120 (1)	117 (2)	120 (1)	115 (2)	119 (2)
C(*n*1)–C(*n*3)–C(*n*2)	117 (1)	115 (1)	117 (1)	110 (1)	110 (2)
C(*n*1)–N(*n*1)–C(*n*11)	123 (1)	121 (2)	122 (1)	126 (1)	119 (2)
C(*n*1)–N(*n*1)–C(*n*12)	121 (1)	120 (2)	122 (1)	118 (1)	121 (2)
C(*n*11)–N(*n*1)–C(*n*12)	116 (1)	119 (3)	116 (2)	116 (2)	120 (2)
C(*n*2)–N(*n*2)–C(*n*21)	124 (1)	118 (2)	122 (2)	125 (1)	117 (2)
C(*n*2)–N(*n*2)–C(*n*22)	122 (1)	126 (1)	123 (1)	116 (2)	127 (2)
C(*n*21)–N(*n*2)–C(*n*22)	115 (2)	116 (2)	115 (1)	119 (1)	117 (1)

Table 5. *Dihedral angles* (°) *between best least-squares planes through the groups* O(*nm*), C(*nm*), C(*n*3), N(*nm*), C(*nm*1), C(*nm*2)

n	*m*		*n*	*m*	
1	1	38 (2)	4	1	37 (2)
1	2		4	2	
2	1	38 (3)	5	1	56 (2)
2	2		5	2	
3	1	49 (2)			
3	2				

Table 6. *Interatomic distances* (Å) *for the three hexafluorophosphate anions*

	$n=1$	$n=2$	$n=3$
P(*n*)–F(*n*1)	1·48 (1)	1·60 (2)	1·53 (2)
P(*n*)–F(*n*2)	1·56 (2)	1·57 (2)	1·53 (2)
P(*n*)–F(*n*3)	1·49 (3)	1·59 (2)	1·57 (2)
P(*n*)–F(*n*4)	1·54 (2)	1·52 (2)	1·48 (3)
P(*n*)–F(*n*5)	1·47 (2)	1·57 (1)	1·52 (3)
P(*n*)–F(*n*6)	1·52 (4)	1·54 (1)	1·45 (3)

Interatomic distances and angles for the ligands are given in Tables 3 and 4 respectively. All values are within the expected range, with the minor exception of some C—O distances which are somewhat too long. This effect was also observed in the Sm and Er complexes (Castellano & Becker, 1981) and is probably significant. Each of the groups C(*nm*), O(*nm*), N(*nm*), C(*nm*1), C(*nm*2), with $n = 1, \ldots, 5$, $m = 1, 2$, is planar to within experimental accuracy. The dihedral angle between the two moieties of the same TMMA is different in each ligand. The relevant angular values are given in Table 5. As in the complexes of Sm and Er, the dihedral angles seem to have no correlation with the bite distance span by the ligands (Castellano & Becker, 1981).

All PF_6^- groups have an approximately octahedral configuration and show some amount of disorder, as indicated by the high value of their temperature factors. P—F distances are given in Table 6. The corresponding mean values for each of the PF_6^- groups are 1·51, 1·57 and 1·51 Å respectively.

Discussion

As indicated by the previous study of Vicentini & Becker (1977), five TMMA groups are coordinated to the cation. Four of them act as bidentate ligands with the O atoms of their carbonyl groups pointing to the central ion and a fifth one coordinated just through one of its carbonyl O atoms. The coordination number of the complex is therefore nine.

It is known that nine-coordination polyhedra are always described in terms of the tricapped trigonal prism (TCTP) of point symmetry D_{3h} or the capped square antiprism (CSAP) of point symmetry C_{4v} (Drew, 1977). Very often, however, the coordination polyhedron does not approximate to one with non-trivial symmetry, as in the present case. When this happens, the best that can be done is to decide which of the ideal polytypes is closer to the one observed. This requires the definition of a comparison criterion and many have been proposed to systematize the procedure. We have adopted the one by Guggenberger & Muetterties (1976), which is simple and, at least in the present case, discriminates quite convincingly between the two possibilities. Table 7 shows the fairly good agreement between observed dihedral angles of triangular faces and the corresponding theoretical values calculated by Guggenberger & Muetterties for the idealized CSAP. Also the normalized mean distances for the four types of edges in the CSAP are in close agreement with those for the theoretical hard-sphere model (with $n = 6$ in the formula $E = \sum r_{ij}^{-n}$, $i \neq j$, for the repulsion energy), as shown in Table 8. These facts, together with the lack of any angle between opposite triangular faces close to 0° (the closest value being 16°) is another important parameter to discriminate against a possible TCTP polytype.

Table 7. *Characteristic dihedral angles (°) of the coordination polyhedron*

Idealized values of Guggenberger & Muetterties (1976) are in parentheses.

O(11)O(12)O(31)–O(21)O(41)O(51)	161 (3)	(163·5)
O(31)O(51)O(52)–O(11)O(22)O(41)	164 (2)	
O(41)O(22)O(21)–O(31)O(52)O(12)	139 (3)	(128·2)
O(11)O(22)O(12)–O(51)O(21)O(52)	135 (2)	
O(21)O(22)O(12)O(52)–O(11)O(31)O(51)O(41)	4·7 (3)	(0·0)

Table 8. *Observed and theoretical dimensions (Å) of the coordination polyhedron*

Edges are labeled as in Table 2.

Edge type	Mean distance	Normalized distance*	Theoretical value†
c	2·89 (2)	1·14	1·13
*s*1	3·36 (3)	1·32	1·32
*s*2	2·86 (2)	1·13	1·13
l	2·96 (3)	1·17	1·18

* Normalized according to a mean La—O value of 2·54 Å.
† Corresponding to $n = 6$, see text.

As pointed out by Drew (1977), the CSAP has four types of edges of which all but one, namely that of the capped square face *s*1, are suitable to take chelate bites. This observation is fully realized in the present case: one ligand spans an *s*2-type edge [O(21)—O(22)], two span *l*-type edges [O(11)—O(12)] and [O(51)—O(52)], and another ligand spans a *c*-type edge [O(31)—O(32)]. Edges spanned by one TMMA group are systematically shorter than those of the same type not spanned by the chelate ligand. These constraints appear to be responsible for the distortion of the coordination polyhedron from the ideal C_{4v} symmetry; however, it is probably just the chelated nature of the ligands that determines the (approximate) C_{4v} configuration, since, according to the calculations of Guggenberger & Muetterties, the CSAP polytype is not, like the TCTP one, at an energy minimum.

Compared with the transition from the Er to the Sm series, the one from the Sm to the La shows a more dramatic effect of the 'lanthanide contraction' in that, rather than just modifying the arrangements of ligands around the ion, the increased ionic radius permits the accommodation of a new TMMA group in the coordination polyhedron.

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