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The Disordered Structures of the Addition Compounds of Europium and Lanthanum Perchlorates with Diphenylphosphinamide

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Abstract

The crystal structures of the title compounds $Ln(ClO_4)_3\cdot 6C_{12}H_{12}NOP$ with Ln = Eu^{3+}, La^{3+}, have been determined from diffractometric X-ray data and refined to final *R*-factors of 12.4% and 13.3% from 450 and 454 independent reflections above background respectively. For the Eu compound the space group is *F*23 with a = 20.29(1) Å, V = 8353(5) Å, M = 1753.6, Z = 4, Dc = 1.40 g cm^{-3}, λ(Mo$K\alpha$) = 0.71069 Å, μ = 9.46 cm^{-1} and for the La compound is *Pa*3 with a = 19.98(1) Å, V = 7976(7) Å, M = 1740.5, Z = 4, Dc = 1.45 g cm^{-3}, λ(Mo$K\alpha$) = 0.71069 Å, μ = 7.48 cm^{-1}. The lanthanide atoms are sited on special positions of high point symmetry (23 and $\bar{3}$ respectively). Both cations are six-coordinated to the phosphoryl oxygens of diphenylphosphinamide (DPPA, $C_{12}H_{12}NOP$) groups, which form an octahedron (Eu compound) and a trigonal antiprism (La compound). The phosphoryl groups are aligned with the lanthanide cation in the Eu complex but form a La–O–P angle of 157(1)° in the other case. The presence of a strong fluorescence band $^5D_0 \rightarrow {}^7F_2$ in the Eu complex, forbidden on symmetry grounds, is attributed to vibronic interactions. A splitting of the infrared $\nu_{P=O}$ band in the La complex is explained in terms of inequivalent environments produced by disordered DPPA ligands.

Introduction

The preparation of anhydrous diphenylphosphinamide (DPPA) adducts of the lanthanide perchlorates has been described [11]. Compounds of general formula $Ln(ClO_4)_3\cdot$6DPPA (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) were prepared and characterized by analysis; infrared spectra, molar conductance in nitromethane and nitrobenzene and X-ray powder patterns. The compounds were found to belong to three isomorphous series: one containing elements of lanthanum and cerium, a second from praseodymium to europium and a third from gadolinium to lutetium and yttrium. Absorption and emission spectra of $Eu(ClO_4)_3\cdot$6DPPA have also been reported [1]. The experimental evidence indicates that in the europium complex the cation is coordinated through the phosphoryl oxygens to six DPPA molecules with a local environment of point symmetry O_h, distorted, in the solid phase, to C_{4v}.

No fluorescence data are available for any members of the first and third isomorphous series.

To interpret the spectroscopic and chemical results we have undertaken the crystal structure determination of the title compounds, which belong to the first and second isomorphous series respectively, as part of a series of structural studies of lanthanides with organic ligands [2, 3].

No compound belonging to the third isomorphous series produced single crystals appropriate for diffractometric structure determination.

Experimental

The compounds were prepared as described in the literature [1].

In both crystals, diffraction measurements were carried out on a CAD-4 Enraf-Nonius diffractometer. Cell dimensions and the orientation matrices for data collection were calculated by least squares from 25 centered reflections using graphite monochromated Mo$K\alpha$ radiation. Diffraction intensities for reflections having θ in the range 1–22° were measured using a variable scan speed between 2.8–6.7° min^{-1} determined by a fast prescan of 6.7° min^{-1}. The intensity of one standard reflection was, in both cases, essentially constant for the duration of the experiment. Data were corrected by Lorentz and polarization effects but not for absorption or extinction.

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In both crystals a complete octant of the reciprocal space was measured and the independent set was obtained by averaging the Laue equivalents. The corresponding agreement R-factor [4] was 0.054 for the europium and 0.051 for the lanthanum complex.

The europium complex crystal was octahedral with edges of approximately 0.25 mm. Of the 475 independent reflections measured, 450 had $I > 2\sigma(I)$.

The lanthanum complex crystal was a fragment of irregular shape with maximum and minimum linear dimensions of about 0.30 and 0.25 mm respectively. Of the 1637 independent reflections measured, 454 had $I > 3\sigma(I)$.

Structures solution and refinement proceeded as follows:

Europium Complex

Diffraction symmetry indicated a cubic space group with an F centered lattice. A few small violations to the systematic absences expected from centering and the low occupation number $Z = 4$ determined from the observed density, clearly indicated the presence of disorder. Since $Z = 4$, the europium atom site is fixed by the space group symmetry.

The structure refined in space group $F23$, the lowest symmetry group (approximately) consistent with the systematic extinctions. A difference map phased on the europium atom placed on special position at ¼, ¼, ¼ (local point symmetry 23), produced the only crystallographic independent phosphoryl group located on the two-fold axis through the heavy atom. The rest of the map was too noisy to be further interpreted. A difference map phased on the heavy atom and the phosphoryl group was not significantly better then the previous one. The R-factor at this stage was 38%. A previous crystal structure determination of DPPA [5] had shown that there is not a molecular two-fold axis along the phosphoryl group, as is indeed expected on stereochemical grounds. On the assumption that this two-fold symmetry is also absent in the present case, it followed that all atoms in the DPPA groups other than oxygen and phosphorus should be disordered. To proceed further, the position of the phenyl group atoms was investigated by calculating structure factors from the partial structure (europium, phosphorus and oxygen atoms) plus a rigid phenyl ring located on a series of stereochemically reasonable positions and orientations until a minimum R-factor was attained. A phenyl group was generated at a P–C fixed distance of 1.81 Å (as in the pure substance) with the O–P–C angle set at the tetrahedral value 109.5°. This ring was rotated around the P–C bond and the O–P bond in intervals of 5 degrees. At each of these positions the R-factor was calculated for a subset of structure factors with amplitudes and sine-theta values lower than certain conveniently chosen limits to enhance the contribution of the light atoms. An occupancy of 0.5 was attributed to all carbon atoms. Two independent and stereochemically consistent sites were found. The phenyl atoms were refined anisotropically about these positions as rigid groups (hydrogen atoms included with a common U-value of 0.05 Å^2) with the P–C distance constrained to the value 1.81 Å with a standard deviation of 0.02 Å. The R-factor dropped to about 15%.

A subsequent difference map showed five more peaks in positions which could be attributed to chlorine atoms of the perchlorate groups. Refinement of the occupancy factors of these atoms, with their U-values set to 0.09 Å^2 and the rest of the structure fixed, gave final occupancy factors which added up to 0.28, which compares well with the value of 0.25 expected for the overall chlorine occupancy in the unit cell. Only one of the peaks, however, gave a significant contribution to the chlorine occupancy (0.166) and since refining the other four chlorine atoms does not add to a meaningful interpretation of the structure we decided not to include them in the model. None of the oxygen atoms of the ClO_4^- groups nor the nitrogen atom of the ligand could be located. This incomplete model gave a final R-factor of 12.4%.

Lanthanum Complex

Laue symmetry and systematic absences unambiguously indicated space group $Pa3$. As in the europium structure $Z = 4$ and the heavy atom is fixed by the space group symmetry. A difference map phased on the heavy atom placed on the special position ½, ½, ½ of point symmetry $\bar{3}$ showed the oxygen and phosphorus atoms of the only independent DPPA group. Alternate cycles of isotropic least squares and difference maps allowed localization of all non-hydrogen atoms of the cation. Two peaks on the 3-fold axis were attributed to disordered chlorine atoms of perchlorate groups. Fixing the temperature factors of these atoms to the common value 0.06 Å^2, their occupation number refined to about 1/6 (Cl(1)) and 1/3 (Cl(2)) respectively, thus giving an overall unit cell occupation of 12 chlorine atoms, as expected. An unusually high isotropic temperature factor suggested that the La atom could be disordered. To test this hypothesis, a lanthanum atom with half occupation was placed close to the special position ½, ½, ½ and its location on the 3-fold axis was allowed to refine. The refinement converged with the atom at 0.25 Å of the $\bar{3}$ centre and a dramatic drop in the R-factor from 24 to 14%. A similar effect on the R-factor value was observed when the lanthanum atom, with its position fixed at the centre of symmetry on the 3-fold axis, was allowed to refine anisotropically. This was the scheme chosen for the

TABLE I. Positional Parameters and Equivalent *B* Values ($Å^2$). B's Calculated Following Hamilton [8].

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B* (iso)
a) Eu complex				
Eu	0.25	0.25	0.25	3.6(1)
P	0.25	0.25	0.0654(3)	9.1(7)
O	0.25	0.25	0.138(1)	5(1)
Cl	0	0.330(2)	0	4(1)
C(1)	0.188(2)	0.1915(9)	0.039(2)	9(1)
C(2)	0.140(2)	0.2096(9)	−0.007(2)	9(1)
C(3)	0.092(2)	0.1645(9)	−0.026(2)	9(1)
C(4)	0.092(2)	0.1012(9)	0.000(2)	9(1)
C(5)	0.139(2)	0.0831(9)	0.047(2)	9(1)
C(6)	0.187(2)	0.1283(9)	0.066(2)	9(1)
C(7)	0.318(2)	0.220(2)	0.015(1)	21(1)
C(8)	0.365(2)	0.180(2)	0.044(1)	21(1)
C(9)	0.427(2)	0.173(2)	0.015(1)	21(1)
C(10)	0.442(2)	0.208(2)	−0.042(1)	21(1)
C(11)	0.395(2)	0.249(2)	−0.072(1)	21(1)
C(12)	0.333(2)	0.255(2)	−0.043(1)	21(1)
b) La complex				
La	0.5	0.5	0.5	9(2)
O(1)	0.099(1)	0.045(2)	0.451(2)	8(1)
P	0.1428(7)	0.0680(8)	0.3987(7)	7.1(7)
N	0.115(2)	0.049(3)	0.326(2)	12(1)
C(1)	0.152(2)	0.1577(9)	0.403(1)	14(1)
C(2)	0.164(2)	0.1949(9)	0.345(1)	14(1)
C(3)	0.177(2)	0.2634(9)	0.350(1)	14(1)
C(4)	0.177(2)	0.2948(9)	0.412(1)	14(1)
C(5)	0.165(2)	0.2576(9)	0.470(1)	14(1)
C(6)	0.152(2)	0.1890(9)	0.465(1)	14(1)
C(7)	0.226(1)	0.034(2)	0.409(1)	11(1)
C(8)	0.250(1)	0.021(2)	0.473(1)	11(1)
C(9)	0.313(1)	−0.007(2)	0.482(1)	11(1)
C(10)	0.352(1)	−0.023(2)	0.426(1)	11(1)
C(11)	0.327(1)	−0.011(2)	0.362(1)	11(1)
C(12)	0.264(1)	0.018(2)	0.353(1)	11(1)
Cl(1)	0.3730(8)	0.3730(8)	0.3730(8)	*
O(Cl1)	0.4118(9)	0.4118(9)	0.4118(9)	11(1)
O′(Cl1)	0.365(4)	0.403(3)	0.314(2)	*
Cl(2)	0.139(1)	0.139(1)	0.139(1)	12.3(7)
O(Cl2)	0.100(1)	0.100(1)	0.100(1)	33(1)
O′(Cl2)	0.156(4)	0.105(2)	0.194(2)	25(1)

TABLE II. Bond Lengths (Å) and Angles (°).

a) Eu complex

		O–P–C(1)	107(1)
Eu–O	2.27(2)	O–P–C(7)	124(1)
P–O	1.47(2)	C(1)–P–C(7)	98(2)
P–C(1)	1.81(3)	P–C(1)–C(2)	120(2)
P–C(7)	1.81(3)	P–C(1)–C(6)	119(2)
		P–C(7)–C(8)	118(3)
		P–C(7)–C(12)	118(3)

b) La complex

		La–O–P	157(1)
La–O	2.40(3)	O–P–N	112(2)
P–O	1.44(3)	O–P–C(1)	110(2)
P–N	1.60(4)	N–P–C(1)	108(2)
P–C(1)	1.80(1)	O–P–C(7)	111(2)
P–C(7)	1.81(1)	N–P–C(7)	109(2)
Cl(1)–O(Cl1)	1.34(2)	C(1)–P–C(7)	106(2)
Cl(1)–O′(Cl1)	1.33(2)	P–C(1)–C(2)	120(1)
Cl(2)–O(Cl2)	1.35(2)	P–C(1)–C(6)	119(1)
Cl(2)–O′(Cl2)	1.34(2)	P–C(7)–C(8)	119(1)
		P–C(7)–C(12)	120(1)

final model. A difference map at this stage showed some small peaks around the chlorine atoms that were interpreted as the oxygens of the perchlorate groups.

The anisotropic refinement with the DPPA rings treated as rigid groups (including hydrogen atoms placed on stereochemical grounds with a common U-value of 0.06 $Å^2$) with a P–C distance constrained to the value 1.81(2) Å, and the perchlorates treated as rigid tetrahedral groups with a Cl–O distance constrained to the value 1.34(2) Å, gave a final *R*-factor of 13.3%. The anisotropic thermal tensor of the atoms Cl(1) and O′(Cl1) rendered non positive definite values.

In the cases of both Eu and La the shifts of the last cycle were all less than 10% of the corresponding standard deviations. The scattering factors used were those given by Cromer and Waber [6] and the anomalous dispersion corrections were those of Cromer and Ibers [7]. All the calculations were performed on a Vax Computer with the SHELX 76 system of programs [4]. The final positional parameters and equivalent isotropic temperature factors calculated as described by Hamilton [8] are given in Table I and interatomic distances and angles are given in Table II.

Discussion

The coordination around the Eu atom is shown in Fig. 1. Figure 2 shows the La cation complex. The main result of this paper is that in spite of different degrees of disorder in both structures the O_h local symmetry of the Eu structure and the D_{3d} local symmetry for the La structure could be unambiguously determined.

In the europium complex the cation is coordinated to the phosphoryl oxygen of six DPPA groups in a crystallographic octahedral configuration. The phosphoryl group is aligned with the europium atom along a two-fold axis and with an Eu–O interatomic distance of 2.27(2) Å, identical to the one in $Eu(AsF_6)_3 \cdot 6(C_5H_{12}N_2O)$ [9].

The high local symmetry of the special position

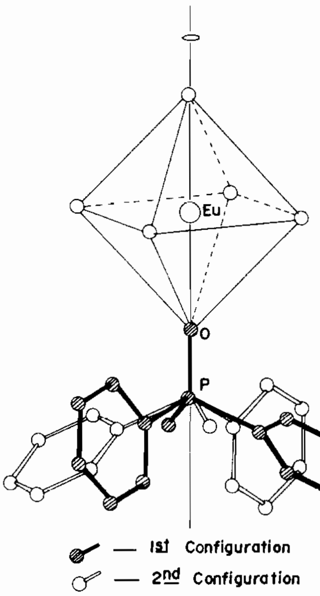

Fig. 1. Schematic representation of the Eu ion environment, showing one of the independent DDPA groups in its two disordered occupation sites.

for the europium atom enforces all DPPA atoms other than oxygen and phosphorus to be disordered. There are two independent positions with half occupation for one of the phenyl groups (the other is generated by the two-fold axis).

The fluorescence spectrum of the europium complex shows two strong bands corresponding to the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ respectively (Fig. 3) [1]. This fact was initially attributed to an approximate O_h local symmetry distorted towards C_{4v}. In the light of our present results this effect may be attributed to dynamic distortions of the O_h symmetry due to temperature effects. This view is further supported by the fact that the relative intensity of the 'forbidden' $^5D_0 \rightarrow {}^7F_2$ band decreases with temperature.

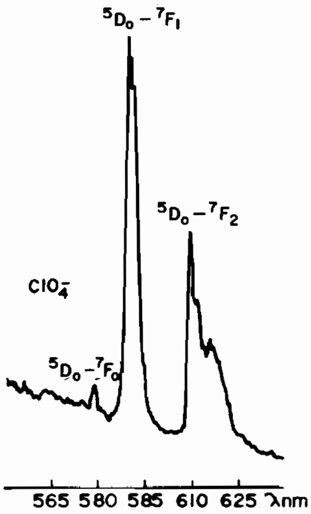

Fig. 3. The fluorescence spectrum of the Eu complexes from reference 1.

In the lanthanum complex the cation is also coordinated to the phosphoryl oxygen of six DPPA groups but in a trigonal-antiprismatic configuration. The La–O interatomic distance is 2.40(3) Å, much shorter than the average La–O distance of 2.54(1) in the complex of lanthanum hexafluorophosphate with N,N,N′,N′-tetramethylmalonamide [3]. This effect is partially due to the different environment and coordination values in the two cases but we also believe that the La–O distance is underestimated in the present case. This is because the disorder of the La mentioned in the previous section gives rise to an unusually high apparent temperature factor which in turn produces an apparent shortening of the interatomic distances involving that atom, as described by Busing and Levy [10]. Diagonalizing the La thermal tensor with an orthogonal matrix which transforms the direction [100] into [111]

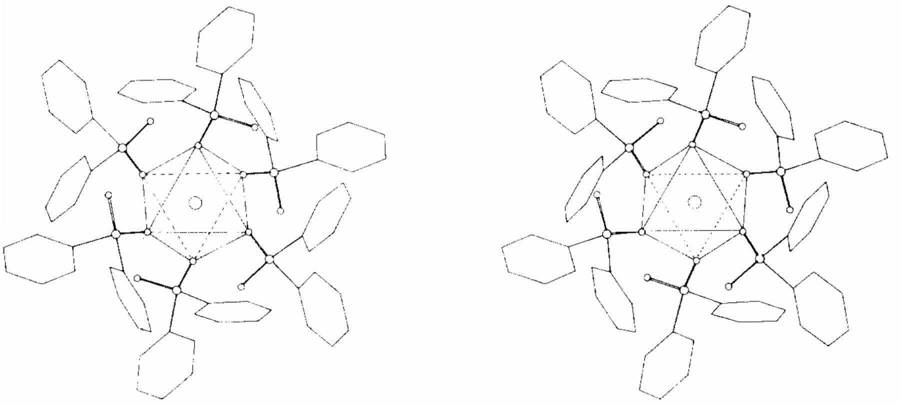

Fig. 2. Stereoscopic view of the La complex cation down its three-fold axis.

$$\begin{bmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{6} & 1/\sqrt{6} & -2/\sqrt{6} \end{bmatrix}$$

gives the tranformed values U'_{11} = 0.278(4) Å^2 and U'_{22} = U'_{33} = 0.031(4) Å^2 which clearly show the anomalous apparent thermal motion along the 3-fold axis mentioned before. As explained in the description of the refinement procedure, this high apparent thermal vibration of the La atom is probably due to a two-fold positional disorder of this atom along the 3-fold axis. This interpretation is consistent with the fact that the infrared $\nu_{P=O}$ band is split in the solid state [11].

The lanthanum and europium environment differ, besides their coordination symmetry, in that the phosphoryl group, aligned with the cation in the europium case, is twisted in the lanthanum structure with a La–O–P angle of 157(1)°. We found no obvious reason for this unusual arrangement.

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