The Crystal and Molecular Structure of the Complex $[Eu(NO_3)_3(Ph_3AsO)_3](H_2O)_4$

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Several europium(III) adducts with unidentate O-donor ligands such as PyNO, Me_3NO, HMPA (hexamethylphosphoramide), DMSO, Ph_3PO and Ph_3AsO have been recently synthesized and studied [1], for which different stoichiometries are obtainable depending on the reaction conditions. The definition of the coordination geometries around the metal is difficult by using techniques such as IR, electronic or Mössbauer spectroscopy, so that an extensive X-ray work has been planned to clarify the structural properties of these compounds, and we report here the crystal structure of $[Eu(NO_3)_3(Ph_3AsO)_3](H_2O)_4$.

Experimental

Another complex, $[Eu(NO_3)_3(Ph_3AsO)_4]$(acetone), was obtained as colourless crystals from a concentrated acetone solution of $Eu(NO_3)_3 \cdot 6H_2O$ and Ph_3AsO in a 1:6 molar ratio; melting point 265 °C(dec). *Anal.* Calc.: C, 53.4; H, 3.9; N, 2.5. Found: C, 53.0; H, 3.9; N, 2.4%.

Upon heating this compound at 100 °C *in vacuo* for 6 h, the complex $Eu(NO_3)_3(Ph_3AsO)_4$ was obtained as white powder. *Anal.* Calc.: C, 53.1; H, 3.7; N, 2.6. Found: C, 53.1; H, 3.7; N, 2.5%. In its IR spectrum the band due to acetone is absent, while those of the nitrate groups remain virtually unchanged and the ν(As–O) is at 893 cm^{-1}. The position of this band for both complexes, slightly increased with respect to that of the free ligand (880 cm^{-1}), is in agreement with the literature data [2].

However, the samples obtained for the monoacetonate adduct were not good enough for an X-ray analysis, and all attempts to obtain suitable crystals of $Eu(NO_3)_3(Ph_3AsO)_4$ from methylene chloride (or *sym*-dichloroethane)/n-hexane mixtures were unsuccessful because the compound invariably released one molecule of Ph_3AsO giving colourless crystals of $Eu(NO_3)_3(Ph_3AsO)_3$.

X-ray Data for $[Eu(NO_3)_3(Ph_3AsO)_3](H_2O)_4$

A crystal of maximum dimensions 0.2 mm was used for the X-ray measurements. Data collection was performed on a Philips diffractometer with Mo Kα radiation. Cell dimensions were determined by a least-squares refinement of 25 medium-angle settings.

Crystal data for $EuC_{54}H_{53}N_3O_{16}As_3$ are: FW = 1375.7, monoclinic, space group $P2_1/c$; a = 22.591(4), b = 11.312(6), c = 24.477(4) Å; β = 99.25(3)°, U = 6173 Å^3, D_c = 1.48 g/cm^3 for Z = 4; μ(Mo Kα) = 27.8 cm^{-1}. The crystal was stable under irradiation, but of a total of 7449 reflections read, the intensities of which were corrected for Lp and for absorption [3], only 3572 with $I > 3\sigma(I)$ could be considered as observed, indicating a relatively low degree of crystallinity of the compound.

Solution of the structure was achieved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. Phenyl groups were refined as rigid bodies. At convergence, the residual conventional R factor was 0.087, based on the observed reflections. The function minimized was $\Sigma w(\Delta F)^2$ with $w = 1$. The SHELX [4] programs package and its scattering factors were used in the calculations, but scattering factors for Eu were those of ref. 5.

Final atomic parameters are listed in Table 1; selected bond lengths and angles are reported in Table 2.

X-ray Structure for $[Eu(NO_3)_3(Ph_3AsO)_3](H_2O)_4$

As shown in the Fig. 1, the Eu(III) ion is nonacoordinate, being directly bonded to three chelate nitrate ions and to three Ph_3AsO neutral ligands. As expected, owing to the geometrical constraints imposed by the rigid structure of the nitrato groups, the coordination polyhedron does not conform to any of the configurations commonly found in nonacoordinated complexes. However, if each nitrato group is considered as occupying a single coordination site, then the coordination polyhedron can be described as a highly distorted octahedron. The neutral ligands occupy the meridional positions; the mean plane defined by the metal and the three oxygen atoms from Ph_3AsO is approximately perpendicular to that defined by the metal and the nitrogen atoms (the dihedral angle between these planes is 95.0(4)°). The angles between opposite ligands vary from 154° for O(10)–Eu–O(11) to 174° for N(1)–Eu–N(2), whereas the values are 87° (both) for adjacent O–Eu–O and 93° and 81° for adjacent N–Eu–N angles.

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TABLE 1. Atomic coordinates

Atom	*x/a*	*y/b*	*z/c*
Eu(1)	0.24015(6)	0.02950(12)	0.14962(6)
As(1)	0.3854(1)	−0.0961(2)	0.1010(1)
As(2)	0.1562(1)	0.3157(2)	0.1773(1)
As(3)	0.1806(1)	0.0123(2)	−0.0081(1)
N(1)	0.3307(11)	0.2207(21)	0.1604(13)
O(1)	0.3705(9)	0.2915(19)	0.1651(11)
O(2)	0.2953(8)	0.2115(16)	0.1169(9)
O(3)	0.3248(7)	0.1561(18)	0.1990(10)
N(2)	0.1546(12)	−0.1702(23)	0.1513(11)
O(4)	0.2086(8)	−0.1845(16)	0.1384(8)
O(5)	0.1184(9)	−0.2529(20)	0.1462(15)
O(6)	0.1431(8)	−0.0694(18)	0.1652(9)
N(3)	0.2596(10)	−0.0197(20)	0.2706(9)
O(7)	0.2836(9)	−0.0789(19)	0.2385(8)
O(8)	0.2270(9)	0.0613(16)	0.2492(10)
O(9)	0.2670(8)	−0.0399(20)	0.3200(9)
O(10)	0.3206(7)	−0.0514(16)	0.1204(8)
O(11)	0.1785(8)	0.1826(15)	0.1632(8)
O(12)	0.1920(6)	0.0277(12)	0.0549(6)
O(13)	0.5427(10)	0.2046(18)	0.6071(11)
O(14)	0.8770(7)	0.3276(15)	0.6835(8)
O(15)	0.0725(8)	−0.0652(18)	0.3634(7)
O(16)	0.4129(8)	0.4279(17)	0.8919(8)
C(1)	0.4532(8)	−0.0722(23)	0.1594(8)
C(2)	0.4928(8)	−0.1647(23)	0.1762(8)
C(3)	0.5414(8)	−0.1468(23)	0.2183(8)
C(4)	0.5505(8)	−0.0362(23)	0.2435(8)
C(5)	0.5110(8)	0.0562(23)	0.2267(8)
C(6)	0.4623(8)	0.0382(23)	0.1846(8)
C(7)	0.4015(11)	−0.0150(29)	0.0386(10)
C(8)	0.3926(11)	−0.0681(29)	−0.0134(10)
C(9)	0.4036(11)	−0.0044(29)	−0.0596(10)
C(10)	0.4234(11)	0.1123(29)	−0.0536(10)
C(11)	0.4322(11)	0.1654(29)	−0.0015(10)
C(12)	0.4213(11)	0.1017(29)	0.0445(10)
C(18)	0.4177(10)	−0.3147(23)	0.0553(10)
C(13)	0.3809(10)	−0.2586(23)	0.0879(10)
C(14)	0.3429(10)	−0.3253(23)	0.1154(10)
C(15)	0.3416(10)	−0.4481(23)	0.1102(10)
C(16)	0.3783(10)	−0.5042(23)	0.0775(10)
C(17)	0.4164(10)	−0.4375(23)	0.0500(10)
C(20)	0.0817(10)	0.4883(25)	0.1139(11)
C(21)	0.0610(10)	0.5505(25)	0.0653(11)
C(22)	0.0835(10)	0.5243(25)	0.0168(11)
C(23)	0.1266(10)	0.4360(25)	0.0169(11)
C(24)	0.1473(10)	0.3739(25)	0.0654(11)
C(19)	0.1249(10)	0.4001(25)	0.1139(11)
C(30)	0.0736(10)	0.1895(18)	0.2278(10)
C(25)	0.0989(10)	0.3008(18)	0.2234(10)
C(26)	0.0835(10)	0.3946(18)	0.2553(10)
C(27)	0.0427(10)	0.3771(18)	0.2917(10)
C(28)	0.0174(10)	0.2658(18)	0.2962(10)
C(29)	0.0328(10)	0.1720(18)	0.2642(10)
C(31)	0.2221(8)	0.4082(19)	0.2156(8)
C(32)	0.2581(8)	0.3580(19)	0.2614(8)
C(33)	0.2993(8)	0.4279(19)	0.2958(8)
C(34)	0.3045(8)	0.5479(19)	0.2844(8)
C(35)	0.2685(8)	0.5981(19)	0.2386(8)
C(36)	0.2273(8)	0.5282(19)	0.2042(8)
C(37)	0.2189(7)	−0.1227(16)	−0.0283(10)
C(38)	0.2430(7)	−0.1227(16)	−0.0774(10)
C(39)	0.2705(7)	−0.2242(16)	−0.0937(10)
C(40)	0.2740(7)	−0.3258(16)	−0.0610(10)
C(41)	0.2499(7)	−0.3258(16)	−0.0120(10)
C(42)	0.2224(7)	−0.2242(16)	0.0043(10)
C(43)	0.2064(9)	0.1403(17)	−0.0445(9)
C(44)	0.2531(9)	0.2098(17)	−0.0174(9)
C(45)	0.2728(9)	0.3079(17)	−0.0440(9)
C(46)	0.2458(9)	0.3364(17)	−0.0977(9)
C(47)	0.1991(9)	0.2669(17)	−0.1248(9)
C(48)	0.1794(9)	0.1688(17)	−0.0982(9)
C(49)	0.0963(6)	−0.0134(18)	−0.0366(8)
C(50)	0.0752(6)	−0.1267(18)	−0.0514(8)
C(51)	0.0151(6)	−0.1440(18)	−0.0737(8)
C(52)	−0.0240(6)	−0.0479(18)	−0.0812(8)
C(53)	−0.0030(6)	0.0654(18)	−0.0664(8)
C(54)	0.0571(6)	0.0826(18)	−0.0440(8)

TABLE 2. Selected bond lengths (Å) and angles (°) with e.s.d. in parentheses

Eu–O(2)	2.60(2)	Eu–O(10)	2.25(2)
Eu–O(3)	2.54(2)	Eu–O(11)	2.28(2)
Eu–O(4)	2.53(2)	Eu–O(12)	2.40(1)
Eu–O(6)	2.54(2)	As(1)–O(10)	1.68(2)
Eu–O(7)	2.55(2)	As(2)–O(11)	1.64(2)
Eu–O(8)	2.53(2)	As(3)–O(12)	1.53(2)
O(2)–Eu–O(3)	48.4(7)	O(10)–Eu–O(11)	153.9(7)
O(4)–Eu–O(6)	50.2(7)	O(10)–Eu–O(12)	87.4(6)
O(7)–Eu–O(8)	48.3(7)	O(11)–Eu–O(12)	87.4(6)
N(1)–Eu–N(2)	173.8(8)	N(3)–Eu–O(11)	89.6(5)
N(1)–Eu–N(3)	93.4(6)	N(3)–Eu–O(10)	104.0(5)
N(2)–Eu–N(3)	80.6(6)	N(1)–Eu–O(12)	107.0(7)
N(3)–Eu–O(12)	158.8(3)	N(2)–Eu–O(12)	79.2(6)
As(1)–O(10)–Eu	173(1)		
As(2)–O(11)–Eu	160(1)		
As(3)–O(12)–Eu	162(1)		

The overall configuration of this compound strictly resembles that of the parent $[Eu(NO_3)_3(Ph_3PO)_3](acetone)_2$ and $[Eu(NO_3)_3(Ph_3PO)_2EtOH]$ complexes [6] and most structural details agree well with those already determined. Thus, for example, the Eu–O (nitrate) bond lengths (mean value 2.55 Å) and the subtended angles (mean value 49°) are fully comparable, and the Eu–O–As angles are spread over a relatively wide range, as are the Eu–O–P angles in the mentioned compounds.

A difference occurs in that the Eu–O(12) bond distance (2.40 Å), which is *trans* to a nitrato group,

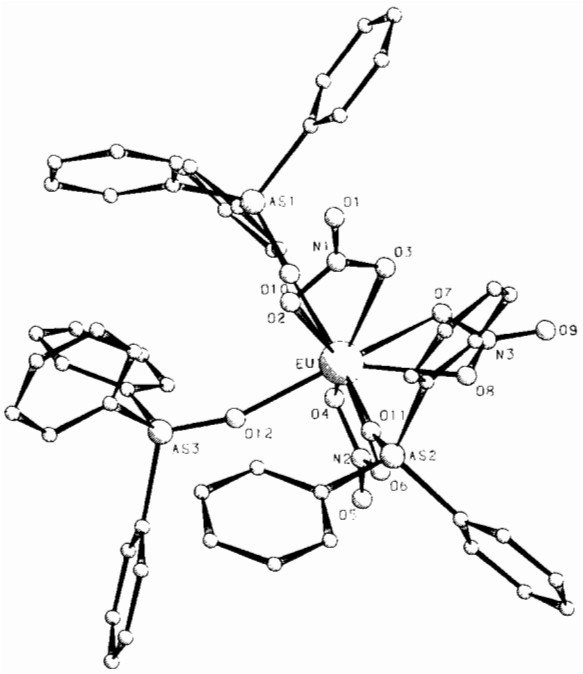

Fig. 1. Structure of $Eu(NO_3)_3(Ph_3AsO)_3 \cdot 4H_2O$.

is significantly longer than the Eu–O(10) and Eu–O(11) distances (2.25 and 2.28 Å respectively) which are *trans* to one another, while the corresponding As–O(12) distance is shorter than the two other ones. Even if the quality of the recorded data is rather poor, there is no indication of disorder around O(12), the thermal parameters of which are absolutely normal. Thus, these values seem to suggest some sensitivity of Ph_3AsO towards the charged group in the *trans* position.

Four clathrate water molecules are also present in the crystal and apparently not involved in strong hydrogen bonding, the O···O contact distances being all longer than 3.3 Å.

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