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Coordination Chemistry and Structure Characterization of $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$

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Abstract

The crystal structure of a cryptate complex of europium, $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$, has been determined from three-dimensional single-crystal X-ray diffraction data collected on a computer-automated diffractometer. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 14.815(5)$, $b = 8.828(2)$, $c = 13.302(4)$ Å, $\alpha = 91.57(2)$, $\beta = 92.64(3)$, $\gamma = 86.90(3)^\circ$ and $Z = 2$. The structure was solved by a heavy atom method and refined by a blocked-matrix least-squares procedure to a conventional R index of 0.029 for 5422 reflections. The molecule is composed of cations $(C_{18}H_{36}O_6N_2EuNO_3)^{2+}$ and anions $[Eu(NO_3)_5 \cdot H_2O]^{2-}$. In the cation, the europium(III) ion enclosed in a [2.2.2] molecule is coordinated with eight oxygen and two nitrogen atoms, forming a 10-coordinate complex ion (cryptate), while the other europium(III) ion is bonded to eleven oxygen atoms in the anion.

Introduction

Because of their special coordination functions, cryptate compounds play an important part in such fields as bionics, biophysics, medicine and pesticides, etc. But very few research results have been reported so far on lanthanide cryptate compounds [1–5], of which only three structures have been determined [6–8]. As part of a further study of the structural character of this type of compound, we have been interested in the coordination chemistry of the cryptate complex of europium. We report here the structure analysis result of $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$ which was synthesized and analysed in our laboratory.

Experimental

Preparation of $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$

Stoichiometric amounts of the [2.2.2] ligand and $Eu(NO_3)_3$ from which water was removed *in vacuo* were separately dissolved in CH_3CN. Some precipitate formed immediately after the two solutions were mixed. The precipitate was then refluxed. After the flask was cooled, the solution was allowed to stand overnight and crystallized. Finally, the crystalline product was filtered, washed with CH_3CN and dried under vacuum at room temperature for several hours. *Anal.* Calc. for $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$: C, 20.20; H, 3.58; N, 10.47. Found: C, 20.51; H, 3.50; N, 10.69%.

X-ray Crystallography

Data reduction

An R3 computer-automated four-circle diffractometer using Mo Kα ($\lambda = 0.71069$) radiation with a graphite crystal monochromator was employed for data collection. The unit cell dimensions were obtained by a least-squares fitting of 25 strong reflections. Data were collected by using the $\theta-2\theta$ scan technique with a variable scan rate from 4.0–29.3 °/min. All crystallographic data are given in Table I.

The data were reduced by applying an LP factor and empirical absorption corrections.

Solution and refinement of the structure

The structure was solved in the triclinic space group $P\bar{1}$. The position of the independent Eu atom was found by solution of the three-dimensional Patterson function. Subsequent Fourier and differ-

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TABLE I. Crystallographic Data for $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$

Formula weight	1070.46
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	14.815(5)
b (Å)	8.828(2)
c (Å)	13.302(4)
α (deg)	91.57(2)
β (deg)	92.64(3)
γ (deg)	86.90(3)
V (Å^3)	1734.79(2)
Z	2
Crystal size (mm)	0.1 × 0.15 × 0.3
D (calc.) (g/cm^3)	2.05
μ (cm^{-1})	37.08
Range 2θ (deg)	3–50
No. measured data	6330
No. unique observed	5422
R	0.029

ence syntheses gave the positions of the remaining atoms. All positional parameters and temperature factors for non-hydrogen atoms (Table II) were refined anisotropically, while those for hydrogen atoms isotropically. The final R index was 0.029. The computational work was carried out on an Eclipse S/250 minicomputer.

Results and Discussion

Description of the Structure

The structure contains two crystallographically distinct ions: $(C_{18}H_{36}O_6N_2EuNO_3)^{2+}$ and $[Eu(NO_3)_5 \cdot H_2O]^{2-}$. In the cation, which is of considerable interest (Fig. 1), the Eu(III) ion is ten-coordinate to the eight donor atoms of the cryptate and to two oxygen atoms of an NO_3^- group. In the free [2.2.2] ligand, two nitrogen atoms are bridged by three symmetrically located strands, each of which contains two oxygen and six carbon atoms. It was found by examining the torsion angles between pairs of best planes through the amine nitrogen atoms and the two other oxygen atoms of each strand that upon formation of the complex ion the ligand is opened somewhat due to the presence of the NO_3^- group. The angle between the planes separated by the NO_3^- is 158.3°, and between the other two pairs 88.7° and 87.9°, respectively. The geometry of the coordination polyhedron of the cation can be described in terms of a distorted bicapped square antiprism (Fig. 2), having the two nitrogen atoms in axial positions and the eight oxygen atoms at the vertices of the two squares. Compared with the structure of $Eu(ClO_4)[2.2.2](ClO_4)_2 \cdot MeCN$ [9], it is further distorted. As a result, the N(6)–Eu(1)–N(7) angle is 177.6(2)°; the two

TABLE II. Atomic Parameters (× 10^4) and Equivalent Temperature Factors U^* (× 10^3 Å^2) for $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$

Atom	x	y	z	U^*
Eu(1)	2019(1)	8705(1)	6939(1)	30(1)
Eu(2)	3178(1)	4461(1)	1871(1)	32(1)
O(1)	1418(3)	9973(5)	8549(3)	68(1)
O(2)	3049(2)	6531(3)	6570(3)	47(1)
O(3)	1933(3)	6444(4)	7980(4)	82(2)
O(4)	1032(2)	7331(5)	5733(4)	91(2)
O(5)	2287(3)	9051(4)	5106(3)	64(1)
O(6)	3131(3)	9234(4)	8346(3)	61(1)
O(7)	2108(2)	11524(3)	6951(3)	46(1)
O(8)	892(2)	10657(3)	6270(3)	48(1)
O(9)	977(3)	13082(4)	6538(4)	69(2)
O(10)	4690(2)	4998(4)	2680(3)	47(1)
O(11)	3576(2)	6459(4)	3174(3)	48(1)
O(12)	4941(3)	6757(4)	3811(3)	67(1)
O(13)	2402(2)	1962(4)	1797(3)	54(1)
O(14)	3854(2)	1705(4)	1852(3)	61(1)
O(15)	3059(4)	−295(4)	1834(4)	100(2)
O(16)	4622(2)	3873(4)	741(3)	52(1)
O(17)	3289(2)	3488(4)	96(3)	53(1)
O(18)	4472(3)	2835(5)	−761(3)	77(2)
O(19)	1676(3)	4746(5)	966(3)	64(1)
O(20)	1967(3)	6742(4)	1849(3)	68(1)
O(21)	658(3)	6569(7)	1056(5)	106(2)
O(22)	2047(2)	4453(4)	3236(3)	50(1)
O(23)	3332(3)	3301(4)	3613(3)	57(1)
O(24)	2253(4)	3393(5)	4680(3)	79(2)
O(25)	3641(2)	6711(4)	981(3)	52(1)
N(1)	4420(3)	6095(4)	3241(3)	42(1)
N(2)	3105(3)	1079(4)	1826(3)	52(2)
N(3)	4146(3)	3384(5)	10(3)	48(1)
N(4)	1414(3)	6040(6)	1286(4)	62(2)
N(5)	2543(3)	3709(4)	3868(3)	47(1)
N(6)	326(4)	8064(6)	7577(5)	91(3)
N(7)	3722(3)	9333(4)	6392(4)	49(1)
N(8)	1315(3)	11804(4)	6584(3)	43(1)
C(1)	3706(4)	6626(6)	5811(5)	54(2)
C(2)	4278(4)	7926(6)	6106(5)	62(2)
C(3)	2985(4)	5069(5)	7001(4)	57(2)
C(4)	2701(6)	5356(8)	8014(6)	80(3)
C(5)	1205(5)	6140(11)	8561(6)	112(4)
C(6)	308(5)	6757(11)	8183(10)	196(7)
C(7)	−78(5)	9480(10)	8064(8)	99(4)
C(8)	534(5)	10100(11)	8859(7)	114(4)
C(9)	194(7)	6809(14)	5899(7)	161(6)
C(10)	−250(6)	7725(14)	6706(12)	172(7)
C(11)	1278(7)	7014(11)	4796(7)	123(5)
C(12)	1624(8)	8380(10)	4358(5)	131(5)
C(13)	3611(5)	10392(7)	5550(5)	74(3)
C(14)	3040(6)	9738(7)	4687(5)	92(3)
C(15)	4096(4)	9291(9)	8189(5)	73(3)
C(16)	4196(4)	10107(7)	7263(6)	73(3)
C(17)	2892(6)	9749(11)	9299(5)	110(4)
C(18)	2061(6)	10543(10)	9314(5)	111(3)

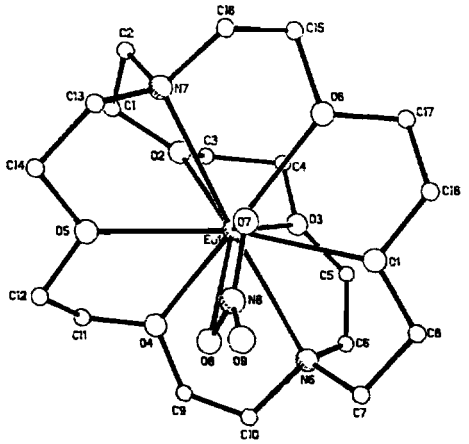

Fig. 1. Perspective view of the $(C_{18}H_{36}O_6N_2EuNO_3)^{2+}$ cation.

TABLE III. Bond Lengths (Å) for $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$

Eu(1)–O(1)	2.561(4)	Eu(1)–O(2)	2.440(3)
Eu(1)–O(3)	2.473(4)	Eu(1)–O(4)	2.461(5)
Eu(1)–O(5)	2.518(3)	Eu(1)–O(6)	2.488(4)
Eu(1)–O(7)	2.499(3)	Eu(1)–O(8)	2.487(3)
Eu(1)–N(6)	2.775(6)	Eu(1)–N(7)	2.748(4)
Eu(2)–O(10)	2.504(3)	Eu(2)–O(11)	2.514(3)
Eu(2)–O(13)	2.540(4)	Eu(2)–O(14)	2.581(4)
Eu(2)–O(16)	2.690(4)	Eu(2)–O(17)	2.499(3)
Eu(2)–O(19)	2.485(4)	Eu(2)–O(20)	2.623(4)
Eu(2)–O(22)	2.526(4)	Eu(2)–O(23)	2.555(4)
Eu(2)–O(25)	2.483(3)	O(1)–C(8)	1.388(9)
O(1)–C(18)	1.460(9)	O(2)–C(1)	1.441(7)
O(2)–C(3)	1.436(6)	O(3)–C(4)	1.448(9)
O(3)–C(5)	1.397(9)	O(4)–C(9)	1.376(12)
O(4)–C(11)	1.332(11)	O(5)–C(12)	1.499(10)
O(5)–C(14)	1.440(9)	O(6)–C(15)	1.458(7)
O(6)–C(17)	1.389(8)	O(7)–N(8)	1.266(5)
O(8)–N(8)	1.271(5)	O(9)–N(8)	1.211(5)
O(10)–N(1)	1.265(5)	O(11)–N(1)	1.274(5)
O(12)–N(1)	1.218(5)	O(13)–N(2)	1.266(6)
O(14)–N(2)	1.264(6)	O(15)–N(2)	1.219(6)
O(16)–N(3)	1.255(6)	O(17)–N(3)	1.278(6)
O(18)–N(3)	1.229(6)	O(19)–N(4)	1.256(6)
O(20)–N(4)	1.261(6)	O(21)–N(4)	1.220(7)
O(22)–N(5)	1.266(5)	O(23)–N(5)	1.262(6)
O(24)–N(5)	1.226(6)	N(6)–C(6)	1.428(13)
N(6)–C(7)	1.500(11)	N(6)–C(10)	1.441(15)
N(7)–C(2)	1.502(7)	N(7)–C(13)	1.476(8)
N(7)–C(16)	1.496(8)	C(1)–C(2)	1.496(8)
C(3)–C(4)	1.442(10)	C(5)–C(6)	1.480(12)
C(7)–C(8)	1.475(13)	C(9)–C(10)	1.483(17)
C(11)–C(12)	1.480(14)	C(13)–C(14)	1.515(10)
C(15)–C(16)	1.461(11)	C(17)–C(18)	1.384(12)

squares composed of O(2), O(5), O(6), O(7) and O(1), O(3), O(4), O(8), respectively, make an angle of 5.9° with each other. But it can be seen from the displacements of composing atoms to the least-squares

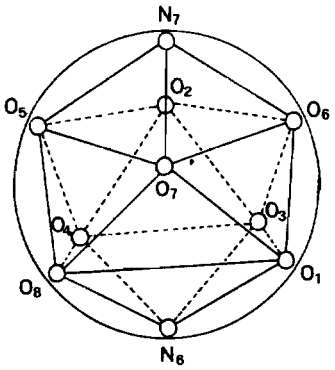

Fig. 2. Coordination polyhedron of the $(C_{18}H_{36}O_6N_2\text{-}Eu(NO_3)^{2+}$ cation.

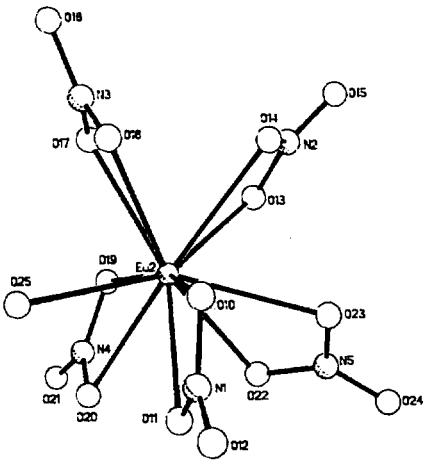

Fig. 3. Perspective view of the $[Eu(NO_3)_5 \cdot H_2O]^{2-}$ anion.

planes (all <0.12 Å) that coplanarity of the two squares is rather good.

Similar to $Eu(ClO_4)[2.2.2](ClO_4)_2 \cdot MeCN$, the Eu–N (2.775 and 2.748 Å), Eu–O(nitrate) (2.499 and 2.487 Å), and Eu–O(ether) distances (2.440–2.561 Å) (Table III) are shorter than the corresponding ones in the 12-coordinate lanthanum complex [6]. In the cation, the Eu–O(nitrate) distance (mean 2.493 Å) is about the same as Eu–O(ether) (mean 2.491 Å). This may indicate that the two oxygen atoms of the nitrate group are as strongly bonded to the Eu(III) ion as are the other six oxygen atoms of the ether.

In the anion (Fig. 3), the Eu(III) ion is coordinated with five bidentate NO_3^- and one oxygen of water to form a 4:5:2 polyhedron. The mean values of bond lengths are Eu–O(nitrate) = 2.552 and Eu–O(water) = 2.483 Å, respectively. It has been shown experimentally that all five nitrate groups are almost perfectly planar and their local symmetry is very close to C_{2v}.

With respect to the mean value of the N–O distance (1.245 Å) and O–N–O angle (120°) (Tables

TABLE IV. Bond Angles (°) for $C_{18}H_{36}O_6N_2Eu_2(NO_3)_6 \cdot H_2O$

O(1)–Eu(1)–O(3)	80.2(1)	O(1)–Eu(1)–O(4)	121.8(1)
O(3)–Eu(1)–O(4)	84.4(2)	O(2)–Eu(1)–O(5)	64.1(2)
O(2)–Eu(1)–O(6)	84.5(1)	O(2)–Eu(1)–O(7)	135.5(1)
O(2)–Eu(1)–O(8)	147.2(1)	O(3)–Eu(1)–O(8)	134.5(1)
O(4)–Eu(1)–O(8)	74.7(1)	O(5)–Eu(1)–O(6)	124.7(1)
O(5)–Eu(1)–O(7)	80.8(1)	O(6)–Eu(1)–O(7)	76.1(1)
N(6)–Eu(1)–N(7)	177.6(2)	O(10)–Eu(2)–O(11)	50.9(1)
O(13)–Eu(2)–O(14)	49.6(1)	O(16)–Eu(2)–O(17)	49.0(1)
O(19)–Eu(2)–O(20)	49.5(1)	O(22)–Eu(2)–O(23)	50.2(1)
C(8)–O(1)–C(18)	112.2(5)	C(1)–O(2)–C(3)	116.3(4)
C(4)–O(3)–C(5)	116.8(6)	C(9)–O(4)–C(11)	111.7(7)
C(12)–O(5)–C(14)	115.7(5)	C(15)–O(6)–C(17)	113.2(5)
O(10)–N(1)–O(11)	116.1(4)	O(10)–N(1)–O(12)	121.6(4)
O(11)–N(1)–O(12)	122.3(4)	O(13)–N(2)–O(14)	116.2(4)
O(13)–N(2)–O(15)	121.7(5)	O(14)–N(2)–O(15)	122.1(5)
O(16)–N(3)–O(17)	116.7(4)	O(16)–N(3)–O(18)	122.8(4)
O(17)–N(3)–O(18)	120.4(4)	O(19)–N(4)–O(20)	116.8(4)
O(19)–N(4)–O(21)	120.5(5)	O(20)–N(4)–O(21)	122.5(5)
O(22)–N(5)–O(23)	116.9(4)	O(22)–N(5)–O(24)	120.4(5)
O(23)–N(5)–O(24)	122.6(4)	C(6)–N(6)–C(7)	113.4(8)
C(6)–N(6)–C(10)	104.4(8)	C(7)–N(6)–C(10)	106.7(7)
C(13)–N(7)–C(16)	108.7(4)	C(2)–N(7)–C(13)	111.3(5)
C(2)–N(7)–C(18)	108.6(4)	O(7)–N(8)–O(9)	122.4(4)
O(7)–N(8)–O(8)	115.8(3)	O(8)–N(8)–O(9)	121.9(4)
O(2)–C(1)–C(2)	107.3(5)	N(7)–C(2)–C(1)	112.5(5)
O(2)–C(3)–C(4)	106.1(5)	O(3)–C(4)–C(3)	108.4(6)
O(3)–C(5)–C(6)	115.6(7)	N(6)–C(6)–C(5)	115.1(7)
N(6)–C(7)–C(8)	111.9(6)	O(1)–C(8)–C(7)	109.6(7)
O(4)–C(9)–C(10)	110.6(9)	N(6)–C(10)–C(9)	115.2(8)
O(4)–C(11)–C(12)	109.8(8)	O(5)–C(12)–C(11)	108.3(6)
N(7)–C(13)–C(14)	111.2(5)	O(5)–C(14)–C(13)	107.9(6)
O(6)–C(15)–C(16)	107.7(5)	N(7)–C(16)–C(15)	110.5(5)
O(6)–C(17)–C(18)	114.0(6)	O(1)–C(18)–C(17)	112.1(6)

III and IV) observed for the symmetrical nitrate group, the terminal N–O bonds are shortened (average 1.222 Å), while those involving the coordinated oxygen atoms are lengthened (average 1.265 Å). Accordingly, the mean value of the O–N–O angles of which the oxygen atoms are bonded to the Eu(III) ion is 116.4°, and other is 121.8°. This obviously results from the formation of coordination bonds between oxygen atoms and the central metal ion.

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