The Crystal and Molecular Structure of Tris-(2,2,6,6-tetramethylheptane-3,5-dionato)lutetium(III)

Shigeki Onuma, Hironao Inoue,* and Shuzo Shibata
Department of Chemistry, Shizuoka University, Oya, Shizuoka 422

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The crystal and molecular structure of tris-(2,2,6,6-tetramethylheptane-3,5-dionato)lutetium(III) has been determined by X-ray diffraction method. The space group is $Pmn2_1$, and the unit cell is orthorhombic with $a=17.713(4)$, $b=10.638(2)$, $c=9.973(3)$ Å, and $Z=2$. The structure is isomorphous with the erbium analogue. The atomic parameters of the molecule (except for hydrogen atoms) were refined by the block-diagonal least-squares method to an R of 0.053. Three chelate rings are planar. One of them lies in the crystallographic mirror plane, and the other two rings are symmetrically related to each other with respect to this mirror plane. Six oxygen atoms of the three β-diketones form a distorted trigonal prism around the central lutetium ion, the average Lu–O distance being 2.19 Å.

The anhydrous lanthanide complexes of 2,2,6,6-tetramethylheptane-3,5-dione, H(thd), are volatile.[1] Among them the complexes of La to Dy are monoclinic and those of Ho to Lu are orthorhombic.[2,3] Crystal structure analyses were carried out on the tris-thd chelates of praseodymium[3] and erbium;[4] the praseodymium chelate is dimeric and each Pr atom is surrounded by seven oxygen atoms in a monocapped trigonal prism, while the erbium chelate is monomeric and the coordination polyhedron is approximately trigonal prismatic, giving a sixfold coordination. The present study was undertaken to determine the crystal and molecular structure of the anhydrous tris-thd chelate of the most heavy element of lanthanides.

Experimental

Single-crystals of anhydrous tris-thd chelate of lutetium were prepared by sublimation. They are transparent prisms. It was, however, noticed that the crystals become opaque and amorphous slowly when exposed to X-rays in the atmosphere. The crystal was, therefore, sealed in a glass capillary tube to avoid such changes.

Approximate cell constants were determined from Weissenberg photographs, and they were refined by a least-squares method using 23 higher angle reflections measured on a Rigaku Denki automatic four-circle single-crystal diffractometer with Mo$K\alpha_1$ radiation ($\lambda=0.70926$ Å). They are given in Table 1 with other crystal data.

The intensity data were collected on a single-crystal diffractometer using Zr-filtered Mo$K\alpha$ radiation at room temperature. The ω–2θ scan technique was employed at a speed of 2°/min in 2θ. The intensities of three reflections (002, 010 and 400) were checked every 50 reflection measurements. The fluctuations were less than 1%, and no appreciable decomposition of crystal was observed. A total of 2360 accessible reflections with $2\theta<55°$ were measured. The data were corrected for the Lorentz and polarization factors, but not corrected for absorption. Reflections whose amplitude $|F|$ were less than three times their standard deviations were not included in the subsequent calculations. The number of observed reflections was 1731.

Table 1. Crystal data

Lu(thd)$_3$, $LuC_{33}H_{57}O_6$
Molecular weight 724.8
Orthorhombic
$a=17.713(4)$
$b=10.638(2)$
$c=9.973(3)$ Å
Space group $Pmn2_1$
Volume of a unit cell 1879.2(8) Å^3
Density, calculated for $Z=2$: 1.286 g cm^{-3}
Number of electrons per unit cell $F(000)=634$
(without hydrogen atoms)

Structure Determination and Refinement

The crystal structure of Lu(thd)$_3$ was supposed to be isomorphous with that of Er(thd)$_3$[4] because the cell constants and systematic absences are similar. Therefore, the atomic parameters of Er(thd)$_3$ were used as initial values and they were refined by a block-diagonal least-squares method. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$, where the weighting function w was unity. Positional and anisotropic thermal parameters

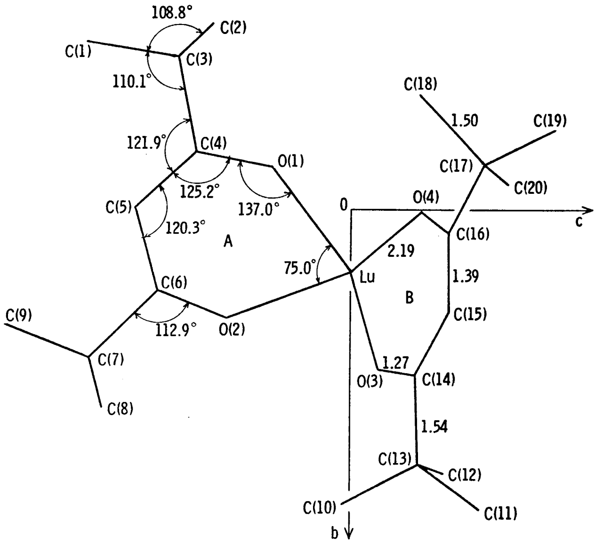

Fig. 1. Projection of the molecular skeleton along the a-axis.
The numbering system of atoms and average bond lengths (l/Å) and angles (φ/°) are also indicated.

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* Rigaku Denki Company, Ltd., Matsubaracho, Akishima, Tokyo 196.

Table 2. The final atomic parameters and their estimated standard deviations in parentheses ($\times 10^4$)
Anisotropic temperature factors are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Lu	0	977(1)	0	39(0)	72(1)	116(1)	0	0	26(4)
O(1)	0	−675(13)	−1284(16)	65(7)	93(15)	123(19)	0	0	19(28)
O(2)	0	1708(13)	−2039(16)	63(7)	77(13)	138(21)	0	0	10(28)
C(1)	0	−2567(31)	−4359(34)	335(58)	134(36)	120(39)	0	0	−84(65)
C(2)	−674(16)	−2874(22)	−2312(42)	129(18)	166(28)	779(119)	201(39)	−401(80)	−346(99)
C(3)	0	−2337(16)	−2845(28)	55(10)	43(15)	198(38)	0	0	−15(41)
C(4)	0	−908(20)	−2547(23)	30(6)	100(19)	137(27)	0	0	−64(46)
C(5)	0	−26(20)	−3552(25)	55(10)	84(20)	156(31)	0	0	55(46)
C(6)	0	1282(20)	−3229(22)	29(7)	115(23)	125(27)	0	0	−16(42)
C(7)	0	2303(22)	−4315(27)	49(10)	120(25)	183(36)	0	0	124(53)
C(8)	687(13)	3107(21)	−4116(24)	69(10)	222(30)	265(37)	−101(31)	−38(33)	246(60)
C(9)	0	1792(23)	−5725(23)	147(22)	110(25)	75(26)	0	0	76(45)
O(3)	800(7)	2477(9)	443(12)	62(5)	93(9)	201(24)	−11(11)	−85(17)	41(21)
O(4)	920(6)	55(9)	1141(12)	51(5)	82(9)	168(15)	−7(11)	−7(15)	21(21)
C(10)	1647(21)	4542(19)	−173(55)	306(32)	190(26)	288(59)	−376(51)	54(150)	−14(125)
C(11)	1203(21)	4637(21)	2088(38)	197(27)	137(26)	615(91)	−139(46)	429(89)	−360(85)
C(12)	2512(17)	4070(21)	1527(50)	95(14)	142(26)	1156(139)	−91(37)	−395(79)	81(122)
C(13)	1709(10)	3971(14)	1106(19)	60(8)	78(13)	197(24)	−16(19)	−34(24)	11(36)
C(14)	1413(10)	2581(13)	1056(15)	59(8)	86(13)	109(17)	−14(17)	−12(20)	3(27)
C(15)	1840(9)	1578(13)	1604(17)	50(7)	74(12)	147(21)	−22(16)	2(21)	19(28)
C(16)	1568(8)	382(14)	1584(16)	32(5)	110(15)	141(20)	6(15)	−24(17)	29(30)
C(17)	1994(9)	−699(13)	2192(18)	46(6)	101(16)	163(23)	14(17)	−37(22)	44(33)
C(18)	2061(12)	−1780(16)	1104(24)	74(10)	106(17)	281(37)	50(23)	−76(34)	−46(46)
C(19)	1546(14)	−1216(24)	3382(26)	84(12)	305(41)	254(39)	95(39)	75(38)	414(71)
C(20)	2808(11)	−362(19)	2614(29)	64(10)	144(24)	343(49)	32(25)	−107(41)	79(60)

of atoms except hydrogen were refined until all the parameter shifts became less than one tenth of the estimated standard deviations. The conventional R was 0.053 for the observed reflections.** At this final stage of refinement the difference Fourier map was flat and unreasonable electron density regions were not found, though no evidence of the hydrogen atoms were obtained.

The atomic scattering factors for carbon and oxygen atoms were taken from Ref. 5, and those for lutetium ion were from the table of Cromer and Waber.[6] The calculations were carried out using UNICS programs[7] at the Computer Center of the University of Tokyo. The refined parameters of atoms, the numbering of which is indicated in Fig. 1, are listed in Table 2.

Results and Discussion

The crystal consists of monomeric Lu(thd)$_3$ units, and in this unit there are two crystallographically independent chelate rings A and B. All the atoms of the forming the ligand A lie in the crystallographic mirror plane except two methyl carbon atoms of C(2) and C(8), which are accompanied with symmetrically related methyl carbon atoms. Projection of the unit along the a-axis (on the mirror plane) was shown in Fig. 1. The other two chelate rings of B are symmetrically related to each other. The angle between the A and B planes is about 117°. The chelate ring is nearly planar as indicated in Table 3 and the folding is about 3.5°. The interatomic distances and angles are listed in Table 4 and the average values are shown in Fig. 1. A comparison of the average values with those for other lanthanide complexes (Table 5) seems to indicate that the structure of the skeleton remains unchanged independent of the atomic number of the central atom and that the structure of the acetylacetonato ring is nearly the same as that reported by Lingafelter and Braun.[8]

Table 3. Least-squares plane by 8 atoms of the chelate ring B and their deviations from the plane (d/Å)

$0.4542x'-0.1571y'-0.8769z'+0.2095=0$
(x', y' and z' are in Ångstrom units)

Lu	0.046	C(15)	0.023
O(3)	0.052	C(16)	0.022
O(4)	−0.057	C(13)	−0.046
C(14)	−0.009	C(17)	0.014
C(10)	0.927	C(18)	1.200
C(11)	−1.424	C(19)	−1.301
C(12)	0.215	C(20)	0.243

The oxygen atoms coordinated to the central lutetium ion form a distorted trigonal prism as shown in Fig. 2, and this coordination polyhedron is the same as that found in Er(thd)$_3$. Metal-oxygen and oxygen-oxygen (bite) distances of β-diketone lanthanide complexes are summarized in Table 6. A constant bite cannot be found. The oxygen-oxygen distances widely range in these complexes probably because of the molecular

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** The table of the observed and calculated structure factors ($\times 10$) is kept as Document No. 7610 at the Chemical Society of Japan.

TABLE 4. DISTANCES (l/Å) AND ANGLES (φ/°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Lu –O(1)	2.174(16)	Lu –O(3)	2.179(12)	O(1)–Lu –O(2)	74.9(0.6)	O(3)–Lu –O(4)	75.0(0.4)
Lu –O(2)	2.177(16)	Lu –O(4)	2.216(12)	Lu –O(1)–C(4)	137.2(1.5)	Lu –O(3)–C(14)	136.7(1.1)
O(1)–C(4)	1.284(28)	O(3)–C(14)	1.251(21)	Lu –O(2)–C(6)	138.2(1.5)	Lu –O(4)–C(16)	135.8(1.1)
O(2)–C(6)	1.270(28)	O(4)–C(16)	1.278(20)	O(1)–C(4)–C(5)	125.8(2.2)	O(3)–C(14)–C(15)	125.8(1.6)
C(4)–C(5)	1.373(34)	C(14)–C(15)	1.417(24)	O(2)–C(6)–C(5)	123.9(2.1)	O(4)–C(16)–C(15)	125.3(1.5)
C(5)–C(6)	1.428(34)	C(15)–C(16)	1.361(23)	C(4)–C(5)–C(6)	120.1(2.2)	C(14)–C(15)–C(16)	120.6(1.6)
C(3)–C(4)	1.549(36)	C(13)–C(14)	1.570(26)	O(1)–C(4)–C(3)	112.2(2.0)	O(3)–C(14)–C(13)	112.9(1.5)
C(6)–C(7)	1.534(35)	C(16)–C(17)	1.503(24)	C(5)–C(4)–C(3)	122.1(2.1)	C(15)–C(14)–C(13)	121.2(1.5)
C(1)–C(3)	1.530(44)	C(10)–C(13)	1.417(58)	C(5)–C(6)–C(7)	122.0(2.1)	C(15)–C(16)–C(17)	122.1(1.5)
C(2)–C(3)	1.426(50)	C(11)–C(13)	1.505(42)	O(2)–C(6)–C(7)	114.0(2.0)	O(4)–C(16)–C(17)	112.5(1.4)
C(7)–C(8)	1.501(36)	C(12)–C(13)	1.487(53)	C(4)–C(3)–C(1)	110.3(2.3)	C(14)–C(13)–C(10)	110.4(2.6)
C(7)–C(9)	1.508(36)	C(17)–C(18)	1.586(30)	C(4)–C(3)–C(2)	108.8(2.6)	C(14)–C(13)–C(11)	105.4(1.9)
		C(17)–C(19)	1.530(31)			C(14)–C(13)–C(12)	113.3(2.3)
		C(17)–C(20)	1.544(34)	C(6)–C(7)–C(8)	108.1(2.0)	C(16)–C(17)–C(18)	108.4(1.5)
O(1)–O(2)	2.644(23)	O(3)–O(4)	2.677(17)	C(6)–C(7)–C(9)	113.8(2.1)	C(16)–C(17)–C(19)	109.1(1.6)
						C(16)–C(17)–C(20)	113.6(1.7)
				C(1)–C(3)–C(2)	107.7(2.7)	C(10)–C(13)–C(11)	109.7(2.9)
				C(8)–C(7)–C(9)	109.2(2.1)	C(10)–C(13)–C(12)	107.3(3.2)
						C(11)–C(13)–C(12)	110.7(2.7)
				O(1)–Lu –O(4)	86.8(0.5)	C(18)–C(17)–C(19)	108.0(1.7)
				O(2)–Lu –O(3)	85.9(0.5)	C(18)–C(17)–C(20)	106.6(1.7)
				O(1)–Lu –O(3)	135.3(0.5)	C(19)–C(17)–C(20)	110.9(1.8)
				O(2)–Lu –O(4)	129.6(0.5)		

TABLE 5. AVERAGE BOND LENGTHS AND ANGLES OF THE CHELATES

	Pr[3)]	Er[4)]	Lu[a)]
C_c–O	1.28 Å	1.27 Å	1.27 Å
C_c–C_s	1.42	1.40	1.39
C_c–C_t	1.56	1.56	1.54
C_t–C_m	1.53	1.52	1.50
$C_cC_sC_c$	124.1°	122.6°	120.3°
$C_cC_tC_m$	109.4	110.0	110.1
$C_sC_cC_t$	121.1	122.3	121.9

The subscripts c, s, t and m mean carbonyl, secondary, tertiary and methyl, respectively. a) Present study.

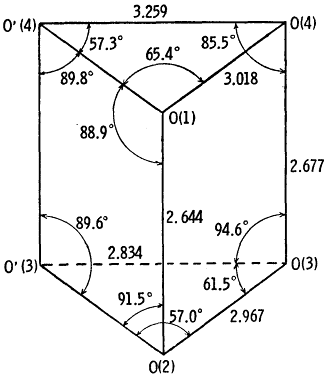

Fig. 2. Distorted trigonal prism formed by oxygen ligand atoms.
Primed and unprimed atoms of the same number are related by the mirror plane.

constraints. The metal-oxygen distances, however, remarkably correlate with the atomic number of the metal. The distances are nearly equal to the sum of the ionic radii[9)] of the metal (+3 for six coordination) and oxygen. The deviations are probably dependent on the kind of ligands (acac, thd and fod), and the coordination number of the metal (6 to 9). For example, the M–O lengths in fod complexes are generally smaller than those in thd complexes and the M–O lengths in six coordination complexes are smaller than those for seven coordination complexes (monohydrate or anhydrous dimer).

The four crystallographically independent *t*-butyl groups of the chelate rings A and B have nearly the same orientation with respect to the corresponding chelate rings. It is interesting to note that this orientation is the same as that in $Ni(thd)_2$[10)] but is the opposite of $Zn(thd)_2$[11)] (180° rotation about the C_3 axis of *t*-butyl group). To check the rotational configuration of the *t*-butyl group, the least-squares calculations were examined using the same structural parameters as listed

TABLE 6. AVERAGE METAL-OXYGEN[a)] AND OXYGEN-OXYGEN (BITE) DISTANCES FOR LANTHANIDE CHELATES[b)]

	M–O	O–O		Ref.
La	2.47 Å	2.78 Å	$La(acac)_32(H_2O)$	12)
Pr	2.42	2.78	$Pr_2(fod)_62(H_2O)$	13)
Pr	2.45	2.83	$Pr_2(thd)_6$	3)
Eu	2.35	2.81	$Eu(thd)_3(py)_2$	14)
Dy	2.28	2.74	$Dy(thd)_3H_2O$	15)
Ho	2.29	2.79	$Ho(dpp)_3H_2O$	16)
Er	2.21	2.67	$Er(thd)_3$	4)
Yb	2.23	2.76	$Yb(acac)_3H_2O$	17)
Yb	2.25	2.75	$Yb(acac)_3H_2O\ 0.5(C_6H_6)$	18)
Lu	2.17	2.57	$Lu(fod)_3H_2O$	19)
Lu	2.19	2.66	$Lu(thd)_3$	Present study

a) Oxygen atoms of M–O and O–O means carbonyl oxygen atoms. b) fod: 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, dpp: 1,3-diphenyl-1,3-propanedione.

in Table 2 except 180° rotation of *t*-butyl groups of the ring A and/or B. In these cases the *R* values did not increase significantly ($\sim$0.07), but the C_t–C_m lengths became unreasonably small (1.0—1.3 Å). However, uncertainty concerning the positions of the methyl groups may remain, if the high temperature factors observed for the methyl carbon atoms are interpreted as static disorder rather than as thermal motion.[3]

All the intermolecular distances are about twice the van der Waals radius for a methyl group or longer, except a distance of 3.65 Å between C(12)(x,y,z) and C(2)$(0.5-x, -y, 0.5+z)$.

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