

## Crystal Structure of Tris-(2,2,6,6-tetramethylheptane-2,5-dionato) Erbium(III)

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The crystal structure of the tris erbium salt of 2,2,6,6-tetramethylheptane-3,5-dione,  $\text{Er}(\text{thd})_3$ , has been determined by three-dimensional X-ray methods, using 1637 intensities obtained by counter methods with  $\text{Mo K}\alpha$  radiation at room temperature. There are two formula units per orthorhombic unit cell with dimensions of  $a = 17.825$  (8),  $b = 10.627$  (10),  $c = 9.950$  (4) Å. The structure was obtained by full-matrix least-squares refinement of atomic and anisotropic thermal parameters to a conventional  $R = 0.041$ . The space group is  $Pmn2_1$  and the molecules are arranged in almost trigonal fashion in layers lying approximately along (010). The erbium ion is coordinated by six oxygen atoms and the coordination geometry is almost ideally trigonal prismatic. The relationship between this structure and the known structures of hydrated and dimeric lanthanide diketonates is discussed.

### Introduction

The lanthanides La to Gd form monoclinic dimeric chelates  $\text{Ln}_2(\text{thd})_6$  with 2,2,6,6-tetramethylheptane-3,5-dione on crystallization from n-hexane or from the vapour phase (Erasmus & Boeyens, 1970) whereas the thd chelates of Ho to Lu are obtained as orthorhombic crystals under the same conditions. (Mode & Smith, 1969). The compounds of both Tb and Dy crystallize in the monoclinic and orthorhombic forms from hexane and the vapour, respectively (Erasmus & Boeyens, 1970). From hexane, exposed to the atmosphere, triclinic crystals of  $\text{Eu}(\text{thd})_3 \cdot \text{H}_2\text{O}$  and  $\text{Dy}(\text{thd})_3 \cdot \text{H}_2\text{O}$  have also been obtained, (Erasmus & Boeyens, 1971). The structures of the monoclinic and hydrated triclinic phases have been determined (Erasmus & Boeyens, 1970, 1971). The structure of the orthorhombic phase has not been determined previously and has been assumed to be monomeric (Boeyens, 1971). This structure is reported here.

Attempts to recrystallize  $\text{Er}(\text{thd})_3$  prepared by the method of Eisentraut & Sievers (1968) from n-hexane resulted in the formation of three types of crystals with slightly different habits. One of these was found to be triclinic and similar to the hydrates of Eu and Dy. Both the other two types are orthorhombic and the large difference in cell sizes suggests that they contain dimeric and monomeric species, respectively. The structure type characterized by the large unit cell (possibly hydrated) is still being studied and only the structure of the anhydrous  $\text{Er}(\text{thd})_3$  crystal with the smaller unit cell is described in this paper.

### Crystal data

Preliminary cell dimensions of the anhydrous orthorhombic  $\text{Er}(\text{thd})_3$  crystals were published by Mode & Smith (1969) and refinement of these values (suitably interchanged to match the standard setting of the space group) on an automatic four-circle diffractometer by

a method of least-squares (Busing & Levy, 1967) yielded the following results:

$$\begin{aligned} a &= 17.825 \text{ (8) \AA} \\ b &= 10.627 \text{ (10)} \\ c &= 9.950 \text{ (4)}. \end{aligned}$$

A positive test for pyro-electricity on the simple device described by Herbstein & Schoening (1957) together with the observed absences of  $h0l$  for  $h+l \neq 2n$  identified space group No. 31 in *International Tables for X-ray Crystallography* (1965). The proper setting,  $Pmn2_1$ , was confirmed by the detailed analysis of the structure. The measured density of  $1.26 \text{ g.cm}^{-3}$  (Boudreaux, 1968) yields  $z = 2$ ,  $\rho_x = 1.26 \text{ g.cm}^{-3}$ .

### Determination of the structure

Intensity data for the sphere with  $\sin \theta/\lambda \leq 0.596$  were collected on a Hilger & Watts single-crystal diffractometer using Zr-filtered  $\text{Mo K}\alpha$  radiation. An  $\omega$  scan mode was used, counting for a total of 300 seconds per reflexion. This was done in 50 steps of  $0.02^\circ$  and counting for 6 seconds per step. Corrections for background were made by measuring the general background as a function of  $\theta$  between two lattice rows and subtracting the scaled values from the measured integrated peak intensities. A total of 1844 reflexions were measured. 207 of these were not significantly above the background. Periodic checks on the strong 600 and 013 reflexions confirmed that there was no appreciable crystal decomposition. Absorption corrections were not applied because the factors stay almost constant for a crystal of radius 0.015 cm,  $\mu R = 0.37$ . Lp corrections were applied using a standard computer program.

The fractional  $y$  coordinate of the Er ion was obtained from a Patterson synthesis and three-dimensional Fourier syntheses were calculated for both possible settings of the space group ( $P2_1nm$  and  $Pmn2_1$ ). Only the latter yielded electron density maxima which made chemical sense when interpreted as representing

the light atoms. The initial confusion, because of a pseudo mirror plane along (001), disappeared once all the atoms had been placed correctly. The trial parameters were refined by full-matrix least squares with the program *ORFLS* of Busing, Martin & Levy (1962) on an IBM 360/65 computer. Apart from fractional atomic coordinates, isotropic individual temperature factors were refined until the conventional *R* value reached 0.10. Anisotropic thermal parameters were introduced and refinement with unitary weights was continued until all parameter shifts were less than 0.1 of the estimated standard deviations. At this stage  $R = \sum |\Delta F| / \sum F_o = 0.041$  and the weighted  $R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2} = 0.049$ . Further refinement was sought by the introduction of a weighting scheme based on counting statistics (Stout & Jensen, 1968), but no visible improvement resulted. It yielded  $R = 0.047$  and  $R_w = 0.052$ . The estimated standard deviations were uniformly higher than before and no difference in the calculated bond lengths was observed. The results given here are based on the refinement with unitary weights for all observed reflexions.

The refined parameters, according to the nomenclature of Fig. 1, are listed in Table 1 and the structure factors on an absolute scale ( $F_{000}$  for non-hydrogen atoms = 628) in Table 2. A difference Fourier synthesis computed from these structure factors was completely featureless and provided no evidence of hydrogen atoms or other unexplained regions of electron density.

It is not surprising that the hydrogen atoms were not found from the difference map. Apart from the heavy Er atom the anisotropic refinement would tend to compensate for them.

### Description of the structure

The stereoscopic packing diagram, Fig. 2, shows that the crystal is made up of monomeric  $\text{Er}(\text{thd})_3$  units. One of the chelate rings lies in a mirror plane and the other two are symmetry related across this mirror plane. Although not demanded by symmetry, the chelate

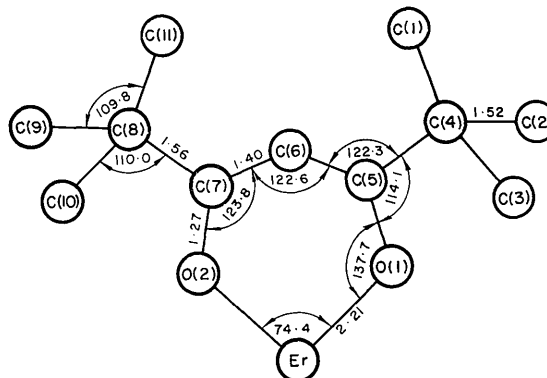


Fig. 1. Schematic drawing to illustrate the atomic numbering system used for the two chelate rings I and II. Averaged bond lengths and angles are also shown.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and individual thermal parameters ( $\times 10^4$ ) and their standard deviations with respect to the number of digits

The two crystallographically independent chelate rings are numbered in Roman numerals and the atoms associated with each ring according to the scheme of Fig. 1.

$$T = \exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2hl\beta_{23})]$$

	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Er	0	0945 (0.6)	0	44.1 (0.2)	71.6 (0.6)	117.5 (0.8)	0	0	15.1 (1.9)
O(1)	$\frac{1}{2}$ *	0747 (11)	3726 (13)	69 (7)	83 (12)	105 (15)	0	0	-9 (11)
O(2)	0	1679 (11)	7980 (14)	68 (7)	77 (11)	131 (18)	0	0	4 (12)
C(1)	$\frac{1}{2}$ *	2673 (25)	0641 (31)	344 (27)	104 (27)	172 (40)	0	0	33 (28)
C(2)	4290 (14)	2889 (20)	2680 (36)	128 (15)	199 (28)	822 (101)	105 (18)	203 (34)	251 (45)
C(4)	$\frac{1}{2}$ *	2381 (15)	2137 (21)	61 (9)	53 (14)	142 (25)	0	0	-6 (16)
C(5)	$\frac{1}{2}$ *	0969 (18)	2484 (20)	46 (8)	102 (19)	133 (25)	0	0	1 (20)
C(6)	$\frac{1}{2}$ *	0046 (17)	1489 (21)	54 (8)	87 (18)	131 (24)	0	0	23 (18)
C(7)	0	1250 (16)	6758 (23)	47 (8)	69 (17)	165 (30)	0	0	7 (19)
C(8)	0	2325 (24)	5655 (38)	85 (16)	110 (29)	169 (38)	0	0	65 (29)
C(9)	0690 (11)	3117 (18)	5884 (22)	74 (9)	206 (25)	285 (34)	-53 (13)	-15 (15)	54 (26)
C(11)	0	1832 (26)	4266 (29)	130 (21)	125 (34)	79 (29)	0	0	-24 (27)
O(1)	0818 (6)	2457 (8)	0507 (11)	59 (4)	86 (8)	241 (21)	-7 (5)	-43 (7)	30 (9)
O(2)	0937 (6)	0042 (7)	1195 (10)	62 (5)	79 (8)	154 (13)	-3 (5)	-4 (7)	14 (9)
C(1)	1701 (20)	4550 (20)	-0269 (31)	276 (28)	200 (26)	198 (59)	-159 (24)	15 (30)	-4 (28)
C(2)	1248 (18)	4616 (18)	2221 (33)	187 (22)	122 (21)	560 (71)	-70 (19)	184 (36)	-139 (34)
C(3)	2509 (16)	4102 (19)	1729 (52)	108 (14)	139 (22)	1303 (154)	-29 (17)	-227 (40)	23 (60)
C(4)	1729 (10)	3970 (11)	1144 (18)	68 (7)	57 (11)	200 (23)	-20 (8)	-12 (11)	-5 (15)
C(5)	1431 (8)	2573 (12)	1091 (15)	52 (6)	89 (13)	146 (18)	-16 (7)	-10 (9)	-6 (13)
C(6)	1857 (8)	1571 (11)	1637 (15)	57 (6)	79 (11)	154 (19)	-5 (7)	-7 (9)	2 (13)
C(7)	1587 (8)	0354 (12)	1645 (14)	46 (6)	101 (13)	134 (18)	-3 (7)	-7 (8)	1 (13)
C(8)	2961 (9)	0711 (12)	7259 (16)	58 (7)	91 (14)	173 (21)	11 (8)	16 (10)	-19 (14)
C(9)	2908 (12)	1802 (14)	6161 (24)	93 (11)	102 (15)	322 (37)	15 (11)	50 (17)	17 (22)
C(10)	3409 (12)	1229 (19)	8469 (20)	90 (10)	252 (29)	217 (28)	38 (15)	-34 (15)	-156 (26)
C(11)	2182 (10)	0367 (18)	7668 (21)	63 (8)	168 (22)	263 (33)	18 (11)	57 (14)	-19 (23)

\* These values are not scaled.



Table 3. Deviations from planarity of the chelate ring in general position as the distances of the atoms from the best plane

$$-0.46204u + 0.15371v + 0.87343w = 0.18796 \text{ obtained by least squares}$$

$u, v, w$  are Ångstrom coordinates.

Er	O(1)	O(2)	C(4)	C(5)	C(6)	C(7)	C(8)
-0.034	-0.020	0.086	0.031	0.001	-0.038	-0.007	-0.020

Table 4. Observed molecular bond lengths

	I	II	Av.	Dy(thd) <sub>3</sub> ·H <sub>2</sub> O
Er—O(1)	2.200 (12)	2.228 (9)	2.212	
Er—O(2)	2.156 (14)	2.263 (10)		
O(1)—C(5)	1.258 (22)	1.245 (16)	1.272	1.28
O(2)—C(7)	1.298 (24)	1.286 (15)		
O(1)—O(2)	2.683 (16)	2.665 (11)	2.674	2.74
C(5)—C(6)	1.394 (25)	1.417 (18)	1.399	1.40
C(7)—C(6)	1.403 (24)	1.381 (17)		
C(5)—C(4)	1.539 (24)	1.577 (16)	1.555	1.55
C(7)—C(8)	1.585 (31)	1.518 (18)		
C(4)—C(1)	1.520 (34)	1.536 (33)	1.520	1.54
C(4)—C(2)	1.478 (22)	1.535 (28)		
C(4)—C(3)		1.514 (30)		
C(8)—C(9)	1.508 (23)	1.596 (23)		
C(8)—C(10)		1.545 (22)		
C(8)—C(11)	1.478 (31)	1.492 (21)		

### Discussion

This structure represents the first example of a monomeric anhydrous lanthanide chelate. Other known structures of lanthanide tris-chelates include those of hydrates (Erasmus & Boeyens, 1971; Zalkin, Temple-

ton & Karraker, 1969; Cunningham, Sands, Wagner & Richardson, 1969; Boeyens & de Villiers, 1971), dimers (Erasmus & Boeyens, 1970), hydrated dimers (de Villiers & Boeyens, 1971) and various adducts (Watkins, Cunningham, Phillips, Sands & Wagner, 1969; Richardson, Corfield, Sands & Sievers, 1970). In these structures the lanthanides are either seven or eight coordinate. The seven-coordination polyhedra usually have the geometry of a monocapped trigonal prism. Superficial examination suggests that the capped trigonal prisms found for acetylacetonates (acac) are different from those found for thd and fod (=1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione) complexes. The relationship between the two types of capped trigonal prism is illustrated in Fig. 5. The top and base triangles of the acac type (e.g., Cunningham *et al.*, 1969) are *ABC* and *DEF*, with cap *G* on face *ACFD*. The distance *AE* is longer than the normal nearest neighbour approach. In the case of thd and fod hydrates (e.g., Erasmus & Boeyens, 1971) the triangles *ABE* and *GCF* are the top and base of the prism with cap *D* on face *AEFG*. *AC* is now longer than a nearest neighbour approach. The factor which decides between the two types of monocapped prism is thus whether *AE* or *AC* is the nearest neighbour ap-

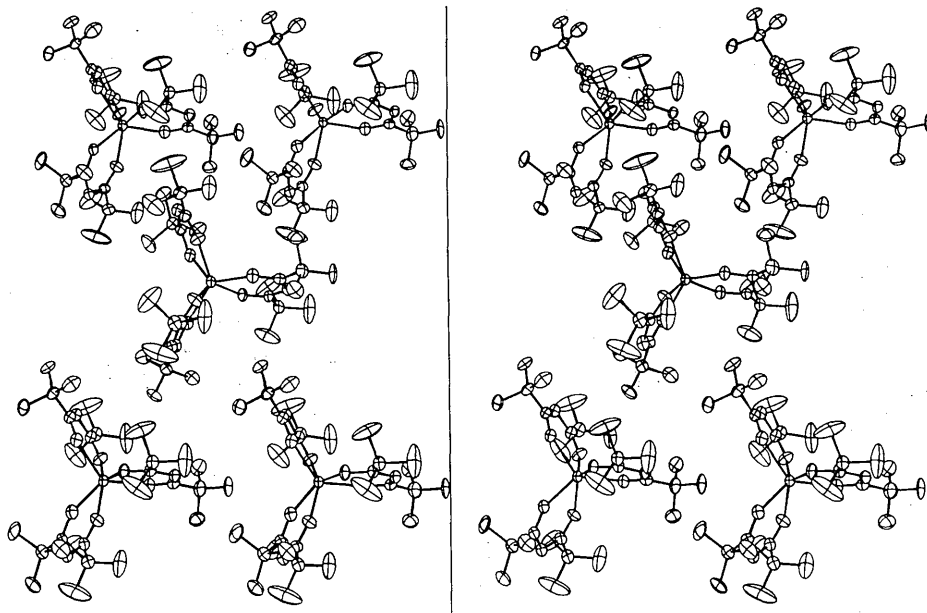


Fig. 2. Stereoscopic packing diagram of the structure as viewed approximately along [010]. All stereoscopic drawings were prepared with the help of the program ORTEP of Johnson (1965).

proach. The bites are indicated by dotted lines: *AD*, *BE* and *CG*.

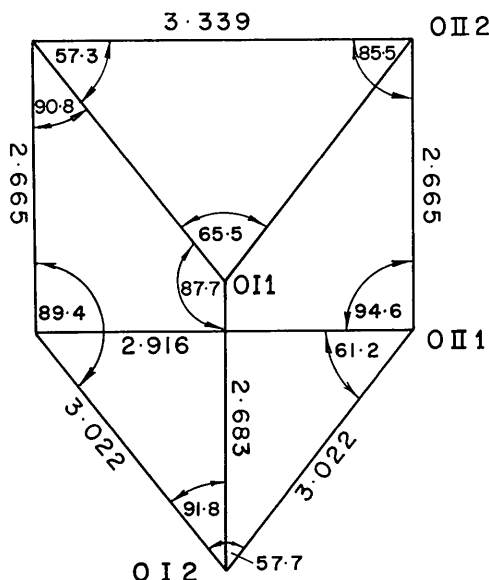


Fig. 3. Schematic drawing of the trigonal prismatic coordination of oxygen atoms around the central erbium ion to illustrate the actually observed geometry.

In both cases atom *F* represents the oxygen of the water molecule, which is thus not the cap. Should the present structure type thus be representative of all anhydrous lanthanide tris chelates, it follows that hydration involves chemical attack by water to replace one of the oxygen ligand atoms in the trigonal prismatic arrangement around the central ion. This dangling oxygen is then drawn back into the coordination sphere as the cap.

In the anhydrous dimeric chelates of *thd* and *fod*, which are also seven coordinated, the same geometry is found (*e.g.* Erasmus & Boeyens, 1970) as in the hydrates where atom *F* represents the oxygen of the neighbouring second half of the dimer in which it is designated as atom *G* and is shared between the two metal ions. Atom *G* in the first half of the dimer is shared in an equivalent fashion with the neighbouring metal ion. The correspondence between the hydrates and the anhydrous dimers is obvious and could indicate that dimerization occurs *via* hydration.

The packing of the molecules in the crystal can be described as an almost trigonal array within layers approximately perpendicular to [010] and is shown in Fig. 2. The bulkiness of the *t*-butyl groups is probably the only factor preventing trigonal crystallographic symmetry. It is noted that some of the *t*-butyl groups

Table 5. Observed bond angles

	I	II	Av.	Dy(thd) <sub>3</sub> ·H <sub>2</sub> O
O(1)—Er—O(2)	76.0 (0.4)	72.8 (0.3)	74.4	
Er—O(1)—C(5)	136.0 (1.3)	138.8 (0.9)	137.7	134.4
Er—O(2)—C(7)	138.2 (1.1)	137.6 (0.8)		
O(1)—C(5)—C(6)	124.5 (1.9)	125.2 (1.2)	123.8	124.7
O(2)—C(7)—C(6)	121.6 (1.8)	123.7 (1.3)		
O(1)—C(5)—C(4)	113.8 (1.7)	113.9 (1.2)	114.1	114.6
O(2)—C(7)—C(8)	113.3 (1.9)	115.3 (1.2)		
C(6)—C(5)—C(4)	121.8 (1.8)	121.0 (1.3)	122.3	120.6
C(6)—C(7)—C(8)	125.2 (2.2)	121.0 (1.3)		
C(5)—C(6)—C(7)	123.8 (2.0)	121.3 (1.3)	122.6	123.0
C(5)—C(4)—C(1)	114.8 (1.8)	109.6 (1.5)	110.0	109.3
C(5)—C(4)—C(2)	105.9 (1.2)	104.9 (1.4)		
C(5)—C(4)—C(3)		114.2 (1.4)		
C(7)—C(8)—C(9)	107.3 (1.8)	107.3 (1.3)		
C(7)—C(8)—C(10)		107.8 (1.3)		
C(7)—C(8)—C(11)	113.1 (2.3)	114.9 (1.4)		
C(1)—C(4)—C(2)	106.4 (1.7)	116.2 (1.9)	109.8	109.3
C(1)—C(4)—C(3)		110.2 (2.4)		
C(2)—C(4)—C(3)	117.7 (3.2)	101.7 (2.3)		
C(9)—C(8)—C(10)	109.4 (2.5)	107.8 (1.4)		
C(9)—C(8)—C(11)	109.8 (1.7)	108.0 (1.5)		
C(10)—C(8)—C(11)		110.8 (1.5)		

Table 6. Comparison of some variable parameters with the corresponding values obtained for other lanthanide chelates, referenced in the text

	Pr <sub>2</sub> (thd) <sub>6</sub>	Nd <sub>2</sub> (thd) <sub>6</sub>	Dy(thd) <sub>3</sub> ·H <sub>2</sub> O	Er(thd) <sub>3</sub>	Lu(fod) <sub>3</sub> ·H <sub>2</sub> O
Bite (Å)	2.83	2.77	2.74	2.67	2.63
O—M—O(°)	70.4	71.6	73.6	74.4	75.8
M—O (Å)	2.41	2.38	2.30	2.21	2.17

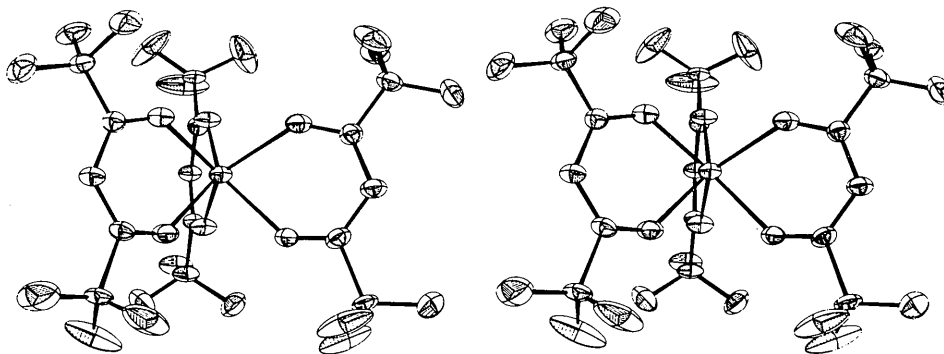


Fig. 4. Stereoscopic drawing to illustrate the conformation of the molecule. The atoms are represented by 20% probability thermal ellipsoids.

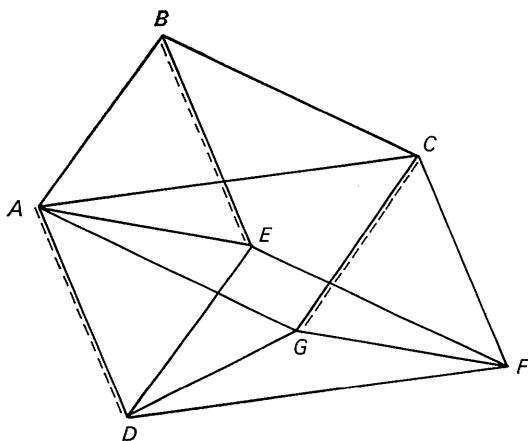


Fig. 5. Schematic drawing to illustrate the relationship between the capped trigonal prisms characteristic of  $\text{Ln}(\text{acac})_3 \cdot \text{H}_2\text{O}$  (cap G) and  $\text{Ln}(\text{thd})_3 \cdot \text{H}_2\text{O}$ ,  $\text{Ln}(\text{fod})_3 \cdot \text{H}_2\text{O}$  (cap D) chelates. The bites of the chelate rings are shown as dotted lines.

point into the layers and some of them slightly outwards. The carbon atoms of the methyl groups constituting the latter show the highest thermal motion as expected.

In conclusion it is instructive to compare the variable parameters: bite,  $d(\text{M}-\text{O})$  and  $\text{O}-\text{M}-\text{O}$  angle with those obtained for the lanthanide chelates  $\text{Pr}_2(\text{thd})_6$  (Erasmus & Boeyens, 1970),  $\text{Nd}_2(\text{thd})_6$  (Burns, 1970),  $\text{Dy}(\text{thd})_3 \cdot \text{H}_2\text{O}$  (Erasmus & Boeyens, 1971) and  $\text{Lu}(\text{fod})_3 \cdot \text{H}_2\text{O}$  (Boeyens & De Villiers, 1971). As shown in Table 6 there is a regular variation of these values with atomic number and the effect of coordination does not appear to be drastic.

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