# Structural and Thermal Studies of Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium(IV)

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The crystal structure of the title compound, $Ce(thd)_4$, was solved from single-crystal X-ray diffraction data. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a$ = 12.40(1), $b$ = 21.37(2), $c$ = 37.89(2) Å, $\beta$ = 91.89(6) ° and $Z$ = 4. Anisotropic refinement of Ce and O and isotropic refinement of C atoms gave $R$ = 0.096 for 7644 reflections. The asymmetric unit of the structure consists of two discrete $Ce(thd)_4$ molecules both having Ce atoms surrounded by eight oxygen atoms from four different thd ligands. The Ce–O distances vary within a rather limited range of 2.29(1)–2.37(1) Å. The $Ce(thd)_4$ molecules are joined together by weak van der Waals type interactions or very weak hydrogen bonds.

Thermoanalytical (TG and DSC) and mass-spectrometric studies showed that $Ce(thd)_4$, sublimes above 200 °C and that the main species found in the mass spectrum are $Ce(thd)_3$ and $Ce(thd)_2$.

Alkaline earth and rare earth metals have generally only a few volatile compounds which have vapour pressures high enough for use in chemical vapour deposition (CVD) of thin films. The β-diketonato complexes of these elements, however, are readily volatile and stable enough for gas-phase thin-film growth.[1] In particular, the thd-chelates (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) of rare earth and alkaline earth metals have recently been applied in the CVD preparation of high-$T_c$ superconducting thin films.[2-4] They have also been successfully used in the growth of the semiconducting layers for electroluminescent (EL) thin-film devices by the atomic layer epitaxy (ALE) process.[5-7] $Ce(thd)_4$ is needed for doping of SrS films in order to obtain a blue-emitting EL device.[8] The process involves, besides volatilization, the reduction of Ce(IV) to its trivalent state by $H_2S$.

The crystal structures of rare earth β-diketonates were extensively studied in the 1960s and early 1970s. For example, the structures of acetylacetonato complexes as tri-,[9] di-[10] and monohydrates[11] and that of the phenyl-substituted monohydrate[12] are known. For the thd-chelates of trivalent rare earth ions the anhydrous dimeric[13] and monomeric[14] structures, as well as the monohydrate[15] and fluorine-substituted[16] structures, have been reported. A common feature for all structures is that the β-diketonate acts as a bidentate ligand, but simultaneously one of the oxygen

atoms may also bind to two different metal ions, thus satisfying the requirements of a high coordination number for these large ions. The latter behaviour has been found in the structures of lighter lanthanoids, as they have a tendency to form dimers. Further bridging does not take place, but the structures generally contain discrete molecules packed together by very weak hydrogen bonds. This structural feature explains the volatility of these complexes.

As regards Ce(IV) β-diketonato complexes, structural studies are limited. However, two structure types have been reported for tetrakis(acetylacetonato)cerium(IV).[17,18] In the present paper the crystal structure and thermal behaviour of $Ce(thd)_4$ are reported and compared with literature data.

## Experimental

*Preparation of the crystals.* The $Ce(thd)_4$ powder was synthesized following a literature method.[19] The starting materials, 2,2,6,6-tetramethyl-3,5-heptanedione and $CeCl_3$ were commercial, analytically pure reagents. The $Ce(thd)_4$ powder was sublimed and recrystallized from a hexane–ethanol mixture.

*X-Ray measurements.* X-Ray intensity data were collected at room temperature on a Rigaku AFC5S diffractometer using $MoK_\alpha$ radiation. Details of crystal data and structure refinement are presented in Table 1. The weak reflections were rescanned up to three times depending on the intensity of the reflection. The intensities were corrected for Lorentz and polarization effects and an empirical absorption correction program DIFABS[20] was also employed. In

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*Table 1.* Summary of crystal data, intensity collection and structure refinement for Ce(thd)$_4$.

**Crystal data**

| | |
|---|---|
| Formula | [Ce(C$_{11}$O$_2$H$_{19}$)$_4$]$_2$ |
| Mol. wt. | 1762.53 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 12.40(1) |
| b/Å | 21.37(2) |
| c/Å | 37.89(1) |
| β/° | 91.89(6) |
| V/Å$^3$ | 10036(13) |
| Z | 4 |
| $d_{calc}$/g cm$^{-3}$ | 1.166 |
| Radiation | MoK$_\alpha$ ($\lambda$ = 0.71069 Å) |
| μ(MoK$_\alpha$)/cm$^{-1}$ | 9.62 |
| Crystal size/mm$^3$ | 0.20×0.15×0.35 |
| Crystal description | Red, prismatic |

**Data collection and structure refinement**

| | |
|---|---|
| Data collection | ω-Scan |
| Scan speed/° min$^{-1}$ | 4.0 |
| No. of data collected | 18975 |
| No. of unique data $I_{obs}>2\sigma(I_{obs})$ | 7644 |
| Solution | Direct methods |
| Abs. correction | Empirical[20] |
| No. of variables | 685 |
| Weighting scheme | $w = [\sigma^2(F_o)]^{-1}$ |
| $R$ ($R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$) | 0.096 |
| $R_w$ ($R_w = [(\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma wF_o^2)]^{\frac{1}{2}}$) | 0.105 |
| Maximum peak in difference map / e$^-$ Å$^{-3}$ | 1.10 |

all calculations the crystallographic program package TEX-SAN[21] was used. The positions of the cerium atoms were located by direct methods. The subsequent difference electron density calculations gave the positions of the other non-hydrogen atoms. In the final calculations Ce and O atoms had anisotropic and C atoms isotropic temperature factors. The use of anisotropic temperature factors for C atoms did not improve the $R$-value and standard deviations but resulted in unrealistic bonding geometries for methyl carbons. The hydrogen atoms could not be located and the they were not included in the calculated model. Tables of anisotropic temperature factors and the observed and calculated structure factors are available from one of the authors (R.S.) upon request. The figures were drawn with the program PLUTO.[22]

*Thermoanalytical and mass-spectrometric measurements.* For the TG and DSC measurements Perkin-Elmer series 7 instruments were used. The sample size in the TG measurements was about 10 mg and in the DSC measurements 5 mg. The heating rate was 10 °C min$^{-1}$ and measurements were carried out in a dynamic argon atmosphere. The molecular formulas of the volatilized species in vacuum were determined in separate experiments using a VG 7070E mass spectrometer.

## Results and discussion

*Crystal strucure.* The final atomic coordinates of all non-hydrogen atoms are listed in Table 2. Table 3 gives the bond lengths and Table 4 the bond angles within the complex. The standard deviations found in the bond lengths and angles are rather large, but this is not uncommon in high-molecular-weight structures.[23] The reasons for the high $R$-value (9.6%) and large standard deviations may be as follows: (i) the crystal diffracted poorly, only 7644 of 18975 reflections having $I > 2\sigma(I)$; (ii) the structure may contain pseudosymmetry, $\pm(\frac{1}{2}-x, y, \frac{1}{2}-z)$; (iii) weak intermolecular forces are present which can be seen in high thermal motion of the methyl groups. These problems could have been partly avoided by taking low-temperature measurements, but facilities for these were not available.

The structure of Ce(thd)$_4$ contains two symmetry-independent discrete Ce(thd)$_4$ molecules in which the coordination spheres around the Ce atoms are similar but not identical (Fig. 1). Both metal atoms are coordinated to eight oxygen atoms from four bidentate thd ligands. The geometrical shape of the coordination polyhedra is close to square antiprismatic. The situation is similar to that found in the structure of Nb(thd)$_4$, but in that case the unit cell contains only four Nb(thd)$_4$ molcules.[24] If the chelating
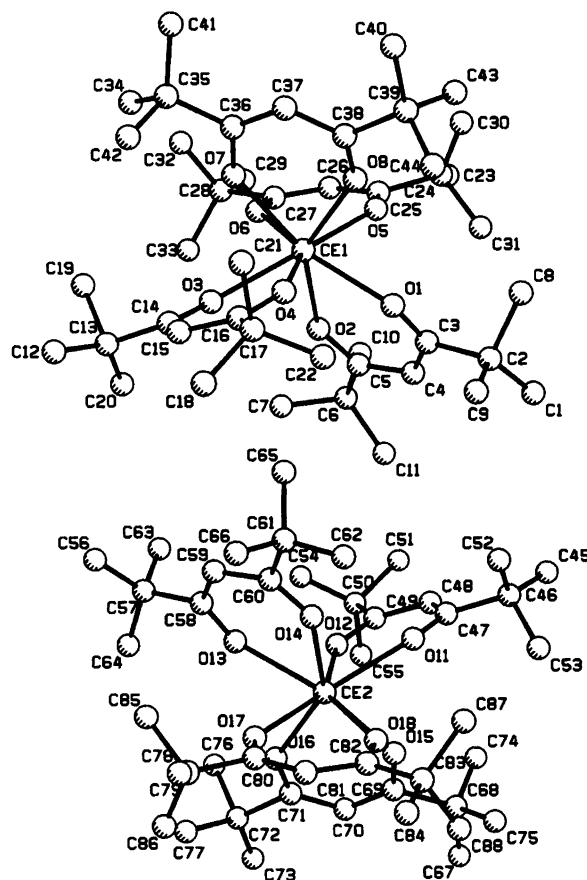


*Fig. 1.* Schematic drawing of the asymmetric unit showing the atomic labelling.

*Table 2.* Atomic positional parameters and equivalent isotropic temperature factors for Ce(thd)$_4$.[a]

| Atom | x | y | z | $B_q/Å^2$ | Atom | x | y | z | $B_q/Å^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Molecule 1 | | | | | Molecule 2 | | | | |
| Ce(1) | 0.60583(8) | 0.05591(5) | 0.62633(3) | 3.58(6) | Ce(2) | 0.88080(8) | 0.06322(5) | 0.87821(3) | 3.98(6) |
| O(1) | 0.5751(9) | 0.1432(5) | 0.6618(3) | 4.4(6) | O(11) | 0.865(1) | 0.1578(6) | 0.8488(3) | 5.0(7) |
| O(2) | 0.750(1) | 0.0707(6) | 0.6656(4) | 5.6(8) | O(12) | 1.036(1) | 0.0816(6) | 0.8483(4) | 5.4(7) |
| O(3) | 0.629(1) | −0.0400(5) | 0.6531(4) | 4.9(7) | O(13) | 0.916(1) | −0.0285(6) | 0.8456(4) | 5.8(8) |
| O(4) | 0.457(1) | 0.0320(6) | 0.6576(4) | 5.3(7) | O(14) | 0.746(1) | 0.0507(6) | 0.8355(3) | 4.9(7) |
| O(5) | 0.697(1) | 0.1347(6) | 0.5981(4) | 5.3(7) | O(15) | 0.968(1) | 0.1357(5) | 0.9156(3) | 5.0(7) |
| O(6) | 0.743(1) | 0.0120(6) | 0.5941(3) | 4.7(7) | O(16) | 0.999(1) | 0.0100(6) | 0.9159(4) | 5.6(8) |
| O(7) | 0.520(1) | −0.0126(6) | 0.5864(4) | 5.0(7) | O(17) | 0.776(1) | −0.0127(6) | 0.9041(4) | 5.8(8) |
| O(8) | 0.473(1) | 0.1080(5) | 0.5941(3) | 4.7(7) | O(18) | 0.744(1) | 0.1111(6) | 0.9083(3) | 4.9(7) |
| C(1) | 0.643(2) | 0.284(1) | 0.7129(8) | 11.0(9) | C(45) | 0.950(3) | 0.307(2) | 0.810(1) | 15(1) |
| C(2) | 0.570(2) | 0.238(1) | 0.6951(6) | 6.4(5) | C(46) | 0.878(2) | 0.262(1) | 0.8247(6) | 5.5(5) |
| C(3) | 0.630(1) | 0.178(1) | 0.6814(5) | 4.6(4) | C(47) | 0.924(2) | 0.197(1) | 0.8336(5) | 4.7(4) |
| C(4) | 0.735(2) | 0.166(1) | 0.6947(5) | 5.3(5) | C(48) | 1.035(1) | 0.184(1) | 0.8247(5) | 4.9(4) |
| C(5) | 0.789(2) | 0.112(1) | 0.6863(6) | 4.9(5) | C(49) | 1.080(2) | 0.125(1) | 0.8321(5) | 4.6(4) |
| C(6) | 0.910(2) | 0.100(1) | 0.7010(7) | 6.7(6) | C(50) | 1.199(2) | 0.107(1) | 0.8204(6) | 5.8(5) |
| C(7) | 0.925(2) | 0.031(1) | 0.7040(8) | 9.8(8) | C(51) | 1.241(2) | 0.159(1) | 0.7933(7) | 9.0(7) |
| C(8) | 0.511(2) | 0.270(1) | 0.6605(8) | 10.1(8) | C(52) | 0.775(3) | 0.248(2) | 0.806(1) | 13(1) |
| C(9) | 0.480(2) | 0.218(1) | 0.7174(8) | 12(1) | C(53) | 0.830(2) | 0.287(1) | 0.8574(9) | 12(1) |
| C(10) | 0.982(3) | 0.119(2) | 0.671(1) | 13(1) | C(54) | 1.195(2) | 0.048(1) | 0.8024(7) | 7.9(6) |
| C(11) | 0.927(3) | 0.139(2) | 0.735(1) | 15(1) | C(55) | 1.267(2) | 0.113(1) | 0.8520(8) | 9.5(8) |
| C(12) | 0.540(2) | −0.198(1) | 0.6833(8) | 11.4(9) | C(56) | 0.850(3) | −0.171(2) | 0.7949(9) | 13(1) |
| C(13) | 0.625(2) | −0.147(1) | 0.6760(6) | 5.8(5) | C(57) | 0.927(2) | −0.122(1) | 0.8130(8) | 8.1(7) |
| C(14) | 0.574(1) | −0.0826(9) | 0.6675(5) | 4.3(4) | C(58) | 0.864(2) | −0.062(1) | 0.8229(6) | 5.4(5) |
| C(15) | 0.463(1) | −0.0727(9) | 0.6779(5) | 5.0(4) | C(59) | 0.768(2) | −0.048(1) | 0.8064(6) | 5.9(5) |
| C(16) | 0.415(1) | −0.013(1) | 0.6738(5) | 4.4(4) | C(60) | 0.715(2) | 0.009(1) | 0.8135(6) | 4.9(5) |
| C(17) | 0.300(1) | −0.0018(9) | 0.6858(5) | 4.6(4) | C(61) | 0.607(2) | 0.024(1) | 0.7936(6) | 6.0(5) |
| C(18) | 0.267(2) | −0.050(1) | 0.7161(6) | 7.4(6) | C(62) | 0.562(3) | 0.082(2) | 0.806(1) | 14(1) |
| C(19) | 0.666(2) | −0.169(1) | 0.6389(8) | 11.3(9) | C(63) | 1.004(4) | −0.105(2) | 0.786(1) | 20(2) |
| C(20) | 0.725(2) | −0.134(1) | 0.6955(8) | 12(1) | C(64) | 0.989(3) | −0.142(2) | 0.844(1) | 18(2) |
| C(21) | 0.225(2) | −0.010(1) | 0.6532(6) | 6.4(5) | C(65) | 0.620(2) | 0.027(1) | 0.754(1) | 11.4(9) |
| C(22) | 0.298(2) | 0.064(1) | 0.7026(6) | 6.1(5) | C(66) | 0.531(3) | −0.025(2) | 0.802(1) | 17(1) |
| C(23) | 0.930(3) | 0.221(2) | 0.565(1) | 15(1) | C(67) | 1.158(3) | 0.208(2) | 0.979(1) | 14(1) |
| C(24) | 0.819(2) | 0.209(1) | 0.5712(7) | 7.4(6) | C(68) | 1.081(2) | 0.203(1) | 0.9490(7) | 6.4(6) |
| C(25) | 0.787(2) | 0.141(1) | 0.5830(5) | 4.9(4) | C(69) | 1.048(2) | 0.136(1) | 0.9371(6) | 5.1(5) |
| C(26) | 0.856(2) | 0.091(1) | 0.5746(6) | 5.5(5) | C(70) | 1.111(2) | 0.084(1) | 0.9479(6) | 5.6(5) |
| C(27) | 0.831(2) | 0.0311(9) | 0.5809(5) | 4.7(4) | C(71) | 1.074(2) | 0.025(1) | 0.9372(6) | 6.3(5) |
| C(28) | 0.908(2) | −0.025(1) | 0.5706(6) | 6.5(5) | C(72) | 1.143(2) | −0.033(1) | 0.9508(8) | 9.2(7) |
| C(29) | 1.019(2) | 0.002(1) | 0.5578(8) | 10.2(8) | C(73) | 1.239(3) | −0.018(2) | 0.977(1) | 15(1) |
| C(30) | 0.739(3) | 0.230(2) | 0.546(1) | 13(1) | C(74) | 1.138(2) | 0.230(1) | 0.9197(8) | 10.8(9) |
| C(31) | 0.812(3) | 0.248(2) | 0.605(1) | 15(1) | C(75) | 0.984(2) | 0.240(1) | 0.9582(8) | 12(1) |
| C(32) | 0.848(2) | −0.065(1) | 0.5444(8) | 10.5(8) | C(76) | 1.209(3) | −0.056(2) | 0.918(1) | 15(1) |
| C(33) | 0.941(2) | −0.062(1) | 0.6049(8) | 9.8(8) | C(77) | 1.065(2) | −0.089(1) | 0.9575(8) | 10.6(8) |
| C(34) | 0.515(2) | −0.113(1) | 0.5427(7) | 9.2(7) | C(78) | 0.531(5) | −0.089(2) | 0.923(1) | 24(2) |
| C(35) | 0.410(2) | −0.076(1) | 0.5474(6) | 5.9(5) | C(79) | 0.640(2) | −0.082(1) | 0.9227(8) | 8.5(7) |
| C(36) | 0.437(2) | −0.012(1) | 0.5645(5) | 4.5(4) | C(80) | 0.683(2) | −0.014(1) | 0.9159(6) | 5.2(5) |
| C(37) | 0.372(1) | 0.0390(9) | 0.5592(5) | 4.6(4) | C(81) | 0.618(2) | 0.036(1) | 0.9253(6) | 5.8(5) |
| C(38) | 0.392(2) | 0.0974(9) | 0.5747(5) | 4.7(4) | C(82) | 0.656(2) | 0.0985(9) | 0.9215(5) | 4.4(4) |
| C(39) | 0.319(2) | 0.156(1) | 0.5665(6) | 6.4(5) | C(83) | 0.583(2) | 0.150(1) | 0.9320(6) | 6.2(5) |
| C(40) | 0.227(2) | 0.143(1) | 0.5371(7) | 9.2(7) | C(84) | 0.480(3) | 0.130(2) | 0.949(1) | 13(1) |
| C(41) | 0.352(2) | −0.069(1) | 0.5107(8) | 10.4(8) | C(85) | 0.657(3) | −0.121(2) | 0.890(1) | 13(1) |
| C(42) | 0.343(2) | −0.114(1) | 0.5745(8) | 10.3(8) | C(86) | 0.700(4) | −0.107(2) | 0.952(1) | 20(2) |
| C(43) | 0.393(2) | 0.208(1) | 0.5521(7) | 7.6(6) | C(87) | 0.556(2) | 0.193(1) | 0.9002(7) | 9.4(7) |
| C(44) | 0.272(2) | 0.177(1) | 0.6010(7) | 8.6(7) | C(88) | 0.653(2) | 0.188(1) | 0.9601(8) | 11.5(9) |

[a]The equivalent isotropic temperature factors for the atoms are of the form $B_q = 4/3\Sigma_i\Sigma_j\beta_{ij}a_i \cdot a_j$.

systems are taken into account the coordination polyhedron for Nb(thd)$_4$ is $D_4$(llll), while for Ce(thd)$_4$ it is $D_2$(ssss). In the Ce acetylacetonato complexes the coordination polyhedra are distorted Archimedean antiprisms of the $D_2$(ssss) type.[17,18] The Ce–O distances in the present structure around Ce1 vary between 2.29(1) and 2.34(1) Å and those around Ce2 between 2.29(1) and 2.37(1) Å. These values are typical of those found in Ce(IV) com-

*Table 3.* Intramolecular bond distances (in Å) for Ce(thd)$_4$ with standard deviations in parentheses.[a]

| Molecule 1 | | Molecule 2 | |
| --- | --- | --- | --- |
| Ce1–O1 | 2.34(1) | Ce2–O11 | 2.31(1) |
| Ce1–O2 | 2.31(1) | Ce2–O12 | 2.29(1) |
| Ce1–O3 | 2.30(1) | Ce2–O13 | 2.37(1) |
| Ce1–O4 | 2.29(1) | Ce2–O14 | 2.31(1) |
| Ce1–O5 | 2.31(1) | Ce2–O15 | 2.34(1) |
| Ce1–O6 | 2.32(1) | Ce2–O16 | 2.31(1) |
| Ce1–O7 | 2.34(1) | Ce2–O17 | 2.31(1) |
| Ce1–O8 | 2.30(1) | Ce2–O18 | 2.31(1) |
| O1–C3 | 1.24(2) | O11–C47 | 1.26(2) |
| O2–C5 | 1.26(2) | O12–C49 | 1.25(2) |
| O3–C14 | 1.27(2) | O13–C58 | 1.28(2) |
| O4–C16 | 1.27(2) | O14–C60 | 1.27(2) |
| O5–C25 | 1.27(2) | O15–C69 | 1.26(2) |
| O6–C27 | 1.28(2) | O16–C71 | 1.26(2) |
| O7–C36 | 1.30(2) | O17–C80 | 1.25(2) |
| O8–C38 | 1.25(2) | O18–C82 | 1.25(2) |

[a]The C–C distances are excluded but are available upon request.

plexes containing oxoligands; for instance, in Ce(acac)$_4$[17,18] the Ce–O range is 2.30–2.37 Å.

For the tetravalent cerium ion an oxygen coordination number of eight is the most common, and in the tetrakis complexes the square antiprism coordination polyhedron is more common than a dodecahedron.[25] Also, in the β-diketonato complexes of trivalent rare earths the eighth coordination and antiprism as coordination polyhedron appear usual, but the fluorinated complexes crystallize in dodecahedral geometry.[25]

The geometry of various coordination polyhedra can be studied by calculating the δ-values.[26] The theoretical δ-values for an idealized $D_{4d}$ antiprism are 0.0, 0.0, 52.4 and 52.4°. In the present structure the observed values for the sphere around Ce1 (O1, O5, O7 and O3 describe the shape) are 9.5, 4.3, 53.5 and 53.3°, while those around Ce2 (O11, O15, O17 and O13) are 12.5, 5.1, 54.8 and 54.8°. The distortions from the antiprismatic structures of Ce acetylacetonato complexes are also quite large, and the coordination polyhedron in α-Ce(acac)$_4$ can even be approximated as a $C_{2v}$ bicapped trigonal prism.[27] The thd ligand is much larger and bulkier than the acetylacetonato ligand, and thus the packing may also force the two Ce atoms to adopt a certain distorted coordination polyhedron. An interesting feature is that molecule 1 (Ce1) can be obtained from molecule 2 (Ce2) by rotating, for example, the atoms O11, O12, O13 and O14 by 90° around the $C_2$ axis.

The thd ligands coordinate bidentately without bridging to the Ce atoms. The geometry of the ligand is very close to that found in Nb(thd)$_4$. The C–O distances [1.24(2)–1.30(2) Å] and intra-ring O···O distances [2.66(2)–2.73(2) Å] (Table 5) are also typical for β-diketonato complexes. The C–C distances in the ligand vary, as would be expected. If the carbon atoms are labelled as carbonyl ($C_c$), double

bond ($C_d$), tertiary ($C_t$) and methyl carbons ($C_m$), the $C_c$–$C_d$ distances are usually the shortest, ranging from 1.35(3) to 1.46(2) Å, indicating the existence of a delocalized double bond. The other distances $C_c$–$C_t$ and $C_t$–$C_m$ are normal within 3 e.s.d.s for single carbon–carbon bonds, ranging from 1.42(3) to 1.62(3) Å, with the exception of C78–C79, which was 1.36(5) Å. A similar situation has also been observed in the Nb(thd)$_4$ structure.[25] Within the ligand the $C_t$–$C_c$(O)–$C_d$–$C_c$–$C_t$ atoms form planes and the Ce atoms are also not far from these planes. In the planar Ce–O–$C_c$–$C_d$–$C_c$–O rings the average angles are: O–Ce–O 70.5°, Ce–O–$C_c$ 138°, O–$C_c$–$C_d$ 125° and $C_c$–$C_d$–$C_c$ 120° (Table 4).

The high thermal parameters of methyl groups are characteristic for all known β-diketonate structures. This can be interpreted either as high thermal motion or static disorder. In any case, this indicates very weak and poorly directed intermolecular interactions. The structure (Fig. 2) is made of layers of molecules 1 and 2. In a layer there are rows

*Table 4.* Intramolecular bond angles (in °) for Ce(thd)$_4$ with standard deviations in parentheses.[a]

| Molecule 1 | | Molecule 2 | |
| --- | --- | --- | --- |
| O1–Ce1–O2 | 70.0(4) | O11–Ce2–O12 | 70.7(4) |
| O1–Ce1–O3 | 118.5(5) | O11–Ce2–O13 | 119.1(5) |
| O1–Ce1–O4 | 74.4(4) | O11–Ce2–O14 | 73.5(4) |
| O1–Ce1–O5 | 77.1(4) | O11–Ce2–O15 | 75.1(5) |
| O1–Ce1–O6 | 139.5(4) | O11–Ce2–O16 | 140.2(4) |
| O1–Ce1–O7 | 142.5(4) | O11–Ce2–O17 | 141.1(4) |
| O1–Ce1–O8 | 78.0(4) | O11–Ce2–O18 | 78.4(4) |
| O2–Ce1–O3 | 75.8(5) | O12–Ce2–O13 | 73.2(5) |
| O2–Ce1–O4 | 108.6(5) | O12–Ce2–O14 | 105.8(5) |
| O2–Ce1–O5 | 79.5(5) | O12–Ce2–O15 | 79.0(5) |
| O2–Ce1–O6 | 80.2(5) | O12–Ce2–O16 | 82.3(5) |
| O2–Ce1–O7 | 146.0(4) | O12–Ce2–O17 | 144.9(4) |
| O2–Ce1–O8 | 143.0(4) | O12–Ce2–O18 | 143.7(4) |
| O3–Ce1–O4 | 70.3(4) | O13–Ce2–O14 | 71.4(5) |
| O3–Ce1–O5 | 142.8(4) | O13–Ce2–O15 | 140.8(5) |
| O3–Ce1–O6 | 77.9(4) | O13–Ce2–O16 | 77.8(5) |
| O3–Ce1–O7 | 77.0(5) | O13–Ce2–O17 | 76.0(5) |
| O3–Ce1–O8 | 137.9(4) | O13–Ce2–O18 | 141.0(4) |
| O4–Ce1–O5 | 145.1(4) | O14–Ce2–O15 | 144.3(4) |
| O4–Ce1–O6 | 143.2(4) | O14–Ce2–O16 | 143.9(5) |
| O4–Ce1–O7 | 80.6(5) | O14–Ce2–O17 | 79.2(5) |
| O4–Ce1–O8 | 78.9(4) | O14–Ce2–O18 | 82.6(4) |
| O5–Ce1–O6 | 70.9(4) | O15–Ce2–O16 | 71.4(4) |
| O5–Ce1–O7 | 112.1(5) | O15–Ce2–O17 | 117.4(5) |
| O5–Ce1–O8 | 75.8(4) | O15–Ce2–O18 | 74.8(4) |
| O6–Ce1–O7 | 74.4(4) | O16–Ce2–O17 | 75.2(5) |
| O6–Ce1–O8 | 116.0(5) | O16–Ce2–O18 | 111.9(5) |
| O7–Ce1–O8 | 70.0(4) | O17–Ce2–O18 | 70.9(4) |
| Ce1–O1–C3 | 137(1) | Ce2–O11–C47 | 139(1) |
| Ce1–O2–C5 | 140(1) | Ce2–O12–C49 | 139(1) |
| Ce1–O3–C14 | 140(1) | Ce2–O13–C58 | 136(1) |
| Ce1–O4–C16 | 141(1) | Ce2–O14–C60 | 137(1) |
| Ce1–O5–C25 | 137(1) | Ce2–O15–C69 | 137(1) |
| Ce1–O6–C27 | 136(1) | Ce2–O16–C71 | 135(1) |
| Ce1–O7–C36 | 138(1) | Ce3–O17–C80 | 135(1) |
| Ce1–O8–C38 | 141(1) | Ce2–O18–C82 | 140(1) |

[a]The angles involving carbon atoms are excluded but are available upon request.

Table 5. Intramolecular oxygen–oxygen distances (in Å) in Ce(thd)$_4$ with standard deviations in parentheses.

| Atom | Atom | Distance | Atom | Atom | Distance |
|------|------|----------|------|------|----------|
| O1 | O2 | 2.66(2) | O11 | O12 | 2.67(2) |
| O1 | O3 | 3.99(2) | O11 | O13 | 4.03(2) |
| O1 | O4 | 2.80(2) | O11 | O14 | 2.76(2) |
| O1 | O5 | 2.90(2) | O11 | O15 | 2.83(2) |
| O1 | O6 | 4.37(2) | O11 | O16 | 4.35(2) |
| O1 | O7 | 4.33(2) | O11 | O17 | 4.36(2) |
| O1 | O8 | 2.92(2) | O11 | O18 | 2.92(2) |
| O2 | O3 | 2.83(2) | O12 | O13 | 2.78(2) |
| O2 | O4 | 3.73(2) | O12 | O14 | 3.67(2) |
| O2 | O5 | 2.95(2) | O12 | O15 | 2.95(2) |
| O2 | O6 | 2.98(2) | O12 | O16 | 3.03(2) |
| O2 | O7 | 4.44(2) | O12 | O17 | 4.40(2) |
| O2 | O8 | 4.37(2) | O12 | O18 | 4.37(2) |
| O3 | O4 | 2.64(2) | O13 | O14 | 2.73(2) |
| O3 | O5 | 4.37(2) | O13 | O15 | 4.43(2) |
| O3 | O6 | 2.91(2) | O13 | O16 | 2.94(2) |
| O3 | O7 | 2.89(2) | O13 | O17 | 2.88(2) |
| O3 | O8 | 4.29(2) | O13 | O18 | 4.41(2) |
| O4 | O5 | 4.39(2) | O14 | O15 | 4.42(2) |
| O4 | O6 | 4.37(2) | O14 | O16 | 4.39(2) |
| O4 | O7 | 2.99(2) | O14 | O17 | 2.95(2) |
| O4 | O8 | 2.83(2) | O14 | O18 | 3.05(2) |
| O5 | O6 | 2.69(2) | O15 | O16 | 2.71(2) |
| O5 | O7 | 3.86(2) | O15 | O17 | 3.97(2) |
| O5 | O8 | 2.83(2) | O15 | O18 | 2.82(2) |
| O6 | O7 | 2.82(2) | O16 | O17 | 2.82(2) |
| O6 | O8 | 3.92(2) | O16 | O18 | 3.83(2) |
| O7 | O8 | 2.66(2) | O17 | O18 | 2.68(2) |

with alternating molecules 1 and 2. The molecules are totally enveloped by the methyl groups, and thus a high volatility of the complex can be expected.

*Thermal studies.* The TG curve for Ce(thd)$_4$ is straightforward containing only a rapid weight loss around 250 °C. The remaining weight is only 1.8 %. This means that the complex volatilizes nearly completely at temperatures above 250 °C and that decomposition under moderate heating rates in an inert atmosphere can be neglected.
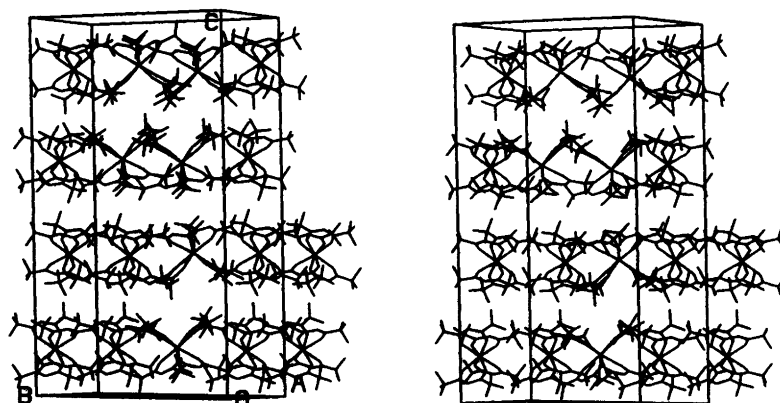


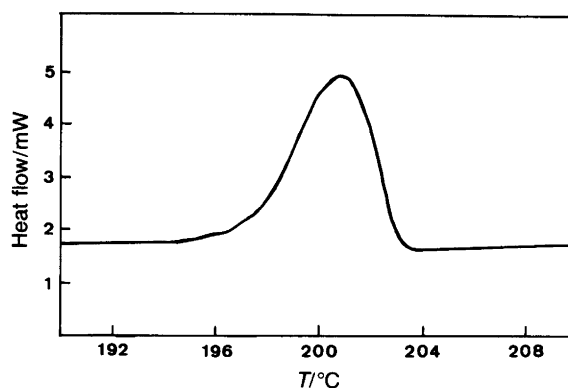Fig. 3. DSC curve for Ce(thd)$_4$.

The DSC measurements corroborated that the complex does not decompose but volatilizes. Owing to experimental differences between the TG and DSC measurements sublimation occurred at a lower temperature in DSC. The endothermic peak was found at 201 °C and the enthalpy for the process was recorded as 30.6 J g$^{-1}$ (Fig. 3). The thermal behaviour of Ce(thd)$_4$ closely resembles that of the trivalent rare earth thd complexes.[28]

In the thermally excited mass spectrum of Ce(thd)$_4$ the main peak ($m/z = 689$) corresponds to a molecule with the stoichiometry of Ce(thd)$_3$ (Fig. 4). The peaks around 510 correspond to Ce(thd)$_2$. A small molecular peak around 880 is also observable. The peaks below 150 correspond to the dissociation fragments of the ligand. No dimeric units were detected in the spectrum.

Because of the difference in the oxidation number the mass spectrum of Ce(thd)$_4$ differs from that of the trivalent rare earth complexes, where Ln(thd)$_2$ and Ln(thd) were the main components. Although the conditions for the determination of the mass spectrum (ultra-high vacuum) and for the growth of thin films in flow-type ALE (or CVD) equipment are different, it seems plausible to assume that the behaviour of Ce(thd)$_4$ would also differ slightly for film growth as compared to the thd chelates of the trivalent rare earths. No experimental data are yet
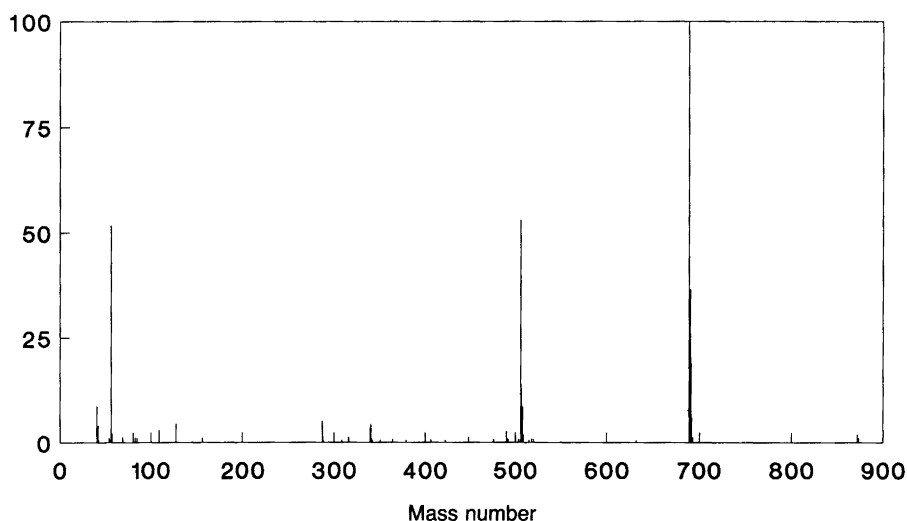


Fig. 2. Stereoscopic drawing of the unit cell.

*Fig. 4.* High-resolution mass spectrum of Ce(thd)$_4$.

available, however, but comparative studies are being planned.

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