

Yttrium tetramethylheptanedionates: syntheses, crystal and molecular structures and thermal behaviours of $Y(\text{thd})_3 \cdot \text{H}_2\text{O}$ and $Y(\text{thd})_3$ (thd = ${}^t\text{BuC}(\text{O})\text{CHC}(\text{O}){}^t\text{Bu}$)

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Abstract

$Y(\text{thd})_3(\text{H}_2\text{O})$ (I) has been prepared from yttrium nitrate via the aqueous method; its drying yielded $Y(\text{thd})_3$ (III). The sublimation of compound II, resulting from the reaction of yttrium isopropoxide with thdH, also yielded $Y(\text{thd})_3$. Compounds II and III have been characterized by elemental analysis, IR, ${}^1\text{H}$ ${}^{13}\text{C}\{{}^1\text{H}\}$ and ${}^{89}\text{Y}$ NMR spectroscopies and mass spectrometry. The thermal behaviour of each compound has been studied by TG and DT analyses. Compounds I and III crystallize in the triclinic ($P\bar{1}$) and orthorhombic ($Pmn2_1$) systems, respectively. The crystal structure determinations reveal centrosymmetric dimeric associations arising from hydrogen bonding between the water molecules and ketonic oxygen atoms for I whereas monomeric $Y(\text{thd})_3$ units with all thd rings in a chelating position are observed for III. The relationship between the crystal structures of I and III has been studied.

Introduction

Yttrium tris-tetramethylheptanedionate ($Y(\text{thd})_3$) has been the most widely used molecular precursor of yttrium for deposition of high T_c superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films [1], since metal-organic chemical vapour deposition (MOCVD) reveals to be a very interesting technique in this area. The choice of this yttrium β -diketonate compound is based on its thermal stability and high volatility reported by Berg and Acosta [2].

The usual preparation of yttrium tris-tetramethylheptanedionate was described by Eisentraut and Sievers in 1965 [3]; the molecular structures of the following yttrium β -diketonates $Y(\text{acac})_3 \cdot 3\text{H}_2\text{O}$ (acac = $\text{MeC}(\text{O})\text{CHC}(\text{O})\text{Me}$) [4], $Y(\text{bzac})_3 \cdot \text{H}_2\text{O}$ (bzac = $\text{PhC}(\text{O})\text{CHC}(\text{O})\text{Me}$) [5] and $\text{Cs}[Y(\text{hfac})_4]$ (hfac = $(\text{CF}_3)_2\text{C}(\text{O})\text{CHC}(\text{O})(\text{CF}_3)$) [6] have only been described. Recently Gleizes *et al.* presented the X-ray crystal structure of $Y(\text{thd})_3 \cdot \text{H}_2\text{O}$ and $Y(\text{thd})_3$ [7]. At the same time, Rees *et al.* mentioned the structural characterizations of $Y(\text{thd})_3 \cdot \text{H}_2\text{O}$ and $[Y(\text{tmod})_3]_2$ (tmod = 2,2,7-trimethyloctane-3,5-dionato) [8]; complete details of the

preparation and collection and refinement of diffraction data will be published.

Here we describe the syntheses as well as the complete characterization including X-ray diffraction crystal structures of $Y(\text{thd})_3 \cdot \text{H}_2\text{O}$ and $Y(\text{thd})_3$. The vapor phase decomposition of these species is also discussed.

Experimental

${}^1\text{H}$, ${}^{13}\text{C}$ NMR and IR spectra were run on Bruker AC-250 and IR FT Nicolet ZDX spectrometers. The ${}^{89}\text{Y}$ NMR spectrum was measured at 14.707 MHz and ${}^{89}\text{Y}$ chemical shifts are reported with respect to YCl_3 (2 M) in D_2O and are negative to high field. IR spectra were obtained as nujol mulls between KBr plates. Mass spectra were recorded on a 300 DX JEOL instrument by electronic impact. Thermogravimetric and differential thermal analyses were performed under argon atmosphere with heating rates of 5 and 10 $^\circ\text{C}/\text{min}$, respectively. Analytical data were obtained from the Centre de Microanalyses du CNRS.

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TABLE 1. Crystallographic and experimental data of Y(thd)₃·H₂O (a) and Y(thd)₃ (b)

| | (a) | (b) |
|------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| Empirical formula | C ₃₃ H ₅₉ O ₇ Y | C ₃₃ H ₅₇ O ₆ Y |
| Formula weight | 656.7 | 638.7 |
| Crystal dimensions (mm) | 0.30 × 0.30 × 0.35 | 0.32 × 0.32 × 0.40 |
| Crystal system | triclinic | orthorhombic |
| <i>a</i> (Å) | 11.566(4) | 17.865(4) |
| <i>b</i> (Å) | 14.571(5) | 10.628(2) |
| <i>c</i> (Å) | 14.811(3) | 9.972(2) |
| α (°) | 119.01(2) | 90 |
| β (°) | 99.98(2) | 90 |
| γ (°) | 106.78(3) | 90 |
| Volume (Å ³) | 1941 | 1893 |
| Space group | $P\bar{1}$ | $Pmn2_1$ |
| Z value | 2 | 2 |
| <i>D_c</i> (g/cm ³) | 1.13 | 1.12 |
| Diffractometer | Enraf-Nonius CAD4 | Siemens P3 |
| <i>F</i> (000) | 704 | 684 |
| Radiation | Mo K α (0.71073 Å) | Mo K α (0.71073 Å) |
| μ (Mo K α) (cm ⁻¹) | 15.0 | 15.8 |
| Temperature (K) | 293 | 293 |
| No. observations | 2912 ($I \geq 2\sigma(I)$) | 871 ($I \geq 3\sigma(I)$) |
| No. variables | 378 | 93 |
| <i>R</i> ; <i>R_w</i> ^a | 0.050; 0.068 | 0.077; 0.085 |
| Residual electron density (e Å ⁻³) | 0.4 to -0.4 | 0.8 to -0.6 |

^aThe quantity minimized in the least-squares procedure is $w(|F_o| - |F_c|)^2$. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Synthesis from yttrium nitrate via the aqueous method

According to the method of Eisentraut and Siever [3], sodium hydroxide (30 mmol) in ethanol (50 ml) was dripped into an ethanol solution (50 ml) of thdH (30 mmol). The solution turned deep yellow. Y(NO₃)₃·6H₂O (Strem Chemicals) (10 mmol) dissolved in a 50:50 mixture of water and ethanol (50 ml) was added and the volume was reduced by half by evaporating *in vacuo*. The white precipitate was filtered and dried in a desiccator. Yield 80–90%. The resulting powder corresponded to Y(thd)₃. *Anal.* Found: C, 62.0; H, 9.1; O, 15.1; Y, 13.8. Calc. for C₃₃H₅₇O₆Y: C, 62.0; H, 9.0; O, 15.0; Y, 13.9%. TGA (5 °C/min, Ar) showed a single loss of weight of 100% in the range 100–300 °C.

Crystals of the aquo species Y(thd)₃(H₂O) (I) were obtained by recrystallizing the still wet white precipitate in heptane. The formula was derived from a X-ray single crystal structure determination.

Synthesis from yttrium isopropoxide in organic medium

All manipulations were performed under argon, using Schlenk tubes and vacuum-line techniques with solvents purified by standard methods. 2,2,6,6-Tetramethyl-3,5-heptanedione [H(thd)] was first purified according to the method described in ref. 9. Y₅O(OⁱPr)₁₃ was prepared according to the procedure of Mazdiyasi and co-workers [10] slightly modified and recently characterized by X-ray diffraction [11].

Hthd (3.6 ml, 15.0 mmol) was added to a solution of Y₅O(OⁱPr)₁₃ (1.33 g, 1.08 mmol) in 40 ml of toluene. The solution became pale yellow and was stirred at reflux temperature for 5 h. The mixture was then concentrated to dryness and a pale yellow powder was obtained. Its recrystallization in toluene gave colourless crystals of II. Yield 92% based on Y. *Anal.* Found: C, 61.8; H, 9.2; Y, 12.8. Calc. for C₃₃H₅₇O₆Y: C, 62.0; H, 8.9; Y, 13.9%. IR (cm⁻¹): 1597–1575 ν_s (C=O), 1554 ν_s (C=C), 1407 ν_{as} (C=O), 1293 ν_{as} (C=O), 1189 δ (C–H), 800 π (C–H), 614 ν (Y–O), 491–475 ν_s (Y–O), C(CH₃)₃, 1378–1359 π (C–H), 1247–1229 ν (C–C). ¹H NMR (CDCl₃, ppm): 5.7s (CH, 1H); 1.13s (CH₃, 18H). ¹³C{¹H} NMR (CDCl₃, ppm): 201.5 (CO); 91.6 (CH); 40.6 (Me₃C); 28.3 (CH₃). ⁸⁹Y NMR (CD₂Cl₂, ppm): 163s. MS (*m/z*, EI): Y₂(thd)₃(ⁱBuCOCHCO)₃ (5%), Y(thd)₃ (15%), Y(thd)(ⁱBuCOCHCO) (65%), Y(thd)₂ (100%), thdH (4%), (ⁱBuCOCHCO) (6%); (ⁱBuCO) (3%), (ⁱBu) (27%). TGA (5 °C/min, Ar) percentage of weight loss in the range 100–330 °C: 98. Melting point: 145 °C. DTA: endothermic peak at 183 °C.

This compound sublimes at 135 °C/10⁻¹ mmHg to give Y(thd)₃ (III) which have the same ¹H, ¹³C NMR as well as IR and MS data. *Anal.* Found: C, 62.7; H, 9.1; Y, 13.9. Calc. for C₃₃H₅₇O₆Y: C, 62.0; H, 8.9; Y, 13.9%. TGA (5 °C/min, Ar) percentage of weight loss in the range 200–330 °C: 97. DTA: endothermic peak at 170 °C. Single colourless crystals of Y(thd)₃ suitable

TABLE 2. Final atomic fractional coordinates and equivalent isotropic displacement parameters for $Y(thd)_3(H_2O)$ (starred values are truly isotropic)

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U</i> (Å ²) |
|--------------------|------------|-------------|------------|----------------------------|
| Y | 0 04676(7) | -0.00277(6) | 0.18857(5) | 0.0377(7) |
| O _w | 0.0420(8) | 0.1026(5) | 0.1104(5) | 0.051(7) |
| H _w (1) | -0.017(7) | 0 098(6) | 0.074(6) | 0.05(3)* |
| H _w (2) | 0.09(1) | 0.11(1) | 0.072(9) | 0.05(3)* |
| O(11) | 0.1332(5) | -0.0868(4) | 0.0548(4) | 0.048(6) |
| O(21) | 0.0653(5) | -0.1449(4) | 0.1977(4) | 0 050(6) |
| C(111) | 0 172(1) | -0.285(1) | -0.1493(9) | 0 13(2) |
| C(211) | 0 387(1) | -0.171(1) | -0.003(1) | 0.12(3) |
| C(311) | 0 280(1) | -0.083(1) | -0.067(1) | 0.11(3) |
| C(11) | 0 2594(9) | -0.1712(9) | -0.0416(7) | 0.06(1) |
| C(21) | 0.1918(7) | -0.1519(7) | 0.0417(6) | 0.052(9) |
| C(31) | 0.1944(8) | -0.2087(7) | 0.0951(7) | 0.06(1) |
| C(41) | 0.1285(8) | -0.2050(6) | 0.1674(6) | 0.049(9) |
| C(51) | 0.1284(9) | -0.2773(7) | 0.2146(7) | 0.06(1) |
| C(151) | -0.012(1) | -0.3678(9) | 0.1647(9) | 0.10(2) |
| C(251) | 0.170(1) | -0.1986(8) | 0.3387(8) | 0.09(2) |
| C(351) | 0.218(1) | -0.336(1) | 0.191(1) | 0 09(2) |
| O(12) | -0.1153(5) | -0.0456(4) | 0.2456(4) | 0.050(6) |
| O(22) | -0.1417(5) | -0.1393(4) | 0.0285(3) | 0.046(5) |
| C(112) | -0.172(1) | -0.101(1) | 0.3901(9) | 0.12(2) |
| C(212) | -0.331(2) | -0.054(1) | 0.323(1) | 0.13(4) |
| C(312) | -0.375(1) | -0.255(1) | 0.2467(9) | 0 11(2) |
| C(12) | -0.2769(9) | -0.1420(8) | 0 2892(7) | 0 06(1) |
| C(22) | -0 2182(8) | -0.1367(7) | 0 2057(6) | 0 049(9) |
| C(32) | -0 2759(7) | -0.2262(6) | 0.0938(6) | 0.053(9) |
| C(42) | -0.2399(7) | -0.2268(6) | 0.0097(6) | 0.048(8) |
| C(52) | -0.3081(9) | -0.3309(7) | -0.1112(6) | 0.057(9) |
| C(152) | -0.3644(9) | -0.2944(8) | -0.1821(7) | 0.08(1) |
| C(252) | -0.418(1) | -0.4335(7) | -0.1295(7) | 0.08(1) |
| C(352) | -0.207(1) | -0.3707(7) | -0.1479(7) | 0.07(1) |
| O(13) | 0.0797(5) | 0.1713(4) | 0.3366(4) | 0.048(5) |
| O(23) | 0.2599(5) | 0.0929(4) | 0.2923(4) | 0.054(6) |
| C(113) | 0.011(1) | 0.309(1) | 0 496(1) | 0.11(2) |
| C(213) | 0.237(1) | 0.444(1) | 0.6078(9) | 0.13(3) |
| C(313) | 0.132(1) | 0 420(1) | 0.440(1) | 0.11(3) |
| C(13) | 0.139(1) | 0 3581(7) | 0 4936(7) | 0.06(1) |
| C(23) | 0.1749(9) | 0.2609(6) | 0.4221(6) | 0 047(9) |
| C(33) | 0.3020(8) | 0.2720(7) | 0 4501(6) | 0.053(9) |
| C(43) | 0.3373(7) | 0.1882(7) | 0.3851(7) | 0.048(9) |
| C(53) | 0.4775(8) | 0.2031(7) | 0.4209(7) | 0.06(1) |
| C(153) | 0.4734(9) | 0.1073(8) | 0.4376(8) | 0 08(1) |
| C(253) | 0 5280(9) | 0.188(1) | 0.3314(8) | 0.08(2) |
| C(353) | 0.5719(9) | 0.3198(8) | 0.5296(8) | 0.09(1) |

for X-ray diffraction studies were obtained by sublimation.

X-ray single crystal structure determination

Measurements were made either on an Enraf-Nonius CAD4 (cpd I) or a Siemens P3 (cpd III) diffractometer using Mo K α radiation ($\lambda_{K\alpha} = 0.71073$ Å). Experimental conditions and crystallographic parameters are presented in Table 1. Cell parameters and an orientation matrix for data collection were derived from the least-squares refinement of 25 accurately refined reflections. Intensity data were corrected for Lorentz and polar-

ization effects. An empirical absorption correction was applied using program DIFABS [12]. The Y atoms were located from a Patterson map using SHELXS 86 [13] and the remaining atoms were found by successive electron density map calculations using SHELX 76 [14]. Anomalous dispersion effects [15] were included in the calculation of *F* values using the anomalous dispersion terms $\Delta f'$ and $\Delta f''$ from the compilation due to Cromer [16]. All calculations were performed on a Alliant VFX-80 (cpd I) or Dec VAX 3100 (cpd III) computer.

Y(thd)₃(H₂O) (I)

The crystal system was found to be triclinic. The refinement of the structure was successfully carried out in the space group $P\bar{1}$. A total of 5151 independent reflections out to 22.5° in θ was collected of which 2912 had $I \geq 2\sigma(I)$ and were used in the structure analysis. The intensities were corrected for an overall decrease of 25% probably due to some water loss (the crystal was not mounted in a capillary).

All non-hydrogen atoms were refined anisotropically. The water hydrogen atoms could be refined isotropically. CH and CH₃ groups were treated as rigid groups. In the last cycle of refinement, the maximum (variable shift)/(e.s.d.) ratio was 0.24 for the 'BuC atoms and 0.11 for the other atoms. No significant features showed up in the final difference Fourier map.

Y(thd)₃ (III)

Based on the systematic absences $h0l$, $h+l=2n+1$ and the successful structure solution and refinement of the structure, the space group was determined to be $Pmn2_1$ (No. 31). Data were collected by using the ω - 2θ scan technique at a scan speed varying from 1.5 to 14.6°/min in ω . Background counts were recorded on each side of the reflection with the ratio of peak counting time to background counting time equal to 2:1. A total of 1023 reflections out to 20° in θ was collected of which 966 were unique and 871 were considered observed ($I \geq 3\sigma(I)$) and were used in the analysis. The intensities of three representative reflections, that were measured after every 100 reflections, remained constant throughout data collection, indicating crystal and electronic stability. Only the yttrium atom was allowed to more anisotropically in order to keep the ratio of observation to parameter close to 10. Hydrogen atoms were placed in calculated positions (C-H=1.08 Å) and were not further refined but recalculated after each cycle. The criteria for the satisfactory complete analysis were the ratios of the r.m.s. shift to standard deviation being less than 0.1 and no significant features in the final different map.

TABLE 3. Selected interatomic distances (Å) and bond angles (°) for Y(thd)₃(H₂O) (standard deviations in parentheses)

| | | | | | |
|---------------------------------------------------|-----------|--------------------------------------------------------|----------|---------------|----------|
| Around Y | | | | | |
| Y–O _w | 2.334(9) | O _w –Y–O(11) | 80.9(3) | O(21)–Y–O(12) | 80.3(2) |
| Y–O(11) | 2.337(6) | O _w –Y–O(21) | 155.7(2) | O(21)–Y–O(22) | 89.5(2) |
| Y–O(21) | 2.207(7) | O _w –Y–O(12) | 116.9(3) | O(21)–Y–O(13) | 124.8(2) |
| Y–O(12) | 2.237(6) | O _w –Y–O(22) | 80.1(2) | O(21)–Y–O(23) | 83.3(2) |
| Y–O(22) | 2.337(4) | O _w –Y–O(13) | 78.1(2) | O(12)–Y–O(22) | 73.3(2) |
| Y–O(13) | 2.268(5) | O _w –Y–O(23) | 97.7(3) | O(12)–Y–O(13) | 75.4(2) |
| Y–O(23) | 2.238(4) | O(11)–Y–O(21) | 75.5(2) | O(12)–Y–O(23) | 126.3(2) |
| | | O(11)–Y–O(12) | 142.6(2) | O(22)–Y–O(13) | 127.7(2) |
| | | O(11)–Y–O(22) | 78.4(2) | O(22)–Y–O(23) | 157.1(2) |
| | | O(11)–Y–O(13) | 142.0(2) | O(13)–Y–O(23) | 73.1(2) |
| | | O(11)–Y–O(23) | 78.8(2) | | |
| Water molecule | | | | | |
| O _w –H _w (1) | 0.76(9) | H _w (1)–O _w –H _w (2) | 92(11) | | |
| O _w –H _w (2) | 0.89(15) | Y–O _w –H _w (1) | 128(7) | | |
| | | Y–O _w –H _w (2) | 128(10) | | |
| H bonds and intermolecular van der Waals contacts | | | | | |
| O _w –O _w ⁱ | 2.884(10) | O _w –H _w (1)··O(11) ⁱ | 159(9) | | |
| O _w –O(11) ⁱ | 2.759(10) | O _w –H _w (2)··O(22) ⁱ | 163(14) | | |
| O _w –O(22) ⁱ | 2.717(10) | | | | |
| H _w (1)–O(11) ⁱ | 2.03(9) | | | | |
| H _w (2)–O(22) ⁱ | 1.86(16) | | | | |
| C(211)–C(311) ⁱⁱ | 4.023(3) | | | | |
| C(351)–C(352) ^{iv} | 3.96(2) | | | | |
| C(112)–C(112) ⁱⁱⁱ | 3.81(2) | | | | |
| C(212)–C(252) ^v | 3.76(2) | | | | |
| C(312)–C(252) ^{vi} | 3.73(2) | | | | |
| C(152)–C(253) ⁱ | 3.82(2) | | | | |

Code of equivalent positions: ⁱ = $-x, -y, -z$; ⁱⁱ = $1-x, -y, -z$; ⁱⁱⁱ = $-x, -y, 1-z$; ^{iv} = $-x, -1-y, -z$; ^v = $x-1, y, z$; ^{vi} = $-1-x, -1-y, -z$.

Results and discussion

Synthesis, spectroscopic and thermal data

The aquo yttrium complex Y(thd)₃(H₂O) is obtained when the synthesis is performed in the presence of water according to the method of Eisentraut and Sievers [3]. Single crystals can be grown from n-heptane solution. The water easily evolves upon drying in a desiccator yielding anhydrous Y(thd)₃. However since the aqueous method often yielded hydrated β-diketonate complexes, we prepared anhydrous tris(tetramethylheptanedionate) of yttrium from yttrium isopropoxide Y₅O(OⁱPr)₁₃ with an excess of thdH by refluxing in toluene. This method was first used for the synthesis of anhydrous tris(acetylacetonates) of praseodymium and neodymium by Mehrotra *et al.* [17] and it was extended to the synthesis of pure tris β-diketonates of the other lanthanide elements [18]. The advantage of the anhydrous β-diketonate of lanthanide and related elements is based on the study of Berg and Acosta [2] who demonstrated that the lack of volatility observed for the lanthanide acetylacetonate and trifluoroacetylacetonate chelates is attributed to the fact that only hydrates of these chelates were formed, which decomposed at elevated temperatures *in vacuo* to form po-

lymeric compounds. The crystallized compound II obtained from this method sometimes may present as a solvate Y(thd)₃·ⁱPrOH depending on the drying time. This formula is in accordance with elemental and thermogravimetric analyses which occurred in a two-step process: a first weight loss in the range 100–180 °C corresponds to the removal of one molecule of ⁱPrOH and a second rapid weight loss in the range 200–340 °C is attributed to the sublimation of Y(thd)₃. The ⁱPrOH molecule can be removed upon longer drying time as shown by IR, ¹H and ¹³C NMR spectroscopies and mass spectrometry. The ⁸⁹Y NMR spectrum exhibits a single signal at 163 ppm which indicates that complex II is monomeric in solution.

Each of the two syntheses, after sublimation of the resulting compound, yielded Y(thd)₃. The IR spectrum displays essentially the absorption bands of the ligands as well as the ν(Y–O) stretching vibrations at 614, 419 and 475 cm⁻¹ which explains the coordination of the chelate by oxygen atoms on the Y centre. The ¹H and ¹³C{¹H} NMR spectra reveal a single average environment for the β-diketonate groups. These spectroscopic results are in agreement with its solid-state structure. The electronic impact mass spectral data exhibit the parent molecular ion. The most intense peak results

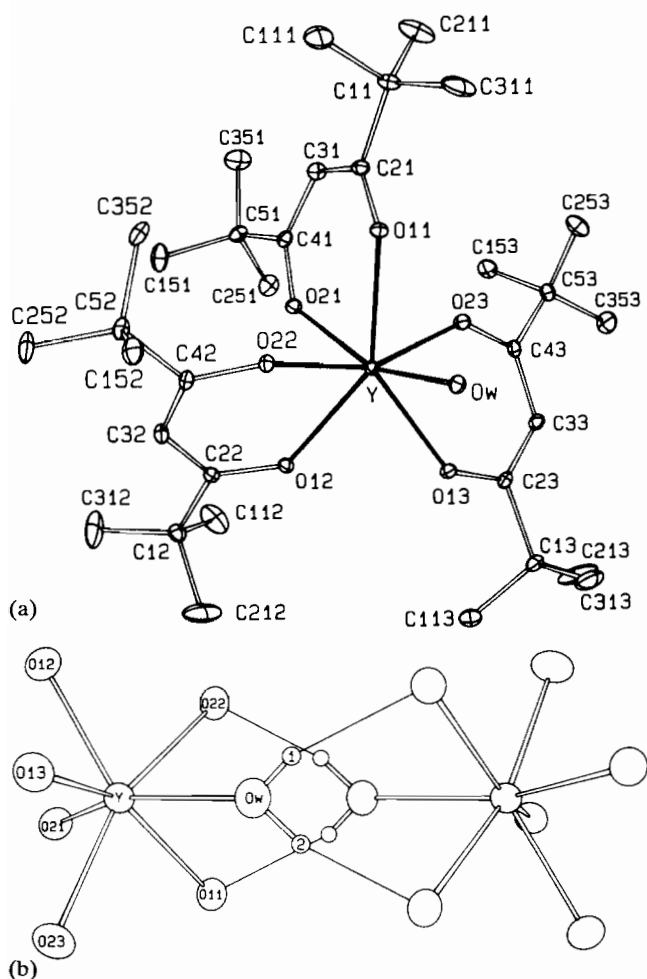


Fig. 1. (a) An ORTEP view of the $Y(thd)_3 \cdot H_2O$ molecule with the atom numbering scheme (5% probability ellipsoids). (b) A close view to the hydrogen bonds giving rise to the dimeric association (20% probability ellipsoids).

from the loss of a thd fragment from the parent monomer. Only one peak of low relative abundance with the m/z value higher than that of the molecular ion is observed and corresponds to the $Y_2(thd)_3(BuCOCHCO)_3$ ion. It probably results from the combination of two fragments stemming from the parent monomer.

$Y(thd)_3$ is soluble in common organic solvents (hexane, toluene, $CHCl_3$, etc.). It is stable to thermal decomposition. The thermogravimetric analysis performed on the sublimed compound $Y(thd)_3$ shows that the product sublimes between 200 and 340 °C. It is in agreement with previous results reported in the literature [19]. Differential thermal analysis confirms the sublimation by an endothermic peak at 170 °C.

Structure of $Y(thd)_3(H_2O)$ (I)

The final positions and equivalent isotropic thermal motion coefficients are given in Table 2, and a selection of bond lengths and angles is given in Table 3. The

TABLE 4. Final atomic fractional coordinates and isotropic displacement parameters for $Y(thd)_3$ (starred value corresponds to equivalent isotropic displacement parameters)

| | x | y | z | U_{iso} |
|--------|------------|-------------|-------------|-----------|
| Y(1) | 0.5 | 0.9064(2) | 0.5 | 40(1)* |
| O(11) | 0.5 | 0.0757(15) | 0.3803(18) | 51(5) |
| O(12) | 0.5 | -0.1666(17) | 0.3013(20) | 57(5) |
| C(11) | 0.5 | 0.1013(26) | 0.2574(30) | 59(8) |
| C(12) | 0.5 | 0.0047(23) | 0.1540(28) | 49(7) |
| C(13) | 0.5 | -0.1200(24) | 0.1908(30) | 51(8) |
| C(14) | 0.5 | 0.2358(23) | 0.2224(27) | 43(7) |
| C(14A) | 0.5 | 0.2745(53) | 0.0784(59) | 289(42) |
| C(14B) | 0.4358(19) | 0.2993(33) | 0.2917(41) | 190(17) |
| C(15) | 0.5 | -0.2237(28) | 0.0716(34) | 62(10) |
| C(15A) | 0.5 | -0.1755(35) | -0.0638(35) | 91(14) |
| C(15B) | 0.5640(15) | -0.3068(23) | 0.0966(30) | 112(9) |
| O(21) | 0.5941(7) | -0.0037(10) | 0.6245(13) | 49(3) |
| O(22) | 0.5846(8) | -0.2462(11) | 0.5560(13) | 62(4) |
| C(21) | 0.6570(11) | -0.0351(16) | 0.6709(20) | 48(5) |
| C(22) | 0.6841(12) | -0.1583(18) | 0.6661(23) | 67(6) |
| C(23) | 0.6438(11) | -0.2597(16) | 0.6162(20) | 55(5) |
| C(24) | 0.7033(11) | 0.0692(17) | 0.7276(21) | 58(6) |
| C(24A) | 0.6612(16) | 0.1243(27) | 0.8432(33) | 125(10) |
| C(24B) | 0.7092(14) | 0.1780(20) | 0.6221(26) | 92(8) |
| C(24C) | 0.7838(12) | 0.0346(21) | 0.7774(25) | 81(7) |
| C(25) | 0.6713(12) | -0.3934(18) | 0.6222(22) | 60(6) |
| C(25A) | 0.7487(21) | -0.4129(30) | 0.6691(41) | 168(14) |
| C(25B) | 0.6697(18) | -0.4545(28) | 0.5121(50) | 173(13) |
| C(25C) | 0.6200(18) | -0.4682(29) | 0.7055(38) | 154(13) |

TABLE 5. Selected bond distances (Å) and angles (°) of $Y(thd)_3$ (standard deviations in parentheses)

| Bond lengths | |
|---------------------------------------|-----------|
| Y(1)–O(11) | 2.160(17) |
| Y(1)–O(12) | 2.128(19) |
| Y(1)–O(21) | 2.298(12) |
| Y(1)–O(22) | 2.286(13) |
| Bond angles | |
| O(12)–Y(1)–O(11) | 77.8(7) |
| O(21)–Y(1)–O(11) | 87.2(4) |
| O(21)–Y(1)–O(12) | 130.9(3) |
| O(22)–Y(1)–O(11) | 136.6(3) |
| O(22)–Y(1)–O(12) | 80.2(5) |
| O(22)–Y(1)–O(21) | 71.3(4) |
| Intermolecular van der Waals contacts | |
| C(14B)...C(25A) ⁱ | 3.76(3) |
| C(25B)...C(25A) ⁱⁱ | 3.98(3) |
| C(14B)...C(25B) ⁱⁱⁱ | 3.90(3) |

ⁱ = $x-0.5, 1-y, z-0.5$; ⁱⁱ = $1.5-x, 1-y, z-0.5$; ⁱⁱⁱ = $1-x, y, z$.

structure was found to be isostructural with $Dy(thd)_3(H_2O)$ previously described by Erasmus and Boeyens [20]. It is made of centrosymmetric dimeric entities (one per unit cell) arising from hydrogen bonding between the water molecules and ketonic oxygen atoms. Figure 1 shows the $Y(thd)_3(H_2O)$ molecule with the atom numbering scheme (Fig. 1(a)) and a close view of the dimeric association (Fig. 1(b)). As they did not

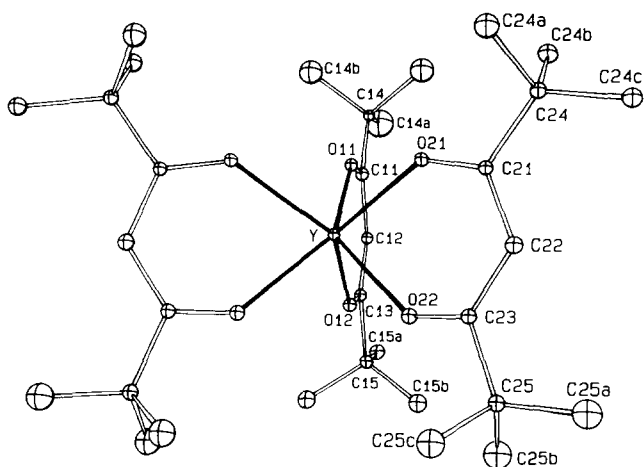
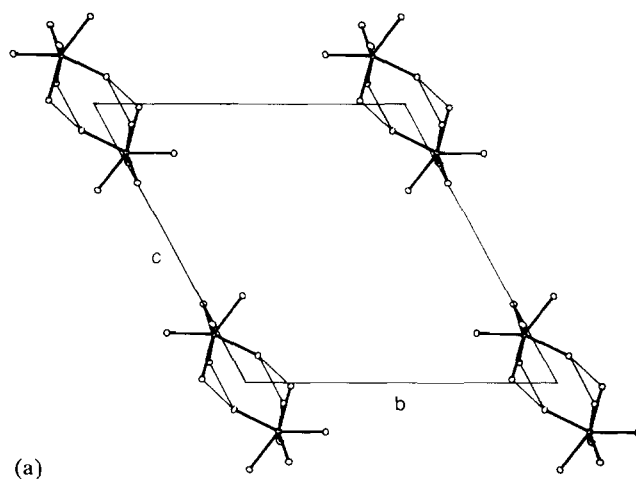


Fig. 2. An ORTEP view of the $Y(thd)_3$ molecule with the atom numbering scheme (5% probability ellipsoids)

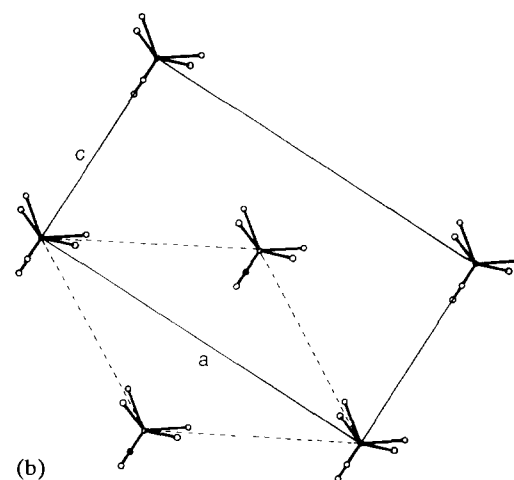
know hydrogen positions, Erasmus and Boeyens were unable to define the hydrogen bonding scheme. In the present work the positions of the water hydrogen atoms H(1) and H(2) have been refined. They are both involved in hydrogen bonds as shown in Fig. 1. Ketonic oxygen atoms O(11) and O(22) which belong to different ligands are bound to H(1) and H(2), respectively (Table 3). Consistently enough, O(11) and O(22) and the water oxygen are the farthest oxygens from yttrium: $Y-O(11)=2.337(6)$, $Y-O(22)=2.337(4)$, $Y-O_w=2.334(9)$ Å. These values do not differ from one another significantly and are on the average 0.1 Å larger than the other yttrium–oxygen distances.

Structure of $Y(thd)_3$ (III)

The final positional parameters together with isotropic temperature factors of the X-ray structure of the anhydrous and sublimed compound $Y(thd)_3$ are given in Table 4. Bond distances and angles are given in Table 5. The structure of $Y(thd)_3$ is shown in Fig. 2. $Y(thd)_3$ has been found to be isostructural with $Er(thd)_3$ previously structurally characterized by de Villiers and Boeyens [21]. The structure consists of monomeric $Y(thd)_3$ units where all thd rings occupy a terminal chelating position. One of these rings lies in a mirror plane and the others are symmetry related across this mirror plane. Although no symmetry constraint is applied to the latter, they also exhibit a planar O–C₃–O ring. The yttrium atom is hexacoordinated in a roughly trigonal prism environment ($O(11)-O(21)=3.08(2)$, $O(21)-O(21')=3.36(2)$, $O(12)-O(22)=3.08(2)$, $O(22)-O(22')=3.02(3)$ Å). The $Y-O(21)$ and $Y-O(22)$ bond lengths fall in the range of the values previously reported in the literature [4, 5], whereas the $Y-O(11)$ and $Y-O(12)$ bond lengths appear rather short. The shortening of these two $Y-O$ bonds can probably be



(a)



(b)

Fig. 3. (a) The arrangement of the dimers around the vertices of the pseudo hexagonal lattice of (100) planes for $Y(thd)_3 \cdot H_2O$. (b) The arrangement of the molecules in the pseudo B-centered rectangular lattice of (010) planes for $Y(thd)_3$ and the corresponding pseudo primitive hexagonal cell (dashed lines). For sake of clarity, Y and O atoms only have been drawn.

attributed to the symmetry constraint imposed upon O(11) and O(12).

Relationship between the crystal structures of I and III

In both structures the unit cell contains two yttrium atoms, with a volume of 1941 Å³ for $Y(thd)_3(H_2O)$ and 1893 Å³ for $Y(thd)_3$. The difference of 48 Å³ is consistent with the departure of two water molecules. It is noteworthy that both these structures consist of stacked layers in which the molecules have a nearly close-packing arrangement. The layers are repeated by translation along the *a* axis for $Y(thd)_3(H_2O)$ and along the *b* axis for $Y(thd)_3$ which means that close packing does not occur along the stacking directions. Within a layer, the molecules are located at the vertices of a nearly hexagonal lattice. This is quite obvious for the (100) planes in $Y(thd)_3(H_2O)$: $b=14.571$, $c=14.811$ Å,

$\alpha = 119.01^\circ$ (Fig. 3(a)). The interlayer distance is equal to 10.27 Å. In $Y(\text{thd})_3$, the molecules are located near vertices and centres of the rectangular cells of planes (010). The yttrium atoms related by the 2_1 screw axis are alternatively located at ± 0.9 Å from the (010) mean plane. If one does not take into account these deviations, the ordering of the molecules about (010) appears to be nearly B-centered (Fig. 3(b)). The a/c ratio is close to $\sqrt{3}$ ($a = 17.865$, $c = 9.972$ Å), which implies that there is a nearly hexagonal primitive cell and therefore a nearly close packing of molecules. This cell is drawn with dashed lines in Fig. 3(b): it has an a parameter of approximately 10 Å that is about $\sqrt{2}$ times shorter than that of the pseudo hexagonal cell of $Y(\text{thd})_3(\text{H}_2\text{O})$. From these observations, it may be inferred that upon water evolution, the rearrangement of molecules takes place within the layers; the pseudo hexagonal array of dimers (2 yttrium atoms per unit cell) is replaced by a pseudo hexagonal array of monomers having consequently a unit cell half as big (1 yttrium atom per unit cell). The interlayer distance is about the same in both structures (10.3 Å in I, 10.6 Å in III).

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