Syntheses, Structures, and Polymorphism of β -Diketonato Complexes – Co(thd)₃

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Dedicated to Professor Rudolf Hoppe on the Occasion of his 85th Birthday

Abstract. Oxidation of Co(thd)₂ dissolved in different solvents has been investigated in air and oxygen atmosphere. In oxygen atmosphere and at the boiling point of the solvents this treatment leads to oxidation of CoII to CoIII, but also to degradation of some of the thd ligands and formation of a new mixed-ligand complex. Three pure-cultivated crystalline Co(thd)₃ phases are reported: 1 (room-temperature phase), 2 (low-temperature phase), and 3 (metastable phase) and in addition there exists an amorphous Co(thd)₃ phase (4) with approximate composition $Co(thd)_3 \cdot xH(thd)$; x =0.06. Reaction of metal(II) oxides (MO, M = Mn, Fe, and Co) with H(thd) under air or O₂ atmosphere is an easy direct route to $M(\text{thd})_3$ complexes. Structure determinations are reported for $Co(thd)_3$ (1-3) based on single-crystal X-ray diffraction data. Modification 1 crystallizes in space group $P\bar{3}c1$ with a = b =18.8100(10), c = 18.815(2) Å at 295 K; R(wR2) = 0.180, modification 2 in space group C2/c with a = 28.007(12), b = 18.482(8),

1 Introduction

For more than a century [1] it has been commonly recognized that metal-organic complexes with β -diketonato ligands such as (acac)⁻ [= (C₅H₇O₂)⁻; derivative of H(acac) = C₅H₈O₂ = acetylacetone = pentane-2,4-dione] and (thd)⁻ [= (C₁₁H₁₉O₂)⁻; derivative of H(thd) = C₁₁H₂₀O₂ = 2,2,6,6-tetramethylheptane-3,5-dione; alternatively dpm for dipivaloylmethane] have remarkable thermal stability. More recently their suitable sublimation properties have given them a unique niche for utilization as precursors in the growth of thin films.

The structural arrangement of these β -diketonato complexes has naturally occupied the scientific community over the century-long period [1-3]. In fact, the first crystal structure determinations of the $M(\operatorname{acac})_3$ complexes with $M = \operatorname{Sc}$, Fe, Ga, and In were performed [3] already in the infancy of the X-ray diffraction.

The interest in the structural aspects of the metal β -diketonato complexes has been maintained over the years and

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c = 21.356(9) Å, $\beta = 97.999(5)^{\circ}$ at 100 K; R(wR2) = 0.211, and modification **3** in space group *Pnma* with a = 19.2394(15), b =18.8795(15), c = 10.7808(8) Å at 100 K; R(wR2) = 0.193. The molecular structures of **1**-**3** all comprise a central Co atom octahedrally co-ordinated by the ketonato O atoms of three thd ligands. The transformation between modifications **1** and **2** is of a fully reversible second-order character. Modifications **1** and **3** are, on the other hand, related by a quasi-reversible cycle. Heat treatment (specifically sublimation) of **1** leads to **3** whereas re-crystallization or prolonged storage at room temperature is required to regenerate **1**. Co(thd)₃ has sufficient thermal stability to permit sublimation without degradation. The various forms of Co(thd)₃ are all diamagnetic, viz. a confirmation of the Co^{III} valence state.

Keywords: Co(thd)₃; Crystal structure; Polymorphism; Oxidation; Thermal stability; Diamagnetism

large amounts of information have been collected. However, there are still holes in our knowledge and new questions keep on popping up. The present report concerns $Co(thd)_3$. As seen from the compilation in Fig. 1, this complex belongs to the category for which structural information is lacking and one of the main intentions of the present ongoing project has been to contribute to the mending of the incompletenesses in Fig. 1. For natural reasons there are more structural information available for the $M(acac)_2$ and $M(acac)_3$ series with the simpler acac ligand than for the homologous thd complexes.

A closer inspection of the structural data behind the references in Fig. 1 unveils a couple of notable features. First, there appear apparently unmotivated breaks in the structural systematics both along columns and rows of the matrix in Fig. 1. Second, several complexes appear with more than one modification (see the number in the upper left corner of the boxes in Fig. 1). However, these at first glance, only trend-breaking traits are probably to a large extent intimately interwoven. This is nicely illustrated in a most interesting, recent article by Geremia and Demitri [30]. This remarkable report accounts for a total of five structurally distinct modifications of Mn(acac)₃ which are interrelated as low-/high-temperature modifications and metastable variants obtained by re-crystallization from different solvents. With this valuable erudition in mind we approached the targeted structural investigation of Co(thd)₃.



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| | Sc | Ti | v | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|----------------------|------|------|----------|----------|----------|----------|----------|----------|----------|------|
| M(acac) ₂ | | | | 1 | 1 | 1 | 2 | 1 | 1 | 1 |
| | | | | [4] | [5] | [6, 7] | [8, 9] | [10, 11] | [12, 13] | [14] |
| M(thd) ₂ | | | Unstable | Unstable | Unstable | Unstable | 1 | 1 | 1 | 1 |
| | | | | | | | [15, 16] | [17] | [18-20] | [21] |
| M(acaca)3 | 1 | 1 | 3 | 1 | 5 | 1 | 1 | | | |
| | [22] | [23] | [24-26] | [27] | [28-30] | [31, 32] | [33-36] | | | |
| M(thd)3 | 1 | | | | 1 | 1 | | | | |
| | [37] | | | | [38] | [39] | | | | |

Fig. 1 Accessibility of crystal structure data for $M(\operatorname{acac})_2$, $M(\operatorname{thd})_2$, $M(\operatorname{acac})_3$, and $M(\operatorname{thd})_3$ complexes of $M = \operatorname{Sc}-\operatorname{Zn}$ as indicated by the references in appropriate boxes. Shaded boxes mark complexes that are likely to be non-existent for valence reasons. Empty boxes refer to complexes that either have not been synthesized or not properly structure determined. The number in the upper left corner of the boxes mediates how many crystallographically distinct modifications that have been reported for the particular complex.

Attention has also been paid to the preparation of $Co(thd)_3$ along different routes, e.g., by reacting Co^{III} salts with H(thd) under basic conditions [40, 41] or from Co^{II} salts and H(thd) with H₂O₂ as oxidizing agent [42–46]. We also report on the preparation of the $M(thd)_3$ complexes of M = Mn, Fe, and Co by direct reaction of M^{II} oxides, H(thd), and O₂ (g).

2 Experimental Section

Reactants and solvents

CoCl₂·6H₂O (Fluka, p.a., ≥98 %), MnO (Aldrich, 99 %), FeO (Aldrich, 99.9 %), CoO (Sigma-Aldrich, 99.99+ %), NiO (L. Light, 99.95 %), H(thd) (Aldrich, purum, ≥98 %), absolute ethanol (Arcus, prima), methanol (Merck, p.a.), hexane (Fluka, p.a., ≥99.5 %), heptane (Fluka, p.a., ≥99.5 %), and H₂O₂ [Prolabo (BHD), ~33 %] were used as reactants and/or solvents without further purification.

Syntheses

All syntheses were performed in round-bottomed flasks equipped with reflux condenser and magnetic stirrer. The reaction mixtures were refluxed at the boiling point (b. p.) for different periods of time and exposed to oxygen or inert atmosphere as specified below. Unless otherwise mentioned all solid products were filtered through a sinter-glass funnel and washed. The products were then dried under vacuum and finally cleaned by sublimation (Büchi-type B-580 sublimation apparatus at *ca.* 0.5 mbar pressure) and/or recrystallized from various solvents. The phase purity of all final products was ascertained by powder X-ray diffraction (PXD).

Several batches of $Co(thd)_3$ were prepared according to different procedures. (In the following text the various modifications of a given complex are usually referred to by bold-faced numbers.) The room-temperature stable modification of $Co(thd)_3$ (1) was obtained phase pure (overall yield *ca*. 25 %) by oxidizing $CoCl_2 \cdot 6H_2O$ with aqueous solutions of H_2O_2 in the presence of H(thd) as described in Ref. [42].

Modification 1 was also prepared by oxidation of $Co(thd)_2$ with O_2 from air or oxygen flasks (with control experiments under inert atmospheres for prolonged reaction periods): (i) H(thd) used as

both reactant and solvent. $[0.0028 \text{ mol of } Co(thd)_2 \text{ and } ca. 30 \text{ mL} H(thd); 5 hours (h) at b. p., cooled to room temperature (r. t.), filtered, vacuum dried at 60 °C, and finally re-crystallized from EtOH; dark-green crystalline product of 1, yield$ *ca.* $95 %.] (ii) Hexane used (with strict measures to avoid fire ignition) as solvent. <math>[0.0064 \text{ mol of } Co(thd)_2 \text{ was refluxed in } ca. 200 \text{ mL of hexane; 3} days (d) at b. p., otherwise as specified above, yield$ *ca.* $75 %.] (iii) EtOH (absolute) used as solvent. <math>[0.0064 \text{ mol of } Co(thd)_2 \text{ and } ca.$ 150 mL EtOH; 5 h at b. p., filtered off, cooled to r. t., left for opento-air evaporation until dryness, re-dissolved in EtOH, the entire procedure repeated twice, final product treated as for procedure i, yield *ca.* 45 %.]

As a somewhat modified variant of the above procedure i, CoO was introduced as starting material. This series of syntheses was soon extended to include the monoxides of M = Mn, Fe, and Ni for which we report successful synthesis of $M(thd)_3$ from MnO, FeO, and CoO. First 0.015 mol of MO was refluxed with 30 mL of H(thd) for 24 h in O₂ atmosphere. The reaction was then stopped and the mixture was cooled to r. t. The liquid phase was evaporated until dryness under vacuum, the thus formed $M(thd)_3$ was extracted by acetone, and afterwards this solvent was evaporated at r. t., either open-to-air or under vacuum. The products were finally purified by sublimation and re-crystallization from EtOH.

Elemental analysis for various samples of the different modifications of Co(thd)₃ ($C_{33}H_{57}O_6Co$) gave virtually identical results for all samples tested; typical: C 65.58 (calc. 65.11), H 9.52 (9.44), O 15.46 (15.77), Co 9.48 (9.68) %.

Powder X-ray diffraction (PXD)

All samples were characterized by PXD at 22 °C with a Siemens D5000 diffractometer (capillary geometry) using monochromatic CuK α_1 radiation ($\lambda = 1.540598$ Å) from an incident-beam Ge monochromator. The detector was a Brown PSD. The diffraction patterns were collected over the 20 range 3–90° and auto-indexed with help of the DICOVL [47] and TREOR [48] program packages and unit-cell dimensions (calibrated to Si standard) were obtained by least-squares refinements using the METRIC program [49].

Single-crystal X-ray diffraction (SXD) analysis

Crystals were mounted on thin glass fibers on brass pins. Intensity data were collected at 295 and 100 K (MoKa radiation) on a Bruker D8 Apex II diffractometer equipped with an Oxford Cryosystems Cryostream, Plus device. The data were integrated with SAINT [50] and corrected for absorption using SADABS [51]. Structures were solved using direct methods with the program SIR2004 [52] or SHELXS [53] and refined using full-matrix least squares against $|F|^2$ with the SHELXL [54] program suite. All nonhydrogen atoms were refined allowing for anisotropic displacement parameters. Hydrogen atoms were assigned to idealized positions and refined with isotropic thermal parameters proportional to the thermal parameter of the atom to which they are attached. The r. t. modification 1 undergoes a phase transition upon cooling to 100 K. The space group of the low-temperature modification 2 (C2/c) is a subgroup of the space group of 1 ($P\overline{3}c1$). Due to disorder of the molecules in 2, restraints idealizing the tert-butyl groups were applied in the structural refinement of this modification. The crystal structure of the metastable modification 3 of Co(thd)₃ suffers even more from disorder of the *tert*-butyl groups.

Crystal data, data collection information, unit-cell dimensions, and R factors for the reported structures are listed in Table 1. The good agreement between the observed and calculated PXD patterns for modifications 1 and 3 in Fig. 2 provides additional evidence for the correctness of structures discussed in Sect. 3.7.

Table 1 Crystallographic data for $Co(thd)_3$, modifications 1-3.

| Modification | 1 | 2 | 3 |
|---|--------------|------------|---|
| Formula | C33H57O6C0 | C33H57O6C0 | C ₃₃ H ₅₇ O ₆ Co |
| $M / g \text{ mol}^{-1}$ | 608.72 | 608.72 | 608.72 |
| T/K | 295 | 100 | 100 |
| Crystal system | trigonal | monoclinic | orthorhombic |
| Space group | $P\bar{3}c1$ | C2/c | Pnma |
| a/Å | 18.8100(10) | 28.007(12) | 19.2394(15) |
| b / Å | 18.8100(10) | 18.482(8) | 18.8795(15) |
| c / Å | 18.815(2) | 21.356(9) | 10.7808(9) |
| α/° | 90 | 90 | 90 |
| β/° | 90 | 97.999(5) | 90 |
| γ/\circ | 120 | 90 | 90 |
| $V/Å^3$ | 5765.2(8) | 10947(8) | 3915.9(5) |
| Ζ | 6 | 12 | 4 |
| $D / \text{g cm}^{-3}$ | 1.052 | 1.108 | 1.033 |
| μ / mm^{-1} | 0.48 | 0.51 | 0.47 |
| 20 range / ° | 4.4-36 | 4.6-36.2 | 4.3-39.4 |
| No. reflections measured | 41164 | 29174 | 12422 |
| R _{int} | 0.078 | 0.121 | 0.037 |
| No. unique reflections | 3497 | 6843 | 1824 |
| No. observed reflections | 1551 | 3815 | 1276 |
| No. parameters / restraints | 238 / 6 | 569 / 0 | 329 / 47 |
| $R1$ $[I>2\sigma(I)]$ | 0.050 | 0.069 | 0.059 |
| wR2 (all data) | 0.180 | 0.211 | 0.193 |
| GOF | 0.99 | 1.02 | 1.07 |
| Final difference peaks/eÅ ⁻³ | -0.62/0.33 | -0.45/0.72 | -0.17/0.28 |



Fig. 2 Observed (black) and calculated (grey) PXD patterns for $Co(thd)_3$, modifications 1 and 3. Top: 1 (295 K; trigonal); bottom: 3 (295 K; orthorhombic). The calculated PXD pattern for modification 3 (metastable) is based on atomic co-ordinates derived from SXD data at 100 K. The experimental patterns contain reflections (marked asterisks) from Si standard.

Elemental analysis

All elemental analyses were determined by the standard combustion technique at Ilse Beetz.

Thermal analysis

Thermogravimetric (TG) analysis was performed with a Perkin-Elmer TGA7 and DTA system in N₂ atmosphere. Quartz containers were used as sample holders. The heating rate was 5 °C min⁻¹, the temperature interval covered was 40–700 °C, and the sample mass was 15–30 mg.

Magnetic susceptibility

Magnetic susceptibility measurements were performed (temperature range 2–300 K, magnetic field 1 kOe) with a superconducting quantum-interference-device instrument (Magnetic Property Measurement System; Quantum Design). The sample mass was 15-30 mg and the samples were contained in gelatine holders during the measurements.

3 Results and Discussion

3.1 Oxidation of Co^{II} to Co^{III}

Solutions of Co(thd)₂ in organic solvents such as EtOH have dark-red to purple color. On exposure to air at r. t. (e.g., during slow evaporation) the solution gradually becomes dark-green and finally deposition of a dark solid product which proved to be a mixture of **1** and an unidentified colorless solid phase. The yield of **1** depends on the exposure time and the solvent used. The observed darkening of the solution appears as almost black. [Deoxygenated ethanolic solutions of Co(thd)₂ remain unaffected even after prolonged refluxing at b. p. for more than a week.] The formation of **1** accordingly implies oxidation of Co^{III} to Co^{III} by the oxygen dissolved in the solvent. The instability of the oxidation state Co^{II} in solution is well recognized [42, 44, 55].

For reactions performed in O_2 atmosphere it is found that virtually complete oxidation of Co^{II} to Co^{III} had occurred. However, solid products thus obtained with EtOH as solvent proved to be contaminated with a new mixed-ligand complex. Structure determination (which will be reported separately) has shown that this complex has the composition Co₃(thd)₃(OEt)₄(*tert*-BuCOO). Some thd groups have been oxidized and degraded to smaller species like *tert*-BuCOO (C₅H₉O₂) which in turn enters as ligand in the complex.

3.2 Role of H(thd) as reactant and solvent during oxidation of $Co(thd)_2$

When H(thd) was used as both reactant and solvent during oxidation experiments with $Co(thd)_2$ it was found that the solid product obtained after evaporation of the solvent at r.

t. consisted of 1 as the only crystalline phase. However, TG investigation suggested that the product also contained at least one other phase [the solvated variant (4) of 1 discussed below] which accordingly had to be amorphous. For reactions performed in pure O₂ atmosphere under refluxing conditions and short reaction periods (only a few hours) the PXD characterization showed that a new, third crystalline modification of $Co(thd)_3$ (3; metastable phase, see Sect. 3.5) was contained in the product in addition to 1 and 4. Heat treatment of product mixtures of 1, 3, and 4 at 125-130 °C converted the entire batches into Co(thd)₃ (according to TG and elemental analyses), but PXD examination unveiled mixtures of 1 and 3. The composition of the amorphous phase 4 is stipulated as Co(thd)₃·xH(thd); $x \approx 0.06$ (x roughly estimated from the TG data); the possibility of a hydrated variant was ruled out by a series of experiments in which appropriate amounts of H₂O were added to reaction mixtures at various stages of the process. Thus there exist at least three distinct crystalline phases with the composition $Co(thd)_3$ (modifications 1-3). 2 is a low-temperature variant of 1, and 3 is metastable to 1 as demonstrated by the finding that 3 is converted to 1 by re-crystallization from hexane or EtOH or storing at r. t. for a prolonged period of time. In addition to modifications 1-3 comes then the just mentioned amorphous solvated form (4).

3.3 Oxidation of Co(thd)₂ in hexane or heptane

With hexane as solvent instead of EtOH, (the rest of the procedure kept unchanged) no solid product was obtained on filtration. The solid products obtained after evaporation of the solvent were either pure $Co(thd)_2$ (preparation in inert atmosphere and drying under vacuum) or mixtures of $Co(thd)_2$, 1, and an unidentified colorless solid (the same procedure but open-to-air evaporation at r. t.). When the experiments were performed in O₂ atmosphere mixtures of 1 and 3 or 3 and 4 were obtained.

On the other hand, when heptane was used instead of hexane somewhat different results were obtained under O_2 atmosphere. Mixtures of **1** and **3** (yield *ca.* 40 %) together with an amorphous solid (recovered after filtration of the solution) were obtained on evaporation of the solvent under vacuum. Elemental analyses of the amorphous phase gave an empirical composition close to $C_7H_{12}O_4Co =$ (RCOO)Co(OOCR') (R = CH_3CH_2CH_2 and R' = CH_3CH_2). This shows that some degradation and/or oxidation of thd groups has occurred as consequences of the comparatively high b. p. (98–99 °C) of heptane.

3.4 Reaction between the monoxides of Mn, Fe, and Co and H(thd) in O_2 atmosphere

The monoxides of Mn, Fe, and Co react with H(thd) in O_2 atmosphere to form $M(thd)_3$ in different yields and with reaction rate depending on temperature, oxygen partial pressure, and the particular *MO* reactant under investigation. At r. t. there is almost neglectable reaction in air.

However, for refluxing at the b. p. the rates have increased to moderate even in air and the yields have increased correspondingly. The reaction is faster in pure oxygen atmosphere and the yields have become quite appreciable for synthesis at b. p.: 78 % for Mn(thd)₃; 60 % for Fe(thd)₃; and 85 % for Co(thd)₃ (note: the yield specifications refer to amounts obtained after sublimation cleaning). The conclusion is accordingly that these monoxides can be oxidized directly to $M(thd)_3$ by oxygen in the presence of H(thd). The yields are good and the only real disadvantage with this method is that it involves the rather expensive chemical ingredient H(thd). The complete elimination of the last traces of the H(thd) solvent by evaporation is also a challenge, but this can be overcome by a final re-crystallization treatment.

A similar procedure for preparation of the corresponding acac complexes has been patented by *Chaudhari* et al. [56], but their recipes involve the use of the more powerful oxidizing agent H_2O_2 .

Attempts to prepare Ni(thd)₃ with the same method have so far been in vain. There are certain indications of onset of an analogous reaction by the formation of a thin creamy brownish surface cover on the reaction mixture [NiO, H(thd), and $O_{2(solv.)}$], but this step could not be advanced into amounts which could be pursued by characterization methods.

3.5 Sublimation and thermal stability

Modifications 1 and 3 can be subjected to total sublimation, (*ca.* 90 °C and *ca.* 0.5 mbar; according to TG: onset at *ca.* 150–160 °C, completed at *ca.* 260–280 °C under N₂ atmosphere, 5 °C min⁻¹). The solid product, obtained on sublimation of 1 is 3 according to PXD. Hence, sublimation treatment of 1 leads to the metastable modification 3 of Co(thd)₃. The subsequent conversion of 3 back to 1 provide an additional proof for 3 as a proper (but metastable) modification of Co(thd)₃. Crystals of 3 are obtained by subjecting 1 to sublimation at 90–100 °C. If only powder specimens of 3 are needed we recommend heat treatment of Co(thd)₃ in evacuated sealed tubes at 100–110 °C followed by quenching to r. t. Through the just described cycle process the conversion of modification 1 to 3 and back again to 1 becomes quasi reversible.

The TG analyses of phase **4** were based on samples where this phase was mixed with **1** and/or **3** (phase **4** was never prepared phase pure in this study). The TG curves for such mixtures showed an initial 2-3% weight loss between *ca*. 95 and 115 °C, whereas the rest of the TG curves followed the course for complexes **1** and **3**.

Slight temperature shifts (at most *ca.* 10 °C) seen between the TG curves for phases 1, 3, and 4 (above *ca.* 115 °C) can easily be attributed to variations in sample characteristics (e.g., particle size).

3.6 Magnetic properties

The various variants of $Co(thd)_3$ (1, 2, 3, and 4) exhibit the unequivocal characteristics of diamagnetism, viz. a small

negative [$\chi_g \approx -0.16 \times 10^{-6}$ e.m.u./g; as-observed average for all variants] virtually temperature-independent magnetic

susceptibility. These findings are in full accordance with the expectations for proper Co^{III} complexes.

251



Fig. 3 X-ray molecular structures of $Co(thd)_3$ modifications 1–3. (a) The two crystallographically independent molecules of 1 at 295 K. Atomic labeling schemes are indicated, hydrogen atoms and labeling of the *tert*-butyl groups are omitted for clarity. Thermal displacement ellipsoids are drawn at the 50 % probability level. (b) The two crystallographically independent molecules of 2 at 100 K. Atomic labeling schemes are indicated, hydrogen atoms and labeling of the *tert*-butyl groups are omitted for clarity. Thermal displacement ellipsoids are drawn at the 50 % probability level. (c) The carbon atoms (atomic labeling scheme indicated) of the two enantiomeric forms of modification 3 at 100 K. Light grey shading and black toning are used to emphasize the disorder. It is renounced to show thermal displacement parameters for the carbon atoms and the hydrogen atoms of the *tert*-butyl groups are omitted for clarity.

Table 2 Selected bond lengths/Å and angles/° for $Co(thd)_3$

| a. Modification 1 (| (295 K) | | |
|------------------------------|--------------------------|---------------------------------------|------------------------------|
| C1-C2 | 1 541 (5) | C9 - C10 | 1 390 (4) |
| C_{2}^{-01} | 1.272(4) | C10-03 | 1.370(1) 1 274(4) |
| $C_{2}^{2}-C_{3}^{2}$ | 1 377 (4) | C10-C11 | 1 519 (5) |
| $C3-C2^i$ | 1 377 (4) | Co1-01 | 1 876 (2) |
| C7-C8 | 1.526 (5) | $C_{0}^{2}-O_{3}^{2}$ | 1.870(2) |
| $C_{8}^{-}O_{2}^{2}$ | 1.320(3) 1.273(4) | $C_{02} = 02$ | 1.868(2) |
| $C_{8}^{-}C_{9}^{0}$ | 1.275(1) 1.398(4) | 002 02 | 1.000 (2) |
| $01^{ii} - C_01 - 01$ | 175.05(13) | $03 - C_02 - 02^{vi}$ | 89 21 (11) |
| $01 - C_{01} - 01^{iii}$ | 89 / 3 (13) | $03 - C_0 2 - 02^v$ | 175 45 (10) |
| $01 - Co1 - 01^{i}$ | 96 26 (13) | $03 - C_{02} - 02$ | 95 51 (10) |
| $01 - Co1 - 01^{iv}$ | 87.26 (10) | $03^{vi} = C_0 2 = 02$ | 87.85 (11) |
| $O_{3^{v}} - C_{02} - O_{3}$ | 87.61 (11) | 02 002 02 | 07.05 (11) |
| Symmetry codes: (| i) v x $1/2 - z$ (ii) - | -x = x + y = 1/2 - z; (iii) | $x = y = y \frac{1}{2} = z$ |
| (iv) -y, x-y, z; (v) | 1 - x + y, 1 - x, z; (y) | vi) 1-y, x-y, z. | , <u>,</u> <u>,</u> <u>,</u> |
| b. Modification 2 (| (100 K) | | |
| C1-C2 | 1.522 (10) | C27-O6 | 1.264 (8) |
| C2-C8 | 1.518 (11) | C27-C28 | 1.532 (9) |
| C2-C3 | 1.527 (10) | C28-C29 | 1.529 (10) |
| C2-C9 | 1.554 (11) | C28-C32 | 1.533 (9) |
| C3-O1 | 1.252 (8) | C28-C33 | 1.540 (9) |
| C3-C4 | 1.411 (10) | C35-C36 | 1.526 (9) |
| C4-C5 | 1.399 (10) | C36-C42 | 1.520 (9) |
| C5-O2 | 1.272 (8) | C36-C43 | 1.522 (9) |
| C5-C6 | 1.532 (10) | C36-C37 | 1.535 (9) |
| C6-C7 | 1.508 (11) | C37-O7 | 1.280 (7) |
| C6-C10 | 1.519 (11) | C38-C39 | 1.398 (9) |
| C6-C11 | 1.534 (10) | C39-O8 | 1.264 (7) |
| C12-C13 | 1.498 (10) | C39-C40 | 1.527 (9) |
| C13-C20 | 1.533 (10) | C40-C45 | 1.521 (9) |
| C13-C14 | 1.534 (10) | C40-C41 | 1.538 (9) |
| C13-C19 | 1 570 (11) | C40 - C44 | 1 543 (9) |
| C14 - O3 | 1 270 (7) | C46 - C47 | 1 525 (9) |
| C14 - C15 | 1 378 (9) | C47 - C51 | 1.523(9) 1.503(9) |
| C15-C16 | 1 397 (9) | C47 - C48 | 1.505(9) 1 541(9) |
| C16 - O4 | 1.357(5) | C47 - C50 | 1.545(10) |
| C16 - C17 | 1.205(7) 1.517(9) | C48 - 09 | 1.345(10) 1.265(7) |
| $C10^{-}C17$ | 1.517(0) 1.462(10) | C48 - C49 | 1.203(7) 1.402(8) |
| C17 - C21 | 1.102(10) 1.500(11) | $C_{01} = 05$ | 1.102(0) 1.858(4) |
| C17 - C22 | 1.500(11) 1.532(11) | $C_{01} = 06$ | 1.850(4) |
| $C_{23} = C_{24}$ | 1.332 (11) | $C_{01} = 02$ | 1.868(4) |
| $C_{23} = C_{24}$ | 1 494 (9) | $C_{01} = 03$ | 1.000(4) 1 872(4) |
| $C_{24} - C_{25}$ | 1.151 (9) | $C_{01} = 04$ | 1.876(4) |
| $C_{24} = C_{20}$ | 1.524(0) 1.565(11) | $C_{01} = 01$ | 1.870(4) 1.881(4) |
| $C_{24} = C_{50}$ | 1.303 (11) | $C_{0}^{2} = 08$ | 1.865(4) |
| $C_{25} = C_{26}$ | 1.278 (8) | $C_{02} = 0.000$ | 1.803(4) 1.872(4) |
| $C_{25} C_{20} C_{20}$ | 1.308 (0) | $C_{02} = 07$ | 1.872(4) |
| 05-Co1-06 | 1.550(5) | 02 - 01 = 01 | 1.077(4) |
| 05 - Col = 00 | 90.2(2) | 02 - 01 - 01 | 93.3(2) 174.7(2) |
| 05-001-02 | 1/0.2(2) | 03-001-01 | 1/4.7(2) |
| 00-001-02 | 00.0(2) | $O_{4}^{2} = C_{01}^{2} = O_{1}^{01}$ | 00.7 (2) 00.6 (2) |
| 05 - 001 - 03 | 90.1 (2) | 08 - 002 - 08 | 89.0(3) |
| $O_{2} = C_{01} = O_{2}$ | 01.3 (2) | $O_{0} = C_{02} = O_{0}^{0}$ | 173.0(2) |
| 02 - 001 - 03 | 01.0 (2) | $00 - 002 - 09^{\circ}$ | 0/.4(2) |
| 05 - 001 - 04 | 07.0 (2) | $09 - 002 - 09^{-1}$ | 95.8 (5) 05.6 (2) |
| 00-001-04 | 1/5.0 (2) | 08 - 02 - 07 | 95.0 (2) |
| 02 - 001 - 04 | 89.4 (2) | 09 - 002 - 07 | 87.6 (2) |
| 05-01-04 | 95.7 (2) | 08 - 002 - 07 | 88.2 (2) |
| 05-001-01 | $\delta/.1(2)$ | 09-002-07 | 88.9 (2) |
| 00-001-01 | 88.6 (29) | | |
| | | | |

Symmetry codes: (i) 2-x, y, 1/2-z.

3.7 Crystal structures

The crystal structures of 1 (295 K), 2 (100 K), and 3 (100 K) comprise packed mononuclear Co(thd)₃ molecules. The inner core of these complex units consists of Co surrounded by six oxygen atoms (from three different bi-dentate thd ligands) in somewhat deformed octahedral configurations. The atomic arrangement at the Co(O_{ket.})₆ cores (see Fig. 3)

Table 2(continued)

| c. Modification 3 (100 | K, metastable) | | |
|------------------------|----------------|--------------------------------------|------------|
| C1-O1 | 1.17 (2) | C7-C8 | 1.36 (2) |
| C1-C2 | 1.44 (2) | C8-C9 | 1.46 (2) |
| C2-C3 | 1.40 (2) | C9-O4 | 1.172 (14) |
| C3-O2 | 1.29 (2) | Co1-O2 ⁱ | 1.855 (5) |
| C4-O2 | 1.17 (2) | Co1-O2 | 1.855 (5) |
| C4-C5 | 1.35 (2) | Co1-O4 | 1.857 (6) |
| C5-C6 | 1.41 (2) | Co1-O3 | 1.864 (8) |
| C6-O3 | 1.14 (2) | Co1-O1 | 1.867 (5) |
| C7-O1 | 1.14 (2) | Co1-O1 ⁱ | 1.867 (5) |
| O1-C1-C2 | 124.0 (2) | O2 ⁱ -Co1-O3 | 92.3 (2) |
| C3-C2-C1 | 122.0 (2) | O2-Co1-O3 | 92.3 (2) |
| O2-C3-C2 | 123.0 (2) | O4-Co1-O3 | 179.7 (3) |
| O2-C4-C5 | 1310.0 (2) | O2 ⁱ -Co1-O1 | 179.5 (2) |
| C4-C5-C6 | 121.0 (2) | O2-Co1-O1 | 91.9 (3) |
| O3-C6-C5 | 121.4 (13) | O4-Co1-O1 | 92.7 (2) |
| O1-C7-C8 | 126.0 (2) | O3-Co1-O1 | 87.5 (3) |
| C7-C8-C9 | 124.0 (2) | O2 ⁱ -Co1-O1 ⁱ | 91.9 (3) |
| O4-C9-C8 | 119.7 (13) | O2-Co1-O1 ⁱ | 179.5 (2) |
| O2i-Co1-O2 | 88.6 (4) | O4-Co1-O1 ⁱ | 92.7 (2) |
| O2i-Co1-O4 | 87.5 (2) | O3-Co1-O1 ⁱ | 87.5 (3) |
| O2-Co1-O4 | 87.5 (2) | O1-Co1-O1 ⁱ | 87.6 (4) |
| Symmetry codes: (i) x, | , 1/2-y, z. | | |

is virtually identical with $Co-O_{ket.}$ bond distances in the range 1.86–1.88 Å (Table 2) and $O_{ket.}-Co-O_{ket.}$ bond angles from 86.8 to 96.2°. The refinement reliability factors [*wR2* (all data), see Table 1] came out somewhat larger than desirable, but we attribute this grievance to imperfections of the simple model presently used to account for structural disorder and thermal vibrations. This imperfection is, e.g., particularly conspicuous in the large scatter of the bond distances within the ketonato rings of complex 3 (Table 2c).

The X-ray molecular structures of modifications 1-3 of Co(thd)₃ match closely those in corresponding parts of Co(acac)₃ [36]. The actual crystal structures of Co(thd)₃ and Co(acac)₃ differ, however, with regard to the packing of the molecular species. This distinction clearly originates from the space demands of the larger and more bulky *tert*-butyl groups of the thd ligands.

There are two possible chiral isomers for the Co(thd)₃ molecules, a left helical Λ form and a right helical Δ form. Since **1** and **2** crystallize in centrosymmetric space groups their asymmetric unit contains two crystallographically independent Co(thd)₃ molecules which correspond to the two possible isomers. In modification **1** at 295 K the majority of the *tert*-butyl groups are rotationally disordered (Fig. 3a), whereas they are well localized in modification **2** at 100 K (Fig. 3b). The involved transformation is concomitant with the change of space group.

Instead of occupying two distinct positions in the crystal structure, the isomeric $Co(thd)_3$ molecules are located in a disordered fashion on the same position in the metastable modification **3** where they are transformed into each other by a mirror plane (Fig. 3c). The *tert*-butyl groups of the two enantiomers here superimpose on approximately the same position in a manner which facilitates the packing of such disordered molecules.

As mentioned the space groups of the structures of modifications 1 and 2 are related as super- versus sub-group symmetry, and the unit-cell volume per formula unit increases from **2** at 100 K to **1** at 295 K is some 5.1 %. The most easily recognized distinction between these structures is the increased thermal movements of the atoms, in particular the onset of rotational disorder of the *tert*-butyl groups, on going from 100 to 295 K. This is probably the driving force of the change in crystal symmetry. Attempts have been made to determine the transformation temperature by differential scanning calorimetry (DSC), but these efforts have hitherto been in vain. Nevertheless, we feel confident that the transition is to be classified as second order.

The relation between 1 and 3 is, as pointed out in Sect. 3.5, not governed by a reversible transformation process although it is also for these modifications of Co(thd)₃ possible to identify corresponding unit-cell directions. As a proper metastable phase 3 exhibits a less efficient packing of the complex molecules than 1 [the unit-cell volume per formula unit is 1.9 % larger in 3 at 100 K than 1 at 295 K; noting also that $V(1) / V(3) \approx 3/2$].

When we wanted to continue our bond-valence analyses with the structural data for the Co(thd)₃ modifications we experienced an unexpected discrepancy. Applying the Co^{III}–O bond-valence parameter of *Brese* and *O'Keeffe* [57] (1.70 Å) to the mutually consistent interatomic Co–O distances in the various modifications of Co(thd)₃ one obtains bond valences in the range of 0.613-0.652 and some 25 % too larger bond-valence sums for Co (3.73-3.83). The ketonato oxygen atoms, on the other hand, obtain normal bond-valence sums of around two. So the approach which worked quite satisfactory for various thd complexes of V^{IV} [58] and Co^{II} [16] gives unsatisfactory valence states for Co in Co(thd)₃. The unavoidable conclusion appears therefore to be that the tabulated bond-valence parameter for Co^{III}–O is incorrect.

An appreciable change of the Co^{III}–O bond-valence parameter to 1.61 Å would indeed give the expected valence of 3 and thus remove the discrepancy. However, the tabulated bond-valence parameters in Ref. [57] and parallel sources are extracted from large collections of selected structural data. Hence, unless the tabulated value of 1.70 Å represents a trivial misprint, one would be confronted with a much larger problem if one without further ado alters the parameter to say, the mentioned value 1.61 Å. However, the rescue for the bond-valence concept appears paradoxically to be that it is too simple. It is well recognized that bond distances depend not only on overall valence, but vary also with chemical bond character, spin state, and co-ordination environment (viz. co-ordination number as well as co-ordination geometry). According to such a more varied picture of bond valence a given valence state may be allowed to take several parameter values.

Available supporting information: CCDC 650381-650383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. *Acknowledgements.* This project has received financial support from the Research Council of Norway.

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