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Synthesis and Crystal Structure of $[Cr(thd)_2(OEt)]_2$

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Abstract. The mixed-ligand complex $[Cr(thd)_2(OEt)]_2$ [$(thd)^-$ = anion of H(thd) = $C_{11}H_{20}O_2$ = 2,2,6,6-tetramethylheptane-3,5-dione] appears as by-product when EtOH/H_2O is used as solvent during preparation of $Cr(thd)_3$. $[Cr(thd)_2(OEt)]_2$ can be difficult to separate from $Cr(thd)_3$ by sublimation, but separation is easily accomplished by extracting $Cr(thd)_3$ with acetone. A detailed account for the sublimation behavior of $[Cr(thd)_2(OEt)]_2$/$Cr(thd)_3$ mixtures is advanced. Good yields of $[Cr(thd)_2(OEt)]_2$ are obtained when $CrCl_3$, H(thd), and Na(EtO) react in absolute EtOH. $[Cr(thd)_2(OEt)]_2$ is obtained in the form of green needle-shaped crystals by recrystallization from toluene. The crystal structure is triclinic [a = 10.2919(15), b = 10.6686(16), c = 14.194(3) Å, α = 106.559(2), β = 107.869(2), and γ = 98.326(2)° at 295 K; space group $P\bar{1}$. The complex contains two crystallographic equivalent chromium atoms, which are bridged by two *cis*-configured ethoxy groups, the four remaining sites in the octahedral coordination around each chromium atom being occupied by oxygen atoms from two thd ligands. The bond lengths and angles concur with the findings for related molecular complexes. The temperature dependence of the magnetic susceptibility of $[Cr(thd)_2(OEt)]_2$ follows Curie–Weiss law with Weiss constant $\theta \approx -65$ K and $\mu_p = 3.87\ \mu_B$.

1 Introduction

The official policy of the Editorial Board of the annual series Inorganic Syntheses is to provide the scientific community with “detailed and foolproof procedures for preparation” of inorganic substances [1]. Each reported procedure “should be the best one available”, with special attention on “yield and purity of product”. With such high ambitions the success of the project will depend crucially on competence, practical skill, attitude to details, skepticism to unexpected events, dedication to commission, etc. of the originators as well as the checkers of the reports.

In 1987 a report appeared in this periodical [2] on the synthesis of $Cr(thd)_3$ [$(thd)^-$ = anion of H(thd) = $C_{11}H_{20}O_2$ = 2,2,6,6-tetramethylheptane-3,5-dione]. Strictly speaking the preparation of $Cr(thd)_3$ does not qualify for classification among “outstanding syntheses”, but reference [2] satisfies most of the other criteria set for such reports. Reference [2] *inter alia* makes no secret of lacking phase purity of the as-synthesized products. The present authors [3] have confirmed that the “purple platelets” and “ruby-red needle-shaped” ingredients of the products correspond to polymorphs of $Cr(thd)_3$. Reference [2] moreover mentions a “light green, slightly less volatile, contaminant” (alternatively referred to as “fluffy powder”), which apparently caused some problems for both originators and checkers during sublimation treatment of products. This paper focuses on this material with emphasis on formation, sublimation, and crystal and molecular structure.

Reference [2] does not specify the relative amounts of $Cr(thd)_3$ and $[Cr(thd)_2(OEt)]_2$ in the as-synthesized products, but the use of the term contaminant may lead one to imagine small amounts. The present authors, on the other hand, have established [3] that some 5 wt.-% of the as-synthesized products, made according to the recipe in reference [2], consist of $[Cr(thd)_2(OEt)]_2$. Moreover there appear to be snags (sect. 3.2) associated with the use of sublimation to separate the main product $Cr(thd)_3$ from the by-product $[Cr(thd)_2(OEt)]_2$. It is highly relevant to establish what causes the appearance of $[Cr(thd)_2(OEt)]_2$ in synthesis of $Cr(thd)_3$ according to the recipe of reference [2]. Other natural questions are: Where in the procedure does it form? How does it manifest itself? Can measures be taken to prevent its occurrence or can its abundance be reduced? How can $[Cr(thd)_2(OEt)]_2$ be separated from $Cr(thd)_3$? Some $[Cr(thd)_2(OEt)]_2$–$Cr(thd)_3$ relations have been briefly touched on in reference [3].

2 Experimental Section

2.1 Reactants and Solvents

$CrCl_3\cdot 6H_2O$ (Aldrich, ≥ 96 %), H(thd) (Aldrich, purum, ≥ 98 %), urea (Aldrich, 99 %), sodium (Merck, rod), HNO_3 (Prolabo, 68–70 %), KOBu-*tert* (Fluka, ≥ 97.0 %), absolute (abs.) ethanol (Arcus, prima), methanol (Merck, p.a.), 1-propanol (Aldrich, 99.5 %), 2-propanol (Fluka, ≥ 99.5 %), *tert*-BuOH (Merck, p.a.), acetone (Prolabo, for HPLC), 1,4-dioxane (Fluka, p.a., ≥ 99.5 %), acetonitrile (Merck, for GC, ≥ 99.8 %), toluene (Merck, p.a.), tetrahydrofuran (Prolabo, p.a.), benzene (Fluka, p.a., ≥ 99.5 %), and hexane (Fluka, p.a., ≥ 99.5 %)

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were used as reactants and/or solvents, mostly without further purification. Methanol, ethanol, and toluene were dried, distilled, and stored over molecular sieves.

2.2 Syntheses

Syntheses were performed in round-bottomed flasks equipped with reflux condenser and magnetic stirrer. The reaction mixtures were heated under reflux at boiling temperature (b.t.) or heated at fixed lower temperatures for different periods of time. Solid products were filtered through a sinter-glass funnel, washed, dried under vacuum, and finally sublimed (Büchi-type B-580 apparatus at ca. 0.05 mbar pressure) and/or recrystallized from various solvents. The phase purity of the final products was checked by powder X-ray diffraction (PXD).

$[Cr(thd)_2(OEt)]_2$ was prepared along three different routes. First, it appeared [3] as a by-product (ca. 5 wt.-%) during syntheses of $Cr(thd)_3$ according to the recipe in reference [2] [modified through the use of 1:3 stoichiometric proportions of the reactants $CrCl_3{\cdot}6H_2O$ and H(thd)].

Second, a parallel route started by heating $Cr(thd)_3$ in abs. EtOH to reflux. After some 5 days (d) the reaction mixture was cooled to room temperature, the solvent was evaporated, afterwards the solid product was treated with acetone to remove unreacted $Cr(thd)_3$, and finally recrystallized from toluene {result ca. 5 wt.-% $[Cr(thd)_2(OEt)]_2$}.

A third approach adopted an analogous procedure to that used for the synthesis of $[Cr(thd)_2(OMe)]_2$ [4]. $CrCl_3{\cdot}6H_2O$ was used instead of the more expensive $CrC1_3{\cdot}3THF$ and converted to $CrCl_3$ by heating at 200 °C for 1 d under vacuum. Anhydrous $CrCl_3$ (0.04 mol) was added to abs. EtOH (ca. 70 mL) in a round-bottomed flask. In another flask sodium (0.12 mol) was added to abs. EtOH (ca. 100 mL) and stirred until all the sodium had reacted. The clear colorless solution of sodium ethoxide thus obtained was added together with H(thd) (0.08 mol) to the suspension of $CrCl_3$, and the resulting mixture was heated to reflux with stirring for 1 d. The mixture was left to cool to room temperature, afterwards the mixture was filtered and the green solid product was dried under vacuum at 40 °C for 5 h and purified by recrystallization, first from benzene or hexane and afterwards from toluene. This procedure gave a yield of ca. 93 % and well developed crystals. The elemental analysis for $[Cr(thd)_2(OEt)]_2$ ($C_{48}H_{86}O_{10}Cr_2$) gave C 62.20 (calcd. 62.18), H 9.33 (9.35), O 17,40 (17.25), Cr 11.07 (11.22) %.

The preparation of $[Cr(thd)_2(OMe)]_2$ was repeated according to a completely analogous procedure to that described for $[Cr(thd)_2(OEt)]_2$. Attempts were also made to prepare other homologous alkoxides (viz. $[Cr(thd)_2(OR)]_2$ with R = 1-Pr, 2-Pr, and *tert*-Bu).

2.3 Elemental Analysis

The elemental analysis was done by the standard combustion technique at Birmingham University (UK). The analysis of chromium was determined as follows. Excess of 68 % HNO_3 was added to an accurately weighed amount of $[Cr(thd)_2(OEt)]_2$ and after careful stirring this mixture was heated at 100–150 °C until dryness. The crust thus obtained was transferred to an oven and heated in air at progressively increasing temperature (to 550 °C in steps of 50 °C) until a constant weight (at room temperature) had been reached. Calculations were based on the postulate that the end product was stochiometeric Cr_2O_3 (confirmed by PXD).

2.4 X-ray Diffraction

All samples were characterized by PXD at 22 °C with a Siemens D5000 diffractometer (capillary geometry) using monochromatic Cu-$K_{\alpha1}$ radiation (λ = 1.540598 Å) from an incident-beam germanium monochromator, and position-sensitive detector (Brown); silicon (a = 5.431065 Å) served as internal standard. The diffraction patterns were collected over the 2θ range 3–90° and indexed with use of DICVOL [5] and TREOR [6]. Unit-cell dimensions were obtained by least-squares refinements (METRIC [7]).

Crystals were mounted on thin glass fibers on brass pins. Single-crystal X-ray diffraction (SXD) data were collected at 295 K with a Bruker D8 Apex II diffractometer (Mo-K_α radiation). The data were integrated with SAINT [8] and corrected for absorption using SADABS [9]. The crystal structures were solved by direct methods with the program SIR2004 [10] or SHELXS [11] and refined using full-matrix least-squares against $|F|^2$ with SHELXL as implemented in Farrugia's WinGX suite [12]. All non-hydrogen atoms were refined allowing for anisotropic displacement parameters (introduced for chromium already from the beginning and for carbon and oxygen at the penultimate stage before the hydrogen atoms were added). Hydrogen atoms were assigned to idealized positions and refined with isotropic thermal parameters proportional to the thermal parameter for the atoms, to which they are attached (riding model).

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the CCDC Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ. Copies of the data can be obtained on quoting the depository number CCDC-786172. (Fax: +44-1223-336-033; www.ccdc.cam.ac.uk/data_request/cif; E-Mail: deposit@ccdc.cam.ac.uk).

2.5 Magnetic Measurements

Magnetic susceptibility measurements were performed (temperature range 2–300 K, magnetic field 1 kOe) with a 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 Genesis of $[Cr(thd)_2(OEt)]_2$

There is much evidence for the existence of a complex with the well defined composition $[Cr(thd)_2(OEt)]_2$. It appears in admixture with $Cr(thd)_3$ in syntheses of the later [2], but can also be obtained as a pure phase by other procedures (vide infra). It is accordingly appropriate to dwell briefly on reactants and experimental terms used in these syntheses.

The recipe of reference [2] starts with $CrCl_3{\cdot}6H_2O$ and H(thd) as reactants and $EtOH/H_2O$ as reaction medium. Since both reactants exhibit weak acidity, such mixtures will remain unreacted even after protracted heating at b.t. A base is clearly required to promote the reaction. For this purpose, reference [2] introduces urea, which gives NH_3 upon hydrolysis:

$$CO(NH_2)_{2(solv.)} + H_2O_{(solv.)} \rightarrow CO_{2(g)} + 2NH_{3(solv.)} \quad (1)$$

at temperatures near b.t.

The appearance of product mixtures of $Cr(thd)_3$ and $[Cr(thd)_2(OEt)]_2$ in these syntheses is a direct consequence of the water-containing medium: $CrCl_3{\cdot}6H_2O$ and H(thd) in refluxing EtOH/H_2O. The following scheme is suggested:

$$Cr^{3+}_{(solv.)} + 3H(thd)_{(solv.)} + 3NH_{3(solv.)} \rightarrow Cr(thd)_{3(solv.)} + 3NH_4{}^{+}_{(solv.)} \quad (2)$$

$$Cr(thd)_{3(solv.)} \rightleftarrows Cr(thd)_{3(s)} \quad (3)$$

$$Cr(thd)_{3(solv.)} + 2EtOH \rightleftarrows [Cr(thd)_2(OEt)]_{2(solv.)} + 2H(thd)_{(solv.)} \quad (4)$$

$$[Cr(thd)_2(OEt)]_{2(solv.)} \rightleftarrows [Cr(thd)_2(OEt)]_{2(s)} \quad (5)$$

As also established in reference [2], $[Cr(thd)_2(OEt)]_2$ is less soluble in EtOH/H_2O than $Cr(thd)_3$ and this is evidently the cause of its appearance as a minor phase in the product mixture. The balance between the constituents of the product is in any case regulated through Equations (2)–(5). The reversibility of Equation (4) was tested by heating 1:2 stoichiometric mixtures of $[Cr(thd)_2(OEt)]_2$ and H(thd) dissolved in (i) EtOH/H_2O, (ii) abs. EtOH, and (iii) H(thd) heated to reflux. The experiments with EtOH/H_2O as solvent turned out somewhat inconclusive. A faint red coloring of the liquid phase indicated that the anticipated reaction had commenced, but the process had then discontinued. This is in agreement with poor solubility of $[Cr(thd)_2(OEt)]_2$ in EtOH/H_2O.

$[Cr(thd)_2(OEt)]_2$ is obtained from $Cr(thd)_3$ and EtOH according to the forward direction of Equation (4) [solv. here denoting abs. EtOH; 5 d heating to reflux gave ca. 5 wt.-% $[Cr(thd)_2(OEt)]_2$ and 95 wt.-% unreacted $Cr(thd)_3$]. Since $[Cr(thd)_2(OEt)]_2$ dissolves poorly in abs. EtOH, the absence of the reverse reaction is in accordance with expectations. However, the reversibility of Equation (4) was ascertained by the use of H(thd) as both reactant and solvent. For example, heating a mixture of $[Cr(thd)_2(OEt)]_2$ and H(thd) to reflux for one day gave (semi-quantitatively assessed) $Cr(thd)_3$ in amounts corresponding to the proportions of the starting mixtures.

An essential inference from the present study is the confirmation of the reversibility of Equation (4), which in turn is controlled [Equation (3) and (5)] by the relative solubilities of $Cr(thd)_3$ and $[Cr(thd)_2(OEt)]_2$ in the solvent concerned. The basis for the inevitable occurrence of $Cr(thd)_3$/$[Cr(thd)_2(OEt)]_2$ mixtures in synthesis according to the urea-based recipe of reference [2] is laid by use of water-containing ingredients. The relative amounts in the product mixtures can to some extent be changed, but since H_2O has to be present according to Equation (1), both complexes should appear in the product. However, turning to water-free ingredients phase-pure $[Cr(thd)_2(OEt)]_2$ can be prepared according to:

$$2CrCl_{3(solv.)} + 6Na(OEt)_{(solv.)} + 4H(thd)_{(solv.)} \rightarrow [Cr(thd)_2(OEt)]_{2(s)} + 4EtOH + 6NaCl_{(s)} \quad (7)$$

The introduction of Na(OEt) from the very beginning makes the use of urea and thus Equations (1) and (2) become superfluous. With $CrCl_3$ and H(thd) as other reactants and abs. EtOH as solvent, $[Cr(thd)_2(OEt)]_2$ is obtained phase-pure in about 93 % yield. This approach mimics the synthesis of $[Cr(thd)_2(OMe)]_2$ [4] and preparation of the last mentioned complex was repeated (some 90 % yield) according to the presently modified procedure.

3.2 Sublimation of $Cr(thd)_3$ and $[Cr(thd)_2(OEt)]_2$ Mixtures

The present findings show that sublimation (under commonly used conditions) can be a rather laborious way to separate $Cr(thd)_3$ and $[Cr(thd)_2(OEt)]_2$. There are indeed other ways based on solvent extraction to perform this task. However, since reference [2] goes quite far toward recommending use of sublimation for purification of $Cr(thd)_3$, we will give a brief account of our experience with the application of sublimation on $Cr(thd)_3$/$[Cr(thd)_2(OEt)]_2$ mixtures.

Let us consider two series of experiments, one in which the sublimation temperature (s.t.) was set at 90 °C and another with s.t. = 180 °C. The deposition temperature (d.t.; viz. the temperature at the cold finger) was kept at 50 °C in both series. The seemingly trivial change of s.t. from 90 to 180 °C caused a major change in the sublimation process. For the s.t. at 90 °C series the process commenced with good speed, but soon after the sublimation rate started to decline, and went asymptotic to nil. PXD showed that the purple sublimate consisted of $Cr(thd)_3$. The unsublimed part had become covered at this stage with a thin layer of green-colored $[Cr(thd)_2(OEt)]_2$. Afterwards, the entire batch of unsublimed material was subjected to gentle crushing and thorough mixing and submitted to renewed sublimation treatment. The evolution of the resumed sublimation process once again followed the course just described. In fact, the crushing/mixing-sublimation treatment had to be repeated about 20 times over two weeks in order to fully separate $Cr(thd)_3$ from $[Cr(thd)_2(OEt)]_2$.

The process at s.t. = 180 °C developed differently. The sublimation rate remained largely unaltered during the process, and the characteristic light green cover-layer on the remnants at the evaporation source was reduced almost to invisibility. Most of a 5 g batch of raw material was sublimed after 30 min treatment at 180 °C. PXD of the sublimate after this treatment showed a mixture $Cr(thd)_3$ and $[Cr(thd)_2(OEt)]_2$. This finding appears to conflict the following statement in reference [2]: “If the sublimation temperature is maintained near 180 °C, the light green solid will not sublime at the pressure specified”.

The distinction between the behavior at s.t. = 90 and 180 °C can be explained by different volatility of $Cr(thd)_3$ and $[Cr(thd)_2(OEt)]_2$. In accordance with its lower molecular mass and presumably weaker intermolecular van der Waals interactions, $Cr(thd)_3$ obtains a significant sublimation pressure at lower temperature than $[Cr(thd)_2(OEt)]_2$. This concurs with the fact that $[Cr(thd)_2(OEt)]_2$ is detected in the sublimates from the 180 °C series, but absent in the 90 °C series.

The participation of sublimation of $[Cr(thd)_2(OEt)]_2$ in the s.t. = 90 °C series is manifested as the thin green cover-layer on the source material, which gradually renders evaporation of $Cr(thd)_3$ difficult and eventually blocks the sublimation process. Even though both complexes are volatile at 90 °C, the sublimation pressure of $[Cr(thd)_2(OEt)]_2$ is low and the flight range is short. At onset, the $Cr(thd)_3$ at the evaporation source has large surface areas free for $[Cr(thd)_2(OEt)]_2$, viz. numerous locations are accessible for sublimation. However, some $[Cr(thd)_2(OEt)]_2$ will also become vaporized, but for s.t. = 90 °C these species cannot travel far from their original location and they will eventually deposit on available colder spots left behind from the sublimation of a $Cr(thd)_3$ species. Once a $[Cr(thd)_2(OEt)]_2$ species has settled on such a spot, this spot becomes blocked for further sublimation, and when all such surface sites are blocked the sublimation will necessarily cease. The sublimation process can be recommenced by the creation of unblocked $Cr(thd)_3$ source surface (e.g., by cautious crushing).

According to these findings we cannot recommend sublimation as a means to separate $Cr(thd)_3$ from $[Cr(thd)_2(OEt)]_2$. The use of an s.t., which is low enough to ensure satisfactory separation demands intermediate crushing of the raw material, whereas high s.t. leads to vapor-phase transport of both compounds. Instead one can take advantage of the different solubility of $Cr(thd)_3$ and $[Cr(thd)_2(OEt)]_2$ in various solvents.

3.3 Crystal and Molecular Structure of $[Cr(thd)_2(OEt)]_2$

The structure of $[Cr(thd)_2(OEt)]_2$ was solved by direct methods, but in this case it was also possible to predict essential features of the crystal and molecular structures from knowledge on related complexes [3, 4, 13–15]. The refinements of the crystal structure of $[Cr(thd)_2(OEt)]_2$ run fairly smoothly and converged at somewhat high, but acceptable values for the reliability factors (Table 1) without introducing explicit descriptions of disorder.

Table 1. Single-crystal data and relevant parameters used in the refinements of the crystal structure of $[Cr(thd)_2(OEt)]_2$. Estimated standard deviations are given in parentheses.

Empiric formula	$C_{48}H_{86}Cr_2O_{10}$
M	927, 1894
T /K	295(3)
Crystal system	Triclinic
Space group	$P\bar{1}$
a /Å	10.2919(15)
b /Å	10.6686(16)
c /Å	14.194(3)
α /°	106.559(2)
β /°	107.869(2)
γ /°	98.326(2)
V /Å^3	1375.0(4)
Z	1
D /g•cm^{-3}	1.120
μ(Mo-K_α)$^{-1}$ /mm	0.443
F(000)	502
Crystal size /mm	0.17 × 0.22 × 0.53
Radiation /Å	0.71073
θ min., max. /°	2.1, 18.3
No. reflections meas.	6373
No. unique reflect.	1963
R_{int}	0.015
Obs. data [$I > 2\sigma(I)$]	1734
No. parameters	272
R_1 [$I > 2\sigma(I)$]	0.0719
wR_2 (all data)	0.1907
GOF	1.086
Min. max. resid. /e•Å^{-3}	–0.27, 0.79

Unit-cell dimensions and space groups are included in Table 1. The molecular structure of $[Cr(thd)_2(OEt)]_2$ is shown in Figure 1. Table 2 gives a surveying extract of selected bond lengths and angles, in which the various categories of bonds are represented by the range, over which the individual distances are distributed and the averages. The Cr–O_{ket} and Cr–O_{alk} bonds are here, as in $Cr(thd)_3$ [3], fairly free to adopt lengths adjusted to the size of Cr^{III} and O^{II}, whereas the O_{ket}–C_{ket}, C_{ket}–C_{ket} and O_{alk}–C_{alk} bonds can retain lengths characteristic for their bonding situation in the chelate rings and alkoxide bridges. The crystal packing in the unit cell of $[Cr(thd)_2(OEt)]_2$ is shown in Figure 1 (c).

Valence-state accounting according to the bond-valence scheme [16] shows an acceptable balance (Table 2). The bond-valence sum for chromium came out consistently some 10 % too high (3.26), whereas the corresponding sums for O_{ket} and O_{alk} deviated from two by ca. 7 % for O_{ket} (2.14) and ca. 2 % for O_{alk} (2.05). From the empirical bond length versus bond-order relation for carbon [17, 18] it follows that the effective valences of C_{ket} and C_{alk} are close to four. The CrO_6 configuration in the central part is almost regular octahedral and the Cr–O_{ket} bond length [individual values within 1.932(6)–1.967(6) Å] is adequately accounted for by the bond-valence model (Table 2). The very similar and nearly 90° intra- and interligand O_{ket}–Cr–O_{ket} angles imply that there cannot occur significant bonding interaction across the ca. 2.75 Å $O_{ket.}$•••$O_{ket.}$ bite and non-bite separations. The arrangement (interatomic distances and angles) in the O_{ket}–C_{ket}–C_{ket}–C_{ket}–O_{ket} section of the chelate ring is virtually the same as in $Cr(acac)_3$ [19–21] and $Cr(thd)_3$ [3]. The adjusting influence of the *tert*-butyl side groups on the shape of the chelate ring, to which it belongs, is quite marginal. Least-squares fitted planes through the chelate ring show deviation from the mean plane by 0.16(2) Å for both non-equivalent rings of the $[Cr(thd)_2(OEt)]_2$ structure.

The crystal and molecular structures of $[Cr(thd)_2(OEt)]_2$ (Figure 1) carry all essential characteristics of $[Cr(thd)_2(OMe)]_2$ [4], $[Cr(acac)_2(OMe)]_2$ [15], substitutional derivatives [13, 14] thereof, and analogous complexes of iron [22]. The crystal structure comprises dimeric $[Cr(thd)_2(OEt)]_2$ units, which are well separated from each other. The arrangement of the six oxygen atoms around the central chromium atom is octahedral [slightly more distorted than in $Cr(thd)_3$]. Compared with $Cr(thd)_3$ two ketonato oxygen atoms (O_{ket}) have been replaced by the oxygen (O_{alk}) atoms of two *cis*-configured ethoxy groups, which bridge the two chromium atoms of the dimeric unit. The implications of the less symmetric octahedral $Cr(O_{ket})_4(O_{alk})_2$ arrangement and the bridging $Cr_2(O_{alk})_2$ regions are surprisingly small. The $Cr_2(O_{alk})_2$ bridge is a molecular building brick with special bond-geometry demands, which, however, appear to be fully satisfied through the formation of the strictly planar $Cr_2(O_{alk})_2$ arrangements (imposed by the inversion center). The Cr–Cr distance across the bridging region [3.053(2) Å] is short enough to permit direct Cr–Cr orbital overlap. The consequent intramolecular magnetic exchange interaction serves to couple the moments antiferromagneticly in accordance with the low-temperature magnetic susceptibility data.

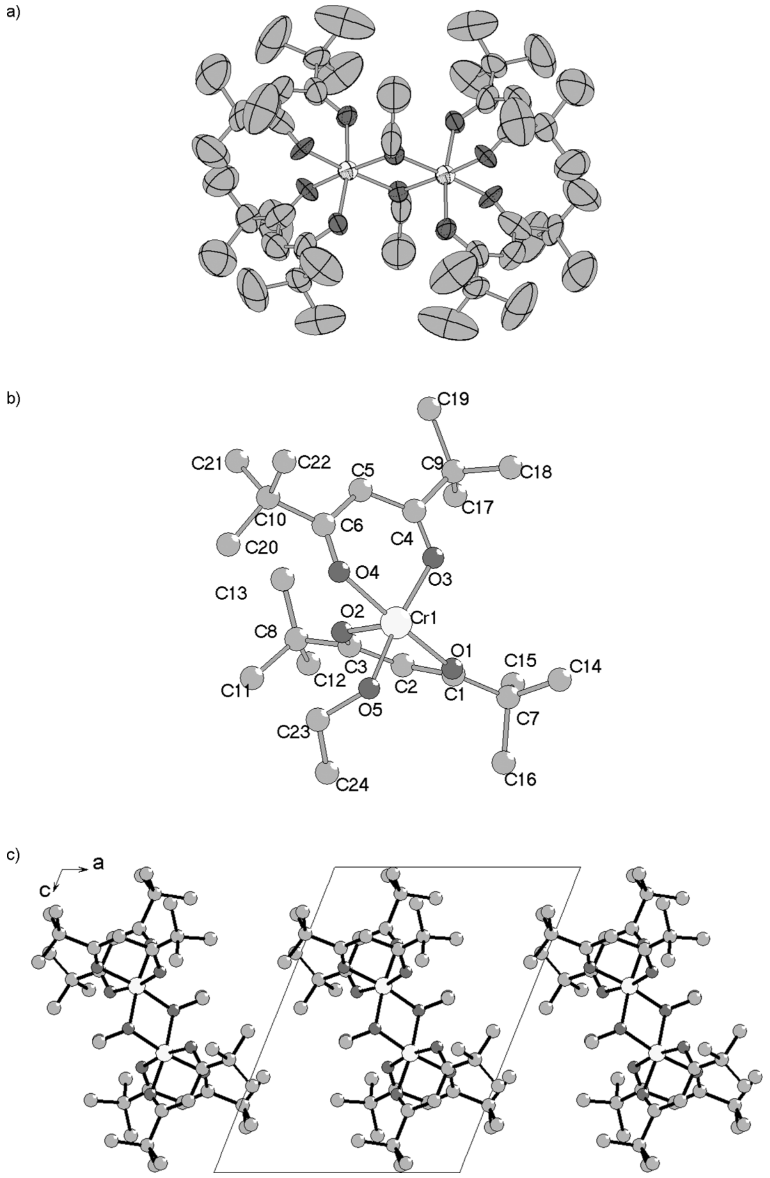

Figure 1. (a) X-ray molecular structure of $[Cr(thd)_2(OEt)]_2$ (at 295 K). Hydrogen atoms are systematically omitted. Thermal displacement ellipsoids are drawn at the 50 % probability level. See references [4, 13–17] for illustrations of related structures. (b) Atomic labeling scheme for chromium, oxygen, and carbon atoms in the asymmetric unit. (c) Packing of the $[Cr(thd)_2(OEt)]_2$ molecules in the crystal structure.

3.4 Magnetic Susceptibility

The $\chi_g^{-1}(T)$ relation (corrected for induced diamagnetism [23]) for $[Cr(thd)_2(OEt)]_2$ shows a positive (upward) curvature for $T < 50$ K, which evidences the presence of intramolecular antiferromagnetic exchange interaction between the chromium atoms (vide supra). Above this temperature the Curie–Weiss law is followed, with $\theta = -65$ K and $\mu_p = 3.87\ \mu_B$. The magnetic moment of $[Cr(thd)_2(OEt)]_2$ is in good agreement with the reported values for Cr^{III} complexes in the literature.

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Table 2. Range and average bond lengths ($d_{\min}$ to $d_{\max}$ and d_{av} in Å) and bond angles ($\varphi_{\min}$ to $\varphi_{\max}$ and φ_{av} in deg.) together with individual bond valences ($v_i = \exp[(D_i–d_i)/ b]$; D_i and b from reference [16]) and bond valence sums ($V = \sum v_i$) for $[Cr(thd)_2(OEt)]_2$.

$Cr–O_{ket}$ Range: 1.943(6)–1.967(6) Average: 1.952 $Cr–O_{alk}$ Gauge: 1.944(5)	$O_{ket}–Cr–O_{ket}$ Range: 89.0(3)–89.3(3) Average: 89.2 [92.7]; non-bonding $O_{ket}–Cr–O_{alk}$ Range: 92.5(2)–95.4(2) Average: 94.1 $O_{alk}–Cr–O_{alk}$ Gauge: 76.5(2)
$v_{Cr–Oket} = 0.54$ $v_{Cr–Oalk} = 0.55$ $V_{Cr} = 4 \cdot v_{Cr–Oket} + 2 \cdot v_{Cr–Oalk} = 2.16 + 1.10 = 3.26$	
$O_{ket}–C_{ket}$ Range: 1.181(14)–1.251(12) Average: 1.216 $O_{alk}–C_{alk}$ Gauge: 1.408(12)	$Cr–O_{ket}–C_{ket}$ Range: 126.7(6) –130.0(7) Average: 128.1 $Cr–O_{alk}–C_{alk}$ Gauge: 127.4(5)
$v_{Oket–Cket} = 1.60$ $v_{Oalk–Calk} = 0.95$ $V_{Oket} = v_{Oket–Cket} + v_{Oket–Cr} = 1.60 + 0.54 = 2.14$ $V_{Oalk} = v_{Oalk–Calk} + 2 \cdot v_{Oalk–Cr} = 0.95 + 1.10 = 2.05$	
$C_{ket}–C_{ket}$ Range: 1.422(15)–1.475(16) Average: 1.460	$O_{ket}–C_{ket}–C_{ket}$ Range: 122.1(10) –125.2(11) Average: 123.7 $C_{ket}–C–C_{ket}$ Range: 121.6(10)–122.4(11) Average: 122.0

[8] *SAINT*, Area-Detector Integration Software, V7.12A, Bruker-Nonius, WI, **2004**.

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