Syntheses, Crystal Structures, and Thermal Stabilities of Polymorphs of Cr(thd)₃

Mohammed A. K. Ahmed,^[a] Helmer Fjellvåg,^[a] Arne Kjekshus,^{*[a]} Renie K. Birkedal,^[a] Poul Norby,^[a] David S. Wragg,^[a] and Nalinava Sen Gupta^[a]

Keywords: Chromium; Cr(thd)3; Crystal structure; Polymorphism; Thermal stability

Abstract. The syntheses, crystal structures, and thermal stabilities of six polymorphs of Cr(thd)₃ [(thd)⁻ = anion of H(thd) = $C_{11}H_{20}O_2$ = 2,2,6,6-tetramethylheptane-3,5-dione] were studied using X-ray diffraction and differential scanning calorimetry. Compound 1 is thermodynamically stable below ca. 110 °C and forms plate-shaped crystals $[a = 9.927(5), b = 18.010(5), c = 21.427(5) \text{ Å}, \text{ and } \beta = 95.461(5)^{\circ} \text{ at}$ 295 K; space group C2/c]. Its crystal structure is isotypic with Mn(thd)₃. Polymorph 4 is metastable to 1, and the only way to prepare 4 appears to be by precipitation from solution. Crystals of 4 are needle shaped $[a = 28.54(3), b = 19.14(2), c = 21.92(2) \text{ Å, and } \beta = 97.31(2)^{\circ}$ at 295 K; space group C2/c] and this structure is isotypic with monoclinic Co(thd)₃. Modifications 2, 2*, and 5 also appear as needleshaped crystals [orthorhombic: a = 18.97(7), b = 18.69(7), and c =10.62(5) Å for **2** and tetragonal: a = b = 18.93(5) and c = 10.57(4) Å for 5, both at 110 K]. Crystals of 2 and 5 have limited lifetime, which

1. Introduction

The 3d metal complexes of beta diketones are both useful and interesting. They are used as reagents for NMR spectroscopic purposes [1-3], catalysts for oligomerization and polymerization [4] and precursors in atomic layer deposition (ALD) of thin films [5] among other things. From a structural point of view, they provide an excellent example of temperature dependent rotational disorder. This paper aims at clarifying basic chemistry issues [6] involved with synthesis and purification of β -diketonato complexes. It is specifically focused on Cr(thd)₃, which is frequently mentioned in the literature [1-3, 7-21].

Our research group [6] has recently given a brief overview on accumulated structural knowledge on (acac)⁻ [= anion of $H(acac) = acetylacetone = C_5H_8O_2 = pentane-2,4-dione]$ and $(\text{thd})^{-}$ [= anion of H(thd) = C₁₁H₂₀O₂ = 2,2,6,6-tetramethylheptane-2,4-dione] complexes of the 3d metals (M). Some of the several completely blank spots on structural information along the $M(acac)_2$, $M(acac)_3$, $M(thd)_2$, and $M(thd)_3$ series are aimed

University of Oslo P.O. Box 1033 Blindern

0315 Oslo, Norway

depends on storage temperature and exposure to X-rays. The conversion sequence is: $5 \rightarrow 2 \rightarrow 1$, where the first step takes 3 to 4 h and the second some 20 h. Attempts to establish detailed accounts of the orthorhombic Co(thd)₃-type structure of 2 and 2* by SXD were unsuccessful due to disorder. The structural distinction between 2 and 2* appears to be associated with rotational disorder among the Cr(thd)₃ molecules. 2* and 3 are high-temperature modifications with stability range ca. 155-200 and ca. 200-235 °C, respectively [Cr(thd)₃ melts at ca. 235 °C]. Quenched 2* can be retained as metastable at room temp. for some weeks, whereas 3 is not quenchable. High-temperature PXD data show that 3 is cubic [a = 13.357(4) Å at 225 °C; with strong rotational disorder of the molecules]. There are only minor variations in bond lengths and angles between 1 and 4 or from 100 to 295 K, and disorder is limited.

to be filled by the present ongoing project. Recent findings ([6] and references cited therein) suggest that the occurrence of polymorphs is more the rule than the exception for these β diketonato complexes.

The incomplete structural data available for these complexes makes it difficult to see a pattern along the series from M =Sc to Zn [6]. Insight into the structural features at and around room temp. is limited, and there is virtually no information available for higher temperatures. The structural situation just below the melting point of molecular complexes is of general interest since the molecular units may be expected to exhibit appreciable orientational (rotational) disorder just before melting sets in [22]. A first theoretical foundation for a research specialty on "rotational motion of molecules in crystals" was laid by Pauling [23] and Stern [24] in 1930/31, and the experimental activities really flourished in the late 1930's. Significant contributions to the progress came from this department [25–27], inter alia demonstrating that owing to steric hindrance the rotation of the molecular units cannot be entirely free [27].

With access to unit-cell dimensions and atomic co-ordinates of sufficiently high precision it becomes highly meaningful to search for structural details as well as coarser traits, which differ between polymorphs of Cr(thd)₃. It is of particular interest to explore the atomic arrangement around the central chromium atom (viz. identify variations in Cr-O_{ket} bond lengths and Oket-Cr-Oket bond angles). The β-diketonato skeletons are

^{*} Prof. Dr. A. Kjekshus

Fax: +47-22855441

E-Mail: arne.kjekshus@kjemi.uio.no

[[]a] Center for Materials Science and Nanotechnology Department of Chemistry



also natural targets for careful attention. Focal points of interest are here planarity versus non-planarity of the chelate ring and whether there are significant variations in O_{ket} - C_{ket} and C_{ket} - C_{ket} distances and associated angles. Another aspect, which deserves attention is variations in disorder either in the connection between the diketonato ligands and the central chromium atom (viz. a major source of rotational disorder) or within the *tert*-butyl groups. Temperature induced changes in disorder as well as distinctions in modes of disorder between polymorphs are of interest in this context. However, designing appropriate models for such disorder is challenging and, in general, the extent of disorder is difficult to quantify. Moreover, disorder is intimately correlated with the thermal motions of the atoms.

2. Experimental Section

2.1 Reactants and Solvents

CrCl₃·6H₂O (Aldrich, ≥ 96 %), H(thd) (Aldrich, purum, ≥ 98 %), urea (Aldrich, 99 %), 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 %) 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

All syntheses were performed in round-bottomed flasks equipped with reflux condenser and magnetic stirrer. The reaction mixtures were refluxed at boiling temperature (b.t.) or heated at fixed lower temperatures for different periods of time. Unless otherwise mentioned the solid products were filtered through a sinter-glass funnel, washed, dried under vacuum, and finally subjected to sublimation (Büchi-type B-580 apparatus at ca. 0.05 mbar pressure) followed by deposition on the cold finger at 50–90 °C and/or recrystallized from various solvents. The phase purity of all final products was ascertained by PXD.

Apart from a scale-up by a factor of 3 and use of proper 1:3 stoichiometry for the CrCl₃·6H₂O to H(thd) content of the reaction mixture, the preparation of Cr(thd)₃ mostly followed reference [14]. The reaction mixture of CrCl₃·6H₂O (0.033 mol), H(thd) (0.100 mol), urea (1.0 mol) distilled H₂O (75 mL), and abs. EtOH (195 mL) was heated under reflux at boiling temperature for 1 to 5 d with stirring. After cooling to room temp., distilled water (300 mL) was added and the mixture was stirred for 1 h. The liquid phase was filtered off through a sinter-glass funnel and the solid product washed several times with distilled water and then dried under vacuum at 60 °C for 1 d, sublimed at 90-180 °C and/or recrystallized from various solvents (overall total yield ca. 77 %). Cr(thd)₃ was obtained as a deep purple crystalline solid in three polymorphs [plate- (1) and/or needle-shaped (2 and 4) crystals] depending on the purification treatment; bold-faced numbers designate the polymorphs. Elemental analysis for various phase-pure samples of modifications 1, 2, and 4 of Cr(thd)₃ (C₃₃H₅₇O₆Cr) gave virtually identical results; typical: C 65.88 (calcd. 65.86), H 9.48 (9.55), O 15.88 (15.95), Cr 8.64 (8.64) %.

Several procedures were tried for preparation of crystals of the various polymorphs of Cr(thd)₃. Crystals grown from solutions appeared, in general, to provide specimens of better quality for SXD work than those obtained by sublimation. The specific crystal specimens used for collection of SXD data were prepared as follows.

1 and 4 were crystallized from solutions of $Cr(thd)_3$ in acetonitrile (either from saturated solution at b.t. and left for slow cooling to room temp. or from diluted solution left for slow evaporation of the solvent at room temp.). Suitable single crystals of these polymorphs were selected on inspection of the products with an optical microscope.

2 (and its tetragonal variant **5** in favorable cases) was (were) obtained in the form of seemingly single-crystal specimens by sublimation of $Cr(thd)_3$ at 180 °C (s.t.) and deposition at 90 °C (d.t.). Initial SXD tests of several of these specimens also suggested that they could be good single crystals. However, attempts to solve the structure demonstrated that these crystals were burdened with severe disorder. Another difficulty for SXD work with **2** is its limited lifetime on exposure to X-ray.

2* was obtained in attempts to improve the crystal quality of 2 by heat treatment of the specimens in sealed, thin-walled silica-glass tubes at 130–160 °C for a few days, followed by quenching in ice-water, but these endeavors resulted in even more severely disordered specimens.

2.3 Powder X-ray Diffraction (PXD)

All samples were characterized by PXD at room temp. with a Siemens D5000 diffractometer (capillary geometry) using monochromatic Cu- $K\alpha_1$ radiation ($\lambda = 1.540598$ Å) from an incident-beam germanium monochromator and a position-sensitive detector (Braun); Si (a = 5.431065 Å) served as internal standard. The diffraction patterns were collected over the 2θ range 3–90° and auto-indexed with help of the DICVOL [28] and TREOR [29] program packages. Unit-cell dimensions were obtained by least-squares refinements using the METRIC program [30].

The variable-temperature PXD measurements were collected on the same instrument. Samples were packed between plugs of silica wool in 0.7 mm internal diameter silica-glass capillaries. The capillaries were mounted in a flow cell [31] and nitrogen was flowed over the sample during heating. The temperature at the position of the sample was calibrated using the thermal expansion of silver as external standard.

2.4 Single-crystal X-ray Diffraction (SXD) Analysis

Crystals were mounted on thin glass fibers clamped on brass pins. Diffraction data were collected at temperatures between 100 and 485 K on a Bruker D8 Apex II diffractometer (Mo- K_{α} radiation) equipped with an Oxford Cryosystems Cryostream Plus cooling device. The data were integrated with SAINT [32] and corrected for absorption using SADABS [33]. Structures were solved by direct methods with the program SIR2004 [34] or SHELXS [35] and refined using full-matrix least-squares against $|F|^2$ with SHELXL as implemented in *Farrugia*'s WinGX suite [36]. 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 parameters for the atoms to which they are attached (riding model).

Table 1. Single-crystal data and relevant parameters used in structure refinements of complexes 1 and 4. Estimated standard deviations are given in parentheses.

	1 (295)	4 (295)	4 (110)	
Empiric formula	C ₃₃ H ₅₇ O ₆ Cr	C ₃₃ H ₅₇ O ₆ Cr	C ₃₃ H ₅₇ O ₆ Cr	
M	601.033	601.033	601.033	
T/K	293	293(2)	110	
Crystal system	Monoclinic	Monoclinic	Monoclinic	
Space group	C2/c	C2/c	C2/c	
a /Å	9.927(5)	28.54(3)	27.924(3)	
b /Å	18.010(5)	19.14(2)	18.6192(19)	
c /Å	21.427(5)	21.92(2)	21.627(2)	
α /°	90.00	90.00	90.00	
β /°	95.461(5)	97.312(16)	98.296(1)	
γ /°	90.00	90.00	90.00	
$V/Å^3$	3813(2)	11877(21)	11126.7(19)	
Ζ	4	12	12	
$D/g \cdot cm^{-3}$	1.048	1.010	1.078	
$\mu(Mo-K_{\alpha}) / mm^{-1}$	0.335	0.322	0.344	
<i>F</i> (000)	1308	3924	3924	
Crystal size /mm	$0.30\times0.60\times0.80$	$0.30 \times 0.40 \times 1.00$	$0.21 \times 0.27 \times 0.91$	
Radiation /Å	0.71073	0.71073	0.71073	
θ min, max / °	1.9, 21.6	1.6, 22.1	1.9, 26.5	
No. reflections meas.	8616	41984	43366	
No. unique reflect.	2213	7304	11477	
R _{int}	0.206	0.040	0.023	
Obs. data $[I > 2\sigma(I)]$	686	4722	9155	
No. parameters	183	560	542	
$R_1 \left[I > 2\sigma(I) \right]$	0.0755	0.0652	0.0473	
wR_2 (all data)	0.2463	0.2222	0.1442	
GOF	0.91	1.04	1.02	
Min, max resid /e•Å ⁻³	-0.29, 0.18	-0.22, 0.31	-0.40, 0.55	

Information on the crystals, data collection, and reliability factors for the reported structures is recorded in Table 1 together with unit-cell dimensions and space-group assignments.

CCDC-786169, -786170, and -786171 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

2.5 Elemental Analysis

Elemental analysis was done by standard combustion technique at Ilse Beetz or Birmingham University (UK).

2.6 Thermogravimetric and Thermal Analysis

Thermogravimetric (TG) analysis was performed with a Perkin–Elmer TGA7 system in a nitrogen atmosphere. Silica-glass containers were used as sample holders. The heating rate was 5 and/or 10 °C·min⁻¹, the temperature interval covered was 30–700 °C, and the sample mass was 15–30 mg.

Differential scanning calorimetry (DSC) was made with a Perkin– Elmer Pyris 1 system. Coarsely powdered specimens were contained in sealed 50 μ L aluminum pans during the measurements and (as an extra measure against oxidation) the containers were surrounded by flowing nitrogen gas. The heating rate was 5 and/or 10 °C·min⁻¹, the temperature range covered was 30–500 °C, and the sample mass was 2–3 mg. The temperature scale was calibrated against various standards. Transition temperatures assessed from parallel runs on 4–6 different samples rarely differed more than \pm 0.3 °C. Enthalpy was calculated on the bases of the melting enthalpy of the Perkin–Elmer indium standard. Transition enthalpies were determined by integration of the heat-flow peaks, values obtained in parallel runs agree within \pm 2 J·g⁻¹; data mentioned in text and illustrations refer to rounded averages.

2.7 Magnetic Susceptibility

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 Syntheses and Product Purification

The as-synthesized batches of $Cr(thd)_3$ according to the recipe in reference [14], contained two (occasionally three) phases with **4** as the major constituent, the mixed ligand complex $[Cr(thd)_2(OEt)]_2$ as by-product, and irregularly small amounts of **1** (vide infra). The instructions in reference [14] certainly provide a good yield of $Cr(thd)_3$ (some 90–95 %), but the byproduct $[Cr(thd)_2(OEt)]_2$ may cause some trouble if sublimation is chosen for purification. An account of synthesis (including sublimation), crystal structure, etc. for $[Cr(thd)_2(OEt)]_2$ is to be published separately [37]. An efficient means to clean $Cr(thd)_3$ contaminated by $[Cr(thd)_2(OEt)]_2$ is to take advantage of the high solubility of $Cr(thd)_3$ and low solubility of $[Cr(thd)_2(OEt)]_2$ in acetone. With acetone as solvent virtually complete separation is attained already after one recrystallization. An alternative approach could be to shift to MeOH–H₂O as solvent since $[Cr(thd)_2(OMe)]_2$ [38] appears to cause less trouble than $[Cr(thd)_2(OEt)]_2$ for sublimation of $Cr(thd)_3$.

Attempts to perform these syntheses at a temperature between room temp. and ca. 50 °C were unsuccessful, almost certainly, owing to insufficient access to the NH₃ at temperatures where the hydrolysis has not really commenced [37]. The visual-inspection-based description of the products in reference [14] refers to the same phases as observed in this study, viz. green fluffy powder, purple platelets, and ruby-red needles refer to [Cr(thd)₂(OEt)]₂, 1, and 4, respectively. Reference [14] does not provide information about the relative amounts of the three phases. The present findings strongly suggest that refluxing of the reaction mixtures for 1 d at ca. 90 °C is sufficient to ensure that the reaction is completed and equilibrium established. Modification 4 is evidently the kinetically preferred polymorph of Cr(thd)₃ under these conditions. The unsystematic appearance of the small amount of 1 in the as synthesized batches may possibly be attributed to temperature fluctuations in the reaction mixtures, whereas the formation of the [Cr(thd)₂(OEt)]₂ as by-product is controlled by a different reaction scheme [37].

Several solvents for growth of crystals were tested in this study, e.g., acetone, ethanol, ethanol–water, methanol, methanol–hexane, 2-propanol, and acetonitrile. The crystal growth was performed at selected temperatures between room temp, and boiling temp., starting from nearly saturated solution, which was left for gradual evaporation of the solvent. The trend in these experiments is that when the crystallization took place below 50 °C mostly phase-pure **1** was obtained, mixtures of **1** and **4** occurred when the crystallization took place at 55–80 °C, whereas essentially phase-pure **4** was found at and above 90 °C.

The choice of deposit between 50 and 90 °C in the sublimation-induced crystal growth of Cr(thd)₃ appeared as a convenient coincidence. Polymorphs 1 and 2 divide the accessible d.t. interval between them, compound 1 rules from 50 to ca. 85 °C and compound 2 from 85 to 90 °C. Small amounts of 2, which occur sporadically in the batches of 1 and vice versa are attributed to temperature fluctuations at the cold-finger (in particular above 80 °C). Two significant observations should be emphasized: (i) Modification 4 has never been observed in any of the numerous batches of Cr(thd)₃ treated by sublimation. The present findings show that preparation of phase-pure 4 demands dissolving and subsequent crystallization of Cr(thd)₃ from a suitable solvent. (ii) A systematic re-examination of the hundreds of PXD diagrams of as-synthesized, crystallized, and sublimed products shows that 2 undergoes a change to 1 on storing at room temp.

The limited insight on polymorphs 1, 2, and 4 gained from the synthesis work will be carried on to following sections where also the perspective of polymorphs 2^* , 3, and 5 are considered to get a more general picture.

3.2 Magnetic Susceptibility

The temperature dependence of the reciprocal magnetic susceptibility for Cr(thd)₃ is virtually identical for the polymorphs **1**, **2**, and **4** and closely follow (correction for induced diamagnetism [39]) the Curie law with a paramagnetic moment $\mu_p = 3.85 \ \mu_B \ (S = 1.49 \approx 3/2 \ \text{according to the "spin-only" approximation)}$. The findings concur with the expectations for Cr(thd)₃ as an ideal mononuclear Cr^{III} complex with regard to valence.

3.3 Structure Determinations and Refinements

Already from the unit-cell dimensions it is inferred that 1, 2, and 4 are isotypic (concept defined as in reference [40]) with Mn(thd)₃ [41], o-Co(thd)₃ (o = orthorhombic) [6], and m-Co(thd)₃ (m = monoclinic) [6], respectively. Owing to the similar atomic sizes and the almost equal X-ray scattering factors of the metal atoms of these complexes, the virtually identical appearance (with regard to peak locations as well as intensity distribution) of corresponding pairs of observed PXD diagrams further strengthen the claim of isotypism, and the structures of the prototypes should provide quite reasonable approximations for the corresponding chromium complexes.

The refinements of the crystal structures of **1** and **4** (with starting models from direct methods or the $Mn(thd)_3$ - and m-Co(thd)₃ structures, respectively) run rather smoothly and the structures show little evidence of disorder. This result has been confirmed from data collected with several specimens of each type.

The situation for 2 and 2^* is quite different. Several of the numerous crystal specimens of these variants gave data with promising good internal reliability factors (around 0.03) and, to begin with, we expected that refinements should proceed as smoothly as for 1 and 4. As soon as the six oxygen atoms of the ligands-to-central-atom attachments had been identified and accepted, another set (B) of six oxygen atoms turned up, related to the first set (A) by a rotational shift of approximately 45° (see Figure 1). Despite numerous attempts with different models to account for the implied disorder it proved impossi-



Figure 1. Mode of rotational disorder in the Cr-to-O attachment in 2^* as obtained in attempts to solve the structure by direct methods (see text). The abundance of disorder-form A relative to B is roughly 1:1, rotation angle between A and B is approximately 45° , and preliminary Cr–O distances range from 1.88 to 1.96 Å. The octahedral arrangements in A (black lines) and B (grey, narrower lines) are emphasized on the right.

ble to bring the structure-determination/refinement process significantly beyond the rather trivial Cr–O stage. This result was surprising in view of the close match between PXD data for o-Cr(thd)₃ and o-Co(thd)₃.

Several nice-looking crystals of **2** were tested, but apart from providing unit-cell dimensions, the SXD data for these proved to be unsuitable for structure determination. Similar observations were made for **2*** (which differs from **2** by post-annealing at 130–160 °C). The crystal imperfections, which render the structure determination/refinement difficult, appear to differ for **2** and **2***. The crystals of **2** are less burdened with rotational disorder of the Cr(thd)₃ molecules than **2***, but instead **2** undergoes structural rearrangements as a function of time (while retaining the external crystal shape).

Somewhat surprisingly the SXD efforts unambiguously established that there also exists a tetragonal (shorthand designations 5 and t) modification of $Cr(thd)_3$. 5 comes upon the scene as a short-lived forerunner for 2 in sublimation-treated samples (s.t. = 180 °C, d.t. = 90 °C). 5 is accordingly the first stage in a time-ruled conversion process $5 \rightarrow 2 \rightarrow 4$ and does not occur as a symmetry-motivated (t between o and c) intermediate in the temperature-determined succession $2^* \rightarrow 3$. Time and efforts were wasted in our search for 5 because we overlooked the clear message that the axial a/b ratio of 2 approaches one with decreasing temperature (e.g., a/b = 1.07, 1.02, and 1.01 at 410, 295, and 110 K, respectively). Besides the usual sources of error in determinations of unit-cell dimensions by SXD, evaluations for 2 and 5 pick up additional uncertainties through the temperature- and time-variations of the lattices. For 5 in particular, as the first rather short-lived member of the genesis series $5 \rightarrow 2 \rightarrow 4$, one must work relatively fast and cool to increase the lifetime to observe its existence. The structural evolution from 5 via 2 to 1 necessarily has a significant impact on the crystal quality of 5 and 2. This is probably the main reason for the obstacles we have experienced in attempts to resolve the crystal structure of 2 from SXD data. Representative unit-cell dimensions at 110 K are proposed as a = b =18.93(5) and c = 10.57(4) Å for 5 and a = 18.97(7), b =18.69(7) and c = 10.60(5) Å for 2. These may vary depending on the synthesis process used. [5 was occasionally noticed, but not measured at 295 K; a = 19.43(5), b = 19.08(5), and c =10.79(3) Å for 2 at 295 K.] There is reasonable consistency between unit-cell dimensions derived by SXD and PXD.

Apart from possible implications of the disorder (e.g., alteration of the space group symmetry), the assignment of **2** as isotypic with o-Co(thd)₃ is appropriate. This relation (viz. the implicit close match between corresponding atomic co-ordinates) can be utilized to derive fairly accurate estimates for interatomic distances and angles in the inner parts of these molecular complexes. Like o-Co(thd)₃ [6], **2** carries disorder, but the disorder in these complexes appears to be limited to the outer *tert*-butyl groups. The disorder in **2*** appears to be of a different character and concerns essentially the entire complex. In fact, coupled orientational disorder and large anisotropic thermal motions are precisely the ingredients which favor formation of spherical shaped molecules. This, in turn,

Table 2. Range and average bond lengths $(d_{\min} \text{ to } d_{\max} \text{ and } d_{av} \text{ in } \text{Å})$ and bond angles $(\varphi_{\min} \text{ to } \varphi_{\max} \text{ and } \varphi_{av} \text{ in } \circ)$ together with individual bond valences $(v_i = \exp[(D_i - d_i) / b]; D_i \text{ and } b$ from reference [42]) and bond valence sums $(V = \sum v_i)$ for modifications 1 and 4 of Cr(thd)₃. Intra- and interligand O_{ket}-Cr-O_{ket} bond angles are differentiated and data for the later category appear in square brackets. Bonds outside chelate ring not included.

1 (295 K)	
Cr-O _{ket} Range: 1.932(6)-1.938(8)	O _{ket} -Cr-O _{ket} Range: 90.6(3)-91.3(5) [86.5(3)-92.6(4)] Average: 90.8 [89.7]
$v_{Cr-O} = 0.56; V_{Cr} = 6 \cdot v_{Cr-O} = 3.36$ $O_{ket} - C_{ket}$	Cr-O _{ket} -C _{ket}
Range: $1.189(14) - 1.262(11)$ Average: 1.244 $v_{0-C} = 1.48; V_0 = v_{0-Cr} + v_{0-C} = 2.04$	Range: 126.9(8)–128.5(10) Average: 127.2
C _{ket} -C _{ket} Range: 1.393(15)–1.440(18) Average: 1.413	O _{ker} -C _{ket} -C _{ket} Range: 122.4(16)–124.0(12) Average: 123.1
	C _{ker} -C _{ker} -C _{ket} Range: 120.9(15)-126.0(11) Average: 123.3
4 (295 K) Domain of Cr1	
Cr1– O_{ket} Range: 1.944(3)–1.954(3) Average: 1.949 $v_{Cr1=0} = 0.54; V_{Cr1} = 6 \cdot v_{Cr1=0} = 3.24$	$O_{ker}{-}Cr1{-}O_{ket}$ Range: 89.71(14)–89.91(14) [89.93(14)–90.29(14)] Average: 89.8 [90.1]
$O_{ket}-C_{ket}$ Range: 1.265(15)-1.270(5) Average: 1.267	Cr1–O _{ket} –C _{ket} Range: 128.1(3)–128.5(3) Average: 128.4
C_{ket} -C _{ket} -C _{ket} Range: 1.374(7)–1.385(5) Average: 1.381	O _{ker} -C _{ket} -C _{ket} Range: 123.3(5)–124.3(5) Average:123.9
	C _{ket} -C _{ket} -C _{ket} Range: 125.1(5)-126.4(7) Average: 125.9
Domain of Cr2	
$Cr2-O_{ket}$ Range: 1.942(4)-1.959(4) Average: 1.947	$O_{ket}\text{-}Cr2\text{-}O_{ket}$ Range: 89.70(15)–90.00(16) [89.13(15)–91.04(15)] Average: 89.8 [90.1]
$O_{ket}-C_{ket}$ Range: 1.253(5)–1.281(6) Average: 1.267	Cr2–O _{ket} -C _{ket} Range: 127.5(3)–128.8(3) Average: 128.4
C _{ket} –C _{ket} Range: 1.375(7)–1.397(6) Average: 1.386	Oker-Cker-Cket Range: 123.0(5)–124.4(5) Average: 123.6 Cker-Cker-Cket
	Range: 124.6(5)–127.0(5) Average: 125.7
4 (110 K) Domain of Cr1	
Cr1–O _{ket} Range: 1.9453(14)–1.9487(14) Average: 1.947	O _{kef} -Cr1-O _{ket} Range: 89.82(6)-90.10(8) [89.75(6)-90.41(6)] Average: 89.9 [90.0]
$v_{CrI-O} = 0.55, v_{CrI} = 6 \cdot v_{CrI-O} = 3.30$ $O_{ker} - C_{ket}$ Range: 1.267(2)–1.275(2) Average: 1.271	Cr1–O _{ket} –C _{ket} Range: 128.50(13)–128.74(13) Average: 128.6
$v_{O-C} = 1.38; V_O = v_{O-Cr1} + v_{O-C} = 1.93$ C _{ket} -C _{ket}	O _{ket} -C _{ket} -C _{ket}
Range: 1.395(3)–1.399(3) Average: 1.397	Range: 124.2(2)–124.6(2) Average: 124.4 C _{ker} -C _{ker} -C _{ket}
	Range: 124.0(2)–124.4(2) Average: 124.2
Domain of Cr2	
Cr2 $-O_{ket}$ Range: 1.941(2)–1.952(2) Average: = 1.947 $V_{red} = 0.55$; $V_{red} = 6_{2}V_{red} = 3.30$	$\begin{array}{l} O_{ket}\text{-}Cr2\text{-}O_{ket} \\ \text{Range: } 89.64(6)\text{-}89.98(6) \ [88.48(7)\text{-}91.50(6)] \\ \text{Average: } 89.8 \ [90.0] \end{array}$
$C_{ket} - C_{ket}$ Range: 1.255(2)–1.281(3) Average: 1.271	Cr2–O _{ket} -C _{ket} Range: 126.66(14)–129.10(14) Average: 128.0
$v_{O-C} = 1.38; v_O = v_{O-Cr2} + v_{O-C} = 1.93$ $C_{ket} - C_{ket}$ Range: 1.385(3)–1.399(3) Average: 1.394	O _{ket} -C _{ket} -C _{ket} Range: 122.2(3)–124.5(2) Average: 123.7
	C _{tet} -C _{ket} -C _{ket} Range: 124.0(2)-125.3(2) Average:124.5



strongly influences the intra- and intermolecular interactions [22], which govern melting, sublimation, decomposition etc.

All structure information on **3** $[c-Cr(thd)_3]$ was obtained through the use of high-temperature PXD within its narrow stability region (200–235 °C). Preparation and examination of single crystals of **3** would necessarily be subject to similar temperature restrictions. Even if single crystals of **3**, against considerable odds, should become available their utilization for structure determination is likely to be hampered by extensive disorder which is evidently more complex and pronounced in **3** than **2***.

A juxtaposition of the interatomic distances in 1 and 4 (Table 2) shows a few smaller irregularities, which indicate that the experimental data are impeded with certain shortcomings. The possibility of collecting new SXD data was carefully considered, but was rejected in view of the very few atomic coordinates that appear to be affected by such defects. To gain insight into how such errors can arise, attention was focused on the electron-density distribution. For example, the co-ordinates of atom C4 in the crystal structure of 1 appear to be incorrect since the O-Cket and Cket-Cket bonds, which involve this atom are, respectively, shorter and longer than the corresponding bonds in other chromium acac and thd complexes. Gradients in the charge distribution at and near the C4 site indicate how the misplacement of this atom has come about. For utilization of the present structural data for bonding considerations a couple of obviously incorrect interatomic distances and angles may simply be neglected.

3.4 Crystal and Molecular Structures

Unit-cell dimensions and space groups are included in Table 1. As for m-Co(thd)₃ [6], the crystal structure of 4 comprises both the left (Λ) and right (Δ) helical forms of the chiral isomers of Cr(thd)₃. A complete listing of the refined positional and thermal parameters for the chromium, oxygen, and carbon atoms in 1 and 4 are given in the electronic deposit. The supplementary material also contains the Cr–O_{ket}, O_{ket}– C_{ket}, and C_{ket}–C_{ket} bond lengths and corresponding bond angles specified according to the numbering of the atoms in Figure 2. Table 2 gives a surveying extract of these data, in which the various categories of bonds are represented by the range over which the individual distances and the averages are distributed.

The molecular structure of $Cr(thd)_3$ is nearly identical in **1** and **4** and also essentially unchanged between 110 and 295 K. Octahedral CrO_6 co-ordination rules in the central part of the complex, whereas the diketonato chelate ring with its side groups dominates in the outskirts. However, perfectly regular octahedral arrangement for the Cr–O bonds appears to be incompatible with bonding demands of the chelate ring, the mutual competition resulting in a compromise through which both parts relinquish a little.

It is well established that bond angles, in general, are more flexible than bond lengths toward perturbations. Applied to the molecular structures of the $Cr(thd)_3$ polymorphs this guidance anticipates that the $Cr-O_{ket}$ bonds are fairly free to adopt lengths adjusted to the size of Cr^{III} and O^{II} , while the $O_{ket}-C_{ket}$

and C_{ket} - C_{ket} bonds can retain lengths characteristic for their bonding situation in the chelate ring (for illustration see figure 8 of reference [43]).

Valence-state accounting according to the bond-valence scheme [42] shows (Table 2) an acceptable balance. The bond-valence sums (V) for chromium came out consistently some 10 % too high (3.24–3.36), whereas the corresponding sums for O_{ket} only deviated from two by about 3 % (1.93–2.05). The valence states for C_{ket} cannot be assessed in the same way, but considerate estimates on the basis of the empirical bond length versus bond-order relation for carbon [44, 45] show that the effective valences of C_{ket} and C_{alk} are close to four.

The use of structural data for $Cr(acac)_3$ and $Cr(thd)_3$ from gas-phase electron diffraction (ED) [46] and density-functional-theory (DFT) calculations [46–48] gives a bond valence of nearly three for chromium ($V_{Cr} = 3.03$), whereas the deviations for O_{ket} increase somewhat. These changes reflect the 0.01–0.02 Å elongation of the bonds in free molecules compared to the solid state (viz. a measure of the perturbations caused by the intermolecular van der Waals type interactions). However, a further meditation on various aspects of bond-valences falls outside the scope of this paper.

The following knowledge is gained on the structure and bonding in molecular Cr(thd)₃. (1) The valence states of the individual constituents are Cr^{III}, O^{II}, and C^{IV}. (2) The CrO₆ configuration in the central part is close to regular octahedral and the Cr-Oket bond length [individual values within the range 1.932(6)–1.967(6) Å] is adequately accounted for by bond-valence accounting. (3) The very similar and nearly 90° intra- and interligand Oket-Cr-Oket angles imply that there cannot be a significant bonding interaction across the ca. 2.75 Å Oket ••• Oket bite and non-bite separations. (4) The atomic arrangement (viz. interatomic distances and angles) in the Oket-Cket-Cket-Oket part of the chelate ring is virtually the same in Cr(acac)₃ [47, 49, 50] and Cr(thd)₃. (5) The adjusting influence of the *tert*-butyl side groups on the shape of the chelate ring to which it belongs is quite marginal, whereas the influence on packing modes in the solid state is more decisive. (6) Points (1)–(5) can be generalized to cover the entire $M(acac)_2$, $M(\text{acac})_3$, $M(\text{thd})_2$, and $M(\text{thd})_3$ series.

Least-squares fitted planes through the whole or parts of the chelate ring can unveil deviation from planarity as atoms located significantly above or below the mean plane. Already the representation of the molecular structures of **1** and **4** in Figure 2 suggests that some of the chelate rings of the Cr(thd)₃ complexes are non-planar. The deviation from planarity varies with the particular complex and chelate ring as well as with temperature, but the actual magnitude of the departures is rather small. For one of the non-equivalent rings of complex **1** (295 K), the maximum deviation from the mean plane is 0.12(2) Å, whereas the departure in the non-equivalent ring only amounts to 0.03(2) Å. We are unable to see a pattern in the available information on non-planarity of chelate rings in acac and thd complexes. Therefore, we hesitate to speculate on possible impacts on the π -conjugated electrons of the rings.

The molecular structures of $Cr(thd)_3$ in 1 and 4 are very similar at and below room temp. and the disorder within their



Figure 2. (a) X-ray molecular structures of Cr(thd)₃ in 1 (295 K), 4 (295 K), and 4 (110 K). Illustrations of 4 at both 110 and 295 K are included to visualize increased thermal motion. Two identical units of 1 are shown to display the absence of chirality compared to the two independent units of 4. Note that the separation between the units for 1 and 4 does not represent the real separation in the crystal structure. Hydrogen atoms are systematically omitted. Thermal displacement ellipsoids are drawn at 50 % probability level. See references [41, 6] for illustrations of the isotypic complexes $Mn(thd)_3$ and m-Co(thd)₃ of 1 and 4, respectively. (b) Atomic labeling schemes (identical for 4 at 110 and 295 K) for chromium, oxygen, and carbon atoms in the asymmetric units of 1 and 4.

ligands (which certainly plays a major role in 2, 2^* , 3, and 5) is small. Nevertheless the packing of the molecular units in the crystal structures of 1 and 4 differs. On the basis of our findings it is tempting to suggest that the distinctions between these packing arrangements along the *a* axes directions reflect

slightly different starting points and initial routes (see section 3.4) which $Cr(thd)_3$ can take to gradually approach spherical shape with disorder as the main means. The progressive removal of restrictions on symmetry is instrumental in this process. It is indeed sad that it has hitherto proved impossible to

obtain single crystals suitable for full SXD exploration of the crystal and molecular structures of $2, 2^*, 3$, and 5. Detailed insight into the structural features of these polytypes is probably the key to a better understanding of properties of rotational disordered crystals.

3.5 Relation Between the Polymorphs

The present examination of the phase relationship between the polymorphs above room temp. was performed with TG, DSC, and HT-PXD (used in scanning and fixed temperature modes as well as room temp. PXD of specimens quenched from selected annealing temperatures). The dynamic nature of scanning techniques makes such methods sensitive to instrumental design and in particular to the experimental settings for heating/cooling rate and atmosphere. Careful calibrations are therefore needed to obtain reasonable consistency between transition temperatures derived by different scanning techniques, which inevitably only provide approximations to the equilibrium transition temperatures. Considerable experience may be needed to make the most correct choice from a set of scattered values from different sources.

The onset s.t. ≈ 140 °C according to TG is higher than the lowest s.t. ≈ 80 °C observed for incipient evaporation with the sublimation apparatus (s.t. = 90 °C). Moreover, the TG findings ensure that Cr(thd)₃ can be subjected to sublimation without decomposition below a certain temperature (guaranteed 300 °C under the present conditions).

The DSC curves for modifications 1, 2, and 4 (Figure 3) show that $Cr(thd)_3$ undergoes several phase transition with temperature. Essentially identical DSC characteristics were obtained above ca. 155 °C regardless which of these [stable (1) or long-time metastable (2 and 4)] polymorphs provided the test specimen is phase pure (especially with regard to [Cr(thd)₂(OEt)]₂ [37]). The present DSC curves contain one feature more than the DTA curve for Cr(thd)₃ reported by *Yoshida* et al. [9], who only recorded an un-assigned peak at ca. 200 °C in addition to the signature of melting at 236 °C.

HT-PXD scans of the same polymorphs (Figure 4) confirm that each of these polymorphs is subject to three phase changes above room temp. After indexing of the HT-PXD data (Figure 4), these transitions could be identified as $1 \rightarrow 2^*, 2 \rightarrow$ 2^* , and $4 \rightarrow 2^*$, for the first steps, followed by the common sequence of transitions $2^* \rightarrow 3 \rightarrow$ melt. As seen from the start and end temperatures for the later transitions (recorded below the peaks in Figure 3) the DSC data exhibit excellent reproducibility. [The transition enthalpies (which were included because they were available) also show good reproducibility.] The transitions labeled $1 \rightarrow 2^*$, $2 \rightarrow 2^*$, and $4 \rightarrow 2^*$ are necessarily free to adopt unequal start temperatures since the initial phases are different. Neither are the end temperatures obliged to be equal since the advancing transformation to the strongly disordered 2* state may take different routes. The broad, smeared look of the peaks appears to support such a point of view.

HT-PXD scans of polymorphs 1, 2, and 4 (Figure 4) covey essentially the same general view of the temperature induced



TEMPERATURE / °C

Figure 3. Differential scanning calorimetric (DSC) data for modifications (a) **1**, (b) **2**, and (c) **4** of Cr(thd)₃ at 5 °C·min⁻¹ heating rate. (d) DSC cooling curve (5 °C·min⁻¹) for Cr(thd)₃ from melt. Temperatures (in °C; averages of 3–5 runs) for the start and end of phase changes are indicated (below the peaks) together with the amount of energy involved (in J·g⁻¹; average of 3–5 runs; printed in slanted numbers).

phase changes in $Cr(thd)_3$ as the DSC scans. (Note that the temperature intervals cited on the illustrations in Figure 4 refer to stability regions assigned to the specified polymorphs as opposed to transition regions stated on Figure 3.) However, the ability of the present HT-XPD setup to detect transient phases and pinpoint phase transition temperature is poorer than that of the DSC equipment. Accordingly it is appropriate to attribute more weight to transition temperatures derived by DSC than assessments based on inspection of HT-PXD scans. However, when supplementary information from fixed-temperature HT-PXD and room temp. PXD of quenched specimens are introduced, stipulation of transition temperatures becomes a matter of discernment. Figure 5 summarizes, on a temperature scale, all available information on relations between the polymorphs of Cr(thd)₃. Efforts were made to provide the best possible estimates for transition temperatures. Polymorph 5 is not incorporated in Figure 5 because of its obviously special formation and evolution progression. The absence of the reverse of the $2 \rightarrow 2^*$ in the DSC and HT-PXD cooling curves provides circumstantial evidence for the claimed substantial enhancement of disorder at the $2 \rightarrow 2^*$ transition.



Figure 4. HT-PXD scans for modifications 1, 2, and 4 of $Cr(thd)_3$. The combined effect of heating rate, diffractometer speed, and scan range amounts to a temperature difference of 12 min between two successive scans. To ease inspection of the illustrations, scans which contain reflections from two adjacent modifications (regarding 2* see text) are omitted, and the thus created interruptions are artificially expanded. Temperatures (in °C) for the extension of the phase regions according to HT-PXD are marked.

Approximate representations of the thermal expansion of the lattices of the different polymorphs of Cr(thd)₃ (Figure 6) have been extracted from the HT-PXD scans. The juxtapositioned curves for the temperature variation of the unit-cell volumes per formula unit [V/Z, Figure 6(d)] is of particular interest in the present context. The succession 1, 4, and 2 of the volume expansion curves supports the inference that 1 is stable relative to 4, which in turn is more stable than 2. The discontinuities in the volume expansion, which is evident at the $1 \rightarrow 2^*$ and $4 \rightarrow 2^*$ transitions comply with first-order character nature of these transitions. The steep increase in volume above ca. 150 °C is compatible with the rapid increase in disorder and lattice defects in general anticipated as the melting temperature is approached.

There are clear relationships between the unit cells of the different polymorphs (Table 1 and Figure 7). Expressed in terms of polymorph 2, vectorial equations for the relations are: $\mathbf{a_1} = -\mathbf{a_2}/3 + 2\mathbf{c_2}/3$, $\mathbf{b_1} = \mathbf{b_2}$, $\mathbf{c_1} = -\mathbf{a_2} + \mathbf{c_2}$, for $\mathbf{2} \rightarrow \mathbf{1}$; $\mathbf{a_3} = \mathbf{a_2}/2 + \mathbf{b_2}/2$, $\mathbf{b_3} = -\mathbf{a_2}/2 + \mathbf{b_2}/2$, $\mathbf{c_3} = 5\mathbf{c_2}/4$ ($\mathbf{a_3} = \mathbf{b_3} = \mathbf{c_3}$ imposed) for $\mathbf{2} \rightarrow \mathbf{3}$; $\mathbf{a_4} = \mathbf{a_2} + 2\mathbf{c_2}$, $\mathbf{b_4} = \mathbf{b_2}$, $\mathbf{c_4} = -\mathbf{a_2} + \mathbf{c_2}$ for $\mathbf{2} \rightarrow \mathbf{4}$; and $\mathbf{a_1} = \mathbf{a_4}/3$, $\mathbf{b_1} = \mathbf{b_4}$, $\mathbf{c_1} = \mathbf{c_4}$ for $\mathbf{4} \rightarrow \mathbf{1}$ (5 represents a special configuration of 2, in which $\mathbf{a_2} = \mathbf{b_2}$). These equations describe the structural correspondence between the unit cells of the polymorphs with a relative accuracy of better than some 5 %.



Figure 5. Summary of relations between the different modifications of $Cr(thd)_3$ as extracted from Figure 3 and Figure 4, as well as supplementary results collected under fixed temperature conditions or derived from quenched samples. Transition temperatures (in °C) are marked.

4. Conclusions

On combining the evidences presented in Figures 3– 3<figr4><figr5><figr6><figr7> we arrive at the conclusion that the $2 \rightarrow 2^*$ transition belongs together with $1 \rightarrow 2^*$ and $4 \rightarrow 2^*$ in the first-order category, whereas the $2^* \rightarrow 3$ and $3 \rightarrow$ melt transitions are of second order. It may be mentioned that it is the progressively increasing rotational disorder which facilitate the second order character of the latter transitions.

The stability of the various polymorphs at room temp. complies with the evolution pattern monoclinic–orthorhombic–cubic–melt on increasing temperature (Figure 5). These findings are in accordance with the conceptions for rotationally disordered molecules in crystals. The increase in crystal symmetry is a means to facilitate increase in rotational disorder within a molecular complex like $Cr(thd)_3$ and the disorder together with the thermal motions within the molecular units serve to accumulate energy, which ultimately leads to sublimation, melting or thermal decomposition. The conversion temperature gives a measure of disorder a given structure can tolerate.

Acknowledgement

The authors are grateful to cand. scient. *Ole Bjørn Karlsen* and *Dr*: *Hiroshi Okamoto* for help with DSC and magnetic susceptibility measurements, respectively.



Figure 6. Temperature variation (slightly smoothed) of relative unitcell dimensions for modifications **1**, **2** and **2***, and **4** of Cr(thd)₃. The monoclinic angle β for **1** and **4** contracts slightly on increasing temperature (95.2 and 96.9° at 110 °C, respectively). (d) Juxtapositioned molar unit-cell volume versus temperature for Cr(thd)₃. The volume expansion above ca. 200 °C should be regarded as tentative (experimental data of relatively low precision in relation to rapid exponential-like changes).



Figure 7. Relation between the unit cells of the different polymorphs of $Cr(thd)_3$; 1 or 4 versus 2 and 3 versus 2 (Vectorial equations for the relations are given in the text. Note that the cell indicated for 3 is only pseudo-cubic; oblique angle 89.1°).

References

- G. C. Levy, U. Edlund, J. G. Hexem, J. Magn. Reson. 1975, 19, 259.
- [2] G. C. Levy, U. Edlund, C. E. Holloway, J. Magn. Reson. 1976, 24, 375.
- [3] G. C. Levy, J. J. Dechter, J. Kowalewski, J. Am. Chem. Soc. 1978, 100, 2308.
- [4] [4] slit4>J. W. Freeman, J. L. Buster, R. D. Knudsen, US Patent 5856257, 1999.
- [5] G. Carta, M. Natali, G. Rossetto, P. Zanella, G. Salmaso, S. Restello, V. Rigato, S. Kaciulis, A. Mezzi, *Chem. Vap. Dep.* 2005, 11, 375.
- [6] M. A. K. Ahmed, H. Fjellvåg, A. Kjekshus, P. D. C. Dietzel, Z. Anorg. Allg. Chem. 2008, 634, 247.
- [7] G. S. Hammond, D. C. Nonhebel, C.-H. S. Wu, *Inorg. Chem.* 1963, 2, 73.
- [8] E. W. Berg, N. M. Herrera, Anal. Chim. Acta 1972, 60, 117.
- [9] I. Yoshida, H. Kobayashi, K. Ueno, Bull. Chem. Soc. Jpn. 1974, 47, 2203.
- [10] K. Ueno, H. Kobayashi, I. Yoshida, Mem. Fac. Eng. Kyushu. Univ. 1978, 38, 83.
- [11] F. Wilkinson, C. Tsiamis, J. Phys. Chem. 1981, 85, 4153.
- [12] H. Dreeskamp, H. Kluge, I. Koch, Miner. Kohlechem. 1985, 324.
- [13] H. Dreeskamp, H. Kluge, Fuel 1985, 64, 1696.
- [14] D. Stille, J. R. Doyle, J. E. Finholt, G. E. Mcguire, *Inorg. Synth.* 1986, 24, 183.
- [15] M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrao, J. Chem. Thermodyn. 1987, 19, 645.
- [16] C. Tsiamis, C. C. Hadjikostas, S. Karageorgiou, G. Manoussakis, *Inorg. Chim. Acta* 1988, 143, 17.
- [17] T. Matsuura, H. Takenawa, T. Suzuki, R. Hirota, K. Sasaki, J. Radioanal. Nucl. Chem. Lett. 1990, 146, 223.
- [18] J. C. Machado, A. O. Porto, C. F. Carvalho, W. F. Magalhaes, A. Marques-Netto, J. Phys. 1993, 3, 201.
- [19] F. Magalhaes, A. O. Porto, J. C. Machado, G. Duplâtre, *Mater. Sci. Forum* 1995, 175–178, 719.
- [20] A. O. Porto, W. F. Magalhaes, C. F. Carvalho, J. C. Machado, J. Radioanal. Nucl. Chem. 1995, 198, 151.
- [21] O. Nilsen, H. Fjellvåg, A. Kjekshus, Thermochim. Acta 2003, 404, 187.
- [22] W. I. Dunning, in: *The Plastically Crystalline State*, (Ed.: J. N. Sherwood) Wiley, Chichester, **1979**.
- [23] L. Pauling, Phys. Rev. 1930, 36, 430.
- [24] T. E. Stern, Proc. Roy. Soc. London 1931, A130, 551.

A. Kjekshus et al.

- [25] C. Finback, O. Hassel, Z. Phys. Chem. 1936, B32, 130; C. Finback, O. Hassel, Z. Phys. Chem. 1936, B32, 433; C. Finback, O. Hassel, Z. Phys. Chem. 1937, B35, 25; C. Finback, O. Hassel, Z. Phys. Chem. 1937, B36, 25; C. Finback, O. Hassel, Z. Phys. Chem. 1937, B37, 75; C. Finback, O. Hassel, Z. Phys. Chem. 1937, B37, 301.
- [26] O. Hassel, A. M. Sommerfeldt, Z. Phys. Chem. 1938, B40, 391.
- [27] C. Finbak, Arch. Math. Naturvidenskab. 1938, B42, No. 1; C. Finbak, Tidssk. Kjemi Bergvesen 1937, 145; C. Finbak, Tidssk. Kjemi Bergvesen 1938, 101.
- [28] A. Boultif, D. J. Louer, J. Appl. Crystallogr. 1991, 24, 987.
- [29] P.-E. Werner, Program *TREOR*, Version 5, University of Stockholm, Stockholm, **1988**; P.-E. Werner, L. Eriksson, M. Westdahl, *J. Appl. Crystallogr.* **1985**, *18*, 367.
- [30] WIN-INDEX Professional Powder Indexing, Version 3.0, Siemens AG Analytical, System AUT, Karlsruhe, 1996.
- [31] P. Norby, J. Am. Chem. Soc. 1997, 119, 5215.
- [32] Area-Detector Integration Software, V7.12A; Bruker-Nonius, WI, 2004.
- [33] Bruker-Nonius, Madison, WI, 2004.
- [34] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. D. Caro, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 2005, 38, 381.
- [35] G. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112.
- [36] L. J. Farrugia, J. Appl. Crystallogr. 1999, 32, 837.
- [37] M. A. K. Ahmed, H. Fjellvåg, A. Kjekshus, N. Sen Gupta, D. S. Wragg, Z. Anorg. Allg. Chem. 2010, 636, accepted.

- [38] H. R. Fischer, D. J. Hodgson, E. Pedersen, *Inorg. Chem.* 1984, 23, 4755.
- [39] P. E. Selwood, Magnetochemistry, Interscience, New York, 1956.
- [40] U. Müller, Inorganic Structural Chemistry, Wiley, Chichester, 2007, p. 10.
- [41] P. Magnus, A. H. Payne, M. J. Waring, D. A. Scott, V. Lynch, *Tetrahedron Lett.* 2000, 41, 9725.
- [42] N. E. Brese, M. O'Keeffe, Acta Crystallogr., Sect. B 1991, 47, 192.
- [43] B. A. Kolesov, I. K. Igumenov, Spectrochim. Acta 1984, 40A, 233.
- [44] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca 1960.
- [45] C. A. Coulson, Valence, Oxford University Press, Oxford, 1953.
- [46] S. Samdal, Private communication.
- [47] I. Diaz-Acosta, J. Baker, W. Cordes, P. Pulay, J. Phys. Chem. 2001, A105, 238.
- [48] I. Diaz-Acosta, J. Baker, J. F. Hinton, P. Pulay, Spectrochim. Acta 2003, 59A, 363.
- [49] E. A. Shugam, L. M. Shkol'nikova, Dokl. Akad. Nauk SSSR 1960, 133, 386.
- [50] B. Morosin, Acta Crystallogr. 1965, 19, 131.

Received: April 7, 2010 Published Online: August 16, 2010