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On the Nature of the Polymeric Organotin(IV) Chromates(VI), [(Me₃Sn)₂CrO₄] and [(Me₃Sn)₃CrO₄(OH)]. An Extension of Non-consolidated Earlier Findings

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The powder X-ray diffractogram of the compound [(Me₃Sn)₂CrO₄] (**1**) is found to be practically superimposable with that of its structurally well-understood molybdenum homologue (**3**). In contrast to the layered topology of **1**, as expressed by the formula ${}_{\infty}^2[\text{Cr}\{\mu\text{-OSn}(\text{Me}_3\text{O})_2\}]$, the structural motif of its formal derivative [(Me₃Sn)₃CrO₄(OH)] (**2**) involves a distorted-diamondoid pattern in accord with the formula ${}_{\infty}^3[\text{Cr}\{\mu\text{-OSn}(\text{Me}_3\text{O})\}\{\mu\text{-OSn}(\text{Me}_3\text{O})(\text{H})\text{Sn}(\text{Me}_3\text{O})\}]$. In the lattice of **2**, actually two equivalent, mutually interpenetrating frameworks are held together by *inter-framework* O–H···O hydrogen bonds. While **1** appears to be surprisingly reluctant to incorporate interlayer guest cations via facile oxidation/reduction reactions, its thermal analysis reflects an appreciably high energy content which even exceeds that of the 1:1 addition product of **1** and Me₃SnOH, **2**.

Owing to our interest both in coordination polymers of the type [(Me₃E)₂MO₄] (E = Sn or Pb, M = Mo or W) [4,5], and supramolecular systems involving the building block {(Me₃Sn)₂(μ-OH)}⁺ [6,7], which was shown to be also present in the structure of **2** [2], our attention has likewise been focused on **1** and **2**. In the following, we are going (i) to present, and to interpret, the powder X-ray diffractogram (XRD) of **1**, (ii) to describe a simple synthesis of **2** in bulk quantities, (iii) to visualize the proper structure of **2** and (iv) to report on several observations reflecting the chemical stability, and reactivity, of **1** and **2**.

INTRODUCTION

Almost three decades ago, Domingos and Sheldrick attempted to elucidate the crystal structure of the earlier reported [1] coordination polymer [(Me₃Sn)₂CrO₄], **1**, but, assumedly owing to partial hydrolysis during the crystallization experiments, only a few single crystals of the *new* species [(Me₃Sn)₃CrO₄(OH)], **2**, were obtained. While the crystal structure of the latter could successfully be solved [2], neither that of **1** has been reported later, nor has **2** ever been prepared in sizeable quantities. Moreover, the supramolecular architecture of **2** in total has never been deduced from the available crystallographic data, although organosilicon, -germanium, -tin and -lead chromates were extensively reviewed in 1988 [3].

RESULTS

X-ray Powder Diffractogram (XRD) of [(Me₃Sn)₂CrO₄] (**1**)

In contrast to the two water-insoluble coordination polymers [(Me₃Sn)₂MO₄] with M = Mo and W [4,5], their chromium-containing homologue **1** is very soluble both in water and numerous polar organic solvents [1]. In agreement with the earlier observations [2], a solvent suitable for the generation of single crystals of **1** could so far not be found. Even in methanol, in which **1** was prepared [1], colour changes after some hours indicate chemical instability, presumably owing to slow oxidation of the alcohol.

The X-ray powder diffractogram (XRD) of **1** shown in Fig. 1(a) displays numerous sharp reflections

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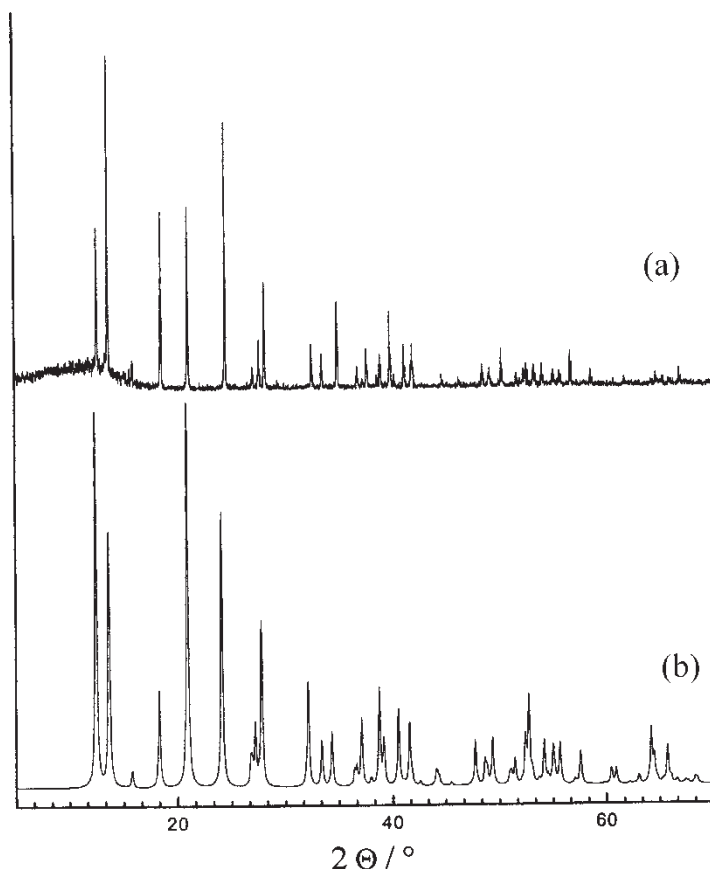


FIGURE 1 Comparison of the experimental XRD of **1** (a) with the simulated XRD of **3** (b).

between $2\theta = 10^\circ$ and 60° and, apart from a flat halo around $2\theta \sim 10^\circ$, an unperturbed base line, indicating that the product obtained after non-delayed methanol evaporation was essentially crystalline. Comparison with the simulated XRD of $[(\text{Me}_3\text{Sn})_2\text{MoO}_4]$, **3** [Fig. 1(b)] the crystal structure of which is known from a single-crystal X-ray study [4,5] reveals immediately a pronounced resemblance, suggesting strongly that **1** and **3** should be isostructural. After indexing and refinement of the lattice parameters, in making use of those of **3** [4,5] as input data, a of **1** turns out to amount to 7.255 Å, and c to 25.880 Å. As expected, the unit cell of **1** is slightly smaller than that of **3**. According to XRDs almost superimposable with that of **3**, the related compounds $[(\text{Me}_3\text{Pb})_3\text{MoO}_4]$ and $[(\text{Me}_3\text{Sn})_3\text{WO}_4]$ had already been considered to be isostructural with **3** [4,5]. Although **3** involves tetrahedral $\text{Mo}(\mu\text{-O})_4^-$ and trigonal bipyramidal $(\mu\text{-O})_2\text{SnMe}_3$ units (sharing all of the bridging oxygen atoms), the overall structure of **3** is layered and not a three-dimensional framework [4,5]. In view of the *molecular* nature of the earlier reported esters $(\text{Me}_3\text{EO})_2\text{CrO}_2$, which are either liquid at room temperature ($\text{E} = \text{Si}$) [8], or melt at 61°C ($\text{E} = \text{Ge}$) [9], the polymeric architecture of **1** is remarkable and essentially due to the preference of tin for pentacoordination.

Preparation of $[(\text{Me}_3\text{Sn})_3\text{CrO}_4(\text{OH})]$, **2**

As the dissolution and recovery, respectively, of **1** (and probably also of **2**) in, and from, suitable solvents is most likely to be accompanied by equilibria involving the disruption and back-formation of Sn—O bonds, it seemed to be promising to attempt the synthesis of **2** according to Eq. 1:



in the hope that finally, after solvent removal, exclusively the envisaged product **2** would remain. However, in solvents like methanol, acetonitrile or acetone, which are polar enough to dissolve **1** completely, the initially orange–yellow colour of **1** darkened continuously (towards reddish brown), suggesting at least partial decomposition. Interestingly, in diethyl ether and tetrahydrofuran (THF) in which **1** is only sparingly soluble, its colour turned almost instantaneously lemon yellow after suspension of **1** in the clear solution of Me_3SnOH . Actually, the crystals of “authentic **2**” are also reported [1,2] to be yellow in colour.

The XRD of the yellow residue resulting after filtration from the yellowish THF solution, washing and drying is shown in Fig. 2(a). For comparison,

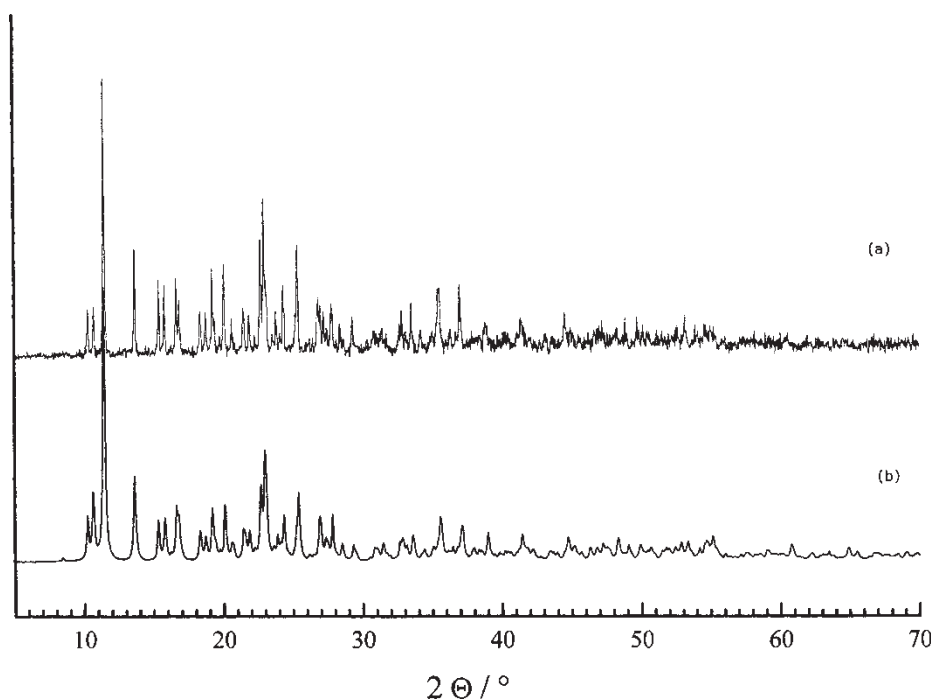


FIGURE 2 Comparison of the experimental (a) with the simulated (b) XRD of authentic 2.

also the simulated XRD of authentic 2 is included in this figure. The XRD of this product differs clearly from that of 1 (Fig. 1), indicating that 1 had been subjected to a chemical reaction, and a very satisfactory correspondence with the simulated XRD of authentic 2 can be seen. The reaction according to Eq. 1 was also repeated with Et₂O as solvent. Again, a yellow residue was obtained as the dominating product, the IR spectrum of which turned out to be identical with that of 2. Here, the solvent had been evaporated in total, and probably for this reason the XRD of the yellow residue displayed again all of the reflections expected for 2 along with a small number of additional ones. On the other hand, the IR spectra of the two residues were superimposable.

Supramolecular Architecture of Authentic 2

According to the crystal structure analysis of 2 reported by Domingos and Sheldrick [2], tetrahedrally coordinated chromium atoms are interconnected alternately either by $-\text{O}(3)-\text{Sn}(1)\text{Me}_3-\text{O}(4)-$ or by $-\text{O}(1)-\text{Sn}(3)\text{Me}_3-\text{O}(5)-\text{Sn}(2)-\text{O}(2)-$ spacers, in that two infinite, nonlinear chains intersect at each chromium site (the numbering of the atoms following strictly that used in Ref. 2). There are, in addition, substantial *inter-chain* $\text{O}(5)-\text{H}\cdots\text{O}(3')$ hydrogen bonds. In view of the fact that the structure of 3 involves likewise infinite chains (containing both tetrahedrally coordinated Mo atoms and $-\text{O}-\text{Sn}(\text{Me}_3)-\text{O}-$ spacers of trigonal bipyramidal configuration), although here a *layered*

lattice results [3], a clear-cut visualization of the supramolecular architecture of 2 appeared to be strongly desirable.

Straightforward application of the CERIUSt² software on the published crystallographic data has led to the unforeseen result that 2 spans a three-dimensional, distorted-diamonoid framework. However, because of the large voids to be found therein, the final crystal lattice consists of two equivalent and independent, mutually interpenetrating frameworks. Comparatively compact packing may already be deduced from the crystallographic density of 2 (2.08 g cm^{-3}), which exceeds considerably e.g. that of $[(\text{Me}_3\text{Sn})_3\text{Co}(\text{CN})_6]$ (1.534 g cm^{-3}) [10]. One of the quasi-adamandoid cages building up each basic framework of 2 is shown in Fig. 3 in which, for better clarity, chromium atoms bridged by either a $-\text{O}-\text{Sn}-\text{O}-$ or $-\text{O}-\text{Sn}-\text{O}-\text{Sn}-\text{O}-$ spacer are also connected by (shorter or longer) straight lines. On the surface of each cage, two kinds of chair-configured hexagons emerge (one with two long and four short edges, and the other with two short and four long edges). The number of ring atoms per hexagon is 28 and 32, respectively. A related coordination polymer, 4, involving tetracoordinate copper(I) and both $\{\text{CNSn}(\text{Me}_3)\text{NC}\}^-$ anions and pyrazine (pyz) molecules as spacers has recently been described [11]. Presumably owing to the lower number of space-demanding Me_3Sn groups per formula unit $[\text{Cu}\{\mu-\text{CNSn}(\text{Me}_3)\text{NC}\}(\mu-\text{pyz})]$ of 4, the latter consists of *three* independent, interpenetrating sub-frameworks.

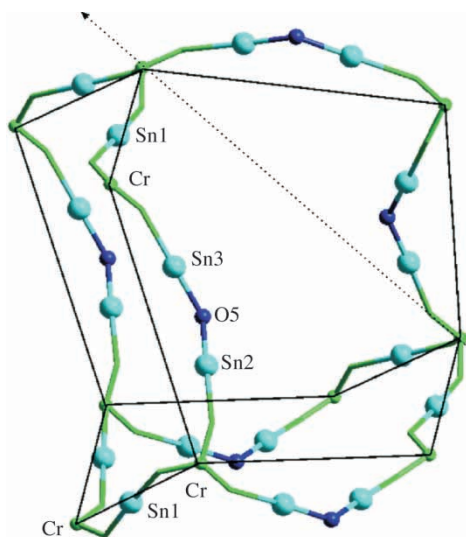


FIGURE 3 One of the adamantoid Cr_{10} cages that constitute the crystal structure of **2**. “Neighbourhood” Cr atoms are also connected by straight lines to indicate the distorted diamondoid framework more clearly. Methyl groups have been omitted, and only the oxygen atoms designated as O5 (generating hydrogen bonds) are reproduced as spheres. The dotted arrow corresponds to the *c*-axis (see also Fig. 5).

The two intra-framework $\text{Cr}\cdots\text{Cr}$ distances of **2** amount to ca. 7.2 and 11.2 Å, while the corresponding $\text{Cu}\cdots\text{Cu}$ separations in **4** are only slightly shorter (7.1 and 10.8 Å). Figure 4 illustrates how the Cr_{10} -cages of two independent sub-frameworks of **2** interpenetrate. The dotted line refers to one of the inter-framework $\text{O}(5)\text{—H}\cdots\text{O}(3')$ hydrogen bonds, which is shown in better resolution in the insert of the figure. As each formula unit contains one OH group, the abundance of inter-framework hydrogen bonds in the final lattice is considerable and also

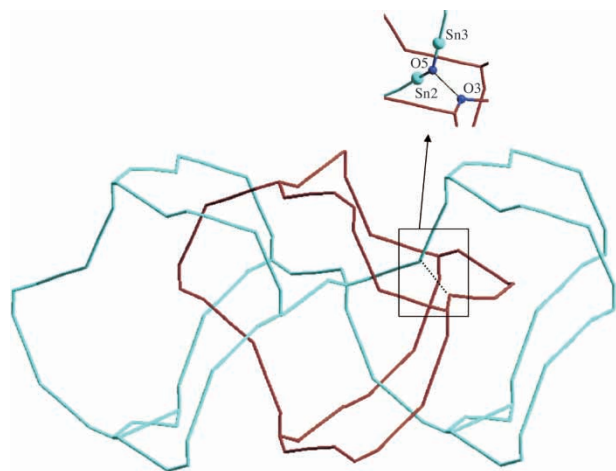


FIGURE 4 Visualization of fragments of two interpenetrating sub-frameworks of **2** (methyl groups have been omitted). The insert magnifies the surroundings of one of the *inter*-framework $\text{O5}\text{—H}\cdots\text{O3}'$ hydrogen bonds.

likely to help stabilizing the final lattice after the interpenetration of just two sub-frameworks. Cu_{10} -cages with the two slightly longer edges $\{\text{N}(\text{CN})_2\}^-$ (dca) and 1,2-bis(4-pyridyl)ethene (bpe) have most recently been found to build up the coordination polymer $\beta\text{-[Cu}(\mu\text{-dca})(\mu\text{-bpe})]$ the lattice of which involves even five interpenetrating sub-frameworks [12].

As interpenetrating diamondoid frameworks of any degree of interpenetration should always be perforated by relatively wide, straight channels parallel to the direction of translation of the subsequent frameworks [13], the crystal structure of **2** was likewise inspected for the occurrence of corresponding channels. In fact, notably wide channels of a square-like cross section (Fig. 5) were not found to extend along the main diagonal of a Cr_{10} cage (as usually for ideal diamondoid frameworks), but along a shorter $\text{Cr}\cdots\text{Cr}$ vector (as indicated in Fig. 3 by a dotted arrow). The distance between parallel-oriented channel walls is ca. 10 Å, which value matches well that of the diameter of the likewise rectangular channels in polymeric $[(\text{Me}_3\text{Sn})_3\text{M}(\text{CN})_6] = {}^3_\infty[\text{M}\{\mu\text{-CNSn}(\text{Me}_3)\text{NC}\}_3]$ systems ($\text{M} = \text{Co}, \text{Fe}$) [10]. We have also re-inspected the structure of **4** and found that here rectangular channels extend along the main diagonal of a distorted-diamondoid Cu_{10} cage. It should be recalled that these channels are always partially occupied by methyl groups of the Me_3Sn building blocks which usually rotate rapidly about their $\text{X}\text{—Sn}\text{—X}$ axes ($\text{X} = \text{either O or N}$).

Chemical Properties of **1** and **2**

Owing to the presence of chromium in its highest oxidation state, both **1** and **2** might be considered as potentially strong oxidants. Quite surprisingly, however, neither **1** nor **2** oxidizes pyrrole to cationic polypyrrole. Thus, in contrast to e.g. $[(\text{Me}_3\text{Sn})_3\text{Fe}^{\text{III}}(\text{CN})_6]$ the colour of which changes instantaneously from orange to black in the presence of gaseous or liquid pyrrole [14,15], contamination of **1** or **2** with a drop of pyrrole does not cause any colour change. On the other hand, grinding of **1** with $[\text{Co}(\text{C}_5\text{H}_5)_2]$ (“cobaltocene”) under an atmosphere of nitrogen affords a dark green powder, which decomposes again rapidly when contacted with water or a polar organic solvent. Interestingly, the chromate(V) anion, $[\text{CrO}_4]^{3-}$ is reported to be green in colour [16], suggesting here the incorporation of cobaltocenium guest cations between the layers of reduced $(\text{Cr}(\text{VI}) \rightarrow \text{Cr}(\text{V}))$. Unexpectedly, however, more than 50% of the cobaltocene used for the tribochemical reaction could readily be recovered by sublimation *in vacuo* at ca. 55°C, leaving a solid residue of still greenish appearance. This behaviour contrasts with

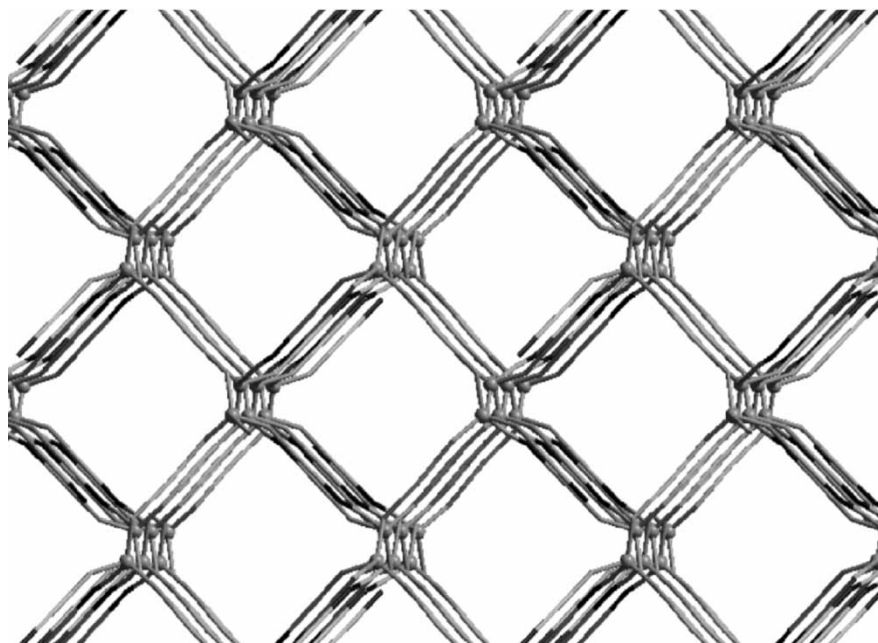
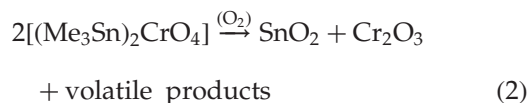


FIGURE 5 Perspective of the supramolecular architecture of **2** along its *c*-axis (see also Fig. 3). Methyl groups occupying the voids have been omitted.

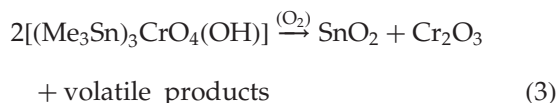
the strictly irreversible formation of $[\text{Co}(\text{C}_5\text{H}_5)_2](\text{Me}_3\text{Sn})_3\text{Fe}^{\text{II}}(\text{CN})_6$ from $[\text{Co}(\text{C}_5\text{H}_5)_2]$ and $[(\text{Me}_3\text{Sn})_3\text{Fe}^{\text{III}}(\text{CN})_6]$ [17,18]. The XRD of the residue obtained after cobaltocene removal was of low quality and had no resemblance to the XRD of **1**. As a small portion of the primary grinding product happened to be pyrophoric, any further tribochemical experiments involving **1** or **2** were strictly avoided.

Thermochemical Studies

According to the XRDs of the final green residues of the TG-DTA runs of **1** and **2** (Fig. 6) up to 1000°C , mixtures of the two oxides SnO_2 and Cr_2O_3 were exclusively generated in either case. The total weight loss (TG) of **1** (of 67.1%) might roughly be rationalized by Eq. 2 (theoretical weight loss: 65.9%), in that three quarters of the tin present in **1** would belong

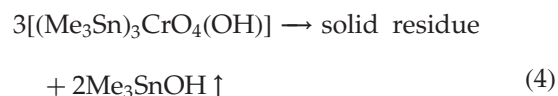


to the volatile fraction. Correspondingly, the total weight loss of **2** (experimental: 77.10%, theoretical: 75.76%) might follow Eq. 3, which is slightly idealized in view of the composition of **2**. The weight loss of the first step of the TG curve of **2**:



exceeds strongly that to be expected for exclusive liberation of H_2O . Assuming, on the other hand, only

extrusion of Me_3SnOH , the experimental weight loss of 18.6% might readily be rationalized by Eq. 4 (theoretical weight loss: 19.3%). Both the



comparatively high temperature of the first TG-DTA event of **2** (pristine Me_3SnOH is known to sublime at 80°C) and the lower yield in liberated Me_3SnOH rule out the view that the reaction product of **1** and Me_3SnOH might simply be a mixture of **1** and Me_3SnOH . In principle, instead of two equivalents of Me_3SnOH , also the stannoxane $(\text{Me}_3\text{Sn})_2\text{O}$ and H_2O (1:1) might escape.

The DSC plots of **1** and **2** (Fig. 7) agree with the corresponding DTA curves in view of both the number of distinct events and the characteristic temperatures. Quite surprisingly, the second of the two strongly exothermic DSC events of both samples is not accompanied by a TG step, suggesting that the intermediate(s) resulting around 210°C are still comparatively rich in energy, but still metastable below ca. 250°C . On the other hand, the lattice energy of the final $\text{SnO}_2\text{—Cr}_2\text{O}_3$ mixture is known to be notably higher than the recrystallization energy reflected by the DSC result. For further comparison, also the DSC plot of the considerably more stable homologue **3** of **1** is included in Fig. 7. Interestingly, the decomposition temperatures observed during attempts to determine potential melting points correspond for **1** and **2** to the second exothermic DSC signals, but for **3** to the (first) endothermic peak.

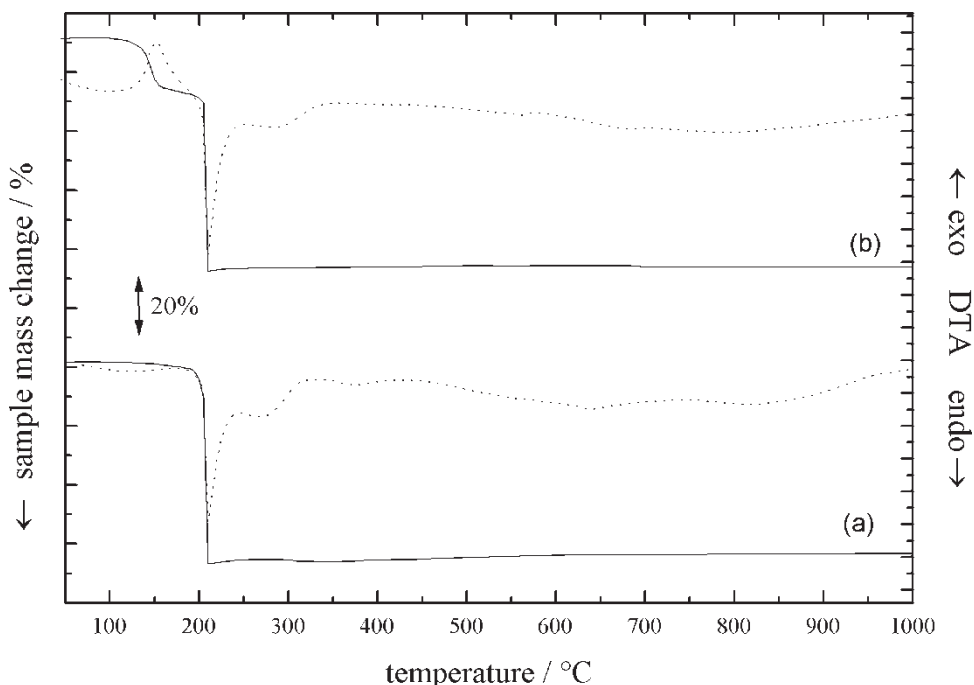


FIGURE 6 Comparison of the TG/DTA plots of **1** (a) and **2** (b).

CONCLUSIONS

Compound **1** is remarkable in that it seems to be the first $(R_3E)_2CrO_4$ system confirmed to be polymeric, and not molecular (as suggested for $R = Me$ and $E = Si$ [8] and Ge [9]). Its triethyl lead-containing, insoluble, but light-sensitive homologue [19] (decomp. temp. $190^\circ C$) might be supramolecular, too. On the other hand, the likewise light-sensitive compounds $(Ph_3E)_2CrO_4$ with $E = Ge$ (decomp. temp. $185^\circ C$) and Sn (decomp. temp. $80^\circ C$) are reported to dissolve readily even in nonpolar organic solvents [20], and might therefore better be ascribed to the molecular ester type. Actually, the more space-demanding phenyl groups are expected to impede pentacoordination of E . Both the good solubility of **1** in H_2O and polar organic solvents and a notable stabilization of the oxidation number $+6$ of the chromium centre owing to the presence of $\{Cr(OSnMe_3)_4\}$ fragments have so far inhibited the facile access to well-defined host-guest intercalation derivatives of **1**. The nature of the metastable phase observed during the TG studies of **1** at ca. $200^\circ C$ still deserves a more detailed investigation.

The supramolecular architecture of **2** based upon distorted-diamonoid frameworks that are perforated by nanometre-sized, straight channels is unexpected. The interpenetration of two, and not three or more (*vide supra*), equivalent frameworks could be dictated by the ease of formation of appropriate *inter-framework* $O-H \cdots O$ hydrogen bonds. Recently, Batten and Robson [21,22] have

pointed out that there might be numerous successful crystallographic structure analyses in the literature, wherein, nevertheless, conclusive information on framework *interpenetration* is either hidden or missing. Another challenge would be the successful preparation of the molybdenum homologue, $[(Me_3Sn)_3MoO_4(OH)]$ of **2**. Probably owing to the low solubility of **3** in H_2O , $MeOH$, CH_2Cl_2 etc., our route employed for the synthesis of **2** has so far not been successful. As the molybdenum (or tungsten) homologue(s) of **2** are expected to be less vigorous oxidants, they might be more suitable candidates for solid-state reactions with potential guest systems.

EXPERIMENTAL

Preparations

Bis(trimethyltin) chromate, $[(Me_3Sn)_2CrO_4]$ (**1**) and trimethyltin hydroxide, Me_3SnOH , were prepared according to literature procedures [1,23].

$[(Me_3Sn)_3CrO_4(OH)]$, **2**

Compound **1** (100 mg, 0.225 mmol) was suspended in a clear solution of Me_3SnOH (50 mg, 0.276 mmol) in either THF (12 cm^3) or Et_2O (15 cm^3). In both cases the colour of the solid changed quickly from orange-yellow to lemon yellow. After stirring overnight (room temperature), filtration, washing of the residue with small amounts of either THF or Et_2O

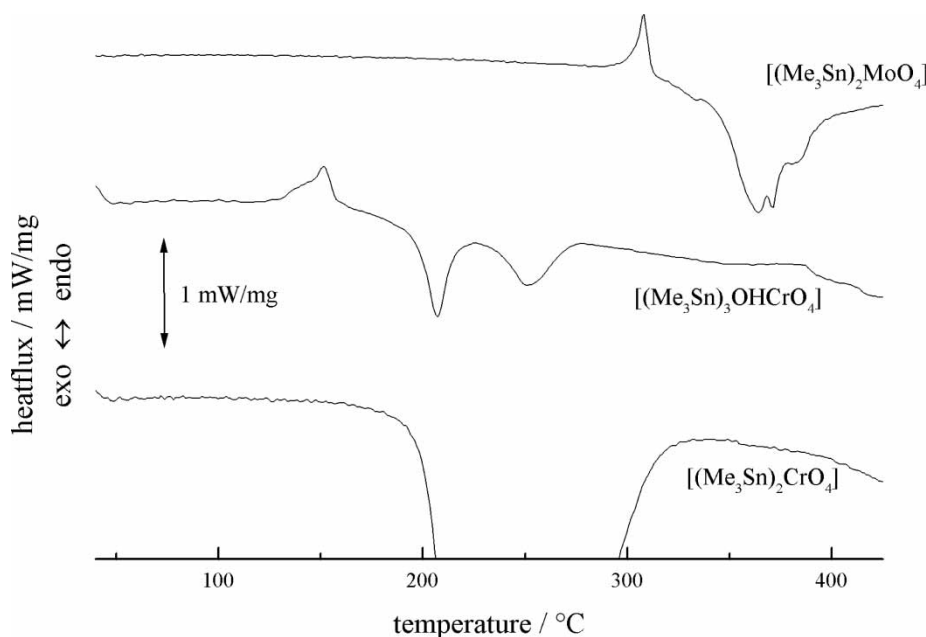


FIGURE 7 Comparison of the DSC plots of 1 (a), 2 (b) and 3 (c).

and drying at air, a bright yellow powder was obtained (from THF: 112.0 mg, 0.180 mmol, 79.5%; from Et₂O: 120.0 mg, 0.192 mmol, 85.2%). Elemental analysis C, 17.41; H, 4.22 (from THF); C, 17.03; H, 4.43% (from Et₂O). C₉H₂₈O₅CrSn₃ requires C, 17.31; H, 4.52%. $\nu_{\max}/\text{cm}^{-1}$ (IR, 1000–500) 923 vs, 909 vs, 881 s, 836 m, 777 vs, 732 vs, 548 s, 518 m. Compound 1 displayed absorptions at 886 vs, 744 vs and 555 m cm⁻¹ only. A reaction of 1 with Me₃SnOH in a molar ratio of 1:2 (THF) resulted likewise in the formation of pure 2.

Tribochemical Reaction of 1 with [Co(C₅H₅)₂]

Using a thick glass rod with a spherical end as a pestle, equimolar quantities of 1 (110.0 mg, 0.247 mmol) and [Co(C₅H₅)₂] (46.7 mg, 0.247 mmol) were ground together in a suitable, solid Schlenk tube under an atmosphere of dry N₂ (for ca. 1 h). Although the colour changed from almost black (cobaltocene) to dark green, more than 50% of the cobaltocene (26.0 mg, 0.137 mmol, 55.6%) could be recovered simply by sublimation *in vacuo*, keeping the Schlenk tube in an oil bath of ca. 55°C. IR of the green product, $\nu_{\max}/\text{cm}^{-1}$ (1000–500): 856 vs, 728 vs, 557 s, 502 w.

Methods

IR spectra were obtained on a Perkin-Elmer IR-1720 spectrometer, and X-ray powder diffractograms on a Bruker axs D8 Advance diffractometer (CuK α). Powder diagrams were simulated with CERIUSt²

4.0 (MSI), for the 2 θ range 5–70°. Crystallographic data for 2 and 3 are available from the Cambridge Crystallographic Data Centre. TG/DTA-studies were carried out on a Netzsch STA 409 C instrument, and DSC studies both on a Mettler DSC 27 HP and on a Netzsch DSC 204 instrument.

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