



## A homoleptic chromium(III) carboxylate†

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**Structurally characterized chromium(III) carboxylates form clusters with a variety of bridging groups introduced from aqueous reaction conditions. The first homoleptic monomeric chromium(III) carboxylate has been prepared using an anhydrous salt metathesis synthetic route. The carboxylate groups coordinate the chromium in a bidentate chelate yielding an aliphatic soluble complex. The complex was characterized by a variety of methods including high energy X-ray diffraction, FD-MS, IR and Raman spectroscopy, complemented by DFT modeling.**

Chromium(III) carboxylates exhibit a rich structural diversity from simple dimers to high nuclearity clusters.<sup>1–3</sup> The metal centres are usually bridged by a combination of carboxylate, oxide and hydroxyl moieties with the latter groups introduced, intentionally or inadvertently, *via* the presence of water in the reaction system.<sup>4,5</sup> The quintessential and most studied metal triangular complex species,  $\text{Cr}_3\text{O}(\text{RCO}_2)_6(\text{H}_2\text{O})_3^+$ , was synthesized as early as 1908 by Alfred Werner and its derivatives were later used to evaluate the theoretical framework for molecular magnetic interactions.<sup>6,7</sup> These trimeric species are commonly referred to in the literature as “basic chromium carboxylates” or simply “chromic carboxylates”.<sup>8</sup> Similar confusing nomenclature was recently noted for copper carboxylates.<sup>9</sup>

Chromium(III) carboxylates are used commercially in a variety of applications including catalytic and materials applications.<sup>10,11</sup> The currently accessible chromium(III) carboxylates suffer from several disadvantages as catalyst precursors.<sup>12</sup> These compounds often contain coordinated or residual water and carboxylic acid molecules. These protic sources are incompatible with many catalyst activators (*i.e.* alkylaluminiums)

and require excess activator and ligand to ensure viable catalytic activity. Ionic and high nuclearity chromium clusters have negligible solubility in aliphatic solvents requiring the use of less desirable aromatic, chlorinated or polar solvents.

A monomeric, neutral chromium(III) carboxylate could overcome these challenges. The synthesis of tris(methacrylate) chromium(III) has been proposed in the literature; however, the characterization is not persuasive.<sup>13</sup> The proposed compound was prepared under aqueous conditions that lead to cluster formation (*vide supra*). Additionally, the chromium complex was insoluble in common organic solvents and the structural characterization was based on unassigned IR peaks. In an older report, reaction of chromium(VI) oxide with carboxylic acid anhydrides was proposed to produce  $\text{Cr}(\text{O}_2\text{C}_3\text{H}_7)_3$ ; however, the complex was only soluble in methanol and contained non-equivalent carboxylate groups in the IR spectra inconsistent with a monomeric structure.<sup>14</sup> We present the synthesis and unambiguous characterization of a monomeric, homoleptic chromium(III) carboxylate soluble in aliphatic solvents.<sup>15,16</sup>

3.1 equivalents dry sodium 2-ethylhexanoate (NaEH: 10.01 g, 60.2 mmol) dissolved in anhydrous tetrahydrofuran (60 mL) was added to a slurry (100 mL THF) containing  $\text{CrCl}_3(\text{THF})_3$  (7.27 g, 19.4 mmol) and stirred for 24 h producing a green solution and a white precipitate (NaCl). The solvent was removed under vacuum and the green solid was extracted with cyclohexane (400 mL), filtered through Celite and dried under vacuum producing the glassy green solid  $\text{Cr}(\text{EH})_3 \cdot (\text{NaEH})_{0.1}$  (**1**) in good yield (7.10 g, 73%) (Fig. 1). No residual THF C–O stretches were observed in the FT-IR spectra. The material was soluble in pentane, toluene and diethyl ether but was insoluble in methanol and acetone. Numerous attempts to crystallize the complex were unsuccessful. Anhydrous starting materials and solvents were critical to successful preparation of **1**. Reactions performed using THF with a water content above 20 ppm W (measured by Karl–Fischer titration) produced only  $\text{Cr}_3\text{O}(\text{EH})_6(\text{H}_2\text{O})_3^+$ .

Many metal carboxylates exist as liquid crystals; however, complex **1** did not produce diffraction peaks when analysed by

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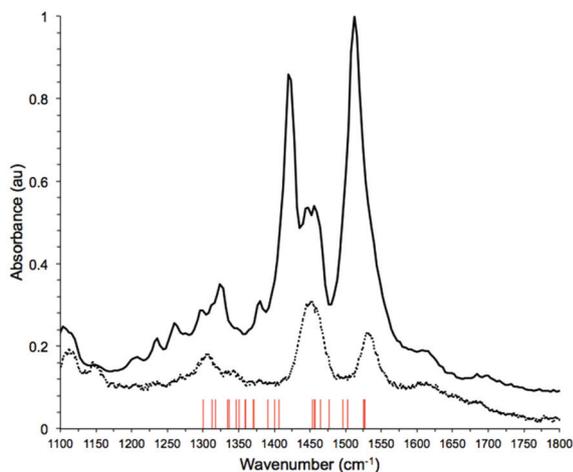


Fig. 1 Calculated frequencies (red vertical bars) and experimental IR (black solid line) and Raman (dotted black line) spectra of **1**.

powder X-ray diffraction nor was birefringence detected by polarized light.<sup>17</sup> Elemental analysis was consistent with the proposed chemical composition [%C expt. (predicted), 59.5 (59.8); %H, 9.7 (9.4); %Cl, <0.1 (0)]. ICP-OES analysis demonstrated the presence of chromium (12.4%) and sodium (0.5%) although the chromium concentration measured higher than predicted (%Cr 10.4; %Na 0.5). The relative Na/Cr molar ratio (0.09) reflects the starting stoichiometric excess and demonstrates NaEH carry-through supporting the proposed complex formulation as  $\text{Cr}(\text{EH})_3 \cdot (\text{NaEH})_{0.1}$ . A stoichiometric excess of sodium 2-ethylhexanoate was necessary for full substitution of the chlorides. Stoichiometric reaction of 3.0 equiv. NaEH per equiv. Cr in THF produced material containing 0.5% chloride content even at extended reaction times (72 h) while 4.0 equiv. NaEH left copious amounts of sodium (5.3 wt%).

FT-IR and Raman spectroscopy are well-established diagnostic probes of carboxylate coordination mode in metal complexes.<sup>18</sup> The difference in wavenumbers between the antisymmetric and symmetric  $\text{CO}_2$  stretches ( $\Delta$ ) distinguishes between monodentate or free ion ( $>200 \text{ cm}^{-1}$ ), bridging ( $200\text{--}100 \text{ cm}^{-1}$ ) and bidentate ( $<100 \text{ cm}^{-1}$ ) carboxylate bonding geometries.<sup>19</sup> The IR spectra of **1** (Fig. 1) shows an antisymmetric carboxylate stretch at  $1515 \text{ cm}^{-1}$  and a symmetric carboxylate stretch in the  $\sim 1455 \text{ cm}^{-1}$  spectroscopic region yielding a low  $\Delta$  of  $\sim 60 \text{ cm}^{-1}$ . These data support bidentate carboxylate coordination of the chromium centre and differentiates **1** from the alternative trimeric species  $\text{Cr}_3\text{O}(\text{EH})_6(\text{H}_2\text{O})_3^+$  (**2**:  $\Delta \approx 165 \text{ cm}^{-1}$ ).<sup>20</sup> The assignment of all  $\nu_{\text{CO}_2}$  stretches was supported by computational modelling (*vide infra*).

The geometries of monomeric chromium(III) 2-ethylhexanoate ( $\text{Cr}(\text{EH})_3$ ) and comparative trimeric  $\mu_3$ -oxo-hexakis- $(\mu_2$ -2-ethylhexanoato- $O,O'$ )-triaquo-trichromium(III) cation (**2**) were optimized using unrestricted DFT with the B3LYP hybrid functional<sup>21,22</sup> as implemented in Gaussian09 quantum chemistry code.<sup>23</sup> The Dunning's 'cc-pVDZ'<sup>24–26</sup> basis set was used for all elements. Normal mode coordinate analysis confirmed the

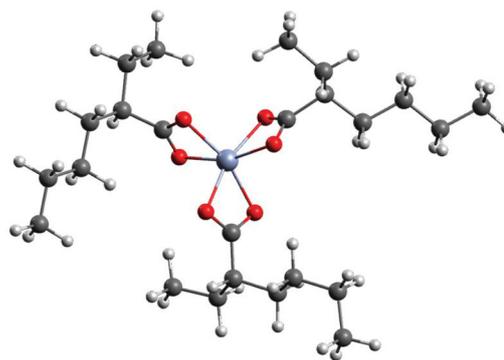


Fig. 2 DFT optimized structure of monomeric  $\text{Cr}(\text{EH})_3$ .

structure to be a local minimum. DFT calculations converged on a quartet ground spin state for  $\text{Cr}(\text{EH})_3$ , while **2** had a doublet ground spin state ( $T = 0 \text{ K}$ ) which is consistent with low temperature experimental data.<sup>27</sup>

The DFT optimized  $\text{Cr}(\text{EH})_3$  structure shows several interesting features (Fig. 2). The three carboxylate alkyl chains radiate from the  $\text{CrO}_6$ -core to form a propeller-shaped molecule. This conformation minimizes steric interaction between the secondary alkyl groups but also leaves the chromium center exposed in the axial positions. This steric unsaturation suggests that  $\text{Cr}(\text{EH})_3$  should react rapidly with Lewis bases; indeed, exposure of a methylcyclohexane solution of **1** to  $\frac{1}{2}$  equivalent  $\text{H}_2\text{O}$  per chromium rapidly formed a violet colored solution. The chromium coordination geometry is that of a distorted octahedron with the  $\text{CrO}_6$  core maintaining  $D_3$  symmetry.  $\kappa^2$ - $O,O'$ -Coordination of the carboxylate ligands enforces a small average bite angle ( $\angle \text{O-Cr-O} = 65^\circ$ ) and leads to bending of the average axial  $\text{O-Cr-O}$  bond angle to  $162^\circ$ . Additionally, the average carboxylate  $\text{O-C-O}$  bond angle ( $116^\circ$ ) is reduced from that of the free ion ( $123^\circ$ ).<sup>28</sup>

Table 1 presents the vibrational normal modes associated with the carboxylate groups, as their characteristic absorptions reflect the differences in molecular structure of Cr-carboxylate complexes. The assignment of the experimental frequencies is based on the observed band frequencies and intensities in the infrared and Raman spectra confirmed by atomic displacements vibrational mode analysis establishing a one-to-one correlation between observed and theoretically calculated frequencies. Notably, the strong band at  $1420 \text{ cm}^{-1}$  in the deconvoluted IR spectrum of **1** is assigned mostly to the CH bending modes of the alkyl chains of the 2-ethylhexanoate ligand based

Table 1 Frequencies and assignments of the vibrational modes associated with the  $\text{CO}_2$  groups of **1** and **2** based upon B3LYP/cc-pVDZ optimized structures

Frequencies ( $\text{cm}^{-1}$ )	<b>1</b>	<b>2</b>
$\nu_{\text{antisym}}$	1510–1527	$\sim 1650$
$\nu_{\text{sym}}$	1452–1464	$\sim 1485$
$\Delta$ (difference)	$\sim 60$	$\sim 165$

on the calculated vibrational data. Additionally, 2-ethylhexanoic acid was absent from the spectra and the region between 3200–3600  $\text{cm}^{-1}$  exhibited no OH stretch frequencies consistent with maintenance of an anhydrous synthetic environment. Only the monomer bidentate structure  $\text{Cr}(\text{EH})_3$  shows good agreement with the experimental IR/Raman spectra of **1**, since the spectroscopic region above  $\sim 1540 \text{ cm}^{-1}$  does not show the computationally predicted intense antisymmetric  $\text{CO}_2$  band of the trimeric Cr species **2**.

Field Desorption Mass Spectrometry (FD-MS) study of **1** showed a significant peak at  $m/z$  481.28 corresponding to the molecular ion peak of the ionized  $\text{Cr}(\text{EH})_3$  monomer ( $\text{C}_{24}\text{H}_{45}\text{O}_6\text{Cr}^+$ ). A unique fragmentation peak at  $m/z$  127.11 was also observed consistent with C–O cleavage of the coordinated 2-ethylhexanoate group to produce the corresponding acylium ion ( $\text{C}_8\text{H}_{15}\text{O}^+$ ). Neither peak was observed in an authentic sample of basic trimeric chromium(III) 2-ethylhexanoate. Peaks corresponding to trimeric  $\text{Cr}_3\text{O}(\text{EH})_7^+$  and tetrameric  $\text{NaCr}_4\text{O}_2(\text{EH})_9^+$  were observed in **1** at  $m/z$  1173.68 and 1551.91 respectively. It was not possible to verify product purity *via* this technique since FD-MS is known to facilitate oligomerization during ionization.<sup>29</sup>

High-energy X-ray diffraction was used to further probe the structure of **1**. X-rays with an incident energy of 115 keV were used at beamline 11-ID-C of the Advanced Photon Source (APS), with a Mar345 image plate detector. The data were analysed using the FIT2D and PDFgetX2 analysis packages.

A plot of the  $g(r)$  distribution on the  $r$  region that spans the intramolecular interactions of interest is shown in Fig. 3 along with bonding pair assignments from Table 2. All major bonding pairs are well-matched by the experimental data and align closely with their predicted values. Significantly, no Cr...Cr bond pairs are evident between the 3–4 Å region further supporting characterization of **1** as a monomer.

The magnetic susceptibility of **1** under an applied field of 1 T was measured by SQUID over the temperature range

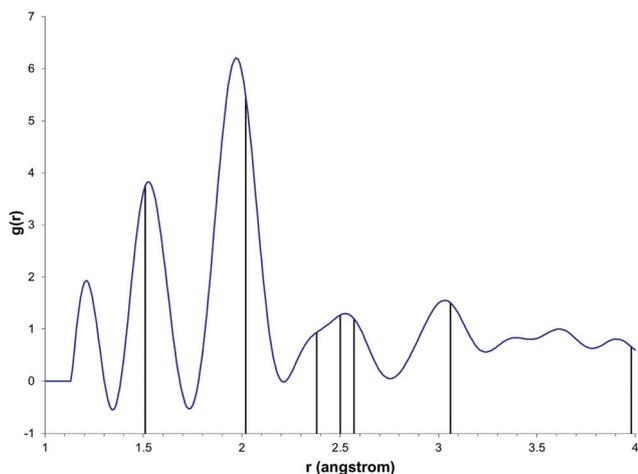


Fig. 3 Plot of  $g(r)$  versus  $r$  for calculated (black) and experimental (blue) **1**.

Table 2 Average B3LYP/cc-pVDZ optimized structural parameters of monomer  $\text{Cr}(\text{EH})_3$

Labels	Length (Å)
$\text{C}_{\text{carbox}}-\text{C}_{1(\text{chain})}$	1.51
$\text{C}_{(\text{chain})}-\text{C}_{(\text{chain})}$ (adjacent)	1.55
$\text{Cr}-\text{O}_{\text{carbox}}$	2.02
$\text{O}-\text{O}_{\text{intra}}$	2.18
$\text{Cr}-\text{C}_{\text{carbox}}$	2.38
$\text{C}_{\text{carbox}}-\text{C}_{2(\text{conjugate})}$	$\sim 2.5$
$\text{C}_{(\text{chain})}-\text{C}_{(\text{chain})}$ (conjugate)	$\sim 2.57$
$\text{O}-\text{O}_{\text{inter}}$	3.06
$\text{O}-\text{O}_{\text{inter}}$	3.98

5–325 K. The room temperature effective magnetic moment ( $3.4\mu_{\text{B}}$ ) is consistent with that predicted for a high spin  $d^3$  ion ( $\mu_{\text{eff}} = 3.9\mu_{\text{B}}$ ). The UV/VIS spectrum of **1** also supports the Cr(III) oxidation state assignment. The room temperature electronic spectrum of **1** in the visible region exhibits two broad absorption peaks at  $\lambda_{\text{max}}(\text{ethylbenzene})/\text{nm}$  448 ( $\epsilon/\text{M}^{-1} \text{ cm}^{-1} = 54$ ) and 600 ( $\epsilon/\text{M}^{-1} \text{ cm}^{-1} = 47$ ) as expected for a quartet ground spin state in a pseudo-octahedral coordination environment.

The effective magnetic moment ( $\mu_{\text{eff}}$ ) decreases monotonically with decreasing temperature going from  $3.4\mu_{\text{B}}$  at 325 K to  $1.0\mu_{\text{B}}$  at 5 K (Fig. 4). The temperature dependent decrease in  $\mu_{\text{eff}}$  shows antiferromagnetic behaviour. Modelling the spin interactions was not attempted since the exact nature of this magnetic interaction is unknown. However, while antiferromagnetic behaviour is most commonly thought of in terms of a through-bond exchange mechanism, examples exist of through-space exchange leading to antiferromagnetism.<sup>30</sup>

In conclusion, the first monomeric, neutral homoleptic chromium(III) carboxylate has been synthesized by anhydrous salt metathesis. This is the first time this structural type has been unambiguously characterized for chromium(III). Rigorous anhydrous conditions before and after synthesis are necessary to achieve and maintain complex stability. Unlike trimeric basic chromium(III) carboxylates, the complex is soluble in aliphatic solvents and is water and acid-free making it compatible with catalyst activators intolerant of protic sources.

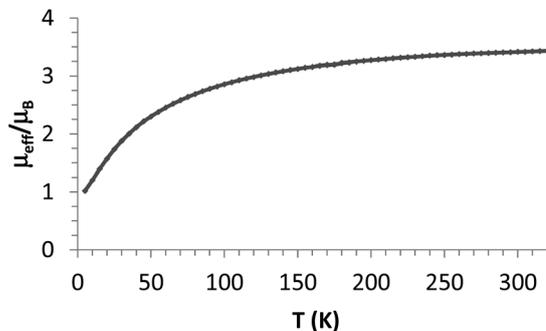


Fig. 4 Temperature dependence of the effective magnetic moment of **1** under an applied field of 1 T.

## Conflicts of interest

There are no conflicts to declare.

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