



Synthesis, crystal structure and magnetic properties of trinuclear chromium(III) basic carboxylate assembly: $[\text{Cr}_3\text{O}(\text{salH})_7(\text{H}_2\text{O})_2]$ ($\text{salH}_2 = \text{salicylic acid}$), a new member of $[\text{Cr}_3\text{O}]$ family



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ABSTRACT

Synthesizing a novel trinuclear chromium(III) basic carboxylate complex could give rise to new materials with interesting properties. Complex $[\text{Cr}_3\text{O}(\text{salH})_7(\text{H}_2\text{O})_2]$ is formed in a one-pot, self-assembly reaction when the inert reaction mixture is exposed to dioxygen. The structural property of the complex has been acquired by single-crystal X-ray crystallography and further characterized by elemental analysis (EA), infrared (IR), UV–Visible (UV–Vis), fluorescence spectroscopy and thermo gravimetric and differential thermal analysis (TG–DTA). X-ray structural analysis shows a slightly distorted equilateral of the Cr triangle. The most important feature of the title complex is the unusual framework of the $[\text{Cr}_3\text{O}]$ family due to a terminal $\text{Ph}(\text{OH})\text{CO}_2^-$ ion of Cr(2) center, which is unique among the structurally characterized (μ_3 -oxo)-trichromium(III) complexes. Variable-temperature magnetic susceptibility studies indicate that the total spin value of the ground state is $1/2$.

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1. Introduction

Oxygen-centered trinuclear metal complexes have been known for over a century [1]. Especially in 1965, the first structure of the $[\text{Cr}_3\text{O}(\text{OOCR})_6\text{L}_3]$ was determined by X-ray diffraction [2], and the research of the $[\text{M}_3\text{O}]$ clusters have aroused great scientific interest. Most of the M_3O clusters are of general type $[\text{M}_3\text{O}(\text{OOCR})_6\text{L}_3]$ ($\text{M} = \text{Cr, Mn, Fe, Ru}$; $\text{R} = \text{an organic group, L} = \text{water, methanol or pyridine etc.}$). Within this family, these multinuclear carboxylate assemblies of Cr(III) have been of considerable interest, which are a structural and functional mimetic of chromodulin [3] and a safer potential therapeutic agent for Type II diabetes [4].

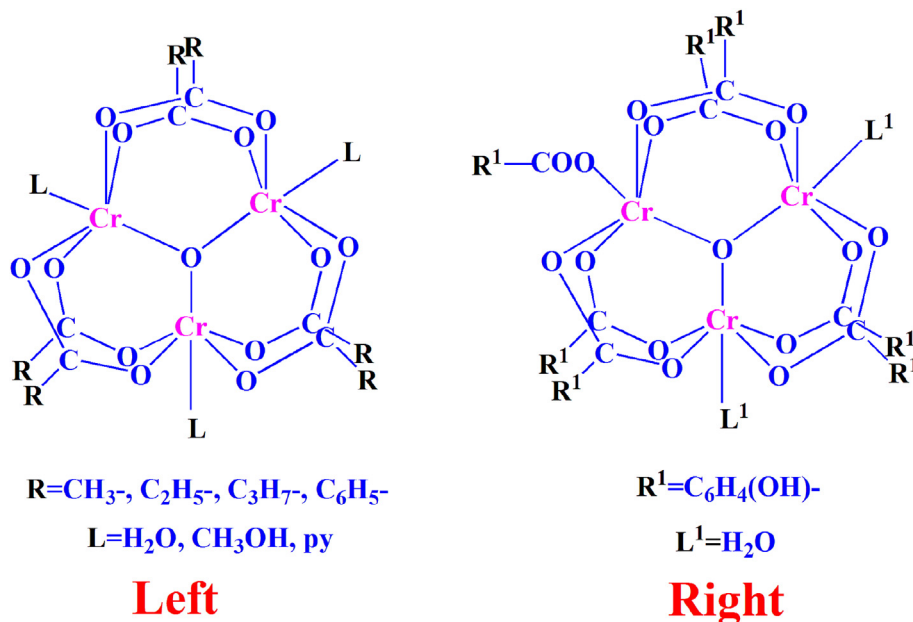
Perusal of the literature [5] reveals that most of M_3O complexes are widely used as models for testing magnetic and electronic properties. For instance, several multinuclear complexes of Fe(III) and Mn(III) have been proven to be single molecule magnets [6–9]. However, molecule magnets of this type containing Cr(III) centres are very limited [5f,10]. In fact, trinuclear Cr(III) complexes have normal magnetic property called spin frustration [11], because the

three pairwise interactions are antiferromagnetic. The ground state of these trinuclear Cr(III) assemblies with net $S_T = 1/2$ then is of intermediate spin, intermediate between the highest and the lowest spins possible for the three metal ions. The unpaired electrons of each $\text{Cr(III)} \cdots \text{Cr(III)}$ center attempt to have their spins aligned in opposite direction, but it is impossible for a triangle of Cr(III) ions, leaving the Cr(III) ions “frustrated” and resulting in a degenerate ground state. Owing to the magnetic Jahn–Teller effect [10], a subtle distortion of the equilateral Cr triangle is formed, and the symmetry lowering is often observed by spectroscopy or structural analysis.

According to some literature [5f,10,12] report, these trinuclear Cr(III) carboxylate assembly units could potentially serve as new materials with interesting properties. The ligand salicylic acid (salH_2) was chosen originally because of its abundant utility, such as antipyretic, analgesic, anti-inflammatory and bioactivity, etc [13], the similar structure with that of aspirin. Based on the above thought, herein, we synthesized a new trinuclear complex, $[\text{Cr}_3\text{O}(\text{salH})_7(\text{H}_2\text{O})_2]$, in contrast to the reported carboxylate-bridged clusters. Although their structures are similar, the major difference among them is that the complex reported in this article is neutral molecule with $[\text{Cr}_3\text{O}]^{7+}$ connected with seven salicylic acid ligand (see Scheme 1 Right). To our knowledge, this kind of

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Scheme 1. Schematic structural features of the known $[\text{Cr}_3\text{O}]$ family (L), and our new complex (R).

Cr(III) centres with salicylic acid ligand was first reported, thus adding a new member for the $[\text{Cr}_3\text{O}]$ family. Toward this end, syntheses, crystal structure, spectra TG–DTA and magnetic properties of $[\text{Cr}_3\text{O}(\text{salH})_7(\text{H}_2\text{O})_2]$ are presented.

2. Experimental

2.1. General procedures

All chemicals were of analytical reagent grade and used without further purification.

Microanalytical data (C, H and N) were obtained with a Perkin–Elmer model 240 C elemental analyzer. The FT-IR spectra were determined on a Nicolet is5 infrared spectrometer by dispersing samples in KBr disks in the $4000\text{--}400\text{ cm}^{-1}$. The crystal data of the title complex were collected on Bruker [Smart2000] diffractometer. The thermo gravimetric analysis was carried out under nitrogen condition on a Rigaku Thermo plus Evo TG 8120 instrument at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$, from 35 to $800\text{ }^\circ\text{C}$. The UV–Visible absorption spectra were recorded on Cary 50 Bio spectrometer and the fluorescence spectroscopy were performed on a Varian Cray Eclipse fluorescence spectrometer.

2.2. Synthesis

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5506 g, 2.06 mmol) was added to ethanol (20 ml) and stirred under reflux for 10 min to give a green–purple solution. Then, sodium salicylate ($\text{NaO}_2\text{C}(\text{OH})\text{Ph}$) (0.6613 g, 4.13 mmol) was added and the reflux continued for another 3 h to give a deep green solution. After cooling of the solution at room temperature, Et_2O (30 ml) was added and the precipitated NaCl was removed by filtration. The final solution was evaporated to produce a green powder, which was dissolved in cold ethanol (15 ml). Green crystals, suitable for X-ray structure analysis, were grown by slow evaporation at room temperature of the green ethanol solution after two weeks. The crystals were filtered off and dried in vacuo. Yield: 1.58 g (68%). The dried solid analyzed as solvent-free, i.e., Anal. Calc. for $\text{C}_{49}\text{H}_{39}\text{Cr}_3\text{O}_{24}$ (%): C, 50.34; H, 3.34. Found: C, 49.72; H, 3.48.

2.3. X-ray Crystallography and structure solution

A single crystal with suitable dimensions for X-ray diffraction analyses was mounted on a glass rod, the crystal data were collected with a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo–K α radiation (0.71073 Å) at 293 K. In all cases intensity data were measured by thin-slice χ or ω - and ω -scans. The method used to solve the structure was direct method and the structure was further expanded using Fourier difference techniques with the SHELXTL-97 program package [14]. Absorption corrections were carried out using the SADABS program supplied by Bruker [15]. The anisotropic refinement was applied for all non-hydrogen atoms while hydrogen atoms in all samples were included in idealized positions and their Uiso values were set to ride on the Ueq values of the parent carbon, nitrogen or oxygen atoms. Details of the crystallographic data collection, structural determination and refinement are summarized in Table 1. Selected bond lengths (Å) and angles ($^\circ$) of complex are shown in Table S1. For crystallographic

Table 1
Summary of crystal structure details for complex $[\text{Cr}_3\text{O}(\text{salH})_7(\text{H}_2\text{O})_2]$.

Formula	C49 H39 Cr3 O24
Crystal system	Triclinic
Space group	P-1
Formula weight	1167.80
<i>a</i> (Å)	12.8373(12)
<i>b</i> (Å)	15.8346(16)
<i>c</i> (Å)	18.2007(18)
α ($^\circ$)	79.2310(10)
β ($^\circ$)	76.0510(10)
γ ($^\circ$)	80.423(2)
<i>V</i> (Å ³)	3498.7(6)
<i>Z</i>	2
<i>T</i> (K)	298(2)
λ (Å)	0.71073
ρ (g·cm ⁻³)	1.109
Rint	0.0553
R_1 [$I > 2\sigma(I)$] ^a	0.0811,
wR_2 [$I > 2\sigma(I)$]	0.1968,

^a $R = \sum (|F_o - F_c|) / \sum |F_o|$. $wR_2 = \{ \sum [w(|F_o - F_c|)^2] / \sum [w|F_o|^2] \}^{1/2}$.

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