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Synthesis and structural characterization of *tris*(methacrylato)chromium(III)

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A straightforward synthetic route to produce *tris*(methacrylato)chromium(III), $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$, by reacting sodium methacrylate with an aqueous solution of CrCl_3 gave a blue microcrystalline powder, insoluble in most common solvents. Electronic spectroscopy (UV-Vis), electron paramagnetic resonance (EPR), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), were employed to characterize $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$. Morphology and elemental composition of this compound were determined using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX), respectively. Spherical particles of approximately 2.5 μm in diameter were obtained. Thermal stability of the product was investigated via thermogravimetric analysis (TGA). The spectroscopic studies revealed that the coordination sphere around the chromium ion corresponds to a chelating bidentate carboxylate-Cr(III) complex. Thermal stability above 350°C, and spherical shape particles of few micrometers in diameter, suggest a potential application of this novel compound as a catalyst in oxidation reactions.

Keywords: Chromium(III) complexes; Methacrylate ligand; X-ray photoelectron spectroscopy

1. Introduction

Several chromium(III) carboxylate complexes have been used as catalysts. For instance, α -olefins can be polymerized at high levels of activity employing a supported chromium(III) compound obtained from the reaction of a chromium(III) carboxylate and an aluminum alkoxide as catalyst [1]. These types of catalysts are the new generation of the well known Phillips catalyst [2]. Moreover, patented commercial products containing chromium(III) are very useful for different manufacturing industries. Tanning agents contain a complex formed between chromium ions and an acrylate or methacrylate polymer and further include an organically bound thio group,

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which is present in the polymer or in a mercapto compound added to the tanning agents [3]. Also, there is an effective method of reacting oxirane-containing compounds with carboxylate-containing compounds at temperatures at or around ambient, in the presence of active chromium(III) tricarboxylate salts. These compounds are powerful catalysts for reactions of oxirane compounds with both organic carboxylic acids and cyclic primary imides [4]. Chromium(III) methacrylate is the basis of a series of products of Dupont, known commercially as Volan, which are useful as coupling agents and adhesion promoters for various composites [5]. Although methacrylate-metal compounds have been known for many years [6], to date none has been obtained as a single crystal; consequently, very little is known about the structure of these materials. There are relatively few recent studies based on infrared spectroscopy, for methacrylate-metal ion complexes, including our investigation on the aluminum(III) methacrylate monomer [7–9]. Further research is needed exploring structural characteristics of these potential functional materials.

In this article, we report an easy synthesis of the microcrystalline and micrometric novel tris(methacrylato)chromium(III), $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$, and its structural and morphological characterization employing X-ray photoelectronic and IR spectroscopic methods, scanning electron microscopy, electron paramagnetic resonance and thermogravimetric analysis.

2. Experimental

2.1. Synthesis of tris(methacrylato)chromium(III)

Reagent grade methacrylic acid (MAc) (Aldrich), NaHCO_3 (Aldrich) and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (J.T. Baker), were employed without purification. De-ionized water was used to prepare all the solutions. Briefly, NaHCO_3 (aq) (1.23 g, 14.66 mmol) was added to an equivalent amount of $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOH}$ (1.22 g, 14.16 mmol), and the solution was stirred for 30 min at room temperature. Then, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (1.30 g, 4.88 mmol) was poured, while stirring, to the freshly prepared sodium methacrylate ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COONa}$) solution. This mixture was stirred for two hours at 40°C . $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ precipitated as a blue powder, which was isolated by filtration, washed thoroughly with de-ionized water and vacuum-dried.

2.2. Structural characterization

$\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ morphology was analyzed and imaged with a PHILIPS XL-30 scanning electron microscope (SEM) at 25 kV equipped with a detector for energy dispersive X-ray analysis (EDAX). Samples were fixed on a support with a copper film and sputter-coated with gold to a thickness of $\sim 200 \text{ \AA}$.

Electronic spectra (200–3000 nm) were obtained at room temperature using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Samples were prepared as Nujol mulls pressed between quartz plates.

Electron paramagnetic resonance analyses were carried out at room temperature using a Varian E-15 spectrometer operated at the X-band as follows: scan range 2000 G, time constant 3 s, modulation amplitude 2×10^0 , received gain 2.5×10^1 , microwave

power 1.0 mW, modulation frequency 100 kHz, microwave frequency 9.5 GHz, and the field was set at 320 mT. Sample was run in the powder form at room temperature and diphenylpicrylhydrazyl (DPPH) ($g=2.0036$) was used as a field reference.

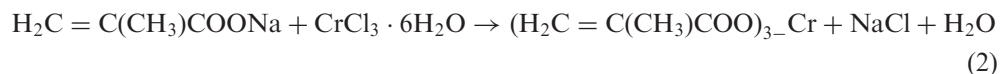
FTIR spectra were obtained with a Nicolet-FTIR 550 spectrophotometer using KBr pellets. Thermal degradation of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ was performed using a TA Instruments TGA-51 calibrated with a standard of calcium oxide. Experiments were conducted from 20 to 800°C, with a heating rate of 10°C min⁻¹, under nitrogen; sample weight was around 10 mg.

X-ray photoelectron spectroscopy (XPS) was performed on a VG Microtech MultiLab ESCA 3000 using an X-ray source 8025 photoelectron spectrometer equipped with a dual Mg/Al anode. The excitation radiation was Mg-K α X-ray ($h\nu=1253.6$ eV). The X-ray generator was operated at 15 kV and 16 mA beam density. The vacuum during analysis was maintained at 8×10^{-9} mb. The sample surface was etched during one minute with Ar ions at 3 kV in 0.11 $\mu\text{A cm}^{-2}$. The peak positions were referenced to the background carbon 1s photo peak at 285.00 eV. High resolution XPS spectra for Cr, O and C were fitted with the program SDP v 4.1 [10]. The XPS spectrum was obtained at 55° of the normal surface in the constant-pass energy mode, $E_0=50$ eV and 20 eV for survey and high-resolution narrow scan, respectively. The atomic relative sensitivity factor (RSF) was corrected using the transmission function of the analyzer [11] and by reference to Cr_2O_3 and CrN.

3. Results and discussion

3.1. Synthesis of tris(methacrylato)chromium(III)

$\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ was obtained following the synthetic route used by Galvan, *et al.* [12] to prepare iron(III) methacrylate, according to the following reactions:



Maintaining the reaction temperature at 40°C is critical for the formation of the desired product, and to avoid homopolymerization of methacrylate. A yield of ~75% was achieved, as determined by gravimetric measurements. A solubility test was performed for $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$, which was insoluble in water, ethanol, isopropanol, acetone, tetrahydrofuran and ethyl ether.

3.2. Structural characterization

3.2.1. Electronic spectroscopy (UV-Vis). Figure 1 shows the UV-Vis spectrum of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$. Three electronic transitions can be observed at 248, 416 and 576 nm. These electronic transitions have been observed in many complexes of chromium(III). The bands at higher wavelength (figure 1) correspond to the spin-allowed transitions: ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$, respectively, and the band at lower

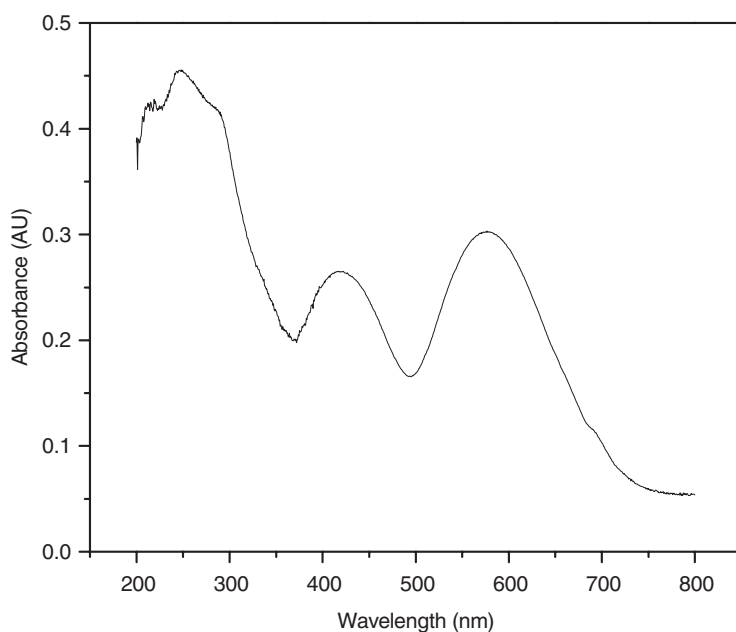


Figure 1. UV-Vis spectrum of *tris*(methacrylato)chromium(III).

wavelength is attributed to charge transfer. Therefore, our results are in agreement with established transitions, indicating that in $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ the chromium ion exhibits an oxidation state of III and an octahedral coordination sphere [13].

3.2.2. Electron paramagnetic resonance (EPR). Figure 2 shows the EPR spectrum of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$. A single line with $g = 1.979$ can be observed due to the presence of Cr^{3+} . The EPR spectrum obtained is expected for a spin $S = 3/2$, where the allowed EPR transitions $+3/2 \rightarrow +1/2$, $+1/2 \rightarrow -1/2$, and $-1/2 \rightarrow -3/2$ coincide and a single line results. This is in agreement with the extensive magnetic resonance investigations that have been carried out on Cr^{3+} in different crystal fields (cubic, tetragonal and orthorhombic) [14, 15].

3.2.3. Infrared spectroscopy (FT-IR). FT-IR spectra for $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ (figure 3) show the bands for water, a narrow band at 3690 cm^{-1} (O–H stretching of coordinated water) and a broad band at $3600\text{--}3200\text{ cm}^{-1}$ O–H from adsorbed water [9] and at 1645 cm^{-1} a double bond carbon-carbon band, at 939 cm^{-1} the bending vibration of a terminal vinyl group, and at 520 cm^{-1} for Cr–O. In general, the spectrum shows the characteristic infrared absorptions of metal-methacrylates [16], a strong asymmetric and a weak symmetric stretching mode of the carboxylate ion at 1528 and 1423 cm^{-1} , respectively, and the absence of a C=O stretching vibration at 1700 cm^{-1} . According to our IR results and the investigations carried out by Deacon and Phillips in studies on carboxylate complexes, $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ should possess a chelating bidentate structure for the methacrylate [17].

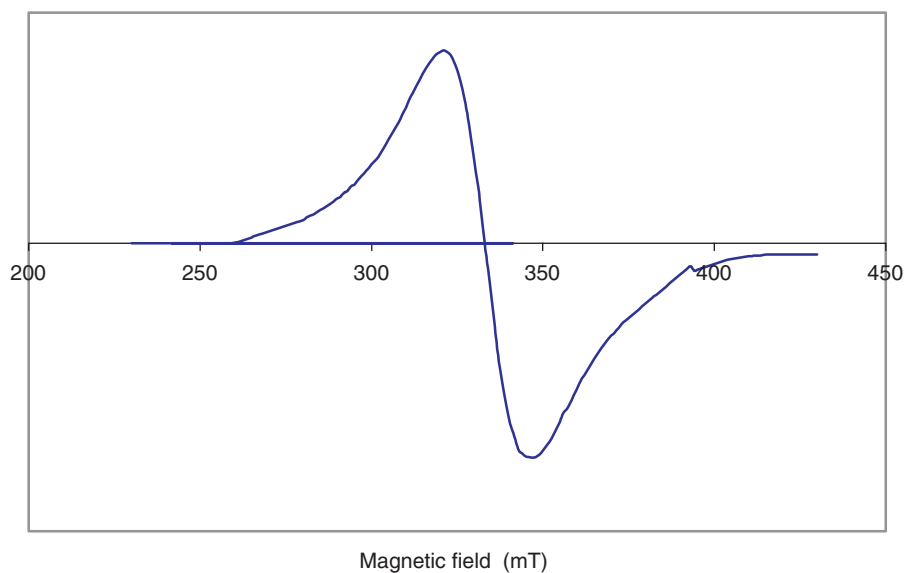


Figure 2. EPR spectrum of *tris*(methacrylato)chromium(III).

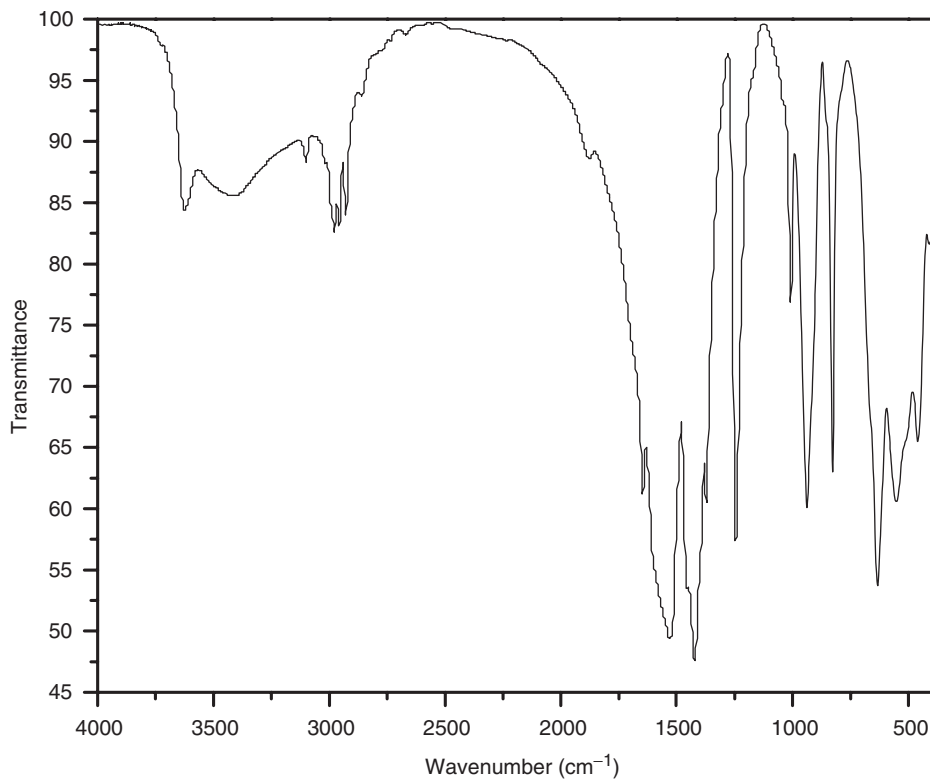


Figure 3. FT-IR spectrum of *tris*(methacrylato)chromium(III).

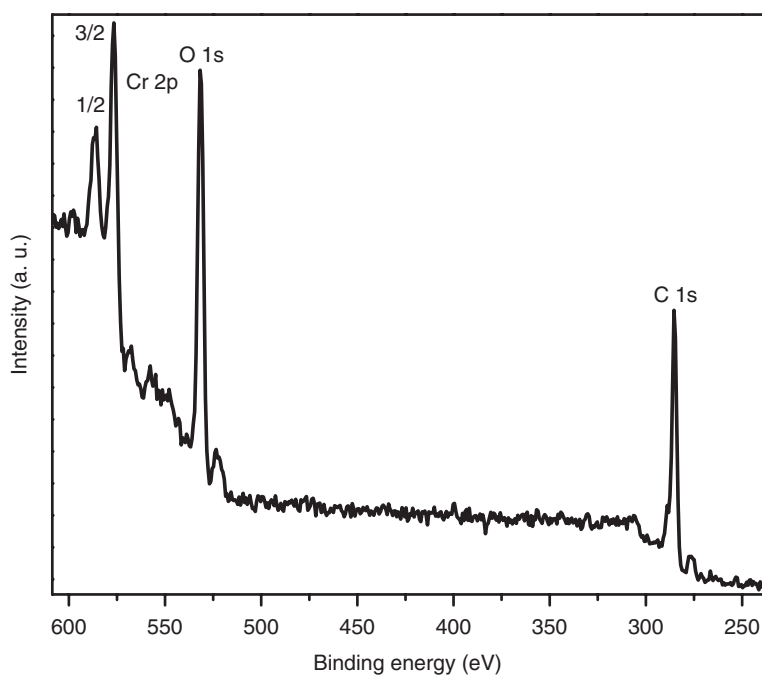


Figure 4. XPS survey spectrum of *tris*(methacrylato)chromium(III).

3.2.4. X-ray photoelectron spectroscopy. Figure 4 shows the XPS survey spectrum of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$. The expected elements C, O and Cr were detected with a Cr elemental concentration of $\sim 8.7\%$. Figure 5 shows the high-resolution XPS spectra of C 1s, O 1s and Cr 2p regions for the sample after 1 min of etching. From the fitting of Cr 2p and O 1s regions, the peaks at 577.26 eV for Cr $2p_{3/2}$ and 586.55 eV for $2p_{1/2}$ correspond to Cr^{3+} for Cr–O, and the O 1s peak, positioned at 533.44 eV, can be assigned to Cr–O. The other peaks of the high resolution spectra for C 1s and O 1s correspond to C=O (289.33 eV), CH_2 (286.56 eV), CH_3 (285.00 eV) and C=C (285.80 eV) for core level C 1s, respectively. In addition, the region for O 1s has two peaks, which correspond to those of poly(methacrylic acid) [18], at O=C (532.39 eV) and O–C (533.44 eV). Thus, the XPS study shows that chromium in $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ has an oxidation state of III. The electronically four different types of carbon, two types of oxygen and one type of chromium for $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ are consistent with the IR results. A plausible structure of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ is depicted in figure 6.

3.2.5. Scanning electron microscopy (SEM). EDAX studies showed that only carbon, oxygen and chromium are in $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ (figure 7). SEM images in figure 8 show the morphological characteristics of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$, with a spherical shape of approximately 2.5 μm diameter. For use as a catalyst, the size of the particles is appropriate [19–22].

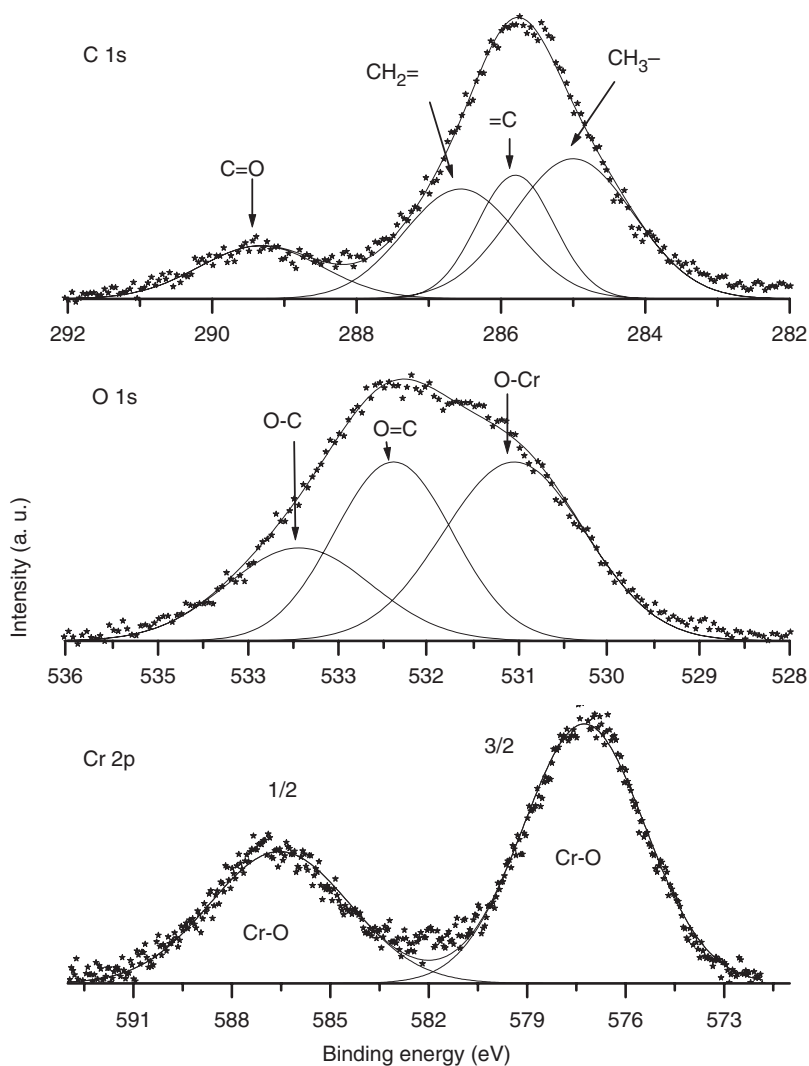


Figure 5. XPS C 1s, O 1s and Cr 2p spectra of *tris*(methacrylate)chromium(III).

3.2.6. Thermogravimetry analysis (TGA). Thermogram of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ is shown in figure 9. Two distinct mass loss regions around 75–200°C and 450°C are seen in the TGA plot. The first corresponds to the loss of adsorbed water; then, there is a continual decrease in weight between 100 and 200°C, which can be due to loss of coordinated water [23]. This is in agreement with the IR analysis of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$, which revealed bands corresponding to adsorbed and coordinated water in this compound. The second stage of mass loss corresponds to degradation of the compound. The thermal decomposition behavior shown by $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ reveals that it is stable below 300°C; therefore, it could be used as a catalyst in mild to medium temperature reactions, such as the liquid

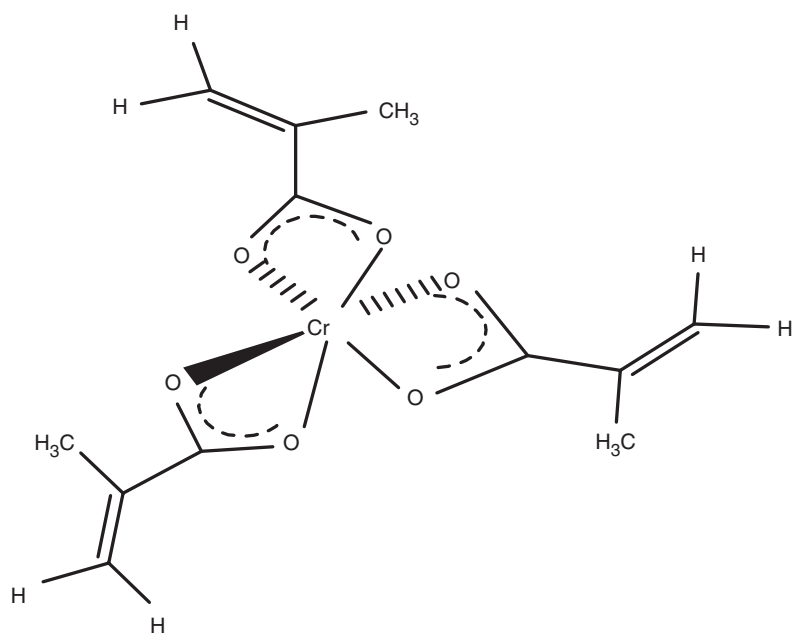


Figure 6. Proposed chemical structure of *tris*(methacrylate)chromium(III).

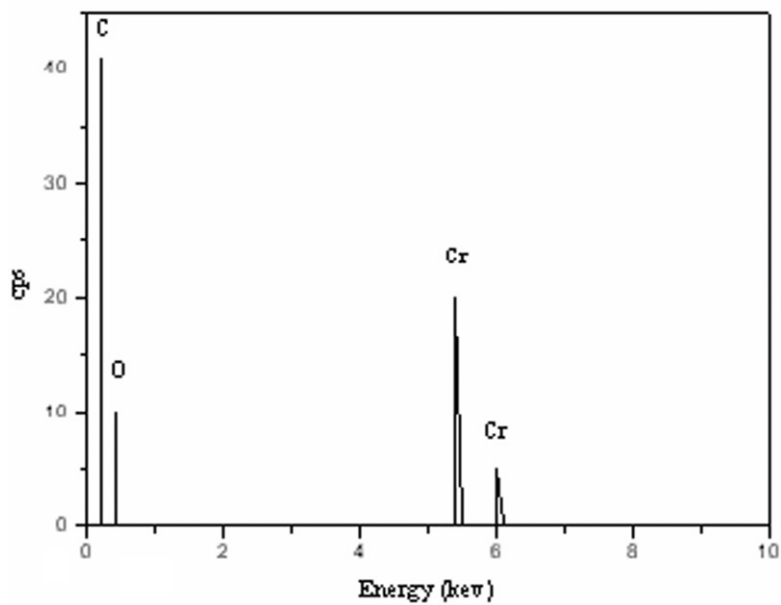


Figure 7. EDAX spectrum of *tris*(methacrylate)chromium(III).

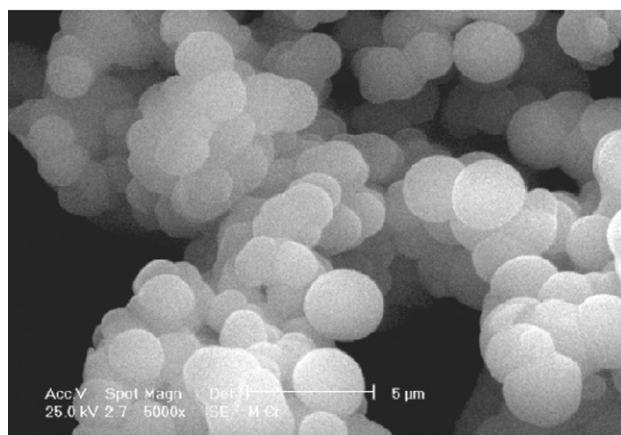


Figure 8. SEM image of *tris*(methacrylato)chromium(III).

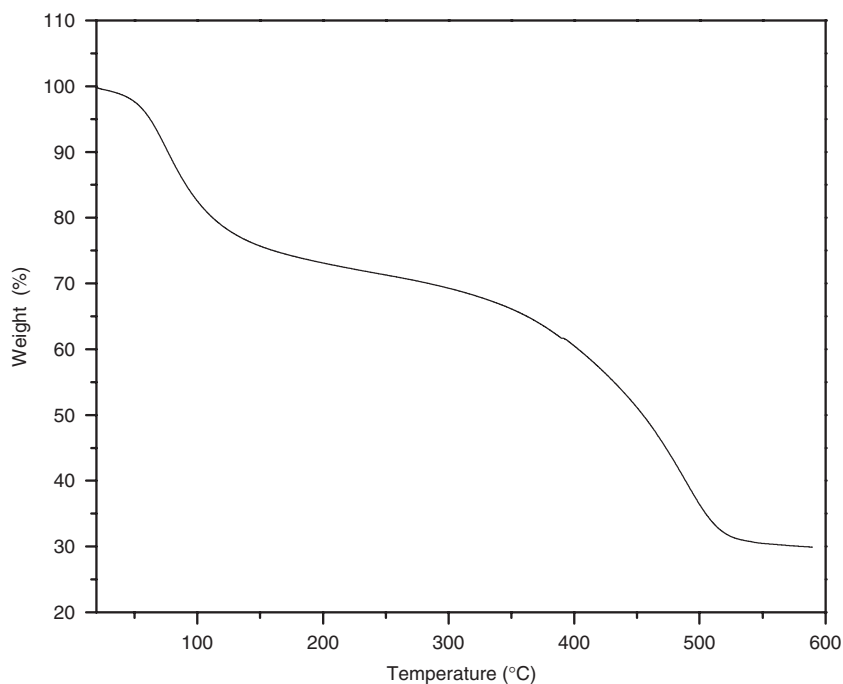


Figure 9. TG curve of *tris*(methacrylato)chromium(III).

phase oxidation of benzene and cyclohexane with H_2O_2 , at temperatures between 80–100°C, where a Cr(III) complex is used as a catalyst [24].

4. Conclusion

In conclusion tris(methacrylato)chromium(III), $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$, which has a submicrometric size, was obtained by an easy synthetic procedure. IR spectroscopy and

XPS of $\text{Cr}(\text{O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_3$ revealed a chelating bidentate coordination of the methacrylate ligands around the Cr ions. Some coordination polymers cannot be obtained as single crystals suitable for X-ray diffraction studies; therefore, the use of spectroscopic methods to elucidate the structure of such coordination monomers and polymers offers an alternative to get insight about these important materials and their potential applications. The reported results imply an important perspective for this chromium(III) carboxylate compound to be used as a catalyst in oxidation and polymerization reactions.

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