Chapter II: Synthesis of chromium(III) oxo-centered carboxylate complexes

2.1 Introduction

In the recent patent literature, Gan et al. [1-4] reported a novel route for the synthesis of trinuclear oxo-centered carboxylate complexes. In addition, they also pointed out that a specific starting material is not essential; any complex able to produce chromium salt could be used for the preparation of these types of clusters. Knowing that metal-ligand interactions may have some effect on the properties and activities of a complex in chemical reactions, a decision was made to synthesize two (μ-oxo)-centered carboxylate assemblies of chromium using different starting materials and to observe their catalytic effect in the polymerization of ethylene.

2.2 Experimental

2.2.1 Materials:

Chromium(III) chloride hexahydrate [$CrCl_3.6H_2O$] and trichloroacetic acid (Cl_3CCO_2H) were purchased from ACRŌS ORGANICS. In addition, chromium(III) nitrate nonahydrate [$Cr(NO_3)_3.9H_2O$] and trifluoroacetic acid (F_3CCO_2H) were supplied by R&M Chemicals and SIGMA-ALDRICH respectively. All solvents were analytical grade and were used as received.

2.2.2 Synthesis of Diaqua-μ_3-oxido-hexakis(μ_2-trichloroacetato-κ^2*O*:*O*')(trichloroacetato-κ*O*)-trichromium(III) trihydrate: [$Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$

$CrCl_3.6H_2O$ was refluxed with Cl_3CCO_2H in a variety of ratios and times. Evolution of brown acidic fumes was observed forty five to sixty minutes after starting the reflux. Green solutions obtained were filtered hot and cooled overnight at room temperature. The resulting light green precipitate was properly washed with chloroform to remove the excess of unreacted acid. The products were then vacuum dried at 60°C for 15 hours. The green powder obtained was weighed and analyzed.

2.2.3 Synthesis of Trinuclear trans-μ_3-oxo tris(bistrifluoroacetatoaquochromium(III))nitro hydrate: $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$.

Commercial $Cr(NO_3)_3.9H_2O$ and F_3CCO_2H were mixed, melted and heated at different ratios and times. NO_2 was evolved in the form of reddish-brown gas. The resulting solutions were immediately filtered and allowed to cool at room temperature. The mixtures were filtered and the precipitates were mixed and stirred with chloroform for at least two hours to remove the excess of F_3CCO_2H. They were then filtered off and dried under vacuum. The green prismatic products obtained were weighed and used for analysis.

2.3 Analysis of chromium(III) complexes

2.3.1 Elemental analysis

a- CHN&S elemental analyses

The percentage of carbon, hydrogen and nitrogen was carried out using an Eager 300 CHN&S elemental analyzer.

b- Titration

Both complexes were analyzed for their chromium content through a well known titrametric method [5]. About 20 mg of each sample was analyzed after oxidizing the chromium(III) salt (Cr^{3+}) content to dichromate (Cr^{6+}). The required amount of sample was first dissolved in 100 mL of water. The mixture was heated when required to get a homogeneous solution. The green solution was acidified with sulfuric acid (H_2SO_4) and later treated with 2 mL of silver nitrate 0.1 M solution to precipitate the halide ions present in the system. This was followed by a treatment with an excess of potassium persulphate. The mixture was then boiled for about 20 min to fully oxidize ions Cr^{3+} to Cr^{6+} and destroy the unreacted potassium persulphate. The orange solution obtained was cooled at room temperature. After cooling, concentrated hydrochloric acid (HCl) and potassium iodide (KI) were added followed by drops of starch solution. The mixture was then titrated against standardized sodium thiosulphate solution. From the number of moles of chromium obtained by titration, the percentage of chromium in each complex could be determined.

2.3.2 Thermogravimetry analysis (TGA)

Thermal analyses were carried out using a Perkin Elmer TGA model 6 instrument and the measurements were done with about 20 mg of sample, under nitrogen atmosphere flow rate of 20 mL/min and in a temperature range of 50-900 ºC with a heating rate of 10 ºC/min.

2.3.3 Fourier Transfer Infra red spectroscopy (FTIR)

FTIR spectra were recorded at room temperature, within the range of 4000-400 cm^{-1}, using a Perkin Elmer FTIR spectrometer model RX-1. About 20 mg of each complex was mixed and ground with the required amount of dried potassium bromide (KBr). The mixture was then pressed into a KBr disc before recording the spectrum.

2.3.4 Magnetic Susceptibility measurement

The magnetic susceptibility of complexes were determined by the Gouy method [6], at room temperature using $Hg[Co(NCS)_4]$ as calibrating agent. Each complex was first finely ground then pressed into a glass tube, previously weighed. In addition, the mass susceptibility (X_g) was obtained through the gouy balance with the full tube and the calculation of molar susceptibility (X_m) was made by multiplying the mass susceptibility (X_g) by the molecular weight (M_w) of each complex. The corrected molar susceptibility (X_m^{corr}) was obtained by the formula molar susceptibility (X_m) - diamagnetic susceptibility (X_{dia}). The obtained X_m^{corr} was then used to calculate the magnetic susceptibility of the complex through the formula: $\mu_{eff} = 2.828(X_m^{corr}.T)^{1/2}$. In addition, the number of unpaired electrons was calculated through the formula: $\mu_{eff} = [n(n+1)]^{1/2}$.

2.3.5 Single crystal X-ray structure determination.

The X-ray diffraction experiments were carried out by means of a Bruker SMART APEX diffractometer operating with graphite-monochromated Mo-Kα radiation (λ=0.71073Å) from a fine focus tube. The intensity data collection was carried out using the ω scan mode. Reflections were measured and the intensities were corrected for absorption by means of a multi scan method [7]. Data reduction of measured intensities was by the SAINT program package [8]. X-SEED [9] was used for the molecular graphics. The structure solutions, obtained using automatic direct methods, and the refinement, using full-matrix least-squares on F^2, were done by means of the SHELXTL97 system of programs [10].

a. X-ray diffraction experiments of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$

About 5 mg of chromium complex was dissolved into 5 mL of acetonitrile and kept in the refrigerator. After three days, dark green prismatic crystals, suitable for single X-ray were grown and a crystal of 0.25 x 0.20 x 0.15 mm was chosen for the analysis. Over 29,000 reflections were measured at temperature of 100 (2) K. Cell parameters were obtained from 9535 reflections in the range of $2.2^o \leq \theta \geq 28.2^o$.

Hydrogen atom sites were located from difference Fourier maps but refined with a mixture of independent and constrained refinements.

b. X-ray diffraction experiments of $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$

In comparison with the first complex, the X-ray crystal of $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ was obtained directly from the preparation. A shiny green, hexagonal shaped crystal with dimensions 0.50 x 0.50 x 0.10 mm was selected and subjected to room temperature [293 (2) K] diffraction studies. Over 11,000 reflections were collected and the unit cell parameters were obtained from 1694 reflections in the range of $2.10^o \leq \theta \geq 30.54^o$.

2.4 Results and discussion

Both complexes are stable at ambient atmosphere. They are soluble in polar solvents such as water, methanol, ethanol, isopropyl alcohol, acetone, acetonitrile and tetrahydrofuran and partially soluble in ethyl methylketone. They are insoluble in non polar solvents such as toluene, hexane and chloroform.

2.4.1 Influence of reactant ratio and reflux time on the synthesis

(i). Chromium(III) trichloroacetate:

$$CrCl_3.6H_2O + Cl_3CCO_2H \longrightarrow [Cr_3\text{-}(\mu\text{-}O)(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$$

The appropriate reaction conditions were determined through trial and error and were essential to maximize the product yield. From earlier synthesis[1], it appeared that a poor yield could be obtained when the Cr / Cl_3CCO_2H ratio was 1:4 and the refluxing time was five hours. Monitoring the refluxing time and the ratio of reactants improved the percentage yield as summarized in Table 2.1. It appears that the percentage yield of the product obtained when the ratio of chromium salt to Cl_3CCO_2H is 1:6 and refluxing time of 10 hours (90 %) has similar yield (g) with the one produced during 8 hours with an increase of Cr salt:Cl_3CCO_2H ratio to 1:8. It is important to point out that in all cases; the crude product was green and slightly hygroscopic but became fine and powdery when dried under vacuum. Table 2.1 summarizes the conditions and results from the reactions.

Table 2.1: Changes in ratio of reactants, refluxing time and the corresponding % yield

Ratio of Cr salt: Cl_3CCO_2H	Reaction time (hrs)	Observation	Product yield (%)
1:6	6	Fine green solid formed during synthesis	78
1:6	10	Fine green solid formed during synthesis	90
1:8	8	Fine green solid formed during synthesis	90
1:8	10	Fine green solid formed during synthesis	92
1:10	6	Fine green solid formed during synthesis	80
1:10	10	Fine green solid formed during synthesis	95

(ii). Chromium(III) trifluoroacetate:

$$Cr(NO_3)_3.9H_2O + F_3CCO_2H \longrightarrow [Cr_3\text{-}(\mu\text{-}O)(F_3CCO_2)_6.3(H_2O)]NO_3.H_2O$$

Chromium(III) trifluoroacetate was conveniently obtained by reaction of chromium(III) nitrate nonahydrate and trifluoroacetic acid in moderate excess. The resulting product was immediately obtained after cooling overnight at room temperature. It was properly washed with chloroform and was suitable for all analyses, including single-crystal X-ray, without any recrystallization. Table 2.2 summarizes the reaction conditions and percentage yield of products obtained.

Table 2.2: Changes in ratio of reactants, refluxing time and the corresponding % yield

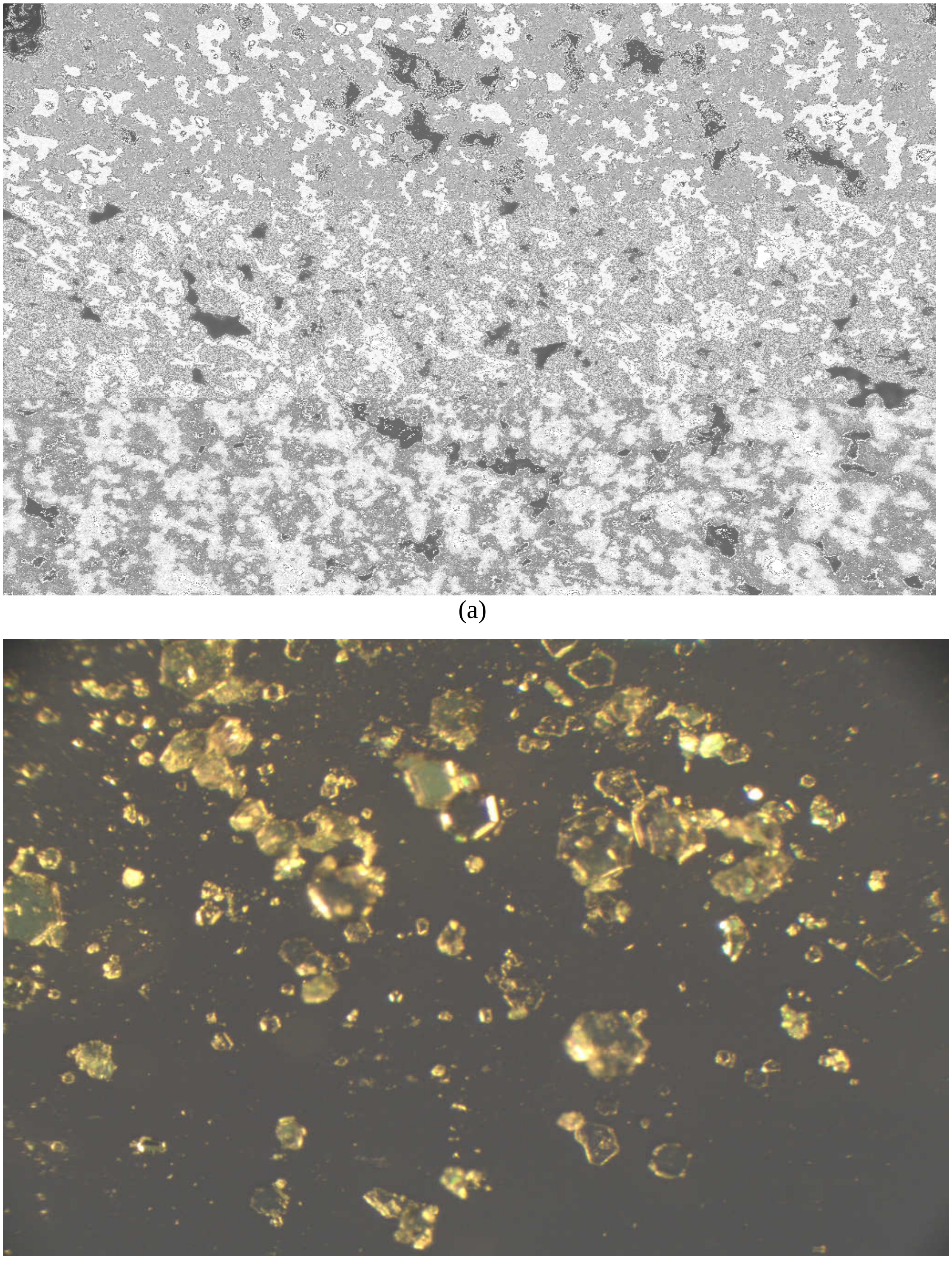
Ratio of $Cr:F_3CCO_2H$	Refluxing time (hrs)	Observation	Product yield (%)
1:4	5	Little green solid formed after refrigeration for two months	2
1:4	8	Dark green product obtained after refrigeration for two weeks	13
1:4	10	Dark green product obtained upon cooling overnight at room temperature	39
1:6	6	Dark green product obtained upon cooling overnight at room temperature	67
1:8	6	Dark green product obtained upon cooling overnight at room temperature	70
1:10	6	Dark green product obtained upon cooling overnight at room temperature	92

Experimental results show that it is difficult to obtain the product in good yield when the ratio of acid to chromium salt is less than 4. Repeated attempts to obtain better product yield were unsuccessful. When the acid to Cr ratio was less than 4, only a viscous green solution was obtained and the yield was negligible after keeping in the refrigerator for months. This was also reported by Jelan [1] and Ooi [2], who made similar observations while synthesizing the monochloroacetate chromium(III) complex. The reaction solution at acid to Cr ratio of 4 produced only 2.39% after refluxing for 5 hours and refrigerating for two months. However, the yield is improved with longer refluxing time. In addition, it is also observed that the higher the ratio of acid to Cr, with same reaction time, the better the yield.

2.4.2 Morphology of the complexes

An optical microscope and Phenom desktop scanning electron microscope (SEM) were used to visualize the particle morphology and size distribution of the complex (Figure 2.1 and Figure 2.2). One can see a clear difference in both complexes, the complex of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ is green powder, appearing as a block of grass when looked with an optical microscope (figure 2.1 (a)). In comparison, the complex of $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ (figure 2.1 (b)) is dark green, shining, hexagonal shaped and its crystal is easily separated. Additionally, it should be noted that, pictures from both complexes were unclear at magnifications above 5,000 when visualized using the SEM instrument.

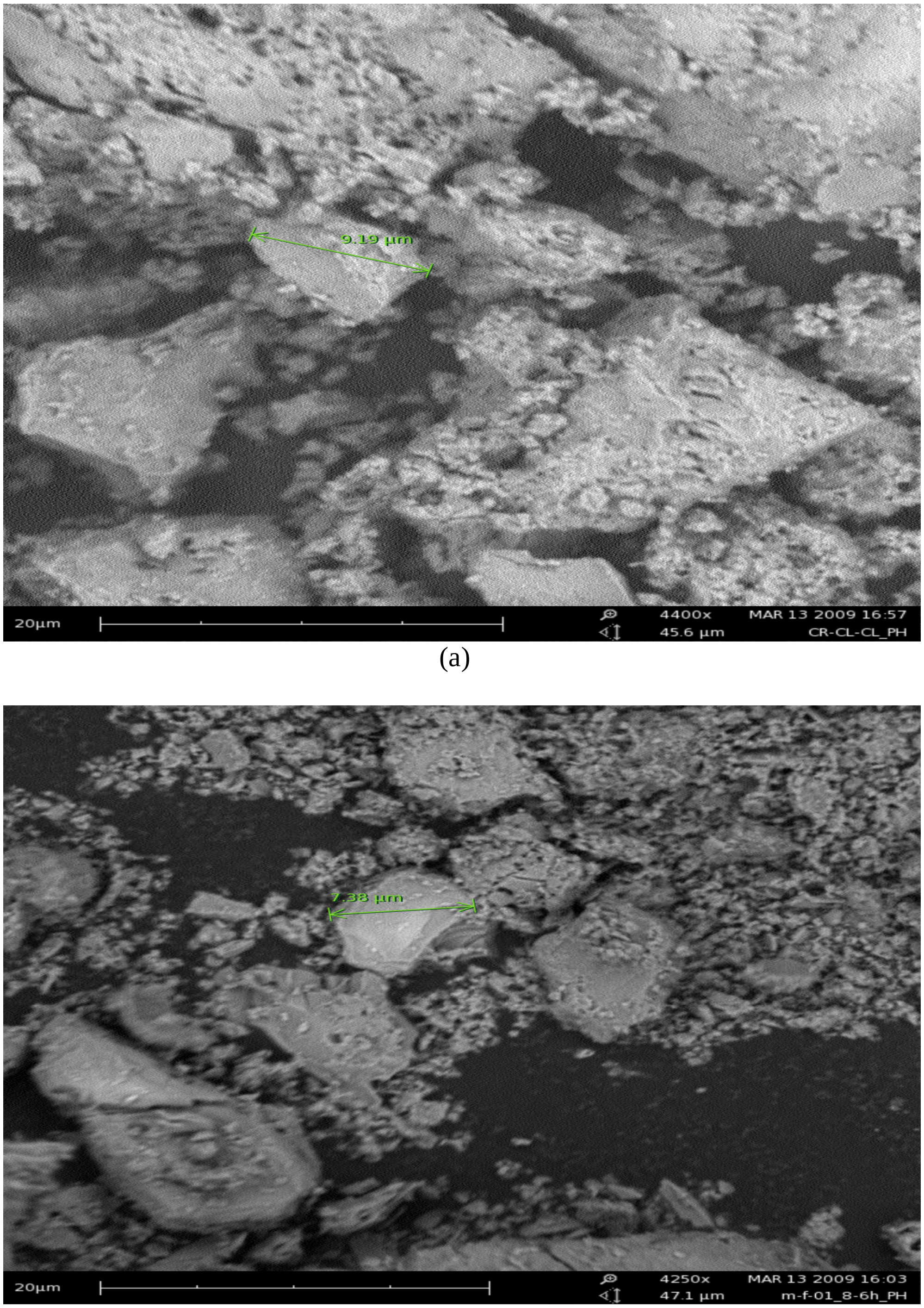
Knowing that the physical state of a catalyst can affect the microstructure of the produced polymer [11, 12], this difference of particle size and particle size distribution was kept in mind when the resulting HDPE particle morphology was investigated.



(a)

(b)

Figure 2.1: Optical micrographs of complex $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ (a) and complex $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ (b)



(a)

(b)

Figure 2.2: Phenom SEM imaging of complex $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ at magnification 4400 (a) and complex $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ at magnification 4250 (b)

2.4.3 Elemental analysis

The titration method has been discussed in full in section 2.3.1-b. The calculations of chromium content in each sample were made following the chemical equation bellow:

$$\underset{n_1 (mol)}{6\,(S_2O_3)^{2-}} + 2\,Cr^{6+} \longrightarrow 3\,(S_4O_6)^{2-} + \underset{n_2\ (mol)}{2\,Cr^{3+}}$$

From the equation, it is known that:

$$1\ \text{mol Cr}^{6+} = 1\ \text{mol Cr}^{3+} \tag{1}$$

and

$$1\ \text{mol of }S_2O_3^{2-} = 1/3\ \text{mol of Cr}^{3+} \tag{2}$$

therefore,

$$M_1V_1\ (\text{mol}) = [(1/3\ \text{mol of Cr}^{3+}) \times 52]\ \text{g of Cr} \tag{3}$$

thus

$$\text{Percentage of Cr}^{3+}\ (\%) = \frac{\text{weight of Cr calculated}\ \ (g)}{\text{weight of complex}\ \ (g)} \times 100 \tag{4}$$

Where,

M_1 = concentration of standardized thiosulphate solution,
V1 = volume of standardized thiosulphate solution used during titration

Carbon, hydrogen, nitrogen content were determined using an CHN&S elemental analyzer and Table 2.3 shows the experimental results obtained from titration with standard sodium thiosulphate and CHN&S elemental analyses and their respective calculated values.

Table 2.3: Analytical data of Complex 1 and Complex 2

Product	Elemental analyses							
	Complex 1				Complex 2			
	Cr[b]	C[a]	H[a]	N	Cr[b]	C[a]	H[a]	N[a]
Experimental (%)	11.32	12.97	0.33	-	15.91	14.83	0.85	1.14
Calculated (%)	11.30	12.02	0.72	-	15.85	14.65	0.82	1.42

Complex 1 = $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$; complex 2 =$[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$

[a] = Elemental analysis; [b] = Titration with standard $Na_2S_2O_3$

These data agree with the structure of $[Cr_3O(Cl_3CCO_2)_6.(H_2O)_2.Cl_3CCO_2].3H_2O$ for Complex 1 and $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ for complex 2. The presence of water, shown in each formula, was confirmed by TGA, FTIR and single-crystal X-ray studies. The experimental value of hydrogen is found lower in sample 1. This is probably due to the lost of the hydrated water by the time of the CHN&S analysis was carried out. Similar observation has previously been reported[2].

2.4.4 Thermogravimetry analyses (TGA)

The dehydration and thermal decomposition studies of the complexes were carried out under nitrogen flow at temperature range of 50 - 900^oC. A continuous record of weight change as function of time and temperature was obtained as shown in Figure 2.3 for $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ and Figure 2.4 for $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$.

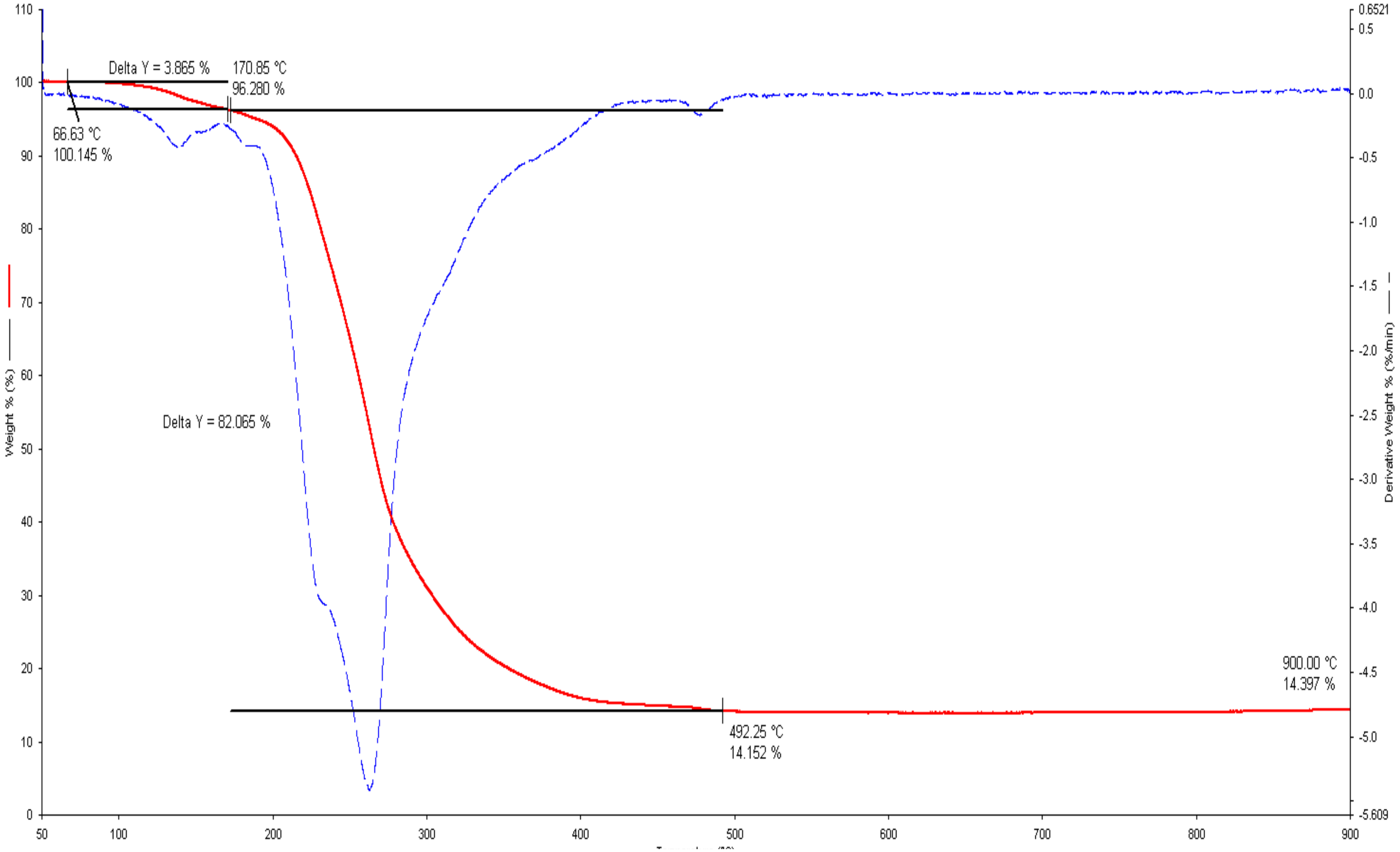
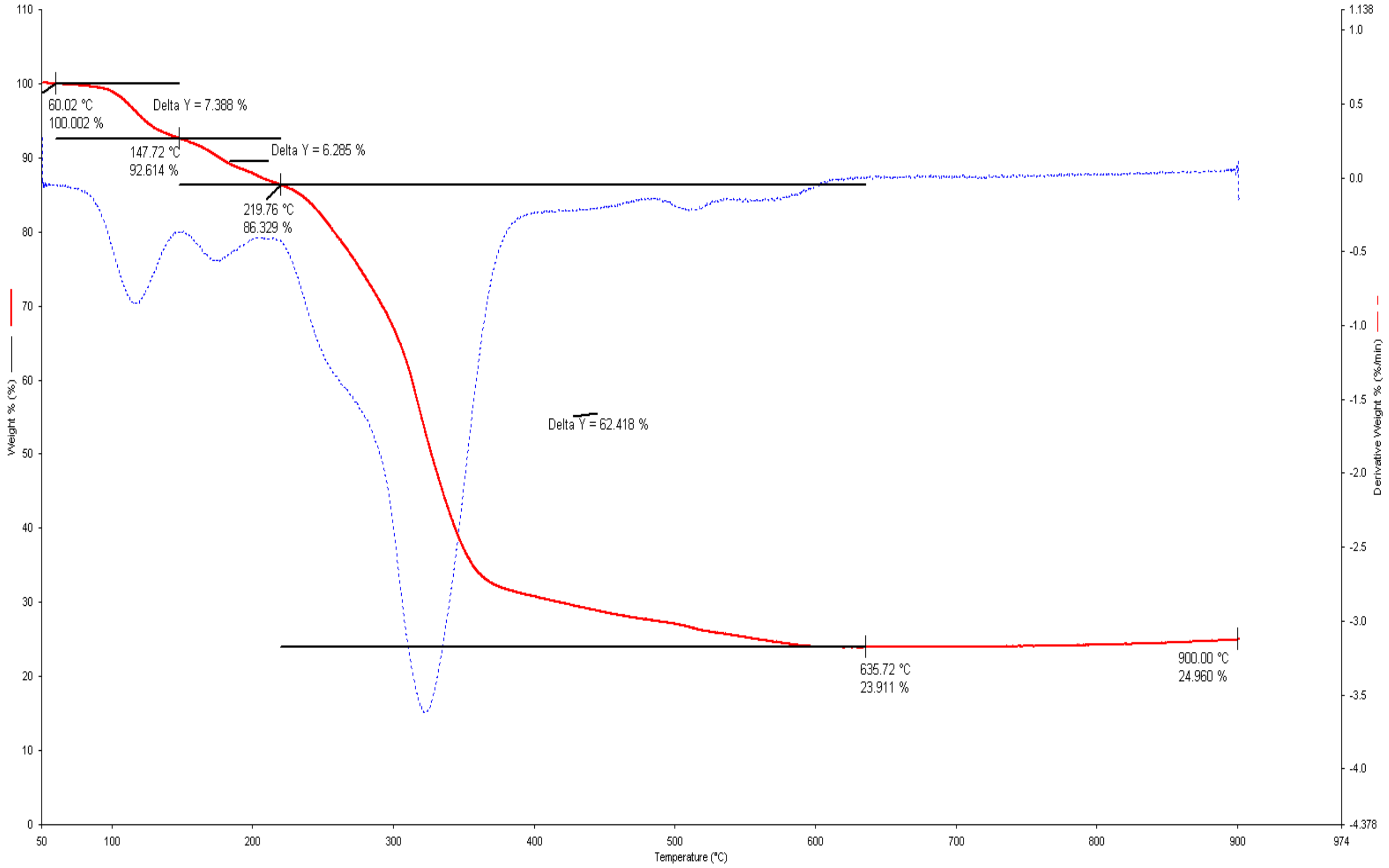


Figure 2.3: TGA thermogram of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ in nitrogen atmosphere.



Figurre 2.4.: TGA thermogram of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ in nitrogen atmosphere.

The thermogravimetric analyses data for the complexes are presented in Table 2.4. As evident from the data, the complex of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ decomposes in two steps. The complex, which has five molecules of water (three hydrates and two coordinated water) dehydrates in two steps, but both steps are not individualized. The first step of the decomposition of the complex (67 – 171 ^oC) corresponds to the elimination of the three lattice water molecule. The second step of decomposition of the complex corresponds to the loss of the coordinated water molecules and the seven trichloroacetate. The TGA curve of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ compound does not show any plateau after the elimination of the coordinated molecule of water. Thus this is followed by a complete decomposition of the complex and it can be concluded that no stable intermediate is formed after dehydration of the complex. Furthermore, its total weight loss during the decomposition is 86 %. The remaining 14 % of the residue at 492 °C corresponds to the oxide formula of CrO. Previous workers reported similar observation [1].

The complex of $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ decomposes in three steps over the temperature range of 50 – 900 °C. The first step in the range of 60 – 148 ^oC corresponds to the total dehydrates (one lattice and three coordinated H_2O molecules) of the complex. The second step in the range of 148 – 220 ^oC corresponds to the loss of the NO_3^- anion. The third step of decomposition, which occurred between 220 – 636 ^oC, corresponds to the decomposition of the six molecules of (F_3CCO_2). Although this last step corresponds to the decomposition F_3CCO_2, a small break at about 400^oC is observed in the curve but the step corresponding to the loss of mass due to individual fragment(s) could not be unambiguously resolved in TG. Recent literature reported similar observation [45, 52-53]. The total weight loss of the complex at 636 ^oC is 76% and the remaining 24% residue corresponds to the oxide formula of Cr_2O_3. A similar observation has been reported before [3].

It is important to point out that an increase of 0.2 % and 1% in the percentage of residue was observed respectively when $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ was heated above 492 °C and $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ above 636 ^oC. These may be due to the chromium metal being in a different oxidation state when the complex is overheated.

Table 2.4: TGA data of chromium(III) oxo-centered carboxylate complexes

Complex	Temperature range (ºC)	Percentage weight loss (%)		Probable molecule decomposed
		Found	Calculated	
Complex (I)	67 - 171	3.9	3.9	3 H_2O (H)
	492	14.2	14.6	Residue (CrO)
Complex (II)	60 - 148	7.4	7.3	1 H_2O (H) + 3 H_2O (C)
	148 - 220	6.3	6.3	NO_3^-
	636	23.9	23.2	Residue (Cr_2O_3)

H = Hydrate molecule, C = Coordinated molecule
Complex (I) = $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$
Complex (II) = $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$

2.4.5 Infrared Spectroscopy

The infrared spectra of both complexes are very similar over the range of 4000-400 cm^{-1} and most bands are readily assigned by comparison with the fundamental vibration frequencies and assignments of carboxylate complexes of chromium(III) and iron(III) reported previously [1-3,13-17]. Table 2.5, lists the data obtained and their corresponding spectra are shown in Figures 2.5 and 2.6.

Table 2.5: Infrared frequencies of the two trinuclear oxo-centered carboxylate complexes

Peak assignments (cm^{-1})	Complex (I)	Complex (II)
$\upsilon_{asym}(Cr_3\text{-}O)$	647 m, sh	661 m, sh
υ_{asym} (Cr-O’)	401 s, sh	382 s, sh
$\upsilon_{asym}(COO^-)$	1684, s, sh	1705 s, sh
$\upsilon_{sym}(COO^-)$	1408 s, sh	1495 m, sh
$\sigma(COO^-)$	689 s, sh	712 w, sh
$\pi(COO^-)$	625 w, sh	626 m,sh
$\upsilon_{asym}(NO_3^-)$	-	1363 s,sh
$\upsilon_{sym}(NO_3^-)$	-	1196 s, sh
$\upsilon(H_2O)$, $\upsilon(CH)$	3504-3167 b	3691-3114 b
$\upsilon(M\text{-}H_2O)$	752 s, sh	735 s, sh
C-Cl_3 stretching	831 s, sh 865 s, sh 981 m, sh	-
C-F_3 stretching	-	780 s, sh 819 w, sh 868 m,sh

s = strong; m = medium; w = weak; sh = sharp; b = broad
Complex1 = $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$
Complex 2 = $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$

The FTIR spectra of both complexes show strong and broad bands in the region of 3691 – 3114 cm^{-1}, which are characteristic of asymmetric and symmetric OH stretching modes of lattice or coordinated water molecules.

According to both Johnson and co-workers and Itoh and co-workers, the carboxylate stretching frequencies for free sodium acetate occur at 1578 cm^{-1} for $\upsilon_{asym}(COO^-)$ and 1414 cm^{-1} for $\upsilon_{sym}(COO^-)$ [14, 18]. However, the bands assigned to $\upsilon_{asym}(COO^-)$ in the spectra $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ and $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ are slightly raised to 1684 cm^{-1} and 1705 cm^{-1}

respectively, but $\upsilon_{sym}(COO^-)$ is decreased to 1408 cm^{-1} for the complex of trichloro carboxylate but increased to 1495 cm^{-1} for the trifluoro carboxylate. Thus the separation between the symmetric and antisymmetric stretching modes of the carboxylate groups of coordinated trichloro and trifluoro ligands are 276 cm^{-1} and 210 cm^{-1} respectively, and the separation is characteristic of a bridging mode of coordination between two metal ions [19]. This large difference between $\upsilon_{asym}(COO^-)$ and $\upsilon_{sym}(COO^-)$ may be due to the presence of halide group acting as electron withdrawing groups onto the carbonyl group. Related observations were reported by Gillette [20] while studying halogen acetic acid complexes; he observed that the frequency rose progressively in the carbonyl absorption through the series of mono- to trichloroacetic acid. Bellamy [13] also reported that the substitution of α-halogen resulted in the carbonyl absorption to rise toward higher frequencies. Thus, a shift in the carbonyl stretching frequency to higher wavenumber reflects the influence of the electronegative group (ligands) in the molecule.

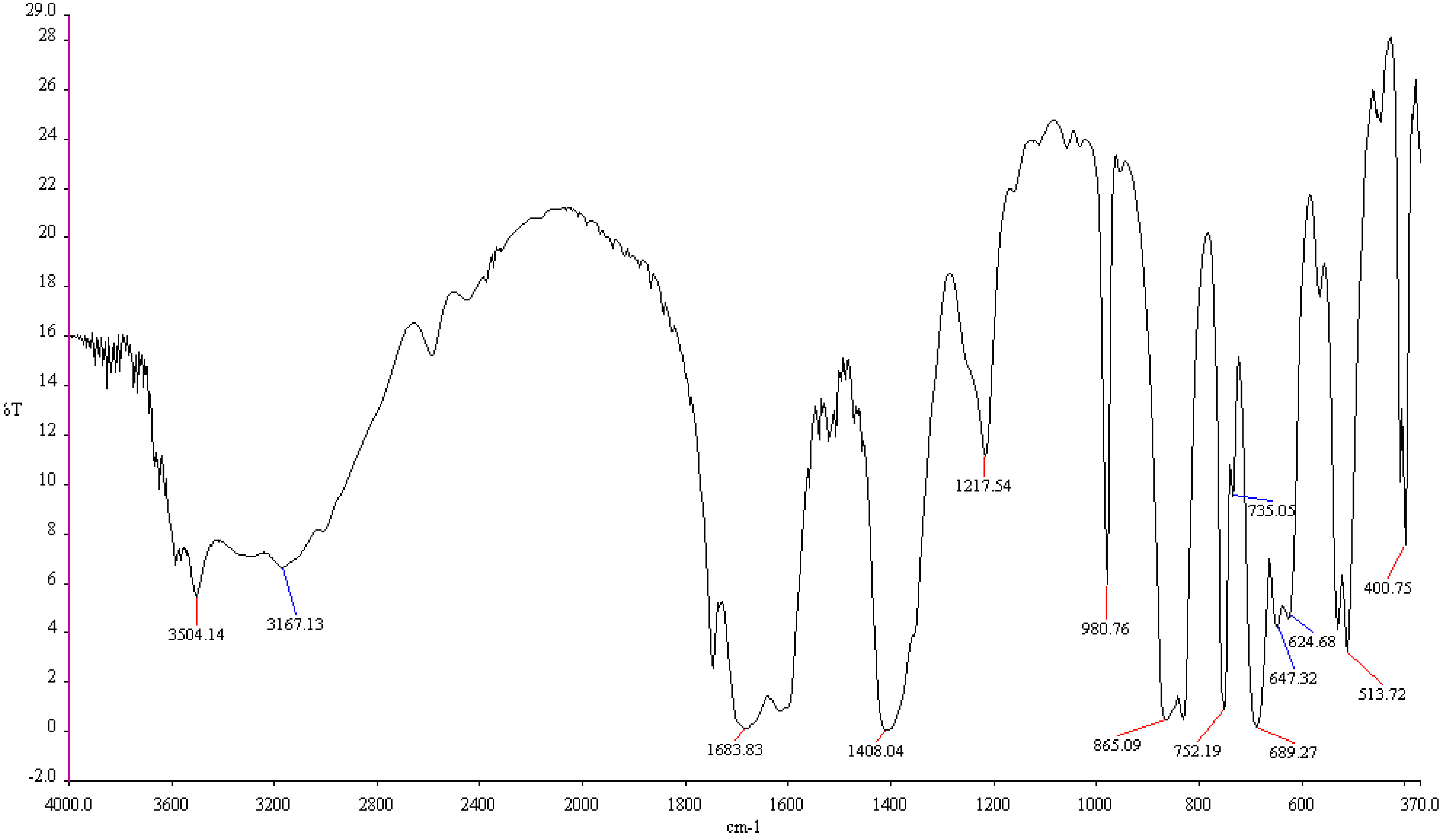


Figure 2.5: FTIR spectrum of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$

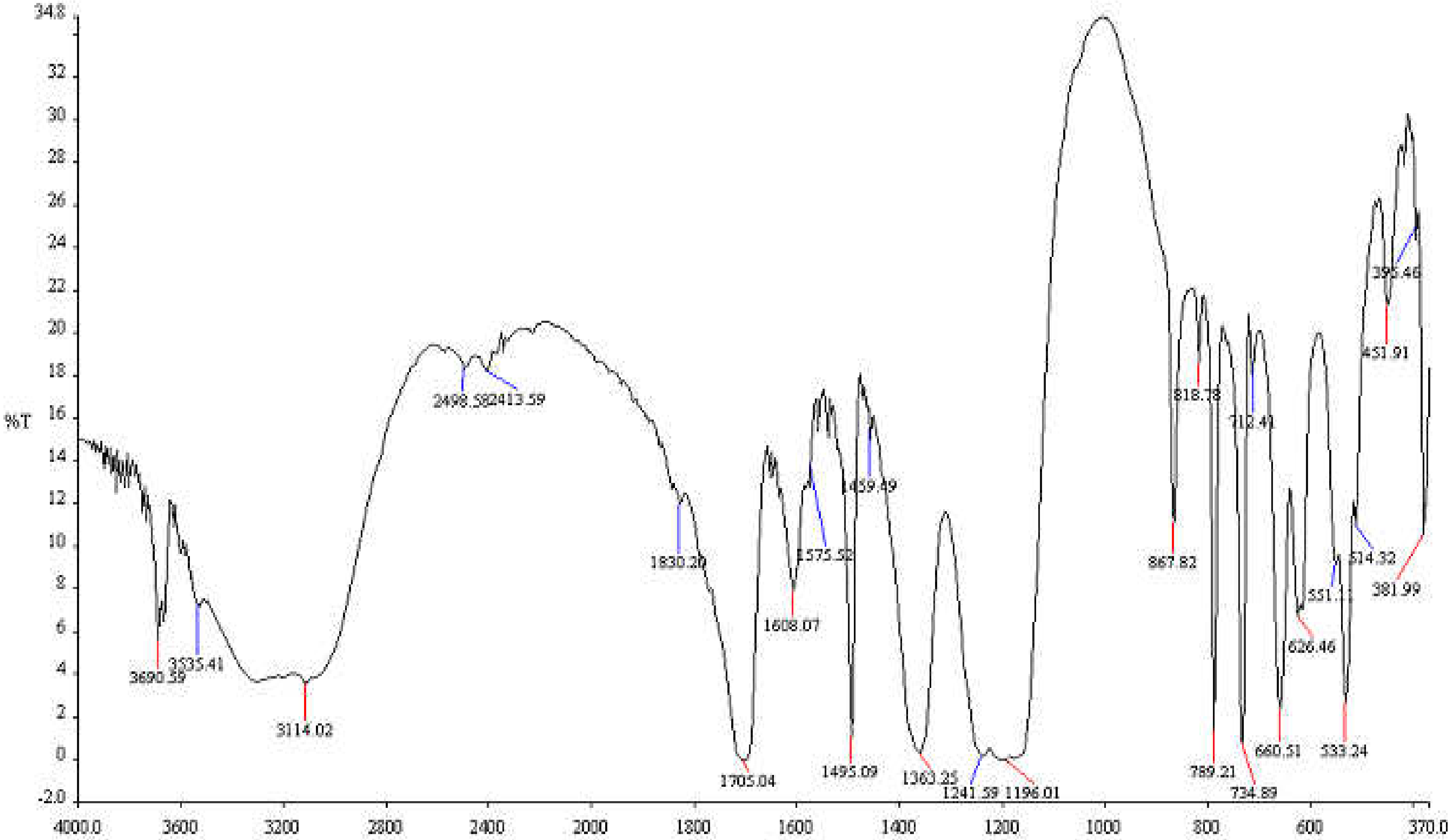


Figure 2.6: FTIR spectrum of $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$

The two strong bands, observed at 752 cm^{-1} and 735 cm^{-1} in the infrared spectra of trichloro and tifluoro acetate complexes respectively are assigned to vibrations due to coordinated water. The presence of these bands in aquo complexes is visible when the metal-oxygen band has sufficient covalent character and hydrogen bonds are present. This was first suggested by Fujita and co-workers [21]. It was later confirmed by Nakagawa et al. [22], assigned the bands at 800 cm^{-1}, 541 cm^{-1} and 490 cm^{-1} to rocking, wagging and metal-oxygen stretching modes respectively while studying the infrared spectrum of $[Cr(H_2O)_6]Cl_3$; and Gamo [23], who assigned the bands at 880-650 cm^{-1} of inorganic salts to the rocking mode of coordinated water. Thus the assignment of each vibration frequency of coordinated water molecules in each complex is in agreement with the spectrum of aquo carboxylate complexes.

Two regions of particular interest for trinuclear complexes lie between 700 – 500 cm^{-1} and 460 – 360 cm^{-1}. Both Holt and co-worker [24] and Johnson et al. [25] have assigned new bands in these particular regions to metal-oxygen stretching frequencies. In particular, Johnson has reported that for trinulcear carboxylate complexes, $\upsilon_{asym}(M_3\text{-}O)$ modes occur in the higher of the two ranges while $\upsilon_{asym}(M\text{-}O')$ modes with O’ denoting a carboxylate oxygen present in coordinated acetate ligands, are observed at about 400 cm^{-1}. The infrared spectra of both complexes were examined in both of these ranges so further comment on the low frequency vibrational spectrum of these carboxylate complexes of chromium(III) is necessary.

In the infrared spectra, the strong band observed at 689 cm^{-1} for the trichloro acetate ligand complex and the weak band shown at 712 cm^{-1} in the tifluoro acetate complex are assigned to the absorption of the symmetric O-C-O deformation mode: $\sigma(COO^-)$ [25]. In addition, those observed at approximately 625 cm^{-1} and 626 cm^{-1} for trichloro and tifluoro acetate respectively are assigned to $\pi(COO^-)$ by comparison with previous literature [18]. It is important to point out that the presence of $\sigma(COO^-)$ and $\pi(COO^-)$ frequencies vibration in the range of 700 cm^{-1} to 500 cm^{-1}, complicate the peak assignment of the vibration of metal-oxygen [$\upsilon_{asym}(M_3\text{-}O)$] which occurs in the same range [25]. Thus, the antisymetric stretching frequencies of Cr_3-O [$\upsilon_{asym}(Cr_3\text{-}O)$] are observed at 647 cm^{-1} and 661 cm^{-1} and other oxygen-metal stretching band were observed at 401 cm^{-1} and 382 cm^{-1} respectively for trichloro and tifluoro acetate complexes. These last vibration frequencies are assigned to υ_{asym}(Cr-O) by comparison with past literature [26-28].

The infrared spectra of both complexes show multiple strong absorption bands at approximately 850 cm^{-1}, 865 cm^{-1} and 981 cm^{-1} for the complex of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ and 780 cm^{-1}, 819 cm^{-1} and 868 cm^{-1} for $[Cr_3O(F_3CCOO)_6.3H_2O]$ $NO_3.H_2O$. These peaks are respectively characteristic of C-Cl_3 and C-F_3 stretching absorption modes by comparison with previous literature [29-31]. This is in agreement with previous observations by Grivas et al. [32, 33], who reported that the absorption bands of F_3C-group vary in number from two to five absorption bands even for the simple molecule.

The most notable difference between the infrared spectra of both complexes is the presence of two strong bands at 1363 cm^{-1} and 1196 cm^{-1} in the infrared spectrum of $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$. These peaks are assigned, by comparison with previous literature [34, 35], to the absorption frequencies of $\upsilon_{asym}(NO_3^-)$ and $\upsilon_{sym}(NO_3^-)$ respectively. It is important to point out that, the third fundamental mode of vibration of NO_3^- (υ_2), absorbing near the region of 800 cm^{-1} according to Newman et al. [34], is missing. This band might have overlapped with another band which was assigned to C-F group vibration.

An important feature of the spectrum of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ is the absence of the two extra peaks in the region of 1300-1580 cm^{-1}, characteristic of free trichloroacetate anion. According to Jelan [1], this absence means that the trichloroacetate ligand is coordinated to the chromium ion. This has been confirmed by single-crystal X-ray crystallography [36].

The resulting spectra of both complexes clearly resemble those of Cr_3-(μ-O) carboxylate systems. Thus it can be concluded that the two complexes synthesized have similar structure to those of known trinuclear oxo-centered acetate complexes of vanadium, iron, chromium, rhodium and ruthenium metal complexes reported in the literature.

2.4.6 Magnetic susceptibility studies

The method of determination of the effective magnetic moment of the complexes has been discussed in full in section 2.3.4. The magnetic moment of oxo-centered trinuclear chromium carboxylate clusters have been discussed in detail by earlier workers by means of spin Hamiltonian [37-40]:

$$H = J_0(S_1.S_2 + S_1.S_3) + (J_0 + J_1)S_2.S_3$$

Where S_1, S_2 and S_3 are the spins of the three chromium atoms and J_0 and J_1 are the exchange integrals. Consequently, the magnetic moment of these complexes are generally in the range of 3.1 – 3.5 B.M. at temperature range of 290-298 K.

Room temperature magnetic moment values found are: 2.39 and 2.99 B.M (Table 2.6) for $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ and $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ respectively. According to Kettle [41], chromium(III) complexes in an octahedral form and d^3 configuration have the “spin only” value of their Cr^{3+} ion around 3.87 B.M. thus, the values obtained here are lower than the calculated “spin only” value for Cr^{3+}. It is common to trinuclear carboxylate complexes of chromium(III) containing a central μ_3-O core [42] and could be interpreted as being due to the presence of super exchange interactions [37] between Cr^{3+} ions, providing π-pathways through central O-atom in the complexes. In other words, the Cr^{3+} ions of the trinuclear oxo-centered chromium(III) (S = +3/2) assemblies are antiferromagnetically coupled resulting in an S = +1/2 ground state [43-45]. Table 2.6, presents the experimental results for the effective magnetic moment of both complexes. It can be concluded that the magnetic moment μ_{eff} corresponds to an intermediate number of unpaired electrons for each metal atom. The same feature has been reported in literature [46].

Table 2.6: Effective magnetic moment per metal atom of chromium(III) carboxylate complexes at 297K.

Compound	μ_{eff} / B.M.
$[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$	2.39
$[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$	2.99

2.4.7 Single-crystal X-ray structure analyses

The infrared analyses of the complexes revealed the presence of acetate ligands, bridging across the chromium metal centers. The single-crystal X-ray data for both complexes are summarized in Table 2.7. They are consistent with a planar triangular arrangement of chromium atoms, a central μ_3-O atom and six halide acetate ligands which bridge across the metal centers using both oxygen atoms of the carboxylate group. In addition, the X-ray analysis confirms that the structures are $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ from the reaction of $CrCl_3.6H_2O$ and

Cl_3CCO_2H and $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ from $Cr(NO_3)_3.9H_2O$ and F_3CCO_2H reflux.

Table 2.7: Single-crystal X- ray data for both chromium(III) carboxylate complexes

Identification code	$[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2$ $3C_2H_3N$	$[Cr_3O(F_3CCO_2)_6.3H_2O]$ $NO_3.H_2O$
Empirical formula	Cr_3 C_{20} H_{13} Cl_{21} $O_{17}N$	Cr_3C_{12} H_8 F_{18} N O_{20}
Formula weight (g/mol)	1467.78	984.13
Temperature (K)	100 (2)	293 (2)
Wavelength (λ)	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$	Hexagonal, $P6_3/m$
Unit cell dimensions	a = 11.631 (6) Å, b =19.481 (1) Å c = 22.949 (1) Å β = 95.355 (1) ^{o}	a = b = 9.895 (4) Å c = 19.393 (18) Å, σ =120 ^{o}
Volume	5177.0 (5) $Å^3$	1644.24 (18) $Å^3$
Z / Calculated density	4 / 1.883 $Mg.m^{-3}$	2 / 1.834 $Mg.m^{-3}$
Absorption coefficient	1.926 mm^{-1}	1.134 mm^{-1}
F(000)	2876	890
Crystal size (mm)	0.25 x 0.20 x 0.15	0.50 x 0.50 x 0.10
Theta range for data collection	2.2 – 28.2^o	2.10 - 30.54^o
Limiting indices	$-15 \leq h \leq 1$, $-25 \leq k \leq 25$, $-29 \leq l \leq 29$	$-14 \leq h \leq 13$, $-5 \leq k \leq 14$, $-24 \leq l \leq 26$
Collected / unique reflections	29504 / 11718 [R_{int} = 0.029]	11101 / 1694 [R_{int} = 0.0267]
Completeness to theta = 25.00	100.0 %	100.0 %
Absorption correction	Multi-scan	Multi-scan
Max. / min. transmission	0.778 / 0.667	0.8951 / 0.6010
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	11718 / 72 / 624	1694 / 0 / 124
Goodness-of-fit on F^2	1.04	0.997
Final R indices [I>2sigma(I)]	R1 = 0.041, wR2 = 0.118	R1 = 0.0378, wR2 = 0.1020
R indices (all data)	R1 = 0.0788, wR2 = 0.1717	R1 = 0.0481, wR2 = 0.1083
Largest diff. peak / hole	1.42 $e.A^{-3}$ / -2.234 $e.A^{-3}$	0.753 $e.A^{-3}$ / -0.330 $e.A^{-3}$

$[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3C_2H_3N$ is the structure of the crystal obtained from the recrystallization of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ in acetonitrile.

a. crystal structure of $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$

The resulting product from the reaction between $CrCl_3.6H_2O$ and Cl_3CCO_2H was a green powder. Thus, a dark green prismatic crystal, suitable for single-crystal X-ray analysis was obtained from its recrystallization in acetonitrile solution. The details of the crystallography and structure parameters have been published [36].

In this recrystallized compound, the three lattice water molecules in $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ have been replaced by three solvate C_2H_3N ligands. The trinuclear $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3C_2H_3N$ molecule has an oxygen (O) atom that is connected to one coordinated monodentate trichloroacetate anion, and two water molecules coordinated to Cr^{III} atoms. The three metal atoms are the vertices of an equilateral triangle. Each of the six remaining carboxylate groups bridges a Cr–O–Cr fragment. The cluster interacts with the three solvate molecules through water–acetonitrile O—H---N hydrogen bonds. Adjacent clusters are linked by a water–carboxylate O—H---O hydrogen bonds. These hydrogen bonds, where water molecules are involved as donor, give rise to a helical chain that is parallel to the y-axis [36]. One of the seven trichloroacetate (CCl_3) groups is found to be disordered over two sites. The six C—Cl distances are restrained to within 0.01 Å of each other, as are the Cl···Cl distances. The anisotropic displacement parameters of the disordered Cl atoms are restrained to be nearly isotropic. The disorder refined to a 0.636 (12):0.364 (12) site occupancy ratio. The water hydrogen atoms are located in a difference Fourier map and are refined with a distance constraint of O—H 0.84 (1) Å; their temperature factors are fixed relative to the atoms to which they are attached. Methyl-H atoms are generated geometrically (C—H = 0.98 Å), and are included in the refinement using the riding model approximation with $U_{iso}(H) = 1.5U_{eq}(C)$. The final difference Fourier map had a large peak in the vicinity of the disordered Cl atoms, but was otherwise featureless.

Figure 2.7 shows the thermal ellipsoid plot of $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3C_2H_3N$ at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. For clarity, the minor disorder component is not shown. Hydrogen bonds are denoted by dashed lines.

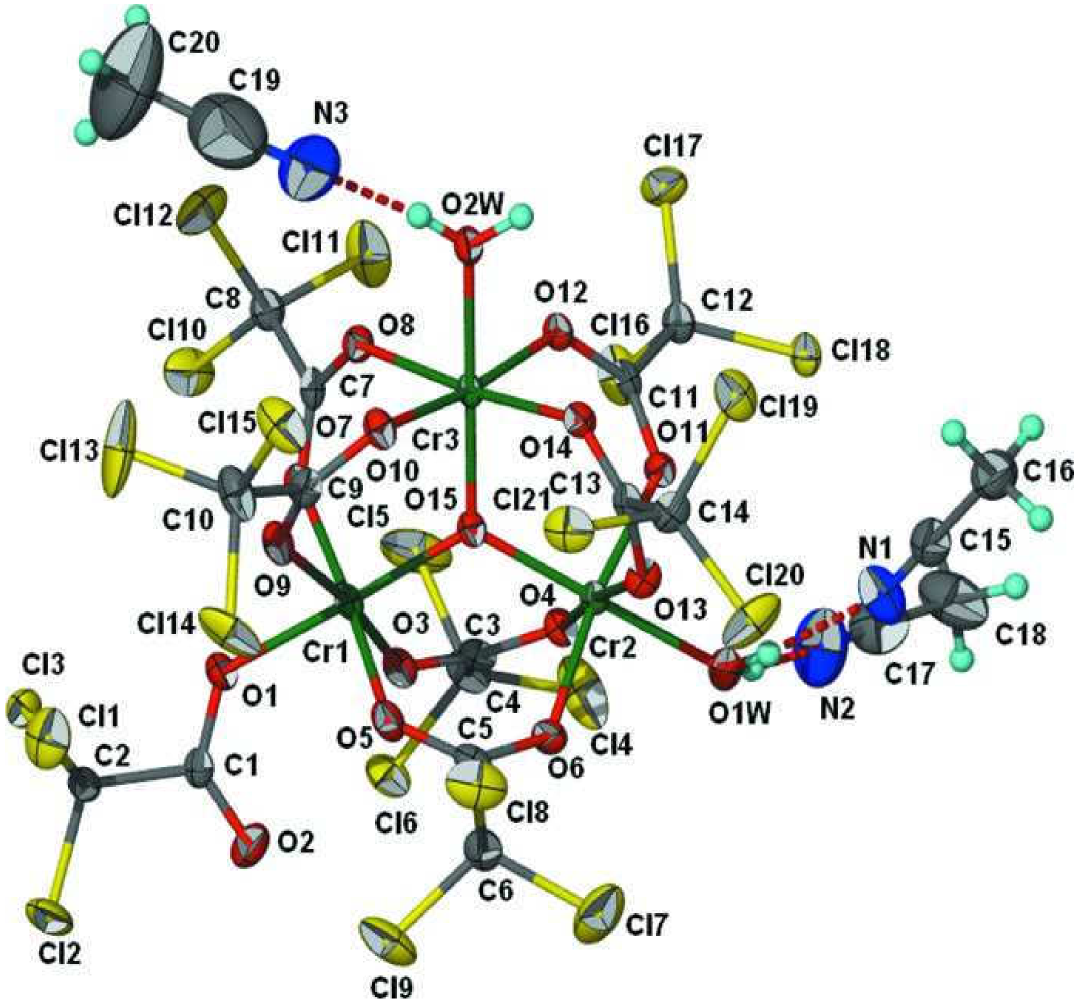


Figure 2.7: Thermal ellipsoid plot of $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3C_2H_3N$

Tables below detail the fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$) (Table 2.8), atomic displacement parameters ($Å^2$) (Table 2.9), geometric parameters (Å, °) (Table 2.10) and hydrogen-bond geometry (Å, °) (Table 2.11) of $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3C_2H_3N$ compound.

Table 2.8: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) of $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3C_2H_3N$

atoms	x	y	z	U_{iso} */U_{eq}	Occ. (<1)
Cr1	0.74255(4)	0.76778(3)	0.70072(2)	0.01404(12)	
Cr2	0.68641(4)	0.73747(3)	0.83719(2)	0.01277(11)	
Cr3	0.72390(4)	0.60693(3)	0.74830(2)	0.01179(11)	
Cl1	0.96872(8)	0.85657(6)	0.56393(4)	0.0333(2)	
Cl2	0.89615(9)	0.99687(5)	0.57400(4)	0.0345(2)	
Cl3	0.73830(8)	0.89677(4)	0.52068(3)	0.02158(18)	
Cl4	0.36046(10)	0.88419(6)	0.80350(5)	0.0431(3)	
Cl5	0.35756(9)	0.81589(5)	0.69151(5)	0.0430(3)	
Cl6	0.46821(8)	0.94801(4)	0.70989(4)	0.02438(19)	
Cl7	0.98178(10)	0.88074(7)	0.90381(5)	0.0451(3)	
Cl8	1.09295(9)	0.78569(5)	0.83228(5)	0.0346(2)	
Cl9	1.03479(9)	0.92225(5)	0.78947(5)	0.0356(2)	
Cl10	0.44418(9)	0.70978(5)	0.55064(4)	0.0322(2)	
Cl11	0.38086(9)	0.61375(7)	0.63683(5)	0.0399(3)	
Cl12	0.53908(9)	0.57331(5)	0.55303(4)	0.0336(2)	
Cl13	0.9998(4)	0.6385(3)	0.58065(14)	0.0556(10)	0.636(12)
Cl14	1.1108(2)	0.71821(13)	0.67552(16)	0.0352(8)	0.636(12)
Cl15	1.0981(8)	0.5711(3)	0.6842(4)	0.0316(13)	0.636(12)
Cl13'	0.9729(10)	0.6101(9)	0.5847(3)	0.105(5)	0.364(12)
C1l4'	1.1068 (6)	0.7141(3)	0.6463(8)	0.103(3)	0.364(12)
Cl15'	1.1046(14)	0.5774(5)	0.6926(7)	0.0252(17)	0.364(12)
Cl16	0.31914(8)	0.66992(5)	0.78820(4)	0.0287(2)	
Cl17	0.35454(8)	0.52405(5)	0.79999(4)	0.0292(2)	
Cl18	0.37880(7)	0.61005(4)	0.90215(3)	0.01931(17)	
Cl19	0.93022(8)	0.51554(5)	0.92623(4)	0.0272(2)	
Cl20	0.99064(8)	0.65247(6)	0.96451(4)	0.0344(2)	
Cl21	1.07222(7)	0.60054(5)	0.85829(4)	0.02607(19)	
O1	0.7710(2)	0.82999(12)	0.63619(10)	0.0187(5)	
O2	0.8135(3)	0.93428(14)	0.67484(11)	0.0281(6)	
O3	0.6252(2)	0.83313(12)	0.72363(10)	0.0179(5)	
O4	0.55621(19)	0.79526(12)	0.80588(10)	0.0163(5)	
O5	0.8720(2)	0.81086(13)	0.74973(10)	0.0197(5)	
O6	0.8001(2)	0.81248(12)	0.83713(10)	0.0184(5)	
O7	0.6175(2)	0.72533(12)	0.64643(10)	0.0178(5)	
O8	0.6429(2)	0.61373(12)	0.66921(9)	0.0160(5)	
O9	0.8600(2)	0.71060(12)	0.66684(10)	0.0184(5)	
O10	0.8769(2)	0.61126(12)	0.71653(10)	0.0168(5)	
O11	0.57304(19)	0.66600(12)	0.85012(10)	0.0155(5)	
O12	0.56962(19)	0.58956(12)	0.77652(9)	0.0147(5)	
O13	0.81379(19)	0.68469(12)	0.87790(10)	0.0169(5)	
O14	0.81080(19)	0.58767(12)	0.82463(9)	0.0151(5)	
O15	0.71611(19)	0.70351(11)	0.76204(9)	0.0136(4)	
O1W	0.6544(2)	0.77209(13)	0.91690(10)	0.0190(5)	
H1W1	0.684(3)	0.747(2)	0.9440(15)	0.059(17)*	
H1W2	0.5872(17)	0.783(2)	0.9250(17)	0.034(13)*	
O2W	0.7303(2)	0.50636(12)	0.73377(10)	0.0171(5)	

H2W1	0.759(4)	0.4871(18)	0.7053(11)	0.032(12)*
H2W2	0.726(4)	0.4790(17)	0.7610(12)	0.050(15)*
N1	0.7157(3)	0.67991(19)	1.00764(16)	0.0338(8)
N2	0.4284(4)	0.7968(3)	0.94552)	0.0556(12)
N3	0.8447(5)	0.4523(3)	0.6464(2)	0.0685(15)
C1	0.8074(3)	0.89117(17)	0.63661(14)	0.0157(6)
C2	0.8515(3)	0.91082(17)	0.57647(14)	0.0172(7)
C3	0.5520(3)	0.82935(16)	0.75960(14)	0.0158(6)
C4	0.4390(3)	0.86978(19)	0.74313(17)	0.0229(7)
C5	0.8757(3)	0.82309(17)	0.80318(15)	0.0173(7)
C6	0.9912(3)	0.85391(19)	0.83110(15)	0.0215(7)
C7	0.5957(3)	0.66336(18)	0.64181(13)	0.0156(6)
C8	0.4943(3)	0.64175(18)	0.59620(15)	0.0196(7)
C9	0.9091(3)	0.65627(17)	0.68302(14)	0.0161(6)
C10	1.0241(3)	0.64354(16)	0.65623(14)	0.0254(8)
C11	0.5281(3)	0.62049(17)	0.81711(14)	0.0142(6)
C12	0.3999(3)	0.60421(18)	0.82725(14)	0.0177(7)
C13	0.8484(3)	0.62681(17)	0.86503(14)	0.0144(6)
C14	0.9565(3)	0.59973(18)	0.90309(15)	0.0187(7)
C15	0.7356(3)	0.6309(2)	1.03291(16)	0.0255(8)
C16	0.7599(4)	0.5680(2)	1.0658(18)	0.0342(9)
H16A	0.8074	0.5785	1.1023	0.051*
H16B	0.8016	0.5360	1.0424	0.051*
H16C	0.6872	0.5470	1.0750	0.051*
C17	0.3472(4)	0.7913(2)	0.9685(2)	0.0423(11)
C18	0.2451(4)	0.7862(3)	0.9985(3)	0.0504(13)
H18A	0.2630	0.7620	1.0356	0.076*
H18B	0.1858	0.7609	0.9742	0.076*
H18C	0.2167	0.8324	1.0062	0.076*
C19	0.8283(8)	0.4449(4)	0.5933(4)	0.091(2)
C20	0.8044(9)	0.4336(6)	0.5267(3)	0.126(4)
H20A	0.8704	0.4102	0.5119	0.189*
H20B	0.7925	0.4781	0.5071	0.189*
H20C	0.7350	0.4053	0.5187	0.189*

Data obtained from reference [36]

Table 2.9: Atomic displacement parameters (Å^2) of [$Cr_3O(CCl_3CO_2)_6.2H_2O$]$CCl_3CO_2.3C_2H_3N$

Atoms	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.0128(3)	0.0158(3)	0.0139(2)	0.0004(2)	0.00299(19)	0.00348(19)
Cr2	0.0104(2)	0.0147(3)	0.0134(2)	-0.00009(19)	0.00208(18)	0.00052(19)
Cr3	0.0095(2)	0.0149(3)	0.0112(2)	0.00076(19)	0.00208(18)	0.00201(18)
Cl1	0.0189(5)	0.0495(6)	0.0329(5)	0.0045(4)	0.0097(4)	-0.0016(4)
Cl2	0.0441(6)	0.0272(5)	0.0306(5)	-0.0214(4)	-0.0047(4)	0.0062(4)
Cl3	0.0244(4)	0.0247(4)	0.0147(4)	-0.0056(3)	-0.0031(3)	-0.0002(3)
Cl4	0.0320(6)	0.0450(6)	0.0567(7)	0.0210(5)	0.0277(5)	0.0231(5)
Cl5	0.0313(6)	0.0279(5)	0.0645(7)	-0.0076(4)	-0.0240(5)	0.0102(5)
Cl6	0.0246(4)	0.0168(4)	0.0320(5)	0.0038(3)	0.0037(3)	0.0075(3)
Cl7	0.0338(6)	0.0700(8)	0.0317(5)	-0.0181(5)	0.0043(4)	-0.0204(5)
Cl8	0.0231(5)	0.0291(5)	0.0492(6)	0.0034(4)	-0.0098(4)	0.0042(4)
Cl9	0.0253(5)	0.0303(5)	0.0495(6)	-0.0113(4)	-0.0057(4)	0.0172(4)
Cl10	0.0359(5)	0.0282(5)	0.0291(5)	0.0015(4)	-0.0152(4)	0.0076(4)
Cl11	0.0192(5)	0.0669(8)	0.0334(5)	-0.0113(5)	0.0016(4)	0.0109(5)
Cl12	0.0399(6)	0.0328(5)	0.0258(5)	0.0067(4)	- 0.0081(4)	-0.0095 (4)
Cl13	0.0395(16)	0.112(3)	0.0170(11)	0.0297(15)	0.0124(9)	0.0041(11)
Cl14	0.0124(10)	0.0279(10)	0.0660(18)	-0.0058(7)	0.0066(10)	0.0156(10)
Cl15	0.0214(19)	0.0290(15)	0.047(3)	0.0084(12)	0.0165(17)	0.0106(15)
Cl3'	0.076(6)	0.221(13)	0.020(2)	0.086(7)	0.014(3)	-0.001(5)
Cl4'	0.050(3)	0.058(3)	0.214(9)	0.025(2)	0.084(5)	0.081(4)
Cl5'	0.017(2)	0.030(3)	0.029(3)	0.012(2)	0.0058(17)	0.008(2)
Cl16	0.0158(4)	0.0420(6)	0.0283(5)	0.0072(4)	0.0009(3)	0.0121(4)
Cl17	0.0231(5)	0.0326(5)	0.0336(5)	-0.0133(4)	0.0119(4)	-0.0121(4)
Cl18	0.0165(4)	0.0251(4)	0.0174(4)	-0.0001(3)	0.0070(3)	0.0011(3)
Cl19	0.0242(5)	0.0303(5)	0.0259(4)	0.0024(4)	- 0.0043(3)	0.0115(4)
Cl20	0.0232(5)	0.0452(6)	0.0318(5)	0.0122(4)	- 0.0136(4)	-0.0189(4)
Cl21	0.0117(4)	0.0285(5)	0.0387(5)	0.0009(3)	0.0060(3)	-0.0024(4)
O1	0.0216(13)	0.0186(12)	0.0162(11)	-0.0034(10)	0.0031(9)	0.0034(9)
O2	0.0416(17)	0.0240(14)	0.0190(13)	0.0025(12)	0.0051(11)	-0.0055(10)
O3	0.0166(12)	0.0177(12)	0.0201(12)	0.0016(9)	0.0046(9)	0.0038(9)
O4	0.0140(12)	0.0170(12)	0.0182(11)	0.0018(9)	0.0027(9)	0.0030(9)
O5	0.0162(12)	0.0244(13)	0.0186(12)	-0.0050(10)	0.0022(9)	0.0053(10)
O6	0.0168 (12)	0.0189(12)	0.0201(12)	-0.0048(9)	0.0053(9)	-0.0020(9)
O7	0.0180(12)	0.0196(12)	0.0156(11)	0.0002(9)	0.0007(9)	0.0041(9)
O8	0.0174(12)	0.0169(12)	0.0135(11)	0.0015(9)	0.0003(9)	0.0011(9)
O9	0.0163(12)	0.0211(12)	0.0186(12)	0.0029(10)	0.0064(9)	0.0052(9)
O10	0.0132(11)	0.0190(12)	0.0188(11)	0.0022(9)	0.0049(9)	0.0041(9)
O11	0.0138(11)	0.0172(12)	0.0158(11)	-0.0017(9)	0.0039(9)	0.0000(9)
O12	0.0114(11)	0.0182(12)	0.0148(11)	-0.0002(9)	0.0032(8)	0.0013(9)
O13	0.0129(11)	0.0203(12)	0.0172(11)	0.0032(9)	-0.0001(9)	-0.0012(9)
O14	0.0132(11)	0.0164(11)	0.0154(11)	0.0001(9)	-0.0001(9)	0.0023(9)
O15	0.0124(11)	0.0150(11)	0.0138(11)	0.0027(9)	0.0035(8)	0.0023(8)
O1W	0.0174(13)	0.0230(13)	0.0173(12)	0.0018(10)	0.0050(10)	-0.0007(10)
O2W	0.0216(13)	0.0163(12)	0.0140(11)	0.0016(10)	0.0046(9)	0.0022(9)
N1	0.0257(18)	0.038(2)	0.038(2)	0.0025(15)	0.0060(15)	0.0135(16)
N2	0.047(3)	0.076(3)	0.046(3)	0.011(2)	0.013(2)	0.000(2)
N3	0.089(4)	0.057(3)	0.067(3)	-0.005(3)	0.046(3)	- 0.022(3)

C1	0.0133(16)	0.0204(17)	0.0135(15)	0.0014(13)	0.0016(12)	0.0020(12)
C2	0.0181(17)	0.0179(16)	0.0154(15)	-0.0046(13)	0.0001(13)	0.0015(12)
C3	0.0132(16)	0.0124(15)	0.0217(16)	0.0001(12)	0.0014(12)	0.0016(12)
C4	0.0183(18)	0.0192(18)	0.031(2)	0.0029(14)	0.0032(14)	0.0066(14)
C5	0.0150(16)	0.0137(15)	0.0234(17)	-0.0021(12)	0.0023(13)	0.0028(13)
C6	0.0162(17)	0.0268(19)	0.0212(17)	-0.0045(14)	0.0004(13)	0.0014(14)
C7	0.0144(16)	0.0225(17)	0.0106(14)	0.0022(13)	0.0040(12)	0.0026(12)
C8	0.0195(17)	0.0212(17)	0.0177(16)	0.0015(14)	0.0005(13)	0.0033(13)
C9	0.0112(15)	0.0218(17)	0.0152(15)	0.0011(13)	0.0013(12)	- 0.0005(12)
C10	0.0178(18)	0.031(2)	0.0286(19)	0.0065(15)	0.0093(14)	0.0119(15)
C11	0.0100(15)	0.0182(16)	0.0145(15)	0.0012(12)	0.0022(11)	0.0065(12)
C12	0.0139(16)	0.0223(17)	0.0175(16)	0.0006(13)	0.0049(12)	0.0013(13)
C13	0.0083(15)	0.0206(17)	0.0146(15)	-0.0007(12)	0.0022(11)	0.0023(12)
C14	0.0129(16)	0.0236(18)	0.0191(16)	0.0021(13)	- 0.0012(13)	-0.0023(13)
C15	0.0207(19)	0.032(2)	0.0237(18)	-0.0009(16)	0.0027(14)	0.000(16)
C16	0.046(3)	0.028(2)	0.028(2)	0.0033(18)	- 0.0004(18)	0.0012(16)
C17	0.036(3)	0.039(3)	0.052(3)	0.008(2)	0.005(2)	- 0.004(2)
C18	0.035(3)	0.036(3)	0.082(4)	0.002(2)	0.018(3)	0.008(2)
C19	0.110(6)	0.059(4)	0.112(7)	0.002(4)	0.052(5)	- 0.005(4)
C20	0.133(9)	0.177(10)	0.073(6)	0.024(7)	0.036(5)	- 0.032(6)

Data obtained from reference [36]

Table 2.10: Geometric parameters (Å, °) of $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3C_2H_3N$

Cr1—O15	1.930(2)	Cl21—C14	1.768(4)	Cl17—C12	1.745(4)
Cr1—O1	1.965(2)	O1—C1	1.264(4)	Cl18—C12	1.762(3)
Cr1—O3	1.973(2)	O2—C1	1.212(4)	Cl19—C14	1.759(4)
Cr1—O9	1.978(2)	O3—C3	1.242(4)	Cl20—C14	1.759(3)
Cr1—O5	1.980(2)	O4—C3	1.250(4)	O15—Cr1—O1	177.60(10)
Cr1—O7	2.003(2)	O5—C5	1.246(4)	O15—Cr1—O3	93.62(9)
Cr2—O15	1.909(2)	O6—C5	1.246(4)	O1—Cr1—O3	88.40(10)
Cr2—O11	1.959(2)	O7—C7	1.236(4)	O15—Cr1—O9	94.83(9)
Cr2—O13	1.966(2)	O8—C7	1.252(4)	O1—Cr1—O9	83.11(10)
Cr2—O4	1.968(2)	O9—C9	1.243(4)	O3—Cr1—O9	171.35(10)
Cr2—O6	1.971(2)	O10—C9	1.247(4)	O15—Cr1—O5	91.45(10)
Cr2—O1W	2.017(2)	O11—C11	1.249(4)	O1—Cr1—O5	89.66(10)
Cr3—O15	1.911(2)	O12—C11	1.244(4)	O3—Cr1—O5	94.78(10)
Cr3—O8	1.970(2)	O13—C13	1.242(4)	O9—Cr1—O5	86.86(10)
Cr3—O14	1.975(2)	O14—C13	1.248(4)	O15—Cr1—O7	91.71(9)
Cr3—O10	1.986(2)	O1W—H1W1	0.839(10)	O1—Cr1—O7	87.10(10)
Cr3—O2W	1.990(2)	O1W—H1W2	0.849(10)	O3—Cr1—O7	87.27(10)
Cr3—O12	1.993(2)	O2W—H2W1	0.850(10)	O9—Cr1—O7	90.63(10)
Cl1—C2	1.769(4)	O2W—H2W2	0.826 (10)	O5—Cr1—O7	176.12(10)
Cl2—C2	1.757(3)	N1—C15	1.131(5)	O15—Cr2—O11	94.11(10)
Cl3—C2	1.770 (3)	N2—C17	1.130(6)	O15—Cr2—O13	93.23(9)
Cl4—C4	1.752(4)	N3—C19	1.225(10)	O11—Cr2—O13	92.54(10)
Cl5—C4	1.787(4)	C1—C2	1.564(4)	O15—Cr2—O4	93.81(9)
Cl6—C4	1.752(4)	C3—C4	1.549(5)	O11—Cr2—O4	87.48(10)
Cl7—C6	1.762(4)	C5—C6	1.554(5)	O13—Cr2—O4	172.95(10)
Cl8—C6	1.778(4)	C7—C8	1.560(5)	O15—Cr2—O6	94.50(10)
Cl9—C6	1.741(4)	C9—C10	1.543(5)	O11—Cr2—O6	171.16(10)
Cl10—C8	1.754(3)	C11—C12	1.562(4)	O13—Cr2—O6	84.97(10)
Cl11—C8	1.772(4)	C13—C14	1.555(4)	O4—Cr2—O6	93.95(10)
Cl12—C8	1.768(4)	C15—C16	1.453(5)	O15—Cr2—O1W	179.24(10)
Cl13—C10	1.734(4)	C16—H16A	0.9800	O11—Cr2—O1W	85.21(10)
Cl14—C10	1.802(4)	C16—H16B	0.9800	O13—Cr2—O1W	86.47(10)
Cl15—C10	1.744(5)	C16—H16C	0.9800	O4—Cr2—O1W	86.50(10)
Cl3'—C10	1.813(6)	C17—C18	1.429(7)	O6—Cr2—O1W	86.17(10)
Cl4'—C10	1.705(5)	C18—H18A	0.9800	O15—Cr3—O8	93.43(9)
Cl5'—C10	1.757(6)	C18—H18B	0.9800	O15—Cr3—O14	93.95(9)
Cl16—C12	1.780(4)	C18—H18C	0.9800	O8—Cr3—O14	172.40(10)
C19—C20	1.544(11)	C20—H20A	0.9800	C20—H20B	0.9800

C20—H20C	0.9800	C3—C4—Cl6	110.7(2)
Cl4—C4—Cl6	110.0(2)	C3—C4—Cl5	104.4(2)
Cl4—C4—Cl5	109.6(2)	Cl6—C4—Cl5	109.6(2)
O6—C5—O5	128.5(3)	O6—C5—C6	116.1(3)
O5—C5—C6	115.4(3)	C5—C6—Cl9	110.7(2)
C5—C6—Cl7	112.2(2)	Cl9—C6—Cl7	109.9(2)
C5—C6—Cl8	105.4(2)	Cl9—C6—Cl8	110.6(2)
Cl7—C6—Cl8	107.91(19)	O7—C7—O8	129.4(3)
O7—C7—C8	117.2(3)	O8—C7—C8	113.4(3)

C7—C8—Cl10	112.6(2)	C7—C8—Cl12	109.6(2)
Cl10—C8—Cl12	109.56(19)	C7—C8—Cl11	106.5(2)
Cl10—C8—Cl11	108.88(19)	Cl12—C8—Cl11	109.6(2)
O9—C9—O10	128.8 (3)	O9—C9—C10	114.1(3)
C9—C10—Cl4'	116.4(4)	C9—C10—Cl13	110.0(3)
C9—C10—Cl15	113.5(4)	Cl4'—C10—Cl15	115.9(5)
Cl13—C10—Cl15	110.6(4)	C9—C10—Cl5'	111.8(7)
Cl4'—C10—Cl5'	111.8(5)	Cl13—C10—Cl5'	117.6(7)
O15—Cr3—O10	94.39(10)	C9—C10—Cl14	105.0(2)
O8—Cr3—O10	91.54(10)	Cl13—C10—Cl14	109.1(2)
O14—Cr3—O10	86.09(10)	Cl15—C10—Cl14	108.5(3)
O15—Cr3—O2W	179.43(10)	Cl5'—C10—Cl14	102.3(5)
O8—Cr3—O2W	86.22(10)	C9—C10—Cl3'	101.2(4)
O14—Cr3—O2W	86.41(10)	Cl4'—C10—Cl3'	108.1(4)
O10—Cr3—O2W	86.07(10)	Cl5'—C10—Cl3'	106.4(5)
O15—Cr3—O12	93.18 (9)	Cl14—C10—Cl3'	129.9(5)
O8—Cr3—O12	86.73(9)	O12—C11—O11	128.9(3)
O14—Cr3—O12	94.66(9)	O12—C11—C12	117.1(3)
O10—Cr3—O12	172.32(10)	O11—C11—C12	113.9(3)
O2W—Cr3—O12	86.35(10)	C11—C12—Cl17	112.9(2)
C1—O1—Cr1	130.9(2)	C11—C12—Cl18	110.7(2)
C3—O3—Cr1	132.3(2)	Cl17—C12—Cl18	110.02(18)
C3—O4—Cr2	125.6(2)	C11—C12—Cl16	104.2(2)
C5—O5—Cr1	126.5(2)	Cl17—C12—Cl16	109.59(19)
C5—O6—Cr2	129.5(2)	Cl18—C12—Cl16	109.25(18)
C7—O7—Cr1	126.0(2)	O13—C13—O14	129.3(3)
C7—O8—Cr3	131.6(2)	O13—C13—C14	115.9(3)
C9—O9—Cr1	132.6(2)	O14—C13—C14	114.8(3)
C9—O10—Cr3	126.0(2)	C13—C14—Cl19	109.4(2)
C11—O11—Cr2	131.5(2)	C13—C14—Cl20	111.2(2)
C11—O12—Cr3	125.8(2)	Cl19—C14—Cl20	109.58(19)
C13—O13—Cr2	127.4(2)	C13—C14—Cl21	106.9(2)
C13—O14—Cr3	131.1(2)	Cl19—C14—Cl21	110.30(19)
Cr2—O15—Cr3	120.38(11)	Cl20—C14—Cl21	109.49(19)
Cr2—O15—Cr1	119.25(12)	N1—C15—C16	179.3(5)
Cr3—O15—Cr1	120.35(11)	C15—C16—H16A	109.5
Cr2—O1W—H1W1	112(3)	C15—C16—H16B	109.5
Cr2—O1W—H1W2	122(3)	H16A—C16—H16B	109.5
H1W1—O1W—H1W2	108.1(17)	C15—C16—H16C	109.5
Cr3—O2W—H2W1	126(3)	H16A—C16—H16C	109.5
Cr3—O2W—H2W2	120(3)	H16B—C16—H16C	109.5
H2W1—O2W—H2W2	110.6(18)	N2—C17—C18	178.2(6)
O2—C1—O1	131.0(3)	C17—C18—H18A	109.5
O2—C1—C2	117.9(3)	C17—C18—H18B	109.5
O1—C1—C2	111.2(3)	H18A—C18—H18B	109.5
C1—C2—Cl2	112.6(2)	C17—C18—H18C	109.5
C1—C2—Cl3	108.5(2)	H18A—C18—H18C	109.5
Cl2—C2—Cl3	109.03(18)	H18B—C18—H18C	109.5
C1—C2—Cl1	108.6(2)	N3—C19—C20	178.0(9)
Cl2—C2—Cl1	109.29(19)	C19—C20—H20A	109.5
Cl3—C2—Cl1	108.81(18)	C19—C20—H20B	109.5
O3—C3—O4	128.4(3)	H20A—C20—H20B	109.5

O3—C3—C4	115.3(3)	C19—C20—H20C	109.5
O4—C3—C4	116.3(3)	H20A—C20—H20C	109.5
C3—C4—Cl4	112.4(2)	H20B—C20—H20C	109.5

Data obtained from reference [36]

Table 2.11: Hydrogen-bond geometry (Å,°) of
$[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3C_2H_3N$

D —H··· A	D —H	H···A	D ··· A	D—H··· A
O1W—H1W1···N1	0.84(1)	1.97(2)	2.791(4)	166(5)
O1W—H1W2···N2	0.85(1)	1.97(1)	2.810(5)	173(4)
O2W—H2W1···N3	0.85(1)	1.88(1)	2.719(5)	171(4)
O2W—H2W2···O2	0.83(1)	1.81(1)	2.613(3)	165(4)

Symmetry codes: (i) - x +3/2, y -1/2, - z+3/2.
Data obtained from reference [36]

b. crystal structure of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$

In comparison with the $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3H_2O$ compound which needed to be recrystallized in acetonitrile, the resulting product from $Cr(NO_3)_3.9H_2O$ and F_3CCO_2H reaction is directly suitable for single-crystal X-ray data collection and structure determination.

In the trichromium(III, III, III) complex $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$, the three oxygen atoms, from coordinated water molecules are in symmetry related sites and complete an octahedral arrangement around each chromium atom in the compound. The cation is located on the twofold axis; consequently, the Cr_3O triangle is planar. The NO_3 group and lattice H_2O molecule are situated outside the trinuclear unit on the threefold axis. All metals are equivalent and distances between chromium and oxygen atoms are similar. A perspective diagram of the unit cell of the compound is shown in Figure 2.8.

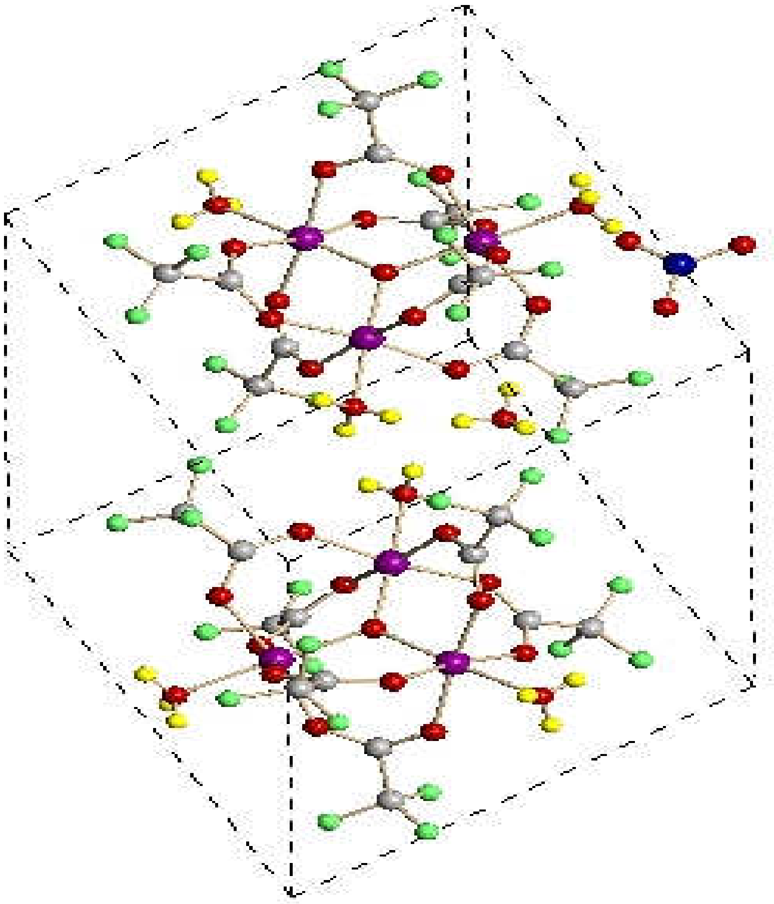


Figure 2.8: Unit cell plot of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$

With a pleasingly low crystallographic R-factor, of 3.8%, the structure of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ is easy to rationalize for charge balance. The 3x(+3) formal charges on the Cr atoms are counterbalanced by the six acetate anions plus the central O(2-) atom and one extra nitrate anion on its own in the crystal lattice. Because there appeared to be a destructive phase change near -170 ^{o}C, the data collection was carried out at room temperature and rotational disorder is apparent in the location of residual peaks of electron density of the compound. A perspective diagram, of the cationic moiety of the compound (Figure 2.9) is shown and referred to throughout this description. In this plot, most fluorine atoms have been omitted deliberately to give a clearer picture of the structure.

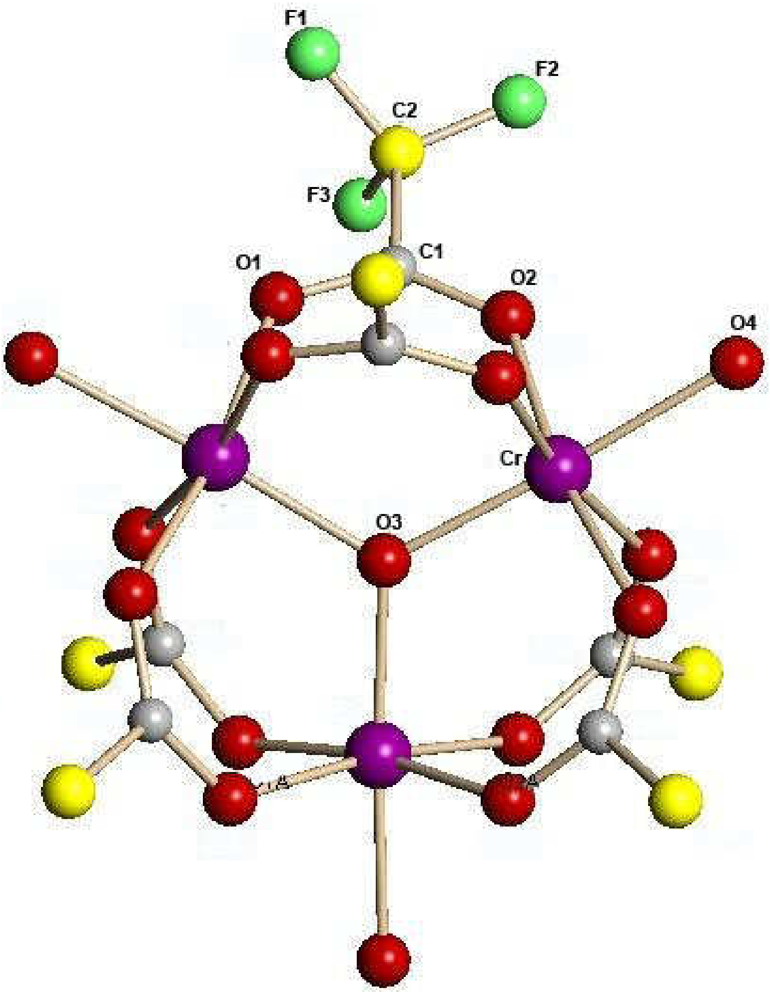


Figure 2.9: Cationic moiety plot of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$

The X-ray structure of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ has been reported elsewhere [46] but its full data are detailed here. Tables below detail the atomic coordinates (x 10^{-4}) and equivalent isotropic displacement parameters (Å^2 x 10^{-3}) (Table 2.12), bond lengths (Å) and angles (°) (Table 2.13) and anisotropic displacement parameters (Å^2 x 10^{-3}) (Table 2.14) of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ compound.

Table 2.12: Atomic coordinates (x 10^{-4}) and equivalent isotropic displacement parameters ($Å^2$ x 10^{-3}) of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$

Atom	x	y	z	U(eq)
Cr	1232(1)	6264(1)	2500	24(1)
O(1)	4167(2)	9532(2)	3215(1)	41(1)
O(2)	1631(2)	7740(2)	3261(1)	37(1)
O(3)	3333	6667	2500	24(1)
O(4)	-944(3)	5965(3)	2500	35(1)
N(1)	0	10000	7500	45(1)
O(5)	295(3)	8917(3)	7500	60(1)
O(6)	3333	6667	6707(3)	88(1)
C(1)	2832(2)	8911(2)	3460(1)	31(1)
C(2)	2693(3)	9722(4)	4112(2)	52(1)
F(1)	3448(6)	11218(4)	4049(3)	102(2)
F(2)	1271(6)	9273(8)	4283(4)	91(2)
F(3)	3267(13)	9346(13)	4634(3)	123(3)
F(1')	1520(30)	8890(40)	4422(11)	147(12)
F(2')	3840(30)	10070(40)	4511(12)	128(12)
F(3')	90(50)	1070(30)	956(10)	179(14)

In this table, U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2.13: Bond lengths (Å) and angles (°) for $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$

Cr-O(3)	1.9115(4)	O(2)-C(1)	1.236(3)
Cr-O(1)#1	1.9673(16)	O(3)-Cr#4	1.9115(4)
Cr-O(1)#2	1.9673(16)	O(3)-Cr#2	1.9115(4)
Cr-O(2)	1.9728(16)	O(4)-H(1)	0.77(4)
Cr-O(2)#3	1.9728(16)	O(4)-H(2)	0.97(9)
Cr-O(4)	2.022(2)	N(1)-O(5)#5	1.243(2)
O(1)-C(1)	1.241(3)	N(1)-O(5)	1.243(2)
O(1)-Cr#4	1.9673(16)	N (1)-O(5)#6	1.243(2)
C(1)-C(2)	1.540(3)	C(2)-F(1')	1.20(2)
C(2)-F(3')	1.281(13)	C(2)-F(2')	1.266(17)
C(2)-F(2)	1.289(5)	C(2)-F(1)	1.288(5)
C(2)-F(3)	1.302(9)	F(1)-F(3')	0.53(4)
F(1)-F(2')	1.63(3)	F(2)-F(1')	0.60(5)
F(2)-F(3')	1.81(3)	F(3)-F(2')	0.70(4)
F(3)-F(1')	1.61(3)		
O(3)-Cr-O(1)#1	95.93(5)	O(3)-Cr-O(1)#2	95.93(5)
O(1)#1-Cr-O(1)#2	89.54(12)	O(3)-Cr-O(2)	92.95(5)
O(1)#1-Cr-O(2)	170.48(7)	O(1)#2-Cr-O(2)	86.10(8)
O(3)-Cr-O(2)#3	92.95(5)	O(1)#1-Cr-O(2)#3	86.10(8)
O(1)#2-Cr-O(2)#3	170.48(7)	O(2)-Cr-O(2)#3	96.92(10)
O(3)-Cr-O(4)	176.87(7)	O(1)#1-Cr-O(4)	86.29(7)
O(1)#2-Cr-O(4)	86.29(7)	O(2)-Cr-O(4)	84.99(7)
O(2)#3-Cr-O(4)	84.99(7)	C(1)-O(1)-Cr#4	129.84(15)
C(1)-O(2)-Cr	132.13(14)	Cr-O(3)-Cr#4	120.0
Cr-O(3)-Cr#2	120.0	Cr#4-O(3)-Cr#2	120.0
Cr-O(4)-H(1)	112(3)	Cr-O(4)-H(2)	104(5)
H(1)-O(4)-H(2)	107(5)	O(5)#5-N(1)-O(5)	120.0(4)
O(5)#5-N(1)-O(5)#6	120.000(1)	O(5)-N(1)-O(5)#6	120.0(1)
O(2)-C(1)-O(1)	129.1(2)	O(2)-C(1)-C(2)	116.8(2)
O(1)-C(1)-C(2)	114.1(2)	F(1')-C(2)-F(3')	114.8(18)
F(1')-C(2)-F(2')	108.1(16)	F(3')-C(2)-F(2')	102.2(17)
F(1')-C(2)-F(2)	28(2)	F(3')-C(2)-F(2)	89.5(17)
F(2')-C(2)-F(2)	127.6(12)	F(1')-C(2)-F(1)	129.9(17)
F(3')-C(2)-F(1)	23.8(17)	F(2')-C(2)-F(1)	79.5(17)
F(2)-C(2)-F(1)	109.1(4)	F(1')-C(2)-F(3)	80.1(18)
F(3')-C(2)-F(3)	128.3(14)	F(2')-C(2)-F(3)	31.5(17)
F(2)-C(2)-F(3)	105.0(5)	F(1)-C(2)-F(3)	108.5(5)
F(1')-C(2)-C(1)	111.4(11)	F(3')-C(2)-C(1)	109.9(9)
F(2')-C(2)-C(1)	110.1(10)	F(2)-C(2)-C(1)	113.4(3)
F(1)-C(2)-C(1)	111.7(3)	F(3)-C(2)-C(1)	108.9(5)
F(3')-F(1)-C(2)	77(2)	F(3')-F(1)-F(2')	124(2)
C(2)-F(1)-F(2')	49.7(8)	F(1')-F(2)-C(2)	68(2)
F(1')-F(2)-F(3')	110(3)	C(2)-F(2)-F(3')	45.1(8)
F(2')-F(3)-C(2)	71(2)	F(2')-F(3)-F(1')	114(3)
C(2)-F(3)-F(1')	47.1(9)	F(2)-F(1')-C(2)	84(3)
F(2)-F(1')-F(3)	131(3)	C(2)-F(1')-F(3)	52.7(13)
F(3)-F(2')-C(2)	77.0(18)	F(3)-F(2')-F(1)	124(3)
C(2)-F(2')-F(1)	50.8(11)	F(1)-F(3')-C(2)	78.9(15)
F(1)-F(3')-F(2)	117(2)	C(2)-F(3')-F(2)	45.5(10)

Symmetry transformations used to generate equivalent atoms:

#1	-y+1,x-y+1,-z+1/2	#2	-y+1,x-y+1,z	#3	x,y,-z+1/2,
#4	-x+y,-x+1,z	#5	-y+1,x-y+2z	#6	-x+y-1,-x+1,z

Table 2.14: Anisotropic displacement parameters (Å x 10^{-3})
for $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr	18(1)	19(1)	35(1)	0	0	9(1)
O(1)	30(1)	29(1)	60(1)	-12(1)	8(1)	11(1)
O(2)	28(1)	36(1)	44(1)	-9(1)	2(1)	14(1)
O(3)	18(1)	18(1)	36(2)	0	0	9(1)
O(4)	23(1)	27(1)	58(2)	0	0	15(1)
N(1)	27(1)	27(1)	80(4)	0	0	14(1)
O(5)	34(1)	29(1)	121(3)	0	0	18(1)
O(6)	82(2)	82(2)	100(4)	0	0	41(1)
C(1)	32(1)	29(1)	35(1)	-2(1)	2(1)	17(1)
C(2)	48(1)	52(2)	48(1)	-16(1)	6(1)	19(1)
F(1)	102(3)	46(2)	111(4)	-39(2)	47(3)	2(2)
F(2)	48(2)	99(3)	112(4)	-55(3)	20(2)	26(2)
F(3)	159(8)	204(8)	45(2)	-13(3)	-14(3)	120(7)
F(1')	150(20)	144(18)	50(7)	-26(9)	69(10)	4(13)
F(2')	86(11)	240(30)	85(13)	-117(18)	-63(10)	100(16)
F(3')	440(40)	155(18)	86(10)	14(11)	34(16)	250(30)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^*2 U_{11} + ... + 2 h k a^* b^* U_{12}]$

In conlusion, the results of X-ray studies on chromium complexes with trichloroacetic acid and trifluoroacetic acid confirm the trinuclear structure on both complexes. In the $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3H_2O$, the three lattice molecules of water have been replaced by three molecules of solvate acetonitrile during the recrystallization. The results obtained indicate that the cationic moiety of the $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ compound is similar to that in the trinuclear acetate [1, 38, 47-51] with the M_3O system having symmetry close to D_3h and with a nearly octahedral environment of each metal atom.

The trinuclear unit in $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3C_2H_3N$ compound is neutral with the terminal ligands of two H_2O molecules and one Cl_3CCO_2, in contrast to the structure of $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ which is cationic.

A comparison of $[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3H_2O$ (complex 1) and $[Cr_3O(F_3CCO_2)_6.3H_2O]NO_3.H_2O$ (complex 2) shows that the replacement of a hard ligand (NO_3^- in complex 2) by a softer stabilizing ligand (C_2H_3N in complex 1) results in a change of the complex type (cationic in complex 2 and neutral in complex 1). This has previously been commented on by Glazunova et al. while studying similar type of complexes [46].

2.5 Conclusion

Two chromium(III) carboxylate complexes have been synthesized in a simple refluxing reaction which does not required an inert atmosphere. Long refluxing time is necessary to obtain high yield, possibly due to the slow formation of the trinuclear skeleton. Both complexes produced are stable in ambient atmosphere and their structure analyses agree with their stoichiometry.

On the basis of finding from the elemental analyses, FTIR spectroscopy, thermogravimetry analyses (TGA), magnetic studies and single-crystal X-ray crystallography of both complexes, their structures are as established and depicted in Figure 2.7 and Figure 2.8, in which chromium(III) is situated in an octahedral environment and there are six carboxylate ions in between two chromium(III) ions. Infrared spectra suggested the bridging nature of the six carboxylate anions as did with $v_{asym}(Cr_3O)$ vibrations in the complexes. Their magnetic moment values are in support of an octahedral environment around the chromium(III) ion and single-crystal X-ray studies show the trinuclear nature of the complexes. Both complexes are chemically and physically different from their chromium salt starting material ($CrCl_3.6H_2O$ for complex 1 and $Cr(NO_3)_3.9H_2O$ for complex 2). Moreover, in combination with $AlEt_2Cl$, they form high activity catalyst systems for the polymerization of ethylene.

2.6 References

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