CHAPTER 3

RESULTS AND DISCUSSION: CHARACTERIZATION OF CATALYSTS

3.1 Synthesis of Chromium(III) Trinuclear Oxo-Carboxylate Complexes

(a) Chromium(III) Monocholoroacetate Complex, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$

The synthesis method of Cr(III) monochloroacetate had been described in Chapter 2, Section 2.1.1. Fine powdery solids were obtained. The solids were slightly hygroscopic, soluble in water, methanol, ethanol and isopropyl alcohol but insoluble in chloroform and toluene. Suitable reaction conditions are important to maximize the yield. The best conditions had to be determined through trial and error. Table 3.1 summarizes the synthesis and product yield obtained.

Table 3.1: Synthesis and yield of chromium(III) monochloroacetate complex

Ratio of chromium nitrate to monochloroacetic acid	Refluxing time/hr	Yield/ g	Percentage yield / %	Observation
1:4	6	5.00	66.5	Green solid obtained upon cooling
1:6	6	5.56	74.0	Green solid obtained upon cooling
	8	5.75	76.4	Green solid obtained upon cooling
1:8	8	6.54	87.0	Green solid obtained upon cooling
1:10	8	7.05	93.8	Green solid obtained upon cooling

Experimental results showed that high yield could be achieved by higher ratio of monochloroacetic acid to chromium nitrate. Time of refluxing also played an important role in obtaining higher yield. Longer reaction time increased the yield. When the ratio of chromium nitrate to monochloroacetic acid was 1:10, very fine powdery green solids were obtained.

(b) Chromium(III) Dichloroacetate Complex, $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$

The complex synthesized is soluble in water, ethanol, propanol and isopropyl alcohol but insoluble in chloroform. Increasing the ratio of the dichloroacetic acid to chromium nitrate salt improved the product yield. Table 3.2 shows that large excess of dichloroacetic acid would ensure that high product yield can be obtained.

Table 3.2: Synthesis and yield of chromium(III) dichloroacetate complex

Ratio of chromium nitrate to dichloroacetic acid	Refluxing time/hr	Yield/ g	Percentage yield / %	Observation
1:6	6	4.45	49.7	Green solid product obtained two weeks later
1:12	6	5.13	57.4	Green solid product obtained two weeks later
	13	6.88	76.9	Green solid product obtained two weeks later
1:13	15	7.53	84.2	Green solid product obtained two weeks later

1:15	15	8.12	90.8	Green solid product obtained two weeks later
1:16	15	8.30	95.0	Green solid product obtained two weeks later

When the ratio between chromium nitrate and dichloroacetic acid is 1:6, a green product with low yield, 49.7% is obtained. However, lengthening the refluxing hour and increasing the ratio of the reagents to 1:15 and 1:16 improved the yield to 90.8% and 95.0% respectively.

(c) Chromium(III) Trichloroacetate Complex, $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$

Green products were formed during synthesis. The results of trichloroacetate chromium(III) complex synthesis are shown in Table 3.4. Increasing the refluxing time to 10 hours improved the product yield to 90.8%.

Table 3.3: Synthesis and yield of chromium(III) trichloroacetate complex

Ratio of chromium nitrate to trichloroacetic acid	Refluxing time/hr	Yield/ g	Percentage yield / %	Observation
1:6	6	8.58	79.3	Fine green solid formed during synthesis
1:6	8	9.20	85.0	Fine green solid formed during synthesis
1:6	10	9.82	90.8	Fine green solid formed during synthesis

(d) Chromium(III) Acetate Complex, $[Cr_3O(CH_3CCOO)_6.3H_2O]NO_3.7H_2O$

Chromium(III) acetate complex obtained from this synthesis is soluble in water, methanol and ethanol but insoluble in toluene and chloroform. A good yield was obtained at $Cr(NO_3).9H_2O$: CH_3COOH ratio of 1:13 and refluxing time of 13 hours.

Table 3.4: Synthesis and yield of chromium(III) acetate complex

Ratio of chromium nitrate to acetic acid glacial	Refluxing time/hr	Yield/ g	Percentage yield / %	Observation
1:11	6	3.57	57.1	Dark green solid obtained upon cooling
	8	3.99	63.8	Dark green solid obtained upon cooling
1:12	8	4.52	72.4	Dark green solid obtained upon cooling
	13	5.27	84.4	Dark green solid obtained upon cooling
1:13	13	5.77	92.4	Dark green solid obtained upon cooling

3.2 Characterization of Chromium(III) Trinuclear Oxo-Carboxylate Complexes

(a) Titrimetric method

$$Cr_2O_7^{2-} + 6\,I^- + 14\,H^+ \longrightarrow 3\,I_2 + 2\,Cr^{3+} + 7\,H_2O$$

$$I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_2O_6^{2-}$$

Chromium content were calculated as follows:

Standardized thiosulphate solution

$$\text{Number of mole} = \frac{M_1V_1}{1000}$$

$$= \text{x mole}$$

where

M_1 = concentration of standardized thiosulphate solution

V_1 = titration volume of standardized thiosulpate solution

Chromium(III), Cr^{3+}

$$\text{Number of mole} = \frac{x}{3}$$

$$= \text{y mole}$$

$$\text{Percentage of } Cr^{3+} = \frac{(52\text{ y})\text{ g}}{(\text{Weight of chromium sample})\text{ g}} \times 100\ \%$$

Table 3.5 shows the data obtained from chromium content determination. The results were in well agreement with the proposed formula.

Table 3.5: Comparison of Cr^{3+} content obtained from titration with theoretical values

Complex	Theoretical %Cr	Experimental %Cr	Catalyst formula
Chomium(III) monochloroacetate	17.3	17.3	$Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$
Chromium(III) dichloroacetate	14.5	14.6	$[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$
Chromium(III) trichloroacetate	12.0	12.0	$[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$
Chromium(III) acetate	20.3	20.4	$[Cr_3O(CH_3CCOO)_6.3H_2O]NO_3.7H_2O$

(b) FT-IR Spectroscopy

The synthesized chromium(III) carboxylate complexes were mixed with KBr powder at 1:100 and pressed into pellet by using a KBr press. The pellets were then scanned through FT-IR spectrometer in the range of 4000-400 cm^{-1}. Absorption bands were assigned by referring to the fundamental vibration frequencies of known carboxylate compounds[1-3] and information provided by previous works[4-5]. Band assignments of the corresponding complexes were listed in Table 3.6 while FT-IR spectra of $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$ and $Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ complexes were shown in Figure 3.1 and Figure 3.2 respectively.

All four spectra showed characteristic peaks of water of crystallization and coordination water in the range of 3568-2962 cm^{-1}. Strong and broad absorption bands in this region indicated the symmetric and antisymmetric OH stretching[3] of water molecules. According to Bellamy[1], C-H stretching mode appeared at the range of 3050-2940 cm^{-1}.

Absorption of the free carboxylic acid was not observed in all the spectra. Instead, two strong bands of asymmetric and symmetric bridging carboxyl (COO^-) stretching absorption were observed at around 1679-1611 cm^{-1} and 1457-1428 cm^{-1}. In the bridging mode, both υ_{asym} (COO^-) and υ_{sym} (COO^-) shift in the same direction thus causing their separation close to that of free ionic form in the range of 100-200 cm^{-1}.[6] For Cr(III) acetate complex, the difference between the two υ (COO^-) is 154 cm^{-1}, indicating the presence of bridging acetate ligand.

The electron withdrawing effect of chloro group on the acetate bridge could be seen from the separation between asymmetric and symmetric COO^- stretch. Table 3.7 shows the separation between $\upsilon_{asym}(COO^-)$ and $\upsilon_{sym}(COO^-)$ of the chromium complexes. As the number of chlorine atom present in the complex increases, the υ_{asym} (COO^-) increases while

Table 3.6: FT-IR band assignments of Cr(III) complexes

Band Assignments (cm-1)	Complexes			
	1	2	3	4
$\upsilon(H_2O)$ $\upsilon(CH)$	2967-3452 *b*	2962-3568 *b*	3012-3547 *b*	3015-3539 *b*
$\upsilon_{asym}(COO^-)$	1611 *s*	1647 *s*	1667 *s*	1679 *s*
$\upsilon_{sym}(COO^-)$	1457 *s*	1438 *s*	1428 *s*	1428 *s*
$\upsilon_{asym}(NO_3^-)$	1385 *s*	1384 *s*	1384 *s*	1384 *s*
$\upsilon(C\text{-}O)$	1298 *w*	1267 *m*	1234 *m*	1313 *m*
$\upsilon_{sym}(NO_3^-)$	1038 *m*	1037 *w*	1039 *w*	1040 *w*
$\upsilon(C\text{-}Cl)$	-	801 *m*	826 *s* 791 *m*	861 *s* 832 *m*
$\upsilon(M\text{-}H_2O)$	700 *m*	702 *m*	726 *m*	757 *m*
$\delta(COO^-)$	677 *m*	660 *m*	662 *m*	691 *m*
$\upsilon_{asym}(Cr_3\text{-}O)$	664 *m*	652 *m*	647 *m*	640 *m*
$\pi(COO^-)$	623 *m*	549 *m*	534 *m*	585 *m*

Abbrevations: *s* = strong; *m* = medium; *w* = weak

Complex 1 = $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$

Complex 2 = $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$

Complex 3 = $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$

Complex 4 = $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$

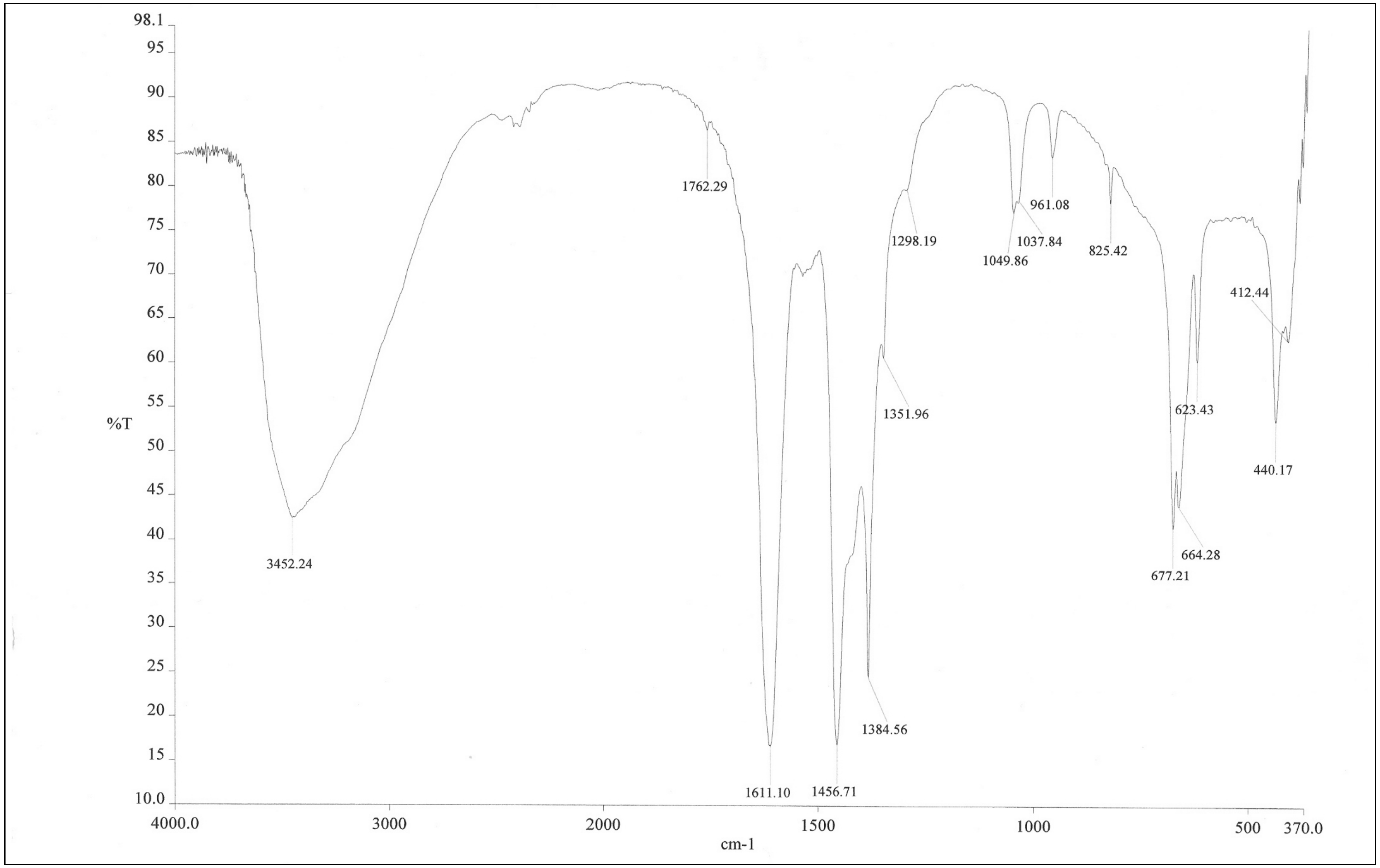

Figure 3.1: FT-IR spectrum of $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$ complex

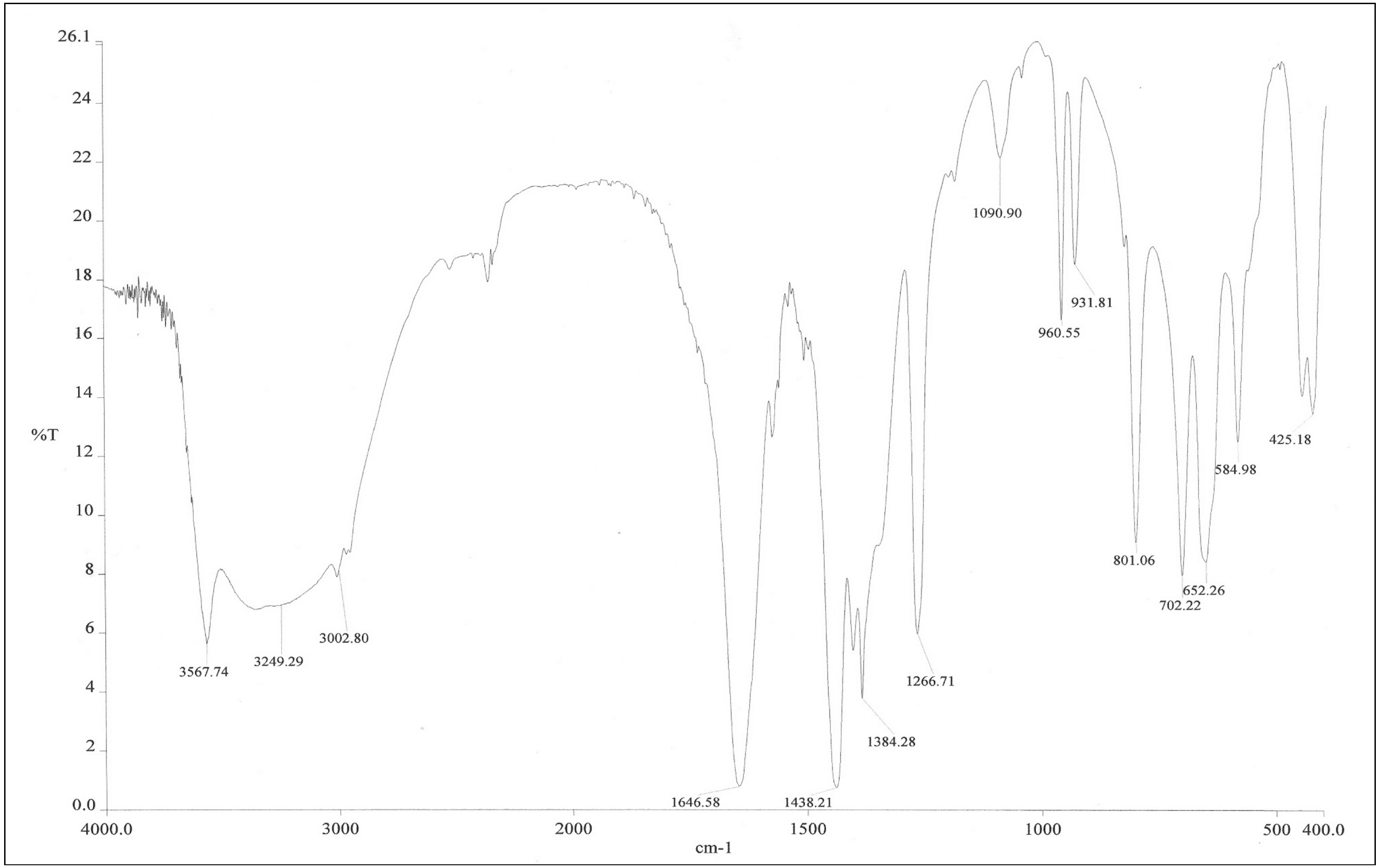

Figure 3.2: FT-IR spectrum of $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ complex

the υ_{sym} (COO$^-$) decreases. This will cause the separation between two frequencies become larger.[3,7] Besides, the large separation might also be attributed to larger metal-metal separation produced by electron withdrawing groups.[8] The Δυ of the chromium complexes increases in the order of

Δυ Cr(III) trichloroacetate > Δυ Cr(III) dichloroacetate > Δυ Cr(III) monochloroacetate > Δυ Cr(III) acetate

Table 3.7: υ_{asym} (COO$^-$), υ_{asym} (COO$^-$) and Δυ(COO$^-$) values of chromium(III) complexes

Chromium(III) complexes	υ_{asym}(COO$^-$) (cm^{-1})	υ_{sym}(COO$^-$) (cm^{-1})	Δυ(COO-) (cm^{-1})
$[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$	1611	1457	154
$[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$	1647	1438	209
$[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$	1667	1428	239
$[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$	1679	1428	251

Δυ(COO-) = υ_{asym}(COO$^-$) - υ_{sym}(COO$^-$)

Nitrate anion gives rise to two absorption bands in the spectra. A sharp band observed at 1385-1384 cm^{-1} was assigned to υ_{asym}(NO$_3^-$)[9] while υ_{sym}(NO$_3^-$)[10] appeared to be medium to weak band in the region of 1037-1040 cm^{-1}. Medium band observed at 801 cm^{-1} in the spectrum of Cr(III) monochloroacetate sample corresponds to the stretching of C-Cl[11-12]. For Cr(III) dichloroacetate and Cr(III) trichloroacetate complexes, two C-Cl stretching peaks were observed. Splitting of the C-Cl stretching frequency into two might be due to the different conformations which are possible.[13]

H-O-H rocking mode of coordinated water molecules was found to appear the range of 900-600 cm^{-1} by several authors.[14-16] Absorption at 700 cm^{-1} in Cr(III) acetate has been assigned to υ(M-H_2O). The mono-, di- and trichloro acetate complexes show OH_2 rocking absorption at 702, 726 and 757 cm^{-1} respectively.

Infrared absorption in the region of 691-660 cm^{-1} was attributed to the symmetric O-C-O deformation mode. Johnson et al.[4] assigned the band at 673 cm^{-1} to δ(COO^-) for $[Cr_3O(CH_3COO)_6 3H_2O]NO_3.xH_2O$ complex. Assignment for asymmetric stretching frequencies of Cr_3O was complex due to the absorption by coordinated ligands in the same region.[17] $\upsilon_{asym}(M_3\text{-}O)$ are expected to lie in the region of 700-500 cm^{-1}. Chromium complexes synthesized showed $\upsilon_{asym}(Cr_3\text{-}O)$ absorption 664-640 cm^{-1}. Besides, bands at 623 cm^{-1}, 549 cm^{-1}, 534 cm^{-1} and 585 cm^{-1} in four spectra were assigned to π(COO^-).

(c) TGA

The trinuclear chromium(III) carboxylate complexes were heated in the temperature range of 50-900ºC at a rate of 20°C/min under nitrogen atmosphere to study the thermal decomposition of the compounds. The complexes were in hydrated form that contained water of hydration and water of coordination[18-19] Water molecules are eliminated according to their binding strength in the compounds. Water of hydration is weakly bonded to the chromium complex via hydrogen bonding while water of coordination is coordinated to the chromium ion in the complex. Therefore, water of hydration is the first to be eliminated on heating and this decomposition usually occurs at temperature below 150°C. Water of coordination should eliminate at temperature above 200°C. Table 3.8 listed the calculated and observed weight losses of the chromium(III) complexes at corresponding temperature ranges.

Table 3.8: Decomposition of chromium(III) carboxylate complexes in nitrogen atmosphere

Complex	Temperature range/ °C	Weight loss/ %		Number of molecules
		Found	Calculated	
$[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$	57-166 166-259	9.4 14.3	9.4 14.1	4 H_2O 6 H_2O
$[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$	61-124 124-287	6.4 12.8	6.0 12.8	3 H_2O 3 H_2O + NO_2 + ½ O_2
$[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$	51-229	12.2	12.5	4 H_2O + NO_2 + ½ O_2
$[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$	113-179	2.8	2.8	2 H_2O

The TGA curve shown in Figure 3.3 is the thermal decomposition of chromium(III) acetate, $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$. The first and second decomposition steps are due to dehydration process. Thermogram shows weight losses at about 9.4% and 14.3% at temperature 57-166°C and 166-259°C which correspond to the elimination of a total of ten water molecules. The results were not able to differentiate between the water of hydration and water of coordination. Weight loss at temperature ranges 259-759°C is due to the decomposition of organic compounds. Chromium(III) acetate complex decomposed slowly until a constant weight was attained, which corresponds to the remaining chromium oxide, Cr_2O_3.[20]

TGA curve for chromium(III) monochloroacetate of formula $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ is shown in Figure 3.4. The first weight loss from 61-124°C (6.4%) corresponded to the elimination of three molecules water of hydration. The obtained weight loss agrees well with the calculated weight loss. The subsequent weight loss of 12.8% at 124-287°C is due to the decomposition of water of coordination and nitrate anion. Further heating resulted in the elimination of organic compounds. Reaction schemes for the decomposition of water molecules and nitrate anion of chromium(III) monochloroacetate are as below:

$$[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O \longrightarrow [Cr_3O(ClCH_2COO)_6.3H_2O]NO_3 + H_2O$$

$$[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3 \longrightarrow [Cr_3O(ClCH_2COO)_6]NO_3$$

$$2\,[Cr_3O(ClCH_2COO)_6]NO_3 \longrightarrow 2\,[Cr_3O(ClCH_2COO)_6]^+ + 2NO_2 + O_2$$

The decomposition of chromium(III) dichloroacetate, $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$ involved more steps than the other chromium complexes, as shown in Figure 3.5. However, dehydration and decomposition of nitrate anion of chromium(III) dichloroacetate occurred in one single step. The 12.2% weight loss corresponded to the elimination of two water of hydration, two water of coordination and nitrate anion. During the decomposition of water of hydration, water of coordination and nitrate anion also started to eliminate at the same time thus only a drop in weight was observed at temperature ranges 51-229°C. The complex then decomposed gradually until a constant weight of 17.3% was obtained.

Figure 3.6 shows the thermal decomposition of chromium(III) trichloroacetate complex, $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$. The 2.8% weight loss obtained in the first step (113-179°C) is due to the release of two water of hydration. A grand weight loss of 70.9% was obtained at temperature 179-392°C. This showed that further decomposition of the complex occured in a single step thus the elimination of water of coordination could not be differentiate from other compounds.

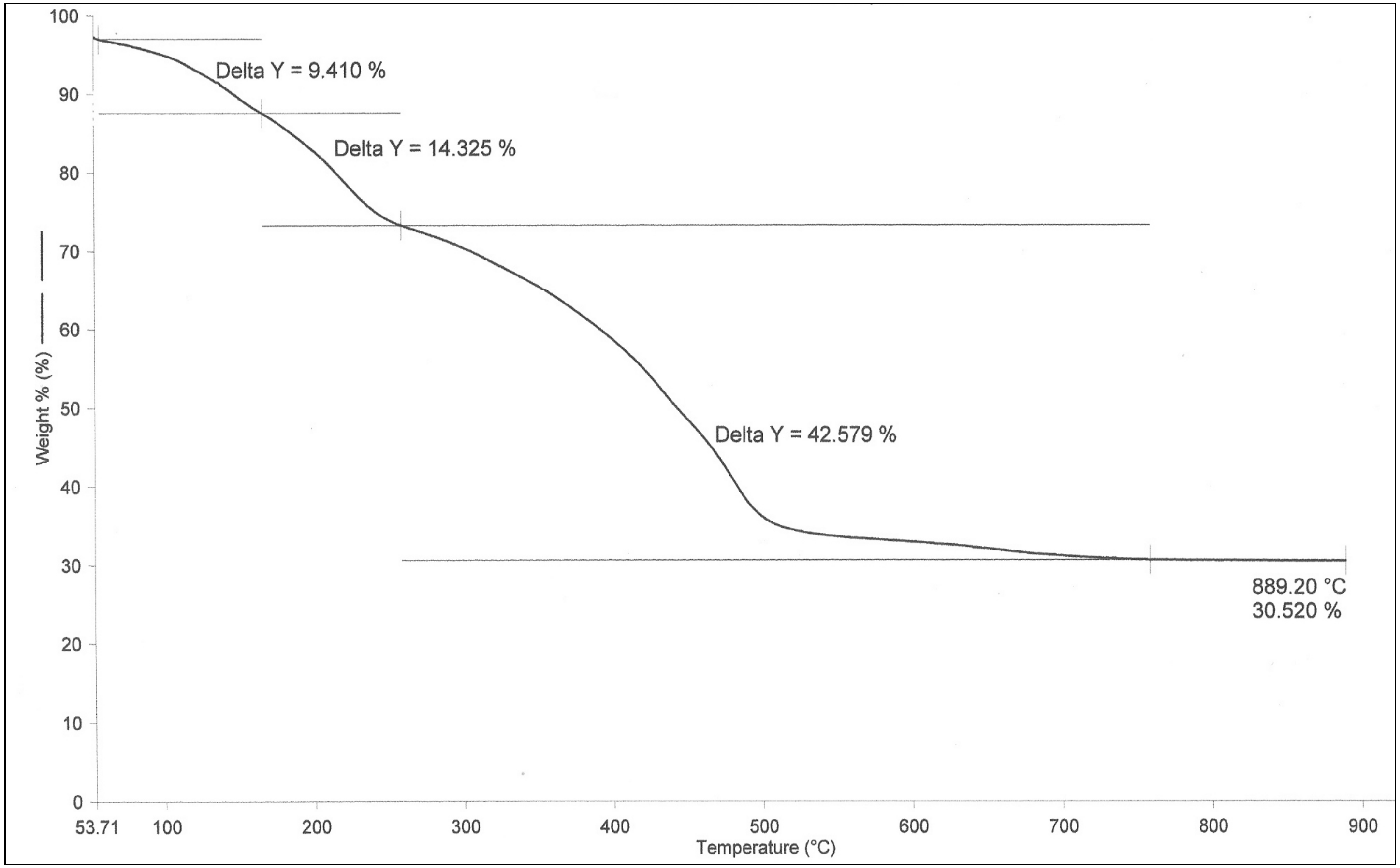

Figure 3.3: TGA thermogram for the decomposition of $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$ complex

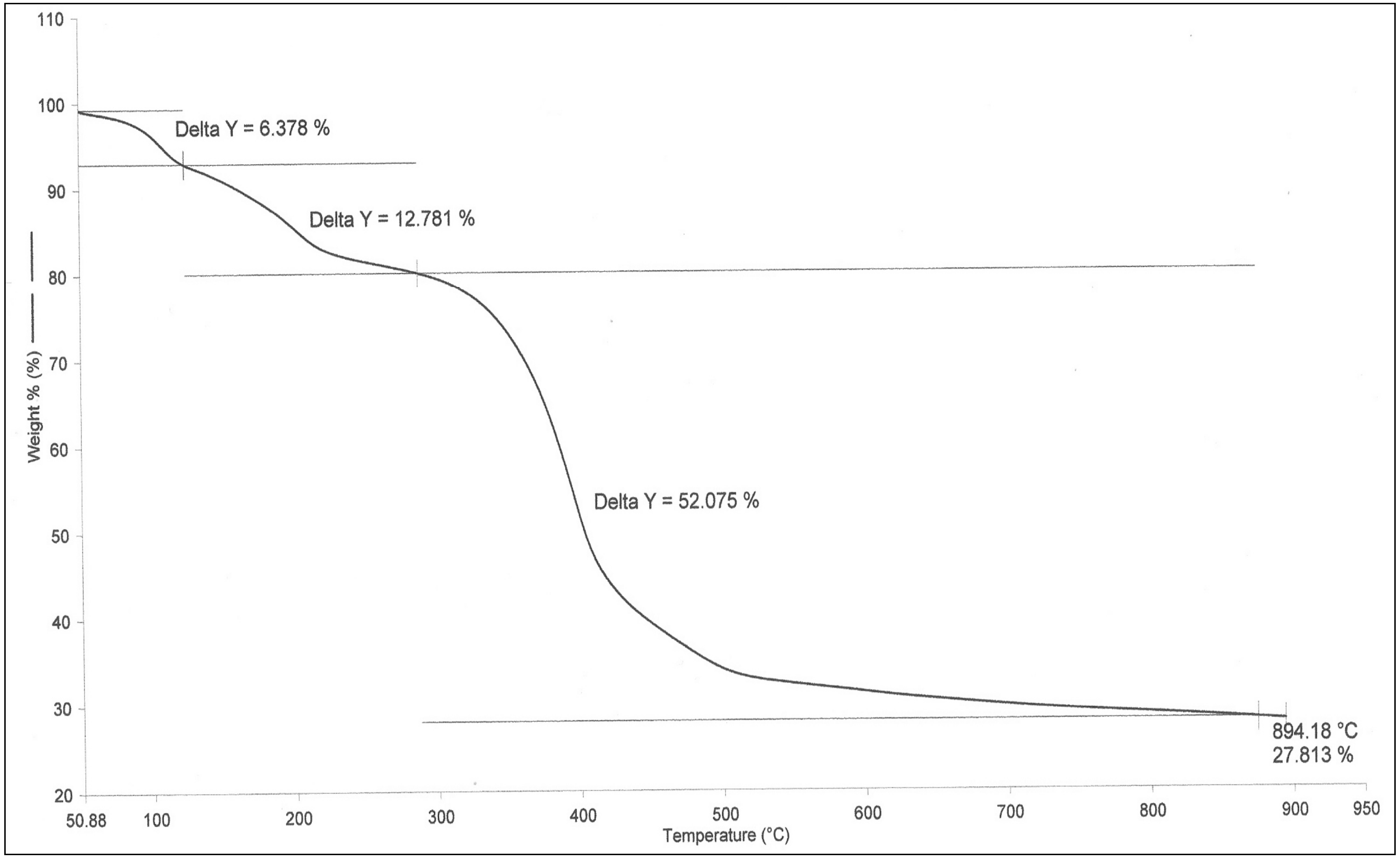

Figure 3.4: TGA thermogram for the decomposition of $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ complex

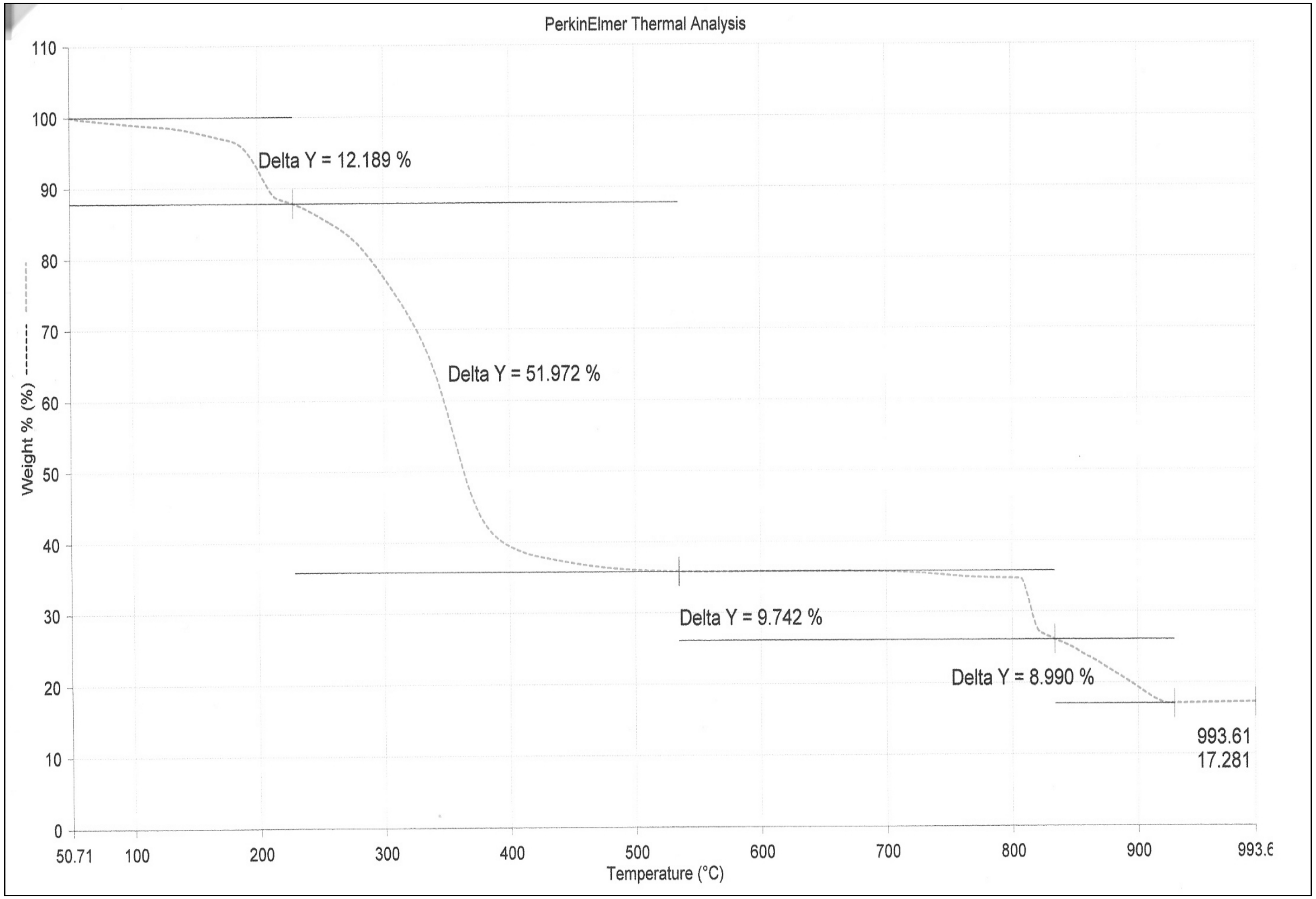

Figure 3.5: TGA thermogram for the decomposition of $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$ complex

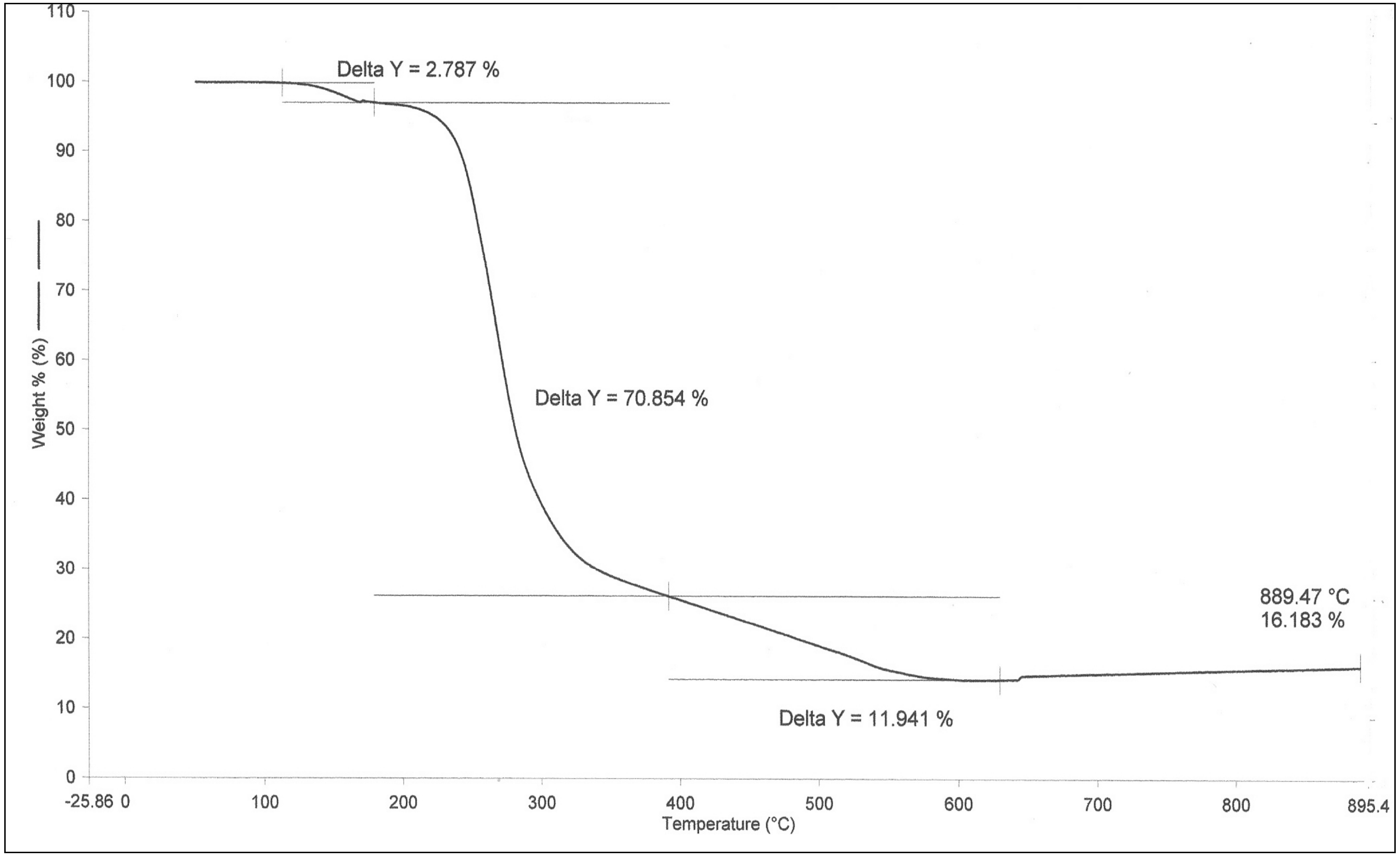

Figure 3.6: TGA thermogram for the decomposition of $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$ complex

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