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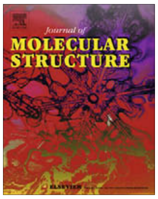

Synthesis, spectral and thermal characterization of nano-sized, oxo-centered, trinuclear carboxylate-bridged chromium(III) complexes of hydroxycarboxylic acids

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ABSTRACT

Complexes of the type $[Cr_3O(OOCR^*)_3(OOCR)_3]^+$ [$R^* = C_6H_4OH$, (R′); $C_6H_5CH(OH)$, (R″) or $(C_6H_5)_2C(OH)$, (R‴) and $R = C_{15}H_{31}$ or $C_{17}H_{35}$] were synthesized by substitutions of acetate ions from their respective acetato complexes, in toluene under reflux. The characterization of the complexes were carried out by spectral (infrared, electronic, FAB mass and powder XRD) studies, elemental analyses, molar conductance and magnetic susceptibility measurements. Their thermal decompositions have been studied by using dynamic, nonisothermal thermogravimetry (TG) and differential scanning calorimetry (DSC). Infrared spectra suggested bidentate and bridging nature of both the carboxylate and hydroxycarboxylate anions along with $\nu_{asym}(Cr_3O)$ vibrations in the complexes. FAB mass spectrometry showed trinuclear nature of the complexes. Molar conductance value of the complexes showed the complexes were 1:1 electrolyte. Magnetic moment values and electronic spectra of these complexes were in support of an octahedral environment around the chromium(III) ion. X-ray diffraction data indicated the nano-sized powder.

1. Introduction

Trinuclear, oxo-centered, carboxylate-bridged complexes of the general composition $[M_3O(OOCR)_6(L)_3]^+$ (M = 3-d metal atom, RCOOH = carboxylic acid, L = terminal ligand like water, methanol, pyridine, etc.) represents one of the most intensely studied class of polynuclear compounds [1]. These species have been of continual interest for several reasons: they serve as a suitable models to study electronic and magnetic metal–metal interactions in clusters [2–7], they display properties of homogeneous catalysts in various oxidation reactions [8]. They behave as precursors for clusters of higher nuclearity whose unusual structural design and physical properties open new opportunities for experimental modeling of biocatalysis and their structural variations allow a close examination of parameters affecting the metal–ligand aggregates [9,10]. In recent years, these multinuclear carboxylate assemblies of chromium(III) have been increasingly used as functional biomimetic models to study insulin related functions of the unique low-molecular-weight chromium-binding-oligopeptide (LMWCr) [11–13] which have been proposed as possible nutritional supplements and therapeutics for adult-onset diabetes [14].

Perusal of the literature reveals that a number of transition metals form complexes with hydroxycarboxylic ligands [15–17], but studies on chromium(III) complexes with such ligands are very limited. It has also been found that the mixed-ligand complexes of chromium(III) with higher fatty acids and hydroxycarboxylic acids are not reported so far. In view of these objectives, we report here synthesis of some μ_3-oxo-tri(carboxylato)tri(hydroxycarboxylato) chromium(III)acetate complexes following substitutions of acetate ions of the μ_3-oxo-tri(acetato)tri(carboxylato)chromium(III)acetate. Coordination behaviour of the ligands has been discussed to arrive at their structure on the basis of spectral, thermal and magnetic studies.

2. Experimental

2.1. Materials and physico-chemical measurements

All the reactions were carried out under anhydrous conditions. Organic solvents (Qualigens) were dried and distilled before use by standard methods [18]. Carboxylic acids were used after distillation under reduced pressure (mp of palmitic acid: 63 °C and stearic acid: 70 °C). Hydroxycarboxylic (salicylic, mandelic and benzilic) acids (BDH) were used after purification. Chromium was estimated gravimetrically as lead chromate [19]. Acetic acid in the collected azeotrope was estimated with standard sodium hydroxide using phenolphthalein indicator.

Electronic spectra were recorded on a Cary 2390 spectrophotometer in Nujol, infrared spectra were recorded on a Perkin-Elmer model 125 FTIR spectrophotometer in KBr discs in the range 4000–400 cm^{-1}. FAB mass data were obtained on a JEOL SX 102/ DA-6000 mass spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix from CDRI Lucknow. Powder X-ray diffraction data were

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collected on a MiniFlex2 goniometer from MANIT Bhopal, India. Molar conductances were measured on century CC-601 digital conductivity meter at 10^{-2}–10^{-3} molar solutions in nitrobenzene. Elemental analyses (C, H) were done on a Haraleus 1108 analyzer. TG-DSC curves were obtained by using a NETZSCH STA 409 PG/PC instrument under a nitrogen atmosphere (flow rate of 100 ml min^{-1}) with a heating rate 10 °C min^{-1}. Magnetic susceptibility data were obtained from polycrystalline samples on a Gouy balance using $Hg[Co(SCN)_4]$ as a calibrant.

2.2. Synthesis of $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$

A solution of salicylic acid (0.82 g; 5.91 mmol) in toluene was added to a toluene solution of $[Cr_3O(OOCCH_3)_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$ (2.50 g; 1.97 mmol) [5]. The reaction mixture was refluxed for 13 h with slow and continuous fractionation of acetic acid–toluene azeotrope (bp 106 °C). The progress of the reaction was followed by estimating the CH_3COOH content in the collected azeotrope. Excess solvent was removed under reduced pressure (1.5 mm/60 °C) to yield a yellowish-green solid. This was purified by reprecipitation from benzene–methanol mixture (1:4 ratio). Other mixed-ligand complexes were synthesized following the same procedure and the analytical results are summarized in Table 1.

3. Results and discussion

A number of trinuclear, oxo-centered, mixed carboxylato complexes of chromium(III) of the general formula $[Cr_3O(OOCCH_3)_3(OOCR)_3](OOCCH_3)$ were synthesized by the substitutions of acetate ions from $[Cr_3(OOCCH_3)_7(OH)_2]$ (μ_3-oxo-(aqua)heptakis(acetato)chromium(III)) with long chain carboxylic acids in 1:3 molar ratios using toluene as a solvent, and the product obtained were reprecipitated with benzene–methanol mixture (1:4 ratio).

$$[Cr_3(OOCCH_3)_7(OH)_2] + 3RCOOH \xrightarrow[\text{Reflux}]{\text{Toluene}}$$
$$[Cr_3O(OOCCH_3)_3\underset{\mathbf{A}}{(OOCR)_3}](OOCCH_3) + H_2O\uparrow + 3CH_3COOH\uparrow \qquad (1)$$

where $R = C_{15}H_{31}$ or $C_{17}H_{35}$.

Table 1
Analytical and conductance results for the chromium(III) complexes.

Reactants[a] (g; mmol)	Product[b] (Colour) (% yield)	Found (Calculated)				Conductance (Ω^{-1} cm^2 mol^{-1})
		CH_3COOH in azeotrope (g)	Cr	C	H	
$[Cr_3O(OOCCH_3)_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$ (2.50; 1.97) + R′COOH (0.82; 5.91)	$[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$ (Yellowish green) (76) (**1**)	0.31 (0.36)	10.40 (10.36)	59.10 (59.07)	8.19 (8.24)	41
$[Cr_3O(OOCCH_3)_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$ (2.32; 1.71) + R′COOH (0.71; 5.14)	$[Cr_3O(OOCR')_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$ (Green) (78) (**2**)	0.34 (0.31)	9.85 (9.82)	60.52 (60.48)	8.61 (8.57)	37
$[Cr_3O(OOCCH_3)_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$ (3.00; 2.36) + R″COOH (1.08; 7.09)	$[Cr_3O(OOCR'')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$ (Dark green) (84) (**3**)	0.40 (0.43)	10.15 (10.09)	59.87 (59.80)	8.41 (8.40)	32
$[Cr_3O(OOCCH_3)_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$ (3.20; 2.36) + R″COOH (1.08; 7.10)	$[Cr_3O(OOCR'')_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$ (Dark green) (84) (**4**)	0.38 (0.43)	9.55 (9.56)	61.04 (61.12)	8.65 (8.72)	45
$[Cr_3O(OOCCH_3)_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$ (2.63; 2.07) + R‴COOH (1.42; 6.22)	$[Cr_3O(OOCR''')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$ (Green) (79) (**5**)	0.35 (0.37)	8.76 (8.80)	64.31 (64.28)	8.10 (8.00)	39
$[Cr_3O(OOCCH_3)_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$ (2.50; 1.85) + R‴COOH (1.27; 5.26)	$[Cr_3O(OOCR''')_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$ (Dark green) (83) (**6**)	0.31 (0.33)	8.45 (8.40)	65.24 (65.25)	8.27 (8.30)	33

[a] Reflux about 13–16 h, C_6H_4OH; (R′), $C_6H_5CH(OH)$; (R″) and $(C_6H_5)_2C(OH)$; (R‴).
[b] Reprecipitated product in benzene–methanol mixture (1:4).

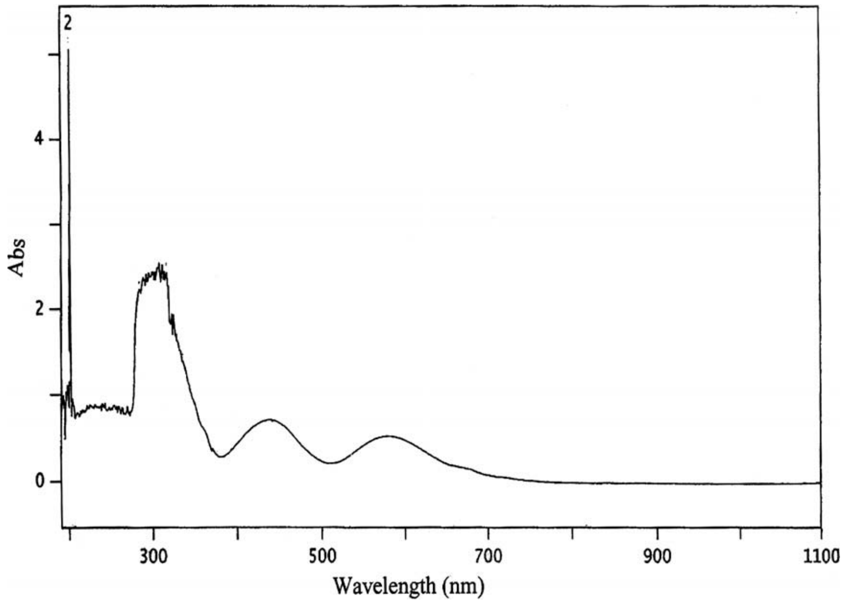

Fig. 1. Room-temperature electronic spectrum of $[Cr_3O(OOCR'')_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$.

Table 2
Electronic spectral transitions (cm^{-1}) and magnetic moment values for the complexes.

Complexes[a]	Observed transitions from $^4A_{2g}$ (F) to			B (cm^{-1})	β	μ_{eff} (B.M.)
	$^4T_{2g}$ (F) (ν_1, 10 Dq)	$^4T_{1g}$ (F) (ν_2)	$^4T_{1g}$ (P) (ν_3)			
$[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$	17110	22882	36715	551	0.60	3.40
$[Cr_3O(OOCR')_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$	16880	23215	36743	621	0.66	3.36
$[Cr_3O(OOCR'')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$	16695	23105	36471	633	0.68	3.39
$[Cr_3O(OOCR'')_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$	17271	22728	36797	514	0.55	3.33
$[Cr_3O(OOCR''')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$	16630	23015	36329	630	0.67	3.38
$[Cr_3O(OOCR''')_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$	16770	22780	36262	582	0.62	3.34

[a] $R' = C_6H_4OH$; $R'' = C_6H_5CH(OH)$; and $R''' = (C_6H_5)_2C(OH)$.

Table 3
Thermoanalytical results for the chromium(III) complexes.

Complex	Step	Decomp.	TG weight loss (%)		DSC		Inference
		Temp. (°C)	Found	Cacld.	Temp. (°C)	Peak	
1	1st	184–334	10.95	10.30	312	Exo[a]	Liberation of $3CH_3OH$ and CH_3COO^- moieties
	2nd	334–452	53.29	50.92	425	Endo[b]	Liberation of all fatty acid groups
	3rd	452–528	26.13	27.33	507	Exo[a]	Liberation of salicylic acid
		>528					Cr_2O_3 as residue
2	1st	192–340	10.63	9.76	318	Exo[a]	Liberation of $3CH_3OH$ and CH_3COO^- moieties
	2nd	340–462	55.04	53.52	452	Exo[a]	Liberation of all fatty acid groups
	3rd	462–530	23.47	25.88	518	Exo[a]	Liberation of salicylic acid
		>530					Cr_2O_3 as residue
3	1st	172–328	12.37	10.02	315	Exo[a]	Liberation of $3CH_3OH$ and CH_3COO^- moieties
	2nd	328–435	47.23	49.53	419	Endo[b]	Liberation of all fatty acid groups
	3rd	435–530	29.91	29.31	522	Exo[a]	Liberation of mandelic acid
		>530					Cr_2O_3 as residue
4	1st	185–340	12.01	9.51	325	Endo[b]	Liberation of $3CH_3OH$ and CH_3COO^- moieties
	2nd	340–425	51.22	52.14	418	Endo[b]	Liberation of all fatty acid groups
	3rd	425–535	28.15	27.80	515	Exo[a]	Liberation of mandelic acid
		>535					Cr_2O_3 as residue
5	1st	172–318	7.13	8.74	290	Exo[a]	Liberation of $3CH_3OH$ and CH_3COO^- moieties
	2nd	318–436	48.50	43.16	405	Endo[b]	Liberation of all fatty acid groups
	3rd	436–520	35.44	38.40	512	Exo[a]	Liberation of benzilic acid
		>520					Cr_2O_3 as residue
6	1st	175–320	10.23	8.34	302	Exo[a]	Liberation of $3CH_3OH$ and CH_3COO^- moieties
	2nd	320–445	48.39	45.74	418	Exo[a]	Liberation of all fatty acid groups
	3rd	445–530	32.65	36.66	510	Exo[a]	Liberation of benzilic acid
		>530					Cr_2O_3 as residue

Note. (+) a, exo (exothermic); (−) b, endo (endothermic); Calcd. calculated ; Temp, temperature ; Decomp., decomposition.

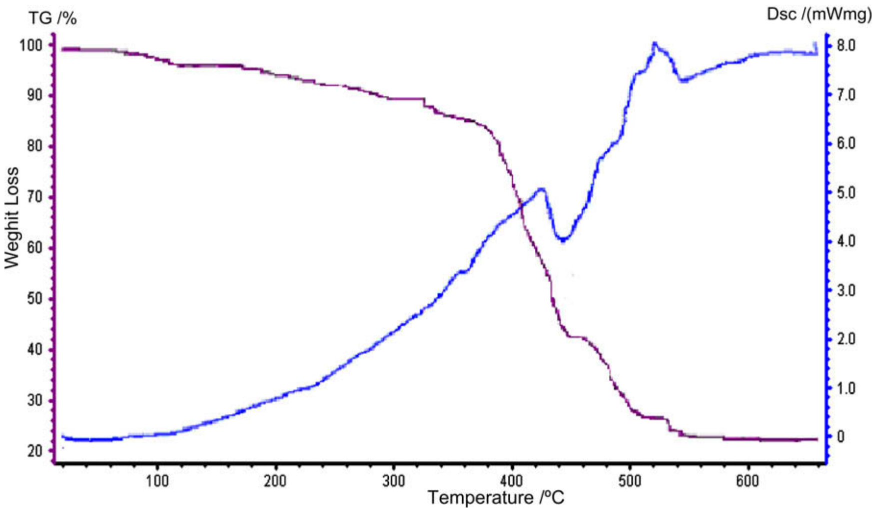

Fig. 2. Thermogram of $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$.

$$\mathbf{A} + CH_3OH = [Cr_3O(OOCCH_3)_3(OOCR)_3](OOCCH_3) \cdot 3CH_3OH$$

The acetate ions of these products were further substituted with hydroxycarboxylic (salicylic, mandelic or benzilic) acids in refluxing toluene and products were finally reprecipitated from their benzene solution by adding an excess of methanol:

$$[Cr_3O(OOCCH_3)_3(OOCR)_3](OOCCH_3) \cdot 3CH_3OH + 3R^*COOH \xrightarrow[\text{Reflux}]{\text{Toluene}} [Cr_3O(OOCR^*)_3(OOCR)_3](OOCCH_3) + 3CH_3COOH\uparrow + 3CH_3OH\uparrow \quad (2)$$

where $R^* = C_6H_4OH$ (R′), $C_6H_5CH(OH)$ (R″) or $(C_6H_5)_2C(OH)$ (R‴).

$$[Cr_3O(OOCR^*)_3(OOCR)_3](OOCCH_3) + \underset{(\text{Excess})}{CH_3OH} \rightarrow [Cr_3O(OOCR^*)_3(OOCR)_3](OOCCH_3) \cdot 3CH_3OH \quad (3)$$

All the above reactions were carried out in toluene because of the advantage that it forms an azeotrope with acetic acid (bp 106 °C) liberated during the course of reactions which could be fractionated out to push the reaction in the forward direction. The reactions were facile and their progress could be followed by estimating the acetic acid content in the collected azeotrope. All the complexes isolated during the present investigations are non-volatile coloured solids. The complexes were soluble in non-polar organic solvents including benzene, toluene, chloroform, dichloromethane, etc. The values of molar conductances in nitrobenzene were found in the range 33–45 $ohm^{-1} cm^2 mol^{-1}$ which clearly indicated that all the complexes were 1:1 electrolyte [20]. The complexes did not have sharp melting point and all of them were decomposed at around 425–535 °C temperature.

Table 4
FAB mass data of $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3).3CH_3OH$.

Peak position	Expected fragmentation species	Calcd. mol. wt.
1472	$[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3){\cdot}2CH_3OH$	1473
1413	$[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)$	1409
1347	$[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3]^+$	1350
1095	$[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_2]^{2+}$	1094
842	$[Cr_3O(OOCR')_3(OOCC_{15}H_{31})]^{3+}$	839
578	$[Cr_3O(OOCR')_3]^{4+}$	583

3.1. Infrared spectra

In FTIR spectra of the synthesized complexes, the characteristic ν (C=O) and δ (O—H) of free carboxylic acids at 1710 and 935 cm^{-1}, respectively, were found absent. The O—H stretching vibration of free hydroxyl group of hydroxycarboxylic acid was noticed at ~3400 cm^{-1} in the IR spectra of the complexes, which indicated that the hydroxyl group of hydroxycarboxylic acid was not bound to chromium and it was remained in free state. Two strong bands were found in the range 1640–1585 and 1436–1400 cm^{-1} which could be assigned due to (ν_{asym}OCO) (antisymmetric) and (ν_{sym}O-CO) (symmetric) vibrations of the carboxylate ions, respectively [21]. The differences between the symmetric and antisymmetric stretches, $\Delta[\nu_{asym}(OCO) - \nu_{sym}(OCO)]$ were in the range 150–160 cm^{-1}, which were less than that for monodentate $NaOOCCH_3$ (184 cm^{-1}) [22]. This indicated the carboxylate groups of both carboxylic acids and hydroxycarboxylic acids were coordinated to chromium in a bidentate and bridging mode involving coordination of both the oxygen atoms of the ligands [22]. A medium band observed at ~680 cm^{-1} was attributed to δ (CO_2) of bridging carboxylate anion [22]. The broad band observed at ~3150 cm^{-1} was assigned to the O—H stretching of coordinated methanol [6,7]. An absorption near 540 cm^{-1} could be assigned to asymmetric stretching of the Cr_3O core [23]. The bands below 500 cm^{-1} may be ascribed to Cr—O vibrations [22].

3.2. Electronic spectra and magnetic moments

The electronic spectrum of a representative complex $[Cr_3O(OOCR'')_3(OOCC_{17}H_{35})_3](OOCCH_3){\cdot}3CH_3OH$ is given in (Fig. 1 and Table 2). The spectra of the complexes exhibited two spin–allowed bands at 16,630–17,271 and 22,728–23,215 cm^{-1} which could be assigned to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}$ (F) (ν_1) and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}$ (F) (ν_2), respectively. These bands suggested an octahedral environment around chromium(III) in the complexes and the lowest energy band (ν_1) is equal to the crystal field splitting i.e. 10 Dq [24]. The position of the third band ${}^4A_{2g}$ (F) $\rightarrow {}^4T_{1g}$ (P) (ν_3), the Racah parameter (B) and the nephelauxetic ratio (β) have been calculated using Eqs. (4)–(6) given by Underhill and Billing [25]

$$340\,Dq + 18(\nu_2 + \nu_3)Dq + \nu_2 \cdot \nu_3 = 0 \quad (4)$$

$$B = \nu_3 + \nu_2 - 30\,Dq/15 \quad (5)$$

$$\beta = B_{complex}/B_{free\ ion} \quad (6)$$

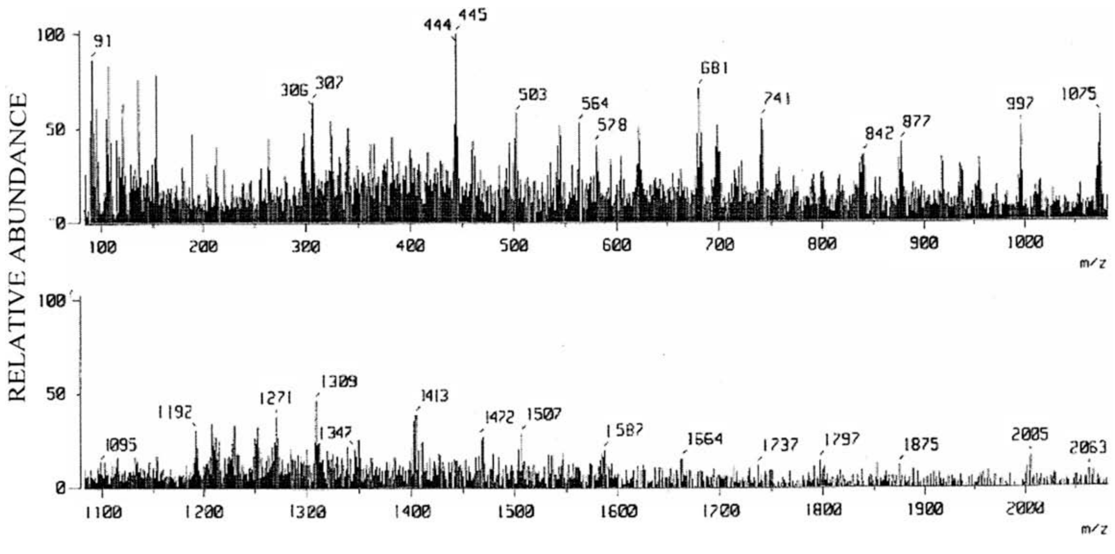

Fig. 3. FAB mass spectrum of $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3){\cdot}3CH_3OH$.

Table 5
Powder XRD data of $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot3CH_3OH$.

Peak No.	2 Theta (°)	Flex width	*d*-Value	Intensity	*I*/*Io*
1	19.400	1.176	4.5717	169	22
2	21.400	0.941	4.1487	798	100
3	24.000	0.941	3.7048	323	41
4	59.000	1.176	1.5643	21	3

The values of *B* and β were found 514–633 cm^{-1} and 0.62 ± 0.07, respectively (Table 2). The reduction of Racah parameter from the free Cr^{3+} value (933 cm^{-1}) [24] suggested considerable covalent character of metal–ligand bonds in these complexes.

The magnetic moment of oxo-centered trinuclear chromium carboxylate complexes have been explained in detail by earlier workers [26,27]. The magnetic moment of these complexes were found in the range 3.37 ± 0.03 B.M. at room temperature (T = 298 K) and the values are given in Table 2. These values are lower than the calculated $\mu_{s.o.}$ value for Cr^{3+} (d^3 system, 3.87 B.M.) which could be interpreted due to the presence of superexchange interactions [26] between Cr^{3+} ions. In these complexes Cr—O—Cr bridge shows weak antiferromagnetic interactions and the oxygen atom provides π-pathways for antiferromagnetic behaviour. In other words, Cr^{3+} ions of trinuclear oxo-centered chromium(III) (S = +3/2) assemblies are antiferromagnetically coupled resulting in an S = +1/2 ground state [23]. This is similar to the trinuclear carboxylates of chromium(III) containing a central μ_3—O core [28].

3.3. Thermal studies

The details of TG and DSC data for the complexes are given in Table 3 and a thermogram of complex $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot3CH_3OH$ is given in Fig. 2. The complexes were decomposed in three steps and the pattern of decomposition is given below:

1. $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot3CH_3OH \xrightarrow[184-334\ ^\circ C]{\text{Temp.range}} Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3 + CH_3COOH + 3CH_3OH$
2. $Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3 \xrightarrow[334-452\ ^\circ C]{\text{Temp.range}} [Cr_3O(OOCR')_3]^{4+}$ + gaseous product
3. $[Cr_3O(OOCR')_3]^{4+} \xrightarrow[452-528\ ^\circ C]{\text{Temp.range}} Cr_2O_3$ + gaseous product

The end product in all the cases was Cr_2O_3 which was confirmed by estimation of chromium gravimetrically.

3.4. FAB mass, powder XRD and structural elucidation

FAB mass spectrum of a representative complex $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot3CH_3OH$ has been recorded (Fig. 3) and positions of the peaks are given in Table 4. The peaks revealed a distinctive set of ions with masses corresponding to the cation and fragments of parent ions derived by loss of the ligands [29].

Single crystals of the complexes could not be prepared to get the XRD and hence the powder diffraction data were obtained for structural characterization. The powder X-ray diffraction spectrum for $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot3CH_3OH$ was recorded (Fig. 4) and the peaks have been indexed by the crystal system (Table 5). The lattice parameters (d, 2θ, height and area) indicated the pattern of the sample matched well with those of other trinuclear chromium(III) oxo-carboxylate assemblies reported earlier [11,26,27]. With the help of the data obtained from the powder XRD, the particle size of the complexes has been calculated using the standard equation given by Scherrer [30].

$$D = K\lambda/(\beta\cos\theta) \tag{7}$$

where, D is the average size of the crystal gain; K is constant (=0.94); λ is X-ray wavelength (=1.5406 Å); θ is Bragg diffraction angle; β is integral peak width of the diffraction peak.

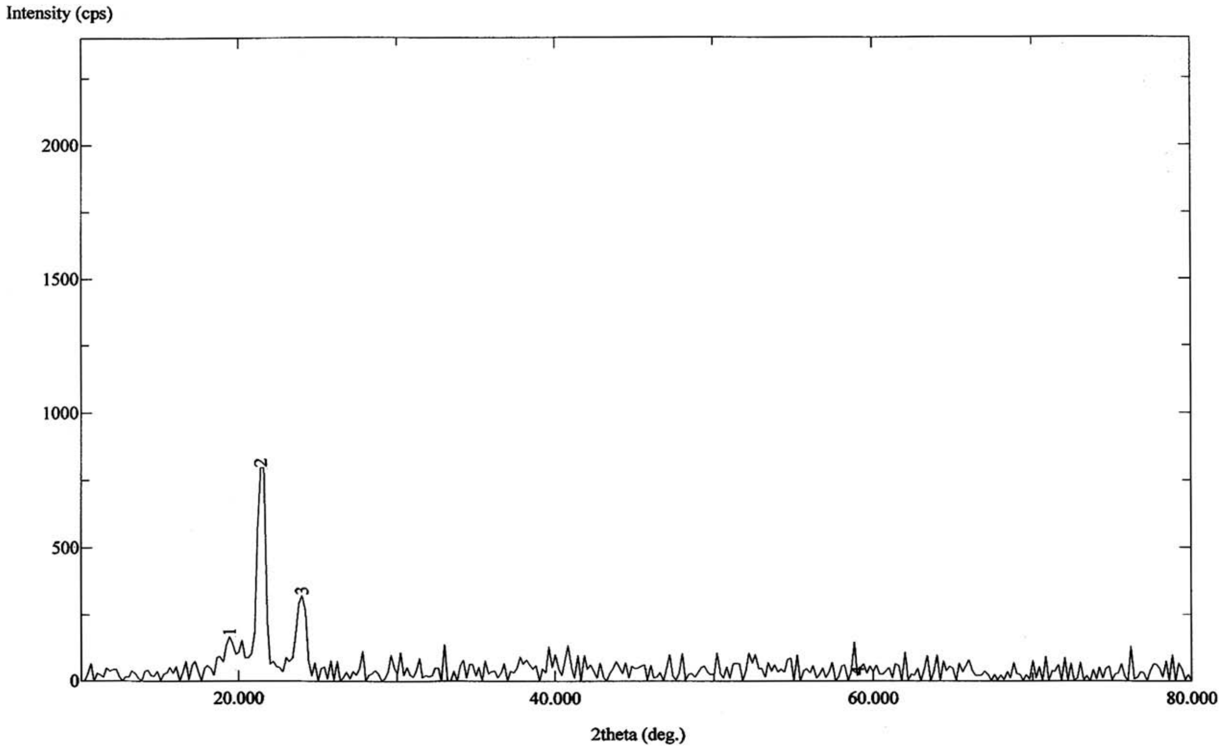

Fig. 4. Powder XRD spectrum of $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot3CH_3OH$.

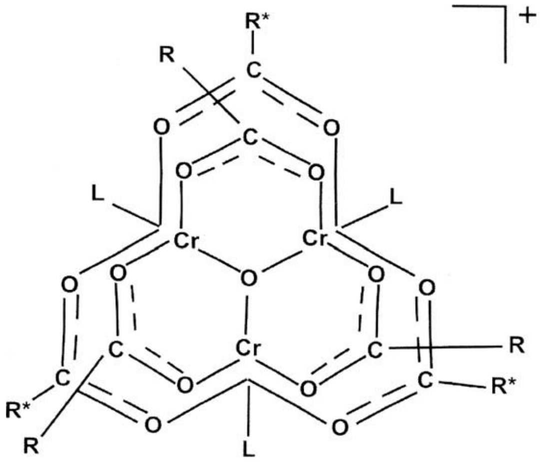

Fig. 5. Proposed structure for $[Cr_3O(OOCR^*)_3(OOCR)_3(L)_3]^+$ (where: $R^* = C_6H_4OH$; (R′), $C_6H_5CH(OH)$; (R″) or $(C_6H_5)_2C(OH)$; (R‴); $R = C_{15}H_{31}$ or $C_{17}H_{35}$ and $L = CH_3OH$).

The size for the representative complex was obtained 15.0 nm and on this basis it could be concluded that the complex $[Cr_3O(OOCR')_3(OOCC_{15}H_{31})_3](OOCCH_3)\cdot 3CH_3OH$ is a nano-sized oxo-bridged complex of chromium(III) with an octahedral structure. On the basis of spectral, thermal and magnetic studies, a plausible structure for the complexes is established (Fig. 5) in which chromium(III) is situated in an octahedral environment and one carboxylate and one hydroxycarboxylate ligands are bridged between two chromium atoms.

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