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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).

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

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).

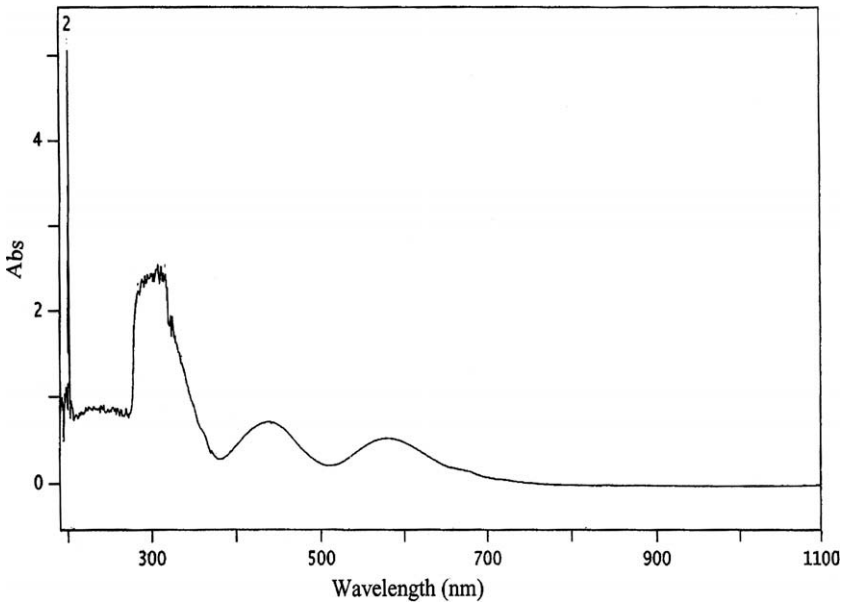

Fig. 1. Room-temperature electronic spectrum of $[Cr_3O(OOCR'')_3(OOCC_{17}H_{35})_3](OOCCH_3)\cdot 3CH_3OH$.