

## SHORT COMMUNICATION

### SYNTHESIS AND CHARACTERIZATION OF TWO NOVEL TRINUCLEAR OXO-CENTERED, OF CHROMIUM AND IRON COMPLEXES CONTAINING UNSATURATED CARBOXYLATE BRIDGING LIGAND

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**ABSTRACT.** Two novel oxo-centered trinuclear compounds,  $[M_2M'O(C_3H_3O_2)_6(H_2O)_3]^+$  ( $M = Cr, M' = Cr, Fe$ ) have been synthesized. The complexes were characterized by elemental analysis, infrared and electronic spectroscopy and thermogravimetric analysis (TGA). These complexes contain unsaturated carboxylate bridging ligands that cause them to have potential scopes for polymerization in the solid state by cross-linking of substituents. Bridging coordination modes for carboxylates were indicated by presence of  $\nu_{asym}(M_2M'O)$  vibrations in the infrared spectra.

**KEY WORDS:** Oxo-centered complexes, Chromium complex, Iron complex, Unsaturated carboxylate

## INTRODUCTION

Oxo-centered carboxylate-bridged trinuclear complexes of the type  $[M_3(\mu_3-O)(\mu-RCO_2)_6L_3]^{n+}$  are an important class of compounds in metal chemistry. They are known with a wide variety of metal ions (M), bridging carboxylate anions ( $RCO_2^-$ ), and monodentate terminal ligands (L) as well as with mixed-valence and mixed-metal combinations [1-5].

Complexes of this structure contain a triangular arrangement of metal ions bridged by a central  $\mu_3$ -oxo atom. Each carboxylate anion spans two metal centres at the periphery of the  $[M_3(\mu_3-O)]^{6+}$  core, while the neutral monodentate ligands occupy the remaining coordination sites on each metal centre, and as a result the coordination around the metal centre is approximately octahedral (Figure 1).

Interest in these compounds has arisen for several reasons. First, some of these complexes are active as homo-generous catalysts for a variety of oxidation reactions [6, 7]. Secondly, in the particular case of chromium(III), complexes that belong to the general structural formula have exciting biological properties. Thus, compound  $[Cr_3O(O_2CET_3)_6(H_2O)_3](NO_3)$  is a functional biomimetic [8] for the low-molecular-weight chromium-binding substance (LMWCr); the latter has been identified as the biologically active form of chromium in mammals, activating the kinase activity of insulin receptor in the presence of insulin [9]. These carboxylate complexes have an additional interest when the carboxylate ligand is unsaturated, because there is a potential scope for further polymerization in the solid state by cross-linking of substituents [10]. One important application of such polymerization reactions is in the quest for dental filling materials as a substitute for amalgams and to produce active material as selective metallic sieves [11].

In this paper, we report synthesis, elemental analysis, IR and UV-Vis data of two new trinuclear complexes containing acrylic acid as bidentate-bridged ligand, with the general formula  $M_2M'O(C_3H_3O_2)_6(H_2O)_3]^+$  ( $M = Cr, M' = Cr, Fe$ ). It is interesting to emphasize that title compounds constitute the rare examples of the  $\mu_3$ -oxo-heterotrinuclear clusters containing acrylic acid as bidentate-bridged ligands.

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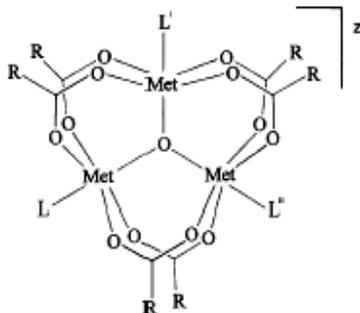


Figure 1. The proposed structure of the cluster unit  $[M_3O(RCOO)_6(L)_3]^n$ .

## EXPERIMENTAL

### Methods and materials

C, H and N analysis were carried out on a Thermo Finnigan Flash model EA 1112 elemental analyzer (Italy), atomic absorption analysis were carried out on a Shimadzu model AA-670 atomic absorption spectrometer (Japan). IR spectra of KBr disc were recorded on a Buck 500 spectrometer (USA). UV-Vis spectra were recorded in the range of 200-700 nm by the Agilent 8453 spectrophotometer (Italy). TG studies were performed on a Cahn 200 microbalance (UK).

Reagents, carboxylic acid and metal salts used in this study were purchased from Merck (Germany).

### Synthesis

#### Preparation of $[Cr_3O(C_3H_3O_2)_6(H_2O)_3]Cl$ (1)

2 g (7.5 mmol) of  $CrCl_3 \cdot 6H_2O$  were dissolved in 10 mL of water and solution containing 1 mL (15 mmol) acrylic acid and 0.795 g (7.5 mmol) sodium carbonate in 15 mL of water were gradually added with continuous stirring. The mixture was left at ambient temperature. After several days, the green crystals were collected, washed with ether and dried in vacuum (yield: 80%).

Elemental analysis: calc. for  $C_{18}H_{24}O_{16}ClCr_3$ ; C: 31.42, H: 3.49, Cr: 22.69%. Found: C: 31.25, H: 3.37, Cr: 22.51%.

#### Preparation of $[Cr_2FeO(C_3H_3O_2)_6(H_2O)_3]NO_3 \cdot 3H_2O$ (2)

1.33 g (5 mmol)  $CrCl_3 \cdot 6H_2O$  and 1 g (2.45 mmol)  $Fe(NO_3)_3 \cdot 9H_2O$  were dissolved in 10 mL of water and solution containing 1 mL (15 mmol) of acrylic acid and 0.795 g (7.5 mmol) of sodium carbonate in 15 mL of water were gradually added with continuous stirring. The mixture was left at ambient temperature. After two weeks, the dark crystals were collected, washed with ether and dried in vacuum (yield: 75%).

Elemental analysis: calc. for  $C_{18}H_{30}O_{22}NCr_2Fe$ ; C: 27.98, H: 3.88, N: 1.81, Cr: 13.47, Fe: 7.23%. Found: C: 27.79, H: 3.68, N: 1.66, Cr: 13.25, Fe: 7.1%.

## RESULTS AND DISCUSSION

### Infrared spectroscopy

Selected bands of the infrared spectra of the prepared compounds are given in Table 1. The  $\nu_{as}(\text{CO}_2)$  and  $\nu_s(\text{CO}_2)$  strong bands are at 1592 (**1**), 1585 (**2**) and 1446 (**1**), 1443 (**2**)  $\text{cm}^{-1}$ , respectively. The difference [ $\Delta\nu = \nu_{as}(\text{CO}_2) - \nu_s(\text{CO}_2)$ ] is 146  $\text{cm}^{-1}$  for **1** and 142  $\text{cm}^{-1}$  for **2**. These values are less than the  $\Delta\nu$  value for  $\text{NaO}_2\text{C}_3\text{H}_5\cdot\text{H}_2\text{O}$  of ( $\approx 200 \text{ cm}^{-1}$ ), as expected for the bidentate bridging ligand of carboxylates. The presence of ionic  $\text{NO}_3^-$  in **2** follows the spectrum of this compound through the appearance of the  $\nu_3(\text{E})$  [ $\nu_d(\text{NO})$ ] mode of the  $\text{D}_{3h}$  ionic nitrate at 1375  $\text{cm}^{-1}$ . A medium intensity band at 1649  $\text{cm}^{-1}$  (**1**) and 1646  $\text{cm}^{-1}$  (**2**) showed double band (C=C) in acrylic acid ligand. For the identification of the  $\text{M}_3\text{O}$  fragment M-O bonds, IR spectra in the range of 400-800  $\text{cm}^{-1}$  were analyzed [12]. The band for the asymmetric vibration associated with the  $\text{M}^{\text{III}}_2\text{M}^{\text{II}}(\mu_3\text{-O})$  unit splits into two components,  $\text{A}_1$  and  $\text{B}_2$  [13]. These spectra showing the characteristic bands for the valence oscillations  $\nu_{as}(\text{Cr}_2\text{FeO})$  in the region 445  $\text{cm}^{-1}$  ( $\text{A}_1$ ) and 410  $\text{cm}^{-1}$  ( $\text{B}_2$ ) were identified, and  $\nu_{as}(\text{Cr}_3\text{O})$  was observed at 520  $\text{cm}^{-1}$ .

The IR spectra of the complexes exhibit a medium to strong band at 3382-3388  $\text{cm}^{-1}$  assignable to the  $\nu(\text{OH})$  vibration of the solvate/coordinated water molecules. The broadness and the relatively low frequency of this band are both indicative of strong hydrogen bonding.

Table 1. Selected IR bands ( $\text{cm}^{-1}$ ) for the prepared complexes.

Compound	$\nu_{\text{sym}}(\text{COO})$	$\nu_{\text{asym}}(\text{COO})$	$\nu(\text{C}=\text{C})$	$\nu(\text{NO}_3)$	$\nu(\text{OH})$	$\nu(\text{M}_3\text{O})$
1	1446	1592	1649	—	3388	520
2	1443	1585	1646	1375	3384	445,410

### Electronic spectroscopy

The electronic spectra of trinuclear complexes can be interpreted in a good approximation in the terms of d-d transitions of individual metal ions, together with ligand-metal charge transfer transitions. Electronic spectra of these complexes are recorded in the range 200-700 nm in dichloromethane solution.

The visible spectra of pseudo-octahedral Cr(III) complexes are expected to display two dominant d-d bands, corresponding to the spin-allowed  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  and  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$  (F) transitions. These bands appeared at 587 and 443 nm for **1** and 552 and 430 nm in the spectra of **2**. The reflectance spectra of complexes show moderate broad bands in the UV region indicating  $\pi \rightarrow \pi^*$  double bond in acrylic ligand. The UV-Vis data which can be assigned and characterized on the basis of earlier reports [14] are given in Table 2.

Table 2. Diffuse reflectance spectra of the complexes.

Compound	Transitions ( $\pi \rightarrow \pi^*$ ) (nm)	Transitions (d $\rightarrow$ d) (nm)
1	208	443,587
2	201	430,552

### Thermal study

These ionic crystals have so high melting point that they decompose before melting. For determining decomposition point of these complexes, TGA technique was used. On TG curves

of the investigated compounds, it is possible to notice that the basic processes of decomposition finish in the range 280-320 °C.

The first stage of decomposition corresponds to removal of solvent molecules (for **2**) and some quantity of intrasphere H<sub>2</sub>O.

The subsequent second process for both clusters is characterized by several super positioned processes: removal of coordinated molecules of H<sub>2</sub>O, decomposition of acrylic acid anions and reorganization of the complexes with the formation of the final product, M<sub>2</sub>M'O<sub>4</sub>, with a small quantity of impurities [15].

### CONCLUSIONS

Two important new oxo-centered complexes were prepared and characteristics of vibrational bands were studied. The observed frequencies  $\nu_{\text{asym}}(\text{CO}_2)$  and  $\nu_{\text{sym}}(\text{CO}_2)$  for the carboxylate ligands support the presence of bridging coordinated carboxylates in these complexes. The visible spectra may be interpreted on the basis of an octahedral environment for Cr(III) in these complexes.

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