



Preparation, Spectral and Thermal Characterization of Two Novel Mixed-Valent and Metal Trinuclear Oxo-centered Complexes

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Two new oxo-centered trinuclear monochloroacetate complexes, $[\text{Mn}_2\text{Mn}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{py})_3]$ (**1**) and $[\text{Cr}_2\text{Fe}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3].\text{NO}_3$ (**2**), were synthesized and characterized by elemental analysis, infrared and electronic spectroscopy and thermogravimetric analysis. These compounds have a typical μ_3 -oxo trinuclear structure: (a) three metal atoms are situated in the apexes of the equilateral triangle; (b) μ_3 -oxygen atom and six monochloroacetate ligands fulfill the bridge functions and (c) the monodentate Py or H_2O ligands complete the octahedral geometry of the metal ions.

Key Words: Oxo-centered complexes, Monochloroacetic acid, Infrared spectroscopy, Electronic spectroscopy.

INTRODUCTION

The universality of carboxylic acids as ligands and the extraordinary wide binding facilities of their acid residues favour the existence of a great variety of carboxylate-based complexes¹⁻³. This class of compounds is active with respect to alkane activation, the catalytic activity being dependent on the carboxylate and metal identities^{4,5}. A number of trinuclear oxo-bridged complexes with the general formula $[\text{M}_2\text{M}'\text{O}(\text{RCOO})_6(\text{L})_3].n\text{Solv}$ are known in a variety of 3d transition metals (M; M'), carboxylate ligands (R-CO₂), monodentate ligands (L) and solvent molecules (Solv)⁶⁻⁸. These compounds containing metal-oxo-carboxylate fragments exhibit a wide range of structural features and diverse chemical reactions. Polynuclear carboxylates of 3d transition metals have been attracting renewed interest because of their intramolecular magnetic exchange interactions^{9,10} and their application as the simple models of oligonuclear active sites in metalloproteins¹¹⁻¹³. Oxo-centered trinuclear iron complexes with a variety of organic ligands have been used to study several physio-chemical phenomena by various spectroscopic methods^{14,15}. Several such complexes have been structurally as well as spectroscopically characterized in detail. These are, however, limited to clusters coordinated by relatively small organic ligands. General view of the trinuclear oxo-centered complexes is illustrated in Fig. 1.

In previous studies, we reported mixed-bridged and mixed-metal trinuclear oxo-centered complexes with saturated and unsaturated carboxylate ligands¹⁶⁻¹⁹. In the present study

we report the synthesis of two new homo and hetero trinuclear compounds $[\text{Mn}_2\text{Mn}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{py})_3]$ (**1**) and $[\text{Cr}_2\text{Fe}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3].\text{NO}_3$ (**2**) together with the results of infrared and electronic spectroscopy and elemental analysis.

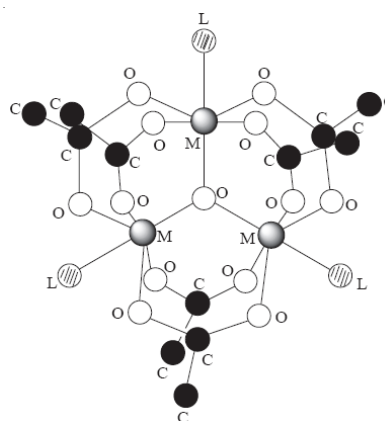


Fig. 1. Schematic representation of the oxo-centered trinuclear clusters structure $[\text{M}_3\text{O}(\text{RCOO})_6(\text{L})_3]^{2-}$

EXPERIMENTAL

All starting materials, except (N-n-Bu₄MnO₄), used in this study were analytical grade and purchased from Merck.

N-n-Bu₄MnO₄: This material was prepared, as outlined in the literature²⁰, by mixing aqueous solutions of KMnO₄, (5.00 g, 31.6 mmol) and N-n-Bu₄Br (12.00 g, 37.2 mmol) with

vigorous stirring to give a total volume of *ca.* 200 mL. The immediate purple precipitate was collected by filtration, washed thoroughly with distilled water and diethyl ether and dried in vacuum at ambient temperature: yield > 90 %.

The carbon, hydrogen and nitrogen contents were determined by a Thermo Finnigan Flash 1112 EA microanalyzer. Atomic absorption analysis for determination of iron(III), chromium(III) and manganese(III, II) contents were carried out on a Shimadzu model AA-670 atomic absorption spectrometer. The IR spectroscopy on KBr pellets was performed with a Buck 500 and Thermo Nicolet Nexus 870 FTIR spectrometer and an Agilent 8453 spectrophotometer was used to obtain ultraviolet-visible spectra. TG studies were performed on a Cahn 200 microbalance.

Synthesis of $[\text{Mn}_2\text{Mn}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{py})_3]$ (1): $\text{Mn}(\text{OOCMe})_2 \cdot 4\text{H}_2\text{O}$ (10 mmol, 2.5 g) and monochloroacetic acid (54 mmol, 5 g) were dissolved in a solvent mixture comprising pyridine (7 mL) and absolute ethanol (15 mL). The resulting solution was stirred while solid $\text{N-}n\text{-Bu}_4\text{MnO}_4$ (3.5 mmol, 1.25 g) was added in small portions and stirred to give a dark brown homogeneous solution. This solution was stirred for 0.5 h and then gray solid was collected by filtration, washed with ether and dried in vacuum. Appropriate black crystals were obtained by slow volatilizing the solution of $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_5\text{CH}_3$ of the complex after 4 days. (Yield: 75 %), m.p.: 180 °C, Anal. calc. for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_{13}\text{Cl}_6\text{Mn}_3$: C, 33.1; H, 2.77; N, 4.29; Mn, 16.85 %. Found: C, 32.96; H, 2.65; N, 4.15; Mn, 16.65 %.

Synthesis of $[\text{Cr}_2\text{Fe}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3] \cdot \text{NO}_3$ (2): 0.9 g (2.25 mmol) $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.404 g (1 mmol) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 20 mL distilled water and a solution containing 2.9 g (30 mmol) monochloroacetic acid were gradually added. Then the solution was mixed with sodium carbonate to control the final pH for 4-5 with continuous stirring. The resulting solution was refluxed for 2 h and then after 3 days of standing in darkness at room temperature, the product, consisting of black crystals of title complex (2), was collected and washed with ether and dried under vacuum. (Yield: 80 %), m.p.: 270 °C, anal. calc. for $\text{C}_{12}\text{H}_{18}\text{NO}_{19}\text{Cl}_6\text{Cr}_2\text{Fe}$: C, 16.94; H, 2.11; N, 1.67; Cr, 12.21; Fe, 6.56 %. Found: C, 17.07; H, 2.18; N, 1.95; Cr, 11.97; Fe, 6.65 %.

RESULTS AND DISCUSSION

Infrared spectroscopy: Infrared spectroscopy is a reliable technique for the characterization of metal carboxylate complexes. The most useful characteristic bands of metal carboxylates are a strong asymmetric CO_2 stretching vibration ($\nu_{\text{CO}_{\text{asym}}}$) and a somewhat weaker symmetric CO_2 stretching vibration ($\nu_{\text{CO}_{\text{sym}}}$)²¹. The metal-ligand interaction for carboxylate ligands in oxo-centered complexes is presented in Fig. 2. The bands corresponding to the coordinated mode (Structure II) are situated at different frequencies relative to values for the free carboxylate ion (Structure I), usually taken as those of the sodium or potassium salts²².

The IR spectra at room temperature of compounds **1** and **2** are shown in Fig. 3. These spectra indicate a single pair of carboxylate stretching vibrations at 1654 and 1394 cm^{-1} for (1), 1640 and 1436 cm^{-1} for (2) assigned to $\nu_{\text{asym}}(\text{COO})$ and

$\nu_{\text{sym}}(\text{COO})$, respectively. For identification of the metal-oxygen bonds of M_3O group, IR spectra in the range of 800-400 cm^{-1} were used²³. The band observed for asymmetric vibration associated with the $\text{M}_2\text{M}'\text{O}$ unit splits into two components, A_1 and B_2 ²⁴. These spectra show the characteristic bands for the valence oscillations $\nu_{\text{as}}(\text{Cr}_2\text{FeO})$ in the region 585 cm^{-1} (A_1) and 435 cm^{-1} (B_2) and $\nu_{\text{as}}(\text{Mn}_3\text{O})$ is observed at 540 cm^{-1} . The IR spectrum of complex (2) exhibits a medium band at 3570 cm^{-1} assignable to the $\nu(\text{OH})$ vibration of the coordinated water molecules. All data of IR spectroscopy for these compounds are given in Table-1.

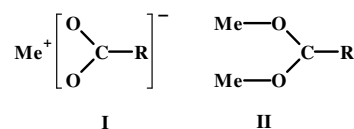


Fig. 2. Structure of metal carboxylates according to the type of metal-ligand interaction. (I) Ionic or uncoordinated form, (II) bidentate bridging coordination

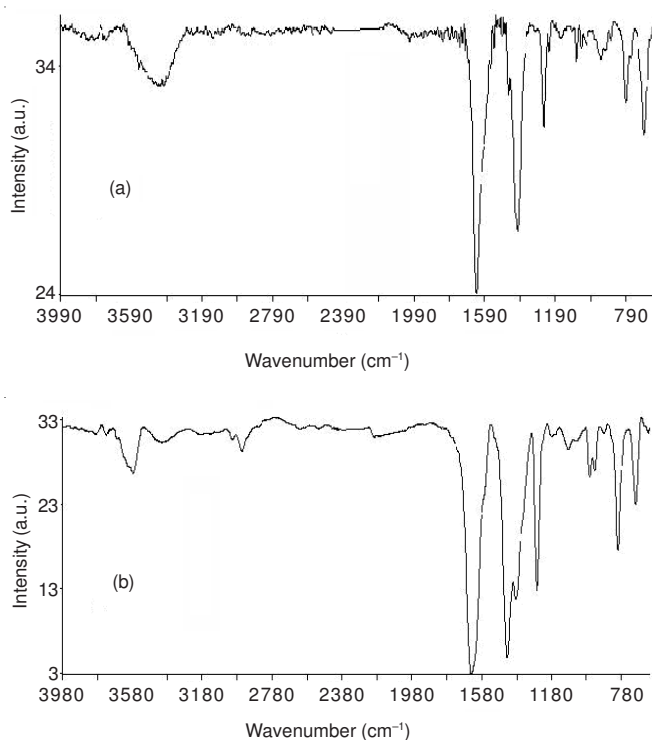


Fig. 3. IR spectra of $[\text{Mn}_2\text{Mn}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{py})_3]$ (a) and $[\text{Cr}_2\text{Fe}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3] \cdot \text{NO}_3$ (b)

TABLE-1
SELECTED IR BANDS (cm^{-1}) FOR COMPLEXES

Compound	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\nu(\text{M}_3\text{O})$	$\nu(\text{C-H})$	$\nu(\text{C-Cl})$	$\nu(\text{O-H})$
1	1654	1394	540	3036	822	-
2	1640	1436	435-585	2970	819	3570

Electronic spectroscopy: Oxo-centered complexes involve electronic transitions that are similar to the other inorganic compounds. One of them is *d-d* transition which is relevant to the electronic transitions between splitting *d* orbitals and another one is charge transfer (CT) transition which consists of LMCT or MLCT. Therefore, UV-VIS spectroscopy

is one of the useful methods for characterizing oxo-centered complexes. The electronic spectra of the complexes were recorded in the range 200-700 nm in dichloromethane solution and the obtained results can be characterized on the basis of earlier reports²⁵ (Table-2). Complex **1** exhibits a strong band at 255 nm, which is due to the ($\pi \rightarrow \pi^*$) transition of pyridine ligand. Another broad band in the region 480 nm, which can be assigned to the transition from 5E_g to $^5T_{2g}$, should be attributed to the existence of Mn(III) (d^4) ion in this complex.

TABLE-2
ELECTRONIC ABSORPTION SPECTRAL DATA OF **1** AND **2**
COMPLEXES IN DICHLOROMETHANE SOLUTION

Compound	Transitions ($\pi \rightarrow \pi^*$) (nm)	Transitions ($d \rightarrow d$) (nm)
1	255	480
2	213	450, 580

The UV-VIS spectra for complex **2** are shown in Fig. 4. The two spin-allowed bands in the regions 450 and 580 nm, could be assigned to the transition from $^4A_{2g}$ (F) to $^4T_{2g}$ (F) (v_1) and $^4T_{1g}$ (F) (v_2), respectively, can be attributed to the presence of Cr(III) (d^3) ion in complex **2**. The position of the third band $^4A_{2g}$ (F) to $^4T_{1g}$ (P) (v_3), the Racah parameter (B) and the nephelauxetic ratio (β) have been calculated using eqn. (1) - (3) given by Underhill and Billing²⁶:

$$340 Dq - 18(v_2 + v_3)Dq + v_2 - v_3 = 0 \quad (1)$$

$$B = v_2 + v_3 - 30 Dq/15 \quad (2)$$

$$\beta = B_{\text{complex}}/B_{\text{free ion}} \quad (3)$$

The values of interelectronic repulsion parameter (B) and the covalency factor (β) were found 560 cm^{-1} and 0.62 ± 0.07 , respectively. The reduction of Racah parameter from the free Cr^{3+} value (933 cm^{-1})²⁷ suggests considerable covalent character of metal-ligand bonds in complex **2**.

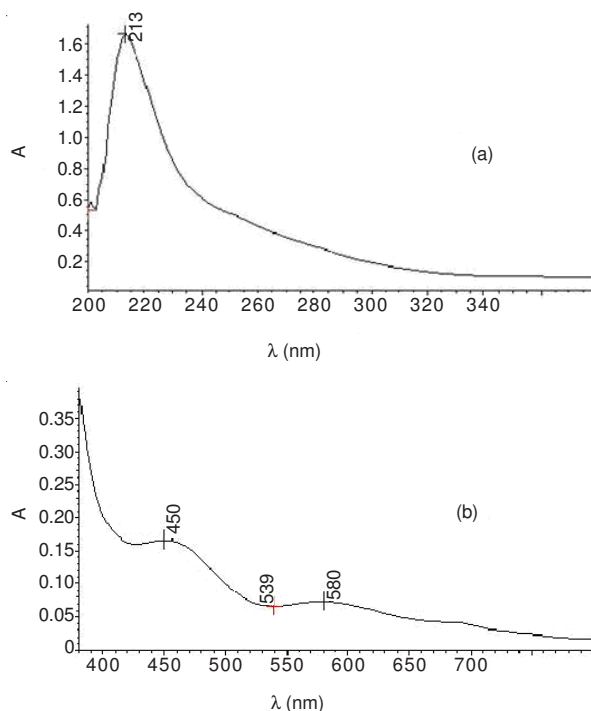


Fig. 4. UV (a) and VIS (b) spectra of the $[\text{Cr}_2\text{Fe}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3].\text{NO}_3$

Besides, the UV spectrum of this complex exhibits a strong band at 213 nm, which is a cause of ($\pi \rightarrow \pi^*$) transitions of carboxylate groups.

Thermal study: These ionic crystals have high melting point that they decompose before melting. For determining decomposition point of these complexes, TGA technique was used. The thermogram of complex $[\text{Cr}_2\text{Fe}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3].\text{NO}_3$ is given in Fig. 5. From TG curve, it is possible to notice that the investigated compound was decomposed in three steps. The first stage of decomposition corresponds to removal of solvent molecules and some quantity of intrasphere H_2O . The subsequent second process is characterized by several super positioned processes: removal of coordinated molecules of H_2O and decomposition of monochloro acetate anions and third step is continued by reorganization of the complex with the formation of the final product, $\text{M}_2\text{M}'\text{O}_4$, with a small quantity of impurities²⁸.

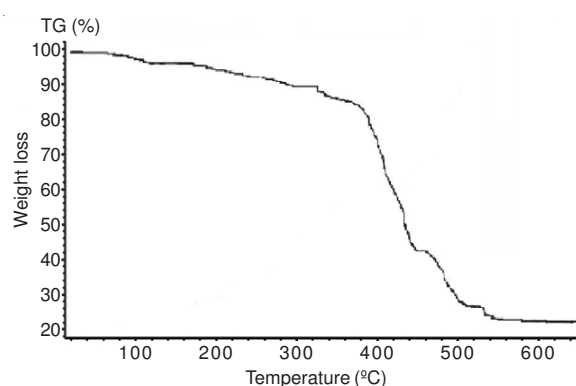


Fig. 5. TGA curve of the $[\text{Cr}_2\text{Fe}(\text{O})(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3].\text{NO}_3$

Conclusion

Two new oxo-centered trinuclear complexes with the general formula $[\text{M}_2\text{M}'\text{O}(\text{CH}_2\text{ClCOO})_6(\text{L})_3]$ where $\text{M} = \text{Mn}$, $\text{M}' = \text{Mn}$, $\text{L} = \text{py}$ (**1**); $\text{M} = \text{Cr}$, $\text{M}' = \text{Fe}$, $\text{L} = \text{H}_2\text{O}$ (**2**) have been obtained and studied by elemental analysis, thermal investigation, UV-VIS and IR spectroscopy. All compounds have a similar μ_3 -oxo structure. The IR investigations of these compounds show intensive absorption bands, which are assigned to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ vibrations. Furthermore, the three metal ions are bound to a central oxygen atom and adjacent metal ions are bridged by two carboxylate ligands. In addition, for mixed metal complex **2**, the atomic absorption data show a statistical 1:2 disorder of iron and chromium atoms, respectively.

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