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Preparation and characterization of novel oxo-centered basic carboxylate bridging trinuclear complexes

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ABSTRACT

Three new oxo-centered trinuclear complexes, one of them a mixed-valence complex $[Mn_3O(CH_3CO_2)_6(Py)_3]$ (1) and the others, mixed-metal complexes of $[FeCr_2O(CH_3CO_2)_6(Py)_3]$ Py (2) and $[Fe_2CoO(CH_3CO_2)_6(Py)_3]Py$ (3) were synthesized by the direct reaction between metal nitrates and acetic acid. These complexes were characterized by elemental analyses (CHN), atomic absorption spectroscopy and spectral (IR, electronic) studies. These are new type of oxo-bridged mixed-metal complexes in which the carboxylate acid. The UV spectra of the complexes exhibited a strong band in the region 265nm which is related to the ($\pi \rightarrow \pi^*$) transitions of the carboxylate ligand. The IR spectra of these compounds showed two strong stretching vibrations bands, indicating a bridging coordination mode of the carboxylic group of the ligand in the complexes. In this work as well for first time aniline was used as axial ligand which form fine crystalline compounds.

Keywords: mixed-valence; oxo-centered; trinuclear complexes; spectroscopy; carboxylic ligand; IR spectra.

INTRODUCTION

Interest in trinuclear oxo-bridged manganese complexes of general composition $[Mn_3O(O_2CR)_6L_3]$ draws from three quarters. First, there is a need to characterize polynuclear manganese complexes as models for the water oxidation center of photosynthetic electron transport chains. The studies of trinuclear oxo-centered manganese complexes of the general formulation $\frac{1}{2}[Mn_3O(CH_3CO_2)_6(Py)_3]$; (L^{1/4}a neutral donor group) play an important role in our understanding of the interaction of manganese cluster [1,8]. Trinuclear, oxo-centered, carboxylate complexes of transition metals of general composition $[M_3O(O_2CR)_6L_3]^{n+}$ and $[M(III)_2M(II)O(O_2CR)_6L_3]$ (Fig. 1) have been of interest for several

years.1–2 Compounds containing metal-oxo-carboxylate fragments exhibit a wide range of structural features and diverse chemical reactions. They have attracted attention as versatile intermediates as precursors to larger assemblies.[7-11] Interest in these compounds arose for several reasons. Firstly, they form a rare class of compounds, which serve as important models to test theories of magnetic coupling between metal ions in multinuclear systems; likewise the structural variations shown by these metallic clusters have yielded important information on the parameters which govern stability within metal-ligand aggregates. Secondly, the polynuclear structure leads to the formation of mixedvalence and mixed-metal derivative, which give opportunities to study the electronic and magnetic interactions between homo-and heterometal centers in close proximity in a defined geometry. There is also the possibility of generating spin-frustrated species. Thirdly, several of these complexes are active as homogeneous catalysts for a variety of oxidation reactions.[5,6] In view of this, the spectroscopic, magnetic and redox properties of these complexes have been extensively studied. Surprisingly, little attention has been paid to the consideration of substitution properties, with only a few reports of comparative studies regarding the redox properties when the terminal ligand L changes. There is interest in establishing how substitution in the carboxylate bridge affects the lability of the terminal ligand and the redox potential of the metal centers. These carboxylate complexes are of additional interest when the carboxylate is unsaturated, because there is a potential scope for further polymerization in the solid state by cross-linking of the substituent [7,10,11,12]. In this paper, the important of these complexes are promising as potential homogeneous redox catalysts in the oxidation of hydrocarbons, alcohols.

MATERIALS AND METHODS

The C, H and N analyses were realized on a Thermo Finnigan Flash model EA1112 elemental analyzer at the Faculty of chemistry, tabriz University. The atomic absorption analyses were performed on a Shimadzu model AA-670 atomic absorption spectrometer. The IR spectra of KBr discs (4000–600 cm⁻¹) were recorded on a Buck 500 spectrometer. The electronic spectra were registered in the range 600–200 cm⁻¹ on a Perkin-Elmer 1600 spectrometer. The reagents, p-chlorobenzoic acid (99 %), iron (99 %), cobalt (99%) and manganese (99 %) nitrate and solvents were obtained commercially from Merck Chemicals and used as received. The nitrogen base (pyridine) was dried following the standard procedures.10 Sodium p-chlorobenzoate was obtained from sodium carbonate and p-chlorobenzoic acid in a 1:2 molar ratio and water as solvent.

- Preparation of $[Mn_3O(CH_3CO_2)_6(Py)_3]$ (1)

A mixture of MnCl₂·4H₂O (2.93, 15mmol) and KMnO₄, (0.26 g, 1.6 mmol), and C₂H₄O₂(20ml) dissolved in distilled water (6.66ml) and pyridine(13.3ml) was refluxed for 4h at 55 °C. The dark brown crystals were filtered off after 2weeks, washed with water and dried in air . Yield: 57%; m.p.: 290 °C. Anal. Calcd. For C, 52.7; H, 5.37; N, 6.84; Fe, 7.8; Co5.3 %. Found: C, 51.84; H, 5.32; N,5.99; Fe, 9.8; Co, 5.9%. IR (selected data, KBr, cm⁻¹):3420.73,1597.89.50,1443.03.11,622.72.

- Preparation of $[FeCr_2O(CH_3CO_2)_6(Py)_3] Py$ (2)

A mixture of FeCl₂·4H₂O (5 g, 25mmol) and NaC₂H₃O₂ (5 g, 83 mmol), and C₂H₄O₂(15ml) dissolved in distilled water (25ml) was refluxed for 2h. and mixture solution was refluxed for 2h at 75 °C. and it was allowed to cool at 20 °C. . The dark brown crystals were filtered off, washed copiously with Et₂O and dried *in vacuo*. This yielded black crystals which were collected by filtration, washed with ether, and dried in *vacuo*. A mixture of This dry crystals

(0.88g, 1.49mmol) and $\text{CrC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$ (0.66 g, 1.76 mmol), dissolved in pyridine (80ml). mixture solution was refluxed for 3h at 60 °C. This yielded black crystals after 4 days, were washed with pyridine, and dried *in vacuo*. Yield: 30 % m.p.: 298 °C. Anal. Calcd. For C, 25.89; H, 4.33; N, 6.76; Fe, 7.8; Cr 5.7%. Found: C, 24.29; H, 4.11; N 6.90; Fe, 9.2; Cr, 5.7 %. IR (selected data, KBr, cm^{-1}): 3446, 1587.22, 1424.23, 66.92

-Preparation of $[\text{Fe}_2\text{CoO}(\text{CH}_3\text{CO}_2)_6(\text{Py})_3]$ (3)

A mixture of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.04 g, 5 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.75g, 2 mmol), dissolved in $\text{NaC}_2\text{H}_3\text{O}_2$ (4.12 g, 68 mmol) was refluxed for 24h. and The resulting dark red solution was allowed to cool and stored for 3 days at 20 °C. The brown crystals were filtered off, washed copiously with Et_2O and dried *in vacuo*. 1g of this Complex was dissolved in pyridine (12.5 ml). This yielded black crystals which were collected by filtration, washed with ether, and dried *in vacuo*. Yield: 55 %; m.p.: 295 °C. Anal. Calcd. For C, 43.80; H, 4.43; N, 6.65; Fe, 7.8; Co 5.3 %. Found: C, 43.71; H, 4.49; N 6.53; Fe, 9.2; Co, 5.3 %. IR (selected data, KBr, cm^{-1}): 1220, 51, 160.50, 1414.11, 55.7

RESULTS AND DISCUSSION

Complexes are few. The synthetic procedures almost invariably employed polymeric Mn(III) acetate, which can be readily obtained from the oxidation of $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ with KMnO_4 in hot glacial acetic acid. Reaction of this material with an excess of a neutral donor group L led to discrete units of the formulation $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{L})_3]z$.

The solvents of choice are EtOH and pyridine which ensure solubility of all the reactants; the cleanest reactions are obtained when an excess of carboxylic acid is also present, otherwise low yields or intractable brown gel-like precipitates result. The synthetic strategy was to react together particular ratios of Mn(VII):Mn(II) to yield products in the intermediate metal oxidation state range +2.67 to +3.00 characteristic of Mn_3O units. However, it was noticed that small changes in the Mn(VII):Mn(II) ratio had no noticeable effect on the identity of the products or their yields. As was registered previously, 10 redox reactions involving solvent, atmospheric oxygen, or reagent impurities could compensate for an excess or lack of Mn(II), for example, over that required to yield the preferred product. A Mn(VII):Mn(II) ratio of 3.15:8.15 has now become the routinely employed stoichiometry and has provided access to complex 1. This ratio should, in theory, provide an average metal oxidation of +3.39 according to Eq. (1) but cleanly leads instead to either $\text{Mn}_2(\text{III})\text{Mn}(\text{II})$ species, or $\text{Mn}_3(\text{III})$ species:



IR Spectroscopy

The IR spectral data of the complexes are given in Table I. The observed vibrational frequencies, $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$, for the carboxylate ligand support the presence of bridging coordinated carboxylates in all the complexes. For the mixed-metal complexes, it appears from the carboxylate stretching frequencies that all six ligands are approximately equivalent and they are best represented as bidentate bridges. For a new series of trinuclear mixed-metal complexes, Naranwal *et al.* [8] assigned the IR spectra and identified the vibrational modes of the central M_3O core. They found that the reduction in site geometry from D_{3h} to C_{2v} lifted the degeneracy of the asymmetric M_3O stretches and two bands were seen. In the IR spectrum of complex, strong bands at 1423 and 1587 cm^{-1} were evident. They are attributed to the $\nu_{\text{sym}}(\text{COO})$ and $\nu_{\text{asym}}(\text{COO})$ modes, respectively.

The difference ($\Delta\nu = \nu_{\text{asym}}(\text{COO}) - \nu_{\text{sym}}(\text{COO})$) is 164 cm^{-1} . Presence of ionic nitrate in this complex follows from the IR spectrum through the appearance of a relatively weak band at 1380 cm^{-1} . For the identification of the metal–oxygen bands of the M_3O groups, the IR spectra in the range $800\text{--}400 \text{ cm}^{-1}$ were used. The strong band observed at $430\text{--}690 \text{ cm}^{-1}$ is attributed to the $\nu(\text{M}_2\text{M}')$ vibration.

Spectroscopy

The electronic spectra of the trinuclear complexes can be interpreted to a good approximation in terms of the individual metal ions, together with ligand–metal charge transfer transitions. The electronic spectra of the complexes were recorded in the range $50000\text{--}15000 \text{ cm}^{-1}$ in dichloromethane solution. The spectra of the mixed–metal complexes show the characteristic bands provided by both metal ions. The UV spectra of these complexes exhibited a strong band in the region 42500 cm^{-1} , which is related to the $(\pi \rightarrow \pi^*)$ transitions of the pyridine (Py) ligand. The bands are shifted to higher energy when $\text{L} = \text{pyridine}$. The electronic spectroscopy data are given in Table II, which can be assigned and characterized based on other literature.

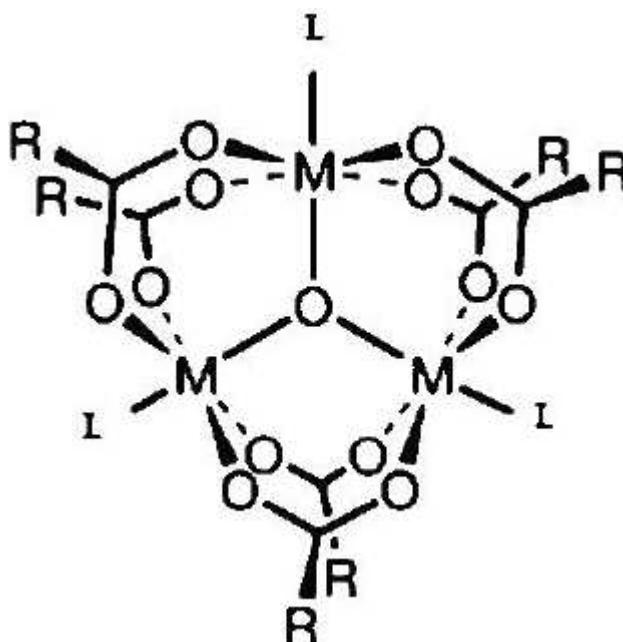


Fig. 1. Structure of the cluster unit $[\text{M}_3\text{O}(\text{RCOO})_6(\text{L})_3]^{2-}$.

Table I. Selected IR bands (cm^{-1}) for the complexes 1–3

Compound	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\nu(\text{M}_3\text{O})$
1	1597.89	1443.03	629.72
2	1587.96	1423.73	662.77
3	1610.50	1440.11	655.76

Table II. Diffuse reflectance spectra of complexes

Compound	Transition $\pi \rightarrow \pi^*$, nm	Transition $d \rightarrow d$, nm
1	225	490
2	260	520
3	265	510

CONCLUSION

In this study, three new oxo-centered basic acetatebridging complexes were prepared by the direct method of reaction between metal nitrate and sodium acetate. These compounds were characterized by elemental analyses (CHN), atomic absorption spectroscopy, as well as by IR and electronic spectroscopy. The IR spectra show two strong bands and the observed stretching vibrations indicated the presence of a bridging coordination mode of carboxylic ligand. In addition, for mixed-metal complexes, the atomic absorption data show a statistical 2:1 disorder of iron and manganese or cobalt atoms, respectively.

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