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Research Article

Synthesis and Characterization of Two New Oxo-centered Trinuclear Complexes of Manganese and Iron

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ABSTRACT

Two new oxo-centered trinuclear complexes, one of them a mixed-valence complex $[Mn_2MnO(CCl_3CO_2)_6(Py)_3]$ (1) and the other, mixed-metal complex of $[Fe_2MnO(CCl_3CO_2)_6(H_2O)_3].NO_3$ (2) were synthesized by the direct reaction between metal nitrates and trichloroacetic 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 ligand is trichloroacetic acid. The UV spectra of the complexes exhibited a strong band in the region 213 and 257 nm which is related to the ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions of the pyridine and H_2O ligands, respectively. 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.

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

1. Introduction

Transition-metal carboxylate chemistry has played a key role in the conceptual development of modern inorganic chemistry [1]. The current interest in the trinuclear, oxo-centered metal carboxylate assemblies of the general composition $[M_3O(OOCR)_6L_3]^+$ (where M= trivalent 3-d metal, L= monodentate ligand) is due to these complexes have served as important models to test theories of magnetic and electronic coupling between metal ions [2,3]. Electron transfer interactions, and subtle distortions from regular structures, can be detected by their effects on molecular vibrations. These are valuable precursors for the synthesis of higher nuclearity clusters exhibiting interesting magnetic properties. 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 liability 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 substituents [4,5]. Trinuclear μ_3,-oxo-bridged iron carboxylate complexes have been studied in great detail [6,7], whereas analogous mixed-valence manganese-carboxylate complexes have been the object of only limited investigation to date.

In previous studies, we reported fabrication of some trinuclear oxo-centered complexes with saturated and unsaturated carboxylate ligands [8]. In this paper, the syntheses and characterization of mixed-valence and mixed-metal clusters are reported. These are, however, limited to clusters coordinated by relatively small organic ligands. General view of the trinuclear oxo-centerd complexes is illustrated in Fig. 1.

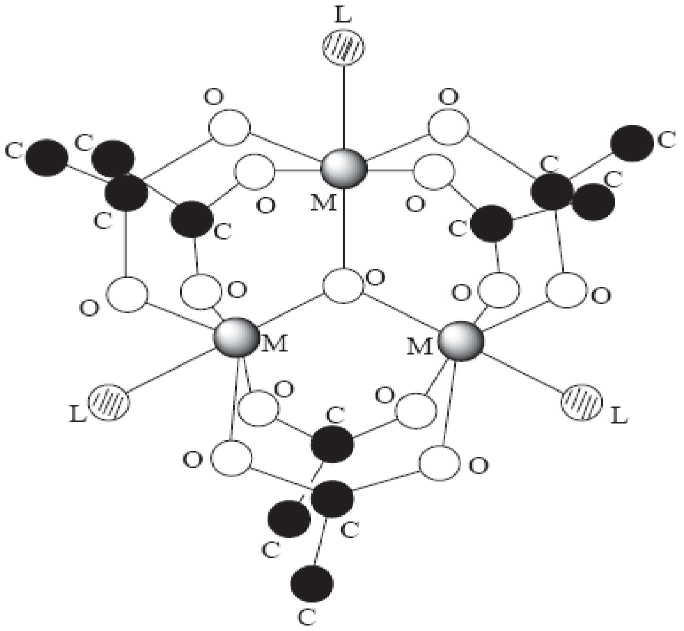


Fig. 1. Schematic representation of the oxo-centered trinuclear clusters structure [M3O(RCOO)6(L)3]z

2. Experimental

2.1. Materials

All starting materials, except (N-n-Bu$_4$MnO$_4$), used in this study were analytical grade and purchased from Merck.

***2.2. N-n-Bu4MnO4*;** This material was prepared, as outlined in the literature [6], by mixing aqueous solutions of KMnO$_4$, (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 C, H and N analyses were realized on a Thermo Finnigan Flash model EA1112 elemental analyzer. 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 the range 600–200 nm on a Perkin-Elmer 1600 spectrometer.

2.3. Preparation of [$Mn_2MnO(CCl_3CO_2)_6(Py)_3$]

N-n-Bu_4Br (12 g, 37.2 mmol) was added to an aqueous solution of $KMnO_4$ (5 g, 31.6 mmol) under vigorous stirring. The immediately formed purple precipitate was collected by filtration, washed thoroughly with distilled water and diethyl ether and dried in vacuo at room temperature. Then $Mn(OOCMe)_2.4H_2O$ (10 mmol, 2.5 g) and trichloroacetic acid (54 mmol, 8.83 g) were dissolved in a solvent mixture comprising pyridine (7 ml) and absolute ethanol (15 ml). The resulting solution was stirred while solid N-*n*-Bu_4MnO_4 (3.5 mmol, 1.25 g) was added in small portions and stirred to give a dark brown homogeneous solution. This solution was allowed to stand undisturbed for 48 h, and the resulting large octahedral-shaped crystals were collected by filtration, washed with pyridine, and dried in vacuum. (Yield: 72%), m.p.: 185 °C, Anal. Calc. for $C_{27}H_{15}Cl_{18}Mn_3N_3O_{13}$: C, 23.26; H, 1.07; N, 3.01; Mn, 11.84%. Found: C, 22.96; H, 1.15; N, 3.11; Mn, 11.65%.

2.4. Preparation of [$Fe_2MnO(CCl_3CO_2)_6(H_2O)_3$].$NO_3$

A mixture of $Fe(NO_3)_3.9H_2O$ (1.08 g, 2.68 mmol) and $Mn(NO_3)_2.4H_2O$ (0.34 g, 1.34 mmol), dissolved in 25 ml deionezed water was refluxed for 10 min and $NaCCl_3CO_2$ (2.22 g, 12 mmol) was added and the reflux continued for 5 h. The resulting brown solution was allowed to cool and stored for 2 days at 20 °C. The black crystals were filtered off, washed copiously with Et_2O and dried in vacuum. (Yield: 85%), m.p.: 275 °C, Anal. Calc. for $C_{12}H_6Cl_{18}Fe_2MnNO_{22}$: C, 10.89; H, 0.45; N, 1.06; Fe, 8.47; Mn, 4.16%. Found: C, 10.64; H, 0.62; N, 1.14; Fe, 8.85; Mn, 4.39%.

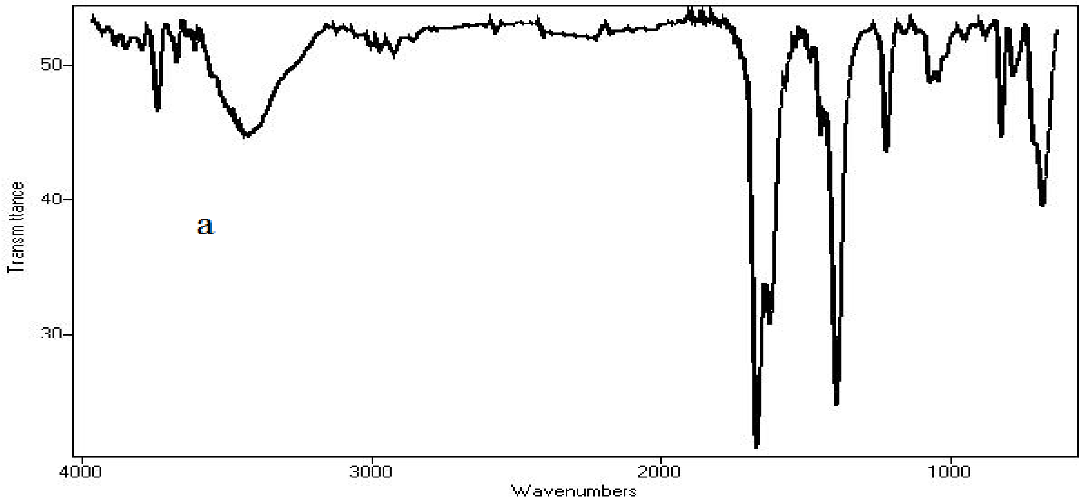
3. Results and discussion

3.1. IR Spectroscopy

The IR spectrum of this complex is shown in Fig. 2 that indicates the presence of carboxylate, H_2O and {M_2MO} groups. The observed vibrational frequencies υ_{asym}(COO) and υ_{sym}(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, Cannon et al. assigned the IR spectra and identified the vibrational modes of the central M_3O core [7].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. These spectra indicate a single pair of carboxylate stretching vibrations at 1601 and 1425 cm^{-1} for (1), 1615 and 1430 cm^{-1} for (2) assigned to υ_{asym}(COO) and υ_{sym}(COO), respectively. The difference ($\Delta\upsilon = \upsilon_{asym}(COO) - \upsilon_{sym}(COO)$) is 176 and 185 cm^{-1}. In the IR spectrum of complex 2, the characteristic vibration frequencies for H_2O groups appear at ~3500–3600 cm^{-1}. For identification of the metal-oxygen bonds of M_3O group, IR spectra in the range of 800-400 cm^{-1} were used [9]. The band observed for asymmetric vibration associated with the $M_2M'O$ unit splits into two components, A_1 and B_2 [10]. These spectra show the characteristic bands for the valence oscillations $\upsilon_{as}(Fe_2MnO)$ in the region 565 cm^{-1} (A_1) and 420 cm^{-1} (B_2) and $\upsilon_{as}(Mn_3O)$ is observed at 580 cm^{-1}. All data of IR spectroscopy for these compounds are given in Table 1.

Table 1. Selected IR bands (cm^{-1}) for complexes

Compound	ν_{asym} (COO)	ν_{sym} (COO)	ν (M_3O)	ν (C-H)	ν (C-Cl)	ν(O-H)
1	1601	1425	580	3036	824	–
2	1615	1430	420-565	2970	816	3570



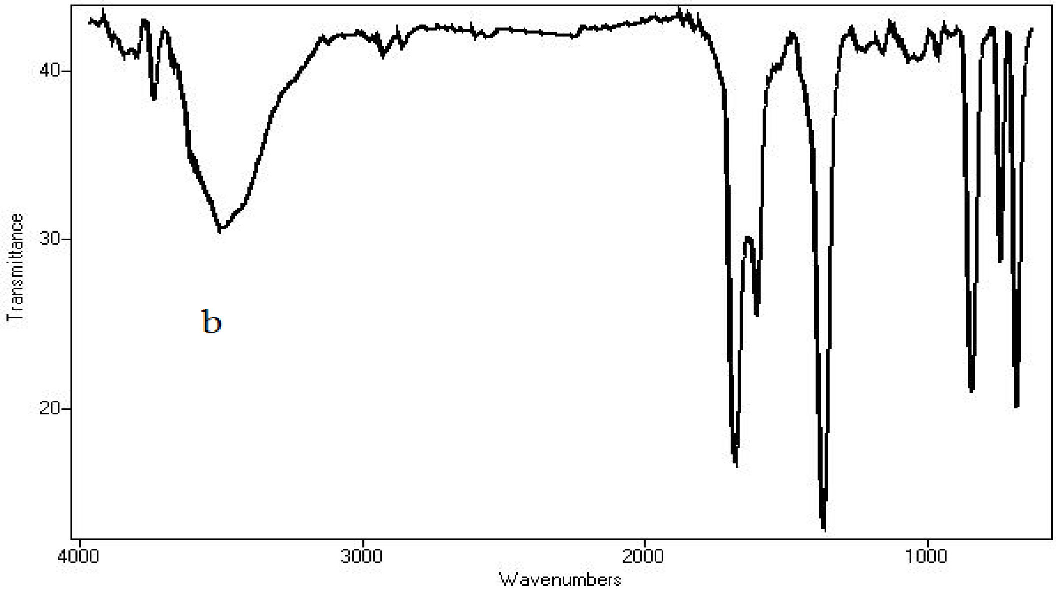


Fig.2. IR spectra of [$Mn_2Mn(O)(CCl_3COO)_6(py)_3$] (a) and [$Fe_2Mn(O)(CCl_3COO)_6(H_2O)_3$].$NO_3$ (b) (KBr pellet)

3.2. Electronic 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 200-600 nm in dichloromethane solution. The spectra of the oxo-centered complexes 1 and 2 show the characteristic bands provided by both metal ions. The UV spectra of the complex 1 and 2 (Fig.3) exhibited a strong bands in the region 257 and 213 nm which is related to the ($\pi \rightarrow \pi^*$) transitions of the pyridine (Py) ligand [8] and ($n \rightarrow \pi^*$) transition of the water ligand.

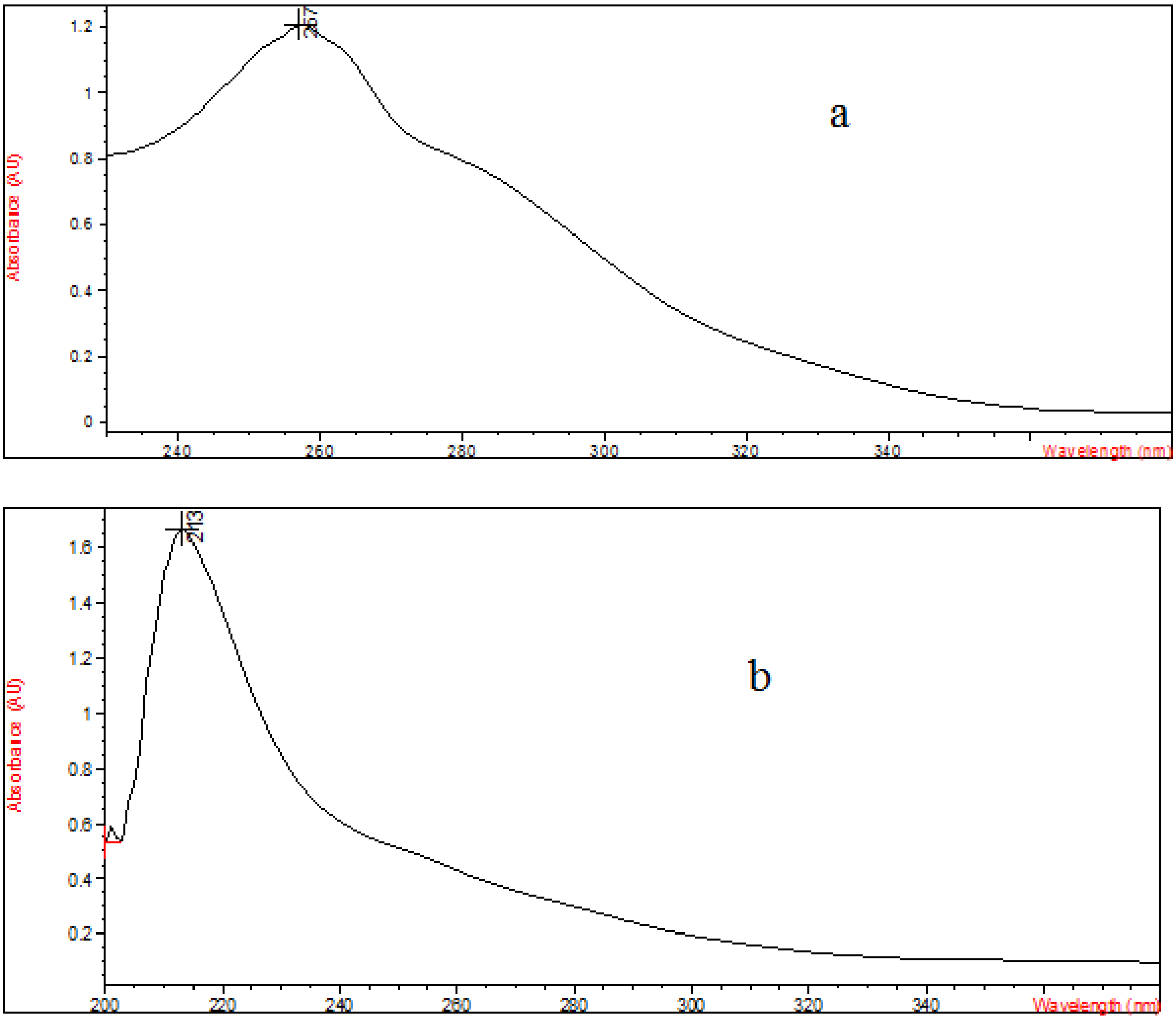


Fig. 3. UV spectra of the [Mn2MnO(CCl3CO2)6(Py)3] (a) [Fe2MnO(CCl3CO2)6(H2O)3].NO3 (b)

The Vis spectra for complex 1, 2 are shown in Fig. 4. As is obvious in this Figure, broad band in the region 480 nm, which can be assigned to the transition from ^{5}Eg to $^5T_2$g, should be attributed to the existence of Mn$^{(III)}$ (d^4) ion in this complexes these data can be assigned and characterized based on other literature [11].

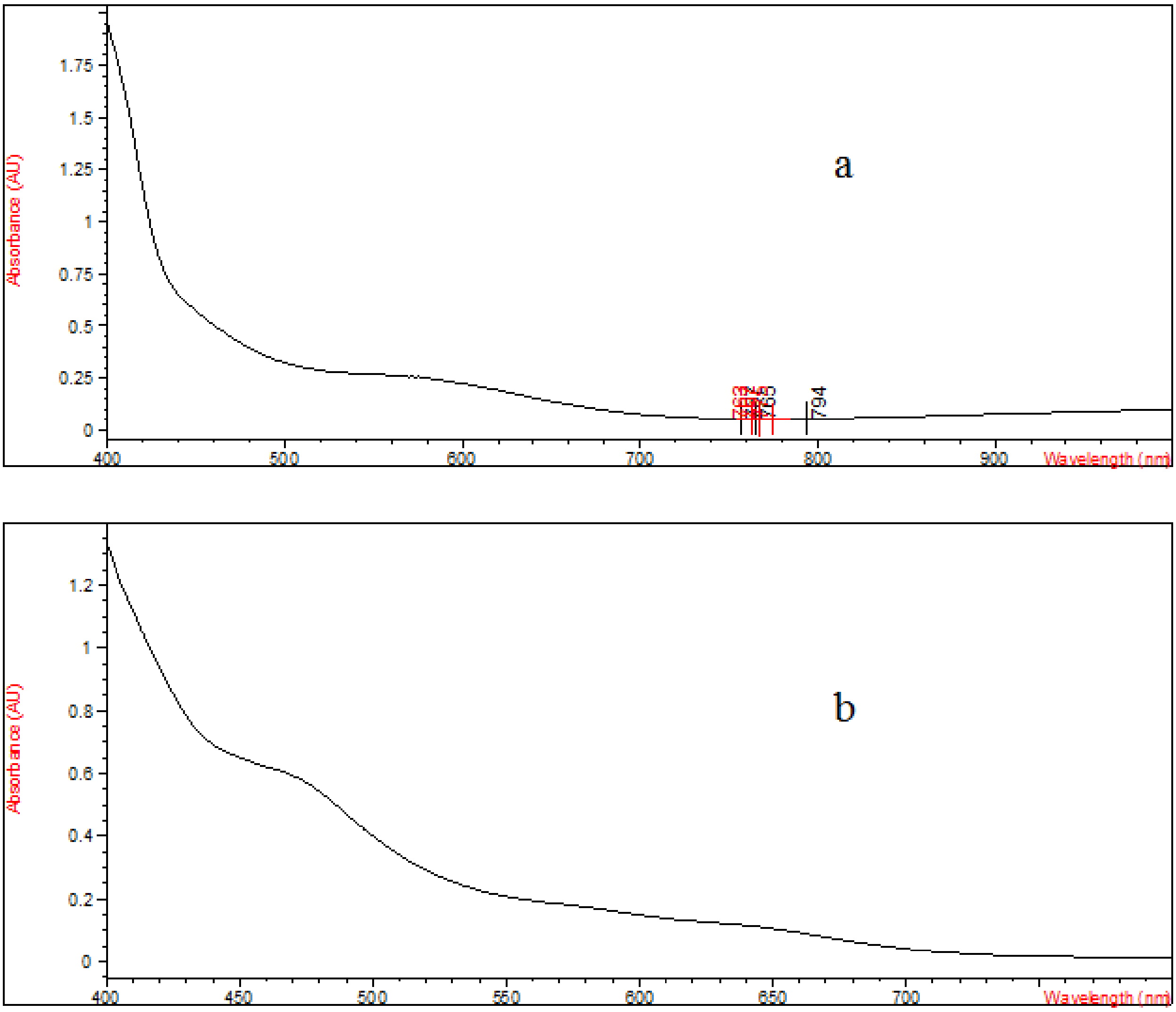


Fig. 4. Vis spectra of the [Mn2MnO(CCl3CO2)6(Py)3] (a) [Fe2MnO(CCl3CO2)6(H2O)3].NO3 (b)

4. Conclusions

Two new Oxo-centered trinuclear complexes with the general formula $[M_2M'O(CCl_3COO)_6(L)_3]$ where M = Mn, M' = Mn, L = py (**1**); M = Fe, M' = Mn, L = H_2O (**2**) were prepared and studied by elemental analysis (CHN), electronic and infrared spectroscopy and atomic absorption spectroscopy. All compounds have a similar μ_3-oxo structure. The IR investigations of these compounds show intensive absorption bands, which are assigned to υ_{asym}(COO) and υ_{sym}(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 2:1 disorder of iron and manganese atoms, respectively.

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