



J. Serb. Chem. Soc. 75 (7) 929–934 (2010)
JSCS–4018

Preparation and characterization of novel oxo-centered basic *p*-chlorobenzoic bridging trinuclear complexes

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(Received 25 August 2009, revised 2 February 2010)

Abstract: Three new oxo-centered trinuclear complexes, one of them a mixed-valence complex $[\text{Mn}_3\text{O}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{Py})_3]\text{Py}$ (**1**) and the others, mixed-metal complexes of $[\text{Fe}_2\text{MnO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{Py})_3]\text{NO}_3$ (**2**) and $[\text{Fe}_2\text{CoO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{Py})_3]$ (**3**) were synthesized by the direct reaction between metal nitrates and *p*-chlorobenzoic 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 *p*-chlorobenzoic acid. The UV spectra of the complexes exhibited a strong band in the region $42,500\text{ cm}^{-1}$ which is related to the ($\pi \rightarrow \pi^*$) transitions of the pyridine 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.

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

INTRODUCTION

Trinuclear, oxo-centered, carboxylate complexes of transition metals of general composition $[\text{M}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^{n+}$ and $[\text{M}(\text{III})_2\text{M}(\text{II})\text{O}(\text{O}_2\text{CR})_6\text{L}_3]$ (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.^{3,4} 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.

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doi: 10.2298/JSC090825066K

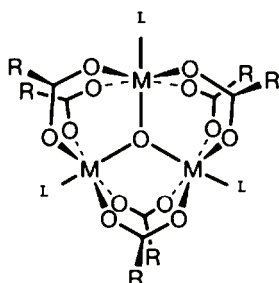


Fig. 1. Structure of the cluster unit $[M_3O(RCOO)_6(L)_3]^{2-}$.

Secondly, the polynuclear structure leads to the formation of mixed-valence 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.⁷

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 substituents.^{8,9}

In this paper, the syntheses and characterization of heterometallic clusters in solution phase are reported.

EXPERIMENTAL

The C, H and N analyses were realized on a Thermo Finnigan Flash model EA1112 elemental analyzer at the Faculty of Science, Ferdowsi University of Mashhad, India. The atomic absorption analyses were performed on a Shimadzu model AA-670 atomic absorption spectrometer. The IR spectra of KBr discs ($4000\text{--}600\text{ cm}^{-1}$) were recorded on a Buck 500 spectrometer. The electronic spectra were registered in the range $600\text{--}200\text{ cm}^{-1}$ 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 $[Mn_3O(C_7H_4O_2Cl)_6(Py)_3]Py$ (I)

n-Bu₄NMnO₄ was prepared by a literature method.¹¹ *n*-Bu₄NBr (12 g, 37 mmol) was added to an aqueous solution of KMnO₄ (5.0 g, 32 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 (yield > 90%).

Warning: *n*-Bu₄NMnO₄ is potentially explosive and must be treated with care!

Mn(O₂CMe)₂·4H₂O (0.80 g, 3.3 mmol) and C₇H₅O₂Cl (3.8 g, 25 mmol) were dissolved in a solvent mixture comprising dry pyridine (3 ml) and absolute EtOH (25 ml). The resulting solution was stirred while solid *n*-Bu₄NMnO₄ (0.46 g, 1.3 mmol) was added in small portions to give a brown-green homogeneous solution, from which the precipitation of a brown-green product began almost immediately. The stirring was continued for 1 h and the product was left undisturbed overnight in a refrigerator. The brown-green precipitate was filtered, washed copiously with cold EtOH, and dried *in vacuo*. Yield: 65 %; m.p.: 190 °C; Anal. Calcd. for C₆₂H₄₄C₁₆Mn₃N₄O₁₃ (FW 1426.7): C, 52.14; H, 3.08; N, 3.92; Mn, 18.6 %. Found: C, 52.22; H, 3.15; N, 3.99; Mn, 18.3 %. IR (selected data, KBr, cm⁻¹): 540 (*m*), 715 (*s*), 1405 (*s*), 1595 (*s*), 2940 (*m*).

Preparation of [Fe₂MnO(C₇H₄O₂Cl)₆(Py)₃]NO₃ (2)

A mixture of Fe(NO₃)₃·9H₂O (1.08 g, 2.68 mmol) and Mn(NO₃)₂·4H₂O (0.34 g, 1.3 mmol), dissolved in 25 ml dry pyridine was refluxed for 10 min and NaC₇H₄O₂Cl (2.0 g, 12 mmol) was added and the reflux continued for 5 h. The resulting deep brown solution was allowed to cool and stored for 2 days at 20 °C. The black crystals were filtered off, washed copiously with Et₂O and dried *in vacuo*. Yield: 75 %; m.p.: 230 °C; Anal. Calcd. for C₅₇H₃₉C₁₆Fe₂MnN₄O₁₆ (FW 1414.5): C, 48.35; H, 2.75; N, 3.95; Fe, 7.8; Mn, 4.3 %. Found: C, 48.95; H, 2.60; N, 3.82; Fe, 7.6; Mn, 4.1 %. IR (selected data, KBr, cm⁻¹): 434 (*m*), 549 (*m*), 715 (*s*), 1410 (*s*), 1598 (*s*), 2900 (*m*).

Preparation of [Fe₂CoO(C₇H₄O₂Cl)₆(Py)₃] (3)

A mixture of Fe(NO₃)₃·9H₂O (1.08 g, 2.68 mmol) and Co(NO₃)₂·6H₂O (0.39 g, 1.3 mmol), dissolved in 25 ml of dry pyridine was refluxed for 10 min and NaC₇H₄O₂Cl (2.0 g, 12 mmol) was added and the reflux continued for 4 h. 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 Et₂O and dried *in vacuo*. Yield: 70 %; m.p.: 185 °C. Anal. Calcd. for C₅₇H₃₉C₁₆CoFe₂N₃O₁₃ (FW 1356.6): C, 50.41; H, 2.87; N, 3.09; Fe, 8.2; Co, 4.3 %. Found: C, 50.59; H, 2.81; N, 3.20; Fe, 8.1; Co, 4.2 %. IR (selected data, KBr, cm⁻¹): 440 (*m*), 543 (*m*), 710 (*s*), 1402 (*s*), 1600 (*s*), 2950 (*m*).

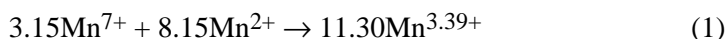
RESULTS AND DISCUSSION

The analytical data for the complexes are given in Table I. They are in close agreement with the calculated data and strongly support the presence of trinuclear metal complexes. Mixed-metal oxo-centered complexes were prepared from metal nitrates and sodium *p*-chlorobenzoate in dry pyridine to obtain the expected products.

TABLE I. Analytical data, color and melting point of the complexes 1–3

Compound	Color	Found (Calcd.), %			M.p., °C
		C	H	N	
1	Brown-green	52.22 (52.14)	3.15 (3.08)	3.99 (3.92)	190
2	Deep-brown	48.95(48.35)	2.60 (2.75)	3.82 (3.95)	230
3	Brown	50.59 (50.42)	2.81 (2.87)	3.20 (3.10)	185

Prior reports of the synthesis and properties of trinuclear oxo-centered Mn 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.¹² Reaction of this material with an excess of a neutral donor group L led to discrete units of the formulation $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{L})_3]^\pm$. As part of our continuing development of *n*- Bu_4NMnO_4 as a reagent for inorganic syntheses in non-aqueous solvents, its use for the synthesis of Mn_3O -type complexes was explored and it was found to work extremely well. 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,¹³ 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 II. 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.¹⁴ For a new series of trinuclear mixed-metal complexes, Cannon *et al.*² 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 **2**, strong bands at 1410 and 1598 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 188 cm^{-1} .¹⁵ The 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 800–400

cm^{-1} were used. The strong band observed at 430–560 cm^{-1} is attributed to the $\nu(\text{M}_2\text{M}')$ vibration.¹⁶

TABLE II. Selected IR bands (cm^{-1}) for the complexes **1–3**

Compound	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\nu(\text{M}_3\text{O})$	$\nu(\text{C-H})$	$\nu(\text{C-X})$
1	1405	1595	540	2940	715
2	1410	1598	434–549	2900	715
3	1402	1600	440–543	2950	710

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 50000–15000 cm^{-1} in dichloromethane solution. The spectra of the mixed–metal complexes **2** and **3** 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.¹⁷ The bands are shifted to higher energy when L = pyridine. The electronic spectroscopy data are given in Table III, which can be assigned and characterized based on other literature.¹⁸

TABLE III. Diffuse reflectance spectra of complexes

Compound	Transition $\pi \rightarrow \pi^*$, nm	Transition d \rightarrow d, nm
1	244	470–530
2	247	459–574
3	254	440–558–677(<i>sh</i>)

CONCLUSIONS

In this study, three new oxo-centered basic *p*-chlorobenzoic bridging complexes were prepared by the direct method of reaction between metal nitrate and sodium *p*-chlorobenzoate. 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.

ИЗВОД

ДОБИЈАЊЕ И КАРАКТЕРИСАЊЕ НОВИХ ОКСО-ЦЕНТРИРАНИХ ТРИНУКЛЕАРНИХ КОМПЛЕКСА СА МОСТОВНО ВЕЗАНОМ *p*-ХЛОРБЕНЗОЕВОМ КИСЕЛИНОМ

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Три нова оксо-центрирана тринуклеарна комплекса, мешовито-валентни $[\text{Mn}_3\text{O}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{Py})_3]\text{Py}$ (**1**) и два мешовито-метална $[\text{Fe}_2\text{MnO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{Py})_3]\text{NO}_3$ (**2**) и $[\text{Fe}_2\text{CoO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{Py})_3]$ (**3**) су добијена директном реакцијом металног нитрата и *p*-хлорбензоове киселине и окарактерисана елементалном анализом (CHN), атомском апсорпционом спектроскопијом и спектралном (IR, електронском) анализом. Ово је нови тип оксо-мостовних мешовито-металних комплекса са карбоксилатним лигандом *p*-хлорбензоовом киселином. UV спектри ових комплекса имају јаку траку у области 42500 cm^{-1} која припада ($\pi \rightarrow \pi^*$) прелазима пиридинског лиганда. IR спектри садрже две јаке траке вибрација истезања указујући на мостовни начин координације карбоксилатног лиганда.

(Примљено 25. августа 2009, ревидирано 2. фебруара 2010)

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