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Synthesis and characterization of novel oxo-bridged, trinuclear mixed-metal complexes of Cr(III) and Fe(III)

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Abstract: Two new heterotrimeric *p*-chlorobenzoates, $[\text{Fe}_2\text{CrO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{py})_3]\text{NO}_3$ (**1**) and $[\text{Cr}_2\text{FeO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{py})_3]\text{NO}_3$ (**2**) were prepared as nitrate salts and characterized by elemental analyses (CHN), spectroscopic (infrared, electronic) studies and atomic absorption spectroscopy. These complexes are a new type of oxo-bridged mixed-metal complex in which the carboxylate ligand is *p*-chlorobenzoic acid. Bridging coordination modes for the carboxylates were indicated by the presence of $\nu_{\text{asym}}(\text{M}_2\text{M}'\text{O})$ vibrations in the infrared spectra.

Keywords: carboxylates; oxo-bridged complexes; *p*-chlorobenzoic acid; IR spectra.

INTRODUCTION

Transition-metal carboxylate chemistry has played a key role in the conceptual development of modern inorganic chemistry. Extensive structural and physicochemical studies of these compounds were crucial for increasing the understanding of the bonding and electronic interactions between proximate metal centers, topics with implications ranging from industrial catalysis and industrial magnetism to the structure and function of mixed-metal compounds.^{1–3} The current interest in trinuclear, oxo-centered metal carboxylate assemblies of the general composition $[\text{M}_3\text{O}(\text{RCOO})_6(\text{L})_3]^z$ (where M is a trivalent 3d metal, L is a monodentate ligand, such as methanol, pyridine (py), *etc.*, and *z* is +1 for $\text{M}(\text{III})_2\text{M}'(\text{III})$ and 0 for $\text{M}(\text{III})_2\text{M}'(\text{II})$) is due to these complexes having served as important models to test theories of electronic coupling between metal ions^{4,5} (Fig. 1).

Heterotrimeric complexes have been known for more than half a century, $[\text{Fe}(\text{III})_2\text{M}(\text{II})\text{O}(\text{MeCOO})_6(\text{H}_2\text{O})_3]$ complexes (M = Co, Ni) were originally prepared in 1928 by Weinland and Holtmeier⁶ and the structures proved in 1980 by Yokubov.⁷

These heterotrimeric complexes exhibited antiferromagnetic exchange interactions and the central O atom provided the main super exchange pathway,⁸ in which the *p*-orbitals of the oxygen atom in the M_3O plane were especially effect-

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tive. It is apparent that the number of d-electrons in $M(III)_2M'(III)O$ compounds is one less than that in $M(III)_2M'(II)O$ compounds, hence the chemical properties of these complexes may be quite different.⁹

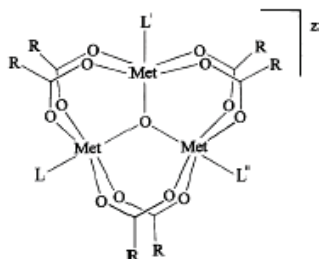
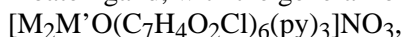


Fig. 1. Structure of the cluster unit $[M_3O(RCOO)_6(L)_3]^z$.

This paper describes the synthesis of new trinuclear oxo-centered complexes containing a *p*-chlorobenzoate ligand, with the general formula:



where M, M' = Fe, Cr.

EXPERIMENTAL

Materials and analytical methods

Organic solvents (Qualigens) were dried and distilled before use by standard methods. All reagents used in this study were of analytical grade and purchased from the Merck Company.

C, H and N analyses were performed on a Thermo Finnigan Flash model EA1112 elemental analyzer. Atomic absorption analyses were performed on a Shimadzu model AA-670 atomic absorption spectrometer. IR spectra of KBr discs ($600\text{--}4000\text{ cm}^{-1}$) were recorded on a Buck 500 spectrometer.

Preparation of $[Fe_2CrO(C_7H_4O_2Cl)_6(py)_3]NO_3$ (1)

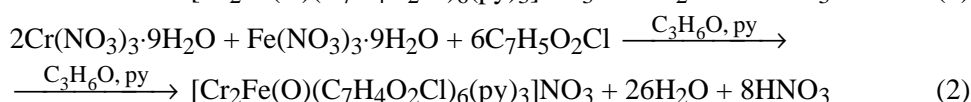
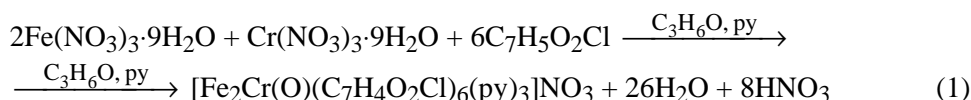
$C_7H_5O_2Cl$ (1.6 g, 10 mmol) was dissolved in pyridine (3.0 ml)–acetone (20 ml) mixture and stirred, then a mixture of $Fe(NO_3)_3 \cdot 9H_2O$ (0.80 g, 2.0 mmol) and $Cr(NO_3)_3 \cdot 9H_2O$ (0.40 g, 1.0 mmol) was added and refluxed for 2 h. The resulting brown solution was allowed to cool and stored for 3 days at $20\text{ }^\circ\text{C}$. The brown crystals were filtered off, washed copiously with Et_2O and dried *in vacuo* (yield: 70 %); m.p.: $267\text{ }^\circ\text{C}$. Anal. Calcd. for $C_{57}H_{39}Cl_6CrFe_2N_4O_{16}$ (1411.5 g/mol): C, 48.45; H, 2.76; N, 3.96; Fe, 6.2; Cr, 2.9. Found: C, 47.65; H, 2.66; N, 3.72; Fe, 6.2; Cr 2.8 %. IR (selected data, KBr, cm^{-1}): 310 (w), 435 (m), 572 (m), 740 (s), 1415 (s), 1607 (s), 3000 (m).

Preparation of $[Cr_2FeO(C_7H_4O_2Cl)_6(py)_3]NO_3$ (2)

$Cr(NO_3)_3 \cdot 9H_2O$ (1.5 g, 4.0 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.40 g, 1.0 mmol) and $C_7H_5O_2Cl$ (1.6 g, 10 mmol) were dissolved in a solvent mixture comprising acetone (20 ml) and pyridine (3.0 ml) and refluxed for 3 h to give a red-purple solution. After cooling, purple crystals were grown by slow evaporation at room temperature ($20\text{ }^\circ\text{C}$) for 3 days. The crystals were filtered off, washed copiously with Et_2O and dried *in vacuo* (yield: 75 %); m.p.: $275\text{ }^\circ\text{C}$. Anal. Calcd. for $C_{57}H_{39}Cl_6Cr_2FeN_4O_{16}$ (1407.6 g/mol): C, 48.59; H, 2.77; N, 3.97; Cr, 7.1; Fe, 3.8. Found: C 48.52; H 2.66; N 3.89; Cr 7.0; Fe 3.4 %; IR (selected data, KBr, cm^{-1}): 305 (w), 441 (m), 565 (m), 710 (s), 1413 (s), 1611 (s), 2870 (m).

RESULTS AND DISCUSSION

Mixed-metal oxo-centered complexes were synthesized by the reaction of Fe(III) and Cr(III) nitrates with *p*-chlorobenzoic acid and pyridine in acetone under reflux (Eqs. (1) and (2)):



After cooling the products to room temperature, the crystals were grown by slow evaporation for 3 days. The use of acetone as the solvent was a very suitable choice for these reactions because this solvent cannot covalently link to the metal ions as a terminal ligand.

The complexes had sharp melting points and both decomposed at around 350–400 °C.

Infrared spectra

In the infrared spectra of both complexes, one band was observed in the region 2800–3000 cm⁻¹, which indicates the presence of C–H aromatic stretching vibration of the carboxylic acid. The IR data for compounds **1** and **2** are given in Table I. A band at ≈ 710 cm⁻¹ (C–Cl stretching) was also found in the spectra of the complexes. Two strong bands were observed at ≈ 1610 cm⁻¹ and ≈ 1415 cm⁻¹, corresponding to ν_{asym}(OCO) and ν_{sym}(OCO) stretching vibrations, respectively. The coordination mode of the carboxylate ligand can be assigned on the basis of the difference (Δν ≈ 195 cm⁻¹) of these two frequencies, which indicates the presence of a bridging mode of coordination of the ligand in the complexes¹⁰ (Fig. 2).

TABLE I. Selected IR bands (cm⁻¹) for the complexes

Complex	ν _{asym} (COO)	ν _{sym} (COO)	ν(M ₃ O)	ν(C–H)	ν(C–Cl)
1	1415	1607	435–572	3000	740
2	1413	1611	441–565	2870	710

For a new series of trinuclear mixed-metal complexes, Cannon and co-workers¹¹ assigned the IR spectra and identified the vibrational modes of the central M₃O core. They found that a reduction in the site geometry from D_{3h} to C_{2v} lifted the degeneracy of the asymmetric M₃O stretching vibrations and two bands were seen. IR spectra in the range 400–800 cm⁻¹ were used for the identification of the metal–oxygen bands of the M₃O groups.¹² The band observed for the asymmetric vibration associated with the M₂M'O unit was split into two

components, A_1 and B_2 .¹³ These spectra showed characteristic bands for the valence oscillations $\nu_{\text{asym}}(\text{M}_2\text{M}'\text{O})$ around 570 (A_1) and 450 cm^{-1} (B_2).

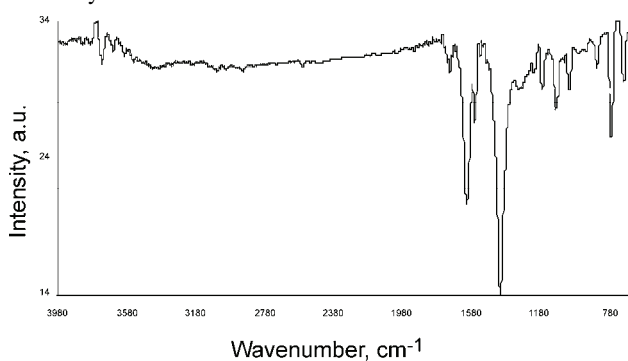


Fig. 2. IR spectrum of $[\text{Cr}_2\text{FeO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{py})_3]\text{NO}_3$.

Electronic spectroscopy

Oxo-centered complexes involve electronic transitions that are similar to other inorganic compounds. Thus, UV–Vis spectroscopy is one of the useful methods for characterizing oxo-centered complexes.

Electronic spectra of the complexes were recorded in the range 15000–50000 cm^{-1} in dichloromethane solution. The spectra exhibited two spin-allowed bands in the regions 17250 and 22200 cm^{-1} , which could be assigned to the transition from ${}^4A_{2g}(\text{F})$ to ${}^4T_{2g}(\text{F})$ (ν_1) and ${}^4T_{1g}(\text{F})$ (ν_2), respectively. These bands should be attributed to the existence of Cr(III) (d^3) ion in these complexes. The room-temperature electronic spectrum of complex **2** is shown in Fig. 3.

The spectra may be interpreted on the basis of an octahedral environment for chromium(III) in these complexes. The position of the third spin-allowed transition ν_3 (${}^4A_{2g}(\text{F})$ to ${}^4T_{2g}(\text{P})$) could be calculated together with the ligand field splitting energy ($10 Dq$), the interelectronic repulsion parameter (B) and the covalency factor (β) using the equations of Underhill and Billing:¹⁴

$$340Dq^2 - 18(\nu_2 + \nu_3)Dq + \nu_2\nu_3 = 0 \quad (1)$$

$$B = (\nu_3 + \nu_2 - 3\nu_1)/15 \quad (2)$$

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

The values of the interelectronic repulsion parameter (B) were found to be below the free ion value for the chromium(III) ion (933 cm^{-1}),¹⁵ which indicates a considerable covalent nature of the metal–ligand bond in both the complexes, with the covalency factor (β) varying in the range 0–7.0. The UV spectra of these complexes exhibit a strong band in the region 41,000 cm^{-1} which is related to ($\pi \rightarrow \pi^*$) transitions of pyridine (py) ligand. The bands are shifted to higher energy when $L = \text{py}$. The electronic spectroscopy data are given in Table II, which were assigned and characterized on the basis of literature data.¹⁶

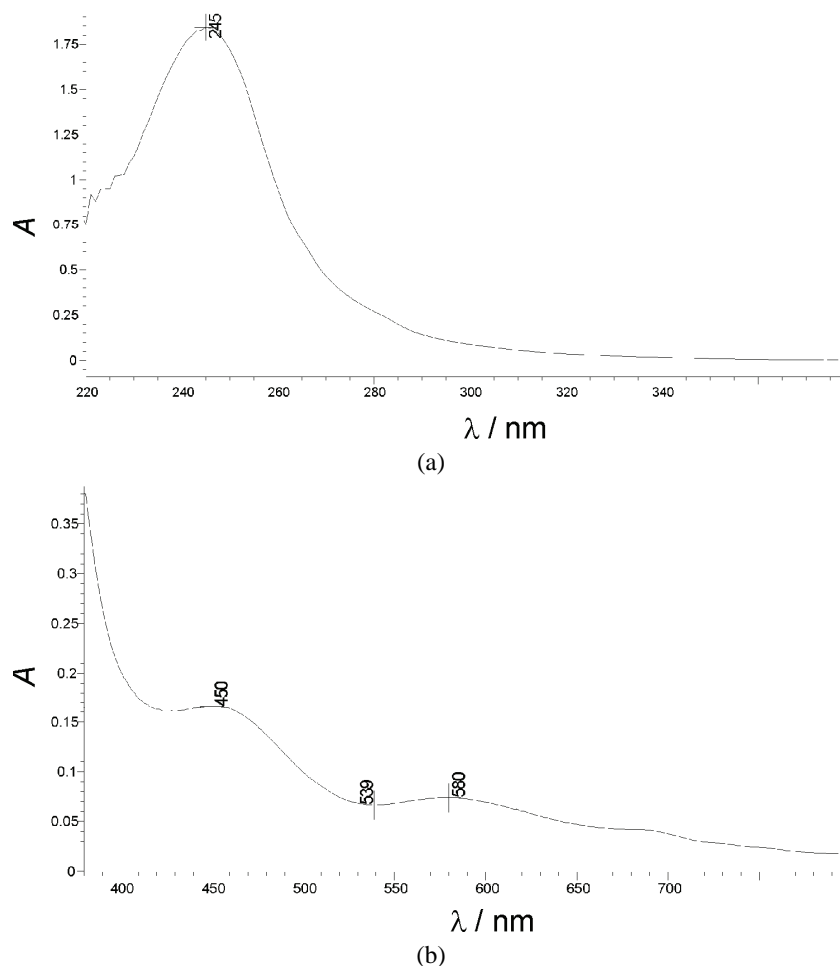


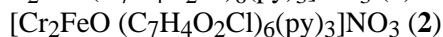
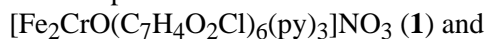
Fig. 3. UV (a) and Vis (b) spectra of $[\text{Cr}_2\text{FeO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{py})_3]\text{NO}_3$.

Table II. Electronic absorption spectral data of complexes **1** and **2** in dichloromethane solution

Compound	Transitions ($\pi \rightarrow \pi^*$), nm	Transitions ($d \rightarrow d$), nm
1	247	459–598
2	245	450–580

CONCLUSIONS

In this study, two new complexes of the formula:



were prepared by the direct reaction of the metal ions with the carboxylic acid. These compounds were characterized by elemental analyses (CHN), infrared and electronic spectroscopy and atomic absorption spectroscopy.

The IR spectra of these compounds showed two strong bands at ≈ 1610 and $\approx 1415 \text{ cm}^{-1}$, corresponding to $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ stretching vibrations. The difference in these values indicates a bridging mode of coordination of the carboxylic ligand in these complexes.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НОВИХ ТРИНУКЛЕАРНИХ МЕШОВИТО
МЕТАЛНИХ КОМПЛЕКСА Cr(III) И Fe(III) СА ОКСО КООРДИНАЦИЈОМ

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Добијена су два нова хетеротринуклеарна *p*-хлоробензоата: $[\text{Fe}_2\text{CrO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{py})_3]\text{NO}_3$ (**1**) и $[\text{Cr}_2\text{FeO}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_6(\text{py})_3]\text{NO}_3$ (**2**) и окарактерисана елементалном (CHN) и спектралном анализом (инфрацрвеном и електронском) и атомском апсорпционом спектроскопијом. Ово је нови тип мешовито металних комплекса са оксо координацијом у којима је карбоксилатни лиганд *p*-хлоробензоева киселина. Ови типови координације карбоксилата су доказани присуством $\nu_{\text{asym}}(\text{M}_2\text{M}'\text{O})$ вибрацијама у инфрацрвеним спектрима.

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