

Heterotrinnuclear Carboxylates of Chromium(III) and Iron(III): Mixtures or Pure Compounds?

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Complexes of the general form $[\text{Cr(III)}_{3-x}\text{Fe(III)}_x\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^+$ ($x = 1, 2$) have been a subject of intense investigation for the past several decades.^{1–9} These species have in general been prepared by heating a mixture of simple inorganic salts of Cr^{3+} and Fe^{3+} (in the desired ratio) in the presence of the appropriate acid anhydride^{3e} or by heating a mixture of the freshly prepared metal hydroxides in the appropriate carboxylic acid,⁹ yields of crystalline materials are generally high. The products have been characterized by a variety of techniques including elemental analysis, bulk magnetic susceptibility measurements,^{1,3d–f} electrochemistry,^{2,3f} polycrystalline EPR,^{1,3d–f} X-ray crystallography,^{4,8} electronic spectroscopy,^{3,5,6} vibrational spectroscopy,^{3g,7} and Mössbauer spectroscopy.^{3f} In all these studies, it has been assumed or “determined” that the mixed-metal product is pure or essentially so. By extending recent NMR and mass spectral studies on the homotrinnuclear species $[\text{M(III)}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^+$ ($\text{M} = \text{Cr(III)}, \text{Fe(III)}, \text{or Mn(III)}$)¹⁰ to their heteronuclear analogues, this laboratory has determined that the products of the above reactions are mixtures of the desired heteronuclear complex and the other possible hetero- and homonuclear analogues and that interpretation of results from previous investigations should take this into consideration.

Experimental Section

Materials. All chemicals were used as received. $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}^{11}$ and $[\text{Fe}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}^{12}$ were prepared as described elsewhere. The complexes “ $[\text{Cr}_{3-x}\text{Fe}_x\text{O}(\text{O}_2\text{CR})_6(\text{H}_2\text{O})_3]\text{NO}_3$ ” ($x = 1, 2$; $\text{R} = \text{Me}, \text{Et}, \text{Ph}$) were prepared and recrystallized as described by

Zelentsov et al.^{3d} The hydrated nitrate salts of Cr^{3+} and Fe^{3+} in a 2:1 or 1:2 ratio (9.9 total mmol) were heated in a mixture of ethanol (5 mL) and the appropriate acid anhydride (20 mmol); after the resulting solutions were allowed to cool, the products were isolated by filtration. This procedure, which is a simple extension of that of Starke used to prepare the homotrinnuclear Cr(III) and Fe(III) complexes,¹³ is that most often used to prepare the heteronuclear materials.^{3,4,5} The analogues where the terminal aquo ligands are replaced with pyridine were prepared by recrystallizing the complexes from hot pyridine. “ $\text{Cr}_2\text{-FeO}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3\text{O}_2\text{CMe}$ ” and “ $[\text{Cr}_2\text{FeO}(\text{O}_2\text{CMe})_6(\text{py})_3]\text{ClO}_4$ ” were also prepared from the trivalent metal hydroxides exactly as described by Johnson et al.⁷ This synthetic procedure for preparing heteronuclear assemblies by heating the metal hydroxides in the appropriate carboxylic acid has also been widely utilized.^{6,7,9} All products reproduced faithfully previously reported infrared and electronic spectra.^{6,7}

Instrumentation. ¹H NMR spectra were obtained using a Bruker AM-360 spectrometer at ca. 23 °C. Chemical shifts are reported on the δ scale (shifts downfield are positive) using the solvent protio impurity signal(s) as a reference. Infrared spectra (as Nujol mulls) were recorded using a Perkin-Elmer 283 B spectrophotometer. A Hewlett-Packard 8451A spectrophotometer was used to obtain ultraviolet–visible spectra. Fast atom bombardment mass spectra were obtained using a VG Autospec high resolution mass spectrometer.

Results and Discussion

Previous results from electronic, infrared, and Mössbauer spectroscopic studies of heteronuclear species prepared by the methods described above have conclusively shown that heteronuclear complexes were generated in these reactions; i.e., the products were not simply mixtures of the homonuclear chromium and iron assemblies. However, assumptions were then made that the products were the pure heteronuclear materials and not statistical mixtures of products containing Cr_3O , $\text{Cr}_2\text{-FeO}$, Fe_2CrO , and Fe_3O cores. Yet, each characterization technique utilized to date possesses inherent difficulties not allowing for distinction to be made between the pure or mixed situation. For example, Mössbauer spectroscopy is blind to the presence of the trichromium material; elemental analysis and magnetic susceptibility measurements are bulk techniques; the g values of a series of these complexes vary from only 1.93 to 1.96 (± 0.01), making distinctions by EPR difficult;^{1c} and difficulties with electrochemical studies have been described previously.¹⁴ Given recent successful characterization of the homonuclear species by NMR^{10,15} and mass spectrometry,^{10,16} these techniques appeared able to address this issue.

The mass spectrum of $[\text{Fe}_2\text{CrO}(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})_3]\text{NO}_3$ prepared by the Zelentsov method is shown in Figure 1 and in tabular form in Table 1. The terminal aquo ligands are readily lost such that the molecular ion is not observed and the ion resulting from loss of all three terminal ligands is the largest mass ion of those retaining the M_3 core in the spectrum.^{10b} The data clearly indicate the ability of FAB mass spectra to differentiate the $\text{Cr}_3\text{-}$, $\text{Cr}_2\text{Fe-}$, $\text{Fe}_2\text{Cr-}$, and $\text{Fe}_3\text{-}$ containing species. The result is a pattern of intense peaks which differ by four units for each metal change. Similar results are obtained regardless of the choice of carboxylate. The mass spectra indicate that the purported complexes containing “ Cr_2FeO ” cores are mixtures of the heteronuclear complex and the homonuclear Cr_3 complex; the purported “ Fe_2Cr ” complexes are mixtures of species containing

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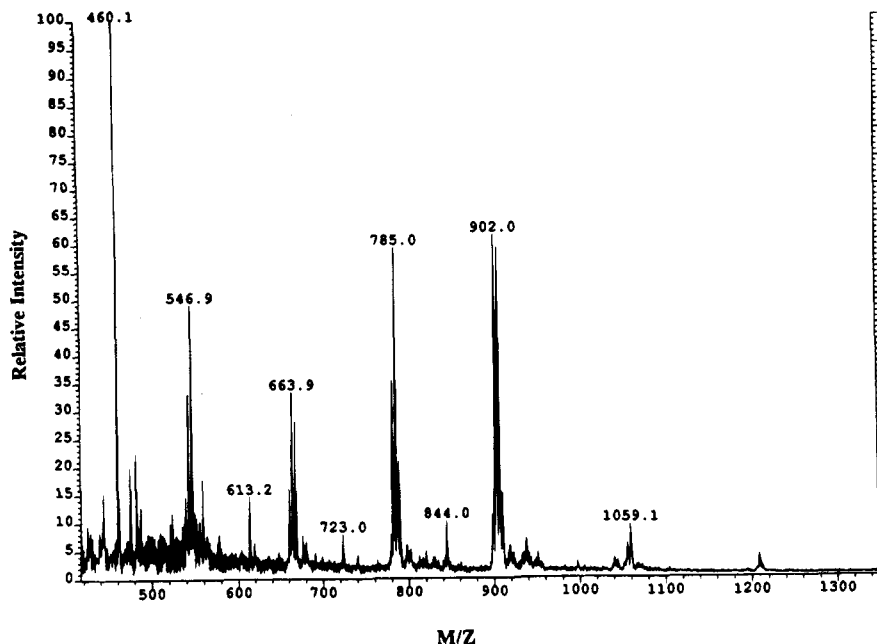


Figure 1. FAB-mass spectrum of $[\text{Fe}_2\text{CrO}(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})_3]^+$ in 3-nitrobenzyl alcohol. The most intense peak has been scaled to 100.

Table 1. Selected Mass Spectral Data for $[\text{Fe}_2\text{CrO}(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})_3]^+$

mass	rel. height (%)	assignt
460.1390	100.00	
538.8641	11.20	$\text{Cr}_2\text{FeO}(\text{O}_2\text{CR})_3^+$
542.8296	29.82	$\text{Fe}_2\text{CrO}(\text{O}_2\text{CR})_3^+$
546.8559	43.26	$\text{Fe}_3\text{O}(\text{O}_2\text{CR})_3^+$
659.9036	12.64	$\text{Cr}_2\text{FeO}(\text{O}_2\text{CR})_4^+$
663.8866	30.38	$\text{Fe}_2\text{CrO}(\text{O}_2\text{CR})_4^+$
667.9072	25.50	$\text{Fe}_3\text{O}(\text{O}_2\text{CR})_4^+$
781.0236	32.13	$\text{Cr}_2\text{FeO}(\text{O}_2\text{CR})_5^+$
785.0225	57.05	$\text{Fe}_2\text{CrO}(\text{O}_2\text{CR})_5^+$
789.0166	18.89	$\text{Fe}_3\text{O}(\text{O}_2\text{CR})_5^+$
902.0172	56.14	$\text{Cr}_2\text{FeO}(\text{O}_2\text{CR})_6^+$
906.0035	55.31	$\text{Fe}_2\text{CrO}(\text{O}_2\text{CR})_6^+$
909.9910	13.20	$\text{Fe}_3\text{O}(\text{O}_2\text{CR})_6^+$

all four possible M_3O cores. Both crude and recrystallized material have been examined; recrystallization only slightly varies the ratio of the particular species, probably simply enhancing the relative concentration of the least soluble species. Likewise, recrystallization from pyridine has only minor effects with the exception that higher mass ions possessing one, two, or three bound pyridine ligands are observable.

The difference in the number of species present between the "Cr₂Fe" and "Fe₂Cr" complexes reflects the relative reaction rates of Cr³⁺ and Fe³⁺, with larger quantities of the more labile ferric ions generating all four possible products. These results are not surprising given the differences in the kinetics of formation of the heteronuclear species as a function of stoichiometry as determined by Nikol'skii and co-workers.² As a result of the relative inertness to substitution of Cr(III) complexes, multinuclear Cr(III) species bridged by multiple ligands which form in the reaction mixture are not prone to dissociate and, thus, accumulate (especially at high Cr(III) concentrations). As the Cr(III)-rich species tends to be less soluble than their iron analogues, the distribution of species tends to be skewed. (As a result, recrystallization of these heteronuclear species as well as complexes of the form $\text{Cr}_2\text{MO}(\text{O}_2\text{CR})_6\text{L}_3$ where M is a divalent metal results in enhancement or generation of the corresponding Cr(III)₃ species.¹⁸) Not surprisingly the mass spectra of products generated from the second method via the metal hydroxides are similar to those of products generated via the other route.

The ¹H NMR spectra of these species confirm the mass spectral results. For example, the spectrum of $[\text{Cr}_2\text{FeO}(\text{O}_2\text{-CMe})_6(\text{H}_2\text{O})_3]\text{NO}_3$ contains at least three paramagnetically shifted resonances (Figure 2a). One of these signals corresponds to the methyl hydrogens of the homonuclear Cr₃ species.^{10a} The remaining two resonances, which occur in a 2.0:1.0 ratio, are readily assigned to the acetate methyl hydrogens of a heteronuclear species, presumably with a Cr₂Fe core as identified by the mass spectra. Of the six acetates contained in a Cr₂Fe complex, four should bridge between a chromic center and a ferric center while only two bridge between two chromic centers; thus, the most intense signal represents acetate ligands bridging between two nonidentical centers, while the less intense signal represents acetate ligands bridging between chromic centers. The weak feature at ca. 31 ppm may arise from a small amount of the Fe₂Cr or Fe₃ species. Similar results are observed in the methylene proton region of the spectrum of $[\text{Cr}_2\text{FeO}(\text{O}_2\text{CCH}_2\text{-CH}_3)_6(\text{H}_2\text{O})_3]\text{NO}_3$ (Figure 2b). Integration of the signals for the sample of recrystallized material gives an overall Cr to Fe ratio of 3:1, quite different than the 2:1 ratio in the starting materials. However, the spectrum of the crude product prior to recrystallization yields a 2.7:1 Cr:Fe ratio. Yet, weak additional signals from the Fe₃- and Fe₂Cr-containing species are present; thus, the crude product reflects the Cr:Fe ratio of the starting materials.

For the purported Fe₂Cr analogues in the methyl and methylene regions, at least five resonances (although broad and overlapping) can be discerned including resonances from both homonuclear materials (not shown).

The ratio of products determined by integration of the NMR resonances differs substantially from that obtained in the mass spectral studies. The NMR-derived ratios should be more accurate.¹⁷ The trinuclear species undergo significant gas phase chemistry, resulting in the production of smaller mass ions;^{10,16}

(17) All ¹H NMR spectra were collected with delay times of 1.0 or 0.5 s. T₁ values for the methyl or methylene protons are in the range 0.2–0.7 ms. For example, in parts a and b of Figure 2, the values are as follows: 21.0 ppm, 0.45 ms, and 26.1, 0.38; 36.9, 0.22, and 23.5 ppm, 0.41 ms, and 26.1, 0.40; 40.9, 0.22, respectively. Values for the acetate methyl signals of Fe₃ species are also in this range (Wu, F.-J.; Kurtz, D. M., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6563); the value for the methylene signal of $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_2\text{CH}_3)_6(\text{H}_2\text{O})_3]^+$ was found to be 0.70 ms.

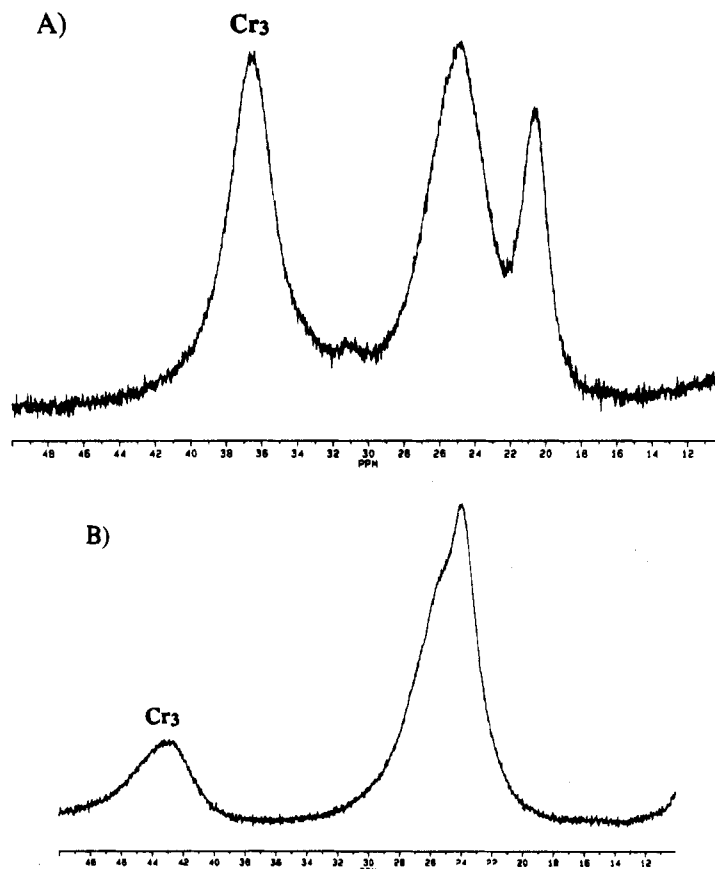


Figure 2. ^1H NMR of (a) the methyl region of $[\text{Cr}_2\text{FeO}(\text{OAc})_6(\text{H}_2\text{O})_3]^+$ in D_2O solution and of (b) the methylene region of $[\text{Cr}_2\text{FeO}(\text{O}_2\text{CCH}_2\text{CH}_3)_6(\text{H}_2\text{O})_3]^+$ in D_2O solution.

the extent of this chemistry varies between Fe_3 and Cr_3 assemblies.¹⁶ As a result, more fragmented ions as shown in Figure 1 display an increase in the relative ratio of Fe_3 - and Fe_2Cr -containing species compared to Cr_3 - and Cr_2Fe -containing species. (However, mass spectral control studies of mixtures of the two homonuclear cations reveal no evidence for the generation of heteronuclear species).

In conclusion, ^1H NMR and mass spectral studies provide conclusive evidence for the formation of heteronuclear carboxylates of $\text{Cr}(\text{III})$ and $\text{Fe}(\text{III})$, yet the products of these

reactions are mixtures of the heteronuclear species and homonuclear species. The distribution of products is not purely statistical but reflects the difference in reaction rate of $\text{Cr}(\text{III})$ and $\text{Fe}(\text{III})$ complexes.

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Supplementary Material Available: Figures S1–S5, showing comparisons of experimental and theoretical FAB-mass spectra (5 pages). Ordering information is given on any current masthead page.

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