

## Notes

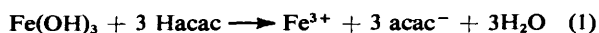
### Novel Synthesis of Tris(acetylacetonato)iron(III)

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The reaction of iron(III) hydroxide with acetylacetone, in the absence of any buffer, readily gives highly crystalline tris(acetylacetonato)iron(III),  $[\text{Fe}(\text{acac})_3]$ , in very high yield. Its mass spectrum provides evidence for rearrangement to give  $\text{Fe}-\text{CH}_3$  species.

Known methods of the synthesis of tris(acetylacetonato)iron(III),  $[\text{Fe}(\text{acac})_3]$ , have some limitations in scope. The reaction between metallic iron and acetylacetone (Hacac) in the presence of oxygen<sup>1</sup> is extremely slow. The aqueous reaction between iron(III) chloride and acetylacetone in the presence of a large amount of sodium acetate as buffer<sup>2,3</sup> may contaminate the product. The synthesis due to Dunne and Cotton<sup>4</sup> involving the reaction between  $[\text{Fe}(\text{CO})_5]$  and acetylacetone requires the preparation and handling of the toxic air-sensitive metal carbonyl. The present report describes a novel synthesis of  $[\text{Fe}(\text{acac})_3]$  directly from iron(III) hydroxide and acetylacetone, without the use of any buffer, and characterization of the compound [equation (1)].



#### Experimental

Reagent-grade iron(III) chloride and acetylacetone were used. Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the calibrant. Molar conductance measurements were made using a Philips PR 9500 conductivity bridge.

The mass spectra were recorded on a Varian MAT CH-5 mass spectrometer using a direct insertion probe. The operation conditions were electron energy, 70 eV (1 eV  $\approx 1.6 \times 10^{-19}$  J); source temperatures of 50, 100, and 150 °C; resolution, 1 000; and accelerating voltage, 8 kV. The mass spectrometric observations were made with the field of ionising current sufficiently strong to trap primary ions.

**Synthesis of Tris(acetylacetonato)iron(III),  $[\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3]$ .**—Anhydrous iron(III) chloride (4.0 g, 24.7 mmol) was dissolved in water (6 cm<sup>3</sup>) with gentle warming. Ammonia solution (specific gravity 0.880, 9 cm<sup>3</sup>, excess) was added slowly with constant stirring. The mixture was heated on a steam-bath for 15–20 min, and the precipitate of iron(III) hydroxide was then filtered off and washed with water until free from chloride.

The moist iron(III) hydroxide and acetylacetone (12.0 g, 120 mmol) were placed in a small conical flask, the neck of which was plugged with cotton wool, and the whole was heated on a steam-bath for 35 min. On cooling, large red crystals of  $[\text{Fe}(\text{acac})_3]$  were obtained which were dried on filter paper and recrystallised from ethanol. Yield, 7.8 g (90%), m.p. 175 °C [Found: *M* (mass spectrum), 353; *C*, 51.2. Calc. for  $\text{C}_{15}\text{H}_{21}\text{FeO}_6$ : *M*, 353; *C*, 51.05%]. Molar conductance ( $\text{H}_2\text{O}$ ): 8  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Magnetic moment (295 K): 5.92 B.M. (B.M. =  $0.927 \times 10^{-23} \text{ A m}^2$ ) (lit.,<sup>3</sup> 5.90 B.M.).

#### Results and Discussion

Recently  $[\text{Mn}(\text{acac})_3]$  was synthesised by the reaction of  $[\text{MnO}_4]^-$  with acetylacetone<sup>5</sup> by exploiting the electron-transfer reaction between them. The weak acidity of Hacac in a polar medium and the absence of any reaction of water with  $[\text{Fe}(\text{acac})_3]$  constitute the basis of the present synthesis. The method described leads to the rapid synthesis of  $[\text{Fe}(\text{acac})_3]$  in a very high yield. Analogous methods have been used with success for the synthesis of  $[\text{Co}(\text{acac})_3]$  from  $\text{CoO}(\text{OH})$  and  $[\text{Mn}(\text{acac})_3]$  from  $\text{MnO}(\text{OH})$ . The pH of the solution recorded immediately after the formation of the compound was found to be ca. 5 which concurs with that maintained by using a large amount of sodium acetate<sup>2,3</sup> in the synthesis of  $[\text{Fe}(\text{acac})_3]$  from  $\text{FeCl}_3$ .

The i.r. spectrum of the compound is unambiguous and exhibits the typical pattern of chelated acetylacetonates ( $\text{acac}^-$ ) in agreement with those of various  $[\text{M}(\text{acac})_3]$ <sup>5,6</sup> compounds. The mass spectra were obtained using a direct insertion probe to introduce the sample into the ionisation chamber without prior heating. The other conditions, except the source temperatures, were similar to those maintained in our earlier experiments.<sup>7</sup>

The spectrum run at 150 °C parallels those previously reported<sup>8,9</sup> showing the molecular ion at *m/z* 353 (intensity 16%) and the most dominant peak at *m/z* 254 assigned to  $[\text{Fe}(\text{acac})_2]^+$  with the major fragmentation pathway being  $[\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3]^+ \longrightarrow [\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2]^+ \longrightarrow [\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_4\text{H}_4\text{O}_2)]^+ \longrightarrow [\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)]^+ \longrightarrow [\text{Fe}(\text{C}_4\text{H}_4\text{O}_2)]^+ \longrightarrow \text{Fe}^+$ . The metastable peaks at *m/z* 182.7, 224.9, 100.8, and 126.5 support the fragmentation path. The two additional, metastable-supported signals at *m/z* 170 and 71 have been assigned to the fragment ions  $[\text{Fe}(\text{CH}_3)(\text{C}_5\text{H}_7\text{O}_2)]^+$  and  $[\text{Fe}(\text{CH}_3)]^+$  respectively, providing evidence for easy methyl migration from carbon to metal presumably favoured by the formation of a new bond between the metal atom and  $\text{CH}_3$ .

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