

Notes

Novel Synthesis of Tris(acetylacetonato)iron(III)

Mihir K. Chaudhuri* and Soumitra K. Ghosh

Department of Chemistry, North-Eastern Hill University, Shillong-793003, India

The reaction of iron(III) hydroxide with acetylacetonone, 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 acetylacetonone (Hacac) in the presence of oxygen¹ is extremely slow. The aqueous reaction between iron(III) chloride and acetylacetonone in the presence of a large amount of sodium acetate as buffer^{2,3} may contaminate the product. The synthesis due to Dunne and Cotton⁴ involving the reaction between $[\text{Fe}(\text{CO})_5]$ and acetylacetonone 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 acetylacetonone, without the use of any buffer, and characterization of the compound [equation (1)].



Experimental

Reagent-grade iron(III) chloride and acetylacetonone 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 cm³) with gentle warming. Ammonia solution (specific gravity 0.880, 9 cm³, 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 acetylacetonone (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 (H_2O): 8 Ω^{-1} cm² mol⁻¹. Magnetic moment (295 K): 5.92 B.M. (B.M. = 0.927×10^{-23} A m²) (lit.,³ 5.90 B.M.).

Results and Discussion

Recently $[\text{Mn}(\text{acac})_3]$ was synthesised by the reaction of $[\text{MnO}_4]^-$ with acetylacetonone⁵ 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^{2,3} in the synthesis of $[\text{Fe}(\text{acac})_3]$ from FeCl_3 .

The i.r. spectrum of the compound is unambiguous and exhibits the typical pattern of chelated acetylacetonates (acac^-) in agreement with those of various $[\text{M}(\text{acac})_3]$ ^{5,6} 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.⁷

The spectrum run at 150 °C parallels those previously reported^{8,9} 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 CH_3 .

Acknowledgements

Our thanks are due to C.S.I.R. (New Delhi) for the award of a fellowship (to S. K. G.).

References

- 1 R. G. Charles and S. Barnartt, *J. Phys. Chem.*, 1958, **62**, 315.
- 2 A. Hantzsch and C. H. Desch, *Liebigs Ann. Chem.*, 1902, **323**, 1.
- 3 D. Nicholls, 'The Chemistry of Iron, Cobalt, and Nickel' in 'Pergamon Texts in Inorganic Chemistry,' Pergamon Press, Oxford, 1975, vol. 24, p. 1045.
- 4 T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 263.

- 5 M. N. Bhattacharjee, M. K. Chaudhuri, and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 1982, 669.
- 6 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley-Interscience, New York, 1970, p. 248.
- 7 M. K. Chaudhuri, H. S. Dasgupta, N. Roy, and D. T. Khathing, *Org. Mass Spectrom.*, 1981, **16**, 303, 534.
- 8 C. G. McDonald and J. S. Shannon, *Aust. J. Chem.*, 1966, **19**, 1545.
- 9 G. M. Bancroft, C. Reichert, and J. B. Westmore, *Inorg. Chem.*, 1968, **7**, 870.

Received 29th April 1982; Paper 2/708