Anhydrous Iron(III) Nitrate

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PENTACARBONYLIRON and dinitrogen tetroxide react[1] to give the salt $[NO]^+ [Fe(NO_3)_4]^-$ but the simple iron(III) nitrate has not been previously described. We now report isolation of the latter as a yellow–brown involatile solid by treatment of either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with excess of N_2O_4 at 0°. Analysis of three products from $Fe_2(CO)_9$ and three from $Fe_3(CO)_{12}$ gave Fe between 22·55 and 23·25% and N between 17·25 and 17·65%; $Fe(NO_3)_3$ requires Fe = 23·1% and N = 17·4%.

The product has low thermal stability and decomposes slowly at room temperature and rapidly at *ca.* 70° under reduced pressure to give iron(III) oxide. It is soluble in polar solvents such as acetic acid, acetone, acetonitrile, and nitromethane and studies of the conductivity, depression of freezing point, and elevation of boiling point of these solutions indicate that reaction with the solvent has taken place. The product was insoluble in chloroform, toluene, or ether.

The i.r. spectrum of solid mulls showed principal bands (cm.$^{-1}$) at 1597s 1554vs, 1290vs, 1252vs, 1041m, 797m, 767m, and 742m. This spectrum is very similar to that of iron(III) oxide nitrate[2] and the tetranitratoferrate(III) anion[3] and clearly all three compounds contain covalent nitrate groups. Attempts to obtain the Raman spectrum have proved unsuccessful and it is therefore not possible at this stage to discuss the bonding of the nitrate groups;[4] clearly, however, the co-ordination number of the iron is likely to be increased by the use of bridging or bidentate nitrate groups. For a similar reason the assignment of the i.r. bands has been delayed.

The molar susceptibility χ_m was 5517×10^{-6} at 21° and a field strength of 5650 gauss, μ_{eff} = 3·62 B.M. which is very low for a high-spin iron(III) compound. Further, the calculated magnetic moment is somewhat dependent on the field strength suggesting that this system is not magnetically dilute. Some similar results have been reported for iron(III) oxide nitrate.[2]

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