Simple Direct Syntheses of Iron Clathro-chelates Derived from Dimethylglyoxime and Boron Compounds

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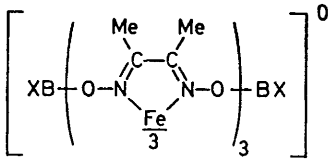
Summary The direct reaction between $\mathrm{Fe^{II}}$ salts with dimethylgloxime and boron trifluoride etherate in alcohol and between $\mathrm{Fe^{II}}$ salts with dimethylglyoxime and boric acid in alcohols or water results in the extremely ready formation of encapsulated metal complexes.

THE relatively new class of encapsulating ligands and their complexes, clathro-chelates,[1–3] are of interest in studies pertaining to analyses of metal ions, limited-pathway racemizations,[4] ion-transport phenomena,[2,5] separation of metal ions through selective sequestration, and stereochemistry.[6–8] We report here six new clathro-chelates which can be prepared by rapid, one step syntheses from mixtures of $\mathrm{Fe^{II}}$ salts, dimethylglyoxime ($\mathrm{dmgH_2}$), and either boric acid or boron trifluoride (see equations and formulae). Reactions according to equation (1) take place

$$\mathrm{Fe^{II}} + 3\mathrm{dmgH_2} + 2\mathrm{B(OH)_3} + 2\mathrm{ROH} \xrightarrow[\text{Heat}]{\mathrm{ROH}} [\mathrm{Fe(dmg)_3(BOR)_2}] + 2\mathrm{H^+} + 6\mathrm{HOH} \qquad (1)$$

$$\mathrm{Fe^{II}} + 6\mathrm{BF_3} + 3\mathrm{dmgH_2} \xrightarrow[\text{excess } \mathrm{BF_3{\cdot}OEt_2}]{\mathrm{Bu^nOH}} [\mathrm{Fe(dmg)_3(BF)_2}] + 6\mathrm{H^+} + 4\mathrm{BF_4^-} \qquad (2)$$

when the starting materials are heated in the appropriate alcohol or in water. The procedure requires less than 1 h and affords yields greater than 50%. However, if the acidity is reduced by adding 0·5—1 mol. equiv. of sodium acetate after the other reactants have been mixed, yields increase to >85%. Reactions according to equation (2) take place when the reactants are mixed together at room temperature, and the crystalline product deposits during several days. However, if *ca.* 5 mol. equiv. of NaOH is added after the other reactants have been mixed, the product is obtained within minutes.



$[\mathrm{Fe(dmg)_3(BX)_2}]$

X = F, OH, OMe, OEt, $\mathrm{OPr^i}$ $\mathrm{OBu^n}$

It seems very likely that the iron ions are serving an 'organizational role' in the reactions by providing a template on which three dmg groups become bound in the *anti*-configuration prior to reaction with the boron-containing fragments.[1]

The cage-like nature of $[\mathrm{Fe(dmg)_3(BF)_2}]$ has been established by single-crystal *X*-ray diffraction.[9] Like other clathro-chelates of the dmg class,[8] this is also intermediate between a trigonal prism and a trigonal antiprism. The formulations of the other five clathro-chelates were assigned by elemental analysis, solution molecular weight measurements, mass spectral measurements, and i.r. and ^{1}H n.m.r. spectra. The strongest peak in the mass spectra (70 eV and *ca.* 250 °C) of all the complexes is the parent ion. This fact coupled with the robust nature of the complexes and the relatively high yields with which they can be prepared suggests that they may well be suitable for analytical purposes. In their Mössbauer spectra the complexes show lower isomer shifts and greater quadrupole splittings than do those of the corresponding low-spin Fe^{II} complexes containing three, symmetrical α-di-imine ligands.[10] Thus the cage ligands as a class seem to be more distorted from octahedral co-ordination than the tris-α-di-imine complexes and also better σ-donors and/or better *d*-π-acceptors.

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