Clathration of Ferrocene and Nickelocene in a Thiourea Host Lattice

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Summary Ferrocene or mixtures of ferrocene and nickelocene form new clathrates with thiourea which show a phase transition at low temperature for high Fe/Ni ratio.

THE ability of thiourea to include a wide variety of organic molecules, such as branched-chain paraffins, fatty acids, and cycloparaffins, is well known.[1] We have found that clathration of metallocenes in the thiourea host lattice channels is also possible.

When ferrocene (*ca.* 0·1 g) is dissolved in 10 ml of a half-saturated solution of thiourea in methanol the mixture, maintained at −15° for some hours, yields orange needles. Alternatively, if a 1:2 mixture of ferrocene and thiourea crystals is heated for 12 h at 140° in a sealed evacuated tube a powdered phase results with properties and structure identical to the needles. When alone, nickelocene does not form a clathrate with thiourea but can be included when accompanying ferrocene (up to Ni/Fe *ca.* 0·4) or cyclohexane. Green needles then result, most of them polycrystalline. Nickelocene can be easily distinguished from ferrocene by its i.r. absorption band at 773 cm^{-1}.[2]

The stoicheiometry of the pure ferrocene clathrate has been obtained by colorimetry after decomposing the clathrate in boiling ether which dissolves ferrocene but not thiourea. The measured ratio of thiourea to ferrocene molecules is 3·0, a value equal to that found for the cyclohexane clathrates.

The *X*-ray rotating-crystal pattern of a ferrocene clathrate needle is similar to that of the known thiourea clathrates.[1a] Reflections can be indexed in the same rhombohedral unit cell; when referred to hexagonal axes, measured parameters are $a = 16{\cdot}40$ Å and $c = 12{\cdot}50$ Å, thus showing an appreciable distortion of the host lattice in the *a* direction with respect to the cyclohexane clathrate where $a = 15{\cdot}80$ Å.

The ferrocene clathrate exhibits a well-defined, apparently first-order, reversible phase transition at 162 K. The corresponding enthalpy variation, estimated from differential thermal analysis (DTA) peaks, is 290 ± 30 cal mol^{-1}

ferrocene. This should be compared with the behaviour of pure ferrocene crystals which undergo a sharp phase transition at 163·9 K immediately followed by a progressive transformation up to 169 K. The ΔH for the overall transition has been measured as 204 cal mol^{-1} and it has been suggested that rotational disorder of the π rings occurs in the high-temperature ferrocene phase.[3] However, the ferrocene clathrate transition is also comparable to that of cyclohexane thiourea clathrate (T = 128 K, ΔH = 300 cal mol^{-1} cyclohexane[4]). Thus the nature of the former could well be different from that observed in pure ferrocene crystals. Clathrates prepared with the maximum value of the nickelocene/ferrocene ratio do not show any DTA peak.

One possible explanation for the fact that the ferrocene clathrate forms readily while the nickelocene clathrate does not is the size of the clathrated species. Ferrocene appreciably distorts the thiourea host lattice from its normal size. Since nickelocene is a bit larger than ferrocene (for the gaseous species, Ni–C = 2·196 Å, Fe–C = 2·064 Å)[5] a filling factor of 40% for nickelocene could induce a destabilization of the host lattice. All attempts at clathrating ruthenocene (Ru–C = 2·21 Å[6]) were unsuccessful.

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