X-Ray Crystallographic Studies on Ferrocene included in a Thiourea Host Lattice

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X-Ray crystallographic studies on a 3 : 1 thiourea–ferrocene clathrate have been carried out at 295 and 100 K. The crystal structure of the high-temperature form has been determined from diffractometer data by Patterson and Fourier methods. Crystals are rhombohedral, space group $R\bar{3}c$ with $Z = 6$ in a unit cell based on the hexagonal setting of $a = 16.360(3)$ and $c = 12.395(2)$ Å. The structure has been refined by least-squares methods to R 0.079 for 711 observed reflections. It consists of thiourea molecules which form a honeycomb of channels by spiralling with a pitch of 120° parallel to the c axis. Within these channels, sites of point symmetry 32 are occupied by the ferrocene iron atoms. The cyclopentadienyl rings are disordered and the time-averaged picture shows regions of three-dimensionally delocalised cyclopentadienyl electron density around the iron atoms.

CHANNEL-INCLUSION compounds formed between urea and thiourea host lattices and a wide range of guest molecules such as paraffins and fatty acids have been known for some time.[1-4] Urea usually forms inclusions with straight-chain compounds whereas thiourea forms clathrates with branched and cycloparaffins. Interest in these compounds was initially aroused because of the possibility of their application in the oil industry. Experimental work on systems containing organic guest molecules includes crystallographic studies [1,3,4] on a number of urea and thiourea compounds, i.r.,[5-7] dielectric-absorption,[8] and wide-line n.m.r. measurements [9] on some urea systems, and thermal studies [10] on some thiourea compounds. The total picture provided by these investigations is one in which the enclosed molecules are loosely held by the host lattices thereby permitting considerable degrees of molecular motion.

More recently, the list of guest molecules has been extended by the addition of metallocenes.[11] For steric reasons apparently related to channel diameter, metallocenes with substituted cyclopentadienyl rings do not form clathrates with thiourea, a property exploited for separating substituted from unsubstituted metallocenes.[12] Enclosing ferrocene, $[Fe(\eta\text{-}C_5H_5)_2]$, in the thiourea lattice provides an opportunity for employing iron as a probe in a ^{57}Fe Mössbauer study. We undertook such a study in combination with a crystallographic investigation. The Mössbauer chemical shifts and quadrupole coupling constants obtained at 78 K for ferrocene and the clathrate are in good agreement, thereby confirming that ferrocene is only weakly held by the thiourea lattice. At 295 K the spectrum is markedly different, its main feature being a negligible quadrupole splitting. This phenomenon would be consistent with appreciable motions of the clathrated ferrocene molecules at room temperature and attendant fluctuations in the electric-field-gradient (e.f.g.) tensor which result in a collapsed quadrupole doublet. At the lower temperature, the motions are effectively frozen and the relaxation effect is absent. These effects have been confirmed recently by Gibb.[13]

We report here the results of a single-crystal *X*-ray diffraction study performed at 295 K, and the changes in reflections which accompany the reversible phase transition observed on cooling down to 100 K.

EXPERIMENTAL

Preparation.—Crystals of the thiourea–ferrocene clathrate, $[Fe(\eta\text{-}C_5H_5)_2]\cdot 3(NH_2)_2CS$ were prepared by mixing hot solutions of ferrocene (0.93 g) in benzene (10 cm^3) and thiourea (1.5 g) in methanol (40 cm^3).

Crystal Data.—$C_{13}H_{22}FeN_6S_3$, $M = 413.85$, Rhombohedral, in the hexagonal setting, $a = 16.360(3)$, $c = 12.395(2)$ Å, $U = 2\,873.1$ Å^3, $D_m = 1.41$ g cm^{-3} (flotation), $Z = 6$, $D_c = 1.44$ g cm^{-3}, $F(000) = 1\,296$, Mo-K_α radiation, $\mu = 10.9$ cm^{-1}. Absent reflections were consistent with space groups $R3c$ and $R\bar{3}c$; the structure solution was successful in the latter. Space group $R\bar{3}c$ implies $\bar{3}$ or 32 point symmetries for the six iron atoms and two-fold symmetry for the 18 thiourea molecules in the unit cell.

Intensity-data Collection and Structure Refinement.—A crystal, with dimensions *ca.* 0.49 × 0.40 × 0.28 mm, was mounted about the c axis and intensity data were collected at room temperature by the θ—2θ technique on a Picker FACS I automatic diffractometer ($2\theta_{\text{max.}}$ 58.8°) using monochromatised Mo-K_α radiation. Of the 920 reflections measured, 711 were classified as observed, *i.e.* $I_{\text{net}} > 2.58\sigma(I)$. The crystal was stable under data collection. Data were corrected for Lorentz and polarisation effects, but not for absorption. Scattering factors for the lighter atoms were taken from ref. 14 and for iron from ref. 15; solution and refinement was carried out using the '*X*-ray '76' system of programs.[16]

It was apparent from the presence of iron–sulphur vector peaks at $W = \frac{1}{4}$ in a Patterson map that the iron atoms must occupy the special positions with point symmetry 32. A difference-Fourier synthesis based on the

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thiourea and iron positions revealed that the cyclopentadienyl rings are disordered; least-squares refinement of the ordered atoms converged to a conventional R of 0.126 with anisotropic temperature factors. Electron density attributable to the cyclopentadienyl carbon atoms is almost completely smeared out around the central iron atom. Partial carbon atoms were fitted to weak maxima contained within this delocalisation. A final R of 0.079 was obtained with anisotropic temperature factors.

The atomic positions are given in Table 1, and Table 2 contains the interatomic distances and valence angles. Thermal parameters and observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 22148 (4 pp.).*

Examination at Low Temperature.—A crystal was mounted on a Syntex $P\bar{1}$ diffractometer fitted with a modified Enraf–Nonius gas-flow cryostat.[17] The temperature in the N_2 stream was *ca.* 105 K at the coldest point.

TABLE 1

Final positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Fe	0 000	0 000	2 500
S	3 064(2)	0 000	2 500
C(1)	4 113(6)	0 000	2 500
N	4 461(5)	−0.147(5)	1 581(6)

TABLE 2

Selected distances (Å) and angles (°), with estimated standard deviations in parentheses

Thiourea			
S–C(1)	1.716(9)	N–C(1)	1.347(9)
N–C(1)–N	118(1)	S–C(1)–N	120.7(8)

DISCUSSION

Thiourea Host Lattice.—The host-lattice part of the crystal structure (Figure 1 and ref. 3) is built up from thiourea molecules which are aligned along trigonally intersecting two-fold axes thereby forming a honeycomb of channels (diameter 10.0 Å) parallel to the c axis. These channels enclose point symmetries $3, \bar{3}$ and 32. The bond lengths and angles for the thiourea molecules are similar to those found in orthorhombic thiourea.[18]

Ferrocene Guest Molecule.—Ferrocene adopts the staggered (D_{5d}) form in the solid [19] and the eclipsed (D_{5h}) form in the vapour phase.[20] In the latter, inter-ring and Fe–C distances are 3.319(5) and 2.064(1) Å respectively. The barrier to ring rotation ($D_{5d} \longrightarrow D_{5h}$) is very low (5 kJ mol^{-1}), and the form adopted in the clathrate may therefore depend on the orientation of the molecule with respect to the host lattice. Ferrocene iron atoms of the clathrate occupy the 32 sites within the channels of the thiourea lattice. Figure 2 contains the relevant sections of a three-dimensional Fourier synthesis which shows some of the regions of delocalised cyclopentadienyl electron density around the iron atoms. We already have some information about the iron environment from Gibb's detailed ^{57}Fe Mössbauer study on the unusual temperature-dependent relaxation of the e.f.g. tensor. The absence of a significant quadrupole splitting at 300 K is typical of a motional narrowing effect caused by a rapid reorientation of the e.f.g. tensor, the principal axis of which coincides with the molecular axis. This effect was interpreted as being due to an even distribution of populations with their molecular axes aligned along the x, y, and z directions respectively.

There are three ways in which the ferrocene molecule can align itself: (*i*) the molecular axis coincides with the channel trigonal axis; (*ii*) the molecular axis lies perpendicular to the channel axis; and (*iii*) the molecular axis is inclined at varying angles, less than 90°, to the channel axis. The regions of delocalised electron density observed around the iron atoms clearly reflect three-dimensional disorder of the cyclopentadienyl rings which precludes a model based *solely* on the two-dimensionally disordered alternative (*i*). Moreover, alternative (*i*) would result in a distance of only 2.88 Å, and hence significant repulsions, between rings on neighbouring ferrocene molecules. This could be the driving force behind the tilting of the ferrocene axis away from the channel axis. In this connection it is interesting to note that [Ni(η-C_5H_5)$_2$], where the intramolecular ring distance is larger (3.66 Å), can only form an inclusion compound with thiourea when accompanying ferrocene (Ni : Fe *ca.* 0.1 : 1) or cyclohexane.[5]

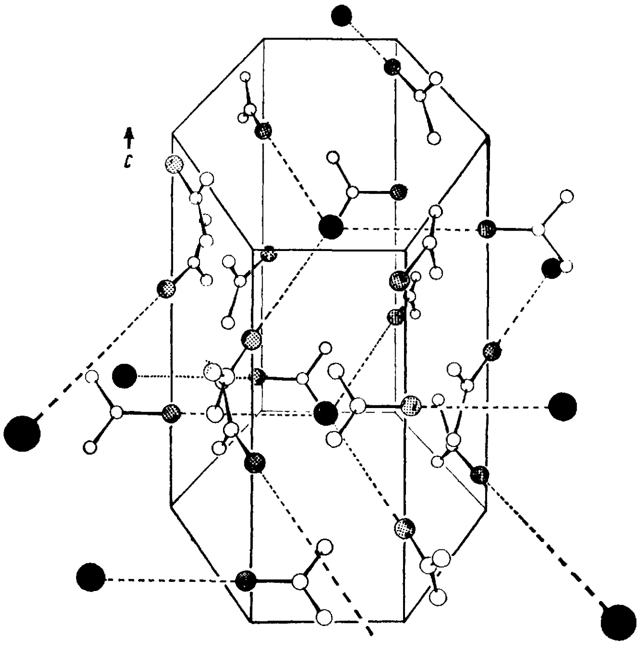

FIGURE 1 Perspective drawing of part of a channel in the thiourea host lattice (sulphur atoms shaded). Positions occupied by ferrocene iron atoms are represented by filled circles. Disordered cyclopentadienyl carbons are omitted

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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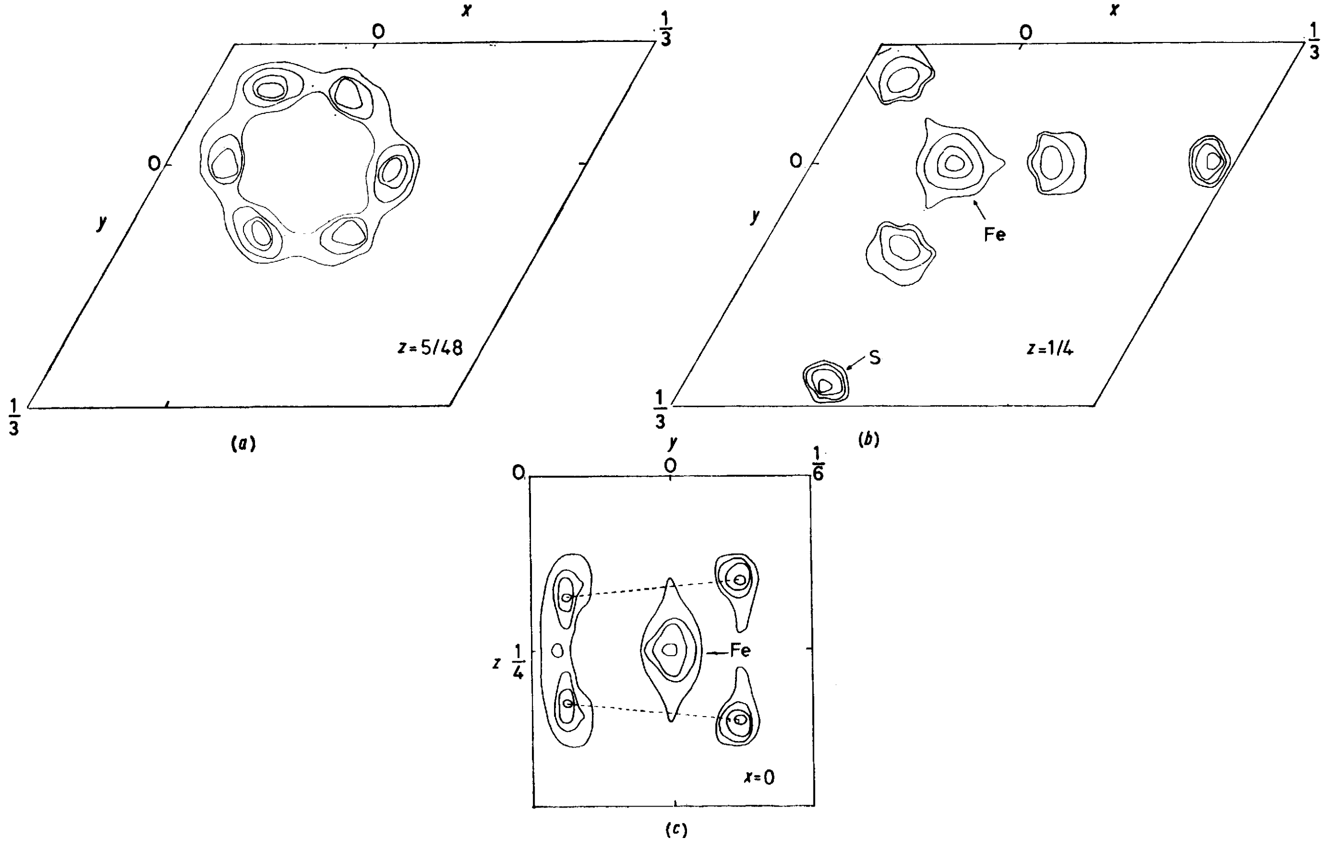

FIGURE 2 Sections through a Fourier synthesis showing disordered cyclopentadienyl electron density perpendicular to c at (a) $z = 5/48$, (b) $z = \frac{1}{4}$, and (c) parallel to x through iron

The partial carbon atoms used to describe the delocalised rings formally account for 98% of the total carbon electron density and lie at distances ranging from 1.9(1) to 2.4(1) Å from the iron atom. It is not possible to estimate the fraction of the ferrocene population which is aligned along the channel axis. The time-averaged picture of such contributions is constrained by interaction between the five-fold molecular axis and the three-fold channel axis. Thus, for fractions based either on the eclipsed or staggered forms, each cyclopentadienyl carbon atom appears in *at least* three or six positions respectively, depending on the molecular form. Any ring rotation would result in overlap of these. Clearly, even for a fraction as high as one third (see above), these contributions would in effect result in a ring of delocalised electron density. On the other hand, the extent of the electron-density distributions and their weak maxima must be a consequence of overlapping electron-density contributions from the various types of disorder. In particular, the maxima situated on the two-fold axes ($z = \frac{1}{4}$) would not be inconsistent with partial overlap of ferrocene molecules in the D_{5d} form disordered around the three-fold channel axis. Because of inter-ferrocene repulsions associated with the molecular axis coinciding with the channel axis, the disorder may take the form of co-operative oscillations with a pitch of 120° between the xy plane and the z axis.

Low-temperature Phase.—First-order phase changes and order–disorder transitions have been established for several urea [21-23] and thiourea [10] clathrates. In the case of the ferrocene clathrate the phase transition is

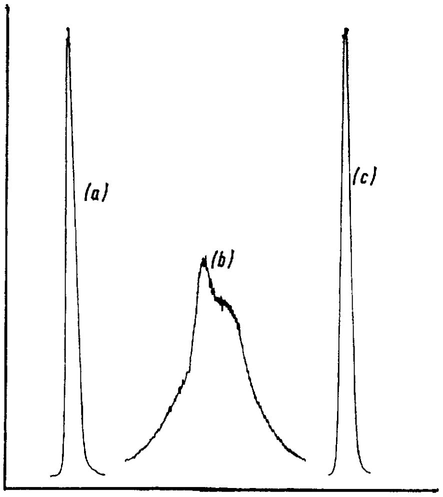

FIGURE 3 Diffractometer tracings (2θ scans) of a typical reflection: (a) initially at room temperature, (b) on cooling to 100 K, and (c) immediately after removing the cooling gas stream

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reported[11] to occur at 162 K. Room-temperature diffractometer 2θ scans were carried out on a number of reflections obtained from a ferrocene clathrate crystal chosen for the low-temperature study. The scans were well defined and characteristic for a single crystal [Figure 3(*a*)]. A number of such scans were then monitored whilst the cold gas stream (see above) was moved slowly towards the crystal. At a certain point in the temperature gradient the originally sharp well defined peaks became considerably broadened [Figure 3(*b*)] indicating that the crystal was no longer single. The transition, single–non-single crystal, was reversible [Figure 3(*c*)]. Slight movement of the gas stream away from the crystal was enough for an apparently immediate reversion to the original high-temperature reflection curve. The broad 2θ scans associated with reflections from the low-temperature phase which precluded low-temperature data collection could arise either from a large increase in the misalignment of the mosaic which constitutes almost all real single crystals, and which is reduced on returning to the high-temperature form, or to the effect of twinning associated with a change to lower symmetry. The latter interpretation is consistent with the similar effect shown by the photographic diffraction pattern of the low-temperature form of the n-hexadecane ($C_{16}H_{34}$)–urea clathrate.[24]

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