# The Red Form of Bis(1,10-phenanthroline)dithiocyanatoiron(II)†

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The red compound of composition $[Fe(phen)_2(NCS)_2]\cdot nH_2O$ (phen = 1,10-phenanthroline) obtained by the Schilt aqueous preparation has been reinvestigated. It is probably better formulated as $[Fe(phen)_3]_2[Fe(NCS)_4][NCS]_2\cdot 3H_2O$. It readily loses water and isomerizes to the violet *cis*-$[Fe(phen)_2(NCS)_2]$. Mössbauer, i.r., and other data for the red compound supporting the above formulation are reported.

In contrast with *cis*-bis(1,10-phenanthroline)dithiocyanatoiron, *cis*-$[Fe(phen)_2(NCS)_2]$, the red hydrated compound, with the same proportions of ligands and metal, obtained by the Schilt and Fritsch[1] aqueous preparation gives a Mössbauer spectrum characteristic of low-spin $Fe^{II}$. Cunningham *et al.*[2] have prepared analogous compounds using a number of substituted phenanthrolines. Their data are inadequate to decide whether these compounds contain one or two molecules of water per iron atom. Measurement of the magnetic susceptibilities of the substituted phenanthroline complexes, in the temperature range 298—80 K, gave values of $\mu_{eff.}$ between 2.35 and 2.71 B.M. The parameters of the Mössbauer spectra were similar to those later reported for the phen complex[3] ($\delta$ 0.35 mm s$^{-1}$ with respect to soft iron, $\Delta$ 0.16 mm s$^{-1}$, isomer shift corrected). They suggested that these complexes contain $Fe^{II}$ in the $S = 1$ state. Although these authors did not make measurements on the hydrated unsubstituted phenanthroline complex, Driver and Walker[4] have found a value $\mu_{eff.} = 2.68$ B.M. for the red compound.

Teodorescu[3] examined the red hydrated complex formed using phen in more detail, paying particular attention to the differences between its i.r. spectrum and that of *cis*-$[Fe(phen)_2(NCS)_2]$. In most respects the room-temperature spectrum of the red compound closely resembles that of the low-temperature, low-spin form of *cis*-$[Fe(phen)_2(NCS)_2]$.

Some time ago some measurements were made in this laboratory of the Mössbauer spectrum of the red complex at low temperatures. Unexpectedly, a component with parameters corresponding to high-spin $Fe^{II}$ appeared.[5] No such component could be detected at room temperature but the high-spin component reappeared each time measurements were made on the sample at low temperature. A preliminary account of these and related observations has been given.[6] Such unusual inverse spin cross-over behaviour warranted a detailed study.

## Experimental

*Materials.*—(*a*) The compound *cis*-$[Fe(phen)_2(NCS)_2]$ was prepared by the pyridine method of Madeja and König[7] as elaborated by Schilt and Fritsch.[1]

(*b*) *The red compound. Method* (*i*). The aqueous preparation of $[Fe(phen)_2(NCS)_2]$ given by Schilt and Fritsch[1] was used. The aged precipitate was washed with a little ethyl alcohol and dried in a desiccator over a silica gel.

*Method* (*ii*). A similar preparation, but in which the thiocyanate is added to the iron(II) solution before the 1,10-phenanthroline hydrate.

*Method* (*iii*). A solution of $[Fe(phen)_3]Cl_2$ was added to a solution of iron(II) chloride in potassium thiocyanate solution. The ratio of thiocyanate to iron in this solution was 8:1 and it contained half as much iron as the $[Fe(phen)_3]Cl_2$ solution. The precipitates from both methods (*ii*) and (*iii*) were aged, filtered off, washed with a little ethyl alcohol, and dried in a desiccator as in method (*i*).

(*c*) *Reference compounds.* $[Fe(phen)_3]Cl_2$. The hydrated compound was prepared by the method described by Inskeep.[8] It was dehydrated *in vacuo* at 373 K.

$[Fe(phen)_2Cl_2]$. This was prepared from the previous compound by extraction with hot carbon tetrachloride as described by Baker and Bobonich.[9]

$[Fe(phen)_3][NCS]_2$. The precipitate obtained by mixing cold saturated solutions of $[Fe(phen)_3]Cl_2$ and KNCS was separated, washed in ice–water, and dried *in vacuo*.[10]

The salt $[NMe_4]_2[Fe(NCS)_4]$ was prepared as described by Forster and Goodgame.[11]

*Measurements.*—Infrared spectra were recorded using a Perkin-Elmer 983 spectrophotometer. Room-temperature spectra were recorded using Nujol mulls between caesium iodide discs and in pressed caesium iodide discs. Measurements at 80 K were made on caesium bromide or iodide discs using a Specac P/N 21 000 low-temperature cell. Some measurements at 80 K were made on powdered material pressed between silver chloride plates. The spectrometer and low-temperature cryostat used to record Mössbauer spectra have been described previously.[12] N.m.r. spectra were obtained on a Bruker WH 400 spectrometer. Multiple sweeps were necessary.

Conductivity measurements were made at room temperature (293 K) using a Wayne Kerr Autobalance Bridge 8641 and a Jones-Bollinger type cell. The cell constant, determined with 0.01 and 0.001 mol dm$^{-3}$ KCl solutions, was 6.032 ohm$^{-1}$ cm$^{-1}$.

Magnetic susceptibility measurements were made on a Gouy balance fitted with a cryostat allowing operation at room temperature and 80 K.

## Results

*Composition.*—All the preparations gave products in which the ratio of iron: phenanthroline: thiocyanate was 1:2:2. Pure anhydrous *cis*-$[Fe(phen)_2(NCS)_2]$, prepared by method (*a*),[1] or by solvent leaching of phenanthroline from $[Fe(phen)_3][NCS]_2$,[9] is always violet in colour and gives a violet streak on unglazed porcelain. The products from preparations (*b*) (*i*)—(*iii*), called the 'red compound,' vary from bright to very dark red, but always give a red streak on porcelain.

For some time we had difficulties because the magnetic, Mössbauer, and i.r. characteristics of the red compound seemed variable. Once the i.r. spectra permitted us to distinguish the red compound from *cis*-$[Fe(phen)_2(NCS)_2]$ (see below) it became apparent that this irreproducibility arose because several of the preparations gave mixtures of the above two compounds

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† *Non-S.I. unit employed:* B.M. ≈ 9.27 × $10^{-24}$ A m$^2$.

and the red compound rather easily isomerizes to give *cis*-$[Fe(phen)_2(NCS)_2]$.

Only method (*b*) (*i*) gives the pure red compound and isomerization can readily be induced by treatment with some solvents, or on storage, or by heating to about 350 K. The mean of eight analyses of five different preparations, using this method, each shown by its i.r. spectrum to be pure, gave: C, 56.95; H, 3.25; Fe, 9.95; N, 15.0; S, 11.3 {$[Fe(phen)_2(NCS)_2]\cdot H_2O$ requires C, 56.75; H, 3.30; Fe, 10.15; N, 15.5; S, 11.65%}. The mean weight loss on heating to 383 K for 1 h was 3.53% (required for $1H_2O$: 3.27%). A thermogravimetric run in dry nitrogen at a heating rate of 2° C min$^{-1}$ showed a weak endothermic peak at about 350 K.

*Effect of Solvents.*—The red compound dissolves readily in dimethyl sulphoxide, acetonitrile, nitromethane, nitrobenzene, pyridine, and dimethylformamide. In acetonitrile fairly rapid isomerization and precipitation of the insoluble *cis*-$[Fe(phen)_2(NCS)_2]$ takes place. Rather slower isomerization occurs in nitromethane and nitrobenzene. In dimethyl sulphoxide and dimethylformamide there is no evidence of isomerization, but the n.m.r. and conductivity data show these are not stable solutions. The compound is slightly soluble in ethyl alcohol, acetone, water, and dichloromethane, but these solvents encourage isomerization which takes place rapidly in acetone. The compound is practically insoluble in diethyl ether, dioxane, and di-isopropyl ether. It cannot be recrystallized from any of these solutions, so that macrocrystalline samples for diffraction studies cannot be obtained.

*Infrared Spectra.*—Spectra were recorded under the same conditions for the red compound, *cis*-$[Fe(phen)_2(NCS)_2]$, *cis*-$[Fe(phen)_2Cl_2]$, $[Fe(phen)_3]Cl_2$, $[Fe(phen)_3][NCS]_2$, and $[Fe(phen)_3][ClO_4]_2$. The spectra of the first two of these compounds were examined at 293 and 80 K. Most of the differences between the spectra of the red compound and *cis*-$[Fe(phen)_2(NCS)_2]$, reported by Teodorescu,[3] were confirmed. The significant regions of the spectra showing differences are the ν(C=N) stretching region (2 150—1 950 cm$^{-1}$), the 900—600 cm$^{-1}$ region, and the low-frequency region where δ(NCS) and the Fe–N stretch frequencies are found. The results for the *cis* compound were in good agreement with those reported by König and Madeja.[13]

(*a*) 2 150—1 950 cm$^{-1}$. The results are given in Table 1. Although, as remarked by Teodorescu,[3] the spectrum of the red compound resembles that of the low-spin form of *cis*-$[Fe(phen)_2(NCS)_2]$, it is readily distinguishable in this frequency region. The room-temperature spectra of the two compounds are also easily distinguished, but the bands are broad and overlap sufficiently that one cannot distinguish one as an impurity in the other. The compounds $[Fe(phen)_3]Cl_2$ and *cis*-$[Fe(phen)_2Cl_2]$ only give weak broad bands in this region, at 2 063 and 2 076 cm$^{-1}$ for the latter compound and at $<2\,000$ cm$^{-1}$ for both compounds.

(*b*) *Between* 1 800 *and* 900 cm$^{-1}$. There are generally only small differences in position and intensity of the i.r. absorption bands shown by the six compounds mentioned above (ignoring any bands associated with the $ClO_4^-$ in the last compound). The spectrum of the red compound is closest to that of low-spin *cis*-$[Fe(phen)_2(NCS)_2]$. This has been recorded by König and Madeja.[13]

In the 900—600 cm$^{-1}$ region there are some useful differences between the spectra of the different compounds. A room-temperature comparison of the red compound from preparation (*b*) (*i*), *cis*-$[Fe(phen)_2(NCS)_2]$, and *cis*-$[Fe(phen)_2Cl_2]$ is shown in Figure 1. The product from preparation (*b*) (*i*) gave a similar spectrum to that from (*b*) (*iii*).

Comparison of the spectra showed the following. (*i*) The red

**Table 1.**

| Red compound | | *cis*-$[Fe(phen)_2(NCS)_2]$ | | $[Fe(phen)_3]$-$[NCS]_2$ |
|---|---|---|---|---|
| 293 K | 80 K | 293 K | 80 K | 293 K |
| | | | 2 116vs | |
| 2 107w,br | | 2 100w | 2 108vs | |
| | | 2 095w | | |
| 2 088m (sp) | 2 087m (sp) | | 2 080w | |
| 2 075w (sh) | 2 072vw (sh) | 2 074s | | |
| | | 2 062s | 2 064w | 2 067 (sh) |
| 2 063 (sh) | 2 050s,br | | | 2 052s |
| 2 052s | 2 042s,br | | | 2 041s |
| | | 2 020w | | |

w = Weak; m = moderate; s = strong; v = very; br = broad; sp = sharp; sh = shoulder.

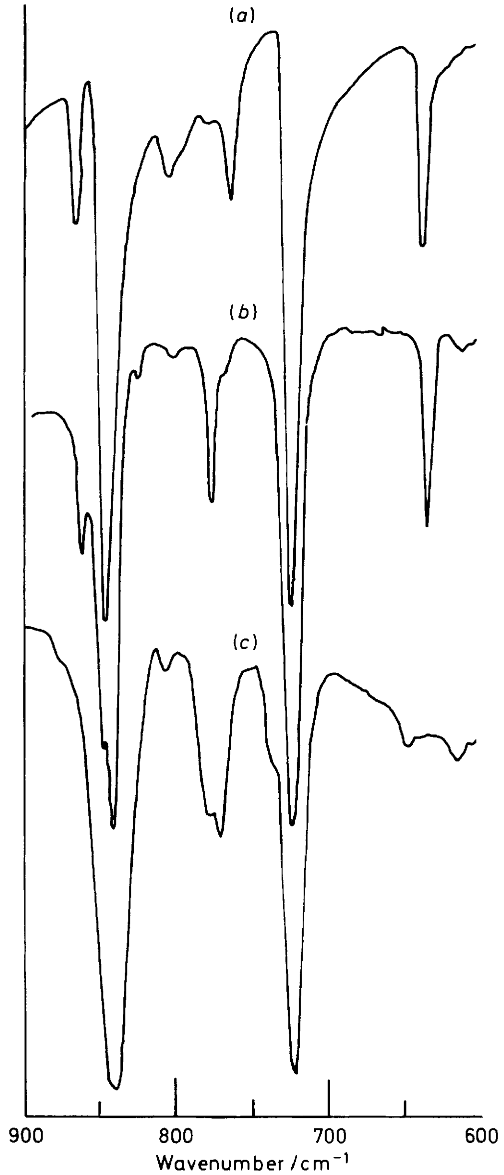

**Figure 1.** I.r. spectra in the region 600—900 cm$^{-1}$: (*a*) *cis*-$[Fe(phen)_2(NCS)_2]$, (*b*) *cis*-$[Fe(phen)_2Cl_2]$, and (*c*) the red compound

**Table 2.** Infrared bands (cm$^{-1}$) in the 600—200 cm$^{-1}$ region

| $[Fe(phen)_3]Cl_2$ | $[Fe(phen)_3][NCS]_2$ | Red compound | | *cis*-$[Fe(phen)_2(NCS)_2]$ | | *cis*-$[Fe(phen)_2Cl_2]$ |
|---|---|---|---|---|---|---|
| 293 K | 293 K | 293 K | 88 K | 293 K | 88 K | 293 K |
| 561m | 561m | 561m | 562m | | 560w | 571m |
| | 545vw (sh) | 547vw (sh) | | | | |
| 531s | 530s | 529s | $\left.\begin{matrix}532\\528\end{matrix}\right\}$s | 528vw | 533m *<br>529m * | 530w |
| 511w | 511w | 510w-m | 512w | 513m-w | 513m | — |
| | | | | | 503m | |
| 498vw | 493w | 495vw | 490vw | 498w | | 497w |
| | | 486 (sh) | | 483m † | 480m † | 482m-w |
| | 476w | 481m,br | 483m | 474m † | 476m-s † | |
| | 460w | 460w | 459w | 457vw | 455w | |
| 433vw | 430w-m | $\left.\begin{matrix}431\\425\end{matrix}\right\}$w | 435m | 431m | 432w | 438w |
| | | | | 420m-s | | 420m-s |
| | | | | | 379m * | |
| 370vw | 372vw | 370vw | | 370vw | 371w * | |
| 297s | 297s | 299s | 294s | | 299m | |
| | | 283s (sh) | 286s (sh) | 283s (sp) | 286w | 285s |
| | | | | | | 255s |
| | 247m,br | 250m-w | | 249s (br) * | | |
| 245m,br | | 244 (sh) | | 244 (sh) * | 243m | 243m |
| | | 230w-m | | 220m * | | 227w |
| | | 213w | | | 212m | |
| 208m | 204w,br | 208w,br | | | | 203m-s |

compound and the $[Fe(phen)_3]^{2+}$ salts showed no absorption at 637 cm$^{-1}$ and only a very weak shoulder at 865 cm$^{-1}$. Both the *cis* compounds show medium-strong absorptions at these frequencies. These two bands are sufficiently isolated to serve to detect mixtures of the two compounds. The absence of the band at 637 cm$^{-1}$ was adopted as a criterion of purity of the red compound and served to show that the product from preparation (*b*) (*ii*), as well as aged or solvent-treated products, contained both isomers.

(*ii*) Neither *cis*-$[Fe(phen)_2X_2]$ compound gives the shoulder at 737 cm$^{-1}$. At 88 K the band at 723 cm$^{-1}$ splits into a triplet for both *cis* compounds but not the others.

(*iii*) The very strong absorption at *ca.* 840 cm$^{-1}$, shown by all six compounds, is resolved into a doublet at 88 K.

(*iv*) A weak absorption at 642—645 cm$^{-1}$ is seen for the $[Fe(phen)_3]^{2+}$ salts and the red compound.

(*v*) The above bands are fairly certainly associated with the phenanthroline ligands.[1,11] Now ν(C–S) might be expected in this region, but its identification is much more speculative. At low temperatures König and Madeja[13] assigned a sharp band of medium to strong intensity, appearing in the low-spin (88 K) spectrum of *cis*-$[Fe(phen)_2(NCS)_2]$ at *ca.* 807 cm$^{-1}$, to the C–S bond. However, all six compounds show a weak rather broad absorption near 805 cm$^{-1}$.

In the other spectra none of the C–S stretching frequencies can be identified unambiguously. The band at 804 cm$^{-1}$, or the shoulder at about 790 cm$^{-1}$, may be related to the high-spin state of *cis*-$[Fe(phen)_2(NCS)_2]$. But the sharp band at 780 cm$^{-1}$ seen in the spectrum of *cis*-$[Fe(phen)_2Cl_2]$ almost disappears for the high-spin thiocyanate while another sharp band of medium intensity is seen at 764 cm$^{-1}$. The latter might also be due to a C–S stretch.

(*vi*) For the red compound the situation is marginally simpler. Supposing the band at 780 cm$^{-1}$, also found for *cis*-$[Fe(phen)_2(NCS)_2]$ and at about 744 cm$^{-1}$ for the $[Fe(phen)_3]^{2+}$ salts, to be a phenanthroline band, it would appear that the medium-intensity band at 770 cm$^{-1}$ and also perhaps an absorption producing the shoulder on the band at 723 cm$^{-1}$, at about 745 cm$^{-1}$, may both be due to C–S stretches.

The free NCS$^-$ of $[Fe(phen)_3][NCS]_2$ seems only to produce a shoulder (at about 747 cm$^{-1}$) on the band at 723 cm$^{-1}$. At 88 K the spectrum of the red compound shows only small shifts in band maxima and a sharpening, leading to separation of the medium-intensity bands at 772 and 787 cm$^{-1}$. A shoulder appears between these two bands at 776 cm$^{-1}$.

(*c*) 600—200 cm$^{-1}$ *region.* The bands marked with an asterisk in Table 2 have been shown to shift on substitution of $^{54}$Fe by $^{57}$Fe.[14] The bands marked with a dagger have been attributed to δ(NCS).[13] Attention is drawn to the following points. (*i*) The $[Fe(phen)_3]^{2+}$ salts, the red compound, and low-spin *cis*-$[Fe(phen)_2(NCS)_2]$ all show bands at *ca.* 561 and 298 cm$^{-1}$. The absorption at *ca.* 530 cm$^{-1}$ which yields a doublet at low temperatures is of medium or strong intensity for the above group, but weak or very weak for the high-spin *cis* compounds. (*ii*) The spectrum of the red compound is little changed between 293 and 88 K. It does not show the bands at 379 or 220 cm$^{-1}$ found for low-spin *cis*-$[Fe(phen)_2(NCS)_2]$. (*iii*) The bands at 474—483 cm$^{-1}$ are probably due to δ(NCS). These bands only appear for compounds containing NCS, except for that at 482 cm$^{-1}$ in *cis*-$[Fe(phen)_2Cl_2]$. (*iv*) The absorption at *ca.* 298 cm$^{-1}$ serves to reveal the red compound in mixtures with the *cis* compound.

*Mössbauer Spectra.*—Using the i.r. absorption at 637 cm$^{-1}$ to monitor the samples before and after measurements, samples of the red compound, prepared by method (*b*) (*i*) and *cis*-$[Fe(phen)_2(NCS)_2]$ prepared by the pyridine method were examined at temperatures between 298 and 52 K. The high-spin component in the spectrum of the red compound could only be resolved at < 250 K. A single sample of the red compound was measured repeatedly at different temperatures throughout this range, then it was heated to 360 K and the spectrum measured at several temperatures. The parameters extracted from the spectra, as well as the appearance of the band at 637 cm$^{-1}$, showed that the red compound had changed to *cis*-$[Fe(phen)_2(NCS)_2]$. The chemical shifts, δ, for the different species, calculated with respect to the centre of the spectrum of soft iron, are shown in Figure 2. The values are consistent with singlet and

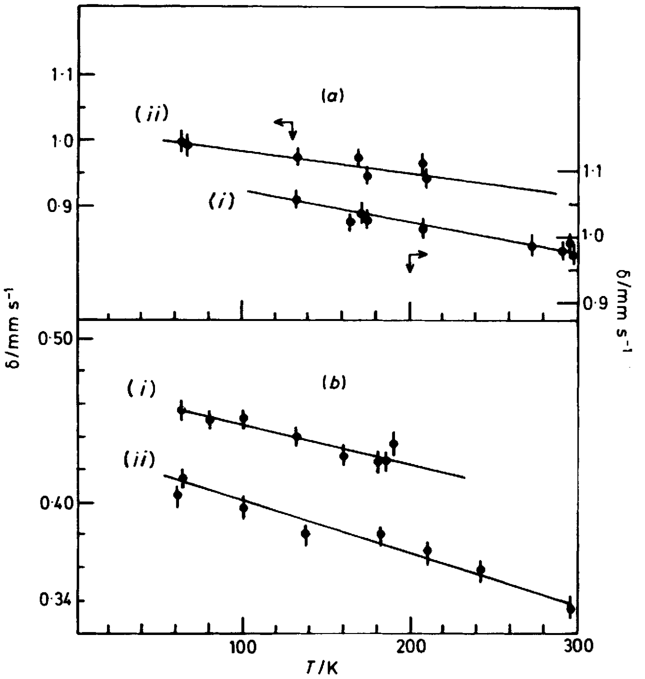

Figure 2. The chemical shift as a function of temperature: (a) high-spin component, (b) low-spin component; (i) *cis*-[Fe(phen)$_2$(NCS)$_2$], (ii) the red compound

pentuplet states for the iron(II). Similar data for the quadrupole splitting, Δ, are given in Figure 3. It will be seen that the splitting for the high-spin species found at low temperatures with the red compound changes rapidly with temperature. Also, that the anomaly in the quadrupole splittings, for the *cis* compound, near the transition temperature, found by Ganguli *et al.*[15] is observed. The change in the intensity of this high-spin component with temperature is shown in Figure 4.

*Other Data.*—(a) To learn more about the nature of the red compound, conductivity measurements were made on some solutions in non-aqueous solvents. A fresh 0.001 mol dm$^{-3}$ solution in acetonitrile, prepared on the assumption of one iron atom per molecule, gave a molar conductivity of 94.1 ohm$^{-1}$ cm$^2$ mol$^{-1}$ which decreased quickly to 60 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in 5 min. A similar result was obtained in nitromethane, the initial value of 113 ohm$^{-1}$ cm$^2$ mol$^{-1}$ falling to 56 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in 90 min. Both these solutions had deposited some *cis*-[Fe(phen)$_2$(NCS)$_2$] while ageing. In dimethyl sulphoxide, on the other hand, the initial molar conductivity of 47.1 ohm$^{-1}$ cm$^2$ mol$^{-1}$ rose to 58.1 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in 24 h and continued to change with age.

In view of the conductivities of the fresh solutions, it seems safe to suppose the red compound is an electrolyte, but that the solutions are unstable, either because of isomerization or solvolysis. In dimethyl sulphoxide, *cis*-[Fe(phen)$_2$(NCS)$_2$] slowly dissolves producing a solution like that obtained from the red compound.

(b) *Magnetic susceptibility and effective magnetic moment.* Assuming a molecular weight of 550.47, one iron atom per molecule, the solid red compound gave $\mu_{\text{eff.}} = 2.97$ B.M. at 298 K and 3.02 B.M. at 80 K. Such a value would be compatible with an $S = 1$ state for the iron.

(c) An n.m.r. study of the solutions seemed likely to yield useful information. A comparison of the $^1$H n.m.r. spectra of fresh solutions of the red compound and of [Fe(phen)$_3$][ClO$_4$]$_2$ in deuterium oxide gave the data in Table 3. Initially the linewidths of the two spectra were equal with the full width at half maximum about 2 Hz. However, the lines of the solution of the red compound gradually broadened and the spectrum changed.

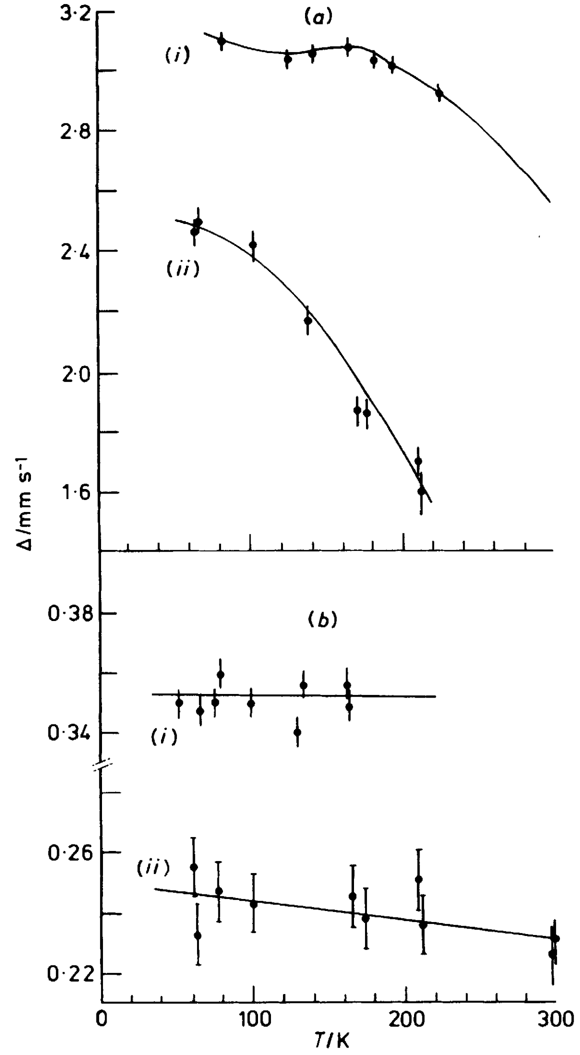

Figure 3. Quadrupole splitting as a function of temperature. Details as in Figure 2

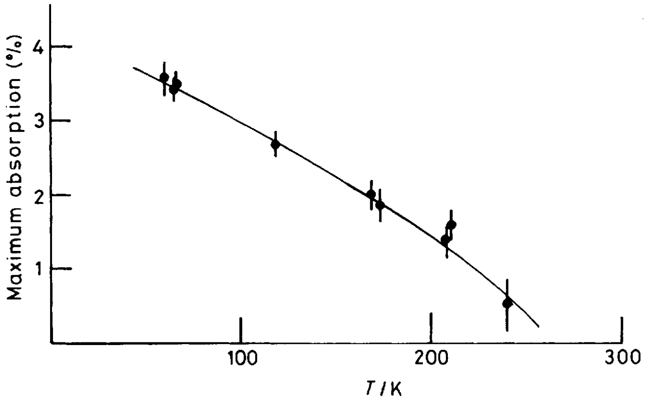

Figure 4. Maximum absorption as a function of temperature for the high-spin component of the red compound

**Table 3.** Proton n.m.r. data

| Resonance | $[Fe(phen)_3][ClO_4]_2$ | Red compound |
|---|---|---|
| (1) | 8.595 (d), $J_1$ = 8.162 | 8.589 (d), $J_1$ = 8.168 |
| (2) | 8.227 (s) | 8.219 (s) |
| (3) | 7.727 (d), $J_2$ = 5.121 | 7.732 (d), $J_2$ = 5.084 |
| (4) | 7.549 (dd), $J_1$ = 8.197,<br>$J_2$ = 5.291 | 7.542 (dd), $J_1$ = 8.041,<br>$J_2$ = 5.341 |

The integrated intensities of groups (1)—(4) were equal. Chemical shifts in p.p.m. with reference to tetramethylsilane, $J$ values in Hz.

A fresh solution of the red compound in deuteriated acetone also showed essentially the same spectrum as a solution of $[Fe(phen)_3][ClO_4]_2$ in this solvent, *i.e.*: (1) 8.827 (d), $J_1$ = 8.212; (2) 8.427 (s); (3) 8.041 (d), $J_2$ = 5.224; (4) 7.794 (dd) p.p.m., $J_1$ = 8.197, $J_2$ = 5.251 Hz. A further coupling of $J_3$ = 1.137 Hz was shown by each of the lines of the doublets (1) and (3). Supposing the lowest-field group (1) arises from the 2,9 positions of the phenanthroline rings, as has been suggested by Constable,[16] then the coupling of 8.212 Hz must be due to the 2,3 and 8,9 positions and that at 1.137 Hz to the 2,4 and 7,9. Group (3) corresponds to the 4,7 positions, the singlet to the 5,6-positions, and group (4) to the 3,8 positions. The coupling at 5.251 Hz is then due to the 3,4 and 7,8 positions.

The lines of the spectrum of the red compound soon broadened (after *ca.* 2 h) and *cis*-$[Fe(phen)_2(NCS)_2]$ eventually precipitated. In the interval before precipitation the lines sharpened and another spectrum appeared, in addition to that reported above. The parameters of the new spectrum were: (1) 9.22 (d), $J_1$ = 3.3; (2) 8.73 (d), $J_2$ = 8.7; (3) 8.16 (s); (4) 7.96 (dd) p.p.m., $J_1$ = 3.3, $J_2$ = 8.7 Hz. The integrated intensities of each group were the same.

Measurements were also made on solutions of the red compound in dimethyl sulphoxide, but the spectrum changed on ageing and one of the doublets overlapped the doublet of doublets.

Like the conductivity data, the n.m.r. data confirm the instability of solutions of the red compound. However, fresh solutions always suggest the presence of $[Fe(phen)_3]^{2+}$. Certainly the spectra are too simple to correspond to any *cis*-$[Fe(phen)_2X_2]$ species. It is also noteworthy that although the red compound is paramagnetic the solution n.m.r. spectra showed as narrow linewidths as those of the $[Fe(phen)_3][ClO_4]_2$ solutions.

The compound *cis*-$[Fe(phen)_2(NCS)_2]$ very slowly dissolved in dimethyl sulphoxide giving a red solution whose n.m.r. spectrum resembles that of the solution of the red compound. The concentration obtained was so small that satisfactory measurement was impossible.

## Discussion

In the absence of material suitable for a crystal structure, there are few other data relevant to the nature of the red compound that can be sought. Fortunately, the above results lead to fairly firm conclusions. It is unlikely that the considerable differences in the properties of *cis*-$[Fe(phen)_2(NCS)_2]$ and the red compound are entirely due to the water of crystallization, which seems to be loosely incorporated, as the thermobalance measurement showed. By prolonged pumping *in vacuo* at room temperature about half a molecule of water can be removed with the production of only small amounts of *cis*-$[Fe(phen)_2(NCS)_2]$. A few samples containing about $0.5H_2O$ were obtained in which no *cis*-$[Fe(phen)_2(NCS)_2]$ could be detected by i.r. spectroscopy and the Mössbauer characteristics of the red compound were retained.

The appearance of the high-spin component in the low-temperature Mössbauer spectrum could be explained in two ways. (*a*) An inverted spin cross-over yielding a high-spin species at low temperatures. Such a possibility is theoretically improbable and is inconsistent with our data in two respects. The intensity of the low-spin component of the spectrum shows no diminution when the high-spin component appears. Secondly, the i.r. spectrum of the red compound shows no important changes between 293 and 80 K. Such differences as are found comprise modest frequency and intensity changes and, principally, a reduction in linewidths. (*b*) There are two iron environments in the solid with widely different Debye temperatures.

There are indeed a rather large number of different compounds having the empirical formula $[Fe(phen)_2(NCS)_2]\cdot H_2O$. One of these, however, $[Fe(phen)_3]_2[Fe(NCS)_4][NCS]_2\cdot 3H_2O$ seems to fit all the experimental data. This compound can be expected to be an electrolyte in the solvents used. The ready isomerization to *cis*-$[Fe(phen)_2(NCS)_2]$ suggests the ligands are moderately substitution labile and so in solutions in the stronger donor solvents solvolysis occurs with formation of more ions probably from the $[Fe(NCS)_4]^{2-}$.

The fresh solution can be expected to show the n.m.r. spectrum of $[Fe(phen)_3]^{2+}$. This species is diamagnetic so that narrow-line spectra are obtained. The second spectrum appearing in acetone, where the precipitation of *cis*-$[Fe(phen)_2(NCS)_2]$ shows the ligands are moderately substitution labile, might be due to an intermediary in the isomerization reaction such as $[Fe(phen)(NCS)_2]$ or perhaps $[Fe(phen)(NCS)_4]^{2-}$.

Only the $[Fe(NCS)_4]^{2-}$ component, in the above formulation, will be paramagnetic. Thus the $\mu_{eff.}$ for this component will be $\sqrt{3}$ times the value of *ca.* 3.0 B.M. calculated above. Such a value, 5.2 B.M., is quite appropriate to this complex anion.

The Mössbauer data provide still stronger support for the above formulation. The rapid change in the quadrupole splitting with temperature and the low intensity of the spectrum due to the high-spin component are both characteristic of quasi-tetrahedral high-spin $Fe^{II}$. The compound $[NMe_4]_2[Fe(NCS)_4]$ was investigated some years ago by Edwards *et al.*[17] They reported a chemical shift of 0.97 mm $s^{-1}$ with respect to soft iron and a quadrupole splitting of 2.10 mm $s^{-1}$ at 77 K. More significantly, this quadrupole splitting decreased rapidly with temperature and the intensity of the spectrum was so low that the spectrum could not be seen above 195 K. The tetragonal Jahn–Teller distortion of $[Fe(NCS)_4]^{2-}$, leading to a separation of the two lowest-lying *d* orbitals by about 100 $cm^{-1}$, is responsible for the rapid change in quadrupole splitting with temperature. Our data are compatible with a separation of the two levels of about this magnitude. It is indeed these two effects of changing temperature on the Mössbauer parameters that lead us to suggest $[Fe(NCS)_4]^{2-}$ and two free $NCS^-$, rather than $[Fe(NCS)_6]^{4-}$. Mössbauer data are also available[18] for $K_4[Fe(NCS)_6]\cdot 4H_2O$: chemical shift 1.33 mm $s^{-1}$ with respect to soft iron; quadrupole splitting *ca.* 0.4 mm $s^{-1}$. Unfortunately, these data only refer to room-temperature measurements, but a 4 or 5% maximum absorption ('dip') at the line peak was found at this temperature. This does not seem compatible with our data.

Edwards *et al.*[17] attributed the absence of detectable absorption lines for $[NMe_4]_2[Fe(NCS)_4]$ at above *ca.* 200 K to scattering and absorption effects from the sulphur in the samples, but since the Mössbauer spectrum due to the $[Fe(phen)_3]^{2+}$ component maintains a reasonable intensity over the temperature range 60—300 K in the same material, it seems the low intensity and strong temperature dependence of the spectrum of $[Fe(NCS)_4]^{2-}$ must reflect a much lower Debye temperature than for $[Fe(phen)_3]^{2+}$.

Epstein[19] obtained $\delta$ = 0.30 and $\Delta$ *ca.* 0.3 mm $s^{-1}$ for some

$[Fe(phen)_3]^{2+}$ salts, values not incompatible with the data for our low-spin component.

The i.r. data also support the above formulation. There is no evidence for any transition taking place on cooling to 60 K. The red compound displays all those absorptions that are characteristic of the $[Fe(phen)_3]^{2+}$ salts, *e.g.* at 1 615, 1 252, and 737 $cm^{-1}$. It does not show any of the bands characteristic of the *cis*-$[Fe(phen)_2X_2]$ species, *e.g.* at 1 304 and, especially, at 637 $cm^{-1}$. The absorption at 865 $cm^{-1}$ is very weak for the $[Fe(phen)_3]^{2+}$ salts and the red compound. Where there are noticeable shifts in frequency and/or changes in intensity between the spectra of *cis*-$[Fe(phen)_2X_2]$ and those of the $[Fe(phen)_3]^{2+}$ salts, the red compound behaves like the latter compounds. However, the strong band at *ca.* 298 $cm^{-1}$ in the spectra of all the $[Fe(phen)_3]^{2+}$ salts and the red compound also appears in the spectrum of low-spin (88 K) *cis*-$[Fe(phen)_2(NCS)_2]$.

The C–N and C–S stretch regions do not provide positive confirmation of the above formulation, but the data are entirely compatible with this formula. The Fe–N region is more interesting. Comparison of the spectra of the $^{54}Fe$ and $^{57}Fe$ compounds enabled Takemoto and Hutchinson[14,20] to identify the Fe–N stretch frequencies for the high- and low-spin states of *cis*-$[Fe(phen)_2(NCS)_2]$. They assigned these bands on the same basis as proposed by Clark and Williams[21] for various $[M(NCS)_2L_2]$ and $[M(NCS)_2L_4]$ complexes (L = a nitrogen donor, *e.g.* pyridine). The value for Fe–N(phen) has been confirmed in several $[Fe(phen)_3]^{2+}$ salts.[22] Thus, they suggest: ν(Fe–N)(phen) 220 (high spin), 371/379 $cm^{-1}$ (low spin); ν(Fe–N)(NCS) 252 (high spin), 529 $cm^{-1}$ (low spin). Now the above formulation, involving low-spin Fe–N(phen) and high-spin tetrahedral Fe–NCS, implies bands around 370—380 $cm^{-1}$ and at a higher frequency than 252 $cm^{-1}$ for the latter vibration. In fact a very weak absorption is observed at about 370 $cm^{-1}$ for all the $[Fe(phen)_3]^{2+}$ salts as well as for the red compound. However, it is curious that a strong absorption is also found at *ca.* 530 $cm^{-1}$ for all these compounds as well as for low-spin (88 K) *cis*-$[Fe(phen)_2(NCS)_2]$. As far as the Fe–NCS stretch is concerned, the red compound shows a band at 250 $cm^{-1}$ and a shoulder at about 283 $cm^{-1}$ to the strong ligand band at 299 $cm^{-1}$. The former would seem rather low for tetrahedral $[Fe(NCS)_4]^{2-}$.

*Relation to Other Investigations.*—Recently König *et al.*,[23] having noted some peculiarities in the Mössbauer spectra of some of the supposedly spin-triplet complexes of iron(II) of the type [Fe(di-imine)$_2$(L–L)] (type A), *e.g.* where L–L is oxalate, made, by aqueous methods, some complexes involving iron(III) of the type (B), $[Fe^{II}(\text{di-imine})_3]_2[Fe^{III}(L\text{–}L)_3]\cdot0.5(L\text{–}L)$. These compounds, which are very difficult to distinguish from type A by classical analysis, seem to duplicate most of the properties of the latter. They suggest that many of the type A products are really of type B and that spin-triplet species are probably not involved. The aqueous preparations of the type A complexes may lead to oxidation and they doubt that type A are entirely iron(II) complexes. Such oxidation appears doubtful because the preparations show no sign of being sensitive to the presence of air and indeed it has been shown that the iron(III) complex $[(phen)_2Fe\text{–}O\text{–}Fe(phen)_2][NCS]_4$ is reduced[4] in aqueous media by thiocyanate to yield the red compound. In our case the isomerization of the red compound to the known *cis*-$[Fe(phen)_2(NCS)_2]$ completely excludes the presence of iron(III).

Our data suggest that the type A compounds may in fact be entirely iron(II) derivatives, analogous to our $[Fe(phen)_3]_2[Fe(NCS)_4][NCS]_2\cdot3H_2O$. A more extensive study of their Mössbauer and i.r. spectra seems essential.

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