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The reaction of 1,1′-bis-(chlorocarbonyl)ferrocene with tetrathia-diaza-18-crown-6

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Abstract

The reaction of 1,1′-bis-(chlorocarbonyl)ferrocene (1) with tetrathiadiaza-18-crown-6 (2) gives the dimeric cryptand 1,1″,1′,1‴-bis(1,4,10,13-tetrathia-7,16-diazacyclooctadecane-7,16-diyldicarbonyl)bisferrocene (4) and not the expected monomeric cryptand 3. An X-ray crystal structure study of 4 is reported and shows that the carbonyl groups are mutually *cis/trans/cis/trans* in the solid state. In solution, however, multinuclear magnetic resonance shows that the molecule is fluxional, and at least two diastereomeric species are detected at low temperatures (below 243 K). The dimeric cryptand can be reduced to 1,1″,1′,1‴-bis(1,4,10,13-tetrathia-7,16-diazacyclo-octadecanedimethylene)bisferrocene (5).

Key words: Iron; Ferrocene; Thia-aza-crown

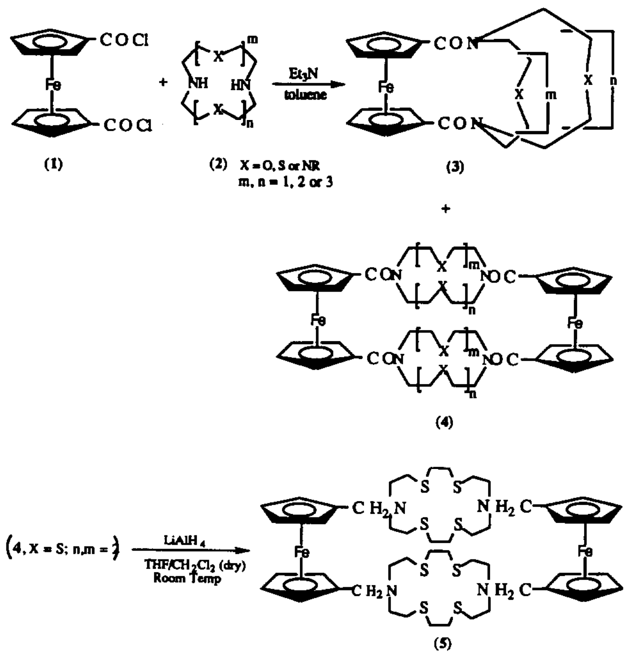
1. Introduction

During the last decade we have studied the synthesis, structure and coordinating properties of a range of electroactive macrocycles and cryptands containing metallocene units [1–10], Scheme 1: These compounds are usually prepared by the condensation of metallocene bis-acid chlorides (1) with diazamacrocycles (2) and, with X = O, the products contain both the monomeric cryptand (3) and dimeric cryptand (4), which may be separated by either fractional crystallization or column chromatography. Both sets of compounds bind metal cations using the amide carbonyl groups as the primary coordinating functions and these complexes have been studied extensively by multinuclear magnetic resonance [10] and X-ray crystallography [11,12]. Solution and solid state studies showed that, in the complexes, the carbonyl groups which are normally *trans* in the host cryptands [6,8,13,14] become *cis* on coordination with cations and that the macrocyclic heteroatoms may also be involved in the coordination sphere. It was therefore a rational step to examine analogous cryptands with sulphur (*i.e.* X = S) rather than with oxygen as the macrocyclic heteroatoms and this paper presents the results of this study.

2. Results and discussion

The reaction of 1,1′-bis-(chlorocarbonyl)ferrocene (1) (M = Fe) with the diazacrown (2) (X = S; *m*, *n* = 2)

Diagram



Scheme 1.

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was carried out in toluene at room temperature under the usual conditions and in the presence of triethylamine to remove the HCl formed. [†] The triethylamine hydrochloride was filtered off, the solvent removed *in vacuo* and the residue chromatographed on alumina to give an orange crystalline solid which, on the basis of its ^1H and ^{13}C spectra, was at first thought to be the monomer **3** (X = S). A single-crystal X-ray study of crystals formed slowly from a mixture of $CDCl_3$ and CD_2Cl_2, however, revealed (Fig. 1) that the isolated material was, in fact, a centrosymmetric dimer **4**. The crystalline material, redissolved in $C_2D_2Cl_4$, gave ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra at 360 K (Table 1) identical with those

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[†] Reaction at 70°C as usually employed with **2** (X = O) was found to give a complex mixture of products including a large proportion of polymer.

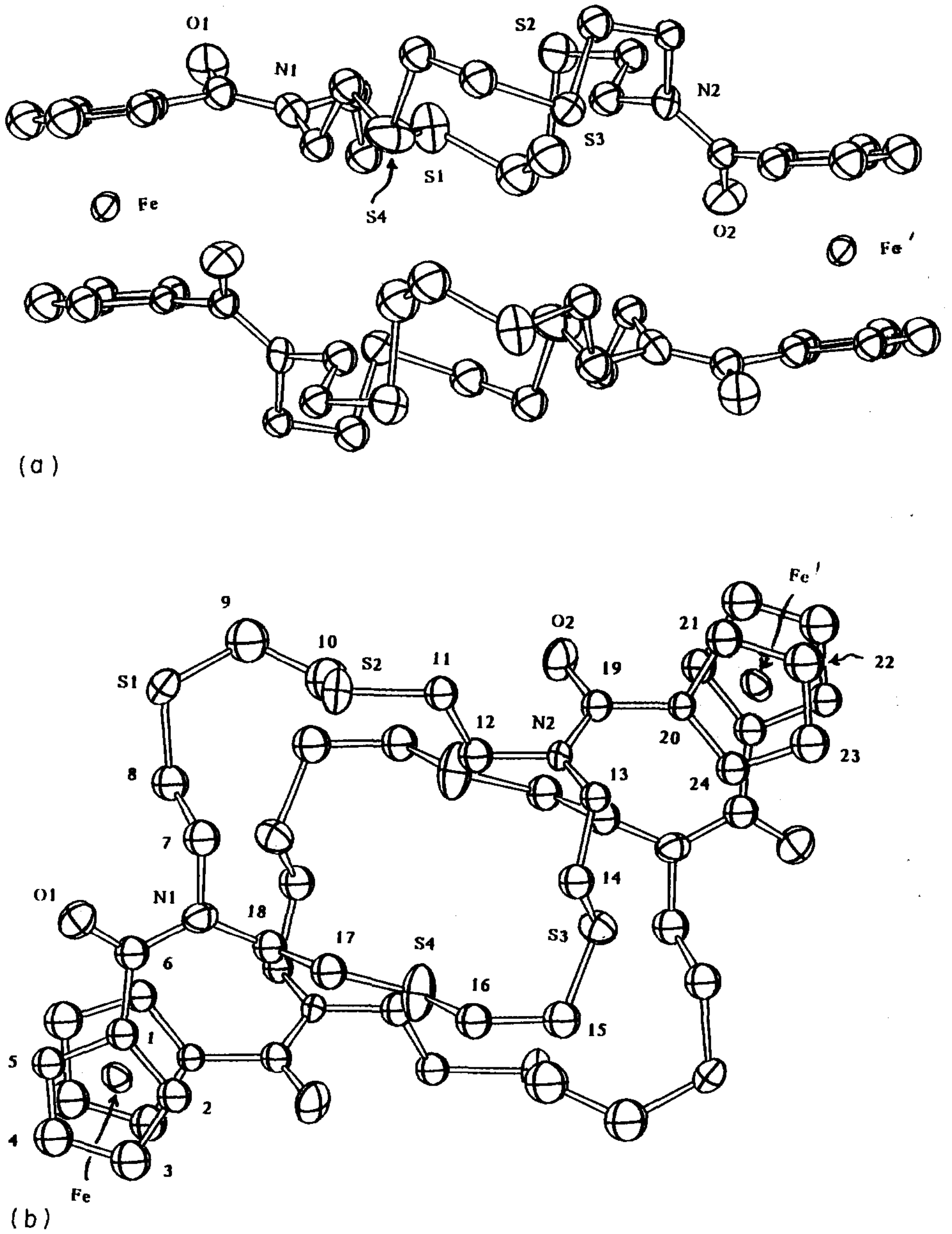


Fig. 1. Molecule **4**: (a) section showing the disposition of macrocyclic rings relative to the ferrocene units; (b) plan of molecule showing the configuration of the carbonyl groups and the eclipsed ferrocene rings. The unit cell of **4** contains two molecules of $CDCl_3$ not shown in the figure. The carbon and three chlorine atoms are listed as C(25), Cl(1), Cl(2) and Cl(3) in Table 1.

TABLE 1. The ^1H and ^{13}C nuclear magnetic resonance spectra of **4** ($X = S$; $m,n = 2$) in $C_2D_2Cl_4$ at 360 K and in CD_2Cl_2 at 260 K relative to tetramethylsilane

^1H NMR			^{13}C NMR (S/N, Fc–CH, 70/1)		
δ (ppm)	Integration	Assignment	δ (ppm)	DEPT	Assignment
In $C_2D_2Cl_4$ at 360 K					
4.61 (t)	4	cpd (2,5)	169.8	0	C=O
4.42 (t)	4	cpd (3,4)	80.6	0	*ipso*-C
3.72 (t)	8	NCH_2	72.5	+	cpd (2,5)
2.89 (t)	8	SCH_2	71.3	+	cpd (3,4)
2.85 (s)	16	SCH_2	49.4	−	NCH_2
			33.4	−	SCH_2
			31.5	−	SCH_2
In CD_2Cl_2 at 260 K [a]					
4.66			171.9 [b]	0	C=O
4.64	4	cpd (2,5)	171.7	0	
4.61 [b]			82.3 [b]	0	*ipso*-C
4.56 [b]			81.7	0	
			74.8	+	
4.45	4	cpd (3,4)	74.5(2)	+	
			74.2	+	cdp-C
			73.6	+	
3.77–3.42 (br mult)	8	NCH_2	73.3(2)	+	
			73.0	+	
			52.6 [b]	−	NCH_2
2.94–2.75 (br mult)	16	SCH_2	52.1	−	
			50.4 [b]	−	
			49.8	−	
			35.2	−	SCH_2
			34.9	−	
			34.6	−	
			34.1	−	
			33.9(2)	−	
			31.7	−	
			31.0	−	

[a] Unequal amounts (about 60:40) of two isomers observed; ^{13}C, S/N, Fc–CH(av.), 8/1.
[b] Major isomer.

obtained at 360 K from the original isolated material. At ambient temperature both the ^1H and the ^{13}C NMR spectra became broad, indicating fluxional molecular processes which were becoming slow on the NMR time scale. At 260 K in CD_2Cl_2, the ^1H and ^{13}C spectra became much more complex. In particular the ^{13}C NMR spectrum showed two sets of peaks in a ratio of 60:40 including two carbonyl carbon atoms, two ipso (cpd) carbon atoms, eight cpd carbon atoms, four NCH_2 carbon atoms and eight SCH_2 carbon atoms assigned by a combination of chemical shift and DEPT spectroscopy. These data are readily explained in terms of restricted rotation on the NMR time scale about the cpd–CO–N bond system (*cf.* **4**; X = O) [1], giving rise to two diastereomeric dimer molecules, which probably involve *cis*(crown)/*trans*(Fc)/*cis*/*trans* and *trans*/*trans*/*trans*/*trans* configurations of the carbonyl groups. The former is consistent with the solid state structure and is therefore likely to be the most stable configuration in solution.

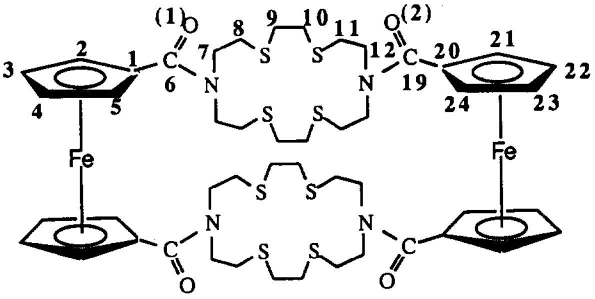
There are a few features of the solid state structure which require comment, especially with respect to the oxygen analogue of **4** [15]. A selection of bond lengths and bond angles is shown in Table 2 in accordance with the numbering system given in Fig. 1(b). The amide C–N bond lengths (N(1)–C(6) and N(2)–C(19)) at 1.350 (14) Å and 1.366 (15) Å respectively and the carbonyl bond lengths at 1.247 (13) Å and 1.234 (15) Å respectively are close to those expected and are very similar to those found in analogous cryptands [6,8,12,14]. The amide functions are essentially planar but the *cis*(crown)/*trans*(Fc)/*cis*/*trans* configuration of the carbonyl groups in **4** (X = S) (Fig. 1(a)) contrasts with the oxygen analogue where the configurations are *trans*/*trans*/*trans*/*trans*. The amide functions are also tilted out of the planes of the respective cpd rings (by 53.3° for C(6) and 65.6° for C(19)) and, whereas the C(6) carbonyl group tilts away from Fe, C(19) tilts towards the Fe atom (Fig. 1(a)). In contrast, the oxygen analogue has all the carbonyl functions tilted towards the Fe atoms. Furthermore, the cpd rings in **4** (X = O) are staggered whereas those in **4** (X = S) are eclipsed (Fig. 1(b)). The N–C and S–C bond lengths all correspond to conventional single bonds and the bond angles at sulphur vary, as expected, between 97.4 and 103.3°. Presumably it is these bond lengths and bond angles which cause the difference between the structures of the oxygen and sulphur analogues. The distance between the cpd ring centroid in each ferrocene unit is 3.292(2) Å, which allows considerable space between the macrocyclic rings for complex formation, a feature which will be discussed in a subsequent paper.

The dimer may be reduced by the elegant method of Gokel and coworkers [16] to produce the dimer **5** in good yield. The ^1H and ^{13}C NMR data associated with this compound are easily assigned and are reported in Table 3. Clearly the molecule is highly fluxional, since only seven carbon signals are observed at ambient and cooling the system to 233 K has no effect on the spectrum. This system offers an opportunity to study complex formation with soft metal cations, and this will also be discussed in a subsequent paper.

3. Experimental details

1,1'-Bis-(chlorocarbonyl)ferrocene (**1**) was prepared as described previously [1] and tetrathiadiaza-18-crown-6 (**2**) was obtained from Aldrich. NMR spectra were obtained on a Bruker AM 360 spectrometer fitted with a quad (^1H, ^{13}C, ^{31}P and ^{19}F), variable-temperature probe using the deuterated solvent ($CDCl_3$–CD_2Cl_2 or $C_2D_2Cl_4$) as the internal lock and tetramethylsilane as internal reference.

TABLE 2. Selected bond lengths and bond angles



	Bond lengths (Å)		
Fe–C(1)/Fe–C(24)	2.039(41)–2.063(13)		
cpd, C–C	1.349(17)–1.451(18)		
C(1)–C(6)	1.494(14)		
C(19)–C(20)	1.499(16)		
C(7)–C(8)/C(17)–C(18)	1.550(18)–1.489(16)		
S(1)–C/S(4)–C	1.804(14)–1.829(13)		
	C–N bond lengths (Å)		**C=O bond lengths**
N(1)–C(6)	1.350(14)	O(1)–C(6)	1.247(13)
N(1)–C(7)	1.471(13)	O(2)–C(19)	1.234(15)
N(1)–C(18)	1.480(16)		
N(2)–C(19)	1.366(15)		
N(2)–C(12)	1.453(15)		
N(2)–C(13)	1.480(14)		
	Bond angle (deg.)		**Bond angle (deg.)**
C(8)–S(1)–C(9)/C(16)–S(4)–C(17)	99.7(6)/98.7(6)		
C(6)–N(1)–C(7)	123.9(8)	C(19)–N(2)–C(12)	127.2(9)
C(6)–N(1)–C(18)	118.2(9)	C(19)–N(2)–C(13)	116.1(9)
C(7)–N(1)–C(18)	116.0(8)	C(12)–N(2)–C(13)	116.7(9)
O(1)–C(6)–N(1)	120.2(10)	O(2)–C(19)–N(2)	119.7(11)
O(1)–C(6)–C(1)	121.3(10)	O(2)–C(19)–C(20)	118.3(10)
N(1)–C(6)–C(1)	118.5(9)	N(2)–C(19)–C(20)	122.0(10)

3.1. Synthesis of 1,1″;1′,1″-bis-(1,4,10,13-tetrathia-7,16-diazacyclooctadecane-7,16-diyldicarbonyl)bisferrocene (4) X = S

A three-necked flask equipped with a mechanical stirrer, was flushed with nitrogen and then charged with triethylamine (150 mg, 1.53 mmol) in toluene (100 ml). A solution of 1,1′-bis(chlorocarbonyl)ferrocene (260 mg, 7.65 mmol) in toluene (200 ml) was placed in a pressure-equalized dropping funnel. In a second similar dropping funnel was placed 1,4,10,13-tetrathia-7,16-diaza-cyclo-octadecane (250 mg, 7.65 mmol) in toluene (100 ml). The two solutions were added dropwise, simultaneously during 1 h to the vigorously stirred mixture in the flask at room temperature and the mixture was then stirred for 4 days. During that time, the colour of the solution changed from red to pale orange, and a fine white precipitate of triethylamine hydrochloride was formed. The precipitate was filtered off, and the solvent was then removed from the filtrate to leave an oily orange residue, which crystallized on standing. This material was chromatographed on a column of alumina with CH_2Cl_2–0.5% MeOH as eluent. An orange band was collected, and upon removal of solvents under vacuum yielded the dimer as an orange powder (yield, 350 mg (82%); melting point

TABLE 3. The ^1H and ^{13}C nuclear magnetic resonance data of **5** in $CDCl_3$ relative to tetramethylsilane

^1H NMR			^{13}C NMR (*S*/*N*, Fc–CH, 35/1)	
δ (ppm)	Integration	Assignment	δ (ppm)	Assigment
4.133 (br)	4	cpd	82.6	*ipso*-C (C(1))
4.129 (br)			70.5	cpd-(C(2),(5/3),(4))
3.58 (s)	2	Fe–CH_2–N	68.8	
			54.1	$N(CH_2)_2$ (C(7))
2.84 (s)	4	$N(CH_2)_2$	53.5	Fe–(CH_2)–N (C(6))
2.65 (br)	8	SCH_2	32.7	S CH_2 (C(8))
			30.2	S CH_2 (C(9))

(m.p.), 223°C). Relative molecular mass fast-atom bombardment (RMM FAB) (thioglycerol matrix): 1129 (M + 1). Anal. Found: C, 50.75; H, 5.80; N, 4.81. Calculated for $C_{48}H_{64}N_4O_4S_8Fe_2$: C, 51.06; H, 5.71; N, 4.96%. NMR data are as shown in Table 1.

3.2. Reduction of 4 (X = S) to 1,1″:1′,1‴-bis-(1,4,-10,13)-tetrathia-7,16-diazacyclo-octadecane-7,16-dimethylene)bisferrocene (5)

To a solution of 4 (X = S) (100 mg, 0.09 mmol) in anhydrous dichloromethane (10 ml) and tetrahydrofuran (2 ml) was added $LiAlH_4$ (20 mg, 0.53 mmol) with vigorous stirring, and the mixture was stirred under nitrogen for 2 days at room temperature. The solution was then diluted with dichloromethane and saturated aqueous sodium potassium tartate was added. The organic layer was separated, washed with water (2 × 10 ml) and dried over magnesium sulphate. The solvent was removed to obtain an oily orange liquid which was chromatographed on alumina with CH_2Cl_2–1% MeOH as eluant. A pale-yellow band was collected and upon removal of the solvents under vacuum yielded 5 as a pale-yellow powder (yield, 70 mg (75%); m.p. 168–70°C). RMM (FAB) (thioglycerol matrix: 1073 (M + 1). The NMR data are reported in Table 3.

TABLE 4. Fractional atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms. (the estimated standard deviations in parenthesis apply to the last or last two digits)

	x	*y*	*z*	B_{iso} (Å)
Fe	−0.33625(16)	0.50561(14)	−0.26844(14)	2.95(8)
S(1)	−0.0271(3)	0.2765(3)	0.0593(3)	3.91(16)
S(2)	0.1222(4)	−0.0117(3)	0.1493(4)	6.0(3)
S(3)	0.4489(4)	−0.0875(3)	−0.3244(3)	4.92(19)
S(4)	0.3578(3)	0.1877(3)	−0.3184(3)	4.57(19)
Cl(1)	−0.6948(3)	0.8501(3)	0.4260(3)	5.11(19)
Cl(2)	−0.9686(4)	0.8699(3)	0.4914(3)	6.06(22)
Cl(3)	−0.8312(4)	0.6413(4)	0.5834(4)	9.5(3)
O(1)	−0.0567(8)	0.3409(7)	−0.3268(7)	4.5(5)
O(2)	0.5827(8)	−0.3001(8)	0.0071(7)	4.9(5)
N(1)	0.0496(8)	0.3624(7)	−0.2011(7)	2.8(5)
N(2)	0.3956(9)	−0.1948(8)	0.0179(7)	3.4(5)
C(1)	−0.1424(9)	0.4923(9)	−0.2578(8)	2.28(19)
C(2)	−0.2144(11)	0.5015(10)	−0.1617(9)	3.25(22)
C(3)	−0.2886(12)	0.6142(11)	−0.1943(11)	4.3(3)
C(4)	−0.2616(12)	0.6719(12)	−0.3136(11)	4.7(3)
C(5)	−0.1713(11)	0.5959(11)	−0.3550(10)	3.9(3)
C(6)	−0.0478(10)	0.3934(10)	−0.2642(9)	2.87(21)
C(7)	0.0889(10)	0.4384(9)	−0.1489(9)	2.70(20)
C(8)	0.1102(11)	0.3652(10)	−0.0246(10)	3.67(24)
C(9)	0.0392(12)	0.1927(11)	0.1915(10)	4.0(3)
C(10)	0.1578(11)	0.1132(10)	0.1837(10)	3.78(24)
C(11)	0.2816(11)	−0.0570(10)	0.1036(10)	3.76(24)
C(12)	0.2731(11)	−0.1666(10)	0.0726(9)	3.40(23)
C(13)	0.4280(11)	−0.1184(11)	−0.1033(10)	3.94(25)
C(14)	0.3912(11)	−0.1760(11)	−0.1775(10)	3.9(3)
C(15)	0.3072(13)	0.0014(12)	−0.3773(11)	5.2(3)
C(16)	0.2437(13)	0.0848(13)	−0.3228(12)	5.4(3)
C(17)	0.2432(11)	0.3090(10)	−0.3082(9)	3.27(22)
C(18)	0.1432(11)	0.2645(10)	−0.2081(9)	3.54(24)
C(19)	0.4832(12)	−0.2863(10)	0.0652(10)	3.50(24)
C(20)	0.4642(10)	−0.3696(10)	0.1874(9)	3.05(22)
C(21)	0.5292(11)	−0.4878(10)	0.2279(9)	3.28(23)
C(22)	0.5020(12)	−0.5426(11)	0.3406(11)	4.7(3)
C(23)	0.4190(12)	−0.4659(12)	0.3790(11)	4.6(3)
C(24)	0.3954(11)	−0.3578(10)	0.2841(9)	3.39(23)
C(25)	−0.8425(11)	0.7778(10)	0.4638(10)	3.69(24)

3.3. Collection of crystal X-ray data

The material was crystallized by slow evaporation of a CD_2Cl_2–$CDCl_3$ solution from which well-formed orange crystals were obtained. Crystals mounted for X-ray structure analysis in the normal way deteriorated rapidly as did one coated in epoxy resin. A successful mounting was achieved, however, by coating a columnar crystal, 0.13 mm × 0.13 mm × 0.75 mm, in silicone grease and gently sliding it into the narrow neck of a Lindeman glass capillary which was then sealed.

Data were collected on a Picker four-circle automated diffractometer in the 2θ range 5–45° using Zr-filtered Mo Kα X-radiation and pulse-height analysis. Data were collected using 2° scans in θ–2θ mode. Fearing deterioration, scanning was at 4° min^{-1}, twice the normal speed. The intensity of a standard reflection measured every 100 intensity values did not change by more than ±2% from the mean, except that, at the very end of the data collection (affecting approximately 300 reflections), the standard fell monotonically in intensity by 5% and was still falling when data collection was completed. This loss in intensity was automatically corrected for in the data reduction routine. Absorption corrections were carried out using the NRCVAX program [17].

3.4. Crystal data

The crystal data were as follows: $[FeC_{24}H_{32}N_2O_2S_4]_2 \cdot 2CDCl_3$; molecular weight = 1370.16; triclinic, space group, $P\bar{1}$; $a = 10.504(14)$ Å, $b = 11.993(8)$ Å and $c = 13.142(9)$ Å; $\alpha = 65.70(5)°$, $\beta = 80.73(9)°$ and $\gamma = 84.39(9)°$; $V = 1499.9$ Å^3; $Z = 1$; $D_{calc} = 1.517$ g cm^{-3}; μ(Mo Kα) = 10.656 cm^{-1}. Cell parameters were obtained from the automated alignment of ten reflections in the 2θ range 31–37°. Of the 3907 intensities measured, 2266 were significant at $2.5\sigma(I)$. The intensity distribution was centric and the structure was solved by direct methods using SOLVER [17]. Refinement was by the full-matrix least-squares method. Atoms other than those of carbon and hydrogen were refined anisotropically. Carbon atoms were refined isotropically; hydrogen atoms were positioned theoretically (C–H, 1.08 Å) and given the same isotropic temperature factors as the carbon atoms to which they are attached. The final $R = 0.069$ and $R_w = 0.074$ with a weighting scheme based on counting statistics. Fractional atomic coordinates and isotropic (or equivalent isotropic) temperature factors are given in Table 4. Anisotropic temperature factors, hydrogen atomic coordinates and structure factor tables have been deposited at the Cambridge Crystallographic Centre.

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