Influence of Electronic Conjugation and Steric Effects on the Crystal Structures of Imino- and Hydrazido-derivatives of Ferrocenecarbaldehyde†

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The crystal and molecular structures of $[Fe(C_5H_5)(C_5H_4CH{=}NC_6H_4X\text{-}p)]$ (X = Br or F) have been determined. The two compounds have markedly different molecular conformations. These are compared with the structures of two series of related ferrocenyl compounds and it is found that the major driving force for the molecular conformation is intra- rather than inter-molecular interaction. The compounds all have electron-withdrawing C=N groups which have previously been shown to act as electron sinks. All the structures have bond lengths in keeping with this finding, though a major steric interaction disguises some bond-length information which would have shed more light on the overall electronic structure of the molecule. The value of Mössbauer spectroscopic data as a complement to the X-ray structural findings is demonstrated.

The ability to control and manipulate molecular arrangement in the solid state has become a desirable goal for chemists. Indeed in the long term this will be a necessity, as it is now well established that both ionic and molecular solids can possess technologically important physical properties which are dependent on their structure. Piezo- and pyro-electric properties, electrical conductivity, superconduction, ferromagnetism and other magnetic effects all arise from interactions between molecules. Non-linear optical materials do not demand such interactions, but the relative orientation of the molecules or ions in a solid critically affects the performance of second harmonic generation.

We have reported on a series of ferrocenyl Schiff-base derivatives containing a donor–conductor–acceptor (D–π–A) motif designed for second harmonic generation. Of the materials so far tested, only one, $[Fe(C_5H_5)(C_5H_4CHNC_6H_4\text{-}NO_2\text{-}p)]$, has displayed any activity.[1] In an attempt to rationalize the factors which affect the relative orientation of donor and acceptor groups and understand their influence on molecular packing arrangements (or *vice versa*), we have continued to investigate the structures of these compounds.[2]

We report here the crystal and molecular structures of the related compounds $[Fe(C_5H_5)(C_5H_4CHNC_6H_4X\text{-}p)]$ (X = F **1** or Br **2**). These structures are discussed in relation to other ferrocene Schiff-base complexes[1–7] and also to a series of substituted *N*-benzylideneanilines.[8–12]

We have recently shown from Mössbauer spectroscopic studies that the –C=N– entity when connected to the ferrocenyl moiety acts as an electron sink,[6] which effectively blocks transfer of electron density to the attached acceptor; it is not a good 'conductor'. The inclusion of this entity in the design of a non-linear optical material is therefore not desirable. The present findings reinforce this conclusion.

Results and Discussion

The bond lengths and angles for compounds **1** and **2** are presented in Tables 1 and 2, and the molecular structures and atom labelling schemes in Figs. 1 and 2. The major features of these structures are bond lengths which give indications about π-electron density in the rings and the Schiff-base region, and the torsion angles between the rings and the *trans* imino unit. In both structures the *trans* C(10)–C(11)–N–C(12) unit is within 1° of being planar, but both the cyclopentadienyl and phenyl rings twist out of this plane.

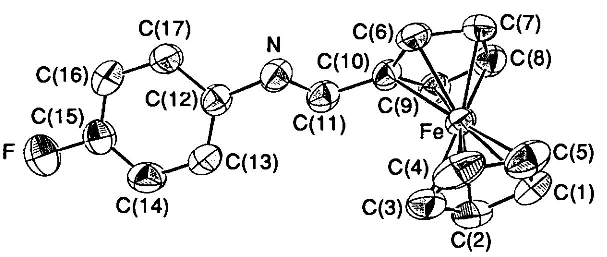

Fig. 1 Molecular structure and atom labelling scheme for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CH{=}NHC_6H_4F\text{-}p)]$ **1**

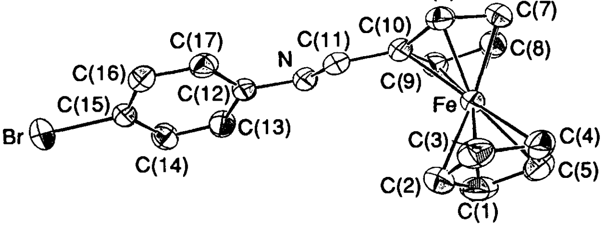

Fig. 2 Molecular structure and atom labelling scheme for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CH{=}NHC_6H_4Br\text{-}p)]$ **2**

Ferrocene Structurally Based Classes.—We have previously[13] divided ferrocene derivatives into classes A–C on the basis of the internal and the exocyclic C–C distances of the cyclopentadienyl ring: A has a fulvenoid structure with the exocyclic C–C distance < 1.45 Å, B has three continuous short C–C distances and exocyclic distance > 1.48 Å, and C has equal internal distances and exocyclic bond 1.45–1.48 Å. Such distances are shown in Table 3 for compounds **1** and **2** and some related compounds; **1** and **2** are readily classified as type A.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Bond distances (Å) and angles (°) for complex **1**

Fe–C(1)	2.026(4)	C(2)–C(3)	1.403(6)
Fe–C(2)	2.030(4)	C(3)–C(4)	1.398(6)
Fe–C(3)	2.038(4)	C(4)–C(5)	1.392(7)
Fe–C(4)	2.034(4)	C(6)–C(7)	1.412(5)
Fe–C(5)	2.028(4)	C(6)–C(10)	1.428(5)
Fe–C(6)	2.037(4)	C(7)–C(8)	1.429(6)
Fe–C(7)	2.045(4)	C(8)–C(9)	1.399(5)
Fe–C(8)	2.050(4)	C(9)–C(10)	1.418(5)
Fe–C(9)	2.025(4)	C(10–C(11)	1.452(5)
Fe–C(10)	2.037(3)	C(12)–C(13)	1.383(5)
F–C(15)	1.359(4)	C(12)–C(17)	1.389(5)
N–C(11)	1.259(5)	C(13)–C(14)	1.385(6)
N–C(12)	1.424(5)	C(14)–C(15)	1.369(6)
C(1)–C(2)	1.393(6)	C(15)–C(16)	1.351(6)
C(1)–C(5)	1.409(6)	C(16)–C(17)	1.369(5)
C(11)–N–C(12)	117.8(3)	C(9)–C(10)–C(11)	124.9(4)
C(2)–C(1)–C(5)	108.0(4)	N–C(11)–C(10)	122.8(4)
C(1)–C(2)–C(3)	108.3(4)	N–C(12)–C(13)	124.8(3)
C(2)–C(3)–C(4)	107.4(4)	N–C(12)–C(17)	116.7(3)
C(3)–C(4)–C(5)	108.8(4)	C(13)–C(12)–C(17)	118.5(3)
C(1)–C(5)–C(4)	107.5(4)	C(12)–C(13)–C(14)	120.9(4)
C(7)–C(6)–C(10)	107.8(4)	C(13)–C(14)–C(15)	118.1(4)
C(6)–C(7)–C(8)	108.0(4)	F–C(15)–C(14)	118.4(4)
C(7)–C(8)–C(9)	107.9(4)	F–C(15)–C(16)	119.0(4)
C(8)–C(9)–C(10)	108.8(4)	C(14)–C(15)–C(16)	122.5(4)
C(6)–C(10)–C(9)	107.5(3)	C(15)–C(16)–C(17)	119.3(4)
C(6)–C(10)–C(11)	127.6(4)	C(12)–C(17)–C(16)	120.7(4)

Numbers in parentheses are estimated standard deviations (e.s.d.s) in the least significant digits.

Table 2 Bond distances (Å) and angles (°) for complex **2**

Br–C(15)	1.906(4)	C(2)–C(3)	1.415(7)
Fe–C(1)	2.051(4)	C(3)–C(4)	1.400(6)
Fe–C(2)	2.043(4)	C(4)–C(5)	1.414(6)
Fe–C(3)	2.045(4)	C(6)–C(7)	1.415(6)
Fe–C(4)	2.049(4)	C(6)–C(10)	1.428(6)
Fe–C(5)	2.046(4)	C(7)–C(8)	1.414(7)
Fe–C(6)	2.035(4)	C(8)–C(9)	1.412(6)
Fe–C(7)	2.052(4)	C(9)–C(10)	1.436(6)
Fe–C(8)	2.049(4)	C(10–C(11)	1.443(5)
Fe–C(9)	2.046(4)	C(12)–C(13)	1.396(6)
Fe–C(10)	2.042(4)	C(12)–C(17)	1.395(6)
N–C(11)	1.277(5)	C(13)–C(14)	1.370(6)
N–C(12)	1.410(5)	C(14)–C(15)	1.378(6)
C(1)–C(2)	1.416(7)	C(15)–C(16)	1.375(6)
C(1)–C(5)	1.408(7)	C(16)–C(17)	1.379(6)
C(11)–N–C(12)	120.4(3)	C(6)–C(10)–C(11)	125.9(4)
C(2)–C(1)–C(5)	107.8(4)	C(9)–C(10)–C(11)	126.7(4)
C(1)–C(2)–C(3)	107.7(4)	N–C(11)–C(10)	121.7(4)
C(2)–C(3)–C(4)	108.3(4)	N–C(12)–C(13)	116.4(4)
C(3)–C(4)–C(5)	108.0(4)	N–C(12)–C(17)	125.6(4)
C(1)–C(5)–C(4)	108.2(4)	C(13)–C(12)–C(17)	118.0(4)
C(7)–C(6)–C(10)	108.1(4)	C(12)–C(13)–C(14)	121.5(4)
C(6)–C(7)–C(8)	108.2(4)	C(13)–C(14)–C(15)	119.0(4)
C(7)–C(8)–C(9)	108.6(4)	C(14)–C(15)–C(16)	121.3(4)
C(8)–C(9)–C(10)	107.7(4)	C(15)–C(16)–C(17)	119.5(4)
C(6)–C(10)–C(9)	107.4(4)	C(12)–C(17)–C(16)	120.7(4)

Numbers in parentheses are e.s.d.s in the least significant digits.

Compound **10**[1] also readily fits into class A. The *p*-nitro derivative[2] **3** nearly fits into this class except that the exocyclic bond length is 1.466(6) Å (see Table 3). However, as no similar structural motif was found in our previous classification (which covered the 41 then known substituted ferrocene structures[13]), it is possible to suggest that **3** is a fulvenoid structure and that class A should allow for longer exocyclic C–C distances. Additional support for this assignment is to be found in the C=N bond length,[1] which is long, and the near coplanarity of the $C_5H_4CH{=}N$ part of the molecule. This is in keeping with the suggestion that some delocalization of electron density is found over the $C_5H_4CH{=}N$ part.[3] In compound **10** the $CH{=}N{-}N{=}CHC_6H_4NO_2$ section is very nearly planar, in keeping with extended delocalized bonding.

Only half the compounds in Table 4 show an exocyclic C–C bond length $\leqslant 1.45$ Å, *i.e.* **1**, **2**, **4**, **6**, **8** and **10**. The remaining five are classified as follows: **3**, class A (with an extended exocyclic C–C bond length); **5**, C; **7**, B; **9**,C; **11**, unclassified because it has N bound to the cyclopentadienyl ring.

The C=N *Bond Lengths*.—One of the purposes of this work is to estimate the extent to which the C=N unit can act as a conductor in the D–π–A or D–σ–A motif (where σ signifies only a sigma and no π conduction). It might be expected that good conduction would be related to conjugation with substituents on C and N, and be reflected in elongation of the C=N bond length. There is unfortunately no standard non-conjugated C=N bond length, although several workers have attempted to find one.[14–16] Bernstein and Izak[8] record lengths of 1.21(1) and 1.237(3) Å which are probably the shortest, and to any reasonable degree of significance are shorter than those in any ferrocene derivatives or in any of the benzylideneanilines discussed in this paper (see Table 4). It may therefore be regarded as established that all the compounds in Table 4 have some degree of conjugation involving the C=N bond. The monosubstituted ferrocenes in Table 4 show a remarkable constancy of C=N distance for nine compounds. The mean value for **1**–**11** (excluding **5** and **8**) is 1.26(2) Å. Compound **8** has a longer value by 4.3 standard deviations, but of the others only **1** and **6** show deviations $\geqslant 2\,\sigma$. The distance in the bromide **2** is longer than that in the fluoride by 2.7 σ. The disubstituted ferrocene **5** shows four different distances (there are two inequivalent molecules in the unit cell) which appear to be longer on average than those of the first group, but the standard deviations are rather large.

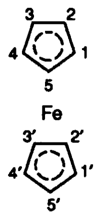
A possibly more sensitive indicator of conjugation has been found by adding the lengths of the exocyclic C–C, C=N and N–R bonds to give an overall bond length (o.b.l.). These o.b.l.s show an increasing relationship with the quadrupole splittings observed in the ^{57}Fe Mössbauer spectra;[1,6] it has been shown that electron withdrawal from ferrocene reduces the observed quadrupole splitting,[1,2] and Table 4 indicates that electron withdrawal from ferrocene reduces the o.b.l. (except for compound **3**, see below). The Mössbauer data of course reflect conjugation only between C=N and the ferrocene ends of the molecules.

Molecular Packing Forces and Torsion Angles.—Conjugation may also be studied by reference to torsional twisting of groups attached at either end of the C=N bond. However, it is necessary to take into account the possibility that intermolecular forces may be a factor in determining torsion angles. In the unit cell of compound **5** there are two independent but chemically equivalent molecules, with four unrelated C=N units. Each unit exhibits hydrogen bonding between the pyridinium hydrazide and acetate anion, and there is a range of 13.1–30.6° in the dihedral angle (α) between the cyclopentadienyl rings and the pyridine rings. Owing to the chemical equivalence it must be concluded that intermolecular forces play a major role in determining these particular torsions.

Compound **4** contains the same (but unprotonated) pyridyl hydrazone unit as that in **5**, but there is no hydrogen bonding in the lattice. Its bond lengths and angles correspond closely to those in **5**, indicating strongly that intermolecular forces do not affect bond angles or lengths. The dihedral angle, α, is close to the highest of the angles found in **5**.

Bernstein and co-workers[8,10–12,17] carried out extensive studies on benzylideneanilines and concluded that the molecular conformation could be determined by intermolecular forces between large halogen atoms on adjacent molecules.

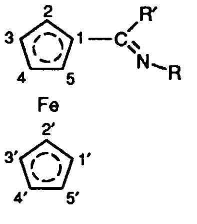
Table 3 Carbon–carbon bond lengths (Å) for cyclopentadienyl rings and relevant exocyclic C–C bonds in substituted ferrocenes



								Average C–C				
Compound	Substituent at C^1		C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(5)–C(1)	ring	unsubstituted ring	Exocyclic C–C	Average error	Ref.
1	$CH=NC_6H_4F$-*p*		1.418	1.399	1.429	1.412	1.428	1.421	1.399	1.452	0.006	This work
2	$CH=NC_6H_4Br$-*p*		1.436	1.412	1.414	1.415	1.428	1.421	1.411	1.443	0.007	This work
3	$CH=NC_6H_4NO_2$-*p*		1.426	1.398	1.430	1.414	1.425	1.423	1.399	1.466	0.006	2
4	$CH=N-NH(2-C_5H_4N)$		1.433	1.437	1.407	1.422	1.427	1.431	1.414	1.456	0.005	3
5*	$[CMe=N-NH(2-C_5H_5N)]_2^+$	A_1	1.464	1.369	1.451	1.483	1.413	1.445	—	1.451	0.020	4
		A_2	1.440	1.472	1.432	1.403	1.432	1.445	—	1.472	0.020	
		B_1	1.428	1.459	1.458	1.457	1.457	1.454	—	1.454	0.020	
		B_2	1.446	1.426	1.404	1.377	1.520	1.443	—	1.464	0.020	
10	$CH=N-N=CHC_6H_4NO_2$-*p*		1.417	1.415	1.427	1.409	1.443	1.422	1.420	1.445	0.007	1
11	$NCHC_6H_4OH$-*o*		1.468	1.406	1.436	1.427	1.403	1.435	1.401	—	0.013	7

* Ferrocene disubstituted at C^1, $C^{1'}$.

Table 4 Exocyclic bond lengths (Å) of a number of closely related substituted ferrocenes



Compound	R′	R	Exocyclic C–C	C=N	N=R ($R = C_{aryl}$)	o.b.l.[a]	Ref.
Monosubstituted ferrocenes							
1	H	C_6H_4F-*p*	1.452(5)	1.259(5)	1.424(5)	4.135(9)	This work
2	H	C_6H_4Br-*p*	1.443(5)	1.277(5)	1.410(5)	4.132(9)	This work
3	H	$C_6H_4NO_2$-*p*	1.466(6)	1.279(6)	1.418(5)	4.163(10)	2
4	H	NHC_5H_4N-2	1.456(5)	1.274(5)	—	—	3
6	H	Ph	1.455(8)	1.251(8)	1.347(8)	4.053(14)	6
7	Me	Ph	1.494(6)	1.269(5)	1.413(5)	4.176(9)	6
8	Ph	Ph	1.448(10)	1.308(9)	1.398(9)	4.154(16)	6
9	H	CH_2Ph	1.464(7)	1.262(7)	—	—	6
10	H	$N{=}CHC_6H_4NO_2$-*p*	1.445(6)	1.272(7)	—	—	1
11[b]	H	$(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)$	—	1.278(11)	—	—	7
Disubstituted (hetero) ferrocenes substituted at C^1, $C^{1'}$							
5	Me	$NH(2\text{-}C_5H_5N)^+$	1.451(14)	1.310(18)	—	—	4
			1.472(14)	1.284(19)	—	—	
			1.454(15)	1.292(19)	—	—	
			1.464(19)	1.269(18)	—	—	

[a] o.b.l. = Overall bond length (addition of exocyclic C–C, C=N and N–R bonds). [b] This compound has C_6H_4OH at the normal ferrocenyl position and the R is the ferrocenyl moiety.

Table 5 Twist angles for a number of closely related substituted ferrocenes

Compound	α	β	δ	Δ/mm s^{-1}	Structure
1	50.80(15)	12.68(73)	38.12(32)	2.31(1)	This work
2	11.21(66)	13.72(95)	24.88(54)	2.31(1)	This work
3	65.80(17)	13.37(71)	52.79(39)	2.25(1)	2
4	27.5(2)	—	—	2.28(1)	3
5	13.1–30.6	—		2.27(1)	4
6	19.0(6)	7.06(6)	12.0(6)	2.28(1)	6
7	93.9(3)	8.3(3)	85.6(6)	2.33(1)	6
8	73.4(6)	11.4(6)	62.0(6)	2.31(1)	6
9	99.6(3)	18.8(3)	—	2.29(1)	6
10	—	3.54	—	—	1
11	—	10.7(3)	—	—	7

α = Angle between cyclopentadienyl and phenyl ring planes, β that between cyclopentadienyl and C–C=N–C planes, and δ that between the six-membered ring and C–C=N–C planes; Δ = Mössbauer spectroscopic quadrupole splitting from ref. 6.

However, in the absence of hydrogen bonding or large atoms and groups, there appears to be no direct evidence that the conformations are other than intramolecular. (This does not apply to the *sense* of a torsion angle which must be determined by an agency outside a molecule.)

The torsion angles δ shown in Table 5 for compounds **1**–**3** and **6**–**8** represent torsional twisting of the R-ring substituents on N. It has previously been shown[2] that the prime factor in this torsion is the relief of steric interaction between the substituent R′ on C(11) and one of the *ortho* hydrogens on the six-membered ring. Allowing for the relative sizes of the R′ substituents, it must be concluded that small δ angles represent sufficiently strong conjugation between C=N and R to overcome at least partially the steric interaction of R′ and the *ortho* hydrogen on the six-membered ring.

Compounds **1**–**3** and **6** are closely related. Compound **3** where $R = C_6H_4NO_2$-*p* shows the most effective electron withdrawal from ferrocene as measured by the quadrupole splitting (Δ). The o.b.l. is the largest of these four compounds and is out of line with the observed previously stated trend. This compound also shows one of the largest δ angles and hence poor conjugation of C=N with the nitrophenyl system. Thus the presence of the *p*-NO_2 group in **3** causes the greatest electron-withdrawing properties and results in a D–σ–A-motif.[6] Clearly, however, if the N–R bond (Table 4) of 1.418(5) Å were considered alone without the Mössbauer data, the conclusion that it is predominantly a single bond when compared to the lengths for compounds **1**, **2** and **6** (which must have some double-bond character masked by steric repulsion) could not have been drawn.

The torsion angles, β, between the cyclopentadienyl ring and the C=N unit are quite small. The only steric interaction which might be expected to affect this angle is between the closest cyclopentadienyl hydrogens and the lone pair on N; the small angles probably reflect conjugation between the cyclopentadienyl ring and C=N, but may not necessarily indicate a strong effect as the steric interaction would be weak. When R′ = Ph, as in compound **8**, it is R′ which twists strongly out of the C=N plane to avoid steric interaction with ferrocenyl, leaving the ferrocenyl cyclopentadienyl ring in conjugation with C=N. This signifies that ferrocenyl is a better electron donor than is phenyl to the C=N group, consistent with our previous findings.[18]

From the preceding discussion it is apparent that the N–C_{aryl} bond lengths may have considerable double-bond character due to electron delocalization, but this is masked in the structures by steric interactions causing twisting of the molecule (δ angles). Thus the N–C_{aryl} bonds found in compounds **6** and **8** (which are short) as well as those of **1**–**3** and **7** are all partially delocalized into the –C–CH=N– and the phenyl ring bonds. Where no CH=N hydrogen steric interactions are present as in compound **10** the molecule is essentially planar throughout, thus this linking group may offer potential for the development of a suitable conductor.

Significantly, compound **11** which is also a Schiff base has a N=CHC_6H_4OH-*o* moiety which is nearly planar[7] (and is in keeping with the structure of compound **10** for the N=$CHC_6H_4NO_2$-*p* part of the molecule). The mean dihedral angle β between the N=CHC_6H_4OH-*o* moiety and the cyclopentadienyl ring is 10.7(3)°. Compound **11** has no N at the CH position compared to **1**–**10** and thus no steric H···H interaction at this point and it therefore does not twist. Moreover, the lone pair at N appears to be involved in a strong hydrogen bond with the H atom of the OH group and this reinforces (or causes) the planarity. Another point of interest is that the dihedral angle β is fairly consistent with those for compounds **1** and **2**.

Conclusion

The following facts now emerge: (*a*) all the compounds in Table 4 have C=N bonds that are in conjugation with the C_5H_4 ring of the ferrocenyl units; (*b*) there is no steric interaction of any consequence between the C_5H_4 ring and the -R′C=N- entity, and the resultant β angles are consequently small; (*c*) there are considerable steric interactions between the CH=N hydrogen and the *o*-hydrogens of the six-membered rings in structures **1**, **2** and **6**; (*d*) the steric interactions [above] mask the delocalization of electron density into the N–R (R = C_{aryl}) bonds, as they reduce the ideal π-orbital overlap in compounds **1**, **2** and **6**; and (*e*) intermolecular forces will be too weak to affect the bonding and conformations of compounds **1**–**11**, except that the sign of δ may be due to intermolecular forces.

The conclusion made from Mössbauer spectroscopic studies[6] that the C=N bond acts as an electron sink (an electron-withdrawing group relative to the ferrocenyl moiety) is in keeping with the structural data in Tables 1–5. Indeed, it is now apparent that the C=N group by its electron-withdrawing power is the dominant force controlling the molecular conformation. The Mössbauer spectroscopic studies give information on electron distribution, particularly the amount of electron withdrawal from ferrocenyl. The crystal structures show the atomic arrangement, but in the presence of steric interactions the bond lengths may not relate directly to bond strengths. However, if both techniques are available, the joint information gives a better understanding of the bonding in a molecule.

Experimental

Crystals of complexes **2** and **1** (prepared as previously described[1,2]) having approximate dimensions 1.16 × 0.47 × 0.33 and 0.83 × 0.41 × 0.33 mm respectively were mounted on glass fibres in random orientation. Preliminary examination and data collection were performed with Mo-Kα radiation (λ = 0.7107 Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite-crystal incident-beam monochromator. Accurate unit-cell dimensions and crystal orientation matrices were determined by least-squares refinement of the setting angles of 25 centred reflections (Table 6). The space groups were determined by systematic absences and from Harker planes in the Patterson functions. Inversion symmetry was detected statistically from E maps. The usual corrections for Lorentz and polarization factors were made. For each structure an empirical absorption correction was made after scanning nine reflections each at 36 different azimuthal angles (ψ scan). Both structures were determined by the heavy-atom method using SHELXS 86;[19] subsequent full-matrix least-squares refinement and Fourier-difference synthesis using MOLEN[20] located all remaining atoms, except hydrogen (Tables 7 and 8). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms

Table 6 Crystal data and details of refinement for compounds **1** and **2**

Crystal	**1**	**2**
Molecular formula	$C_{17}H_{14}FFeN$	$C_{17}H_{14}BrFeN$
M	307.15	368.06
Space group	$P2_1/c$	$P2_1/a$
a/Å	5.831(1)	11.132(3)
b/Å	10.961(3)	10.5712(8)
c/Å	21.580(4)	13.224(3)
β/°	95.96(1)	112.94(1)
U/Å^3	1372(1)	1433.1
D_c/g cm^{-3}	1.486	1.706
μ(Mo-Kα)/mm^{-1}	1.0951	3.8
θ range for lattice parameters/°	19.38–23.2	22.98–24.87
Minimum, maximum transmittance	77.0464, 99.5145	74.3838, 99.8823
No. of measured reflections	2700	2828
No. of independent reflections	2657	2682
No. of observed reflections	1919 $[I > 3\sigma(I)]$	2217 $[I > 1.5\sigma(I)]$
h, *k*, *l* ranges	0–6, 0–13, −25 to 25	0–13, 0–12, −15 to 15
Variation of standards (average) (%)	1.4	0.34
R	0.033	0.0324
R′	0.042	0.0478
Maximum, minimum difference peaks/e Å^{-3}	0.486, −0.305	0.381, −0.784
Weighting scheme, *w*	$1/[\sigma^2(F) + (0.02F)^2 + 1]$	$1/[\sigma^2(F) + (0.02F)^2 + 1]$
S	0.66	1.231
F(000)	632	736

Details in common: monoclinic; 18 °C; ω–2θ scans; 2θ 3–50°; three standard reflections every 120 min; refinement on *F*; maximum shift/error < 0.01.

Table 7 Final atomic coordinates for complex **1**

Atom	x	y	z
Fe	0.029 85(9)	0.090 79(5)	0.171 73(2)
F	0.525 7(5)	0.532 3(2)	−0.145 6(1)
N	0.378 4(5)	0.184 3(3)	0.030 8(1)
C(1)	−0.188 3(7)	0.134 5(4)	0.235 4(2)
C(2)	−0.202 3(7)	0.221 7(4)	0.188 2(2)
C(3)	0.016 3(8)	0.274 1(4)	0.186 7(2)
C(4)	0.164 3(7)	0.218 6(4)	0.233 5(2)
C(5)	0.040 7(8)	0.132 1(4)	0.263 6(2)
C(6)	0.292 0(7)	0.007 1(3)	0.133 0(2)
C(7)	0.171 0(7)	−0.079 0(3)	0.165 8(2)
C(8)	−0.063 6(7)	−0.079 6(3)	0.139 1(2)
C(9)	−0.085 8(7)	0.006 4(3)	0.091 0(2)
C(10)	0.132 7(6)	0.059 8(3)	0.085 7(1)
C(11)	0.177 9(7)	0.153 5(3)	0.041 0(2)
C(12)	0.401 2(6)	0.275 9(3)	−0.014 9(1)
C(13)	0.264 2(7)	0.378 8(4)	−0.023 3(2)
C(14)	0.304 9(7)	0.465 9(4)	−0.067 3(2)
C(15)	0.484 5(7)	0.447 2(4)	−0.102 3(2)
C(16)	0.620 2(7)	0.347 2(4)	−0.095 7(2)
C(17)	0.580 8(7)	0.261 7(3)	−0.051 8(2)

Table 8 Final atomic coordinates for complex **2**

Atom	x	y	z
Br	0.231 48(5)	0.145 14(5)	1.035 04(4)
Fe	−0.122 55(5)	0.920 35(5)	0.642 79(4)
N	−0.046 1(3)	0.555 3(3)	0.704 0(3)
C(1)	0.064 1(4)	0.980 4(5)	0.675 5(4)
C(2)	0.051 2(4)	0.942 6(5)	0.773 5(4)
C(3)	−0.045 6(4)	1.019 3(5)	0.786 5(4)
C(4)	−0.092 3(4)	1.103 2(4)	0.697 9(4)
C(5)	−0.025 2(4)	1.079 3(4)	0.628 6(4)
C(6)	−0.280 1(4)	0.821 3(4)	0.641 8(4)
C(7)	−0.317 1(4)	0.898 9(4)	0.547 5(4)
C(8)	−0.241 1(4)	0.864 8(4)	0.487 1(3)
C(9)	−0.156 9(4)	0.765 3(4)	0.542 8(3)
C(10)	−0.180 8(3)	0.736 7(4)	0.639 4(3)
C(11)	−0.115 0(4)	0.642 6(4)	0.721 5(3)
C(12)	0.011 8(3)	0.461 4(4)	0.783 9(3)
C(13)	0.120 4(4)	0.400 1(4)	0.778 5(3)
C(14)	0.185 8(4)	0.307 9(4)	0.852 9(3)
C(15)	0.141 1(4)	0.273 4(4)	0.932 4(3)
C(16)	0.032 2(4)	0.329 2(4)	0.938 3(3)
C(17)	−0.032 5(4)	0.422 3(4)	0.864 1(3)

in calculated positions were included in structure-factor calculations but not refined. Killean and Lawrence[21] weights were used in each refinement. All computations were performed on a MicroVax computer. Atomic scattering factors were taken from ref. 22. Diagrams were drawn using ORTEP.[23] Final atomic coordinates are given in Tables 7 and 8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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