A New Series of Neutral Nitrosyl(η^4-tetraphenylcyclobutadiene)iron(0) Complexes: Crystal and Molecular Structure of (*NN*-Diethyldithiocarbamato-*SS'*)nitrosyl(η^4-tetraphenylcyclobutadiene)iron(0) †

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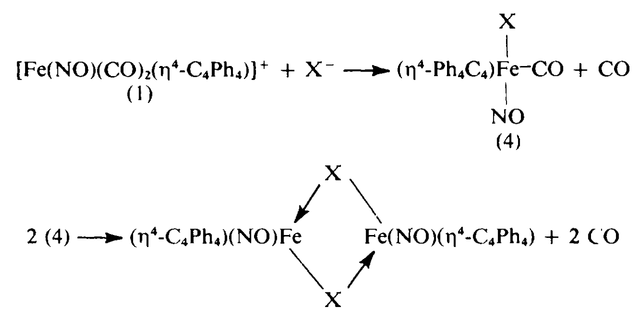
Reactions of the cationic nitrosyl(η^4-tetraphenylcyclobutadiene)iron(0) complexes $[Fe(NO)(CO)_2(\eta^4\text{-}C_4Ph_4)]^+$ (1) and $[Fe(NO)(CO)(PPh_3)(\eta^4\text{-}C_4Ph_4)]^+$ (2) with uni- and bi-dentate anionic nucleophiles have been investigated. Complex (2) reacts with Cl^- to give $[FeCl(NO)(PPh_3)(\eta^4\text{-}C_4Ph_4)]$ (3). Reaction of (1) with X^- (X = Cl, NCO, NCS, NO_2, or N_3) yields polynuclear complexes $[\{FeX(NO)(\eta^4\text{-}Ph_4C_4)\}_n]$ (5) where *n* is probably 2. With potentially chelating anions (1) yields the mononuclear complexes $[FeZ(NO)(\eta^4\text{-}C_4Ph_4)]$ [Z = NO_3 (6), pentane-2,4-dionate (7), or S_2CNEt_2(8)]. The structure of (8) has been established by an *X*-ray crystallographic analysis. Crystals are monoclinic, $a = 11.383(2)$, $b = 16.211(3)$, $c = 15.529(4)$ Å, $\beta = 93.23(2)°$, $Z = 4$, and space group $P2_1/n$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculation to $R = 0.027$ and $R' = 0.031$ for 2 998 reflections with $I > 3\sigma(I)$. The iron atom is co-ordinated to four carbon atoms of tetraphenylcyclobutadiene [Fe–C 2.061(2), 2.070(2), 2.034(2), and 2.065(2) Å], to the two S atoms of the dithiocarbamato-ligand [Fe–S 2.317(1) and 2.316(1) Å], and to the N atom of the nitrosyl ligand [Fe–N 1.649(3), N–O 1.167(3) Å]. The nitrosyl ligand is slightly bent [Fe–N–O 170.4(3)°].

Although the reactions of the cationic η^4-tetraphenylcyclobutadieneiron(0) complex, $[Fe(NO)(CO)_2(\eta^4\text{-}C_4Ph_4)]^+$ (1), with neutral Lewis bases have received extensive study,[1] the behaviour of (1) towards anionic nucleophiles does not appear to have been investigated. Herein we describe the synthesis of a new series of neutral nitrosyl(η^4-tetraphenylcyclobutadiene)iron(0) complexes which result from the reaction of (1) and related species with unidentate and bidentate anions. The full *X*-ray crystallographic characterisation of one of these complexes, $[Fe(S_2CNEt_2)(NO)(\eta^4\text{-}C_4Ph_4)]$ (8), is also described.



$$[Fe(NO)(CO)_2(\eta^4\text{-}C_4Ph_4)]^+ \ (1) + X^- \longrightarrow (\eta^4\text{-}Ph_4C_4)Fe(X)(CO)(NO) \ (4) + CO$$

$$2\,(4) \longrightarrow (\eta^4\text{-}C_4Ph_4)(NO)Fe(\mu\text{-}X)_2Fe(NO)(\eta^4\text{-}C_4Ph_4) + 2\,CO$$

[X = Cl (5a), NCO (5b), NCS (5c), NO_2 (5d), or N_3 (5e)]

Scheme.

Results and Discussion

The triphenylphosphine-substituted derivative of (1), $[Fe(NO)(CO)(PPh_3)(\eta^4\text{-}C_4Ph_4)]^+$ (2) (as its PF_6^- salt) reacted rapidly with one equivalent of $[N(PPh_3)_2]Cl$ in acetone to yield a brown carbonyl-free product, (3). Microanalytical data (Table 1) agreed with the formulation of (3) as the neutral complex $[FeCl(NO)(PPh_3)(\eta^4\text{-}C_4Ph_4)]$. Consistent with this formulation, the i.r. spectrum of (3) (Table 1) showed a single strong ν(NO) absorption at 1 760 cm^{-1} (CH_2Cl_2), *ca.* 65 cm^{-1} to lower wavenumber than that of its cationic precursor (2).[2] On the basis of this result we anticipated that (1) would react with Cl^- to yield an analogous monocarbonyl complex $[FeCl(NO)(CO)(\eta^4\text{-}C_4Ph_4)]$ (4). This was not observed. Instead, the reaction of (1) with $[N(PPh_3)_2]X$ (X = Cl, NCO, NCS, NO_2, or N_3) led to the formation of brown microcrystalline carbonyl-free solids (5a)—(5e) in 60—80% yield. Unlike (3), complexes of type (5) were very sparingly soluble in polar organic solvents and gave microanalytical data (Table 1) in agreement with the formulation $[\{FeX(NO)(\eta^4\text{-}C_4Ph_4)\}_n]$. The complexes (5a)—(5c) and (5e) exhibited a single strong ν(NO) i.r. band in the region 1 745—1 765 cm^{-1} (Table 1) consistent with the presence of a linear terminal (NO^+) nitrosyl ligand. Formation of (5) may be rationalised in terms of the reaction sequence outlined in the Scheme. It is likely that monocarbonyl complexes of type (4) are the initial products of the reaction. However, it appears that these compounds then undergo intermolecular condensation with loss of the remaining CO group and generation of [Fe–X–Fe] bridges. Although higher degrees of aggregation are possible we believe that the dimeric structure illustrated in the Scheme is the most likely possibility for (5). We have been unable to verify this suggestion experimentally as the complexes were insufficiently soluble for molecular weight determination by solution methods and the microcrystalline solids did not contain crystals suitable for an *X*-ray crystallographic study. For the same reason we are at present unable to specify the relative disposition of the C_4Ph_4 and nitrosyl ligands with respect to the (presumed) $Fe(\mu\text{-}X)_2Fe$ core (possible *cis–trans* isomerism) or the mode of attachment of the bridging pseudohalide ligands (possible linkage isomerism). The i.r. spectra of complexes (5a)—(5c) show only a single sharp ν(NO) band and this may be taken as tentative evidence that only one isomeric form is present. The species which we have formulated as the nitrito-complex $[\{Fe(NO_2)(NO)(\eta^4\text{-}C_4Ph_4)\}_n]$ (5d) shows a more complex pattern of ν(NO) bands: two strong absorptions at 1 766 and

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† *Supplementary data available* (No. SUP 23767, 23 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles, least-squares plane data, stereoview of unit cell, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Microanalytical and i.r. data for nitrosyl(η^4-tetraphenylcyclobutadiene) complexes

	Microanalysis [a] (%)				I.r.[b] (cm^{-1})	
Complex	C	H	N	Other	ν(NO)	Other
(3)	74.4 (74.65)	5.2 (4.75)	1.8 (1.9)	5.0 [c] (4.8)	1 760	
(5a)	69.9 (70.4)	4.3 (4.2)	2.85 (2.95)	7.0 [c] (7.4)	1 765	
(5b)	72.3 (71.9)	4.3 (4.15)	5.5 (5.8)		1 745	ν(NCO) 2 160
(5c)	69.4 (69.6)	4.3 (4.05)	5.2 (5.6)	5.95 [d] (6.4)	1 745	ν(NCS) 2 130
(5d)	69.0 (68.85)	4.25 (4.15)	5.45 (5.75)		1 742 (sh), 1 750, 1 766	ν(NO_2) 1 450, 1 140
(5e) [e]	70.9 (71.45)	3.8 (4.15)	6.5 (6.85)		1 745br	ν(NCO) 2 160 ν(N_3) 2 060
(6)	66.8 (66.7)	4.15 (4.0)	5.35 (5.55)		1 765	ν(NO_3) 1 522, 1 252
(7)	73.7 (73.2)	5.2 (5.05)	2.35 (2.6)		1 730	
(8)	67.5 (67.1)	4.9 (5.1)	5.25 (4.75)	10.5 [d] (10.85)	1 735	

[a] Calculated values in parentheses. [b] All absorptions are strong. Spectra recorded in KBr discs except for compounds (6)—(8) which were in CH_2Cl_2 solution; sh = shoulder, br = broad. [c] Chlorine. [d] Sulphur. [e] Calculated values are for a 4.5 : 1.0 mixture (5b) : (5e) (see text).

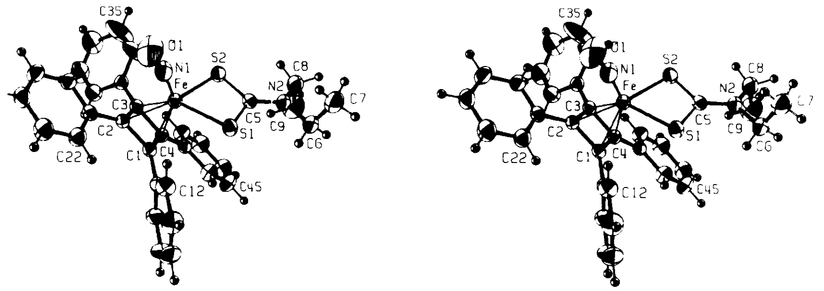


Figure. Stereoview of (8) showing the crystallographic numbering scheme

1 750 cm^{-1} and a strong shoulder at 1 742 cm^{-1}. This led us initially to consider whether (5d) might not be a dinitrosyl complex, *i.e.* $[Fe(NO)_2(\eta^4\text{-}C_4Ph_4)]$, since $[N(PPh_3)_2]NO_2$ is known to be capable of functioning as a source of the nitrosyl ligand *via* atom-transfer redox reactions with co-ordinated CO.[3] This possibility was eliminated on the basis of the microanalytical data obtained for (5d) (Table 1) and the fact that no CO_2 was evolved during the reaction of (1) with $[N(PPh_3)_2]NO_2$. We conclude, therefore, that more than one isomeric form must be present in solid (5d) but we have insufficient evidence to determine the nature of the isomerism involved.

Reaction of the cation (1) with $[N(PPh_3)_2]N_3$ gave an insoluble mixture of the azido-complex (5e) formed by direct displacement of CO by N_3^- and the isocyanato-complex (5b) which arises from attack of N_3^- on a co-ordinated carbonyl group.[4] The i.r. spectrum of the inseparable mixture (Table 1) indicated that the isocyanato-complex was the major product and microanalytical data were compatible with a 4.5 : 1.0 ratio of (5b) to (5e).

Reaction of (1) with $[N(PPh_3)_2]NO_3$ yielded a nitrato-complex $[\{Fe(NO_3)(NO)(\eta^4\text{-}C_4Ph_4)\}_n]$ (6) which differed from (5a)—(5e) in being reasonably soluble in polar solvents such as CH_2Cl_2. This raised the possibility that (6) might actually be a monomeric complex in which the nitrato-ligand was *OO'*-chelated to the iron atom. The i.r. spectrum of (6) showed bands at 1 522 and 1 252 cm^{-1} assignable to the nitrato-ligand (CH_2Cl_2 solution) but we were unable to make an unambiguous decision between the possible bidentate bridging or chelating co-ordination modes of the ligand on the basis of this information. Furthermore, crystals of (6) were of insufficient quality to allow an *X*-ray crystallographic determination of the molecular structure. Less ambiguous results were obtained with the classically chelating anions pentane-2,4-dionate (pd) and *NN*-diethyldithiocarbamate ($Et_2NCS_2^-$). Complex (1) reacted smoothly with Tl(pd) and $[N(PPh_3)_2][S_2CNEt_2]$ to give the new complexes $[FeZ(NO)(\eta^4\text{-}C_4Ph_4)]$ (7; Z = pd) and (8; Z = S_2CNEt_2) in 45 and 62% yields respectively. Like (6), both (7) and (8) were soluble in polar organic solvents. An *X*-ray crystallographic investigation of (8) confirmed the monomeric structure for this complex and thus, by reasonable implication, for (6) and (7) also.

Crystals of (8) contain discrete monomeric molecules separated by normal van der Waals contacts. A stereoview of (8) with the crystallographic numbering scheme is shown in the Figure. Details of the molecular dimensions are in Table 2. The co-ordination at Fe has approximate mirror symmetry, the mirror plane passing through Fe, N(1), C(2), and C(4) with S–Fe–N(nitrosyl) 104.9(1) and 106.9(1), N(1)–Fe–C(2) 93.7(1), S(1)–Fe–C(4) 98.6(1), and S(2)–Fe–C(4) 92.9(1)°. The Fe–C(η^4-C_4Ph_4) distances [2.034(2)—2.070(2) Å], the C–Fe–C angles involving adjacent C atoms in the cyclobutadiene ligand [41.2(1)—41.8(1)°] and the C–C bond lengths within the cyclobutadiene ring [1.454(3)—1.464(3) Å] are all in excellent agreement with the analogous dimensions reported for a variety of other Fe^0 cyclobutadiene complexes.[5] The cyclobutadiene ring is almost planar with an average deviation from the best least-squares plane through the four carbon atoms of 0.016 Å corresponding to a fold angle of 2.5(5)°. The length of the normal from the iron atom to the mean plane of the C_4 ring is 1.779 Å. The phenyl carbon atoms bonded to the C_4 ring are bent (5.8—12.7°) out of the C_4 plane in a direction away from the Fe atom; the phenyl groups are also rotated about the exocyclic C–C bonds out of the C_4 plane so that the dihedral angles between the mean plane of the C_4 portion of the ligand and those of the phenyl substituents are 54.4 [C(11)—C(16)], 11.1 [C(21)—C(26)], 99.8 [C(31)—C(36)], and 16.7° [C(41)—C(46)] respectively.

The *NN*-diethyldithiocarbamato-ligand bonds to Fe *via* a

Table 2. Selected molecular dimensions for [Fe(S_2CNEt_2)(NO)(η^4-C_4Ph_4)] (8), with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

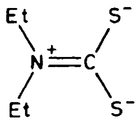
Fe–S(1)	2.317(1)	Fe–C(4)	2.065(2)	C(6)–C(7)	1.496(5)	C(3)–C(4)	1.464(3)
Fe–S(2)	2.316(1)	S(1)–C(5)	1.715(3)	C(8)–C(9)	1.501(5)	C(1)–C(11)	1.475(3)
Fe–N(1)	1.649(3)	S(2)–C(5)	1.715(3)	N(1)–O(1)	1.167(3)	C(2)–C(21)	1.468(3)
Fe–C(1)	2.061(2)	N(2)–C(5)	1.317(3)	C(1)–C(2)	1.454(3)	C(3)–C(31)	1.484(3)
Fe–C(2)	2.070(2)	N(2)–C(6)	1.470(4)	C(1)–C(4)	1.466(3)	C(4)–C(41)	1.459(3)
Fe–C(3)	2.034(2)	N(2)–C(8)	1.470(4)	C(2)–C(3)	1.461(3)		

Mean phenyl C–C distance 1.375(4) Å

(*b*) Bond angles (°)

S(1)–Fe–S(2)	75.2(1)	C(1)–Fe–C(3)	61.1(1)	C(5)–N(2)–C(8)	121.2(2)
S(1)–Fe–N(1)	104.9(1)	C(1)–Fe–C(4)	41.6(1)	C(6)–N(2)–C(8)	117.0(2)
S(1)–Fe–C(1)	92.2(1)	C(2)–Fe–C(3)	41.7(1)	N(2)–C(6)–C(7)	111.8(3)
S(1)–Fe–C(2)	131.0(1)	C(2)–Fe–C(4)	59.5(1)	N(2)–C(8)–C(9)	111.5(3)
S(1)–Fe–C(3)	140.3(1)	C(3)–Fe–C(4)	41.8(1)	C(1)–C(2)–C(3)	91.1(2)
S(1)–Fe–C(4)	98.6(1)	Fe–S(1)–C(5)	86.8(1)	C(1)–C(2)–C(21)	135.0(2)
S(2)–Fe–N(1)	106.9(1)	Fe–S(1)–C(5)	86.8(1)	C(3)–C(2)–C(21)	133.5(2)
S(2)–Fe–C(1)	131.1(1)	Fe–N(1)–O(1)	170.4(3)	C(2)–C(3)–C(4)	89.1(2)
S(2)–Fe–C(2)	141.5(1)	Fe–C(1)–C(11)	127.6(2)	C(2)–C(3)–C(31)	132.3(2)
S(2)–Fe–C(3)	99.8(1)	Fe–C(2)–C(21)	126.7(2)	C(4)–C(3)–C(31)	134.7(2)
S(2)–Fe–C(4)	92.9(1)	Fe–C(3)–(31)	133.2(2)	C(1)–C(4)–C(3)	90.5(2)
N(1)–Fe–C(1)	122.0(1)	Fe–C(4)–C(41)	126.9(2)	C(1)–C(4)–C(41)	135.7(2)
N(1)–Fe–C(2)	93.7(1)	S(1)–C(5)–S(2)	111.1(1)	C(3)–C(4)–C(41)	133.2(2)
N(1)–Fe–C(3)	114.0(1)	S(1)–C(5)–N(2)	124.2(2)	C(2)–C(1)–C(4)	89.3(2)
N(1)–Fe–C(4)	152.4(1)	S(2)–C(5)–N(2)	124.7(2)	C(2)–C(1)–C(11)	135.9(2)
C(1)–Fe–C(2)	41.2(1)	C(5)–N(2)–C(6)	121.8(2)	C(4)–C(1)–C(11)	133.7(2)

pair of equivalent Fe–S bonds [2.317(1), 2.316(1) Å] which are well within the range of Fe–S distances observed in other low-spin iron dithiocarbamato-complexes.[6] The two bonds from sulphur to the dithiocarbamate carbon are also identical in length [1.715(3) Å] and the C–N distance [1.317(3) Å] is appreciably shorter than would be anticipated for a C–N single bond. Within the diethyldithiocarbamato–iron portion of the complex the FeS_2CNC_2 fragment is planar to within 0.125 Å with the terminal methyl groups lying 1.45 and 1.56 Å above and below this plane respectively. These results suggest a major contribution from the resonance form below to the ground state of the co-ordinated dithiocarbamate ligand in (8).



The nitrosyl ligand has normal temperature factors and is well resolved with no evidence of disorder. The dimensions and geometry of the FeNO unit [Fe–N 1.649(3), N–O 1.167(3) Å, and Fe–N–O 170.4(3)°] allow the ligand to be formally classified as NO^+ as required for (8) by the 18-electron rule. In (8) the Fe–N distance is shorter and the N–O distance longer than those found in the isoelectronic Fe^0 complex dicarbonyl(nitrosyl)(1—3-η-4-*exo*-trimethylphosphoniocyclobut-2-en-1-yl)iron hexafluorophosphate (9) [Fe–N 1.680(9), N–O 1.148(8) Å].[7] This implies a reduced degree of Fe^0 to NO^+ π-bonding in the latter complex as compared to (8) and may be rationalised in terms of (*a*) the difference in net charge between the two complexes and (*b*) the contrasting electronic effects of the two π-acceptor CO ligands in (9) compared with the strongly σ-donating dithiocarbamato-ligand in (8).

Experimental

Complexes (1) and (2),[2] [N(PPh_3)$_2$]X (X = Cl, NCO, NCS, NO_2, N_3, and Et_2NCS_2),[8] and Tl(pd)[9] were prepared by literature methods. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer (calibrated with polystyrene film). Microanalyses were carried out by the staff of the Microanalytical Laboratory of University College, Cork.

Preparation of the Complexes (3), (5a)—(5e), *and* (6)—(8).—The following procedure, with minor variations, is typical. A stirred solution of (1) (1.29 g, 2.0 mmol) in acetone was treated portionwise, under N_2, with solid [N(PPh_3)$_2$]Cl (1.15 g, 2.1 mmol). Gas was evolved and the solution became brown. After *ca.* 1 h the brown insoluble product was collected by filtration, washed with a little acetone and diethyl ether and dried *in vacuo* over P_2O_5 to yield (5a) (0.85 g, 88%). The more soluble (3) and (6)—(8) were isolated by removal of the solvent *in vacuo*, solution of the residue in ether or CH_2Cl_2 and precipitation with n-hexane. Analytical and i.r. data are in Table 1. Crystals of (8) suitable for *X*-ray studies were obtained by slow concentration of a solution in CH_2Cl_2–hexane.

Crystal Data for [Fe(S_2CNEt_2)(NO)(η^4-C_4Ph_4)] (8).—$C_{33}H_{30}FeN_2OS_2$, $M = 590.6$, Monoclinic, $a = 11.383(2)$, $b = 16.211(3)$, $c = 15.529(4)$ Å, $\beta = 93.23(2)°$, $U = 2\,860.81$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}, $F(000) = 1\,088$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 6.4 cm^{-1}. Space group $P2_1/n$ from systematic absences: $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$.

A dark brown prismatic crystal (dimensions 0.32 × 0.15 × 0.12 mm) of (8) was set up on a PDP8/A controlled Enraf-Nonius CAD-4 diffractometer equipped with Mo-K_α radiation monochromatized by a graphite crystal. 25 Reflections in the range $9 < \theta < 12°$ were used to obtain accurate cell constants and an orientation matrix. The intensities of the unique reflections with $2 < \theta < 22.5°$ were measured by the ω/2θ scan method. Of the 4 109 reflections collected, 2 998 with $I > 3\sigma(I)$ were considered observed, and after correction for Lorentz and polarisation factors, were used in all subsequent calculations. The intensities of three well separated reflections, monitored as standards at regular intervals did not change significantly over the period of the data collection.

Table 3. Final fractional co-ordinates for non-hydrogen atoms (Fe × 10^5, others × 10^4) with estimated standard deviations in parentheses

Atom	x	y	z
Fe	75(3)	16 387(2)	21 408(2)
S(1)	−238(1)	321(1)	2 645(1)
S(2)	−694(1)	869(1)	929(1)
O(1)	2 429(2)	1 920(2)	2 009(2)
N(1)	1 439(2)	1 738(2)	2 024(2)
N(2)	−1 179(2)	−683(1)	1 415(1)
C(1)	−852(2)	2 164(2)	3 101(2)
C(2)	−167(2)	2 784(2)	2 674(2)
C(3)	−914(2)	2 699(2)	1 882(2)
C(4)	−1 638(2)	2 104(1)	2 323(2)
C(5)	−760(2)	52(2)	1 626(2)
C(6)	−1 111(3)	−1 377(2)	2 024(2)
C(7)	−85(4)	−1 926(2)	1 877(3)
C(8)	−1 781(3)	−834(2)	567(2)
C(9)	−3 088(4)	−723(3)	594(3)
C(11)	−910(2)	1 853(2)	3 990(2)
C(12)	39(3)	1 465(2)	4 429(2)
C(13)	−55(3)	1 189(2)	5 265(2)
C(14)	−1 086(4)	1 293(2)	5 671(2)
C(15)	−2 014(3)	1 669(2)	5 253(2)
C(16)	−1 936(3)	1 946(2)	4 415(2)
C(21)	789(2)	3 350(2)	2 948(2)
C(22)	1 193(3)	3 396(2)	3 800(2)
C(23)	2 066(3)	3 950(2)	4 056(2)
C(24)	2 540(3)	4 468(2)	3 478(2)
C(25)	2 143(3)	4 433(2)	2 627(2)
C(26)	1 271(2)	3 881(2)	2 358(2)
C(31)	−1 103(2)	3 238(2)	1 114(2)
C(32)	−1 633(3)	3 989(2)	1 199(2)
C(33)	−1 828(4)	4 509(2)	508(2)
C(34)	−1 511(4)	4 293(2)	−277(2)
C(35)	−1 023(6)	3 546(3)	−377(2)
C(36)	−796(5)	3 022(2)	312(2)
C(41)	−2 771(2)	1 717(2)	2 098(2)
C(42)	−3 460(2)	1 984(2)	1 385(2)
C(43)	−4 549(3)	1 648(2)	1 186(2)
C(44)	−4 982(3)	1 033(2)	1 691(2)
C(45)	−4 310(3)	752(2)	2 397(2)
C(46)	−3 214(2)	1 089(2)	2 600(2)

Structure Solution and Refinement.—The Fe atom was located from an unsharpened Patterson map and a subsequent heavy-atom phased F_o synthesis revealed the positions of all non-hydrogen atoms. Initial refinement[10] of the positional parameters by full-matrix least-squares methods lowered R to 0.104 and a difference map showed maxima consistent with the expected location of all hydrogen atoms. The latter were positioned geometrically (C–H = 0.95 Å) and in subsequent cycles overall $U_{iso.}$ values were refined for all protons. The non-hydrogen atoms were then allowed anisotropic motion and full-matrix refinement converged with $R = 0.027$ and $R' = 0.031$. A final difference map showed no significant features. In the final stages of refinement weighting factors were derived from the counting statistics. Scattering factors for non-hydrogen atoms[11] and for hydrogen atoms[12] were used in the calculations and allowance was made for anomalous dispersion.[13] Final fractional co-ordinates are given in Table 3.

Acknowledgements

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