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X-RAY STRUCTURE OF (*N*-HETEROCYCLIC)(η^4-DIENE)-DICARBONYLIRON(0) COMPOUNDS

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Summary

(*N*-Heterocyclic)(η^4-diene)dicarbonyliron(0) compounds, where the *N*-heterocycles are quinoline and pyrazine and the diene is the diethyl ester of the hexa-2,4-dien-1,6-dioic acid (diethyl muconate) were studied by X-ray diffraction. The measurements demonstrated that the *N*-heterocycle occupies different positions of a tetragonal pyramid in these compounds. Quinoline occupies a basal position and pyrazine an apical position. This is discussed in terms of the π-bonding ability of the ligands.

Introduction

With a few exceptions five coordinated iron(0) compounds in the solid state assume square pyramidal configurations, with the positioning of the ligands in the basal or apical sites being assigned to relatively stronger or weaker π-bonding ability.

The photochemical reaction of pentacarbonyliron with excess diethyl muconate produces the bis(diethyl muconate)carbonyliron compound [1]. It was shown by X-ray diffraction that its structure is that of a square pyramid with the two dienes occypying basal/basal coordination sites and with the carbonyl in the apical position [2]. In this case, the stronger π-bonding CO ligand coordinates in an unfavorable position due to the steric hindrance for basal/apical diene coordination. The exchange of one of the dienes for a diazadiene, such as 2,2′-bipyridine, 2-benzoylpyridine or 2-benzoylpyridine-*p*-methoxyanil, produces a (diene)(diazadiene)monocarbonyliron compound which also shows a square pyramidal configuration [3]. In this case the entering bidentate nitrogen-containing ligand occupies an apical/basal position, thus distorting the pyramid in the C_4 axis direction. When the synthesis of the same class of compounds is carried out in the opposite way, i.e., exchange of a diazadiene by a diene in a bis(diazadiene)monocarbonyliron com-

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pound, it is possible to isolate a (diene)(diazadiene)monocarbonyliron compound with both bidentate ligands occupying the basal positions of a less distorted square pyramid [4]. More recently, we treated bis(diethyl muconate)monocarbonyliron with monodentate *N*-heterocyclic ligands in an attempt to exchange one diene for two heterocycles to obtain a compound similar to that observed from reactions with 2,2′-bipyridine. However, the reaction yielded a crystalline product with the composition (diene)(*N*-heterocycle)dicarbonyliron, where the *N*-heterocycle was pyridine, pyrazine and quinoline [5]. The same products were obtained by the photochemical substitution of one CO in (diene)$(CO)_3Fe$ by the corresponding *N*-heterocycle. Similar compounds have also been prepared where the diene is replaced by benzylideneacetone and the heterocycle by a phosphine [6]. In this case X-ray structural analysis showed a somewhat complicated structure which can be approximated as a distorted square pyramid with the benzylideneacetone and the two carbonyls on the base and the phosphine in the apical position.

In this work we report the solid state structures of two (*N*-heterocyclic)(η^4-diene)dicarbonyliron compounds prepared with the *N*-heterocycles quinoline (compound **1**) and pyrazine (compound **2**). We show that these heterocycles occupy different coordination sites although this difference can not be detected by measurements made in solution, such as ^1H or ^{13}C NMR [5].

Experimental

The compounds were prepared and purified according to reference [5].

X-Ray structure determination. The following features were common to both

TABLE 1

CRYSTAL DATA AND DETAILS OF DATA COLLECTION AND REFINEMENT FOR COMPOUNDS **1** AND **2**

	1	**2**
Formula	$C_{21}H_{21}O_6NFe$	$C_{16}H_{18}O_6N_2Fe$
M	439.25	390.18
Space Group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 4)
a (Å)	7.766(2)	10.390(2)
b (Å)	9.644(2)	19.754(4)
c (Å)	14.917(2)	9.051(2)
α (°)	84.12(2)	90
β (°)	74.99(2)	108.27(2)
γ (°)	76.54(2)	90
Z	2	4
V (Å^3)	1048.4	1764.0
D_o (flotation) (g cm^{-3})	1.39	1.47
D_c (g·cm^{-3})	1.391	1.469
r (mm^{-1})	0.78	0.92
F(000)	228	202
Crystal size (mm)	0.14×0.16×0.09	0.14×0.06×0.14
Unique reflections	3427	3400
Observed reflections	1589	967
$[I > 3\sigma(I)]$	1589	967
Structure solution	Heavy atom (Fe)	Heavy atom (Fe)
R	0.058	0.066

TABLE 2

ATOMIC COORDINATES FOR COMPOUND **1**, WITH STANDARD DEVIATIONS IN PARENTHESES

Fe	0.4940(2)	0.2044(1)	0.2369(1)	4.76(6)
O(1)	0.181(1)	0.3685(9)	0.3635(5)	9.5(5)
O(2)	0.289(1)	0.1248(8)	0.1184(5)	8.7(5)
O(3)	0.8914(8)	0.3653(7)	0.2307(4)	6.8(4)
O(4)	0.6873(8)	0.4396(7)	0.3622(4)	6.3(4)
O(5)	0.372(1)	−0.1396(8)	0.2564(5)	9.2(5)
O(6)	0.224(1)	−0.0598(8)	0.3966(5)	9.3(5)
N	0.5792(9)	0.3557(7)	0.1410(4)	4.5(3)
C(1)	0.303(1)	0.311(1)	0.3104(6)	5.7(5)
C(2)	0.370(1)	0.156(1)	0.1636(7)	6.0(5)
C(3)	0.529(1)	0.4915(9)	0.1635(6)	5.3(5)
C(4)	0.593(1)	0.6033(9)	0.1101(8)	6.1(6)
C(5)	0.714(1)	0.576(1)	0.0261(7)	6.2(6)
C(6)	0.883(1)	0.405(1)	−0.0929(7)	6.4(6)
C(7)	0.924(1)	0.270(1)	−0.1216(6)	7.4(6)
C(8)	0.859(1)	0.163(1)	−0.0663(7)	6.8(6)
C(9)	0.747(1)	0.1873(8)	0.0223(5)	5.2(5)
C(10)	0.697(1)	0.3274(8)	0.0534(5)	4.3(4)
C(11)	0.766(1)	0.4365(9)	−0.0038(6)	5.0(5)
C(12)	0.652(2)	0.653(1)	0.4333(9)	8.8(8)
C(13)	0.749(1)	0.571(1)	0.3497(7)	7.0(6)
C(14)	0.768(1)	0.346(1)	0.2959(6)	5.2(5)
C(15)	0.686(1)	0.2206(9)	0.3136(6)	5.2(4)
C(16)	0.757(1)	0.1103(9)	0.2478(6)	5.6(5)
C(17)	0.656(1)	0.008(1)	0.2545(6)	6.6(5)
C(18)	0.486(1)	0.0202(9)	0.3233(6)	6.1(5)
C(19)	0.357(2)	−0.067(1)	0.3195(8)	6.8(6)
C(20)	0.074(2)	−0.132(2)	0.3964(9)	11.1(1)
C(21)	0.114(2)	−0.262(2)	0.442(1)	15.6(1)

compounds. Intensities were measured on a CAD-4 diffractometer, ω–2θ scanning mode, graphite-monochromated Mo-K_α radiation, in the range $2° < 2\theta < 50°$ and reduced to structure factors after Lorentz, polarization and absorption corrections. Cell constants were refined from 2θ values of selected strong reflections in the range 18–22°. Crystal data and further details are given in Table 1. The program system SHELX [7] was used for the structure solution and full-matrix least-squares refinement.

One of the ethyl groups present in compound **2** is disordered. Hydrogen atoms were included in the refinement using a riding model and constant isotropic thermal factor equal to 6 Å^2. The weighting scheme was $w^{-1} = \sigma^2(F_0) + g\,F_0^2$, with $\sigma(F_0)$ from counting statistics. Atomic coordinates and relevant derived parameters are given in Tables 2 to 5.

A representation of compounds **1** and **2**, as well as the numbering used, is given in Fig. 1 and 2, respectively.

Discussion

As shown in Fig. 1 and 2, a square pyramidal structure is observed for both compounds in the solid state, as expected for five-coordinated iron(0) complexes

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND **1**, WITH STANDARD DEVIATIONS IN PARENTHESES

Fe–C(1)	1.772(8)	C(9)–C(10)	1.41(1)
Fe–C(2)	1.79(1)	C(10)–C(11)	1.40(1)
Fe–N	2.038(6)	C(10)–N	1.399(9)
Fe–C(15)	2.14(1)	C(12)–C(13)	1.48(2)
Fe–C(16)	2.074(8)	C(13)–O(4)	1.44(1)
Fe–C(17)	2.052(9)	C(14)–O(4)	1.34(1)
Fe–C(18)	2.091(8)	C(14)–O(3)	1.21(1)
C(1)–O(1)	1.14(1)	C(14)–C(15)	1.46(1)
C(2)–O(2)	1.14(2)	C(15)–C(16)	1.44(1)
C(3)–N	1.33(1)	C(16)–C(17)	1.39(2)
C(4)–C(3)	1.39(1)	C(17)–C(18)	1.44(1)
C(5)–C(4)	1.37(1)	C(18)–C(19)	1.46(2)
C(5)–C(11)	1.40(1)	C(19)–O(5)	1.20(1)
C(6)–C(7)	1.36(2)	C(19)–O(6)	1.33(1)
C(6)–C(11)	1.42(1)	C(20)–O(6)	1.49(2)
C(7)–C(8)	1.36(2)	C(20)–C(21)	1.37(2)
C(8)–C(9)	1.39(1)		
C(2)–Fe–C(1)	96.2(5)	C(9)–C(8)–C(7)	121.5(9)
N–Fe–C(1)	100.2(3)	C(10)–C(9)–C(8)	118.3(8)
N–Fe–C(2)	91.3(4)	C(9)–C(10)–N	119.5(7)
C(15)–Fe–C(1)	95.6(4)	C(11)–C(10)–N	120.9(7)
C(15)–Fe–C(2)	167.3(3)	C(11)–C(10)–C(9)	119.7(7)
C(15)–Fe–N	91.3(3)	C(6)–C(11)–C(5)	120.6(9)
C(16)–Fe–C(1)	134.0(4)	C(10)–C(11)–C(5)	119.8(7)
C(16)–Fe–C(2)	127.6(4)	C(10)–C(11)–C(6)	119.6(8)
C(16)–Fe–N	93.1(3)	O(4)–C(13)–C(12)	106.9(8)
C(16)–Fe–C(15)	39.8(3)	C(14)–O(4)–C(13)	116.1(7)
C(17)–Fe–C(1)	133.5(4)	O(3)–C(14)–O(4)	123.3(9)
C(17)–Fe–C(2)	98.5(4)	C(15)–C(14)–O(4)	110.8(7)
C(17)–Fe–N	123.1(3)	C(15)–C(14)–O(3)	125.9(8)
C(17)–Fe–C(15)	69.7(4)	C(14)–C(15)–Fe	118.7(6)
C(17)–Fe–C(16)	39.1(4)	C(16)–C(15)–Fe	67.6(5)
C(18)–Fe–C(1)	94.7(4)	C(16)–C(15)–C(14)	117.6(7)
C(18)–Fe–C(2)	94.3(4)	C(15)–C(16)–Fe	72.6(5)
C(18)–Fe–N	163.4(3)	C(17)–C(16)–Fe	69.6(5)
C(18)–Fe–C(15)	80.0(4)	C(17)–C(16)–C(15)	116.8(7)
C(18)–Fe–C(16)	71.2(4)	C(16)–C(17)–Fe	71.3(5)
C(18)–Fe–C(17)	40.5(3)	C(18)–C(17)–Fe	71.2(5)
O(1)–C(1)–Fe	173.4(9)	C(18)–C(17)–C(16)	119.0(5)
O(2)–C(2)–Fe	178.8(8)	C(17)–C(18)–Fe	68.3(5)
C(3)–N–Fe	118.9(5)	C(19)–C(18)–Fe	118.9(7)
C(10)–N–Fe	124.8(5)	C(19)–C(18)–C(17)	120.3(8)
C(10)–N–C(3)	116.3(6)	O(5)–C(19)–C(18)	124.6(9)
C(4)–C(3)–N	125.3(7)	O(6)–C(19)–C(18)	111.5(9)
C(5)–C(4)–C(3)	118.9(8)	O(6)–C(19)–O(5)	124 (1)
C(11)–C(5)–C(4)	118.8(9)	C(20)–O(6)–C(19)	116.1(9)
C(11)–C(6)–C(7)	119.2(9)	C(21)–C(20)–O(6)	106 (1)
C(8)–C(7)–C(6)	121.7(8)		

with a diene ligand [8]. However, it is very interesting that, in spite of the similarity of the *N*-heterocyclic ligands, their positioning around the central iron atom is different. As shown in the schematic representation in Fig. 3, in compound **1**, the

TABLE 4

ATOMIC COORDINATES FOR COMPOUND 2, WITH STANDARD DEVIATIONS IN PARENTHESES

Fe	0.2345(2)	0.3861(1)	0.3073(2)	3.36(6)
O(1)	0.333(1)	0.2551(6)	0.440(2)	7.6(5)
O(2)	0.519(1)	0.4257(6)	0.395(1)	7.6(5)
O(3)	−0.1313(9)	0.3054(4)	0.267(1)	4.4(3)
O(4)	0.021(1)	0.2357(5)	0.221(1)	6.1(4)
O(5)	0.221(1)	0.5827(6)	0.194(1)	6.9(5)
O(6)	0.353(1)	0.5177(5)	0.098(2)	8.9
N(1)	0.1837(9)	0.4279(5)	0.482(1)	3.1(3)
N(2)	0.109(1)	0.4873(6)	0.725(1)	4.1(4)
C(1)	0.288(1)	0.3048(8)	0.385(2)	4.5(5)
C(2)	0.407(2)	0.4113(7)	0.361(2)	4.5(5)
C(3)	0.206(1)	0.4937(7)	0.519(2)	3.5(4)
C(4)	0.169(1)	0.5217(6)	0.641(2)	3.7(5)
C(5)	0.088(1)	0.4242(8)	0.691(2)	4.2(5)
C(6)	0.127(1)	0.3928(7)	0.572(1)	3.4(4)
C(7)	−0.322(2)	0.272(1)	0.333(3)	9.4(9)
C(8)	−0.198(2)	0.2469(8)	0.312(2)	5.6(6)
C(9)	−0.021(1)	0.2904(8)	0.222(2)	3.7(5)
C(10)	0.034(1)	0.3537(6)	0.180(2)	3.3(4)
C(11)	0.126(1)	0.3488(7)	0.093(2)	3.8(5)
C(12)	0.196(1)	0.4074(8)	0.078(2)	4.8(5)
C(13)	0.168(1)	0.4673(7)	0.144(2)	3.7(5)
C(14)	0.248(2)	0.5285(8)	0.147(2)	5.3(6)
C(15)	0.413(3)	0.583(1)	0.051(3)	6.0
C(15′)	0.464(2)	0.573(1)	0.135(2)	6.0
C(16)	0.532(2)	0.603(1)	0.182(3)	6.0
C(16′)	0.443(3)	0.615(1)	−0.440(2)	6.0

nitrogen atom of quinoline occupies a basal position of the square pyramid together with a carbonyl, *trans* to the diene moiety while in compound **2**, the nitrogen atom of pyrazine coordinates to the apical position of the square pyramid leaving the basal plane to the two carbonyls and the diene moiety.

These differences are remarkable, taking into account that both complexes were obtained by either of two reaction routes, i.e. the thermal substitution of a diene ligand in a bis(diethylmuconate)monocarbonyliron(0) complex by a heterocycle and a carbonyl or the photochemical substitution of a CO in the (diethylmuconate)tricarbonyliron(0) complex by a heterocycle [5].

In case of the thermal reaction, the starting complex has, in the solid state, a structure with the two dienes in the basal plane of a square pyramid and the stronger π-bonding carbonyl ligand in the apical position [2]. As observed for substitution reactions in iron(0) complexes, the reaction mechanism may involve, as a first step, the opening of one of the iron–diene bonds and coordination of the *N*-heterocycle [9]. The second step would be the dissociation of the remaining η^2-diene with coordination of the CO. In both cases the structure of this product in solution is expected to be an equilibrium between a square pyramid and a trigonal bipyramid, though stereochemical nonrigidity in solution has been observed for other pentacoordinated complexes in solution [10]. The difference in behavior occurs during crystallization of the complexes with the formation of the square

TABLE 5

BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND **2**, WITH STANDARD DEVIATION IN PARENTHESES.

Fe–C(1)	1.79(2)	C(7)–C(8)	1.44(4)
Fe–C(2)	1.79(2)	C(8)–O(3)	1.47(2)
Fe–N(1)	2.00(1)	C(9)–O(3)	1.36(2)
Fe–C(10)	2.12(1)	C(9)–O(4)	1.17(2)
Fe–C(11)	2.06(1)	C(9)–C(10)	1.47(2)
Fe–C(12)	2.04(2)	C(10)–C(11)	1.40(3)
Fe–C(13)	2.14(2)	C(11)–C(12)	1.40(2)
C(1)–O(1)	1.12(2)	C(12)–C(13)	1.40(2)
C(2)–O(2)	1.13(2)	C(13)–C(14)	1.46(3)
C(3)–N(1)	1.34(2)	C(14)–O(5)	1.21(2)
C(3)–C(4)	1.39(3)	C(14)–O(6)	1.33(3)
C(4)–N(2)	1.32(2)	C(15)–O(6)	1.54(3)
C(5)–N(2)	1.30(2)	C(15)–C(16)	1.47(4)
C(5)–C(6)	1.38(3)	C(15′)–O(6)	1.54(3)
C(6)–N(1)	1.33(2)	C(15′)–C(16′)	1.47(4)
C(2)–Fe–C(1)	88.8(7)	C(5)–C(6)–N(1)	123(2)
N(1)–Fe–C(1)	100.7(7)	C(5)–N(2)–C(4)	115(2)
N(1)–Fe–C(2)	99.5(6)	O(3)–C(8)–C(7)	107(2)
C(10)–Fe–C(1)	94.2(6)	C(9)–O(3)–C(8)	111(1)
C(10)–Fe–C(2)	164.1(7)	O(4)–C(9)–O(3)	124(2)
C(10)–Fe–N(1)	95.3(6)	C(10)–C(9)–O(3)	109(1)
C(11)–Fe–C(1)	93.4(7)	C(10)–C(9)–O(4)	127(2)
C(11)–Fe–C(2)	125.1(7)	C(9)–C(10)–Fe	121(9)
C(11)–Fe–N(1)	133.5(6)	C(11)–C(10)–Fe	67.9(8)
C(11)–Fe–C(10)	39.2(7)	C(11)–C(10)–C(9)	118(1)
C(12)–Fe–C(1)	121.9(8)	C(10)–C(11)–Fe	72.8(9)
C(12)–Fe–C(2)	95.0(7)	C(12)–C(11)–Fe	69.4(9)
C(12)–Fe–N(1)	135.2(6)	C(12)–C(11)–C(10)	117(2)
C(12)–Fe–C(10)	70.2(7)	C(11)–C(12)–Fe	71(1)
C(12)–Fe–C(11)	40.0(7)	C(13)–C(12)–Fe	74(1)
C(13)–Fe–C(1)	160.9(7)	C(13)–C(12)–C(11)	118(2)
C(13)–Fe–C(2)	93.5(7)	C(12)–C(13)–Fe	66.6(9)
C(13)–Fe–N(1)	97.6(6)	C(14)–C(13)–Fe	123(1)
C(13)–Fe–C(10)	78.7(6)	C(14)–C(13)–C(12)	121(2)
C(13)–Fe–C(11)	69.9(6)	O(5)–C(14)–C(13)	123(2)
C(13)–Fe–C(12)	39.1(6)	O(6)–C(14)–C(13)	113(2)
O(1)–C(1)–Fe	174 (2)	O(6)–C(14)–O(5)	124(2)
O(2)–C(2)–Fe	178 (2)	C(15)–O(6)–C(14)	114(2)
C(3)–N(1)–Fe	122 (1)	C(15′)–O(6)–C(14)	117(2)
C(6)–N(1)–Fe	125 (1)	C(15′)–O(6)–C(15)	30(1)
C(6)–N(1)–C(3)	115 (1)	C(16)–C(15)–O(6)	108(2)
C(4)–C(3)–N(1)	121 (2)	C(16′)–C(15′)–O(6)	108(2)
N(2)–C(4)–C(3)	124 (1)		

pyramid structure detected in the solid state; in compound **1** the heterocycle rearranges to occupy the basal position and in compound **2** the apical position.

A simpler substitution mechanism may occur in the photochemical reaction. The first step involves photolysis of an iron-carbonyl bond and addition of the heterocycle in a trigonal bipyramidal complex, with subsequent rearrangement in solution to the equilibrium mixture of square pyramid trigonal bipyramid. During crystalli-

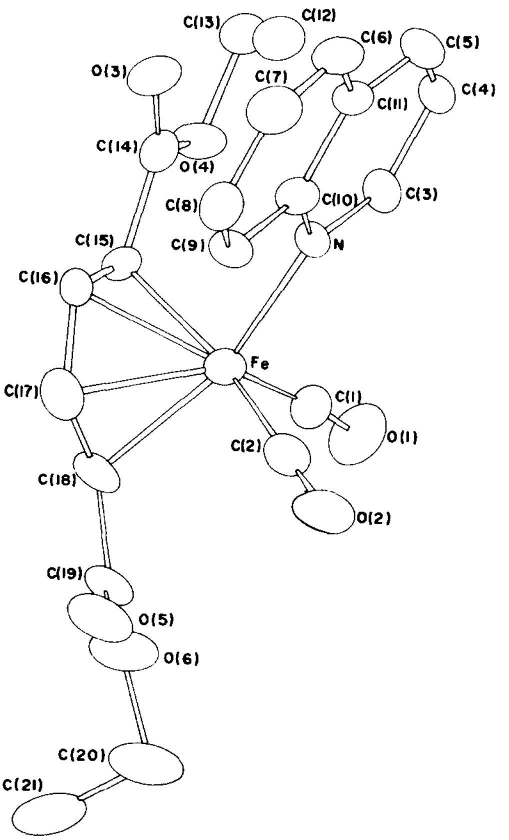

Fig. 1. Molecular structure of compound **1**, showing the atom labelling scheme.

zation, compounds **1** and **2** are formed, with the observed structure, as in the previous case.

The fact that one ligand coordinates in the apical and the other in the basal position could be related to the π-bonding ability of the ligands. As suggested by molecular orbital theory, better π-bonding ligands preferentially occupy the basal position, where overlap with the occupied t_{2g} metal orbitals is favored. Thus, the crystallization of the compound with quinoline in the basal position suggests that this ligand is a better π-ligand in comparison to pyrazine. On the other hand, as we observe in Fig. 1, the quinoline ring is located parallel to one of the ester groups of the diene ligand, suggesting a possible π–π interaction between the ester and the quinoline π-system. This reinforces the overlap cited above and gives preference to this structure. Basal coordination preference has been also observed for the isonitrile ligand in $(\eta^4\text{-}C_6H_8)(CO)_2(CNC_2H_5)Fe$ [11], at low temperature, as well as for a series of other similar complexes [12]. This was assigned to the donor capacity of the ligand in comparison to CO. Steric hindrance reasoning would have lead us to an opposite conclusion, since the bulkier quinoline ligand would be expected to occupy the less hindered, apical, position.

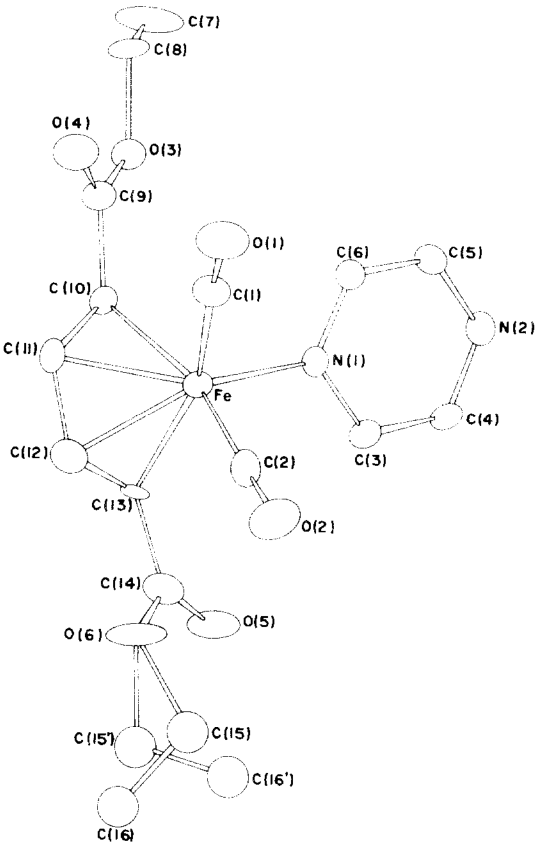

Fig. 2. Molecular structure of compound **2**, showing the atom labelling scheme.

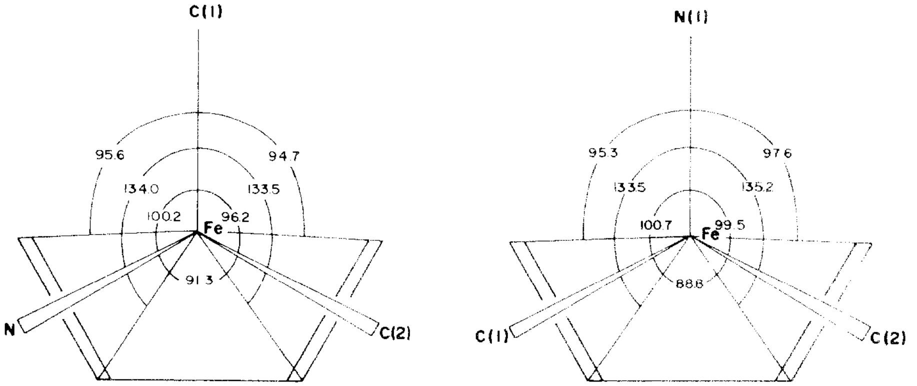

Fig. 3. Schematic representation of the coordination polyhedra in compound **1** (left) and compound **2** (right).

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