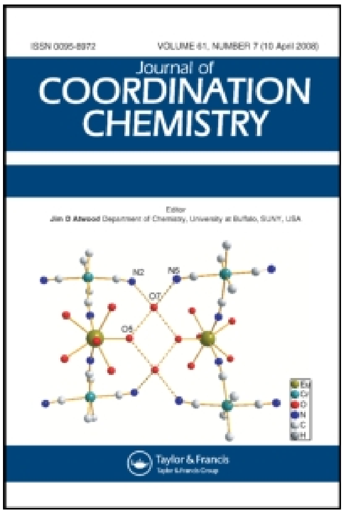

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SECONDARY ENAMINES AS LIGANDS. I. SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF GROUP VIII METALS WITH 2-(2-PYRIDINYLMETHYL)AMINO-3-(2-PYRIDINYLMETHYLENE)AMINO-2-BUTENEDINITRILE (PPH). CRYSTAL STRUCTURE OF THE IRON(II) COMPLEX $[Fe\{(PP)_2H\}]PF_6.2H_2O$

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SECONDARY ENAMINES AS LIGANDS. I. SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF GROUP VIII METALS WITH 2-(2-PYRIDINYLMETHYL)AMINO-3-(2-PYRIDINYLMETHYLENE)AMINO-2-BUTENEDINITRILE (PPH). CRYSTAL STRUCTURE OF THE IRON(II) COMPLEX $[Fe\{(PP)_2H\}]PF_6.2H_2O$

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Complexes of 2-(2-pyridinylmethyl)amino-3-(2-pyridinylmethylene)amino-2-butenedinitrile, (PPH), have been prepared with Fe(II), Co(II) and Ni(II). The complexes have the general formula $[M\{(PP)_2H\}]PF_6 \cdot 2H_2O$. Two dimorphs of the Fe(II) complex have been obtained, and single crystal x-ray structures of them have been completed. The molecular structures in the orthorhombic and monoclinic forms are closely related.

Keywords: Enamines, complexes, structures, synthesis, X-ray

INTRODUCTION

Diaminomaleonitrile (2,3-diamino-2-butenedinitrile, DAMN) is one, and by far the most easily available, of the rare compuonds carrying two vicinal $-NH_2$ groups on a carbon-carbon double bond. This compound can be used, as with the other more common 1,2-diamines, in the syntheses of polydentate ligands. Thus, three macrocycles[1-3] and monomeric[4] and polymeric[5] analogs of salen‡ were prepared from DAMN. Complexes of these Schiff-type bases were also investigated.[2-5]

We report here a new approach to the synthesis of ligands derived from DAMN. This approach is based on two features of DAMN chemistry: In mild reaction conditions only monocondensation is observed when DAMN is reacted with carbonylic compounds[6] and it is possible to reduce selectively the iminic function of a monocondensate product[7] to obtain a secondary enamine group. We note that non-cyclic secondary enamines can in principle coordinate to a transition metal center both through the double bond and the nitrogen atom. However, due to the well-known poor stability of these compounds, their coordination chemistry has been scarcely investigated. As far as we know only one example of the former coordination mode is

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‡ salen = *N,N'*-ethylenebis(salicylideneimine).

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known[8] and very few of nitrogen coordination.[9] We report here the synthesis of the ligand 2-(2-pyridinylmethyl)amino-3-(2-pyridinylmethylene)amino-2-butenedinitrile (PPH) and of its complexes with group VIII ions. The x-ray structure of the complex $[Fe\{(PP)_2H\}]\ PF_6 \cdot 2H_2O$ is presented.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker WH 270 spectrometer, using TMS as internal reference. Electronic spectra were obtained on a Perkin Elmer 320 spectrophotometer. IR spectra were recorded on a Perkin Elmer 457 spectrophotometer in Nujol mulls. Magnetic susceptibilities were measured by the Gouy method at 20° on a Bruker Magnet DM6 instrument. Measurements of molecular conductivities were made with 10^{-3} M nitromethane solutions using an Orion 101 conductimeter. Elemental analyses were performed by Analitische Laboratorium, Elbach, West Germany and by EFI, Naples, Italy.

Synthesis of PPH

The title compound was obtained by properly adapting a general procedure already described.[7] A solution of 15 g (0.138 mol) of DAMN, 14.86 g (0.138 mol) of pyridine-2-carboxyaldehyde and 3 drops of concentrated H_2SO_4 in 180 cm^3 of THF was stirred for 2 h. 2-amino, 3-(2-pyridinylmethylene)amino-2-butenedinitrile, identified by ^{1}H NMR spectroscopy (δ in CD_3COCD_3: 2.95 (NH_2, 2 H, bs), 7.4–8.7 (Ar-H, 4 H, m), 8.45 (CH=N, 1 H, s)) partially precipitates as a yellow solid. As its isolation is unnecessary, methanol (85 cm^3) was added to the slurry, followed by sodium borohydride (3.78 g, 0.100 mol) in portions over a 20 min period at 0°. The resulting solution was stirred for 20 min, concentrated to 80 cm^3 and poured into 500 cm^3 of cold water. The dark red precipitate was collected by filtration and dried (22.1 g). Chromatography on Florisil with methylene chloride as eluant gave 12.4 g (yield 46%) of 2-amino,3-(2-pyridinylmethyl)amino-2-butenedinitrile as light orange crystals which separated on cooling from the eluate after the solvent was partially evaporated: ^{1}H NMR (CD_3COCD_3)δ 4.45 (CH_2, 2 H, d), 5.2 (NH, NH_2, 3 H, bs), 7.2–8.6 (Ar-H, 4 H, m).

A slurry of 5.0 g (25.1 mmol) of the above compound, 2.7 g (25.1 mmol) of pyridine-2-carboxyaldehyde, 100 cm^3 of absolute ethanol and one drop of concentrated H_2SO_4 was stirred for 4 h. The resulting greenish solid was collected and dried (6.5 g). This crude product was dissolved in methylene chloride and filtered through a Florisil bed and recovered by evaporation of the solvent. Recrystallization from methylene chloride – propanol gave 5.4 g (75%) of PPH as yellow crystals. *Anal.* Found C 66.7; H 4.2; N 29.1%. $C_{16}H_{12}N_6$ requires C 66.66; H 4.19; N 29.15%. ^{1}H NMR (CD_2Cl_2): δ 4.70 (CH_2, 2 H, s), 7.30 (NH, 1 H, bs), 7.25–8.60 (Ar-H, 8 H, m), 8.37 (CH=N, 1 H, s). IR (nujol): 3310 (NH), 2260, 2220 (CN), 1630, 1610, 1570 (C=N and pyridyl ring) cm^{-1}. MP 140°C dec. $\lambda_{max}^{acetone}$ (log ε): 379 (4.31), 485 (2.06) nm.

Synthesis of metal complexes

$[Fe\{(PP)_2H\}]PF_6 \cdot 2H_2O$.

A solution of PPH (0.288 g, 1 mmol) in 80 cm^3 of methanol and a solution of $FeCl_2 \cdot 4H_2O$ (0.100 g, 0.5 mol) in 20 cm^3 of methanol were mixed. An instantaneous darkening of the solution was observed, but no precipitation occurred. A methanol solution of NH_4PF_6 (0.500 g, 3.1 mmol) was slowly added without stirring. During 3 h, dark-red crystals of $[Fe\{(PP)_2H\}]PF_6 \cdot 2\ H_2O$ were formed in 75% yield. *Anal.* Found C 47.4; H 3.25; N 20.5; Fe 6.9%. $C_{32}H_{27}N_{12}O_2FePF_6$ requires C 47.31; H 3.35; N 20.69; Fe 6.87%.

^{1}H NMR (CD_3COCD_3): δ 4.19, 4.81 (CH_2, 2 H, AB q); 7.05 - 8.90 (*CH*=N and Ar-*H*, 9 H, m). IR (nujol): 2240, 2200 (CN); 1605, 1520 (C=N and pyridyl ring) cm^{-1}. Λ = 106 Ω^{-1} cm^2 mol^{-1}. $\lambda_{max}^{acetone}$ (log ε): 397 (4.25), 490 (3.88) nm. The compound is diamagnetic.

[Co{(PP)$_2$H}]PF$_6$·H$_2$O and [Ni{(PP)$_2$H}]PF$_6$·2H$_2$O.

By following a procedure similar to that described for the iron complex, the title compounds were obtained.

[Co{(PP)$_2$H}]PF$_6$·2 H$_2$O: dark purple crystals (80% yield). *Anal.* Found C 46.8; H 3.1; N 20.4; Co 6.9%. $C_{32}H_{27}N_{12}O_2CoPF_6$ requires C 47.13; H 3.34; N 20.61; Co 7.23%. IR (nujol): 2190 (CN); 1605, 1515 (C=N and pyridyl ring) cm^{-1}. Λ = 103 Ω^{-1} cm^2 mol^{-1}. $\lambda_{max}^{acetone}$ (log ε): 338 (4.12), 520 (4.29) nm. μ_{eff} = 5.1 B.M.

[Ni{(PP)$_2$H}]PF$_6$·2 H$_2$O: bright red crystals (80% yield). *Anal.* Found C 47.5; H 3.2; N 20.2; Ni 7.0%. $C_{32}H_{27}N_{12}O_2NiPF_6$ requires C 47.14; H 3.34; N 20.61; Ni 7.20%. IR (nujol): 2190 (CN); 1605, 1525 (C=N and pyridyl ring) cm^{-1}. Λ = 92 Ω^{-1} cm^2 mol^{-1}. $\lambda_{max}^{acetone}$ (log ε): 342 (4.22), 508 (4.56) nm. μ_{eff} = 3.6 B.M.

X-ray data collection and solution of the structure of [Fe{(PP)$_2$H}]PF$_6$·2H$_2$O.

The crop of dark-red crystals obtained from the reaction mixture resulted to be mainly formed of disordered crystals. On careful examination, orthorhombic and monoclinic (with orthorhombic face-centred pseudosymmetry) single crystals could be selected.

Orthorhombic form.

A single crystal (0.4 × 0.2 × 0.02 mm) was selected for the crystallographic study. Accurate cell parameters were obtained by least-squares refinement of the setting angles of 22 reflections at medium ϑ (19° ≤ 2ϑ ≤ 21°), using MoKα filtered radiation and Enraf-Nonius CAD-4F diffractomer on line with a PDP 11/34 Digital computer. 2208 independent reflections (ϑ_{max} = 22°) were collected at room temperature, using the ω-2ϑ scan mode. During the data collection a maximum scan time of 90 sec was set for each reflection and the intensities of three standard reflections were monitored every 3 h (4% variation) in order to check the crystal and equipment stability. The relatively low linear absorption coefficient (μ = 56.5 cm^{-1}) made absorption corrections unnecessary. The space group *Pbcm* (no 57)[10] was assumed and confirmed by the successful refinement of the structure. The structure was solved by direct methods, using program MULTAN.[11] A difference Fourier synthesis based on the coordinates of all the atoms of the complex plus the P atom indicated that the PF_6^- ion was partially disordered and that two water solvent molecules were present per cation. The refinement of the structure (Fe and P anisotropic) was carried out by full matrix (on P) least-squares cycles using the 677 observed reflections ($I \leq 2.5\ \sigma(I)$). As the number of observations per parameter is low, full anisotropic refinement of the structure was not pursued. For the same reason a comprehensive treatment of the disorder for the PF_6^- and the water molecules was not attempted and the fluorine and oxygen atoms were refined starting from the positions corresponding to the maxima of the electron density map. At convergence the discrepancy *R* factor was 0.096 and R_w = 0.113 with weights obtained by counting statistics. All the hydrogen atoms, except those of the water molecules, were included in the last refinement cycles at idealized positions and the thermal parameters set equal to those of parent atoms.

Monoclinic form

A single crystal (0.5 × 0.2 × 0.02 mm) and MoKα radiation were used for the experimental work. The space group is the monoclinic *P2/c* (no 13).[10] Cell parameters

TABLE I
Crystal Data

	Orthorhombic form	Monoclinic form
formula	$[Fe\{(C_{16}H_{11}N_6)_2H\}]PF_6 \cdot 2H_2O$	
formula weight	812.46	
space group	*Pbcm*	*P2/c*
a, Å	9.420(2)	13.350(6)
b, Å	16.634(6)	9.338(5)
c, Å	21.894(4)	16.752(9)
β, degrees		126.73(6)
V, Å^3	3430(3)	1683(4)
Z	4	2
D_m, g/cm^3	1.58	1.59
D_x, g/cm^3	1.573	1.603
λ Mo*Kα* (Å)	0.71073	0.71073
ϑ_{max}, degrees	22	25
No. of indep. refl.	2208	2773
No. of refl. above 2.5σ	677	1291
R	0.096	0.066
R_w	0.113	0.072

were determined by least-squares refinement of the setting angles of 18 reflections with $18° \leq 2\vartheta \leq 20°$. 2773 independent reflections were collected ($\vartheta_{max} = 25°$) and all the X-ray work was carried out using the same procedure previously described for the orthorhombic form. The refinement of the positional and anisotropic temperature parameters for all non-hydrogen atoms provided the discrepancy index $R = 0.066$ for the 1291 observed reflections with $I \geqslant 2.5\,\sigma(I)$ and $R_w = 0.072$. The H atoms, except those of the water molecules, were generated at the expected positions and included in the last refinement cycles with thermal parameters equal to the B_{eq} values of the parent atoms. During all the crystallographic work, the equipment of the 'Centro di Metodologie Chimico-fisiche dell Università di Napoli' and the SDP package was used. Scattering factors were taken from Cromer and Waber.[12] Table I summarizes some crystal data for the two forms and final atomic parameters with esd in parentheses are given in Table II*.

RESULTS AND DISCUSSION

The preparation of PPH and its complexes is schematized below:

$$H_2NC(CN){=}C(CN)NH_2 \xrightarrow{C_5H_4NCHO} H_2NC(CN){=}C(CN)N{=}CHC_5H_4N \rightarrow$$

$$\xrightarrow{NaBH_4} H_2NC(CN){=}C(CN)NH\text{-}CH_2C_5H_4N \xrightarrow{C_5H_4NCHO}$$

$$\longrightarrow C_5H_4NCH{=}NC(CN){=}C(CN)NH\text{-}CH_2C_5H_4N \quad (PPH) \xrightarrow{MCl_2}$$

$$\longrightarrow [M\{(PP)_2H\}]^+Cl^- \quad (M = Fe, Co, Ni)$$

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*List of structure factors, hydrogen atoms parameters and anisotropic thermal parameters have been deposited.

TABLE II

Final positional parameters and isotropic or equivalent temperature factors* (A²) with esd in parentheses.

	Orthorhombic form				Monoclinic form			
Atom	*x/a*	*y/b*	*z/c*	B_{iso}/B_{eq}	*x/a*	*y/b*	*z/c*	B_{eq}
Fe	0.5554(5)	0.25	0.0	2.2(1)	0.0	0.4463(2)	0.2500(0)	2.77(4)
N(1)	0.699(2)	0.212(1)	−0.0567(9)	2.6(5)	0.1164(5)	0.2978(7)	0.2673(4)	3.2(2)
N(2)	0.556(2)	0.336(1)	−0.0574(9)	2.4(4)	0.1166(4)	0.4463(7)	0.3914(3)	2.7(2)
N(3)	0.425(3)	0.514(1)	−0.1192(10)	5.2(6)	0.2392(6)	0.5740(9)	0.6286(4)	4.9(2)
N(4)	0.203(3)	0.489(1)	0.0453(9)	4.6(5)	−0.0862(5)	0.8019(9)	0.4485(4)	4.7(2)
N(5)	0.410(2)	0.318(1)	0.0422(9)	2.2(4)	−0.0839(5)	0.5897(7)	0.2779(4)	2.8(2)
N(6)	0.166(2)	0.222(1)	0.0596(8)	1.9(4)	−0.1196(5)	0.8314(7)	0.1638(4)	3.6(2)
C(1)	0.777(3)	0.146(1)	−0.0534(11)	2.3(6)	0.1110(6)	0.2181(9)	0.1977(5)	3.6(2)
C(2)	0.880(3)	0.123(2)	−0.0978(12)	4.3(7)	0.1991(7)	0.1180(9)	0.2175(5)	4.0(2)
C(3)	0.896(3)	0.172(2)	−0.1492(13)	3.9(7)	0.2990(7)	0.0997(9)	0.3157(5)	4.4(2)
C(4)	0.816(3)	0.242(2)	−0.1542(11)	3.9(6)	0.3100(6)	0.1775(10)	0.3906(5)	3.9(2)
C(5)	0.721(2)	0.263(1)	−0.1070(9)	2.1(5)	0.2168(6)	0.2760(9)	0.3643(5)	3.1(2)
C(6)	0.639(3)	0.333(1)	−0.1042(11)	2.9(3)	0.2145(6)	0.3630(9)	0.4340(5)	3.3(2)
C(7)	0.462(2)	0.397(1)	−0.0425(10)	2.0(5)	0.0898(6)	0.5393(9)	0.4393(4)	3.0(2)
C(8)	0.439(3)	0.462(2)	−0.0851(13)	4.8(7)	0.1720(6)	0.5612(9)	0.5448(5)	3.4(2)
C(9)	0.391(2)	0.385(1)	0.0116(10)	2.5(6)	−0.0224(6)	0.6129(9)	0.3742(5)	2.9(2)
C(10)	0.288(3)	0.445(1)	0.0280(10)	2.4(6)	−0.0611(6)	0.7176(9)	0.4148(5)	3.4(2)
C(11)	0.349(2)	0.311(1)	0.1027(10)	2.1(5)	−0.2081(6)	0.6479(9)	0.2097(5)	3.1(2)
C(12)	0.254(2)	0.238(2)	0.1071(11)	3.1(6)	−0.2180(6)	0.7467(9)	0.1345(5)	3.4(2)
C(13)	0.242(3)	0.192(1)	0.1597(12)	3.5(6)	−0.3253(6)	0.7577(10)	0.0379(5)	3.7(2)
C(14)	0.145(3)	0.128(2)	0.1628(12)	4.2(7)	−0.3304(7)	0.8537(11)	-0.0285(6)	5.0(3)
C(15)	0.060(3)	0.114(1)	0.1110(11)	3.9(6)	−0.2295(7)	0.9382(11)	0.0045(5)	4.7(2)
C(16)	0.071(3)	0.161(1)	0.0614(12)	3.3(6)	−0.1271(6)	0.9231(9)	0.0997(5)	4.0(2)
P	0.193(1)	0.4898(8)	0.25	4.5(3)	0.5	0.1864(4)	0.75	4.3(1)
F(1)	0.189(3)	0.491(1)	0.184(1)	14.6(9)	0.5	0.0281(12)	0.75	15.7(4)
F(2)	0.173(4)	0.584(2)	0.25	10.9(10)	0.5	0.3405(12)	0.75	20.9(6)
F(3)	0.031(5)	0.481(3)	0.25	16.8(15)	0.4836(6)	0.1827(9)	0.6492(4)	10.5(2)
F(4)	0.207(4)	0.396(2)	0.25	10.8(10)	0.3655(6)	0.1839(15)	0.6980(6)	18.5(5)
F(5)	0.363(6)	0.497(3)	0.25	23.6(22)				
OW(1)	0.615(6)	0.399(3)	0.25	20.(2)	0.462(1)	0.580(1)	0.8414(8)	19.2(5)
OW(2)	0.515(7)	0.257(4)	0.25	24.(3)				

*$B_{eq} = 4/3\ \Sigma_i\ \Sigma_j\ b_{ij}a_ia_j$

The cationic complexes were precipitated as hexafluorophosphates. The complexes have conductivities in nitromethane which indicate that they are uni-univalent electrolytes, in agreement with the above general formula.

The observed diamagnetism of the iron complex is in line with the low spin state in an octahedral environment. The main absorption maxima in the visible absorption spectrum are similar to those observed for other octaheral Fe(II) complexes of terdentate ligands with imine functions.[13] For these complexes these types of bands are ascribed to electron transfer from the metal to the ligand. The magnetic moment of the cobalt complex at 20° is 5.1 B.M. This value is within the typical range of the moments exhibited by octahedral Co(II) complexes.[14] The electronic spectra show a band at 520 nm (log $\varepsilon = 4.29$). In an octahedral geometry, energy and intensity of this band can be accounted for on the basis of a large charge-transfer contribution.[15]

In the case of the nickel complex the ground for a reasonable assignment of the geometry from electronic spectra and magnetic measurements seems poor. The magnetic moment (3.6 B.M.) is near the lower limit for tetrahedral Ni(II) complexes.[14] An intense band at 508 nm, which appears to be substantially charge-transfer, is not diagnostic for geometry assignment.

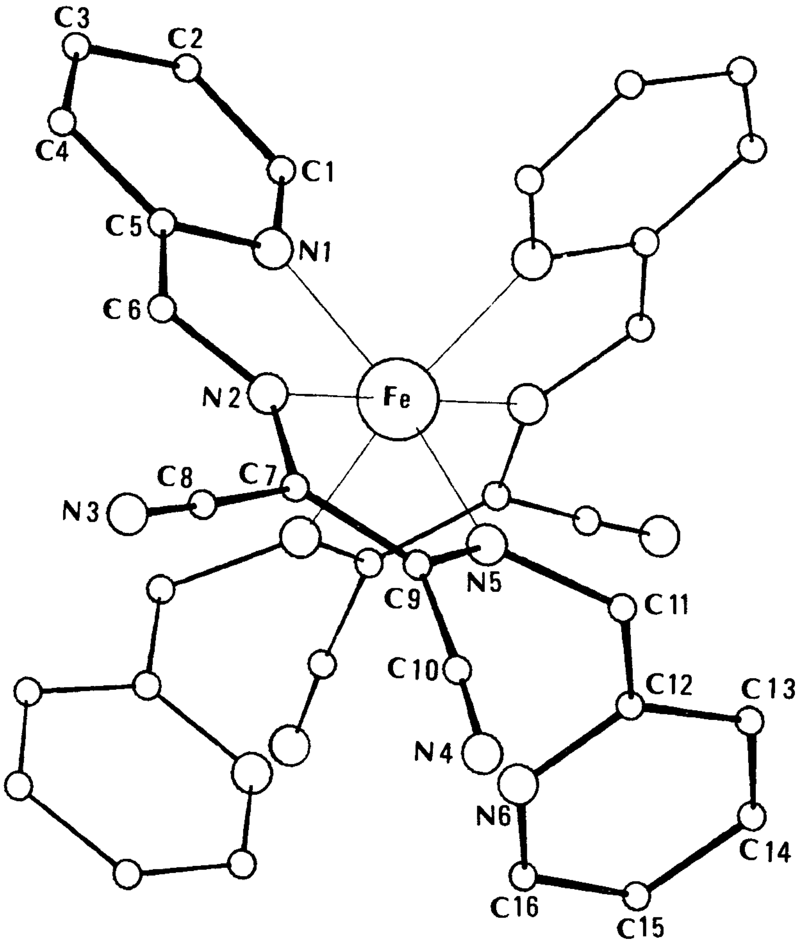

FIGURE 1 Molecular structure with the atomic numbering scheme used.

For all complexes deprotonation of the enaminic function is clearly indicated by the IR spectra. In fact no band attributable to NH stretching is observed. For the free ligand PPH the NH stretching is observed at 3310 cm^{-1}.

Description of the structure of $[Fe\{(PP)_2H\}]PF_6 \cdot 2H_2O$

In the two crystal forms the complex is present as single charged cations with octahedral coordinated metal ions bonded to two terdentate ligands. A view of the complex in the monoclinic structure is shown in Fig. 1, together with the numbering scheme used. Inter-atomic distances and angles are given in Table III. The lower accuracy of the orthorhombic structure is caused by the smaller number of reflections observed for this form. However the overall geometry of the complex is strictly similar in the two crystal forms and for this reason only the geometrical parameters of the monoclinic structure will be discussed in detail.

TABLE III

Bond distances (Å) and bond angles (°), with their esd in parentheses, for the orthorhombic (o) and monoclinic (M) forms.

Bond distances

	O	M		O	M
Fe-N(1)	1.94(2)	1.976(6)	C(4)-C(5)	1.41(3)	1.393(11)
Fe-N(2)	1.90(2)	1.904(4)	C(5)-C(6)	1.39(3)	1.440(8)
Fe-N(5)	2.01(2)	1.978(5)	C(7)-C(8)	1.44(3)	1.431(7)
N(1)-C(1)	1.33(3)	1.351(7)	C(7)-C(9)	1.37(3)	1.396(9)
N(1)-C(5)	1.42(3)	1.369(7)	C(9)-C(10)	1.44(3)	1.455(9)
N(2)-C(6)	1.29(3)	1.309(9)	C(11)-C(12)	1.51(3)	1.505(8)
N(2)-C(7)	1.39(3)	1.373(7)	C(12)-C(13)	1.39(4)	1.381(8)
N(3)-C(8)	1.15(3)	1.134(7)	C(13)-C(14)	1.40(4)	1.402(10)
N(4)-C(10)	1.14(3)	1.133(9)	C(14)-C(15)	1.41(4)	1.363(12)
N(5)-C(9)	1.31(3)	1.319(5)	C(15)-C(16)	1.34(4)	1.351(9)
N(5)-C(11)	1.45(3)	1.445(9)	P-F(1)	1.44(2)	1.485(12)
N(5)-C(12)	1.36(3)	1.352(9)	P-F(2)	1.59(3)	1.447(12)
N(6)-C(16)	1.35(3)	1.333(8)	P-F(3)	1.54(5)	1.568(7)
C(1)-C(2)	1.42(4)	1.392(11)	P-F(4)	1.56(3)	1.454(6)
C(2)-C(3)	1.40(4)	1.375(8)	P-F(5)	1.60(6)	
C(3)-C(4)	1.40(4)	1.383(9)			

Bond angles

	O	M		O	M
N(1)-Fe-N(2)	80(1)	80.3(4)	C(4)-C(5)-C(6)	126(4)	124.6(10)
N(1)-Fe-N(5)	163(1)	162.3(4)	N(2)-C(6)-C(5)	113(4)	113.3(10)
N(2)-Fe-N(5)	83(1)	82.1(4)	N(2)-C(7)-C(8)	120(4)	122.3(10)
Fe-N(1)-C(1)	128(3)	129.3(8)	N(2)-C(7)-C(9)	114(3)	113.0(9)
Fe-N(1)-C(5)	114(2)	113.9(7)	C(8)-C(7)-C(9)	126(4)	124.6(10)
C(1)-N(1)-C(5)	118(3)	116.8(9)	N(3)-C(8)-C(7)	177(5)	177.7(12)
Fe-N(2)-C(6)	120(3)	119.0(7)	N(5)-C(9)-C(7)	120(3)	117.8(10)
Fe-N(2)-C(7)	113(2)	115.0(7)	N(5)-C(9)-C(10)	123(3)	123.2(10)
C(6)-N(2)-C(7)	127(3)	126.0(7)	C(7)-C(9)-C(10)	116(3)	118.8(10)
Fe-N(5)-C(9)	110(2)	112.0(7)	N(4)-C(10)-C(9)	174(4)	177.0(12)
Fe-N(5)-C(11)	130(2)	127.9(7)	N(5)-C(11)-C(12)	111(3)	112.3(9)
C(9)-N(5)-C(11)	119(3)	119.0(10)	N(6)-C(12)-C(11)	118(3)	118.6(10)
C(12)-N(6)-C(16)	122(3)	120.0(10)	N(6)-C(12)-C(13)	118(4)	118.9(10)
N(1)-C(1)-C(2)	124(4)	124.8(10)	C(11)-C(12)-C(13)	123(4)	122.5(10)
C(1)-C(2)-C(3)	118(4)	116.7(11)	C(12)-C(13)-C(14)	121(4)	120.1(11)
C(2)-C(3)-C(4)	120(4)	121.4(11)	C(13)-C(14)-C(15)	117(4)	119.0(12)
C(3)-C(4)-C(5)	119(4)	118.3(11)	C(14)-C(15)-C(16)	121(4)	118.4(12)
N(1)-C(5)-C(4)	121(3)	122.0(10)	N(6)-C(16)-C(15)	121(4)	123.6(11)
N(1)-C(5)-C(6)	113(3)	113.4(10)			

The bis(terdentate) complexes have the *abf* structure, for which two enantiomorphous forms are possible. Both are present in the two crystal structures. The donor atoms are the pyridine N(1), the iminic N(2) and the enaminic N(5) nitrogens. The coordination polyhedron is a slightly distorted octahedron with crystallographic C2 symmetry.

The Fe-N(2) distance (1.904(4)Å) is slightly shorter than the other two Fe-N distances. On the average their values are well within the range expected for the low spin state of the iron ion,[16] in agreement with the observed diamagnetism of the

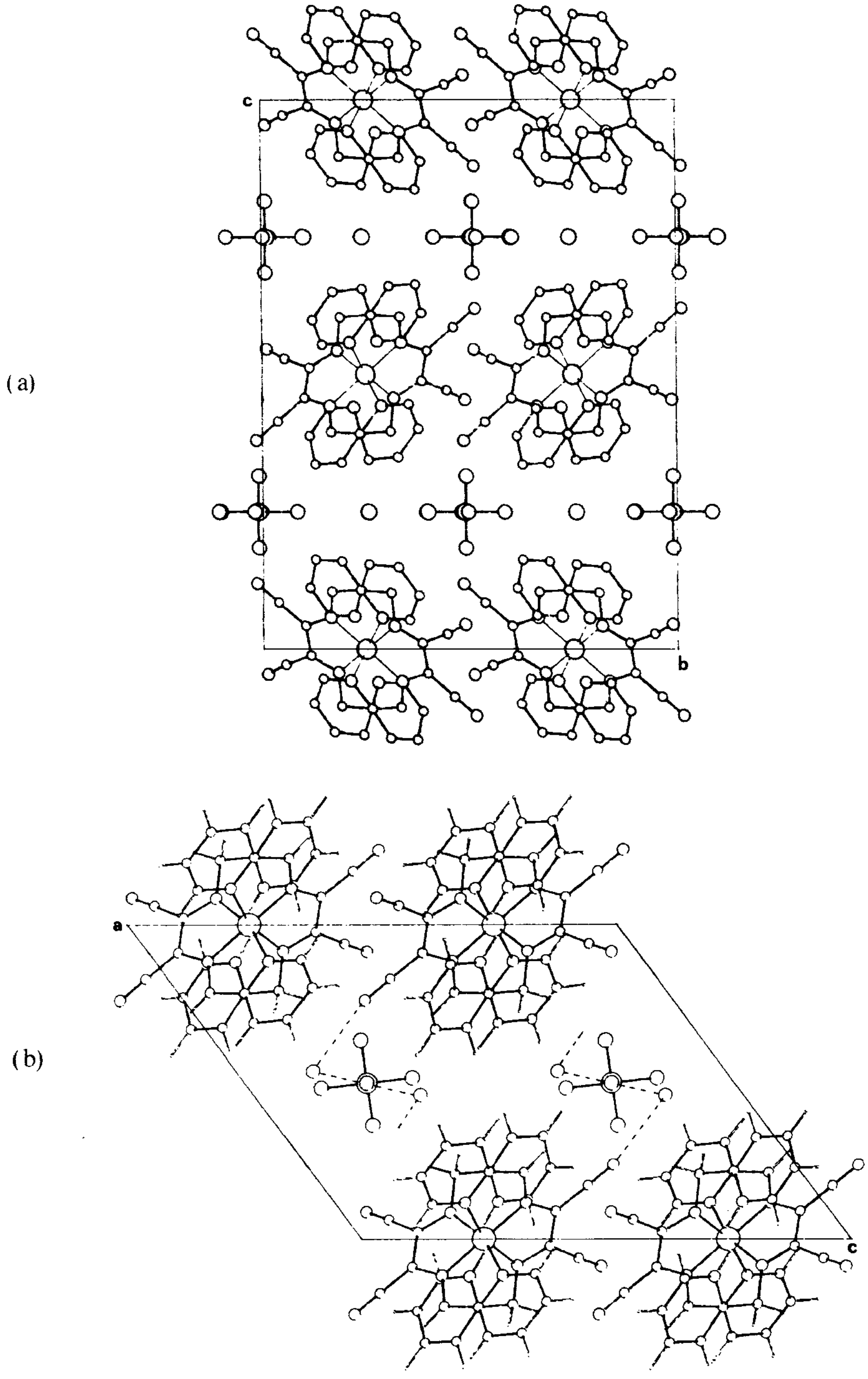

FIGURE 2 Crystal packing for the orthorhombic (a) and for the monoclinic (b) forms of the iron complex.

complex. The two five-membered chelate rings are fully planar. Indeed, with the exception of the methylene group and the attached uncoordinated pyridine ring, the ligand is planar and the atoms deviate at most 0.05(1)Å from the best plane. This is in agreement with the extensive conjugation between the coordinated aromatic pyridine ring and the diaminomaleonitrile group, as indicated by the values of the bond lengths and in particular by the shortening of the C(5)–C(6) bond compared to the value of the C(11)–C(12) bond (1.440(8) and 1.505(8) Å respectively). The values of the torsion angles about the N(5)-C(11) and C(11)-C(12) bonds are such that the plane of the uncoordinated pyridine ring is orthogonal to the rest of the ligand (90.9°) and nearly parallel to the coordinated diaminomaleonitrile group of the second ligand (10.5°). The intramolecular stacking of these two groups, at a vertical distance of 3.2Å, contributes to the stability of the complex. In addition the two uncoordinated pyridine nitrogens interact through the molecular diad axis forming a linear N-H· · ·N intramolecular hydrogen bond (N(6)· · ·N(6′) = 2.74(1)Å). This interaction implies that one of the two pyridine nitrogens is protonated. For symmetry reasons, the proton must be statistically placed on either side of the mid-point between N(6) and N(6′), while the two nitrogens act either as acceptor or as donor in the same hydrogen bond. It is worth noting that the value of 120(1)° for the C(12)–N(6)–C(16) bond angle is intermediate between the values expected for a protonated and unprotonated pyridine ring respectively.[17]

The crystal packing is organized in layers parallel to (100). Within the layers, the molecules of the complex are held together by van der Waals forces and stacking interactions involving the uncoordinated pyridine rings and the diaminomaleonitrile groups. The layers repeat by translation along the *a* axis and are separated by the PF_6^- anions, which have the phosphorus and two fluorine atoms sets on a crystallographic diad axis (Fig. 2a). The high values of the thermal parameters of the PF_6^- group and their anisotropy indicate that this group undergoes a marked oscillation about the F(3)-P axis, and justify qualitatively the observed pattern of the P–F bond lengths. The water molecule is hydrogen bonded to N(3) and to the fluorine atom F(2) on the diad axis, which in turn is linked through a second water molecule to the N(3) of the next layer, thus forming a sequential scheme of hydrogen bonds which stabilize the packing of layers (N(3)· · ·O(W2) = 2.98(1)Å, O(W1)· · ·F(2) = 2.93(1)A). In the orthorhombic crystals the layers, parallel to (010), are strictly conserved; in this case however two adjacent layers are related by mirror symmetry (Fig. 2b). The distance between the layers is slightly longer than in the monoclinic structure and the PF_6^- ions are placed on the mirror plane. In this case the water molecule and the PF_6^- anions are more disordered and no precise scheme for the hydrogen bonds is given. The strict similarity in the packing explains also the occurrence of the two crystal forms in the same crystallization batch.

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