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Syntheses of Iron(III) Aroyl Hydrazones Containing Pyridoxal and Salicylaldehyde. The Crystal and Molecular Structure of Two Iron(III)-pyridoxal Isonicotinoyl Hydrazone Complexes*

TERRANCE B. MURPHY**, NORMAN J. ROSE, VERNER SCHOMAKER and ALEJANDRO ARUFFO†

Department of Chemistry, University of Washington, Seattle, Wash. 98195, U.S.A.

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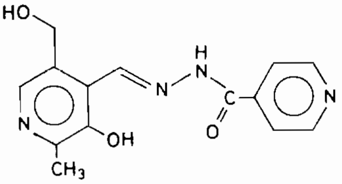
Abstract

Iron(III) complexes of three aroyl hydrazones, pyridoxal isonicotinoyl hydrazone (H_2pih), pyridoxal benzoyl hydrazone (H_2pbh), and salicylaldehyde benzoyl hydrazone (H_2sbh), were synthesized and characterized. In aqueous medium at pH 7, [Fe(pih)(Hpih)]·$3H_2O$ is formed. In acidic methanol, a 1:1 ligand-to-metal complex is formed, [$FeCl_2$(H_2pih)]Cl (**1**), whereas in aqueous medium at low pH *cis*-[$FeCl_2$(H_2pih)(H_2O)]Cl·H_2O (**2**) is formed. Compounds **1** and **2** are high-spin d^5 with $\mu_{eff} = 5.88$ μ_B and 5.93 μ_B (298 K). The crystal structures of **1** and **2** show that H_2pih acts as a tridentate neutral ligand in which the phenolic and hydrazidic protons have shifted to the pyridine nitrogen atoms. The coordination polyhedron of **1** is 'square' pyramidal, whereas that of **2** is pseudo-octahedral. Compound **1** is triclinic, space group $P\bar{1}$, with $a = 12.704(2)$ Å, $b = 8.655(2)$ Å, $c = 8.820(2)$ Å, $\alpha = 105.42(1)°$, $\beta = 89.87(1)°$, $\gamma = 107.60(1)°$, $V = 888$ Å^3, and $Z = 2$; **2** is monoclinic, space group $P2_1/c$, with $a = 15.358(4)$ Å, $b = 7.304(3)$ Å, $c = 17.442(4)$ Å, $\beta = 101.00(2)°$, $V = 1921$ Å^3, and $Z = 4$.

Introduction

In recent years, there has been considerable interest in natural iron chelators and their synthetic analogs [2–6]. Among these, the thiosemicarbazones have been investigated as potential antineoplastic agents [7–9], and others have been screened as trypanocides against African trypanosomiasis [10]. Another major reason for interest in natural and synthetic chelators is their clinical application in the treatment of iron-loading anemias, such as thalassemia, which cause the accumulation of excess iron in the tissues of the heart, lungs, and liver, and result in early adult death [11]. The iron chelator in clinical use today is desferrioxamine B (DFO), a naturally occurring trishydroxamic acid. Although highly specific for iron(III), DFO is not effective when taken orally and is thus administered by subcutaneous infusions over long periods of time. Because subcutaneous infusion is costly, the search for a more effective iron-chelator has continued.

In 1979, Ponka *et al.* [12] reported that the new iron-chelating agent, pyridoxal isonicotinoyl hydrazone (PIH), is effective at removing iron from reticulocytes. PIH is the Schiff base resulting from the condensation of pyridoxal with isonicotinic acid hydrazide*.



Since the preliminary report of Ponka *et al.* [12], several investigators have studied the efficacy of PIH and other structurally similar Schiff bases as ***in vitro*** and ***in vivo*** iron chelators [13–20]. It has also been found recently that PIH and other related tridentate chelators appear to be unusually potent inhibitors of DNA synthesis and cell growth in a variety of human and rodent cell lines grown in culture [21] and that an iron(III)–PIH complex will stimulate cell proliferation and differentiation as effctively as transferrin [22].

In the light of the original report of Ponka *et al.* [12] the synthesis of iron(III) complexes of PIH, pyridoxal benzoyl hydrazone (PBH), and salicylal-

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*Taken in part from ref. 1.

**Author to whom correspondence should be addressed. Present address: Department of Chemistry, Ithaca College, Ithaca, N.Y. 14850, U.S.A.

†Present address: Department of Biochemistry, Harvard University, Cambridge, Mass. 02138, U.S.A.

*In this paper, PIH represents the neutral, generic molecule, H_2pih the form where the hydrazidic and phenolic hydrogen atoms have been transferred to the pyridine nitrogen atoms, and $Hpih^-$ and pih^{2-} the anion and dianion of the molecule.

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dehyde benzoyl hydrazone (SBH) was undertaken. These studies were done in part to determine the mode by which PIH binds to iron, with a view to better understanding the iron(III)–PIH interaction *in vivo*. In this paper we report the synthesis and characterization of iron(III) complexes of these ligands and the X-ray structural analysis of two iron(III)–PIH compounds. A preliminary report of the crystal structures has appeared [23].

Experimental

Instrumentation

IR spectra (600–200 cm^{-1}) were recorded on either an IBM model 98 FT-IR or on a Perkin-Elmer 283 spectrophotometer with samples prepared as Nujol mulls between CsI plates. The remaining IR spectra were recorded on a Perkin-Elmer 727B spectrophotometer as Nujol or Kel-F mulls between KBr or CsI plates. The mass spectrum of PIH was measured on a Hewlett-Packard 5985 mass spectrometer at ionizing voltage 70 eV. UV and visible spectra were recorded on a Cary 219 spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer 650-10S fluorescence spectrophotometer. ^1H NMR spectra were run in D_2O on a Varian EM-360 spectrometer at 60 MHz. Chemical shifts, δ, are reported in ppm downfield from t-butanol. All pD values were calculated by adding 0.40 to the pH reading [24].

Room temperature magnetic susceptibilities were measured by the Faraday method with Hg[Co-$(NCS)_4$] as the calibrant [25] and are corrected by Pascal's constants [26]. The apparatus consisted of a Varian Associates V-4005 four-inch electromagnet and a Cahn model 4100 electrobalance. Melting points were obtained on a Thomas-Hoover apparatus in open capillaries and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan or Canadian Microanalytical Service, Ltd., Vancouver, B.C., Canada.

Materials

All solvents and starting materials were reagent grade where possible. Pyridoxal hydrochloride (Sigma Chemical Co.), benzoic acid hydrazide, and isonicotinic acid hydrazide (Aldrich Chemical Co.) were used without further purification.

Syntheses

PIH

The method of Sah [27] was used. When the crystalline product is recrystallized from methanol, the solubility decreases remarkably, and more than recrystallization is likely to be involved. For example, in a typical case, *ca.* 3 g of undried, crude product was stirred rapidly in 135 ml of methanol at 40 °C. The solution cleared (less than 1 min), and was filtered by gravity, with crystallization beginning immediately. To redissolve this recrystallized PIH required a total of 300–400 ml of boiling methanol. Adding 150–200 ml petroleum ether to such a solution once again induces crystallization. Yield of recrystallized product (pale yellow crystals): 75%; m.p. 261 °C dec (lit. [27] m.p. 261–262 °C dec); UV-Vis λ_{max} (MeOH): 214 nm (ϵ 24 000 M^{-1} cm^{-1}), 289(sh) (18 000), 297 (19 000), 306(sh) (17 000), 342 (9700) tailing off to 490 nm. Fluorescence spectrum: λ_{max} (MeOH) emission, 530 nm; λ_{max} (MeOH) excitation, 375 nm (primary), 337 nm (secondary). Mass spectrum: m/e (relative intensity) 286.1 (M^+, 5.5), 150.1 (92), 149.0 (66), 106.0 ($C_5H_4NCO^+$, 100), 78.1 (87). NMR (D_2O, pD = 11.6): δ (ppm from t-BuOH) 7.63 (s, 1H), 7.37 (d, 2H, $J = 5$ Hz), 6.53 (d, 2H, $J = 5$ Hz), 6.23 (s, 1H), 3.31 (s, $-CH_2-$), 1.13 (s, $-CH_3$).

PBH

To 2.04 g (10.0 mmol) of pyridoxal hydrochloride in 20 ml water were added 1.36 g (10.0 mmol) of benzoic acid hydrazide in 40 ml ethanol/water (1:1) and, with stirring, 1.0 g (12 mmol) of anhydrous sodium acetate in 10 ml water. The mixture was heated for 20 min on a steam bath and then cooled to room temperature. The resulting crude product was recrystallized as pale yellow crystals from ethanol/ether. Yield: 55%; m.p. 221–222.5 °C dec (lit. [28] m.p. 230 °C). *Anal.* Calcd for $C_{15}H_{15}N_3O_3$: C, 63.15; H, 5.20; N, 14.73. Found: C, 63.16; H, 5.32; N, 14.78. UV-Vis λ_{max} (MeOH): 230 nm(sh) (ϵ 8600 M^{-1} cm^{-1}), 286(sh) (12 000), 295 (14 000), 305(sh) (12 000), 339 (5600), 400(br) (930). Fluorescence spectrum: λ_{max} (MeOH) emission, 448 nm; λ_{max} (MeOH) excitation, 410 nm (primary), 400 nm (secondary). NMR (D_2O, pD = 12.1): δ (ppm from t-BuOH): 7.64 (s, 1H), 6.64 (m, 2H), 6.29 (m, 4H), 3.27 (s, $-CH_2-$), 1.10 (s, $-CH_3$).

SBH

This was prepared by literature methods [29]. This ligand appears to exist in two forms: from heated reaction mixtures, pale yellow crystals, m.p. 168–169 °C, from reactions run at room temperature, white crystals m.p. 181 °C. Recrystallization from hot $EtOH/H_2O$ gives crystals with the lower m.p. Both forms give the same iron–SBH complex (*vide infra*).

Dichloro(pyridoxal isonicotinoyl hydrazone) iron(III) chloride (1)

To a solution made by dissolving 0.27 g (1.0 mmol) $FeCl_3 \cdot 6H_2O$ in 10 ml absolute methanol was added 0.29 g (1.0 mmol) solid PIH with continuous stirring. The resulting red-brown solution cleared in about 2 min as the PIH dissolved, and a red-brown solid began to form. After stirring *ca.* 20 min, the solid was collected, washed with methanol, then ether, and air dried. Yield: 0.38 g, 85%. Recrystallization from methanol/ether yields red crystals, m.p. 260 °C (dec). *Anal.* Calcd for $C_{14}H_{14}N_4O_3Cl_3Fe$: C, 37.49; H, 3.15; N, 12.49; Cl, 23.71; Fe, 12.45. Found: C, 37.48; H, 3.20; N, 12.34; Cl, 22.69, 23.36, 23.22; Fe, 11.84. Magnetic susceptibility (297.9 K): $\chi_g^T = 3.19 \times 10^{-5}$, $\mu_{eff} = 5.88\ \mu_B$.

Cis-dichloroaquo(pyridoxal isonicotinoyl hydrazone) iron(III) chloride monohydrate (2)

$[FeCl_2(H_2pih)]Cl$ (0.25 g, 0.56 mmol) was dissolved in 20 ml H_2O and ~5 g NaCl was added with stirring. The solution was filtered and allowed to stand several days. The red-brown micro-crystalline product was collected and dried overnight *in vacuo* over P_4O_{10}. Yield: 0.16 g, 60%. No suitable method was found for recrystallizing the product. However, crystals suitable for X-ray diffraction studies were obtained when 6.8 g of NaCl was used in the synthesis. The solution was then stirred for 10 min, and the solid which had formed was filtered off. After allowing the mother liquor to stand for 7 days, 0.07 g of crystals were collected. *Anal.* Calcd for $C_{14}H_{18}N_4O_5Cl_3Fe$: C, 34.70; H, 3.74; N, 11.56; Cl, 21.95. Found: C, 34.73; H, 3.28; N, 11.46; Cl, 22.31. Magnetic susceptibility (298.2 K): $\chi_g^T = 2.99 \times 10^{-5}$, $\mu_{eff} = 5.93\ \mu_B$.

Dichloro(pyridoxal benzoyl hydrazone) iron(III) chloride monomethanolate (3)

To a solution of $FeCl_3 \cdot 6H_2O$ (0.21 g (0.78 mmol) in 23 ml methanol) was added 0.22 g (0.77 mmol) solid PBH. After stirring for 2 min, the resulting clear red-brown solution was filtered and left standing for 2 days. Yellow-brown crystals were collected, washed with methanol, then ether, and air dried. Yield: 0.16 g, 43%; m.p. 230 °C dec. The product can be recrystallized by dissolving in methanol and using ether to induce crystallization. *Anal.* Calcd for $C_{16}H_{19}N_3O_4Cl_3Fe$: C, 40.07; H, 3.99; N, 8.76; Cl, 22.18; Fe, 11.65. Found: C, 40.08; H, 3.90; N, 8.62; Cl, 23.15; Fe, 11.66. Magnetic susceptibility (297.2 K): $\chi_g^T = 3.04 \times 10^{-5}$, $\mu_{eff} = 5.94\ \mu_B$.

Cis-dichloro(salicylaldehyde benzoyl hydrazonato)-(methanol) iron(III) (4)

To 0.54 g (2.0 mmol) $FeCl_3 \cdot 6H_2O$ in methanol (20 ml) was added 0.48 g (2.0 mmol) SBH. The resulting deep green solution was filtered and cooled to 5 °C for 1 day. Fine, green crystals were collected, washed twice with ethanol, and then with ether. Yield: 0.40 g, 50%. *Anal.* Calcd for $C_{15}H_{15}O_3N_2Cl_2Fe$: C, 45.26; H, 3.80; N, 7.04; Cl, 17.81. Found: C, 45.21; H, 3.65; N, 7.01; Cl, 18.30. Magnetic susceptibility (297.7 K): $\chi_g^T = 3.61 \times 10^{-5}$, $\mu_{eff} = 5.89\ \mu_B$.

(Pyridoxal isonicotinoyl hydrazonato)(pyridoxal isonicotinoyl hydrazonato(2−)) iron(III) monohydrate monomethanolate (5)

PIH (0.79 g, 2.76 mmol) was dissolved in a solution containing 0.17 g of 97.8% NaOH (4.16 mmol) in 45 ml methanol. $FeCl_3 \cdot 6H_2O$ (0.38 g, 1.41 mmol) dissolved in 10 ml methanol was added, and the resulting deep red-brown solution was filtered and allowed to stand. Tiny black crystals, appearing within 1 h, were collected after 24 h, washed twice with methanol/ether (1:1) and twice with ether, and dried in air; yield 0.80 g, 86%. Attempts to recrystallize this product from hot methanol (in which it is reasonably soluble) were not successful. The product can be dissolved in boiling methanol, but the IR spectra of the precipitate upon cooling and of the starting material are slightly different; a second 'recrystallization' yields a material that is no longer soluble in boiling methanol and has a different IR spectrum. Because of these changes, characterization was undertaken on the original microcrystalline product. *Anal.* Calcd for $FeC_{28}H_{25}O_6N_8 \cdot H_2O \cdot CH_3OH$: C, 51.57; H, 4.63; N, 16.59; Fe, 8.27. Found: C, 51.78; H, 4.64; N, 16.59; Fe, 8.48. Numerous attempts were made to obtain X-ray diffraction data on these crystals, either coated with glue or sealed in glass capillaries together with an aliquot of mother liquor, but in all cases they ceased to diffract after a few hours in the X-ray beam.

Crystallographic Data

Intensity measurements were made at ambient temperature on a Picker FACS-I diffractometer with Nb-filtered (3-mil) Mo K_α radiation ($\lambda = 0.71069$ Å) with a take-off angle of 2°. Data were collected using $\theta/2\theta$ scans at a scan rate of 2° in 2θ/minute. Crystallographic computations were performed on a VAX 11/780 computer with programs available in the X-RAY system, version 1976 [30], or programs locally available from the Laboratory for Crystallography, Department of Chemistry, University of Washington. The atomic scattering factors used for chlorine, oxygen, nitrogen, and carbon were taken from Cromer and Mann [31], for iron from Doyle and Turner [32], and for hydrogen from Stewart *et al.* [33].

$[FeCl_2(H_2pih)]Cl$ (1)

A thin needle ($0.38 \times 0.10 \times 0.05$ mm) was mounted along *b*. Photographs indicated triclinic symmetry; the intensity statistics suggested that the crystal was centric; and a successful model was found with space group $P\bar{1}$.

Least-squares adjustment of the positions of 28 reflections (14 pairs at $\pm 2\theta$, $27° \leqslant 2\theta \leqslant 41°$) gave $a = 12.704(2)$ Å, $b = 8.655(2)$ Å, $c = 8.820(2)$ Å, $\alpha = 105.42(1)°$, $\beta = 89.87(1)°$, $\gamma = 107.60(1)°$, $V = 888$ Å^3. Other parameters: $Z = 2$, $d_{\text{calc}} = 1.678$ g/cm^3, $d_{\text{obs}} = 1.65$ g/cm^3, $F(000) = 454$, $M_r = 448.5$.

The intensities were measured twice with the same crystal and then averaged (*vide infra*): 20 second background counts at each side of the peak; 3496 $\pm h$, $\pm k$, $l \geqslant 0$ reflections, $3° \leqslant 2\theta \leqslant 50°$; five standard reflections, monitored every 250 reflections (every 300 reflections for the second set), indicated no decay. Equivalent reflections in each data set were averaged, after which the two sets were combined by summing the two net intensities ($I_{\text{sum}} = I_1 + I_2$, $I_i = S_i - T_iB_i$) and their estimated variances ($\sigma_{\text{sum}}{}^2 = \sigma_1{}^2 + \sigma_2{}^2$, $\sigma_i{}^2 = S_i + T_i{}^2B_i + P^2I_i{}^2$) for each reflection, where S_i is the scan count, T_i the ratio of scan and total background times, B_i the total background count, and P the so-called instability constant, which was taken as zero, the indicated value from the standards being small (~0.5%). Intensities were converted to F and $\sigma(F)$ values by X-RAY [30], which gave 3133 inequivalent F_o s, 2416 of which were greater than three times their σ values.

Trial positions of the iron and three chlorine atoms were deduced from a three-dimensional Patterson map. In subsequent electron density maps the positions of the remaining non-hydrogen atoms were obtained. The hydrogen atoms were given bond lengths (CH or NH) of 1.0 Å and, except for the methyl hydrogen atoms and the hydroxy methyl hydrogen atom, H(31), the obvious nominal directions. The methyl hydrogen atoms were found in a Fourier difference map, and H(31), which was not clearly indicated by the difference map, was placed along the line between its oxygen O(3), and Cl(3). Non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement was done on F with $1/\sigma_{(F)}{}^2$ weights. (The hydrogen positions were fixed, but most of their U values were isotropically refined. For H(31) and H(142), the isotropic U was fixed at 0.127 Å^2.) Anomalous dispersion terms (f′ and f″ from ref. 34) were included for all non-hydrogen atoms. The refinement (see Tables I and III) converged at $R = 0.065$, $R_w = 0.042$, GOF = 1.81, with last-cycle shift/e.s.d. 0.029 maximum and 0.0033 average. The final difference Fourier map showed excursions of electron density of 1.7, 0.8, 0.6, and 0.5 e/Å^3 in the vicinity of the iron and chlorine atoms, respectively. There was one peak of 0.7 e/Å^3 near H(143), but placing H(143) in that location gave a CH distance that was much too long, and H(143) was left in its present location.

TABLE I. Final Positional Parameters With their Estimated Standard Deviations for [$FeCl_2(H_2pih)$]Cl, (1).

Atom	x	y	z
Fe(1)	−0.13496(8)	0.17465(13)	0.30402(11)
Cl(1)	−0.1146(2)	−0.0588(2)	0.1479(2)
Cl(2)	−0.2509(1)	0.2554(2)	0.1754(2)
Cl(3)	−0.4670(1)	0.2814(3)	0.8667(2)
O(1)	−0.2496(3)	0.0960(6)	0.4424(5)
O(2)	−0.0061(3)	0.3516(6)	0.2883(5)
O(3)	0.4129(3)	0.4409(6)	0.6728(5)
N(1)	−0.4532(5)	−0.1688(7)	0.8326(7)
N(2)	−0.1103(4)	0.1235(7)	0.6218(6)
N(3)	−0.0474(4)	0.1993(6)	0.5168(6)
N(4)	0.2850(4)	0.5153(7)	0.2932(6)
C(1)	−0.4076(5)	−0.0779(8)	0.6070(8)
C(2)	−0.4851(5)	−0.1528(9)	0.6962(9)
C(3)	−0.3459(6)	−0.1134(9)	0.8915(8)
C(4)	−0.2660(5)	−0.0341(9)	0.8060(8)
C(5)	−0.2960(5)	−0.0134(8)	0.6644(7)
C(6)	−0.2132(5)	0.0744(8)	0.5683(7)
C(7)	0.0570(5)	0.2655(8)	0.5604(8)
C(8)	0.1366(5)	0.3522(8)	0.4679(8)
C(9)	0.2518(5)	0.4010(8)	0.5116(7)
C(10)	0.3235(5)	0.4808(8)	0.4191(8)
C(11)	0.1778(6)	0.4741(8)	0.2468(8)
C(12)	0.0980(5)	0.3889(8)	0.3366(8)
C(13)	0.2962(5)	0.3670(8)	0.6522(8)
C(14)	0.1445(6)	0.5140(9)	0.1045(8)

Atom [bonded to]	x	y	z
H(1)[C(1)]	−0.431(4)	−0.069(6)	0.502(5)
H(2)[C(2)]	−0.565(4)	−0.195(7)	0.658(6)
H(3)[C(3)]	−0.325(5)	−0.129(7)	0.994(7)
H(4)[C(4)]	−0.187(4)	0.010(6)	0.848(5)
H(7)[C(7)]	0.085(4)	0.257(6)	0.663(6)
H(10)[C(10)]	0.405(4)	0.514(6)	0.445(6)
H(11)[N(1)]	−0.511(6)	−0.225(8)	0.895(8)
H(31)[O(3)]	0.444(6)	0.429(9)	0.769(8)
H(41)[N(4)]	0.340(5)	0.576(7)	0.231(6)
H(131)[C(13)]	0.263(4)	0.417(6)	0.748(6)
H(132)[C(13)]	0.278(4)	0.243(5)	0.635(5)
H(141)[C(14)]	0.103(5)	0.597(8)	0.136(7)
H(142)[C(14)]	0.212(6)	0.565(9)	0.055(8)
H(143)[C(14)]	0.096(6)	0.407(9)	0.026(8)

[$FeCl_2(H_2pih)(H_2O)$]$Cl \cdot H_2O$ (2)

A red-brown crystal (0.085 × 0.15 × 0.26 mm) was mounted along *b*. Oscillation and Weisenberg photographs indicated monoclinic symmetry, and systematic absences ($h0l$ for l odd and $0k0$ for k odd) indicated the space group to be $P2_1/c$. Least-squares adjustment of the positions of 28 reflections (14 pairs at $\pm 2\theta$, $14° \leqslant 2\theta \leqslant 26°$) gave $a = 15.358(4)$ Å, $b = 7.304(3)$ Å, $c = 17.442(4)$ Å, $\beta = 101.00(2)°$, $V = 1921$ Å^3. Other parameters: $Z = 4$, $d_{\text{calc}} = 1.675$ g/cm^3, $d_{\text{obs}} = 1.65$ g/cm^3, $F(000) = 988$, MW = 484.5.

TABLE II. Final Positional Parameters With their Estimated Standard Deviations For $[FeCl_2(H_2pih)(H_2O)]Cl \cdot H_2O$, (**2**).

Atom	*x*	*y*	*z*
Fe(1)	0.74655(7)	0.49723(22)	0.16493(6)
Cl(1)	0.6626(2)	0.7686(4)	0.1678(1)
Cl(2)	0.8013(1)	0.5061(4)	0.2961(1)
Cl(3)	0.1605(1)	0.5975(3)	0.4962(1)
O(1)	0.6374(3)	0.3466(8)	0.1672(3)
O(2)	0.8369(3)	0.6227(9)	0.1247(3)
O(3)	0.8414(4)	0.5329(9)	−0.2229(3)
O(4)	0.8187(4)	0.2499(9)	0.1630(3)
O(5)	0.5435(6)	0.1408(14)	0.3609(5)
N(1)	0.3464(4)	0.0406(11)	0.0948(4)
N(2)	0.6135(4)	0.3499(10)	0.0317(4)
N(3)	0.6938(4)	0.4403(9)	0.0452(3)
N(4)	0.9737(4)	0.7263(10)	−0.0105(4)
C(1)	0.4453(5)	0.1893(13)	0.0268(5)
C(2)	0.3663(5)	0.1080(13)	0.0272(5)
C(3)	0.4042(6)	0.0566(15)	0.1632(5)
C(4)	0.4857(6)	0.1375(14)	0.1657(5)
C(5)	0.5072(6)	0.2098(12)	0.0959(5)
C(6)	0.5915(5)	0.3076(12)	0.0995(5)
C(7)	0.7276(5)	0.4721(13)	−0.0161(4)
C(8)	0.8120(5)	0.5631(11)	−0.0128(4)
C(9)	0.8458(5)	0.5842(12)	−0.0830(4)
C(10)	0.9259(6)	0.6632(12)	−0.0800(5)
C(11)	0.9445(5)	0.7181(12)	0.0572(5)
C(12)	0.8623(5)	0.6346(12)	0.0571(5)
C(13)	0.7952(5)	0.5055(15)	−0.1607(4)
C(14)	0.9997(5)	0.7939(12)	0.1283(5)

Atom [bonded to]	*x*	*y*	*z*
H(1)[C(1)]	0.457(3)	0.240(8)	−0.021(3)
H(2)[C(2)]	0.322(4)	0.097(9)	−0.023(4)
H(3)[C(3)]	0.388(4)	0.009(10)	0.212(3)
H(4)[C(4)]	0.529(5)	0.146(12)	0.216(4)
H(7)[C(7)]	0.694(3)	0.432(8)	−0.068(3)
H(10)[C(10)]	0.951(5)	0.676(11)	−0.129(4)
H(11)[N(1)]	0.288(5)	−0.021(13)	0.093(4)
H(31)[O(3)]	0.798(6)	0.568(13)	−0.269(5)
H(41)[N(4)]	1.033(4)	0.781(9)	−0.010(3)
H(42)[O(4)]	0.827(6)	0.151(14)	0.203(5)
H(43)[O(4)]	0.826(6)	0.201(13)	0.111(5)
H(51)[O(5)]	0.481(6)	0.178(13)	0.354(5)
H(52)[O(5)]	0.565(5)	0.143(13)	0.418(5)
H(131)[C(13)]	0.785(3)	0.371(8)	−0.154(3)
H(132)[C(13)]	0.735(3)	0.563(7)	−0.174(3)
H(141)[C(14)]	1.008(5)	0.699(11)	0.170(4)
H(142)[C(14)]	0.969(4)	0.903(9)	0.146(3)
H(143)[C(14)]	1.059(4)	0.831(9)	0.118(4)

Intensity data: 10-second backgrounds were measured at each side of the peak; 2650 $\pm h, k \geqslant 0, l \geqslant 0$ reflections, $2° \leqslant 2\theta \leqslant 56°$. A survey mode was used during the collection of the $35° < 2\theta \leqslant 56°$ shell of data, any reflection being passed over if its preliminary 2-second peak count was <18. Five standards monitored every 250 reflections gave P = 0.01, used in $\sigma_I^2 = S + T^2B + P^2I^2$, *vide supra*. The total number of inequivalent reflections was 2299, of which 2005 had $F_0 \geqslant 3\sigma(F_0)$ and were used in the final structure determination.

The positions of the iron and two of the chlorine atoms were obtained from a three-dimension Patterson map and the rest of the non-hydrogen atoms were found in subsequent Fourier difference maps. The bonds to hydrogen atoms (OH, NH, CH) were all set at 1.0 Å and, except for the methyl group, the water molecule, and hydroxy methyl hydrogen (H(31)), in the obvious nominal directions. The methyl directions were taken from a Fourier difference map, the water directions to give linear hydrogen bonds, and the H(31) direction so as to be structurally reasonable. Full-matrix least-squares refinement was done on F with $1/\sigma_{(F)}^2$ weights (The positions of all hydrogen atoms were fixed, but most of their U values were isotropically refined. For H(31), H(42), H(43), H(51), and H(52) the isotropic U was fixed at 0.127 Å^2). Anomalous dispersion terms were included for all non-hydrogen atoms. The refinement (see Tables II and IV) converged at R = 0.069, R_w = 0.052, GOF = 1.57, with last-cycle shift/e.s.d. 0.133 maximum and 0.0056 average. In the final Fourier difference map, the largest peak (1.2 e/Å^3) was near the iron atom, and the second and third largest peaks were 0.7 and 0.5 e/Å^3.

Results and Discussion

Syntheses

1:1 Complexes

Equimolar amounts of $FeCl_3 \cdot 6H_2O$ and PIH dissolved in methanol yield red-brown crystals of **1**. The amount of water present during synthesis is crucial, and in a typical $[FeCl_2(H_2pih)]Cl$ synthesis, it amounts to *ca.* 1%, primarily due to the use of $FeCl_3 \cdot 6H_2O$. If, however, methanol is used that contains more than 1% water, a mixture of **1** and **2** is formed. Stirring this mixture in absolute methanol converts it to **1**. When methanol is used that contains 10% water, a new product, which has not been fully characterized, is formed*. Thus, in methanol, the range of water concentration associated with the formation of **2** is greater than 1% but less than 10%.

Compound **1** is readily soluble in water giving an acidic solution (pH ~2 for a 0.05 M solution) which

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*If the synthesis of $[FeCl_2(H_2pih)]Cl$ is attempted in 95% EtOH, the only product is again this uncharacterized material.

TABLE III. Bond Distances (Å) and Angles (deg) for $[FeCl_2(C_{14}H_{14}N_4O_3)]Cl$, (1).

Coordination polyhedron			
Fe–O(1)	1.977(4)	Fe–Cl(1)	2.209(2)
Fe–O(2)	1.908(4)	Fe–Cl(2)	2.235(2)
Fe–N(3)	2.111(6)		
Ligand			
C(1)–C(2)	1.375(10)	C(7)–C(8)	1.454(10)
C(2)–N(1)	1.325(11)	C(8)–C(9)	1.418(9)
N(1)–C(3)	1.354(9)	C(9)–C(10)	1.374(9)
C(3)–C(4)	1.386(10)	C(10)–N(4)	1.352(10)
C(4)–C(5)	1.378(10)	C(11)–N(4)	1.334(9)
C(5)–C(1)	1.397(9)	C(11)–C(12)	1.432(10)
C(5)–C(6)	1.502(9)	C(12)–C(8)	1.405(11)
C(6)–O(1)	1.283(9)	C(11)–C(14)	1.481(11)
C(6)–N(2)	1.292(8)	C(12)–O(2)	1.307(8)
N(2)–N(3)	1.389(8)	C(13)–C(9)	1.497(10)
N(3)–C(7)	1.289(8)	C(13)–O(3)	1.416(7)
Coordination polyhedron			
O(1)–Fe–Cl(2)	91.86(16)	O(1)–Fe–Cl(1)	104.67(15)
O(1)–Fe–N(3)	74.49(18)	N(3)–Fe–Cl(1)	102.12(17)
N(3)–Fe–O(2)	82.64(20)	O(2)–Fe–Cl(1)	105.39(15)
O(2)–Fe–Cl(2)	94.89(18)	O(1)–Fe–O(2)	145.32(18)
Cl(2)–Fe–Cl(1)	108.12(8)	N(3)–Fe–Cl(2)	149.15(16)
Chelate rings			
C(6)–O(1)–Fe	115.2(4)	C(7)–N(3)–Fe	129.7(5)
O(1)–C(6)–N(2)	125.6(6)	N(3)–C(7)–C(8)	123.3(7)
C(6)–N(2)–N(3)	107.6(5)	C(7)–C(8)–C(12)	119.3(6)
N(2)–N(3)–Fe	115.4(3)	C(8)–C(12)–O(2)	125.2(6)
N(2)–N(3)–C(7)	114.8(6)	C(12)–O(2)–Fe	132.0(5)
Ligand			
C(5)–C(1)–C(2)	119.4(7)	C(9)–C(10)–N(4)	120.9(6)
C(1)–C(2)–N(1)	119.9(6)	C(10)–N(4)–C(11)	124.3(6)
C(2)–N(1)–C(3)	123.1(6)	C(12)–C(11)–N(4)	118.1(7)
N(1)–C(3)–C(4)	118.4(7)	C(11)–C(12)–C(8)	118.4(6)
C(3)–C(4)–C(5)	120.3(6)	C(12)–C(8)–C(9)	120.6(6)
C(4)–C(5)–C(1)	118.8(6)	C(11)–C(12)–O(2)	116.3(7)
C(4)–C(5)–C(6)	122.6(6)	C(12)–C(11)–C(14)	122.0(6)
C(1)–C(5)–C(6)	118.6(6)	C(14)–C(11)–N(4)	119.9(6)
C(5)–C(6)–O(1)	118.1(5)	C(13)–C(9)–C(8)	122.3(6)
C(5)–C(6)–N(2)	116.3(6)	C(10)–C(9)–C(13)	120.0(6)
C(7)–C(8)–C(9)	120.1(7)	C(9–C(13)–O(3)	109.4(5)
C(8)–C(9)–C(10)	117.7(7)		

appears to be stable indefinitely. When large quantities of NaCl are added to this solution, crystals of the water adduct, 2, are formed. This adduct is also obtained when aqueous solutions of 1 are taken to dryness. Drying 2 14 h *in vacuo* at ~1 torr over P_4O_{10} does not remove the water from the structure. Aqueous solutions containing PIH and iron(III) in a 2:1 molar ratio at pH 1.4 deposit the 1:1 product 2 when large amounts of LiCl are added. Thus, 2 may well be the thermodynamically favored iron(III)–PIH complex at low pH in the presence of excess Cl^-.

2:1 Complexes

When 1 is dissolved in water and three equivalents of base are added, a solid is formed (pH ~7), which by analysis has the composition Fe(pih)(Hpih)·$3H_2O$. This product can also be formed when PIH

TABLE IV. Bond Distances (Å) and Angles (deg) for $[FeCl_2(C_{14}H_{14}N_4O_3)(H_2O)]Cl{\cdot}H_2O$, (**2**).

Coordination polyhedron			
Fe–O(1)	2.012(6)	Fe–N(3)	2.131(6)
Fe–O(2)	1.905(6)	Fe–Cl(1)	2.370(3)
Fe–O(4)	2.122(7)	Fe–Cl(2)	2.282(2)
Ligand			
C(1)–C(2)	1.352(12)	C(7)–C(8)	1.449(11)
C(2)–N(1)	1.364(12)	C(8)–C(9)	1.426(12)
N(1)–C(3)	1.350(10)	C(9)–C(10)	1.351(12)
C(3)–C(4)	1.377(14)	C(10–N(4)	1.371(10)
C(4)–C(5)	1.424(13)	N(4)–C(11)	1.342(11)
C(5)–C(1)	1.393(11)	C(11)–C(12)	1.403(12)
C(5)–C(6)	1.469(12)	C(12)–C(8)	1.413(10)
C(6)–O(1)	1.287(9)	C(12)–O(2)	1.313(10)
C(6)–N(2)	1.327(11)	C(11)–C(14)	1.471(11)
N(2)–N(3)	1.379(9)	C(9)–C(13)	1.539(11)
N(3)–C(7)	1.295(10)	C(13)–O(3)	1.420(10)
Coordination polyhedron			
Cl(2)–Fe–O(1)	98.3(2)	O(4)–Fe–O(1)	88.5(3)
O(1)–Fe–N(3)	75.5(2)	O(1)–Fe–Cl(1)	89.9(2)
N(3)–Fe–O(2)	84.3(2)	Cl(1)–Fe–O(2)	92.4(2)
O(2)–Fe–Cl(2)	101.6(2)	O(2)–Fe–O(4)	89.1(3)
Cl(2)–Fe–O(4)	87.0(2)	O(2)–Fe–O(1)	159.8(2)
O(4)–Fe–N(3)	85.4(2)	O(4)–Fe–Cl(1)	178.4(2)
N(3)–Fe–Cl(1)	94.4(2)	N(3)–Fe–Cl(2)	170.3(2)
Cl(1)–Fe–Cl(2)	93.0(1)		
Chelate rings			
Fe–O(1)–C(6)	114.6(5)	Fe–N(3)–C(7)	129.5(5)
O(1)–C(6)–N(2)	125.3(8)	N(3)–C(7)–C(8)	123.1(6)
C(6)–N(2)–N(3)	109.3(6)	C(7)–C(8)–C(12)	122.8(7)
N(2)–N(3)–Fe	114.9(5)	C(8)–C(12)–O(2)	122.9(7)
N(2)–N(3)–C(7)	115.5(6)	C(12)–O(2)–Fe	136.4(5)
Ligand			
C(5)–C(1)–C(2)	120.4(8)	C(9)–C(10)–N(4)	120.5(8)
C(1)–C(2)–N(1)	120.9(7)	C(10)–N(4)–C(11)	123.4(7)
C(2)–N(1)–C(3)	120.9(7)	N(4)–C(11)–C(12)	118.1(7)
N(1)–C(3)–C(4)	120.4(8)	C(11)–C(12)–C(8)	120.3(8)
C(3)–C(4)–C(5)	119.3(7)	C(12)–C(8)–C(9)	118.2(7)
C(4)–C(5)–C(1)	118.0(8)	O(2)–C(12)–C(11)	116.7(7)
C(4)–C(5)–C(6)	119.3(7)	C(12)–C(11)–C(14)	122.5(8)
C(1)–C(5)–C(6)	122.6(8)	N(4)–C(11)–C(14)	119.4(7)
C(5)–C(6)–O(1)	118.1(8)	C(8)–C(9)–C(13)	120.7(7)
C(5)–C(6)–N(2)	116.6(7)	C(10)–C(9)–C(13)	119.7(7)
C(7)–C(8)–C(9)	119.0(6)	C(9)–C(13)–O(3)	112.2(7)
C(8)–C(9)–C(10)	119.4(7)		

and $FeCl_3{\cdot}6H_2O$ in a 2:1 ratio are stirred in water and three equivalents of base are added. We conclude that a 2:1 ligand-to-metal complex is the preferred product in aqueous media near pH 7. This conclusion is consistent with the observations of Ponka *et al.* [12] who conducted spectrophotometric studies with iron(III) and PIH showing that a 2:1 ligand-to-metal complex is formed at pH 7.4. When the 2:1 complex is stirred in water and additional base is added, it dissolves forming a clear, deep red-brown solution (pH ~11).

In methanol, black crystals of the 2:1 complex $Fe(pih)(Hpih){\cdot}MeOH{\cdot}H_2O$ are formed when 3 equivalents of methanolic NaOH are added to a mixture containing PIH and $FeCl_3 \cdot 6H_2O$ in a molar ratio of 2:1. This material converts to $Fe(pih)(Hpih) \cdot 3H_2O$ upon stirring in water. In an attempt to prepare $K[Fe(pih)_2]$, the method of Burrows and Bailar [35] was used. When 4 equivalents of KOH are added to an ethanolic mixture containing PIH and $Fe(NO_3)_3 \cdot 9H_2O$ in a molar ratio of 2:1, and the reaction volume reduced, a very soluble, brown, crystalline material is formed. However, repeated attempts to recrystallize this material from absolute methanol gave products with differing IR spectra and elemental analyses. The crude, brown, crystalline material, when dissolved in water, gives a brown precipitate with an identical IR spectrum to that of $Fe(pih)(Hpih) \cdot 3H_2O$.

Crystal Structures

The structures (see Figs. 1 and 2) of **1** and **2** consist of discrete cations, chloride anions, and, in **2**, water molecules held together by electrostatic interactions and hydrogen bonds.

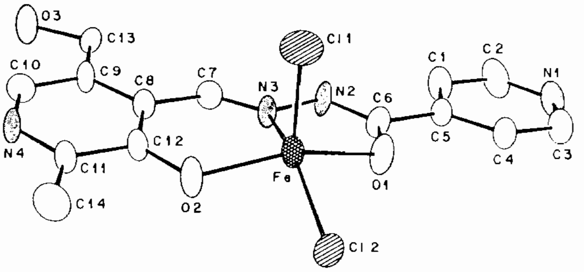

Fig. 1. ORTEP drawing of the $[FeCl_2(H_2pih)]^+$ cation (**1**) showing the 50% probability thermal ellipsoids. The hydrogen atoms and the chloride counter-ion have been omitted.

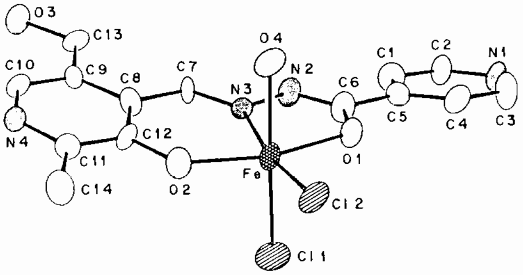

Fig. 2. ORTEP drawing of the $[FeCl_2(H_2pih)(H_2O)]^+$ cation (**2**) showing the 50% probability thermal ellipsoids. The chloride counter-ion, the uncoordinated water molecule, and the hydrogen atoms have been omitted.

In **1** the iron penta-coordination polyhedron is roughly square-pyramidal, the least-squares plane defined by O(1), N(3), O(2), and Cl(2) lying 0.54 Å below Fe and Cl(1) at the apex above. The structure of the $[FeCl_2(H_2pih)(H_2O)]^+$ complex is similar except for the addition of a water molecule to the polyhedron, which becomes roughly octahedral. The iron atom is slightly displaced (0.09 Å) toward Cl(1) from the least-squares plane of O(2)–Cl(2)–O(1)–N(3).

In both structures, the iron atom is bonded to O(2), phenolate, and O(1), carboxylate, with Fe–O(2), 1.908(4) Å, 1.905(6) Å, shorter than Fe–O(1), 1.977(4) Å, 2.012(6) Å. The shorter iron–phenolate distance is most likely due to the greater negative charge on the phenolic oxygen atom. The Fe–O(2) distances are within the range of values found for other high-spin iron(III) structures [36]. The Fe–O(water) distance of 2.122(7) Å in **2** is longer than for most iron(III) structures reported in the literature [37], the range being 1.98 to 2.14 Å. This large Fe–O distance is also seen in the similar structure $[FeCl_2(Hsbh)(MeOH)]$ [38], where the Fe–O(methanol) distance is 2.17 Å, the longest Fe–O(alcohol) distance reported to date. In both of these structures, the oxygen atoms are *trans* to a chlorine atom, and thus part of the bond lengthening may be due to a *trans* influence of the chlorine atom [39]. This lengthening of Fe–O bonds *trans* to a chlorine atom has also been reported in the structure *cis*-$[FeCl_2(H_2O)_4]^+$, in which the two Fe–O bonds *trans* to the chlorine atoms are 2.095(8) Å and 2.116(7) Å, whereas the two Fe–O bonds *trans* to each other are 2.004(8) Å and 2.035(8) Å [39].

In **1** and **2**, the chlorine atoms are *cis*, with considerably shorter iron–chlorine distances in **1**, the five-coordinate structure, than in **2**, the six-coordinate structure. This is consistent with the usual trend toward shorter metal–ligand distance as the coordination number decreases.

Moreover, in **2**, the lesser lengthening of Fe–Cl(2) and the greater lengthening of Fe–Cl(1) relative to **1** can be understood in terms of ligand–ligand repulsions and electronic effects. In **1**, contacts between the equatorial chlorine atom, Cl(2), and O(1) and O(2) are less than the sum of the van der Waals radii of oxygen and chlorine, whereas distances between the axial chlorine atom Cl(1) and the equatorial ligating atoms are near the respective sums of the van der Waals radii. This difference in ligand–ligand repulsions may account for the equatorial Fe–Cl bond being 0.026 Å longer than the axial Fe–Cl bond. In **2**, where the sixth ligand, H_2O, forces the iron atom to move toward the plane of the tridentate ligand, the situation is reversed, the equatorial Fe–Cl bond being 0.088 Å shorter than the axial Fe–Cl bond. This trend of Fe–Cl distances is seen in other *cis*-dichloro iron(III) complexes [38, 40, 41].

Electronic effects may also influence the Fe–Cl distances. Bonding between the Fe d orbital and the π^* orbital of the imine would remove electron density from the Fe atom, effectively increasing the π donation of the *trans* atom, in this case Cl(2), and, in turn, shortening the Fe–Cl(2) distance. Such a Cl–Fe–N interaction should be about the same in the five- and

TABLE V. Bond Distances (Å) in the Linkage C(7)–N(3)–N(2)–C(6)–O(1)[a].

Compound	Coordination number	Distance (Å)				Reference
		C(7)–N(3)	N(3)–N(2)	N(2)–C(6)	C(6)–O(1)	
$PPH\cdot HCl\cdot H_2O$	–	1.284(6)	1.347(7)	1.353(7)	1.228(8)	44
$[FeCl_2(dapsc)]Cl\cdot 2H_2O$	7	1.289(10)	1.359(10)	1.372(10)	1.245(11)	45
$[FeCl_2(Hsbh)(MeOH)]$	6	1.293(3)	1.380(4)	1.336(4)	1.256(4)	38
$[FeCl_2(H_2pih)(H_2O)]Cl\cdot H_2O$	6	1.295(10)	1.379(9)	1.327(11)	1.287(9)	this work
$[FeCl_2(H_2pih)]Cl$	5	1.289(8)	1.389(8)	1.292(8)	1.283(9)	this work

[a] dapsc = 2,6-diacetylpyridenebis(semicarbazone); PPH = Pyridoxal picolinoyl hydrazone.

six-coordinate PIH complexes and have about the same effect on the Fe–Cl equatorial bonding. The Fe–Cl axial distances, on the other hand, should depend on the atom *trans* to Cl(1). In the five-coordinate complex, Cl(1) has no *trans* partner and in the six-coordinate complex, Cl(1) has a *trans* partner which is a π donor. In this respect, it is interesting to note that Fe–Cl(equatorial) only increases 0.047 Å from $[FeCl_2(H_2pih)]^+$ to $[FeCl_2(H_2pih)(H_2O)]^+$, whereas Fe–Cl(axial) increases by 0.161 Å. A similar explanation can be advanced in comparing the Fe–Cl distances for $[FeCl_2$(1,3-dibenzoyl-2-azapropenato)(EtOH)] [40] and $[FeCl_2(H_2pih)(H_2O)]Cl\cdot H_2O$. In the former case, the O–C–C–N–C–C–O ligand unit is charged –1 and it is expected to be a better π acceptor than the ligand unit O–C–C–C–N–N–C–O of $[FeCl_2(H_2pih)(H_2O)]Cl\cdot H_2O$ which has a –2 charge. Thus more interaction of a π character in the former can take place between the Fe and the equatorial Cl, causing the Fe–Cl equatorial distance (2.216 Å) [40] to be shorter than the Fe–Cl equatorial distance (2.282 Å) in 2.

In both iron(III)–PIH structures, the coordinated ligand remains neutral, transferring the protons from the phenolic oxygen atom, O(2), and the hydrazidic nitrogen atom, N(2), to the pyridine nitrogen atoms N(1) and N(4). Thus the actual ligand in **1** and **2** is a zwitterion, a pattern seen in other complexes containing vitamin B_6 moieties [42]. As expected the C–N–C bond angles fall in the range given by Singh [43] for protonated nitrogen atoms of pyridine rings.

Comparison of bond lengths in the C(7)–N(3)–N(2)–C(6)–O(1) linkage with an isomer of the free ligand and similar iron(III) complexes (Table V) indicates the following: (1) C(7)N(3) is virtually unchanged in all five structures and is typical of a double bond; (2) N(2)–C(6) in the PIH and SBH complexes is shorter than in the free ligand, being 0.06 Å shorter in the five-coordinate complex; (3) C(6)–O(1) is slightly longer in the seven-coordinate and SBH complexes, but significantly longer in the PIH complexes (*ca.* 0.06 Å). In the free ligand [44] the linkage between the two pyridine rings is best represented as [C=N–NH–C=O]. Upon complexation to a metal ion, the ligand can either lose or retain the hydrazidic proton. If it retains the proton, the pattern of bond distances will vary little from those in the free ligand. This is seen in the seven-coordinate structure and in the SBH complex [45, 38], in both of which the hydrazidic hydrogen atom is retained, although involved in hydrogen bonding. In the PIH complexes, however, the hydrazidic hydrogen atom has been lost. In these complexes the shortened N(2)–C(6) distances and the increased C(6)–O(1) distances are consistent with a conjugated representation (C=N–N=C–O). This is particularly clear in the case of the five-coordinate complex where the C(7)–N(3) and N(2)–C(6) distances are clearly indistinguishable. Although the hydrazidic nitrogen atom is deprotonated in the six-coordinate PIH structure, the N(2)–C(6) bond is not as short as in the five-coordinate case. This is probably due to the hydrogen bond which is connected to the hydrazidic nitrogen atom in the six-coordinate structure but not in the five-coordinate structure. This hydrogen bond would tend to withdraw electron density from the chain of atoms and thus increase the N–C distance. Clearly, the interatomic distances in the ligand backbone are predictively sensitive to whether the hydrazidic nitrogen atom is protonated, deprotonated, or hydrogen bonded. We assume the C=N–N=C–O linkage characteristic of **1** is retained in solution over a large pH range and the primary protonation–deprotonation reactions involve the pyridine groups. In this context, we propose that maintaining the $[Fe(pih)_2]^-$ ion in aqueous solution would require very basic conditions considering that this anion contain four pyridine groups. In fact, the hydrolysis of this anion would be expected to lead to neutral species such as Fe(pih)(Hpih)·$3H_2O$ previously mentioned.

Both structures are held together by hydrogen bonds. In **1**, these bonds are between the free chloride ion Cl(3), the protonated pyridine nitrogen atoms N(1) and N(4), and O(3) of the hydroxymethyl group (Table VI). For **2**, the chloride ion, Cl(3), is involved in three hydrogen bonds, two with the protons on the pyridine nitrogen atoms, N(1) and N(4), and one with a hydrogen bonded to both

TABLE VI. Possible Hydrogen Bonds in [$FeCl_2(H_2pih)$]Cl, (**1**).

Atoms[a]	Distance (Å)	Angle (deg)
N(4)–H(41)•••Cl(3)^{i}	3.046(6)	172(4)
O(3)–H(31)•••Cl(3)^{ii}	3.114(6)	144(6)
N(1)–H(11)•••Cl(3)^{iii}	3.127(7)	142(5)
N(1)–H(11)•••O(3)^{iv}	3.209(7)	98(4)
N(1)–H(11)•••Cl(2)^{v}	3.601(6)	119(6)

[a] The roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: i = $-x, -y + 1, -z + 1$; ii = $x + 1, y, z$; iii = $-x - 1, -y, -z + 2$; iv = $x - 1, y - 1, z$; v = $-x - 1, -y, -z + 1$.

Cl(2) and Cl(3), appearing to form a bifurcated hydrogen bond (Table VII). The N–H•••Cl bond of 3.046(6) Å and the O–H•••Cl bond of 3.064(6) Å are considerably shorter than the average bond distances for these type of bonds as given by Pimentel and McClellan [46].

TABLE VII. Possible Hydrogen Bonds in [$FeCl_2(H_2pih)(H_2O)$]Cl•H_2O, (**2**).

Atoms[a]	Distance (Å)	Angle (deg)
O(4)–H(42)•••O(3)^{i}	2.844(8)	179(8)
O(5)–H(52)•••N(2)^{i}	2.969(10)	177(8)
O(4)–H(43)•••Cl(3)^{iii}	3.064(6)	180(8)
N(4)–H(41)•••Cl(3)^{iv}	3.126(7)	177(5)
N(1)–H(11)•••Cl(3)^{ii}	3.201(7)	137(6)
N(1)–H(11)•••Cl(2)^{iii}	3.238(8)	123(6)
O(5)–H(51)•••Cl(1)^{iii}	3.247(9)	177(7)
O(3)–H(31)•••Cl(1)^{v}	3.360(6)	152(7)

[a] The roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: i = $x, -y + 1/2, z + 1/2$; ii = $x, -y + 1/2, z - 1/2$; iii = $-x + 1, y - 1/2, -z + 1/2$; iv = $x + 1, -y + 3/2, z - 1/2$; v = $x, -y + 3/2, z - 1/2$.

Infrared Spectra

Some major bands for the ligands and the complexes along with their possible assignments are given in Table VIII. The broad absorption between 3300 cm^{-1} and 2600 cm^{-1} for the ligands is attributed to OH and NH groups involved in intramolecular hydrogen bonding [47]. The PIH complexes show bands in this same region and are attributed to hydrogen bonding. The complexes also show weak absorptions near 2000 cm^{-1}. Bands like these have been associated with the zwitterion form of pyridoxal [48] and of amino acids [49] and have been attributed to vibrational modes of the pyridinium group. This is consistent with the structure of these complexes and it should be noted that these bands are missing for [$FeCl_2(Hsbh)(MeOH)$], a compound with no pyridine nitrogen atoms [38]. In all complexes

TABLE VIII. Selected Infrared Bands (cm^{-1}) of the Ligands and Complexes[a].

Ligands			
SBH	PBH	PIH	Assignment
3267m	3185s,b	3140m	ν_{N-H}
3300–2800b	3100–2700b	3300–2600b	ν_{O-H}H bonded
1672s	1650s	1676s	$\nu_{C=O}$ Amide I
1621s	1605m	1613w	$\nu_{C=N}$
1606s	1582m	1597w	$\nu_{C=N}$
1580s			
1537s	1560s	1555s	Amide II
1271s	1285s	1298s	ν_{C-O} Amide III
1263s,sh		1284s	ν_{C-O} Amide III

Complexes					
1	**2**	**3**	**4**	**5**	Assignment
–	3480m	3315	3360m	–	ν_{OH}
3280s	3500–2650m,b	2750s	–	3500–2500m,b	ν_{OH} H-bonding
2610s	2780m				ν_{OH} H-bonding
2040w	2010w	2010w	–	2080w	Pyridinium moiety vibrations
1980w	1935w	1955w	–		Pyridinium moiety vibrations
1637m	1657m	1600s	1602s	1595s	$\nu_{C=N}$
1595s	1635m	1595s,sh	1592s		
	1586s				
–	1612m	–	–	–	δ_{O-H}
363s	352s	358s	354s		ν_{Fe-Cl}

[a] Intensities: s = strong; m = medium; w = weak; b = broad; sh = shoulder.

the amide I band of the ligand disappears, indicative of coordination of the carboxylate oxygen atom to the iron atom. For **2**, the 1612 cm^{-1} band is assigned as the H–O–H deformation. This assignment is supported by observing the spectrum of a sample recovered from D_2O.

The far IR spectra for complexes **1**–**4** show a strong to medium band between 352–363 cm^{-1}. Previous workers report that iron(III)–chlorine stretches occur in this region [50–52]. The complexes $Fe(pih)(Hpih){\cdot}3H_2O$ and $Fe(pih)(Hpih){\cdot}MeOH{\cdot}H_2O$, which contain no chlorine, show no bands in this region. On this basis, the strong to medium band between 352 and 363 cm^{-1} is assigned to an iron–chlorine stretching vibration. The iron–chlorine stretch for **1** occurs at a higher energy (363 cm^{-1}) than for **2** (352 cm^{-1}), and this is consistent with the trend of higher metal–halogen stretching frequencies with decrease in coordination number [53] and with decreased mean bond distances.

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Supplementary Material

Listings of the Gaussian amplitudes and the calculated atomic coordinates for the hydrogen atoms (Tables S-1, S-2), least-squares planes and atomic deviations therefrom (Tables S-3, S-4), and structure factors for both compounds (Tables S-5, S-6) (42 pages) have been deposited with the Editor-in-Chief.

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