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THE COORDINATION CHEMISTRY OF MIXED PYRIDINE–PHENOL AND PHENANTHROLINE–PHENOL LIGANDS; THE CRYSTAL STRUCTURE OF 2-(2-HYDROXYPHENYL)-1,10-PHENANTHROLINE (HL) AND THE CRYSTAL STRUCTURE AND PROPERTIES OF [FeL$_2$][PF$_6$]

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Abstract—The crystal structures of the N,N,O-terdentate ligand 2-(2-hydroxyphenyl)-1,10-phenanthroline (HL) and its Fe(III) complex [FeL$_2$][PF$_6$] (**1**) have been determined. In HL, an intramolecular O—H···N hydrogen bond between the phenolic OH and the adjacent nitrogen atom of the phenanthroline fragment constrains these two donor atoms to be *cisoid*, with the proton 'chelated'. The molecules of HL are associated into pairs in the crystal *via* a face-to-face aromatic π-stacking interaction. Complex **1** has a conventional distorted octahedral structure; sections of the aromatic ligands overlap between adjacent molecules to form an interleaved stack. It is high-spin down to 83 K, and its EPR spectrum (frozen glass at 77 K) is entirely typical of a rhombically distorted high-spin Fe^{III} site.

We are currently examining the structural and physico-chemical properties of transition metal complexes with the mixed-donor ligands 6-(2-hydroxyphenyl)-2,2′-bipyridine and 2-(2-hydroxyphenyl)-1,10-phenanthroline (HL). The structures of the complexes have been shown to vary in an unpredictable manner according to a fine balance between the stereoelectronic preferences of the metal centres and non-covalent interactions between the ligands, such as aromatic π-stacking and hydrogen-bonding. We have so far observed mononuclear complexes with Cr^{III},[1] Ru^{III},[1,2] Ni^{II}[3] and Pd^{II},[4] phenolato-bridged dinuclear complexes with Cu^{II} and Ni^{II},[3,5] and an unusual tetranuclear chain-like Mn^{II} complex.[6] For redox-active metals we have shown that their redox potentials may be varied over a wide range by control of the numbers of the pyridyl and phenolate donors in the ligand set.[1,2] We describe here the properties and crystal structure of the mononuclear Fe^{III} complex [FeL$_2$][PF$_6$] (**1**), together with the crystal structure of the free ligand HL.

EXPERIMENTAL

General details of the syntheses and apparatus used are as described previously.[1-5] The variable-temperature magnetic susceptibility of **1** was recorded with a Faraday balance calibrated with HgCo(NCS)$_4$ as described previously.[7]

Preparation of **1**

This was prepared by reaction of HL with FeCl$_2\cdot$4H$_2$O (0.5 equiv.) in methanol at room tem-

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Table 1. Crystal, data collection and refinement details for HL and **1**

	HL	**1**
Formula	$C_{18}H_{12}N_2O$	$C_{36}H_{22}F_6FeN_4O_2P$
Formula weight	272.3	743.4
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	12.245(3)	21.712(6)
b (Å)	18.990(5)	11.946(5)
c (Å)	11.907(3)	24.782(11)
β (°)	102.83(2)	98.37(3)
Cell volume (Å^3)	2699.7(12)	6359(4)
Molecules/unit cell	8	8
ρ_{calc} (g cm^{-3})	1.340	1.553
μ(Mo-K_α) (cm^{-1})	0.85	6.01
F(000)	1136	3016
Crystal dimensions (mm)	0.75 × 0.3 × 0.25	0.7 × 0.3 × 0.2
Unique reflections measured	4751	7300
Collection method	Wyckoff ω-scan	Wyckoff ω-scan
2θ range (°)	5.0–50.0	3.0–55.0
Index ranges	$0 \leqslant h \leqslant 14; 0 \leqslant k \leqslant 22; -14 \leqslant l \leqslant 13$	$0 \leqslant h \leqslant 28; 0 \leqslant k \leqslant 15; -32 \leqslant l \leqslant 31$
Refinement method	Full matrix least-squares on F [2049 data with $F \geqslant 4\sigma(F)$]	Full-matrix least-squares on all F^2 data
Final residuals	$R_1 = 0.055$; $R_w = 0.049^a$	$wR_2 = 0.188^b$ ($R_1 = 0.062$)^c
Weighting factors	$g = 0.0002^a$	$a = 0.0904$; $b = 16.2507^b$
Largest difference peak and hole (e Å^{-3})	0.16, −0.16	1.37, −0.67

[a] $R_1 = \Sigma ||F_o|-|F_c||/\Sigma|F_o|$ and $w^{-1} = [\sigma^2(F_o)+gF_o^2]$.

[b] Structure was refined on F_o^2 using all data: $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sigma^2(F_o^2)+(aP)^2+bP]$ and $P = [\max(F_o^2, 0)+2F_c^2]/3$.

[c] The value in parentheses is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$.

perature. After heating and stirring for 10 min a dark green solution was obtained, from which the complex was precipitated in *ca* 90% yield by addition of KPF_6. The crude dark green solid was recrystallized from acetonitrile–ether. FAB MS $m/z = 598$ [$M^+ - PF_6$]. Found: C, 57.9; H, 3.2; N, 7.2. Calc. for $C_{36}H_{22}N_4FeF_6O_2P$: C, 58.1; H, 3.0; N, 7.5%. UV–vis, λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1}): 228 (10), 291 (7.3), 398 (sh, 1.3).

Crystal structure determinations

Crystals of HL were grown by slow evaporation of a methanol solution, and crystals of **1** were grown by vapour diffusion of ether into an acetonitrile solution. The crystals selected were sealed in glass capillary tubes saturated with the recrystallization solvent. Data were collected using a Siemens R3m/V four-circle diffractometer (293 K, Mo-K_α X-radiation, graphite monochromator, $\bar{\lambda} =$ 0.71073 Å. The data were corrected for Lorentz and polarization effects, and the data for **1** were also corrected for X-ray absorption effects using an empirical method based on azimuthal scan data.[8] An absorption correction for the data from HL was not necessary. Details of the crystal data and intensity collection are summarized in Table 1. The structure of HL was solved by direct methods; the structure of **1** was solved by conventional heavy-atom methods. Successive difference Fourier syntheses were used to locate all non-hydrogen atoms. The hydroxyl hydrogen atoms in HL were refined with fixed isotropic thermal parameters and all remaining hydrogen atoms in both structures were included in calculated positions. The structure of HL has two crystallographically independent molecules of HL in the asymmetric unit and both have essentially identical bond lengths and angles. In complex **1** the asymmetric unit contains two halves of the PF_6 anions which lie on an inversion centre and astride a two-fold axis, respectively. All initial calculations were performed with a DEC microVax II computer with the SHELXTL PLUS systems of programs.[8] The final least-squares refinement on F^2 for **1** was carried out on a Silicon Graphics Indigo R4000 computer using SHELX-93.[8] Scattering factors with corrections for anomalous dispersion were taken from ref. 9. Selected bond lengths and angles are listed in Tables 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises atom coordinates, thermal parameters, and remaining bond lengths and angles.

RESULTS AND DISCUSSION

We have noted previously that the ^{1}H NMR chemical shifts of the phenolic protons of HL and related ligands are high (16.3 ppm for HL in $CDCl_3$),[3,5] which we ascribed to the presence of an intramolecular N···O—H hydrogen-bonding interaction between the phenolic OH group and the nitrogen atom of the adjacent heterocyclic ring. The proton would therefore be bound in an N,O-bidentate chelate pocket, with these two donor atoms necessarily in a *cisoid* arrangement. This may be compared with polypyridine ligands, which tend to adopt a mutually *transoid* arrangement of adjacent lone pairs when unbound,[10] but which become *cisoid* on protonation so that each proton may be bound within a 2,2′-bipyridyl chelating site.[11] This is confirmed by the crystal structure, which reveals that the asymmetric unit contains two crystallographically independent molecules of HL (Fig. 1). The ligands are essentially planar with the phenol rings in a *cisoid* conformation relative to the central heterocyclic rings, permitting intramolecular hydrogen bonds (average O—H 0.92 and average H···N 1.71 Å); full details of bond lengths and angles are given in Table 2. The molecules are associated into stacked pairs in the crystal (Fig. 1),

Table 2. Internuclear distances (Å) and angles (°) for the two crystallographically independent molecules of HL

	$n = 1$	$n = 2$		$n = 1$	$n = 2$
N(n11)—C(n12)	1.325(6)	1.325(6)	N(n11)—C(n16)	1.362(5)	1.357(5)
C(n12)—C(n13)	1.395(6)	1.395(6)	C(n13)—C(n14)	1.361(6)	1.361(6)
C(n14)—C(n15)	1.389(7)	1.402(7)	C(n15)—C(n16)	1.409(6)	1.396(6)
C(n15)—C(n41)	1.438(6)	1.446(6)	C(n16)—C(n22)	1.451(7)	1.446(6)
N(n21)—C(n22)	1.351(6)	1.353(5)	N(n21)—C(n26)	1.350(7)	1.339(6)
C(n22)—C(n23)	1.416(6)	1.411(5)	C(n23)—C(n24)	1.409(9)	1.399(7)
C(n23)—C(n42)	1.416(8)	1.428(6)	C(n24)—C(n25)	1.349(8)	1.353(6)
C(n25)—C(n26)	1.422(7)	1.411(6)	C(n26)—C(n32)	1.468(7)	1.476(6)
C(n31)—C(n32)	1.398(7)	1.397(6)	C(n31)—C(n36)	1.388(7)	1.388(6)
C(n31)—O(n00)	1.346(6)	1.347(6)	C(n32)—C(n33)	1.409(8)	1.408(7)
C(n33)—C(n34)	1.354(8)	1.368(7)	C(n34)—C(n35)	1.379(9)	1.363(8)
C(n35)—C(n36)	1.363(9)	1.363(8)	C(n41)—C(n42)	1.350(9)	1.340(7)

	$n = 1$	$n = 2$		$n = 1$	$n = 2$
C(n12)—N(n11)—C(116)	116.8(3)	116.9(3)	N(n11)—C(n12)—C(113)	124.5(4)	124.4(4)
C(n12)—C(n13)—C(114)	118.5(5)	118.4(4)	C(n13)—C(n14)—C(115)	119.4(4)	119.5(4)
C(n14)—C(n15)—C(116)	118.5(4)	117.9(4)	C(n14)—C(n15)—C(141)	122.5(4)	122.3(4)
C(n16)—C(n15)—C(141)	119.0(5)	119.8(4)	N(n11)—C(n16)—C(115)	122.1(4)	123.0(4)
N(n11)—C(n16)—C(122)	117.4(4)	118.2(4)	C(n15)—C(n16)—C(122)	120.4(4)	118.9(3)
C(n22)—N(n21)—C(126)	121.4(4)	120.7(3)	C(n16)—C(n22)—N(121)	119.6(4)	118.6(4)
C(n16)—C(n22)—C(123)	117.9(4)	120.2(4)	N(n21)—C(n22)—C(123)	122.6(5)	121.1(4)
C(n22)—C(n23)—C(124)	115.6(5)	117.4(4)	C(n22)—C(n23)—C(142)	120.4(5)	118.6(4)
C(n24)—C(n23)—C(142)	124.0(4)	124.0(4)	C(n23)—C(n24)—C(125)	121.1(5)	120.8(4)
C(n24)—C(n25)—C(126)	121.3(6)	119.6(4)	N(n21)—C(n26)—C(125)	117.9(5)	120.3(4)
N(n21)—C(n26)—C(132)	116.8(4)	116.2(3)	C(n25)—C(n26)—C(132)	125.3(5)	123.5(4)
C(n32)—C(n31)—C(136)	119.0(5)	120.5(4)	C(n32)—C(n31)—O(100)	123.8(4)	122.9(4)
C(n36)—C(n31)—O(100)	117.2(4)	116.6(4)	C(n26)—C(n32)—C(131)	121.1(5)	121.6(4)
C(n26)—C(n32)—C(133)	120.3(4)	121.9(4)	C(n31)—C(n32)—C(133)	118.6(5)	116.5(4)
C(n32)—C(n33)—C(134)	120.9(5)	122.0(5)	C(n33)—C(n34)—C(135)	120.0(6)	120.2(5)
C(n34)—C(n35)—C(136)	120.4(5)	119.8(5)	C(n31)—C(n36)—C(135)	121.0(5)	121.0(4)
C(n15)—C(n41)—C(142)	120.6(5)	120.6(4)	C(n23)—C(n42)—C(141)	121.7(4)	121.8(4)

Table 3. Selected internuclear distances (Å) and angles (°) for **1**

Fe(1)—O(40)	1.884(3)	Fe(1)—O(10)	1.893(3)	Fe(1)—N(51)	2.134(3)
Fe(1)—N(21)	2.137(3)	Fe(1)—N(62)	2.153(3)	Fe(1)—N(32)	2.162(3)
O(40)—Fe(1)—O(10)	94.67(12)	O(40)—Fe(1)—N(51)	87.08(11)	O(10)—Fe(1)—N(51)	102.12(11)
O(40)—Fe(1)—N(21)	98.98(11)	O(10)—Fe(1)—N(21)	86.58(12)	N(51)—Fe(1)—N(21)	169.03(11)
O(40)—Fe(1)—N(62)	164.59(12)	O(10)—Fe(1)—N(62)	91.33(13)	N(51)—Fe(1)—N(62)	77.78(12)
N(21)—Fe(1)—N(62)	95.54(12)	O(40)—Fe(1)—N(32)	89.38(11)	O(10)—Fe(1)—N(32)	163.67(11)
N(51)—Fe(1)—N(32)	93.86(11)	N(21)—Fe(1)—N(32)	77.16(11)	N(62)—Fe(1)—N(32)	88.81(11)
C(11)—O(10)—Fe(1)	131.0(2)	C(41)—O(40)—Fe(1)	132.8(2)		

with an average separation of 3.5 Å between the overlapping sections of the rings, which is entirely typical of stacked aromatic rings.[4,12] There is no evidence for hydrogen bonding between the components of each pair.

Reaction of $FeCl_2 \cdot 4H_2O$ in methanol with two equivalents of HL ligand rapidly results in a dark green solution due to formation of an Fe^{III} complex by aerial oxidation; the complex is therefore cationic and was isolated as its hexafluorophosphate salt. The formulation of $[FeL_2][PF_6]$ for **1** was confirmed by FAB mass spectrometry and elemental analysis. The crystal structure of **1** is depicted in Fig. 2a. The $[FeL_2]^+$ cation is approximately octahedral, with the ligand–metal–ligand bite angles varying between 77° and 102° (Table 3). Bond lengths are typical for high-spin Fe^{III} complexes. The crystallographically independent ligands are not planar but have a slight twist (15.6 and 20.8°) between the terminal phenolate ring and the phenanthrolinyl fragment, a common feature of complexes with these ligands. The most interesting feature of the structure is the way in which phenanthrolinyl fragments of adjacent complex units overlap in an alternating fashion to give an interleaved stack, with stacking distances (from an atom in one ligand to the mean plane of the other) varying between 3.3 and 3.8 Å (Fig. 2b). We have recently observed how intermolecular stacking interactions between aromatic ligand fragments can be of overriding importance in determining the nature of the crystal packing.[12]

Cyclic voltammetry of complex **1** revealed a reversible, one-electron wave ($\Delta E_p = 80$ mV at a scan rate of 0.2 V^{-1}; cathodic and anodic peak currents equal) at $E_{1/2} = -0.67$ V vs the ferrocene/ferrocenium couple (Fc/Fc^+); we assign this to an Fe^{II}/Fe^{III} couple. There is also a reversible ($\Delta E_p = 70$ mV) ligand-based reduction at -2.12 V vs Fc/Fc^+ and a totally irreversible ligand-based oxidation at $+0.97$ V vs Fc/Fc^+. The stabilization of the Fe^{III} oxidation state is a consequence of

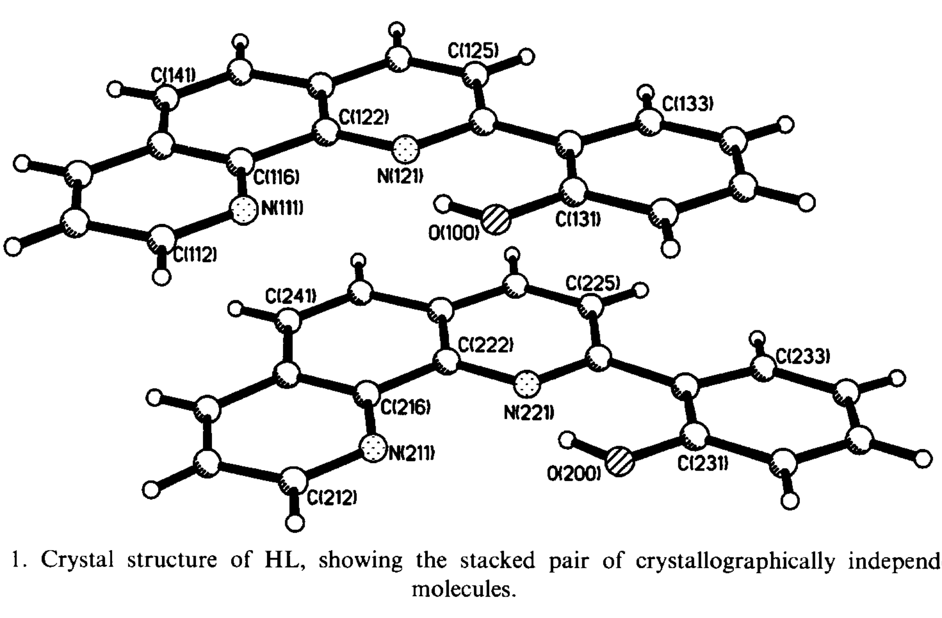

Fig. 1. Crystal structure of HL, showing the stacked pair of crystallographically independent molecules.

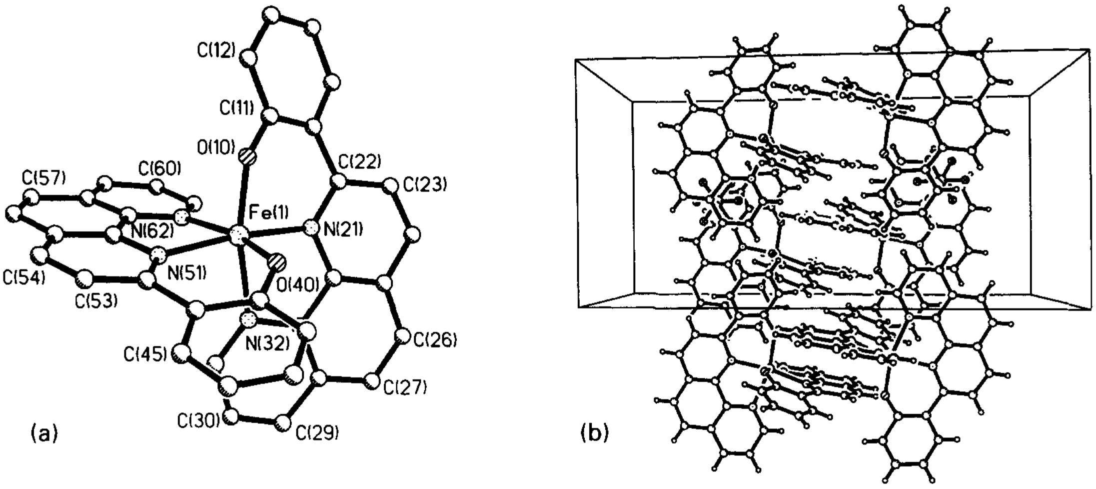

Fig. 2. Structure of the cation of **1**, showing the mononuclear unit with numbering scheme (a) and the interleaved stack in the crystal formed from overlapping sections of the aromatic ligands (b).

the donor set, containing two phenolate donors (e.g. the potential of the iron-based redox couple in $[Fe(terpy)_2]^{2+/3+}$ is +1.13 V vs Ag/AgCl in MeCN).[13]

We examined the magnetic susceptibility of **1** between 83 and 299 K. The magnetic moment was found to be $\mu_{eff} \approx 5.9$ B.M. over most of the temperature range, apart from a slight decrease (to 5.6 B.M.) below 100 K which we ascribe to the presence of a small amount of an antiferromagnetically coupled impurity. The complex is therefore in the high-spin state over this temperature range (consistent with the observed bond lengths in the crystal structure) and shows no spin-crossover behaviour, unlike other Fe^{III} complexes with similar donor sets.[14] It is interesting to note the dramatic difference between this simple mononuclear structure and the tetranuclear structure of $[Mn_4L_6]^{2+}$. Since the metal ions of both complexes have a high-spin *d*5 configuration, with no stereoelectronic preferences, the difference is most likely due to electrostatic effects: the electrostatic repulsion between a chain of closely-spaced metal ions (3.3–3.4 Å) in $[Mn_4L_6]^{2+}$ may become prohibitive if the metals all carry a +3 charge rather than +2.

The EPR spectrum of **1** in a frozen glass (MeCN–THF, 1 : 1) at 77 K shows a weak inflexion at $g = 4.28$, a strong inflexion at $g = 2.16$ and a weak negative-going feature split into a doublet with peaks at $g = 1.95$ and 1.94. The spectrum is similar in all of these respects to those of some other high-spin Fe^{III} complexes:[16] the signal at $g = 4.28$ is a transition between the middle Kramers doublet and is particularly characteristic of rhombically-distorted Fe^{III} complexes, including iron–tyrosinate proteins.[16]

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