

A novel blue luminescent high-spin iron(III) complex with interlayer O–H···Cl bridging: Synthesis, structure and spectroscopic studies

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Abstract

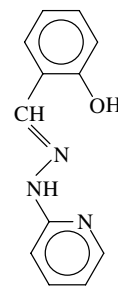
A blue luminescent high-spin ($s = 5/2$) iron(III) complex, $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl}$ (**2**), was synthesized with the acyclic tridentate salicylaldehyde 2-pyridyl hydrazone ligand, H_2L^1 (**1**), and it can subsequently be deprotonated and methylated into blue luminescent iron(III) complexes, $[\text{Fe}^{\text{III}}(\text{L}^2)_2]\text{Cl}$ (**3**) and $[\text{Fe}^{\text{III}}(\text{MeL}^1)_2]\text{Cl}$ (**4**) respectively. On excitation at 390 nm, the ligand and the complexes display fluorescence in the blue region ($\lambda_{\text{em}} = 440\text{--}450$ nm) of the spectrum. The association constant, ($K_{\text{ass}} = 4.6421 \times 10^4$ at 298 K) and the thermodynamic parameters for complex **2** have been determined by UV–Vis spectroscopy. The iron(III)–iron(II) reduction potentials lie near -0.2 V versus SCE. The X-ray crystal structure of the complex, $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl} \cdot \text{H}_2\text{O}$ (**2**), was determined, revealing meridional binding of the two ligands affording a *cis*- FeN_4O_2 geometry with alternate chlorine and water molecules at the interface of the main molecule, resulting in interesting interlayer O–H···Cl bridging.

Keywords: Blue luminescent; Binding constant; High-spin iron(III); Structure; Interlayer O–H···Cl bridging

1. Introduction

Luminescent organic and coordination compounds are a fascinating class of molecules that have wide applications in trace metal analysis, metal signaling, construction of optical devices and sensor molecules [1–4]. Amongst green, blue and red, stable blue luminescent complexes, useful for electro luminescent displays [5], are still rare and very challenging to prepare [6]. In recent years, the design and synthesis of a blue luminescent iron(III) complex [7] has become a very active area of research as a result of the demand for more sensitive and selective chemosensors for *in vivo* and *in vitro* purposes [8]. The above objective has

been realized using salicylaldehyde 2-pyridyl hydrazone, H_2L^1 (**1**), that can provide metal complexes with special electronic



H_2L^1

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and structural properties [9]. Complexes of **1** were screened for their antitumor and antimicrobial activities [10], but their luminescence properties have barely been investigated [11]. In the present investigation we have synthesized a series of novel blue luminescent high-spin ($s = 5/2$) iron(III) complexes using ligand **1** as the blue light emitting species [11a]. Interestingly, the photophysical and chemical properties of the iron(III) complex can be modulated by controlling the degree of protonation of the ligand or by insertion of a nucleophile. Emphasis will be given to understanding the binding phenomenon via the binding constant and thermodynamic calculations for the complexation equilibrium. Other important features scrutinized include absorption, emission, redox and magnetic studies. The X-ray structure of one of the iron(III) complexes authenticates an FeN_4O_2 coordination with interesting $\text{Cl} \cdots \text{H}-\text{O}$ bonding [12].

2. Experimental

2.1. Materials

All starting materials and solvents were purchased from Aldrich Chemical Company and were used without further purification unless otherwise stated.

2.2. Physical measurements

A Perkin–Elmer 2400 C Elemental Analyzer was used to collect microanalytical data (C, H, N). A Sartorius CP64 balance was used for weighing purposes. IR data were collected with the help of a FTIR Perkin–Elmer L 120-000 A. The UV–Vis spectra of the ligand and its complexes were measured on a Shimadzu UV-1601 spectrophotometer and corrected for backgrounds due to solvent absorption. Fluorescence spectra were recorded with a Perkin–Elmer LS 50B Luminescence Spectrometer. For binding constant measurements, solutions were prepared at a fixed concentration of H_2L^1 (1.0×10^{-5} M) and at a concentration of the metal ions ranging from 1.0×10^{-6} M to 10.0×10^{-6} M at room temperature. Electrochemical measurements were performed under a nitrogen atmosphere on a Versastat II PAR Electrochemistry system using solvents and supporting electrolyte (TEAP) prepared and purified as before [13]. The reference electrode was a saturated calomel electrode (SCE). Solution electrical conductivities were measured with the help of a Philips PR 9500 bridge, the solute concentration being 10^{-3} M. For spectroscopic and electrochemical studies HPLC grade solvents were used.

2.3. X-ray crystallography

Single crystals of $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl} \cdot \text{H}_2\text{O}$ (**2**), were grown by slow diffusion of hexane into a dichloromethane solution of the complex, followed by slow evaporation. A rod shaped crystal was mounted on a glass fiber. Intensity data

for complex **2** was collected at 173 K (-100 °C) by the ω -scan method over the 2θ range 1.78 – 29.27° on a Stoe Mark II-Image Plate Diffraction System [14a] equipped with a two-circle goniometer and using Mo $\text{K}\alpha$ graphite monochromated radiation ($\lambda = 0.71073$ Å). Structure solution and refinement were done by direct methods using SHELXS-97 and SHELXL-97 programs [14b,14c]. The structure was successfully solved in the space group $P2_1/c$. Of the 5990 independent reflections, 5006 satisfying $I > 2\sigma(I)$ were used for the structure solution. The NH H atoms were located from Fourier difference maps and refined isotropically. The water H atoms were located from Fourier difference maps. They were refined isotropically with the O–H bond lengths restrained to be $0.82(2)$ Å. The remainders of the H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. All non-hydrogen atoms were refined anisotropically. An absorption correction was applied using MULscanABS in PLATON [14d]. The molecular structure and crystallographic numbering scheme are illustrated in the PLATON drawing [14d].

Molecular formula $\text{C}_{24}\text{H}_{22}\text{ClFeN}_6\text{O}_3$, M 533.78, monoclinic, space group $P2_1/c$, $a = 11.9163(6)$ Å, $b = 20.4137(9)$ Å, $c = 9.4770(5)$ Å, $\beta = 106.028(4)^\circ$, $V = 2215.72(19)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.600$ g cm⁻³, absorption coefficient $\mu = 0.844$ mm⁻¹, crystal dimensions: $0.39 \times 0.36 \times 0.25$ mm, $F(000)$: 1100, θ range for data collection: 1.78 – 29.27 ($^\circ$), index ranges: $-16 \leq h \leq 16$, $-27 \leq k \leq 27$, $-13 \leq l \leq 12$, reflections collected/unique: 31762/5990, significant unique reflections: 5006 with $I > 2\sigma(I)$, refinement method: full-matrix least-squares on F^2 , data/parameters/restraints: 5990/332/2, goodness-of-fit on F^2 : 1.045, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0348$, $wR_2 = 0.0797$, R indices (all data): $R_1 = 0.0454$, $wR_2 = 0.0856$, weighting scheme: $w = 1/[(\sigma F_o)^2 + (0.0395P)^2 + 0.9534P]$, where $P = (F_o^2 + 2F_c^2)/3$, largest difference peak and hole ($\text{e}/\text{Å}^3$): 0.542 and -0.584 .

$R_1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$ (based on F), $wR_2 = [(\sum w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ (based on F^2), $\text{GOF} = ((\sum (|F_o| - |F_c|)^2) / (N_o - N_v))^{1/2}$ with N_o = number of observed reflections and N_v = number of parameters.

2.4. Syntheses

2.4.1. Salicylaldehyde 2-pyridyl hydrazone H_2L^1 (**1**)

The ligand was prepared by the same general procedure as before [15].

2.4.2. Iron complexes

$[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl}$ (**2**): To a stirred methanolic solution of anhydrous ferric chloride (0.03 g, 0.2 mmol) was added a solution of H_2L^1 (**1**), (0.085 g, 0.4 mmol) in methanol (5 ml) and the resulting brown solution was stirred for 0.5 h. The solvent was evaporated on a rotary evaporator, and on recrystallization from methanol deep brown crystals of $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl}$ (**2**), were obtained. Yield 89%. Selected FTIR data, ν (cm^{-1}): 3356, 1623, 1594, 1574,

1537, 1515, 1376, 1355, 1332, 1287, 1250, 1205, 1150, 1139, 1103, 1121, 1030, 1003, 933, 880, 858, 794, 766, 753, 655, 604, 522, 469, 426. *Anal. Calc.* for $C_{24}H_{20}N_6O_2FeCl \cdot H_2O$: C, 54.01; H, 4.12; N, 15.75. Found: C, 54.02; H, 4.14; N, 15.74%.

$[Fe^{III}(L^2)_2]Cl$ (**3**): Anhydrous ferric chloride (0.03 g, 0.2 mmol) in methanol (5 ml) was added to a methanolic solution (5 ml) of **1** (0.085 g, 0.4 mmol), previously deprotonated by adding NaOH (0.016 g, 0.4 mmol). A green colored solution was obtained which on evaporation yielded shining greenish brown crystalline solids of $[Fe^{III}(L^2)_2]Cl$ (**3**). Yield 85%. Selected FTIR data, ν (cm^{-1}): 3362, 3011, 2921, 2842, 1614, 1538, 1482, 1469, 1427, 1328, 1285, 1202, 1150, 1100, 1058, 1031, 1008, 931, 881, 848, 753, 604, 429, 469. *Anal. Calc.* for $C_{24}H_{18}N_6O_2FeCl$: C, 56.11; H, 3.50; N, 16.36. Found: C, 55.12; H, 3.56; N 16.38%.

$[Fe^{III}(MeL^1)_2]Cl$ (**4**): To a methanolic solution of $[Fe^{III}(HL^1)_2]Cl$ (**2**), (0.1 g, 0.2 mmol) 1 ml methyl iodide was added and stirred for 0.5 h at room temperature resulting in a reddish brown solution. The solvent was evaporated and the complex was recrystallized from methanol and finally dried over fused calcium chloride to obtain $[Fe^{III}(MeL^1)_2]Cl$ (**4**), as reddish brown crystalline solids. Yield 80%. Selected FTIR data, ν (cm^{-1}): 3383, 1621, 1538, 1496, 1358, 1324, 1286, 1148, 1105, 855, 765, 694, 526, 430, 376. *Anal. Calc.* for $C_{26}H_{24}N_6O_2FeCl$: C, 57.43; H, 4.41; N, 15.46. Found: C, 57.42; H, 4.40; N, 15.44%.

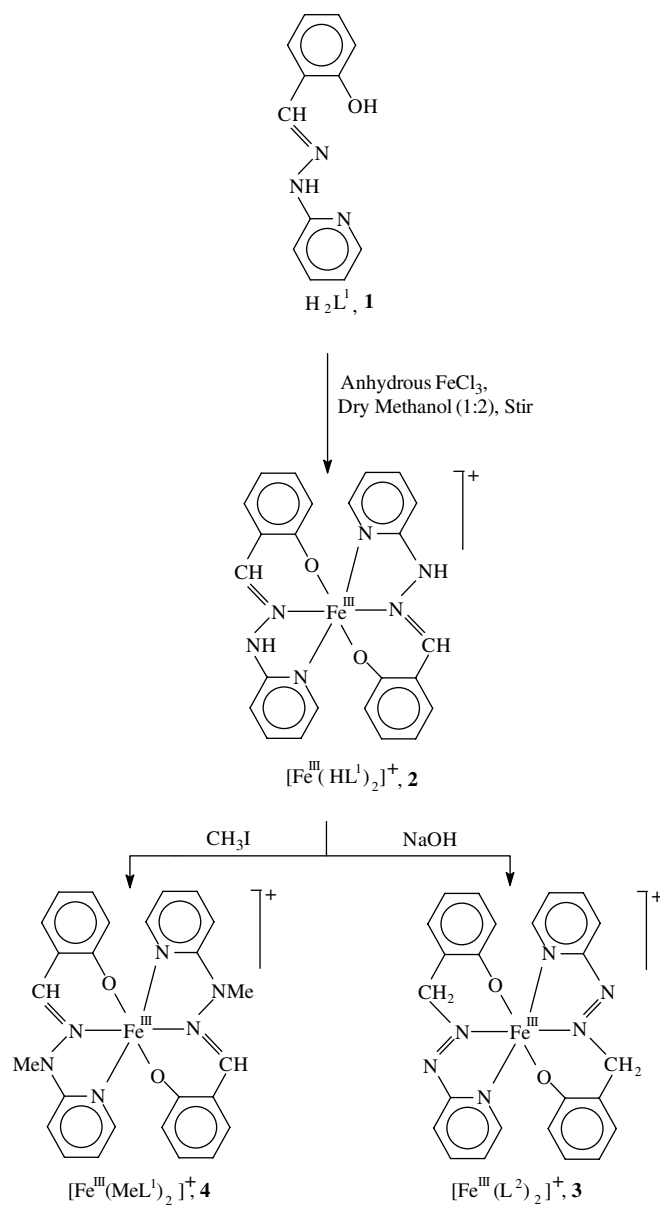
3. Results and discussion

3.1. Syntheses and characterization

The ligand system H_2L^1 (**1**), used in the present work is tridentate in nature, incorporating imine, phenolic and pyridyl functions as potential donor sites. The 1:2 reaction of H_2L^1 with anhydrous ferric chloride in methanol at room temperature afforded deep brown colored blue luminescent $[Fe^{III}(HL^1)_2]Cl$ (**2**), in excellent yields, which can subsequently be deprotonated into luminescent green colored $[Fe^{III}(L^2)_2]Cl$ (**3**), followed by methylation leading to another luminescent reddish brown complex, $[Fe^{III}(MeL^1)_2]Cl$ (**4**). The synthetic routes for complexes **2**, **3** and **4** are depicted in Scheme 1. All the complexes are highly soluble in acetonitrile, methanol and ethanol. They are 1:1 electrolytes ($\Lambda = 130\text{--}134 \Omega^{-1} \text{cm}^2 \text{M}^{-1}$) in acetonitrile. The room temperature (298 K) magnetic moments of complexes **2**, **3** and **4** lie in the range 5.56–5.84 μ_B , indicating a high-spin configuration (d^5 , $t_{2g}^3 e_g^2$, $s = 5/2$) with FeN_4O_2 coordination.

3.2. Absorption and Emission Spectra of H_2L^1 and its Iron(III) Complexes

All the spectroscopic measurements were carried out in degassed methanol at room temperature. The bands appearing in the UV region (240–395 nm) are characteristic of the ligand H_2L^1 (**1**) (Fig. 1). In the complexes these



Scheme 1.

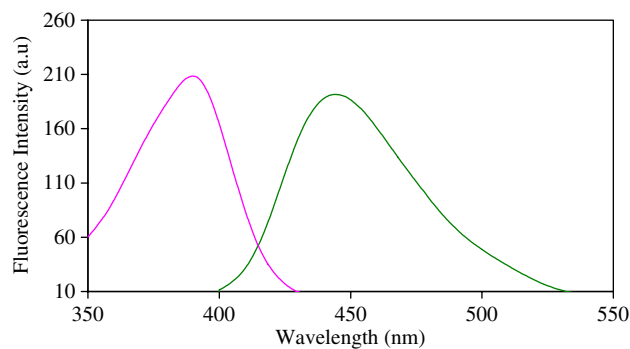


Fig. 1. Excitation (—) and emission (—) spectra of H_2L^1 (**1**), in degassed methanol at 298 K.

ligand centred bands are accompanied by multiple bands extending into the visible region (400–460 nm). The excitation and emission spectra of the ligand and the complexes are listed in Table 1. On excitation at 390 nm, the ligand H_2L^1 (**1**), strongly fluoresces in the blue region (444 nm) due to an intraligand $^1(\pi-\pi^*)$ transition [11a]. Upon complexation with iron(III), the emission peak is slightly red shifted with a significant quenching in emission intensity, as observed in $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl}$ (**2**). Subsequent quenching is observed in the deprotonated complex, $[\text{Fe}^{\text{III}}(\text{L}^2)_2]\text{Cl}$ (**3**), and the methylated complex, $[\text{Fe}^{\text{III}}(\text{MeL}^1)_2]\text{Cl}$ (**4**), with a slight shift in emission wavelength (Table 1). Thus all the complexes **2**, **3** and **4** emit strongly in the blue region (400–460 nm) of the spectrum (Fig. 2). During excitation, the ligand **1** and complex **2** undergo an auto increment in fluorescence intensity at room temperature, without the influence of any external reagent, viz. acid, alkali, excess metal or ligand, possibly due to the internal photo induced azo-imine tautomerism (Scheme 2) [16,17]. The rate of increment is the highest for ligand **1**.

Deprotonation of the imine form, $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl}$ (**2**), stabilizes the azo form, $[\text{Fe}^{\text{III}}(\text{L}^2)_2]\text{Cl}$ (**3**), with a decreased rate of increment. Complex **3** was isolated and characterized (FTIR $\nu_{\text{N}=\text{N}} \sim 1450 \text{ cm}^{-1}$). Interestingly, the increment is totally stopped in the methyl substituted complex, $[\text{Fe}^{\text{III}}(\text{MeL}^1)_2]\text{Cl}$ (**4**), due to the unavailability of the $-\text{NH}$ proton required for the intramolecular tautomerism [16,17].

3.3. Thermodynamics of binding

The association constant (K_{ass}) of complex **2** can be estimated spectrophotometrically (Fig. 3) according to Eq. (1) [18], where X represents the absorption intensity, C_{H} and C_{G} are the corresponding concentrations of the ligand and the metal ion.

The K_{ass} (UV-Vis) was found to be 4.6421×10^4 at 298 K. The temperature dependence of the binding constant was studied between 298 and 308 K, and the values of the

$$X = X_0 + (X_{\text{lim}} - X_0)/2C_0\{C_{\text{H}} + C_{\text{G}} + 1/K_{\text{ass}} - [(C_{\text{H}} + C_{\text{G}} + 1/K_{\text{ass}})^2 - 4C_{\text{H}}C_{\text{G}}]^{1/2}\} \quad (1)$$

Table 1
Spectral characteristics of iron(III) complexes of H_2L^1

Compounds	Excitation		Emission		F/F_0^a
	λ_{exc} (nm)	$\log \epsilon$	λ_{em} (nm)	Intensity (a.u)	
H_2L^1 (1)	390	5.10	444.49	536.84	
$[\text{Fe}^{\text{III}}(\text{HL}^1)_2]^+$ (2)	390	4.58	449.04	438.51	0.81
$[\text{Fe}^{\text{III}}(\text{L}^2)_2]^+$ (3)	390	4.32	451.32	235.18	0.47
$[\text{Fe}^{\text{III}}(\text{MeL}^1)_2]^+$ (4)	390	4.39	444.11	129.54	0.24

^a The ratio of fluorescence intensity of the metal complexes of H_2L^1 in the presence of metal (F) and in the absence of metal (F_0). The concentrations of metal and H_2L^1 being 10^{-6} mol/L and 10^{-5} mol/L respectively.

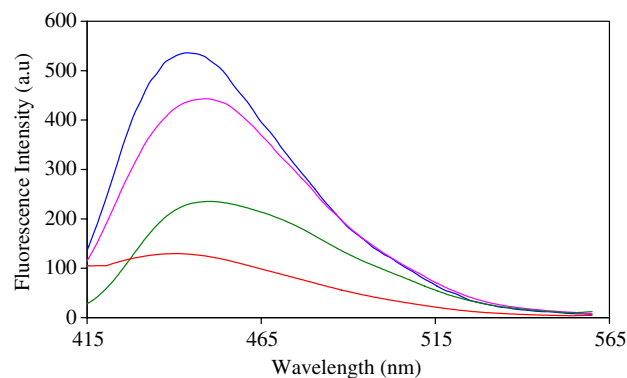
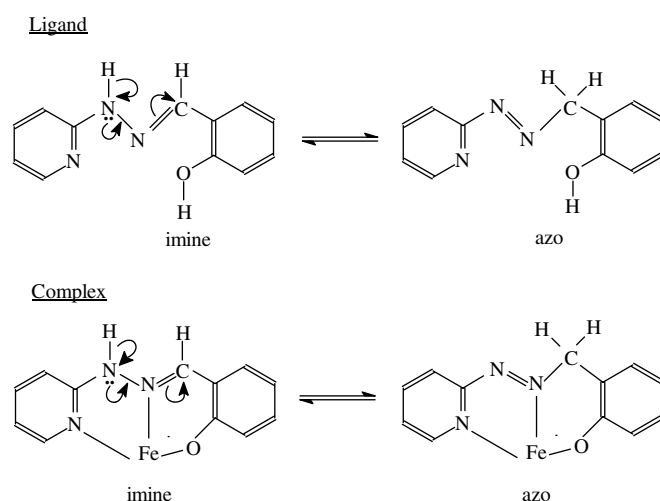


Fig. 2. Emission spectra of ligand **1** (—) and complexes **2** (—), **3** (—), **4** (—), (1×10^{-5} M) in degassed methanol (pH = 7.0), $\lambda_{\text{exc}} = 390$ nm, at 298 K.



Scheme 2.

thermodynamic parameters ($\Delta G^0 = -6401.04 \text{ cal/M}$, $\Delta H^0 = -636.36 \text{ cal/M}$, $\Delta S^0 = 23.62 \text{ cal/M/deg}$) were obtained at 298 K in degassed methanol. It is seen that the binding process is favoured by a negative ΔH^0 and positive ΔS^0 . A variable temperature UV-Vis titration was performed to monitor the variation of the dissociation constant with temperature, which often gives clues as to the nature of the forces involved in the interaction.

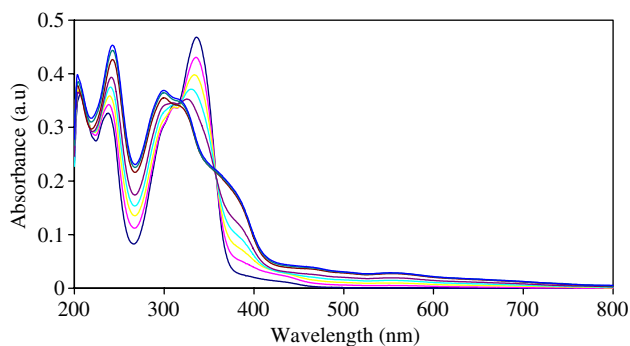


Fig. 3. UV absorbance spectra of H_2L^1 (1.0×10^{-5} M) upon addition of iron(III) (1.0×10^{-6} M – 1.0×10^{-5} M) in degassed methanol (pH = 7.0) at 298 K.

3.4. Electrochemistry

The redox properties of the complexes have been studied in acetonitrile (0.1 M TEAP) solution by cyclic voltammetry (CV) using a platinum-working electrode. $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl}$ (**2**), displays a quasi-reversible ($\Delta E_p = 140$ mV) one-electron cyclic response near -0.15 V versus the saturated calomel electrode (SCE). The response is assigned to the $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]^+ / [\text{Fe}^{\text{II}}(\text{HL}^1)_2]$ reduction. Isolation of $[\text{Fe}^{\text{II}}(\text{HL}^1)_2]$ in the pure state is difficult

due to rapid air oxidation of the bivalent species. In the deprotonated complex $[\text{Fe}^{\text{III}}(\text{L}^2)_2]\text{Cl}$ (**3**), an irreversible couple is observed at a lower potential, possibly due to the predominance of the azo tautomer over the imine form [19].

3.5. X-ray structure of $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl} \cdot \text{H}_2\text{O}$

The molecular structure of complex **2** has been established by single crystal X-ray diffraction. A view of $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl} \cdot \text{H}_2\text{O}$ (**2**), is shown in Fig. 4. The water molecules and chloride ions occur as discrete entities in the lattice and participate in intermolecular hydrogen bonding. The two ligands span meridionally, binding the metal in a hexadentate FeN_4O_2 fashion, utilizing pairs of pyridyl-N, phenolato-O and imine-N, resulting in a *cis* configuration for the FeN_4O_2 sphere. The angles at the metal centre between the *cis* positioned donor pairs span the range $73.27(5)$ – $97.58(5)^\circ$ and those between *trans* positioned pairs are $154.08(5)$ – $155.30(5)^\circ$. The two tridentate ligands have the same gross structures with little conformational change. The five-membered FeN_3C chelate rings are relatively planar. The r.m.s. deviations of the five fitted atoms are 0.0535 for ring $[\text{Fe}1, \text{N}1, \text{C}5, \text{N}2, \text{N}3]$ and 0.0164 for ring $[\text{Fe}1, \text{N}4, \text{C}17, \text{N}5, \text{N}6]$. The six-membered FeC_3NO chelate rings are also relatively planar, with the

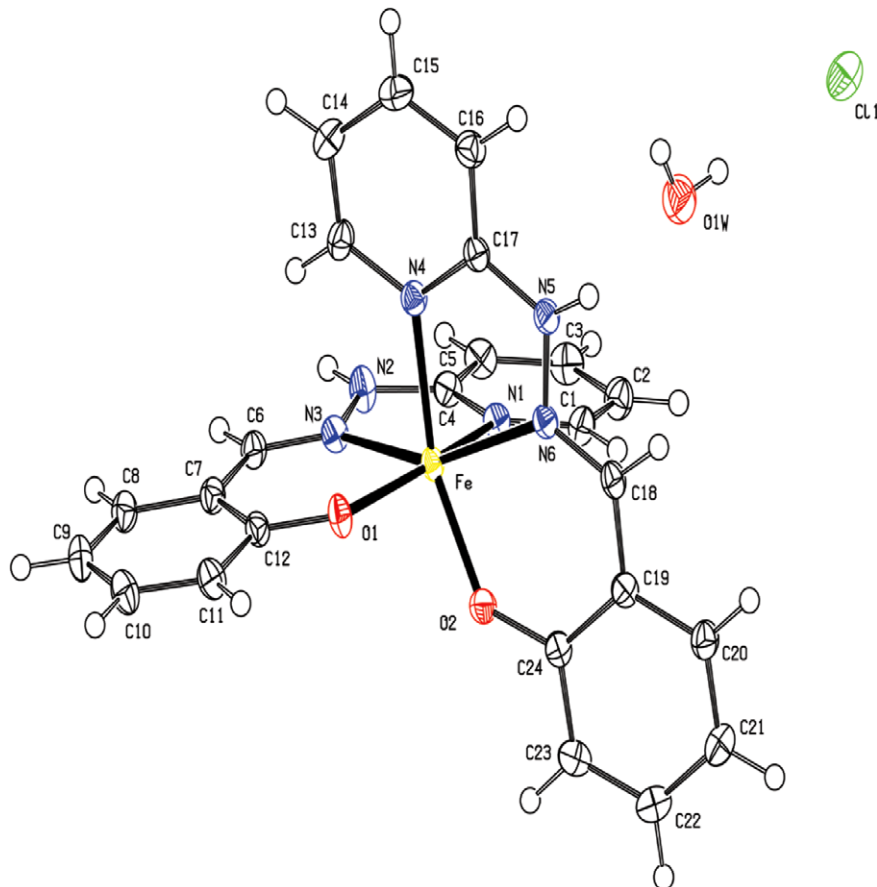


Fig. 4. Perspective view and atom labelling scheme for $[\text{Fe}^{\text{III}}(\text{HL}^1)_2]\text{Cl} \cdot \text{H}_2\text{O}$ (**2**). All atoms are represented by their 50% thermal probability ellipsoids.

r.m.s deviations of the six fitted atoms being 0.0124 for ring [Fe1, O1, C12, C7, C6, N3], and 0.0759 for ring [Fe1, O2, C24, C19, C18, N6]. The four Fe–N lengths are virtually same, the average value being 2.159(1) Å, as expected for high-spin iron(III) complexes (2.1 Å) [20]. The Fe–O_{phenolate} bond length, 1.9041(12) Å, is almost equal to other high-spin iron(III) complexes (~1.89 Å) [21]. The two imine (–NH) bond lengths are almost the same, the average value is 1.373(2) Å, longer than the N=N bond length, 1.28 Å [22]. The bond distance of N(3)–C(6) is 1.295(2) Å and that of N(6)–C(18) is 1.296(2) Å, which is normal for C=N [23] (See Tables 2 and 3).

3.6. Hydrogen bonding

In complex **2**, there is one strong N(5)–H(5A)···O(1w), 2.841(2) Å, and one weak N(2)–H(2A)···Cl(1), 3.111(2) Å intermolecular hydrogen bond, as expected for N–H···O (~2.90 Å) [24] and N–H···Cl (~3.08 Å) [12]. These N–H···O and N–H···Cl hydrogen bonds undergo weak interactions with chloride and water molecules present in the crystal lattice. The crystal packing diagram (Fig. 5) clearly shows this interlayer O–H···Cl bridging (O(1w)–H(1wA)–Cl(1), 3.162(2) Å; O(1w)–H(1wB)–Cl(1), 3.199(2) Å) at the interface of the main molecule [12].

Table 2
Selected bond lengths (Å) and bond angles (°) for [Fe^{III}(HL¹)₂]Cl · H₂O (**2**)

<i>Bond lengths</i>			
Fe–N(1)	2.1583(14)	Fe–O(1)	1.9069(12)
Fe–N(3)	2.1551(13)	Fe–O(2)	1.9013(12)
Fe–N(4)	2.1590(14)	N(2)–N(3)	1.3730(20)
Fe–N(6)	2.1672(13)	N(5)–N(6)	1.3742(19)
N(2)–H(2A)–Cl(1 ^a)	3.1107(15)	N(5)–H(5A)···O(1W)	2.8410(20)
O(1W)–H(1WA)–Cl(1)	3.1623(18)	O(1W)–H(1WB)···Cl(1 ^b)	3.1991(18)
<i>Bond angles</i>			
N(1)–Fe–N(4)	97.58(5)	O(1)–Fe–N(4)	90.74(5)
N(1)–Fe–N(6)	90.41(5)	O(1)–Fe–N(6)	114.28(5)
N(3)–Fe–N(1)	73.43(5)	O(2)–Fe–N(1)	91.62(6)
N(3)–Fe–N(4)	88.98(5)	O(2)–Fe–N(3)	116.90(5)
N(3)–Fe–N(6)	154.39(5)	O(2)–Fe–N(4)	154.08(5)
N(4)–Fe–N(6)	73.27(5)	O(2)–Fe–N(6)	82.52(5)
O(1)–Fe–N(1)	155.30(5)	O(2)–Fe–O(1)	90.86(5)
O(1)–Fe–N(3)	83.56(5)		

Symmetry transformations used to generate equivalent atoms: ^a $x - 1, y, z$; ^b $x, -y + 1/2, z + 1/2$.

Table 3
Hydrogen-bonds for [Fe^{III}(HL¹)₂]Cl · H₂O (**2**) [(Å) and (°)]

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
N(2)–H(2A)···Cl(1 ⁱ)	0.87(2)	2.24(2)	3.1107(15)	172(2)
N(5)–H(5A)···O(1W)	0.82(2)	2.05(2)	2.841(2)	162(2)
O(1W)–H(1WA)···Cl(1)	0.775(17)	2.395(18)	3.1623(18)	171(3)
O(1W)–H(1WB)···Cl(1 ⁱⁱ)	0.798(18)	2.406(18)	3.1991(18)	173(3)

Symmetry transformations used to generate equivalent atoms: (i) $x - 1, y, z$; (ii) $x, -y + 1/2, z + 1/2$.

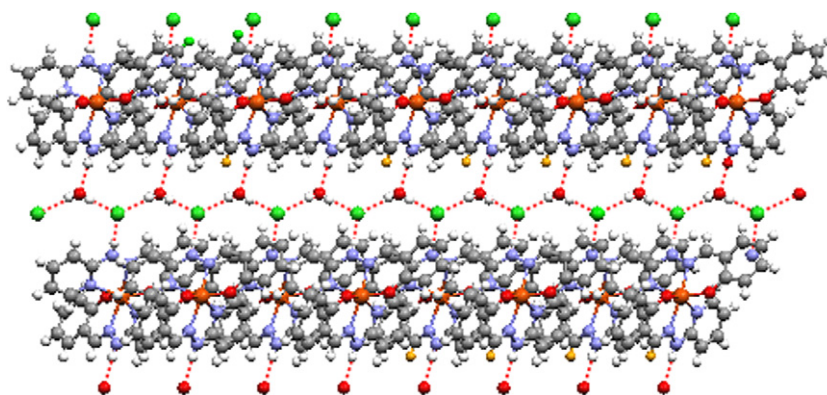


Fig. 5. Packing diagram along the *b* axis exhibiting alternate Cl(1) (●)···H–O(1w) (●) bonding in [Fe^{III}(HL¹)₂]Cl · H₂O (**2**).

4. Conclusion

A series of blue luminescent high-spin ($s = 5/2$) iron(III) complexes of H_2L^1 have been successfully designed and synthesized. Deprotonation and insertion of a nucleophile into the parent complex significantly modulates the photo-physical and chemical properties. Moreover, the ligand and its iron(III) complex undergo photoinduced intramolecular azo-imine tautomerism. The association constant (K_{ass}) and thermodynamic calculations clearly revealed that the binding process is favoured by a negative ΔH^0 and positive ΔS^0 . The X-ray structure of complex **2** shows that the acyclic tridentate H_2L^1 (**1**), span meridionally, binding the metal in a hexadentate FeN_4O_2 fashion, utilizing pairs of pyridyl-N, phenolato-O and imine-N, resulting in a *cis* configuration for the FeN_4O_2 coordination sphere. The complex also displays bridging interlayer hydrogen bonding.

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Appendix A. Supplementary material

CCDC 632086 contains the supplementary crystallographic data for $[Fe^{III}(HL^1)_2]Cl \cdot H_2O$ (**2**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.03.053.

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