

A new chromogenic agent for iron(III): Synthesis, structure and spectroscopic studies

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Abstract. A heterocyclic hydrazone ligand, diacetyl monoxime-2-pyridyl hydrazone, HL, **1**, was investigated as a new chromogenic agent for selective detection of Fe³⁺. The ligand **1**, undergoes 1 : 2 complexation with Fe³⁺ and Ni²⁺ to form complexes [Fe^{III}(HL)₂]Cl₃, **1a** and [Ni^{II}(HL)₂]Cl₂, **1b** respectively. The iron(III) complex **1a** gives a characteristic absorption peak at 487 nm with distinct reddish-pink colouration. The change in colour can easily be distinguished from other metal complexes by the naked eye. No obvious interference was observed in presence of other metal ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺, Mn²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Co²⁺, Pb²⁺, Hg²⁺, Cd²⁺). The bands appearing in the UV region (200–340 nm) are characteristics of the ligand, HL, **1**. In the complexes [Fe^{III}(HL)₂]Cl₃, **1a**, and [Ni^{II}(HL)₂]Cl₂, **1b**, these ligand centered bands are accompanied by multiple bands extending into the visible region (350–500 nm). The association constants (K_{ass} , UV-Vis) were found to be $(6.4865 \pm 0.004) \times 10^5$ for the complex **1a** and $(1.1960 \pm 0.002) \times 10^5$ for the complex **1b** at 298 K determined by the UV-Vis spectroscopy. On excitation at 285 nm, the ligand HL, **1** strongly emits at 364 nm due to an intraligand¹ ($\pi - \pi^*$) transition. The complexes are luminescent (λ_{ex} 285 nm, λ_{em} 365 nm) with F/F_0 0.75 for **1a** and 0.81 for **1b**. In both the cases, the 1 : 2 binding is confirmed by Job's method. Molecular structure of the complex **1b** has been determined by single crystal X-ray diffraction studies. Here, two crystallographically distinct but metrically very similar molecules making an enantiomeric pair constitute the asymmetric unit in which both metal atoms are tris chelated in meridional geometry.

Keywords. Chromogenic agent; luminescent compounds; spectroscopy; thermodynamic parameters; structure.

1. Introduction

The recognition of ions and molecules is an essential part of supramolecular chemistry.^{1–5} The design and synthesis of chemosensors for heavy and transition metal ions are currently a task of prime importance for medical, environmental and biological applications.^{6–9} Presently one of the most attractive approaches focuses on the research of novel colourimetric metal ion sensors which allows naked eyes a real time and space detection of the change of colour upon metal ion binding without use of any spectroscopic instrument.^{10–14} Chemosensors not only possess simplicity and high sensitivity, but are capable of specific recognition of particular ions in presence of related ones.^{15–17} Iron is the most abundant essen-

tial transition metal and it plays very important roles in various biological processes.¹⁸ A few systems have been designed as selective chemosensors for iron (II)/iron (III) or total iron content.^{13,19–23} In our present work, we report a highly selective colourimetric chromogenic agent for iron(III) with a diacetyl monoxime-2-pyridyl hydrazone ligand, HL, (**1**), because it would be useful now-a-days to develop simple-to-use, naked eye diagnostic tools.

2. Experimental

2.1 Materials

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

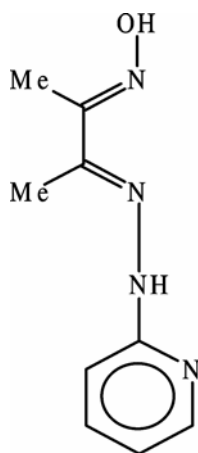
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2.2 Physical measurements

A Perkin Elmer 2400 C elemental analyser was used to collect microanalytical data (C, H, N). Sartorius CP64 balance was used for weighing purpose. FTIR data were collected with the help of FTIR 8400 Shimadzu Spectrophotometer. The UV-Vis spectra of the ligand and its complexes were measured on Shimadzu UV-1700 spectrophotometer and corrected for background due to solvent absorption. Emission spectra were carried out with a Perkin Elmer LS 50B Luminescence Spectrometer. For binding constant measurements solutions were prepared at a fixed concentration of HL, **1** (1.0×10^{-5} M) and at a concentration of metal ions ranging from $(1.0 \text{ to } 10.0) \times 10^{-6}$ M at room temperature. Electrochemical measurements were performed in aqueous medium under nitrogen atmosphere on a Versastat II PAR Electrochemistry system using a platinum electrode. NH_4PF_6 was used as a supporting electrolyte and the potentials are referenced to the Ag/AgCl electrode. Solution electrical conductivities were measured with the help of a Philips PR 9500 bridge, the solute concentration being 10^{-3} M. For spectroscopic measurements HPLC grade solvents were used.

2.3 X-ray structure determination of $[\text{Ni}^{\text{II}}(\text{HL})_2]\text{Cl}_2$, **1b**

The plate-like brown coloured crystals of $[\text{Ni}^{\text{II}}(\text{HL})_2]\text{Cl}_2$, **1b**, were grown by slow evaporation of methanol at room temperature and mounted on a glass fibre. Intensity data for the complex **1b** was



HL, **1**

collected at 173 K (-100°C) by the ω -scan method over the 2θ range $1.36\text{--}25.71^\circ$ on a Stoe Mark II-Image plate diffraction system²⁴ equipped with a two-circle goniometer and using $\text{MoK}\alpha$ graphite monochromated radiation ($\lambda = 0.71073 \text{ \AA}$). Structure solution and refinement were done by direct methods using SHELXS-97 and SHELXL-97 programs.^{25–27} The structure was successfully solved in space group $P2_1/c$. Of the 10986 independent reflections, 8494 satisfying $I > 2\sigma(I)$ were used for structure solution. All non-hydrogen atoms were refined anisotropically. An absorption correction was applied using MULScanABS in PLATON.²⁸ The molecular structure and crystallographic numbering scheme are illustrated in the PLATON drawing.²⁸ Details regarding the crystallographic structure determination are given in table 1. We were unable to crystallize the iron(III) complex **1a**, but the elemental analysis and the stoichiometric studies (*vide supra*) confirm the 1 : 2 binding in $[\text{Fe}^{\text{III}}(\text{HL})_2]\text{Cl}_3$, **1a**.

Table 1. Crystallographic data for $[\text{Ni}^{\text{II}}(\text{HL})_2]\text{Cl}_2$, **1b**.

Compound	1b
Formula	$\text{C}_{18}\text{H}_{38}\text{Cl}_2\text{N}_8\text{NiO}_9$
Formula mass	640.17
$T(\text{K})$	173(2) K
Wavelength (\AA)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (\AA)	11.881(4)
b (\AA)	17.824(7)
c (\AA)	28.953(9)
α ($^\circ$)	90
β ($^\circ$)	108.427(2)
γ ($^\circ$)	90
V [\AA^3]	5817.2
Z	8
D_{calc} (g/cm^{-3})	1.462
μ (mm^{-1})	0.908
$F(000)$	2688
Limiting indices	$-14 < h < 14, -21 < k < 21, -35 < l < 35$
Reflns collected/unique	10986/8494
Refinement method	Full-matrix least-squares on $ F $
Data/restraints/parameters	10986/4/578
GOF on F^2	1.039
$R1^{[a]}, wR2^{[b]}$ [$I > 2\sigma(I)$]	$R1 = 0.0841, wR2 = 0.1974$
$R1^{[a]}, wR2^{[b]}$ (all data)	$R1 = 0.0670, wR2 = 0.1876$
Largest diff. peak and hole ($\text{e}\text{\AA}^{-3}$)	1.232, -1.326

^a $R_1 = [\sum||F_o| - |F_c||] / \sum|F_o|$ (based on F); ^b $wR_2 = [(\sum(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ (based on F^2)

2.4 Syntheses of ligand and complexes

2.4a *Diacetyl monoxime-2-pyridyl hydrazone ligand, HL, 1*: The ligand was prepared by the same general procedure as before.^{29,30}

2.4b *Synthesis of $[Fe^{III}(HL)_2]Cl_3$, 1a*: To a stirred methanolic solution of anhydrous iron(III) chloride (0.03 g, 0.2 mmol) was added a solution of HL, **1**, (0.03 g, 0.4 mmol) in methanol (5 ml) and the resulting reddish-pink solution was stirred for 0.5 h. The solvent was evaporated by rotary evaporator and recrystallized from methanol. Yield. 0.10 g, 84%. Anal. calc. for $C_{18}H_{24}N_8O_2Cl_3Fe$: C 39.53, H 4.39, N 20.49; found C 39.56, H 4.38, N 20.50%. Selected FTIR data, ν (cm^{-1}): 3425, 3271, 2925, 1649, 1616, 1554, 1481, 1448, 1319, 1282, 1259, 1218, 1110, 1091, 931, 817, 769, 626, 524, 499, 464. UV-Vis (CH_3OH), λ_{max} (nm) (ϵ , $M^{-1} cm^{-1}$): 487(8400), 350 (27000), 287 (32000), 240 (40000).

2.4c *Synthesis of $[Ni^{II}(HL)_2]Cl_2$, 1b*: To a stirred methanolic solution of $NiCl_2 \cdot 6H_2O$ (0.04 g, 0.2 mmol) was added a solution of HL, **1**, (0.03 g, 0.4 mmol) in methanol (5 ml) and the resulting brown solution was stirred for 0.5 h. The solvent was evaporated by rotary evaporator and on recrystallization from methanol deep brown crystals of the complex was obtained. Yield 0.11 g, 86%. Anal. calc. for $C_{18}H_{38}Cl_2N_8NiO_9$: C 33.74, H 5.93, N 17.49; found C 33.76, H 5.94, N 17.48%. Selected FTIR data, ν (cm^{-1}): 3398, 3164, 3109, 3060, 2968, 2918, 1645, 1616, 1573, 1481, 1427, 1380, 1309, 1280, 1251, 1222, 1135, 1060, 1010, 966, 902, 806, 773, 526, 476. UV-Vis (CH_3OH), λ_{max} (nm) (ϵ , $M^{-1} cm^{-1}$): 448 (8500), 352 (29000), 289 (34000), 240 (40000).

2.5 Stoichiometry calculation

The metal to ligand ratio (n) for the complexation reaction was ascertained by Job's method of continuous variation.

2.5a *Job's method of continuous variation*: This method is performed by preparing several solutions consisting of varying amounts of the metal ion and the ligand, however the sum of the metal ion concentration and the ligand concentration is constant for each solution. The absorbance of each solution is measured and plotted against the mole fraction of

metal ion or the mole fraction of ligand. The mole fraction of the metal, M , is defined as

$$\text{Mole fraction} = C_m / (C_m + C_l),$$

where C_m = the concentration of the metal and C_l = the concentration of the ligand.

3. Results and discussion

3.1 Synthesis and characterization

The ligand HL, **1** used in the present work is tridentate in nature incorporating pyridyl, imine and oxime N-atoms as potential donor sites. It reacts with anhydrous $FeCl_3$ and $NiCl_2 \cdot 6H_2O$ in methanol at room temperature in 1:2 molar ratio to afford reddish-pink and brown coloured complexes $[Fe^{III}(HL)_2]Cl_2$, **1a** and $[Ni^{II}(HL)_2]Cl_2$, **1b** in high yields. The elemental analysis data are consistent with their empirical formulae. All the complexes are soluble in methanol and sparingly soluble in water. Room temperature (298 K) magnetic moments of complexes **1a** and **1b** are $4.9 \mu_B$ ($S = 2$) and $2.84 \mu_B$ ($S = 1$) respectively, corresponding to the high spin configuration in both the cases.

3.2 Spectral studies

All the spectroscopic measurements were carried out in degassed methanol at room temperature. The bands appearing in the UV region (200–340 nm) are characteristics of the ligand, HL, **1**. In the complexes these ligand centered bands are accompanied by multiple bands extending into the visible region (350–500 nm). On excitation at 285 nm, the ligand HL, **1** strongly emits at 364 nm due to an intraligand $^1(\pi-\pi^*)$ transition. The complexes are luminescent ($\lambda_{ex} = 285$ nm, $\lambda_{em} = 365$ nm) with F/F_0 0.75 for **1a** and 0.81 for **1b**. The absorption maxima of the ligand are decreased linearly with increase of metal ion concentration (1×10^{-6} M). With M^{2+} /ligand HL mole ratio 1:2, a characteristic peak is developed at 487 nm for the iron(III) complex **1a** with clear isosbestic point at 327 nm (figure 1). The absorption peak generated in the visible region is maximum red shifted in case of complex **1a**, with a distinct colour change from yellow to reddish-pink which can easily be read through naked eyes without any spectroscopic instrument (figure 2). In order to study the effects of other metal ions, competition experiments were conducted in presence of Fe^{3+} that is also

mixed with Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} , Hg^{2+} , Cd^{2+} ions at 10^{-5} M. No obvious interference was observed in presence of other metal ions as shown in table 2. Thus the ligand HL, **1** can be effectively used as a chromogenic agent for Fe^{3+} .

3.3 Thermodynamics of binding

The association constant (K_{ass}) of complexes can be estimated spectrophotometrically (figure 1) according to the (1),^{29,31} where X represents the absorption intensity, X_{lim} represents the absorption intensity at full complexation, C_0 is the initial concentration of the ligand, C_{H} and C_{G} are the corresponding concentrations of the ligand and metal ion during titration. The K_{ass} (UV-Vis) was found to be $(6.4865 \pm 0.004) \times 10^5$ for **1a** which was higher than **1b** (K_{ass} (UV-Vis) $1.1960 \pm 0.002) \times 10^5$) at 298 K.

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

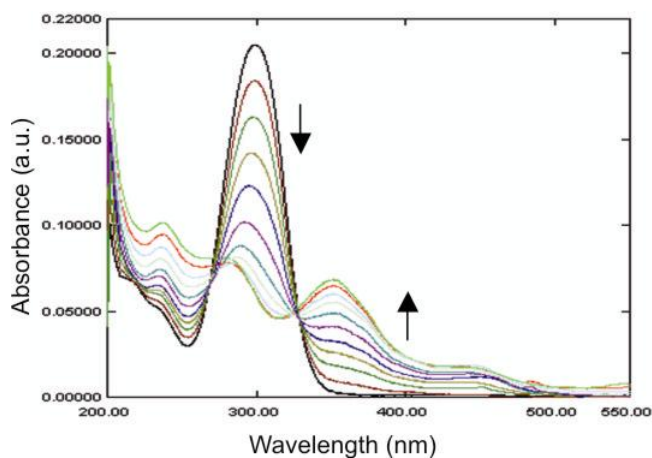


Figure 1. Absorbance spectra of HL, **1**, (1.0×10^{-5} M) upon addition of Fe(III), (1.0×10^{-6} M – 1.0×10^{-5} M) in degassed methanol (pH = 7.0) at 298 K.



Figure 2. The photograph of ligand HL, **1** in methanol solution after the addition of different metal ions and the mixture (Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+}).

The temperature dependence of binding constant was studied between 293–308 K and the values of the thermodynamic parameters for the binding were obtained by variable temperature UV-Vis titration in degassed methanol at 298 K. The standard Gibbs energy change, ΔG^0 , the standard enthalpy change, ΔH^0 and the standard entropy change, ΔS^0 which are listed in table 3, are calculated using Vant Hoff's equation. The stoichiometry (n) of the complexes **1a** and **1b** is confirmed by the Job's plot (table 3).

3.4 Metal redox

The redox properties of **1a** and **1b** have been studied in double distilled deionized water by cyclic voltammetry using a platinum working electrode. The complex **1a** exhibits quasi reversible single reductive response ($E_{\text{Fe(III/II)}}$, 0.10 V; $\Delta E_{\text{p}} = 280$ mV vs Ag/AgCl) and the complex **1b** shows single oxidative response ($E_{\text{Ni(II/III)}}$, 0.70 V; $\Delta E_{\text{p}} = 240$ mV vs Ag/AgCl) under nitrogen atmosphere. A representative diagram of the cyclic voltammogram of the complex **1a** is shown in figure 3.

Attempted isolation of the bivalent species for **1a** did not succeed due to its rapid oxidation in air.

3.5 Molecular Structure of $[\text{Ni}^{\text{II}}(\text{HL})_2]\text{Cl}_2$, **1b**

The molecular structure of $[\text{Ni}^{\text{II}}(\text{HL})_2]\text{Cl}_2$, **1b** clearly shows that ligand binds to the metal in a tridentate manner utilizing pyridyl, imine and oxime N-atoms as potential donor sites. Selected bond distances and angles are listed in table 4. In complex **1b**, two crys-

Table 2. Interference of metal ions in the Fe^{3+} detection.

Fe^{3+} + metal ions	Absorbance (at 487 nm)
$\text{Fe}^{3+} + \text{Ca}^{2+}$	0.124
$\text{Fe}^{3+} + \text{Mg}^{2+}$	0.122
$\text{Fe}^{3+} + \text{Al}^{3+}$	0.122
$\text{Fe}^{3+} + \text{Hg}^{2+}$	0.123
$\text{Fe}^{3+} + \text{Zn}^{2+}$	0.120
$\text{Fe}^{3+} + \text{Cu}^{2+}$	0.116
$\text{Fe}^{3+} + \text{Cd}^{2+}$	0.123
$\text{Fe}^{3+} + \text{Pb}^{2+}$	0.122
$\text{Fe}^{3+} + \text{Mn}^{2+}$	0.122
$\text{Fe}^{3+} + \text{Co}^{2+}$	0.119
$\text{Fe}^{3+} + \text{Ni}^{2+}$	0.117
Fe^{3+}	0.124

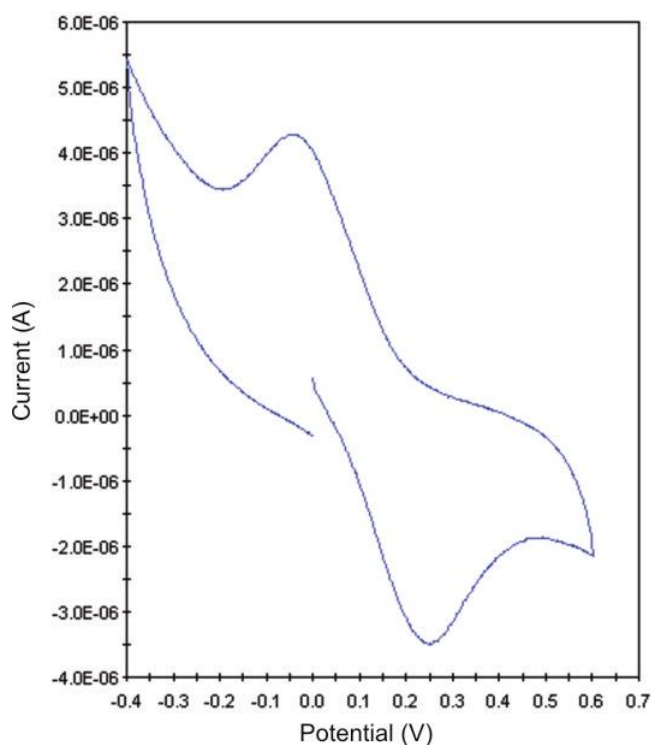
FeCl_3 (1.0×10^{-5} M) was added to the solution of ligand HL, **1** (1.0×10^{-5} M) in the presence of other metal ions (1.0×10^{-5} M)

Table 3. Binding and thermodynamic parameters for **1a** and **1b**.

Complexes	K_{ass}	ΔG^0 (cal/M)	ΔH^0 (cal/M)	ΔS^0 (cal/M/deg)	n
$[\text{Fe}^{\text{III}}(\text{HL})_2]^{3+}$, 1a	$(6.4865 \pm 0.004) \times 10^5$	(-7976.05 ± 1.37)	(-245.9 ± 2.01)	(25.94 ± 0.054)	0.56
$[\text{Ni}^{\text{II}}(\text{HL})_2]^{2+}$, 1b	$(1.1960 \pm 0.002) \times 10^5$	(-6968.37 ± 4.06)	(-399.33 ± 2.21)	(22.04 ± 0.032)	0.53

Table 4. Selected bond distances (Å) and angles (°) for $[\text{Ni}^{\text{II}}(\text{HL})_2]\text{Cl}_2$, **1b**.

Bond lengths			
Ni(1)–N(1)	2.047(4)	Ni(1)–N(3)	2.023(4)
Ni(1)–N(4)	2.170(4)	Ni(1)–N(5)	2.078(3)
Ni(1)–N(7)	2.003(4)	Ni(1)–N(8)	2.136(3)
Ni(2)–N(11)	2.003(4)	Ni(2)–N(12)	2.120(3)
Ni(2)–N(13)	2.085(3)	Ni(2)–N(15)	1.998(4)
Ni(2)–N(16)	2.149(4)	Ni(2)–N(9)	2.076(3)
Bond angles			
N(1)–Ni(1)–N(4)	154.08(15)	N(1)–Ni(1)–N(5)	92.74(14)
N(1)–Ni(1)–N(7)	103.39(14)	N(1)–Ni(1)–N(8)	91.97(14)
N(3)–Ni(1)–N(1)	78.8(2)	N(3)–Ni(1)–N(4)	75.25(14)
N(3)–Ni(1)–N(5)	99.40(15)	N(3)–Ni(1)–N(7)	176.85(14)
N(3)–Ni(1)–N(8)	106.35(15)	N(4)–Ni(1)–N(5)	90.30(13)
N(4)–Ni(1)–N(7)	102.43(14)	N(4)–Ni(1)–N(8)	96.38(13)
N(5)–Ni(1)–N(7)	78.38(14)	N(5)–Ni(1)–N(8)	154.25(14)
N(7)–Ni(1)–N(8)	75.90(14)	N(9)–Ni(2)–N(15)	99.24(15)
N(9)–Ni(2)–N(13)	91.18(14)	N(11)–Ni(2)–N(12)	76.18(14)
N(9)–Ni(2)–N(16)	93.69(14)	N(11)–Ni(2)–N(15)	176.2(2)
N(11)–Ni(2)–N(13)	99.01(15)	N(12)–Ni(2)–N(13)	95.56(14)
N(11)–Ni(2)–N(16)	107.32(14)	N(12)–Ni(2)–N(16)	91.27(14)
N(12)–Ni(2)–N(15)	106.63(14)	N(13)–Ni(2)–N(16)	153.66(14)
N(13)–Ni(2)–N(15)	78.21(15)	N(9)–Ni(2)–N(11)	78.06(14)
N(15)–Ni(2)–N(16)	75.46(14)	N(9)–Ni(2)–N(12)	154.08(15)

**Figure 3.** Cyclic voltammogram of $[\text{Fe}^{\text{III}}(\text{HL})_2]\text{Cl}_3$, **1a** in aqueous solution (pH = 7.2) at room temperature.

tallographically distinct but metrically very similar molecules making an enantiomeric pair constitute the asymmetric unit in which both metal atoms are *bis* chelated in meridional geometry as shown in figure 4.

Selected bond lengths of the complex, **1b** has been reported as Ni(1)–N(1) 2.047(4) Å, Ni(1)–N(3) 2.023(4) Å, Ni(1)–N(4) 2.170(4) Å, Ni(1)–N(5) 2.078(3) Å, Ni(1)–N(7) 2.003(4) Å, Ni(1)–N(8) 2.136(3) Å, Ni(2)–N(11) 2.003(4) Å, Ni(2)–N(12) 2.120(3) Å, Ni(2)–N(13) 2.085(3) Å, Ni(2)–N(15) 1.998(4) Å, Ni(2)–N(16) 2.149(4) Å, Ni(2)–N(9) 2.076(3) Å. The four five-membered rings are almost planar. The NiN_6 coordination spheres are distorted from octahedral geometry as can be seen from the angles at the metal centres. The angles at the metal centre between the *cis*-positioned donor pairs span the range $75.25(14)^\circ$ – $106.35(15)^\circ$ and those between the *trans*-positioned pairs are $154.08(15)$ – $176.85(14)^\circ$ for the centre Ni(1), whereas for the centre Ni(2) the angles at the metal centre between the *cis*-positioned donor pairs span the range $75.46(14)^\circ$ – $107.32(14)^\circ$ and those

between the *trans*-positioned pairs are $153.66(14)^\circ$ – $176.2(2)^\circ$. The average Ni–N_{ox} distance is $\sim 2.14 \text{ \AA}$ which is much longer than the reported Ni–N_{ox} distance $\sim 2.04 \text{ \AA}$,³² where oxime is deprotonated.

4. Conclusion

In conclusion, we have designed a highly selective chromogenic agent for detection of iron(III) via design of a heterocyclic hydrazone ligand, diacetyl monoxime-2-pyridyl hydrazone HL, **1**. The ligand shows a remarkable colour change with iron(III) from yellow to reddish-pink that exhibits a characteristic absorption peak at 487 nm. The change in colour can easily be distinguished from other metal complexes by the naked eye. No obvious interference was observed in presence of other metal ions (Ca^{2+} , Mg^{2+} , Al^{3+} , Pb^{2+} , Hg^{2+} , Cd^{2+} , Mn^{2+} , Na^+ , K^+ , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}). The association constant (K_{ass} , UV-Vis) was found to be $(6.4865 \pm 0.004) \times 10^5$ for the complex **1a** and $(1.1960 \pm 0.002) \times 10^5$ for the complex **1b** at 298 K determined by the UV-Vis spectroscopy. On excitation at 285 nm, the ligand **1** strongly emits at 364 nm due to an intraligand $^1(\pi - \pi^*)$ transition. Both the complexes are also luminescent ($\lambda_{\text{ex}} = 285 \text{ nm}$, $\lambda_{\text{em}} = 365 \text{ nm}$, F/F_0 0.75 for **1a** and 0.81 for **1b**). The 1 : 2 binding of the Fe^{3+} and Ni^{2+} with the ligand in the complexes **1a** and **1b** is confirmed by Job's method. In complex **1b**, two crystallographically distinct but metrically very similar molecules making an enantiomeric pair constitute the asymmetric unit in which both metal atoms are *tris* chelated in meridional NiN₆ geometry.

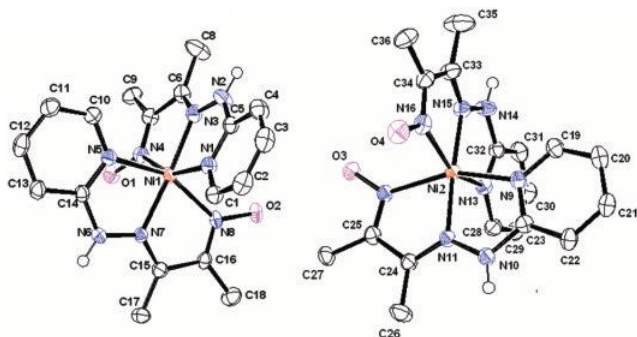


Figure 4. Molecular structure of the complex, $[\text{Ni}^{\text{II}}(\text{HL})_2]\text{Cl}_2$, **1b** with thermal ellipsoids drawn at the 50% probability level. The water molecules have been omitted for clarity.

Supplementary material

Crystallographic data for the complex $[\text{Ni}^{\text{II}}(\text{HL})_2]\text{Cl}_2$, **1b** in the CIF format has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 715865. 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; e-mail: deposit@ccdc.cam.ac.uk.

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