



REGULAR ARTICLE

# *N*-(acyl)-*N'*-(ferrocenylidene)hydrazines and their nickel(II) complexes: Syntheses, structures and physical properties<sup>†</sup>

G NARENDRA BABU and SAMUDRANIL PAL\*

School of Chemistry, University of Hyderabad, Hyderabad, Telengana 500 046, India  
E-mail: spal@uohyd.ac.in

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**Abstract.** The Schiff bases *N*-(acyl)-*N'*-(ferrocenylidene)hydrazines (HFcah (**1**) and HFcbh (**2**), where acyl = acetyl in **1** and benzoyl in **2** and H represents the dissociable amide proton) were synthesized in high yields (74 and 81%) by condensation reactions of equimolar amounts of ferrocene-carboxaldehyde and the corresponding acylhydrazines in presence of acetic acid in refluxing methanol. Reactions of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, the Schiff bases (**1** and **2**) and NaOAc·3H<sub>2</sub>O in 1:2:4 mole ratio in refluxing methanol afforded the diamagnetic iron(II)-nickel(II)-iron(II) species [Ni(Fcah)<sub>2</sub>] (**3**) and [Ni(Fcbh)<sub>2</sub>] (**4**) in 60 and 68% yields, respectively. Both Schiff bases and the two trinuclear complexes were characterized by elemental (CHN) analysis, mass spectrometric, various spectroscopic (IR, UV-Vis and <sup>1</sup>H NMR) and cyclic voltammetric measurements. Molecular structures of **2**, **3** and **4** were determined by single crystal X-ray diffraction studies. The cyclopentadienide rings in the ferrocene moieties are essentially in eclipsed conformation in all three structures. Deprotonated Schiff base ligands in each complex (Fcah<sup>-</sup> in **3** and Fcbh<sup>-</sup> in **4**) act as five-membered chelate ring forming azomethine-N and amidate-O donors and assemble a square-planar *trans*-N<sub>2</sub>O<sub>2</sub> coordination environment around the nickel centre. The redox active **1–4** exhibit an iron centred redox couple in the potential range 0.23–0.50 V (vs. Ag/AgCl).

**Keywords.** Nickel (II); ferrocene; acylhydrazones; crystal structures; physical properties.

## 1. Introduction

Since the discovery of ferrocene and elucidation of its structure,<sup>1–4</sup> it has attracted enormous attention due to its exceptional stability, electron-transfer properties and benzene-like versatile reactivity. These properties have led to the development of a vast number of ferrocene derivatives and their applications in a wide range of research areas such as catalytic organic synthesis, biological and medicinal chemistry, agrochemicals and materials science.<sup>5–15</sup> Consequently, there is a continuous endeavour to design and synthesize ferrocene containing new molecules, which will have potential utility as functional materials or catalysts in organic synthetic reactions. Recently, we have reported a dipalladium(II) complex with a ferrocene containing diphosphine ligand<sup>16</sup> and its application as catalyst in C-C cross coupling reactions.<sup>17</sup> In

the present work, we have explored the coordination chemistry of the Schiff bases *N*-(acetyl/benzoyl)-*N'*-(ferrocenylidene)hydrazines with nickel(II). The reason for choosing these Schiff bases, other than having the redox active ferrocene moiety, is the presence of high oxidation state promoting O-coordinating amide functionality which can provide transition metal ion complexes with interesting electron transfer behaviour, a prerequisite for molecular materials and redox catalysts. Herein, we report the syntheses, structures and physical properties of the Schiff bases HFcah (**1**) and HFcbh (**2**) and their corresponding nickel(II) complexes [Ni(Fcah)<sub>2</sub>] (**3**) and [Ni(Fcbh)<sub>2</sub>] (**4**) containing the angular trinuclear iron(II)-nickel(II)-iron(II) array (Scheme 1).

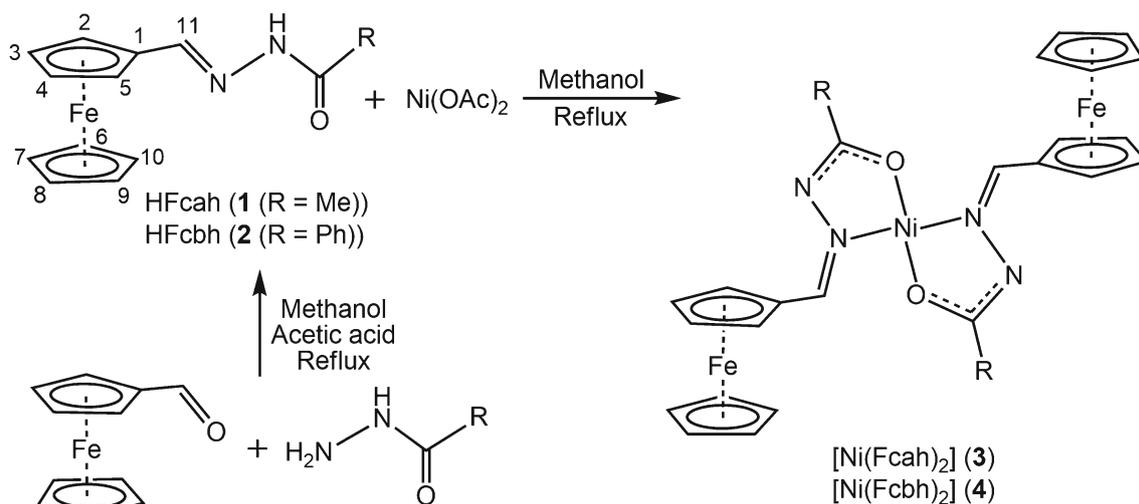
## 2. Experimental

### 2.1 Materials

All the chemicals used in this work were of analytical grade available commercially and were used as supplied without any

\*For correspondence

<sup>†</sup>Dedicated to Professor K. C. Kumara Swamy on the occasion of his 60th birth anniversary.



**Scheme 1.** Syntheses of *N*-(acyl)-*N'*-(ferrocenyldene)hydrazines and their Ni(II) complexes

further purification. Solvents used were purified by standard methods.<sup>18</sup>

## 2.2 Physical measurements

Elemental (CHN) analysis data were obtained with the help of a Thermo Finnigan Flash EA1112 series elemental analyser. Purity of the Schiff bases was checked using a Shimadzu LCMS 2010 liquid chromatograph mass spectrometer. A Bruker Maxis ESI-TOF spectrometer was used to record the high-resolution mass spectra. Magnetic susceptibility measurements were performed using a Sherwood Scientific balance. A Digisun DI-909 conductivity meter was used to measure the solution electrical conductivities. Infrared spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrophotometer. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used to collect the electronic spectra. The <sup>1</sup>H NMR spectra were acquired on a Bruker 400 MHz spectrometer. A CH-Instruments model 620A electrochemical analyser was employed for cyclic voltammetric measurements.

## 2.3 Synthesis of HFcah (1)

A mixture of acetylhydrazine (0.37 g, 5 mmol) and ferrocene-carboxaldehyde (1.07 g, 5 mmol) was taken in methanol (30 mL) and a few drops of acetic acid were added. The resulting mixture was refluxed for 12 h. The dark brown solid separated was filtered off and recrystallized from chloroform. Yield: 1.01 g (74%). Anal. Calcd. for C<sub>13</sub>H<sub>14</sub>FeN<sub>2</sub>O: C, 57.81; H, 5.22; N, 10.37%. Found: C, 57.72; H, 5.26; N, 10.26%. LCMS *m/z* for {M + H}<sup>+</sup> found (calcd.): 271.15 (270.97). Selected IR bands:  $\nu$  (cm<sup>-1</sup>) = 3187 (amide-NH), 1671 (amide-CO), 1605 (azomethine-CN). UV-Vis in CH<sub>2</sub>Cl<sub>2</sub>:  $\lambda_{\max}$  (nm) ( $\epsilon$  (10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>)) = 460 (0.05), 340<sup>sh</sup> (0.12), 292 (1.42), 250 (1.33). <sup>1</sup>H NMR in CDCl<sub>3</sub>:  $\delta$  (ppm) = 9.52 (s, 1H, NH), 7.68 (s, 1H, H<sup>11</sup>), 4.61 (s, 2H, H<sup>2</sup>, H<sup>5</sup>), 4.40

(s, 2H, H<sup>3</sup>, H<sup>4</sup>), 4.22 (s, 5H, H<sup>6-10</sup>), 2.34 (s, 3H, R = CH<sub>3</sub>). CV data in CH<sub>2</sub>Cl<sub>2</sub>: E<sub>1/2</sub> (V) ( $\Delta E_p$  (mV)) = 0.23 (160).

## 2.4 Synthesis of HFcbh (2)

To a methanol solution (30 mL) of benzoylhydrazine (0.68 g, 5 mmol) and ferrocene-carboxaldehyde (1.07 g, 5 mmol) few drops of acetic acid were added and the mixture was boiled under reflux for 9 h. The brown solid formed was collected by filtration and recrystallized from chloroform. Yield: 1.34 gm (81%). Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>FeN<sub>2</sub>O: C, 65.08; H, 4.85; N, 8.43%. Found: C, 65.17; H, 4.91; N, 8.36%. LCMS *m/z* for {M + H}<sup>+</sup> found (calcd.): 333.15 (332.98). Selected IR bands:  $\nu$  (cm<sup>-1</sup>) = 3191 (amide-NH), 1638 (amide-CO), 1605 (azomethine-CN). UV-Vis in CH<sub>2</sub>Cl<sub>2</sub>:  $\lambda_{\max}$  (nm) ( $\epsilon$  (10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>)) = 456 (0.09), 360<sup>sh</sup> (0.23), 300 (1.43), 258 (1.12). <sup>1</sup>H NMR in CDCl<sub>3</sub>:  $\delta$  (ppm) = 9.05 (s, 1H, NH), 8.27 (s, 1H, H<sup>11</sup>), 7.87 (s, 2H, *ortho* Hs of R = Ph), 7.57–7.49 (m, 3H, *meta* and *para* Hs of R = Ph), 4.74 (s, 2H, H<sup>2</sup>, H<sup>5</sup>), 4.45 (s, 2H, H<sup>3</sup>, H<sup>4</sup>), 4.24 (s, 5H, H<sup>6-10</sup>). CV data in CH<sub>2</sub>Cl<sub>2</sub>: E<sub>1/2</sub> (V) ( $\Delta E_p$  (mV)) = 0.36 (130).

## 2.5 Synthesis of [Ni(Fcah)<sub>2</sub>] (3)

A mixture of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.25 g, 1 mmol), HFcah (0.54 gm, 2 mmol) and NaOAc·3H<sub>2</sub>O (0.55 g, 4 mmol) was taken in 30 mL of methanol and heated to boiling under reflux for 8 h. The brown solid precipitated was filtered off, washed first with water (20 mL) and then with methanol (2 × 10 mL portions) and finally dried in vacuum. Yield: 0.36 g (60%). Anal. Calcd. for C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>Fe<sub>2</sub>Ni: C, 52.32; H, 4.39; N, 9.39%. Found: C, 52.41; H, 4.32; N, 9.45%. HRMS *m/z* for {M + H}<sup>+</sup> found (calcd.): 597.02 (597.60). Selected IR bands:  $\nu$  (cm<sup>-1</sup>) = 1614 (amidate-CO), 1552 (amidate-CN-NC-azomethine). UV-Vis in CH<sub>2</sub>Cl<sub>2</sub>:  $\lambda_{\max}$  (nm) ( $\epsilon$  (10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>)) = 475 (0.32), 377 (1.41), 330<sup>sh</sup> (1.28), 295 (1.56), 263 (1.57). <sup>1</sup>H NMR in CDCl<sub>3</sub>:  $\delta$  (ppm) = 6.83 (s, 1H, H<sup>11</sup>), 5.03 (s, 2H, H<sup>2</sup>, H<sup>5</sup>), 4.49 (s, 2H, H<sup>3</sup>, H<sup>4</sup>),

4.31 (s, 5H, H<sup>6-10</sup>), 1.95 (s, 3H, R = CH<sub>3</sub>). CV data in CH<sub>2</sub>Cl<sub>2</sub>: E<sub>1/2</sub> (V) (ΔE<sub>p</sub> (mV)) = 0.50 (210).

## 2.6 Synthesis of [Ni(Fcbh)<sub>2</sub>] (4)

To 30 mL of methanol, Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.25 g, 1 mmol), HFcbh (0.67 gm, 2 mmol) and NaOAc·3H<sub>2</sub>O (0.55 g, 4 mmol) were added and the mixture was boiled under reflux for 8 h. The brick-red solid formed was collected by filtration, washed with water (20 mL) followed by 2 x 10 mL portions of methanol and finally dried in vacuum. Yield: (0.49 g, 68%). Anal. Calcd. for C<sub>36</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Fe<sub>2</sub>Ni: C, 59.97; H, 4.19; N, 7.77%. Found: C, 59.85; H, 4.25; N, 7.71%. HRMS m/z for {M + H}<sup>+</sup> found (calcd.): 721.05 (721.63). Selected IR bands: ν (cm<sup>-1</sup>) = 1614 (amidate-CO), 1585 (amidate-CN-NC-azomethine). UV-Vis in CH<sub>2</sub>Cl<sub>2</sub>: λ<sub>max</sub> (nm) (ε (10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>)) = 488 (0.64), 390 (1.97), 335<sup>sh</sup> (2.23), 305 (2.98), 265<sup>sh</sup> (2.62). <sup>1</sup>H NMR in CDCl<sub>3</sub>: δ (ppm) (J<sub>H-H</sub> (Hz)) = 8.03 (8) (d, 2H, *ortho* Hs of R = Ph), 7.51-7.42 (m, 3H, *meta* and *para* Hs of R = Ph), 7.18 (s, 1H, H<sup>11</sup>), 5.19 (s, 2H, H<sup>2</sup>, H<sup>5</sup>), 4.60 (s, 2H, H<sup>3</sup>, H<sup>4</sup>), 4.34 (s, 5H, H<sup>6-10</sup>). CV data in CH<sub>2</sub>Cl<sub>2</sub>: E<sub>1/2</sub> (V) (ΔE<sub>p</sub> (mV)) = 0.47(210).

## 2.7 X-ray crystallography

X-ray quality crystals of the Schiff base HFcbh (2) were obtained as 2·CDCl<sub>3</sub> from its CDCl<sub>3</sub> solution in a NMR tube. On the other hand, single crystals of the complexes [Ni(Fcah)<sub>2</sub>] (3) and [Ni(Fcbh)<sub>2</sub>] (4) were grown by slow evaporation of their solutions in chloroform-acetonitrile (1:1) mixture. Complex 3 crystallized as it is without any solvent molecule, while complex 4 formed a chloroform solvate 4·CHCl<sub>3</sub>. X-ray intensity data for 2·CDCl<sub>3</sub> were collected at 298 K on a Bruker-Nonius SMART APEX CCD single crystal diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The SMART and the SAINT-Plus packages<sup>19</sup> were used for data collection and reduction, respectively. A Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used to acquire X-ray intensity data from 3 and 4·CHCl<sub>3</sub> at 298 K. Data collection and reduction were performed using APEX2 and SAINT-Plus packages, respectively.<sup>20</sup> Absorption corrections were done with the help of SADABS program.<sup>21</sup> The structures of 2·CDCl<sub>3</sub>, 3 and 4·CHCl<sub>3</sub> were solved by direct method in the space groups P3<sub>1</sub>, P2<sub>1</sub>/c and P2<sub>1</sub>/n, respectively. The asymmetric unit of each of 2·CDCl<sub>3</sub> and 4·CHCl<sub>3</sub> contains one complex molecule and a solvent molecule, while that of 3 contains one molecule of the complex. Each structure was refined on F<sup>2</sup> by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in the structure factor calculations at idealized positions by using a riding model. The SHELX-97 programs<sup>22</sup> accessed

via the WinGX package<sup>23</sup> were used for structure solution and refinement. The structural illustrations were prepared using ORTEP-3 for Windows.<sup>24</sup> Selected crystal data and refinement summary for all three structures are listed in Table 1.

## 3. Results and Discussion

### 3.1 Synthesis and characterization

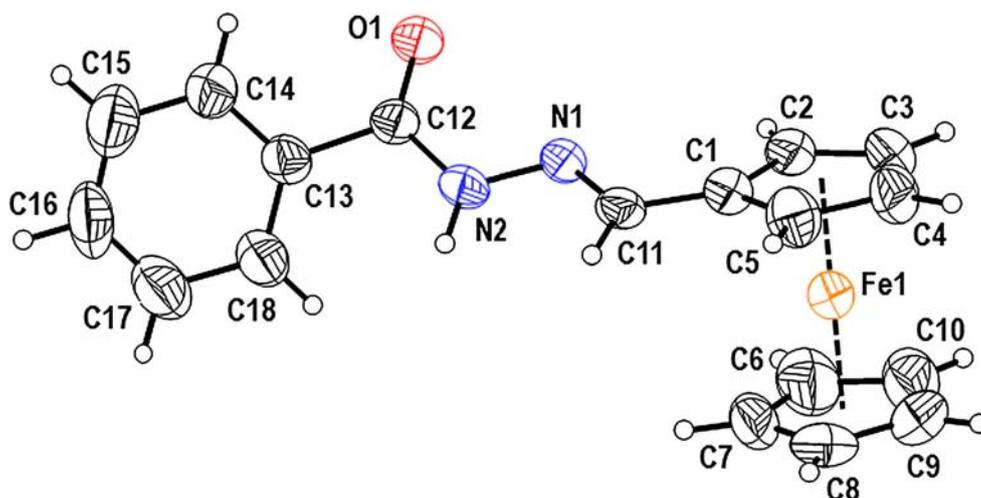
The Schiff bases HFcah (1) and HFcbh (2) were synthesised in very good yields (74 and 81%) by condensation reactions of equimolar amounts of ferrocene-carboxaldehyde and the corresponding acylhydrazines (acetylhydrazine and benzoylhydrazine) in methanol in presence of a few drops of acetic acid (Scheme 1). Both 1 and 2 were characterized by elemental analysis, mass spectrometric and spectroscopic (IR and <sup>1</sup>H NMR) measurements. The characterisation data are consistent with their molecular formulas and structures. The nickel(II) complexes [Ni(Fcah)<sub>2</sub>] (3) and [Ni(Fcbh)<sub>2</sub>] (4) were synthesized in 60 and 68% yields, respectively, by reacting Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, the corresponding Schiff bases and NaOAc·3H<sub>2</sub>O in 1:2:4 mole ratio in boiling methanol. The elemental analysis data of 3 and 4 are in good agreement with their molecular formulas. They are highly soluble in dichloromethane, chloroform, dimethylsulfoxide and dimethylformamide; sparingly soluble in acetonitrile and methanol and insoluble in *n*-hexane and toluene. Room temperature magnetic susceptibility measurements with powdered samples of 3 and 4 revealed their diamagnetic nature. Thus, the nickel centres in each complex are in +2 oxidation state and have square-planar coordination environments. In solution, the electrically non-conducting behaviour of both complexes supports their molecular formulas as neutral species.

### 3.2 X-ray molecular structures

Molecular structures of 2, 3 and 4 determined by single crystal X-ray diffraction analyses are depicted in Figures 1, 2 and 3, respectively. Selected geometric parameters are listed in Table 2. In all three structures, the planar cyclopentadienide (Cp<sup>-</sup>) rings in the FeCp<sub>2</sub> fragments are essentially parallel. The dihedral angles between the two Cp<sup>-</sup> planes span the range 0.16(23)–2.75(21)°. The double-decker FeCp<sub>2</sub> units are in the eclipsed rather than the staggered conformation. The torsion angles involving the opposing corners of the Cp<sup>-</sup> rings are in the ranges 2.80–4.91° for 2, 4.40–6.45° and 2.53–3.47° for 3 and 3.65–4.89°

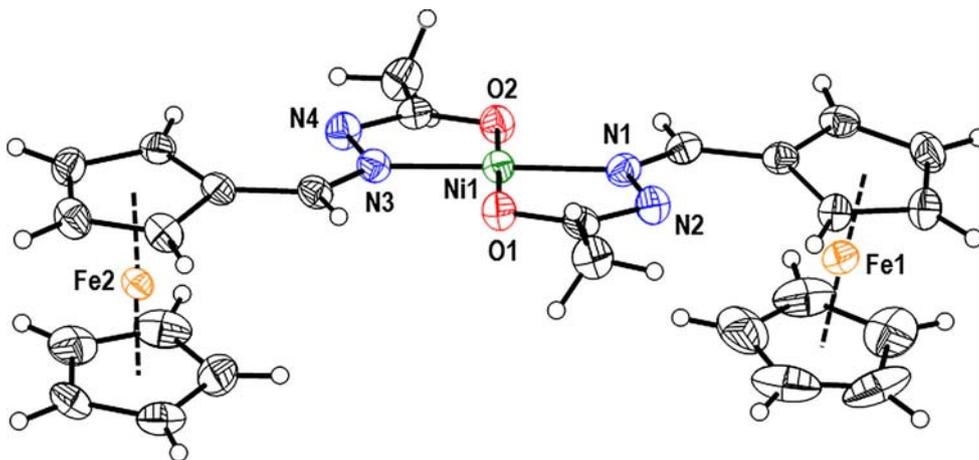
**Table 1.** Selected crystal data and structure refinement summary.

Compound	2·CDCl <sub>3</sub>	3	4·CHCl <sub>3</sub>
Chemical formula	C <sub>19</sub> H <sub>16</sub> DN <sub>2</sub> OCl <sub>3</sub> Fe	C <sub>26</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> Fe <sub>2</sub> Ni	C <sub>37</sub> H <sub>31</sub> N <sub>4</sub> O <sub>2</sub> Cl <sub>3</sub> Fe <sub>2</sub> Ni
Formula weight	452.55	596.92	840.42
Crystal system	Trigonal	Monoclinic	Monoclinic
Space group	<i>P</i> 3 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	12.3802(12)	11.6562(5)	16.5132(13)
<i>b</i> (Å)	12.3802(12)	20.5748(9)	13.1438(11)
<i>c</i> (Å)	11.623(2)	11.5414(4)	16.8401(15)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90	119.312(1)	107.255(3)
$\gamma$ (°)	120	90	90
Volume (Å <sup>3</sup> )	1542.7(4)	2413.52(17)	3490.6(5)
<i>Z</i>	3	4	4
$\rho$ (g cm <sup>-3</sup> )	1.461	1.643	1.599
$\mu$ (mm <sup>-1</sup> )	1.133	1.990	1.624
Reflections collected	14898	28639	63579
Reflections unique	3613	4246	6124
Reflections [ <i>I</i> ≥ 2σ( <i>I</i> )]	2939	3658	4724
Data/restr./param.	3613/1/235	4246/0/318	6124/0/442
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0565, 0.1415	0.0273, 0.0674	0.0648, 0.1750
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0703, 0.1527	0.0350, 0.0706	0.0868, 0.1887
GoF on <i>F</i> <sup>2</sup>	1.027	1.069	1.045
Max./Min. Δρ (e Å <sup>-3</sup> )	0.482/−0.274	0.797/−0.339	1.869/−1.081

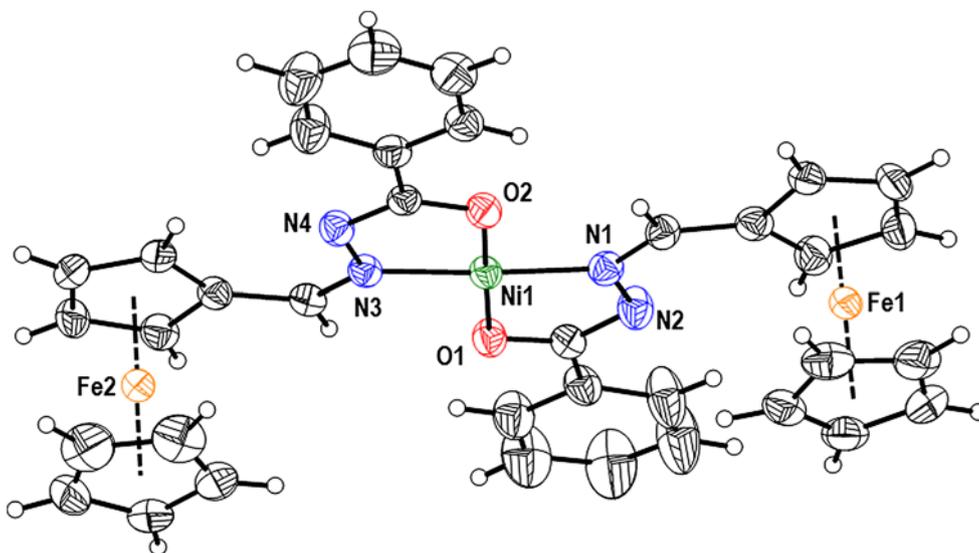
**Figure 1.** Molecular structure of HFcbh (**2**) with the atom labeling scheme. Thermal ellipsoids of all non-hydrogen atoms are drawn at the 40% probability level.

and 10.67–12.03° for **4**. The Fe–Cg (Cg = centroid of Cp<sup>−</sup>) (1.633–1.659 Å) and the Fe–C (Cp<sup>−</sup>) distances (2.004(8)–2.060(7) Å) are comparable with the corresponding distances reported for the eclipsed conformation of FeCp<sub>2</sub>.<sup>25,26</sup> The C=O and the C–N bond lengths of the amide functionality in **2** are shorter (by 0.097 Å) and longer (by 0.047 Å), respectively, when compared with the averages of the corresponding bond lengths in **3** and **4** (Table 2). These differences clearly indicate that the amide functionalities of the ligands in

each complex are deprotonated.<sup>16,27,29,29</sup> Further, the C–O and the C–N distances in the amidate moieties of the ligands in **3** and **4** clearly indicate the delocalisation of the corresponding negative charge over the –(O)CN– fragment. The ligands (Fcah<sup>−</sup> in **3** and Fcbh<sup>−</sup> in **4**) coordinate the nickel centre *via* the azomethine–N and the amidate–O atoms to form two five-membered chelate rings and a *trans*-N<sub>2</sub>O<sub>2</sub> coordination environment in both complexes (Figures 2 and 3). The chelate bite angles (83.4–83.7°) in **3** and **4** are unexceptional and



**Figure 2.** Molecular structure of  $[\text{Ni}(\text{Fcah})_2]$  (**3**). Thermal ellipsoids of all non-hydrogen atoms are shown at the 40% probability level. For clarity only the non-carbon atoms are labeled.



**Figure 3.** Molecular structure of  $[\text{Ni}(\text{Fcbh})_2]$  (**4**). All non-hydrogen atoms are represented by their 40% probability thermal ellipsoids. For clarity the carbon atoms are not labeled.

very similar to those reported earlier for similar chelate ring containing nickel(II) complexes.<sup>28,29</sup> The other two *cis* angles are within  $95.8\text{--}97.2^\circ$ . The *trans* bond angles ( $177\text{--}179^\circ$ ) are very close to the ideal value of  $180^\circ$ . There is no deviation of the metal centre from the plane containing the four coordinating atoms. The root-mean-square deviation from the mean plane constituted by  $\text{NiN}_2\text{O}_2$  is  $0.006\text{ \AA}$  in **3** and  $0.031\text{ \AA}$  in **4**. The Ni–N and the Ni–O bond lengths are within the ranges observed for square-planar nickel(II) complexes having similar coordinating atoms.<sup>28–30,33</sup> Because of the *trans*- $\text{N}_2\text{O}_2$  geometry the iron atoms and the unsubstituted  $\text{Cp}^-$  rings of the two  $\text{FeCp}_2$  units are on the same side of  $\text{NiN}_2\text{O}_2$  plane and, as a result, the shape of the iron(II)–nickel(II)–iron(II) array is angular in each of **3** and **4** (Figures 2

and 3). The average  $\text{Ni}\cdots\text{Fe}$  distance in **3** ( $5.570\text{ \AA}$ ) is slightly shorter than that ( $5.673\text{ \AA}$ ) in **4**. The  $\text{Fe}\cdots\text{Fe}$  distance and the  $\text{Fe}\cdots\text{Ni}\cdots\text{Fe}$  angle are  $10.525\text{ \AA}$  and  $141.73^\circ$  in **3** and  $11.031\text{ \AA}$  and  $152.95^\circ$  in **4**.

### 3.3 Spectroscopic properties

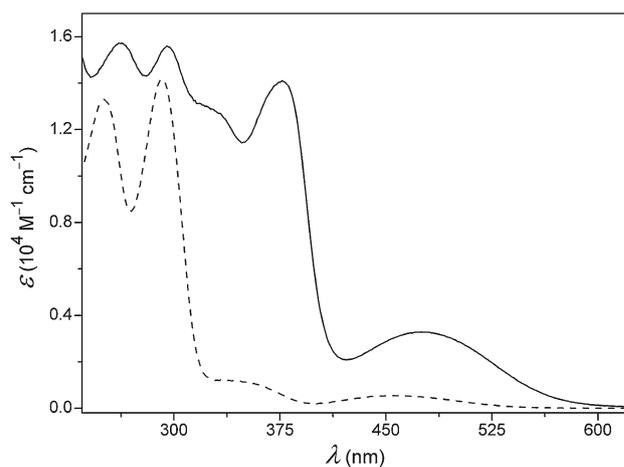
Infrared spectra of **1–4** were recorded by using KBr pellets in the range  $4000\text{--}400\text{ cm}^{-1}$ . A large number of bands have been observed in each spectrum. We have not attempted to assign all the bands except for very few. The free Schiff bases **1** and **2** show the amide-NH stretches at  $3187$  and  $3191\text{ cm}^{-1}$ , respectively. **1** displays a very strong and somewhat broad band at  $1671\text{ cm}^{-1}$  with a shoulder at  $1605\text{ cm}^{-1}$ . These two absorptions have

**Table 2.** Selected bond parameters (Å and °) for **2**·CDCl<sub>3</sub>, **3** and **4**·CHCl<sub>3</sub>.

Compound	<b>2</b> ·CDCl <sub>3</sub>	<b>3</b>	<b>4</b> ·CHCl <sub>3</sub>
Fe-Cg (Cp <sup>-</sup> )	1.633, 1.644	1.645–1.658	1.643–1.659
Fe-C (Cp <sup>-</sup> )	2.004(8)–2.050(7)	2.029(2)–2.056(3)	2.029(6)–2.060(7)
C-O (amide)	1.204(5)	1.296(3), 1.301(3)	1.298(7), 1.308(6)
C-N (amide)	1.349(6)	1.300(3), 1.304(3)	1.305(7), 1.297(7)
C-N (azomethine)	1.265(6)	1.286(3), 1.290(3)	1.306(7), 1.299(7)
Ni(1)-O(1)	–	1.8432(16)	1.846(4)
Ni(1)-O(2)	–	1.8436(16)	1.831(4)
Ni(1)-N(1)	–	1.866(2)	1.867(5)
Ni(1)-N(3)	–	1.857(2)	1.868(4)
O(1)-Ni(1)-O(2)	–	178.97(8)	178.41(18)
O(1)-Ni(1)-N(1)	–	83.52(8)	83.43(18)
O(1)-Ni(1)-N(3)	–	95.97(8)	97.18(18)
O(2)-Ni(1)-N(1)	–	96.90(8)	95.81(18)
O(2)-Ni(1)-N(3)	–	83.60(8)	83.65(18)
N(1)-Ni(1)-N(3)	–	178.99(9)	177.1(2)

been assigned to the amide-CO and the azomethine-CN stretches, respectively. In contrast, the amide-CO and the azomethine-CN stretches for **2** appear as two rather closely spaced strong bands at 1638 and 1605 cm<sup>-1</sup>, respectively. The absence of the amide-NH stretching band in the spectra of the two complexes **3** and **4** is consistent with the deprotonation of the amide functionalities in the corresponding ligands. Two sharp and strong bands observed at 1614 and 1552 cm<sup>-1</sup> for **3** are most likely due to the amidate-CO<sup>34</sup> and the amidate-CN-NC-azomethine<sup>28,35,36</sup> moieties, respectively, of the ligand Fcah<sup>-</sup>. The corresponding bands for Fcbh<sup>-</sup> in **4** have been observed at 1614 and 1585 cm<sup>-1</sup>, respectively.

Electronic absorption spectra of **1-4** were recorded using their dichloromethane solutions. The spectroscopic profile of **1** is very similar to that of **2**. The spectroscopic profiles of **3** and **4** are also comparable to each other. The spectra of **1** and **3** are illustrated in Figure 4 and those of **2** and **4** are depicted in Figure S1 (Supplementary Information). The free Schiff bases (**1** and **2**) exhibit two weak absorptions at ~458 and ~350 nm and two very strong absorptions at ~296 and ~254 nm. Ferrocene and its derivatives are well known to display similar absorption bands at comparable wavelengths.<sup>37-40</sup> Thus, it is very apparent that all four absorption bands observed for **1** and **2** are associated with transitions involving their ferrocene fragments only. The weak absorption bands are typically assigned to the iron centred ligand field transitions, while the following two strong absorptions are attributed to ligand-to-metal and metal-to-ligand charge transfer transitions, respectively.<sup>37-40</sup> In contrast, the nickel(II) complexes (**3** and **4**) display an absorption maximum at ~482 nm of moderate intensity and four strong

**Figure 4.** Electronic absorption spectra of HFcah (**1**) (dashed trace) and [Ni(Fcah)<sub>2</sub>] (**3**) (solid trace) in dichloromethane.

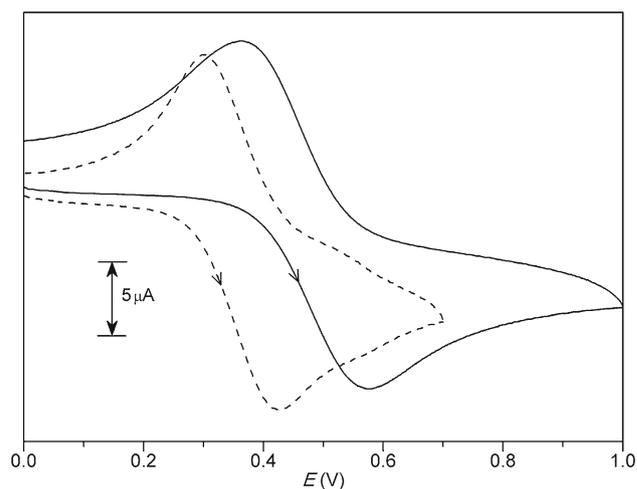
absorptions at ~384, ~333, ~300 and ~264 nm (Figure 4). It is very likely that the first three absorption bands are predominantly due to ligand-to-metal and ligand centred charge transfer transitions associated with the square-planar NiN<sub>2</sub>O<sub>2</sub> chromophore.<sup>41</sup> As for the free Schiff bases (**1** and **2**), the last two absorption bands for the complexes are also assigned to ferrocene fragment centred ligand-to-metal and metal-to-ligand charge transfer transitions, respectively.

The <sup>1</sup>H NMR spectra of **1-4** were obtained using CDCl<sub>3</sub> as solvent and tetramethylsilane as internal standard. The chemical shift data given in the experimental section are according to the numbering scheme shown in Scheme 1. The spectrum of each of the two complexes clearly indicates that its two ligands are equivalent in solution. The amide-NH proton of **1** and **2** appears as a

singlet at  $\delta$  9.52 and 9.05 ppm, respectively. No such signal has been observed in the spectrum of either of **3** and **4** due to deprotonation of the amide functionalities of the coordinated ligands in them. The singlet observed at  $\delta$  7.68 and 8.27 ppm for **1** and **2**, respectively, is assigned to the azomethine proton ( $H^{11}$ ). The singlet corresponding to the azomethine proton ( $H^{11}$ ) resonates at  $\delta$  6.83 and 7.18 ppm for **3** and **4**, respectively. The upfield shift in each case is most likely the consequence of  $\pi$ -backdonation from metal to azomethine.<sup>42</sup> In the cases of **1** and **2**, the four protons of the substituted  $Cp^-$  ring appear as two singlets, each of two-proton, at  $\delta \sim 4.68$  and  $\sim 4.43$  ppm, while the five protons of the unsubstituted  $Cp^-$  ring are observed as a singlet at  $\delta \sim 4.23$  ppm. The corresponding singlets are shifted downfield by  $\delta \sim 0.12$  ppm for **3** and **4**. The three-proton singlet due to the methyl protons of the  $-NHC(=O)Me$  fragment of **1** has been observed at  $\delta$  2.34 ppm, while for **3** the corresponding singlet is shifted upfield by  $\delta$  0.39 ppm, perhaps due to the amide deprotonation and iminolate formation. In the case of **2**, a two-proton singlet observed at  $\delta$  7.87 ppm is assigned to *ortho* protons of the phenyl ring in the  $-NHC(=O)Ph$  fragment, while the *meta* and the *para* protons are observed as a three-proton multiplet centred at  $\delta$  7.53 ppm. In **4**, the *ortho* protons resonate somewhat down-field at  $\delta$  8.03 ppm as a two-proton doublet, while the *meta* and the *para* protons appear slightly upfield at  $\delta$  7.47 ppm as a three-proton multiplet.

#### 4. Redox properties

The electron transfer characteristics of **1–4** were examined by using cyclic voltammetry. The measurements were carried out at 298 K with  $\sim 1 \times 10^{-3}$  M dichloromethane solutions of the compounds containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte under nitrogen atmosphere using a platinum disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. The ferrocenium/ferrocene ( $Fc^+/Fc$ ) couple was observed at  $E_{1/2} = 0.35$  V under identical conditions. All of **1–4** exhibit a quasi-reversible oxidation response with  $E_{1/2}$  value within the range of 0.23–0.50 V. Cyclic voltammograms of **2** and **4** are shown in Figure 5 and those of **1** and **3** are given in Figure S2 (Supplementary Information). One-electron nature of this response has been inferred by comparing the peak currents with those of the ferrocene and other known one-electron redox couples under identical experimental conditions.<sup>35,36,43,44</sup> The oxidation potential (0.23 V) of **1** is somewhat lower than that (0.36 V) of **2**. On the other hand, the oxidation potential (0.50 V) of **3** is very close to that (0.47 V) of **4**. Comparison of these potentials with the potential



**Figure 5.** Cyclic voltammograms (scan rate  $100 \text{ mV s}^{-1}$ ) of HFcbh (**2**) (dashed trace) and  $[\text{Ni}(\text{Fcbh})_2]$  (**4**) (solid trace) in dichloromethane using the experimental conditions described in the text.

(0.35 V) of the unsubstituted ferrocene redox couple clearly indicates that the oxidation response observed for not only **1** and **2** but also for **3** and **4** is iron centred. It is very likely that although the nickel centre is redox silent but its coordination makes the acylhydrazonate fragment more electron withdrawing and consequently, the iron oxidation potentials of the complexes become higher than those of the free Schiff bases.

#### 5. Conclusions

Syntheses and characterization of two Schiff bases  $N$ -(acyl)- $N'$ -(ferrocenylidene)hydrazines (acyl = acetyl and benzoyl) and their diamagnetic nickel(II) complexes containing the angular iron(II)-nickel(II)-iron(II) array are presented. X-ray molecular structures of one of the two Schiff bases and both nickel(II) *bis* chelates of the deprotonated monoanionic azomethine-N and amidate-O coordinating Schiff bases have been determined. In each of the three structures, the cyclopentadienide rings in the ferrocene fragment adopt an eclipsed conformation. The N,O-coordinating ligands form two five-membered chelate rings and a *trans*- $N_2O_2$  square-plane around nickel(II) in both complexes. Analytical and spectroscopic characteristics of all the compounds are congruent with their molecular structures. Both Schiff bases and their two complexes are redox active and display an iron centred oxidation response. We are currently engaged in synthesising and characterising **4d** and **5d** transition metal ion coordination and cyclometallated complexes with these Schiff bases and exploring the possibility of their use as effective catalysts in synthetic organic reactions.

## Supplementary Information (SI)

CCDC 1538071, 1538072 and 1538073 contain the supplementary crystallographic data for **2**-CDCl<sub>3</sub>, **3** and **4**-CHCl<sub>3</sub>, respectively. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by e-mailing to [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk) or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033. Supplementary Figures S1 and S2 are available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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