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RESEARCH ARTICLE

SYNTHESIS & CHARACTERIZATION OF TRANSITION METALS COMPLEXES WITH FERROCENYL SCHIFF BASES

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ABSTRACT

Schiff bases and their complexes are versatile compounds synthesized from the condensation of an amino compound with carbonyl compounds and widely used for industrial purposes and also exhibit a broad range of biological activities including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. A few ferrocenyl Schiff bases have been isolated by the condensation of Formyl ferrocene and acetyl ferrocene with 4-methyl ortho-phenylene diamine, ortho-amino naphthol and ortho-amino naphthoic acid. Reactions of these ferrocenyl Schiff bases with copper(II) cobalt(II) and nickel(II) salts in varied reaction conditions, Yield new complexes of the type $M(L)_2$ and also some mixed ligand complexes of the type $M(L)(X)(NH_3)$ (where HL is mono basic bidentate ferrocenyl Schiff base, $M=Ni(II)$, $Cu(II)$, $Co(II)$ and $X=(OH/Cl)$). Cobalt (III) complexes of the type $Co(L)_2(OH)(NH_3)$ are also isolated. The compounds have been characterized on the basis of elemental analysis, molar conductance, molecular weights, magnetic susceptibilities and spectroscopic (Electronic and infrared) data.

INTRODUCTION

Schiff bases have played a significant role in the development of coordination chemistry and have been implicated as an important point in the development of inorganic biochemistry and optical materials. In the past two decades, the properties of Schiff base metal complexes stimulated much interest for their contributions to single molecule based magnetism, material science, catalysis of many reactions like carbonylation, hydroformylation, oxidation, reduction and epoxidation, their industrial applications and complexing ability towards some toxic metals. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes (Mohamed, *et al.*, A.2008). Schiff base complexes containing nitrogen and oxygen as donor atoms play an important role in biological systems and represents models for metalloproteins and metallo enzymes that catalyse the reduction of nitrogen and oxygen (Singh, *et al.*, 2008) small bioactive ligands with low molecular weight, which also recognize and interact with DNA are of significance as potential artificial gene regulators or cancer chemotherapeutic agents (Pulimamidi, *et al.*, 2009). The medicinal uses and applications Schiff bases and their metal complexes are of increasing clinical and commercial importance. Schiff bases have picked up significance in medicinal and pharmaceutical field because of an expansive range of biological activities like anti-inflammatory, (Sathe, *et al.*, 2011, Sondhi, *et al.*, 2006, Pandey A *et al.*, 2011, Chandramouli C, *et al.*, 2012).

analgesic (Sondhi *et al.*, 2006, Pandey *et al.*, 2011, Chandramouli *et al.*, 2012 Chandramouli *et al.*, 2012) antimicrobial (Chinnasamy *et al.*, 2010, Arif *et al.*, 2011) antispasmodic (Anaconda and Ortega 2015) tuberculosis (Chaubey and Pandeya 2012), anti-cancer (Aboul-Fadl, *et al.*, 2003, Miri *et al.*, 2013) antioxidants (Wei *et al.*, 2006), anthelmintic (Schi Avaji *et al.*, 2009) schiff bases are also administered as catalysts, intermediates in organic synthesis, pigments, dyes, polymeric stabilizers and corrosion inhibitors (Kawamoto & Kushi, 1992). The metal complexes of ferrocene containing Schiff bases have not been thoroughly investigated. It is only recently that some reports on the complexing behaviour of ferrocenyl Schiff bases have been reported (Xu Beng *et al.*, 1992, Lopez *et al.*, 1992; Houlton *et al.*, 1992, Graham *et al.*, 1968). There is a possibility that the ferrocenyl Schiff bases and their metal complexes might have redox active properties and also would have applications in non linear optics and other areas of molecular electronics. In view of the multifarious importance of ferrocene, ferrocenyl chelating ligands and also their metal complexes (Casey *et al.*, 1990). We have synthesized some ferrocenyl Schiff bases by the condensation of formyl ferrocene and acetyl ferrocene with 4-methyl orthophenylene diamine, ortho amino naphthol, and ortho-amino naphthoic acid to study their complexing behaviour. Present work describes the isolation and characterization of ferrocenyl Schiff base ligands (structure-I) and their complexes with copper(II), cobalt(II), cobalt(III) and nickel (II) ions. Of these six bases, only formyl ferrocene-4-methyl ortho phenylene diamine HFfaa and acetyl ferrocene o-amino naphthol, HAFaba were isolated in the solid state and used in the preparation of metal complexes.

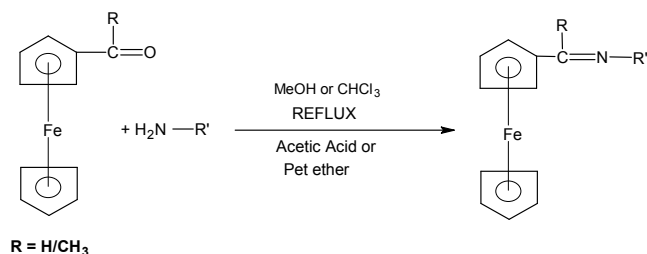
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The metal complexes of other Schiff bases were prepared by in situ method.

MATERIALS AND METHODS

Formylferrocene and acetylferrocene (Fluka and Sigma Chemicals) were used as such and these were also synthesized by the literature method (Graham *et al.*, 1968). The solvents were purified and dried before use by standard procedures (Casey *et al.*, 1990).



HFfmaa: when $R=H$ and $R^1 = -O-C_6H_3-NH_2-CH_3$
 HAFmaa: when $R=CH_3$ and $R^1 = -O-C_6H_3-NH_2-CH_3$
 HFfan: when $R=H$ and $R^1 = -O-C_{10}H_6-OH$
 HAFan: when $R=CH_3$ and $R^1 = -O-C_{10}H_6-OH$
 HFfana: when $R=H$ and $R^1 = -O-C_{10}H_6-COOH$
 HAFana: when $R=CH_3$ and $R^1 = -O-C_{10}H_6-COOH$

Structure-I

Preparation of the ligands 1-{N-(2(4-methyl amino) anilineiminemethyl} ferrocene

Formyl ferrocene (0.001 mol) was dissolved in dry methanol (50 cm³) and 4-methyl ortho-phenylenediamine (0.001 mol) in methanol (50 cm³) was added to it with stirring. The mixture was heated under reflux for 4 h after addition of a few drops of glacial acetic acid. The brown solution was then cooled to ~10°C, whereby a yellow crystalline compounds separated out. It was filtered off, washed with dry methanol and dried in vacuo, yield 70%; m.p. 150°C (dec.).

N-(2(carboxyl) naphthaleneimine ethyl}ferrocene

To the chloroform solution (50 cm³) of acetylferrocene (0.001 mol) was added a solution of ortho-amino naphthoic acid (0.001 mol) in chloroform (50cm³) with stirring and the mixture heated under reflux for 6 h. The solution was then cooled to room temperature and pet. Ether (40–60°) was added dropwise whereby a brown precipitate of HAFana appeared, which was recrystallized from chloroform pet-ether mixture, yield 60%; m.p. 210°C (dec.).

Preparation of complexes

All the complexes were isolated by in situ method. The ligands HFfmaa and HAFna were also used for the preparation of complexes and were found to produce identical complexes compared to in situ preparation. The preparation is summarized below: To an ethanolic solution (60 cm³) of HFfmaa (0.001 mol) [or HAFmaa prepared in situ by the condensation of acetylferrocene and 4-methyl orthophenylene diamine (0.001 mol) in ethanol] was added the metal salt solution (0.001 mol) in ethanol (40 cm³) and the mixture heated under reflux at pH~9 (15% NH₄OH) for 2h on water

bath. The following complexes were isolated, which were filtered and washed with suitable solvents. Ni (Ffmaa)₂H₂O (1), orange yellow crystals (yield 60%) soluble in common organic solvents. Ni(Afmaa)₂H₂O (2), brown crystals (yield, 65%), soluble in organic solvents, Co(Ffmaa)₂ (3), blue violet solid (prepared under nitrogen atmosphere), (yield, 65%). Co(Afmaa)₂ (4), violet solid (prepared under nitrogen atmosphere, (yield, 65%). Co(Ffmaa)₂(OH)(NH₃) (5), brown (prepared in excess of air), yield 80%, Co(Afmaa)₂(OH)(NH₃) (6), brown (prepared in excess of air), (yield 80%). Cu(Ffmaa)₂ (7), brown, (yield, 70%), Cu(Afmaa)₂ (8), brown, (yield, 70%). Cu(Afmaa)₂ (NH₃)₂ (9), isolated from the filtrate of compound (8) on treating with excess NH₄OH as deep brown compound, (yield 25%). Similarly the complexes (10) to (18) were prepared by in situ method. Ni(Ffan) (Cl) (NH₃), (10), brown, (yield, 65%). Ni(Ffan) (OH) (NH₃), (11), brown, (yield, 65%). Ni(Afan) (Cl) (NH₃), (12), brown, (yield, 70%). Co(Ffan)₂ (OH) (NH₃), (13), deep brown (prepared in excess of air), yield, 65%, Co(Ffan) (Cl) (NH₃), (14), brown complex (prepared in dry solvent under nitrogen atmosphere), (yield, 60%), Cu(Ffan) (OH) (NH₃), (15), brown, (yield, 70%). Ni(Ffana) (Cl) (NH₃), (16), red (yield, 70%). Ni(Afana) (Cl) (NH₃), (17) reddish brown, (yield 75%). Cu(Ffana) (Cl) (NH₃), (18), brown, (yield, 65%).

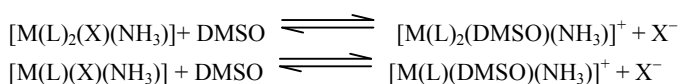
RESULTS AND DISCUSSION

The reactions of 1-formylferrocene and 1-acetylferrocene with 4-methyl-ortho-aminoaniline (4-methyl ortho-phenylenediamine), ortho-aminonaphthol and ortho-aminonaphthoic acid in ethanol and in the presence of glacial acetic acid produced coloured ferrocenyl Schiff base HFfmaa, HAFmaa, HFfan, HAFan, HFfana and HAFana respectively in solution (structure I). However only HFfmaa and HAFna could be isolated in the pure state. Therefore, in situ preparative methods were employed for the syntheses of the metal complexes. However, repetition of preparation with HFfmaa or HAFana afforded the same complexes as obtained by in situ method. The reactions of Ni(OAc)₂4H₂O or NiCl₂6H₂O with HFfmaa and HAFmaa in ethanol at pH ~9 yielded Schiff base complexes (1) and (2) respectively. The identical reactions of Cu(OAc)₂H₂O with HFfmaa and HAFmaa at pH~9 yielded complexes, Cu(Ffmaa)₂, (7) and Cu(Afmaa)₂, (8) respectively. It is interesting to note that the filtrate from (8), on prolong standing in the presence of excess NH₄OH, yielded a complex, Cu(Afmaa)₂(NH₃)₂, (9).

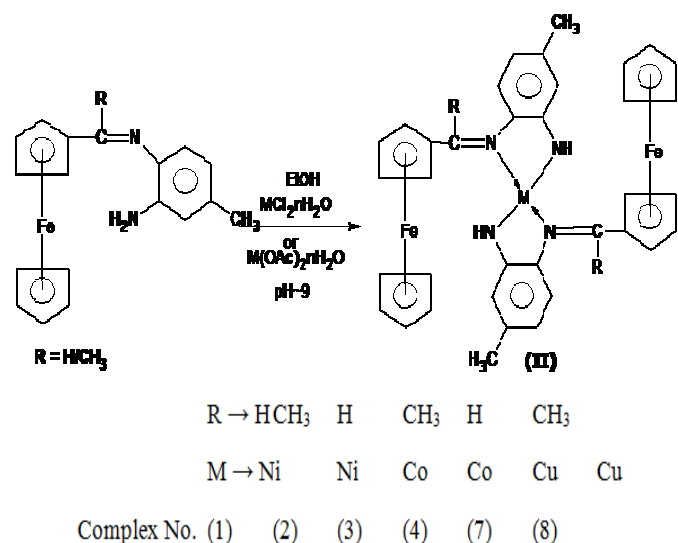
The reaction of NiCl₂6H₂O with the refluxed solution of formylferrocene (or acetylferrocene) and ortho-amino naphthol in ethanol at pH~9 yielded Ni(Ffan) (Cl) (NH₃), (10) or Ni(Afan) (Cl) (NH₃), (12). On the other hand, the use of Ni(OAc)₂4H₂O at pH~9 in place of NiCl₂6H₂O yielded the complex Ni(Ffan)(OH)(NH₃), (11). Similarly in situ reactions of the ligand components and Co(OAc)₂4H₂O at pH~9 (in excess of air) afforded a cobalt(III) complex, Co(Ffan)₂(OH)(NH₃), (13). The same reaction with CoCl₂6H₂O under nitrogen atmosphere, however, gave Co(Ffan)(Cl)(NH₃), (14). Similarly, formylferrocene or acetylferrocene reacts with ortho-amino naphthoic acid in the presence of NiCl₂6H₂O yielding diamagnetic nickel(II) complexes Ni(Ffana)(Cl) (NH₃), (16) and Ni(Afana)(Cl) (NH₃), (17) at pH~9. The replacement of NiCl₂6H₂O by CuCl₂H₂O under identical reaction conditions gave the copper(II) complex, Cu(Ffana)(Cl)(NH₃), (18).

The preparations are summarized in Schemes 1–3

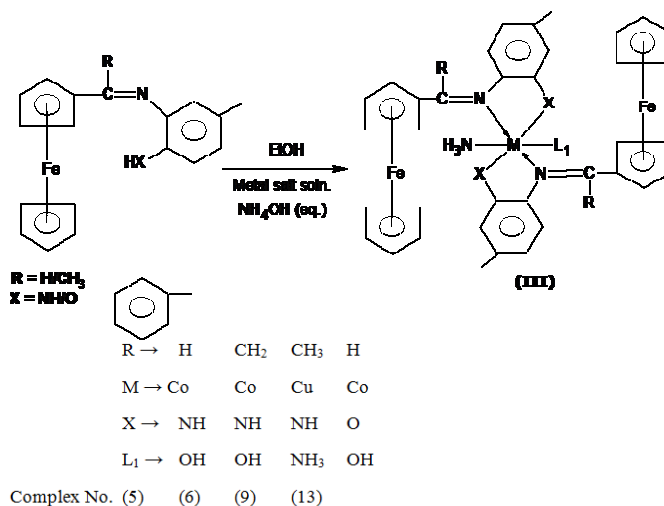
The isolated ligands and complexes are all coloured and stable at room temperature. The ligand HFfaa decomposed at 150°C, while HAFana decomposed at 210°C. The complexes did not melt upto 200°C. The elemental analyses of the solid ligands and the newly synthesized complexes agreed with their formulations (Table 1 and Scheme 1–3). The molecular weights of some of the compounds (measured by Rast’s method) are also in good agreement with these formulations. Both the ligands HAFaa and HAFana are soluble in CHCl₃ and DMSO, while the complexes are soluble in coordinating solvents and also in common organic solvents. The molar conductance values (Table 1) of the complexes measured in DMSO and DMF suggest their nonelectrolytic nature. It has also been observed that on prolong standing at room temperature, the Λ_M values in DMSO solutions of (5), (6), (10)–(15) increased showing the presence of 1:1 electrolytes in solutions. These results may be rationalized by assuming the following equilibria in solutions:



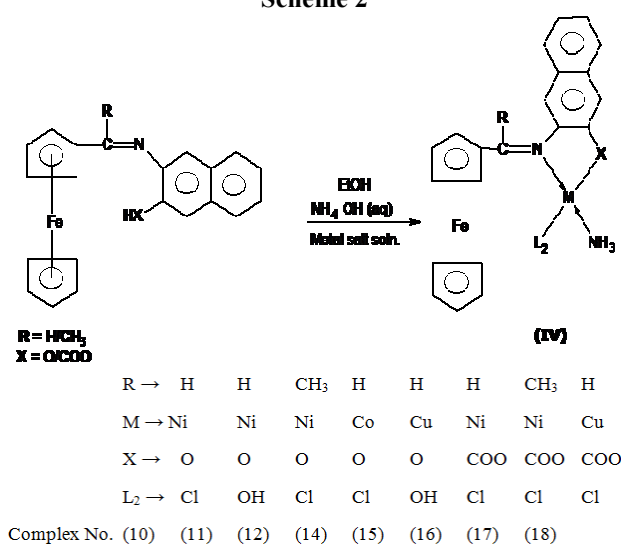
(where M=Cobalt(III) or cobalt(II), nickel(II), copper(II); L=monobasic bidentate ferrocenyl Schiff base; and X=OH⁻ or Cl⁻). The nickel(II) complexes are diamagnetic indicating square planar geometry around nickel(II) ion (Dey, *et al.*, 1991). The diamagnetic cobalt(III) complexes are octahedral (may be distorted). On the other hand cobalt(II) complexes(3), (4) and (14) show magnetic moments in the range 4.1–4.2 B.M. at room temperature. The values suggested tetrahedral arrangement of donor atoms around central cobalt(II) ion (Figgis, B.N. & Nyholm, R.S.1959). The copper(II) complexes, Cu(Ffmaa)₂(7), Cu(Afmaa)₂(8), Cu(Ffan)(OH)(NH₃)(15) and Cu(Ffana)(Cl)(NH₃), (18) exhibit, magnetic moment values in the range 1.78 to 1.81 BM, the values quite close to the spin only value viz., 1.73 B.M. expected for S=1/2 system. These values tentatively suggest a square planar structure for the copper(II) complexes (Figgis and Harris, 1959; Figgis & Lewis, 1964).



Scheme 1



Scheme 2



Scheme 3

The brown copper(II) complex, Cu(Afmaa)₂(NH₃)₂(9) has an effective magnetic moment value of 1.98 B.M. at room temperature suggesting its pseudo- octahedral structure (Figgis, B.N. & Lewis, J., 1964). The contention that the present diamagnetic nickel(II) complexes are square planar is supported by the appearance of spectral bands measured in nujol mull at 700–680 nm and 440–420 nm regions assignable to ¹A_{1g}→¹A_{2g} and ¹A_{1g}→¹B_{1g} transitions respectively in a square planar field around nickel(II) ion. The tetrahedral structure for the present cobalt(II) complexes (3), (4) and (14) have been further supported by the visible spectra in the range 700–650 nm assignable to ⁴A₂→⁴T₁ (P) transition in a pseudo-tetrahedral geometry (Dey, *et al.*, 1970). The other cobalt complexes (5), (6) and (13) are diamagnetic and therefore lead to cobalt(III) species. These complexes show bands in the regions 600–580 nm and 460–410nm assignable to ¹A_{1g}→¹T_{1g} and ¹A_{1g}→¹T_{2g} transitions in an octahedral environment. The copper(II) complexes (7), (8), (15) and (18) may attain square planar structure as inferred above from magnetic moment values. The electronic spectral data also support this annotation. The nujol mull spectra are quite different from the tetrahedral electronic spectral pattern generally observed for tetrahedral copper(II) complexes. The band observed at 19800 cm⁻¹ may be taken as a proof for square planar structure for these copper(II) complexes (Dey &

Sen, 1979). The other copper(II) complexes (9) showed bands (nujol mull) at 17000 cm^{-1} and 12000 cm^{-1} (sh) suggesting either a square planar or distorted octahedral geometry. The infrared spectra of the metal complexes were recorded in KBr phase and important bands along with their tentative assignments have been discussed.

due to the conversion of NH_2 to NH^- and simultaneous coordination with the metal ions (Yngxiang *et al.*, 1989, Tarafder *et al.*, 1981). However, this is entirely tentative propositions. The ligand HAFana show a band at 1710 cm^{-1} for asymmetric stretching of free carboxylic group (Bhare and Kharat, 1981).

Table 1. Characterisation Data of The Ligands And Their Complexes

Compounds	Mol. weight	Colour	Found (Calc.) %					$\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ λ_M	μ_{eff} (B.M.)
			C	H	N	Cl	M		
HFfmaa $\text{C}_{18}\text{H}_{18}\text{N}_2\text{Fe}$		Light yellow	67.84 (67.95)	5.58 (5.66)	8.70 (8.80)	–	–	–	–
HFfana $\text{C}_{22}\text{H}_{17}\text{NO}_2\text{Fe}$		Brown	68.89 (68.95)	4.21 (4.40)	3.50 (3.65)	–	–	–	–
$\text{Ni}(\text{Ffmaa})_2\cdot 2\text{H}_2\text{O}\cdot(1)$ $\text{C}_{36}\text{H}_{38}\text{O}_2\text{N}_4\text{Fe}_2\text{Ni}$	705 (728)	Yellow	59.20 (59.30)	5.10 (5.21)	7.56 (7.68)	–	7.93 (8.06)	3.30	Diamagnetic
$\text{Ni}(\text{Ffmaa})_2\cdot 2\text{H}_2\text{O}\cdot(2)$ $\text{C}_{38}\text{H}_{42}\text{O}_2\text{N}_4\text{Fe}_2\text{Ni}$	–	Brown	60.12 (60.28)	5.42 (5.55)	7.21 (7.40)	–	7.61 (7.76)	–	Diamagnetic
$\text{Co}^{\text{II}}(\text{Ffmaa})_2(3)$ $\text{C}_{36}\text{H}_{34}\text{N}_4\text{Fe}_2\text{Co}$	680 (692)	Blue violet	62.30 (62.37)	4.80 (4.90)	7.94 (8.08)	–	8.40 (8.50)	11.96	4.22
$\text{Co}^{\text{II}}(\text{Ff,aa})_2(4)$ $\text{C}_{38}\text{H}_{38}\text{N}_4\text{Fe}_2\text{Co}$	700 (720)	Violet	63.20 (63.27)	5.12 (5.27)	7.60 (7.77)	–	8.0 (8.17)	–	4.10
$\text{Co}^{\text{III}}(\text{Ffmaa})_2(\text{OH})(\text{NH}_3)(5)$ $\text{C}_{36}\text{H}_{38}\text{ON}_5\text{Fe}_2\text{Co}$	712 (726)	Brown	59.32 (59.45)	5.10 (5.23)	9.47 (9.63)	–	8.0 (8.11)	13.82	Diamagnetic

Compounds	Mol. weight	Colour	Found (Calc.) %					$\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ λ_M	μ_{eff} (B.M.)
			C	H	N	Cl	M		
$\text{Co}^{\text{III}}(\text{Ffmaa})_2(\text{OH})(\text{NH}_3)(6)$ $\text{C}_{38}\text{H}_{42}\text{ON}_5\text{Fe}_2\text{Co}$	732 (754)	Brown	60.30 (60.42)	5.41 (5.56)	9.16 (9.27)	–	7.67 (7.81)	–	Diamagnetic
$\text{Cu}(\text{Ffmaa})_2(7)$ $\text{C}_{36}\text{H}_{34}\text{N}_4\text{Fe}_2\text{Cu}$	672 (697)	Yellow Brown	61.80 (61.95)	4.70 (4.87)	7.95 (8.03)	–	9.0 (9.11)	–	1.78
$\text{Cu}(\text{Afmaa})_2(8)$ $\text{C}_{38}\text{H}_{38}\text{N}_4\text{Fe}_2\text{Cu}$	–	Brown	62.70 (62.87)	5.12 (5.23)	7.60 (7.72)	–	8.63 (8.76)	–	1.81
$\text{Cu}(\text{Afmaa})_2(\text{NH}_3)(9)$ $\text{C}_{38}\text{H}_{44}\text{N}_6\text{Fe}_2\text{Cu}$	729 (759)	Brown	59.92 (60.06)	5.62 (5.79)	10.86 (11.06)	–	8.20 (8.36)	–	1.98
$\text{Ni}(\text{Ffan})(\text{Cl})(\text{NH}_3)(10)$ $\text{C}_{21}\text{H}_{19}\text{ON}_2\text{ClFeNi}$	445 (465)	Yellow Brown	54.02 (55.04)	4.01 (4.09)	5.82 (6.02)	7.50 (7.63)	12.50 (12.62)	5.78	Diamagnetic
$\text{Ni}(\text{Ffan})(\text{OH})(\text{NH}_3)(11)$ $\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}_2\text{FeNi}$	430 (456)	Brown	55.04 (55.19)	4.10 (4.38)	6.0 (6.13)	–	12.70 (12.85)	–	Diamagnetic
$\text{Ni}(\text{Afan})(\text{Cl})(\text{NH}_3)(12)$ $\text{C}_{22}\text{H}_{21}\text{ON}_2\text{ClFeNi}$	–	Brown	55.0 (55.10)	4.21 (4.38)	5.70 (5.84)	7.20 (7.41)	12.10 (12.25)	–	Diamagnetic

Compounds	Mol. weight	Colour	Found (Calc.) %					$\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ λ_M	μ_{eff} (B.M.)
			C	H	N	Cl	M		
$\text{Co}^{\text{III}}(\text{Ffan})_2(\text{OH})(\text{NH}_3)(13)$ $\text{C}_{42}\text{H}_{36}\text{O}_3\text{N}_3\text{Fe}_2\text{Co}$	791 (800)	Deep Brown	62.80 (62.94)	4.36 (4.49)	5.12 (5.24)	–	7.20 (7.36)	14.28	Diamagnetic
$\text{Co}(\text{Ffan})(\text{Cl})(\text{NH}_3)(14)$ $\text{C}_{21}\text{H}_{19}\text{ON}_2\text{ClFe}_2\text{Co}$	448 (465)	Blish Yellow	54.01 (54.15)	3.88	5.91 (6.01)	7.48 (7.62)	12.52 (12.66)	12.15	4.20
$\text{Cu}(\text{Ffan})(\text{OH})(\text{NH}_3)(15)$ $\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}_2\text{FeCu}$	–	Brown	55.71 (55.82)	4.38 (4.43)	6.03 (6.20)	–	13.88 (14.07)	–	1.79
$\text{Ni}(\text{Ffana})(\text{Cl})(\text{NH}_3)(16)$ $\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}_2\text{ClFeNi}$	–	Red	53.40 (53.54)	3.80 (3.85)	5.50 (5.67)	7.02 (7.19)	11.80 (11.90)	–	Diamagnetic
$\text{Ni}(\text{Afana})(\text{Cl})(\text{NH}_3)(17)$ $\text{C}_{23}\text{H}_{21}\text{O}_2\text{ClN}_2\text{FeNi}$	–	Red	54.30 (54.43)	4.0 (4.15)	5.40 (5.52)	6.89 (7.0)	11.40 (11.57)	5.10	Diamagnetic
$\text{Cu}(\text{Ffana})(\text{Cl})(\text{NH}_3)(18)$ $\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}_2\text{ClFeCu}$	450 (448)	Dark Brown	52.85 (53.02)	3.70 (3.81)	5.50 (5.62)	7.0 (7.13)	12.63 (12.76)	–	1.80

Both the ligands HFfmaa and HAFana show strong bands in the region $1650\text{--}1600\text{ cm}^{-1}$ assignable to $\text{C}=\text{N}$ stretching. These bands were lowered by $10\text{--}15\text{ cm}^{-1}$ in the complexes, suggesting the coordination of azomethine nitrogen atom (Kovacic, J.E., 1967, K.Dey, *et al.*, 1982). The infrared spectrum of the ligand HFfmaa shows absorption bands at 3490 cm^{-1} and 3385 cm^{-1} , which may be assigned to $\nu_{\text{asym}}(\text{NH})$ and $\nu_{\text{sym}}(\text{NH})$ respectively. The bending (NH) vibration may be at $\sim 1640\text{--}1600\text{ cm}^{-1}$, which is difficult to assign due to the presence of 'C=N' chromophore and aromatic ring. However, $\nu(\text{NH})$ frequencies (Nakamoto, 1978, Mukherjee, G, *et al.*, 1993, Ricciardi, G, *et al.*, 1991) are lowered considerably in the spectra in this region. Infact, very broad bands in the region $3400\text{--}3300\text{ cm}^{-1}$ were found in the complexes. This may be

The complexes of the ligands HFfana and HAFana exhibit bands in the region $1600\text{--}1570\text{ cm}^{-1}$, which may be attributed to the bonded carboxylate group (Onoda *et al.*, 2004) although the presence of 'C=N' chromophore might complicate this interpretation.

1. The OH stretching frequencies characteristic of the free ligands do not appear in the infrared spectra of the complexes (10)–(15). Bands in the region $560\text{--}440\text{ cm}^{-1}$ can be assigned to $\nu(\text{M}\text{--}\text{N})$ stretching modes⁽⁴⁴⁾ for the complexes (1)–(9). A band in the region $340\text{--}330\text{ cm}^{-1}$ may be assigned to $\nu(\text{M}\text{--}\text{Cl})$ stretching mode⁽⁴⁴⁾. The formation of 'M–O' band in the complexes is supported by the appearance of bands in the The phenolic 'C–O'

stretching vibrations are shifted in the complexes (10)–(15) to higher frequencies by about $(10 \pm 5 \text{ cm}^{-1})$ in relation to the free ligands [$\nu(\text{C}-\text{O})$ in the free ligand observed], at 1520 cm^{-1} , suggesting the coordination of phenolic 'C–O' to nickel(II), cobalt(II), cobalt(III) and copper(II) (Srinivasan, B.R., *et al.*, 2011, Murugavel, R. & Korah, R, 2007), region $500\text{--}380 \text{ cm}^{-1}$, assignable to $\nu(\text{M}-\text{O})$ modes (Crane, J.D., Moreton, D.J. & Rogerson, E. 2004, Starosta, W. & Leciejewicz, J. 2005, Fox, S., *et al.*, 2007, Robin Kumar, *et al.*, 2011, Basudev Maity & Chakarvarty, A.R, 2012, Hari Babu P. & Hussain Reddy, K., 2011). Both the ligands and the complexes showed characteristic bands for ferrocenyl moiety at $\sim 3100\text{--}3000 \text{ cm}^{-1}$, $1440\text{--}1400 \text{ cm}^{-1}$, $1110\text{--}1100 \text{ cm}^{-1}$, $880\text{--}840 \text{ cm}^{-1}$ and $510\text{--}490 \text{ cm}^{-1}$ respectively. The hydroxy complexes (5), (6), (11), (13) and (15) exhibit bands at $1100\text{--}955 \text{ cm}^{-1}$ due to $\nu(\text{M}-\text{OH})$ along with the bands at $\sim 300 \text{ cm}^{-1}$ for $\nu(\text{M}-\text{O})$. Only the nickel(II) complexes (1) and (2) have shown broad bands above 3400 cm^{-1} , which may be assigned to $\nu(\text{OH})$ for lattice water (Wang, Y. & Okabe, N., 2005, Hangan, A., *et al.*, 2010, Chowdhury, P., Pandit, S. & Mondal, B., 2009). The structural formulations of the compounds are tentatively proposed (Scheme 1–3) and are on the basis of their analytical and spectral data.

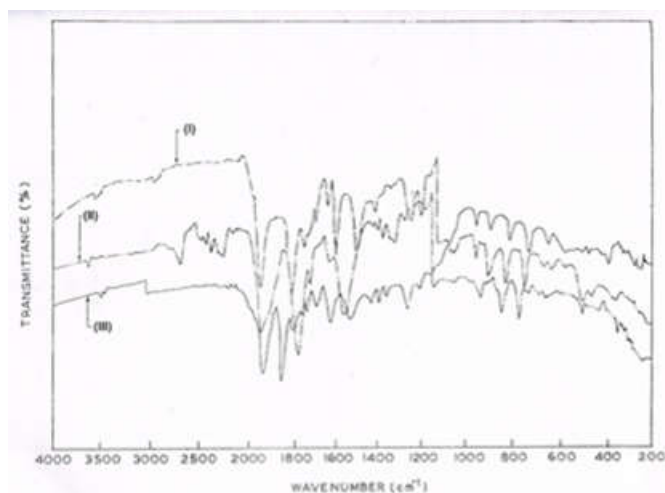


Fig. 1. IR Spectra of complexes $(\text{C}_{36}\text{H}_{38}\text{O}_2\text{N}_4\text{Fe}_2\text{Ni})(\text{II})$ $(\text{C}_{36}\text{H}_{34}\text{N}_4\text{Fe}_2\text{Co})(\text{III})$ $(\text{C}_{36}\text{H}_{34}\text{N}_4\text{Fe}_2\text{Cu})$

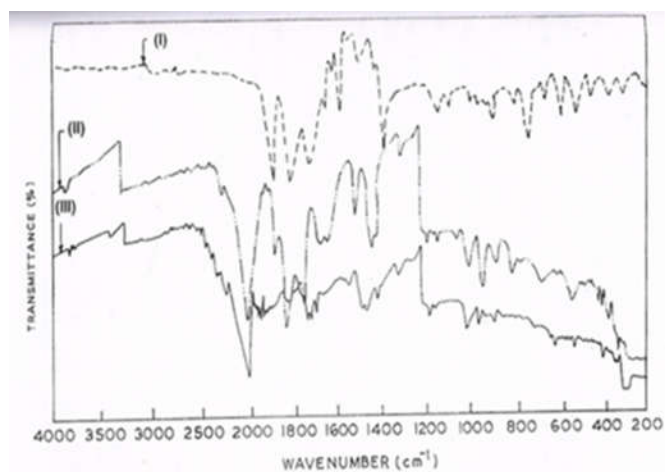


Fig. 2. IR Spectra of complexes $(\text{C}_{22}\text{H}_{21}\text{O}\text{N}_2\text{ClFeNi})(\text{II})$ $(\text{C}_{42}\text{H}_{36}\text{O}_3\text{N}_3\text{Fe}_2\text{Co}_2\text{Co})(\text{III})$ $(\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}_2\text{ClFeCu})$

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