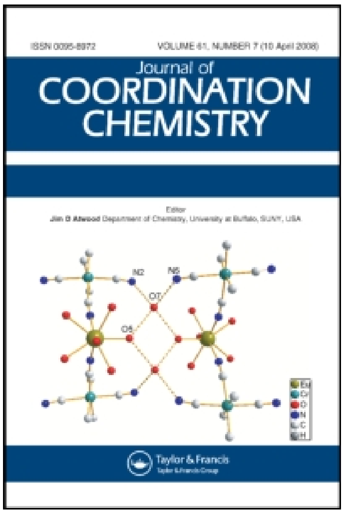

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The synthesis and characterization of (<i>E</i>,<i>E</i>)-dioxime and its transition metal complexes containing 12-membered macrocycles linked to ferrocenyl-methyl groups

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The synthesis and characterization of (*E*,*E*)-dioxime and its transition metal complexes containing 12-membered macrocycles linked to ferrocenyl-methyl groups

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13,14-*bis*(Hydroxyimino)-4,7-*bis*(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrobenzo[k]-4,7-diaza-1,10-dithiacyclododecine[13,14-g]-quinoxaline (H_2L) has been prepared from (*E*,*E*)-dichloroglyoxime and 12,13-diamino-4,7-*bis*(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrobenzo[k]-4,7-diaza-1,10-dithiacyclododecine which was synthesized from 12,13-dinitro-4,7-*bis*(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrobenzo[k]4,7-diaza-1,10-dithia cyclododecine. Mononuclear nickel(II) and copper(II) complexes of H_2L have a metal-ligand ratio of 1 : 2 and the ligand coordinates through two nitrogen atoms, as do most (*E*,*E*)-dioximes. The homotrinuclear $[Cu(L)_2Cu_2(dipy)_2](NO_3)_2$ compound coordinates to the other two copper(II) ions through deprotonated oximate oxygens and two 2,2′-dipyridyl as an end-cap ligand to yield the trinuclear structure. The ligand and its complexes have been characterized on the basis of ^1H, ^{13}C NMR, IR and MS spectroscopy and elemental analyses.

Keywords: (*E*,*E*)-Dioxime; Mixed donor macrocycle; Ferrocene; Nickel(II), Copper(II); Template effect

1. Introduction

The growth of coordination chemistry has been three dimensional, encompassing, breadth, depth, and applications. One development provides the basis for expansion of the domain for complexation by macrocyclic ligands, first to alkali metal ions, complex anions and neutral molecules in host-guest complexes [1].

Forty-eight years ago it was possible to show only a few examples of reasonably well characterized complexes for alkali metals discovery of crown ethers of appropriate ring size to bind alkali metal cations. Since the discovery of the crown ethers, host-guest or supramolecular chemistry has grown enormously giving chemists many opportunities to design and synthesize new compounds, and to investigate their applications [2]. Such compounds contain central hydrophilic cavities with either electronegative or electropositive binding atoms and exterior flexible frameworks exhibiting hydrophobic behaviour.

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Coordination compounds of (*E*,*E*)-dioximes have been widely investigated as analytical reagents [3], as models for biological systems such as vitamin B_{12} [4] and as compounds having columnar stacking thought to be the reason for their semiconducting properties [5]. The presence of mildly acidic hyroxy groups and slightly basic nitrogen atoms makes (*E*,*E*)-dioximes amphoteric compounds which can form corrin-type square-planar, square-pyramidal, tetrahedral or octahedral complexes with transition metal ions [6].

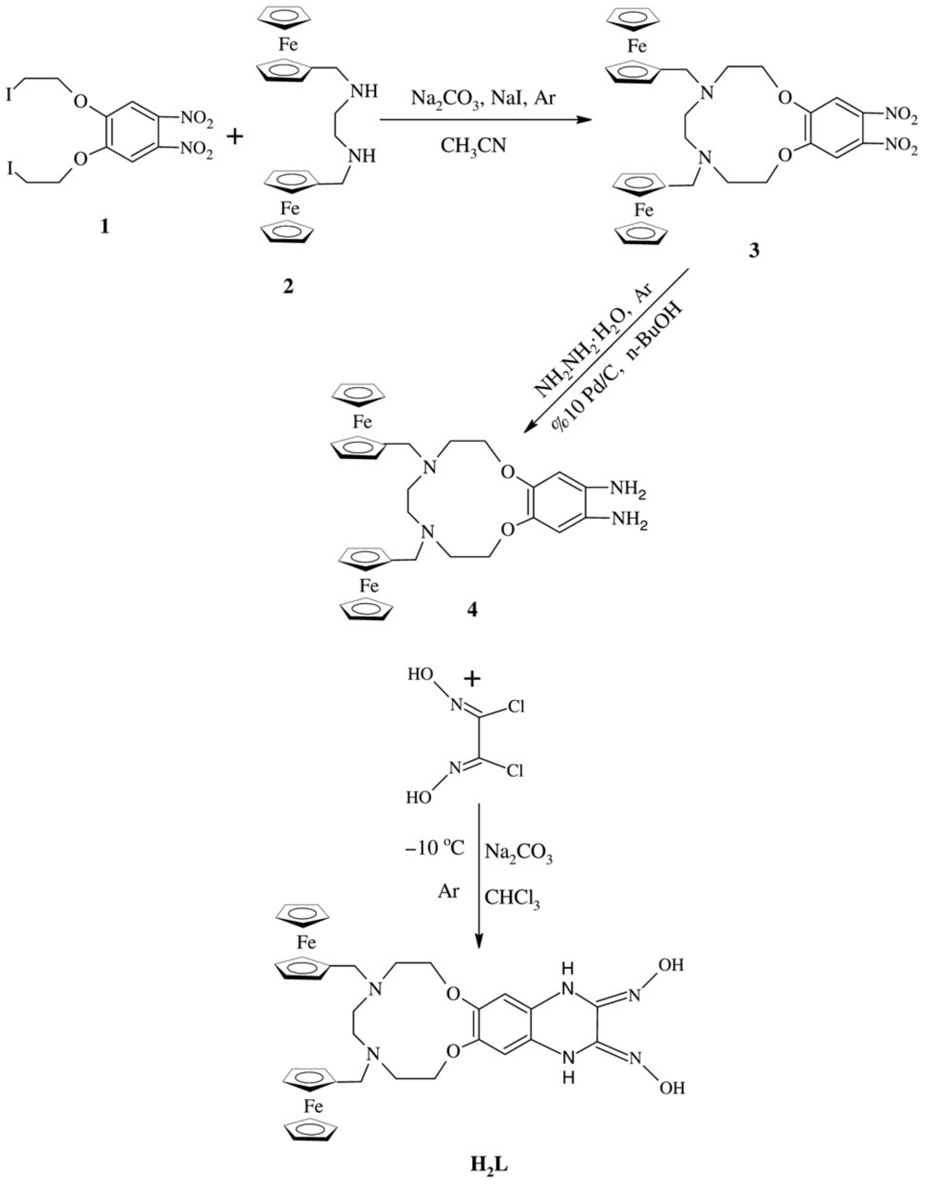
The dependence of the magnitude of the exchange interaction upon the nature of the bridging ligand, such as oximato, in a series of polynuclear complexes has been investigated extensively [7]. One of the best strategies for the synthesis of polynuclear complexes is to use mononuclear complexes, such as $[M(L)]^{2-}$, as ligands which contain potential donor moieties for another metal ion carrying end-cap ligands, such as dipy or phen [8].

This study reports the synthesis and characterization of a (*E*,*E*)-dioxime and its mono- and homotrinuclear transition metal complexes, including synthesis, structure, ^{1}H, ^{13}C NMR, IR, MS spectra, magnetic susceptibility and elemental analysis of ligand and complexes.

2. Results and discussion

The synthesis of 13,14-*bis*(hydroxyimino)-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octa-hydrobenzo[k]-4,7-diaza-1,10-dithiacyclododecine[13,14-g]-quinoxaline [H_2L] was accomplished in a three step procedure as described in scheme 1. First, the dinitro functionalized 13,14-dinitro-4,7-*bis*(ferrocenylmethy)-2,3,4,5,6,7,8,9-octahydrobenzo[k]-4,7-diaza-1,10-dithiacyclododecine (**3**) was prepared in good yield (69.5%) *via* reaction of the appropriate amine (**2**) [9] with 1,2-dinitro-4,5-*bis*(2-iodoethoxy)benzene (**1**) [10] in the presence of finely ground Na_2CO_3 and NaI in refluxing acetonitrile under nitrogen for 94 h. After crystallization, the dinitro derivative of macrocycle **3** was isolated from a mixture of ethylacetate : diethyl ether (1 : 2) and characterized. The ^{1}H-NMR spectrum of **3** showed new signals due to methylene and ferrocenyl methyl protons at $\delta = 3.54$ and 4.13 ppm, respectively. The proton-decoupled ^{13}C-NMR spectrum of this compound is in good agreement with the proposed structure (scheme 1). The new resonances belonging to dinitro substituted phenyl and methylene carbons connected to nitrogen at $\delta = 151.75$ and 52.77 ppm, respectively, and the disappearance of NH protons in the precursor compound **2** could be attributed to the macrocyclization. The carbon resonances belonging to the nonsubstituted cyclopentadienyl ring are equivalent at $\delta = 69.24$ ppm; the other carbon-13 NMR signal at $\delta = 81.89$ ppm appearing at lower field indicates the ipso carbon chemical shifts. The remaining signals around $\delta = 68.79$–67.91 ppm are ascribed to the substituted cyclopentadienyl rings. The disappearance of the N–H stretching vibrations seen in the IR spectrum of the starting material **2** also suggests the formation of **3**. This compound displays the expected molecular ion peak in its mass spectrum at $m/z = 709$ $[M + 1]^+$.

The mixed donor macrocycle dinitro compound **3** was reduced in a high yield (83.5%) to the corresponding diamino compound **4** in *n*-butanol using Pd-activated carbon (10%) and hydrazine hydrate (100%). This compound **4**, apparently sensitive to both heat and air, is pale brown and darkens when left standing at room temperature



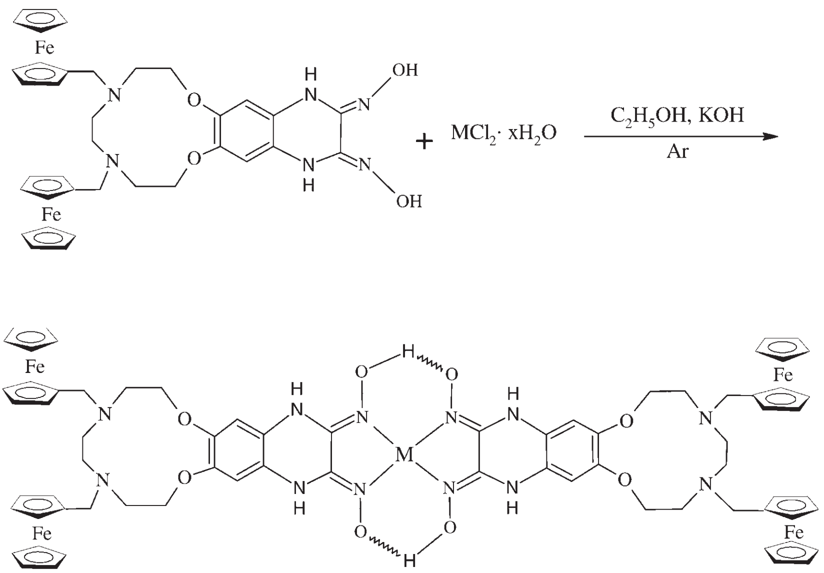
Scheme 1. Ligand synthesis.

for 1 h. In the ^{1}H-NMR spectrum of **4**, there is a broad signal at $\delta = 4.68$ ppm due to the aromatic amine protons confirming the structure. The chemical shifts of **4** show an upfield shift of the aromatic protons at $\delta = 6.62$ ppm from aromatic primary amine instead of nitro groups. The disappearance of the Ar–NO_2 resonance at 1330 cm^{-1} and appearance of Ar–NH_2 stretching and bending vibrations at 3203 and 1613 cm^{-1}, respectively, indicate completion of the reduction. The mass spectrum of **4** shows an expected molecular ion peak at $m/z = 648$ $[M]^+$, which also supports the proposed formulation.

The target compound H_2L was synthesized from diamino substituted macrocycle **4** and cyanogen di-N oxide solution in $CHCl_3$ which was prepared in 56.2% yield by treating a suspension of (*E*,*E*)-dichloroglyoxime in $CHCl_3$ with 0.5 M aqueous Na_2CO_3 at $-15^\circ C$ [11] under nitrogen atmosphere for 12 h. In the ^1H-NMR spectrum of H_2L, the deuterium exchangeable protons of N–OH and NH groups appear as two singlets at $\delta = 11.82$ and 8.82 ppm, respectively. The single signal for N–OH protons indicates that the oxime groups are in the (*E*,*E*)-structure [12]. In the proton-decoupled ^{13}C-NMR spectrum of H_2L, the carbon resonance of azomethine is found at lower field, $\delta = 151.45$ ppm, and this unique signal of the oxime also confirms the (*E*,*E*) form of the *vic*-dioxime [12]. The IR spectrum of this compound suggested the same structure, and the presence of a sharp absorption at $1621\,cm^{-1}$ was strongly indicative of the presence of the azomethine. The disappearance of the NH_2 stretching vibrations along with the appearance of new absorptions at 3181 and $1028\,cm^{-1}$ that indicate O–H and N–O groups that is also in agreement with the structure in scheme 1. The mass spectrum of H_2L exhibited an intense peak at $m/z = 733$ $[M+1]^+$, which is in accord with the proposed formulation.

Complexation of the (*E*,*E*)-dioxime with Ni(II) and Cu(II) was carried out by addition of a solution of $[NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O]$ and an equivalent amount of KOH in ethanol and a hot solution of H_2L in ethanol on a water-bath to afford the 1 : 2 (metal : ligand) complexes $\{[Ni(HL)_2]$ and $[Cu(HL)_2]\}$ (figure 1). Since a distinct decrease in the pH of the solution was observed during complex formation, deprotonation of the ligands with subsequent *N*,*N′* chelation with the (*E*,*E*)-dioxime groups probably occurs. This complexation reaction does not occur in the macrocyclic moieties under the same conditions, which could be attributed to greater affinity of the Ni(II) or Cu(II) for oximato, promoting oxime formation and stability for *bis*(oximato)M [M : Ni(II), Cu(II)] complexes [13]. In these complexes, Ni(II) and Cu(II) are not trapped in the N_2O_2-mixed donor macrocycle, but coordinated through the nitrogen of the oxime groups of two ligands [14]. This indicates that N-substitution of the 12-membered N_2O_2 macrocycle hinders coordination of other metal ions. Both complexes had IR spectra very similar to those of the ligand, except for the shift of the O–H stretching vibrations. The formation of new weak bands around 1693–1703 cm^{-1} indicated O–H$\cdots$O bending vibrations [15]. The shifts of C=N resonances of the Ni(II) and Cu(II) complexes to lower energy at 1610 and $1613\,cm^{-1}$, respectively, are due to *N*,*N′*-coordination to transition metal cations [16]. As shown in figure 1, the Ni(II) or Cu(II) ions are square-planar as expected, with the equatorial plane composed of N_4 donors of the oxime ligands [17]. The magnetic moment of the Cu(II) complex at room temperature is 1.81 BM, typical for mononuclear Cu(II) complexes [18]. The ^1H-NMR spectrum of the diamagnetic nickel(II) complex was characterized by the dis-appearance of the N–OH signal and presence of a new resonance at $\delta = 17.02$ ppm, assigned to formation of the hydrogen bridge which could easily be identified by deuterium exchange [19]. The other chemical shifts of this complex are very similar to those of the precursor free ligand. It is obvious that, upon complexation with Ni(II) cation, the free ligand resonances shifted slightly as expected. In the mass spectrum of this mononuclear complex significant fragment ions for Ni(II) and Cu(II) complexes at $m/z = 1529$ and 1526 could be assigned $[M + 1/2H_2O]^+$ and $[M+1]^+$, repectively.

Nitrate salt of the trinuclear copper(II) complex was synthesized by re-acting the mononuclear copper(II) complex as a ligand in THF with $Cu(NO_3)_2 \cdot 3H_2O$ and 2,2′-bipyridine (bipy) (figure 2) as an end-cap ligand in THF in tolerable yield (36%).



5 M: Ni(II)
6 M: Cu(II)

Figure 1. Complex synthesis.

This complex has a 1 : 2 metal : ligand ratio according to the elemental analysis, in accord with formation of a trinuclear Cu(II) complex. The last two copper ions in this complex need to be tetracoordinate with two nitrogen atoms of bipy and two oxygens of oximate. This complex also contains the dinuclear cation $[Cu(L)_2Cu_2(bipy)_2]^{2+}$, two uncoordinated nitrate anions with sharp and strong resonances at ca $1375\,cm^{-1}$ [20]. The bending vibrations at $1703\,cm^{-1}$ belonging to the mononuclear Cu(II) complex are missing in the IR spectrum of trinuclear complex, indicating that the hydrogen bridges are lost upon chelation. Formation of trinuclear complex is verified by the M^+ peak at m/z 1805 $[M\text{-bipy–Cu–}NO_3^- + 1]^+$. The secondary ion corresponding to the loss of two bipy groups together with two copper and two nitrates also appears at m/z: 1523. The coordination geometry proposed for the trinuclear complex surrounding the whole cation is not coplanar, but bent at the bridging oximate oxygens so that it assumes a butterfly shape [8]. On the other hand, the magnetic susceptibility of this complex ($\mu = 4.73$ BM) closely follows the spin-only formula calculated for the square-planar copper(II) ion and two tetrahedral ones.

3. Experimental

Proton and ^{13}C NMR spectra were recorded on a Varian Mecury 200 spectrometer, using tetramethylsilane as the internal standard. Mass spectra of the ligand and complex were obtained on a Micromass Quatro LC/ULTIMA LC-MS MS spectrometer. IR spectra of the compounds were recorded on a Perkin–Elmer Spectrum One

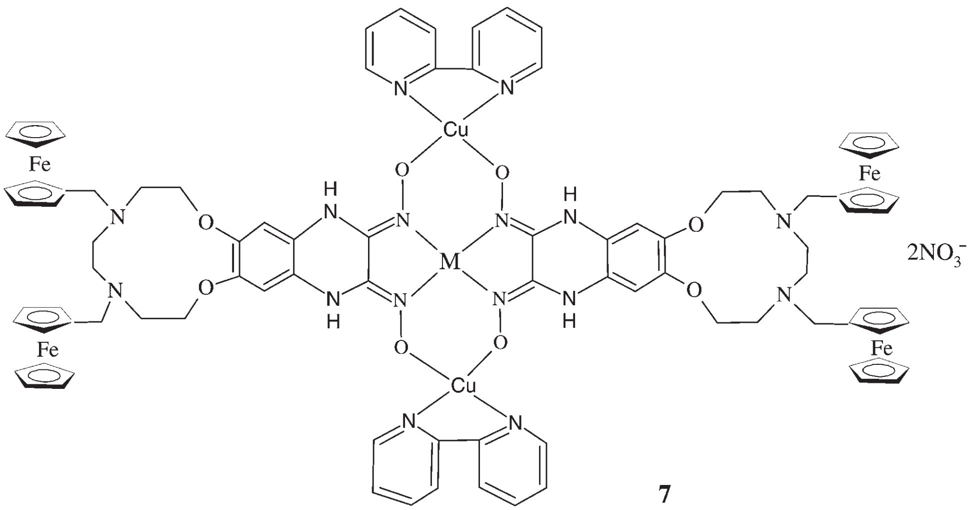


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Figure 2. Trinuclear copper complex.

FT–IR spectrometer at room temperature. Elemental anlysis and metal contents of the ligand and complex were performed on a Hewlett-Packard 185 CHN analyzer and Unicam 929 AA spectrometer, respectively. Magnetic susceptibility was determined on a Sherwood Scientific Cambridge Magnetic Susceptibility Balance at room temperature using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [21]. Melting points were determined on an Electrothermal apparatus and are uncorrected. (*E*,*E*)-Dichloroglyoxime [22], cyanogendi-N-oxide [23], 1,2-dinitro-4,5-*bis*(2-iodoethoxy)benzene [11] and *N*,*N*′-ethylenebis(ferrocenylmethyl)amine [10] were prepared by reported procedures. All solvents were reagent grade and purified according to standard procedures [24].

3.1. *12,13-Dinitro-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrobenzo[k]-4,7-diaza-1,10-dithiacyclododecine (3)*

A round-bottom flask containing dry acetonitrile (150 cm^3) and fitted with a condenser was evacuated, refilled three times with dry nitrogen and connected to a vacuum line. Under dry nitrogen, the flask was charged with **1** (2.02 g, 4 mmol), **2** (1.82 g, 4 mmol) an excess of finely ground anhydrous Na_2CO_3 (0.96 g, 9.04 mmol), and anhydrous NaI (0.28 g, 1.86 mmol); the mixture was refluxed under nitrogen for 94 h. Then the mixture was cooled to room temperature, filtered and washed with acetonitrile. The combined solutions were evaporated to dryness under reduced pressure. The oily product was dissolved in ethyl acetate and then diethyl ether was added to obtain solid product. The yellow product was crystallized from a mixture of ethylacetate : diethyl ether (1 : 2) to give pale yellow crystalline solid. Yield: 1.96 g (69.5%), m.p. 204°C. Anal. Calcd for $C_{34}H_{36}N_4O_6Fe_2$: C, 57.62; H, 5.08; N, 7.90. Found: C, 57.39; H, 5.34; N, 7.61. IR (KBr pellets, cm^{-1}): 3093 (Ar–H), 3065 (C_5H_5), 2924–2851 (C–H), 1591 (Ar–H), 1330 (Ar–NO_2), 1102–1040 (OCH_2). ^{1}H-NMR ($CDCl_3$): δ 7.35 (s, 2H, Ar–H), 4.39 (t, 4H, $ArOCH_2$), 4.13 (m, 18H, C_5H_5), 3.54 (s, 4H, CH_2), 2.95 (m, 8H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 151.75 (C–NO_2), 148.27 (ArCO), 134.16 (ArCH), 71.81 (OCH_2), 68.79–67.91 (C_5H_5), 81.89 (C_5H_5), 69.08 (C_5H_5), 52.77 (NCH_2). MS (*m*/*z*): 709 $[M+1]^+$.

3.2. *12,13-Diamino-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrobenzo[k]-4,7-di-aza-1,10-dithiacyclododecine (4)*

Palladium/activated carbon (10%) (1.2 g) was added to a solution of **3** (1.90 g, 2.4 mmol) in *n*-butanol (100 cm^3) at reflux and 15.7 cm^3 of hydrazine hydrate (100%) was added dropwise at this temperature. The reaction mixture was refluxed and stirred until the foam became colorless (approximately 24 h). At the end of this period, the reaction mixture was cooled to room temperature and filtered through Celite under nitrogen, concentrated to 10 cm^3 under reduced pressure and then allowed to stand in a refrigerator at −18°C overnight under nitrogen. The solvent was removed under reduced pressure and an air sensitive pale brown oily product was obtained. Yield: 1.30 g (83.5%). Anal. Calcd for $C_{34}H_{40}N_4O_2$ Fe_2: C, 62.96; H, 6.17; N, 8.64: Found: C, 62.27; H, 5.98; N, 8.82. IR (NaCl disc, cm^{-1}): 3435–3203 (NH_2), 3095 (Ar–H), 3060 (C_5H_5), 2959–2875 (C–H), 1613 (N–H), 1112–1066 (OCH_2). ^1H–NMR ($CDCl_3$): 6.88 (s, 2H, Ar–H), 4.68 (s, 4H, NH_2), 4.31 ($ArOCH_2$), 4.08 (m, 18H, C_5H_5), 3.36 (s, 4H, CH_2), 2.88 (m, 8H, NCH_2). MS (*m*/*z*): 648 $[M]^+$.

3.3. *13,14-bis(hydroxyimino)-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrobenzo [k]-4,7-diaza-1,10-dithiacyclododecine[13,14-g]-quinoxaline (H_2L)*

A solution of cyanogen di-N-oxide in chloroform (25 cm^3), which was prepared from (*E*,*E*)-dichloroglyoxime (0.31 g, 2 mmol) and aqueous Na_2CO_3 (10 cm^3, 0.5 M), was added with stirring to a cold solution (−15°C) of **4** (0.975 g, 1.5 mmol) in chloroform (50 cm^3) under dry nitrogen; the reaction was continued for 12 h at this temperature. At the end of this period, the reaction mixture was concentrated to 10 cm^3 and solidified by adding 5 cm^3 of diethyl ether. The brown solid was filtered off, washed with diethyl ether, dried *in vacuo* and then crystallized from a mixture of ethanol : diethyl ether (1 : 2) to give pale brown solid product. Yield: 0.615 g (56.2%), m.p. >300°C. Anal. Calcd for $C_{36}H_{40}N_6O_4Fe_2$: C, 59.01; H, 5.46; N, 11.47. Found: 59.36; H, 5.31; N, 11.16. IR (KBr pellets, cm^{-1}): 3291 (N–H), 3181 (O–H), 3088 (Ar–H), 3065 (C_5H_5), 2925–2851, 1621(C=N), 1108–1071 (OCH_2), 1028 (N–O). ^1H-NMR (DMSO-d_6): δ 11.82 (s, 2H, N–OH), 8.82 (s, 2H, NH), 7.17 (s, 2H, Ar–H), 4.47 (m, 4H, $ArOCH_2$), 4.20 (m, 18H, C_5H_5), 3.45 (s, 4H, CH_2), 2.85 (m, 8H, NCH_2). ^{13}C-NMR (DMSO-d_6): δ 151.45 (C=N), 144.23 (ArCO), 130.11 (ArCH), 125.78 (ArCN), 82.17 (C_5H_5), 71.34 ($ArOCH_2$), 68.55–67.41 (C_5H_5), 69.52 (C_5H_5), 49.29 (NCH_2). MS (*m*/*z*): 733 $[M+1]^+$.

3.4. *[Ni(HL)$_2$] (5) and [Cu[HL)$_2$] (6)*

A solution of 0.24 mmol of [$NiCl_2 \cdot 6H_2O$ (0.058 g) or $CuCl_2 \cdot 2H_2O$ (0.0425 g)] in ethanol (10 cm^3) was added to a hot solution of H_2L (0.35 g, 0.48 mmol) in ethanol (45 cm^3) by stirring on a water-bath at 60°C. A distinct change in color from pale brown to brownish red and a decrease in the pH of the solution to 0.98–1.4 was observed. While heating and stirring at 60°C, an equivalent amount of ethanolic solution of KOH (0.1 M) was added dropwise to adjust the pH to 4.0. After heating and stirring the reaction mixture for 4 h on a water-bath, the solid was filtered off, washed several times with water, ethanol and diethyl ether and then dried *in vacuo*.

3.4.1. [Ni(HL)$_2$] (5). The isolated product was an orange solid. Yield: 0.32 g (88.9%), m.p. >300°C. Anal. Calcd for $C_{72}H_{78}N_{12}O_8Fe_4Ni$: C, 56.81; H, 5.12; N, 11.04; Ni, 3.86. Found: C, 57.01; H, 4.84; N, 10.69; Ni, 4.17. IR (KBr pellets, cm^{-1}): 3350 (N–H), 3078 (Ar–H), 3040 (C_5H_5), 2933–2860 (C–H), 1693 (O–H $\cdots$ O), 1610 (C=N), 1591 (Ar–H), 1118–1080 (OCH_2), 1031 (N–O). ^{1}H-NMR (DMSO-d$_6$): δ 17.02 (s, 2H, O–H $\cdots$ O), 8.90 (m, 4H, NH), 7.22 (m, 4H, ArH), 4.41 (m, 8H, ArOCH$_2$), 4.25 (m, 36H, C_5H_5), 3.51 (m, 8H, CH$_2$), 2.97 (m, 16H, NCH$_2$). MS (*m*/*z*): 1529 $[M + 1/2H_2O]^+$.

3.4.2. [Cu(HL)$_2$] (6). The isolated product was a dark green solid. Yield: 0.35 g (92.1%), m.p. >300°C. Anal. Calcd for $C_{72}H_{78}N_{12}O_8Fe_4Cu$: C, 56.65; H, 5.11; N, 11.1; Cu, 4.16. Found: C, 56.93; H, 4.87; N, 11.33; Cu, 3.81. IR (KBr pellets, cm^{-1}): 3342 (N–H), 3069 (Ar–H), 3035 (C_5H_5), 2920–2877 (C–H), 1703 (O–H $\cdots$ O), 1613 (C=N), 1594 (Ar–H), 1129–1092 (OCH_2), 1010 (N–O). MS (*m*/*z*): 1526 $[M + 1]^+$.

3.4.3. [Cu(L)$_2$(CuL$'$)$_2$](NO$_3$)$_2$, (L$'$ = bipy) (7). The mononuclear copper(II) complex of H_2L (0.305 g, 0.2 mmol) was suspended in THF (30 cm^3). A solution of [bipy (0.068 g, 0.5 mmol)] in THF (5 cm^3) and a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.12g, 0.5 mmol) in THF (5 cm^3) was added to the suspension at reflux. After refluxing for 7 h, the reaction mixture was filtered hot and concentrated to 7 cm^3 under reduced pressure. Diethyl ether was slowly added with continuous stirring to precipitate the complex. The product was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.25 g (36%), m.p. >300°C. Anal. Calcd for $C_{92}H_{92}N_{18}O_{14}Fe_4Cu_3$: C, 52.92; H, 4.41; N, 12.08; Cu, 9.13. Found: C, 52.68; H, 4.72; N, 12.37; Cu, 8.84. IR (KBr pel-lets, cm^{-1}): 3336 (N–H), 3087 (Ar–H), 3064 (Ar–H), 3041 (C_5H_5), 2912–2871 (C–H), 1619 (C=N), 1596–1571 (Ar–H), 1138–1103 (OCH_2), 989 (N–O). MS (*m*/*z*): 1805 $[M\text{–dipy-Cu-}NO_3^- + 1]^+$, 1523 $[M\text{-2dipy-2Cu-2}NO_3^-]^+$.

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