

Novel *vic*-dioximes: Synthesis, complexation with transition metal ions, spectral studies and biological activity

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Abstract

A novel, substituted disodium-4-hydroxy-5-[(1*E*,2*E*)-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino}naphthalene-2,7-disulfonate *vic*-dioxime ligand (LH₂) was synthesized from 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid disodium salt and (*E,E*)-monochloroglyoxime at room temperature. The mononuclear Cu^{II}, Ni^{II}, Zn^{II} and Cd^{II} complexes of this *vic*-dioxime ligand were prepared and their structures confirmed by elemental analysis, IR and UV–visible spectroscopy; the ¹H and ¹³C NMR spectra of the LH₂ ligand (**1**) were also recorded. The oxime ligand, LH₂, acts as a bidentate ligand bending through nitrogen atoms in the presence of base. Elemental analyses indicated that the ligand:metal ratio was 2:1 in the cases of Cu^{II} and Ni^{II} complexes and 1:1 in the cases of Zn^{II} and Cd^{II} complexes. The ligand was screened for its antimicrobial activity against the fungi *Rhodotorula rubra*, *Kluyveromyces marxianus*, *Aspergillus fumigatus* and *Mucor pusillus* and this was compared to that of metal complexes derived from it.

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1. Introduction

The preparation of new ligands is perhaps the most important step in the development of metal complexes with unique properties and novel reactivity. In recent years, the chemistry of coordination compounds has seen rapid development in diverse disciplines due to the possible biological applications of these new compounds. Metal chelates play an essential role in the chemistry of living organisms and a large number of metal proteins and other metal complexes of biological importance have been studied [1].

A significant interest in coordination chemistry is the interaction of a central atom with surrounding atoms, ions or molecules. Coordination compounds containing *vic*-dioxime ligands have been known since the beginning of the last

century; the chemistry of transition metal complexes with *vic*-dioxime ligands has been studied in detail and has been the subject of several reviews [2]. Dioxime ligands are known to coordinate metal ions as neutral dioximes and also as mono-anionic dioximates via dissociation of one oxime proton; they are also known to act as bridging ligands via coordination through the oxygens [3,4]. The chemistry of the bis-dioximate complexes of transition metal ions has attracted much attention because of their importance as reference models for vitamin B₁₂ [5,6], dioxygen carriers [7], catalysis in chemical transformations [8,9], intramolecular hydrogen bonding and metal–metal interaction [10–12].

The exceptional stability and unique electronic properties of the complexes can be attributed to their planar structure, which is stabilised by hydrogen bonding. The high stability of complexes prepared from *vic*-dioxime ligands has been used extensively for various purposes [13].

In our previous studies we investigated the synthesis and characterization of new ligands and their various transition

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metal complexes [14–22]. In this paper, a new *vic*-dioxime ligand, disodium 4-hydroxy-5-[[*(1E,2E)*-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]naphthalene-2,7-disulfonate (LH_2) containing an $-\text{SO}_3\text{Na}$ group was synthesized from 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid disodium salt and (*E,E*)-monochloroglyoxime. Mononuclear $\{[\text{M}(\text{LH}_2)]$, where $\text{M} = \text{Ni}^{\text{II}}$, Cu^{II} and $[\text{M}(\text{LH}_2)(\text{OH})_2]$, where $\text{M} = \text{Zn}^{\text{II}}$, $\text{Cd}^{\text{II}}\}$ complexes of LH_2 were obtained with metal:ligand ratio of 1:2 and 1:1, respectively, through *N,N*-coordination. ^1H and ^{13}C NMR, IR and UV–visible data are presented.

2. Experimental

2.1. Materials and measurements

All solvents were of reagent grade and were purified according to standard procedures. All chemicals were of reagent grade quality and were used without purification; (*E,E*)-monochloroglyoxime was prepared as described [23]. Elemental analyses were carried out by the Instrumental Analysis Laboratory of TUBITAK Marmara Research Centre. IR spectra were obtained using KBr discs ($4000\text{--}400\text{ cm}^{-1}$) on a Shimadzu 8300 FTIR spectrophotometer. Electronic spectra were obtained using DMSO on a Shimadzu UV-160 A spectrophotometer while ^1H and ^{13}C NMR spectra were recorded on a Bruker GmbH 300 MHz FT-NMR spectrometer. The pathogenic organisms used were *Rhodotorula rubra*, *Cluyveromyces marxianus*, *Aspergillus fumigatus* and *Mucor pusillus* fungi.

2.2. Synthesis of disodium 4-hydroxy-5-[[*(1E,2E)*-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]-naphthalene-2,7-disulfonate, LH_2 (1)

An excess of solid NaHCO_3 (1.2 g) was added to a solution of 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid disodium salt (0.2387 g, 0.7 mmol) in 50 cm^3 of $\text{EtOH}:\text{H}_2\text{O}$ (1:1). To this was added, dropwise, a solution of (*E,E*)-monochloroglyoxime (0.125 g, 1.02 mmol) in 15 cm^3 of EtOH ; the ensuing mixture was stirred at room temperature. After 5 h, the brown solid product was filtered and washed with cold EtOH and cold water. Recrystallization from hot $\text{EtOH}:\text{H}_2\text{O}$ (1:1) (25 cm^3) yielded a brown crystalline solid that was soluble in water, DMSO and slightly soluble in DMF. Yield: 0.26 g (55%). M.p.: $>250^\circ\text{C}$ (dec.). Elemental analyses for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_9\text{Na}_2\text{S}_2$ (F.W.: 449.32 g/mol): found: C, 31.94; H, 1.89; N, 9.26; S, 14.38%. Calcd.: C, 32.08; H, 2.02; N, 9.35; S, 14.27%. UV–visible (in DMSO) (λ_{max} , nm): 335 (5750), 304 (8700), 290 (11750). ^1H NMR (DMSO- d_6 ; δ , ppm): 12.10 (s, 1H, $\text{C}=\text{N}-\text{OH}$), 11.60 (s, 1H, $\text{C}=\text{N}-\text{OH}$), 8.75 (s, 1H, $\text{H}-\text{C}=\text{N}-$), 6.85–6.70 (m, 1H, 4H, napht.-H), 5.67 (s, 1H, $-\text{NH}-\text{C}=\text{N}$). ^{13}C NMR (DMSO- d_6 ; δ , ppm): 165.70 (napht.-C–OH), 152.20 ($-\text{NH}-\text{C}=\text{N}-\text{OH}$), 147.80 ($\text{H}-\text{C}=\text{N}-\text{OH}$), 138.30 (napht.-C–NH), 133.40 (napht.-C).

2.3. Synthesis of $[\text{Ni}(\text{LH}_2)]$ (2)

A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 g, 0.109 mmol) in 5 cm^3 of hot EtOH was added to a solution of LH_2 (0.04 g, 8.32×10^{-2} mmol) in 30 cm^3 of hot $\text{EtOH}:\text{H}_2\text{O}$ (2:1) at 70°C . After addition, the pH of the solution fell to 2.35 and was adjusted using 0.1 M NaOH in EtOH to 4.5–5.0, at which point precipitation of the complex began. The mixture was heated in a water bath for 3 h to complete the precipitation of the dark red complex, which was filtered, washed with hot EtOH and cold water and dried under vacuum. Yield: 0.021 g (50%). M.p.: $>250^\circ\text{C}$. Elemental analyses for $\text{C}_{24}\text{H}_{16}\text{N}_6\text{Na}_4\text{NiO}_{18}\text{S}_4$ (F.W.: 955.69 g/mol): found: C, 29.95; H, 1.60; N, 8.69; S, 13.31%. Calcd.: C, 30.17; H, 1.69; N, 8.80; S, 13.43%. UV–visible (in DMSO) (λ_{max} , nm): 425 (6200), 324 (9100), 301 (12 800).

2.4. Synthesis of $[\text{Cu}(\text{LH}_2)]$ (3)

A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0072 g, 0.042 mmol) in 10 cm^3 of EtOH was added to a suspension of LH_2 (0.04 g, 8.32×10^{-2} mmol) in 15 cm^3 of $\text{EtOH}:\text{H}_2\text{O}$ (2:1). The colour of the mixture changed and a sharp decrease in pH of the solution to 2.0 was observed. When the pH was increased to 5.0–5.5 with 1% NaOH in EtOH , precipitation began. After the mixture was stirred in a water bath at 60°C for 4 h, the dark-green precipitate was filtered, washed with cold EtOH and H_2O and then dried under vacuum. Yield: 0.019 g (47%). M.p.: $>250^\circ\text{C}$. Elemental analyses for $\text{C}_{24}\text{H}_{16}\text{CuN}_6\text{Na}_4\text{O}_{18}\text{S}_4$ (F.W.: 960.183 g/mol): found: C, 29.91; H, 1.55; N, 8.88; S, 13, 24%. Calcd.: C, 30.02; H, 1.68; N, 8.75; S, 13.36%. UV–visible (in DMSO) (λ_{max} , nm): 350 (2350) (sh), 305 (9050).

2.5. Synthesis of $[\text{Zn}(\text{LH}_2)(\text{OH})_2]$ (4)

A solution of ZnCl_2 (0.15 g, 1.10 mmol) in EtOH (10 cm^3) was added to a solution of LH_2 (0.75 g, 1.55 mmol) in 75 cm^3 of $\text{EtOH}:\text{H}_2\text{O}$ (2:1) at 70°C . An equivalent amount of 1 M aq NaOH solution was added while heating and stirring at this temperature and a brown precipitate, $\text{Zn}(\text{LH}_2)(\text{OH})_2$ (4), was formed. After heating the mixture for 3.5 h in a water bath, the precipitate was filtered, washed with water several times then with EtOH and Et_2O and finally dried under vacuum. Yield: 0.68 g (53%). M.p.: $278\text{--}280^\circ\text{C}$ (dec.). Elemental analyses for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_{11}\text{Na}_2\text{S}_2\text{Zn}$ (548.73 g/mol): found: C, 26.05; H, 1.89; N, 7.77; S, 11.59%. Calcd.: C, 26.27; H, 2.02; N, 7.66; S, 11.69%. UV–visible (in DMSO) (λ_{max} , nm): 547 (18 300), 290 (8950), 280 (11 200).

2.6. Synthesis of $[\text{Cd}(\text{LH}_2)(\text{OH})_2]$ (5)

CdCl_2 (0.0360 g, 0.196 mmol in 10 cm^3 of water) was slowly added, with constant stirring, to LH_2 (0.160 g, 0.332 mmol) in 20 cm^3 of $\text{EtOH}:\text{H}_2\text{O}$ (2:1). The colour of the solution turned to dark yellow and the pH of the mixture was raised to about 7.0 by the addition of 1 M aq NaOH

solution. The reaction mixture was stirred at 70 °C until precipitation was complete and then, it was brought to room temperature and the yellow crystalline complex was filtered, washed with water, EtOH and Et₂O and finally dried under vacuum. The compound is soluble in DMF and DMSO. Yield: 0.080 g (45%). M.p.: >250 °C. Elemental analyses for C₁₂H₁₁CdN₃O₁₁Na₂S₂ (F.W.: 595.752 g/mol): found: C, 24.13; H, 1.74; N, 6.94; S, 10.65%. Calcd.: C, 24.19; H, 1.86; N, 7.05; S, 10.76%. UV–visible (in DMSO) (λ_{max} , nm): 530 (17 500), 295 (9150), 283 (10 900).

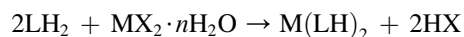
2.7. Biological studies

The *in vitro* growth inhibitory activity of the LH₂ *vic*-dioxime ligand and its complexes was assessed against the fungi *R. rubra*, *K. marxianus*, *A. fumigatus* and *M. pusillus*. The fungi were incubated in Malt Extract Broth (Difco) for 48 h. Mueller Hinton Agar (Oxoid), sterilized in a flask and cooled to 45–50 °C, was placed in sterilized Petri dishes of 9 cm diameter. Fifty microlitres of all the compounds obtained and the standard antibiotics were injected into empty sterilized antibiotic discs of 6 mm diameter (Schleicher & Shüll no: 2668, Germany). The compounds were dissolved in H₂O to provide a final concentration of 2000 ppm. The discs prepared with the complexes were placed on the solid agar medium by applying a slight pressure and the Petri dishes were kept at 4 °C for 2 h. The Petri dishes were then inoculated with fungi and incubated at 25 ± 0.1 °C for 24 h, after which time, the diameter of inhibition zones which had developed was measured. The experiments were repeated three times. Gentamicin (Bioanalyse) and Nystatin (Oxoid) were used as standards.

3. Results and discussion

3.1. Synthesis of the compounds

Disodium 4-hydroxy-5-[[*(1E,2E)*-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]naphthalene-2,7-disulfonate was prepared by the reaction of 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid disodium salt with (*E,E*)-monochloroglyoxime in EtOH–H₂O at room temperature. The product of the condensation reaction of 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid disodium salt with (*E,E*)-monochloroglyoxime is depicted in Fig. 1. The novel *vic*-dioxime ligand, disodium 4-hydroxy-5-[[*(1E,2E)*-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]naphthalene-2,7-disulfonate, gave mononuclear complexes (Fig. 2) with Ni^{II} and Cu^{II} as follows:



LH₂: disodium 4-hydroxy-5-[[*(1E,2E)*-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]naphthalene-2,7-disulfonate;
M: Ni^{II} and Cu^{II};
X: Cl, *n*: 6 and 2.

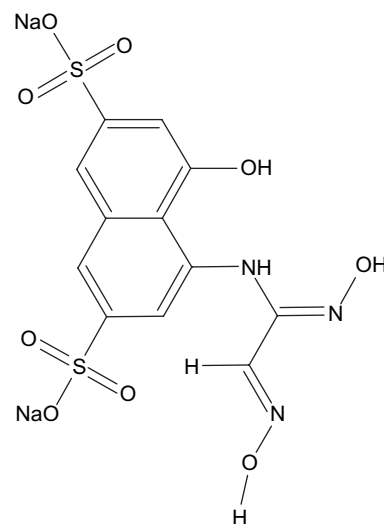
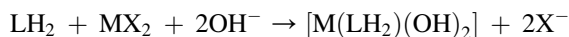


Fig. 1. Disodium 4-hydroxy-5-[[*(1E,2E)*-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]naphthalene-2,7-disulfonate, LH₂.

The general synthesis reaction of [M(LH₂)(OH)₂] (M = Zn^{II} or Cd^{II}) is as follows:



Experimental results of the elemental analyses of the synthesized ligand and its metal chelates were in good agreement with theoretical expectations. Elemental analyses of the complexes indicated that the metal:ligand ratios were 1:2 and 1:1 for the [M(LH)₂] (M = Ni^{II} or Cu^{II}) and [M(LH₂)(OH)₂]

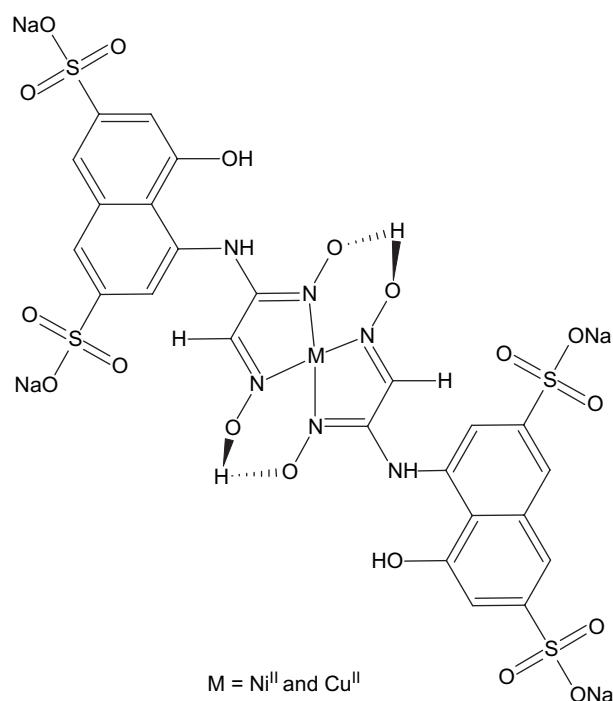


Fig. 2. The proposed structure of the Ni^{II} and Cu^{II} complexes of disodium 4-hydroxy-5-[[*(1E,2E)*-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]naphthalene-2,7-disulfonate.

($M = \text{Zn}^{\text{II}}$ or Cd^{II}) metal complexes, respectively. The level of impurity in the products was determined by TLC. The synthesized ligand and its mononuclear complexes were soluble in water giving stable solutions at room temperature. As single crystals of the new *vic*-dioxime ligand and its transition metal chelates could not be isolated from any organic solution, no definite structures could be determined. However, the analytical and spectroscopic data enabled a prediction of the possible structures as shown in Figs. 1–3.

3.2 ^1H and ^{13}C NMR spectrum of the *vic*-dioxime ligand

The ^1H and ^{13}C NMR spectral results obtained for the LH_2 *vic*-dioxime ligand in $\text{DMSO}-d_6$, together with respective assignments, have been given above in Section 2. The ^1H NMR spectrum of the *vic*-dioxime ligand in $\text{DMSO}-d_6$ showed two singlets at 12.10 and 11.60 ppm, which disappeared upon addition of D_2O and which were assigned to the proton of the hydroxyimino group ($\text{C}=\text{N}-\text{OH}$). The singlets for the oxime groups showed that the LH_2 ligand was in the (*E,E*)-configuration [24]. The red colour of the Ni^{II} complex of LH_2 indicated that the ligand was in the (*E,E*) form, the *anti*-form of the ligand. In the proton NMR spectrum of the ligand, the resonance observed at 8.75 ppm as a singlet was assigned to the azomethine proton of the oxime group ($\text{HC}=\text{N}-$). The ^1H NMR spectrum of LH_2 in $\text{DMSO}-d_6$ revealed a multiplet at 6.85–6.70 ppm corresponding to aromatic protons; a singlet signal of the OH proton on the naphthalene ring was observed at 6.10 ppm [25]. In the spectrum of LH_2 , the NH (amide proton of the amideoxime) proton next to the oxime group appeared as a singlet at 5.67 ppm [26]. In the ^{13}C NMR spectrum of the *vic*-dioxime ligand, the naphth.-C–OH (C_1) and $-\text{NH}-\text{C}=\text{N}-\text{OH}$ (C_{17}) groups were seen at 165.70 and 152.20 ppm, respectively (Fig. 4). The most characteristic

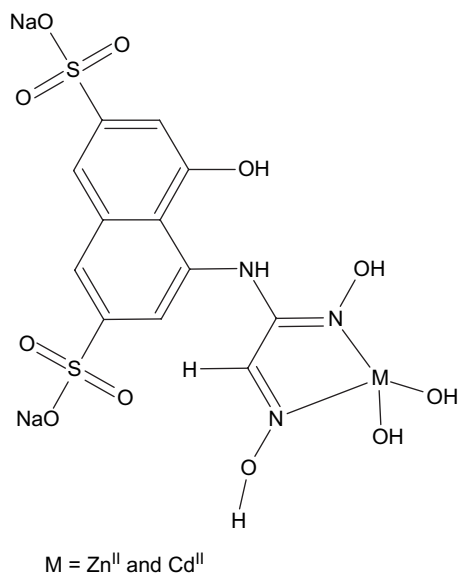


Fig. 3. The proposed structure of the Zn^{II} and Cd^{II} complexes of disodium 4-hydroxy-5-[[[(1*E*,2*E*)-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]naphthalene-2,7-disulfonate.

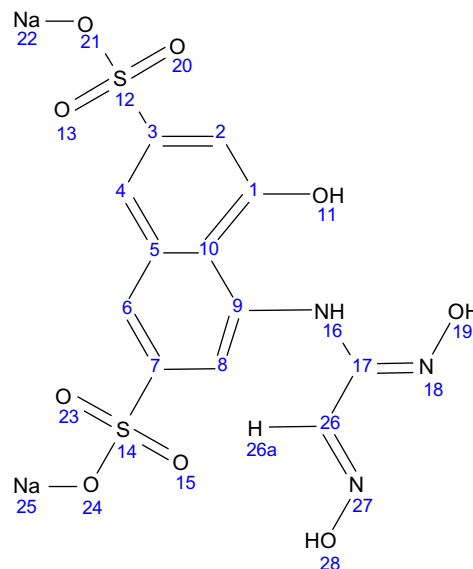


Fig. 4. The numbered structure of disodium 4-hydroxy-5-[[[(1*E*,2*E*)-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]naphthalene-2,7-disulfonate, LH_2 .

signal for $\text{HC}=\text{N}-\text{OH}$ (C_{26}) appeared at 147.80 ppm. In the ^{13}C NMR, carbon resonances of the ligand (C_2-C_{10}) were observed at 138.30–133.40 ppm. These values are in good agreement with the literature.

3.3. IR spectra

The characteristic IR data of the *vic*-dioxime and its metal complexes are listed in Table 1. Generally, oximes are characterized by three IR absorption bands at $3300\text{--}3150\text{ cm}^{-1}$ (O–H str.), $1690\text{--}1620\text{ cm}^{-1}$ ($\text{C}=\text{N}$ str.), and 950 cm^{-1} (N–O str.) [21,27].

In order to study the binding of the dioxime ligand to the metal in the complexes, the IR spectrum of the free oxime ligand was compared with that of the metal complexes. In the IR spectrum of the LH_2 *vic*-dioxime ligand, N–H stretching vibrations were observed at 3360 cm^{-1} as a broad absorption band. O–H, $\text{C}=\text{N}$ and N–O stretching vibrations were obtained at 3246, 1637 and 955 cm^{-1} , respectively [13b]; these values were in harmony with previously reported aminoglyoxime derivatives. Ni^{II} and Cu^{II} complexes of the *vic*-dioxime were square planar and had a metal:ligand ratio of 1:2 (Fig. 2). This structure for *anti*-dioximes was based on the formation of (O–H \cdots O) bands for each molecule; the weak vibrations of these hydrogen bridges were observed at $1715\text{--}1719\text{ cm}^{-1}$ for the Ni^{II} and Cu^{II} complexes.

In the Zn^{II} and Cd^{II} complexes of *vic*-dioxime, two of the four coordination sites of the metal ions were occupied by two nitrogen atoms of the dioxime molecule; the other two groups were hydroxyl ions. The LH_2 complex with Zn^{II} and Cd^{II} had a metal:ligand ratio of 1:1. The IR spectra showed that $\nu(\text{OH})$ vibrations were unchanged as they were in the ligand. The $\text{C}=\text{N}$ absorptions ($1588\text{--}1620\text{ cm}^{-1}$) were slightly lower than those of the *vic*-dioxime (1637 cm^{-1})

Table 1

Characteristic IR bands of the *vic*-dioxime ligand and its metal complexes, (1) LH₂, (2) [Ni(LH)₂], (3) [Cu(LH)₂], (4) [Zn(LH₂)(OH)₂], (5) [Cd(LH₂)(OH)₂] (cm⁻¹, KBr)

Compound	$\nu(\text{N-H})$	$\nu(\text{O-H})$	$\nu(\text{C-H})$	$\nu(\text{O-H}\cdots\text{O})$	$\nu(\text{C=N})$	$\nu(\text{N-O})$	$\nu(\text{M-N})$
(1) LH ₂	3360 s	3246 s	3035 w	—	1637 m	955 m	—
(2) [Ni(LH) ₂]	3350 s	3226 s	3031 w	1715 w	1588 w	950 m	510 w
(3) [Cu(LH) ₂]	3355 s	3225 s	3029 w	1719 w	1593 w	945 m	465 w
(4) [Zn(LH ₂)(OH) ₂]	3361 s	3235 s	3035 w	1705 w	1596 w	980 m	460 w
(5) [Cd(LH ₂)(OH) ₂]	3362 s	3234 s	3040 w	1712 w	1620 w	993 m	475 w

s: Strong, m: medium, w: weak.

and were consistent with *N,N*-chelate coordination [20]. In the ligand spectrum, the band at 1637 was assigned to the C=N group; this was shifted to lower frequencies (17–49 cm⁻¹) after complexation for all metal complexes, indicating the participation of the C=N–OH group in metal coordination. The coordination of nitrogen with the metal atom is expected to reduce the electron density on the azomethine link, and, thus causes a shift in the C=N group of oxime. IR bands in 510–460 cm⁻¹ region were attributed to (M–N) [17,28].

3.4. UV–visible spectra

The electronic spectra of the complexes in 10⁻³ M DMSO solutions at room temperature were recorded. The UV–visible spectra of the *vic*-dioxime ligand and its metal complexes, (1) [LH₂], (2) [Ni(LH)₂], (3) [Cu(LH)₂], (4) [Zn(LH₂)(OH)₂] and (5) [Cd(LH₂)(OH)₂] showed two or three absorption bands between 280 and 450 nm. These bands were assigned to both a charge transfer transition from the metal to anti-bonding orbital of the ligand and to a spin-allowed transition of the ligand. The general character of the spectra was very similar to that of the corresponding complexes of symmetrically disubstituted dioximate ligands. This was probably due to the fact that metal to ligand charge transfer and ligand to metal charge transfer transitions had similar energy differences. The d⁸ metal ion, Ni^{II} exhibits a preference for square planar geometry with dioxime complexes. The decrease in the intensities of the transitions indicates coordination with the nitrogen atoms. The electronic spectra of the Zn^{II}–dioxime and Cd^{II}–dioxime complexes exhibited an M–L charge transfer band at 547 and 530 nm, respectively; these complexes, presumably, were of tetrahedral configuration. The suggested structural formulae of the metal–dioxime complexes under investigation are given in Figs. 2 and 3.

3.5. Biological activity

The free ligand LH₂ and its metal complexes were tested for their inhibitory effects on the growth of *R. rubra*, *K. marxianus*, *A. fumigatus* and *M. pusillus* fungi using the diffusion method [21,29]. It was seen that the transition metal chelates displayed higher activity than the corresponding free ligand against the same microorganism under identical experimental conditions. The possible cause of the increased toxicity of the metal chelates compared to that of the free ligand may be explained in terms of Tweedy's chelation theory [30]. Chelation

reduces the polarity of the central atom mainly because of partial sharing of its positive charge with the donor groups and possible π -electron delocalization within the whole chelate ring. Also, chelation increases the lipophilic nature of the central atom, which subsequently favours its permeation through the lipid layer of the cell membrane [28a,b]. There are other factors which also increase activity such as solubility, conductivity and bond length between the metal and ligand [31]. Of the complexes tested, (2) [Ni(LH)₂] exhibited higher activity against *R. rubra* MC12 and *K. marxianus* fungi and (4) [Zn(LH₂)(OH)₂] showed higher activity against *A. fumigatus* than other complexes (Table 2) while (4) [Zn^{II} complex] showed no activity against *R. rubra* MC12. It was observed that inhibition activity increased with increasing concentration of the compounds used. The variation in the activity of the metal complexes against different organisms depends on the impermeability of the microorganism cells or differences between the ribosomes of microbial cells [13b,32–34]. The biological activities of the compounds are given in Table 2.

4. Conclusions

A novel, *vic*-dioxime ligand, disodium 4-hydroxy-5-[[*(1E,2E)*-*N*-hydroxy-2-(hydroxyimino)ethanimidoyl]amino]-naphthalene-2,7-disulfonate (Fig. 5) derived from 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid disodium salt with (*E,E*)-monochloroglyoxime and its some transition metal complexes have been prepared. The analytical data and spectroscopic studies suggest that the complexes were of the general formula: [M(LH)₂] where M is Ni^{II} or Cu^{II} and [M(LH)(OH)₂] where M is Zn^{II} or Cd^{II}. According to the UV–visible and IR data of the H acid linked *vic*-dioxime ligand, LH₂ (1) is coordinated with the metal ion through the hydroxyimino nitrogens.

Table 2

Antimicrobial activity studies [diameter of inhibition zone (mm); concentration: 2 ppm, 50 μ L/disc]

Compound	<i>Rhodotorula rubra</i>	<i>Kluyveromyces marxianus</i>	<i>Aspergillus fumigatus</i>	<i>Mucor pusillus</i>
(1) LH ₂	—	—	—	—
(2) [Ni(LH) ₂]	16	18	8	8
(3) [Cu(LH) ₂]	9	8	14	7
(4) [Zn(LH ₂)(OH) ₂]	—	10	14	7
(5) [Cd(LH ₂)(OH) ₂]	7	9	10	8

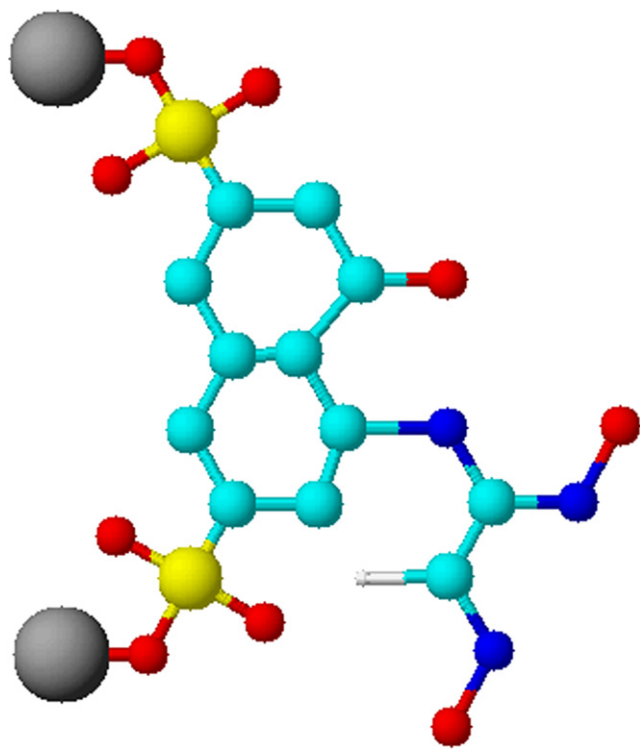


Fig. 5. The conformational structure of the LH_2 vic-dioxime ligand.

Based on the above results, the structure of the coordination compounds under investigation can be formulated as shown in Figs. 2 and 3.

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