Synthesis, complexation, spectral, antibacterial and antifungal activity of 2,4-dihydroxy-5-[(E)-phenyl diazenyl]benzaldehyde oxime

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Abstract: A new substituted salicylaldoxime ligand containing an azo (–N=N–) group, 2,4-dihydroxy-5-[(E)-phenyl diazenyl]benzaldehyde oxime (H$_3$salox) (2), was synthesized by the reaction of 2,4-dihydroxy-5-[(E)-phenyl diazenyl]benzaldehyde (1) with hydroxylamine in ethanolic solution at room temperature. Mononuclear complexes of (H$_3$salox) (2), a bidentate hydroxyaldoxime ligand, were synthesized by reaction with nickel(II), cobalt(II) and copper(II) chloride salts. The complexes, [Ni(H$_2$salox)$_2$] (3), [Cu(H$_2$salox)$_2$] (4) and [Co(H$_2$salox)$_2$] (5) were characterized by elemental analyses (C, H, N), conductivity measurements and infrared and electronic spectral studies. The $^1$H-NMR spectrum of the H$_3$salox (2) ligand was also recorded. The mononuclear Ni(II), Co(II) and Cu(II) complexes of the ligand, (H$_3$salox), have a metal:ligand ratio of 1:2 and the ligand coordinates through the N and O atoms, as is the case with most hydroxyaldoximes. The molar conductivities in DMF solution indicate the non-electrolytic nature of the metal chelates. The antimicrobial activities of the ligand and its metal complexes were estimated for eight bacteria, i.e., Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae, Mycobacterium smegmatis, Pseudomonas aeruginosa, Enterococcus cloacae, Bacillus megaterium and Micrococcus luteus and three fungi, i.e., Kluyveromyces fragilis, Rhodotorula rubra and Saccharomyces cerevisiae.

Keywords: azo; azomethine; oxime; metal complexes.

INTRODUCTION

In recent years, the chemistry of coordination compounds has shown a rapid development in diverse disciplines as a result of the possible use of these new compounds in biological applications. Transition metal complexes with potential biological activity are the focus of extensive investigations. Oximes and azo dyes have often been used as chelating ligands in the field of coordination chemistry and their metal complexes have been of great interest for many years. The biological importance of oximes and their complexes is very well known.$^1$ Different oximes and their metal complexes have shown notable bioactivity as chelating therapeutics, as drugs, as inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxides.$^2,^3$ Transition metal complexes with o-hydroxy aromatic oximes have attracted much attention as they exist as cis- and trans- geometrical isomers. Copper complexes are known to assume trans structures while cobalt complexes have cis structures.$^4$
The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms makes vic-dioximes amphoteric ligands, which form square-planar, square-pyramidal or octahedral complexes with transition metal ions such as Ni(II), Co(II) and Cu(II) as the central atom.\textsuperscript{5} Fig. 1.

In previous papers, the synthesis and characterization of new ligands and their various transition metal complexes were reported.\textsuperscript{6–8} Due to the importance of azo-oxime compounds and in continuance of interest in the syntheses of azo and oxime compounds, the synthesis and spectral properties of a new azo-oxime compound and its metal complexes are reported herein. The proposed structure of the ligand is shown in Fig. 1. \textsuperscript{1}H-NMR, IR and UV-vis data and elemental analyses results of the azo-oxime compounds are presented.

EXPERIMENTAL

Materials and measurements

All chemicals used in the syntheses were of reagent grade and used without further purification. All solvents were of reagent grade and purified according to the standard procedure. Carbon, hydrogen and nitrogen elemental analyses were performed with a model LECO CHNS 932 elemental analyzer. The IR spectra were obtained as KBr discs (4000–400 cm\textsuperscript{-1}) using a Shimadzu 8300 FTIR spectrophotometer. The electronic spectra were obtained in DMF on a Shimadzu UV-160 A spectrophotometer. The \textsuperscript{1}H-NMR spectra were recorded on a Bruker Ultrashield 300 MHz FT-NMR spectrometer.

2,4-dihydroxy-5-[(E)-phenyldiazenyl]benzaldehyde, a-sal (1)

Aniline (0.093 g, 1.0 mmol) was cooled to 0 °C and hydrochloric acid (35.5 %, 0.4 mL) was added. When the mixture had attained room temperature, it was stirred for complete solubilization. The solution was again cooled to 0 °C and NaNO\textsubscript{2} (crystals) (70 mg, 1.0 mmol) was added in 2 min. The suspension was stirred with a glass rod until a deep yellow precipitate was formed (10 min). To this suspension, ice (ca. 10 g) was added in small pieces and the mixture was poured into a suspension of 2,4-dihydroxybenzaldehyde (128 mg, 1.0 mmol) and CH\textsubscript{3}COONa (ca. 3 g) in EtOH (35 mL) at 0 °C. The color changed within a few minutes from blue to red. After 15 min stirring, aqueous sodium carbonate (20 %, 50 mL) was added at 0 °C and the solution was allowed to warm to room temperature and then extracted three times with EtOH (3 x 50 mL). The combined organic layers were washed with water, dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was evaporated under vacuum. Anal. Calcd. for C\textsubscript{13}H\textsubscript{10}N\textsubscript{2}O\textsubscript{3} (FW 242.23): C, 64.46, H, 4.16; N, 11.56 %. Found: C, 64.35; H, 4.24; N, 11.69 %; IR (KBr disc, cm\textsuperscript{-1}): 3422 (O–H), 3062 (Ar–C–H), 1700 (C=O), 1385 (–N=N–); \textsuperscript{1}H-NMR (300 MHz, DMSO-d\textsubscript{6}, δ ppm): 10.20 (OH), 9.95 (CHO), 7.45–7.60 (Ar–H); \textgreek{A}\textsc{M (\textomega \textsuperscript{-1} cm\textsuperscript{-1} mol\textsuperscript{-1}}): 11.

Synthesis of 2,4-dihydroxy-5-[(E)-phenyldiazenyl]benzaldehyde oxime (H\textsubscript{3}salox) (2)

The oxime ligand was prepared by the reaction of hydroxylammoniumchloride (NH\textsubscript{2}OH.HCl) with 2,4-dihydroxy-5-[(E)-phenyldiazenyl]benzaldehyde. NH\textsubscript{2}OH.HCl (0.5 g, 7.2 mmol) and a-sal (1.215 g, 5 mmol) were taken in MeOH. The resulting mixture was neutralized with a few drops of 1 M NaOH solution and refluxed for 4–5 h. The precipitated compound was filtered, washed with cold MeOH and dried under vacuum.

Synthesis of [Ni(H\textsubscript{2}salox)\textsubscript{2}] (3)

A solution of H\textsubscript{3}salox (0.257 mg, 0.001 mol) in EtOH (25 mL) was added drop-wise to a solution of NiCl\textsubscript{2}.6H\textsubscript{2}O (0.12 g, 0.0005 mmol) in EtOH (20 mL) at room temperature under air. The brown solution (pH 8) was stirred for 3 h, during which time it went darker and a dark green solid was formed. The solid was filtered and washed with cold EtOH and dried under vacuum.

Synthesis of [Cu(H\textsubscript{2}salox)\textsubscript{2}] (4)

This dark green complex was prepared by a procedure similar that employed for the synthesis of [Ni(H\textsubscript{2}salox)\textsubscript{2}] but using CuCl\textsubscript{2}.2H\textsubscript{2}O (0.086 g, 0.5 mmol) instead of NiCl\textsubscript{2}.6H\textsubscript{2}O.

Synthesis of [Co(H\textsubscript{2}salox)\textsubscript{2}] (5)

Cobalt(II) chloride hexahydrate (0.12 g, 0.0005 mol) in 10 mL of EtOH was added to a hot EtOH solution of H\textsubscript{3}salox (1:2 molar ratio). The mixture was stirred 5 h at room
temperature with air bubbling, giving a reddish brown precipitate. The precipitate was collected by filtration, washed with cold EtOH, then Et2O and dried in a desiccator.

**Fig. 2.**

Antibacterial and antifungal activities

The new salicylaldoxime derivative ligand and its metal complexes were evaluated for both their *in-vitro* antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Mycobacterium smegmatis*, *Pseudomonas aeruginosa*, *Enterococcus cloacae*, *Bacillus megaterium* and *Micrococcus luteus* and their *in-vitro* antifungal activity against *Kluyveromyces fragilis*, *Rhodotorula rubra* and *Saccharomyces cerevisiae* by the disc diffusion method.9

**RESULTS AND DISCUSSION**

**Synthesis**

2,4-Dihydroxy-5-[*(E*)-phenyldiazenyl]benzaldehyde oxime (H$_3$salox) was prepared by the reaction of 2,4-dihydroxy-5-[*(E*)-phenyldiazenyl]benzaldehyde with hydroxylamine hydrochloride in EtOH at room temperature. The product of the condensation reaction of 2,4-dihydroxy-5-[*(E*)-phenyldiazenyl]benzaldehyde salt with hydroxylamine hydrochloride is depicted in Fig. 1. The new oxime ligand, 2,4-dihydroxy-5-[*(E*)-phenyldiazenyl]benzaldehyde oxime (H$_3$salox), gave mononuclear complexes (Fig. 3) with Ni(II), Co(II) and Cu(II) as follows:

$$2H_3salox + MX_2.nH_2O \rightarrow M(H_2salox)_2 + 2HX + nH_2O$$

where H$_3$salox: 2,4-dihydroxy-5-[*(E*)-phenyldiazenyl]benzaldehyde oxime; M: Ni(II), Co(II) or Cu(II); X: Cl; n: 6 or 2.

**Analytic and spectral data of the ligand and its complexes**

2,4-Dihydroxy-5-[(E)-phenyldiazenyl]benzaldehyde oxime (H$_3$salox)

(2): Yield: 0.61 g (48 %); m.p.: 165 °C. Anal. for Calcd. C$_{13}$H$_{11}$N$_3$O$_3$ (FW: 257.25): C, 60.70, H, 4.31; N, 16.47 %. Found: C, 60.49; H, 4.11; N, 16.47 %; IR (KBr, cm$^{-1}$): 3434 (O–H), 3135 (N–H), 3037 (Ar-C–H), 1716 (O–H–O), 1639 (C=N), 1385 (–N=N–), 960 (N–O); 1H-NMR (300 MHz, DMSO-$d_6$, $\delta$/ ppm): 14.15 (C=N–OH), 10.20 (OH), 8.55 (–CHO), 7.45–7.60 (Ar-H), 6.42 (N–H); UV-vis.( DMF) ($\lambda_{max}$/ nm): 287, 348, 421; $\lambda_M$ ($\Omega$–1 cm$^2$ mol$^{-1}$): 14.

[Ni(H$_2$salox)$_2$] (3): Yield: 0.25 g (89 %); m.p. > 250 °C; Anal. Calcd. for C$_{26}$H$_{20}$NiO$_6$ (FW: 571.17): C, 54.67, H, 3.53; Ni, 10.28 %. Found: C, 54.49; H, 3.61; Ni, 10.36 %; IR (KBr, cm$^{-1}$): 3384 (O–H), 3049 (Ar-C–H), 1710 (O–H–O), 1629 (C=N), 1389 (–N=N–), 935 (N–O), 524 (Ni–O), 418 (Ni–N); UV-vis.(DMF) ($\lambda_{max}$/ nm): 275, 340, 440; $\lambda_M$ ($\Omega$–1 cm$^2$ mol$^{-1}$): 21.

[Cu(H$_2$salox)$_2$] (4): Yield: 0.20 g (69 %); m.p.: > 250 °C; Anal. Calcd. for C$_{26}$H$_{20}$CuO$_6$ (FW: 576.02): C, 54.21, H, 3.50; Cu, 11.01 %. Found: C, 54.34; H, 3.41; Cu, 11.25 %; IR (KBr, cm$^{-1}$): 3448.5 (O–H), 3058 (Ar-C–H), 1716 (O–H–O), 1632 (C=N), 1385 (–N=N–), 939 (N–O), 511 (Cu–O), 424 (Cu–N); UV-vis. (DMF) ($\lambda_{max}$/ nm): 276, 326, 430, 501, 514; $\lambda_M$ ($\Omega$–1 cm$^2$ mol$^{-1}$): 19.

[Co(H$_2$salox)$_2$] (5): Yield: 0.18 g (64 %); m.p.: >250 °C. Anal. Calcd. for C$_{26}$H$_{20}$CoO$_6$ (FW: 571.41): C, 54.65, H, 3.53; Co, 10.31 %. Found: C, 54.47; H, 3.63; Co, 10.39 %; IR (KBr, cm$^{-1}$): 3383 (O–H), 3049 (Ar-C–H), 1720 (O–H–O), 1631 (C=N), 1386 (–N=N–), 941 (N–O).
O), 526 (Co–O), 437 (Co–N); UV-vis.(DMF) (λmax/ nm): 279, 345, 436, 598, 661; ΛM (Ω–1 cm2 mol–1): 23.

The experimental results of the elemental analyses of the synthesized ligand and its metal chelates are in good agreement with theoretical expectations. The elemental analyses of the complexes indicate that the metal-ligand ratios were 1:2 in the [M(H2salox)2] [M = Ni(II), Co(II), or Cu(II)], metal complexes. The level of impurity in the products was checked by TLC. The synthesized ligand and its mononuclear complexes were soluble in water giving stable solutions at room temperature. The low conductances of the chelates support the non-electrolytic nature of the metal complexes. Single crystals of the new oxime ligand and its transition metal chelates could not be isolated from any organic solution, thus, no definite structures could be described. However, the analytical and spectroscopic data enables possible structures, as shown in Figs. 1 and 3, to be predicted.

Fig. 3.

Spectral Characterization

The 1H-NMR data recorded in DMSO-d6 provided further evidence for the structural characteristics of the oxime ligand. The 1H-NMR spectrum of the a-sal compound displayed the presence of a broad singlet signal due to the hydrogen of aldehyde group at 9.95 ppm, which is lower field shifted to 8.55 ppm in the spectrum of the aldoxime ligand through the oximation reaction.10 The spectrum of the H3salox ligand exhibited multiplet signals at 7.45–7.60 ppm due to aromatic protons.11 The strong signals appearing in the chemical shift ranges 6.42–6.45 ppm can be attributed to the hydrogen of the –NH of the keto structure (Fig. 2). In addition, the spectrum of the ligand H3salox showed a singlet signal at 10.20 ppm due to the hydrogen of the –OH group. The 1H NMR spectrum of the ligand showed a signal at 14.20 ppm, which can be attributed to the hydrogen bounded OH proton of the hydroxyimino group.

The electronic spectra of the complexes in 10–3 M DMF solutions at room temperature were recorded. The electronic spectra can often provide quick and reliable information about the ligand arrangement in transition metal complexes. The electronic spectra of the ligand and its metal complexes in DMF showed 3–5 absorption bands between 275 and 661 nm. The ligand showed absorption bands at 421, 348 and 287 nm. These bands are assigned to the n → π* and π → π* transitions, respectively.12 The electronic absorption spectrum of the [Ni(H2salox)2] complex showed weak bands at 647 and 598 nm, which are assigned to the 1A1g → 1B1g and 1A1g → 1A2g transitions, respectively. A d8 metal ion, Ni(II) exhibits a preference for square planar geometry with oxime complexes. The decrease in the intensities of the transitions indicated coordination to the nitrogen atoms. The band at 340 nm is due to the charge-transfer transition and that at 275 nm is due to π → π* transitions. The [Cu(H2salox)2] complex exhibited bands at 514 and 501 nm, which can be assigned to d-d transitions, while absorption band at 430 nm is assignable to the charge-transfer transition. The bands at 326 and 276 nm are assigned to the n → π* and π → π* transitions, respectively. The electronic absorption spectrum of the Co(II) complex showed weak bands at 661 and 598 nm, which can be assigned to the d → d transitions 2B2g → 2Eg and 1A1g → 1B1g. This agrees with square-planar geometry.13 The band at 436 nm is due to the charge-transfer transition, and the bands at 345 and 279 nm are assigned to the n → π* and π → π*
transitions, respectively. The suggested structural formulae of the metal-oxime complexes under investigation are given in Fig. 3.

The IR spectra of the free ligand and metal complexes were recorded in the range 4000–400 cm$^{-1}$ and 400–100 cm$^{-1}$. The infrared spectrum of the substituted salicylaldoxime ligand showed strong and broad bands due to the hydrogen-bonded phenolic OH at o-position in the region 3000–2800 cm$^{-1}$. It also exhibited two separate OH bands due to the oxime OH at 3237 and 3137 cm$^{-1}$ and phenolic OH at 3400 cm$^{-1}$. The IR spectrum of the ligand showed a broad band between 3200 and 3450 cm$^{-1}$, which can be attributed to the phenolic OH group. The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom. The medium bands observed in the 1646–1620 cm$^{-1}$ frequency ranges in the complexes were assigned to the $\nu$(C=N) mode. The shift of the $\nu$(C=N) vibration in all the complexes to a lower frequency suggests that the nitrogen atom of the ring contributes to the complexation. The lower $\nu$(C=N) frequency also indicates stronger M–N bonding. In the IR spectra of the complexes, a band was observed between 430 and 460 cm$^{-1}$, which is attributed to $\nu$(M–N) stretching vibrations.$^{14}$ Another band appeared between 660 and 672 cm$^{-1}$, which is assigned to the interaction of the phenolic oxygen to the metal atom, i.e., the stretching vibrations $\nu$(M–O).

**Biological Activity**

The antibacterial and antifungal activity of the new compounds were tested using the disc diffusion method.$^{15}$ The antibacterial and antifungal activities of the compounds against eight bacteria, namely *E. coli*, *S. aureus*, *K. pneumoniae*, *M. smegmatis*, *P. aeruginosa*, *En. cloacae*, *B. megaterium* and *M. luteus*, and three fungi, namely *K. fragilis*, *R. rubra* and *S. cerevisiae*, are presented in Table I.

The results showed that the bidentate ligand exhibited activity against none of the tested species of bacteria, *E. coli*, *S. aureus*, *K. pneumoniae*, *M. smegmatis*, *P. aeruginosa*, *En. cloacae*, *B. megaterium* and *M. luteus*, nor against the fungi *K. fragilis* and *R. rubra*. The H$_3$salox ligand (2) had the highest effect against the fungus *S. cerevisiae*. The results indicate that the [Ni(H$_2$salox)$_2$] chelate (3) showed no activity except against *S. cerevisiae* under identical experimental conditions. However, the Cu(II) metal chelate of the ligand (4) showed low effects against *S. aureus* and *M. smegmatis* bacteria and *S. cerevisiae* fungus. The [Co(H$_2$salox)$_2$] chelate (5) had the highest activity against *S. cerevisiae* fungus, but it had low activity against *R. rubra* fungus. The complex has no activity against the other bacteria and fungi. The variation in the activity of the different metal complexes against the different microorganisms depends either on the impermeability of the cells of the microbes or differences in the ribosomes in the microbial cells.$^{10,16}$

**CONCLUSIONS**

In this study, a phenolic oxime ligand, 2,4-dihydroxy-5-[(E)-phenyldiazenyl]benzaldehyde oxime (Fig. 1), derived from 2,4-dihydroxy-5-[(E)-phenyldiazenyl]benzaldehyde and hydroxylamine in EtOH, and some of its transition metal complexes were prepared. The analytical data and the spectroscopic studies suggested that the complexes had the general formula [M(H$_2$salox)$_2$], where M is nickel(II), cobalt(II) or copper(II). The molar conductance measurements of the complexes showed their non-electrolytic nature. According to the UV-vis. and IR data of the phenylazo linked oxime
ligand, H$_2$salox (2) was coordinated to the metal ion through the oxime nitrogen and oxygen atom of the hydroxyl group in salicylaldehyde.

Based on the obtained results, the structure of the coordination compounds under investigation can be formulated as in Fig. 3.

СИНТЕЗА, КОМПЛЕКСИРАЊЕ, СПЕКТРАЛНА, АНТИБАКТЕРИЈСКА И АНТИФУНГАЛНА АКТИВНОСТ ОКСИМА 2,4-ДИХИДРОКСИ-5-[(E)-ФЕНИЛДИАЗЕНИЛ]БЕНЗАЛДЕХИДА

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У реакцији између 2,4-дијидрокси-5-[(E)-фенилдизазенил]бензилехида и хидроксилиамина у етаноловом раствору на собној температурі синтетизован је 2,4-оксим дијидрокси-5-[(E)-фенилдизазенил]бензилехида (H$_2$salox) (2). Овај лиганд је употребљен за синтезу монокулеарних Ni(II), Co(II) и Cu(II) комплекса у којима је H$_2$salox лиганд бидентатно координован за испитиване Јоше метала. За карактеризацију [Ni(H$_2$salox)$_2$] $\text{3}, [\text{Cu(H}_2\text{salox)}_2]$ $\text{4}$ и [Co(H$_2$salox)$_2$] $\text{5}$ комплекса употребљене су различите технике, као што су елементална (C, H и N) анализа, кондуктометријска мерења, инфрачврна и електронска апсорпциона спектроскопија. Такође, у овој раду приказан је и 1$^\text{H}$ NMR спектар H$_2$salox (2) лиганда. У испитиваним Ni(II), Co(II) и Cu(II) комплексима H$_2$salox (2) лиганд је координован преко N и O долорских атома, при чему су за један јон метал координован два лиганда. Антибактеријска активност H$_2$salox лиганда и одговарајућих комплекса метала испитана је на осам врста бактерија, као што су: Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae, Mycobacterium smegmatis, Pseudomonas aeruginosa, Enterococcus cloacae, Bacillus megaterium и Micrococcus luteus. Поред тога, испитивана је антифунгала активност на три врсте гљива и то: Micrococcus luteus, Rhodotorula rubra и Saccharomyces cerevisiae.

REFERENCES

TABLE I. Antimicrobial effects of the synthesized compounds, a-sal (1), H$_3$salox (2), [Ni(H$_2$salox)$_2$] (3), [Cu(H$_2$salox)$_2$] (4) and [Co(H$_2$salox)$_2$] (5) (Concentration: 2000 ppm; 50 µl well$^{-1}$).

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– denotes no activity

FIGURE CAPTIONS

Fig. 1. The synthesis reaction of the substituted salicylaldoxime ligand.
Fig. 2. Keto-enol tautomerism in the a-sal compound.
Fig. 3. The proposed structure of the metal complexes of the substituted salicylaldoxime ligand
$\text{NH}_2$ $\xrightarrow{i}$ $\text{N}^+$ $\xrightarrow{ii}$ $\text{N}^+\text{N}^-\text{N}^-\text{N}^-$ $\xrightarrow{iii}$ $\text{N}^+\text{N}^-\text{N}^-\text{N}^-$

$i$: NaNO$_2$/HCl; $ii$: 2,4-dihydroxybenzaldehyde; $iii$: hydroxylammoniumchloride

Fig. 1.
Enol form  \[ \xrightarrow{\text{HOMO}} \]  keto form

Fig. 2.
M = Ni(II), Cu(II) or Co(II)

Fig. 3.