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Synthesis and Biochemical Activity Studies of 2,2'-[propane-1,3-diylbis(oxy)]-2,2'bis-[(benzylideneamino)benzenethiol], ligand and its mononuclear copper(II), nickel(II) and cobalt(II) complexes

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Abstract: A new hexadentate ligand incorporating Shiff base moities has been synthesized and its copper(II), nickel(II) and cobalt(II) complexes have been prepared and characterized by spectral methods. Elemental analyses and spectroscopic data of the Schiff base ligand and its copper(II), nickel(II) and cobalt(II) complexes are consistent with the formation of the ligand and its metal complexes. In addition to the Schiff base ligand (H₂L) and copper (II), nickel(II) and cobalt(II) complexes (5-7) were tested against the morphology of series bacteria. The copper(II), nickel(II) and cobalt(II) complexes exhibit higher activity than Schiff base ligand (H₂L) under identical experimental conditions.

Keywords: Benzenethiol; biological activity; copper(II); nickel(II); cobalt(II) complex.

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Introduction

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The reaction of primary amines with carbonyl compounds yields Schiff bases.^[1] Also the Schiff base derived from the reaction of diketones with diamines represent an important series of chelating agents and are now being widely used the synthesise mono-, di-, and polynuclear transition metal complexes. Schiff bases and their metal complexes play a key role in our understanding of the coordination chemistry of transition metal ions.^[2] There is considerable interest in the chemistry of transition metal complexes of ligands containing oxygen, nitrogen and sulphur donor atoms due to the antitumor, antiviral, antifungal and antibacterial activity and industrial uses.^[3,4]

In the past years, the synthesis, structure and properties of Schiff base complexes have been stimulated much interest for their noteworthy contributions in single molecule-based magnetism, material science,^[5] catalysis of many reaction like carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis.^[6] This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning the metal centered electronic factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalyst. The flexibility of disposition of different donor site is the secret behind their successful performance in mimicking peculiar geometries around the metal centers, leading to very interesting spectroscopic properties with varied magnetic activities.^[7] Copper(II), nickel(II) and cobalt(II) complexes of Schiff base with pseudohalides are well known for their preparational accessibilities, exhibiting the flexibility of the coordination geometry around the metal center.^[8-10] The coordination number usually varies from four to six depending upon the donor site geometry around the metal and above all the steric constraints imposed by the ligand itself.

This article describes the synthesis and characterization of the new ligand, 2,2'-[propane-1,3-diylbis(oxy)]2,2'bis-[(benzylideneamino)benzenethiol], and its copper(II), nickel(II) and cobalt(II) complexes. The properties of the complexes were investigated by magnetic, physical, and spectral methods. Furthermore, the free ligand and copper(II), nickel(II) and cobalt(II) complexes (5-7) were evaluated for antimicrobial activity against one gram-positive bacterium (*Staphylococcus aureus*), a gram-negative bacterium (*Escherichia coli*), and the fungi *Aspergillus niger* and *Trichoderma*. The free ligand and copper(II), nickel(II) and cobalt(II) complexes (5-7) exhibit antibacterial activity against both strains.

Results and Discussion

2,2'-[propane-1,3-diylbis(oxy)]2,2'bis-[(benzylideneamino)benzenethiol], (H2L) was synthesised in EtOH by condensation 2,2'-[propane-1,3-diylbis(oxy)]dibenzaldehyde, (**3**) with 2-aminothiophenol (Scheme 1). The Schiff base ligand and dialdehyde (**3**) were characterized by elemental analysis, ¹H-NMR, ¹³C-NMR, IR and mass spectral data. The Cu(II), Ni(II), and Co(II) complexes of Schiff base (H₂L) have been prepared and characterized by elemental analysis, magnetic moment, Uv-Vis, and mass spectral data. In the proposed structure of the Schiff base ligand (H₂L), N₂S₂O₂ units available for the octahedral complexation of Cu(II), Ni(II), and Co(II) metal ions.

NMR Spectra

The 1H-NMR spectra of dialdehyde (**3**) and Schiff base (H₂L) ligand (in CDCl₃) showed well-resolved signals as expected. The proton ¹H-NMR spectrum of compound **3** showed the following signals: C₆H₄ as multiplet at δ = 7.0-7.85, -CHO singlet at δ = 10.50, -OCH₂- triplet at δ = 4.33, and -CH₂- pentet at δ = 2.43 ppm. The proton NMR spectrum of Schiff base ligand

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(H₂L) showed the following signals: C₆H₄ as multiplet at δ = 7.1-8.1, -N=CH singlet at δ = 8.57, -SH singlet at δ = 8.53, -OCH₂- triplet at δ = 4.6 and -CH₂- pentet at δ = 2.73 ppm. In 8.53 ppm, the singlet disappears on deuterium exchange. In the ¹H-NMR spectra, integrated data are consistent with the formula. Nine resonance signals were observed in the ¹³C-NMR spectra of the dialdehyde (**3**) and Schiff base ligand (H₂L), which was also consistent with the formula for H₂L.

Mass Spectra

The mass spectra of the Schiff base (H₂L) and its Cu(II), Ni(II), and Co(II) complexes were recorded in pyridine solution. The mass spectra (ESI) exhibited the molecular ion at m/z =284 M⁺ for compound **3** and m/z = 498 M⁺ for the free Schiff base ligand, which indicated formation of compound **3** and ligand. The molecular ion peaks appeared (m/z, ESI) at 560.18 M⁺, at 556.41 [M+1]⁺, and at 555.57 M⁺ for the CuL, NiL, and CoL, respectively. The mass spectra showed the formation of the ligand and its Cu(II), Ni(II), and Co(II) complexes.

IR Spectra

Relevant characteristic IR bands were given in Table 1. In generally, the metal complexes exhibited very comparable IR features, suggesting that they were similar structure. The certain bands in the generally complicated IR spectra were used to establish the nature of the metal complexes. The strong band at 1594 cm⁻¹ might be assigned to \Box (C=N) vibration.^[11] In the Cu(II), Ni((II), and Co(II) complexes \Box (C=N) vibrations were shifted to lower frequency (≈10 cm⁻¹), suggesting coordination of metal via nitrogen.^[12] Finally, the peaks appearing between 430 and 480 cm⁻¹ are attributed to \Box (M-N).^[12, 13] The significant shifts in \Box (C=N) upon

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complexation support the concept of coordination of ligand through the Schiff base nitrogen (Fig 1).

Magnetic properties and Electronic Absorption Spectra

Electronic spectra of the Cu(II), Ni(II), and Co(II) complexes were recorded in DMSO (λ cm⁻¹(ε L mol⁻¹ cm⁻¹)). The experimental values are given in Table 2. Electronic spectra of the Cu(II) complex show bands at 13,123 (762), 16,181 (618), and 28,985 (345) cm⁻¹ assignable to a ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition and charge transfer. Electronic spectral data coupled with detected magnetic moment of 1.81 B.M. suggest octahedral geometry.^[12, 14] Ni(II) complex displays bands at 13,422 (1025), 14,285 (700), and 30,303 (355) cm⁻¹ assignable to a ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}(F)$, ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$, and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$, respectively. These electronic transition along with magnetic moment 2.78 B.M. suggest octahedral geometry for Ni(II) complex.^[12, 15] The Co(II) complex shows three bands at 13,450 (750), 14,326 (700), and 33,335 (320) cm⁻¹ assignable to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(P)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$, and ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$ transitions, respectively. These transitions and detected magnetic moment of 3.9 B.M. indicate a high-spin octahedral complex.^[12, 16, 17] The calculated values of ligand field splitting energy (10 Dq), Racah interelectronic repulsion parameter (B), covalent factor (β), ratio v_2/v_1 , and ligand field stabilization energy (LFSE), given in Table 2, support the proposed geometry for the Cu(II), Ni(II), and Co(II) complexes.

Antimicrobial Activity

The Schiff base ligand (H₂L) and its metal complexes were evaluated for antimicrobial activity against one gram-positive bacterium (*S. aureus*), gram-negative bacterium (*E. coli*), and fungi fungi *A. niger* and *Trichoderma*. The results of these studies are given in Table 3. These data showing that the Schiff base ligand and its Cu(II), Ni(II), and Co(II) complexes exhibit

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antibacterial activity against both strains. The Cu(II), Ni(II), and Co(II) complexes exhibit higher activity than the Schiff base ligand under identical experimental conditions. Antibacterial inhibitions were compared with the activity of ciprofloxin as a standard. The Schiff base ligand (H_2L) and its metal complexes showed less activity than the standard. The metal salts used for synthesis of metal complexes exhibit negligibly antimicrobial activities.^[18, 19] Enhancement of activity of the Schiff base after chelation can be explained on the basis of Overtones and Tweedy's concepts.^[20] Antibacterial inhibition was found to increase with increasing concentration of the metal complexes. The studies showed that the Cu((II) complex exhibits higher activity against each class of organism. The activity is related to the nature and structure of the metal complexes.^[21] The higher activity of the Cu(II) complex may be attributed to its higher stability constants. The Schiff base and its metal complexes show more activity against gram-negative E. coli than against gram-positive S. aureus. Antibacterial activity can be ordered as CuL> CoL > NiL, similar to earlier observations.^[12, 22] The Cu(II), Ni(II), and Co(II) metal complexes don't show strong concentration dependence of antimicrobial activity as compared to the antifungal activities of the same complexes. The relation between chelation and toxicity is very complex, expected to be a function of steric, electronic, and pharmacological factors along with mechanistic pathways.^[23] Investigation of antifungal activity of the Schiff base ligand and its Cu(II), Ni(II), and Co(II) metal complexes revealed that all the metal complexes are more toxic than the ligand. The antifungal activity is enhanced several times on being coordinated with metal. The metal complexes activity increases as the stability of the complex increases. The metal complex activities follow the order CuL > CoL > NiL, which is exactly same as the order of stability constants of these complexes. Comparison of activities shows that the Cu(II) complex

is more active than the Schiff base ligand against *A. niger*. The Schiff base ligand (H₂L) activity against *Trichoderma* increases.

Conclusions

In this work, we have demonstrated the synthesis and characterization of the 2,2'-[propane-1,3-diylbis(oxy)]2,2'bis-[(benzylideneamino)benzenethiol], and its copper(II), nickel(II) and cobalt(II) complexes. All the metal complexes have been found to be paramagnetic properties. The metal atom ions were complexed with nitrogen, sulphur and oxygen atoms of the Schiff base ligand in an octahedral geometry. All of data obtained from spectra supported the structural properties of ligand and its metal complexes. The Shiff base ligand and its copper(II), nickel(II) and cobalt(II) complexes (5-7) were evaluated for antimicrobial activity against one gram-positive bacterium (*Staphylococcus aureus*), a gram-negative bacterium (*Escherichia coli*), and the fungi *Aspergillus niger* and *Trichoderma*. The free ligand and copper(II), nickel(II) and cobalt(II) complexes (5-7) exhibit antibacterial activity against both strains.

Experimental and methods

Reagents and Instruments

¹H-NMR and ¹³C- NMR spectra were recorded on a Varian Gemini 200 spectrometer. $CDCl_3$ was used as solvent. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane, using the solvent signal as internal reference. C, H and N contents were determined microanalytically on a Hewlett Packard 85 CHN analyzer, and metal contents were estimated spectrophotometrically. IR spectra were recorded on an ATI Unicam Matson 1000 Model FTIR spectrophotometer and Uv-Vis spectra on an ATI Unicam UV2 Model UV/Vis

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spectrophotometer. Mass spectra [ESI) were recorded on Micromass Quattroo LC-MS/MS spectrophotometer. Room temperature magnetic susceptibility measurements were done on a PAR model 155 vibrating sample magnetometer. All chemicals were of the highest quality available, obtained from local suppliers, and used as received

Sythesis of 2,2'-[propane-1,3-diylbis(oxy)]dibenzaldehyde, (3)

Freshly prepared potassium 2-formylphenolate (3.2 g, 20 mmol) and 1,3-dibrompropane (2 g, 10 mmol) were refluxed for 3 h in dimethylformamide (DMF) (25 mL). The solution was then poured in to ice-water (50 mL) and the solid product filtered off and recrystallised from ethanol with decolourising charcoal. The compound **3**, m.p. 120 °C, was isolated in 80% yield; IR (KBr disc.)/cm⁻¹ 1682 (C=O) and 1240(C-O); ¹H-NMR(CDCl₃)/ppm δ : 10.50 (s, 2H, CHO), 7.0-7.85 (m, 8H, aryl), 4.33 (t, 4H, C -OCH₂), and 2.44 (p, 2H, -CH₂-). MS: (ESI) *m*/*z* = 284 M⁺. Elementel analysis (%): calculated: C, 72.90; H, 5.82; found: C, 72.70; H, 5.8 for C₁₇H₁₆O₄.

Sythesis of 2,2'-[propane-1,3-diylbis(oxy)]2,2'bis-[(benzylideneamino)benzenethiol], (H₂L)

A solution of dialdehyde (**3**) (2.84 g, 10 mmol) and 2-aminothiophenol (2.5 g, 20 mmol) were refluxed for 10 h in EtOH (25 mL). The solution was then poured in to water (50 mL) and the solid product filtered off and recrystallised from ethanol with decolourising charcoal. The compound **3**, m.p. 154.3 °C, was isolated in 60% yield; IR (KBr disc.)/cm⁻¹ 1594 (C=N), and 1238(C-O); ¹H-NMR(CDCl₃)/ppm δ : 8.57 (s, 2H, N=CH), 8.53 (s, 2H, -SH) 7.1-8.1 (m, 16H, aryl), 4.6 (t, 4H, -OCH₂), and 2.73 (p, 2H, -CH₂-). MS: (ESI) *m*/*z* = 498 M⁺. Elementel analysis (%): calculated: C, 69.8; H, 5.3; found: C, 69.9; H, 5.2 for C₂₉H₂₆N₂O₂S₂.

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Sythesis of copper(II), nickel(II) and cobalt(II) complexes (5-7)

Metal complexes (5-7) have been prepared by the same method. A solution of $M(ClO_4)_2.6H_2O$ (1 mmol) in $(CH_3)_2CO$ (25 mL) was added to the ligand (0.5 g, 1 mmol) solution in $(CH_3)_2CO$ (25 mL), and the mixture was boiled under reflux with stirring for 4 h. The products were filtered off, washed with H₂O, EtOH, Et₂O respectively and dried over P₂O₅.

For C₂₉H₂₄CuN₂O₂S₂, (**5**), elementel analysis (%): calculated: C, 62.2; H, 4.3; Cu, 11.3 found: C, 62.1; H, 4.2; Cu, 11.2. MS (ESI): m/z = 560.18 M⁺. Yield, a green-brown solid: 0.4 g (71%). For C₂₉H₂₄NiN₂O₂S₂, (**6**), elementel analysis (%): calculated: C, 62.7; H, 4.4; Ni, 10.6 found: C, 62.6; H, 4.5; Ni, 10.5. MS (ESI): m/z = 556.41 [M+1]⁺. Yield, a pale-red solid: 0.35 g (63%). For C₂₉H₂₄CoN₂O₂S₂, (**7**), elementel analysis (%): calculated: C, 62.7; H, 4.4; Co, 10.6 found: C, 62.7; H, 4.4; Ni, 10.7. MS (ESI): m/z = 555.57 M⁺. Yield, a brown solid: 0.4 g (72%).

Antimicrobial Activity

The antimicrobial activity of the Schiff base ligand and its Cu(II), Ni(II), and Co(II) complexes, the metal salts, and the control (DMSO) was tested *in vitro* against gram-positive bacteria (*Staphylococcus aureus*), and gram-negative bacteria (*Escherichia coli*) by paper disc method.^{[24].} Sterile (10 mm diameter) Whatman number 42 paper discs were soaked in different concentrations of ligand and/or complex (0.5 and 1 mg L⁻¹) in DMSO, dried, and then placed on nitruent agar plates. The plates were then incubated for 24 h at 37 °C and the inhibition zone around each disc was measured. The results obtained were compared with those of ciprofloxin. Three replicates were taken and the average value is given in Table 1. The Schiff base ligand and its Cu(II), Ni(II), and Co(II) complexes, metal salts, and the control (DMSO) were screened

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for antifungal activity against the fungi *Aspergillus niger* and *Trichoderma* at 0.5 and 1 mg L⁻¹ by the mycelia dry weight (MDW) method.^[25] The cultures of fungi were purified by singlespore isolation technique. The glucose nitrate (GN) medium was used for growth of fungi. The mycelia biomass was then dried along with filter paper in an oven at 65 ± 5 °C to constant weight, cooled, and finally weighed. The MDW was obtained by subtracting the weight of myceliumfree filter paper from final dry weight.^[26] Three replicates of each treatment were repeated in all experiments. The MDW was corrected each time by subtracting the dry weight obtained from the incubated flask under similar experimental conditions. The yields of MDW (mg) are presented in Table 1. The percentage error was found to be ±0.01. The percent decrease in MDW to the test compound in each case was calculated and tabulated in terms of average percentage inhibition. The results indicate that the ligand and its Cu(II), Ni(II), and Co(II) complexes arrested the growth of fungi.

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TABLE 1. Characteristic IR bands of the free ligand and its metal complexes (in cm⁻¹)

 \Box (C-O)

 \Box (M-N)

3	1682	-	1240	-
H_2L	-	1594	1238	-
CuL	-	1574	1241	455
NiL	-	1580	1240	430
CoL	-	1578	1236	480

 \Box (C=N)

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Compound

 \Box (C=O)

Complex	Ligand field splitting	Racah interelectronic	Covalent	β	v_2/v_1	LFSE
	energy (Dq cm ⁻¹)	repulsion parameter	factor (β)	(%)		(kcal mol ⁻¹)
		$(B \text{ cm}^{-1})$				
CuL	1312,3	95	-	-	-	37.49
NiL	1342,2	1030	0.2845	6.2	1.06	38.34
CoL	1345,0	971	0.5054	4.9	1.06	38.42

TABLE 2. Ligand field parameter of the metal complexes

TABLE 3. Antibacterial activities of (diameter inhibition zone in mm) and antifungal activity weight (mg) (% inhibion) of the ligand and metal complexes

	Antibacteriyal			Antifungal activiteleri (mg mL ⁻¹)				
	activiteleri(mg mL ⁻¹) E. coli S. aureus		A. niger		Trichoderma			
Compound	0.5	1	0.5	1	0.5	1	0.5	1
Ciprofloxin/kontrol	40	45	42	44	74	72	65	60
H_2L	12	15	10	20	70 (15)	65 (10)	45 (25)	30 (50)
5	20	35	15	25	50 (45)	15 (80)	35 (50)	25 (70)
6	10	15	12	20	50 (40)	20 (80)	30 (50)	25 (65)
7	17	20	15	20	55 (30)	25 (75)	40 (60)	25 (64)

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Scheme 1. Preparation of ligand, bis-{2-[(*E*)-(2-propoxybenzylidene)amino]benzenethiol},(H₂L)

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M=Cu(II) (5), Ni(II) (6), Co(II) (7)



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