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Synthesis, Spectral, Thermal and Biological Studies of Co(III) and Binuclear Ni(II) Complexes with a Novel Amine–Imine–Oxime Ligand[1]

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Abstract—Two different metal complexes of $[Co(HL)(L)(Ac)_2].4H_2O$ (**I**) and $[Ni_2(L)_2(Ac)_2].4H_2O$ (**II**)**,** have been synthesized with newly prepared amine-imine-oxime ligand [HL = 3-(4'-aminobiphenyl-4-ylimino)-butan-2-one oxime, Ac = CH_3COO^-]. This ligand HL was prepared by the condensation of diacetylmonoxime with benzidine. The structure of the ligand and complexes have been proposed by elemental analyses, IR, ^1H, and ^{13}C NMR, electronic spectra, magnetic susceptibility measurements, mass spectra, molar conductivity and thermo gravimetric analysis. The molar conductance measurements of the complexes in DMF solution correspond to non electrolytic nature for the complexes. Octahedral and tetrahedral geometries have been determined to the complexes of Co(III) and binuclear Ni(II) respectively. The ligand and its metal complexes were tested in vitro for their biological effects. Their activities against two gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and one fungal specie (*Candida albicans*) were found. They were inactive against tested gram negative bacteria.

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INTRODUCTION

Oximes and their complexes have played a remarkably role in the development of transition metal chemistry [1–8]. Oxime and dioxime derivatives are very important compounds in the chemical industry and medicine [9]. They have a broad pharmacological activity spectrum, encompassing antibacterial, antidepressant and antifungal activities [10–12]. Some oxime complexes have also anti-carcinogenic activities [9, 13, 14]. Although the numerous oximes and their metal complexes have been investigated, there have been few amine-imine-oxime complexes reported in the literature [15].

In this study, novel metal complexes of $[Co(HL)(L)\cdot(Ac)_2]\cdot 4H_2O$ (**I**) and $[Ni_2(L)_2(Ac)_2]\cdot 4H_2O$ (**II**)**,** have been synthesized with newly prepared amine-imine-oxime ligand [HL = 3-(4'-aminobiphenyl-4-ylimino)-butan-2-one oxime, Ac = CH_3COO^-]. HL was prepared by the condensation of diacetylmonoxime with benzidine. The structure of the ligand and complexes have been proposed by elemental analyses, IR, ^1H, and ^{13}C NMR, electronic spectra, magnetic susceptibility measurements, mass spectra, molar conductivity and thermo gravimetric analysis.

Some literatures [16–18] indicated that in some transition metal complexes with heterocyclic or biheterocyclic are biologically more active than the free ligands. Therefore, the biological activities of the ligand HL and their metal complexes of the Co(III) and Ni(II) are tested against six strains of bacteria (i.e. four gram-positive and two gram-negative bacteria) and against four fungal species (one yeast and three molds).

EXPERIMENTAL

All chemicals and solvents used for the synthesis were of reagent grade. Benzidine, diacetylmonoxime, $Co(CH_3COO)_2\cdot 4H_2O$, $Ni(CH_3COO)_2\cdot 4H_2O$ (Aldrich) were used as received.

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[1] The text was submitted by authors in English.

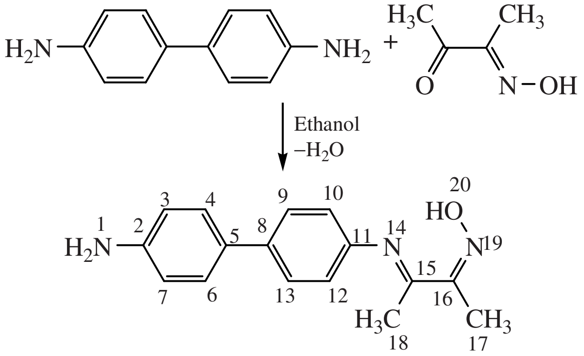
Table 1. Molar conductance and elemental analysis data of the complexes

Compound	Formula (Fw) g mol^{-1}	Molar conductance ($W^{-1}cm^2\ mol^{-1}$)	Mass spectrum, M^+, *m/z*	Elemental analysis							
				Calculated, %				Found, %			
				C	H	N	M	C	H	N	M
HL	$C_{16}H_{17}N_3O$ (267.33)	1.7	268.0 (M + 1) 267.0 (M^+)	71.89	6.41	15.72	–	71.76	6.43	15.36	–
I	$C_{36}H_{47}CoN_6O_{10}$ (782.73)	6.4		55.24	6.05	10.74	7.53	55.23	5.50	11.52	7.03
II	$C_{36}H_{46}N_6Ni_2O_{10}$ (840.17)	4.0		51.46	5.52	10.00	13.97	51.54	5.71	9.87	13.89

Synthesis of Ligand (HL)

A solution of diacetylmonoxime (10 mmol, 10.11 g) in ethanol (30 ml) was added drop wise to a solution of benzidine (10 mmol, 18.42 g) in ethanol. After 1 hour stirring, glacial acetic acid (1.5 ml) was added drop wise to the mixture and refluxed for 24 h. On cooling, the crude product was filtered, washed with water and then recrystallized from ethanol to obtain th ligand as pale yellow crystals (Scheme 1).

Scheme 1. Synthesis of HL



Yield 65% ; mp 238°C; *MS* (*m/z*) (g mol^{-1}) = 268.0 (M + 1), 267.0 (M^+), 250.0, 208.9, 168.0, 104.5, 83.5 (Fig. 1).

The elemental data and molar conductance of the ligand are given in Table 1. In Table 2 electronic spectral data, in Table 3 characteristic IR bands and in Table 4 the ^1H NMR and ^{13}C NMR spectra of the ligand are listed respectively.

Synthesis of the Metal Complexes

A solution of HL (0.27 g, 1 mmol) in ethanol-water (1:1; 20 ml) was added dropwise with stirring at room temperature to a solution of $Co(CH_3COO)_2{\cdot}4H_2O$ or Ni $(CH_3COO)_2{\cdot}4H_2O$ (0.25 g, 1 mmol) in water (20 ml). The mixture was stirred for 30 min at room temperature. The product formed was filtered, washed with warm water, methanol and finally with trichloromethane and dried under vaccum over P_4O_{10} to obtain reddish brown complex $Co(HL)(L)(Ac)_2]{\cdot}4H_2O$ (**I**) (Yield 58%; decomp. 255°C) or brown complex $[Ni_2(L)_2(Ac)_2]{\cdot}4H_2O$ (**II**) (Yield 45 %; decomp. 272°C).

The elemental data and molar conductance of the metal complexes are given in Table 1. In Table 2 magnetic moments and electronic spectral data, in Table 3 characteristic IR bands and in Table 5 thermo gravimetric spectral data of the metal complexes are listed respectively. Schemes 2 and 3 show the proposed structures for the metal complexes **I** and **II** respectively according to the spectral and analytical results. Thermo gravimetric spectra for the complexes **I** and **II** are also presented in Figs. 2 and 3, respectively.

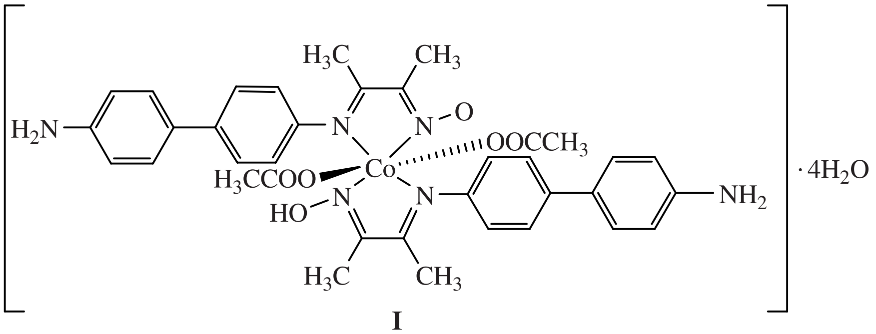
Physical Measurements

The carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba 1106 auto elemental

Table 2. Magnetic moment and electronic spectral data of the ligand and metal complexes

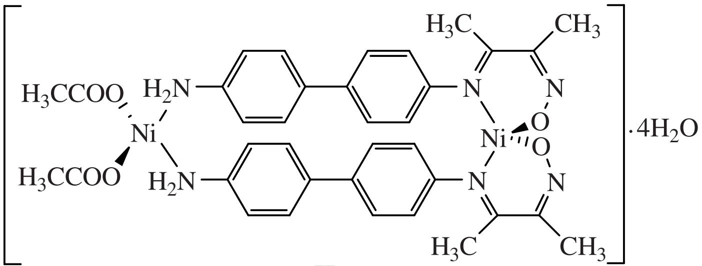
Compound	μ_{eff} (BM)	λ_{max}, nm (ε, l mol^{-1} cm^{-1})	
		d–*d*/CT	*n*–π* azomethine
HL	–	–	378 (189)
I	0.88	585 (164) 415 (145) 335 (195)	
II	2.86	601 (195)	

Scheme 2. Structures of $Co(HL)(L)(Ac)_2]\cdot 4H_2O$ (**I**)



I

Scheme 3. Structures of $Ni_2(L)_2(Ac)_2]\cdot 4H_2O$ (**II**)



II

analyzer. The complexes were analyzed for their metal contents by Perkin Elmer Optima 4300 DW ICP-OES. Magnetic susceptibility measurements at room temperatures were performed using a Sherwood Scientific MK1 model Gouy magnetic balance. UV-vis. spectrum was obtained in the methanol solutions (10^{-3} mol l^{-1}) of the complex with a Unicam UV2 spectrometer in the range of 900–190 nm. The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400 MHz FT–NMR spectrometer, utilizing deuterated dimethylsulphoxide as a solvent and TMS was used as an internal standard. The mass spectrum of HL was recorded by Thermo Finnigan Trace DSQ mass spectrometer interfaced with gas chromatography (GC–MS). FT–IR spectra were recorded in the 4000–400 cm^{-1} region with a Mattson 1000 FT–IR spectrometer using KBr pellets. Thermal analysis curves (DTA, TG and DTG curves) were recorded simultaneously under nitrogen atmosphere with a Shimadzu DTA 50 thermal analyzer. The molar conductivities of the complexes (Λ_M) were recorded using a WTW model 315i conductivity meter.

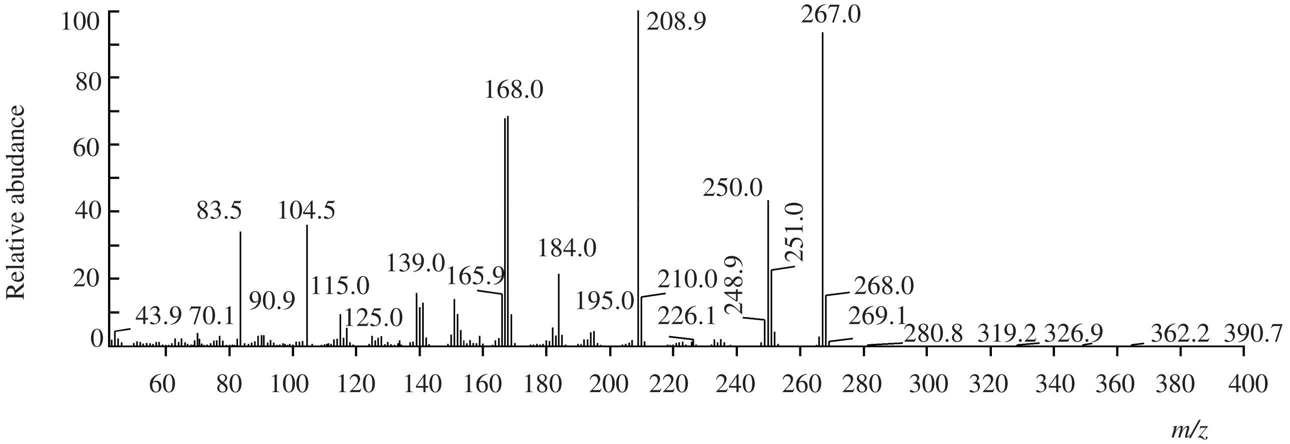


Fig. 1. Mass spectrum of HL.

Table 3. Characteristic IR bands (cm^{-1}) of the ligand and the complexes

Compound	ν(O–H) oxime	ν(NH_2)	ν(C–H) aromatic aliphatic	ν(C=O) acetate	ν(C=N) azomethine	ν(C=N) oxime	ν(N–O)	ν(M–O)	ν(M–N)
HL	3428 s	3340 s 3296 s	3020 w 2920 w	–	1625 vs	1598 s	1020 m	–	–
I	–	3290 s 3261 s	3040 w 2920 w	1700 m	1610 vs	1591 s	1010 m	540 w	444 w
II	–	3321 s 3276 s	3020 w 2890 w	1699 w	1605 vs	1593 s	1090 m	503 w	474 w

Biological Screening

A total of 10 microbial species including 6 bacteria, 3 molds and 1 yeast were used as test organisms in this study. These microorganisms *Staphylococcus aureus* ATCC 6538, *Enterococcus fecalis* ATCC 29212, *Escherichia coli* ATCC 25922, *Salmonella typhimurium* ATCC 14028, *Aspergillus niger* ATCC 10949, were obtained from American Type Culture Collection. *Bacillus subtilis* NRRL –B-209, *Bacillus cereus* NRRRL B-3711, *Candida albicans* NRRL Y–12983, *Aspergillus flavus* NRRL 1957, *A. parasiticus* NRRL 465 were also obtained from USDA, Agriculture Research Service, Peria, USA. Bacterial and fungal cultures of test organisms were maintained on Nutrient Agar and Malt Extract Agar slants at 4°C, respectively, and were sub cultured in Petri dishes prior to use.

The ligand and its metal complexes were tested for their antimicrobial activity against six species of bacteria, and four fungal species using agar well diffusion method. Each compound (100 μl) were poured into the wells and the diameters of inhibition zones (mm) were measured at the end of an incubation period of 24 hours at 37°C for bacteria, and 4 days at 28°C for fungi [19]. Discs saturated with DMSO are used as solvent control. Tetracycline 30 μg/disc and Kanamycine 30 μg/disc were used as reference substance for bacteria.

RESULTS AND DISCUSSION

FT–IR Measurements

The tentative assignment of the most characteristic IR bands were observed and given in Table 3. The broad medium intensity band appearing at ~3400 cm^{-1} is assigned to the characteristic OH_{oxime} absorption for the HL ligand. The bands at 3340 and 3296 cm^{-1} may be assigned to ν(N–H) stretching vibrations of NH_2 group of HL ligand. The relatively weak bands at 3020 and 2920 cm^{-1} are due to the aromatic and aliphatic ν(C–H) vibrations respectively. The absorption bands corresponding to azomethine $\nu(C{=}N)_{azomet}$ and $\nu(C{=}N)_{oxime}$ group is distinct and appears at 1625 and 1598 cm^{-1} of HL ligand. The broad medium intensity band in the region of 1020 cm^{-1} is due to the (N–O) stretching vibrations.

The absorption bands at 3290–3261cm^{-1} and 3321–3276 cm^{-1} are attributed to ν(NH_2) vibrations of complex **I** and **II** respectively. The weak absorption bands at 3040 and 2920 cm^{-1} and 3020 and 2890 cm^{-1} indicate the aromatic and aliphatic ν(C–H) vibrations of **I** and **II** complexes respectively. The bands at 1610 and 1605 cm^{-1} may be assigned to $\nu(C{=}N)_{azomet}$ and 1591 and 1593 cm^{-1} stretching vibrations to $\nu(C{=}N)_{oxime}$

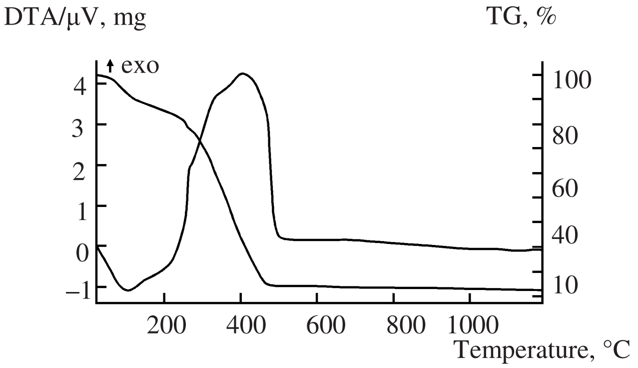


Fig. 2. Thermo gravimetric spectrum for the $Co(HL)(L)(Ac)_2]\cdot 4H_2O$ (**I**).

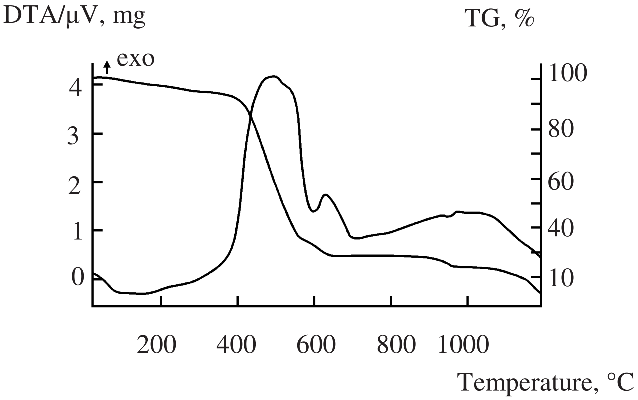


Fig. 3. Thermo gravimetric spectrum for the $Ni_2(L)_2(Ac)]·4H_2O$ (**II**).

for **I** and **II**. When the spectra of the complexes are compared with those of the uncomplexed imine-amine-oxime ligand, the ν(C=N) band are shifted to lower frequency [20,21]. This indicates that the imine nitrogen is coordinated to the metal ion which leads to new absorption bands for ν(M–N) [22, 23]. The acetate groups as coordinated groups to metal ions show carbonyl absorption peaks at the region of 1700 cm^{-1} and which also leads new ν(M–O) bands [20]. The weak bands in the region of 540–503 cm^{-1} are due to the M–O, and 444–474 cm^{-1} are due to the M–N stretching vibrations for the complexes **I** and **II** respectively. In addition, complex **1** exhibits medium band at 1010 cm^{-1}, complex **II** exhibits medium band at 1090 cm^{-1} corresponding to ν(N-O) vibrations. The ν(N–O) vibration for **II** (1090 cm^{-1}) is shifted upper frequency compared with HL (1020 cm^{-1}) [24] indicating that oxime group coordinated to Ni(II) via oxygen atom to give tetrahedral geometry as indicated in [25].

^1H NMR and ^{13}C NMR Spectral Measurements

In order to understand the solution structure of the novel HL ligand ^1H NMR and ^{13}C NMR spectra have been employed. The ^1H NMR assignments are listed in Table 4 and the spectral data for HL are as expected (Scheme 1). The ^1H signals were assigned on the basis of chemical shifts, multiplicities and coupling constants. The two CH_3 protons of HL are easily distinguishable, and they are observed at 2.2 and 2.1 ppm as singlets. In addition, all aromatic protons of HL are also distinguishable and their peaks are between 7.58–6.64 ppm as doublets, in which those have three bond-coupling constants, ~ca. 8.40 Hz. Furthermore, the singlet at 5.2 ppm and 12.05 ppm in the ligand HL are attributed to NH_2 and OH protons respectively.

The ^{13}C NMR spectrum of HL has showed a series of resonance peaks which are in accordance with the

Table 4. The ^1H NMR and ^{13}C NMR spectra of the HL (DMSO-d_6)

^1H NMR spectrum			^{13}C NMR spectrum	
δ, ppm	*J*, Hz	assignment	δ, ppm	assignment
12.05 s, 1H		OH	166.31	C^{15}
7.58 d, 2H	8.44	$CH^{3,7}$	158.07	C^{16}
7.37 d, 2H	8.43	$CH^{4,6}$	150.17	C^{11}
6.79 d, 2H	8.47	$CH^{10,12}$	149.77	C^2
6.64 d, 2H	8.14	$CH^{9,13}$	137.77	C^8
5.2 s, 2H		$NH_2{}^1$	129.06	C^5
2.2 s, 3H		$CH_3{}^{17}$	128.57	$C^{10,12}$
2.1 s, 3H		$CH_3{}^{18}$	127.55	$C^{9,13}$
			121.43	$C^{3,7}$
			116.13	$C^{4,6}$
			17.17	C^{18}
			11.01	C^{17}

Table 5. TG–DTG data of complexes

Comp. no.	Temperature range, °C	DTG_{max}, °C	Weight loss		Assignment
			Found, %	Calculated, %	
I	25–186	98, 113, 145	8.95	9.19	four crystal water molecules
	186–345	214, 255	83.10	83.25	two HL ligands and two acetate anions
			7.95	7.56	metallic cobalt
II	20–145	102, 109, 120, 135	9.46	8.62	four crystal water molecules
	145–386	189, 345	63.62	63.48	two HL ligands
	386–645	415, 448	13.58	14.02	two acetate anions
			13.34	13.88	metallic nickel

number of carbon atoms of the ligand. All of the possible carbon peaks are observed from the ^{13}C NMR spectral data as expected (Scheme 1 and Table 4).

Thermal Analyses

TG–DTG and DTA curves obtained for experiments at 5°C/min under nitrogen atmosphere. In Fig. 2, the first endothermic stage, at 25–186ºC temperature range of **I** (DTG_{max} = 98, 113, 145ºC), corresponds to the loss of the four crystal water molecules (found, %: 8.95, calculated, %: 9.19). The second stage, between 186–345°C, is response to the endothermic decomposition of the two HL ligand and two acetate anions (found, %: 83.10, calculated, %: 83.25; DTG_{max}= 214, 255°C). The final decomposition product is metallic cobalt (found, %: 7.95, calculated, %: 7.56) [26].

In Fig. 3, the first endothermic stage, at 20–145ºC temperature range of **II** (DTG_{max} = 102, 109, 120, 135ºC), also corresponds to the loss of the four crystal water molecules (found, %: 9.46, calculated, %: 8.62). The second stage, between 145–386°C, is response to the endothermic decomposition of the two HL ligand (found, %: 63.62, calculated, %: 63.48; DTG_{max}= 189, 345°C). Following last stage, between 386–645ºC, is related to the decomposition of coordinated acetate anions as an extremely exothermic effect (found, %: 13.58, calculated, %: 14.02; DTG_{max}= 415, 448°C). The final decomposition product is metallic nickel (found, %: 13.34, calculated, %: 13.88) [27].

In addition, the molecular ion peak [267.0 (M^+)] has been observed in mass spectrum as based peak (Table 1 and Fig. 1).

UV–Vis Spectra, Magnetic Moment and Molar Conductivity Measurements

The molar conductance of the complexes of **I** and **II** in 10^{-3} M solutions in DMF lies in the range 6.4 and 4.0 Ω^{-1} cm^2 mol^{-1} (Table 1), consistent with non-electrolytes [28].

Complex **1** shows magnetic moment 0.88 BM at room temperature corresponding to low spin d^6 system for Co(III) which suggest octahedral geometry (Scheme 2 and Table 2). Complex **II** shows magnetic moment 2.86 BM per metal at room temperature corresponding to d^8 system with two unpaired electrons which lies in the range reported for a tetrahedral geometry around Ni(II) ions (Scheme 3 and Table 2) [29].

Table 6. Effect of the ligand and its Co(III) and Ni(II) complexes on the growth of Bacteria and Fungi (zone of inhibition in mm) (well Ø 10mm)[a]

Test microorganisms	Ligand 500μg/well	Co(III) complex 500μg/well	Ni(II) complex 500μg/well	Tetracycline 30μg/disc	Kanamycine 30μg/disc
Gram-positive bacteria					
Bacillus subtilis	–	12±1.2	–	35	25
B. cereus	–	–	–	30	20
Staphylococcus aureus	–	–	20±1.0	30	26
Enterobacter fecalis	–	–	–	15	22
Gram-negative bacteria					
Escherichia coli	–	–	–	28	28
Salmonella typhimirium	–	–	–	20	28
Fungi					
Candida albicans	–	12±1.7	12±1.5	not tested	not tested
Aspergillus niger	–	–	–	not tested	not tested
A. flavus	–	–	–	not tested	not tested
A. fumigatus	–	–	–	not tested	not tested

[a] (–) No zones of inhibition were observed. The tests were carried out in triplicate.

The electronic spectra of the ligand and complexes were recorded in DMF at room temperature. The UV–vis. spectral data of the ligand and complexes are given in Table 2. The aromatic band of the ligand at 271 nm is attributed to benzene rings π–π* transition. The band approach 378 nm is due to the *n*–π* transition of the non-bonding electrons present on the nitrogen of the azomethine groups in the amine-imine-oxime ligand.

The solution state UV–Vis absorption spectrum of the complex **I** shows strong absorptions at 585, 415 and 335 nm. These absorptions correspond to *d*–*d* transitions typical for octahedral low spin cobalt(III) complexes [30]. These transitions are from $^1A_{1g}$ ground state of cobalt(III) to singlet state $^1T_{1g}$ (low energy) and from $^1A_{1g}$ ground state to $^1T_{2g}$ (higher energy). In the complexes of the type CoA_4B_2 (*cis* or *trans*) the $^1T_{1g}$ state split, the splitting in trans isomer being more [31], thus justifying trans geometry with the three absorption peaks in the complex **I**.

The band observed at 601 nm for the complex **II** is in accordance with a tetrahedral configuration and assigned to the $^3T_1 \rightarrow {}^3T_1(P)$ *d*–*d* transition [32].

Biological Activity

The ligand HL and its Co(III) and Ni(II) complexes were screened in vitro for their antibacterial activity against microorganisms. The results of the antibacterial and antifungal activities are summarized in Table 6. Tested microorganisms showed diameters of zone inhibition ranging between 12 and 20 mm. Co(III) complex investigated showed antimicrobial activity against one gram positive bacteria (*Bacillus subtilis).* Ni(II) complex *also* inhibited one gram positive bacteria (*Staphylococcus aureus*) while HL ligand does not present antimicrobial activity against all tested gram positive bacteria. In addition, they were resistant against all gram negative bacteria. The complexes showed activity against only *C. albicans* from fungi.

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