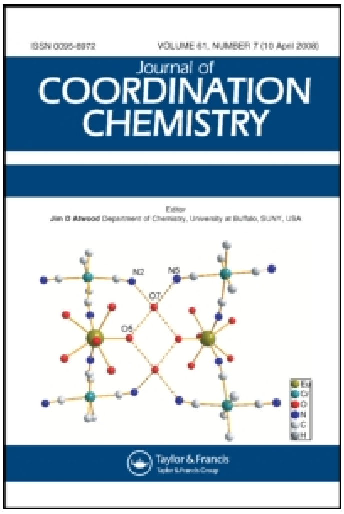

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Synthesis, characterization and biological studies on unsymmetrical Schiff-base complexes of nickel(II), copper(II) and zinc(II) and adducts with 2,2'-dipyridine and 1,10-phenanthroline

A. A. Osowole[a]; G. A. Kolawole[b]; O. E. Fagade[c]
[a] Department of Chemistry, University of Ibadan, Ibadan, Nigeria [b] Department of Chemistry, University of Zululand, Kwadlangezwa, South Africa [c] Department of Botany and Microbiology, University of Ibadan, Ibadan, Nigeria

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Synthesis, characterization and biological studies on unsymmetrical Schiff-base complexes of nickel(II), copper(II) and zinc(II) and adducts with 2,2′-dipyridine and 1,10-phenanthroline

A. A. OSOWOLE†, G. A. KOLAWOLE*‡ and O. E. FAGADE§

†Department of Chemistry, University of Ibadan, Ibadan, Nigeria
‡Department of Chemistry, University of Zululand,
Private Bag X1001, Kwadlangezwa 3886, South Africa
§Department of Botany and Microbiology, University of Ibadan, Ibadan, Nigeria

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A series of metal(II) unsymmetrical Schiff-base complexes, {M($C_{10}H_6$OCH:N$(CH_2)_2$N:C(CH_3)CH:C(CH_3)O), where M=Ni(II), Cu(II) and Zn(II)}, and their 2,2′-dipyridine (bipy) and 1,10-phenanthroline (phen) adducts are synthesized and characterized by microanalysis, magnetic susceptibility, conductance, IR and UV-Vis spectra. The ligand coordinates using the N_2O_2 chromophore to give a two-metal-center four-coordinate square-planar geometry. IR and UV-Vis spectra are consistent with octahedral adducts. The compounds are non-electrolytes in nitromethane and magnetic moments indicate that the complexes are magnetically dilute. The antimicrobial activity of the compounds against ten bacteria and one fungus are reported. The Cu(II) and Zn(II) complexes showed good activity against many of the organisms while their adducts are generally not sensitive. The minimum inhibitory concentrations (MICs) of the sensitive compounds are between 3.0–13.0 mg mL^{-1}.

Keywords: Adducts; Unsymmetrical Schiff base; Antimicrobial; Gentamycin

1. Introduction

Schiff-base complexes of transition metals and adducts have received attention due to their coordination, catalytic and biological activities [1–5]. They, particularly pyrimidinyl Schiff-base chelates of Mn, Co, Ni and Cu, are studied for their probable use as topical anti-infective cream while Co(salen) complexes are used as oxygen carriers [6, 7]. Other Schiff-base complexes of non-cyclopentadienyl semiquinone and aminoacids are of particular interest due to their catalysis and may serve as models for biological studies [8–11]. There are many symmetrical Schiff-base complexes [12–14], and their pyridine, 2,2′-bipyridine and 1,10-phenanthroline adducts [15–17] reported in the literature. Literature is building on complexes of unsymmetrical Schiff bases [18–21]. However, work on Ni(II), Cu(II) and Zn(II) unsymmetrical Schiff-base

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*Corresponding author. Email: gayokola@pan.uzulu.ac.za

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complexes and their 2,2′-bipyridine and 1,10-phenanthroline adducts has not been as widespread [22].

We recently reported [23] metal(II) complexes of an unsymmetrical Schiff base derived from condensation of 2-hydroxy-1-naphthaldehyde and 2,4-pentanedione where the bridging amine was *p*-phenylenediamine and proposed structures where the 1,4-diimino *N* atoms of the Schiff base coordinate to two different metal centers. The work at hand is an extension of this previous work. Here, we report the synthesis, characterization and biological studies on an unsymmetrical Schiff-base ligand (derived from 2-hydroxy-1-naphthaldehyde, ethylenediamine and 2,4-pentanedione), its Ni(II), Cu(II) and Zn(II) complexes, and their 2,2′-bipyridine and 1,10-phenanthroline adducts. The ligand used for this study with the acronym H_2L is shown in equation (1); its metal(II) complexes and adducts are new and are being reported for the first time. The spectral, magnetic and biological properties of these new compounds are also discussed.

2. Experimental

2.1. *Reagents and solvents*

Reagent grade 2,4-pentanedione, 2-hydroxy-1-naphthaldehyde and ethylenediamine were obtained from Aldrich and used as received while nickel(II) acetate tetrahydrate, copper(II) acetate monohydrate and zinc(II) acetate dihydrate were available from BDH chemicals. Solvents were purified by standard methods.

2.2. *Preparation of [$OHC_{10}H_6CH:N(CH_2CH_2)N:C(CH_3)CH:C(CH_3)OH$], H_2L*

The ligand was prepared by modification of a literature method [4]. A mixture of 0.1 mol (6.00 g; 6.70 mL) ethylenediamine, 0.1 mol (17.25 g) of 2-hydroxy-1-naphthaldehyde and 0.1 mol (10.01 g; 10.46 mL) of 2,4-pentanedione in 100 mL of ethanol was refluxed for 2 h. The reaction mixture was cooled in ice and the golden yellow product, which formed, was filtered and washed with ethanol and dried over anhydrous calcium chloride. The yield of the title compound was 17.23 g (50%).

2.3. *Preparation of the metal(II) complexes*

The various complexes were prepared by addition of 5 mmol of $Ni(CH_3COO)_2 \cdot 4H_2O$, (1.24 g); $Cu(CH_3COO)_2 \cdot H_2O$ (1.00 g) or $Zn(CH_3COO)_2 \cdot 2H_2O$ (1.10 g) dissolved in 40% aqueous ethanol to a stirring 5 mmol solution of the ligand (1.48 g) in dried ethanol. The color of the complexes changed in a few minutes. The mixture was refluxed for 2 h and the precipitated solids were filtered, washed with ethanol and dried over anhydrous calcium chloride.

2.4. *Preparation of [$Ni\{OC_{10}H_6CH:N(CH_2CH_2)N:C(CH_3)CH:C(CH_3)O\} \cdot bipy)$], [NiLbipy]*

2,2′-bipyridine (0.78 g, 5 mmol), dissolved in 10 mL of ethanol, was added slowly to a solution of [$Ni\{OC_{10}H_6CH:N(CH_2CH_2)N:C(CH_3)CH:C(CH_3)O\}$] (1.79 g, 5 mmol) suspended in 20 mL of ethanol while stirring. The mixture was refluxed for 2 h and the product formed was filtered, washed with ethanol and dried over anhydrous calcium chloride. A similar procedure was used to prepare the other 2,2′-bipyridine and 1,10-phenanthroline adducts [15–17].

2.5. *Antimicrobial studies*

Laboratory strains of *Escherichia coli*, *Bacillus* sp, *Salmonella typhi*, *Streptococcus faecalis*, *Enterococcus faecalis*; clinical samples of *Klebsilla pneumoniae*, *Staphylococcus aureus*, *Candida albicans* and environmental cultures of *Acinetobacter* sp, *Flavobacterium* sp *and Pseudomonas aeruginosa* were used for screening. Details of the preparation of the agar plates/sample and the procedure for the screening were as previously discussed [23]. All experiments were performed in duplicate and gentamycin was used as a standard drug.

2.6. *Physical measurements*

The elemental analyses for C, H and N were done by Microanalytical Laboratories of the University of Manchester, UK, and the Institute of Organic Chemistry, TuDarmstadt, Germany, while nickel, copper and zinc were determined titrimetrically. The diffuse reflectance spectra were recorded on a Perkin–Elmer λ-20 UV-Visible spectrophotometer. The infrared spectra were measured as KBr discs on a Perkin–Elmer FTIR spectrophotometer in the range 4000–250 cm^{-1} and frequencies are accurate within ±2 cm^{-1}. Magnetic susceptibility was measured on a Johnson Matthey magnetic balance and diamagnetic corrections were calculated using Pascal's constant. Electrolytic conductivities of the soluble compounds in nitromethane were determined using a MC-1, Mark V conductivity meter with a cell constant of 1.0. Single crystal X-ray structural measurements could not be taken on any of the complexes because good crystals were not obtained.

3. Results and discussion

The reactions that led to formation of the metal(II) Schiff-base complexes and their adducts can be represented by equations 1 and 2. The compounds were formed in 20–90% yields.

$$\mathrm{M(CH_3COOH)_2 \cdot \mathit{x}H_2O + H_2L \rightarrow [ML] + 2CH_3COOH + \mathit{x}H_2O} \qquad (1)$$

(where M=Cu(II) $\{x=1\}$, Ni(II) $\{x=4\}$, or Zn(II) $\{x=2\}$)

$$\mathrm{ML + A \rightarrow [MLA]} \qquad (2)$$

(where M=Ni(II), Cu(II), Zn(II); A = 2,2′-bipyridine/1,10-phenanthroline)

The structure of the ligand is provided in figure 1. The formation of this ligand is confirmed by the fact that it crystallized out as yellow solid which analyzes correctly. The alternative formation of an aliphatic Schiff base arising from the condensation of

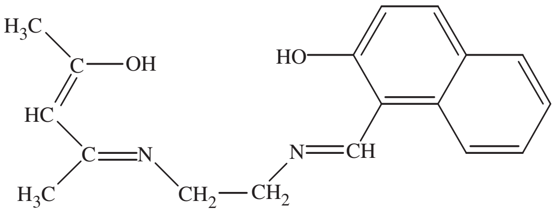

Figure 1. The ligand.

2,4-pentanedione and ethylenediamine is therefore ruled out since this product has been previously reported as straw-colored with a melting point of 111–112°C [24]. Alternatively, the formation of the symmetrical *bis*(2-hydroxynaphthalidene)ethylenediamine and the unsymmetrical analogue could be distinguished from the microanalytical data since they have different molar masses. The microanalyses support the predominant formation of the unsymmetrical Schiff base. The analytical data, colors, percentage yields, melting points/decomposition temperatures and room temperature magnetic moments (μ_{eff}) of the compounds are presented in table 1. These complexes, like those of p-*N*,*N*′-phenylene-*bis*(salicylaldiiminato)metal(II) complexes [23] were non-electrolytes in nitromethane, ($\Lambda\text{m} < 5\,\text{Ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$).

3.1. *Electronic spectra*

The ultraviolet spectra of the compounds are characterized by three to four peaks between 38.45–43.48 and 26.88–34.48 kK, assigned to π–π^* transitions (of various origin) and charge transfer transitions, respectively [25]. The reflectance spectra of the Ni(II) complex, [NiL], showed absorption bands at 18.04 and 23.04 kK assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions of a four-coordinate, square-planar geometry [18]. On the contrary, the adducts, [NiLbipy] and [NiLphen], have three absorption bands in the range 10.00–13.00, 17.24–18.18 and 22.42–23.00 kK, assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) typical of octahedral geometry [26].

Copper(II) complexes are often subjected to Jahn–Teller distortions, resulting in unsymmetrical bands and/or occurrence of additional bands. Up to three transitions can be observed in the visible spectra of copper(II) compounds. The copper(II) complex, $[\text{CuL}]\cdot\text{H}_2\text{O}$, displayed two bands at 18.12 and 24.41 kK assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$ transitions of four-coordinate, square-planar geometry while the adducts [CuLbipy] and [CuLphen] displayed a single prominent unsymmetrical band around 18.10 kK, consistent with a distorted octahedral complex [27]. The high-energy band in the region 26.74–43.48 kK in the zinc(II) complexes are attributed to intraligand π–π^* or charge transfer transitions.

3.2. *Infrared spectra*

The relevant infrared data are presented in table 3. The involvement of the phenoxide O in bonding was confirmed by the disappearance of the ν(OH) band, observed at $3454\,\text{cm}^{-1}$ in the ligand, in the complexes. A new ν(OH) band was, however, observed in

Table 1. Analytical data for the compounds.

Compound (Empirical formula)	Formula weight	Color	Yield %	M.p.dec. T (°C)	Analysis C	Found H	(Cal) N	% Metal	μ_{eff} (B.M.)
H_2L ($C_{18}H_{20}N_2O_2$)	296.41	Yellow	63	183	72.49 (72.94)	6.98 (6.80)	9.05 (9.45)	–	–
[NiL] ($NiC_{18}H_{18}N_2O_2$)	353.10	Orange	56	258–260	61.02 (61.30)	5.32 (5.14)	7.50 (7.93)	16.72 (16.63)	0.49
[NiLbipy] ($NiC_{28}H_{26}N_4O_2$)	509.29	Orange	30	262	66.00 (66.04)	5.05 (5.15)	10.51 (11.00)	11.64 (11.53)	3.1
[NiL(phen)] ($NiC_{30}H_{26}N_4O_2$)	533.29	Orange	20	266–268	67.66 (67.57)	4.49 (4.91)	10.81 (10.51)	11.64 (11.00)	3.2
[CuL] · H_2O ($CuC_{18}H_{20}N_2O_3$)	375.96	Grey	55	180	57.19 (57.51)	4.96 (5.36)	7.88 (7.45)	17.02 (16.90)	2.24
[CuL(bipy)] ($CuC_{28}H_{26}N_4O_2$)	514.11	Green	20	336–338	65.43 (65.41)	5.08 (5.10)	7.51 (7.90)	12.05 (12.36)	2.20
[CuL(phen)] ($CuC_{30}H_{26}N_4O_2$)	538.13	Green	20	328–329	66.97 (66.96)	4.85 (4.87)	10.79 (10.41)	11.79 (11.81)	2.20
[ZnL] ($ZnC_{18}H_{18}N_2O_2$)	359.39	Golden green	90	205	60.73 (60.15)	4.97 (5.05)	7.79 (7.80)	18.22 (18.09)	0
[ZnL(bipy)] ($ZnC_{28}H_{26}N_4O_2$)	515.56	Yellow	76	264–266	65.20 (65.23)	5.05 (5.08)	10.98 (10.87)	12.00 (12.61)	0
[ZnL(phen)] ($ZnC_{30}H_{26}N_4O_2$)	539.58	Yellow	75	308	66.80 (66.78)	5.00 (4.89)	10.91 (10.38)	11.90 (12.05)	0

M.p.dec.T = melting point/decomposition temperature; Calc. = calculated.

Table 2. Electronic spectra for the complexes (kK).

Compound	Absorption region (kK)	Band assignment	Geometry
[NiL]	28.36, 31.68, 32.05	C.T/π–π*	Square-planar
	18.04	$^1A_{1g} \rightarrow {}^1B_{1g}$	
	23.04	$^1A_{1g} \rightarrow {}^1A_{2g}(P)$	
[NiL(bipy)]	29.41, 34.48, 41.70	C.T/π–π*	
	10.00	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	Octahedral
	17.00	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	23.00		
		$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
[NiL(phen)]	29.41, 34.01, 41.70	C.T/π–π*	
	13.00	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	Octahedral
	18.18	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	23.00	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
[CuL] · H_2O	29.06, 32.12, 39.36	C.T/π–π*	
	18.12	$^2B_{1g} \rightarrow {}^2A_{1g}$	Square-planar
	24.41	$^2B_{1g} \rightarrow {}^2E_g$	
[CuL(bipy)]	27.0, 31.25, 38.46	C.T/π–π*	Octahedral
	18.00	d–d	
[CuL(phen)]	26.32, 31.25, 38.45	C.T/π–π*	Octahedral
	18.20	d-d	
[ZnL]	27.66, 31.20, 32.45	C.T/π–π*	Square-planar
[ZnL(phen)]	26.88, 30.30, 34.48, 43.48	C.T/π–π*	Octahedral
[ZnL(bipy)]	26.74, 31.25, 33.33, 41.67	C.T/π–π*	Octahedral

Table 3. Relevant infrared spectral data of the complexes.

Compound	νOH	ν(C=N) + ν(C=C)	νPh/C–O	δC–H	ν(M–N)	ν(M–O)
H_2L	3454s	1638s 1585s 1492s	1403s	996m 941m	–	–
[NiL]	–	1619s 1542s 1457s	1362m 1285m	980m 940m	597s 536s	488s 430s
[NiL(bipy)]	–	1624s 1509s 1454s	1199s 1101s	749vs	531s 503s	497s
[NiL(phen)]	–	1612s 1533s 1460s	1192s 1144s	834vs	595s 531s	495s
[CuL] · H_2O	3500b	1631s 1582s 1458s	1272m 1245m	972m 956m	566s 518s	463s 418s
[CuL(bipy)]	–	1630s 1545s 1460s	1186s 1138s	736 vs	544s 503s	498s
[CuL(phen)]	–	1630s 1542s 1460s	1186s 1143s	828 vs	560s	494s
[ZnL]	–	1630s 1545s 1457s	1300 m 1248 m	976 m	534s	498s 435s
[ZnLbipy]	–	1620s 1545s 1460s	1179s 1144s	749vs	545s	493s
[ZnLphen]	–	1636s 1551s 1460s	1178s 1144s	748vs	558s	494s

Key: b = broad, m = medium, vs = very strong, s = strong.

the complexes at 3500 cm^{-1}, assigned to water in the hydrated complexes. The uncoordinated C=N and C=C stretching vibrations were coupled and observed at 1638–1492 cm^{-1} [15–17]. These bands were shifted to 1607–1458 cm^{-1} upon coordination, thus confirming the involvement of the azomethine *N* in coordination to metal(II). Similarly, upon adduct formation, a further shift of this coupled band was observed at 1606–1440 cm^{-1}. This shift could be attributed to a weakening of the M–N bonds on adduct formation. The very strong bands at 849–734 cm^{-1} in the adducts are attributed to δC–H bands of 2,2′-bipyridine and 1,10-phenanthroline. The bands due to ν(M–O) and ν(M–N) were observed at 488–415 and 595–510 cm^{-1}, respectively.

3.3. *Magnetic susceptibilities*

Generally, square-planar complexes of Ni(II) are diamagnetic while tetrahedral complexes have moments in the range 3.20–4.10 B.M. and octahedral complexes should have moments between 2.90–3.30 B.M. [NiL] gave a moment of 0.49 B.M. and hence is square-planar, although some contamination from tetrahedral species could not be ruled out. The adducts have moments of 3.10 (bipy) and 3.22 B.M. (phen) and consistent with octahedral complexes [28].

A moment of 1.9–2.2 B.M. is usually observed for mononuclear copper(II) complexes, regardless of stereochemistry [28]. The magnetic moments of the copper(II) complexes fall between 2.20–2.24 B.M., expectedly higher than the spin-only moment due to orbital contribution and spin-orbit coupling. The zinc(II) compounds are diamagnetic.

The apparent normal magnetic moments for the four-coordinate complexes could point to possible monomeric complexes, but the low symmetry of the chelating ligand would limit this possibility. Consequently, a dimeric structure (figure 2) is proposed. The obvious distance between the two metal centers, separated by two methylene bridges, is sufficiently large to minimize or obviate any metal-metal interaction, hence the normal magnetic moments.

3.4. *Antimicrobial activity*

The results of the antimicrobial activity of the compounds against various bacteria and a fungus are presented in table 4. All the complexes and the ligand were not effective against all bacteria isolates except [CuL]·H_2O and [ZnL], which were active against eight and six bacteria, respectively. These two complexes, along with [CuLbipy] and [CuLphen], were also active against the only fungus screened. With some of the isolates the activities of [CuL]·H_2O and [ZnL] were comparable to that of gentamycin, but the drug was generally more active.

The minimum inhibitory concentrations (MICs) were determined for the two complexes that gave the highest inhibitory zones and one adduct that was not active with selected organisms. The values were between 3.0–13.0 mg mL^{-1} (table 5). [CuLbipy], with MIC value of 3.0 mg mL^{-1} against *C. albicans*, appears to be the most toxic, while [ZnL] with the highest MIC value of 13.0 mg mL^{-1} appears to be the least toxic. Consequently, toxicity does not appear to contribute to the activity of the two complexes that were most active. Furthermore, the formation of adducts of [CuL′] and [ZnL′] resulted in the complete loss of activity against all the bacteria, but the adducts of [CuL′] showed some activity (inhibitory zones of 11–13 nm) against the fungus. This behavior is at variance with our previous results [23] where the bridging amine was *p*-phenylenediamine. Consequently the nature of the bridging amine may be a factor in the biological activities of the complexes of this class of Schiff bases. This will be explored further in our future work.

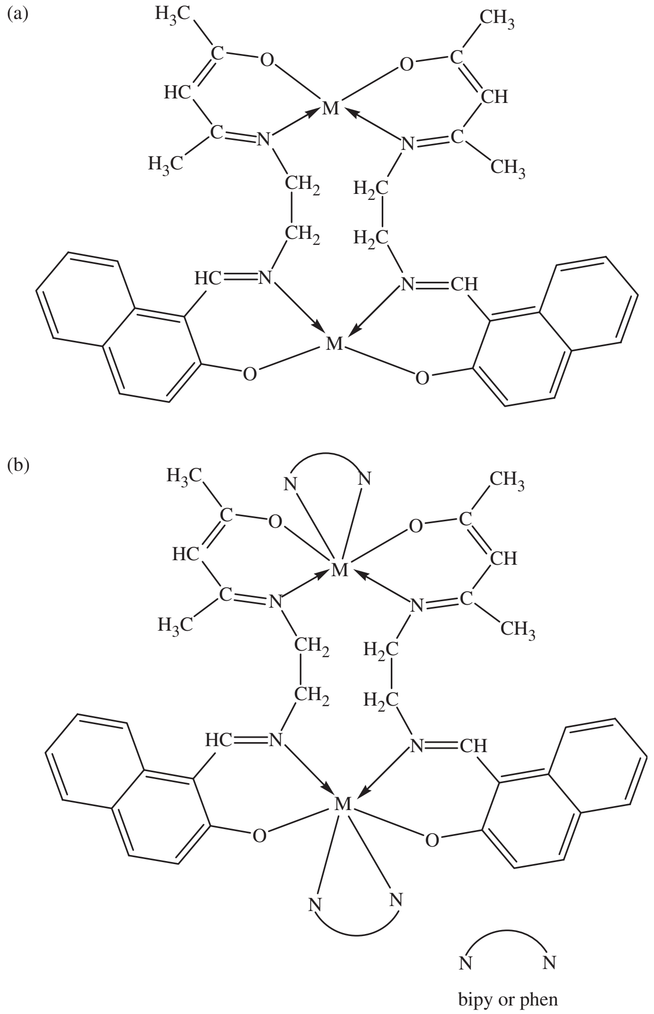

Figure 2. Proposed structures for (a) metal(II) complexes and (b) the adducts.

Table 4. Zones of inhibition in mm of the compounds against various bacterial isolates.

	Zones of inhibition for active compounds				
Organisms	$[CuL] \cdot H_2O$	[CuL(bipy)]	[CuL(phen)]	[ZnL]	Gentamycin[a]
S.aureus	17	R	R	10	15
S. faecalis	13	R	R	R	16
Bacillus sp	17	R	R	11	15
E. coli	15	R	R	R	ND
P. aeruginosa	8	R	R	R	15
S. typhi	R	R	R	R	ND
K. pneumoniae	10	R	R	9	ND
Acinetobacter sp	14	R	R	R	ND
Flavobacterium sp	R	R	R	10	11
E. faecalis	23	R	R	13	ND
C. albicans	12	13	11	10	ND

Key: ND = Not determined; a = positive control; R = Resistant.Methanol was used as negative control and no activity was recorded. The ligand and all the other complexes were not active against all the microbes screened.

Table 5. Minimum inhibitory concentrations (MIC) in mg mL^{-1} for some compounds.

Complexes	Organisms	MIC (mg mL^{-1})
[CuL] · H_2O	*C. albicans*	3
[CuL(bipy)]	*Bacillus* sp.	6
[CuL(phen)]	*S. faecalis*	9
[ZnL]	*Flavobacterium* sp.	13

4. Conclusions

The mixed Schiff-base ligand coordinates to the Ni(II), Cu(II) and Zn(II) ions using the azomethine N and enol O atoms. The assignment of a four-coordinate, square-planar geometry for the metal(II) complexes and six-coordinate octahedral geometry for the 2,2′-bipyridine/1,10-phenanthroline adducts is corroborated by magnetic, infrared and electronic spectral measurements. The Cu(II) and Zn(II) complexes have good activity against most of the organisms used while the ligand, the Ni(II) complex, and the various adducts were generally not sensitive. [CuL] · H_2O and [ZnL] have comparable activity to gentamycin, a broad-spectrum antibiotic, in some isolates.

Square-planar Ni(II) and Cu(II) complexes formed with such a low-symmetry ligand suggest that the four donor atoms of the ligand could not have bonded to one metal center. We have therefore proposed two metal-center complexes, where two ligand molecules bond, bidentate, to each metal center (figure 2), but with the metal centers sufficiently kept apart by the methylene bridges to prohibit metal-metal interaction.

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