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MEDICINAL CHEMISTRY RESEARCH

ORIGINAL RESEARCH

Synthesis, characterization, and antimicrobial activity of some new 2-diazo-benzimidazole derivatives and their Ni(II), Cu(II), and Ag(I) complexes

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Abstract 2-Aminobenzimidazole was diazotized and made to react with active methylene compounds viz: ethylcyanoacetate and malanonitrile. The ligands [**IIIa** and **IIIb**] were isolated, characterized, and then condensed with Ni(II) chloride, Cu(II) chloride, and Ag(I) nitrate. The ligands and complexes were characterized by elemental analysis, IR, ^{1}H NMR, ESR, UV–Visible spectral techniques, and along with thermal studies. The antimicrobial activity of the ligands [**IIIa** ($C_{12}H_{11}N_5O_2$) and **IIIb** ($C_{10}H_6N_6$)] and their metal complexes [**IVa–IVf**] against bacterial strains and fungal strains were investigated. The antimicrobial activity of the above metals and the ligands were discussed.

Keywords 2-Aminobenzimidazole · Dinucleating ligands · Nickel(II), copper(II), silver(I) complexes · Antimicrobial activity

Introduction

Benzimidazole is a heterocyclic aromatic organic compound. It is an important pharmacophore and a privileged structure in medicinal chemistry. The most prominent benzimidazole compound in nature is *N*-ribosyl-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin B_{12} (Barker *et al*., 1960). Various types of benzimidazole ligands have been described in the literature for their chemotherapeutic importance (Boruah and Skibo, 1994; Kubo *et al*., 1993). These compounds have different activities as they can act as bactericides, fungicides, and anticarcinogens (Küçükbay *et al*., 2003; Garuti *et al*., 1999; Gata *et al*., 2003). This ring system is present in numerous antiparasitic, antihelmintic, and anti-inflammatory drugs (El-masry *et al*., 2000). Hunger *et al*. (1960) reported that 1-(dialkyl amino alkyl)benzimidazole ligands, and particularly the 2-amino ligands (Hunger *et al.,* 1961) showed potent analgesic activity. Earlier work has shown that some drugs exhibit increased activity when administered as metal chelates rather than as organic compounds (Mahindru *et al*., 1983). Several metal complexes containing β-diketones, β-ketamines, and other related ligands have been reported by different group of workers (Jayakumar and Natarajan, 1992; Prasanna *et al*., 2001). After the discovery of the chemical nuclease activity of transition metal complexes in the 1980s (Sigman *et al*., 1979; Downey *et al*., 1980), many scientists studied the interaction model and the mechanism of transition metal complexes with DNA and explored the applications of metal complexes in antineoplastic medication, molecular biology, and bioengineering.

In this paper, we report the synthesis, characterization, and antimicrobial activity of some new 2-diazo-benzimidazole derivatives (III) obtained by the diazotization of 2-amino benzimidazole (I). The resulting diazonium salt (II) coupled with active methylene groups (Novinson *et al*., 1976) like ethylcyanoacetate (ECA) and malanonitrile (MN) to yield the compounds **IIIa** and **IIIb**. The ligands [**IIIa** and **IIIb**] were isolated and characterized by

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spectroscopic methods. The ligands were further condensed (Mishra and Jha, 1993) with nickel(II) chloride, copper(II) chloride, and silver(I) nitrate. The complexes were also characterized and screened for antimicrobial activity along with the corresponding ligands.

Experimental

Materials

Reagents viz: 2-amino benzimidazole, ECA, MN, metal chlorides, and metal nitrate were purchased from Across Ltd., and used as such. All the solvents were of analytical grade and were distilled before use.

Measurements

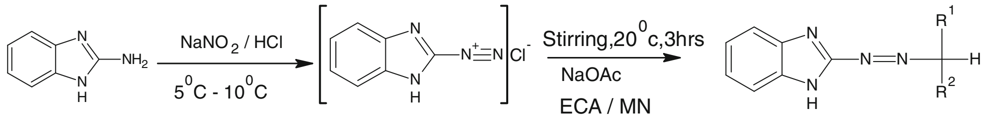
Melting points were determined by open-tube capillary method and are uncorrected. IR spectra were recorded on Thermo Nicolet FTIR spectrophotometer in the 4000–400 cm^{-1} region in KBr pallets at Andhra University, Visakhapatnam. The electronic spectra of the ligands and the complexes were recorded in DMSO solution using a Shimadzu UV-1700 spectrophotometer. ^1H NMR spectra were taken on Perkin Elmer R32, 90 MHz in DMSO-d_6 using TMS as internal reference. ESR spectra were taken on Varion E112 at room temperature and at liquid nitrogen temperature using DPPH as standard at SAIF, IIT Chennai. Thermo gravimetric and differential thermo gravimetric analysis (TG–DTA) were performed in a NETSCH STA under nitrogen atmosphere at SAIF, IIT Chennai. Elemental analysis was carried out at Micro analytical Centre at Andhra University, Visakhapatnam.

Synthesis of dinucleating ligands (**IIIa** and **IIIb**)

2-Amino benzimidazole (I) (0.662 g, 5 mmol) was dissolved in HCl (10 ml) and cooled at 5–10 °C. Cold solution of sodium nitrite (0.7 g, 10 mmol in 10 ml (1 M) of distilled water) was then added dropwise while stirring. After 10–15 min of stirring, ethylcyanoacetate (0.6 ml, 5 mmol) for the preparation of compound **IIIa**, and malanonitrile (0.4 ml, 5 mmol) for the preparation of compound **IIIb** (in separate reactions) were added (Novinson *et al.*, 1976) in the presence of NaOAc [~5 g, 36 mmol in distilled water (10 ml)]. The resulting solution was stirred for 3–4 h at 20 °C and refrigerated overnight. The solid product formed was collected by filtration and crystallized from EtOH. The isolated ligands were characterized by various spectral methods. Ligands described in this study are outlined in Scheme 1 and physical and analytical data is presented in Table 1.

Physical and spectral characteristics of **IIIa** and **IIIb**

IIIa: Ethyl[-*1H*-benzimidazol-2-yldiazenyl](cyano)acetate ($C_{12}H_{11}N_5O_2$): mp 240–242 °C, IR (υ_{max}, KBr cm^{-1}):



I II III

IIIa. $R_1 = CN$, $R_2 = COOC_2H_5$
IIIb. $R_1 = R_2 = CN$

Scheme 1 General procedure for the synthesis of ligands

Table 1 Physical and analytical data of synthesized compounds

Compounds	Color/M.P (°C)[a]	Yield (%)[b]	Found (calc) (%)				
			C	H	N	M	Cl
IIIa [$C_{12}H_{11}N_5O_2$]	Reddish brown/242	85	56.09 (56.03)	4.23 (4.28)	27.27 (27.23)		
IIIb [$C_{10}H_6N_6$]	Light yellow/252	73	57.18 (57.14)	2.81 (2.85)	40.06 (40.00)		
IVa [Ni_2(**IIIa**)$Cl_3(H_2O)_5$]	Brown/>250	70	25.27 (25.22)	3.61 (3.67)	12.31 (12.26)	20.67 (20.56)	18.49 (18.56)
IVb [Cu_2(**IIIa**)$Cl_3(H_2O)_5$]	Brown/>250	60	24.78 (24.80)	3.55 (3.61)	12.08 (12.05)	21.84 (21.91)	18.20 (18.25)
IVc [Ag_2(**IIIa**)$(H_2O)_4$]$2NO_3$	Brown/>250	65	21.32 (21.53)	2.61 (2.84)	14.82 (14.65)	32.40 (32.26)	
IVd [Ni_2(**IIIb**)$Cl_3(H_2O)_5$]	Brown/>250	72	22.87 (22.90)	3.09 (3.05)	16.08 (16.03)	22.55 (22.41)	20.37 (20.24)
IVe [Cu_2(**IIIb**)$Cl_3(H_2O)_5$]	Reddish brown/250	60	22.43 (22.48)	2.97 (2.99)	15.78 (15.74)	23.87 (23.80)	19.90 (19.95)
IVf [Ag_2(**IIIb**)$(H_2O)_4$]$2NO_3$	Brown/>250	60	19.32 (19.29)	2.14 (2.25)	18.04 (18.00)	34.92 (34.70)	

3065 υ (NH), 2310 υ (C≡N), 1628 υ (C=O), 1568 υ (C=N of the ring), 1431 υ (N=N); ^{1}H NMR (DMSO-d$_6$ δ ppm) 8.0 (1H. s. NH), 7.1–7.5 (4H. m. Aromatic H), 3.8 (1H. s. –CH), 3.2 (2H. m. –OCH$_2$), 1.2 (3H. t. –CH$_3$).

IIIb: [-*1H*-Benzoimidazol-2-yldiazenyl]propanedinitrile ($C_{10}H_6N_6$): mp 250–252 °C, IR (υ_{max}, KBr cm^{-1}): 3190 υ (NH), 2226 υ (C≡N), 1574 υ (C=N of the ring), 1423 υ (N=N); ^{1}H NMR (DMSO-d$_6$ δ ppm) 10.2 (1H. s. NH), 7.1–7.5 (4H. m. Aromatic H), 3.2 (1H. s. –CH).

Synthesis of Ni(II), Cu(II), and Ag(I) complexes (**IVa–IVf**)

An ethanolic solution (10 ml) of $NiCl_2 \cdot 6H_2O$ (0.469 g, 2 mmol) for the preparation of complexes **IVa** and **IVd**, $CuCl_2 \cdot 2H_2O$ (0.34 g, 2 mmol) for the preparation of complexes **IVb** and **IVe**, $AgNO_3$ (0.339 g, 2 mmol) for the preparation of complexes **IVc** and **IVf** was added dropwise to the respective ligand [**IIIa** (0.257 g, 1 mmol), **IIIb** (0.210 g, 1 mmol) in separate reactions] solutions in ethanol (10 ml) while stirring followed by the addition of 2–3 drops of triethylamine. The reaction mixture was refluxed for 3–4 h and refrigerated overnight (Mishra and Jha, 1993). The solids thus obtained were filtered and washed successively with ethanol and ether, and dried in vacuum. The physical and analytical data of the isolated complexes are presented in Table 1.

Antimicrobial activity

The in vitro antimicrobial activities of the synthesized dinucleating ligands and their Ni(II), Cu(II), and Ag(I) complexes were studied for their antibacterial and antifungal activities by nutrient agar and potato dextrose agar well diffusion method (Odds, 1989). The synthesized compounds tested against gram positive bacterial strains [*Bacillus subtilis* (*BS*) and *Staphylococcus aureus* (*SA*)], gram negative bacterial strains [*Escherichia coli* (*EC*) and *Klebsiella pneumoniae* (*KP*)], and two fungal strains [*Aspergillus niger* (*AN*) and *Candida albicans* (*CA*)]. 200 ml of nutrient agar growth medium was dispensed into sterile conical flasks, these were then inoculated with 20 µl of cultures, mixed gently, and poured into sterile petri dish. After settling, a 6 mm diameter borer was properly sterilized by flaming and used to make four uniform wells in each petri dish. The wells were loaded with 50 µl of 1 mg/ml different investigated compounds. The solvent DMSO used for reconstituting solvent for diluting the compounds were similarly analyzed for control. Standard antibacterial drug (ampicillin) and antifungal drug (nystatin) were used for comparison under similar conditions. The plates were incubated at 37 °C for 24 h. The above procedure is adopted for fungal assays also, and the medium is potato dextrose agar (instead of nutrient agar), and incubated at 27 °C for 48 h. The zone of inhibition was measured with a Hi-antibiotic zone scale in mm, and the experiment was carried out in duplicate. The results are shown in Table 2.

Results and discussion

The dinucleating ligands (**IIIa** and **IIIb**) form octahedral complexes (**IVa**, **IVb**, **IVd**, and **IVe**) with $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ in ethanol and square-planar complexes (**IVc** and **IVf**) with $AgNO_3$ in ethanol. All the Ni(II), Cu(II), and Ag(I) complexes were stable and non-hygroscopic in nature. The complexes were insoluble in common organic solvents but soluble in DMF and DMSO.

IR spectral studies

The solid-state IR spectra (Sastry *et al.*, 1991; Coucouvanis and Fackler, 1967; Mishra and Jha, 1996) of the free ligands as well as their complexes were recorded in the 4000–400 cm^{-1} region in KBr pallets. The major peaks observed at 3065 cm^{-1} broad, 2310, 1628, 1568, and 1431 cm^{-1} were considered to arise from the υ NH, υ C≡N, υ C=O, υ C=N, and υ N=N, respectively, in the ligand **IIIa**; further peaks observed at 3190, 2226, 1574, and 1423 cm^{-1} were assigned υ NH, υ C≡N, υ C=N, and υ N=N, respectively, in the ligand **IIIb**. The IR spectra of the metal complexes, which showed major peaks at the range 3422–3406 cm^{-1}, were assigned to coordinated υ H_2O molecules. However, peaks observed at the range 1558–1520 cm^{-1} in the spectra of the complexes with all ligands were assigned to coordinated υ C=N vibration of the ring. Further, the υ C≡N observed in the range 2293–2289 cm^{-1} in complexes **IVa** to **IVc**, and

Table 2 Antimicrobial data of the investigated compounds (zone of inhibition in mm) 50 µl of compound from 1 mg/ml

Compounds	EC	KP	BS	SA	AN	CA
IIIa	08.50	09.00	08.00	07.50	08.50	09.00
IIIb	10.75	NA	NA	NA	NA	NA
IVa	12.50	NA	10.75	10.75	9.75	NA
IVb	14.50	5.75	7.25	9.50	19.50	33.00
IVc	10.50	8.15	6.80	7.45	10.00	NA
IVd	12.50	13.00	10.50	14.75	10.75	23.00
IVe	6.25	9.50	NA	10.50	18.25	20.00
IVf	7.25	8.45	NA	9.45	NA	14.25
DMSO	NA	NA	NA	NA	NA	NA
Ampicillin	31.25	NA	29.50	30.50	–	–
Nystatin	–	–	–	–	25	36

EC Escherichia coli, *KP Klebsiella pneumoniae*, *BS Bacillus subtilis*, *SA Staphylococcus aureus*, *AN Aspergillus niger*, *CA Candida albicans*, *NA* not active

2212–2203 cm^{-1} in the complexes **IVd** to **IVf** indicated lowering in wave numbers upon coordination with metal ions. The lowering of C$\equiv$N, N=N, and C=N of the ring upon complexation could be understood in view of the participation of their π electrons in coordination with metal ions (Nakamoto, 1986). Ag(I) complexes show strong bands at 1383 cm^{-1} supporting the presence of uncoordinated nitrate ions (Tavman *et al*., 2009). The bands at 560–450 cm^{-1} were assigned to υ M–N, υ M–O, and υ M–Cl bonds.

^{1}H NMR spectral study of ligands **IIIa** and **IIIb**

The ^{1}H NMR spectra of ligands **IIIa** and **IIIb** which were recorded in DMSO-d_6 showed the following signals: the NH proton signal exhibited at 8.0 ppm (**IIIa**) and 10.2 ppm (**IIIb**). The signals at the region 7.1–7.5 ppm (**IIIa**) and 7.1–7.5 ppm (**IIIb**) were due to aromatic protons. A characteristic proton signal at 3.8 ppm (**IIIa**) and 3.2 ppm (**IIIb**) was assigned to –CH–N=N proton. In addition to this, the ethyl group attached to acetate ion exhibited signals 3.2 ppm to –CH$_2$ and 1.2 ppm to –CH$_3$ group in the ligand **IIIa**. The poor solubility and paramagnetic nature of the metal complexes restricted us from recording their NMR spectra.

Electronic spectral studies

The electronic spectral data of ligands and complexes recorded in DMSO and shown in Table 3, were found to be very similar to those reported earlier for octahedral Ni(II) and Cu(II) complexes (Mishra and Pandey, 1991), and square-planar Ag(I) complexes. In UV spectra, the bands observed $\sim$700(14285 cm^{-1})–630(15873 cm^{-1}) nm in the electronic spectra of Cu(II) complexes have been identified as d–d transition. In these complexes, the bands observed at $\sim$480(20833 cm^{-1})–400(25000 cm^{-1}) nm could be assigned to charge transfer absorption (Wasson *et al*., 1968). The bands observed at higher energy region $\sim$300(33333 cm^{-1}) nm in the electronic spectra of free ligands and metal complexes were found to be very similar and assigned to an intra-ligand transition; Ni(II) complexes showed d–d bands in the regions $\sim$410(24390 cm^{-1})–450(22222 cm^{-1}) nm, $\sim$570(17543 cm^{-1})–590(16949 cm^{-1}) nm, and $\sim$1020 (9803 cm^{-1})–1040(9615 cm^{-1}) nm (Mishra and Jha, 1994). These were assigned to the spin-allowed transitions $^3A_{2g}$ (F) → $^3T_{1g}$ (p)($\surd_3$), $^3A_{2g}$ (F) → $^3T_{1g}$ (F)($\surd_2$), and $^3A_{2g}$ (F) → $^3T_{2g}$ (F)($\surd_1$), respectively, and their well-defined octahedral configuration. The $\surd_2/\surd_1$ ratio $\sim$1.77 lies well within the limit reported for hexa coordinate geometry of the Ni(II) complexes. The spectra of Ag(I) complexes (Yohannes *et al*., 1995) of **IIIa** and **IIIb** showed broad absorption band around 485(20618 cm^{-1}) and 470(21276 cm^{-1}), respectively, and another narrow absorption band around 415(24096 cm^{-1}) and 410(24390 cm^{-1}), respectively. The absorption bands in the Ag (I) complexes are most probably associated with the π–π* electronic transition in the coordinated ligand molecules.

ESR studies

The ESR parameters for the Cu(II) complexes of all ligands at room temperature (RT) as well as liquid nitrogen temperature (LNT) are given in Table 3. The ESR spectra of IVb and IVe at liquid nitrogen temperature are shown in Figs. 1 and 2, respectively. The powder-state spectra of the complex [Cu$_2$ (**IIIa**) Cl$_3$ (H$_2$O)$_5$] at RT and LNT showed four equally spaced lines as expected for Cu(II) ion showing $g_{\|} > g_{\perp}$ which becomes clear in LNT spectra. The values were supportive of octahedral geometry around metal (Mishra *et al*., 1997). Basic spectral characteristics at both temperatures are similar with slightly better resolution (Kumar *et al*., 2001) at LNT. The half-field signal was not observed in any of these spectra indicating that there was no Cu–Cu interaction between the complexes within the molecule; hence it was supportive of di-nuclear complexes. Further, the ^{14}N super hyper fine splitting showing five signals separated at 8G could easily be seen in the spectra

Table 3 UV–Visible and ESR spectroscopic data

S. no	Compounds	UV–Visible spectral data λ_{max} (nm)	ESR spectral data at room temperature (RT) solid			ESR spectral data at liquid nitrogen temperature (LNT)		
			$g_{\|}$	$g_{\perp}$	$A_{\|}$	$g_{\|}$	$g_{\perp}$	$A_{\|}$
1.	**IIIa**	240, 325, 410	–	–	–	–	–	–
2.	**IVa**	300, 410, 480, 500, 620, 825, 970, 1020	–	–	–	–	–	–
3.	**IVb**	410, 515, 630	2.302	2.033	160	2.342	2.023	165
4.	**IVc**	240, 300, 415, 485	–	–	–	–	–	–
5.	**IIIb**	250, 345, 465	–	–	–	–	–	–
6.	**IVd**	400, 450, 570, 630, 650, 1040	–	–	–	–	–	–
7.	**IVe**	450, 480, 590, 630, 700	2.231	2.110	165	2.302	2.116	165
8.	**IVf**	240, 300, 410, 470	–	–	–	–	–	–

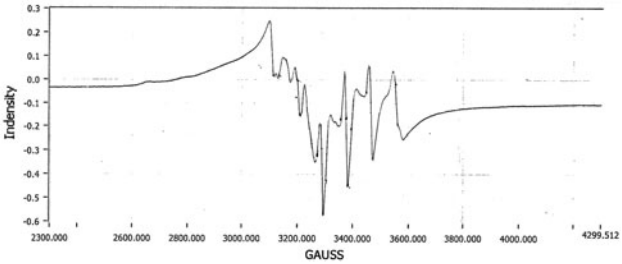


Fig. 1 ESR spectra of **IVb**

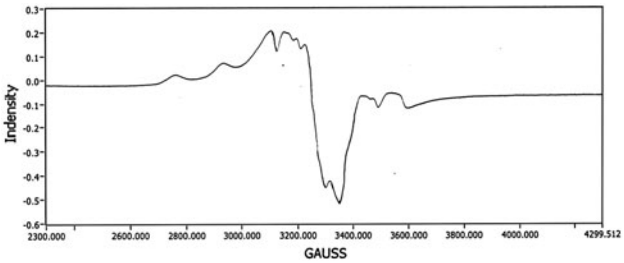


Fig. 2 ESR spectra of **IVe**

of the complexes in solution state at both the temperatures. At LNT this splitting was better resolved showing two nitrogens around Cu(II) ions. However, the difference between two coordination environments O & O in **IIIa**, N & N in **IIIb** could not be identified at this stage.

Thermal analysis

The thermal properties of the prepared complex IVb was examined by TG–DTA. The copper complex (**IVb**) with ligand was heated up to 1400 °C in a nitrogen atmosphere. The TG–DTA results were in good agreement with the formula suggested from the analytical data. The decomposition of the complex proceeded with an endothermic peak at 131.7 °C. At this temperature it lost 2 Cl atoms and 2 water molecules (found: 19 %; calc: 18.41 %). In the second stage, the temperature range 222–350 °C lost 3 water molecules (found: 12 %; calc: 11.40 %). A slow decomposition of the ligand was observed. The weight loss of 14 % at the temperature 350–500 °C is attributed to 2 nitrogen molecules (found: 14 %; calc: 13.34 %). Finally at 500–1300 °C, the TGA curve represents the complete decomposition of organic molecule with the formation of stable metal oxide (2CuO) as the final product. Thermograms of **IVb** complex are shown in Fig. 3.

Antimicrobial activity

The synthesized compounds were screened for antimicrobial activity against two gram negative, two gram positive bacterial strains, and two fungal strains. A comparative study of the ligands and their complexes (inhibition zone in mm Table 2 and graphical representation in Fig. 4) indicates that all the complexes exhibited higher antimicrobial activity than the free ligands. Compounds **IVb** and **IVe** exhibited significant activity against fungal strains *AN* and *CA*. Compounds **IVd** and **IVf** exhibited significant activity against fungal strain *CA*. Compounds **IVa**, **IVc**, **IVe**, and **IVf** had no significant activity against bacterial strains. Compounds **IVb** exhibited moderate activity against *EC* and **IVd** against *SA*. The activity of the complexes can be explained on the basis of the Overtone concept (Anjaneyula and Rao, 1986) and the Tweedy chelation theory (Dharamraj *et al*., 2001). According to Overtone concept of cell permeability, the lipid membrane surrounding the cell favors the passage of only lipid-soluble materials, due to which liposolubility is an important factor controlling the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal ion with donor groups. Furthermore, it increases the delocalization of π electrons over the whole chelate ring and enhances the lipophilicity of the complexes. The lipid and polysaccharides are some important constituents of cell walls and membranes, which are preferred for metal ion interaction. In addition to this, the cell wall also contains many amino phosphates, carbonyl, and cysteinyl ligands, which maintain the integrity of the membrane by acting as diffusion barrier and also provides suitable sites for binding. This increased lipophilicity enhances the penetration of the complexes into lipid membranes which leads to blocking of the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins which restricts further growth of the organism. Further, the mode of action of the compound may involve formation of a hydrogen bond through the azomethine (>N=N–C=N) group with the active centre of cell constituents, resulting in interference with normal cell processes. Antimicrobial activity was more intense for the copper and nickel complexes containing chlorine, which may be due to faster diffusion of the metal complexes through the cell membrane (Calinescu *et al*., 2008). The test results presented in Table 2 showed that copper complexes had the strongest effect against both fungal strains.

Conclusion

A new series of ligand complexes of nickel, copper, and silver were synthesized and their octahedral geometry in nickel, copper complexes, square planar in silver

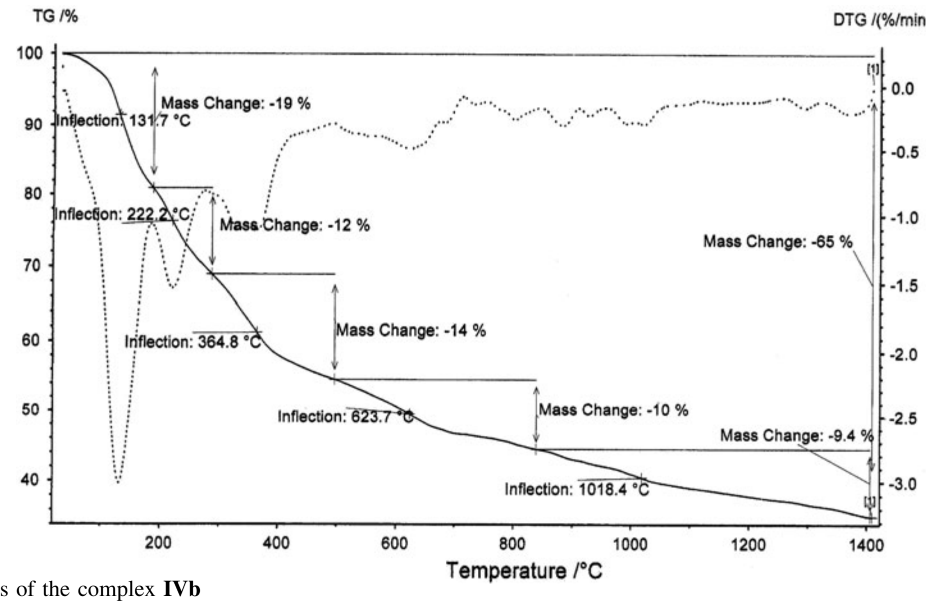


Fig. 3 Thermograms of the complex **IVb**

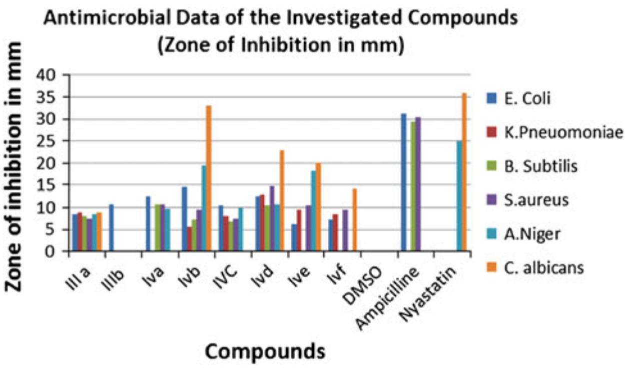


Fig. 4 Antimicrobial activity of investigated compounds

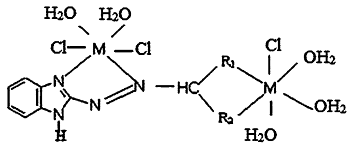


Fig. 5 Tentative structures of Ni(II) and Cu(II) complexes. **IVa** = Ni(II) + **IIIa**; **IVb** = Cu(II) + **IIIa**; **IVd** = Ni(II) + **IIIb**; **IVe** = Cu(II) + **IIIb**

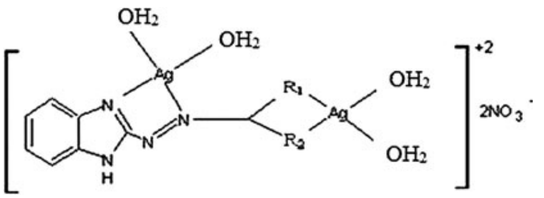


Fig. 6 Tentative structure of Ag(I) complexes. **IVc** = Ag(I) + **IIIa**; **IVf** = Ag(I) + **IIIb**

complexes was observed from their spectral data. A comparative study of the bacterial and fungal growth inhibition values of the ligands and their complexes indicate that complexes exhibit higher antimicrobial activity than the free ligands. Out of all the ligands and metal complexes **IVb**, **IVd**, and **IVe** showed more potent activity against fungal strains than others as expected. In view of the structural formulae of the complexes that exhibit antimicrobial activity, metal moiety plays a significant role in the antimicrobial activity of complexes. Thus, on the basis of above analytical, physical, and spectral data, the tentative structures of complexes are given in Figs. 5 and 6.

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