Turk J Chem
35 (2011) , 393 – 404.

doi:10.3906/kim-1008-860

Synthesis, characterization, and biological activity studies of (E)-N′-((thiophen-2-yl)methylene)benzofuran-2-carbohydrazide and its metal(II) complexes

Madappa B. HALLI*, Vijayalaxmi B. PATIL and Sumathi R. BEVINAMARADA
Department of Chemistry, Gulbarga University, Gulbarga,
585106, Karnataka-INDIA
e-mail: mbhalli@rediffmail.com

Received: 24.08.2010

Metal complexes of the type MLX_2, where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II), and X = Cl and L = TMBC, Schiff base derived from the condensation of benzofuran-2-carbohydrazide with thiophene-2-aldehyde were synthesized. The structure of the complexes was proposed in light of analytical, IR, UV-Vis, ^{1}H-NMR, FAB-MS, ESR spectral data, and magnetic studies. The complexes were soluble in DMF and DMSO. The measured molar conductance values indicated that the complexes were nonelectrolytic in nature. On the basis of these studies, 6 coordinated octahedral polymeric structures were assigned to the Co(II), Ni(II), and Cu(II) complexes, and 4 coordinated tetrahedral geometries to the Zn(II), Cd(II), and Hg(II) complexes. The Schiff base and its metal complexes were tested for antibacterial and antifungal activities by the MIC method. The DNA cleavage activities of all of the complexes were studied by the agarose gel electrophoresis method.

Key Words: Benzofuran, Schiff base, metal complexes, spectral studies, antimicrobial activity, DNA cleavage

Introduction

Metal complexes play an essential role in agricultural, pharmaceutical, and industrial chemistry.[1] Schiff bases have been widely investigated for their antibacterial and antitumor activities.[2–4] The metal complexes of Schiff

*Corresponding author

bases have also received much attention. These complexes play an important role not only in the development of coordination chemistry, but also in catalysis, enzymatic reactions, magnetism, and molecular architectures,[5−7] and they exhibit interesting biological activities.[8−10]

Benzofuran compounds are abundant in nature, particularly among plants. Natural products possessing benzofuran moiety often exhibit useful pharmacological properties. Benzofuran compounds occur in nature in a variety of structural forms. The seed oil of the egonoki plant, which contains a benzofuran derivative called egonal, is an effective synergist for rotenone and pyrethrum against house flies, mosquitoes, aphides, and many other insects.[11] Baker's yeast contains a benzofuran derivative that acts as an antioxidant preventing hemorrhagic liver necrosis in rats and hemolysis of red cells in Vitamin-E deficient rats.[12] Some of the benzofuran derivatives, such as 2-acetylbenzofuran and 2-nitrobenzofuran, are well-known biodynamic agents possessing various pharmacological properties.[13−15] The compound amiodarone hydrochloride, used as an ideal antiarrhythmic drug,[16] contains a 2,3-disubstituted benzofuran moiety.

Thus, the aim of the present work was to synthesize and characterize Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) metal complexes with newly synthesized Schiff base derived from benzofuran-2-carbohydrazide and thiophene-2-aldehyde. The Schiff base and its metal complexes were tested for their antibacterial and antifungal activities. The DNA cleavage activities of all of the complexes were studied by the agarose gel electrophoresis method.

Experimental

All of the chemicals used were of analytical reagent grade (AR) and of the highest purity available. Benzofuran-2-carbohydrazide was synthesized according to the literature procedure.[17] The metal and chloride contents were determined as per Vogel's procedure.[18]

Procedure for synthesis of (E)-N′-((thiophen-2-yl)methylene)benzofuran-2-carbohydrazide (TMBC)

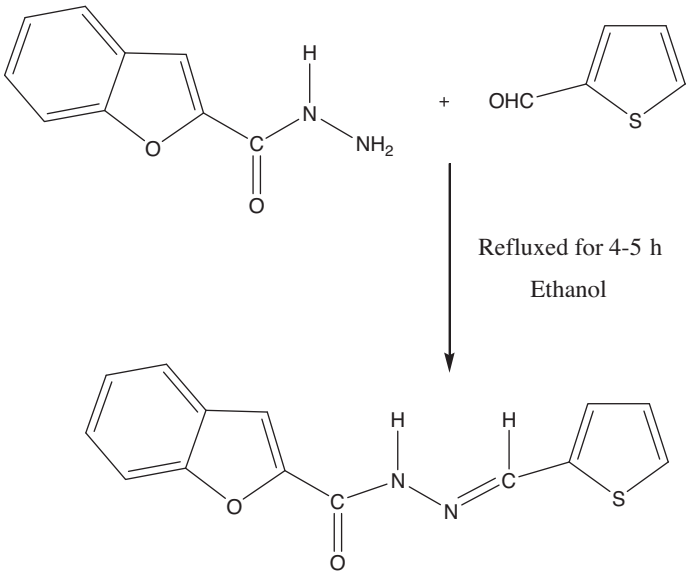
The Schiff base was synthesized by refluxing a mixture of a hot ethanolic solution (30 mL) of benzofuran-2-carbohydrazide (1.76 g, 0.01 mol) and a hot ethanolic solution (20 mL) of thiophene-2-carboxaldehyde (0.9 mL, 0.01 mol) for 4-5 h on a water bath. The light-yellowish crystalline solid that formed during reflux was cooled, filtered, washed with ethanol, and recrystallized from hot ethanol. The synthesis of the Schiff base is shown in the Scheme.

Mol. formula: $C_{14}H_{10}O_2N_2S$ (TMBC); Mol. weight = 270, mp = 218 °C, yield = 75%.

General procedure for synthesis of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes

The metal complexes were synthesized by adding an ethanolic solution (20 mL) of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), or Hg(II) chloride (0.01 mol) to the Schiff base (TMBC) (2.70 g, 0.01 mol) in ethanol (30 mL). The reaction mixture was refluxed on a water bath for 6 h, and on partial removal of the solvent and cooling to

room temperature gave colored, solid complexes that were filtered, washed thoroughly with alcohol, and finally dried over fused $CaCl_2$ in a vacuum (yield: 60%-65%).



Scheme. Synthesis of Schiff base (TMBC).

Physical measurements

Carbon, hydrogen and nitrogen analysis was carried out microanalytically on a PerkinElmer 240C model at the Central Drug Research Institute (CDRI) of Lucknow. The IR spectra of the Schiff base and its Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes were recorded in KBr pellets in the region of 4000-350 cm^{-1} on a PerkinElmer 783 FT-IR spectrophotometer. The electronic spectra of the Co(II), Ni(II), and Cu(II) complexes were recorded on an ELICO SL-164 double beam UV-visible spectrophotometer in the range of 200-1100 nm in DMF (10^{-3} M) solution. The ^{1}H-NMR spectra were recorded in DMSO-d_6 on a Bruker 300 MHz spectrophotometer using TMS as an internal standard. The ESR spectrum of the Cu(II) complex in the polycrystalline state was recorded on a Varian-E-4X band EPR spectrophotometer using TCNE as the 'g' marker (g = 2.00277) at room temperature. The FAB mass spectra were recorded on a JEOL 600H/TSS2000 mass spectrometer using argon (2 kVA as FAB gas). Meta-nitro benzyl alcohol (NBA) was used as the matrix. Molar conductivity measurements were recorded on an ELICO CM-180 conductivity bridge in DMF solution (10^{-3} M) using a dip-type conductivity cell fitted with a platinum electrode, and the magnetic susceptibility measurements were made at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant.

Antibacterial and antifungal assays

The biological activities of the synthesized Schiff base and its Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes were studied for antibacterial and antifungal properties by the agar diffusion method respectively in DMSO solvent against *Escherichia coli*, *Staphylococcus aureus*, and *Salmonella typhi* bacteria and *Aspergillus niger*, *Aspergillus flavus*, and *Cladosporium* spp. fungi.[19,20] The stock solution of the test compound was

prepared by dissolving 10 mg of the test compound in 10 mL of DMSO solvent. The stock solution was suitably diluted with sterilized distilled water to concentrations of 100, 75, 50, 25, and 12.5 μg/mL. The control for each dilution was prepared by diluting 10 mL of solvent instead of stock solution with sterilized distilled water.

The bacteria were subcultured in agar medium. The petri dishes were incubated for 24 h at 37 °C. A standard antibacterial drug, gentamycine, was also screened under similar conditions for comparison. The fungi were subcultured in potato dextrose agar medium. A standard antifungal drug, fluconazole, was used for comparison. The petri dishes were incubated for 48 h at 37 °C. Activity was determined by measuring the diameter of the zone showing complete inhibition.

DNA cleavage experiment

Preparation of culture media

DNA cleavage experiments were done according to the literature.[21] Nutrient broth (10 g/L of peptone, 5 g/L of yeast extract, and 10 g/L of NaCl) was used for the culturing of *Staphylococcus aureus*. After 50 mL of medium was prepared, it was autoclaved for 15 min at 121 °C under 15 lb of pressure. The autoclaved medium was inoculated with the seed culture and incubated at 37 °C for 24 h.

Isolation of DNA

The fresh bacterial culture (1.5 mL) was centrifuged to obtain the pellet, which was then dissolved in 0.5 mL of lysis buffer (100 mM Tris, pH 8.0; 50 mM EDTA; 50 mM lysozyme). To this, 0.5 mL of saturated phenol was added and incubated at 55 °C for 10 min. It was then centrifuged at 10,000 rpm for 10 min, and to the supernatant, an equal volume of chloroform and isoamyl alcohol (24:1) and a one-twentieth volume of 3 M sodium acetate (pH 4.8) was added. This was then centrifuged at 10,000 rpm for 10 min and, to the supernatant, 3 volumes of chilled absolute alcohol were added. The precipitated DNA was separated by centrifugation, and the pellet was dried and dissolved in Tris buffer (10 mM Tris, pH 8.0) and stored in cold conditions.

Agarose gel electrophoresis

Cleavage products were analyzed by the agarose gel electrophoresis method.[21] Test samples (1 mg/mL) were prepared in DMSO. The samples (25 μg) were added to the isolated DNA of *S. aureus*. The samples were incubated for 2 h at 37 °C, and then 20 μL of DNA sample (mixed with bromophenol blue dye at a 1:1 ratio) was loaded carefully into the electrophoresis chamber wells along with a standard DNA marker containing TAE buffer (4.84 g Tris base, pH 8.0; 0.5 M EDTA/1 L) and finally loaded onto the agarose gel, passing the constant 50 V of electricity for about 30 min. The gel was removed and stained with 10 μg/mL of ethidium bromide for 10-15 min, and the bands observed and photographed under the UV transilluminator were used to determine the extent of DNA cleavage. The results were then compared with a standard DNA marker.

Results and discussion

The analytical data showed that all of the complexes had 1:1 stoichiometry (Table 1). The molar conductance values were too low to account for any dissociation of the complexes in DMF, indicating the nonelectrolytic nature of the complexes.[22] All of the complexes were light in color, stable, and nonhygroscopic in nature, and possessed high melting points. The complexes were insoluble in common organic solvents but soluble in DMF and DMSO.

IR spectral studies

The prominent infrared spectral data of the Schiff base and its Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes are presented in Table 2.

The IR bands give valuable information regarding the bonding modes of ligand to metal ions in the complexes. The IR spectrum of the free ligand was compared with the spectra of the metal complexes. The IR spectrum of the Schiff base showed a strong band at 3205 cm^{-1} assigned to the ν (NH) stretch of the CONH group. The shifting of this band to a higher wave number side in the complexes by 7-16 cm^{-1} indicated the noninvolvement of the 'N' of the CONH group in bonding.[23] The strong band observed at 1643 cm^{-1} in the free ligand was assigned to the ν (C=O) stretch of the CONH group.[24] This band shifted to a lower wave number side in all of the complexes by about 23-52 cm^{-1}, indicating the participation of the carbonyl oxygen in coordination.[25] A medium-to-strong intensity band at 1597 cm^{-1} in the free ligand was assigned to the ν (C=N) stretch of the azomethine group based on earlier reports.[26] This band shifted to a lower wave number side in all of the complexes by about 21-46 cm^{-1}, suggesting the participation of azomethine nitrogen in bonding with metal ions.[27] The medium intensity band at 958 cm^{-1} was assigned to the ν (N-N) stretching vibration of hydrazine residue. This band in the complexes shifted slightly to a higher wave number side, confirming the involvement of one of the nitrogens of -N-N- in bonding with the metal ions. Many researchers[28,29] have reported ν (C-O-C) stretching vibrations of furan in the region of 1020-1250 cm^{-1}. In the present case, the ν (C-O-C) stretch was observed at 1226 cm^{-1}, remaining unaltered in the metal complexes and indicating nonparticipation of the furan ring's oxygen atom in the bonding with metal ions.

Metal-ligand vibrations are generally observed in the far-IR region and usually give valuable information regarding the bonding of the ligand to the metal ions. The weak intensity nonligand bands observed in the complexes in the regions of 542-521 cm^{-1} and 468-442 cm^{-1} were assigned to ν (M-O) and ν (M-N) stretching vibrations, respectively.[30] For polymeric complexes in which both terminal and bridging metal-halogen linkages are present, the ν (M-Cl) stretch for the terminal halide is observed at a higher wave number side than that for the bridging halide.[31,32] In the present study, we assigned the broad and weak intensity nonligand bands to the ν (M-Cl) stretch for the terminal halide in the region of 386-442 cm^{-1} and the ν (M-Cl) stretch for bridging in the region of 354-380 cm^{-1} in the case of the Co(II), Ni(II), and Cu(II) complexes, in support of their chloride-bridged polymeric structures. Medium intensity bands in the region of 372-404 cm^{-1} were assigned to the ν (M-Cl) stretch in the Zn(II), Cd(II), and Hg(II) complexes.

Table 1. Elemental analysis, molar conductance, and magnetic susceptibility data for Schiff base (TMBC) and its metal complexes.

Molecular formula of Schiff base/complexes	Mol. weight	Mp (°C)	C%		H%		N%		M%		Cl%		Λ_M^*	μ_{eff} (BM)
			found	calcd	found	calcd	found	calcd	found	calcd	found	calcd		
$C_{14}H_{10}O_2N_2S$ (TMBC)	270	218	62.09	62.21	3.56	3.73	10.11	10.36	-	-	-	-	-	-
$[Co(TMBC)Cl_2]_n$	400.16	>300	41.87	42.02	2.21	2.52	6.76	7.00	14.54	14.73	17.58	17.72	12	4.82
$[Ni(TMBC)Cl_2]_n$	399.91	>300	41.68	42.05	2.23	2.52	6.78	7.00	14.42	14.68	17.56	17.73	20	2.88
$[Cu(TMBC)Cl_2]_n$	404.76	>300	41.23	41.54	2.18	2.49	6.64	6.92	15.48	15.70	17.23	17.52	23	1.66
$[Zn(TMBC)Cl_2]$	406.60	278	41.12	41.35	2.16	2.48	6.53	6.89	15.82	16.08	17.16	17.44	14	-
$[Cd(TMBC)Cl_2]$	453.62	286	36.82	37.07	2.09	2.22	5.92	6.18	24.36	24.78	15.35	15.63	13	-
$[Hg(TMBC)Cl_2]$	541.80	290	30.78	31.04	1.62	1.86	4.94	5.17	36.76	37.02	12.89	13.09	16	-

*Molar conductance values in $ohm^{-1}\,cm^2\,mol^{-1}$.

Table 2. Important infrared frequencies (in cm^{-1}) of Schiff base and its metal complexes.

Compound	ν (NH)	ν (C O)	ν (C N)	ν (N-N)	ν (M-O)	ν (M-N)	ν (M-Cl)t	ν (M-Cl)b	ν (M-Cl)
$C_{14}H_{10}O_2N_2S$ (TMBC)	3205	1643	1597	958	-	-	-	-	-
$[Co(TMBC)Cl_2]_n$	3218	1606	1568	965	534	454	398	365	-
$[Ni(TMBC)Cl_2]_n$	3215	1594	1576	968	523	442	386	354	-
$[Cu(TMBC)Cl_2]_n$	3212	1611	1562	964	542	463	442	380	-
$[Zn(TMBC)Cl_2]$	3221	1591	1551	966	526	468	-	-	404
$[Cd(TMBC)Cl_2]$	3219	1598	1574	962	521	459	-	-	372
$[Hg(TMBC)Cl_2]$	3216	1620	1559	969	539	448	-	-	394

^{1}H-NMR spectral studies

^{1}H-NMR spectra of the Schiff base and its Zn(II) and Cd(II) complexes were recorded in DMSO-d_6. The signal at δ (12.10) (s, 1H) was assigned to the amide proton (-CONH-) and the signal at δ (8.41) (s, 1H) was assigned to the azomethine proton (-N=CH-) of the Schiff base (TMBC). The signal due to (-CONH-) shifted downfield in the spectra of the Zn(II) and Cd(II) complexes in the region of δ (12.36, 12.42) (s, 1H), indicating the coordination of the oxygen of –CONH- with metal ions. The azomethine proton shifted downfield in the region of δ (8.65, 8.73) (s, 1H), supporting the coordination of the 'N' of the –N=CH- group with the metal ions. The aromatic protons at δ (7.06-7.82) (m, 8H) shifted downfield in the complexes. Thus, the ^{1}H-NMR spectral observations supported the assigned geometry.

Mass spectral studies

The FAB mass spectrum of the Schiff base (TMBC) showed a molecular ion peak at m/z 271, which is 1 mass unit more than that of the molecular weight of the Schiff base. The FAB mass spectrum of the Ni(II) complex showed a molecular ion peak at m/z 400, which is the same as that of the molecular weight of the complex. This supports the suggested structure for the complex.

Magnetic properties

The magnetic moments obtained at room temperature are listed in Table 1. The magnetic measurements for the Co(II) and Ni(II) complexes showed magnetic moment values of 4.82 and 2.88 BM, respectively, suggesting consistency with their octahedral environment.[33–35] The Cu(II) complex showed the magnetic moment value of 1.66 BM expected for one unpaired electron, which offers the possibility of a distorted octahedral geometry.[36]

Electronic spectral studies

The electronic spectra of the Co(II), Ni(II), and Cu(II) complexes were recorded in freshly prepared DMF solution (10^{-3} M) at room temperature and the spectral data are presented in Table 3. The electronic spectra of the Co(II) complex showed bands at 16,223 and 20,523 cm^{-1}. These 2 bands are assignable to $^4T_{1g}$ (F) $\rightarrow ^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$ (F) $\rightarrow ^4T_{2g}$ (F) (ν_3) transitions, respectively, in an octahedral environment.[37] The lowest band, ν_1, could not be observed due to the limited range of the instrument used, but could be calculated using the band fitting procedure suggested by Underhill and Billing.[38] The Ni(II) complex exhibited 2 absorption bands, at 15,321 and 25,410 cm^{-1}, assignable to $^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$ (P) (ν_3) transitions, respectively, in an octahedral environment. The Cu(II) complex exhibited a single broad asymmetric band in the region of 13,523-17,369 cm^{-1}. The broadness of the band indicated the 3 transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), $^2B_{1g} \rightarrow ^2B_{2g}$ (ν_2), and $^2B_{1g} \rightarrow ^2E_g$ (ν_3), which are similar in energy and give rise to only 1 broad absorption band. The broadness of the band may have been due to dynamic Jahn-Teller distortion. All of these data suggested a distorted octahedral geometry around the Cu(II) ion. The octahedral geometry[39] was further supported by the values of ligand field parameters, such as the Racah interelectronic repulsion parameter (B′), ligand field splitting energy (10 Dq), covalency factor (β), and ligand field stabilization energy (LFSE).[40] The B′ values for the complexes were lower than the free ion values, which is an indication of the orbital overlap

and delocalization of d-orbitals. The β values obtained were less than unity, suggesting a considerable amount of covalency for the metal-ligand bonds. The β value for the Ni(II) complex was less than that of the Co(II) complex, indicating the greater covalency of the M – L bond.[41]

Table 3. Electronic spectral bands and ligand field parameters of the Co(II), Ni(II), and Cu(II) complexes in DMF (10^{-3} M) solution.

Complexes	Transitions in cm^{-1}			Dq (cm^{-1})	B (cm^{-1})	β	β%	ν_2/ν_1	LFSE (kcal)
	ν_1[a]	$\nu_{2(\varepsilon)}$[b]	$\nu_{3(\varepsilon)}$[b]						
$[Co(TMBC)Cl_2]_n$	7543	16,223 (280)	20,523 (460)	868	941	0.969	3.090	2.151	14.880
$[Ni(TMBC)Cl_2]_n$	9460	15,321 (250)	25,410 (560)	946	823	0.791	20.865	1.620	32.434
$[Cu(TMBC)Cl_2]_n$	13,523-17,369 (360)			1545	-	-	-	-	26.486

[a]Calculated values.
[b]Molar extinction coefficient values are given in parentheses in units of L mol^{-1} cm^{-1}.

ESR spectra of Cu(II) complex

The ESR spectra of the Cu(II) complex in a polycrystalline state was recorded at room temperature. The $g_{||}$ and $g_{\perp}$ values were found to be 2.388 and 2.104, respectively. The g_{av} was calculated to be 2.203. The spectra showed asymmetric bands with $g_{||} > g_{\perp} > 2.00277$, indicating that the unpaired electrons lay predominantly in the d_{x2-y2} orbital with possible mixing of d_{z2} because of low symmetry.[42] The axial symmetry parameter 'G' was determined as $G = (g_{||} - 2.00277)/(g_{\perp} - 2.00277) = 3.794$, suggesting considerable interaction in the solid state.[43]

Antibacterial and antifungal activities

The antibacterial and antifungal activities of the synthesized compounds were tested against *Escherichia coli*, *Staphylococcus aureus*, and *Salmonella typhi* bacteria and *Aspergillus niger*, *Aspergillus flavus*, and *Cladosporium* spp. fungi by the MIC method. The MIC values of the compounds against the growth of microorganisms are summarized in Table 4. A comparative study of the ligand and complexes (MIC values) indicated that the complexes exhibited higher antimicrobial activity than the free ligand. Such increased activity of the complexes can be explained on the basis of Overtone's concept[44] and Tweedy's chelation theory.[45] These complexes also disturb the respiration process of the cell and thus block the synthesis of the proteins, restricting the further growth of the organism. Furthermore, the mode of action of the compound may involve the formation of a hydrogen bond through the azomethine group with the active center of the cell, resulting in interference with the normal cell processes. In general, metal complexes are more active than ligands because metal complexes may serve as a vehicle for the activation of ligands as the principle cytotoxic species.[46]

Table 4. Minimum inhibitory concentration, MIC (μg/mL), of all of the compounds.

Compounds	*E. coli*	*S. aureus*	*S. typhi*	*A. flavus*	*A. niger*	*Cladosporium*
TMBC	50	75	50	75	50	50
$[Co(TMBC)Cl_2]_n$	25	50	25	25	12.50	25
$[Ni(TMBC)Cl_2]_n$	12.50	25	25	12.50	25	12.50
$[Cu(TMBC)Cl_2]_n$	12.50	12.50	12.50	12.50	12.50	12.50
$[Zn(TMBC)Cl_2]$	12.50	12.50	12.50	12.50	12.50	12.50
$[Cd(TMBC)Cl_2]$	25	25	25	50	12.50	25
$[Hg(TMBC)Cl_2]$	25	12.50	12.50	25	12.50	25
Gentamycine	12.50	12.50	12.50	-	-	-
Fluconazole	-	-	-	12.50	12.50	12.50

Electrophoretic analysis

The Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes were studied for their DNA cleavage activity by the agarose gel electrophoresis method and are presented in Figure 1. The gel after electrophoresis clearly revealed that the intensity of all of the treated DNA samples diminished, possibly because of the cleavage of the DNA. The complete cleavage of the DNA was observed for Zn(II) (lane S4), and partial cleavage of DNA was observed for the Ni(II) (lane S2) and Hg(II) (lane S6) complexes. A difference was observed in the bands of the complexes (lanes S1-S6) compared to that of the control DNA of *S. aureus*. This indicates that the control DNA alone did not show any apparent cleavage, while the complexes did. However, the nature of the reactive intermediates involved in the DNA cleavage by the complexes is not clear. The results indicated the important role of metal ions in these isolated DNA cleavage reactions. As the compound was observed to cleave the DNA, it can be concluded that the compound inhibits the growth of the pathogenic organism by cleaving the genome.[47]

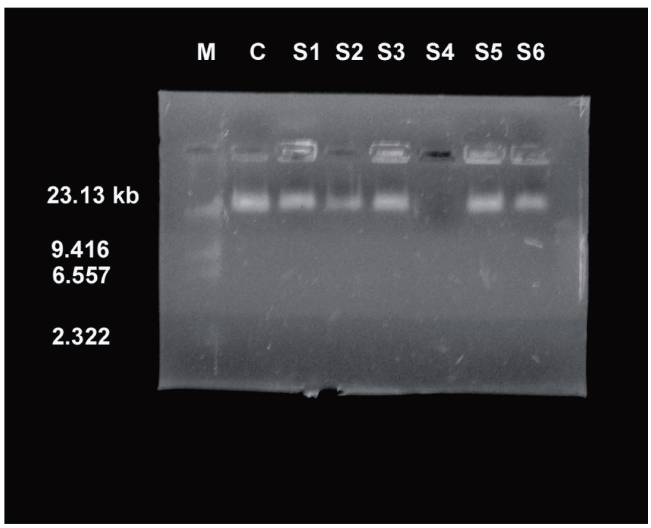
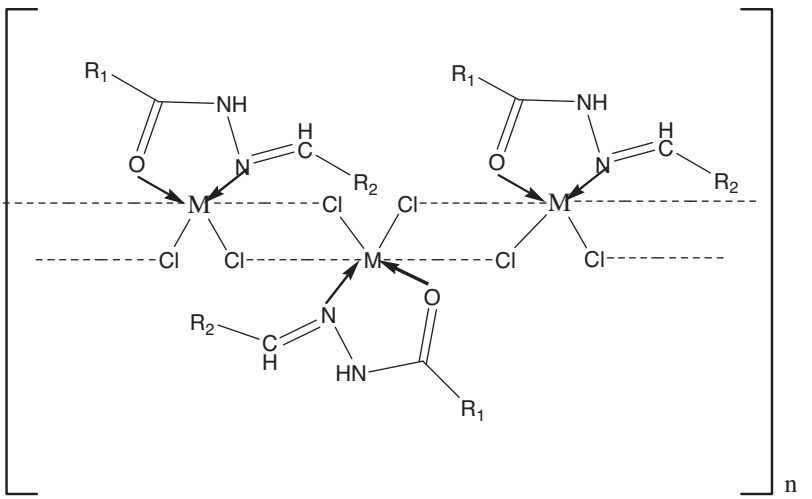


Figure 1. DNA cleavage activity of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) (S1-S6) complexes.

Conclusion

The newly synthesized Schiff base acted as a neutral bidentate ligand. The metal ion was coordinated through the amide oxygen and the nitrogen of the azomethine group. The bonding of ligand to metal ions was confirmed by the analytical data and spectral and magnetic studies. The complexes had higher antibacterial and antifungal activity than the ligand. The DNA cleavage studies revealed that the complete cleavage of DNA was observed for Zn(II) (lane S4), and partial cleavage of DNA was observed for the Ni(II) (lane S2) and Hg(II) (lane S6) complexes. All of these observations together lead us to propose chloride-bridged polymeric octahedral structures for the Co(II), Ni(II), and Cu(II) complexes and tetrahedral structures for the Zn(II), Cd(II), and Hg(II) complexes (Figures 2 and 3).



Where M = Co (II), Ni (II) or Cu (II)

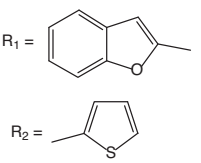
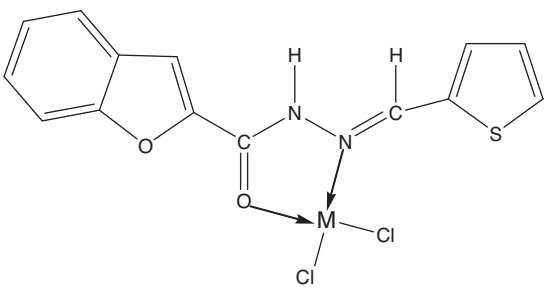


Figure 2. Suggested structure of Co(II), Ni(II), or Cu(II) complexes.



Where M = Zn (II), Cd (II) or Hg (II)

Figure 3. Suggested structure of Zn(II), Cd(II), or Hg(II) complexes.

Acknowledgement

The authors are thankful to the Chairman, Department of Chemistry, Gulbarga University, Gulbarga, for encouragement and facilities. One of the authors (VBP) is thankful to UGC New Delhi for the UGC Research Fellowship for meritorious students under the RFSMS Scheme.

References

1. Kumar, S.; Dhar, D. N.; Saxena, P. N. *J. Scientific and Industrial Research* **2009**, *68*, 181-187.
2. Ugras, H. I.; Basaran, I.; Kilic, T.; Cakir, U. *J. Heterocyclic Chem.* **2006**, *43*, 1679.
3. Chohan, Z. H.; UI-Hassan, M.; Khan, K. M.; Supuran, C. T. *J. Enzyme Inhib. Med. Chem.* **2005**, *20*, 183.
4. Iqbal, A.; Siddiqui, H. L.; Ashraf, C. M.; Bukhari, M. H.; Akram, C. M. *Pharm. Bull.* **2007**, *55*, 1070.
5. Lalehzari, A.; Desper, J.; Levy, C. J. *Inorg. Chem.* **2008**, *47*, 1120.
6. Shit, S.; Sen, S.; Mitra, S.; Hughes, D. L. *Transition Met. Chem.* **2009**, *34*, 269.
7. Xu, B.; Jiang, W.; Zhang, J.; Tang, Y.; Li, J. *Transition Met. Chem.* **2009**, *34*, 293.
8. Bagihalli, G. B.; Avaji, P. G.; Patil, S. A.; Badami, P. S. *Eur. J. Med. Chem.* **2008**, *43*, 2639-2649.
9. Chohan, Z. H.; Arif, M.; Rashid, A. J. *J. Enzyme Inhib. Med. Chem.* **2008**, *23*, 785.
10. Chohan, Z. H.; Arif, M.; Shafiq, Z.; Yaqub, M.; Supuran, C. T. *J. Enzyme Inhib. Med. Chem.* **2006**, *21*, 95.
11. Mastubara, H. *Botyk Kogaku.* **1954**, *19*, 15.
12. Forbes, M.; Zilliikan, F.; Robert. G.; Gyorgy, P. *J. Am. Chem. Soc.* **1985**, *80*, 385.
13. Rahaman, A. H.; Khendel, E. M. *J. Indian. Chem. Soc.* **1981**, *58*, 404.
14. Scherrer, R. A. US Patent 3 37 927, 1975.
15. Kadin, S. B. *J. Med. Chem.* **1972**, *15*, 551.
16. Mason, J. W.; Eng, N. *J. Med. Chem.* **1987**, *31*, 455.
17. Kawas, Y.; Nakayama, M.; Tamatskuri, P. *Bull. Chem. Soc. Japan* **1962**, *35*, 149.
18. Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*, 3rd ed., Longman ELBS, London, 1968.
19. Threlfall, E. J.; Fisher, I. S. T.; Ward, L.; Tschape, H.; Gerner-Smidt, P. *Microb. Drug Resist.* **1999**, *5*, 195-199.
20. Prescott, J. F.; Baggot, J. D.; Walker, R. D. In *Antimicrobial Therapy in Veterinary Medicine*, Iowa State University Press, Ames, Iowa, 2000.
21. Sambrook, J.; Fritsch, E. F.; Maniatis, T. *Molecular Cloning, A Laboratory Manual*, 2nd ed., Cold Spring Harbor Laboratory, Cold Spring Harbor, New York, 1989.
22. Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81-122.
23. Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, 1963.
24. Sutaria, D. H.; Patel, J. R.; Patel, M. N. *J. Indian Chem. Soc.* **1996**, *73*, 309.
25. Rao, C. N. R.; Venkatraghavan, R. *Spectrochim. Acta* **1962**, *18*, 541.
26. Reddy, H. H.; Reddy, P. S. *J. Indian Chem. Soc.* **2002**, *79*, 132.

27. Yang, Z. Y. *Synth. React. Inorg. Met.-Org. Chem.* **2002**, *32*, 903.
28. Singh, B.; Shahi, P.; Singh, P. K., *Indian J. Chem.* **1996**, *35A*, 494.
29. Ahuja, I. S.; Singh, R. *J. Indian Chem. Soc.* **2001**, *78*, 39.
30. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., John Wiley and Sons, New York, 1986.
31. Hiremath, A. C.; Reddy, K. M.; Patel, K. M.; Halli, M. B. *Proc. Natl. Acad. Sci. India* **1993**, *63A*, 341.
32. Satyanarayana, D. N. *Vibrational Spectroscopy*, New Age International Pub., New Delhi, 2004, 406-408.
33. Figgis, B. N.; Lewis, J. In *Progress in Inorganic Chemistry*; Cotton, F. A., Ed.; Interscience, New York, 1964.
34. Baranwal, B. P.; Gupta, T. *Synth. React. Inorg. Met.-Org. Chem.* **2004**, *34*, 1737.
35. Khan, T. A.; Naseem, S.; Azim, Y.; Parveen, S.; Shakir, M. *Trans. Met. Chem.* **2007**, *32*, 706-710.
36. Earnshaw, A. *Introduction to Magnetochemistry*, Academic Press Inc. Limited, London, 1968.
37. Lever, A. B. P. *Inorganic Electronic Spectroscopy*, Elsevier, New York, 1984.
38. Underhill, A. E.; Billing, D. E. *Nature* **1966**, *210*, 834.
39. Mishra, A. P.; Gsutams, S. K. *J. Indian Chem. Soc.* **2004**, *81*, 324.
40. Satyanarayana, D. N. *Electronic Absorption Spectroscopy and Related Techniques*, Universities Press (India) Limited, New Delhi, 2001.
41. Shivakumar, K.; Shashidhar.; Reddy, P. V.; Halli, M. B. *J. Coord. Chem.* **2008**, *61*, 2274-2287.
42. Kivelson, D.; Neiman, R. *J. Chem. Phys.* **1961**, *35*, 149.
43. Hathway, B. J. *Struct. Bonding* **1973**, *14*, 60.
44. Raman, N.; Sakthivel, A.; Rajasekaran, K. *J. Coord. Chem.* **2009**, *62*, 1661.
45. Belaid, S.; Landreau, A.; Djebbar, S.; Benali-Baitich, O.; Bouet, G.; Bouchara, J. P. *J. Inorg. Biochem.* **2008**, *102*, 63.
46. Petering, D. H. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker, New York, 1973.
47. Kulkarni, A.; Patil, S. A.; Badami, P. S. *Eur. J. Med. Chem.* **2009**, *44*, 2904-2912.