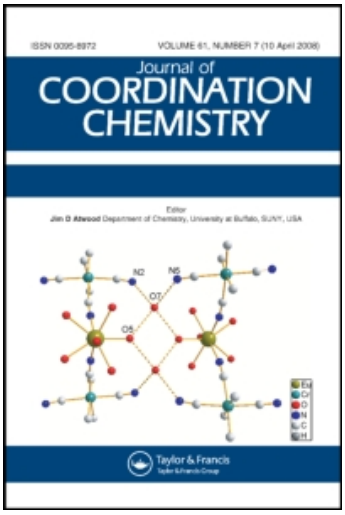

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Synthesis, spectral, electrochemical and antibacterial studies of copper(II) complexes with isatin derived bishydrazone and different co-ligands

Balakrishnan Murukan[a]; Bhageerethi Sindhu Kumari[a]; Kochukittan Mohanan[a]
[a] Department of Chemistry, University of Kerala, Kariavattom Campus, Trivandrum - 695 581, Kerala, India

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Synthesis, spectral, electrochemical and antibacterial studies of copper(II) complexes with isatin derived bishydrazone and different co-ligands

BALAKRISHNAN MURUKAN, BHAGEERETHI SINDHU KUMARI and KOCHUKITTAN MOHANAN*

Department of Chemistry, University of Kerala, Kariavattom Campus, Trivandrum - 695 581, Kerala, India

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A potentially tridentate bishydrazone derived from isatin was prepared by condensing isatin monohydrazone and salicylaldehyde. This ligand is versatile in forming a series of copper(II) complexes in the presence of different coordinating anions. The ligand and metal complexes have been characterized on the basis of elemental analyses, molar conductance values, magnetic susceptibility data, NMR, UV-visible, IR and EPR spectral studies wherever possible and applicable. The spectral studies reveal that the bishydrazone is monobasic tridentate, coordinating through the deprotonated phenolate oxygen, azomethine nitrogen and carbonyl group of the isatin moiety. Analytical data indicate that the complexes possess 1 : 1 metal–ligand ratio. Molar conductance values support the non-electrolytic nature of the complexes and the complexes have been formulated as [Cu(IBS)X]; where X = Cl^-, Br^-, NO_3^-, OAc^-, or ClO_4^- and HIBS = [(2-hydroxybenzaldehyde)-3-isatin]-bishydrazone. Based on the electronic spectral data, and magnetic moment values, a distorted square planar geometry has been proposed for the complexes. The chloride complex [Cu(IBS)Cl] has been subjected to X-ray diffraction and cyclic voltammetric studies. In view of the biological activities of hydrazone derivatives, the ligand and the metallated compounds were screened for the antibacterial activities and the effect of co-ligands on the antibacterial property has also been discussed.

Keywords: Bishydrazone; XRD; Cyclic voltammetry; Antibacterial activity

1. Introduction

Hydrazone derivatives containing heterocyclic moieties have interesting ligational features and have extensive applications in biological, clinical, analytical and various other fields [1–3]. Although much work has been reported with heterocyclic monohydrazones, very little information is available on bishydrazones [4]. A literature survey revealed several metallated monohydrazone derived from isatin but less from bishydrazone [5–7]. Apart from the synthetic, structural and analytical aspects, hydrazones and their metal complexes exhibit innumerable pharmacological activities, such as antibacterial, antifungal, antitumoral, antiviral, antimalarial and anti-HIV

*Corresponding author. Email: drkmohanan@rediffmail.com

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activities [8]. The present communication describes the synthesis and spectral studies of a bishydrazone and its copper(II) complexes containing different co-ligands. The study also highlights some important aspects of anion coordination chemistry [9].

2. Experimental

2.1. *Synthesis of monohydrazone (IM)*

A quantity (1.47 g, 10 mmol) of isatin was dissolved in methanol (40 mL) and was added to a solution of hydrazine hydrate (0.05 g, 10 mmol) dissolved in hot methanol (10 mL). The resulting mixture was refluxed for 3 h on a water-bath and, on cooling, the yellow compound that formed was filtered, washed, dried and recrystallized from methanol. m.p. 226°C (yield 95%).

2.2. *Synthesis of bishydrazone (HIBS)*

Salicylaldehyde (1.22 g, 10 mmol) was dissolved in methanol (10 mL) and was added in small portions to a solution of isatin monohydrazone (1.61 g, 10 mmol) in hot methanol (50 mL). The solution was then refluxed on a water-bath for 4 h. The orange compound, which separated was filtered, washed with methanol and dried in vacuum. The ligand was further purified by recrystallization from methanol. m.p. 337°C (yield 85%).

2.3. *Preparation of copper(II) complexes*

Copper(II) complexes were synthesised by the following general procedure. The appropriate copper(II) salt (10 mmol) [$CuCl_2 \cdot 2H_2O$, $CuBr_2$, $Cu(NO_3)_2 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$, $Cu(ClO_4)_2O \cdot 6H_2O$] dissolved in methanol, was added to a magnetically stirred solution of the ligand (2.65 g, 10 mmol) dissolved in methanol (50 mL). The pH of the solution was adjusted to 6.5–7.0 and the mixture was stirred for 30 min. The resulting solution was then refluxed on a water-bath for 3 h, concentrated and allowed to cool. The complex which separated was filtered, washed successively with methanol and ether then finally dried in vacuum over P_4O_{10}. The yields of the complexes are given in table 1.

2.4. *Antibacterial experiments*

The ligands and their metal complexes were screened for antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus megaterium and Vibrio cholerea* at a concentration of 200 $\mu g\,mL^{-1}$ in DMSO using the agar diffusion method [10, 11] described below:

A molten nutrient agar solution (20 mL) was poured into sterilized petri dishes and allowed to attain room temperature. The seed layer medium was melted and then cooled to about 45°C. The previously grown subculture was added to the seed layer medium aseptically and mixed well. It was immediately raked into the petri dishes and allowed to attain room temperature. Wells were then made with a sterile cork borer

Table 1. Analytical data and other details of the metal complexes.

Compound	Molecular formula	Yield (%)	Analytical data (%)				Molar conductance ($Ohm^{-1}cm^2mol^{-1}$) DMSO	Magnetic moment BM
			Cu	C	H	N		
IM	$C_8H_7N_3O$	95	–	59.59(59.62)	4.32(4.37)	(25.98)26.07	–	–
HIBS	$C_{15}H_{11}N_3O_2$	85	–	67.88(67.91)	4.03(4.17)	15.77(15.84)	–	–
[Cu(IBS)Cl]	$CuC_{15}H_{10}N3O2Cl$	71	17.41(17.49)	49.55(49.59)	2.70(2.77)	11.52(11.56)	7.8	1.88
[Cu(IBS)Br]	$CuC15H_{10}N_3O_2Br$	74	19.54(19.59)	44.11(44.18)	2.44(2.47)	10.30(10.30)	8.6	1.83
[Cu(IBS)NO_3]	$CuC_{15}H_{10}N_4O_5$	73	16.33(16.30)	46.19(46.21)	2.50(2.58)	14.32(14.37)	9.7	1.86
[Cu(IBS)OAc]	$CuC_{17}H_{13}N_3O_4$	74	16.40(16.42)	52.77(52.78)	3.36(3.38)	10.84(10.86)	8.7	1.85
[Cu(IBS)ClO_4]	CuC15H10N3O6Cl	75	14.82(14.87)	42.10(42.16)			8.2	1.82

and to these wells, a definite volume (0.05 mL) of the drug solution was added and the plates were allowed to cool for an hour to facilitate diffusion. The plates were incubated at 37°C for 48 h. At the end of incubation period, the inhibition zones around the wells were measured. Streptomycin was used as the standard antibacterial agent.

2.5. *Physical measurements*

The complexes were analyzed for their metal content by using the atomic absorption spectrophotometer (GBC Avanta). Carbon, hydrogen and nitrogen analyses were performed using a Heraeus Carlo Erba 1108-CHN Analyzer. The electronic spectra of the complexes were recorded on a Hitachi 320 UV-Visible spectrophotometer. Infrared spectra were recorded on a Shimadzu FT IR 8000 spectrophotometer using DMSO as solvent. Proton NMR spectra were recorded in DMSO-d_6 on a JEOL GSX 400NB 400MHz FT NMR spectrometer. Far IR spectra were recorded on a polytec FIR 30 Fourier spectrometer using CsI discs. Molar conductance measurements in DMSO were made at room temperature using a Systronics conductivity meter type 304. Magnetic susceptibility values of the complexes were measured at room temperature with a Gouy type magnetic balance. EPR spectra of the complexes were recorded in the solid state and also in DMSO at the temperature of liquid nitrogen using a Varian-112 EPR spectrometer. Cyclic voltammetric study of the copper(II) complex was performed with a BAS CV-50 analyzer and the X-ray diffraction data were recorded on a Siemens D 5005 model spectrometer.

3. Results and discussion

Formation of the complexes is shown below:

$$CuX_2 + HIBS \rightarrow [Cu(IBS)X] + HX$$
$$(X = Cl, Br, NO_3, OAc \text{ or } ClO_4)$$

The complexes obtained are listed in table 1; all the complexes are fairly stable at room temperature. They are non-hygroscopic solids insoluble in common organic solvents but soluble in DMSO and DMF. The elemental analysis, molar conductance values and magnetic susceptibility measurements enabled the formation these complexes.

3.1. *Structure of the ligand*

Condensation of isatin monohydrazone with salicylaldehyde occurred in 1 : 1 molar ratio to form the bishydrazone viz. [(2-hydroxybenzaldehyde)-3-isatin]-bishydrazone (HIBS) which has been characterized through various spectral studies. The electronic spectrum of the bishydrazone shows absorption bands at 360 and 345 nm assignable to the n–π^* transitions of the ketimine and aldimine moieties, respectively. An infrared spectrum of the bishydrazone exhibited a broad band from 3420–3250 cm^{-1} and centered at 3330 cm^{-1}, which can be attributed to hydrogenbonded OH of the salicylidene moiety. Another band at 3280 cm^{-1} of medium intensity, can be assigned to

Table 2. Proton NMR spectra of mono and bishydrazones.

	Chemical shift (ppm)				
Compound	–OH	–CH=N–	Ring-NH–	Ar–H	$–NH_2$
Isatin monohydrazone (IM)	–	–	9.51	6.80–7.23	5.92
Bishydrazone (HIBS)	11.45	8.81	9.91	6.81-7.79	–

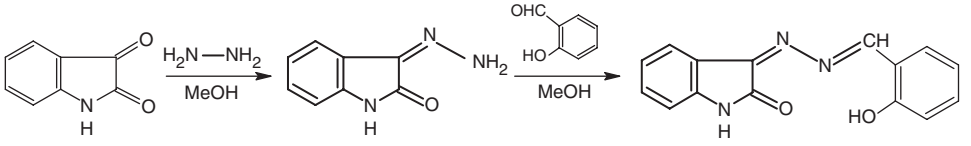

Figure 1. Synthesis of the ligand.

the NH vibrations of the indole ring system. An intense band at 1718 cm^{-1} was due to ν(C=O) of isatin [12]. Vibrations of the aldimine and ketimine groups were observed at 1620 and 1632 cm^{-1} respectively. The phenolic ν(C–O) and hydrazinic ν(N–N) are observed at 1282 and 995 cm^{-1} respectively.

Proton NMR spectrum of the ligand gave the characteristic signal of phenolic proton at 11.45 δ, indicating its involvement in strong intramolecular hydrogen bonding [13]. The signal due to azomethine proton was observed at 8.81 and that of NH of the indole ring was observed at 9.91 δ. Aromatic proton signals were observed in the range of 6.81 to 7.71 δ (table 2). On the basis of the above spectral data an internally hydrogen bonded structure has been assigned for the ligand.

3.2. *Structure of the metal complexes*

Molar conductance measured in DMSO reveal the non-electrolytic nature of the metal complexes [14].

3.2.1. Infrared spectra. Infrared spectral data of the complexes are presented in table 3 along with their tentative assignments. In the metal complexes, the broad band of hydrogen bonded OH in the salicylidene moiety disappeared from 3420–3250 cm^{-1} suggesting deprotonation and formation of a metal-oxygen bond. Consequently, the phenolic ν(C–O) frequency increased by ~40 cm^{-1} showing coordination of the phenolate oxygen [15]. The ν(C=N) vibrational characteristic of the aldimine moiety is shifted to lower frequency by about 20–25 cm^{-1} in the complexes, and clear evidence for the involvement of this group in chelation with metal. The band corresponding to ν(C=O) shifts to lower frequency by about 30–40 cm^{-1} in the spectra of the metal complexes, indicating coordination by carbonyl oxygen. However, the vibrational characteristics of the ring ν(NH) at 3280 cm^{-1} and of ketimine ν(C=N) at 1615 cm^{-1}, remain almost unaffected, indicating their non-involvement in coordination (figure 2). Far infrared spectra of the metal complexes showed several absorption bands, which are not observed in the ligand spectrum; bands appearing at 368 and 298 cm^{-1} are

Table 3. Important IR spectral bands of the ligand (IBSH) and its metal complexes (cm^{-1}).

IBSH	[Cu(IBS)Cl]	[Cu(IBS)Br]	[Cu(IBS)NO_3]	[Cu(IBS)OAc]	[Cu(IBS)ClO_4]	Tentative assignment
3330	–	–	–	–	–	Hydrogen bonded ν(OH)
3280	3281	3280	3279	3282	3280	Indole ring NH
1718	1688	1690	1689	1689	1688	ν(C=O) ring
1615	1613	1612	1611	1610	1612	ν(C=N) ring
1590	1566	1562	1567	1569	1568	ν(C=N) aldimine
1282	1320	1321	1318	1317	1319	ν(C–O) phenolic
995	1010	1006	1009	1012	1009	ν(N–N)
–	417	412	411	416	411	ν(Cu–N)
–	514	518	516	519	515	ν(Cu–O)
–	368	298	–	–	–	ν(Cu–X)

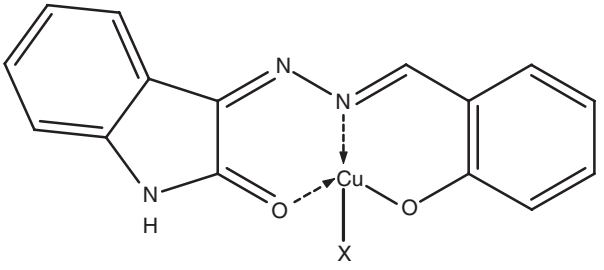

Figure 2. Structure of the metal complex.

assignable to ν(Cu–Cl) and ν(Cu–Br) stretching vibrations, respectively [16]. Further ν(Cu–N) and ν(Cu–O) vibrations have been observed in the range, 410–420 and 510–520 cm^{-1}, respectively, in all the complexes [17].

3.2.2. Coordination by the anions. The ligand has been designed in such a way that the species formed after coordination of one molecule of ligand to the copper(II) species served as a receptor capable of coordinating a univalent anion also, thereby allowing study of anion coordination chemistry, which has extensive applications in various fields [18]. Six different anions have been examined with particular reference to their bonding modes and their impact on antibacterial properties.

In the infrared spectrum of the nitrato complex, three strong bands of the coordinated nitrato group have been observed, at 1386, 1311 and 1000 cm^{-1}, assignable to ν_5, ν_1 and ν_2 modes of vibration, respectively. Since the magnitude of the difference between ν_5 and ν_1 is 75 cm^{-1}, the nitrato group is considered monodentate to the copper(II). In the acetato complex ν_a(COO)is observed at 1616 cm^{-1} and ν_s(COO) is observed at 1400 cm^{-1} in addition to skeletal vibrations of the ligand. The difference between these two frequencies ($\Delta\nu = 216\,cm^{-1}$) supports monodentate coordination of the acetato group [19].

In the perchlorate complex, the diagnostic band at 1110 cm^{-1} (ν_3) is broad due to splitting. The ν_4 vibration also splits into two bands, the difference between these two bands of ν_4 ($\Delta\nu = 35\,cm^{-1}$) indicates monodentate coordination [20].

Table 4. EPR spectual data of the metal complexes.

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^{-4}$ (cm^{-1})	$g_{\parallel}/A_{\parallel}$ (cm)	α^2
[Cu(IBS)Cl]	2.210	2.058	180	122	0.77
[Cu(IBS)Br]	2.243	2.041	178	124	0.79
[Cu(IBS)NO_3]	2.232	2.049	176	127	0.78
[Cu(IBS)OAc]	2.223	2.042	177	125	0.77
[Cu(IBS)ClO_4]	2.201	2.051	176	125	0.75

3.2.3. Electronic spectra and magnetic moment values. In the electronic spectra of the metal complexes the $n \rightarrow \pi^*$ bands were slightly redshifted indicating that no structural alteration of the ligand occurred on metal chelation. The band observed in the region 720–740 nm is attributed to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, in agreement with a distorted square-planar geometry around the copper(II) ion [21]. Magnetic moment values of the complexes at room temperature vary in the range 1.82 to 1.89 BM, indicating the absence of metal-metal interaction in the complexes.

3.2.4. EPR spectra. The X-band EPR spectra of the copper(II) complexes were recorded in the solid state at room temperature and in DMSO at the temperature of liquid nitrogen using DPPH free radical as the '*g*' marker. The EPR spectra of all the complexes are isotropic at room temperature. However, the spectra are anisotropic at liquid nitrogen temperature, characteristic of axial symmetry. The complexes have a well resolved $g_{\parallel}$ and broadened $g_{\perp}$ region. Various Hamiltonian parameters have also been calculated (table 4). The trend $g_{\parallel} > g_{\perp} > g_e$ indicates tetragonal elongation along the *z* axis and the presence of the unpaired electron in the $d_{x^2-y^2}$ orbital [22]. EPR spectral studies are also helpful in revealing the covalent character of the metal–ligand bond [23]. It has been reported that $g_{\parallel}$ values are sensitive to the covalent nature of the metal–ligand bond and that values above 2.3 show ionic character and lower than 2.3 indicate covalent character. In addition to this, the covalency parameter (α^2) of the complexes has been calculated, using the Kievelson and Neiman equation [24].

$$\alpha^2_{Cu} = \frac{-(A_{\parallel})}{0.036} + (g_{\parallel} - 2.002) + \frac{3}{7}(g_{\perp} - 2.002) + 0.04$$

The α^2 values of the complexes indicate considerable covalent character for the metal–ligand bond [25]. Empirical ratio $g_{\parallel}/A_{\parallel}$ is frequently used to evaluate tetrahedral distortions in the tetragonal structure of copper(II) compounds, where the ratio $g_{\parallel}/A_{\parallel}$ close to 100 cm indicates a roughly square planar or tetragonal structure around the copper(II) ion, and the values from 170 to 250 cm indicate a distorted tetrahedral symmetry [26]. Based on this general data, a square planar geometry has been proposed. Thus EPR study of the copper complexes has provided supportive evidence to the optical results. The spectra of the complexes recorded in DMSO, showed four peaks due to coupling of the electron spin of the ^{63}Cu nucleus ($I = 3/2$). The peaks are broad and have the appearance of ill-resolved triplets (figure 3). The breadth of the peaks

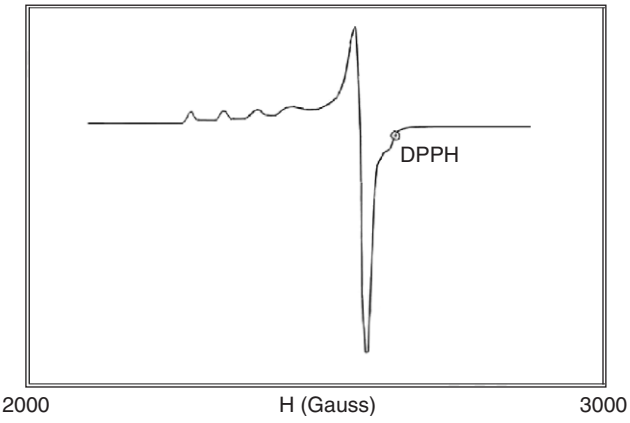

Figure 3. EPR spectrum of [Cu(IBS)NO_3].

and its triplet appearance can be attributed to hyperfine splitting of the nitrogen atom ($I=1$) of the ligand. The triplet appearance is evidence for nitrogen coordination [27].

3.3. *X-ray diffraction*

The crystal structure of the copper(II) complex was studied by powder X-ray diffraction. The X-ray diffraction pattern of the complex indicates high crystallinity of the complex. The diffractogram recorded 14 reflections between 2θ ranging from 5 to 45° with maxima at $2\theta = 7.6488°$ corresponding to interplanar distance $d = 11.7485$ Å. The main peaks have been indexed using computer software by trial and error method [28, 29]. The d_{hkl} values obtained have been compared with calculated values. A comparison of these values show good agreement between the calculated and observed values. The complex was successfully indexed to an orthorhombic crystal system with the lattice constant, $a = 11.6141$ Å; $b = 9.1283$ Å; $c = 5.7990$ Å and unit cell volume 613.0611 $Å^3$.

3.4. *Cyclic voltammetry (CV)*

Electrochemical behaviour of [Cu(IBS)Cl] was examined by means of cyclic voltammetry, employing glassy carbon as working electrode, Ag/AgCl as reference electrode, and platinum wire as auxiliary electrode. The working media consisted of DMSO and Bu_4NPF_6 as the supporting electrolyte. The solution was degassed with argon prior to use and kept under an argon atmosphere throughout the experiment. The measurement was carried out using 2 mM solution at room temperature in the potential range −2.0 to +2.0 V with a scan rate 100 mV sec^{-1}.

In the CV profile, a broad irreversible, single electron response was identified at −0.93 V, which may be assigned to reduction of the ligand; no oxidative response was found. The single-electron reversible couple identified at −0.62 V has been assigned to the metal-centered Cu(II)/Cu(I) couple. At slower scan rate the difference of the peaks (ΔE_p) is close to 57 mV, indicating that the number of electrons transferred is 1 ($n = 1$). Also the ratio of the anodic to cathodic peak current (ip_a/ip_c) approaches one at this scan rate. From the above voltammetric data the electron transfer process can be schematically represented as

$$[Cu(II)(IBS)Cl] + 1e \rightarrow [Cu(I)(IBS)] + Cl^-$$

The electrochemical process is diffusion controlled. However decomplexation and copper metal deposition on the electrode are not observed [30].

3.5. *Antibacterial activity*

Antimicrobial properties of hydrazone complexes have been reported by several investigators. Allured by these observations, biological experiments for evaluating the antibacterial activities of the ligand and complexes have been performed using a reported method [31]. The screening data obtained by using some pathogenic bacteria are presented in the antibacteriogram (figure 4). The ligand is physiologically active and chelation enhanced its activity. This enhancement in activity due to chelation can be explained on the basis of chelation theory [32]. Chelation reduces the polarity of the metal ion considerably, mainly because of the partial sharing of its positive charge with donor groups and the possible π-electron delocalization over the whole chelate ring. Chelation not only reduces the polarity of metal ion, but also increases the lipophilic character of the chelate. As a result of this, interaction between metal ion and the cell walls is favoured resulting in interference with normal cell processes. If the geometry and charge distribution around the molecule are incompatible with the geometry and charge distribution around the pores of the bacterial cell wall, penetration through the wall by the toxic agent cannot take place, preventing toxic reaction within the pores [33].

As a part of the study on anion coordination chemistry, the role of certain anions on the antibacterial property has also been examined. If we examine the antibacterial properties of metal complexes containing different anions, acetate coordinated complexes exhibit more inhibition compared to others. The low activity of NO_3^- and ClO_4^- compounds may be due to greater bonding capacities of these groups towards the copper(II) ion and the lesser activity of Cl^- and Br^- coordinated complexes may due to low lipid solubility. The present system contains a heterocyclic ligand with multi-functional groups giving a greater chance of interaction either with nucleoside bases or with biologically essential metal ions present in the biosystem [34]. Apart from this mode of action, the compounds may form hydrogen bonds through the coordinated anions as well as the azomethine group, with the active centers of the cell constituents resulting in interference with the normal cell processes. Hence it can be concluded that anion coordination also influences the antibacterial properties of metal complexes.

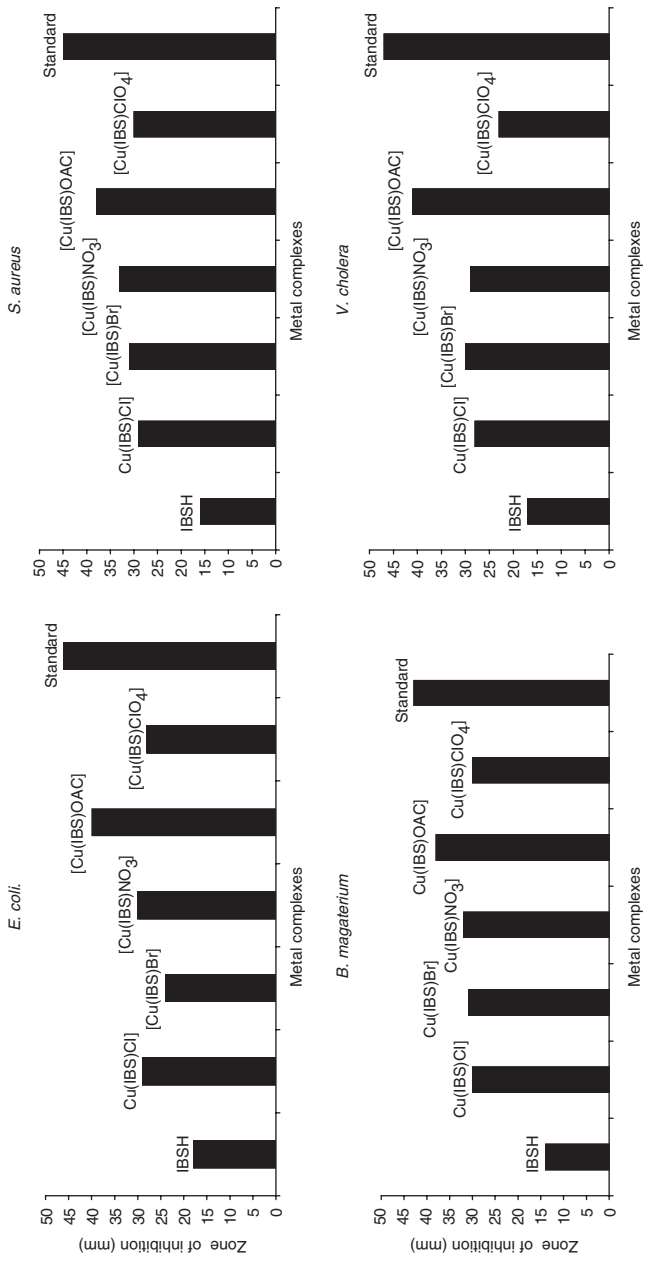

Figure 4. Antibacteriogram.

References

[1] M. Katyal, W.A.E. McBryde. *Technical News Service*, Part I & II, Sarabai M. Chemicals, Baroda (1978).
[2] E.I. Pleskushkina, A.N. Nikolaevskii, T.A. Filippenko. *Russ. J. Appl. Chem.*, **74**, 792 (2001).
[3] C.R. Maria, B.F. Marisa, B. Franco, P. Corrado, P. Giorgio, P. Silvana, S. Monica. *J. Inorg. Biochem.*, **98**, 313 (2004).
[4] K.S. Seshaiah, R. Atmakuru. *Biol. Pharm. Bull.*, **24**, 1149 (2001).
[5] M.B. Ferrari, C. Pelizzi, G. Pelosi, M.C. Rodriguez-Arguelles. *Polyhedron*, **21**, 2593 (2002).
[6] V.V. Lukov, S.I. Levchenkov, S.V. Posokhova, I.N. Shcherbakov, V.A. Kogan. *Russ. J. Coord. Chem.*, **28**, 222 (2002).
[7] B. Bottari, R. Maccari, F. Monforte, R. Ottana, M.G. Vigorita, G. Bruno, F. Nicolo, A. Rotondo, E. Rotondo. *Bioorg. Med. Chem.*, **9**, 2203 (2001).
[8] S.N. Pandeya, S. Smitha, M. Jyoti, S.K. Sridhar. *Acta Pharm.*, **55**, 27 (2005).
[9] P.A. Gale. *Coord. Chem. Rev.*, **199**, 181 (2000).
[10] T.R. Johnson, C.L. Case. *Laboratory Experiments in Microbiology*, Benjemin Cummings, Wesley Longman, Sanfrancisco (2001).
[11] J.G. Collee, J.P. Duguid, A.G. Farser, B.D. Marmion (Eds). *Practical Medical Microbiology*, Churchill Livingstone, New York (1989).
[12] S. Neena, H. Sunita, S. Jyoti, P. Vanita, B.V. Agarwala. *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 1283 (1992).
[13] C.A. Elmer, M. Abdul. *Can. J. Chem.*, **53**, 939 (1975).
[14] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[15] S.M. El-Medani, M.M. Aboaly, H.H. Abdalla, R.M. Ramdan. *Spectr. Lett.*, **37**, 619 (2004).
[16] M.J. Kharodawala, A.K. Rana. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 1483 (2003).
[17] A. Hatzidumitrious, C.A. Bolos. *Polyhedron*, **17**, 1779 (1998).
[18] J. Zhou, S.J. Lancaster, D.A. Walker, S. Beck, M. Thornton-Peth, M. Bochmann. *J. Am. Chem. Soc.*, **123**, 223 (2001).
[19] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York (1997).
[20] R.P. Scholer, A.E. Merbach. *Inorg. Chim. Acta*, **15**, 15 (1975).
[21] N. Nawar, M.A. Khattab, N.M. Hosny. *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 1365 (1990).
[22] B. Singh, B.P. Yadev, R.C. Aggarwal. *Indian J. Chem.*, **23A**, 441 (1984).
[23] G. Marcotrigiano, L. Meuabue, G.C. Pellacani. *Inorg. Chim. Acta*, **46**, 107 (1980).
[24] D. Kivelson, R. Neiman. *J. Chem. Phys.*, **35**, 149 (1961).
[25] J.R. Wasson, C. Trapp. *J. Phys. Chem.*, **73**, 3763 (1969).
[26] J. Muller, K. Felix, C. Maichle, E. Lengfelder, J. Strahle, U. Weser. *Inorg. Chim. Acta*, **233**, 11 (1995).
[27] L.G. Mac Donald, D.H. Brown, W.E. Smith. *Inorg. Chim. Acta*, **63**, 213 (1982).
[28] N.F.M. Hentry, H. Lipson, W.A. Wooster. *Interpretation of X-ray Diffraction Photographs*, McMillan, London (1951).
[29] R.W.M. D'Eye, E. Wait. *X-ray Powder Photography in Inorganic Chemistry*, Butterwoths, London (1960).
[30] A.J. Bard, L.R. Faulkner. *Electrochemical Methods*, John Wiley & Sons, New York (1980).
[31] J.G. Collee, J.P. Duguid, A.G. Farser, B.P Marmion (Ed.). *Practical Medical Microbiology*, Churchill Livingstone, New York (1989).
[32] K.N. Thimmaiah, W.D. Lloyd, G.T. Chandrappa. *Inorg. Chim. Acta*, **106**, 81 (1985).
[33] P. Chakrabarti. *J. Mol. Biol.*, **234**, 463 (1993).
[34] Z.H. Chohan, H. Pervez, A. Rauf, K.M. Khan, C.T. Supuran. *J. Enz. Inhib. Med. Chem.*, **19**(5), 417 (2004).