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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF TRANSITION METAL COMPLEXES OF IMIDAZOLE DERIVATIVE

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ABSTRACT. A series of new biologically active complexes of Zn(II), Cu(II), Co(II) and Ni(II) with imidazole derivative have been synthesized. The synthesized chelating agent and metal(II) complexes were screened for antibacterial activities against four pathogenic species of bacteria namely; *Eschereschi coli*, *Pseudomonas aeruginosa*, *Klesbiella pneumonia* and *Staphylococcus aureus* by agar well diffusion method. The results show that most of the metal complexes were more active than the neat ligand, against these bacterial species as expected.

KEY WORDS: 1,3-Di(1H-imidazol-1-yl)-2-propanol, Coordination compounds, Antimicrobial study

INTRODUCTION

Metal complexes play an important role in many biological systems [1-4]. It has been observed that metal ions have considerable effect on the antimicrobial activity of antibiotics [5-9]. Similarly metal ions are known for their antitumor activity [10-14].

Emerging bacterial resistance to the currently available antibiotics has driven the search for novel prokaryotic targets as well as new molecules which inhibit their activity [15]. Among these novel metal complexes derivatives which show considerable biological activity may represent an interesting approach for designing new antibacterial drugs. This may be due to the dual possibility of both ligands plus metal ion interacting with different steps of the pathogen life cycle [16]. Many of the anticancer drugs are versatile ligands [17], some of which exhibit increased anticancer activity when administered in the form of their metal complexes [18]. It has been suggested that certain type of cancers are virus-caused [19, 20]. The interaction between the metal ion and the ligand with cancer-associated viruses might represent an important route in designing new anticancer therapies [21]. The inverse process, i.e. coordinating a metal ion from an important biomolecule for instance, a zinc finger protein has been used to design novel antiviral therapies, targeted against virus causing infection [22, 23].

In recent age, the role of metal complexes has been increased in relation to antibacterial activity. Literature indicates that ligands/drugs become more bacteriostatic on complexation as compared to unchelated ones [24, 25].

The biological activity of Zn(II), Cu(II), Co(II) and Ni(II) with imidazole derivative (DIPO) (Figure 1) have not been studied earlier. In the present work, biological activity of the above mentioned metal chelates against four pathogenic bacteria (*Escherichia coli*, *Pseudomonas aerogans*, *Kleisbella pneumonia* and *Staphylococcus aureus*) have been studied.

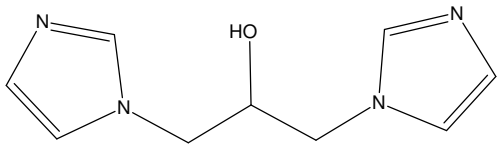

Figure 1. Structure of ligand, 1,3-di(1H-imidazol-1-yl)-2-propanol (DIPO).

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EXPERIMENTAL

Materials

Metal salts used were of analytical grade, obtained from Riedel-de-Haen (Germany) and were used as such without further purification. Imidazole was obtained from Merck-Schuchardt (Germany), potassium hydroxide from Merck (Germany) and epichlorhydrin from AVOCADO, Research Chemicals Ltd, Heysham, Lancs. The partial dehydration of the salts was carried out by drying the hydrated salts in a vacuum oven for several hours at 80–100 ^{o}C. All the solvents were distilled prior to their use.

Synthesis of ligand

The ligand 1,3-di(1H-imidazol-1-yl)-2-propanol (DIPO) was synthesized by reacting imidazol with epichlorohydrin. Imidazol (0.01 mole) in absolute ethanol (10 mL) was added dropwise to (0.007 moles) epichlorohydrin. The reaction mixture was refluxed for about 15 min and then KOH (0.5 g) was added slowly. The reflux was continued for another 4 h. The residue containing solid KCl was filtered off and the filtrate on evaporation through rotary evaporator gave the ligand. The crude product was then recrystallized from ethanol to give the purified product in 86% yield.

Preparation of complexes

All the complexes were prepared using same general procedure. Approximately 10 mmoles of partially dehydrated salts were dissolved in minimum amount of anhydrous ethanol. The ligand DIPO, in excess over 1:2 metal to ligand ratio, was dissolved in the minimum amount of the same solvent with constant stirring, the mixture was stirred and kept at 50 ^{o}C for half an hour, then cooled for about 20 min. The metal complexes precipitated either immediately or on cooling. The product was filtered through sintered glass crucible, washed several times with ethanol and dried under vacuum at 50 ^{o}C. The complexes were recrystallized from suitable solvents.

Instrumentation

Infrared spectra were taken in the range of 4000-600 cm^{-1} on PYE UNICAM Infrared Spectrophotometer in KBr disc. The far IR spectra were examined in KBr discs in the region of 400-200 cm^{-1} (FT-IR SHIMADZU).

The absorption spectra of solution of complexes in the range of 200-900 nm using different solvents were obtained on Jasco DEC-1 Spectrophotometer with 1 cm matched quartz cells.

Molar conductances of the solution of the metal complexes were determined with a conductivity meter type HI 8333. All measurements were carried out at room temperature (30 ^{o}C) with freshly prepared solution.

Magnetic susceptibilities were measured by Gouy method at room temperature using $Hg[Co(SCN)_4]$ as a standard [39], magnetic moments were thus calculated. The cations and anions were estimated by using typical analytical procedure [40].

Antibacterial activity

Agar well diffusion method was used for the determination of biological activities of the synthesized metal complexes. Six wells were cut in seeded agar and one at the center. Two to

eight hours old bacterial inoculums containing 10^4–10^6 colony forming units (CFU)/mL were used in these assays. The wells were dug in the agar media using a sterile metallic borer with centers at least 24 mm. Recommended concentration (120 μL) of the test sample (1 mg/mL in DMSO) was introduced into the respective wells. Other wells were supplemented with DMSO and reference antibacterial drug, maxipime served as negative and positive controls, respectively. These discs/plates were placed in incubator for 24 h at 37 ^oC for drying. After that, sensitivity tests were conducted. Media for different types of bacteria used were blood, agar and nutrient agar. The clear zone around the well was compared against the zone produced by the known concentration of the control drug and the diameter of the inhibition zone was measured [26].

RESULTS AND DISCUSSION

The ligand was analysed by elemental analysis, NMR and mass spectrum and was reported earlier [34], whereas, the complexes were characterized on the basis of elemental analysis, conductance measurement, magnetic susceptibility, IR and electronic spectra (Table 1 and 2). All the obtained data support the proposed tetrahedral geometries. The characteristic bands in the infrared spectra (4000-600 cm^{-1}) of DIPO and its metal complexes are given in Table 2. The IR of DIPO in KBr showed strong absorption at 1511 cm^{-1} and a weak at 1592 cm^{-1} which were assigned to C=N stretching vibrations. C-N exhibited stretching vibrations at 1107 cm^{-1} strongly and at 1080 cm^{-1} weakly. For –OH a broad peak was observed at 3219 cm^{-1}. In metal complexes the bands at 1511 cm^{-1} and 1107 cm^{-1} were shifted to lower frequencies. The solid state infrared spectra of the free ligand and complexes in KBr support tetrahedral coordination [34]. The ligand 1,3-di(1H-imidazol-1-yl)-2-propanol (DIPO) form complexes of the type (MLX_2) where M = Zn(II), Cu(II), Co(II), and Ni(II), X = Cl^-, Br^-. The elemental analysis and molar conductance values support the proposed formula and also that the anions are within the coordination sphere. The magnetic moment of the Co(II) complexes (4.32-4.39 BM) is the characteristic value for the presence of three unpaired electrons. The solution spectra of Co(II) complexes in DMSO exhibit absorption band which could be assigned to $^4A_2(F) \rightarrow {}^4T_1(P)$ ν_3 in T_d symmetry [26, 34], this data also support the tetrahedral stereochemistry of the complex. Magnetic moment of Cu(II) complexes is 1.92-2.06 BM. The Cu(II) solution spectra in DMSO support the C_2v symmetry and reported [34], which resemble to Cu(II) complexes having CuN_2X_2 chromophore [28]. The magnetic moment of Ni(II) complexes (3.14-3.68 BM) is the characteristic value for the presence of two unpaired electrons. The solution spectra of Ni(II) complexes in DMSO exhibit two absorption bands, which could be assigned $^3T_1(F) \rightarrow {}^3T_2(P)$ (ν_3) transition and $^3T_1 \rightarrow {}^3T_2$ (ν_1) transition in T_d symmetry [29]. The solid state infrared spectra of the free ligand and complexes in KBr support tetrahedral coordination.

The conductance data of Zn(II) complexes indicate the non-ionic species. As the complexes of the cyclic diamines have not been reported so far, however, they can be compared with cyclic amidines. In view of the well-known tendencies of Zn(II) to form tetrahedral complexes [35, 36], same structure may be proposed for Zn(II) DIPO complexes with DIPO acting as bidentate ligand. Trzaskowski *et al.* observed by density functional calculations that deprotonated serine and cystein, which are close in structural features to DIPO, forms tetrahedral geometry around the zinc(II) ion with only four ligands around the metal ion [37].

Roe *et al.* also showed that tetrahedral geometry for the Zn^{+2} complexes are the most stable ones [36]. This geometry would also be consistent with the non-electrolytic behavior of the complexes [35-38].

The antibacterial activities of both the ligands and their complexes were tested for the activities against the pathogenic bacteria like *E. Coli*, *P. aeruginosa*, *K. pneumonae* and *S. aureus* compared with maxipime used as a positive control.

Table 1. Physical, analytical, conductance and magnetic moments of DIPO and its complexes.

Compound	Color	Dec. temp. °C	% metal (calc.)	% anion (calc.)	% C (calc.)	% H (calc.)	% N (calc.)	Molar conductance	μ_{effec} (BM)
DIPO	---	--	---	--	55.9 (56.2)	5.9 (6.3)	28.3 (28.9)	--	--
[Zn(DIPO)Cl_2]	White	107	20.1 (19.8)	21.5 (21.6)	32.6 (32.9)	3.5 (3.6)	16.8 (17.0)	2.3	Diamag-netic
[Zn(DIPO)Br_2]	White	104	15.7 (15.5)	38.2 (38.3)	25.7 (25.9)	2.7 (2.9)	13.3 (13.4)	2.7	Diamag-netic
[Co(DIPO)Cl_2]	Light blue	91	18.3 (17.9)	22.0 (22.0)	33.4 (33.5)	3.6 (3.7)	17.0 (17.4)	3.0	4.3
[Co(DIPO)Br_2]	Blue	94	14.3 (14.0)	38.6 (39.0)	26.0 (26.0)	2.8 (3.0)	13.5 (13.6)	3.5	4.4
[Ni(DIPO)Cl_2]	Blue	118	18.3 (18.0)	21.8 (22.0)	33.5 (33.6)	3.6 (3.7)	17.3 (17.4)	6.2	3.4
[Ni(DIPO)Br_2]	Light Blue	114	14.3 (14.1)	38.8 (38.9)	26.2 (26.3)	2.8 (2.9)	13.6 (13.6)	6.6	3.7
[Cu(DIPO)Cl_2]	Bluish green	95	19.4 (19.3)	21.6 (21.7)	32.8 (33.0)	3.5 (3.7)	17.0 (17.0)	3.2	1.92
[Cu(DIPO)Br_2]	Dark green	87	15.3 (15.0)	38.3 (38.5)	25.9 (26.0)	2.8 (2.9)	13.3 (13.5)	3.7	2.06

Table 2. IR data of DIPO and its coordination compounds.

Compound	ν(C-N) cm^{-1}	ν(C=N) cm^{-1}	ν(-OH) cm^{-1}
DIPO	1080 s, 1107 sh	1511 vs, 1592 s	3219 b
[Zn(DIPO)Cl_2]	1020 s, 1198 w	1500 s, 1560 s	3210 b
[Zn(DIPO)Br_2]	1014 w, 1129 w	1480 s, 1570 s	3220 b
[Co(DIPO)Cl_2]	1095 s, 1166 w	1508 s, 1521 vs, 1558 s	3210 b
[Co(DIPO)Br_2]	1070 s, 1160 w	1520 s, 1530 w	3215 b
[Ni(DIPO)Cl_2]	1080 w, 1180 w	1510 s, 1545 w	3210 b
[Ni(DIPO)Br_2]	1089 w, 1180 w	1520 s, 1560 s	3210 b
[Cu(DIPO)Cl_2]	1010 w, 1160 s	1506 s, 1521 sh	3211 b
[Cu(DIPO)Br_2]	1031 vs	1521 s, 1558 w	3210 b

Sh = sharp, w = weak, s = small, b = broad, vs = very small.

Table 3 shows that at lower concentration, no inhibition zone was found in E. coli, while at higher concentration (100 g/20 L and 120 g/20 L) all complexes showed low inhibition zone from 0.5-2.0 mm. Zone of inhibition for maxipime as positive control was 10.6 mm.

Table 3. Results of antibacterial activity of the coordination complexes of DIPO against *Escherichia coli*.

S. No.	Complexes	Concentration of complexes µg/20µL						
		20	40	60	80	100	120	
1	[Zn(DIPO)Cl_2]	-	-	-	-	1.0	1.5	Diameter of inhibition zone of bacteria (mm)
2	[Zn(DIPO)Br_2]	-	-	-	-	1.0	2.0	
3	[Cu(DIPO)Cl_2]	2.0	2.0	3.0	3.0	3.0	4.0	
4	[Cu(DIPO)Br_2]	2.0	2.5	3.0	3.5	3.5	3.5	
5	[Co(DIPO)Cl_2]	-	-	1.0	2.0	2.0	2.5	
6	[Co(DIPO)Br_2]	-	-	1.0	1.5	2.5	3.0	
7	[Ni(DIPO)Cl_2]	2.0	2.0	2.0	2.5	2.5	3.0	
8	[Ni(DIPO)Br_2]	2.0	2.5	2.5	3.0	3.0	3.0	
9	Maxipime						10.6	

Table 4 shows that complexes of Zn(II) show no inhibition zone at all concentrations for *P. aeruginosa*. All other complexes show intermediary inhibition zone (1.0-3.0 mm) at all concentration zone of inhibition for maxipime, as positive control was 12.6 mm.

In Table 5 complexes of zinc and copper show no inhibition zone at lower concentration for K. pneumonae. All other complex showed intermediary inhibition zone (1.3-3.0 mm) at all concentrations. Zone of inhibition for maxipime as positive control was 9.2 mm.

It is revealed from the Tables 3-6 that complexes of zinc have less and other complexes have moderate antibacterial effects. These tables also show that the inhibition effects of the complexes on the bacterial growth are significantly different.

Table 4. Results of antibacterial activity of the coordination complexes of DIPO against *Pseudomonas aerogans*.

S. No.	Complexes	Concentration of complexes μg/20μL						
		20	40	60	80	100	120	
1	$[Zn(DIPO)Cl_2]$	-	-	-	-	-	-	Diameter of inhibition zone of bacteria (mm)
2	$[Zn(DIPO)Br_2]$	-	-	-	-	-	-	
3	$[Cu(DIPO)Cl_2]$	1.5	2.0	3.0	3.5	3.5	4.0	
4	$[Cu(DIPO)Br_2]$	1.0	1.5	2.5	3.0	3.5	3.5	
5	$[Co(DIPO)Cl_2]$	1.0	2.0	2.0	2.5	3.0	3.5	
6	$[Co(DIPO)Br_2]$	1.5	1.5	2.0	2.0	2.5	3.0	
7	$[Ni(DIPO)Cl_2]$	2.0	2.0	2.5	2.5	3.0	3.5	
8	$[Ni(DIPO)Br_2]$	2.0	2.5	2.5	3.0	3.5	4.0	
9	Maxipime						12.6	

Table 5. Results of antibacterial activity of the coordination complexes of DIPO against *Kleisbella pneumonia*.

S. No	Complexes	Concentration of complexes μg/20 μL						
		20	40	60	80	100	120	
1	$[Zn(DIPO)Cl_2]$	-	-	-	-	2.0	2.5	Diameter of inhibition zone of bacteria (mm)
2	$[Zn(DIPO)Br_2]$	-	-	-	-	2.5	2.5	
3	$[Cu(DIPO)Cl_2]$	-	-	-	-	1.5	2.5	
4	$[Cu(DIPO)Br_2]$	-	-	2.0	2.0	2.5	3.0	
5	$[Co(DIPO)Cl_2]$	-	-	2.5	2.5	2.5	3.0	
6	$[Co(DIPO)Br_2]$	-	-	2.5	2.5	3.0	3.5	
7	$[Ni(DIPO)Cl_2]$	-	-	2.5	2.5	3.0	3.5	
8	$[Ni(DIPO)Br_2]$	-	-	2.0	2.0	2.5	2.5	
9	Maxipime						9.2	

Table 6 shows that at lower concentration, no inhibition zone was found for *S. aureus* while at higher concentration, all complexes show intermediary zone of inhibition (0.5-3.0 mm). Zone of inhibition for maxipime as positive control was 11.2 mm.

The biological activity has been enhanced as compared to earlier reported complexes in the same series [30]. The antibacterial potency increases upon complexation as compared to uncomplexed compounds, against the tested bacterial species, thus opening new approaches to find new ways in the fight against antibiotic resistance [31].

It is suggested that the positive charge of the metal ion is partially shared with the donor atoms and there is electron delocalization over the whole chelate ring system having counter anions, which effectively influence the solubility mechanism of the complex [32]. It is however known, that chelation tends to make the ligands act as more powerful and potent bactericidal

agents, thus killing more of the bacteria than the parent ligands, it is suspected that factors, such as solubility, conductivity, dipole moment and cell permeability mechanisms (influenced by the presence of metal ions) may be the possible reasons for increasing this biological activity [33]. The results also indicate that copper and nickel complexes of the bromide ion are found to be potentially active as compared to chloride.

Table 6. Results of antibacterial activity of the coordination complexes of DIPO against *Staphylococcus aureus*.

S. No.	Complexes	Concentration of complexes µg/20µL						
		20	40	60	80	100	120	
1	$[Zn(DIPO)Cl_2]$	-	-	-	1.5	1.5	2.0	Diameter of inhibition zone of bacteria (mm)
2	$[Zn(DIPO)Br_2]$	-	-	-	1.5	2.0	2.5	
3	$[Cu(DIPO)Cl_2]$	0.5	0.5	1.0	1.0	1.0	1.5	
4	$[Cu(DIPO)Br_2]$	0.5	1.0	1.0	1.0	1.5	2.0	
5	$[Co(DIPO)Cl_2]$	1.0	2.0	3.0	3.0	3.5	4.0	
6	$[Co(DIPO)Br_2]$	1.5	2.5	3.0	3.5	4.0	4.0	
7	$[Ni(DIPO)Cl_2]$	2.0	2.0	2.0	3.0	3.0	3.0	
8	$[Ni(DIPO)Br_2]$	2.5	2.5	3.0	3.0	3.5	3.5	
9	Maxipime						11.2	

CONCLUSIONS

Most of the synthesized metal complexes have shown biological activities against the tested four types of pathogenic bacterial species by a well agar method. To counter the increased bacterial, fungal, viral, and microbial, cancer, aids, etc. diseases to the rapid growth in population, investigation of the biological activities of the ligands and their metal complexes would be very interesting and useful to control the respective diseases. The present work will be extended to the synthesis of other ligands, metal complexes and their biological activities.

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