Synthesis, Characterization and Antimicrobial Activity of Cu(ii), Co(ii), Ni(ii) and Mn(ii) Complexes with Desipramine

H.D. Revanasiddappa, B. Vijaya, L. Shiva Kumar and K. Shiva Prasad

Department of Chemistry, Manasagangotri, University of Mysore, Mysore, India

Abstract: A new series of complexes of the type $[M(L)(H_2O)_nX_2]$, where, M=Cu(II), Co(II), Ni(II) and Mn(II); $X= Cl^-, Br^-, CH_3COO^-, ClO_4^-, NO_3^-$,; L= desipramine (DM) has been synthesized and characterized by using FT-IR, ^{1}H-NMR, elemental analyses, molar conductance, ESR and TGA-DTA studies. The spectral result show that ligand DM acts as bidentate ligand coordinating *via* secondary nitrogen -NH- and heterocyclic nitrogen, thus suggesting 1:1 stiochiometry of metal to ligand. Antibacterial and antifungal activities were studied for ligand and its metal complexes. The activity of complexes is found to be more than free ligand.

Key words: Desipramine · Transition metal compounds · Thermodynamics · Antibacterial activity · Antifungal activity

INTRODUCTION

In the last few decades, metal complexes of nitrogen chelating ligands have attracted considerable attention because of their interesting physico-chemical properties and biological relevance, as pharmaceutical and chemotherapeutic agents [1, 2]. A number of *in vitro* and *in vivo* studies have indicated that biologically active compounds become more bacteriostatic and carcinostatic upon chelation [3, 4]. Desipramine (DM) is a dibenzoazapine compound belongs to an important family of antidepressant drugs that inhibits the reuptake of norepinephrine. DM is an active metabolite of imipramine, having wide applicability in pharmacological field *viz.* as antinociceptive [5], antithyroid [6], for detection of blood in urine [7], indeed all these activities are increased upon complexation with the electron acceptors. DM consists of two nitrogen atom as donor sites, which makes stable complexation with transition metals. The survey of the literature reveals that, the use of DM as a ligand with the transition metal for the complexation is the first time and not has been reported so far.

Taking these factors into consideration, it is worthwhile to synthesize metal complexes with DM. The present paper deals with the synthesis of Cu(II), Co(II), Ni(II) and Mn(II) complexes with the ligand DM (10,11-dihydro-*N*-methyl-5H-dibenz[*bf*]azepine-5-propanamine) containing nitrogen as donor atom. These complexes are subjected for characterization and antimicrobial activities.

RESULT AND DISCUSSION

All the prepared metal complexes are crystalline solids. The analytical data collected from the spectral analysis in Table 1, indicate the stiochiometry of metal to ligand was 1:1 suggesting the general formula $[M(DM)(H_2O)_nX_2)]$. The complexes are stable at ordinary conditions and are non-hygroscopic. All the complexes are insoluble in water and common organic solvents but readily soluble in DMF and DMSO. The molar conductance measured in DMF of 10^{-3} M solution and all the complexes fall in the range 12-29 Ohm^{-1} cm^2 mol^{-1} indicating their non-electrolytic behaviour [8]. The molar conductance values of the complexes are given in Table 2.

IR Spectra: In order to study the chelation behaviour between ligand and its complexes, the IR spectrum of the free ligand was compared with the respective complexes (Table 3). The IR spectrum of the DM showed a broad band in the region 2970-2850 cm^{-1} can be assigned to the heterocyclic nitrogen atom attached to the alkyl group [9]. Another broad band in the region 2700-2350 cm^{-1} occurred for DM assigning to the nitrogen of the side chain. These two bands have been totally disappeared in the corresponding IR spectra of the complexes thereby indicating that the nitrogen atom of the side chain is the site of coordination. The new bands in the 462-470 and 434-438 cm^{-1} region for the complexes are ascribed to the

Corresponding Author: H.D. Revanasiddappa, Department of Chemistry, Manasagangotri, University of Mysore, Mysore. India
Tel: +91-821-2419669

Table 1: Analytical data of the prepared complexes

Complex	M.Wt	Yield (%)	Found (Calc.)%				
			C	H	N	O	M
1a. [Cu(L)(H$_2$O)$_2$Cl$_2$]	437.4	66	49.26 (49.43)	5.65 (5.72)	6.30 (6.40)	7.30 (7.31)	14.45 (14.53)
1b. [Cu(L)(H$_2$O)$_2$(ac)$_2$]	482.5	73	54.55 (54.71)	6.36 (6.42)	5.72 (5.80)	19.68 (19.89)	12.14 (12.21)
2a. [Co(L)(H$_2$O)$_2$Cl$_2$]	430.9	75	49.96 (50.12)	5.81 (5.80)	6.47 (6.50)	7.28 (7.42)	13.51 (13.67)
2b. [Co(L)(H$_2$O)$_2$Br$_2$]	519.7	65	41.31 (41.56)	4.80 (4.81)	5.29 (5.39)	6.07 (6.16)	11.25 (11.34)
2c.[Co(L)(H$_2$O)$_2$(NO$_3$)$_2$]	483.9	79	44.52 (44.63)	5.10 (5.16)	8.55 (8.68)	26.33 (26.45)	12.04 (12.18)
2d.[Co(L)(H$_2$O)$_2$(ClO$_4$)$_2$]	558.9	58	38.52 (38.64)	4.38 (4.47)	5.03 (5.00)	28.53 (28.62)	10.41 (10.54)
2e. [Co(L)(H$_2$O)$_2$(ac)$_2$]	477.9	67	55.02 (55.24)	6.45 (6.49)	5.77 (5.86)	19.97 (20.08)	12.24 (12.33)
3a. [Ni(L)(H$_2$O)$_2$Cl$_2$]	430.7	74	49.76 (49.98)	5.75 (5.80)	6.42 (6.50)	7.40 (7.43)	13.55 (13.63)
3b. [Ni(L)(H$_2$O)$_2$Br$_2$]	519.5	70	41.61 (41.58)	4.75 (4.81)	5.30 (5.39)	6.03 (6.15)	11.17 (11.30)
3c. [Ni(L)(H$_2$O)$_2$(ac)$_2$]	477.7	78	55.21 (55.26)	6.40 (6.49)	5.74 (5.86)	19.96 (20.10)	12.20 (12.29)
4a. [Mn(L)(H$_2$O)$_2$Cl$_2$]	426.9	64	50.29 (50.59)	5.68 (5.85)	6.50 (6.56)	7.40 (7.49)	12.75 (12.88)

Table 2: Results of electronic spectra and magnetic moments of the metal complexes

Complex	Electronic spectral bands (cm^{-1})	Λ Ohm^{-1} cm^2 mol^{-1}	μ_{eff} (BM)
1a	14462, 15009, 15847, 31489, 39742	18.2	4.80
1b	14378, 16472, 29387, 40334	21.2	5.22
2a	14798, 15856, 16827, 36331	29.41	4.47
2b	31483, 39618	16.44	5.06
2c	14832, 16437, 31254, 377731	14.04	4.92
2d	16037, 16918, 31258, 39687	17.09	4.21
2e	10247, 21066, 46852	19.89	1.87
3a	14360, 16320, 23562	12.3	3.31
3b	13896, 15307, 20440	12.9	3.18
3c	13415,14529, 20804	14.8	3.19
4a	13588, 16126, 22235	15.9	5.91

Dia = diamagnetic

Table 3: Characteristic IR bands (cm^{-1}) of the ligand and its metal complexes

Compound	(-HN-CH$_3$)	(N-CH$_2$)Hetero	(OH)	(M-N)	(M-X)
DM	2700-2350	2970-2850	-	-	-
1a	-	-	3339	422	328
1b	-	-	3445	406	-
2a	-	-	3460	412	310
2b	-	-	3339	429	340
2c	-	-	3480	424	-
2d	-	-	3500	405	-
2e	-	-	3330	421	-
3a	-	-	3480	415	240
3b	-	-	3500	410	230
3c	-	-	3450	422	-
4a	-	-	3350	435	320

Table 4: ESR data of Copper(II) complexe in DMSO

Complex	g$_{\|}$	g$_{iso}$	g$_\perp$	G	g$_{av}$
1a	2.1329	2.2106	2.0601	2.0931	2.0268

formation of M-N bonds, which further supports the coordination of the tertiary and secondary nitrogen atoms with metal salts. The Far-IR spectra of halide complexes gave sharp bands in the region 230-328 cm^{-1} indicating M-X bond. The spectra of acetate complexes show infrared band at 1600 and at 1340 cm^{-1} corresponding to v_{as}(COO$^-$) and v_s(COO$^-$), respectively. This observation indicates that the acetate groups are unidentately coordinated to metal ion [10]. On the basis of the above interpretation, it is concluded that DM behaves as bidentate ligand. In the spectra of the corresponding complexes a broad band around 3600-3300 cm^{-1} may be assigned to v(OH) of the coordinated water [11]. The presence of coordinated water was also checked from the TG studies.
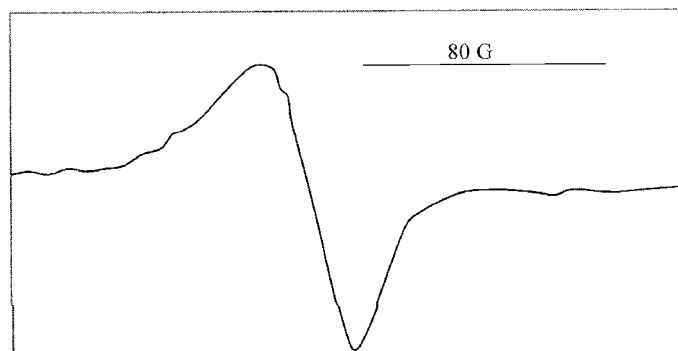
Fig. 1: ESR spectrum of [Cu(DM)(H$_2$O)$_2$Cl$_2$]

^{1}H-NMR Studies: The ^{1}H-NMR spectra of the ligand DM and its chloride salts of Cu(II) and Co(II) complexes have been recorded in DMSO-d$_6$ using TMS as a standard. The ligand DM exhibit a multiplet at δ 1.81-1.88 ppm and δ 7.1 ppm are assigned to alkyl and aromatic protons, respectively. These two multiplets were remains unchanged in the spectra of the complexes. The sharp signal (singlet) at δ 2.47 ppm and a multiplet at δ 3.06 ppm is due to –N-CH$_3$ and -N-CH$_2$ protons of the ligand, which are shifted to downfield around δ 2.85-2.81 and δ 3.33-3.27 ppm, thereby indicating the involvement of secondary nitrogen and heterocyclic nitrogen atom of DM in complexation. Further binding of the secondary -NH proton to metal center is supported by sharp signal at δ 9.23 ppm in DM is shifted to δ 9.76 and 9.89 ppm in the Cu(II) and Co(II) complexes, respectively.

ESR Spectral Studies: The ESR study is useful in understanding the geometry and state of electrons in metal ion of the complexes. In the present study, the ESR spectra of the Cu(II) complexes is recorded in a DMSO solution and related parameters are given in Table 4. The solid-state ESR spectra of some of the complexes exhibit axially symmetric g-tensor parameters with g$_\parallel$ > g⊥ >2.0023, indicating that the copper site has a d$_{x^2-y^2}^2$ ground-state characteristic of tetrahedral, square-planar, or octahedral stereochemistry [12]. In axial symmetry the g-values are given by Eq. 1.

$$G= (g_\parallel -2)/(g⊥-2) = 4 \qquad (1)$$

Where G is the exchange interaction parameter, according to literature [13], for the considerable exchange interaction process between Cu(II) centers in the solid state the value of G ≤4. The calculated G values for the [Cu(DM)(H$_2$O)$_2$Cl$_2$] complex is 2.09, suggesting the presence of exchange coupling between Cu(II) centers

in the solid state (Figure 1). The values of g$_\parallel$ > g⊥ in the complex indicates a geometry of distorted octahedral geometry [14]. The g$_{av}$ values are in agreement with orbitally non-degenerate states which support distorted octahedral geometry [15].

Electronic Spectra and Magnetic Study: The electronic spectra and magnetic moment values of the complexes are presented in Table 2. The magnetic moments of the complexes were measured at room temperature and all the complexes were represented paramagnetic property. The paramagnetic complexes showed magnetic moment in the range 1.87-5.91 B.M. giving evidence for the presence of unpaired electrons, suggesting high-spin distorted octahedral configuration [16].

In the Co(II) complexes 14390-14530 cm^{-1} is assigned to ^{4}T$_{1g}$ (F)→ ^{4}T$_2$g (F). The visible absorption spectra at 14850 cm^{-1} and at 16430 cm^{-1} is attributed to ^{4}T$_1$g → ^{4}A$_2$g (F) and ^{4}T$_1$g (F) → ^{4}T$_2$g (P) transitions, respectively [17]. The more intense bands beyond 36500 cm^{-1}are charge transfer bands. These values are in agreement with the values obtained for known octahedral Co(II) complexes [18]. For the Cu(II) complexes one broad absorption band is observed in the region 10260-11300 cm^{-1} being assigned to ^{2}B$_1$g → ^{2}A$_1$g and ^{2}B$_1$g → ^{2}B$_2$g transitions, while the second band around 18340-22788 cm^{-1} can be attributed to ^{2}B$_1$g → ^{2}Eg transition suggesting a distorted octahedral configuration [19, 20]. Charge transfer origin appears near 30000-40000 cm^{-1}.

Electronic spectra of Ni(II) complexes show two bands in the region 12830-16380 cm^{-1}due to ^{3}A$_2$g → ^{3}T$_1$g (F) (v$_3$) and ^{3}A$_2$g → ^{3}T$_1$g (P) (v$_3$) transitions, respectively, commensurate with octahedral stereochemistry [21]. This facts suggest Ni(II) complexes has octahedral arrangement [22, 23]. The electronic spectral bands for Mn(II) complex observed in the region 13272-13878, 15873-16977 and 2 1 470-22262 cm^{-1} may be assigned to

Table 5: Stepwise thermal degradation data obtained from TGA curves

| Complex | Temp. Range (°C) | Degradation of products | % weight loss | | No.of moles | % Residue [a] | |
			Cal.	Expt.		Cal.	Expt.
1a	158-210	$2 H_2O$	8.24	7.00	2	18.2	15.92
	220-320	DM	60.98	57.16	1		
	390-580	2 Cl	16.23	14.77	2		
1b	135-180	$2 H_2O$	7.43	6.55	2	16.43	15.28
	195-394	DM	55.04	51.36	1		
	460-580	2 ac	24.38	22.83	2		
2a	185-255	$2 H_2O$	8.34	7.88	2	17.23	16.69
	270-440	DM	61.75	60.57	1		
	450-530	2 Cl	16.43	15.98	2		
2b	170-223	$2 H_2O$	6.92	6.14	2	14.37	13.73
	228-330	DM	51.11	50.23	1		
	350-555	2 Br	30.66	28.57	2		
2c	126-206	$2 H_2O$	7.41	6.87	2	15.43	14.34
	218-365	DM	54.88	53.44	1		
	380-630	$2 NO_3$	25.55	24.39	2		
2d	160-192	$2 H_2O$	6.42	6.88	2	13.37	14.73
	210-258	DM	47.54	46.45	1		
	310-560	$2 ClO_4$	35.50	34.51	2		
2e	128-178	$2 H_2O$	7.51	6.86	2	15.63	16.14
	185-290	DM	55.57	54.11	1		
	310-510	2 ac	24.61	23.16	2		
3a	126-178	$2 H_2O$	8.33	7.88	2	17.29	16.92
	194-312	DM	61.66	58.25	1		
	390-585	2 Cl	16.41	15.13	2		
3b	150-175	$2 H_2O$	7.87	7.02	2	16.34	15.89
	178-318	DM	58.27	56.67	1		
	320-525	2 Br	21.00	20.03	2		
3c	110-168	$2 H_2O$	7.51	7.11	2	15.59	16.23
	175-345	DM	55.60	54.23	1		
	366-495	2 ac	24.63	23.15	2		
4a	180-220	$2 H_2O$	8.40	7.88	2	16.57	15.98
	240-430	DM	62.19	61.25	1		
	480-610	2 Cl	16.55	15.38	2		

DM = Desipramine; ac = CH_3COO; [a] = CuO/CoO/NiO/MnO

$^6A_1g \rightarrow {}^4T_1g$ (G), $^6A_1g \rightarrow {}^4T_2 g$ (G) and $^6A_1g \rightarrow {}^4A_1g$, ^4Eg, respectively [24, 25]. Band around 34000 cm^{-1} has been regarded as ligand-metal charge transfer band. These data suggest an octahedral arrangement of ligand around Mn(II) ion [26, 27].

Thermogravimetric Analysis: Thermal analyses of the complexes were recorded on a Perkin Elmer, US TGA-7 analyzer in the atmosphere of air. The temperature scale of the instrument was calibrated with high purity Calcium oxalate. The operational range of the instrument was from ambient to 900°C. About 4.8 mg of the pure sample was subjected for dynamic TG scans at heating rate of 10°C min^{-1}. The TGA ad DTA data's and composition obtained are presented in Table 5. TGA and DTA curves

show three decomposition steps for all the complexes except cadmium complexes which show only two steps of degradation.

First degradation step occurs due to the loss of two coordinated water molecules at the temperature range 110-250°C [28]. The experimental values for the mass loss of the dehydration stage are consistent with the calculated values. The decomposition occurs around 175-440°C corresponds to degradation of two molecules of ligand. The third step of the degradation mechanism is concern to decomposition of outer sphere ions. The remaining final residue is consisting of metal oxides. The probable structure of the metal complexes is depicted in Figure 2, based on the spectral, thermal and magnetic studies.
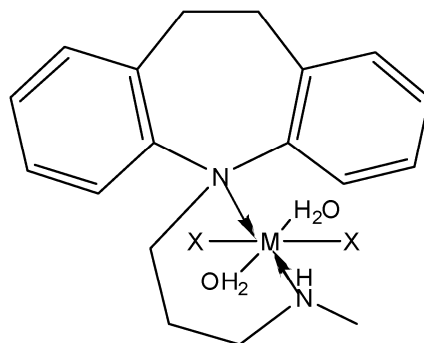
Fig. 2: Suggested structure of $[M(L)(H_2O)_2X_2]$; where L = desipramine ; M = Cu(II) {X=Cl$^-$, CH$_3$COO$^-$}; Co(II) {X= Cl$^-$, Br$^-$, NO$_3^-$, CH$_3$COO$^-$, ClO$_4^-$}; Ni(II) {X= Cl$^-$, Br$^-$, CH$_3$COO$^-$}; Mn(II) {X= Cl$^-$}
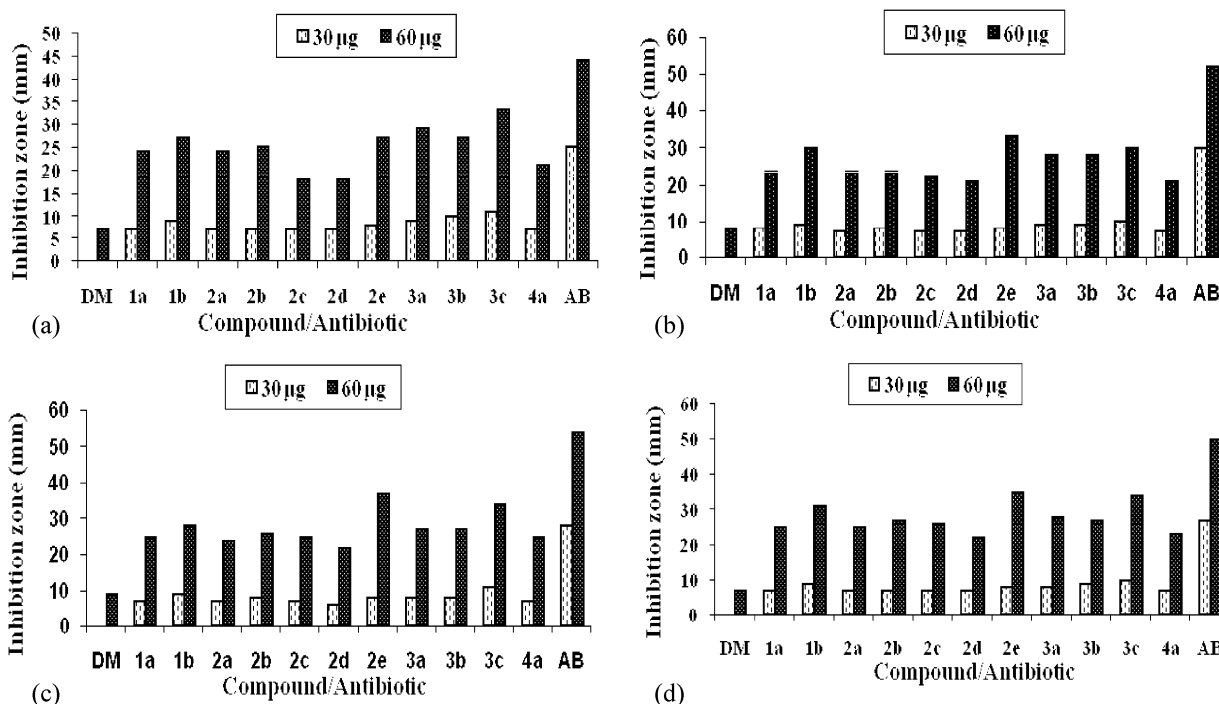

Fig. 3: Effect of desipramine and its complexes on bacteria, (a) *S. aureas* (b) *E. coli*; (c) *P. aregainosa*; (d) *B. subtilius*; is represented in percentage inhibition zone. (DM = desipramine; AB = Antibiotic/Chlormphenicol)
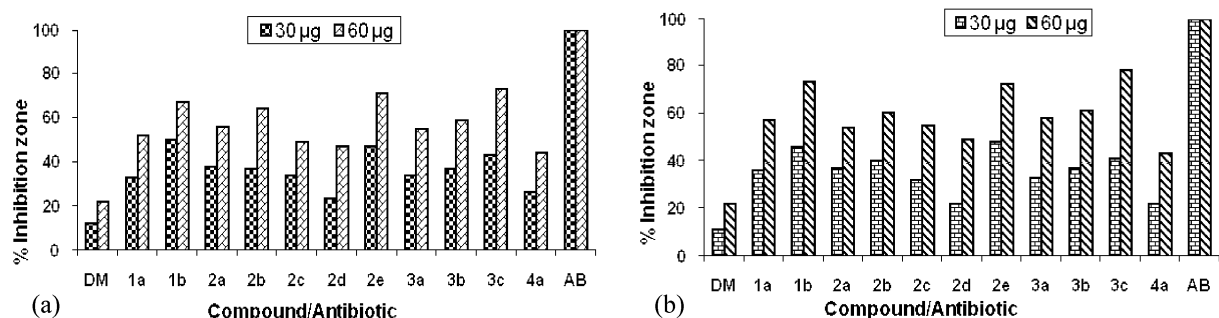

Fig. 4: Effect of desipramine and its complexes on fungi, (a) *A. flavus* and (b) *A. niger* is Represented in percentage inhibition zone. (DM = desipramine; AB = Antibiotic/Griseofulvin)

Table 6: Antibacterial screening data of the ligand and its metal complexes

| Compound | Inhibition zone in mm | | | | | | | |
| | S. aureas | | E. coli | | P. aregainosa | | B. subtilius | |
	30 µg	60 µg	30 µg	60 µg	30 µg	60 µg	30 µg	60 µg
DM	0	7	0	8	0	9	0	7
1a	7	24	8	23	7	25	7	25
1b	9	27	9	30	9	28	9	31
2a	7	24	7	23	7	24	7	25
2b	7	25	8	23	8	26	7	27
2c	7	18	7	22	7	25	7	26
2d	7	18	7	21	6	22	7	22
2e	8	27	8	33	8	37	8	35
3a	9	29	9	28	8	27	8	28
3b	10	27	9	28	8	27	9	27
3c	11	33	10	30	11	34	10	34
4a	7	21	7	21	7	25	7	23
Chlorampenicol	25	44	30	52	28	54	27	50

DMSO showed no inhibition, each value is the average of four replicates

Table 7: Antifungal screening data of the ligand and its metal complexes

| Compound | Percentage Inhibition zone | | | |
| | A. flavus | | A. niger | |
	30 µg	60 µg	30 µg	60 µg
DM	12	22	11	22
1a	33	52	36	57
1b	50	74	50	77
2a	38	56	37	54
2b	40	64	42	59
2c	34	49	32	55
2d	23	47	22	49
2e	47	71	48	72
3a	34	55	33	58
3b	37	59	37	61
3c	43	73	41	78
4a	26	44	22	43
Griseofulvin	100	100	100	100

DMSO showed no inhibition, each value is the average of four replicates

Antimicrobial Studies: The *in vitro* biocidal activities of the ligand and its metal complexes were tested against four bacteria viz., *E. coli, P. aeraginosa* and *B. subtilius* by disk diffusion method [29, 30] and two fungi *A. flavus and A. niger* by using Batemann poisoned food technique [31]. The results of inhibition of bacterial growth and antifungal activity values are presented in Tables 6 and 7 and its graphical representation is showed in Figures 3 and 4.

The result clearly indicates that the compounds have both antibacterial and antifungal activity against the tested organisms. The polarity of metal ion is considerably reduced on chelation with the organic compound which is mainly because of partial sharing of its positive charge with a donor groups and possibly π-electron delocalization over the whole molecule [32]. At 30 µg concentration, the antibacterial and antifungal activity of the complexes was very low compared to

concentration at 60 µg. It shows that as the concentration of the complexes increases, the inhibition zone of bacterial and fungal growth also increases. Among the synthesized complexes Ni(II) complexes showed potent activity. Metal ion with chloro, bromo, sulphate and acetate complexes are having the antimicrobial activity in the order, acetate complex > sulphate complex > bromo complex > chloro complex. This indicates that in addition to the nature of metal ions, the nature of anion in the complex played significant role in antimicrobial activities.

CONCLUSIONS

The present work shows the transition metals involving Cu(II), Co(II), Ni(II) and Mn(II) metal conjugation with antidepressant drug *viz.* desipramine resulting in synergistic enhancement of its antimicrobial activity. Characterization of the prepared complexes were visualized by using FT-IR, ^{1}H-NMR, elemental analyses, molar conductance, ESR and TGA-DTA studies. The spectral studies showed that ligand DM acts as bidentate ligand coordinating *via* secondary nitrogen -NH- and heterocyclic nitrogen, thus suggesting 1:1 stiochiometry of metal to ligand. It is suggested that all the metal complexes have high-spin distorted octahedral configuration except cadmium complexes, which showed tetrahedral geometry. All the prepared complexes have shown potent antimicrobial activity than ligand.

Experimental

Material: The ligand DM is received in the form of desipramine hydrochloride from Smith Kline and Beecham Ltd., India as gift sample and used by neutralizing acid with appropriate base [33]. Among the solvents employed DMF and DMSO were of spectroscopic grade and remaining solvents were of AR grade. The commercial ethanol sample was refluxed over calcium oxide for 6 h, distilled and used.

Physical Measurements: Elemental analyses (C, H, N) were carried out using an Elementar Vario EL-III instrument. FTIR spectra for samples were recorded using Jasco FT-IR- 4100 spectrometer. ^{1}H-NMR spectra were recorded in DMSO-d$_6$ on AMX-400 FT-NMR spectrometer. Electronic spectra of the complexes in the UV-visible region (200-900 nm) were measured using a Jasco UVIDEC-610 double beam spectrophotometer with quartz cells. Electrical conductance measurements of the prepared complexes were done using an Elico CM-180 conductometer. Melting points were determined in an

open capillary tube on Mel-temp apparatus. Magnetic susceptibility data in the room temperature were obtained from Gouy method using Hg[Co(SCN)$_4$] as a calibrant. The TG and DTA patterns of the complexes were recorded on a Perkin Elmer US TGA-7 analyzer in the atmosphere of air. Metal contents in the complexes were analyzed by using standard procedures [34].

General Procedure for the Preparation of Complexes: The complexes were prepared by mixing an ethanolic solution (50 ml, 5 m mol) of ligand DM and the (50 ml, 5 m mol) ethanol solution of metal(II) salts MX$_2$.nH$_2$O {M=Cu, Ni, Co, Mn; X= Cl$^-$, Br$^-$, CH$_3$COO$^-$, ClO$_4^-$, NO$_3^-$, }, with continuous stirring. The mixture was then refluxed on a water bath at 60-70°C for 2 h. The precipitate obtained in each case after cooling to room temperature were filtered and washed several times with alcohol, finally with ether and dried over anhydrous CaCl$_2$. The prepared complexes are listed below.

Antibacterial Activity: Antibacterial activity of ligand and its complexes was studied against bacteria *E. coli, S. aureus, P. aerugenosa, B. subtilius* by employing disk diffusion method [35, 36]. The pure cultures of these organisms were obtained from the Department of Biotechnology, BIET, Davanagere. The sterilized filter paper disks (Whatman 41) were loaded with known volume of the test compound of known strength using micropipette, to get the disk of desired concentration. The disks are placed over the growth media seeded with microorganisms, left for diffusion and incubated at 37±2°C for 24 h. The experiment is carried out with four replicates for each concentration. The Chlorampenicol was used as a standard and DMSO as a control under similar conditions for comparison. For each concentration, the mean diameter of inhibition zone developed (mm) was calculated.

Antifungal Activity: The antifungal studies of ligand and its complexes was tested on the fungal strains namely *A. flavus* and *A. niger* in the growth media by using Batemann poisoned food technique [37]. These fungi were cultured for seven days on Czapek's agar in sterilized petri dishes under 12/12 h light and darkness. The ligand and its metal complexes dissolved in DMSO were added to 10-15 ml of sterilized media to achieve different concentration at 35±2°C and allowed the media for solidification. The test fungi *A. flavus and A. niger* were taken as 2 mm disks from 10 days old pure colonies and placed in the petri plates containing Czapek's agar

nutritive medium. The experiments were carried out in four replicates per treatment and incubation was carried out at $22\pm2°C$ under 12/12 light and darkness. The radical growth of the colony was recorded after 96 h of incubation. The Griseofulvin was used as a standard and DMSO as a control. The average percentage inhibition was calculated by using the reported method.

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