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1-[(2,5-dioxopyrrolidin-1-yl)(phenyl)methyl] urea and 1-[(2,5-dioxopyrrolidin-1-yl)(phenyl)methyl] thiourea and its transition metal (II) complexes: Synthesis, structural characterization and antimicrobial study

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ABSTRACT

Mannich bases 1-[(2,5-Dioxopyrrolidin-1-yl)(phenyl)methyl] urea (USB) and 1-[(2,5-Dioxopyrrolidin-1-yl)(phenyl)methyl] thiourea (TSB) formed by the condensation of succinimide, benzaldehyde and urea/thiourea and its Mn^{II}, Co^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} complexes have been synthesized. Their structures have been elucidated on the basis of analytical, magnetic, electrical conductivity and spectral study as well as elemental analysis. The complexes exhibit octahedral, tetrahedral and tetragonally distorted octahedral geometries. The monomeric and non-electrolytic nature of the complexes is evidenced by their magnetic susceptibility and conductance data. Antimicrobial screening tests gave good results in the presence of metal ion in the ligand system.

KEYWORDS

Mannich bases;
Complexes;
Octahedral;
Tetrahedral;
Antimicrobial activity.

INTRODUCTION

It is well known from literature that the compounds containing amide moiety have a strong ability to form metal complexes and exhibit a wide range of biological activities[1-4]. The coordination chemistry of amide group has received much attention due to its diverse coordinating behavior and the role it plays in biological process[5]. An amide group offers two potential binding sites i.e., through oxygen/sulphur and nitrogen for complexation with protons and metal ions. Urea and related compounds have long been studied for their biological activities[6-9]. Also since N-containing compounds generally exhibit biological activity, an attempt is made to find out the biocidal activity of these complexes against a wide range of antibacterial and antifungal agents.

EXPERIMENTAL

All the reagents used for synthesizing the complexes were of A.R Grade and the solvents used were commercial products of the highest available purity. The micro elemental analysis was carried out on Vario EL III CHNS Elemental Analyzer at STIC, Kochi. Infrared spectrum was recorded in KBr medium on a Spectrum-One Perkin Elmer FTIR instrument. UV-Visible spectrum was recorded in DMF on EZ301 Perkin Elmer spectrophotometer. ^1H NMR spectrum was recorded in DMSO-d_6 using Bruker AVIII 500 MHz NMR at SAIF, IIT Chennai. Magnetic susceptibility measurements of the complexes were carried on Auto Magnetic Susceptibility Balance. Molar conductivity was measured on Systronics Direct Reading Digital Conductivity Meter 304 with dip type conductivity cell using ~10^{-3} M DMF solution of the complexes.

Antimicrobial activity

The *in vitro* biological screening effects were carried out at C.L. Baid Metha College of Pharmacy, Chennai. The complexes were tested against the bacterial species *Staphylococcus aureus*, *Micrococcus luteus*, *Escherichia coli* and *Pseudomonas aeruginosa* and fungal species *Aspergillus niger* and *Aspergillus fumigates* by paper disc diffusion method using nutrient agar and sabouraud dextrose agar as the medium. The test solutions were prepared by dissolving the compounds in DMSO. Ciprofloxacin and Ketoconazole were used as the standard for anti-bacterial and anti-fungal activities respectively.

Synthesis of mannich base (USB)

Urea (12g, 0.2M), succinimide (19.8g, 0.2M) and benzaldehyde (22ml, 0.2M) were taken in equimolar ratio. A concentrated aqueous solution of urea and succinimide was prepared. Benzaldehyde was added in drops with continuous stirring of the solution. The mixture first became oily and slowly turned into a white crystalline mass which was separated by suction filtration and washed several times with distilled water. The product was dried in the air oven at 80°C and recrystallised using acetone by slow evaporation. The percentage yield of the compound was 53 with a melting point in the range 188-190°C.

Synthesis of mannich base (TSB)

Thiourea (15.2g, 0.2M), succinimide (19.8g, 0.2M) and benzaldehyde (22mL, 0.2M) were taken in equimolar ratio. A concentrated aqueous solution of thiourea and succinimide was prepared. Benzaldehyde was added in drops with continuous stirring of the solution. The mixture first became oily and slowly turned into a white crystalline mass which was separated by suction filtration and washed several times with distilled water. The product was dried in the air oven at 80°C and recrystallised using acetone by slow evaporation. The percentage yield of the compound was 15 with a melting point in the range 197-199°C.

Synthesis of metal complexes

All the complexes of USB and TSB were isolated from non-aqueous media using methanol and ethanol. The divalent metal salts were used as such without dehydrating them. The metal chlorides and nitrates were dissolved in ethanol and the metal sulphates were dissolved in methanol. The ligand was dissolved in DMF. The hot ethanolic/methanolic solution of the metal salt was added slowly with constant stirring to the hot DMF solution of the ligand in 1:1 mol ratio. The insoluble complex formed was filtered, washed with appropriate solvent to remove the unreacted metal and ligand, dried in air and then in an air over at 80°C.

RESULTS AND DISCUSSIONS

The analytical data of USB and TSB and its metal complexes are summarized in TABLE 1 and 2. The elemental analyses show that metal ions form 1:1 complexes. All the complexes are coloured except Zn^{II} and Cd^{II} complexes which is purely white and stable at room temperature. All the complexes are soluble in DMF and

TABLE 1 : Analytical data of USB and its complexes

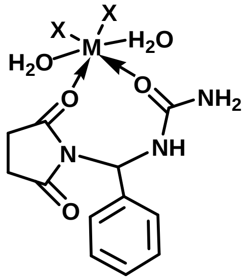
Complex	% C Obs(Cal.)	% H Obs.(Cal.)	% N Obs.(Cal.)	%Metal Obs.(Cal.)	μ_{eff} B.M
USB	58.16(58.35)	5.29(5.30)	16.96(17.01)		
$Mn(NO_3)_2$.USB. $2H_2O$	32.00(31.18)	3.10(3.71)	15.21(15.15)	12.10(11.89)	5.92
$MnSO_4$.USB. $2H_2O$	34.50(33.19)	4.00(3.95)	9.18(9.68)	11.87(12.65)	5.72
$CoSO_4$.USB.$2H_2O$	34.72(32.89)	3.66(3.91)	9.02(9.59)	13.90(13.45)	4.89
$CuCl_2$.USB.$2H_2O$	34.09(34.50)	3.81(4.10)	9.91(10.06)	14.98(15.21)	1.54
$Cu(NO_3)_2$.USB.$2H_2O$	30.02(30.61)	3.26(3.64)	14.35(14.87)	13.36(13.50)	1.70
$ZnSO_4$.USB.$2H_2O$	31.19(32.41)	3.34(3.85)	9.65(9.45)	14.67(14.70)	-
$CdCl_2$.USB	32.89(33.47)	3.15(3.04)	9.34(9.76)	26.03(26.11)	-
$CdSO_4$.USB.$2H_2O$	30.00(29.31)	3.24(3.48)	8.23(8.54)	22.74(22.86)	-
$HgCl_2$.USB	27.56(27.78)	2.95(2.53)	8.04(8.10)	38.47(38.67)	-

TABLE 2 : Analytical data of TSB and its complexes

Complex	% C Obs(Cal.)	% H Obs.(Cal.)	% N Obs.(Cal.)	%Metal Obs.(Cal.)	μ_{eff} B.M
TSB	54.60(54.75)	4.75(4.94)	15.11(15.97)		
$Mn(NO_3)_2$.TSB. $2H_2O$	31.06(30.13)	3.10(3.58)	14.21(14.64)	11.10(11.49)	5.85
$NiSO_4$.TSB.H_2O	33.85(33.05)	3.15(3.47)	9.56(9.64)	13.78(13.46)	3.59
$CuCl_2$.TSB.H_2O	34.09(34.66)	3.81(3.64)	9.91(10.11)	15.98(15.28)	1.95
$Cu(NO_3)_2$.TSB.$2H_2O$	29.17(29.60)	3.20(3.52)	14.13(14.38)	13.54(13.05)	1.98
$ZnSO_4$.TSB. H_2O	31.79(32.55)	3.34(3.41)	9.65(9.49)	14.67(14.77)	-
$CdCl_2$.TSB.H_2O	31.89(31.02)	3.08(3.25)	9.44(9.04)	25.05(24.19)	-
$HgCl_2$.TSB.H_2O	26.56(26.07)	2.95(2.73)	7.04(7.60)	36.47(36.28)	-

DMSO. Molar conductances of the complexes reveal their non-electrolytic nature. The crystal structures of the ligands USB and TSB are already reported[10,11].

In all the complexes of USB, the ν_{NH} band appeared in the region 3390-3542cm^{-1} at a much higher frequency than the free ligand. The $\nu_{C=O}$ band of succinimide appeared at a lower frequency than the free ligand, indicating the coordination of carbonyl oxygen to the metal atom. Mn^{II}, Co^{II}, Cu^{II}, Cd^{II} and Hg^{II} complexes show an increase in ν_{NH}, δ_{NH} and ν_{CNC} frequencies and lowering of $\nu_{C=O}$ of succinimide and urea, indicating that the ligand (USB) acts as a bidentate ligand coordinating through carbonyl oxygen of succinimide and urea. $CuCl_2$ and $ZnSO_4$ complexes show a decrease in ν_{NH}, δ_{NH} and ν_{CNC} frequencies, indicating that the amide N is coordinated to the metal atom in these complexes. TABLE 3 shows the IR absorption bands of USB and its complexes. Mn^{II} and Cu^{II} nitrate complex exhibits $\nu_{as(NO2)}$, $\nu_{s(NO2)}$ and ν_{NO} bands at 1384, 1383 (ν_5), 1341, 1340 (ν_1) and 1005, 1046 (ν_2) cm^{-1} respectively due to the nitrato group. The difference between the ν_5 and ν_1 bands is 43 cm^{-1} in both the complexes suggesting unidentate behavior[12-14] of the nitrato group. Mn^{II} and Co^{II} sulphato complexes shows bands due to 'SO' stretching mode ν_3 of sulphato group at 1125,1018 and 1118, 1019 cm^{-1}. The OSO bending mode ν_4 appears at 668,653,625 and 669,627, 606 cm^{-1} respectively. The ν_1 and ν_2 mode of coordinated sulphato group occurs at 821,468 and 874, 562 cm^{-1}in both these complexes. Absorption bands observed due to sulphato group in the Mn^{II} and Co^{II} sulphato complex are consistent with those normally associated with the bidentate chelating sulphato group[15,12]. Zn^{II} and Cd^{II} sulphato complexes



M = Mn^{II}, Co^{II}, Cu^{II}, and Zn^{II} X = NO_3 and SO_4

Figure 1 : USB and Mn^{II}, Co^{II}, Cu^{II}, Zn^{II} complexes

TABLE 3 : IR absorption bands of the complexes of USB

Compound	ν_{NH}	$\nu_{C=O}$	δ_{NH}	ν_{CNC}	ν_3	ν_4	ν_1	ν_2	ν_5	ν_6
USB	3364	1771, 1689	1533	1111	-	-	-	-	-	-
$Mn(NO_3)_2$.USB. $2H_2O$	3410	1714	1553	1141			1341	1005	1384	823
$MnSO_4$.USB. $2H_2O$	3424	1689	1542	1125	1125, 1018	668, 653, 625	821	468	-	-
$CoSO_4$.USB.$2H_2O$	3390	1638	1547	1118	1118, 1019	669, 627, 606	874	562		
$CuCl_2$.USB.$2H_2O$	3338	1634	1384	1102	-	-	-	-	-	-
$Cu(NO_3)_2$.USB. $2H_2O$	3434	1761	1595	1117	-	-	1340	1046	1383	869
$ZnSO_4$.USB.$2H_2O$	3353	1666	1524	1106	1151, 1141, 1020	659, 635, 623	877	564	-	-
$CdCl_2$.USB	3542	1742	1583	1153	-	-	-	-	-	-
$CdSO_4$.USB.$2H_2O$	3420	1623	1566	1111	1129, 1111, 993	642, 618	883	594		
$HgCl_2$.USB	3434	1693	1533	1177	-	-	-	-	-	-

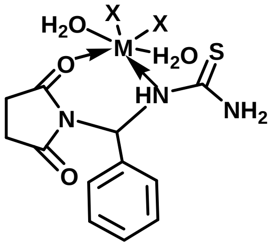
shows bands due to ‘SO’ stretching mode ν_3 of sulphato group at 1151, 1141, 1020 and 1129, 1111, 993 cm^{-1}. The OSO bending mode ν_4 appears at 659,635, 623 and 642,618 cm^{-1} respectively. The ν_1 and ν_2 mode of coordinated sulphato group occurs at 877,564 and 883, 594 cm^{-1} in both these complexes. Absorption bands observed due to sulphato group in the Zn^{II} and Cd^{II} sulphato complexes are consistent with those normally associated with the bidentate chelating sulphato group[12].

In all the complexes of TSB, the ν_{NH} band appeared at a higher frequency than the free ligand except in the case of $NiSO_4$, $CuCl_2$ and $HgCl_2$ complexes where the ν_{NH} band appeared at a lower frequency than the free ligand. TABLE 4 shows the IR absorption bands of TSB and its complexes. The $\nu_{C=O}$ band of succinimide displayed substantial negative shifts than the free ligand, indicating the coordination of carbonyl oxygen to the metal atom. The δ_{NH} and ν_{CNC} bands also suffer negative shifts than the free ligand. The ligand TSB acts as a bidentate ligand coordinating through the carbonyl oxygen of succinimide and one of the amide N in the case of Mn^{II} and Cu^{II} nitrate complexes. In the case of $NiSO_4$, $CuCl_2$, $ZnSO_4$, $CdCl_2$ and $HgCl_2$ complexes, the ligand TSB acts as a tridentate ligand coordinating through the carbonyl oxygen of succinimide, amido S and one of the amido N of thiourea. Mn^{II} and Cu^{II} nitrate complex exhibits $\nu_{as(NO2)}$, $\nu_{s(NO2)}$ and ν_{NO} bands at 1384, 1384 (ν_5), 1352, 1337 (ν_1) and 1018, 1107 (ν_2) cm^{-1} respectively due to the nitrato group. The difference between the ν_5 and ν_1 bands is 32 and 47 cm^{-1} in both the complexes suggesting unidentate behavior[12-14] of the nitrato group. Ni^{II} and Zn^{II} sulphato complexes shows bands due to ‘SO’ stretching mode ν_3 of sulphato group at 1152 and 1098 and 1151, 1112, 1020 cm^{-1}. The OSO bending mode ν_4 appears at 659 and 631 and 647 and 619 cm^{-1} respectively. The ν_1 and ν_2 mode of coordinated sulphato group occurs at 823,470 and 874, 458 cm^{-1} in both these complexes. Absorption bands observed due to sulphato group in the Ni^{II} and Zn^{II} sulphato complexes are consistent with those normally associated with the bidentate chelating sulphato group[12].

TABLE 4 : IR absorption bands of the complexes of TSB

Complex	ν_{NH}	ν_{CO}	$\nu_{C=S} + \nu_{CN} + \delta_{C-N}$	ν_{C-S}	δ_{NH}	ν_{C-N-C}	ν_3	ν_4	ν_1	ν_2	ν_5	ν_6
TSB	3399	1770, 1694	1382	753	1540	1117						
$Mn(NO_3)_2$.TSB. $2H_2O$	3408	1605	1384	765	1529	1117			1352	1018	1384	835
$NiSO_4$.TSB. H_2O	3348	1635	1352	631	1470	1098	1152, 1098	659, 631	823	470		
$CuCl_2$.TSB.H_2O	3341	1631	1352	708	1506	1103	-	-	-	-		
$Cu(NO_3)_2$.TSB.$2H_2O$	3397	1598	1418	757	1494	1107			1337	1107	1384	881
$ZnSO_4$.TSB. H_2O	3409	1616	1340	742	1482	1112	1151, 1112, 1020	647, 619	874	458	-	-
$CdCl_2$.TSB.H_2O	3459	1651	1376	680	1492	1113	-	-	-	-		
$HgCl_2$.TSB. H_2O	3364	1768	1376	738	1495	1106	-	-	-	-		

^1H NMR spectra of the ligand USB and its Zn^{II}, Cd^{II} and Hg^{II} complexes were recorded in DMSO-d_6. In the free ligand the amide protons occur at δ 6.009 and 6.91-6.889 ppm. On coordination to the metal atom the amide protons are shifted downfield. The downfield shift is due to the decrease in electron density on the atoms involved in coordination and consequent deshielding of the protons. The methylene protons of succinimide are shifted upfield. Presence of a broad peak at δ 3.35-3.36 ppm suggests the presence of lattice water in the complex or bulk water in DMSO-d_6. These support the coordination suggested by IR data.



M = Mn^{II}, and Cu^{II} X = NO_3

Figure 2 : TSB and Mn^{II}, Cu^{II} complexes

^1H NMR spectra of the ligand TSB and its Zn^{II}, Cd^{II} and Hg^{II} complexes were recorded in DMSO-d_6. In the free ligand the amide protons occur at δ 7.84

and 7.89- 7.92 ppm. On coordination to the metal atom the amide protons are shifted upfield. The upfield shift is due to modification of electron density upon coordination and the deshielding zone developed around these protons. The methylene protons of succinimide are shifted downfield. These suggest the coordination of amido N or S to the metal atom. Presence of a broad peak at δ 3.34-3.36 ppm suggests the presence of lattice water in the complex or bulk water in DMSO-d_6. These support the coordination suggested by IR data.

The manganese (II) complexes of USB show magnetic moments in the range 5.72-5.92 B.M at room temperature corresponding to five unpaired electrons. The electronic spectra of the Mn^{II} complexes exhibit four weak intensity absorption bands in the range 17605-18049, 23255-23684, 25445-26315 and 32154-36764 cm^{-1}. These bands may be assigned to[16] transitions: $^6A_{1g}\rightarrow{}^4T_{1g}$ (^4G), $^6A_{1g}\rightarrow{}^4E_{1g}$, $^4A_{1g}$ (^4G), $^6A_{1g}\rightarrow{}^4E_g$ (^4D), $^6A_{1g}\rightarrow{}^4T_{1g}$ (^4P). The position of these bands suggests a high spin octahedral environment around the Mn^{II} ion.

The Mn^{II} nitrate complex of TSB show a magnetic moment of 5.85 B.M at room temperature corresponding to five unpaired electrons. The electronic spectra of the Mn^{II} nitrate complex exhibit four weak intensity absorption bands in the range 18021, 24986, 29135 and 31293 cm^{-1}. These bands may be assigned to[16] transitions: $^6A_{1g}\rightarrow{}^4T_{1g}$ (^4G), $^6A_{1g}\rightarrow{}^4E_{1g}$, $^4A_{1g}$ (^4G), $^6A_{1g}\rightarrow{}^4E_g$ (^4D), $^6A_{1g}\rightarrow{}^4T_{1g}$ (^4P). The position of these bands suggests a high spin octahedral environment around the Mn^{II} ion.

At room temperature the Co^{II} sulphate complex of USB show a magnetic moment of 4.89 B.M. corresponding to three unpaired electrons. The electronic spectra of the Co^{II} sulphate complex recorded in DMF solution exhibit absorption in the region 7127, 14945, 18761 and 27624, 34246 cm-1. These bands may be assigned to $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$, $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ respectively. The fourth band is due to charge transfer. The position of these bands suggests an octahedral environment around the Co^{II} ion[17].

The magnetic moments of the Cu^{II} complexes of USB were recorded at room temperature. The complexes show magnetic moments in the range 1.54-1.70 B.M. corresponding to one unpaired electron. The electronic spectra of Cu^{II} complexes in DMF exhibit bands in the range 9141-9174, 12019-12114, 14706-15106 and 24791-26596, 30030-32623 cm^{-1}. These bands may be assigned to $^2B_1g\rightarrow{}^2A_{1g,}$ $^2B_{1g}\rightarrow{}^2B_{2g}$ and $^2Eg\rightarrow{}^2T_{2g}$ (F) respectively. The fourth band may be due to charge transfer. The position of these bands suggests a tetragonally distorted octahedral environment around the Cu^{II} ion.

The magnetic moment of $NiSO_4$ complex of TSB were recorded at room temperature. The complex shows a magnetic moment of 3.59 B.M. The electronic spectra of $NiSO_4$ complex in DMF exhibit bands in the region 9090, 14903, 25252, 11848, 20661 and 36101 cm^{-1}. These bands may be assigned to $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$, $^3A_{2g}(F)\rightarrow{}^1E_g$ and $^3A_{2g}(F)\rightarrow{}^1T_{1g}$. The fourth band may be due to charge transfer. The position of these bands suggests a octahedral environment around the Ni^{II} ion.

The magnetic moments of the Cu^{II} complexes of TSB were recorded at room temperature. The complexes show magnetic moments in the range 1.95-1.98 B.M corresponding to one unpaired electron. The electronic spectra of Cu^{II} complexes in DMF exhibit bands in the range 10449-10526,11820-12020, 15948-16181 and 23365,36232-26584,31034 cm^{-1}. These bands may be assigned to $^2B_1g\rightarrow{}^2A_{1g,}$ $^2B_{1g}\rightarrow{}^2B_{2g}$ and

TABLE 5 : IR Absorption bands due to coordinated water molecules in USB complexes

Complex	ν_{OH}	δ_{HOH}	ρr_{HOH}	ρw_{HOH}	M-O
$Mn(NO_3)_2.USB.2H_2O$	3410	1714	823	600	476
$MnSO_4.USB.2H_2O$	3424	1689	821	605	468
$CoSO_4.USB.2H_2O$	3428	1707	823	602	488
$CuCl_2.USB.2H_2O$	3440	1634	848	607	484
$Cu(NO_3)_2.USB.2H_2O$	3434	1761	869	679	471
$ZnSO_4.USB.2H_2O$	3421	1666	877	623	564
$CdSO_4.USB.2H_2O$	3420	1623	883	618	594

TABLE 6 : IR Absorption bands due to coordinated water molecules in TSB complexes

Complex	ν_{OH}	δ_{HOH}	ρr_{HOH}	ρw_{HOH}	M-O
$Mn(NO_3)_2.TSB.2H_2O$	3408	1605	823	620	467
$NiSO_4.TSB.H_2O$	3348	1635	823	631	470
$CuCl_2.TSB.H_2O$	3441	1631	847	633	477
$Cu(NO_3)_2.TSB.2H_2O$	3397	1598	881	623	470
$ZnSO_4.TSB.H_2O$	3409	1616	874	619	458
$CdCl_2.TSB.H_2O$	3459	1651	864	680	535
$HgCl_2.TSB.\ H_2O$	3364	1768	847	659	458

${}^2Eg \rightarrow {}^2T_{2g}$ (F) respectively. The fourth band may be due to charge transfer. The position of these bands suggests a tetragonally distorted octahedral environment around the Cu^{II} ion[18].

Antimicrobial activity

Antibacterial activities of USB and its metal complexes such as $CuCl_2.USB.2H_2O$ (1C1), $Cu(NO_3)_2.USB.2H_2O$ (1C8), $Mn(NO_3)_2.USB.2H_2O$ (1C10) and $CoSO_4.USB.2H_2O$ (1C14) were studied. These complexes were tested in-vitro against four bacterial species *Staphylococcus aureus*, *Micrococcus luteus*, *Escherichia coli* and *Pseudomonas aeruginosa* by paper disc diffusion method. The results obtained are tabulated in the TABLE 5. The zone of inhibition of the compounds is given in millimeters. The comparative study of the ligand and its complexes indicates that the metal chelates exhibit higher activity than the free ligand. The order of activity towards *Staphylococcus aureus*: 1C14 >1C8 > 1C1> 1C10 > USB; *Micrococcus luteus*: 1C14 > 1C10 > 1C8 > 1C1 > USB; *Escherichia coli*: 1C8 > 1C10 > 1C1 > 1C14 > USB; *Pseudomonas aeruginosa*: 1C1 > 1C8 > 1C14 > 1C10 > USB. Co^{II} sulphate complex shows the highest activity against the *Staphylococcus* aureus and *Micrococcus luteus* bacterial species. The least active against the *Staphylococcus* and *Micrococcus* bacterium is manganous nitrate and cupric chloride complexes. The highest activity against *Escherichia coli* bacterium is shown by cupric nitrate and least by Co^{II} sulphate. The highest activity against *Pseudomonas aeruginosa* is shown by cupric chloride and least by manganous nitrate complexes. The Cu^{II} nitrato complex is having a pseudo tetrahedral geometry and coordinately unsaturated, and hence it exhibits a tendency to get saturated by linking with the protein, leading to the inhibition of its growth. Morever, steric constraints are less for a tetrahedral complex than for an octahedral complex and so the tetrahedral complexes are more active than the octahedral complexes. Co^{II} is an essential micronutrient during transcription and transformation of nucleic acids, and hence its complex has higher activity. These complexes were tested in-vitro against two antifungal species namely *Aspergillus niger* and *Aspergillus fumigates*. The antifungal activities of these compounds were determined by sabouraud dextrose agar medium in paper disc diffusion method. The order of activity towards *Aspergillus niger*: 1C1>1C8>1C14>1C10>USB; *Aspergillus fumigates*: 1C1>1C8>1C10>1C14>USB. The Cu^{II} complexes showed higher activity against both the fungal species. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to combined activity effect of the metal and the ligand. Such increased activity of the metal chelates can be explained on the basis of

TABLE 7 : Antibacterial and antifungal activity of USB and its complexes (zone of inhibition in mm)

Compound	Conc (µl)	S. aureus (mm)	M. luteus (mm)	E. coli (mm)	P. aeru (mm)	A.niger (mm)	A.fumigates (mm)
USB	25	13	17	13	15	12	10
	50	19	19	18	18	23	17
	100	15	21	15	17	27	21
$CuCl_2.USB.2H_2O$ (1C1)	25	13	16	13	19	19	14
	50	19	19	19	23	23	18
	100	21	21	24	28	29	22
$Cu(NO_3)_2.USB.2H_2O$ (1C8)	25	14	19	15	17	16	13
	50	22	22	21	20	20	19
	100	25	24	26	21	23	23
$Mn(NO_3)_2.USB.2H_2O$ (1C10)	25	13	19	14	15	14	13
	50	15	23	18	19	19	17
	100	23	26	20	22	21	20
$CoSO_4.USB.2H_2O$ (1C14)	25	15	19	12	16	15	12
	50	18	24	15	21	18	18
	100	24	27	18	24	22	20

Overtone's concept[19] and the Tweedy's chelation theory[20]. The lipid membrane that surrounds the cell favours the passage of only lipid soluble materials due to which lipophilicity is an important factor which controls the antimicrobial activity. On chelation the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with the donor groups. Further it increases the delocalization of the π-electron over the whole chelate ring and enhances the liposolubility of the complexes. This increased liposolubility enhances the penetration of the complexes into the lipid membrane and blocks the metal binding sites in the enzymes of the microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restrict further growth of the organisms.

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