A New Mannich Base Derived from Benzamide, Benzaldehdye and Pyrrolidine: Preparation, Spectral Characterization and Biological Studies of Some of its Transition Metal Chelates

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Abstract

The synthesis of a new Mannich base ligand N-[Phenyl(pyrrolidin-1-yl)methyl]benzamide was carrying out the reaction between the ethanolic solution of benzamide, benzaldehdye and pyrrolidine. Elemental analysis and spectral data (IR, ¹H NMR, ¹³C NMR, UV-Vis and Mass) confirm the structure of the synthesized ligand. Some transition metal complexes of VO^{IV}, Mn^{II}, Fe^{II}, Ni^{II} and Cu^{II} with the above Mannich base ligand have been prepared and characterized by elemental analysis, conductivity and magnetic measurements, IR, UV and EPR spectral studies. Based on the IR data, it was found that the ligand acts as a neutral bidentate in nature. The complexes are

non-electrolytic in DMF. The presence of the coordinated water molecules in some of the complexes was indicated by IR spectra. It was found that Ni^{II} chloro and nitrato and Cu^{II} sulphato complexes exhibit tetrahedral geometry and the remaining show octahedral geometry. All the synthesized compounds were evaluated in vitro for their antimicrobial activity against six bacterial species and two fungal species using Disc Diffusion technique. Most of them exhibit significant antibiological activity, when compared with standard drugs.

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Keywords: Mannich base, octahedral geometry, metal chelate, antibiological activity

Introduction

Coordination chemistry stands as a landmark in the field of scientific advancement, embracing most diverse branches of science, engineering and technology[1]. Metal complexes of Mannich bases form a group of less investigated compounds. However, recently more efforts are being made to synthesize, characterize and these investigate the biological activities of compounds[2]. Many Mannich base complexes possess very promising biological activities[3-5] as anticancer agents, antibacterial agents, anticonvulsant agents, anti tuberculosis agents, pain-relief agents, anti-dermatitis agents and antimicrobial agents. In addition to their medical uses, some of the complexes have found other uses in the agricultural and industrial fields[6,7]. The reactivity of coordination compounds has dramatically changed as inferred from the present studies. Some interesting reactions of substituted benzamide chelates^[8] of copper and nickel, in which the organic groups attached to nitrogen of the donors are altered, have been reported. The importance and application of metal complexes in analytical chemistry are well known. The Mannich base ligands play an important role in some biological systems and their function is related, at

least in part, to its chelating ability with metals[9]. In view of the importance of such a work and in continuation of our recent work on the synthesis of unreported Mannich base complexes, it was therefore considered worthwhile to synthesize some new benzamide derivatives with pyrrolidine residue. Thus, the synthesis of a new compound *N*-[Phenyl(pyrrolidin-1-yl)methyl]benzamide has been carried out.

Experimental

All the reagents used for synthesizing the ligand and its complexes were of A.R. grade and the solvents used were commercial products of the highest available purity and were further purified by distillation.

Micro elemental data were obtained with Carlo Erba 1108 elemental analyzer. Metal contents were estimated by usual procedure[10], after digesting the complexes with con.HNO₃. Conductance data were obtained in $\sim 10^{-3}$ M DMF solution of the complexes using digital conductivity meter. IR spectra were recorded using Perkin Elmer FT-IR spectrometer by

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using KBr pellets. Absorbance in UV-Visible region was recorded in DMF solution using UV-Visible spectrometer. The ¹H and ¹³C NMR of the ligand were recorded on a Bruker instrument employing TMS as internal reference and DMSO-d₆ as solvent. The FAB mass for the ligand was carried out using Mass spectrometer. The room temperature magnetic susceptibility measurements of the complexes were made by using a Gouy Magnetic Balance.

Synthesis and characterization of the ligand

N-[Phenyl(pyrrolidin-1-yl)methyl]benzamide(PBB) was synthesized by employing the Mannich synthetic route[11]. Benzamide (12.1 g, 0.1 mol) was dissolved in minimum quantity of ethanol. To this solution, benzaldehdye (10 mL, 0.1 mol) followed by pyrrolidine (7.1 mL, 0.1 mol) were added with constant stirring in an ice bath. After 20 days, the pale yellow solid obtained was washed with water and with acetone. The compound was dried in air and then in an air oven and recrystallised from ethanol. It was insoluble in water and soluble in organic solvents.

Molecular formula: $C_{18}H_{20}N_2O$, Yield: 86%, MP: 76-80°C, Mol.wt: 280, FT-IR KBr in cm⁻¹: 3346(NH), 1634(C=O), 3057, 3033(v_{CH} aromatic), 2965, $2873(v_{CH} alicyclic), 2801(v_{CH} aliphatic), 1147(C-N-C),$ $1578(v_{C=C}, v_{C-N})$, $1515(\delta_{NH}$ secondary amide), $1029(\delta_{CH})$ i.p.b benzene), $930(\delta_{CH} + o.p.b \text{ of pyrrolidine})$, 908, 1.5.6 defized by 950(d_{CH} + 0.5.6 df pyrtonume), 908, 868(δ_{NH} wagging and twisting), 719(δ_{CH} o.p.b benzene), 540($\pi_{\text{C=O}}$), 505(o.p.b ring C=C). ¹H NMR (300MHz, DMSO-d₆) δ 8.92(s, NH), 5.86 & 5.83 (d, CH), 7.93 -7.54(m, 5H amido phenyl ring), 7.48 - 7.25(m, 5H aldehydic phenyl ring), 2.56(s, N(CH₂)₂ at α , α^{1}), 1.69(s, (CH₂)₂ at β , β^{1}). ¹³C NMR (300MHz, DMSO-d₆) 168.39 (s,C=O), 141.58- 127.75(m, 6C aldehydic phenyl ring), 127.95(m, 134.83-6C, amido phenyl ring), 70.44(s,methine C), 49.60 (s, Pyrrolidine N(CH₂)₂ at α , α^{1}), 23.71 (s, Pyrrolidine (CH₂)₂ at β , β^{1}). UV-Vis(DMF) $263(n \rightarrow \pi^*)$, $235(\pi \rightarrow \pi^*)$. FABMS m/z $280(C_{18}H_{20}N_2O), m/z = 204 (C_{12}H_{15}N_2O^+), m/z = 126$ $(C_6H_{10}N_2O^+)$, m/z = 70 ($C_4H_8N^+$). Calculated: C 77.14%, H 7.14% and N 10.00%. Found: C 76.91%, H 7.28% and N 9.06%.



Figure 1 PBB (Tentative structure proposed for *N*-[Phenyl(pyrrolidin-1-yl)methyl]benzamide)

Based on the data obtained from various physical[12] and chemical studies[13], the molecular structure of PBB is shown in **Figure 1**.

Synthesis of metal complexes

The methanolic solution of the metal salts was added slowly with constant stirring to the ethanolic solution of the ligand in 2:1 mol ratio at warm condition. The insoluble complexes[14] formed were filtered, washed with ethanol and methanol to remove the unreacted metal and ligand, and then dried at 80°C.

Antimicrobial Screening

Antibacterial and antifungal activities[15] of the ligand and seven of its metal complexes were tested *in vitro* against six bacterial species viz *E.coli*, *P.aeruginosa*, *S.typhi*, *B.subtilis*, *S.pyogenes*, *S.aureus* and two fungal species *A.niger* and *A.flavus* by disc diffusion method⁸ using agar nutrient as medium and gentamycin as control. The paper disc containing the compound (10, 20 and 30 µg/disc) was placed on the surface of the nutrient agar plate, previously spread with 0.1 mL of sterilized culture of microorganism. After incubating this at 37°C for 24 hrs, the diameter of inhibition zone around the paper disc was measured.

Results and Discussion

The percentages of the metal ions, anions and CHN were determined in order to find the stoichiometry[16] of the complexes. The electrical conductance measurements of the $\sim 10^{-3}$ M DMF solutions at room temperature revealed that, all the complexes are non-electrolytes(**Table 1**).

The IR spectrum of the VO^{II}, Mn^{II} and Fe^{II} sulphato complexes registered lower frequency values for the C=O and CNC by about 90, 12 & 14 and 21, 25 & 03 cm⁻¹ (when compared to the free ligand values) respectively. In Ni^{II} chloro & nitrato and Cu^{II} nitrato & sulphato complexes, the carbonyl stretching frequency of the free ligand at 1634 cm⁻¹ suffers a negative shift of 12, 06, 07 & 22 cm⁻¹ and the v_{CNC} of the free ligand at 1147 cm⁻¹ suffers a negative shift of 46, 44, 46 & 55 cm⁻¹. The above data suggest a bidentate coordination of the ligand[17] (**Table.2**).

The IR spectra of the nitrato complexes of Ni^{II} and Cu^{II} show a band at 1305, 1300 (v_1), 1052, 1062(v_2), 1384, 1391(v_5) and 834, 992 (v_6) cm⁻¹ respectively due to the nitrato group. The difference between v_5 and v_1 is 79 and 91 cm⁻¹, which points to the unidentate behaviour of nitrate.

The v_3 of sulphato group bands appear at 1126, 1122, 1144 & 1154 and 1050, 1018, 1017& 1092 and 1013 & 996 cm⁻¹. The corresponding v_4 bands appear at 682, 653, 664 & 659 and 660, 626, 625 & 634 and 648, 607,

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603& 618 cm⁻¹. The v_1 and v_2 modes occur at 771, 823, 828 & 865 and 536, 529, 526 & 498 cm⁻¹ respectively. Absorption bands observed in all the sulphato complexes were associated with the bidentate[18] chelating sulphato group.

Bands appearing at (3657, 3376, 3354, 3548 & 3448), (1645, 1622, 1637, 1627 & 1615), (771, 823, 828, 835 & 848), (682, 653, 665,679 & 596) and (536, 529, 526, 457 & 454) cm⁻¹ are assigned to v_{OH} , δ_{HOH} , ρ_{THOH} , ρ_{WHOH} and v_{M-O} modes respectively of coordinated water[19] in the sulphato complexes of VO^{II}, Mn^{II}, Fe^{II} and Cu^{II} and chloro complex of Cu^{II}.

Far-IR spectrum furnishes information regarding the formation of metal-chloride bond[20] in Cu^{II} chloro complex. The bands observed at 570 & 526, 484, 422 & 380 and 250 cm⁻¹ are assigned to the M-O, M-N and M-Cl stretching modes respectively.

The UV-Visible spectrum[21] of VO^{IV} sulphato complex shows absorption bands at 14499, 16602 and 27030 cm⁻¹ which indicate ${}^{2}B_{2}\rightarrow{}^{2}E_{2}$, ${}^{2}B_{2}\rightarrow{}^{2}B_{1}$ and ${}^{2}B_{2}\rightarrow{}^{2}A_{1}$ transitions. The EPR spectrum of this complex shows only one resolution at g_{||} region; so it can be assumed that g_x and g_y are same or nearly the same[22]. The g value of 1.8903 indicates the strong interaction between the ligand and the metal ion. The complex displays a strong V=O stretching at 771 cm⁻¹. The room temperature magnetic moment value is 1.57 B.M. which suggests a hexa coordinate geometry around VO^{IV} ion(**Figure 2**).



Figure 2 VOSO₄.PBB.H₂O (Tentative structure proposed for VO sulphato complex)

The UV-Visible spectrum[23] of Mn^{II} sulphato complex shows absorption bands at 18049 cm⁻¹ due to ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(G)$ transition, at 24986 cm⁻¹ due to ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}, A_{1g}(G)$ transition, at 29135 cm⁻¹ due to ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}(D)$ transition and at 31274 cm⁻¹ due to ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(P)$ transitions respectively. The magnetic moment value was found to be 5.96 B.M. suggestive of a high spin octahedral geometry (Figure 3).

The electronic spectrum of Fe^{II} sulphato complex exhibits a strong intense band at 11258 cm⁻¹ due to ${}^{5}\text{T}_{2g} \rightarrow {}^{5}\text{E}_{g}$ transition and the CT band at 23402 cm⁻¹ which obscures the other very low intensity d-d absorption bands. The μ_{eff} value of 5.67 B.M. points to a hexa coordinate[23] geometry(**Figure 4**).



Figure 3 MnSO₄.PBB.2H₂O (Tentative structure proposed for Mn sulphato complex)



Figure 4 FeSO₄.PBB.2H₂O (Tentative structure proposed for Fe sulphato complex)

The Ni^{II} chloro and nitrato complexes exhibit bands at 3917 & 3870 cm⁻¹ due to ${}^{3}T_{1g}(F) \rightarrow {}^{3}T_{2g}(F)$ transition, at 8402 & 8413 cm⁻¹ due to ${}^{3}T_{1g}(F) \rightarrow {}^{3}A_{2g}(F)$ transition and at 15036 & 15389 cm⁻¹ due to ${}^{3}T_{1g}(F) \rightarrow {}^{3}T_{2g}(P)$ transition respectively. The charge transfer transition band for the chloro compound occurs at 25675 cm⁻¹ and for the nitrato complex appears at 28561 & 24555 cm⁻¹. The $\mu_{eff.}$ values for the chloro and nitrato complexes are 3.80 and 4.36 B.M. respectively, indicating tetrahedral environment[24] around Ni^{ff} ion(**Figure 5&6**).



Figure 5 NiCl₂.PBB (Tentative structure proposed for VO chloro complex)



Figure 6 Ni(NO₃)₂. PBB (Tentative structure proposed for VO nitrato complex)

The sulphato complex of Cu^{II} exhibits electronic absorption bands: at 9145 cm⁻¹ due to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$, at 11078 cm⁻¹ due to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$, at 12804 cm⁻¹ due to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}(F)$ and the bands observed at 34472 & 35699 cm⁻¹ due to charge transfer transitions. The μ_{eff} value of sulphato complex is 2.78 B.M. which suggests a distorted tetrahedral geometry. Nitrato complex of Cu^{II} exhibits electronic absorption bands at 8245 cm⁻¹ due to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$, 11328 cm⁻¹ due to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$, 14650 cm⁻¹ due to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}(F)$ and the bands at 26392 & 35675 cm⁻¹ are assigned due to charge transfer transitions respectively. The μ_{eff} value (1.89 B.M.) of nitrato complex indicate that the complex is magnetically diluted and has a distorted octahedral geometry[25].

The X band EPR spectra[22] of the nitrato and sulphato complexes of Cu^{II} were recorded at LNT(**Table 3**). The g values of the nitrato complex of Cu^{II} are in the trend, $g_{\parallel} > g_{\perp} > g_{DPPh}$ suggesting that the unpaired electron lies predominantly in the d_{x2-y2} orbital. The complex showed EPR spectra of axial symmetry type indicating planar based distorted octahedral geometry around copper centre.

The g_{||} values of nitrato and sulphato complexes are less than 2.30 indicating the covalent nature. The higher g_{\parallel} values may be due to the coordination of H_2O Cu^{II} ion in the nitrato complex. The axial to the symmetry parameter G value[26] which is a measure of interaction between the metal centers in the crystalline solid for the sulphato complex of Cu^{II} is 4.95 and this suggests the lack of charge interaction between two Cu^{II} centres in the unit cell of the complex. The value of G is less than 4 for the nitrato complex of Cu^{II} . It shows considerable coupling and appreciable misalignment of the local tetragonal axes, leading to an exchange interaction of free electron between two copper centers in the solid state. Based on the above discussions, six coordinated tetragonally distorted octahedral geometry may be assigned to the nitrato complex and pseudo tetrahedral structure for the sulphato complex of Cu¹¹(**Figure 7&8**).



Figure 7 Cu(NO₃)₂.PBB.2H₂O (Tentative structure proposed for Cu nitrato complex)



Figure 8 CuSO₄.PBB (Tentative structure proposed for Cu sulphato complex)

Complex	% C Obs (Cal.)	% H Obs. (Cal.)	% N Obs. (Cal.)	%Metal Obs. (Cal.)	%Anion Obs. (Cal.)	$\Lambda_{ m M}$ ohm ⁻¹ cm ² mol ⁻¹
VOSO ₄ .PBB. H ₂ O	38.70	4.12	4.85	8.99	18.10	31.65
	(39.20)	(3.63)	(5.08)	(9.25)	(17.42)	
MnSO ₄ . PBB.2H ₂ O	39.32	4.04	4.75	10.63	18.00	19.82
	(40.07)	(3.71)	(5.19)	(10.19)	(17.42)	
FeSO ₄ .PBB. 2H ₂ O	36.68	3.10	5.08	9.16	16.97	24.07
	(36.36)	(3.37)	(4.71)	(9.40)	(16.16)	
NiCl ₂ .PBB	42.34	3.29	5.01	10.89	14.19	43.13
	(41.70)	(3.86)	(5.41)	(11.33)	(13.68)	
Ni(NO ₃) ₂ .PBB	38.00	3.90	5.12	9.95	22.14	15.49
	(37.83)	(3.50)	(4.91)	(10.28)	(21.72)	
Cu(NO ₃) ₂ . PBB.2H ₂ O	39.32	4.19	4.96	12.07	21.85	29.41
	(38.71)	(3.94)	(5.02)	(11.39)	(22.22)	
CuSO ₄ .PBB	41.22	4.09	4.95	11.74	18.81	12.55
	(40.83)	(3.78)	(5.29)	(12.01)	(18.15)	

Table 1 Analytical and Conductance Data for VO ^{IV} , Mn ^{II} , Fe ^{II} , Ni ^{II} and Cu ^{II}
Complexes of PBB

Table 2 Important IR Absorption Bands (cm ⁻¹) of PBB and of VO ^{IV} , Mn ^{II} ,
Fe^{II} , Ni^{II} and Cu^{II} Complexes

Compound	v _{NH}	v _{C=0}	V _{CNC}	v ₃	v 4	v 1	v ₂	v 5	v 6
PBB	3346	1634	1147	-	-	-	-	-	-
VOSO ₄ .PBB.H ₂ O	3409	1544	1126	1126,	682,	771	536	-	-
				1050,	660,				
				1013	648				
MnSO ₄ .PBB.2H ₂ O	3376	1622	1122	1122,	653,	823	529	-	-
				1018	626,				
					607				
FeSO _{4.} PBB.2H ₂ O	3354	1620	1144	1144,	664,	828	526	-	-
				1100,	625,				
				1017	603				
NiCl ₂ .PBB	3395	1622	1101	-	-	-	-	-	-
Ni(NO ₃) ₂ .PBB	3401	1628	1103	-	-	1305	1062	1384	992
Cu(NO ₃) ₂ .PBB.2H ₂ O	3548	1627	1101	-	-	1300	1052	1384	834
CuSO ₄ .PBB	3229	1622	1092	1154,	659,	865	475	-	
				1092,	634,				
				996	618				

Table 3 EPR Spectral Parameters of Cu^{II} Complexes

Complex	g∥	g⊥	\mathbf{g}_{av}	G
Cu(NO ₃) ₂ .PBB.2H ₂ O	2.02	1.98	1.99	1.44
CuSO ₄ .PBB	2.09	2.02	2.05	4.95

Compound	1	E. col	li	1	P. aer.			S. typhi.			B. sub			S. pyo			S. aur		
Conc. (µg/disc)	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30	
Control	09	12	17	06	09	15	10	12	16	08	14	18	14	19	22	10	10	18	
PBB	12	15	20	10	13	18	14	17	22	11	14	18	10	12	16	12	17	20	
VOSO ₄ .PBB.H ₂ O	16	18	23	14	19	24	14	19	26	14	19	27	17	23	28	18	23	30	
MnSO ₄ .PBB.2H ₂ O	14	20	21	16	16	21	14	15	21	12	18	24	16	21	26	12	19	25	
FeSO _{4.} PBB.2H ₂ O	18	21	24	17	22	27	20	28	30	23	26	32	18	24	29	25	28	35	
NiCl ₂ .PBB	25	27	36	22	26	39	25	32	40	21	30	39	25	28	35	23	29	39	
Ni(NO ₃) ₂ .PBB	20	26	30	19	24	35	20	27	33	18	22	28	18	20	26	19	24	30	
Cu(NO ₃) ₂ .PBB.2H ₂ O	22	29	32	23	26	32	21	26	32	20	29	31	20	24	31	26	28	34	
CuSO ₄ .PBB	26	32	45	24	28	40	25	34	44	23	31	42	28	32	40	26	32	41	

Table 4 Antibacterial Activity of Ligand and its Complexes

Table 5 Antifungal Activity of Ligand and its Complexes

Compound	1	E. col	i	1	P. aer.			S. typhi.			B. sub			S. pyo			S. aur		
Conc. (µg/disc)	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30	
Control	08	11	14	06	09	10	08	10	16	07	07	12	10	13	14	09	12	15	
PBB	09	13	16	08	12	14	10	12	17	10	13	16	11	15	16	11	14	18	
VOSO ₄ .PBB.H ₂ O	12	15	18	10	13	16	11	13	18	12	14	16	14	14	17	13	15	19	
MnSO ₄ .PBB.2H ₂ O	16	18	20	14	16	18	14	16	20	15	18	21	15	17	20	16	18	24	
FeSO _{4.} PBB.2H ₂ O	15	18	21	12	17	22	16	19	22	14	19	24	15	20	23	17	20	25	
NiCl ₂ .PBB	18	21	24	17	22	27	20	28	30	23	26	32	18	24	29	25	28	35	
Ni(NO ₃) ₂ .PBB	16	20	22	14	18	20	15	18	22	19	20	26	18	18	24	14	20	26	
Cu(NO ₃) ₂ .PBB.2H ₂ O	19	23	28	16	22	29	18	23	28	20	27	37	16	22	35	24	29	40	
CuSO ₄ .PBB	21	29	37	19	24	35	18	23	33	26	30	41	22	29	39	26	31	47	

Antimicrobial activity

The inhibition zone of the compounds under investigation is compared and listed in Tables 4 and 5. It shows that, Cu^{II} sulphato complex exhibits highest antibacterial and antifungal activity against all the eight species mentioned above. They have larger diameters of inhibition zones than the control gentamycin at the same concentration and identical conditions. Antimicrobial activity of metal chelates can be explained on the basis of chelation theory[27]. Chelation reduces the polarity of the copper ion mainly because of the partial sharing of its positive charge with the donor groups and possibly the π -electron delocalization within the whole chelate ring system thus formed during coordination. This process of chelation thus increases the lipophilic nature of the copper ion, which in turn favors its permeation through the lipid layer of the membrane [28]. This in turn, is responsible for increasing the hydrophobic character and liposolubility of the molecule in crossing cell membrane of the microorganism. Hence it enhances the biological utilization ratio and activity of the testing compound. The enhanced activity of the complexes may also be explained on the basis of their solubility[29]. In Cu^{II} sulphato complex, the unsaturated metal center present, achieves higher coordination number by binding with some of the functional groups of the protein. This leads to the increased uptake of the compound by the bacterium and thereby inhibiting its growth. Steric constraints are less for a tetrahedral complex than for an octahedral complex. So the tetrahedral complexes are biologically more active than the octahedral complexes. Transition metal complexes of many O, N, and S donors show higher antibacterial and antifungal activities compared to the respective ligand[30].

Conclusion

 VO^{IV} , Mn^{II} , Fe^{II} , Ni^{II} and Cu^{II} metal chelates of a new Mannich base *N*-[Phenyl(pyrrolidin-1-yl)methyl]benzamide(PBB) were synthesized and characterized by various chemical and spectral analysis. Based on the spectral data, the ligand was found to act as bidentate to the metal ion through CO and CNC groups. Chloro and nitrato complexes of Ni^{II} and Cu^{II} sulphato complex exhibit tetrahedral geometry and the remaining complexes show octahedral geometry. The synthesized ligand and their metal complexes were screened for biological activities. All the compounds showed antibacterial and antifungal activities. The Cu^{II} sulphato complex was more active than the rest.

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