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Synthesis, characterization, stability constant and microbial activity of schiff bases and their Co^{II}, Ni^{II}, Cu^{II} & Zn^{II} Metal Chelates

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Abstract

The three new Schiff bases derived from 4-(p-bromophenyl)-2-amino-thiazole and R-substituted 2-hydroxyacetophenone (R = H, 5-CH_3 and 5-Cl) and transition metals (Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}). The complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility and spectral studies (IR & UV). The metal coordinates with thiazole ring nitrogen atom, azo nitrogen atom and phenolic oxygen atom. The NNO donor ligand acts as a tridentate ligand in all complexes. The complexes have 1:2 (metal-ligand) stoichiometry and an octabedral geometry.

The thermodynamic parameter ΔH, ΔG and ΔS also calculated at elevated temperature (25, 35 & 45 °C) ΔH and ΔG are negative, while ΔS is positive.

The Schiff bases whose antibacterial and antifungal activities are checked and found that they are active and inactive respectively.

Keywords: Schiff base, metal complexes, biological activity, stability constant.

1. Introduction

Hugo Schiff [1] in 1964 described the condensation between aldehyde or ketone and amine leading to a Schiff base (R-CH=N-R) Schiff base ligands are able to coordinate metals through imine (-CH=N-) Nitrogen and other groups containing donor atom.

Schiff base ligands are considered as ‘Privileged Ligands’ [2]. Because they are easily synthesized by condensation between aldehyde or ketone and amine. Schiff bases are able to coordinate many different metals and to stabilize them in various oxidation state due to stereogenic centre or other elements of chirality (plane, axes).

The Chemistry of Schiff bases and their metal complexes is now attending importance in diverse fields like catalysis, medicine, micro and nano analysis, separation of ions, preconcentration technique electrolysis and in agriculture. It is therefore necessary to study in great details new Schiff bases and the metal complexes in view as synthesis, spectral, characterization (UV-Visible, IR, NMR and MASS etc). Structural bonding, stereochemistry, microbial activity.

Now we are in a position to throw light on the new Schiff bases and their metal complexes prepared by the condensation of substituted amino thiazole and substituted Aurones.

Experimental

Preparation of Schiff bases

2. Material and Methods

2.1 Synthesis of aminothiazole

4-(p-bromophenyl)-2-aminothiazole

All chemicals purchased from E-Merk (A.R.grade) and used. The 4-(p-bromophenyl)-2-aminothiazole synthesized by the known literature, methods [3-5]. The filtrate was treated with concentrated ammonia to librale the base. The product (I) obtained was recrystallised from 50% ethanol. M.P. 179 °C (lit 181 °C)

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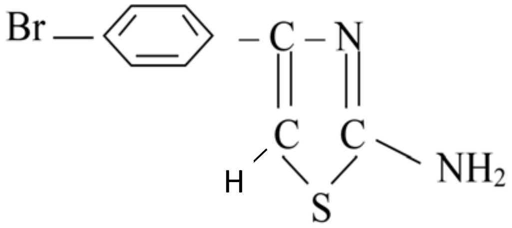

(I)

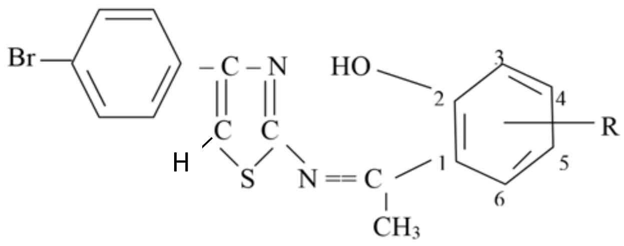
II) Aurones – 1) 2-hydroxy-acetophenone
2) 2-hydroxy-5-methyl acetophenone
3) 2-hydroxy-5-chloroacetophenone
Purchased from E-merk (A.R. Grade)

2.2 Synthesis of amino thiazole Schiff base (ligand)

A solution of 2-hydroxyacetophenone in ethanol was added to the ethanolic solution of 4-(p-bromophenyl)-2-aminothiazole in equimolar quantity. The mixture was refluxed on a water bath for 2 hrs. The Schiff base, thus formed was filtred and recrystallized from ethanol and dried under vacuum purity of the Schiff base was checked by molecular weight determination, elemental analysis and TLC. Elemental analysis and molecular weight listed in table No. 1 and IR frequencies in table No. 2.

Following Schiff base were prepared

1. *N-(2Hydroxyphenylmethylidene-4(p-bromophenyl)-2-aminothizole 2HPMBPAT*
2. *N-(2Hydroxy-5-methyphenymethylidene-4(p-bromophenyl)2-aminothizole 2H5MPMBPAT*
3. *N-(2-Hydroxy-5-chloro-phenyl-methylidene-4(p-bromophenyl)-2-aminothizole 2H5CPMBPAT*



Sr. No.	Ligand	R
1.	2HPMBPAT	H
2.	2H5MPMBPAT	5-CH_3
3.	2H5CPMBPAT	5-Cl

Table 1: Elemental analysis and physical constant data of Schiff bases.

Sr. No.	Schiff base	C% found (cale)	H% found (cale)	N% found (cale)	S% found (cale)	Molecular weight found (cale)
1.	2HPMBPAT ($C_{17}H_{13}N_2$ BrOS) R- H	56.03 (56.19)	3.52 (3.58)	7.68 (7.71)	8.78 (8.81)	359 (363)
2.	2H5MPMBPAT ($C_{18}H_{15}N_2BrOS$) R-5CH_3	57.18 (57.29)	3.91 (3.97)	7.40 (7.42)	8.43 (8.48)	374 (377)
3.	2H5CPMBPAT ($C_{18}H_{15}N_2$ BrOS) R-5CH_3	51.21 (51.25)	2.98 (3.01)	6.97 (7.03)	8.01 (8.04)	3.94 (398)

Table 2: Important IR. Frequencies of the Schiff bases (cm^{-1})

Sr. No.	Schiff base	V_{oH}	$Vc_{=N}$	Vc_{-0}	Phenye and thiazole ring vibrations
1.	2HPMBPAT	~2900bd	1625s	1280s	1580m 1518sh 1484s 1375m 1355m 1205m 1170m 1156s
2.	2H5MPMBPAT	~2900bd	1625s	1284s	1584m 1505sh 1480s 1385m 1350m 1207m 1185m 1162s
3.	2H5CPMBPAT	~2900bd	1625s	1285s	1587m 1505sh 1410s 1390m 1365m 1210m 1190m 1165s

bd = broad, S=strong, m=medium, w=weak, sh=shoulder

2.3 Preparation of metal complex

An ethanol solution 10ml of the appropriate metal salts (II) (0.001M) was added to a stired ethanol solution (25ml) of the respective Schiff base (0.002M). The mixture was refluxed for 2.5 hrs. The resulting mixture was cooled, filtered and reduced to nearly half its volume. The concentrated mixture was kept overnight at room temperature, which result in the formation of solid product. The product thus obtained was filtered washed with ethanol then with ether and dried and crystallized from ethanol gave the desired metal complexes of metal salt. Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} etc.

3. Determination of stability constants

3.1 Proton ligand stability constant

Elico-4T-120 pH meter with combined gass electrode assembly was used for pH measurement. The pH meter was standardized with potassium hydrogen phthalate and phosphate buffer before performing the titrations.

The Schiff base solution was prepared in double distilled ethanol. All the metal ion solution were prepared and standardized by conventional procedures. Sodium perchlorate ($NaCl0_4$) was used to keep the ionic strength constant for different sets. A solution of sodium hydroxide (NaOH) (E-merck) in doubly distilled water was used as the titrant. It was standardized with a standard solution of oxalic acid. All other chemicals used were of reagent grade. The titration were carried out in an atmosphere of nitrogen. All measurements were made at a definite temperature, which were kept constant Julabo F-20 thermostat. The method of Bjerrum and calvin as modified by Irving and Rossotti [6], has been used to determine n^- and P^L values. The experimental procedure envolved the pH-metric titrations of the following solutions against at 0.1M ionic strength to determine n^- and P^L vales of the complexes at 25±1 °C

1. Free acid titration

A mixture of 2.oml of Naclo$_4$ (0.02M) + 1.oml (.1M) + 12ml water + 15ml ethanol.

2. Schiff base titration

A mixture of 2.oml of HCl0$_4$ (0.02M) + 1.oml Nacl0$_4$ (.1M) + 5ml of Schiff base solution (0.02M) + 12ml water + 10ml ethanol.

3. Metal titration

A mixture of 2.oml of Nacl0$_4$ (0.02M) + 1.oml Nacl0$_4$ (.1M) + 5ml of Schiff base solution (0.02M) + 2.0 ml metal perchlorate solution + 10ml water + 10ml ethanol.

In other sets a requisite amount of NaCl0$_4$ was added to maintain the ionic strength at μ = 0.1M was also individually titrated against Na0H at different temperature 35 and 45 °C. The stability constant values are listed in table No. 3.

Table 3: Proton-ligand Stability constants of Schiff bases at constant ionic strength μ = 0.1M NaClO$_4$ at temperature 25, 35 and 45 °C.

Sr. No.	Ligand	Temperature °C	Proton ligand stability constant – pk$_1$	
			Hall-integral	Graphical
1.	2HPMBPAT	25	10.71	10.72
		35	10.62	10.62
		45	10.53	10.51
2.	2H5MPMBPAT	25	11.25	11.26
		35	11.20	11.21
		45	11.14	11.15
3.	2H5CPMBPAT	25	10.92	10.91
		35	10.85	10.87
		45	10.80	10.81

Table 4: Metal-ligand Stability constants of divalent transition metal complexes of Schiff bases at constant ionic strength μ = 0.1MNaCl0$_4$ at different temperature 25, 35 and 45 °C.

Sr. No.	Ligand	Metal ion	Metal-ligand Stability constant			
			Half Integral		Graphical	
			PK$_1$ 25 35 45^{0}C	PK$_2$ 25 35 45^{0}C	PK$_1$ 25 35 45^{0}C	PK$_2$ 25 35 45^{0}C
1.	2HPMBPAT	Co^{II}	8.20, 8.15, 8.10	7.15, 7.10, 7.07	8.21, 8.15, 8.10	7.16, 7.10, 7.08
		Ni^{II}	8.15, 8.09, 8.04	7.09, 7.06, 7.01	8.16, 8.10, 8.05	7.10, 7.06, 7.02
		Cu^{II}	7.90, 7.85, 7.81	6.81, 6.75, 6.65	7.91, 7.85, 7.82	6.80, 6.76, 6.65
		Zn^{II}	7.60, 7.55, 7.49	6.50, 6.45, 6.40	7.61, 7.56, 7.50	6.52, 6.46, 6.41
2.	2H5MAPBPAT	Co^{II}	7.80, 7.76, 7.71	6.70, 6.66, 6.60	7.81, 7.76, 7.72	6.71, 6.66, 6.61
		Ni^{II}	7.55, 7.50, 7.46	6.50, 6.46, 6.40	7.55, 7.52, 7.47	6.51, 6.45, 6.40
		Cu^{II}	7.37, 7.30, 7.26	6.35, 6.24, 6.20	7.38, 7.30, 7.25	6.35, 6.25, 6.20
		Zn^{II}	7.30, 7.27, 7.20	6.21, 6.17, 6.10	7.32, 7.26, 7.21	6.20, 6.16, 6.10
3.	2H5CAPBPAT	Co^{II}	7.55, 7.51, 7.47	6.53, 6.44, 6.40	7.55, 7.50, 7.48	6.55, 6.45, 6.41
		Ni^{II}	7.45, 7.41, 7.36	6.41, 6.35, 6.30	7.45, 7.40, 7.35	6.40, 6.36, 6.30
		Cu^{II}	7.38, 7.33, 7.30	6.30, 6.25, 6.21	7.39, 7.34, 7.30	6.30, 6.25, 6.20
		Zn^{II}	7.31, 7.28, 7.23	6.20, 6.16, 6.13	7.32, 7.28, 7.23	6.20, 6.16, 6.14

4. Result and Discussion

Proton-ligand stability constant (pk) values of ligands. 2HPMBPAT, 2H5MPMBPAT and 2H5CPMBPAT were calculated by using half-integral and graphical method.

Values of ligand contains only one pk values due to dissociable proton of the phenolic-OH group. The protonation of imino nitrogen (HC=N) does not take place in the pH range under study. The pk values are summarized in table No. 3.

The pk values follows the trend

2H5MPMBPAT > 2H5CPMBPAT > 2HPMBPAT

This is explained on the ground of basic nature of azomethine nitrogen and phenolic oxygen[7-8]

Higher values of 2H5CPMBPAT as compaired to 2HPMBPAT may be due to the presence of C1 in the aromatic ring where it behaves more as electron releasing group via stronger mesomeric effect (+M) rather than electron withdrawing group through the donor ability of azomethine nitrogen in 2H5CPMBPAT relative to 2HPMBPAT and hence proton-ligand stability constant value increase.

In ligand 2H5MPMBPAT methyl group is substituted in phenyl ring methyl group has (+I) effect and therefore electron density on phenyl ring increases. Thus azomethine nitrogen and phenolic oxygen becomes more basic due to increase in electron density over them and therefore stability constant values of this ligand is higher that of 2H5CPMBPAT.

4.1 Metal ligand stability constant

The tilration curves of acid, ligand and the metal ions are studied. The metal ion curves shows departure from ligand curves at pH much lower than the pH of hydrolysis of metal ion and therefore the libration of the proton is due to chelation. The metal ligand stability constants were determined by using half integral and graphical method. The values are summarized in table No. 4

The order of stability of Schiff base metal complexes follows the trend. Co^{II}> Ni^{II}> Cu^{II}> Zn^{II} and it is found to be in accordance with the order suggested by Irving and Williams [9].

4.2 Effect of temperature

To study the effect of temperature on complexation, the metal ion, The metal ion Co^{II}> Ni^{II}> Cu^{II}> and Zn^{II} and Schiff bases. 2HPMBPAT, 2H5MPMBPAT and 2H5CPMBPAT complexes for determination of metal ligand stability constant at 25, 35 and 45 °C in ethanol water (50:50%) (v/v) medium and at constant ionic strength μ = 0.1M (NaCl0$_4$).

As thermodynamic parameter (ΔG, ΔH and ΔS) have been calculated and are summarized in table No. 5.

The logk values decreases with increasing in temperature for complexation. The ΔG, ΔH are negative, while ΔS values are positive.

Table 5: Thermodynamic parameters of Schiff base metal complexes.

Sr. No.	Complex	Log K1			-ΔG(KJM01^{-1})			-ΔH(KJM01^{-1})		ΔS(JKM01^{-1})		
		25	35	45	I	II	III	I	II	I	II	III
1.	2HPMBPAT											
	Co^{II}	8.20	8.15	8.10	46.57	47.84	49.09	26.59	28.38	67.01	61.74	65.12
	Ni^{II}	8.15	8.09	8.04	46.29	46.72	48.32	32.50	27.32	46.27	64.02	66.03
	Cu^{II}	7.90	7.85	7.81	44.87	45.84	47.33	26.60	29.43	61.30	54.15	56.25
	Zn^{II}	7.60	7.55	7.49	43.16	43.97	45.39	28.56	35.73	48.99	27.19	30.27
2.	2H5MAPBPAT											
	Co^{II}	7.80	7.76	7.71	44.30	45.56	46.73	21.67	29.43	75.93	53.23	54.40
	Ni^{II}	7.55	7.50	7.46	42.88	44.02	45.21	27.58	30.48	51.34	44.68	46.32
	Cu^{II}	7.37	7.30	7.26	41.86	42.85	44.00	41.37	25.22	1.64	58.18	54.05
	Zn^{II}	7.30	7.27	7.20	41.46	42.67	43.64	17.73	44.14	79.63	04.85	1.57
3.	2H5CAPBPAT											
	Co^{II}	7.53	7.51	7.47	42.88	44.08	45.27	27.28	24.17	79.63	65.70	66.35
	Ni^{II}	7.45	7.41	7.36	42.31	43.01	44.61	23.64	30.48	65.00	41.35	44.43
	Cu^{II}	7.38	7.33	7.30	41.91	43.31	44.24	29.55	18.92	40.79	80.49	79.62
	Zn^{II}	7.31	7.28	7.23	41.52	42.73	43.82	11.82	31.53	99.66	36.96	38.64

4.3 Characterization of Schiff base complexes

The Co^{II}, Ni ^{II}, Cu ^{II} and Zn ^{II} are reddish brown, yellow, greenish blue and brown coloured crystalline solid respectively. They are stable in chloroform benzene and nitro-benzene. The molecular weight determination and very low molar conductance values ($<11\Omega^{-1}$cm mole^{-1}) in nitrobenzene indicates that the complexes are monomeric and non-electrolytic in nature.

4.4 Electronic spectra of complexes

The electronic spectra of the Co^{II} complexes exhibit band at ~8700, ~18200, ~21000 and ~25500 Cm^{-1} occurrence of the first three bands, attributing to transition ${}^4T_{2g} \leftarrow {}^4T_{1g}$ (ν_1) ${}^4A_{2g} \leftarrow {}^4T_{1g}$ (ν_2) and ${}^4T_{2g}$ (p) $\leftarrow {}^4T_{1g}$ (ν_3) respectively, suggests an octahedral geometry for the complexes. An intense band at ~26500 cm^{-1} (ε~1000 dm^3 mole^{-1} cm^{-1}) may be due to ligand to metal (metal ← ligand) charge transfer.

The Ni^{II} complexes display band at ~8200, ~13700, ~24300 and 26400 cm^{-1}. The first three bands corresponding to transitions ${}^3T_{2g}$ (F) $\leftarrow {}^3A_{2g}$ (ν_1), ${}^3T_{2g}$ (F) $\leftarrow {}^3A_{2g}$ (ν_2) and ${}^3T_{2g}$ (p) $\leftarrow {}^3A_{2g}$ (ν_3) respectively, indicates an octahedral geometry for the complexes. The band occurring at 26400 cm^{-1} is sharp and intense (ε~1000 dm^3 mol^{-1} cm^{-1}) and may be due to ligand to metal (metal ← ligand) charge transfer.

The Cu^{II} complexes display three bands in the region 16240-17545cm^{-1}, 22250-3560cm^{-1} and 27465-28150cm^{-1}. The low energy band may be assigned for Cu^{II} in an octahedral configuration [10-11]. Corresponding to the transition ${}^4T_{2g} \leftarrow {}^2E_g$ and to the symmetry forbidden metal←ligand charge transfer. The Zn^{II} complexes exhibits a high intensity band at 28360-28755cm^{-1} assigned to metal←ligand charge transfer and band at 13340-13920cm^{-1} due to transitions ${}^2T_{2g} \leftarrow {}^2E_g$ in a distorted octahedral environment [11].

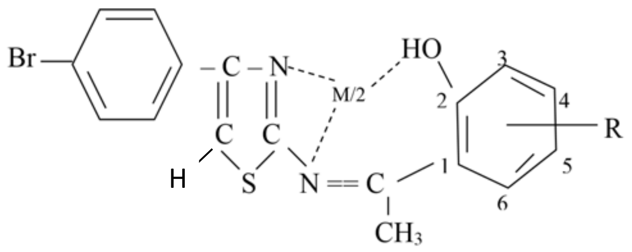
4.5 IR of Schiff base complexes

IR spectra of the Schiff base showed the absence of bands at 1735 and 3420cm^{-1} due to carbonyl ν(c=0) and $\nu(_{NH2})$ stretching, vibration and instead the appearance of a strong new band at 1630cm^{-1} assigned [12-14] to the azomethine ν(C=N) linkage. This suggested that the amino and ketone moieties of the starting reagents no more exist and have been converted in to respective Schiff base linkage. The comparison of infrared spectra of ligand and their metal chelates indicated that the ligand were coordinates to the metal atom in three ways. Thus representing ligands acts as tridentates. The band appearing at 1625 and 1615 cm^{-1} Assigned to azomethine and thiazole ring vibration Schiffed to lower frequency by 10cm^{-1} indicating the participation of azomethine nitrogen in chelation, further conclusive evidence of the coordination of these tridentate ligands with the metal was shown by the appearance of high frequency new band at 455-460 and 530-535. There were in turns assigned to metal oxygen ν(M-0) and metal- nitrogen (M-N) the obsance of ν_{OH} frequency in the complexes indicates the involvement of phenolic-OH in metal-oxygen band formation.

4.6 Magnetic moments of complexes

The values of magnetic moments (Gouy) of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} metal ion complexes. The Co^{II} complexes lies in the range 4.8-5.1BM indicative [15] of three unpaired electrons on per Co^{II} ion in octahedral environment, the Ni^{II} complexes lies in the range 3.0-3.2 BM indicative [16] of two unpaired electrons on per Ni^{II} ion in octahedral environment, the Cu^{II} complexes lies in the rang 1.7-1.9 BM showing one unpaired electron on per Cu^{II} ion suggesting a distorted octahedral geometry. Zn^{II} complexes are diamagnetic.

From above parameters i.e. IR, UV and magnetic movement and molecular weight, the proposed structure of metal complexes are as follows.



Where M = Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} ions

4.7 Biological activities

The compounds were tested *in vitro* for their antibacterial activity against E-coli, Bacillus and Staphylococcus and antifungal activity against A.niger and A.flaves at 50mg/ml concentration using DMF as the solvent by cup plate method. The zone of inhibition were measured. The activity of ligands was compared with that displayed by ampicillin (antibacterial activity) and griseofulvin (antifungal activity) as the standard drugs.

4.8 Antibacterial activity

E coli and ligands 2HPMBPAT, 2H5MPMBPAT and 2H5CPMBPAT exhibited zone of inhibition 6-13 mm where as the standard drug Amphicillin exhibited zone of inhibition 20mm.

Bacillus and Staphylococus and ligand exhibited zone of inhibition 6-16mm against 20mm for amphicillin. Hence concluded to amphicillin for antibacterial activity of ligands. 2HPMBPAT, 2H5MPMBPAT and 2H5CPMBPAT against the above organism by serial dilution technique [17] in DMF in the concentration 5-50 mg/ml.

MIC volues of ligands were fund. The values lie in the range 15-20mg/ml. The activity of ligands is explained on the grounds of chelation theory [18].

4.9 Antifungal activity

All the ligands i.e. 2HPMBPAT, 2H5MPMBPAT and 2H5CPMBPAT tested against A. flavus and A. niger. The ligand 2H5MPMBPAT exhibit zone of inhibition 8mm and the standard drug Griseofulvin exhibited zone of inhibition 20mm. Concluded that ligand possesses lower antifungal activity as compaired to Griseofulvin other ligands are inactive.

5. Conclusion

Proton-ligand Stability constants of metal ions have been calculated by using half integral and graphical method. The reported values of proton ligand stability constants follows trend.

2H5CPMBPAT > 2H5MPMBPAT > 2HPMBPAT

To study the effect of elevated temperature on determination of proton ligand stability constant is of ligands. It was found that with increasing temperature the proton ligand stability constant values decreases.

Metal-ligand stability constants were determined by half integral and graphical methods. The proposed order of stability of the complexes which follows the trend. $Co^{II} > Ni^{II} > Cu^{II} > Zn^{II}$.

The order of stability of the complexes is in accordance with the proposed by Irving and Williams.

The effect of elevated temperature on the determination of metal-ligand stability constants has been studied. It was observed that as the temperature increases the values of stability constants decreases. This suggest that low temperature is favorable for complex formation. The temperature parameter (ΔH, ΔG and ΔS) have been calculated. The ΔH and ΔG values are negative where as ΔS values are positive. The negative values of ΔH and ΔG suggest that the complex formation is thermodynamically favoured. The positive values of ΔS indicates that entropy effect is found to be predominant over enthalpy effect.

The structures of Schiff bases and of their complexes also have been determined on the basis of their physical and spectral data (i.e. IR and UV visible spectra) and magnetic moments.

The Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes are monomeric, non-electrolytic and covalent in nature having 1:2 (metal-legend) stoichiometry and an octahedral geometry. The coordination takes place through the oxygen of phenolic – OH, nitrogen of the azomethine group and a nitrogen of thiazole moiety and thus the ligands behave as tridentate with NNO donor set. The h*x*-values indicate the ligands should be placed in between urea and ammonia in the nephelauxetic series.

Ligands have been screened for the evaluation of antibacterial and antifungal activities by cup plate method. The MIC values have been reported the ligands are found to posseses good antibacterial activity.

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