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The study of transition metal (Co^{ii}, Ni^{ii}, Cu^{ii} & Zn^{ii}) complexes of substituted thiazole ring containing ligands and their biological activity

RP Giram and BN Muthal

Abstract

A series of Schiff bases have been synthesized by reacting 4(p-flurophenyl) 2-aminothiazole and R-substituted Salicylaldehyde (R-H, 5-Me, 5-Br). The bases and their metal complexes were characterized by elemental analysis, UV-visible and Infra-red spectra, magnetic susceptibility and conductivity measurement. The Schiff base complexes act as monomeric and have octahedral in geometry. The ligand coordinated through oxygen atom of phenolic –OH group and the nitrogen atom of azomethine group. The complexes are non-electrolitic in nature.

The stability constants and thermodynamic parameters (ΔH, ΔG & ΔS) were recorded. The –ve ΔG in each cases indicates the complexation is spontaneous. The enthalpy change is exothermic. The positive value of ΔS indicates the reactions are entropically favoured.

The Schiff bases and their metal complexes were screened for antibacterial, antifugal and pesticidal activity.

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

Introduction

The Schiff bases and their transition metal complexes have been amongst the widely studied as a coordination compound in few past years. The Schiff base ligands are able to stabilize many different metals in various oxidation state, controlling the performance of metals in a large variety of useful applications in biological, clinical, analytical and industrial in addition to their important role in catalysis and organic synthesis. Schiff base ligands containing various donor atoms like N, O and S show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ion. Now in recent year new interesting applications found in the field of pesticide and medicine. The metal complexes with tridentate O, N, N type of alternative structure have attracted the attention of chemist [1-5].

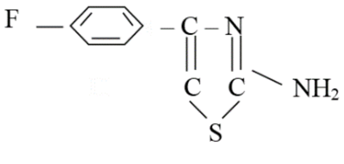
In present communication here we report synthesis, characterization, biological activity, stability constant and thermodynamic parameter of a Schiff base derived from 4-(P-Flurophenyl)-2-aminothiazole and transition metal (Co^{II}, Zn^{II}, Cu^{II}, Zn^{II}) ion complexes.

1. Experimental

Preparation of Schiff bases

1.1 Synthesis of aminothiazole

4-(p-Florophenyl)-2-aminothiazole, Synthesised as reported method [6-8].

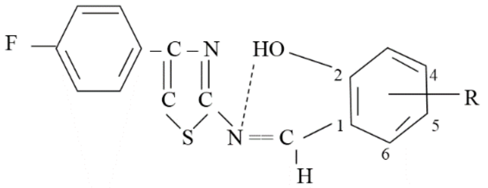


1.2 Synthesis of amino thiazole Schiff base (ligand)

A solution of *Salicylaldehyde* in ethanol was added to the ethanolic solution of 4-(p-florophenyl)-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. IR-Frequencies in table 1.
Following Schiff base were prepared

1. N-(Salicylidene-4(p-florophenyl)-2-aminothizole) SFPAT
2. N-(4-methyl Salicylidene-4 (p-florophenyl)-2-aminothizole) 4MSFPAT
3. N-(5-bromo-Salicylidene-4(p-florophenyl)-2-aminothizole) 5BSFPAT



Sr. No.	Ligand	R
1.	SFPAT	H
2.	4MSFPAT	4-CH_3
3.	5-BSFPAT	5-Br

1.3 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.

1.4 Determination of stability constants

Proton ligand stability constant

The method of Bjerrum and calvin as modified by Irving and Rossotti[9] 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 ± 1^0c

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 $\mu = 0.1$M was also individually titrated against Na0H at different temperature 35 and 45 ^{0}C.

2 Result and Discussion

2.1 Proton-ligand stability constant

Proton-ligand stability constant (pk) values of ligands. SFPAT, 4MSFPAT and 5BSFPAT 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. 2.

The pk values follows the trend
4MSFPAT > 5BSFPAT > SFPAT

This is explained on the ground of basic nature of azomethine nitrogen and phenolic oxygen [10-11].

Higher values of 5BSFPAT as compared to SFPAT may be due to the presence of Br 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 5BSFPAT relative to SFPAT and hence proton-ligand stability constant value increase.

In ligand 4MSFPAT 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 5BSFPAT.

2.2 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. 3

The order of stability of Schiff base metal complexes follows the trend. Zn^{II} > Co^{II}> Ni^{II}> Cu^{II} and it is found to be in accordance with the order suggested by Irving and Williams [12].

2.3 Effect of temperature

To study the effect of temperature on complexation, the metal ion, the metal ion Zn^{II} > Co^{II}> Ni^{II}> and Cu^{II} and Schiff bases. SFPAT, 4MSFPAT and 5BSFPAT complexes for determination of metal ligand stability constant at 25, 35 and 45 ^{0}C in ethanol water (50:50%) (v/v) medium and at constant ionic strength $\mu = 0.1$M ($NaCl0_4$).

As thermodynamic parameter (ΔG, ΔH and ΔS) have been calculated and are summarized in table No. 4.

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

2.4 Electronic spectra of complexes

The electronic spectra of the Co^{II} complexes exhibit band at ~8500, ~18100, ~21400 and ~26100 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 ~8000, ~13300, ~24100 and 26250 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 26250 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 16100-17300cm^{-1}, 22100-23400cm^{-1} and 27200-28000cm^{-1}. The low energy band may be assigned for Cu^{II} in an octahedral configuration [13-14]. 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 28100-28555cm^{-1} assigned to metal←ligand charge transfer and band at 13200-13700cm^{-1} due to transitions $^2T_{2g} \leftarrow {}^2E_g$ in a distorted octahedral environment [14].

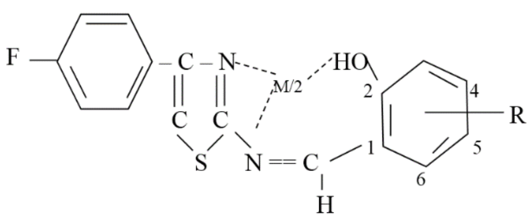
2.5 IR of Schiff base complexes

IR spectra of the Schiff base showed the absence of bands at 1725 and 3410cm^{-1} due to carbonyl ν(c=0) and $\nu(_{NH2})$ stretching, vibration and instead the appearance of a strong new band at 1625cm^{-1} assigned [15-17] 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 1605 cm^{-1} Assigned to azomethine and thiazole ring vibration Schiffed to lower frequency by 20cm^{-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 450-455 and 525-530. 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.

2.6 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 4.7-5.1BM indicative [18] of three unpaired electrons on per Co^{II} ion in octahedral environment, the Ni^{II} complexes lies in the range 3.0-3.3 BM indicative [19] 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

3. 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.

3.1 Antibacterial activity

E coli and ligands SFPAT, 4MSPAT and 5BSFPAT exhibited zone of inhibition 6-12 mm where as the standard drug Amphicillin exhibited zone of inhibition 20mm.

Bacillus and Staphylococus and ligand exhibited zone of inhibition 6-14mm against 20mm for amphicillin. Hence concluded to amphicillin for antibacterial activity of ligands. SFPAT, 4MSPAT and 5BSFPAT against the above organism by serial dilution technique[20] in DMF in the concentration 5-50 mg/ml.

MIC volues of ligands were fund. The values lie in the range 14-19mg/ml. The activity of ligands is explained on the grounds of chelation theory [21].

3.2 Antifungal activity

All the ligands i.e. SFPAT, 4MSPAT and 5BSFPAT tested against A. flavus and A. niger. The ligand 4MSPAT exhibit zone of inhibition 7mm and the standard drug Griseofulvin exhibited zone of inhibition 19mm. Concluded that ligand possesses lower antifungal activity as compaired to Griseofulvin other ligands are inactive.

3.3 Pesticidal activity

The insecticide and pesticide activity of Schiff base were tested against some sessional edible plants chilli. (*Capsicum annum* L) Okra (*Abelmoschus esculents* (L) Moench) Lay's Finger or Bhendi, Tomato. Pesticidal and insecticidal activities of Schiff bases and their Cu^{II} complexes shows much more activity on poisoning [22-25].

In present report Schiff bases and Cu^{II} and Zn^{II} shows complexes shows pesticidal and insecticidal activities. The rate of poisoning is lower than commercial pesticide and insecticide.

4. 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.

4MSPAT > 5BSFPAT > SFPAT

The proposed order of stability of the complexes which follows the trend. $Zn^{II} > Co^{II} > Ni^{II} > Cu^{II}$.

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 whereas 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-legand) 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.

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

Sr. No.	Schiff base	V_{OH}	$V_{C=N}$	V_{C-0}	Phenyl and thiazole ring vibrations
1.	SFPAT	~2900bd	1625s	1275s	1580m 1518sh 1480s 1372m 1352m 1203m 1172m 1160s
2.	4MSFPAT	~2900bd	1625s	1277s	1581m 1508sh 1480s 1382m 1352m 1208m 1184m 1165s
3.	5BSFPAT	~2900bd	1625s	1280s	1580m 1503sh 1413s 1390m 1358m 1213m 1195m 1162s

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

Table 2: Proton-ligand Stability constants of Schiff bases at constant ionic strength μ = 0.1M $NaClO_4$ at temperature 25, 35 and 45 ^{0}C.

Sr. No.	Ligand	Temperature 0_C	Proton ligand stability constant – pk_1	
			Hall-integral	Graphical
1.	SFPAT	25	10.55	10.57
		35	10.50	10.50
		45	10.43	10.41
2.	4MSFPAT	25	11.10	11.12
		35	11.07	11.08
		45	11.05	11.06
3.	5BSFPAT	25	10.80	10.79
		35	10.72	10.71
		45	10.70	10.70

Table 3: Metal-ligand Stability constants of divalent transition metal complexes of Schiff bases at constant ionic strength μ = 0.1M$NaCl0_4$ at different temperature 25, 35 and 45 ^{0}C.

Sr. No.	Ligand	Metal ion	Metal-ligand Stability constant											
			Half Integral						Graphical					
			PK_1			PK_2			PK_1			PK_2		
			25	35	45^{0}C	25	35	45^{0}C	25	35	45 ^{0}C	25	35	45 ^{0}C
1.	SFPAT	Zn^{II}	8.15,	8.10,	8.05	7.10,	7.05,	7.02	8.16,	8.10,	8.05	7.11,	7.05,	7.03
		Co^{II}	8.10,	8.04,	7.99	7.04,	7.01,	6.96	8.11,	8.05,	8.00	7.05,	7.01,	6.97
		Ni^{II}	7.85,	7.80,	7.76	6.76,	6.70,	6.60	7.86,	7.80,	7.77	6.75,	6.71,	6.60
		Cu^{II}	7.55,	7.50,	7.44	6.45,	6.40,	6.35	7.56,	7.51,	7.45	6.47,	6.41,	6.36
2.	4MSFPAT	Zn^{II}	7.75,	7.71,	7.67	6.65,	6.61,	6.55	7.76,	7.71,	7.67	6.66,	6.61,	6.56
		Co^{II}	7.50,	7.45,	7.41	6.45,	6.41,	6.35	7.50,	7.47,	7.42	6.46,	6.40,	6.35
		Ni^{II}	7.32,	7.25,	7.21	6.30,	6.19,	6.15	7.33,	7.25,	7.20	6.30,	6.20,	6.15
		Cu^{II}	7.25,	7.22,	7.15	6.16,	6.12,	6.05	7.27,	7.21,	7.16	6.15,	6.11,	6.05
3.	5BSFPAT	Zn^{II}	7.50,	7.46,	7.42	6.48,	6.39,	6.35	7.50,	7.45,	7.43	6.50,	6.40,	6.36
		Co^{II}	7.40,	7.36,	7.31	6.36,	6.30,	6.25	7.40,	7.35,	7.30	6.35,	6.31,	6.25
		Ni^{II}	7.33,	7.28,	7.25	6.25,	6.20,	6.16	7.34,	7.29,	7.25	6.25,	6.20,	6.15
		Cu^{II}	7.26,	7.23,	7.18	6.15,	6.11,	6.08	7.27,	7.23,	7.18	6.15,	6.11,	6.09

Table 4: 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.	SFPAT											
	Zn^{II}	8.15	8.10	8.05	46.52	47.79	49.04	26.54	28.33	66.96	61.69	65.07
	Co^{II}	8.10	8.04	7.99	46.24	46.67	48.27	32.45	27.27	46.22	63.97	65.98
	Ni^{II}	7.85	7.80	7.76	44.82	45.79	47.28	26.55	29.38	61.25	54.10	56.20
	Cu^{II}	7.55	7.50	7.44	43.11	43.92	45.34	28.51	35.68	48.94	27.14	30.22
2.	4MSFPAT											
	Zn^{II}	7.75	7.71	7.66	44.25	45.51	46.68	21.62	29.38	75.88	53.18	54.35
	Co^{II}	7.50	7.45	7.41	42.83	43.97	45.16	27.53	30.43	51.29	44.63	46.27
	Ni^{II}	7.32	7.25	7.21	41.81	42.80	43.95	41.32	25.17	1.59	58.13	54.00
	Cu^{II}	7.25	7.22	7.15	41.41	42.62	43.59	17.68	44.09	79.58	04.80	1.52
3.	5BSFPAT											
	Zn^{II}	7.48	7.46	7.42	42.83	44.03	45.22	27.23	24.12	79.58	65.65	66.30
	Co^{II}	7.40	7.36	7.31	42.26	42.96	44.56	23.59	30.43	64.95	41.30	44.38
	Ni^{II}	7.33	7.28	7.25	41.86	43.26	44.19	29.50	18.87	40.74	80.44	79.57
	Cu^{II}	7.26	7.23	7.18	41.47	42.68	43.77	11.77	31.48	99.61	36.91	38.59

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