



P-ISSN2349-8528
E-ISSN 2321-4902
IJCS 2016; 4(2): 78-82
© 2016 JEZS
Received: 23-01-2016
Accepted: 26-02-2016

BN Muthal
Shri Shivaji College,
Kandhar Dist. Nanded (MS).

BN Raut
Shri Shivaji College,
Kandhar Dist. Nanded (MS).

AS Tekale
Shri Shivaji College,
Udgir Dist. Latur (MS).

Synthesis and characterization of transition metal ion (Coⁱⁱⁱ, Niⁱⁱⁱ, Cuⁱⁱ & Znⁱⁱ) complexes of Schiff bases derived from aminothiazole and their biological activity

BN Muthal, BN Raut, AS Tekale

Abstract

A series of Schiff bases have been synthesized by reacting 4-(p-fluoro phenyl) 2-aminothiazole and R-substituted Salicylaldehyde (R-H, 5-Me, 5-cl and 5-ome and 2-hydroxy-1-naphthalene. 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-electrolytic in nature.

The stability constants and thermodynamic parameters ($\Delta H, \Delta G$ & 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, antifungal and pesticidal activity.

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

1. 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].

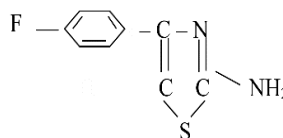
In present communication here we report synthesis, characterization, biological activity, stability constant and thermodynamic parameter of a Schiff base derived from 4-(P-Fluorophenyl)-2-aminothiazole and transition metal (Co^{II}, Zn^{II}, Cu^{II}, Zn^{II}) ion complexes.

Experimental:

Preparation of Schiff bases:

Synthesis of aminothiazole

4-(p-Fluorophenyl)-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-fluorophenyl)-2-aminothiazole in equimolar quantity. The mixture was refluxed on a water bath for 2 hrs. The Schiff base, thus formed was filtered and recrystallized from ethanol and dried

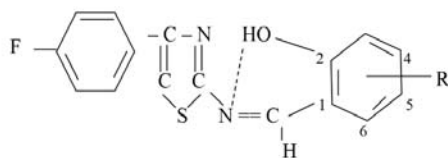
Correspondence

BN Muthal
Shri Shivaji College,
Kandhar Dist. Nanded (MS).

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-fluorophenyl)-2-aminothizole) SFPAT
2. N-(5-methyl Salicylidene-4(p-fluorophenyl)-2-aminothizole) 5MSFPAT
3. N-(5-chloro-Salicylidene-4(p-fluorophenyl)-2-aminothizole) 2CSFPAT



Sr. No.	Ligand	R
1.	SFPAT	H
2.	5MSFPAT	5-CH ₃
3.	5-CSFPAT	5-Cl

1.3 Preparation of metal complex

An ethanol solution 10ml of the appropriate metal salts (II) (0.001M) was added to a stirred 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 Rossotti⁹ has been used to determine n⁻ and P^L values. The experimental procedure involved 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^oc

1. Free acid titration

A mixture of 2.0ml of NaClO₄ (0.02M) + 1.0ml (.1M) + 12ml water + 15ml ethanol.

2. Schiff base titration

A mixture of 2.0ml of HClO₄ (0.02M) + 1.0ml NaClO₄ (.1M) + 5ml of Schiff base solution (0.02M) + 12ml water + 10ml ethanol.

3. Metal titration

A mixture of 2.0ml of NaClO₄ (0.02M) + 1.0ml NaClO₄ (.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 NaClO₄ was added to maintain the ionic strength at μ = 0.1M was also individually titrated against NaOH at different temperature 35 and 45 ^oC.

2 Result and Discussion

2.1. Proton-ligand stability constant

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



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

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

In ligand 5MSFPAT 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 5CSFPAT.

2.2 Metal-ligand stability constant

The titration 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, 5MSFPAT and 5CSFPAT complexes for determination of metal ligand stability constant at 25, 35 and 45^oC in ethanol water (50:50%) (v/v) medium and at constant ionic strength μ = 0.1M(NaClO₄).

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 ~8600, ~18000, ~21500 and ~26000 Cm⁻¹ occurrence of the first three bands, attributing to transition ⁴T_{2g} ← ⁴T_{1g} (ν₁) ⁴A_{2g} ← ⁴T_{1g} (ν₂) and ⁴T_{2g} (p) ← ⁴T_{1g} (ν₃) respectively, suggests an octahedral geometry for the complexes. An intense band at ~26400 cm⁻¹ (ε~1000 dm³ mole⁻¹ cm⁻¹) may be due to ligand to metal (metal ← ligand) charge transfer.

The Ni^{II} complexes display band at ~8100, ~13500, ~24200 and 26300 cm⁻¹. The first three bands corresponding to transitions ³T_{2g} (F) ← ³A_{2g} (ν₁), ³T_{2g} (F) ← ³A_{2g} (ν₂) and ³T_{2g} (p) ← ³A_{2g} (ν₃) respectively, indicates an octahedral geometry for the complexes. The band occurring at 26300 cm⁻¹ is sharp and intense (ε~1000 dm³ 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 $16200\text{-}17400\text{cm}^{-1}$, $22150\text{-}3500\text{cm}^{-1}$ and $27365\text{-}28100\text{cm}^{-1}$. The low energy band may be assigned for Cu^{II} in an octahedral configuration ${}^4\text{T}_{2g} \leftarrow {}^2\text{E}_g$ and to the symmetry forbidden metal \leftarrow ligand charge transfer. The Zn^{II} complexes exhibits a high intensity band at $28200\text{-}28655\text{cm}^{-1}$ assigned to metal \leftarrow ligand charge transfer and band at $13240\text{-}13800\text{cm}^{-1}$ due to transitions ${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$ in a distorted octahedral environment ${}^{[14]}$.

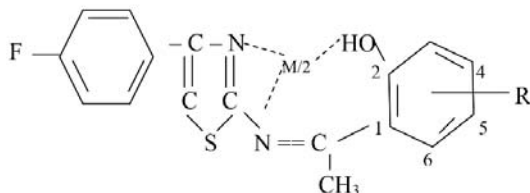
2.5 IR of Schiff base complexes

IR spectra of the Schiff base showed the absence of bands at 1735 and 3420cm^{-1} due to carbonyl $\nu(\text{C}=\text{O})$ and $\nu(\text{NH}_2)$ stretching, vibration and instead the appearance of a strong new band at 1630cm^{-1} assigned ${}^{[15-17]}$ to the azomethine $\nu(\text{C}=\text{N})$ 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 1630 and 1615cm^{-1} Assigned to azomethine and thiazole ring vibration Schiffed to lower frequency by 15cm^{-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 $455\text{-}460$ and $530\text{-}535$. There were in turns assigned to metal oxygen $\nu(\text{M}-\text{O})$ 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 $4.8\text{-}5.1\text{BM}$ indicative ${}^{[18]}$ of three unpaired electrons on per Co^{II} ion in octahedral environment, the Ni^{II} complexes lies in the range $3.0\text{-}3.2\text{BM}$ indicative ${}^{[19]}$ of two unpaired electrons on per Ni^{II} ion in octahedral environment, the Cu^{II} complexes lies in the rang $1.7\text{-}1.9\text{BM}$ 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 $\text{M} = \text{Co}^{\text{II}}$, 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, 5MSPAT and 5CSFPAT exhibited zone of inhibition $6\text{-}12\text{mm}$ where as the standard drug Amphotericin exhibited zone of inhibition 20mm .

Bacillus and Staphylococcus and ligand exhibited zone of inhibition $6\text{-}14\text{mm}$ against 20mm for amphotericin. Hence concluded to amphotericin for antibacterial activity of ligands. SFPAT, 5MSPAT and 5CSFPAT against the above organism by serial dilution technique ${}^{[20]}$ in DMF in the concentration $5\text{-}50\text{mg/ml}$.

MIC volues of ligands were fund. The values lie in the range $15\text{-}20\text{mg/ml}$. The activity of ligands is explained on the grounds of chelation theory ${}^{[21]}$.

3.2 Antifungal activity

All the ligands i.e. SFPAT, 5MSPAT and 5CSFPAT 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 compared 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 prisoning 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.



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

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 hx -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 possess good antibacterial activity.

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

Sr. No.	Schiff base	V_{OH}	$\text{V}_{\text{C=N}}$	$\text{V}_{\text{C-O}}$	Phenyl and thiazole ring vibrations
1.	SFPAT	~2900bd	1630s	1280s	1585m 1520sh 1484s 1370m 1350m 1205m 1170m 1156s
2.	5MSFPAT	~2900bd	1630s	1282s	1580m 1510sh 1482s 1380m 1350m 1210m 1185m 1162s
3.	5CSFPAT	~2900bd	1630s	1282s	1582m 1505sh 1415s 1392m 1360m 1215m 1190m 1160s

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

Table 2: Proton-ligand Stability constants of Schiff bases at constant ionic strength $\mu = 0.1\text{M NaClO}_4$ at temperature 25, 35 and 45 °C.

Sr. No.	Ligand	Temperature 0_{C}	Proton ligand stability constant – $\text{p}K_1$	
			Hall-integral	Graphical
1.	SFPAT	25	10.60	10.62
		35	10.52	10.53
		45	10.45	10.44
2.	5MSFPAT	25	11.15	11.16
		35	11.10	11.10
		45	11.07	11.08
3.	5CSFPAT	25	10.83	10.82
		35	10.74	10.75
		45	10.71	10.72

Table 3: Metal-ligand Stability constants of divalent transition metal complexes of Schiff bases at constant ionic strength $\mu = 0.1\text{M NaClO}_4$ 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°C	PK_2 25 35 45°C	PK_1 25 35 45°C	PK_2 25 35 45°C		
1.	SFPAT	Zn ^{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		
		Co ^{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		
		Ni ^{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		
		Cu ^{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.	5MSFPAT	Zn ^{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		
		Co ^{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		
		Ni ^{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		
		Cu ^{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.	5CSFPAT	Zn ^{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		
		Co ^{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		
		Ni ^{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		
		Cu ^{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		

Table 4: Thermodynamic parameters of Schiff base metal complexes.

Sr. No.	Complex	Log K_1			$-\Delta G(\text{KJM01}^{-1})$			$-\Delta H(\text{KJM01}^{-1})$		$\Delta S(\text{KJM01}^{-1})$		
		25	35	45	I	II	III	I	II	I	II	III
1.	SFPAT											
	Zn ^{II}	8.20	8.15	8.10	46.57	47.84	49.09	26.59	28.38	67.01	61.74	65.12
	Co ^{II}	8.15	8.09	8.04	46.29	46.72	48.32	32.50	27.32	46.27	64.02	66.03
	Ni ^{II}	7.90	7.85	7.81	44.87	45.84	47.33	26.60	29.43	61.30	54.15	56.25
	Cu ^{II}	7.60	7.55	7.49	43.16	43.97	45.39	28.56	35.73	48.99	27.19	30.27
2.	5MSFPAT											
	Zn ^{II}	7.80	7.76	7.71	44.30	45.56	46.73	21.67	29.43	75.93	53.23	54.40
	Co ^{II}	7.55	7.50	7.46	42.88	44.02	45.21	27.58	30.48	51.34	44.68	46.32
	Ni ^{II}	7.37	7.30	7.26	41.86	42.85	44.00	41.37	25.22	1.64	58.18	54.05
	Cu ^{II}	7.30	7.27	7.20	41.46	42.67	43.64	17.73	44.14	79.63	04.85	1.57
3.	HCSFPAT											
	Zn ^{II}	7.53	7.51	7.47	42.88	44.08	45.27	27.28	24.17	79.63	65.70	66.35
	Co ^{II}	7.45	7.41	7.36	42.31	43.01	44.61	23.64	30.48	65.00	41.35	44.43
	Ni ^{II}	7.38	7.33	7.30	41.91	43.31	44.24	29.55	18.92	40.79	80.49	79.62
	Cu ^{II}	7.31	7.28	7.23	41.52	42.73	43.82	11.82	31.53	99.66	36.96	38.64

5. Acknowledgement

Author thanks to UGC and authorities of Shri Shivaji Education Society's Kandhar and Principal, Shri Shivaji College, Kandhar for providing facilities, one of the authors (AST) thanks to the Principal, Shivaji College, Udgir for constant support. Authors thank to Dr. P.G. More for helpful suggestions and constant encouragement.

6. References

- Bhendekar AK, Vijay K, Raut AW. Synthesis of some novel Schiff base of 2-aminopyrimidine and their antimicrobial activity, *Acta ciencia indica (Chemistry)* 2004; 30:29.
- Mohamed GG, Abd El-Wahad ZH. Mixed ligand complexes of bis (phenylimine) Schiff base ligands incorporating pyridinium moiety synthesis, characterization and antibacterial activity, *spectrochim. Acta A* 2005; 61(6):1059.
- More PG, Lawand AS, Dalve NV, Nalawade AM. *J Indian Chem Soc.* 2008; 85:862.
- Magraby MA, Hassan AA. *Indian J Chem* 20B. 256, 1981.
- Chaben I, Oji. *J Indian Chem Soc.* 1984; 61:523.
- Shyam R, Tiwari IC. *Agri Bio Chem.*, 1975; 39:715.
- AI Vogel. A textbook of qualitative organic chemistry 3rd Ed. (ELBS, London), 1961.
- BS Furniss, AJ Hanna Ford, PWG Smith, AR Tatchell. Vogel's practical organic chem. 5th Ed. (Logman Scientific Technical, John Wiley and Sons), 1989.
- Maurya MR, Gopinathan C. *India J Chem.* 1996; 35A:701.
- Irving HM, Rossotti HS. *J Chem Soc.* 1954, 2904.
- Gurkan P, Gunduz N, *J Indian chem Soc.* 1997; 74:713.
- Naikwade SD, Mane PS, Chondhekar TK. *J Indian Chem Soc.* 2001; 78:41.
- Sanyal P, Sar P, Sengupta GP. *J Indian Chem Soc.* 2002; 79:614.
- Pardeshi RK, Palaskar NG, Chondhekar TK. *J Indian Chem Soc.* 2002; 79:958.
- More PG, Muthal BN, Lawand AS. *J Indian Chem Soc.* 2006; 83:36-38.
- Irving H, Williams RJP. *Nature, J Chem Soc.* 1953, 3192. 1948; 162:746.
- Balhausen CJ. *Introduction to ligand fields* McGraw Hill, New York, 1962.
- Liehr AD, *Phys J. Chem.* 1967; 67:1314.
- Kovacic JE, *Spectrochim, Acta*, 1967, 23 A, 183.
- Adams DM. *Metal ligands and related vibrations* Edward Arnold, London, 1967.
- Nakamoto K. *Infrared Spectra of Inorganic and coordination compounds*, John Wiley, New York, 1963.
- Glick MD, Lintvedt RL. *Prog. Inorg. Chem.* 1976; 21:233.
- Barefield EK, Busch DH, Nelson SM. *Quart. Rev.* 1968; 22:457.
- Spooner DI, Sykes G. *Methods in Microbiology*, Academic, London, 1972.
- Srivastava RS. *Inorg. Chem. Acta*, 1981; 56:165.
- Jesmim M, Ali MM, Islam MN, Islam N, Sharirar SM, Khanam JA. *J Sci Foundation.* 2008; 6:49.
- Jesmin M, Ali MM, Salahuddin MS, Habib MR, Khanam JA. *Microbiology* 2008; 36:70.
- Zhu, Wang X, Dang Y, Zhou H, Wu, 2 Liu, Ye D, Zhou Syn Q. & Real *Inorg. And Met. Org. Chem.*, 2000; 30:625.
- Zhu X, Wang C, Dong W, Song F, Hu Z, Dang Y *et al.* *Syn and Rede, Inorg. & Met. Org. Chem.* 2002; 32:475.