

Synthesis, Characterization and Spectral Studies of Schiff base Complexes Derived from Pyridoxal Derivatives and Amidoguanidine

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Received: 21.11.2017

Accepted: 25.11.2017

ABSTRACT

In this paper eight transition metal (II) chelates of the type $[ML_2]$, where L is the uninegative tridentate Schiff base derived from amidoguanidine and pyridoxal derivatives, have been reported. Six coordinated geometry for all the metal (II) complexes have been characterized on the basis of elemental analysis, conductivity measurements, magnetic and spectral data.

Keywords: Amidoguanidine, Schiff Base, IR spectra and Electronic spectra.

INTRODUCTION

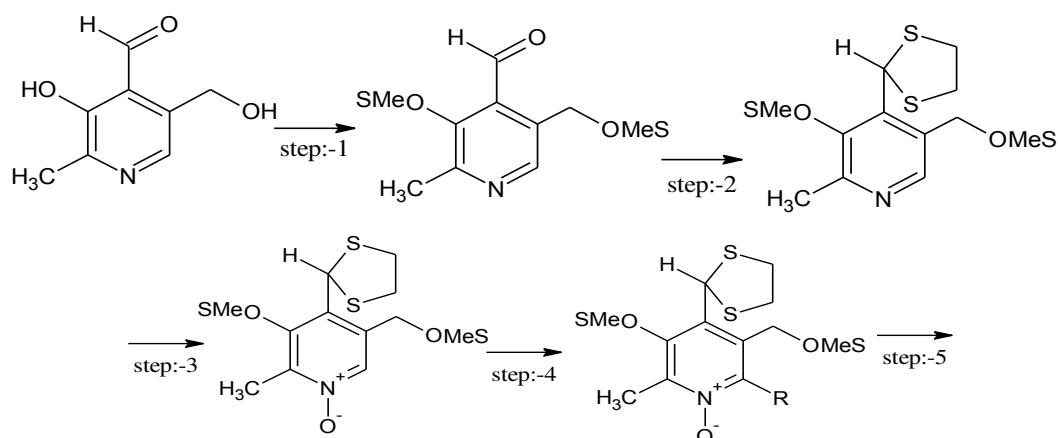
Schiff bases are some of the most widely used organic compounds. They are used as pigments¹, dyes², catalysts³, intermediates⁴ in organic synthesis and as a polymer stabilizer⁵. Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal⁶, antibacterial^{7, 8}, antimalarial⁹, antiproliferative¹⁰, antiinflammatory¹¹, antiviral¹² and antipyretic¹³ properties.

In the present study a series of Schiff bases derived from pyridoxal derivatives and amidoguanidine were synthesized. In order to prepare metal chelates, the newly synthesized uninegative tridentate Schiff bases have been further allowed to react with transition metal (II) salts like Fe (II) chloride and Cu (II) chloride.

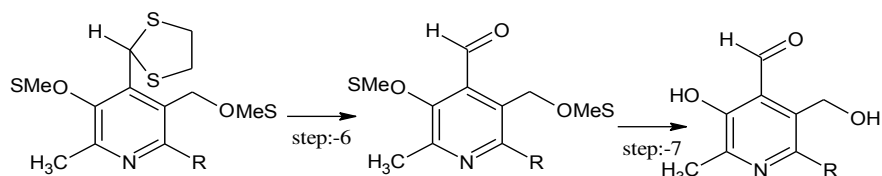
MATERIALS AND METHODS

The chemical used were of BDH, AR or E-Merck and used as such.

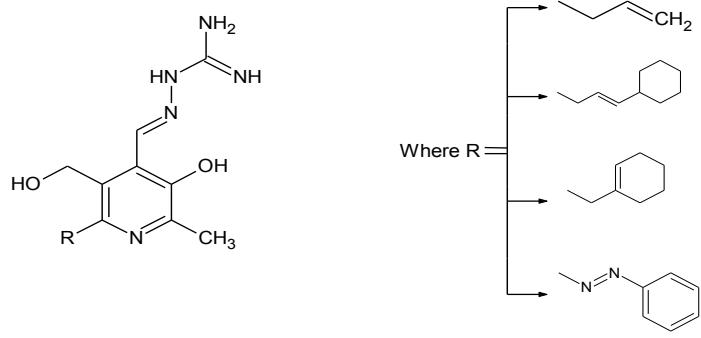
Preparation of ligands: Preparation of ligands has been performed according to following scheme.



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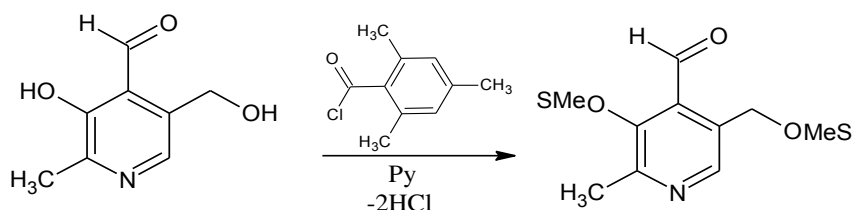


Four ligands have been prepared by using five different “R” substituents. The general structures of the ligands may be shown as:



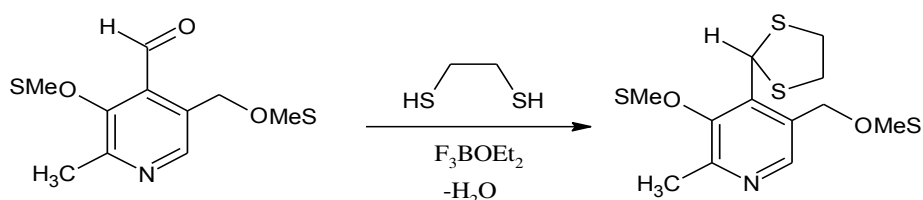
Step 1: Protection of Hydroxyl Groups¹⁴

Reaction:



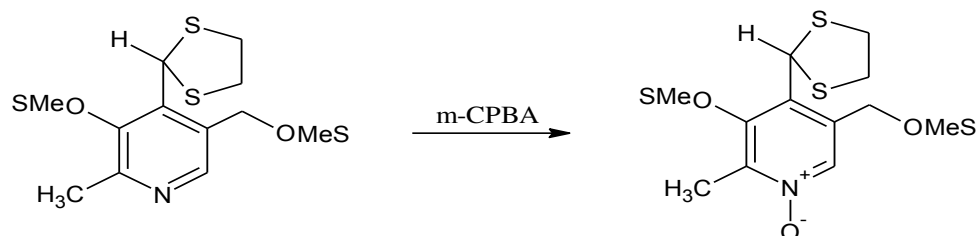
Step 2: Protection of Aldehydic Group¹⁵

Reaction:



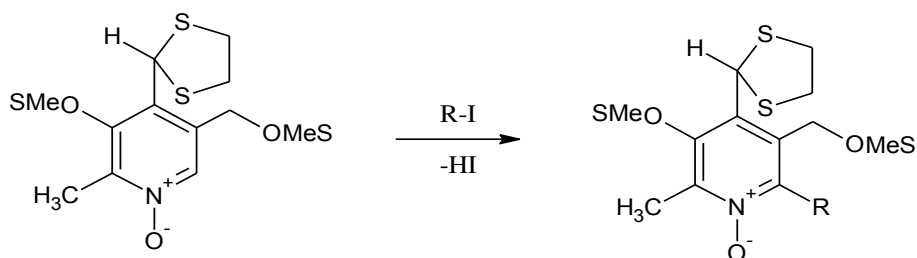
Step 3: Formation of N-oxide of Pyridine Ring¹⁶

Reaction:



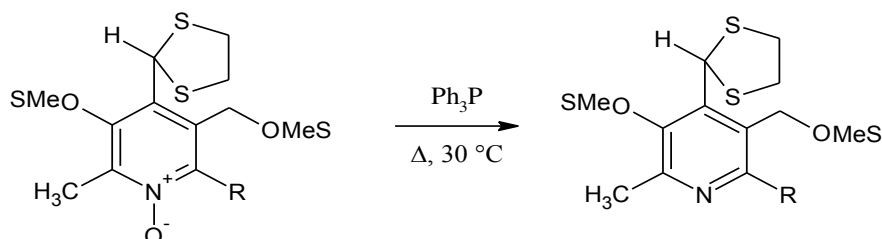
Step 4: Substitution at α -Position of Pyridine Ring¹⁷

Reaction:



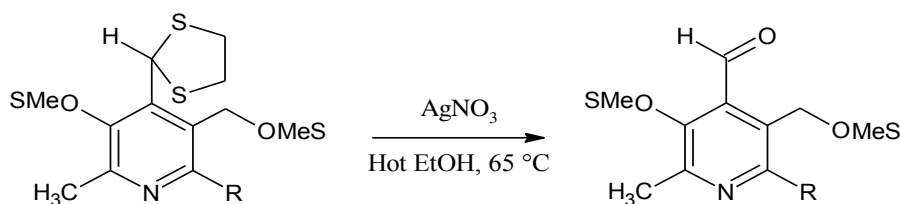
Step 5: Removal of N-oxide of Pyridine Ring¹⁸

Reaction:



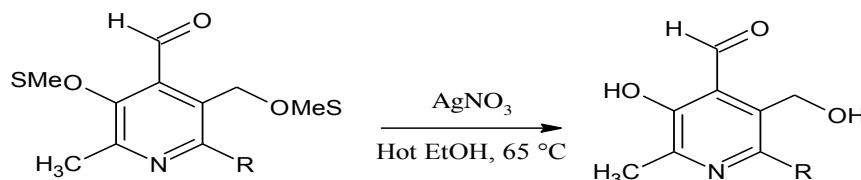
Step 5: Deprotection of Aldehydic group¹⁹

Reaction:



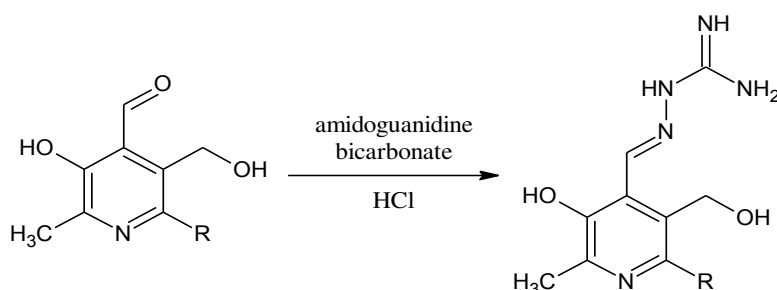
Step 6: Deprotection of Hydroxyl groups²⁰

Reaction:



Step 7: Synthesis of Ligand Amidoguanidine Schiff Base²¹

Reaction:



Procedure:

The 0.5 M methanolic solution of compounds obtained from step-6 was prepared by mixing appropriate amount of the compound in 10 mL methanol. The appropriate amount of amidoguanidine bicarbonate was dissolved in HCl to prepare 0.5 M solution. Both the

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solutions were mixed together with continuous stirring and refluxed for an hour. On cooling yellowish coloured precipitate appeared. The solid mass was filtered, recrystallised from methanol and washed with water and ethanol repeatedly with three times and dried over calcium chloride in desiccator. The melting points of the ligands were determined using open capillary tube in kjeldal flask filled with concentrated sulphuric acid.

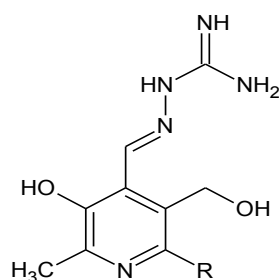
Elemental analysis: The elemental analyses of the compounds are given as:

	L ¹ (Found/Cal)	L ² (Found/Cal)	L ³ (Found/Cal)	L ⁴ (Found/Cal)
C	54.43/54.75	62.32/62.61	60.25/60.57	54.87/54.04
H	6.41/6.46	7.79/7.83	7.15/7.25	5.16/5.20
N	26.32/26.61	20.15/20.29	21.92/22.08	29.78/29.97

The main IR bands of the ligands are assigned in the following table:

Bands (cm ⁻¹)	Assignments
3410	$\nu_{\text{O-H}}$ (str.)
3200	ν_{NH_2} (str.)
2080	$\nu_{\text{O-H}}$ (str. H-bonded)
1585	$\nu_{\text{C=N-H}}$ (str.)
1350	$\nu_{\text{C=N}}$ (str.)

After analysis of the IR spectral bands of the ligands, following structure of the ligands was confirmed.



Where R = Following

-
-
-
-

Preparation of Complexes:

A hot freshly prepared ethanolic solution (10 mL) of metal (II) chlorides (0.05M) were mixed with a hot solution (0.05M) of ligands (0.05M). The mixture was saturated with sodium acetate to maintain the pH ~9. The resulting mixture was then left under reflux for 4 hours. After refluxing for 4 hrs appropriate complexes were precipitated out on cooling the reaction mixture. The coloured complexes were then filtered, washed with methanol and recrystallized from ethanol. The synthesized complexes were obtained in ~60-70% yield. A solubility test of this complex was performed. It was found soluble in dimethyl sulphoxide (DMSO), dimethyl formamide (DMF). It was sparingly soluble in water and insoluble in alcohol, ether and acetone. The purity of the complexes was checked by taking TLC. The thin layer chromatographies of the complexes were performed by using aluminium plates coated with silica gel-60GF254 as the stationary phase. The solvent system was consisted of CHCl₃ and MeOH in 9:1 ratio as mobile phase. Its melting point was determined using open capillary tube in kjeldal flask filled with concentrated sulphuric acid.

Physicochemical Measurements:

Elemental Analysis: The metal complexes were decomposed with fuming nitric acid and

metal content was determined. The C, H and N analytical data are reported in Table 1.

Table 1
Analytical data and conductivity measurement of metal complexes

Sl. No.	Complexes	Elemental analysis				Conductivity ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
		M%	C %	H %	N %	
1.	$[\text{Fe}(\text{L}^1)_2]$	9.49/9.63	49.38/49.67	5.47/5.52	24.14/24.14	8.9
2.	$[\text{Cu}(\text{L}^1)_2]$	10.56/10.82	48.65/49.02	5.41/5.45	23.49/23.83	5.6
3.	$[\text{Fe}(\text{L}^2)_2]$	7.37/7.51	57.76/58.08	6.92/6.99	18.59/18.82	10.9
4.	$[\text{Cu}(\text{L}^2)_2]$	8.21/8.45	57.26/57.48	6.88/6.92	18.43/18.63	18.4
5.	$[\text{Fe}(\text{L}^3)_2]$	8.01/8.12	55.50/55.83	6.33/6.40	20.27/20.35	12.7
6.	$[\text{Cu}(\text{L}^3)_2]$	8.95/9.14	55.02/55.21	6.27/6.32	20.01/20.35	20.5
7.	$[\text{Fe}(\text{L}^4)_2]$	7.41/7.89	50.49/50.86	4.45/4.52	27.33/27.69	30.3
8.	$[\text{Cu}(\text{L}^4)_2]$	8.53/8.88	50.08/50.31	4.41/4.47	27.21/27.39	15.3

RESULT AND DISCUSSION

Elemental analysis, metal ligand ratio and conductivity measurements data indicates these complexes to be non electrolyte established in the form of compound reported. The general composition of the synthesized metal complexes can be represented as $[\text{M}(\text{L})_2]$ [where M = Fe(II), and Cu(II) and L = ligands]. All the synthesized complexes were thermally stable and colored. Observations such as colour, melting point and solubility behaviour for all the complexes were recorded.

Solubility behaviour:

Solubility behaviour of all the synthesized complexes was checked using different solvents such as water, methanol, ethanol, chloroform, acetone, acetonitrile, DMSO and DMF. Both synthesized complexes were found to be insoluble in water and partially soluble in methanol, ethanol, acetone and ethyl acetate. Both complexes were found to be soluble in DMF and DMSO.

Molar conductance:

Molar conductance for both complexes was measured by preparing their 10^{-3} M solutions in DMF as a solvent. The lower values (20 and $35 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) for both complexes with divalent metal ions such as Fe(II) and Cu(II) complexes was recorded. The lower values recorded for divalent metal ion complexes indicate non-electrolytic behaviour of the complexes²¹.

Magnetic properties:

Magnetic susceptibilities were determined on the SES instrument's magnetic susceptibility Guoy's balance (Model EMU-50) at room temperature using copper (II) sulphate as a standard. These magnetic susceptibility values were utilized to calculate magnetic moments using spin only formula $\mu_{eff} = \sqrt{n(n+2)}$ for all the synthesized complexes. The magnetic moment values of Fe (II) complexes lie in the range of 4.92-4.98 B.M. indicating towards d^6 configuration and four unpaired electrons present in this complex³. This means this complex is of six coordinated octahedral geometry. The magnetic moment values of Cu (II) complexes lie in the range of 1.95-2.00 B.M. corresponding to one unpaired electrons in these complex²².

IR and NMR Spectra:

IR spectra were recorded as KBr pellets in the region of $4000\text{-}400 \text{ cm}^{-1}$ on a Perkin-

Elmer Spectrophotometer. IR spectra of all the synthesized complexes have been recorded in the range 4000-400 cm^{-1} . The spectra are interpreted considering few main peaks observed. The ligands have many donor sites such as phenolic hydroxyl, hydroxymethyl, lone pair of electrons of pyridine nitrogen, lone pairs of electrons of nitrogen of amidoguanidine part and the π -electrons of ethylenic carbon-carbon double bond *etc.* As lone pair of phenolic hydroxyl is in conjugation with the aromatic ring, it may not participate in the complexation. The characteristic IR frequency of hydroxymethyl group²³ at $\sim 3450 \text{ cm}^{-1}$ almost remain as such in all metal complexes of ligands indicating the group remain intact from complexation. The characteristic IR frequency of ethylenic carbon-carbon double bond²⁴ at $\sim 1652 \text{ cm}^{-1}$ remain almost as such in all metal complexes of ligands indicating the corresponding π -electrons do not participate in complexation. Perhaps, due to steric hindrance generated by the propenyl group of C-6, the lone pair of nitrogen of pyridine ring is remained separated from complexation²⁵. However, the infrared frequencies in the ligands characteristic of phenolic hydroxyl group and carbon-nitrogen bond of amidoguanidine part have been influenced on complexation with metal²⁺ ions. The highest frequency of the bands of the ligand at $\sim 3200 \text{ cm}^{-1}$ can be assigned to the asymmetric ν_{OH} vibration of the phenolichydroxyl group. This band is absent after complexation in all complexes of ligands indicating the deprotonation²⁶ of $-\text{OH}$ group during condensation before complex formation. It is further confirmed as complexes do show the NMR peak characteristic of proton of phenolichydroxyl group. The band of ligand near $\sim 3420 \text{ cm}^{-1}$ remains almost unaltered in all the complexes of ligands, which indicates²⁷ those NH_2 and NH groups do not participate in complexation. The characteristic bands at $\sim 2460 \text{ cm}^{-1}$, $\sim 2200 \text{ cm}^{-1}$, $\sim 1900 \text{ cm}^{-1}$, $\sim 920 \text{ cm}^{-1}$, $\sim 840 \text{ cm}^{-1}$ and $\sim 780 \text{ cm}^{-1}$ remain unaffected.

In the metal complexes, the most interesting features noted is about doublet band²⁸ observed in the IR spectrum of the ligands nears $\sim 1620 \text{ cm}^{-1}$. The higher one goes up to $\sim 1650\text{--}1680 \text{ cm}^{-1}$ probably due to the bending mode of NH_2 group, which remain almost same and shows that it does not participate in coordination²⁹. The other component, which is due to $\text{C}=\text{NH}$ (imine group) stretching frequency shifts to lower frequencies about $\sim 1600 \text{ cm}^{-1}$ in the complexes, indicating the coordination through this group (*i.e.* $\text{C}=\text{N}$). A sharp band at $\sim 1585 \text{ cm}^{-1}$ observed in free ligand is assigned to $\text{C}=\text{N}$ stretching vibration of Schiff base residue. This band shifts to the lower frequencies in all complexes, which indicates³⁰ that azomethine nitrogen of $\text{C}=\text{N}$ participate in complexation. Thus, on account of infrared spectral properties we can say that the ligands act as uninegative tridentate ligand. The occurrence of bands in between $\sim 420\text{--}455 \text{ cm}^{-1}$, which are characteristics of $\text{M}\text{--}\text{O}$ linkage, proves the coordination of oxygen to the metal ions³¹.

Electronic spectra:

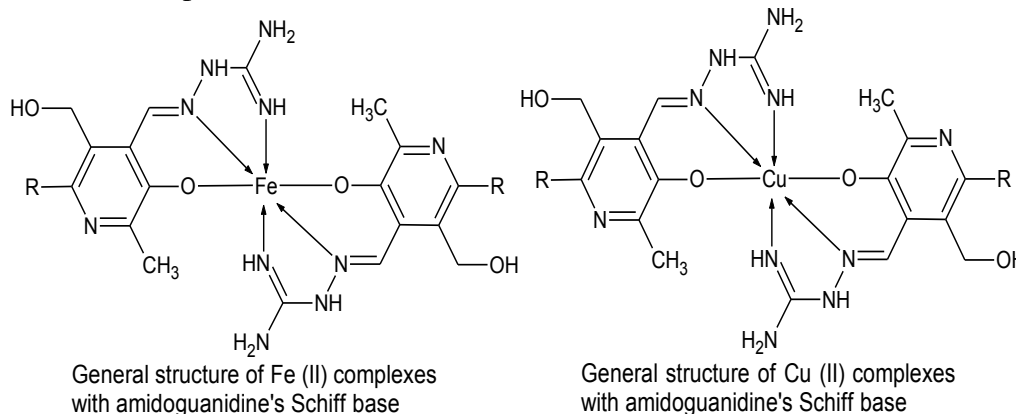
Electronic spectra were recorded in DMSO on a Shimadzu UV-1600 spectrophotometer. Electronic spectra for all the synthesized complexes were recorded in DMSO solvent. The complex formed by Fe (II) ion shows absorption at $\sim 21,235 \text{ cm}^{-1}$ labeling the transition ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}$, which indicates³² octahedral geometry of the complex having four unpaired electron in Fe (II) ion. A great majority of Cu (II) complexes are blue or green in colour. Some of these complexes may be red or brown. This is generally caused by a strong absorption in UV-region arising from charge transfer. These transitions tail off into the blue end of the visible spectrum, thereby causing the complexes to appear red to brown. Cu (II) complexes with ligand are known in a wide variety of structures. In present research work, Cu (II) complex show absorptions ~ 12000 , ~ 15500 and ~ 17000 respectively. They are labeled as ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{A}_{1\text{g}}$, ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{B}_{2\text{g}}$ and ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$ indicating the tetragonal geometry^{33,34} of the complex. The increased bonding partner of the $d_{x^2-y^2}$ copper atomic orbital then leads to larger splitting of the ground state ${}^2\text{E}_{\text{g}}$ than we would anticipate from a purley ionic model³⁵.

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The approximate positions of the 2E_g and 2B_g states can be estimated from the g factors obtained from electron paramagnetic spectra. Thus six coordinated Cu (II) complex is distorted from a regular octahedral with the axial ligands of the octahedron further away from the metal ion than the equatorial ligands due to Jahn-Teller distortion.

CONCLUSION

On the basis of elemental analyses, spectral analyses and magnetic data, following structures of the complexes have been established.



ACKNOWLEDGEMENTS

The authors express their thanks to Prof. S. Jha (Retired), PG. Department of Chemistry, L. N. M. U, Darbhanga, India and to Prof. L. K. Mishra (Retired), Department of Chemistry, Science College, Patna, India for constant encouragement during the course of investigation.

REFERENCES

1. Prabhu, G. V. and Venkappaya, D. 1995. *J. Ind. Chem. Soc.*, 72:511.
2. Sharma, Y. S., Pandey, H. N. and Mathuur, P. 1994. *Polyhedron*, 13:3111.
3. Brown-Ann, W. V. 1990. *Acad. Sci*, 598, 376.
4. Constable, E. C. and Holmes-Inorg, J. M. 1987. *Chim. Acta*, 126:195.
5. Hash, F. P. 1993. *J. Ozols-Proc. Natl. Acad. Sci. (USA)*, 90:5302.
6. Dash, A. C, Nanda, R. K. and Aditya, S. 2001. *J. Indian Chem. Soc.*, 78:707.
7. D. Wester, D. and Palenik, G. J. 1973. *J. Am. Chem. Soc.*, 95:6505.
8. Narang, K. K. and A. Aggarwal, A. 1975. *Ind. J. Chem.*, 13:1072.
9. Yadav, J. S., Reddy, V. S., Eeshwaraiah, B. and Gupta, M. K. 2004. *Tetrahedron Lett.*, 45:5873.
10. Boger, D. L., Boyee, C. W., Labriti, M. A., Schon, C. A. and Q. Jin, Q. 1999. *J. Am. Chem. Soc.*, 121, 54.
11. Singh, C., Parwana, H. K., Singh, G. and Jolly, R. S. 2000. *Asian J. Chem.*, 12:1.
12. Sari, N., and Gurkan, P. 2004. *Z. Naturforsch.*, 59b:692.
13. Manezand, R. M., Pretsch, E. and Bakker, E. 1998. *Chem. Rev.*, 98:3083.
14. Chen, X. T., Bhattacharya, S. K., Zhou, B., Gutteridge, C. E., Pettus, T. R. R. and Danishefsky, S. J. 1999. *J. Am. Chem. Soc.*, 121:6563.
15. Fujita, E., Nagao, Y. K. 1978. *Kanelo-Chem. Pharma. Bull.*, 26:3743.
16. Walters, M. A. and Shay, J. J. 1995. *Tetrahedron Lett.*, 36:7575.
17. Van Ammers, M., J. den Hertog, H., and Haase, B. 1962. *Tetrahedron*, 18:227.

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18. Katrizky, R. and Lam-heterocycles, J. N.1992. 33:1011.
19. Trost, B. M. and Parquette, J. R.1994. *J. Org. Chem.*, 59:7568.
20. Gassman, P. G. and Schenk, W. N.1977. *J. Org. Chem.*, 42:918.
21. Ronald, S. B. and Rao, G. N. 2002. *Proc. Natl. Acad. Sci. India, A* 72: 301.
22. Sailaja, B. B. V., Kebede, T., Rao, G. N. and Rao, M. S. P. 2004. *Proc. Natl. Acad. Sci. India, A* 74:399.
23. Wang, W. S., Lin, J. K., Lin, T. C., Chen, W. S., Jiang, J. K., Wang, H. S., Chiou, T. J., Liu, J. H., Yen, C. C. and Chen, P. M. 2007. *Oncologist* 12: 312.
24. Ronald, S. B. and Rao, G. N. 2002. *J. Indian Chem. Soc.* 79:799.
25. G. N. and Ramakrishna, A. 2006. *J. Indian Chem. Soc.* 83:332.
26. A. Ramakrishna, A. and Rao, G. N.2007. *Proc. Natl. Acad. Sci. India, A* 77:21
27. Zyed, M. A. and Abdallah, S. M. 2005. *Spectrochimica Acta, Part-A*, 61:2231-2238.
28. Mohamed, G. G., El-Gamel, N. E. A. and Nour El-Dien, F. A. 2001. *Synth. React. Inorg. Met. Org. Chem.*, 31:347.
29. Di Stefano, R.2002. *J. Inotg. Biochem.*, 29: (3-4)179-292.
30. K. Nakamoto, K.2009. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part-B*, 6th ed., John Wiley and Sons Inc, New York.
31. Kemp, W. 2004. *Org. Spectroscopy*, 3rd ed.
32. R. K. Agarwal and Himanshu Agarwal: *Synthe. React. Inorg. Met.-Org. Chem.*, 31, 263, 2001.
33. Tendon, S. P., Mehta, P. C.: *J. Chem. Phys.*, 52, 4313, 1970.
34. Singh, B., Sahai, Preeti and Singh, Praveen K., *Indian J. Chem.*, 35A, 494, 1996.
35. A. C. Dash, R. K. Nanda and S. Aditya- *J. Indian Chem. Soc.*, 78, 707, 2001.