RESEARCH VOL. 1, 2015

ISSN 2394–3750
EISSN 2394–3769

SCIENCE & TECHNOLOGY

Synthesis and fungicidal activities of transition metal complexes of the 2- Amino -4- (P- Methoxy Phenyl) Thiazole

Dinkar Malik[1]☼, Sandeep Kumar[1], Punam Yadav[1], Vijai Malik[2]

1.Department of Chemistry, M. S. College, Saharanpur U.P., India
2.Department of Botany, M. S. College, Saharanpur U.P., India

☼**Correspondence to:** Dr. Dinkar Malik c/o Vijai Malik, 21-Mohit Vihar New Madhonagar Saharanpur-247001 (U.P.) Email: vijai.malik@rediffmail.com

Article History
Received: 05 October 2013
Accepted: 23 December 2013
Published: 1 July 2015

Citation
Dinkar Malik, Sandeep Kumar, Punam Yadav, Vijai Malik. Synthesis and fungicidal activities of transition metal complexes of the 2-Amino -4- (P- Methoxy Phenyl) Thiazole. *Science & Technology,* 2015, 1(3), 106-108

ABSTRACT

Transition metal complexes derived from the ligand 2-amino-4-(p-methoxy phenyl) thiazole were prepared and characterized with the help of their elemental analysis, IR, electronic and magnetic susceptibility studies. The complexes is of the type ML_2X_2 (where M = Cu (II), Co (II) and Ni (II), L= 2-amino-4-(p-methoxy phenyl) thiazole and X= ci^-, $CH3COO^-$. IR studies have shown that nitrogen of the amino group and sulphur of the thiazole ring took part in co-ordination. Magnetic and electronic spectral studies have shown that all the complexes are having octahedral geometry. These newly synthesized complexes were also screened for their antifungal activity against different fungi at different concentrations. The activity decreases with decrease of concentration and the metal complexes are less toxic than the parent ligand.

Key Words: Fungicidal activity, Thiazole Complexes, Toxicity

1. INTRODUCTION

Heterocyclic compounds are cyclic compound containing a hetero atom in the ring. The common hetero atoms are oxygen, nitrogen and sulphur. Thiazole derivatives have attracted the interest because in addition to nitrogen atom, it has also sulphur atom which acts as donor site. Such study has been motivated not only by a desire to understand the interaction between the donor site and metal atoms but also by the development of metal complexes into antifungal, antiviral and antibacterial agent. A critical review of literature revealed that no systematic work on transition metal complexes of 2- amino-4-(p-methoxy phenyl) thiazole has been carried out. Khamamkar et al. (2012) studied the synthesis, spectral characterization and biological activity of Schiff's base derived metal complexes. Schiff's base derived complexes of derivatives of DHA were also studied by Mane et al. (2001). Malik et al. (2013) studied the structural and biological aspects of transition metal complexes of the ligand 2-amino-4-(p-hydroxy phenyl) thiazole. The present paper deals with the preparation and characterization of Cu(II), Co(II) and Ni(II) complexes with 2-amino-4-(p-methoxy phenyl)thiazole. Metal complexes play an important role in biological activity. In many cases metal complexes are more potent than free ligands. The newly prepared complexes were also screened for their antifungal activity against different fungi at different concentrations (Bharti et al. 2010).

2. EXPERIMENTAL

2.1. Materials and methods

All the chemicals and reagents used were of analytical grade: otherwise they were purified before use. Organic solvent used was absolute alcohol. IR spectra of the ligand and complexes are recorded in nujolmull. The electronic spectra were recorded in MgO at room temperature on VSU-22 spectrophotometer. The measurements were carried out Guru Nanak Dev University, Amristar. Metal and sulphur contents of these complexes were estimated using the standard procedures reported in literature (Vogal 1961 and Vogal 1958). The estimation of carbon, hydrogen and nitrogen were carried out at BHU, Varanasi and CDRI, Lucknow and results are given in Table 1. Magnetic measurements were carried out at IIT Roorkee at room temperature using Co [Hg (CNS)$_4$] as a calibrant. The ligand 2-amino-4-(p-methoxy phenyl) thiazole was prepared using the procedure reported in the literature (Dodson et al. 1945).

Table 1
Elemental Analysis Data

Complexes	%Calc./ Obs.					
	C	H	S	N	O	M
$C_{10}H_{10}N_2OS$	58.25 58.11	4.85 4.78	15.53 15.46	13.59 13.51	7.77 7.69	-----
$[Cu(C_{10}H_{10}N_2OS)_2Cl_2]$	43.91 43.86	3.65 3.60	11.71 11.62	10.24 10.18	5.85 5.80	11.61 11.50
$[Ni(C_{10}H_{10}N_2OS)_2Cl_2]$	44.28 44.18	3.69 3.62	11.80 11.69	10.33 10.27	5.90 5.82	10.88 10.78
$[Co(C_{10}H_{10}N_2OS)_2Cl_2]$	44.28 44.21	3.70 3.66	11.80 11.73	10.32 10.24	5.90 5.85	10.87 10.79
$[Cu(C_{10}H_{10}N_2OS)_2(CH_3COO^-)_2]$	48.52 48.49	4.38 4.29	10.78 10.66	9.43 9.39	16.17 16.11	10.69 10.58
$[Ni(C_{10}H_{10}N_2OS)_2(CH_3COO^-)_2]$	48.89 48.70	4.41 4.31	10.86 10.81	9.50 9.43	16.29 16.21	10.01 9.94
$[Co(C_{10}H_{10}N_2OS)_2(CH_3COO^-)_2]$	48.89 48.78	4.42 4.37	10.87 10.79	9.50 9.44	16.28 16.22	10.00 9.94

2.2. Preparation of metal complexes

Bis [-amino-4-(p-methoxy phenyl) thiazole] Dichloride/Diacetate ligands and M(II) salts where M= Ni(II), Cu(II) and Co(II) are taken to synthesize the complex. The respective metal salts in dry alcohol were taken into a round bottom flask and mixed with required amount of ligand (1:2ratio). A little amount of alcohol was also added. Then the reaction mixture was refluxed on water bath for at least two hours and then the reaction mixture was concentrated to half of its volume. On keeping for overnight, crystals of metal complexes separate out which were filtered, washed with alcohol and finally with ether and then dried in vacuum. Similarily some complexes of thiazole were also synthesized by many workers (Khalil et al. 2009; Aridoss et al. 2009; Kaergoudar et al. 2008; Dawane et al. 2010; Adibpour et al. 2010; Arshad et al. 2011 and Giri et al. 2009).

3. RESULTS AND DISCUSSION

The infra-red and far infra-red spectra of the ligand and its complexes were recorded to detect the point of co-ordination. This ligand has three donor sites viz. two nitrogen (one on thiazole ring and other on the amino group) and one on ring sulphur. Thiazoles are formally derived from imidazole by replacement of -NH by sulphur in position one makes it better π acceptor due to the availability of empty d-orbital on sulphur atom. The complex formation affects the absorption band due to NH_2 and C-S

vibrations. The band obtained near about 1636 cm^{-1} which is due to ν (C=N) frequencies in the free ligand is completely unaffected after complex formation. This shows that the ring nitrogen does not take any part in the coordination. The band observed at 650 cm^{-1} in the free ligand assigned to asymmetric ν (C-S) is shifted to lower frequency after complexation. But the symmetric ν (C-S) frequency obtained at 685 cm^{-1} completely disappears or intensity of this band is reduced after complexation. The change in asymmetric C-S and disappearance of symmetric C-S band clearly indicates that the ring sulphur of thiazole ring is taking part in complex formation. The ν(N-H) asymmetric and symmetric stretching frequencies appeared in the region 3425 and 3265 cm^{-1} respectively, also decreases due to interaction of lone pair of nitrogen atom of the amino group with π electron system of the conjugated system, which reduces the N-H band strength, thus giving an idea about the point of attachment with metal ion. This shows that the lone pair of electron available on nitrogen atom of amino group is taking part in complex formation. From the above observation it is clear that the nitrogen of the $–NH_2$ group and ring sulphur take part in coordination.

In the electronic spectra of Ni (II) complexes bands were observed in the region 9150-9900 cm^{-1} can be assigned to $^3A_{2g}$ (F) → $^3T_{1g}$ (F), the highest energy transition ν_3 obtained in the region 24400-26500 cm^{-1} may probably be due to $^3A_{2g}$ (F) → $^3T_{1g}$ (P) while the spin allowed transition of the lowest energy ν_1 may be assigned to $^3A_{2g}$ (F) → $^3T_{2g}$ (F) which are characteristic of octahedral Ni(II) ion. The magnetic moment values found in the range 2.80-3.48 B.M. This is a support of high spin octahedral geometry (Earnshaw 1968).

Cobalt complexes show magnetic moment value in the range 4.32 – 4.39 B.M. which are within the range 4.2- 4.8 B.M. for tetrahedral complexes. In present Co (II) complexes three bands at 8505-9000, 16050-17245 and 18000-19000 cm^{-1} were observed which may be assigned for $^4A_2$ (F) → $\nu_3{}^4T_2$, $^4A_2$ (F) → $\nu_2{}^4T_1$ (F) and $^4A_2$ (F) → $\nu_1{}^4T_{1g}$ (P) respectively. Since ν_1 band is very weak due to weak character of $^4T_2$ transition the observed bands are likely to be due to multi-component bands ν_2 and ν_3. The observed splitting of these bands suggests the tetrahedral geometry.

Two bands were observed in electronic spectra of Cu (II) complexes in the region 15300-15400 and 19200-20250 cm^{-1} which may be assigned to $^2B_{1g}$ → $^2A_{1g}$ and $^2B_{1g}$ → $^2E_{1g}$ transitions respectively in a planar field. The magnetic moment values for the Cu(II) complexes lie in the range 1.54-1.57 B.M. which support square planar geometry.

Sulphur and its various compounds are known which function as fungicides and pesticide colloidal sulphur was used as insecticide. The thiazole and their complexes were screened for the fungicidal activity against *Drechlera-tetramera*, *Fusarium-oxysporum* and *Macroohomia-phaseoli*. The metal complexes are less toxic than the free ligand. This might be due to the fact that free sulphur is present in the ligand which is responsible for toxicity however it is co-ordinated to metal in the complex. It is also observed that the ligand as well as their metal complexes is more toxic at higher concentration and the activity decreases with decrease in concentration.

Acknowledgement

We gratefully acknowledge to Dr. K.K. Sharma, Principal M. S. College, Saharanpur (U.P.) for providing necessary facilities.

REFERENCE

1. Adibpour N, Khalaj A, Rajabalian S. Synthesis and antibacterial activity of isothiazolyloxazolidinones and analogous 3(2H)-isothiazolones. *Eur J Med Chem.,* 2010, 45, 19-24
2. Aridoss G, Amirthaganesan S, Kim MS, Kim JT, Jeong YT. Synthesis, spectral and biological evaluation of some new thiazolidinones and thiazoles based on t-3-alkyl-r-2, c-6-diarylpiperidin- 4-ones. *Eur J Med Chem.,* 2009, 44, 4199-4210
3. Arshad A, Osman H, Bagiey MC, Lan CK, Mohamad S, Safirah A, Zahariluddin M. Synthesis and antimicrobial properties of some new thiazolyl coumarin derivatives. *Eur J Med Chem.,* 2011, 1-7
4. Bharti SK, Nath G, Tilak R, Singh SK. Synthesis, anti-bacterial and anti-fungal activities of some novel Schiff bases containing 2,4-disubstituted thiazole ring. *Eur J Med Chem.,* 2010, 45, 651-660
5. Dawane BS, Konda SG, Mandawad GG, Shaikh BM. Poly(ethylene glycol) (PEG-400) as an alternative reaction solvent for the synthesis of some new 1-(4- (4-chlorophenyl)-2-thiazolyl)-3-aryl-5-(2-butyl-4-chloro-1H-imidazol-5yl)-2-pyrazolines and their in vitro antimicrobial evaluation. *Eur J Med Chem.,* 2010, 45, 387-392
6. Dodson RM, King LC. The reaction of ketones with halogens and thiourea *J. Am. Chem. Soc.*, 1945, 67, 2242
7. Earnshaw A, *Magnetochemistry*. Academic Press. New York., 1968
8. Giri RS, Thaker HM, Giordano T, Williams J, Rogers D, Sudersanam V, Vasu KK. Design, Synthesis and characterization of novel 2-(2,4-disubstituted-thiazole-5-yl)-3-aryl-3H-quinazoline- 4-one derivatives as inhibitors of NF-IB and AP-1 mediated transcription activation and as potential anti-inflammatory agents. *Eur J Med Chem.,* 2009, 44, 2184-2189
9. Karegoudar P, Karthikeyan MS, Prasad DJ, Mahalinga M, Holla BS, Kumari NS. Synthesis of some novel 2,4-disubstituted thiazoles as possible antimicrobial agents. *Eur J Med Chem.,* 2008, 43, 261-267
10. Khalil AM, Berghot MA, Gouda MA. Synthesis and antibacterial activity of some new thiazole and thiophene derivatives. *Eur J Med Chem.,* 2009, 44, 4434-4440
11. Khamamkar Ashwini, Pallapothula Rao Venkateshwar. Synthesis, Spectral Characterization and Biological activity of Schiff's base derived metal complexes. J. Ind. Council Chem., Vol.29, No. 1&2. 2012,71-76
12. Malik Dinkar, Yadav Punam, Kumar Sandeep, Malik Vijai Studies on Structural and biological aspects of transition metal complexes of the ligand 2-amino-4-(p-hydroxy phenyl) thiazole. Discovery Pharmacy, Vol. 5, No. 15, Dec. 2013, 15-17
13. Mane PS, Shirodkar SG, Arbad BR, Chondhekar TK I. JC, Sec A; Inorganic, Bio-inorganic, Physical & Analytical Chemistry, 2001, 40A(6), 648
14. Vogal AI. *A Text Book of Quantitative Inorganic Analysis*. 3rd ed. (English Language Book Society and Longman)., 1961
15. Vogal AI. *Quantitative Organic Analysis*., 1958