

Synthesis and Characterization of Complexes of Co (II) and Hg (II) with 2'-Methoxy-2-Thioquinaldine Anilide

Abha Sinha

Associate Professor, Department of Applied Chemistry, Rungta College of Engineering & Technology, Bhilai, Durg, Chhattisgarh, India

Abstract: Sulphur compounds have been the subject of interest for the chemist all over the world due to their chemotherapeutic use for the mankind and animals. In recent few years coordination chemist have shown their interest in synthesizing organo-metallic compounds mainly chelates of metals ions with sulphur and nitrogen containing organic molecules. The ability of nitrogen and sulphur based donors to stabilize different metal ions has sparked interest in bioinorganic systems. They are now a day widely explored owing to their versatile biological activity and prospective use as drugs. So, in the present investigations an attempt is made in the direction of seeking such a co-relation between different physico chemical properties of complexes with ligands (thioamides) having sulphur and nitrogen atoms as potential donors. For this, 2'-methoxy-2-thioquinaldine anilide ligand has been prepared by Willgerdort reaction. In the present study, complexes of the ligand with Co(II), Hg(II) have been prepared and investigated. From the studies of magnetic behaviour, electronic & IR spectra it is concluded that ligand behaves in bidentate manner utilizing sulphur and nitrogen donor atoms.

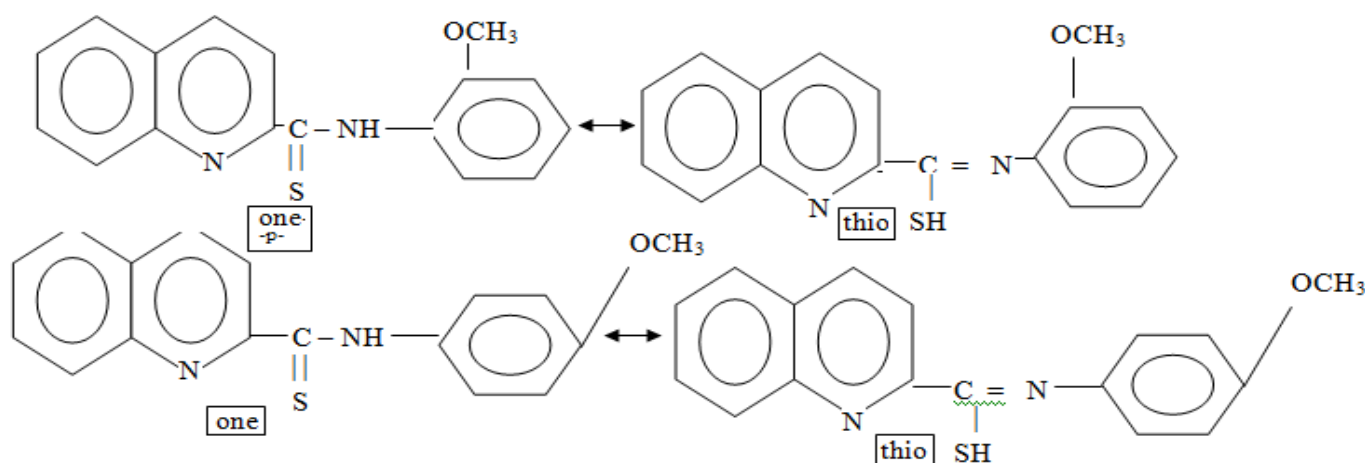
Keywords: Hg (II), Complexes, 2-Thioquinaldine Anilide, potential donor

1. Introduction

Heavy metal ions are of great concern, not only among the scientific community, especially chemists, biologists, and environmentalists, but increasingly among the general population, who are aware of the some of the disadvantages associated with them. In spite of the fact that some heavy metal ions play important roles in living systems, they are very toxic and hence capable of causing serious environmental and health problems. ¹⁻⁶ Some heavy metal ions, such as Zn(II), Cu(II), Co(II) are essential for the maintenance of human metabolism. However, high concentrations of these ions can lead to many adverse health effects. ^{1, 2, 7-20} It is also a fact that others such as Hg(II),

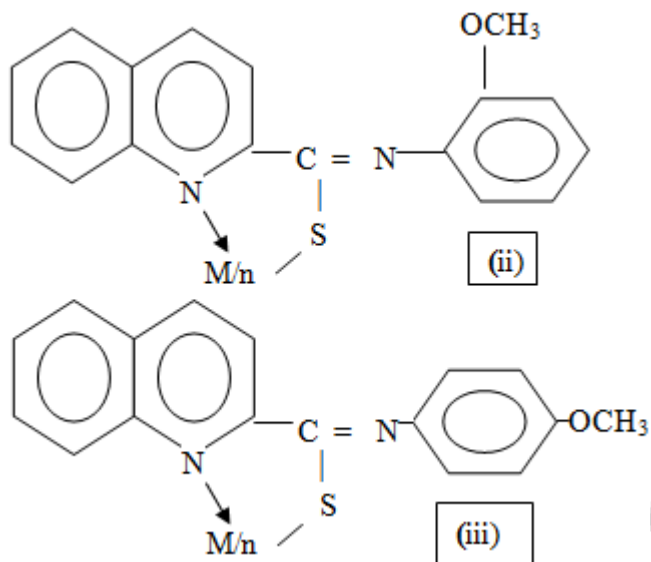
Pb(II), and As(III) are among the most toxic ions known that lack any vital or beneficial effects. Accumulation of these over time in the bodies of humans and animals can lead to serious debilitating illnesses. ^{2,21-30}

Therefore, in recent few years co-ordination chemists have shown their interest in synthesizing the coordination compounds of transition metal ions with the ligand having S & N atoms (thioamides) as ligands. In view of the growing interest of thioamide ligand and their complexes in this work presentation the synthesis and characterization of , 2'-methoxy-2-thioquinaldine anilide and its complexes with Co(II) and Hg(II) ions are reported. The ligand exists in the one-thio tautomeric form as shown:



Structure (i): the one-thio tautomeric form of Ligand

This is bidentate monobasic and form five membered chelate ring with various metal ions (structure-ii and iii).



Structure (ii) & (iii): Metal – Ligand Complexes

2. Experimental

2.1 Preparation of 2'-Methoxy 2-Thioquinaldine anilide:

The ligand 2' – Methoxy 2 – Thioquinaldine anilide was synthesised by Willgerdort reaction. **31**

Meta-toluidine (distilled 1 mol.) quinaldine (distilled 1 mole) and sulphur (powder 1 mole) were mixed in a 250 cc flask fitted with reflux condenser. The mixture was refluxed at 160°C for six hours. The reaction mixture was kept overnight. The solid red crystals obtained were filtered and recrystallised twice from ethanol. The deep yellow

compound obtained was dried in vacuum (0.1 mm of Hg) for 24 hours.

2.2 Preparation of complexes

The complexes of 2' – Methoxy thioquinaldine anilide was prepared by the general procedure as described below: -

2.2.1 Preparation of [Co (L)₂(B)₂] complexes

LH = 2' – Methoxy 2 –thioquinaldine anilide.

.B = Pyridine, α, β, γ -picoline

An aqueous ethanolic solution of hydrated cobalt (II) chloride (0.01 M in 60 cc 90% ethanol) was added slowly to ligand (0.01 M) in pyridine (or approximate base) and ethanol mixture (50 cc of 30% pyridine). The resulting solution was allowed to stand for 20-30 minutes for completion the reaction. The resulting reddish brown solution was diluted with excess of water when a brownish precipitate separated out. The product was filtered, washed without aqueous pyridine and allowed to stand in a KOH desiccator in the atmosphere of pyridine (or approximate base)

2.2.2 Preparation of [Hg(L)₂] 3 H₂O complex:

Mercuric acetate (0.02 M) solution if aqueous ethanol (30 cc) was treated with ligand (0.01M) solution in acetone (30 cc) and refluxed slowly on a steam bath, for half an hour. The yellow granular precipitate was filtered, washed with excess of water and finally with ethanol and then dried in a desiccator over CaCl₂. The dry solids were analysed. Analytical datas have been shown in the table-

Table 1: Results of Elemental Analysis of Complexes:

Compound	% of metal Theo.	Found	% of C Theo.	Found	% of H Theo.	Found	% of O Theo.	Found	% of N Theo.	Found	% of S Theo.	Found
Co(L) ₂ (λ-Pic) ₂	7.07	7.10	66.24	66.28	4.80	4.76	3.84	3.87	10.08	10.11	3.84	3.87
[Hg(L ₂)]3H ₂ O	23.87	23.86	48.55	48.59	3.81	3.88	9.52	9.58	6.66	6.69	3.81	3.85

The metal and sulphur estimations were carried out by standard methods **32, 33** and nitrogen by Kjeldahl method.

3. Results and Discussion

3.1 Magnetic Behaviour of Complexes

Magnetic behavior of certain metal ions play important role in structural determination of complexes. Magnetic behavior of Co (II) complex was calculated.

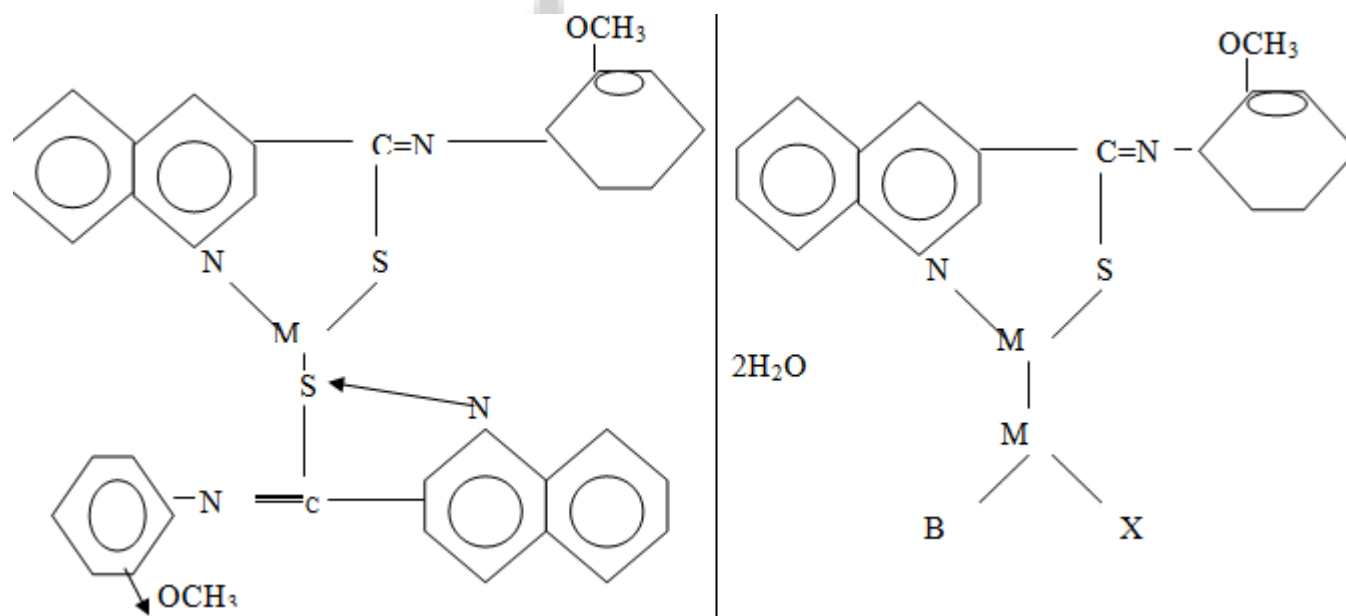
The Co (II) complexes understudies show the magnetic moment value between 2.21 BM to 2.30 BM at room temperature (35°C). These values indicate that the complexes have either four – co-ordinated square planar stereochemistry or six – ordinate low – spin octahedral structure. In present investigation, it is observed that the complexes do not exhibit spectral band similar to high spin tetrahedral or octahedral cobalt (ii) complexes. This band is probably d-d band assignable to ²E_g → ²T_{1g} transition of the complexes. Therefore, it is suggested that the Co (II) complexes have low spin octahedral structure.

3.2 Infrared Spectroscopic Measurement of the Complexes

The infrared spectra of Co(II) complexes have been recorded to find out the sites of ligand with Co(II) ion. The complexes display (C = N) vibration around 1605 -10 cm⁻¹ almost equal to ligand vibrations and second reduces by 10 - 15cm⁻¹ indicating the co-ordination by one (C=N) nitrogen in complexes and one is free i.e. not involved in bonding. In case of adduct complexes, the (C=N) stretch appears as very strong and broad band at probably due to coupling of co-ordinated pyridine (or heterocyclic bases) molecules (C = N) stretching vibrations in the complexes. (C = N) and (C - H) in plane bonding vibrations of the ligand are not affected appreciably in the complexes.

In case of base coordinated complexes definite position of ligands vibration was difficult to assign due to the IR vibrations of pyridine or heterocyclic base molecules. The fourth thioamide vibration of the ligand molecules (785cm⁻¹

in MTQA) which series mainly due to (C=S) stretch, shifts to lower frequencies by 110-120 cm^{-1} indicating the involvement of thiol (C=S) sulphur in bond with central metal atom, In present investigation, the IR spectra could not be determined in far infrared region hence nothing could be suggested about (M-N) or (M-S) vibration. Therefore, it is concluded the ligands (MTQA) is behaving as bidentate in $[\text{Co}(\text{L})_2(\text{B})_2]$.



Structure (iv): str.of $\text{Co}(\text{L})_2(\lambda\text{-Pic})_2$ Structure (v): str.of $\text{Co}(\text{L})_2(\beta\text{-Pic})_2$ where $\text{M} = \text{Co}(\text{II}), \text{Hg}(\text{II})$

5. Acknowledgement

The author is thankful to Dr. H.C. Rai, HOD, Department of Chemistry, BBA Bihar University for suggestions. Thanks to Dr. Manisha Agrawal, HOD, Department of Chemistry, RCET, Bhilai. A great thanks to Management of the Rungta College Of Engineering & Technology for providing the facilities.

References

- [1] Orvig, C.; Abrams, M. J. Chem. Rev. 1999, 99, 2201.
- [2] McRae, R.; Bagchi, P.; Sumalekshmy, S.; Fahrni, C. J. Chem. Rev. 2009, 109, 4780.
- [3] Que, E. L.; Domaille, D. W.; Chang, C. J. Chem. Rev. 2008, 108, 1517.
- [4] Bargossi, C.; Fiorini, M. C.; Montalti, M.; Prodi, L.; Zaccheroni, N. Coord. Chem. Rev. 2000, 208, 17.
- [5] Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. Coord. Chem. Rev. 2000, 205, 59.
- [6] Benounis, M.; Jaffrezic-Renault, N.; Halouani, H.; Lamartine, R.; Dumazet-Bonnamour, I. Mater. Sci. Eng., C 2006, 26, 364.
- [7] Lee, J. W.; Jung, H. S.; Kwon, P. S.; Kim, J. W.; Bartsch, R. A.; Kim, Y.; Kim, S.-J.; Kim, J. S. Org. Lett. 2008, 10, 3801.
- [8] Carol, P.; Sreejith, S.; Ajayaghosh, A. Chem. Asian J. 2007, 2, 338.
- [9] Rhee, H. W.; Choi, H. Y.; Han, K.; Hong, J. I. J. Am. Chem. Soc. 2007, 129, 4524.
- [10] Chang, C. J.; Nolan, E. M.; Jaworski, J.; Okamoto, K.; Hayashi, Y.; Sheng, M.; Lippard, S. J. Inorg. Chem. 2004, 43, 6774.
- [11] Aisen, P.; Wessling-Resnick, M.; Leibold, E. A. Curr. Opin. Chem. Biol. 1999, 2003.
- [12] Touati, D. Arch. Biochem. Biophys. 2000, 373, 1.
- [13] Kim, H. J.; Lee, S. J.; Park, S. Y.; Jung, J. H.; Kim, J. S. Adv. Mater. 2008, 20, 3229.
- [14] Jung, H. S.; Kwon, P. S.; Lee, J. W.; Kim, J. I.; Hong, C. S.; Kim, J. W.; Yan, S.; Lee, J. Y.; Lee, J. H.; Joo, T.; Kim, J. S. J. Am. Chem. Soc. 2009, 131, 2008.
- [15] Georgopoulos, P. G.; Roy, A.; Yonone-Lioy, M. J.; Opiekun, R. E.; Lioy, P. J. J. Toxicol. Environ. Health, Part B 2001, 4, 341.
- [16] Martínez, R.; Zapata, F.; Caballero, A.; Espinosa, A.; Tarraga, A.; Molina, P. Arkivoc 2010, iii, 124.
- [17] High, B.; Bruce, D.; Richter, M. M. Anal. Chim. Acta 2001, 449, 17.
- [18] Tapia, L.; Suazo, M.; Hodar, C.; Cambiazo, V.; González, M. Biometals 2003, 16, 169.
- [19] Metal Ions in Biological Systems; Sigel, H., Ed.; Marcel Dekker: New York, 1981; Chapter 12.
- [20] Waggoner, D. J.; Bartnikas, T. B.; Gitlin, J. D. Neurobiol. Dis. 1999, 6, 221.
- [21] Fluorescent Chemosensors for Ion and Molecule Recognition; Czarnik, A. W., Ed.; American Chemical Society: Washington, DC, 1993.
- [22] de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. Coord. Chem. Rev. 2000, 205, 41.

- [23] de Silva, A. P.; Gunaratne, H. Q. N.; Gunlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* 1997, 97, 1515.
- [24] *Chemosensors of Ion and Molecule Recognition*; Desvergne, J. P., Czarnik, A. W., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997.
- [25] Tchounwou, P. B.; Ayensu, W. K.; Ninashvili, N.; Sutton, D. *Environ. Toxicol.* 2003, 18, 149.
- [26] Vries, W. de; Schütze, G.; Lofts, S.; Meili, M.; Römkens, P. F. A. M.; Farret, R.; Temmerman, L. De; Jakubowski, M. Critical limits for cadmium, lead and mercury related to ecotoxicological effects on soil organisms, aquatic organisms, plants, animals and humans. In *Proceedings of the Expert Meeting on Critical Limits for Heavy Metals and Methods for their Application*, Berlin, Umweltbundesamt, 2-4 December 2002; pp 29-78.
- [27] Drasch, G.; Wanghofer, E.; Roeder, G. *Trace Elem. Electrolytes* 1997, 14, 116.
- [28] Marzec, Z.; Schlegel-Zawadzka, M. *Food Addit. Contam.* 2004, 21, 963.
- [29] Sapunar-Postruznik, J.; Bazulic, D.; Kubala, H.; Balint, L. *Sci. Total Environ.* 1996, 177, 31.
- [30] Wennberg, M.; Lundh, T.; Bergdahl, I. A.; Hallmans, G.; Jansson
- [31] H.D.J. Porter, *J. Am. Chem. Soc.*, 76, 127 (1954)
- [32] A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*. Long-Mans, Green & Co. Ltd., London (1952).
- [33] F.J. Welcher, *Organic Analytical Reagents*, D. Van Nostrand Co. Inc., New Jersey, Vol. 1 and 2 (1948).

Author Profile



Dr. Abha Sinha is an Associate Professor in Department of Applied Chemistry in RCET, Bhilai. She has fourteen years of teaching experience. Her area of interest is to formulate newer compounds for the benefits of living beings.

IJSR