RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.4, No.4 (2011),901-903
ISSN: 0974-1496
CODEN: RJCABP

STRUCTURAL STUDIES ON ISATINE MORPHOLIN-N-THIHYDRAZONE COMPLEXES WITH Pd(II) AND Pt(II)

Irshad Ali[1] and Shashad Ahmad Khan[2]
[1]Dept. of Chemistry, B.N. College, Patna University, Patna.
[2]P.G. Dept. of Chemistry, D.A.V College, Siwan
*E-mail: irshadbnc@yahoo.co.in

ABSTRACT

The complexes of Palladium (II) and Platinum(II) with α-isatinyl morpholine-N-thiohydrazone (H*I*stmth),having composition, [M (H*I*stmth) Cl_2], [M (Istmth)$_2$],[M (*I*stmth) PyCl] have been prepared and characterized by elemental analysis, IR, UV, molar conductivity and magnetic susceptibility measurements. The diamagnetism and ligand to metal ratio in complexes indicated four co-ordinated planar structures of the both Palladium (II) and Platinum (II) complexes.

Keywords: α-isatinyl morpholine-N-thiohydrazone, Palladium(II) and Platinum(II)

INTRODUCTION

The Isatin derivatives and some of their complexes are of much interest because of their potential application in medicine, pharmacy and dye industry.[1] Therefore, the research interests in Isatins derivatives increasing day to day.

The condensation of Isatine (A) with morpholine – N – thiohydrazide (B) in presence of dilute acetic acid yeilds α-isatinylmorpholine-N-thiohydrazone (H*I*stmth), which is potential N, S, and O donor molecule. This ligand coordinates in two different ways with some metals (Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}) to form complexes of the general formula ($ML_2.nH_2O$) behaving as tridentate molecule and with non-transition metals (Zn^{2+}, Cd^{2+}, Hg^{2+}) to form complexes [ML_2] and acting as bidentate ligand with donor sites N & S only. Now we report the preparation and characterization of Pd(II) and Pt(II) complexes with H*I*stmth.

EXPERIMENTAL

Palldium (II) and Platinum (II) chloride were obtained from Johnson Methew London and other Chemicals used were of AR grade. The ligand α-isatinyl morpholine-N-thiohydrazone was prepared as reported in the literature.

The complexes of Pt(II) and Pd(II) of type [M (Istmth)$_2$] were prepared by interaction of ligand and metal chloride solution in 2:1 molar proportion in hot ethanol at pH 5-6 and [M (HIstmth) Cl_2] in 1:1 molar ratio in acidic medium. The complexes [M (Istmth) PyCl] were obtained by adding stoichiometric proportion of pyridine to dichlorocomplex [M (HIstmth) Cl_2].The product was filtered washed with aqueous ethanol followed by ether and dried in vacuum desiccators over $CaCl_2$. The elemental analysis of the complexes is recorded in Table 1.

Infra red spectra of ligands and complexes were recorded on a perkin-Elmer 577 spectrophotometer in the range of 4000-200 com^{-1} and electronic spectra on a Beckmann DU-6 spectrophotometer. The molar conductances of complexes were measured in DMF using Wiss-Werksttter Weithein obb type LBR conductivity meter. Magnetic measurements were made on a Gouy balance using Hg [Co(SCN)$_4$] as calibrant.

The thiol enolic toutomer C exists in highly alkaline medium and strongly coloured due to resonance stabilized structure.

Since the complexes of Palladium (II) and Platinum (II) with (H*I*stmth) have been isolated in acidic medium (pH < 3) as well as in neutral medium (pH_{5-6}) therefore the ligand is expected to coordinate as neutral bidentate molecule or monoanionic chelating molecule. Analysis of Palladium (II) and Platinum (II) complex isolated in acidic medium correspond to composition [M (H*I*stmth) Cl_2] , while the complexes formed in basic medium have composition [*M* (*I*stmth)$_2$] and [M (*I*stmth) PyCl]. (M = Pd^{2+} or Pt^{2+}).

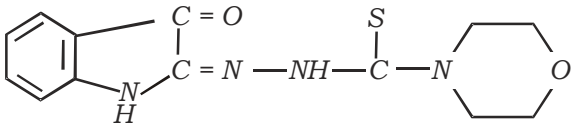
The complexes are diamagnetic and its electrical conductance value in DMF qualitatively occur in the range 5-12 Ohm^{-1} $mole^{-1}$ cm^2 indicating their non-ionic nature.[2]

Table-1:Analytical Results and Physical data of Complexes

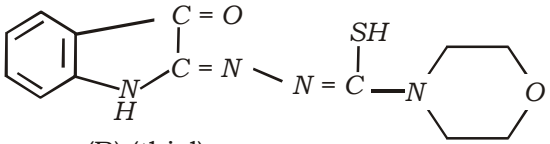
Complexes	Colour	Elemental analysis (%) : Found (Calcd.)					
		M	C	H	N	S	Cl
$Pd(C_{13}H_{14}N_4O_2S)Cl_2$	Deep Orange Red	23.11 (23.40)	34.10 (34.32)	3.21 (3.08)	12.41 (12.32)	7.21 (7.04)	15.34 (15.62)
$Pd(C_{13}H_{13}N_4O_2S)_2$	Orange Yellow	15.71 (15.96)	45.81 (46.80)	4.02 (3.90)	17.01 (16.80)	9.31 (9.61)	-
$Pd(C_{13}H_{13}N_4O_2S)PyCl$	Orange	24.15 (24.17)	35.61 (35.88)	3.02 (2.99)	12.91 (12.42)	7.31 (7.36)	7.93 (8.16)
$Pt(C_{13}H_{14}N_4O_2S)Cl_2$	Light Yellow	35.31 (35.12)	27.69 (28.08)	2.73 (2.52)	9.93 (10.08)	5.83 (5.76)	12.61 (12.78)
$Pt(C_{13}H_{13}N_4O_2S)_2$	Yellowish Brown	25.58 (25.67)	41.18 (41.32)	4.01 (4.31)	14.32 (14.51)	8.59 (7.99)	-
$Pt(C_{13}H_{13}N_4O_2S)PyCl$	Cream	37.31 (37.06)	28.51 (29.64)	2.73 (2.47)	10.73 (10.64)	7.05 (6.08)	6.71 (6.08)

RESULTS AND DISCUSSION

Isatinyl morpholine – N – thiohydrazone (H*I*stmth) exists in thione as well as thiol tautomers (A, B and C).

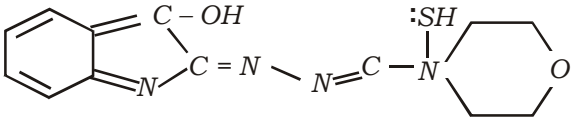


(A) (Thione)



(B) (thiol)

Or



(C)

Fig.-1

Electronic Spectra

The electronic absorption spectrum of 2-isatinylmorpholine-N-thiohydrazone in ethanol shows prominent electronic absorption bands around 237, 267, 332 and 345 nm and these transitions could be attributed to $\sigma - \pi^*$, $\pi - \pi^*$ and $n - \pi^*$ transitions of ligand molecules. The electronic absorption spectra of complexes in ethanol show strong and very broad transitions below 380nm and a shoulder around 410-430nm. The strong absorption is attributed to charge transfer transitions coupled with d – d transition $A_{1g} \rightarrow A_{2g}$ while shoulder at 430nm for palladium complexes is attributed to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition in planar field.[3-5] The charge transfer transition in Pt (II) complexes were observed around 390 and d-d band at 405-410nm assignable $^1A_{1g}$-$^1A_{2g}$ transition in planar field.[3-5]

Infrared Spectra

The I.R. spectrum of ligand was recorded as KBr disc.The ketonic group of ligand shows a preminent band at $1670\ cm^{-1}$. The $\nu\ (CO)$ is not shifted to higher frequency by 5 to 10 cm^{-1} in complexes indicating that CO oxygen is free and not involved in bonding.[6-9] The aldimine (C = N) stretch of free ligand was observed at 1626cm^{-1} which get shifted to1605 ± 5cm^{-1}. The shift of CN stretch to lower wave number suggested the coordinatin of aldimine nitrogen to metal atom. The ligand display thioamide bands located at 1535, 1454, 1220 and 956Cm^{-1}. The thioamide band IV located at 956cm^{-1} is shifted to lower wave number and observed at 760-720cm in [*M* (*I*stmth)$_2$] and [M (*I*stmth) PyCl] type of complexes suggesting bonding of sulphur atom on deprotonation of thiol SH of H*I*stmth. The thioamide band IV in complex [*Pd (*H*I*stmth) Cl_2] (M=Pd^{2+} or Pt^{2+}) is observed near 930cm suggesting that thione tautomer is retained and it acts as bidentate chelating molecule.[10-16]

Thus, from the I.R., UV, magnetic measurements and conductance values four coordinated planar structures are suggested for all Pd(II) and Pt(II) complexes with H*I*stmth,

REFERENCES

1. V .Glover, Halket, P.J. Watkin, A .Clow, B.L. Goodwin and M.J.Sandler, *Neurochemistry*,**51**, 656(1988)
2. (a) J.V Quagliano, J. Fujita, G. Fraz, D.J. Philips and S.Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).(b) W. J. Geary, *Coord. Chem. Rev.*, **8**, 288(1971).
3. J.L. Burmeister and F. Basolo, *Inorg. Chem.* , **3**, 1587(1964).
4. F. Basolo, W.H. Bradley and J.L. Burmeister, *Inorg. Chem.,* **3**, 1202(1964).
5. S.P. Ghosh and L.K. Mishra, *J. Indian Chem. Soc.*, **51**, 308(1974).
6. N.B. Colthup, *J.Opt. Soc Amer.*, **40**, 397(1950)
7. Depaigne-Delay and J. Lecomte, *J. Phys. Radium.*,**7,** 38(1946)
8. R.G. Snyder and J.C. Decius, *Spectro Chim Acta*, **13**, 280(1959).
9. C.N.R. Rao and R. Venkateshraghavan, *Canad. J. Chem.*, **42**, 36(1964).
10. R.D. Bereman, D.M. Baird, J. Bordono and J. Dorfaman, *Polyhedron*, **2**, 25(1983).
11. N.K. Das, M. Nath, J. Zuckerman and D.A. Knight, *Inorg. Chim. Acta.*, **21**, 49(1983).
12. J. Brooks, Y. Babayan, S. Lamansky, P.I.Djuorovich, I. Tsy Ba, R. Bau, M. E.Thompson, *Inorg. Chem.* , **41,** 3055(2002)
13. D.M.Adams, Metal-ligands and related vibrations, Arnold Publication London (1967)
14. K. Nakamato, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons. Inc, NewYork. (1988).
15. M.R. Gajendragad and U. Agrawala, *Z. Anorg. Allgem. Chem.*, 84, 415(1975).
16. J.P. Srivastava, B.K. Sinha, R. Singh, and L.K. Mishra, *J. Inorg Nucl. Chem.,* **39**,1797(1977).

[RJC-861/2011]