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Synthesis and Structural studies of Pd (II) and Pt (II) complexes with 2-thiobenzimidazolyl acetic acid

IRSHAD ALI[1]* and JYOTSANA KUMARI[2]

[1]Department of Chemistry, B.N. College, Patna University, Patna (India).
[2]Research Scholar, Deptt. of Chemistry, B.N. College, Patna (India).

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ABSTRACT

The complexes of Pd(II) and Pt(II) with 2-thiobenzimidazolyl acetic acid have been prepared and characterized .The bonding of ligand and geometry of complexes have been suggested by UV,IR, Spectroscopic methods and resembles with square planar geometry of Pd(II) & Pt(II) Complexes.

Key words: 2-thiobenzimidazolyl acetic acid, Palladium(II), Platinum(II).

INTRODUCTION

Benzimidazole, thiazole, triazole, benzothiazole, imidazole are versatile co-ordinating substances and their complexes, have been studied widely[1-10]. Benzimidazole and Benzothiazole derivatives display vital role in regulating pharmacological activity in biological system and also play antibacterial as well as antifungal properties.[11-12] The complexes of Pt (II) metals are presently subject matter of extensive studies due to their interaction of tumor and cancer cell[13-23]. Thus the complexes of Benzimidazole derivatives with Pd (II) & Pt (II) will be of immense interest. In present paper we report the preparation and characterization of complexes of Pd (II) and Pt (II) with 2-thiobenzimidazolyl acetic acid.

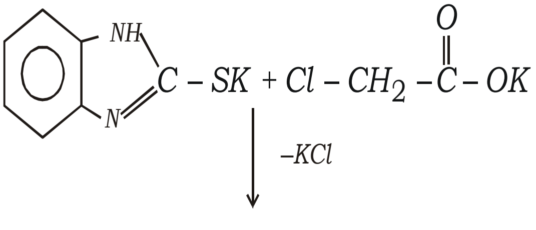
EXPERIMENTAL

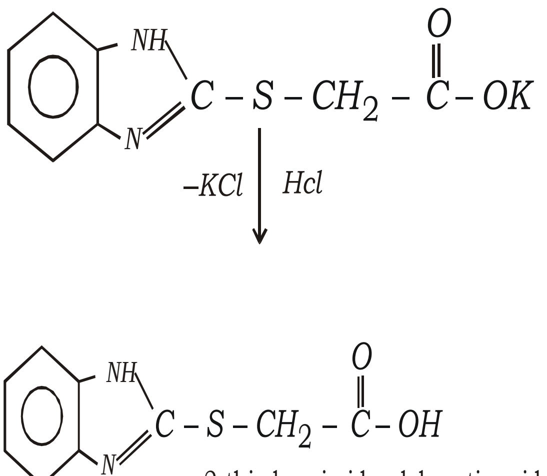
All chemicals used throughout the course of experimental work were procured from BDH or E Merk. Pd (II) and Pt (II) salts used were obtained from Johnson Mathew London.

The infra red spectra of complexes were recorded in KBr pellets on Perkin Elmer 1000 FTIR spectrophotometer. Electronic spectra were recorded in the range 200-850nm on Perkin Elmer lambda-15 UVB vis spectrophotometer. The C,H,N,S, were analyzed on Elementar Analysensysteme GmbH VarioEL. Magnetic susceptibility of complexes were measured by Gouy method at room temperature.

Preparation of Ligand

The ligand 2-thiobenzimidazolyl acetic acid was prepared by reacting alkaline solution of 2-mercaptobenzimidazole with neutralized solution of 2-chloroacetic acid at reflux temperature and standing the solution overnight. The resulting solution on acidification with dil HCl gave the free water insoluble ligard, 2-thiobenzimidazolyl acetic acid (tbah).





2-thio benzimidazolyl acetic acid

Preparation of Complexes

[ML_2] ($M=Pd^{2+}$ or Pt^{2+} and L = tba)

About 0.002 gram mole of aqueous solution of Palladium (II) Chloride or Platinum (II) Chloride was treated with hot ethanolic solution of ligand (0.004, mol,1:2 molar ratio). The resulting solution was neutralized by adding dilute NaOH solution when bis ligated complex (ML_2) separated immediately. The product was digested for 15-20 minutes, cooled and collected on a filter. It was washed with water and dried in a desiccator over $CaCl_{2.}$

Prepraton of [M $(LH)_2$ Cl_2] ($M=Pd^{2+}$ or Pt^{2+} and LH=tbah)

The dichloro complexes of Palladium and Platinum (II) was obtained when stoichiometric proportion of metal chloride and ligand in ethanol were mixed and its p^H was adjusted to 1-2 by adding a dilute HCl. The complexes were obtained on concentrating and cooling the mixed solution at room temperature. The complexes were collected on a filter, washed with a few drops of cold methanol and finally dried as above.

Preparation of [MLBCl] (M = Pd^{2+} or Pt^{2+}, B = NH_3 or Py,and L=tba)

About 0.002 mole of Platinum (II) chloride or Palladium (II) chloride was dissolved in 25ml of aqueous acidic methanol and treated with a little (1ml) Pyridine or conc ammonia. The resulting solution was treated with 1:1 molar ratio of ligand and digested on water bath for one hour. The resulting solution was neutralized and p^H was maintained at 6-7 by adding dilute hydrochloric acid. The solution on concentration yielded light coloured Pt (II) and cream yellow coloured Pd (II) complexes. The complexes were collected, washed with cold ethanol and dried as above. The dried samples of complexes were analysed for metal halogen sulphur and nitrogen.

RESULTS AND DISCUSSION

The result of elemental analysis of complexes correspond to the formula suggested for all complexes [M $(tba)_2$] ($M=Pd^{2+}$ or Pt^{2+}), [M $(tbah)_2$ Cl_2] and [M (tba)BCl] ($M=Pd^{2+}$ or Pt^{2+} and B=Py or NH_3) [Table – I].

Both Pd (II) & Pt (II) complexes were isolated as light yellow or orange or deep brown product. The Complexes are insoluble in cold water but [$M(LH)_2Cl_2$] dissociate into [ML_2] in boiling water. The freshly prepared DMF solution of complexes shown negligible electrical conductance value. (Λ_∞=6-10 Ω^{-1} mol^{-1} cm^2) indicating non ionic nature. The observed value suggested that chloride ion is bonded to metal atom in almost all complexes. The solubility of complexes [ML_2] and [MLBCl] (B = Py or NH_3) are relatively higher than those of [$M(LH)_2Cl_2$] in organic solvents. The Complexes as usual are diamagnetic indicating square planar structure of Palladium (II) and Platinum (II) complexes. The electronic absorption spectra of ligand display three electronic absorption bands located at 215, 245 and 285 nm. In complexes, these electronic bands are observed at relatively higher wave length. The Pd (II) complexes show a medium band at 410 – 420 nm while Platinum (II) complexes show strong absorption below 320nm and a shoulder near 390 nm. The shoulder observed in the complexes can be assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in square planar field. The electronic absorption of complexes [ML(B)Cl] is observed at higher frequency (lower wave length in the complexes) indicating stronger ligand field for species [ML(B)Cl] than others.

The i.r spectra of 2-thiobenzimidazolyl acetic acid shows broad band at 3150 – 3250 cm^{-1} attributable to hydrogen bonded hydroxyl group. The

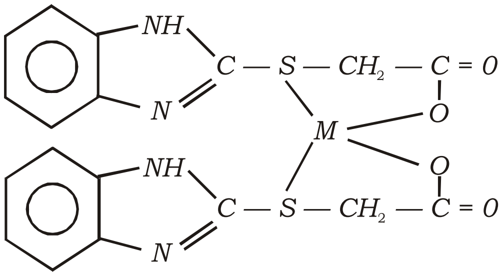
Table 1.

	Elemental Analysis (%) Found (Calculated)				
Complexes	**Metal**	**C**	**H**	**N**	**S**
[Pt (tba)$_2$]	32.25 (32.08)	36.43 (35.46)	3.34 (2.29)	9.47 (9.19)	10.58 (10.50)
[Pd (tba)$_2$]	19.95 (20.44)	42.6 (41.5)	3.01 (2.69)	10.50 (10.76)	12.25 (12.29)
[Pt (tbah)$_2$ Cl$_2$]	28.56 (28.60)	30.50 (31.66)	2.56 (2.34)	7.98 (8.21)	8.25 (9.38)
[Pd (tbah)$_2$ Cl$_2$]	16.98 (17.93)	36.76 (36.40)	2.89 (2.69)	9.87 (9.43)	9.98 (10.78)
[Pt (tba) Py Cl]	37.89 (37.76)	31.98 (32.53)	2.28 (2.32)	8.54 (8.13)	5.98 (6.19)
[Pd (tba) Py Cl]	25.52 (24.86)	40.01 (39.26)	2.78 (2.80)	8.91 (9.81)	8.52 (7.47)
[Pt (tba) (NH$_3$)Cl]	41.82 (42.9)	22.98 (23.75)	2.18 (2.19)	8.89 (9.23)	6.78 (7.03)
[Pd (tba) (NH$_3$)Cl]	28.05 (29.07)	30.01 (29.51)	2.56 (2.73)	10.98 (11.47)	8.65 (8.74)

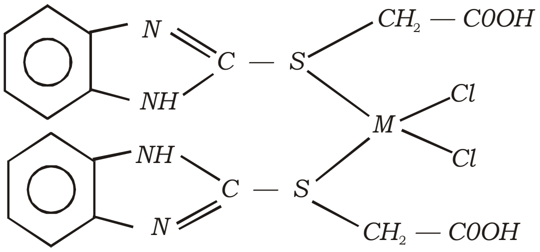
υ(CO) vibration of (COOH) group is also observed at relative lower wave number than the free (CO) group. The strong and broad band observed at 1640 cm^{-1} is attributed to hydrogen bonded carboxylic group. The phenyl and imidazolyl part i.r vibrations are observed at 1590, 1512, 1468, 1365 and 1120 cm^{-1}. These vibrations are also affected in complexes. The i.r. spectra of complex [ML$_2$] and [ML(B)Cl] display υ(CO) vibrations at higher wave number (1680-1690 cm$^{-1)}$ indicating that only one oxygen atom of carboxylic groups is involved in bond formation and there is absence of hydrogen bonding also. The υ(C-S) ether group vibration of ligand molecule is observed at 750 cm^{-1} and it is shifted to lower frequency by 10 to 15 cm^{-1}, suggesting the co-ordination of ether sulphur atom in complexes.

Thus from i.r. spectral studies it is inferred that carboxyl group oxygen and ether sulphur of 2-thiobenzimidazolyl acetic acid are bonding site of ligand molecule in complexes $[ML_2]$ and [M L(B) Cl] (or Pt^{2+}). The IR spectra of ligand and complexes display all characteristic vibration of aromatic ring and aromatic deformation and out of plane bending bands wre observed at appropriate ranges.

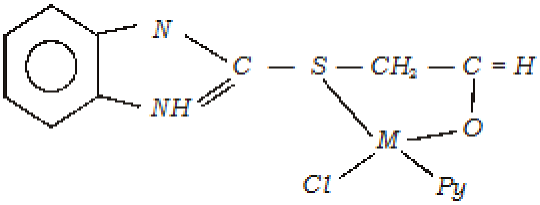
$M = Pd^{2+}$ On the basis of analytical results and physical measurements the following structures for complexes have been tentatively suggested.



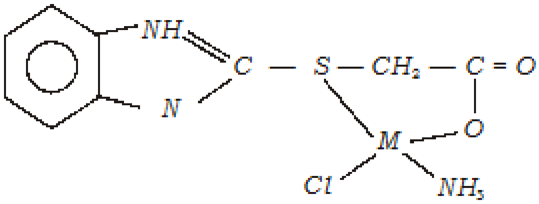
Structure of [ML$_2$]



Structure of $[M(LH)_2Cl_2]$



Structure of [ML(Py)Cl]



(or Pd^{2+})

Structure of $[ML(NH_3)Cl]$

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REFERENCES

1. W. Todd,W.Kajda, Philip J. Squattrito,and S.N. Dubey *Inorg. Chim Acta* 300-302 1082-1089(2000).
2. Udo Beckman, & Sally Brooker, *Coord. Chim. Rev*. 245: 1729 (2003).
3. Robert W. Clark, Philip J., Squattrito, S.N. Dubey *Inorg. Chim. Acta* 293: 61-69 (1999).
4. Abdel Rahman, S.Ferwanah, Abdel M. Awadallah, Boshra M. Awad. *Inorg. Chim. Acta* 358: 4511-4518 (2005).
5. Sudhir Burman, B.N.Sathnaraynan, *J. Inorg. Nucl. Chem*. **43**: 1940- 1942 (1981).
6. C.A Bolos, A.T.Chaviara, D.Nourelatos, Z.Lakovidon *et al*., *Bio-organic & Medical chemistry* **17**: 3142-3151 (2009).
7. S.Pal, D.Das, and C.Sinha, *Inorg Chim. Acta* **313**: 21-29 (2001).
8. Christian Mock, Ina Puscasu, Michel J.Rauterkus. *Inorg. Chim. Acta* **319**: 109-116 (2001).
9. Gang Woolee, Narindra Singh, Doo OK Jang *Tetrahedron Letter* 49,1952-1956, 2008)
10. N. Xi.Q Hung, L.Lu, *Comp. Heterocyclic Chemistry* 143-364 (2008) .
11. Gurupadayya B.M.Gopal, M, Padmashal.B. and Manohara Y.N. *Indian J. Pharmuceutical Sciences,* (2008).
12. Desai, K.G., Ravi, J.P and K.R, *Indian Journal of Chem. Soc.* **3**: 233-244 (2006).
13. A . Furst and R.T. Haro, *Progr. Exp. Tumour Res.,* **12**: 102 (1969).

$M = Pt^{2+}$

14. L.H. Schmidt, *Ann. Rev. Microbiol,* **23**: 427 (1969).
15. F. Basolo and R.G. Pearson, “The trans effect in Metal Complexes Progress in Inorg. Chim..” Edited F.A. Cotton, Vol.4 (1962).
16. W. Laverick, A.H.W. Nials, I.M. Ismail & P.H. Sadler, *Br. J. Cancer Res.,* 732 (1981).
17. B. Rosenberg, “Metal ions in biological systems”, ed. H. Siegel, Marcel Dekker, New York, **2**: 127 (1980).
18. S.J. Lippard *et.al, Inorg. Chem*. **26**: 1524 (1987).
19. Christian Mock, Ina Puscosu, Michale J. Rauterkus , *Inorg. Chim. Acta* **319**: 109-116 (2001).
20. Lloyd R. Kelland, Critical Review in Oncology **15**: 191-219 (1993).
21. H. Beraldo, D. Gambino, *Mini Rev. Med. Chem*. **4**: 31 (2004).
22. A. Gomez Quiroga, C.Navarro, Ranninger *Coord. Chim. Rev*.. **248**: 119 (2004).
23. I.Kucukguzel, S.G.Kucukguzel, S.Rollas, M.Kiraz, *Bio-organic chem.letter* **11**: 1703 (2001).