

# To Investigation structure of Coordination Compounds of Platinum (II) with 2-Amino-4-Methyl Benzothiazole, 2- Amino-6-Methyl Benzothiazole

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## Abstract

The mixed ligand complexes ( $PtL_2Cl_2$ ) where (L=2-amino-6- methylbenzothiazole and 2-amino-4-methylbenzothiazole), have been prepared by the interaction of parent compound ( $PtCl_2$ ) with ligand. The complexes are characterized by elemental analysis, magnetic measurement, electron spin resonance and infrared spectral studies containing Pt (II)  $d^8$  configuration.

## 1. Introduction:

In our recent article, we have synthesized and studied the physiochemical aspects of some mixed ligand complexes of platinum with some substituted benzothiazoles.<sup>[1]</sup> As a part of our programme to synthesize and characterize some neutral mixed ligand complexes of divalent platinum, studies have been extended using some more benzothiazoles derivatives.

Contemporarily, a great deal of interest has been shown to the study of neutral mixed-ligand complexes of platinum having d electronic configuration. No attempts have been made so far to isolate complexes of divalent platinum with some substituted 2- aminobenzothiazoles<sup>[2]</sup>. We, therefore, report here the first synthesis of neutral mixed ligand complexes of platinum with 2- Amino-4-methylbenzothiazole and 2- Amino-6-methylbenzothiazole The present chapter describes the results of such studies<sup>[3-7]</sup>.

## 2. Experimental:

### (a) Materials Employed:

2-Amino-6-methyl benzothiazole and 2-amino-4-methyl benzothiazole were procured from Aldrich Chemical Company, US.A. and used as received.  $PtCl_2$ , and chemicals 2-amino-6-methyl benzothiazole and 2-amino-4-methyl benzothiazole were obtained from TOKYO KASEI Organic Chemical, Japan and B.D.H England. Distilled water used in all the operation.

### (b) Preparation of the Coordination Compound:

#### 1. Preparation of the Coordination Compound [ $Pt(2\text{-Amino-6- methyl BTZ})_2 Cl_2$ ]:

A mixture of  $PtCl_2$  (500mg) and ligand 2-amino-6-methyl benzothiazole (1gm) in water and methanol (50ml) was refluxed at 80°C 5-6 hours until it became a clear yellowish colour solution. This volume was reduced to 5ml and treated with methanol. The resulting brown crystals were collected and washed well with ethanol and acetone. The analytical data are given in table 1.

## 2. Preparation of the Coordination Compound [Pt(2-Amino-4- methyl BTZ)<sub>2</sub>Cl<sub>2</sub>]:

A mixture of PtCl<sub>2</sub> (500mg) and ligand 2-amino-4-methyl benzothiazole (1gm) in water and methanol (50ml) was refluxed at 80°C 5-6 hours until it became a clear white colour solution. This volume was reduced to 5ml and treated with methanol. The resulting white crystals were collected and washed well with ethanol and acetone. The analytical data are given in table 1.

The general reaction for the preparation of coordination compounds of platinum is as follows:

where, L, 2-amino-6-methyl benzothiazole and 2-amino-4-methyl benzothiazole

## 3. Analysis of the Constituents Elements:

(1) Carbon, hydrogen, nitrogen and sulphur present in the investigated complexes were estimated micro-analytically.

**Table 1. Analytical and Electronic Spectral Data of Pt (II) Complexes**

Compound		Found (calc)%						Mol.wt.of	Conductance
M	C	H	N	S	Cl	found	Data		
[Pt(C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> S) <sub>2</sub> Cl <sub>2</sub> ]	32.42	32.00	2.23	9.06	10.23	11.42	593.97	0.050-0.055	
(32.82)	(32.33)	(2.71)	(9.43)	(10.79)	(11.93)	(594.54)	Ω <sup>-2</sup> cm <sup>2</sup> mol <sup>-1</sup>		
[Pt(C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> S) <sub>2</sub> Cl]	32.37	32.00	2.26	9.00	10.26	11.33	593.94	0.050-0.055	
(32.82)	(32.33)	(2.71)	(9.43)	(10.79)	(11.93)	(594.54)	Ω <sup>-2</sup> cm <sup>2</sup> mol <sup>-1</sup>		

## 4. Estimation of Pt:

For the estimation of platinum as ammonium chloroplatinate, dissolved the compound in 5ml of concentrated hydrochloric acid and 20ml of hot water, and then add gradually an equal bulk of half-saturated ammonium chloride solution. Allow to stand for 8 hours, filtered off the precipitate, wash it with ammonium chloride solution, and finally twice with cold water. Transferred the filtered paper and precipitate to a Main-Smith Crucible, heat extremely slowly at first, and ultimately raise to a bright red heat. Repeated heating, cooling and weighting were carried out until weight obtained constant.

### (d) Physical Methods:

#### (i) Molecular Weight Determination:

Molecular weight determination of the synthesized complexes was made by Rast's Method

#### (ii) Magnetic Susceptibility Measurement:

The magnetic susceptibility measurements were made at room temperature by the Gouy Method. A magnetic field strength of 8500 gauss was employed. The apparatus was calibrated using cobalt mercury thiocyanate Hg [Co(NCS)<sub>4</sub>] The diamagnetic corrections were computed using Pascal's Constant <sup>[8,9]</sup> For calculations of effective magnetic moment following equation has been used.

Effective magnetic moment ( $\mu_{\text{eff}}$ ) =  $284 (X^{\text{corr}} \text{ m T})^{1/2}$  where T =temperature in absolute scale and X = corrected molar susceptibility

**(iii) Conductance Measurement:**

Conductance was measured in analytical grade methanol using dip type cell with the help of a Philips Conductivity Bridge

**(iv) Infrared Spectral Measurement:**Infrared spectra (4000-600cm) of the uncoordinated ligands and of the complexes were recorded as Nujol Mulls supported between sodium chloride platex (rock salt regions) on a Perkin Elmer Spectrum RXI Spectrometer.

**(v) <sup>1</sup>H NMR Spectral Measurement:**

<sup>1</sup>H NMR Spectra of the synthesized compounds were recorded on AC 300F Spectrometer (300MH,) using TMS as an internal standard

**(vi) Electron Spin Resonance Spectra:**

Electron Spin resonance spectra of the complexes were recorded at room temperature on a Varium E-3 spectrometer using powdered sample at the microwave frequency 9.53GHz The 'g' values were calculated using the given equation.

where (GHz) = microwave frequency in GHz at which sample operated, and H (G)= field in gauss for the sample

**Properties of the Complexes:**

The analytical and physical data of the ligand and its metal complexes are given in table no 1. The complexes are nonhygroscopic and stable at room temperature. The solubility of these complexes is given in table no 2. They are soluble in DMSO, sparingly soluble in DMF and insoluble in other organic solvent. The colour of these complexes are given in table no 3. They do not possess sharp melting points.

**Table 2. Color and % Yield of the complexes**

S.No.	Compound	Color	% Yield
1.	[Pt(2-Amino-6-Methyl BTZ) <sub>2</sub> Cl <sub>2</sub> ]	Brown	68
2.	[Pt(2-Amino-4-Methyl BTZ) <sub>2</sub> Cl <sub>2</sub> ]	White	57

**Table.3 Solubilities of the Complexes in Different Solvents**

S.No.	Compound	DMF	DMSO	EtOH	MeOH	CHCl <sub>3</sub>
1.	[Pt(2-Amino-6-Methyl BTZ) <sub>2</sub> Cl <sub>2</sub> ]	Sparingly Soluble	Soluble	Insoluble	Insoluble	Insoluble
2.	[Pt(2-Amino-4-Methyl BTZ) <sub>2</sub> Cl <sub>2</sub> ]	Sparingly Soluble	Soluble	Insoluble	Insoluble	Insoluble

BTZ)<sub>2</sub>Cl<sub>2</sub>]

Soluble

### 3. Result and Discussion:

#### (a) Magnetic Measurement:

The magnetic values of synthesized complexes measured at room temperature. An observation shows that the magnetic moment values of the complexes [Pt(2-amino-4-methyl BTZ)<sub>2</sub> Cl<sub>2</sub>] and [Pt(2-amino-6-methyl BTZ)<sub>2</sub> Cl<sub>2</sub>] are zero. Hence, all the complexes are diamagnetic and also the square-planar geometry of compounds is evident from their diamagnetic nature.

#### (b) Conductance Measurement:

The analytical and physical data of the ligand and its metal complexes are given in table no 1. The values of molar conductance are in the range 0.050-0.055 Ω<sup>-2</sup>cm<sup>2</sup>mol<sup>-1</sup> suggesting non-electrolyte nature of the synthesized complexes

#### (c) Infrared Spectroscopy:

The ligand 2-amino-6-methyl benzothiazole and 2-amino-4-methyl benzothiazole possess three possible donor sites, (i) amino nitrogen, (i) tertiary cyclic nitrogen and sulfur of thiazole ring Further the amino group involved in coordination through the nitrogen atom. Coordination through nitrogen of the amino group invariably results in the negative shift in νNH<sub>2</sub> (3105cm<sup>-1</sup>) by at least 60cm<sup>-1</sup> (3045 cm<sup>-1</sup> in 2-amino-6-methyl benzothiazole and 50cm<sup>-1</sup> in 2-amino-4-methyl benzothiazole (3055 cm<sup>-1</sup>). In the complexes of 2-amino-6-methyl benzothiazole and 2-amino-4-methyl benzothiazole, the IR frequency of tertiary cyclic nitrogen and sulfur of thiazole ring are unchanged, suggesting cyclic nitrogen and sulfur of this ligand do not participate in the coordination. IR Spectral Band and their Assignment is given in table 4.

**Table 4. Important IR Spectral Band and their Assignment**

S.No.	Compound	νNH <sub>2</sub>	νC-S <sub>(cyclic)</sub>	νN
1.	[Pt(2-Amino-6-Methyl BTZ) <sub>2</sub> Cl <sub>2</sub> ]	Unchanged(1375cm <sup>-1</sup> )	3045cm <sup>-1</sup>	Unchanged(780-740cm <sup>-1</sup> )
2.	[Pt(2-Amino-4-Methyl BTZ) <sub>2</sub> Cl <sub>2</sub> ]	Unchanged(1375cm <sup>-1</sup> )	3055cm <sup>-1</sup>	Unchanged(780-740cm <sup>-1</sup> )

#### (d) Electron Spin Resonance Spectra:

The electron spin resonance spectral data for the synthesized complexes under this investigation are given in table 5.

The recorded 'g' values in the range 1.982-1.983 are constant Bands at 30150-32240cm is the characteristic of square planer arrangement around the metal ion. These bands can assigned the transitions

$1A_{1g} \rightarrow 1A_{2g}$  ,  $1A_{1g} \rightarrow 1B_{1g}$  In order of increase energy<sup>[10,11]</sup>

**Table 5 Electron Spin Resonance Spectral Data of the Complexes**

S.No.	Compound	Spectral Data	
1.	[Pt(2-Amino-6-Methyl BTZ) <sub>2</sub> Cl <sub>2</sub> ]	30150-32240cm <sup>-1</sup>	<sup>1</sup> A <sub>1g</sub> ----->>>- <sup>1</sup> E <sub>g</sub>
2.	[Pt(2-Amino-4-Methyl BTZ) <sub>2</sub> Cl <sub>2</sub> ]	30150-32240cm <sup>-1</sup>	<sup>1</sup> A <sub>1g</sub> ----->>>- <sup>1</sup> E <sub>g</sub>

**(e) NMR Spectroscopy:**

The spectrum of Pt (II) with 2-Amino-6-methyl benzothiazole and 2-Amino-4-methyl benzothiazole complexes dissolved in DMSO consists of a broad NH, signal at 5.38ppm. At later times, or raising signal the pH, the NH<sub>2</sub> protons exchange completely. Spectrum of aforesaid compounds shown into figure 1 The methyl proton spectrum consists of doublet, due to N-H coupling, flanked by symmetric doublet <sup>195</sup>Pt side bands

**Effect of Coordination on Chemical Shifts:**

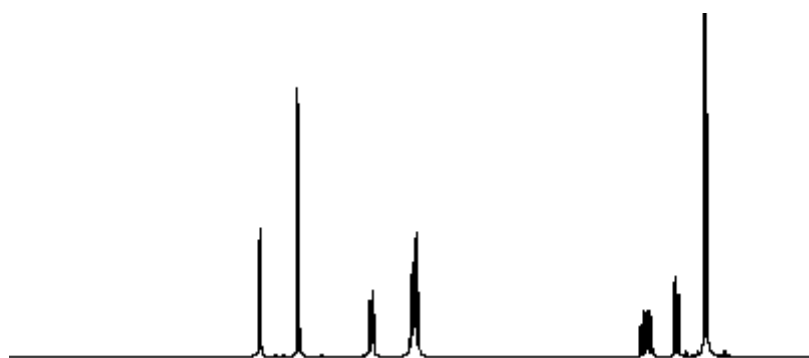
Coordination to Pt invariably produces substantial downfield shifts for ligand protons. The extent of the downfield shift is similar to corresponding protonation shifts and decreases similarly with distance from the coordination site. Among the methyl-substituted glycines, chelation produces a downfield shift about 80% as great as that resulting from single protonation. Not surprisingly, CH<sub>2</sub>, signals of N-coordinated glycines are shifted downfield only half as much as those of chelated glycines, but are much more affected by protonation of the free CO<sub>2</sub> group.

Such observations are the basis for concluding that the α- carboxyl group, rather than the β-carboxyl group, is involved in chelation top Pt in complexes of L-aspartate. For those complexes. the methane proton is more affected by complexing, while the methylene protons are more affected by subsequent titration of the uncomplexed carboxyl For S-methylcysteine, and methionine, the effect of protonation of NH: and CO<sub>2</sub> on CH, shifts is not large, but coordination of NH<sub>2</sub> to Pt produces a downfield shift comparable to the effect of protonation or complexing N for N-CH, groups

Differences in chemical shifts for all ligand protons were negligible for the following pairs of isomers: trans-Pt(L-Asp), and Pt(L-Asp)(D-Asp), trans- Pt(L-Glu) and Pt(L-Glu)(D-Glu), and cis-and trans-Pt (L-Dap). For Pt(L-Hist), chemical shifts of cis and trans isomers are very similar for corresponding protons of corresponding species, except for C-H whose environment in the two isomers varies significantly.

**Platinum-Proton Coupling and Coordination:**

The presence or absence of Pt side bands provides a clear identification of the site of coordination in these complexes. In general, three-bond Pt-N-C-H couplings are between 10 and 60 Hz Coupling through four bonds is negligibly small, except for C<sub>4</sub>-H of histidine which is coupled through four bonds nearly as strongly as is C<sub>4</sub>-H through three bonds<sup>[12]</sup>.



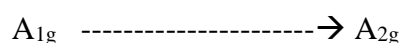
**Figure 1. Proton NMR Spectrum of the sarcosine complex**

Not surprisingly, in view of the known strong tendency of Pt( $\Pi$ ) to coordinate sulfur.  $J_{\text{Pt-S-C-H}}$  values are generally among the largest values observed. A small, but noteworthy, variation in  $J_{\text{Pt-CH}_3}$  was observed for 1:1 complexes of both S-methylcysteine and methionine. Starting with  $\text{Pt}(\text{AA})\text{Cl}_2$  replacement of the Cl cis to the N of AA by  $\text{NH}_3$  decreases  $J_{\text{Pt-CH}_3}$  from  $\sim 55$  to  $\sim 45$  Hz, while replacement of both Cl's by  $\text{NH}_3$  or ethylenediamine has a smaller effect ( $\sim 55$  to  $\sim 50$  Hz).

#### 4. Conclusion

The mixed ligand complexes  $[\text{PtL}_2\text{Cl}_2]$  where (L-2-amino-6-methylbenzothiazole and 2-amino-4-methylbenzothiazole), have been prepared by the interaction of parent compound  $[\text{PtCl}_2]$  with ligand. The complexes are characterized by elemental analysis, magnetic measurement, electron spin resonance and infrared spectral studies containing Pt (II) d configuration. All the complexes are diamagnetic suggesting square planar geometry. It is observed that

- (i) The DMSO solution of the synthesized compounds are nonconducting .
- (ii) All the complexes contain low spin  $d^8$  configuration.
- (iii) The reflectance spectra of the complexes display a shoulder at 340-430 nm, which is attributable to transition



- (iv) All the compounds are thermally stable upto  $280^\circ\text{C}$ .
- (v) All the complexes show anticancer activity.

#### 5. References:

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