

# THE INTERNATIONAL JOURNAL OF SCIENCE & TECHNOLEDGE

## A Study on the Ternary Compounds of Adenine and Guanine with Co (II), Hg (II) in Aqueous Medium

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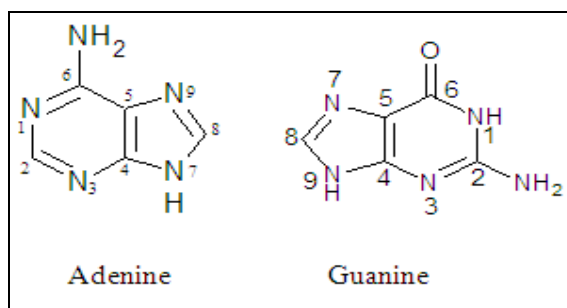
### Abstract

Adenine and guanine formed complexes with Co(II), Hg(II) in aqueous media. The complexes are  $\text{Co}(\text{C}_5\text{H}_4\text{N}_5\text{O})(\text{C}_5\text{H}_4\text{N}_5)(\text{H}_2\text{O})_2$ ,  $[\text{Hg}(\text{C}_5\text{H}_4\text{N}_5\text{O})_2] \cdot (\text{C}_5\text{H}_6\text{N}_5)\text{Cl}$ , formulated on the basis of their metal and chloride contents. Their physico-chemical properties such as solubility, melting point, elemental analysis, IR and UV-visible spectra, magnetic susceptibility, thermogravimetry, differential scanning calorimetry, conductivity were studied.

**Keywords:** Nucleic acids, Adeninium ions, Guaninium ions, Pyrimidine ring, magnetic susceptibilities

### 1. Introduction

It is well known that nucleotides and metal ions are involved in the basic metabolic process of life, participating as substrates in enzymatic reactions in the form of metal ion complexes<sup>[1-5]</sup>. Besides this, in case of removing their toxic effects complex formation is also a possible mechanism for the prevention of toxic metals by combining with one or more reactive groups essential for physiological functions. Such interference in the physiological action is sometimes referred to as toxic metal antagonism. Adenine and guanine are nucleobases found in the nucleic acids DNA and RNA. These nucleobases consist of a fused pyrimidine-imidazole ring system with conjugated double bonds. In acidic medium, ring nitrogen N3 is protonated i.e.  $\text{N}(3)\text{-H}^+$ .



The adenine and guanine complexes are of tetrahedral and octahedral geometries respectively. All are of high spin nature. Anionic guanine functions as bidentate ligand and links through N(3) and N(9), neutral guanines are probably unidentate and coordinate either through N(3) or N(9), Cu(II) complex has a highly distorted octahedral structure, Co(II) and Ni(II) complexes possess pseudooctahedral geometry. Metal-ligand interaction probably takes place through N(7) and O atom of the carbonyl group. They also suggest the guaninium cation (protonated at N(3) and/or N(7)) neutralize the charges of metal anionic species in a cation-anion electrostatic interaction but no coordination with metal at all.

The adenine<sup>[6-11]</sup> and guanine complexes<sup>[12-16]</sup> of several metal ions, such as Co(II), and Hg(II) have been reported earlier. Literature review reveals that N(9), N(7) and N(3) of adenine acts as donor sites, whereas guanine is metalated at N(3) and N(7) though there are other sites, such as N(1) and NH<sub>2</sub> for adenine and O(6) and NH<sub>2</sub> for guanine. Because of this, in the literature there are only a few metal compounds with mixed nucleobases adenine-thymine and cytosine-guanine. Under these circumstances the first attempt of our investigation that is described in this thesis comprises preparation, properties and structural characterization of compounds of some metal ions Co(II), Hg(II) are presented with adenine-guanine.

Moreover we became interested in the chemistry of adenine-metal-guanine compounds to establish under which condition the adenine and guanine molecules are linked to N(7), N(9), N(3) and/or O and started a systematic study of such materials because of their extreme biological significance.

## 2. Experimental

### 2.1. Materials

Guanine was procured from Loba Cheme Pvt. Ltd. Mumbai, India and adenine was procured from BDH Chemicals Ltd., England. Cobalt(II) chloride, mercuric(II) chloride, hydrochloric acid, nitric acid, sodium hydroxide and organic solvents etc., used in all synthetic and analytical work were analar grade, either Aldrich (U.S.A.), E. Merck (Germany) or E. Merck (India).

### 2.2. Equipments

A Fourier transform infrared (FTIR) of 4000-400  $\text{cm}^{-1}$  were recorded as potassium bromide disc on shimadzu(Japan) Pestige-21 Fourier transform infrared spectrophotometer. UV-Visible spectra was measured using spectrophotometer, Model UV-160A, Simadzu (Japan), in the wavelength range, 200-1100nm. Elemental analysis (C, H, N, S) was performed by CHNS/O Element analyzer Model-Vario Micro Cube. Determinations of metals were carried out using laboratory methods. A melting point apparatus, model SMP11 with a thermometer was used for the determination of melting point. Magnetic susceptibility was determined by the SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance (M.S.B.), model no Magway MSB MK1. The thermo gravimetric analysis (TGA) of the complexes was carried out with TGA-50 analyzer, Shimadzu (japan). Platinum pan was used for Co(II) and Hg(II) complexes, while aluminium pan was used for mercury(II). All analysis were carried out in nitrogen medium. The quasi-static thermogravimetric analysis (QSTG) of complex was carried out in a Carbolite calibrated muffle furnace(CWF 11/5). The differential scanning calorimetry (DSC) was performed by using a Shimadzu Thermal Analyzer DT-40. The DSC thermograma were recorded from 50°C to 550°C at a heating rate of 10°C/min. An empty pan was used as a reference. A nitrogen flow of 20 mL/min was used for each DSC run.

### 2.3. Preparation of Complexes

- $\text{Co}(\text{C}_5\text{H}_4\text{N}_5\text{O})(\text{C}_5\text{H}_4\text{N}_5)(\text{H}_2\text{O})_2$**   
 0.4534 g guanine was dissolved in 15.0 mL 1M HCl acid by heating in a beaker. To it an aqueous solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and NaCl (0.7139 g and 0.0878 g respectively in 20 mL) was added. 0.4054 g adenine was dissolved in 10 mL water. Two solutions were mixed together and then 1M NaOH solution was added to this mixture drop wise with constant stirring until the pH was attained 7. Light pink powdery crystals were formed instantaneously. The crystals were allowed to settle for 30 minutes, separated by filtration, washed with water and then with ethanol. They were dried in air and finally over blue silica gel in a desiccator. The color of the compound remains unchanged on exposure to light and air at room temperature.
- $[\text{Hg}(\text{C}_5\text{H}_4\text{N}_5\text{O})_2] \cdot (\text{C}_5\text{H}_6\text{N}_5\text{Cl})$**   
 0.3026 g guanine, was dissolved in 13 mL 1M HCl acid by heating in a beaker. An aqueous solution of mercury(II) chloride,  $\text{HgCl}_2$  and NaCl (0.8024 g and 0.1170 g respectively in 20 mL) was added to guanine solution. 0.2704 g adenine was dissolved in 10 mL water and added with mercury-guanine solution. The pH of the solution was maintained 2.5. Brown crystals were formed after a day. The crystals were separated by filtration, washed with water and then with ethanol. They were dried in air and finally over blue silica gel in a desiccator. The color of the compound remains unchanged on exposure to light and air at room temperature.

## 3. Results and Discussions

The empirical formulae of the complexes have been established on the basis of their metal and chloride contents analyses. Their physical properties viz. yield, colour, melting points, elemental analysis, solubility have been studied, and are tabulated in Table 1.

Compound	Colour	Melting point,	Yield %,	Elemental Analysis Calc. (found%)					Solubility
				C	H	N	Cl	M	
$\text{Co}(\text{C}_5\text{H}_4\text{N}_5\text{O})(\text{C}_5\text{H}_4\text{N}_5)(\text{H}_2\text{O})_2$	Pink	180-200 (d)	64.68	30.46 (31.66)	3.56 (3.17)	35.37 (36.94)	–	16.30 (15.34)	
$[\text{Hg}(\text{C}_5\text{H}_4\text{N}_5\text{O})_2] \cdot (\text{C}_5\text{H}_6\text{N}_5\text{Cl})$	white	250-280 (d)	47.27	20.01 (26.81)	1.941 (2.08)	23.38 (31.27)	12.45 (5.27)	29.71 (29.74)	Soluble in hot $\text{H}_2\text{O}$

Table 1: Metal and Chloride contents and some physical properties of prepared complexes

### 3.1. IR Spectral Analyses

Tentative assignments of some important IR bands of the studied compounds were done on the basis of standard references and those of the guanine, adenine nucleobases are listed in Table 2.

Compounds	$\nu(\text{O-H})/\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu(\text{C-NH}_2)$	$\nu(\text{C-N})$	M-N	M-O
Adenine	3400-3000	1620	–	1250	1150	–	–
Guanine	3500-2500	1660	1680	1250	1110	–	–
A	3600-2900	1690	1700	1250	1120	490	460
B	2600-3000	1670	1670	1250	1120	–	–

Table 2: Tentative IR bands of adenine, guanine and adenine-metal-guanine compounds

The strong and broad bands in the region  $3600\text{-}2600\text{ cm}^{-1}$  indicate the presence of the hydrogen bonded water molecule and/or N-H and aromatic C-H stretching vibrations. Involvement of N-H group in extensive H-bonding may also be the reason for such a broadening of this peak of the compounds or in coordination with metals.

Compare to adenine (at  $1620\text{ cm}^{-1}$ ) its compounds of cobalt with guanine show vibrations at different frequencies in the region  $1670\text{-}1690\text{ cm}^{-1}$  for the  $\nu(\text{C=N})$  vibrations, which indicate the formation of bond with metals by the N(3) of adeninato ion.

All compounds show bands due to  $\nu(>\text{C=O})$  in the region  $1670\text{-}1700\text{ cm}^{-1}$ , while that of guanine is  $1680\text{ cm}^{-1}$ , the shift of the carbonyl absorption compared to that observed in the free guanine molecule (at  $1680\text{ cm}^{-1}$ ) can be explained on the basis of the greater involvement of the  $>\text{C=O}$  group in bonding.

In case of B compound, a new peak appears near  $1550\text{ cm}^{-1}$ , which indicates that the nitrogen of the pyrimidine ring N(3) is protonated i.e.  $\text{N}(3)\text{-H}^+$ .

The peaks of  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  vibrations are in the region of  $450\text{-}550\text{ cm}^{-1}$  for A compound. While the Hg-N, Hg-O stretching vibrations usually appear below  $400\text{ cm}^{-1}$ , and not observed in the above spectrum due to instrumental limitation.

### 3.2. UV-Vis Spectral Analyses

The electrochemical spectral data of the studied adenine-metal-guanine compounds in the UV/Vis region are tabulated in table 3. The bands at shorter wavelengths result from the  $\pi\rightarrow\pi^*$  and  $n\rightarrow\pi^*$  electronic transitions, characteristic spectral properties of heteroaromatic molecule<sup>17</sup>.

Compounds	$\lambda, \text{nm}$
A $[\text{Co}(\text{C}_5\text{H}_4\text{N}_5\text{O})(\text{C}_5\text{H}_4\text{N}_5)(\text{H}_2\text{O})_2]$	225.0, 259.0
B $[\text{Hg}(\text{C}_5\text{H}_4\text{N}_5\text{O})_2].(\text{C}_5\text{H}_6\text{N}_5\text{Cl})$	226.0, 255.0

Table 3: Data for electronic spectral analyses of adenine-metal-guanine compounds

The spectra of cobalt(II) and mercury(II) compounds show an intense absorption band nearly at  $226.0\text{ nm}$ . These high intensity bands at strong field suggest that they are not ligand-field d-d transitions. These may be assigned to  $\sigma\rightarrow\sigma^*$  transitions.

The compounds also show band at about  $260.0\text{ nm}$  possibly due to  $\pi\rightarrow\pi^*$  and  $n\rightarrow\pi^*$  electronic transitions in the ethylenic bonds of the heteroaromatic ring present within the ligand.

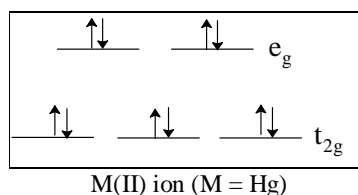
### 3.3. Magnetic Measurement

Magnetic susceptibilities of the compounds were measured and the results are summarized in Table 4.

Compound	$C_{\text{Bal}}$	l, cm	m, g	R	$R_0$	$\chi_g$ , C.G.S. unit	T, K	$\mu_{\text{eff}}$ BM
A	1.0302	2.30	0.1133	278	-031	$6.46\times 10^{-6}$	307	2.45
B	1.0283	2.20	0.0757	-047	-032	$-4.48\times 10^{-7}$	307	-

Table 4: Magnetic measurement data of adenine-metal-guanine compounds

The magnetic susceptibility values of mercury (B) compound is negative due to their diamagnetic properties. It implies that Hg(II) ions has  $d^{10}$  electronic configuration in which all the electrons in  $t_{2g}$  and  $e_g$  levels are paired.



Complexes	$d^n$	Electron configuration	Term symbol	Ground state	$\mu_{\text{eff}}$		Orbital Contribution in octahedral
					Found	Calc	
<b>A</b>	$d^7$	$t_{2g}^5 e_g^2$	$^4F$	$^4T_{1g}$	2.45	3.87	Yes
<b>B</b>	$d^{10}$	$t_{2g}^6 e_g^4$	$^1S$	-	diamagnetic	zero	-

Table 5: The magnetic Properties of the Complexes

### 3.4. Thermal Analysis

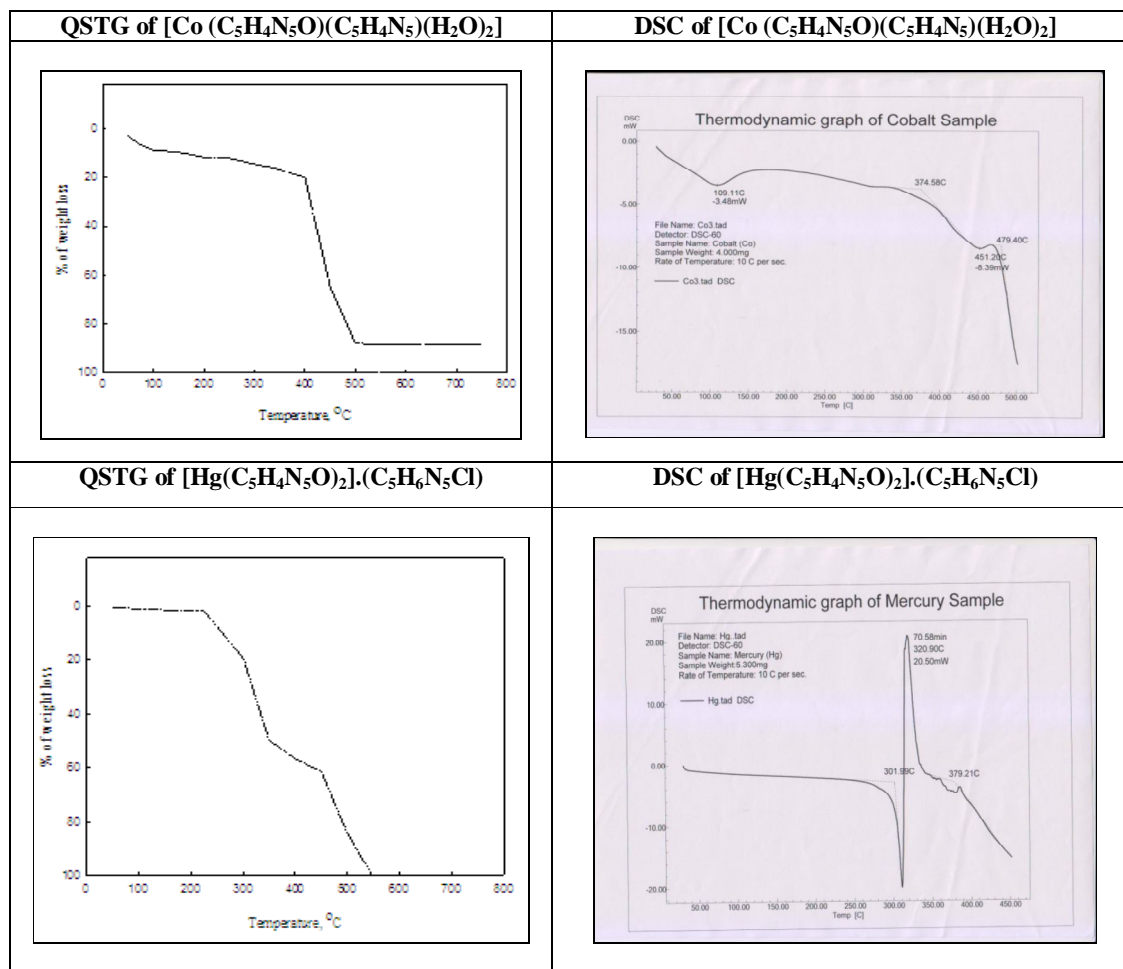
The thermograms obtained from the thermogravimetric analysis of the compounds are plotted in The QSTG curve of cobalt shows that the compound starts decomposition at lower temperature and about 8.89% of weight loss is recorded within the temperature 75-100°C. This corresponds to the loss of two molecules of water (calculated weight loss 9.46%) from the compound.

The curve shows that the mercury compound is sufficiently stable up to 225°C indicating that it contains no loosely bound water molecule. The percentage of weight loss within the temperature range 175-200°C is 3.22%.

Co(II) commence decomposition at very low temperature, ~50°C. After several steps of decomposition these compounds are converted to their corresponding metal oxides. The mercury compound also shows thermal stability up to 200°C, then starts decomposition and sublimes off completely at 550°C.

On the basis of thermal stability the compounds under study are arranged in the following order:

- Hg > Co



### 4. Conductivity Measurement

The capacity of electrolytic conductors to conduct electricity is not the same for all electrolytic conduction. Conductance of these depends on the number of ions, their speeds, size, temperature, concentration etc.

The experimental results of Mercury compound is shown in the Table 6:

Molar concentration (M)	Observed Conductance $\times 10^{-6}$ (S)	Corrected Conductance $\times 10^{-6}$ (S)	Specific Conductance $\times 10^{-4}$ (S cm <sup>-1</sup> )	Molar Conductance $\times 10^4$ (S cm <sup>-1</sup> M <sup>-1</sup> )
0.00001	29.90	17.18	1.96	1.96
0.00005	85.60	72.88	8.31	1.66
0.00010	14.03	01.33	0.15	0.02
0.00050	18.27	05.55	0.63	0.01

Table 6: Molar conductance of the mercury compound of different concentration at 29.6°C  
Conductance of water at 29.6°C =  $12.72 \times 10^{-6}$  S, cell constant = 11.41 cm<sup>-1</sup>

The variation of molar conductance with concentration of the complex is shown in the following figure Fig. 1:

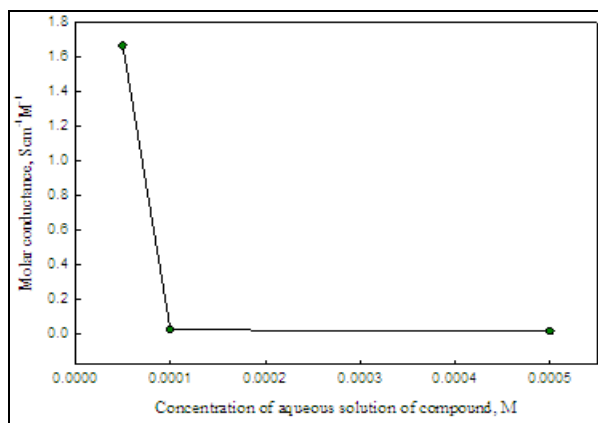
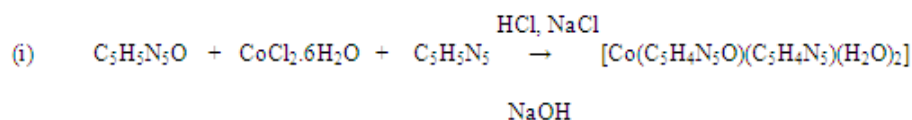


Figure 1: Plots of molar conductance vs. molar concentration of mercury (II) complex

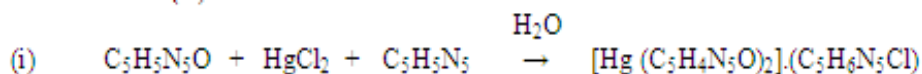
Table 6 shows that the molar conductances increase with increasing dilution suggesting that the compound undergoes some amount of ionic dissociations in its aqueous solution. This is expected because mercury compound in water yields aquated chloride ion and adeninium ion with a positive charge on the N(3) atom. It is also observed in Fig. 1 that its molar conductance decreases rapidly at high concentrations, indicating that the mercury complex compound is behaving as a weak electrolyte in aqueous medium.

## 5. Conclusion

Our investigation demonstrates that the reaction between the divalent transition metal ions, guanine and adenine occur as expected.



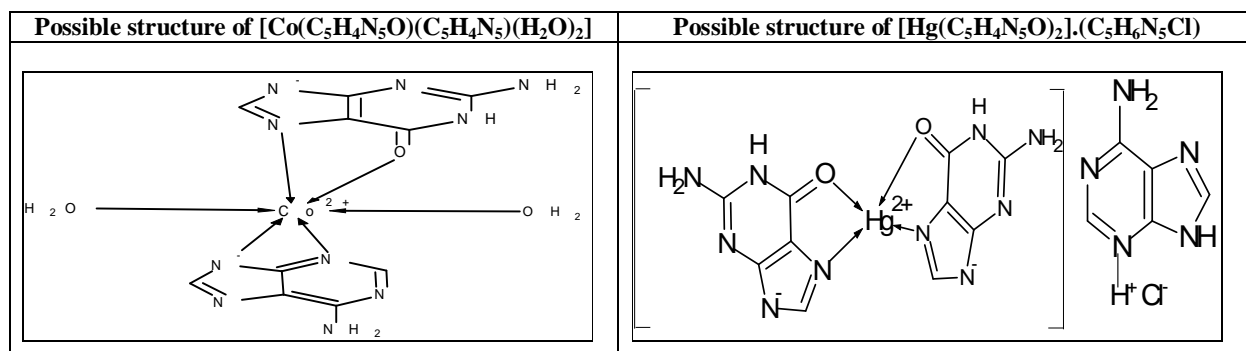
Where M = Co(II)



Where M = Hg(II).

Reactions of adenine and guanine with metal ions Co(II) and Hg(II) gave ternary adenine-metal-guanine compounds. On the basis of their metal and chloride contents the compounds are formulated as  $Co(C_5H_4N_5O)(C_5H_4N_5)(H_2O)_2$ ,  $[Hg(C_5H_4N_5O)_2] \cdot (C_5H_5N_5)Cl$ . Their physico-chemical properties are also supported the revealed formula.

Though it is not very conclusive to ascertain which nitrogen(s) participates in bond formation with the metal ions without single crystal X-ray crystallographic study, however, IR and other techniques used in the present study suggest that possibly N(7) of the adenine, N(7) and O atom of the guanine molecule ligated in Co(II) complex, and both N(7) and O atom of guanine in Hg(II) complexes take part in bonding. The most probable proposed structures of the studied compounds are given below:



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