

## Preparation and Characterization of Adenine Complexes of Co(II), Cu(II) and Zn(II)

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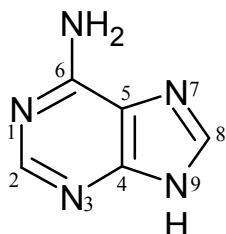
### Abstract

Complexes of divalent cobalt, copper and zinc with adenine were prepared and characterized. The complexes were formulated as  $[\text{Co}(\text{C}_5\text{H}_5\text{N}_5)_2\text{Cl}_2]\cdot\text{H}_2\text{O}$ ,  $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_5)(\text{H}_2\text{O})_3\text{Cl}_2]\cdot\text{H}_2\text{O}$ , and  $[\text{Zn}(\text{C}_5\text{H}_5\text{N}_5)\text{Cl}_3]$  on the basis of their metal and chloride contents. Their solubility, melting point, IR and UV-Visible spectra, magnetic and thermal properties, and conductivity were studied. The cyclic voltammetric study of only Cu(II) complex was also carried out.

### I Introduction

Metal ions mediate the biochemistry of pyrimidine and purine nucleosides, nucleotides, and nucleic acids<sup>1-3</sup>. Recently researches are mainly focused on the synthesis of their metal complexes, specifically with recognized nucleobases<sup>4</sup>. Adenine is one of the two well known purine nucleobases used in forming nucleotides of the nucleic acids. Several metal complexes of adenine have been studied and its binding site(s) has been elucidated<sup>5-13</sup>. Among the four nitrogens N(1), N(3), N(7) and N(9) of adenine, the N(9) is the most basic and hence the most preferred metal binding site<sup>14</sup>. In fact, the geometry of the metal-adenine complexes more specifically the coordination sites of adenine molecule to the metal ions varies significantly on the condition under which they are prepared.

For understanding the bonding sites a schematic representation of the structure of adenine is given below in **Scheme 1**.



**Scheme 1.** Schematic structure of adenine.

In this report we have dealt on the preparation and characterization of the adenine complexes with Co(II), Cu(II), and Zn(II).

### II Experimental

Adenine was purchased from BDH Chemicals Ltd., England. The other chemicals and the solvents that were used in all synthetic and analytical work were analytical grade (BDH and Aldrich products).

#### Materials and methods

Melting points of the compounds were recorded in a paraffin oil bath equipped with a thermometer of recording capacity up to 250°C. Metal and chloride contents were

determined by complexometric method and Volhard's method of analysis respectively. Infrared (IR) spectra of the complexes were recorded on a Shimadzu (Japan) Infrared Spectrometer of model IR - 470 in the range of 400 - 4000  $\text{cm}^{-1}$  using KBr pallets. The UV-Visible spectra of the complexes were recorded using UV-Visible recording Spectrometer, Model UV - 160A, Shimadzu (Japan), in the wavelength range, 200 -1100 nm using water as a solvent. Magnetic susceptibility of the complexes was determined by the Sherwood Scientific Magnetic Susceptibility Balance (M.S.B.), model: Magway MSB Mk1. The quasi-static thermal analysis (QSTG) was carried out in a Carbolite Calibrated Muffle Furnace of the type CWF 11/5. A Computerized Electrochemical System, Model HQ-2040 developed by Advanced Analytics, USA was employed for cyclic voltammetric investigation.

#### Preparation of metal-adenine complexes

##### (i) Bis(adenine)dichlorocobalt(II).monohydrate, $[\text{Co}(\text{C}_5\text{H}_5\text{N}_5)_2\text{Cl}_2]\cdot\text{H}_2\text{O}$

Methanolic solutions of adenine (0.27 g in 60 mL) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.48 g in 20 mL) were mixed together in a beaker. The resulting mixture was kept at room temperature for about 24 hours. Blue crystals of  $[\text{Co}(\text{C}_5\text{H}_5\text{N}_5)_2\text{Cl}_2]\cdot\text{H}_2\text{O}$  were formed. The product was filtered, washed twice with methanol and dried in air first and then over silica gel. Yield 57.60 % (on metal content), Melting point > 250 °C.

The compound is soluble in water, but insoluble in methanol, ethanol, acetone and n-hexane. It is air stable.

##### (ii) (Adenine)triaquadichlorocopper(II).monohydrate, $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_5)(\text{H}_2\text{O})_3\text{Cl}_2]\cdot\text{H}_2\text{O}$

A methanolic solution of adenine (0.54 g in 120 mL) was added to a methanolic solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.68 g in 20 mL). The mixed solution was stirred and kept at room temperature. Green crystals of  $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_5)(\text{H}_2\text{O})_3\text{Cl}_2]\cdot\text{H}_2\text{O}$  were formed immediately. The crystals were filtered, washed twice with methanol and dried in air first and then over silica gel. Yield 55.30 % (on metal content), Melting point > 250 °C.

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The compound is soluble in water, but insoluble in methanol, ethanol, acetone and n-hexane. It is stable in air.

### (iii) Trichloroadeniniumzinc(II), $[\text{Zn}(\text{C}_5\text{H}_6\text{N}_5)\text{Cl}_3]$

Methanolic solutions of adenine (0.14 g in 40 mL) and  $\text{ZnCl}_2$  (0.14 g in 15 mL) were mixed together in a beaker. The resulting mixture was kept at room temperature for about 24 hours. White crystals of  $[\text{Zn}(\text{C}_5\text{H}_6\text{N}_5)\text{Cl}_3]$  were formed. The product was filtered, washed twice with methanol and dried in air first and then over silica gel. Yield 52.33 % (on metal content), Melting point > 250 °C.

The compound is slightly soluble in hot water, but insoluble in methanol, ethanol, acetone and n-hexane. It is air stable.

## III Results and Discussion

The empirical formula of Co(II), Cu(II) and Zn(II) complexes have been determined by their elemental analyses. The metal and chloride contents of the complexes are summarized in Table 1.

**Table 1. Data for elemental analysis of the complexes.**

Compound	% of Metal found	% of Chloride found
$[\text{Co}(\text{C}_5\text{H}_5\text{N}_5)_2\text{Cl}_2] \cdot \text{H}_2\text{O}$	16.09 (14.02)	16.83 (16.89)
$[\text{Cu}(\text{C}_5\text{H}_5\text{N}_5)(\text{H}_2\text{O})_3\text{Cl}_2] \cdot \text{H}_2\text{O}$	19.37 (18.61)	24.07 (20.79)
$[\text{Zn}(\text{C}_5\text{H}_6\text{N}_5)\text{Cl}_3]$	18.50 (21.21)	34.81 (34.75)

Calculated values are given in parentheses.

**IR spectral analysis:** A comparison of several important vibrational frequencies of ligands and their metal complexes is shown in Table 2. The ligand shows a weak absorption peak at about  $3450 \text{ cm}^{-1}$  due to the N-H stretching motion. A similar absorption peak is observed in the Zn(II) complex at  $3500\text{-}3000 \text{ cm}^{-1}$ . However, both Co(II) and Cu(II) complexes show broad absorption bands in the region  $3500\text{-}2800$ . Such broadness of the peak results from the merging of O-H stretchings of water of hydration, N-H and C-H stretchings of ligand.

Characteristic aromatic ring vibrations in the region  $1670\text{-}1360 \text{ cm}^{-1}$  are associated with the interaction of the C=C and C=N vibrations. The strong peaks at  $1670$  and  $1595 \text{ cm}^{-1}$  are also assigned to the coupling of the ring stretchings with the N-H bending motion. Careful investigation of IR spectral

data of adenine and its metal complexes indicates that the interaction between the metal and the ligand possibly occurs through N(7) of adenine in each complex. The significant shifting of the C=N peak in the spectra of the complexes leads us to make this conclusion.

**UV/Vis spectral analysis:** The UV-Vis spectra of the complexes were recorded in aqueous medium. In the cobalt complex, the absorption band at 502 nm can be assigned as  $d \rightarrow d$ , more specifically  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  electronic transition. The band at wavelength 260 nm is a characteristic band of heteroaromatic molecule called benzoid band. For copper complex a broad band has been observed at about 604 nm due to  $d \rightarrow d$  electronic transition. This band, in fact, consists of three nearly superimposed bands from the  $d_{xy}$ ,  $d_z^2$ , and  $d_{xz}$ ,  $d_{yz}$  pair to the  $\sigma$  anti-bonding, and half field  $d_x^2 - y^2$  level. These are the characteristics of Jahn-Teller distortion of simple octahedral complex. The two high intensity bands in the UV-region originate from  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions<sup>15</sup>. No significant absorption band was observed for zinc complex in the visible region. Nevertheless, a weak absorption band at 287.2 nm is found, due to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  electronic transitions.

**Magnetic measurement:** From the magnetic measurements (Table 3) it is found that the  $[\text{Co}(\text{C}_5\text{H}_5\text{N}_5)_2\text{Cl}_2] \cdot \text{H}_2\text{O}$  complex is paramagnetic with a magnetic moment of 3.26 B. M., which corresponds to the presence of 3 unpaired electrons in its 3d orbitals. The complex has tetrahedral geometry with two adenine molecules and two  $\text{Cl}^-$  ions are coordinated to the  $\text{Co}^{2+}$  ion. This is expected, because larger ligands usually favor tetrahedral geometry. Its green color also supports our comment. The  $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_5)(\text{H}_2\text{O})_3\text{Cl}_2] \cdot \text{H}_2\text{O}$  complex reveals paramagnetic magnetic behavior corresponding to one unpaired electron in its 3d levels. It suggests that in the complex copper exists as  $\text{Cu}^{2+}$  ion with an octahedral moiety formed by 2  $\text{Cl}^-$  ions, 1 adenine and 3  $\text{H}_2\text{O}$  molecules around the  $\text{Cu}^{2+}$  ion. A negative value of magnetic susceptibility for Zn(II) complex suggests that it is diamagnetic in nature, i.e. all the electron in five d-orbitals for a  $3d^{10}$  ion are paired.

**Table 2. Some key IR bands (assignments were done on the basis of standard reference) of adenine and its complexes.**

Compound	$\nu(\text{O-H})$ $\text{cm}^{-1}$	$\nu(\text{N-H})$ $\text{cm}^{-1}$	$\nu(\text{C=N})/$ $\delta(\text{N-H}) \text{ cm}^{-1}$	$\nu(\text{C=C})$ $\text{cm}^{-1}$	$\nu(\text{C-NH}_2)$ $\text{cm}^{-1}$	$\nu(\text{C-N})$ $\text{cm}^{-1}$
$\text{C}_5\text{H}_5\text{N}_5$		3450	1670,1595	1440	1250	1120
$[\text{Co}(\text{C}_5\text{H}_5\text{N}_5)_2\text{Cl}_2] \cdot \text{H}_2\text{O}$	3500-2800		1660,1595	1470	1250	1120
$[\text{Cu}(\text{C}_5\text{H}_5\text{N}_5)(\text{H}_2\text{O})_3\text{Cl}_2] \cdot \text{H}_2\text{O}$	3500-2800		1635,1570	1440	1210	1100
$[\text{Zn}(\text{C}_5\text{H}_6\text{N}_5)\text{Cl}_3]$	3500-3000		1660,1595	1470	1220	1170

**Table 3. Magnetic data of the studied complexes.**

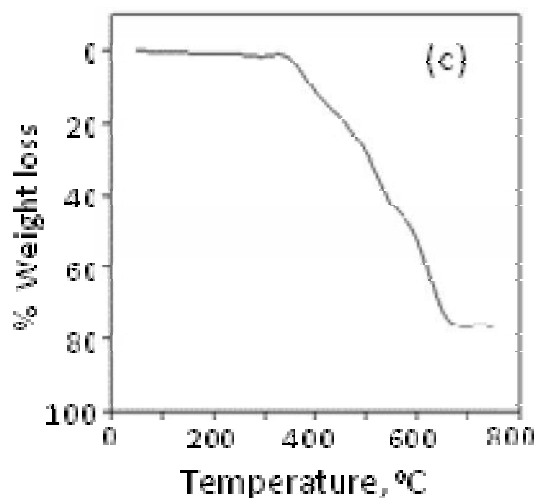
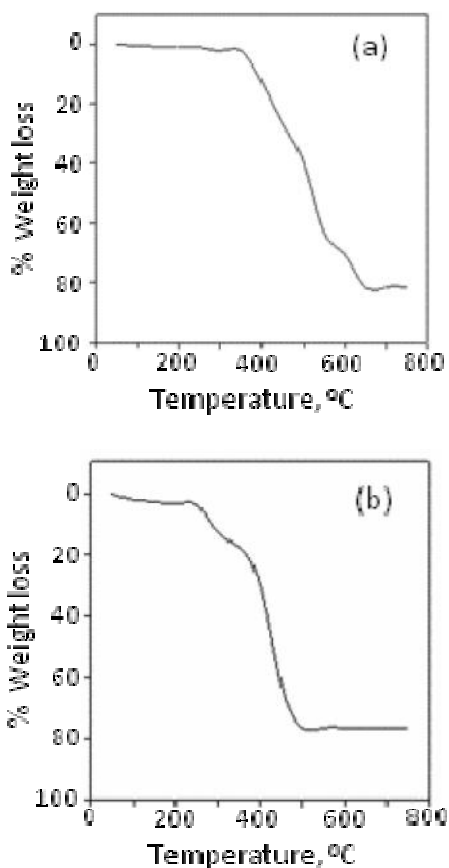
Compounds	$\chi_g \times 10^{-5}$	$\mu_s$
	C. G. S. unit	B. M.
[Co(C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	1.6893	3.2641
[Cu(C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> )(H <sub>2</sub> O) <sub>3</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	0.28761	1.5275
[Zn(C <sub>5</sub> H <sub>6</sub> N <sub>5</sub> )Cl <sub>3</sub> ]	-0.0386	0

$\chi_g$  - Gram susceptibility,  $\mu_s$  - Uncorrected spin magnetic moment.

**Thermal analysis:** Thermal behaviour of the complexes has been investigated by QSTG method. Their decomposition patterns are shown in Fig. 1. All the complexes show high thermal stability.

Cobalt complex is stable up to 350°C which then decomposes rapidly and attains a constant weight at 650°C. The end product is black, about 18.34% of the original weight. It is identified as CoO for which the calculated weight is 17.83%.

The copper complex starts losing weight at 200°C, and upto 300°C about 12.78% weight losses is registered. It corresponds to the loss of two molecules of water (calculated weight loss is 10.54%). The decomposition process is rapid above this temperature and completed by 500°C. About 76.57% of the total weight loss is observed. The residue is black and identified as CuO for which the calculated weight is 23.28%.

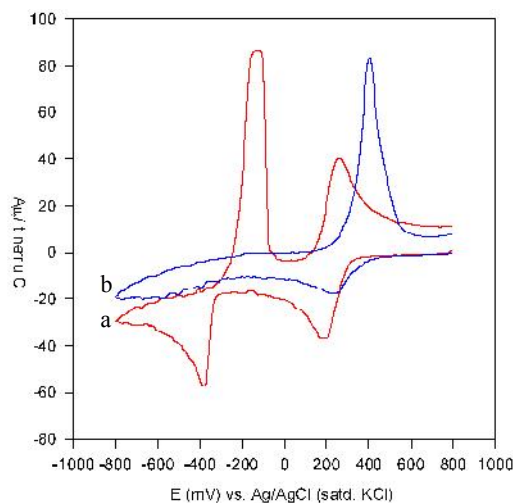


**Fig. 1.** QSTG of (a) [Co(C<sub>5</sub>H<sub>5</sub>N<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>].H<sub>2</sub>O, (b) [Cu(C<sub>5</sub>H<sub>5</sub>N<sub>5</sub>)(H<sub>2</sub>O)<sub>3</sub>Cl<sub>2</sub>].H<sub>2</sub>O and (c) [Zn(C<sub>5</sub>H<sub>6</sub>N<sub>5</sub>)Cl<sub>3</sub>].

The zinc complex undergoes thermal decomposition above 300°C. The decomposition process is rapid and continuous until it attains a constant weight at 650°C. About 81.00% of the total weight loss is registered. The end product is white, characterized as ZnO.

**Conductivity measurement:** The conductivity measurements of Co(II), Cu(II) and Zn(II) complexes in aqueous medium reveal that their molar conductance increases with increasing dilution. These are the characteristics of the complexes that dissociate into different electroactive aquated ions in solution.

**Cyclic voltammetric observation:** The cyclic voltammetric response of 2 mM Cu(II) in 1 M KCl solution at GCE with scan rate of 100 mVs<sup>-1</sup> within the potential window of 800 mV to -800 mV was studied. The recorded voltammogram is shown in Fig. 2(a).



**Fig. 2.** Cyclic voltammograms of (a) 2 mM Cu(II) and (b) Cu(II)-adenine mixture in 1.0 M KCl at GCE with scan rate of 100 mVs<sup>-1</sup>.

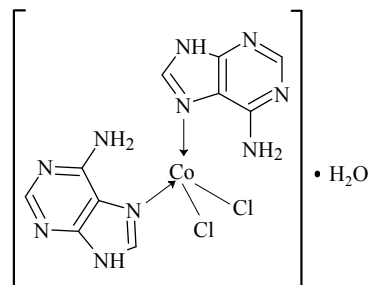
In the forward scan the voltammogram shows two cathodic peaks,  $i_{pc1}$  and  $i_{pc2}$  at about -205.45 and -390.87 mV respectively and in the reverse scan two anodic peaks,  $i_{pa1}$  and  $i_{pa2}$  at about 410.39 and -150.45 mV respectively. Two cathodic peaks correspond to the reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0) species while the two anodic peaks are due to the oxidation of Cu(0) to Cu(I) and Cu(I) to Cu(II) species is in good agreement with previous study<sup>16</sup>. The linear relationship of peak currents and square root of scan rate demonstrates that the electrode process is adsorptive controlled as well as diffusion controlled as shown in previous study<sup>17</sup>.

The voltammogram of Cu(II) in presence of adenine was carried out at scan rate of  $100 \text{ mVs}^{-1}$  within the same potential window as before. The recorded voltammogram is shown in Fig. 2(b). It exhibits a broad cathodic peak at about 275.37 mV, and an anodic peak at about 450.79 mV. The peak current and peak potential of voltammograms recorded for Cu(II) and Cu(II)-adenine system with different scan rates are given in Table 4. The disappearing of both cathodic and anodic peaks and appearing of a new cathodic and an anodic peaks for Cu(II) in presence of adenine suggest that Cu(II)-adenine interaction was occurred. The position of the new appearing cathodic peak at more positive potential indicates a strong participation of copper in complex formation with adenine which makes its reduction process more difficult. The newly appeared anodic peak, associated with the oxidation process of Cu, becomes intense indicated that oxidation of copper has been facilitated in the presence of the ligand. Cyclic voltammetric behavior of Co(II)- and Zn(II)-adenine systems were not carried out yet.

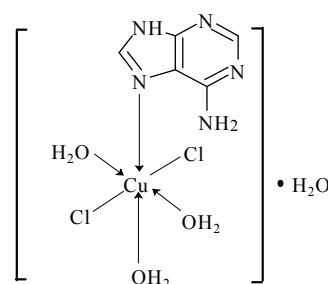
#### IV. Conclusion

Adenine is a purine derivative and form complexes with Co(II), Cu(II) and Zn(II) in methanolic medium. The results

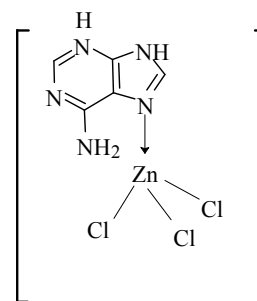
of our studies described and discussed in this report exhibit the following proposed structures of the complexes (Scheme 2).



Bis(adenine)dichlorocobalt(II).monohydrate



(Adenine)trisaquadichlorocopper(II). monohydrate



Trichloroadeniniumzinc(II)

**Scheme 2.** Schematic representation of proposed structures of the complexes.

**Table 4.** The peak currents and peak potentials of the voltammograms of Cu(II) in 1.0 M KCl at 25°C.

Scan rate, $v \text{ mVs}^{-1}$	Anodic peak current $\mu\text{A}$		Cathodic peak current $\mu\text{A}$		Anodic peak potential mV		Cathodic peak potential mV		$\Delta E_p = E_{pa} - E_{pc}$ mV		$i_{pa1}/i_{pc1}$	$i_{pa2}/i_{pc2}$
	$i_{pa1}$ (+)	$i_{pa2}$ (+)	$i_{pc1}$ (-)	$i_{pc2}$ (-)	$E_{pa1}$ (+)	$E_{pa2}$ (-)	$E_{pc1}$ (+)	$E_{pc2}$ (-)	$\Delta E_{p1}$	$\Delta E_{p2}$		
25	20.5	77.2	19.1	31.0	245.8	141.2	193.5	350.4	52.3	208.8	1.07	2.49
50	28.5	86.3	26.1	40.9	256.3	135.9	177.0	366.1	79.3	230.2	1.09	2.11
100	40.5	86.5	36.9	57.3	256.3	130.7	188.3	386.9	68.0	256.2	1.09	1.51
150	51.4	87.0	46.3	75.8	261.0	130.8	188.3	371.3	72.7	240.5	1.11	1.15
200	57.0	87.5	52.4	76.8	261.5	125.5	183.0	397.5	78.5	272.0	1.08	1.14

### Acknowledgement

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