

## Mixed Ligand Binuclear Complexes of Copper(II) and Cadmium(II) with Adenine and 1,4-Diazabicyclo[2.2.2]octane

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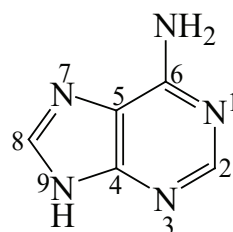
### Abstract

Mixed ligand binuclear complexes of Cu(II) and Cd(II) with adenine (Ade) and 1,4-diazabicyclo[2.2.2]octane (DABCO) have been synthesized at a metal to ligands (M:L:L') molar ratio of 1:1:1 in aqueous medium under ambient conditions. All synthesized complexes are powdery solids of different colours, slightly soluble in hot water and decompose at high temperature. Characterization of the complexes was accomplished using various analytical techniques, e.g. metal and chloride content analysis, Fourier transform spectrophotometer (FT-IR), UV-visible spectrophotometer, magnetic measurement, and thermal analyses. The metal and chloride contents analyses of the complexes reveal to their stoichiometry  $[M_2Cl_2(Ade)_2(H_2O)_2(DABCO)]Cl_2$  [M = Cu(II) or Cd(II)]. Analytical data suggests that they are homo metal symmetric binuclear complexes comprises of two  $[MCl(Ade)(H_2O)]$  moieties in between a DABCO molecule is N,N'-bridge bonded. The arrangements of the ligands around the metal centers are essentially tetrahedral involving N(9) of deprotonated imidazole moiety, one Cl<sup>-</sup> ion, one oxygen from the water molecule and one tertiary N atom from DABCO completing the coordination. Proton migration occurs from N(9) to the N(1) site resulting into a zwitterionic form of adenine, additionally N(3) site of which is hydrogen bonded with the coordinated water molecule. Electrochemical redox behaviour of Cu(II) in presence of adenine and DABCO in the aqueous medium was also studied. It exhibits quasi-reversible one-electron transfer processes.

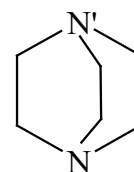
**Keywords:** Nucleic acids, Adenine, DABCO, Infrared spectrum, Thermal analysis.

### I. Introduction

Reactions of metal ions with nucleobases and their derivatives are of great interest and highly relevant because of their chemical and biological demand<sup>1</sup>. The interest of this field is focused on delineating metal centers in biology, which includes the application of inorganic chemistry to investigate structures and functions of biomolecules<sup>2</sup>. There are many functional motivations behind the study of how metal complexes interact with nucleic acids and their constituents. Adenine (Ade) is an essential nucleobase of nucleic acids, comprising of a fused pyrimidine-imidazole ring with conjugated double bonds<sup>3-5</sup>. There are five nitrogen atoms in Ade, and each nitrogen atom has lone electron pair, which makes a suitable ligand for alkali/alkaline earth, terrestrial cations, and transition metal ions<sup>6</sup>. Metal ions are typically bound with N(9)-unsubstituted Ade preferentially to N(9) site (in bridge to N(3)), then to N(7), and finally to N(1) position<sup>7</sup>, and intramolecular interactions among the ligands may also play a role of the stability of the complexes<sup>8</sup>. Addition of a multicoordinated ligand, DABCO into a reaction mixture of metal ions and Ade may cause the reaction to take place in a more selective way. The structural formulae of Ade and DABCO are.



Adenine (Ade)



1,4-diazabicyclo[2.2.2]octane (DABCO)

It is reported that intramolecular interligand hydrogen bonds among the ligands play a crucial role in controlling the site-specific metal bonding to nucleobases. Marzilli and Kistenmacher emphasized the importance of stereospecific interligand interactions, which include hydrogen bonding, electrostatic repulsions, and steric constraints, in determining the specific metal binding to nucleic acid bases<sup>9</sup>. Aoki *et al.* investigated the base- or site-specific metal bonding in the  $[Rh_2(\text{carboxylato or amidato})_4(\text{nucleobase or its derivative})_2]$  system and concluded that the interligand interactions via hydrogen bonding are responsible for site-specific metal bonding to nucleobases<sup>10-13</sup>. Mixed ligand complexes of various metal ions with nucleobases and other ligands have been reported by several workers<sup>10-16</sup>. However, there is no evidence yet in the literature on metal ion-mixed ligand complexes of Ade and DABCO. Consequently, an attempt has been made to study this exciting area involving the interaction of  $MCl_2$  (M = Cu(II) and Cd(II)) with a nucleobase Ade mixed with a diamine, DABCO. The results of our work are presented in this report.

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## II. Experimental

### Chemicals

Adenine was procured from LOBA Chemie Pvt. Ltd., India; DABCO from Sigma-Aldrich, China. Copper(II) chloride dihydrate, cadmium(II) chloride monohydrate, silver nitrate, inorganic acids (HCl, HNO<sub>3</sub>), ammonia, and others organic solvents etc., used in all synthetic and analytical work were analar grade. All chemicals were used as supplied.

### Equipments and Methods

A SMP11 electrothermal melting point apparatus, Shimadzu, Japan was used to determine the melting points of the complexes. The metal content was estimated complexometrically using Na<sub>2</sub>EDTA.2H<sub>2</sub>O as the titrating agent. The chloride content was determined gravimetrically as AgCl. The FTIR spectra of the complexes were recorded using KBr pellet technique at room temperature by a Shimadzu (Japan) Infrared Spectrometer IR-470 in the range of 400-4000 cm<sup>-1</sup>. The absorption spectra were recorded on a UV-visible spectrometer, Model UV-160A, Shimadzu (Japan), in the wavelength range 200-600 nm using water as the reference medium. The magnetic susceptibility of the complexes was measured using the Sherwood Scientific Magnetic Susceptibility Balance (M.S.B.) of model Magway MSB Mk1, Cambridge, England. The quasi-static thermogravimetric (QSTG) analysis was performed in a CWF 11/5 type Carbolite calibrated muffle furnace. Shimadzu Thermal Analyzer (DT-40) was used for recording differential scanning calorimetric (DSC) data of the complexes. Cyclic voltammetric measurements were carried out using a CH 620D Electroanalyzer equipped with a Teflon capped Pyrex-glass micro cell. All measurements were carried out using a three electrodes arrangement consists of GCE as working electrode, Ag/AgCl (satd. KCl) as reference electrode and platinum wire as counter electrode.

### Synthesis of the Complexes

#### (i) [Cu<sub>2</sub>Cl<sub>2</sub>(Ade)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(DABCO)]Cl<sub>2</sub>

Aqueous solutions of CuCl<sub>2</sub>.2H<sub>2</sub>O, adenine and DABCO in a 1:1:1 molar ratio were prepared by dissolving them into least volume of hot distilled water separately and mixed together. The pH of the resultant solution was about 4. It was kept at ambient conditions. A blackish green precipitate was formed within half an hour. The product was filtered, washed with distilled water, and dried in a desiccator over silica gel. The compound is stable in air, and slightly soluble in hot water. Yield, % = 58% (on the basis of copper content). Decomposition temperature: 155-165°C. Copper(II) content

(%): 18.39 (found) and 18.49 (Calcd.); Chloride content (%): 23.6 (found), 20.63 (calcd.).

FTIR bands/cm<sup>-1</sup>: 3440-3325, 3190, 1676, 1644, 1590, 1565, 1465, 1404, 1368, 1340, 1307, 1272, 1204, 1144, 1030, 990, 890, 793, 735, 685, 650, 573, 545 and 418.

#### (ii) [Cd<sub>2</sub>Cl<sub>2</sub>(Ade)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(DABCO)]Cl<sub>2</sub>

Requisite amount of CdCl<sub>2</sub>.H<sub>2</sub>O, adenine and DABCO in the molar ratio (1:1:1) were dissolved into hot distilled water separately and mixed. The measured pH of the resulting solution is 4.5. The solution was then kept at ambient temperature for crystallization. A white precipitate was formed within an hour. The product was filtered, washed with distilled water, and dried in a desiccator over silica gel. The compound is stable in air, and only slightly soluble in hot water. Yield % = 39% (on the basis of cadmium content). Decomposition temperature: > 250°C. Cadmium(II) content (%): 28.90 (found) and 28.64 (Calcd.); Chloride content (%): 17.27 (found), 18.06 (calcd.).

FTIR bands/ cm<sup>-1</sup>: 3430-3330, 3205, 1678, 1654, 1606, 1565, 1468, 1400, 1360, 1350, 1308, 1280, 1210, 1146, 1035, 993, 888, 795, 740, 682, 655, 575, 550 and 447.

## III. Results and Discussion

The synthesized binuclear complexes are powdery solids of different colours, poorly soluble in hot water and decompose at high-temperature. The empirical formulation of the complexes was done on the basis of their metal and chloride ions content. Some of their importance physico-chemical investigations are discussed in the onward sections.

### FTIR Spectral Analysis

The band assignments of ade, DABCO and the synthesized binuclear M(II) complexes have been completed based on literature survey. The characteristics FTIR bands of adenine and DABCO moiety were observed in the prepared complexes. In comparison with the spectra of ligands, their Cu(II) and Cd(II) complexes show numerous vibrational frequencies at different positions and intensities, demonstrating that the ligands are coordinated with M(II) ions. The broad peak(s) that appeared in the region 3440-3325 cm<sup>-1</sup> shows the presence of O-H, N-H, and C-H groups from organic moieties present in the studied complexes. This broadening of the peak is occurring due to the peaks resulting from different merging groups in addition to their interactions within. Hydrogen bond formation among the ligands within the complex also results in a broadening of O-H and N-H stretching vibrations.

The characteristic absorption peaks due to the N–H group of imidazole rings of purine bases are observed at 2600–2800  $\text{cm}^{-1}$  and at 871  $\text{cm}^{-1}$  due to  $\nu(\text{N–H})$  and  $\delta(\text{N–H})$  (out-of-plane) modes respectively. These bands are disappeared in the studied complexes on replacement of the proton by the Cu(II) or Cd(II). The absorption band at 1252  $\text{cm}^{-1}$  is assigned to the C(6)–NH<sub>2</sub> stretching mode attached to an internal C–N stretching vibration for free Ade. This band is shifted to higher region at 1272 and 1280  $\text{cm}^{-1}$  for the Cu(II) and Cd(II) complexes, respectively, because of protonation at the N(1) site and metalation with the ring nitrogen. A similar observation was recorded in the adeninato–Cu<sup>2+</sup> complex<sup>17</sup>. The characteristic C–N:→M(II) stretching band coupled with the deformation of the C–H group is observed at 1204  $\text{cm}^{-1}$  and 1210  $\text{cm}^{-1}$  for the Cu(II) and Cd(II) complexes, respectively. The  $\nu(\text{C–N})$  frequency of free DABCO is observed at 1060  $\text{cm}^{-1}$  while it appears in the complexes at around 1030–1035  $\text{cm}^{-1}$ . The downward shifting of the  $\nu(\text{C–N})$  frequency suggests the involvement of the DABCO ligand in coordination with metal ions. In the region of 900–1000  $\text{cm}^{-1}$ , two absorption bands at 922 and 942  $\text{cm}^{-1}$ , are observed for the ring vibrations of Ade molecule. In the complexes, these bands are also found near 890 and 990  $\text{cm}^{-1}$ . The simultaneous effect of protonation at the N(1) site and metal coordination at the N(9) position in our investigated complexes could possibly account for these variations. Nevertheless, in the adeninium chloride, the band at 922  $\text{cm}^{-1}$  is shifted to a lower frequency by protonation at the N(1) position, and the other band at 942  $\text{cm}^{-1}$  remains unshifted<sup>17</sup>. The complexation sensitive bands appeared in the region of 650–740  $\text{cm}^{-1}$ . The position of these bands varies little with respect to the skeletal ring vibration of free Ade. For the Cu(II) and Cd(II) complexes, the  $\nu\text{N}(1)\text{–H}$  protonation bands appear at 573 and 575  $\text{cm}^{-1}$  along with new bands at 418 and 447  $\text{cm}^{-1}$  due to metal ion coordination, respectively. The  $\delta(\text{NH}_2)$  band of Ade is also shifted to a higher frequency region in the complexes. The tetrahedral arrangement around the Cu(II) or Cd(II) center is thus built up possibly through one nitrogen of the DABCO ligand, one chloride ion, the N(9) site of Ade ligand, and the 4<sup>th</sup> position is decided by a water molecule.

#### UV-vis Spectral Analysis

The synthesized complexes are some extents soluble in distilled water at ambient conditions and aqueous solutions of them were used for measuring their electronic spectra. The UV-visible spectral study shows that free adenine has absorption at 195 and 260 nm while that of DABCO is at

196 nm. Nonetheless, the binuclear Cu(II) complex shows two intense absorption bands at 284 and 300 nm and Cd(II) complex resulting an intense band at 302 nm. These intense band(s) are assigned for  $\pi\rightarrow\pi^*$  and/or  $n\rightarrow\pi^*$  electronic transitions. However, the complexes do not show any bands in the visible region because of their poor solubility in water.

#### Magnetic Susceptibility Measurement

The observed magnetic moment ( $\mu_{\text{eff}}$ ) of  $[\text{Cu}_2\text{Cl}_2(\text{Ade})_2(\text{H}_2\text{O})_2(\text{DABCO})]\text{Cl}_2$  complex is 1.60 BM correspond to the presence of a single unpaired electron. The weak ligands, Cl<sup>-</sup>, ade, aqua and DABCO groups give rise to tetrahedral Cu(II)  $d^9$  complex with the  $d$ -electron configuration of  $e_g^4t_{2g}^5$ . Conversely, the  $[\text{Cd}_2\text{Cl}_2(\text{Ade})_2(\text{H}_2\text{O})_2(\text{DABCO})]\text{Cl}_2$  complex showed negative magnetic susceptibility, purely diamagnetic character of Cd(II) ion. It is expected for  $d^{10}$  system of Cd(II) cation with the  $d$ -electron configuration of  $t_{2g}^6e_g^4$ , irrespective of spin type as well as geometry of its complexes.

#### Thermal Analysis

The quasi-static thermogravimetric analysis of the studied complexes was also carried out and the obtained thermograms are plotted in Fig. 1. The thermogram (Fig. 1) shows that at around 50°C, the  $[\text{Cu}_2\text{Cl}_2(\text{Ade})_2(\text{H}_2\text{O})_2(\text{DABCO})]\text{Cl}_2$  complex begins to lose weight. Total weight loss up to 112°C is 5.86%, which corresponds to the removal of two molecules of water (calculated weight loss is 5.24%). In the temperature range of 150–300°C, a rapid loss of 18.62% of the total weight is observed, which might be due to the loss of coordinated water along with chloride ions. Above 300°C, the decomposition process is very fast and continuous. The end product is ash coloured, possibly CuO, and the percentage of weight is 20.09%, which is close to the calculated value of 23.14%. It is noted that during heating, the sample suffered colour changes at several stages, i.e. dark green to light brown and finally ash coloured. The DSC studies (Fig. 2.) of the complex show that the decomposition process consists of several exotherms. It implies that the oxidative decomposition of the ligand molecules occurs even at lower temperatures.

The QSTG curve of the  $[\text{Cd}_2\text{Cl}_2(\text{Ade})_2(\text{H}_2\text{O})_2(\text{DABCO})]\text{Cl}_2$  complex shows that the compound is thermally stable up to 150°C (Fig. 3). Beyond this temperature, the decomposition commences and the total weight loss up to 200°C is 3.19%. It corresponds to the partial removal of two molecules of coordinated water (calculated weight loss is 4.59%).

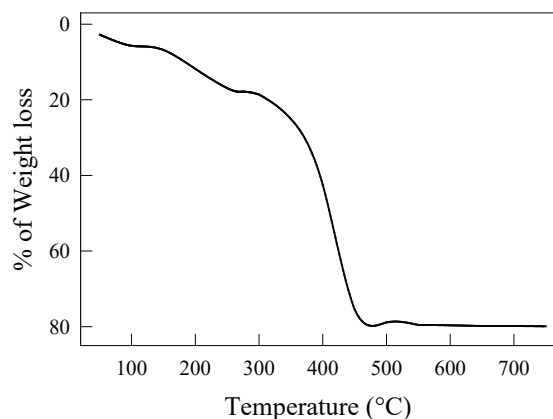


Fig. 1. QSTG graph of  $[\text{Cu}_2\text{Cl}_2(\text{Ade})_2(\text{H}_2\text{O})_2(\text{DABCO})]\text{Cl}_2$ .

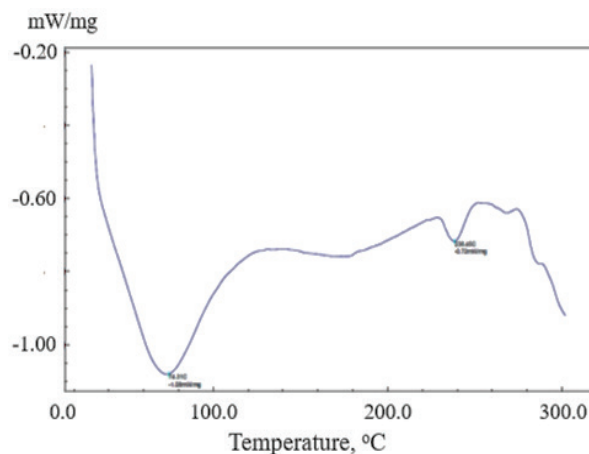


Fig. 2. DSC graph of  $[\text{Cu}_2\text{Cl}_2(\text{Ade})_2(\text{H}_2\text{O})_2(\text{DABCO})]\text{Cl}_2$ .

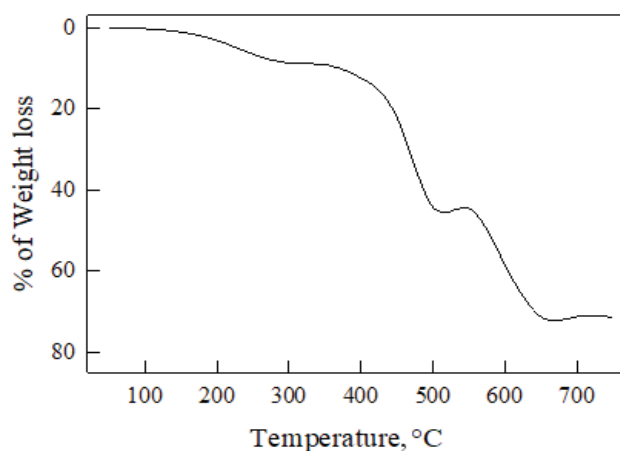


Fig. 3. QSTG graph of  $[\text{Cd}_2\text{Cl}_2(\text{Ade})_2(\text{H}_2\text{O})_2(\text{DABCO})]\text{Cl}_2$ .

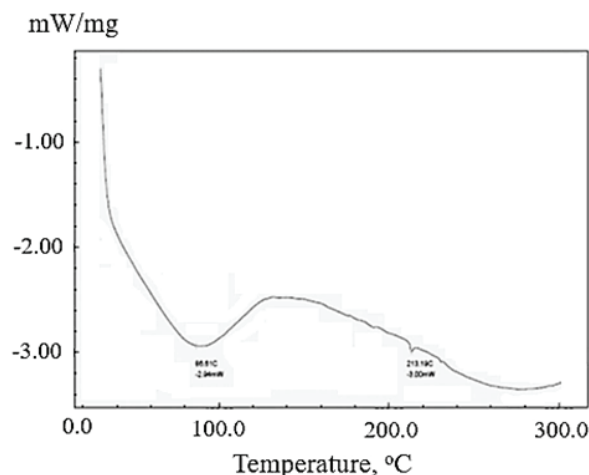


Fig. 4. DSC graph of  $[\text{Cd}_2\text{Cl}_2(\text{Ade})_2(\text{H}_2\text{O})_2(\text{DABCO})]\text{Cl}_2$ .

In the temperature range of 200-400°C, a rapid loss of 17.14% of the total weight is observed and resulting into a conversion of white to light brown product. Above 400°C, the decomposition process is very sharp and continuous. The end product is deep ash, possibly CdO, and attains a constant weight and is characterized by chemical analysis. The percentage of residue is about 28.61% and the calculated conversion value is 32.79%. The DSC measurement of the complex (Fig. 4.) reveals that the decomposition process involves two exotherms up to 300°C. It means that the oxidative breakdown of the ligand molecules undergoes even at lower temperatures.

#### Cyclic Voltammetric Study

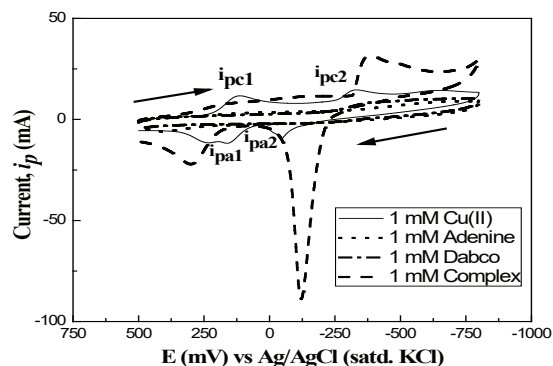
The electrochemical redox behaviour of Cu(II), and Cu(I) in presence of adenine and DABCO at a 1:1:1 molar ratio in an aqueous solution has been investigated. The recorded cyclic voltammogram (CV) of Cu(II) at a scan rate of 100  $\text{mVs}^{-1}$  within the potential window of 500 mV to -800 mV is shown in Fig. 5 (solid line). The voltammogram shows

two reduction waves,  $i_{pc1}$  and  $i_{pc2}$  at about 180.45 mV and -395.87 mV, together with two oxidation waves,  $i_{pa1}$  and  $i_{pa2}$  at about 235.39 mV and -70.50 mV respectively. These results are in agreement with previous studies<sup>18</sup>. Over the whole scan range, the peak current variation with the square root of scan rate establishes that the redox processes are diffusion controlled<sup>19</sup>. The ratio of peak current and the peak potential separation reveal that the Cu(II)/Cu(I) redox couple (corresponding to the first pair) is reversible while the Cu(I)/Cu(0) (corresponding to the second pair) is a quasi-reversible redox process.

A typical voltammogram of Cu(II) in presence of mixed ligands is shown in Fig. 5 (short-dashed line). Interestingly, CV for such a combination exhibits only one cathodic peak (around -393 mV) and two anodic peaks (around -123 mV and 295 mV). Under the identical experimental conditions, the CVs for Ade (dot dot) and DABCO (dash dot) showed no peaks. In presence of mixed-ligands, the peak currents and the peak potentials of Cu(II) are shifted, suggesting that metal-ligands interactions occur in the reaction medium.



The peak potential separation increases with increasing scan rate (Fig. 6) due to the quasi-reversible redox processes. The anodic peak current related to the oxidation process is intense

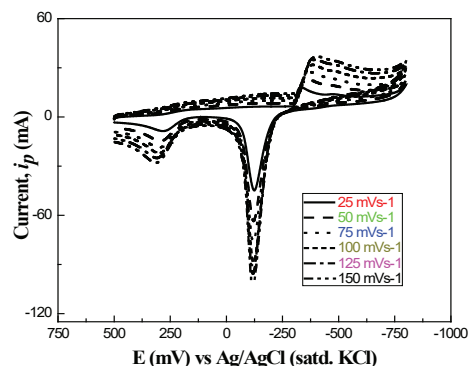


**Fig. 5.** Cyclic voltammograms of Cu(II) (solid), adenine (dot dot), DABCO (dash dot), and Cu(II)-ligands mixture (short dash) in KCl solution at the scan rate of 100 mVs<sup>-1</sup>.

#### IV. Conclusion

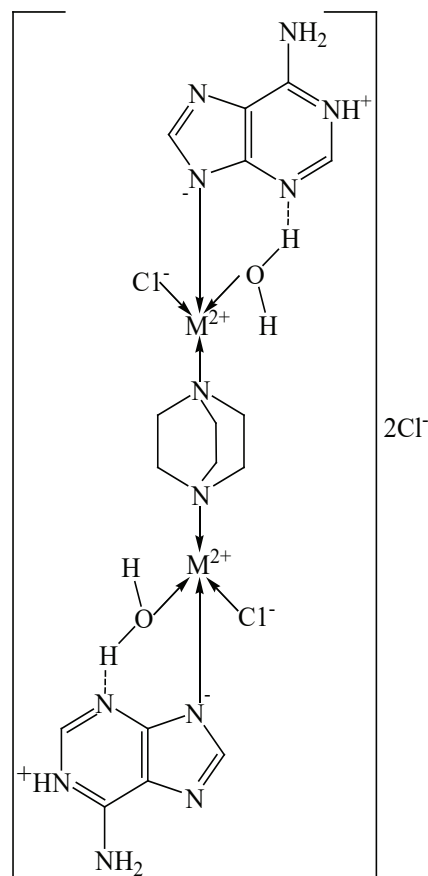
In aqueous medium, the reaction of  $MCl_2 \cdot nH_2O$  (where  $M = Cu(II)$  or  $Cd(II)$ ) with adenine and DABCO produced homo metal symmetric binuclear complexes with the probable proposed formula of  $[M_2Cl_2(Ade)_2(H_2O)_2(DABCO)]Cl_2$ . Investigations of their different physico-chemical properties suggest that nucleobase adenine attains a zwitterionic form and is ligated as a monodentate ligand with the metal ion which is tetrahedrally surrounded by a water molecule, a chloride ion, and a nitrogen atom of the DABCO that essentially acts as a  $\mu$ -type bridging ligand between two homo metal symmetric binuclear moieties. Hence, the best way to represent the general formula of the synthesized complexes is  $[MCl(Ade)(H_2O)(\mu-DABCO)MCl(Ade)-(H_2O)]Cl_2$ . Adenine is coordinated through its imidazolyl ring nitrogen, deprotonated N(9), and possibly there is an interligand hydrogen bonding between N(3) and a water molecule which is further coordinated with the M(II) center. There is another interligand H-bond possibly formed between the nitrogen of DABCO and the hydrogen atom of the aqua ligand. It was reported earlier<sup>14-15</sup> that adenine, in the presence of amino- or imino-ligands, usually coordinates with a metal ion through N(9) after deprotonation. The released proton is attached to N(1), the most basic site (except N(9)) among the four ring nitrogen atoms that exist in the structure of adenine base. This site-specificity may be triggered by interligand interactions such as hydrogen bonding and electrostatic repulsion associated with the steric environment of the M(II) ion. Single crystal X-ray diffraction data may well resolve the structural details of the prepared complexes, and reemphasize the hypothesis proposed for metal-interligand interactions, including site-specific metal binding to adenine. On the basis of our experimental investigations and previous

and reveals the oxidation of copper is significantly facilitated in presence of adenine and DABCO ligands<sup>20</sup>.



**Fig. 6.** Cyclic voltammograms of Cu(II) in presence of adenine and DABCO at different scan rates of 25, 50, 75, 125 and 150 mVs<sup>-1</sup>.

assessments<sup>14-15,17</sup> the most possible general structure of the synthesized complexes is



$[M_2Cl_2(Ade)_2(H_2O)_2(DABCO)]Cl_2$ , ( $M = Cu(II)$  or  $Cd(II)$ )

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