

Synthesis and Characterization of Mixed Ligand Complexes of Copper(II) with Adenine and Dicarboxylic Acids

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Abstract

Three mixed ligand complexes of copper(II) with adenine and dicarboxylic acids have been synthesized. The resulting complexes were characterized by their melting point, solubility, metal content analysis, FT-IR and UV-visible spectroscopy, magnetic measurement, thermal analysis, cyclic voltammetric measurement and X-ray powder diffraction study. The products are microcrystalline powder, slightly soluble in water and decompose at high temperature. Under experimental condition, the ligands adenine (Ade) behaves as a neutral ligand, whereas oxalic acid (OxH_2), succinic acid (SucH_2) and tartaric acid (TarH_2) are doubly deprotonated to form dianionic ligands that are coordinated to the Cu(II) ion. The Cu(II) content analysis of the complexes confine to their stoichiometry $[\text{Cu}(\text{Ade})(\text{L})(\text{H}_2\text{O})]$ ($\text{L} = \text{Ox}, \text{Suc}, \text{or Tar dianion}$). Electrochemical redox behavior of the complexes in their reaction medium was also examined. They exhibit quasi-reversible one-electron transfer processes.

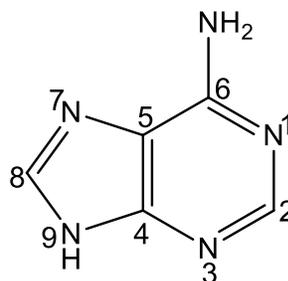
Keywords: Nucleobase, Adenine, Dicarboxylic acid, Infrared spectrum, Magnetic susceptibility.

I. Introduction

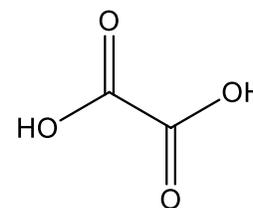
Interactions of metal ions with nucleic acid become highly relevant when the transition metal compounds are applied as chemical probes in the nucleic acid biochemistry or in chemotherapy¹. The two main types of nucleic acids are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), whose molecules consist of many nucleotides linked in a long chain. And again, a nucleotide is made up of three components: a nucleobase, a pentose sugar, and a phosphate group. Adenine² is a derivative of purine, consisting of a fused pyrimidine-imidazole ring system with conjugated double bonds and is an essential nucleobase³⁻⁵ of both DNA and RNA. Since heterocyclic nitrogen of the nucleic acid bases carry lone electron pairs, they are good ligands for alkali/alkaline earth and transition metals cations⁶. Coordination of metal ions to purine bases with unsubstituted N(9) is preferentially first to N(9) (in bridge to N(3)), then to N(7) and then to N(1)⁷. On the other hand, dicarboxylic acids contain two acidic functional groups. Partial or complete deprotonation of dicarboxylic acids makes them excellent candidates for coordination with metal ions in multi-coordinated ways. Addition of a di- or poly carboxylic acid, consisting of hydrogen bonding acceptor groups (OOC-R-COO) in a reaction mixture of metal ion and nucleobase, reaction may take place in a more selective way.

Intramolecular interligand hydrogen bond (H-bond) among the ligands could affect the stability of the complexes. Marzilli and Kistenmacher have primarily demonstrated the importance of stereospecific interligand interactions as factors that affect the specific metal binding to nucleic acid bases, involving hydrogen bonding, electrostatic repulsions, and steric constraints⁸. K. Aoki *et al.* have demonstrated the validity of Marzilli and Kistenmacher's approach in which the base- or site-specific metal bonding in the $[\text{Rh}_2(\text{carboxylato or amidato})_4(\text{nucleobase or its derivative})_2]$ system could be rationalized by interligand interactions⁹⁻¹². In the $[\text{Ni}(\text{nta})(\text{adeninium})(\text{aqua})] \cdot \text{H}_2\text{O}$ complex, the metal ion

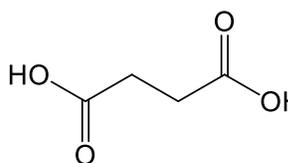
bonding to N(7) for unsubstituted adenine and in this N(7)-bonded metal complex, an interligand H-bond involving the N(6) amino substituent is commonly formed, with carboxylato oxygen(s) of nta ligand, strongly suggesting that the formation of interligand H-bond(s) is a factor that determines the metal binding site, N(7)¹³. However, there is no information yet available in the literature on metal-mixed ligand complexes of adenine and dicarboxylic acids. An attempt has, therefore, been taken to study the interaction between Cu(II) ion and adenine in presence of a dicarboxylic acid. In this report, synthesis and structural characterization of Cu(II) complexes with adenine and dicarboxylic acid such as oxalic acid (OxH_2), succinic acid (SucH_2) or tartaric acid (TarH_2) are presented. The structural formulae of Ade, OxH_2 , SucH_2 , and TarH_2 are given below:



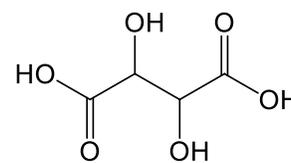
Adenine (Ade)



Oxalic acid (OxH_2)



Succinic acid (SucH_2)



Tartaric acid (TarH_2)

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II. Experimental

Chemicals

Adenine was procured from LOBA Chemie Pvt. Ltd., India; oxalic acid dihydrate from Uni-Chem, India; succinic acid from Thomas Baker (Chemicals) Ltd., India; tartaric acid from Sigma-Aldrich, China. Copper chloride dihydrate, hydrochloric acid, nitric acid, ammonia, and organic solvents etc., used in all synthetic and analytical work were analar grade. All chemicals were used as received.

Methods and Equipments

Melting points were recorded on a SMP11 electrothermal melting point apparatus, Shimadzu, Japan. The Cu(II) content of the complexes was determined complexometrically using Na₂EDTA·2H₂O as the titrating agent. Infrared (IR) spectra of the complexes were recorded on a Shimadzu (Japan) Infrared Spectrometer of model IR-470 in the range of 400-4000 cm⁻¹ using KBr pellets. The UV-visible spectra of the complexes were recorded using UV-visible recording Spectrometer, Model UV-160A, Shimadzu (Japan), in the wavelength range of 200-600 nm using water as the reference solvent. Magnetic susceptibility of the complexes was determined by the SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance (M.S.B.), Cambridge, England, Model: Magway MSB Mk1. The quasi-static thermogravimetric (QSTG) analysis was carried out in a CARBOLITE calibrated muffle furnace of the type CWF 11/5. The thermo-gravimetric analysis (TGA) of the complexes was carried out with TGA-50 analyzer, Shimadzu (Japan) in the temperature range from 20°C to 700°C under nitrogen at a flow rate of 20 mL/min and at a heating rate of 10°C/min. The differential scanning calorimetry (DSC) was performed on a Shimadzu Thermal Analyzer DT-40. Samples were placed in sealed aluminum pans and heated under nitrogen flow (20 mL/min) at a

heating rate of 10°C/min from 50°C to 550°C. An empty pan was used as a reference. Cyclic voltammetric measurement of the complexes was done using CH 620D Electroanalyzer and in Pyrex glass micro cell with a Teflon cap. Three electrode system, GCE as the working electrode, Ag/AgCl (satd. KCl) as the reference electrode and platinum wire as the counter electrode was employed for cyclic voltammetric investigation. Powder X-ray diffraction photograph of a complex was recorded in a PHILIPS PW-1830 X-ray generator equipped with XDC-700 Guinier-Hägg camera, using nickel filtered CuK_α radiation ($\lambda = 1.540981 \text{ \AA}$).

Synthesis of Complexes

Mixed ligands complexes of copper(II) (adenine-aquadicarboxylato-Cu(II)) were synthesized in aqueous/or methanolic solution and at ambient conditions. Aqueous/or methanolic solutions of copper(II) chloride dihydrate, adenine and dicarboxylic acid in 1:1:1 molar ratio were prepared by dissolving the requisite amount of them in minimum volume of hot distilled water/or methanol separately, mixed together and kept the resulting solution at ambient conditions for reaction. The products formed were isolated by filtration, washed with water, and dried in a desiccator over blue silica gel. A summarized synthetic procedure is given in Table 1.

III. Results and Discussion

All complexes are air-stable and non-hygroscopic at ambient conditions. The empirical formulae of the complexes have been established on the basis of their Cu(II) contents. The products are microcrystalline in nature and slightly soluble in water. Some of their physical properties viz. yield, colour, melting point, Cu(II) content have been studied and are tabulated in Table 2.

Table 1. Nominal composition of reactants used for the preparation of complexes.

Dicarboxylic acids	CuCl ₂ ·2H ₂ O	Adenine	Acid	pH	Complexes
Oxalic acid	0.6912 g in 10 mL H ₂ O	0.5447 g in 80 mL H ₂ O	0.5026 g in 20 mL H ₂ O	2.0	[Cu(C ₅ H ₅ N ₅)(C ₂ O ₄)(H ₂ O)]
Succinic acid	0.5215 g in 5 mL H ₂ O	0.4045 g in 60 mL H ₂ O	0.3513 g in 20 mL H ₂ O	3.5	[Cu(C ₅ H ₅ N ₅)(C ₄ H ₄ O ₄)(H ₂ O)]
Tartaric acid	0.1743 g in 10 mL MeOH	0.1362 g in 175 mL MeOH	0.1585 g in 20 mL MeOH	1.5	[Cu(C ₅ H ₅ N ₅)(C ₄ H ₄ O ₆)(H ₂ O)]

MeOH = Methanol

Table 2. Metal content and some physical properties of the complexes.

Compounds	Yield* /%	Colour	m.p. /°C	Metal content /%
[Cu(Ade)(Ox)(H ₂ O)]	38.1	Sky blue	156 (d)	20.13 (20.72)
[Cu(Ade)(Suc)(H ₂ O)]	62.6	Dark green	195 (d)	20.76 (18.98)
[Cu(Ade)(Tar)(H ₂ O)]	59.0	Bluish green	>250	18.75 (17.42)

Ade = C₅H₅N₅, Ox = C₂O₄²⁻, Suc = C₄H₄O₄²⁻ and Tar = C₄H₄O₆²⁻. *The percentage of yield was calculated on the basis of Cu(II) content. =decomposition temperature. The calculated metal contents are in parentheses.

Table 3. Tentative assignments¹⁴ of IR bands of adenine, dicarboxylic acids and their Cu(II) complexes.

Compounds	$\nu(\text{O-H})$ /cm ⁻¹	$\nu(\text{N-H})$ /cm ⁻¹	$\nu(>\text{C=O})$ /cm ⁻¹	$\nu(>\text{COO}^-)$ /cm ⁻¹	$\nu(\text{C=N})$ /cm ⁻¹	$\nu(\text{C-N})$ /cm ⁻¹	$\nu(\text{M-N})$ /cm ⁻¹	$\nu(\text{M-O})$ /cm ⁻¹
Adenine		3297-3119			1672	1150		
OxH ₂	3500-3000		1685					
SucH ₂	3350-2537		1727, 1691					
TarH ₂	3650-3000		1736					
[Cu(Ade)(Ox)(H ₂ O)]	3330-3175			1661, 1461	1550	1321	506	430
[Cu(Ade)(Suc)(H ₂ O)]	3331-3190			1646, 1464	1604	1343	576	440
[Cu(Ade)(Tar)(H ₂ O)]	3370-2755			1660, 1462	1604	1319	560	425

IR Spectral Analysis

The prominent infrared spectral data of adenine, dicarboxylic acids and their Cu(II) complexes are presented in Table 3. The band assignments have been done on the basis of literature survey.

The broad peak(s) in the region 3650-2537 cm⁻¹ indicates the presence of O-H, N-H and C-H groups from inorganic/organic moieties. This broadening of the peak is as a consequence of peaks resulting from different merging groups as well as their interaction within. Formation of hydrogen bonding also results in broadened of O-H and N-H stretchings vibrations bands. In comparison with the spectra of ligands, their Cu(II) complexes show various vibrational frequencies at different positions and intensities indicating that the ligands are coordinated with Cu(II) ion. The characteristic i.r. band of carboxylic acid group observed at 1685-1736 cm⁻¹ in the spectrum of free dicarboxylic acids, is absent in the spectra of their complexes. It supports that dicarboxylic acids are doubly deprotonated before coordination with metal ions in the complexes. The ligated -COO⁻ vibrates at about 1660 and 1462 cm⁻¹ in the spectra of the complexes. The peak separations between $\nu_{\text{asym}}(-\text{COO}^-)$ and $\nu_{\text{sym}}(-\text{COO}^-)$ are found ~198 cm⁻¹ which supported bis-bidentate coordination modes of carboxylate groups. The C=N peak appearing in the ligand at 1672 cm⁻¹ is shifted to 1550-1604 cm⁻¹ in the complexes. The shift of $\nu(\text{C=N})$ frequency values suggests that coordination between the Cu(II) and the adenine possibly occurs through imidazolyl nitrogen N(7) atom of the ligand.

The $\nu(\text{Cu-N})$ and $\nu(\text{Cu-O})$ vibrations of weak intensity appear in the region of 576-425 cm⁻¹. The tetrahedral Cu(II) ion is build up possibly through dicarboxylate oxygens that occupy two of the four directional positions, an adenine ligand at the another directional position through the N(7) site, and the remaining tetrahedral directional position is occupied by a water molecule.

UV-vis Spectral Analysis

All three complexes are slightly soluble in water at room temperature. Their aqueous solutions were used for

Table 5. Magnetic measurement data of the studied complexes at 32°C.

Complexes	C _{Bal}	l, cm	m, g	R	Ro	$\chi_g \times 10^{-8}$, C.G.S. unit	μ_{eff} , BM
[Cu(Ade)(Ox)(H ₂ O)]	0.9963	2.3	0.0923	105	-34	345.09	1.63
[Cu(Ade)(Suc)(H ₂ O)]	0.9927	2.2	0.1358	154	-34	302.34	1.60
[Cu(Ade)(Tar)(H ₂ O)]	0.9954	2.0	0.1355	164	-35	292.38	1.64

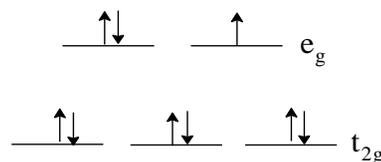
recording their electronic spectra. The spectral data of the complexes are tabulated in Table 4. The UV-visible spectral investigation shows that the complexes show an intense absorption band at ~300 nm due to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ electronic transitions. Due to poor solubility in water the complexes do not show any band in the visible region.

Table 4. Electronic spectral data of the studied compounds.

Complexes	λ /nm
[Cu(Ade)(Ox)(H ₂ O)]	302
[Cu(Ade)(Suc)(H ₂ O)]	308
[Cu(Ade)(Tar)(H ₂ O)]	322

Magnetic Susceptibility Measurement

Magnetic measurements of the complexes were carried out, and the results are gathered in Table 5. The observed magnetic moment (μ_{eff}) of Cu(II) complexes are in the ranges of 1.60-1.64 BM correspond to the presence of one unpaired electron. Cu(II) is a d^9 cation with the d -electron configuration of $t_{2g}^6 e_g^3$ irrespective of spin type as well as geometry of its complexes.



Thermal Analysis

The thermograms obtained from the quasi-static thermogravimetric analysis of the studied complexes are plotted in Fig.1 for comparison. The thermograms show that all the studied Cu(II) complexes start losing weight at around 50°C. Total weight loses up to 150°C are registered 6.38% for [Cu(Ade)(Ox)(H₂O)], 5.78% for [Cu(Ade)(Suc)(H₂O)] and 5.41% for [Cu(Ade)(Tar)(H₂O)], corresponds to the removal of coordinately bonded water molecule from the complexes.

Beyond that, the process of decomposition is relatively rapid and occurs in several steps suggesting that the ligands are lost in fragments. In spite of different colour of the products, the thermal decomposition of all three Cu(II) complexes ends in a black residue and attain a constant weight at about 400-450°C. The residues are being identified as CuO by their chemical analysis. The overall weight loss observed is about 77%, comparable with theoretical mass value. The way of the thermal decomposition of [Cu(Ade)(L)(H₂O)] (L = Ox, Suc, or Tar dianion) is as follows:

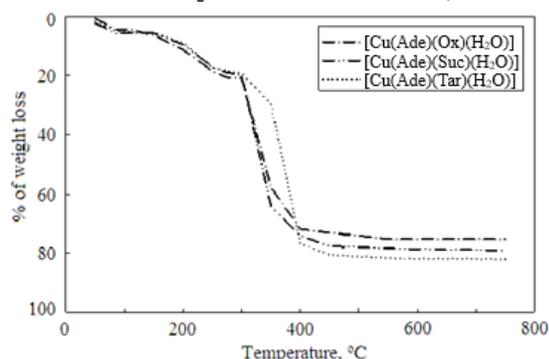
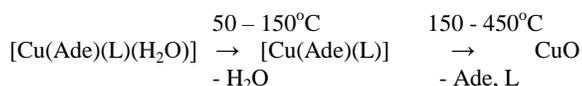


Fig. 1. QSTG graph of [Cu(Ade)(L)(H₂O)] (L = Ox, Suc, or Tar dianion).

The thermogravimetric analyses (TGA) of these complexes were also performed. A similar trend of thermal behavior of above complexes is observed. The differential scanning calorimetric (DSC) analysis shows that the decomposition processes are both endothermic and exothermic in nature.

Cyclic Voltammetric Study

Electrochemical behavior of Cu(II), and Cu(II) with adenine and dicarboxylic acid ligands at 1:1:1 molar ratio in 0.1 M KCl aqueous solution at GCE have been studied. The cyclic voltammogram (CV) of Cu(II) in 0.1 M KCl solution with scan rate of 100 mVs⁻¹ within the potential window of 750 mV to -1000 mV is shown in Fig. 2(solid line). In the forward scan, the voltammogram exhibits two cathodic peaks, *i_{pc1}* and *i_{pc2}* at about 180.45 mV and -395.87 mV respectively, as well as in the reverse scan two anodic peaks, *i_{pa1}* and *i_{pa2}* at about 235.39 mV and -70.50 mV, are observed separately. 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. This behavior apparently reveals that the electrode system follows two step one-electron transfer electrode processes. These findings are in good agreement with the previous studies¹⁵. The variation of peak current with the square root of scan rate over the whole scan range demonstrates that the redox processes are diffusion controlled. Anodic peak and cathodic peak current ratio and the peak potential separation suggest that the Cu(II)/Cu(I) couple (corresponds to first

pair) is reversible and the Cu(I)/Cu(0) (corresponds to second pair) is quasi-reversible redox system.

In presence of Ade and SucH₂ ligands at 1:1:1 molar ratio (Cu(II):Ade:SucH₂), the voltammogram of Cu(II) was recorded in the identical condition and the obtained voltammogram is shown in Fig. 2(short dash). It is interesting that CV for the mixture exhibits only one cathodic peak (around -400 mV) and two anodic peaks (around 280 mV and -180 mV). Although the CVs for Ade (dash) and SucH₂(dash dot) showed no peaks in the identical experimental conditions. The peak currents and the peak potentials of Cu(II) are shifted in presence of ligands relative to those of its free state, indicating metal-ligand interactions take place in the reaction medium. The peak potential separation increases with increasing scan rate (Fig. 3) because of quasi-reversible redox processes. The anodic peak associated with the oxidation process is intense indicates the oxidation of copper is greatly facilitated in the presence of Ade and SucH₂ molecule.

CVs of Cu(II) ion, and Cu(II) in presence of Ade and OxH₂ (Fig. 4), or Cu(II) ion, and Cu(II) along with Ade and TarH₂ (Fig. 5) at identical experimental condition are also recorded and similar behavior is observed.

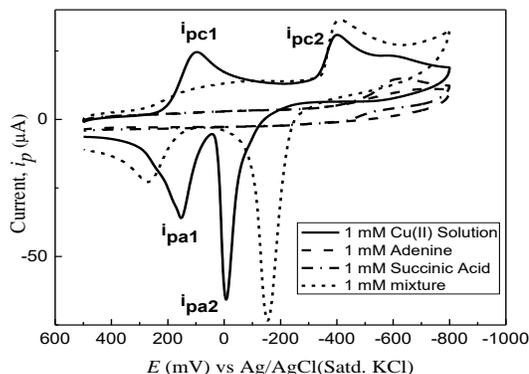


Fig. 2. Cyclic voltammograms of Cu(II)(solid), adenine(dash), succinic acid(dash dot), and Cu(II)-ligands mixture(short dash) solution in KCl solution at the scan rate 100 mVs⁻¹.

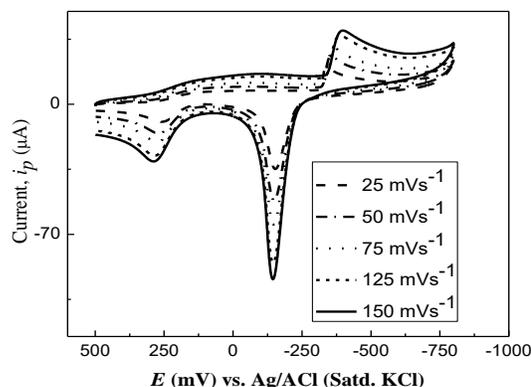


Fig. 3. Cyclic voltammograms of Cu(II) in presence of adenine and succinic acid at different scan rates 25(dash), 50(dash dot), 75(dot), 125(short dash) and 150(solid) mVs⁻¹.

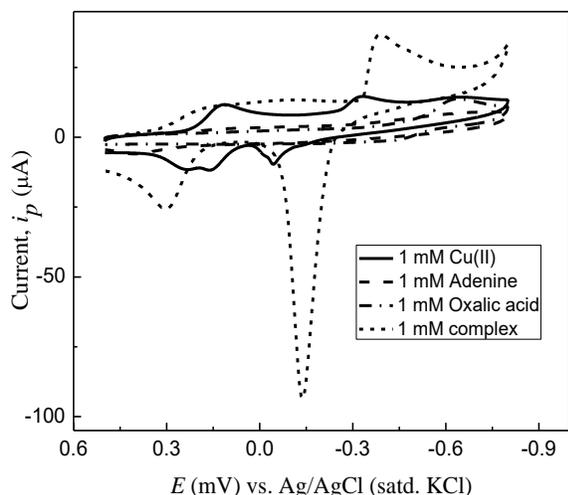


Fig. 4. Cyclic voltammograms of Cu(II)(solid), adenine(dash), oxalic acid(dash dot), and Cu(II)-ligands mixture(short dash) solution in KCl solution at the scan rate 100 mVs⁻¹.

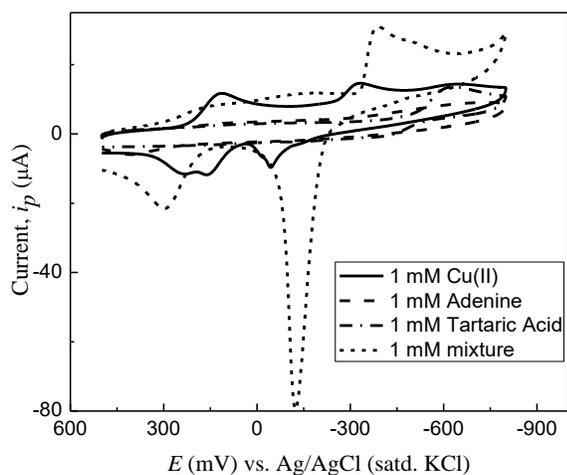


Fig. 5. Cyclic voltammograms of Cu(II)(solid), adenine(dash), tartaric acid(dash dot), and Cu(II)-ligands mixture(short dash) solution in KCl solution at the scan rate 100 mVs⁻¹.

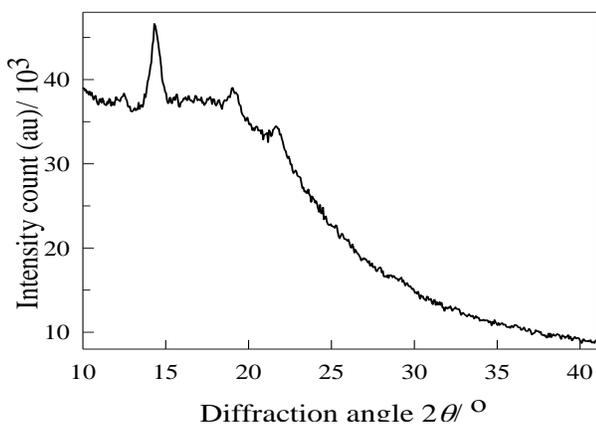


Fig. 6. X-ray powder diffraction of [Cu(Ade)(Suc)(H₂O)].

X-ray Powder Diffraction Studies

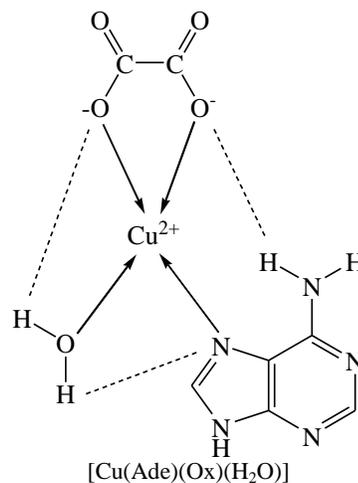
The X-ray powder diffraction of only [Cu(Ade)(Suc)(H₂O)] complex shows a few observable weak diffraction lines (Fig. 6). The d -values of them were calculated. These are presented in Table 6. The cause of showing a few weak lines is that either the complex belongs to a high symmetry crystal system, or it is a poorly crystalline solid which does not diffract well.

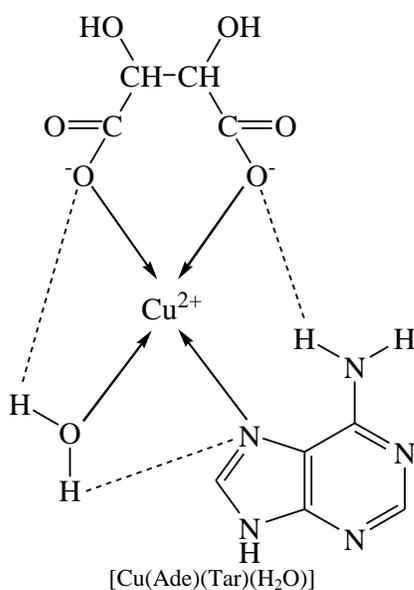
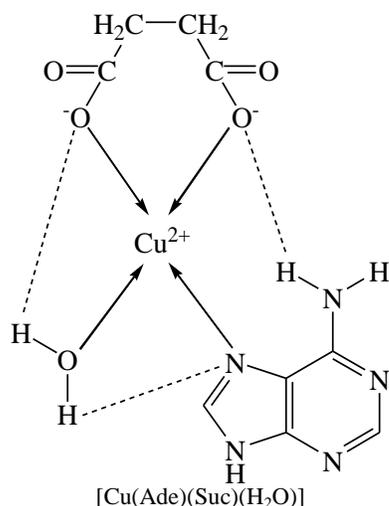
Table 6. The d -values calculated from powder X-ray diffraction of [Cu(Ade)(Suc)(H₂O)].

Relative intensity	l /mm	θ /°	Calcd. d /Å
Strong	24.43	7.16	6.18
Medium	32.51	9.52	4.66
Weak	36.95	10.82	4.10

IV. Conclusion

Reaction of copper(II) with adenine and a dicarboxylic acid like oxalic acid, succinic acid or tartaric acid in aqueous/methanol medium yielded complexes with the proposed formula of [Cu(Ade)(L)(H₂O)] (L = Ox, Suc or Tar dianions). Investigation of their physico-chemical properties indicates that adenine acts as a neutral ligand and dicarboxylic acids act as bidentate anionic ligands after doubly deprotonation. Adenine is coordinated with Cu(II) through N(7) of its imidazolyl ring nitrogen, dicarboxylate anions through carboxylate oxygens and probably there is also an interligand hydrogen-bonding between exocyclic H₂N(6) group with dicarboxylate anion. In major cases, adenine coordinates to metal ion through N(9) or through N(9) and N(3), and in minor cases, through N(7) and through N(3). In case of [Cu(Ade)(L)(H₂O)] (where L = Ox, Suc or Tar dianions) complex the Cu(II) ion shows a coordinating behavior selective for N(7) over N(9) with adenine. This site-selectivity may be caused by interligand interactions such as hydrogen-bonding and electrostatic repulsion associated with the steric environment about the Cu(II) ion. Suitable single crystal preparation and their structural data collection is still our plan to reemphasize the hypothesis on metal ion-interligand interactions. Based on our experimental results and earlier reports, the most probable structures of the studied compounds are given below:





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