Complexes of Copper(II) and Adenine at Various pH: Synthesis and Characterization

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Abstract

The coordination of Cu(II) ion with purine base is pH dependent and versatile. This study describes the synthesis, structural components and coordination behavior of Cu(II) with adenine. Three complexes of Cu(II) with adenine have been prepared at different pH in aqueous solution and ambient conditions. All synthesized complexes are polycrystalline solids of various colors, air-stable and partially soluble in polar solvents. The complexes were characterized by numerous analytical techniques including compositional analyses, Fourier transform infrared and UV-visible analyses, and thermal investigation. The elemental analyses of the complexes established their chemical composition as $[Cu(adeninium)Cl_3]$, $[Cu(adenine)(H_2O)Cl_2]$ and $[Cu(H_2O)_2(adeninato)_2]$. Analytical results suggest that the adenine nucleobase could act as a cationic (pH: 5), or a neutral (pH: 7), or an anionic (pH: 8) monodentate ligand in pH facilitated aqueous solution. In the structure, the purine moiety, chloride ion and aqua groups are situated around the copper(II) center is basically in a tetrahedral arrangements. Protonation or deprotonation of the adenine and intramolecular interligand hydrogen bond assisted the pH dependent versatile coordinating behavior of purine base.

Keywords: Adenine, Complex compounds, Hydrogen bond, Infrared spectrum, Thermogravimetry.

I. Introduction

The interactions of nucleic acids and nucleobases with various metal ions are of great interest in the field of chemistry, biology and inorganic biochemistry[1]. The interest of which is on outlining the metal ions in biology, which includes the uses of bioinorganic chemistry to investigate structures and functions of biomolecules[2]. There are countless purposeful motivations for studying metal complexes of heterocyclic compounds[3]. Adenine (Scheme I) is a purine nucleobase and one of the essential constituent of nucleic acids, consisting of a attached pyrimidine-imidazole ring system through conjugated double bonds[4-6]. The adenine molecule contains five nitrogen atoms in its structure, resultant a suitable and versatile ligand for alkali and alkaline earth, borderline metal ions, and transition metal ions[7]. X-ray crystallographic study also reveal various coordination site(s) of adenine which are susceptible to metal binding. Most of the metal ions are favorably bound to N(9) in a bridge to N(3) site of N(9)-unsubstituted adenine, then to N(7), and finally with N(1) site[8], and intramolecular interligand interactions could also affect the stability of the compounds. In acidic/neutral medium, N(9)-H group associated synthetic adenine favorably interacts with metal ions through N(7) site rather than N(9) position[9], although in alkaline medium deprotonating N(9)-site more effective towards metal ions[10-11].
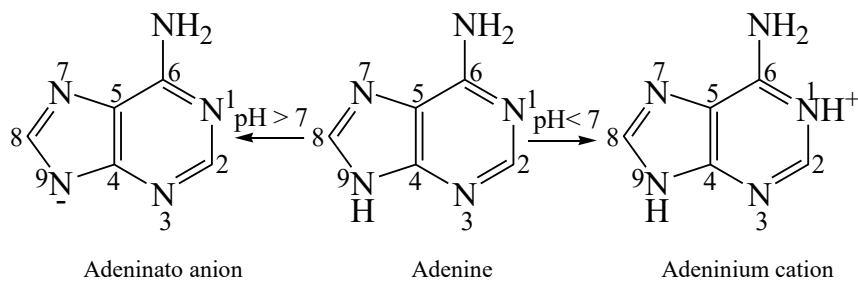
Scheme I: Structural representation of adenine, adeninium and adeninato species.

Weiss[12] prepared various complexes of Cu(II) salts with adenine, determined their constitution with the aid of replacement principle to describe the site combination of adenine. In the crystallographic studies of adenine-copper complex, Sletten[13] described that the metal ion binds to N(7) and the substituent on C(6), forming a five-membered ring.

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An inner complex of the stoichiometry Cu(adeninato)$_2$. 4H$_2$O has been reported in which pairs of Cu(II) ions are bound by four connecting adenine anions and metalation through N(3) and N(9) sites[14]. X-ray diffraction study exhibited the coordination of ZnCl$^-_3$ anion to N(7) site of adeninium cation protonated at N(1) position[15]. In mixed ligands complexes, hydrogen bonding donor(s) or hydrogen bonding acceptor(s) ligands play an important role in directing the base- and site-specific bonding of metal ion with nucleobases[16-21]. Within the crystal structure of [(nta)(adeninium)(aqua)nickel(II)] hydrate, N(1) site of adenine is protonated, resulting monovalent adeninium cation and coordinated with Ni^{2+} ion through the N(7) site[9]. Though, in the [Cu(tren) (adeninato)]$^+$complex ion, the Cu^{2+} ion is coordinated through N(9) site of an adeninato anion[10]. There are many evidence about such motivating and adaptable behavior of adenine, though the results are disseminated. In diverse solvent system (i. e. aqueous, ethanol, acetonitrile etc.), and at various pH (acidic, neutral or basic) values, the reaction of adenine with metal ions possibly will take place in a more selective way. An attempt has, therefore, been taken to work systematically in this exciting field involving the reaction of CuCl$_2$ salt with adenine in aqueous medium. Depending on the pH, adenine forms various complexes with Cu(II). In this report, synthesis, structural constituents and coordination behavior of Cu(II) ion with adenine are presented.

II. Experimental

Chemicals

Adenine was obtained from LOBA Chemie Pvt. Ltd. (India); and Copper(II) chloride dehydrate from Sigma-Aldrich, China. The other chemicals such as Na$_2$EDTA.2H$_2$O, ammonia, hydrochloric acid, nitric acid, silver nitrate, and other solvents etc., used for the preparation and analytical work were high purity analytical quality. The reagents were used without further modification.

Methods and Equipments

Melting points of all three complexes were measured on an electrothermal (SMP11, Shimadzu, Japan). The copper content in each complex was measured by complexometric method using Na$_2$EDTA. 2H$_2$O as the titrant. The chloride content was determined by Volhard's method. The other constituent elements such as carbon, hydrogen and nitrogen content were estimated by CHNS analyzer (vario MICRO cube, Germany). Fourier transform infrared (FTIR) spectrum of each complex was recorded on a spectrophotometer with attenuated total reflectance (ATR) in the range of 600-4000 cm^{-1} (Alpha II, Bruker, Germany). The UV-visible electronic spectra were recorded on a UV-visible spectrometer (UV-160A, Shimadzu, Japan), in the range of 190-700 nm wavelength using distilled water as reference solvent. Thermo gravimetric analysis (TGA) was performed on a thermogravimetric analyzer (TGA 8000, PerkinElmer, USA) in the temperature from 30°C to 700°C in a nitrogen atmosphere at a flow rate of 20 mL/min and at a heating rate of 10°C/min.

Synthesis of Complexes

Complexes of adenine and copper(II) salt were synthesized at different pH values under ambient conditions. Aqueous solutions of CuCl$_2$.2H$_2$O and adenine were prepared by taking and dissolving the required amount of reactants in hot distilled water separately and then mixed together. The pH of the resultant solutions were adjusted using HCl or NaOH solution, heated to reduce the volume and kept the reaction mixer at ambient environment for slow evaporation. The products were collected, carefully washed with distilled water, and dried over silica gel. A summarized preparation procedure is presented in Table1.

Table 1. Starting nominal composition and synthetic conditions of the complexes.

CuCl$_2$.2H$_2$O	Adenine	pH	Time	Colour	Yield/ %	Complex
1.0 g in 50 mL H$_2$O	0.135 g in 50 mL H$_2$O	5	3-4 days	Antique Bronze	33	[Cu(adeninium)Cl$_3$]
1.0 g in 50 mL H$_2$O	0.135 g in 50 mL H$_2$O	7	Instantly	Bluish green	49	[Cu(adenine)(H$_2$O)Cl$_2$]
0.170 g in 20 mL H$_2$O	0.270 g in 100 mL H$_2$O	8	4 days	Blue-violet	60	[Cu(H$_2$O)$_2$(adeninato)$_2$]

III. Results and Discussion

The products are polycrystalline solids of various colors, stable at ambient room-condition and partially soluble in distilled water as well as other polar solvents. All complexes are non-hygroscopic, stable in air, and decompose at high temperature. The chemical composition of each complex is established based on their compositional analysis. The resultant data are given in the Table 2. Various physico-chemical results of the prepared complexes are discussed in the onward parts.

Table 2. Compositional analytical data (%) of synthesized complexes.

Complex	Cu	Cl	C	H	N	T_d /°
[Cu(adeninium)Cl$_3$]	21.21 (20.76)	33.68 (34.75)	22.15 (19.62)	1.48 (1.98)	25.92 (22.88)	~300
[Cu(adenine)(H$_2$O)Cl$_2$]	21.87 (22.10)	24.98 (24.66)	20.93 (20.88)	1.91 (2.45)	23.93 (24.35)	~272
[Cu(H$_2$O)$_2$(adeninato)$_2$]	18.38 (17.28)	-	31.58 (32.65)	3.11 (3.29)	36.80 (38.08)	~248

The first value given is the analyzed value, and the value in parentheses is the calculated value. T_d = Decomposition Temperature.

FTIR Spectral Analysis

FTIR spectral bands of adenine and all synthesized Cu(II) complexes have been assigned on the basis of literature survey[22-23]. The prominent perceived FTIR bands of all three complexes are mentioned in Table 3. In assessment with adenine, copper(II) complexes showed vibrational bands at different positions with dissimilar intensities, demonstrating the coordination of adenine with Cu(II) ion with divergent donor site.

The broad and asymmetric band(s) which observed in the region 3600-3432 cm^{-1} and 3380-3090 cm^{-1} showed the existence of O-H and N-H groups from adenine/ aqueous species existing in the prepared complexes. The stretching modes of –NH$_2$ and –OH groups resulted several bands[2] in the region of 3500–3000 cm^{-1}. The resultant broad peak appeared due to the different merging groups as well as their mutual interactions. Formation of hydrogen bond within the species also resulted broad peak of O-H and N-H stretching vibrations (Fig. 1).

The absorption bands of imidazole[22] (N9)-H group of adenine base at 872 cm^{-1} and 2600-2900 cm^{-1} are missing

due to replacement of proton by Cu(II) ion in the [Cu(H$_2$O)$_2$(adeninato)$_2$] complex, whereas these bands are observed in the [Cu(adeninium)Cl$_3$] and [Cu(adenine) (H$_2$O)Cl$_2$] complexes. In all the complexes the intensity of N-H bands are very weak due to the interligand hydrogen-bonding within the molecule. In the adeninium-Cu(II) complex, a new band found at 3064 cm^{-1} due to the protonation at N(1) site of pyrimidine ring. Such peak is absent in the Cu(II)-adenine/or adeninato complexes which suggests to assign this band to the (N1)-H stretching. In the Cu(II)-adeninato complex, a new band appeared at 1299 cm^{-1} and the peak at 1520 cm^{-1} was missing. Relating to bands of adeninium-, adenine-, or adeninato-Cu(II) complxes, the peak at 1299 cm^{-1} is assignable to Cu(II)←:N-C stretching[23] and the band at 1520 cm^{-1} is due to δ(C-N9-H) mode. In the Cu(II)-adenine complex, an absorption peak occurred at 1241 cm^{-1} because of the (C6–NH$_2$) stretching associated with an internal C–N vibration. This frequency shifted to higher values at 1267 cm^{-1} for adeninato-Cu(II) complex because of metalation through N(9) position of the purine base.
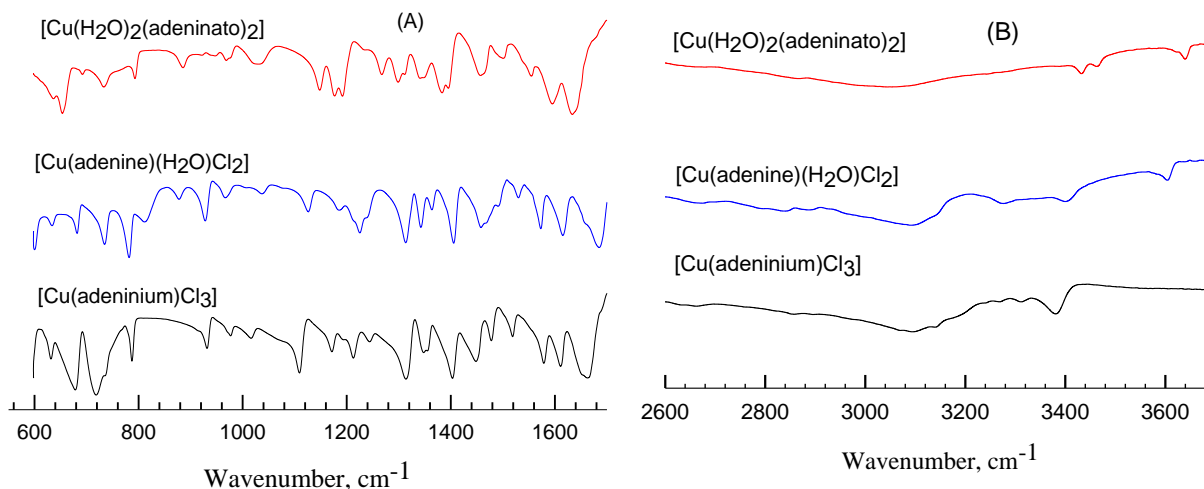

Fig. 1. FTIR spectra of synthesized complexes of wavenumber 600-1700 cm^{-1} (A) and 2600-3700 cm^{-1} (B).

Table 3. Tentative assignments of FTIR bands of Cu(II) complexes.

[Cu(adeninium)Cl₃]	[Cu(adenine)(H₂O)Cl₂]	[Cu(H₂O)₂(adeninato)₂]	Assignments
	3604, 3400	3639, 3466, 3432	νH_2O
3381, 3312, 3266	3276	3247	$\nu_{sym}(NH_2)$
3137, 3094	3092	3089	$\nu_{asym,}(NH_2)$
3064			$\nu(N1-H)$
2892, 2852, 2660	2886, 2836, 2790		$\nu(N9-H)$
2284	2285	2282	$\nu(C-H)$
1810, 1663	1685,1662	1890,1633	δNH_2
1611,1579	1615,1573	1595,1555	$\nu(C=N),\nu(C=C)$
1519	1530		$\delta(C-N9-H)$
1478	1488,1469	1501	δNH_2
1448	1458	1457	imidazole ring
1403	1405	1396	$\delta(N=CH)$
1348	1342	1341	$\nu(C-N),\nu(C=N)$
1314	1313	1313, 1299	$\nu(C-N), (C=N)$
1213, 1243	1225, 1241	1267, 1235	$\nu(C-NH_2)$
1171,1109	1128, 1044	1192, 1176,1148	$\delta(C2-N1=C6), \delta(C5-N7=C8)$
1016	1037	1031	$\delta(C-N-C)$
977	974	969, 941	$\delta(N-C =N)$
931	931	922	rNH_2
879	885		$\delta(N9-H)$out-of-plane
787	784	793	$\delta(C-H)$ + ring vib.
738	736	733	Skeletal ring vib.
678	679	692	δNH_2 wagging
632	634	654	New ring vib.

In the region of wavenumber 900-1000 cm⁻¹, the ring vibrational band at 923 and 938 cm⁻¹of adenine remained unshifted for N(9) coordination, but 923 cm⁻¹ band shifted to lower frequency for N(1) protonation and 938 cm⁻¹ band shifted to higher values for N(7) coordination[22]. The band around 890 cm⁻¹ is observed for protonation of N(9) position in adeninium and adenine moieties, and disappearing of such band resulting adeninato group by which coordination occur with Cu(II) center. The complexation sensitive bands[22] found in the wavenumber region of 630-740 cm⁻¹. The position of these peaks varied little relating to the ring-skeletal vibration of adeninium/adenine/adeninato species. The δ(NH₂) band of the adenine species also changed to a higher wavenumber region in all three complexes. The coordinating groups, chloride, adeninium/or adenine/ or adeninato species, and aqua groups resulted tetrahedral Cu(II) complex.

UV-Vis Spectral Analysis

The prepared complexes are sparingly soluble in distilled water at room-ambient conditions, and the electronic spectra were recorded using theirs aqueous solutions as well as distilled water as a reference solvent. Adenine showed two absorption bands at 205 nm and 260 nm of the UV-visible region. The band appeared at 205 nm may be recognized to π-π* transitions, while the peak at 260 nm may be due to n-π* transition[24,25] where n denotes the non-bonded electron pair of the heteroatom. Nonetheless, each Cu(II) complex (Fig. 2) contributed two intense absorption bands in the ultraviolet region by means of similar peak shapes comparable to adenine. The [Cu(adeninium)Cl₃] complex gave peaks 207 and 261 nm, while the [Cu(H₂O)₂(adeninato)₂] showed electronic bands at 206 and 260 nm, and such absorption peak of the [Cu(adenine)(H₂O)(Cl₂)] complex occurred at 208 and 262 nm. Because of less solubility in distilled water, the complexes showed no absorption band in the visible region.
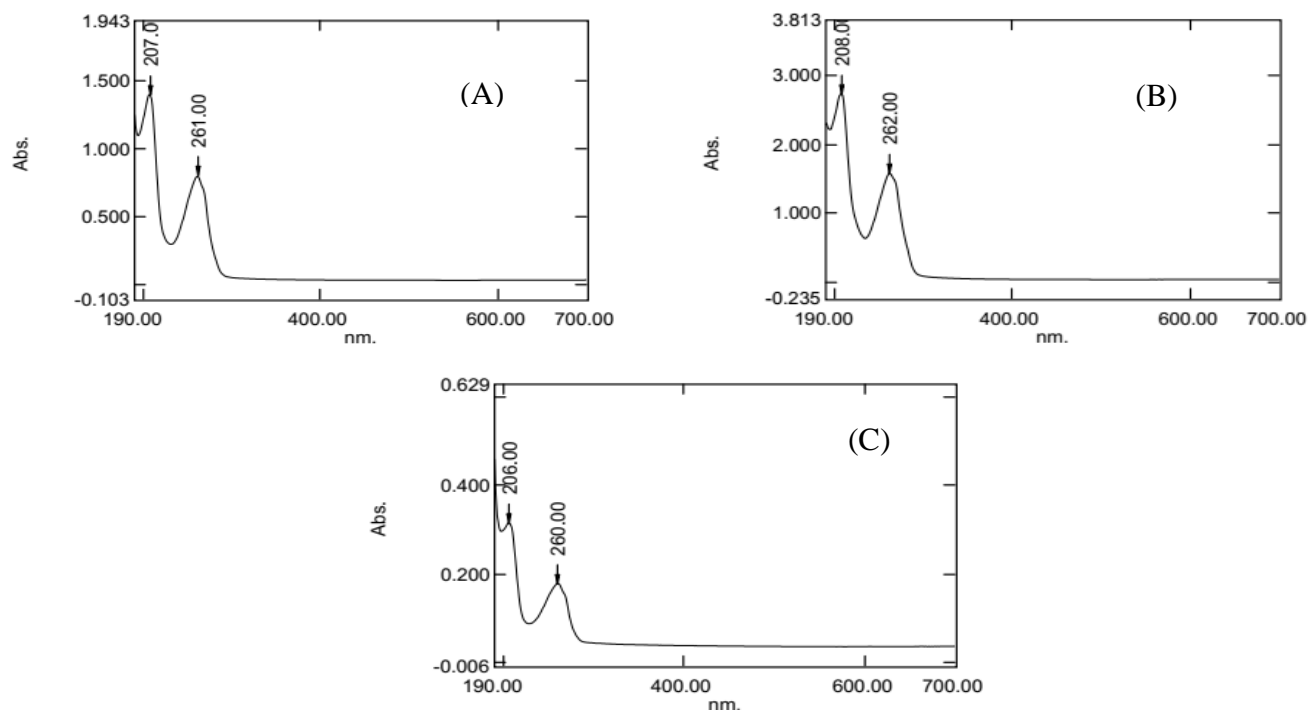
Fig. 2. UV-visible absorption spectra of (A) [Cu(adeninium)Cl$_3$], (B) [Cu(adenine)(H$_2$O)(Cl$_2$)], and (C) [Cu(H$_2$O)$_2$(adeninato)$_2$] complexes.

Thermogravimetric Analysis

The thermogram of adenine is two-step processes involving breaking and decomposition of the pyrimidine-imidazole ring and successive decomposition of the resulting organic species. The thermogram showed that up to 245°C, total weight loss of this purine base is 40%; the second decomposition step is very rapid and up to 390 ^{o}C all the remaining residue is completely removed. A comparative thermograms of the Cu(II) complexes are given in Fig. 3. Adenine shows two important decomposition pathways[2], and the observed TGA profiles of Cu(II) complexes containing purine ligand also show similar decomposition patterns, confirming the presence of adenine. The [Cu(adeninium)Cl$_3$] complex shows roughly three-step thermal decomposition processes: overall weight loss up to 160 ^{o}C is 23.9%, which resembles to the removal of two moles of chloride (calc. 23.2%), in the second step the total weight loss is 11.5% up to 280°C, which reveals the elimination of one mole hydrogen chloride (calc. 11.9%) , and in the final stage total weight loss is 44.6% up to 605°C, which agrees to the elimination of adenine base (calc. 44.2%).
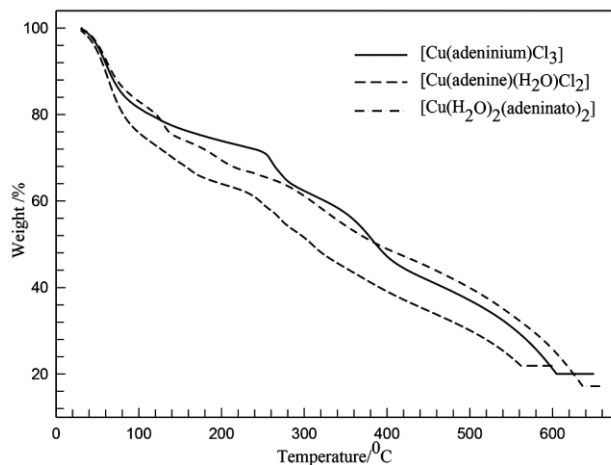

Fig. 3. Thermograms of [Cu(adeninium) Cl$_3$], [Cu(adenine)(H$_2$O)Cl$_2$] and [Cu(H$_2$O)(adeninato)$_2$] complexes.

The thermogravimetric behavior of [Cu(adenine)(H$_2$O)Cl$_2$] is very similar to that of [Cu(adeninium)Cl$_3$] complex. It also follows three-step thermal decomposition and elimination of the constituents species: total weight loss up to 100°C is 24.2%, which suggests the exclusion of two chloride ions (calc. 24.7%) and in the successive step total weight loss is 5.0% up to 150°C which corresponds to elimination of one water molecule (calc. 6.3%); finally the residue is persisted by deduction of 46.6% weight loss around 560°C which indicates the removal of adenine (cal. 47.0%). The thermogram of [Cu(H$_2$O)$_2$(adeninato)$_2$] is continuous and widespread two steps thermal decomposition processes. Initial step are very sharp and probably two water molecules (calc. 9.8%) are removed rapidly up to 120 °C by total weight loss of 9.8%; and uninterruptedly two adeninato species (calc. 72.9%) are eliminated by weight loss of 72.6% up to 635°C. The weight percentage of all three complexes suggest that because of nitrogen atmosphere the residual species is metallic copper.

IV. Conclusion

The reaction of CuCl$_2$.2H$_2$O with adenine produced mononuclear three different copper(II) complexes of various colours with the chemical compositions of [Cu(adeninium)Cl$_3$], [Cu(adenine)(H$_2$O)Cl$_2$] and [Cu(H$_2$O)$_2$(adeninato)$_2$], depending on the pH. Investigations of their physico-chemical characteristics expose that adenine is an adaptable ligand under different pH to form adeninium cation or adeninato anion or exists as neutral adenine molecule. In all three complexes adenine is coordinated as a unidentate ligand with Cu(II) ion which is tetrahedrally centered by the other ligand groups. In alkaline pH, adenine is bonded through its deprotonated N(9) site, imidazolyl-ring nitrogen, while in acidic environment protonation occurs on N(1) site of adenine, the resultant adeninium cation is coordinated with Cu(II) ion using N(7) position. Nonetheless, in neutral aqueous system, adenine also behaves as monodentate ligand and metalation also takes place through N(7) site. In all three cases probably there is intramolecular interligand hydrogen-bonding between C(6)-NH$_2$ and chloride ion, H$_2$O and chloride ion, and N(3) position and aqua group, which also ligated with the Cu(II) ion. On the basis of our experimental characterizations and previous assessments[9-11,18,19] the most possible build up structures of the prepared complexes are given below:
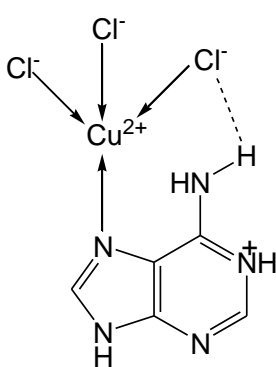
[Cu(adeninium)Cl$_3$]   [Cu(adenine)(H$_2$O)Cl$_2$]   [Cu(H$_2$O)(adeninato)$_2$]
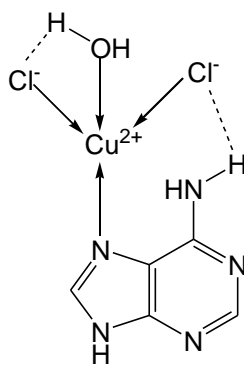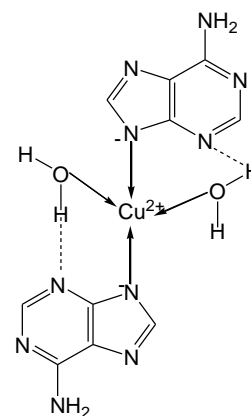
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