

## Preparation, Characterization, Molecular Models and Cyclic Voltammetric Study of Tren Complexes of Cu(II) and Zn(II) [Tren = tris(2-aminoethyl) amine]

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**Abstract :** Two new compounds were obtained by reacting tris(2-aminoethyl)amine, (tren) with Cu(II) and Zn(II) in the ethanol medium. The complexes are  $[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)\text{NO}_3]\text{NO}_3$  and  $[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)\text{ClO}_4]\text{ClO}_4$ . Elemental analyses, IR, UV-visible spectral analysis have been used to characterize the compounds. From X-ray powder photographs the d-values are calculated. Molecular model calculation indicates the distorted trigonal bipyramidal structures for the complexes. Redox behaviour of the copper complex at glassy carbon electrode is irreversible and diffusion controlled.

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### Introduction

Studies on metal complexes of different quadridentate tripodal ligands have been reported [1-5]. Taking in consideration, the ability of forming five coordinated trigonal bipyramidal (tbp) complexes by the quadridentate tripodal ligand, tren, a number of complexes of the ligand with 1st row transition metals and some heavy metals having small ligands at the 5th position of the tbp were prepared and characterized [6-10].

In continuation of our previous study, in the present communication we have reported the preparation of tris (2-aminoethyl)amine complexes of Cu(II) and Zn(II). The copper complex,  $[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)\text{NO}_3]\text{NO}_3$  with  $\text{NO}_3^{1-}$  ion at the 5<sup>th</sup> position of the tbp has been prepared for the first time. The zinc complex  $[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)\text{ClO}_4]\text{ClO}_4$  was prepared before and was used as doping agents for EPR and ENDOR study of corresponding copper complex [9]. The prepared complexes are characterised by chemical analysis and different spectroscopic methods. Redox behaviour of the complexes at glassy carbon electrode has been studied. Molecular model calculations have also been done.

### Experimental

**Materials and methods:** Analytical grade (AR) chemicals and ligand were used in the preparation and analytical works (E Mark, BDH and Wako pure chemicals). Micro-analytical data for C, H, N and Cl were obtained from IMRAM, Tohoku University, Japan. Metal contents were determined by complexometric titration [11]. FTIR spectra were recorded on a Shimadzu 8300 Fourier transform infrared, spectrophotometer and IR spectra were recorded on a Shimadzu IR 470

spectrometer in the range of 4000-400  $\text{cm}^{-1}$  in the form of KBr pellets. Electronic spectra of the complexes were recorded on an UV-160A spectrophotometer between 200-800 nm using nujol mull technique. Melting points were measured in a heating device MEL –TEMP (II), with a FLUKE 51KJ thermometer, USA, in the range of 0-400 °C. The conductance of the aqueous solution of the compounds was measured in the laboratory using a conductometer, CM-55, TOA Electronics Ltd. Tokyo, Japan. The solutions were prepared taking formula weight as the molecular weight. The cyclic voltammograms of the complexes were studied with a computerized custom made potentiostat, Model 2040G, of Advanced Analytics, USA. An ORION pH-meter was used to measure the pH of the solutions. Molecular model calculations were done using the Gaussian 03 software package from Gaussian Inc, USA.

### Preparation and formulation:

**Copper-tren complex,  $[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)\text{NO}_3]\text{NO}_3$  :**  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.89 g in 10 mL) and tris(2-aminoethyl)amine (0.44 g in 10 mL) were dissolved in EtOH separately and were mixed together. The solution became dark blue and after few minutes of mixing blue precipitate was formed. The product was separated by filtration, washed with cold ethanol and dried over silica gel. It is stable in light and atmosphere.

Yield  $\approx$  90% (on metal content), mp = 165-169 °C.

It is soluble in  $\text{H}_2\text{O}$  and insoluble in common organic solvent EtOH, MeOH, and  $\text{CCl}_4$ .

*Calc.* for  $[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)\text{NO}_3]\text{NO}_3$  C 21.54, H 5.44, N 25.18, Cu 19.04; *anal* found C 22.32, H 5.96, N 25.74, Cu 20.42 %

IR bands  $\text{cm}^{-1}$ : 3390(s), 3235(s), 3125(s), 2915(sh), 1582(sh), 1582(s), 1458(sh), 1377(vs), 1228(w), 1197(w), 1157(w), 1182(s), 1059(s), 1011(m), 984(sh), 893(w), 814(w), 575(w), 467(w),

d-values Å: 8.68(w), 6.95(w), 6.84(m), 6.69(w), 6.34(vs), 6.13(s), 5.79(m), 5.00(s), 4.72(w), 4.28(w), 4.20(w), 4.08(w), 3.99(m), 3.91(w), 3.76(w), 3.65(m), 3.55(w), 3.50(w), 3.43(w), 3.36(s), 3.29(w), 3.17(w), 3.08(s), 2.96(w)

#### **Zn-tren Complex, $[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)\text{ClO}_4]\text{ClO}_4$ :**

The preparation procedure of the Zn complex is similar to that of copper complex.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.8922 g in 10 mL) was reacted with the ligand (0.4389 g in 10 mL) in EtOH medium. A separate solution of sodium perchlorate (0.735 g in 10 mL) in EtOH was added to the above reaction mixture. After a few minutes yellowish white powder product was obtained. The product was separated by filtration washed with EtOH and dried over silica gel. It is stable in light and atmosphere.

Yield = 80% (on metal content), mp = 258 -261 °C.

It is soluble in water and insoluble in EtOH, MeOH,  $\text{CCl}_4$ , *Calc.* for  $[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)\text{ClO}_4]\text{ClO}_4$  C 17.55, H 4.42, N 13.65, Cl 17.27, Zn 15.93; *anal* found C 18.56, H 4.44, N 14.16, Cl 16.02 Zn 16.64 %

IR bands  $\text{cm}^{-1}$ : 3405(s), 3235(s), 3120(s), 2910(m), 1635(s), 1586(m), 1524(m), 1466(m), 1383(m), 1305(w), 1135(vs), 1160(vs), 1079(vs), 1085(s), 1085(s), 1005(m), 935(m), 802(m), 626(s), 533(m), 502(m)

d-values Å : 7.74(w), 6.88(w), 6.54(m), 5.95(w), 5.79(m), 5.59(w), 5.09(w), 4.98(w), 4.73(w), 4.54(w), 4.24(m), 4.20(m), 4.10(s), 4.03(m), 3.89(w), 3.83(w), 3.68(w), 3.59(w), 3.49(m), 3.43(w), 3.38(w), 3.34(w), 3.29(w).

#### **Result and discussion**

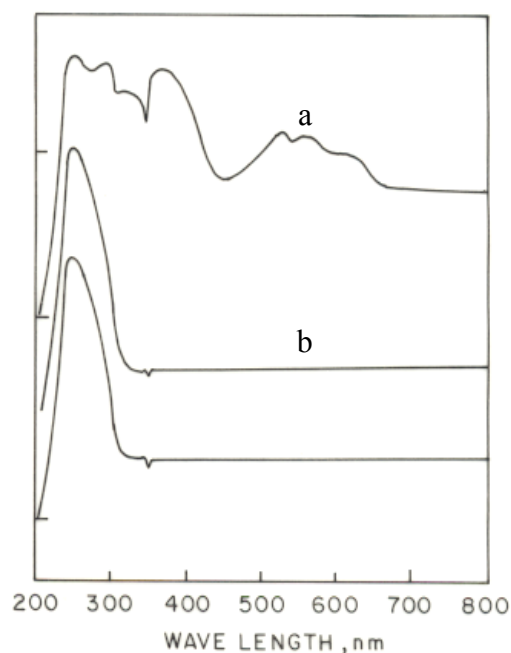
The compositions of the prepared complexes were confirmed by comparing the analytical data for C, H, N, Cl and metal. The experimental and theoretical values are in good agreement. The low melting points of the complexes demonstrates that the metal-ligand bonds are mostly of covalent nature. The molar conductance of the complexes increases rapidly with the dilution of the solutions which indicate that these complexes are weak

electrolytes. A large number of lines in the powder photographs indicate that these crystals are of lower symmetry. Since powder pattern is the finger print property, the d- values of the complexes recorded here would be extremely useful for further study and references.

**Infrared spectra:** The IR spectra of the compounds were studied in detail. Both IR and FTIR were recorded, the spectra are basically same but the bands in FTIR spectra are much sharper. The tentative assignments of the IR bands which are important for understanding of metal ligand bonding have been done on the basis of the standard references and by comparing with the bands of the ligands and other related compounds [12-15]. The ligand tren absorbs due to asymmetric and symmetric NH stretching vibrations at 3345  $\text{cm}^{-1}$  as a doublet and at 2910  $\text{cm}^{-1}$  for CH stretching vibration. Besides, the ligand absorbs strongly for  $\delta$  (NH),  $\nu$  ( $\text{CH}_2$ ) and  $\nu$ (CN) at 1588, 1450 and 1094  $\text{cm}^{-1}$  respectively. Like the ligand, both copper and zinc complexes absorb for NH stretching vibration in the range 3120-3405  $\text{cm}^{-1}$  and for CH stretching vibration in the range 2910-2915  $\text{cm}^{-1}$ . The NH bending mode of vibration of the complexes appear as strong sharp peak at 1582 and 1586  $\text{cm}^{-1}$  respectively.

The copper complex absorbs for asymmetric and symmetric stretching vibration of  $\text{NO}_3^-$  ion at 1377  $\text{cm}^{-1}$  and sharply at 819  $\text{cm}^{-1}$ . The CN stretching vibration appears at 1054  $\text{cm}^{-1}$ . The  $\text{CH}_2$  bending vibration appears as a shoulder at 1458  $\text{cm}^{-1}$ . The Zn complex absorbs very strongly as triplet in the range 1079-1135 $\text{cm}^{-1}$  and very sharply at 629  $\text{cm}^{-1}$  due to asymmetric and symmetric stretching of  $\text{ClO}_4^-$  ion. The CN stretching of the compound is buried in the  $\text{ClO}_4^-$  absorption band and the  $\text{CH}_2$  bending mode of vibration appears as a shoulder at 1452  $\text{cm}^{-1}$ .

**Uv-visible spectra:** The uv-visible absorption spectra of tren and the complexes were investigated. The absorption spectra are compared in Fig. 1 and the bands were assigned on the basis of standard references [16,17]. The ligand tris(2-aminoethyl)amine, has lone pair of electrons on N. It shows absorption bands at 247 resulting from  $n-\sigma^*$  transition of nitrogen lone pair to anti bonding orbital of C-N bond. The Zn complex absorbs identically like the ligand at 240 nm. The copper complex shows many absorption bands, at 250 nm for  $n-\sigma^*$ , at 346 nm for  $n-\pi^*$ , and at 362 nm for CT transition. It also shows a broad absorption in the range 530-640 nm for d-d transition.

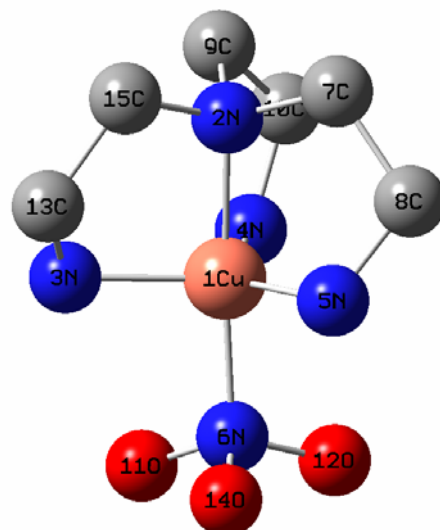


**Figure 1** : Uv-visible spectra of the ligand, tren and its complexes a)  $[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)\text{NO}_3]\text{NO}_3$  and b)  $[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)\text{ClO}_4]\text{ClO}_4$

**Molecular models:** Molecular models of the complexes have been calculated by Hartree Fock[18] method and 3-21G basis set. Full optimisation has been done. The bond lengths and bond angles around the coordination sphere are listed in Table-1. Both the compounds are of trigonal bipyramidal geometry and are distorted from the view point of bond angle and bond length. In both the case equatorial nitrogens are above the equatorial plane due to the pulling tendency of the tripodal ligand. The bond angles in the equatorial plane are unequal. The two axial bonds are not in the same straight line. The Zn-complex is more distorted than the Cu-complex may due to the fact

that  $\text{ClO}_4^-$  contain more O-atoms than in the  $\text{NO}_3^-$  ion. The structure of the Cu-complex is shown in Fig 2.

**Cyclic voltammogram :** A three-electrode electrolysis cell made of borosilicate glass was used to run the cyclic voltammetric experiments. A glassy carbon electrode (GCE) of 3 mm diameter was used as working electrode after polishing with 0.3  $\mu\text{m}$  alumina. The reference electrode used was Ag/AgCl (satd. KCl) made by BAS, USA and the counter electrode was a platinum wire of 0.5 mm diameter. Purging with  $\text{N}_2$  (99.997%) was done using a computer controlled magnetic stirrer.



**Figure 2** : Trigonal bipyramidal structure of Cu-tren complex. Hydrogen atoms and lone pairs are omitted for clarity.

**Table-1** : Energy and bond length and bond angles in the coordination sphere of the zinc and copper complex.

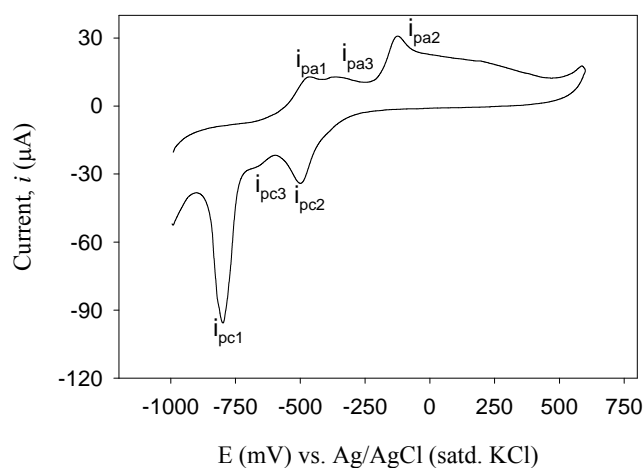
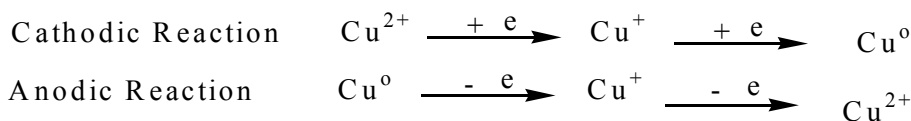
Bond length	Zn-tren	Cu-tren
M(1)-N(2)	2.02732	1.98948
M(1)-N(3)	2.06888	1.98045
M(1)-N(4)	2.01635	1.96502
M(1)-N(5)	2.21989	1.99653
M(1)-5 <sup>th</sup> atom	2.66982	2.00081
<b>Bond angles</b>		
N(5)-M(1)-N(2)	83.59273	89.03741
N(5)-M(1)-N(3)	81.74576	89.32969
N(5)-M(1)-N(4)	82.75010	90.10806
N(3)-M(1)-N(2)	114.31486	122.88646
N(3)-M(1)-N(4)	117.69016	117.41675
N(2)-M(1)-N(4)	123.22597	119.67238
N(2)-M(1)-5 <sup>th</sup> atom	102.48958	88.43853
N(3)-M(1)-5 <sup>th</sup> atom	81.44308	91.11563
N(4)-M(1)-5 <sup>th</sup> atom	103.20800	92.09806
N(5)-M(1)-5 <sup>th</sup> atom	163.04483	178.02532

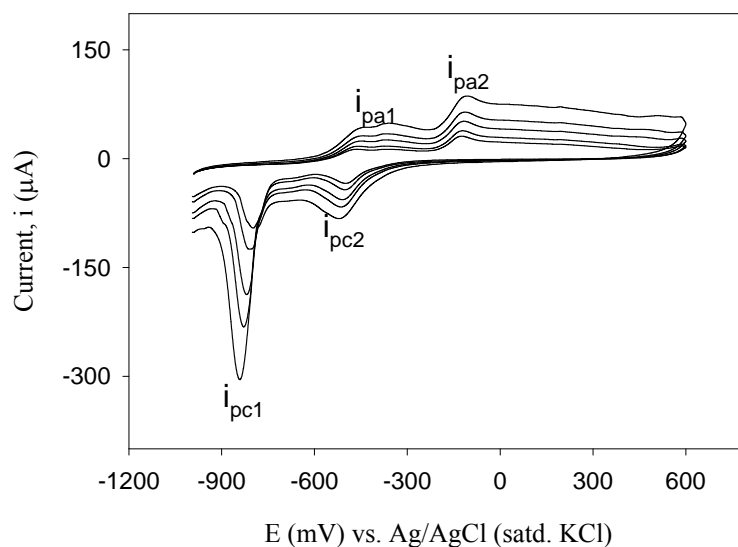
5<sup>th</sup> atom is the coordinating atom of the counter ion coordinated to the metal atom at the axial position of the trigonal bipyramid.

All solutions used in this voltammetric study were made in deionised water. After each use the electrode was cleaned and revived successfully.

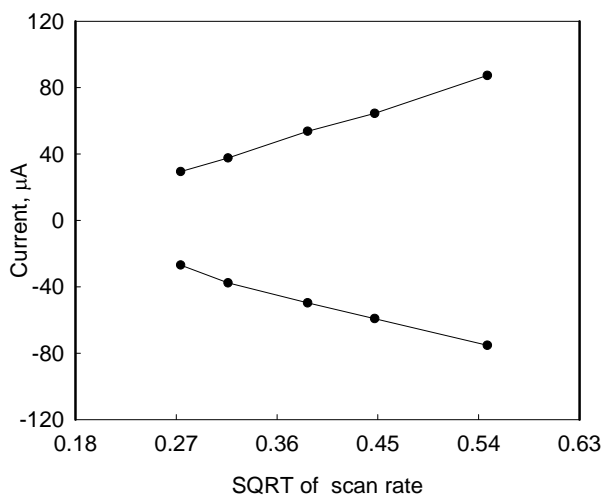
Cyclic voltammogram of 1 mM Cu-tren complex solution at the surface of glassy carbon electrode vs. Ag/AgCl reference electrode in HEPES buffer solution (*pH* 10.0) within the potential window of -1050 to 600 mV with scan rate of 75 mVs<sup>-1</sup> at 30°C is shown in Fig. 3. The voltammogram shows two anodic peaks at about -470 mV (*i*<sub>pa1</sub>) and -125 mV (*i*<sub>pa2</sub>) for two steps oxidation and two cathodic peaks at about -800

mV (*i*<sub>pc1</sub>) and -502 mV (*i*<sub>pc2</sub>) were obtained during reverse scan for the reduction of the neutral species obtained in the forward scan. The first pair (*i*<sub>pa1</sub> and *i*<sub>pc1</sub>) shows peak separation of 329 mV while the second pair, (*i*<sub>pa2</sub> and *i*<sub>pc2</sub>) shows peak separation of 376 mV. During the forward scan, the Cu-tren complex is adsorbed irreversibly and tenaciously on GCE. There is a pre-peak (*i*<sub>pc3</sub>) to the normal CV peak indicating the strong adsorption of the product[19]. The electrode reactions may be shown as

**Figure 3** : Cyclic voltammogram of 1 mM copper-tren complex at GCE in HEPES buffer at pH 10.0 of scan rate 75 mVs<sup>-1</sup> at 30°C



**Figure 4** : Cyclic voltammograms of 1 mM copper-tren complex at GCE in HEPES buffer at pH 10.0 with scan rates: 75, 100, 150, 200 and 300  $\text{mVs}^{-1}$  at 30°C



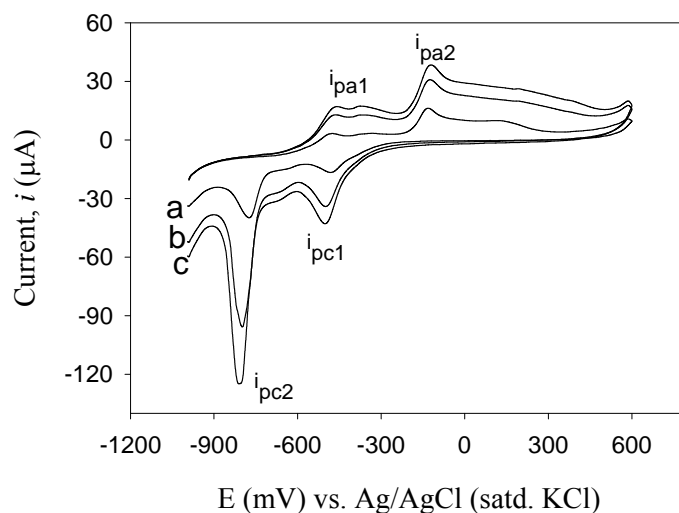
**Figure 5** : Variation of peak current with SQRT of scan rate for first pair of signals

The peak potential separation increases with the increase of the scan rate (Fig.4) indicating the limitation due to charge transfer kinetics and also supports the process of adsorption [20]. It also indicates that  $E_p$  is a function of scan rate ( $v$ ) [21]. The plots of peak currents vs.  $v^{1/2}$ , for both anodic and cathodic peaks are linear (Fig 5). The linear dependence of peak currents on scan rates is indicative of the combination of diffusion and surface control behaviour of the redox system, where the peak currents for dissolved and adsorbed species are proportional to  $v^{1/2}$  and  $v$  respectively [22,23]. For both the couples peak currents ratio is not unity but increase with the increase of scan

rate. These observations indicate that the processes are irreversible and diffusion controlled.

Cyclic voltammograms of Cu-tren complex were studied at various concentrations (0.5 mM, 1.0 mM and 1.5 mM) at pH 10.0 in HEPES buffer at 30°C (Fig. 6). It was found that the anodic and cathodic peak current increase with the concentration of the complex. The linear nature of the peak currents with concentrations of the complex again indicates that the processes are diffusion controlled.

Similar experiments were done with the Zn-complex using the same cell, electrodes, and buffer but no response was obtained.



**Figure 6** : Cyclic voltammograms of (a) 0.5 mM, (b) 1.0 mM and (c) 1.5 mM Copper-tren complex in HEPES buffer with scan rate of 50 mVS<sup>-1</sup>

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