CHAPTER-V

Conformational isomers of Dichloro bis(1,3-diaminopropane)Copper(II): Synthesis, characterization and DFT modeling
Metal ions and the organic ligands are two essential components for designing discrete molecules, however, covalent and hydrogen bonding interactions are important factors which have ability to control the molecular topology of varying conformations [1,2]. Hydrogen bonds play major role in widening of bite angle from the ideal 90° value [3]. Since the energy of hydrogen bond is much lower than a covalent bond, they do not predominantly affect the electrical and magnetic properties of the isomers.

1,3-Diaminopropane may coordinate with Cu(II) ions in bent or planar conformation [4-7]. The reluctance of Cu(II) ion in [Cu(pn)₂Cl₂] to form a regular octahedral structure would permit even more molecular structures similar to [Cu(dien)X₂] (X=Cl, NO₃) which has already been reported [8] to exhibit two different types of solid state electronic spectra. A large number of Cu(II) complexes with 1,3-diaminopropane of conformations have been reported [9-13], although no attempt seems to have been made to explore the possibility of isomer formation.

Utilizing the concept of ring puckering, we have attempted to synthesize three different complexes of Cu(II) with 1,3-diaminopropane which have the same composition but different physical properties and it makes us to believe that they are isomer. The present work describes the structure of compounds belonging to molecular formula [Cu(pn)₂Cl₂] where central atom exhibits conformational isomerism. They have been characterized by elemental and thermal analysis, conductance measurement, IR, electronic and EPR spectra of the isomeric complex.
Quantum mechanical calculations have been carried out to evaluate coordination modes and relative energies of three isomers.

EXPERIMENTAL

Material and methods

1,3-Diaminopropene (pn) (Fluka), CuCl₂H₂O (BDH) were used as supplied. MeOH (RANKEM), HCl and Et₂O (SDFCL) used in this work were of analytical grade.

Synthesis of [Cu(pn)₂Cl₂]

[Cu(pn)₂Cl₂] was synthesized by literature method [14] with a slight modification (Scheme 1.). To a methanolic (25 cm³) solution of CuCl₂.2H₂O (1.66 g, 0.01 mol) 1,3-diaminopropane (1.671 ml, 0.02 mol) dissolved in the same solvent was added slowly. The navy blue precipitate was formed instantaneously along with some blue precipitate in the same reaction vessel. Since the navy blue precipitate gets dissolved in excess of solvent it was recovered by slow evaporation of the solvent. However the blue precipitate remains insoluble and was separated by filtration. The precipitates were washed with diethyl ether and dried in vacuum over CaCl₂. The yellow isomer was prepared by drop wise addition of conc. HCl to navy blue precipitate. It was washed with diethyl ether until it was free from Cl⁻ ions. The compounds were dried in vacuum over CaCl₂.
Physical measurements

Elemental analyses were carried with Carlo-Erba 1106. Molar conductance was measured in DMSO on an ELICO Conductivity Bridge model CM 183. The IR spectra (600-4000 cm\(^{-1}\)) were recorded on an Interspec 2020 FTIR SPECTROLAB, U.K. in KBr pellet. Far IR (200-500 cm\(^{-1}\)) was recorded using CsBr. Electronic spectra were recorded at room temperature on a UV min-1240 Pharm Spec. SHIMADZU UV-vis spectrophotometer in aqueous and DMSO solutions. Chloride content was quantitatively analyzed as AgCl by gravimetric analysis. TGA measurements were carried out on a Mettler Stare SW 8.10 thermal analyzer at CSMCRI-Bhavnagar, India, under nitrogen atmosphere using Al\(_2\)O\(_3\) as reference.

Computational details

Density Functional Theory (DFT) calculations for all the complexes, with spin multiplicity 2, were mainly performed with the Gaussian 09 (G09) code [15]. Optimized geometries were calculated with the widely adopted U-B3LYP [16] functional. For all the atoms except Cu 6-31+g (d,p) basis set was employed while in case of Cu(II) cc-Pvtz-pp basis set was used. For ground state optimization, wave function stability calculations were performed to confirm that the calculated wave functions correspond to the ground state. The presence of one negative frequency was observed in the case of transition state geometries. Franck–Condon electronic excitation spectra were calculated on the optimized structures both in vacuum and in DMSO using the polarized continuum model (PCM) [17] within the Time Dependent-Density Functional Theory (TD-DFT) taking into account the lowest 25 excitations.
Scheme 1. Synthesis of [Cu(pn)$_2$Cl$_2$]
RESULTS AND DISCUSSION

The Cu(II) in [Cu(pn)$_2$Cl$_2$] lies on an inversion centre and is pseudo octahedrally (4+2) coordinated by four nitrogen atoms of two pn and two chloride ions displaying three different spatial conformations namely; boat-boat, chair-chair, and chair-boat arrangements (Fig.1-3). The coordination polyhedron of the Cu(II) ion can be described as axially elongated octahedral, with chloride ions at the axial position. The bite angle N-M-N is always found to be smaller than 90°. The concept of distortion isomerism was first introduced by Gazo [19,20] to describe the distortion in the coordination polyhedra of Cu(II) compounds. Because the term distortion isomerism is often interchangeable with ‘bond stretch isomerism’ we shall use conformational isomerism instead of describing the changes in bond angle [21-23]. It is observed that the driving force behind this conformational freedom is puckering of the six-membered ring, situated at equatorial position to central Cu(II) ion and hydrogen bonding through the hydrogen of pn nitrogen with axial chloro groups. The changes in N-Cu-N and N-Cu-C bond angles and Cu-N bond lengths play a critical role in the existence of these three isomeric forms in solid state [24]. Assuming the site symmetry to be $D_{4h}$ around the central Cu(II) ion, Bersuker and coworkers [25] have shown that the dissimilarity in bond angles and bond lengths can be readily explained by applying the second order Jahn-Teller Effect.

By varying the method of synthesis, 1,3-diaminopropane yielded a set of three complexes of different colors namely; navy blue, blue and yellow. They have Cu(II) ion sitting at the centre of spatial symmetry with 1,3-diaminopropane occupying equatorial position forming a six-membered ring. It is observed that the changes in
reaction conditions i.e. temperature, pH etc. lead to stabilization of systems with similar composition and basic structural motifs. In our case, pH (2-3) of the solvent is responsible for the existence of yellow isomer. Axial position in all the cases is occupied by chloride ion. The optimized axial bond lengths of Cu-Cl are quite longer than Cu-N bond lengths in all complexes. Cu-N bond lengths are found to be similar. The similarity found in equatorial bond lengths can be explained by mixing of solvent electronic states $B_{2g}$ and $A_{1g}$. It is well known that the six-membered ring formed by 1,3-diaminopropane and metal ions possesses great conformational freedom (chair-chair, boat-boat and chair-boat) with chair conformation being thermodynamically more favorable, however, other two conformations are kinetically accessible [26-28].

All the three complexes turn nearly blue when dissolved in water although in the solid state they are stable with sharp melting points (Table 1). However, they give different colors in DMSO and exhibit different absorptions in UV-vis. region. Any of these could not be recrystallized because their solution becomes sticky after standing for fifteen days. The change in color and other physical properties of the complexes are due to non-planarity of the pn molecule. Although the changes are very small, they have a considerable effect on the geometry of the complex. The molar conductance of $10^{-3}$ M solution of the complexes measured in DMSO falls in the range 40-44 S cm$^2$ mol$^{-1}$ [29].
Table 1 Analytical data and physical properties

<table>
<thead>
<tr>
<th>Isomers</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
<th>Analysis, % Found (Calcd.)</th>
<th>Molar conductance (Scm$^2$mol$^{-1}$) DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Navy blue</td>
<td>200</td>
<td>65</td>
<td>(25.44)</td>
<td>(7.06)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>26.03</td>
<td>6.69</td>
</tr>
<tr>
<td>Blue</td>
<td>190</td>
<td>34</td>
<td>(25.44)</td>
<td>(7.06)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24.79</td>
<td>5.97</td>
</tr>
<tr>
<td>Yellow</td>
<td>246</td>
<td>40</td>
<td>(25.44)</td>
<td>(7.06)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25.88</td>
<td>7.24</td>
</tr>
</tbody>
</table>
In order to assess the relative energy differences between the three conformational isomers, viz. boat-boat (1), chair-chair (2) and chair-boat (3) density functional theoretical (DFT) calculations were performed using the hybrid Lee-Yang-Parr (B3LYP) functional. The calculations reveal that the isomer (1) has highest energy and thus least stable, whereas the (2) is most stable. The energy difference between isomers (1) and (3) is 3.12 kJmol\(^{-1}\), whilst those between (1), (2) and (2), (3) are 11.26 and 8.19 kJmol\(^{-1}\), respectively. The selected geometrical parameters for all the isomers are listed in (Table 2). It is evident from the data presented in Table 2 that the differences between all the three isomers arise due to difference in their conformations. Additionally in order to go insight into the mutual transformation of the three conformations, the transition state and intrinsic reaction coordinates calculations were performed (Fig.4). The calculations indicate that the energy difference between the most stable conformer and the transition state is 12.22 kJmol\(^{-1}\). It indicates that transformation of one conformation to another can be accessible at room temperature in the solution phase. It is clear from the transition state that one of the six membered chelates comprising of the Cu(II) and 1,3-diaminopropane ring adopts the twist boat conformation while the other one posses the chair conformation. The structure of transition state clearly indicates that it can be easily transformed to either more stable structure (2) or relatively less stable structure (1).
Table 2 Geometrical parameters for 1, 2 and 3

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td>Cu-N</td>
<td>2.145</td>
<td>2.144</td>
<td>2.130</td>
</tr>
<tr>
<td>Cu-Cl</td>
<td>2.635</td>
<td>2.634</td>
<td>2.732</td>
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</table>

<table>
<thead>
<tr>
<th>Bond angle(°)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Cu-N</td>
<td>88.71</td>
<td>88.73</td>
<td>87.72</td>
</tr>
<tr>
<td>Cl-Cu-Cl</td>
<td>179.92</td>
<td>179.97</td>
<td>175.53</td>
</tr>
<tr>
<td>Cl-Cu-N</td>
<td>93.57</td>
<td>86.43</td>
<td>85.68</td>
</tr>
</tbody>
</table>
Fig. 1 Optimized geometry 1 (Boat-boat conformation)
Fig. 2 Optimized geometry 2 (Chair-chair conformation)
Fig. 3  Optimized geometry 3 (Chair-boat conformation)
Fig. 4 Intrinsic reaction coordinates for the copper complexes
Electronic spectra

The electronic spectra of the complexes (Table 3) in DMSO and aqueous media absorb in 240-310 nm region, which may be attributed to ligand to metal charge-transfer (LMCT) corresponding to $\sigma \, \text{N} \rightarrow d_{x^2-y^2}^2 \text{Cu(II)}$, $\sigma, \pi \, \text{Cl} \rightarrow d_{x^2-y^2}^2 \text{Cu(II)}$ transitions. Zelenak [30] has reported that in tetragonal Cu(II) complexes with long Cu-L bond, CT absorption occurs from equatorial halogen ligand instead of axial ones. This is not a universal phenomenon because Cu-Cl charge transfer (CT) does not seem to be governed by the position of chloro group in an octahedral complex. The M-Cl charge transfer occurs irrespective of the position of chloro group. In case of chloro bridged complex [31] the Cl occupies equatorial position, while in a monomeric octahedral (4+2) complex Cu-Cl exhibits similar CT although it occupies axial position. In the visible region the $d-d$ transition from component of $t_{2g}$ to the $d_{x^2-y^2}$ ($e_g$) was observed as a single peak in 570-600 nm region in all the isomers. No splitting of this band was observed. The electronic spectra of the isomers differ from each other nevertheless these differences are the actual cause for existence of stable isomers. It is concluded that the change in physical properties of [Cu(pn)$_2$Cl$_2$] is due to the non planarity of the pn molecule.

An attempt has been made to assign the electronic transition of the isomers using time-dependent density functional theory (TD-DFT) calculations. The electronic excitations involve transitions mainly from metal–ligand bonding MOs to the $\beta$-spin LUMO, with dominant Cu $d_{z^2}$ character, and to $\beta$-LUMO. Since each absorption line in a TD-DFT spectrum can arise from several single orbital excitations, a description of the transition character is generally not straight forward. However, approximate assignments can be made, although they provide a simplified
representation of the transitions. TD-DFT excitations were calculated both on the gas phase and in the solvent using the PCM (water and DMSO). By comparing the calculated spectra it is evident that transitions exhibit significant solvatochromic effects in comparison to the calculations performed under vacuum. Thus only the PCM model results are presented in table 2. The experimental UV-vis spectra presents a very weak and broad absorption centered at 623, 687 and 635 nm for the complexes 2, 1 and 3, respectively. This lowest energy band is attributed to $d \rightarrow d$ transition from the $d_{z^2}$ orbital of Cu center to $d_{x^2-y^2}$ orbital with slight intermixing of orbitals residing over the nitrogen atoms of pn. The next higher energy band was observed at ~305 nm for complexes 1 and 2 while in the case of 3, the next higher energy band was recorded at 260 nm. These transitions were of ligand-to-metal type with slight intermixing of metal orbitals. The representative selected orbital transitions for the conformer 2 is presented in fig.5.
Table 3  Electronic spectral data

<table>
<thead>
<tr>
<th>Isomers</th>
<th>UV region</th>
<th>Visible region</th>
<th>DMSO Medium</th>
<th>Visible region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ(nm)</td>
<td>Abs.</td>
<td>λ(nm)</td>
<td>Abs.</td>
</tr>
<tr>
<td>Navy blue</td>
<td>250</td>
<td>1.442</td>
<td>576</td>
<td>0.156</td>
</tr>
<tr>
<td>Blue</td>
<td>240</td>
<td>1.147</td>
<td>585</td>
<td>0.128</td>
</tr>
<tr>
<td>Yellow</td>
<td>243</td>
<td>1.316</td>
<td>600</td>
<td>0.635</td>
</tr>
</tbody>
</table>
Fig. 5 Selected orbital transitions for 2 (orbital contour value 0.05 a.u)
Infrared spectra

The free pn molecule exhibits two sharp and well-separated narrow bands in the region 3050-3350 cm\(^{-1}\) arising due to symmetric and asymmetric \(\nu(\text{NH}_2)\) stretching vibrations [32,33]. This band shifts to lower wave number (3010-3275 cm\(^{-1}\)) as a consequence of its coordination to Cu(II) ion forming a six membered ring [34]. In addition, a characteristic medium to weak \(\nu(\text{C-N})\) band observed in the range 1160-1183 cm\(^{-1}\) is also shifted to lower wave number. Stretching vibrations of CH\(_2\) group of pn are in the range 2875-2960 cm\(^{-1}\). A sharp band in the region 1571-1580 cm\(^{-1}\) is attributed to deformation vibration of CH\(_2\) group [35]. It is difficult, however, to make unequivocal assignments of metal ligand vibrations since the interpretation of low frequency spectrum is complicated by the appearance of ligand vibration as well as lattice vibration. In our case \(\nu(\text{Cu-N})\) appears as a strong absorption in the region 450-600 cm\(^{-1}\). In case of MX\(_2\).L\(_2\), where L is a bidentate chelating ligand, X can only occupy axial position in an octahedral compound. The Cu-Cl stretching frequency in the region 250-380 cm\(^{-1}\) in our case, indicates the presence of chloride ligand at axial position [36-38] (Table 4). Many other important bands were also observed due to deformation vibration and skeleton vibrations of CH\(_2\) and NH\(_2\) groups.
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Table 4  Infrared spectral data

<table>
<thead>
<tr>
<th>Isomer</th>
<th>ν(NH$_2$)</th>
<th>ν(CH$_2$)</th>
<th>ν(CH$_2$) def.</th>
<th>ν(C-N)</th>
<th>ν(Cu-N)</th>
<th>ν(Cu-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Navy blue</td>
<td>3256</td>
<td>2919</td>
<td>1580</td>
<td>1172</td>
<td>495</td>
<td>353</td>
</tr>
<tr>
<td></td>
<td>3210</td>
<td>2874</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>3275</td>
<td>2938</td>
<td>1571</td>
<td>1160</td>
<td>501</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>3225</td>
<td>2883</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Yellow</td>
<td>3068</td>
<td>2900</td>
<td>1576</td>
<td>1183</td>
<td>503</td>
<td>354</td>
</tr>
<tr>
<td></td>
<td>3008</td>
<td>2886</td>
<td></td>
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</table>
Thermal analysis

TGA profile of all the isomers is essentially identical and consists of well defined stages (Fig.6-8). They were studied between 50-600 °C range at a heating rate of 10 °C min⁻¹. It was realized while running TGA that these isomers are hygroscopic in nature. The navy blue isomer is stable up to 50 °C. The first decomposition occurs between 50-140 °C corresponding to the loss of one water molecule. The second step (29%) corresponds to disappearance of one water molecule and two chlorine atoms. The third step shows 25% loss in weight which is equal to the expulsion of one molecule of pn. The second pn molecule is lost in the subsequent steps. Finally, 22.53% Cu is left as residue at 600 °C.

The pyrolysis of blue isomer occurs in three steps. The first step between 135-265 °C indicates a weight loss of ~8.71% (exp. 7.23%) which corresponds to 3/2 mole of coordinated water. In the second step one mole of pn and chloride ions are lost simultaneously between (265-370 °C) exhibiting ~35.39% of loss which is in agreement with experimental value (34.74%). The third step indicates a weight loss of ~19.35% (20.29%) in temperature range 370-600 °C corresponding the expulsion of organic moiety [(NH₂)₂(CH₂)₂]. The last step exhibits the loss of [CH₂Cl] in the initial portion of thermogram followed by residue of copper metal at 600 °C.

Thermal degradation of yellow isomer also comprises of includes three steps. The thermogram shows that the yellow isomer is thermally more stable. The first step shows comprises a loss of ~8.71% (exp. 8.45%) corresponding to 3/2 mole of coordinated water between 220-260 °C. The second step shows a loss of ~61.68% (exp. 63.17%) which corresponds to loss of [pn+Cl₂+C₃H₁₀] moiety between 260-400
°C. The nitrogen, ~9.03% (exp. 10.07%), is lost in third step between 400-600 °C. In the end copper metal is left as residue at 600 °C.

Fig. 6 Thermogram of complex 1
Fig. 7 Thermogram of complex 2
Fig. 8 Thermogram of complex 3
EPR spectra

The X- band EPR spectrum of one of the isomeric complexes (Navy blue) was studied in the solid state at room temperature and the following inferences have been drawn. The powder spectrum shows two distinct signals indicating tetragonal environment around the axial-type Cu(II) centre (Fig.8). The value of $g_{||}$ and $g_{\perp}$ have been calculated from the peak position with references to the standard TCNE peak ($g=2.0027$) at magnetic field of 3135 gauss. The tetragonal system provides a strong evidence for the presence of Jahn-Teller distortion and on the basis of $g_{||}$ and $g_{\perp}$ it is proposed that unpaired electron reside in $d_{x^2-y^2}$ orbital. The complex does not show hyperfine splitting. The room temperature g values of $[\text{Cu(pn)}_2\text{Cl}_2]$ ($g_{||}=2.1744$ and $g_{\perp}=2.0666$). It has been reported that for ionic environment $g_{||} > 2.3$ while for a covalent environment covalent environment $g_{||} < 2.3$, indicating that the present complex exhibits considerable covalent character [39]. This suggests distortion from Oh symmetry to $D_{4h}$ symmetry [40] in the Cu(II) complex. The smaller $g_{||}$ indicates increased delocalization of unpaired electrons away from the metal nucleus and has been interpreted in terms of increased covalency in the metal ligand bond.

CONCLUSION

The reaction of 1,3-diaminopropane with copper(II) chloride results in the formation of pseudoctahedral complex, $[\text{Cu(pn)}_2\text{Cl}_2]$ which exists in three isomeric forms. They are distinctly visible, as they are of three different colors and are stable at room temperature. Their existence has been evidenced by elemental and thermal analysis, conductance measurement, IR, electronic and EPR spectra. The existence
and, energy wise relative stability of these isomers are entirely supported by quantum mechanical calculations and molecular simulations based on time dependent density functional theory. They exhibit almost similar electronic spectra and color because the lattice gets ruptured in solution. The main cause behind existence of these isomers is ring puckering.

Fig.9  EPR spectrum of [Cu(pn)$_2$Cl$_2$]
References


