



## ORIGINAL ARTICLE

# Conformational isomers of dichloro *bis* (1,3-diaminopropane) copper(II): Synthesis, characterization and DFT modeling



Seema Yadav <sup>a</sup>, A. Moheman <sup>a</sup>, Abhinav Kumar <sup>b</sup>, Rajendra Prasad <sup>c</sup>,  
K.S. Siddiqi <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India

<sup>b</sup> Department of Chemistry, University of Lucknow, Lucknow 226 007, India

<sup>c</sup> Department of Chemistry, S.G.B. Amravati University, Amravati 444 602, India

Received 14 August 2012; accepted 17 April 2013

Available online 25 April 2013

## KEYWORDS

DFT;  
Inversion center;  
Ring puckering;  
Conformations;  
Propanediamine;  
Octahedral

**Abstract** Three isomers of  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$  in solid state have been synthesized, isolated and characterized by elemental analysis, molar conductance, FTIR, TGA, EPR, electronic spectra and DFT calculation. The molar conductance of 1 mM solution of the complexes measured in DMSO falls in 40–44  $\text{Scm}^2 \text{mol}^{-1}$ . All the isomers in aqueous medium show similar absorption pattern in the UV–visible region of the spectra. They are nearly identical in solution although in the solid state they exist in three distinct colors. The change in the color of complexes is due to change in conformations of the propanediamine molecule. Cu(II) in  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$  lies on an inversion center. It is octahedrally coordinated to four nitrogen of 1,3-diaminopropane (pn) and two chloride ions displaying three different spatial conformations namely chair–chair, chair–boat and boat–boat. The TGA of the complexes suggest that Cu is left as final residue at 600 °C. The entire data have been supported by DFT calculation.

© 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

## 1. Introduction

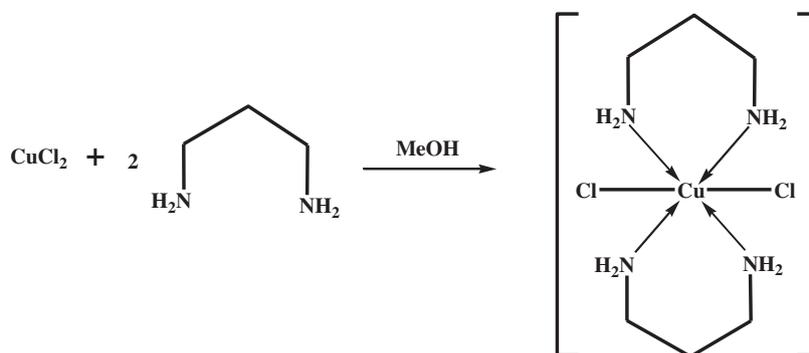
Metal ions and organic ligands are two parent and necessary components for designing of discrete molecules, however,

\* Corresponding author. Mobile: +91 9837284930.  
E-mail address: [ks\\_siddiqi@yahoo.co.in](mailto:ks_siddiqi@yahoo.co.in) (K.S. Siddiqi).  
Peer review under responsibility of King Saud University.

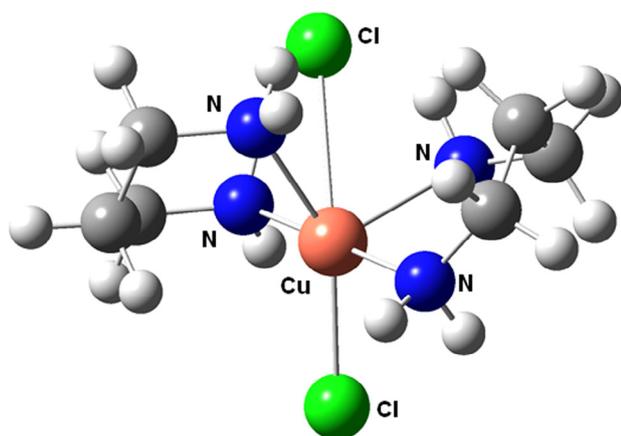


covalent and hydrogen bonding interactions are important factors which have the ability to control the molecular topology of varying conformations (Ribas et al., 1999; Real et al., 2003). Hydrogen bonds play a major role in the widening of bite angle from the ideal 90° value (Allen, 2002). Since the energy of hydrogen bond is much lower than a covalent bond, it does not predominantly affect the electrical and magnetic properties of the isomers.

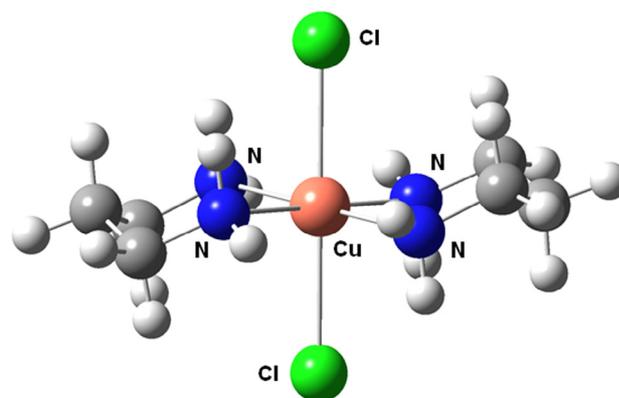
1,3-Diaminopropane may coordinate with Cu(II) ions in bent or planar conformation (Sundberg et al., 1996; Triki et al., 2005; Ribas et al., 1991; Hay et al., 1997). The reluctance



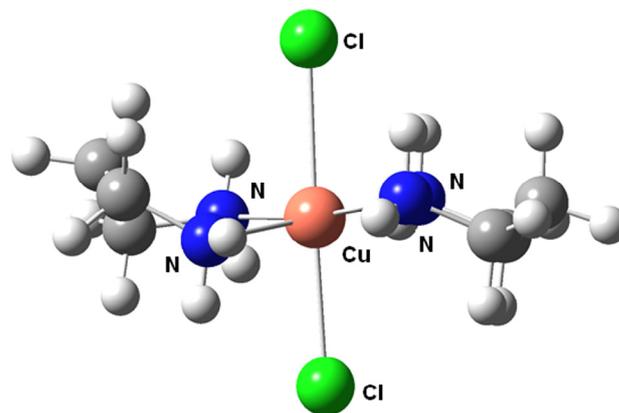
**Scheme 1** Schematic representation of synthesis of  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$ .



**Figure 1** Optimized geometry for (1).



**Figure 2** Optimized geometry for (2).



**Figure 3** Optimized geometry for (3).

of Cu(II) ion in  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$  to form a regular octahedral structure would permit even more molecular structures similar to  $[\text{Cu}(\text{dien})\text{X}_2]$  ( $\text{X}=\text{Cl}, \text{NO}_3$ ) which has already been reported (Siddiqi et al., 2004) to exhibit two different types of solid state electronic spectra. A large number of Cu(II) complexes with 1,3-diaminopropane of varying geometry and conformation have been reported (Navarro et al., 1998; Luo et al., 2003; Thetiot et al., 2003; Sundberg et al., 2001; Sundberg and Uglja, 1997) 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 believe that they are isomers. The present work describes the structure of compounds belonging to molecular formula  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$  where central atom exhibits conformational isomerism. They have been characterized by elemental and thermal analysis, conductance measurement, IR-, electronic- and EPR spectroscopy of the isomeric complexes. Quantum mechanical calculations have been carried out to evaluate coordination modes and relative energy of three isomers.

## 2. Experimental

1,3-Diaminopropane (Fluka) and  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  (BDH) were used as supplied. MeOH (RANKEM), HCl and  $\text{Et}_2\text{O}$  (SDFCL) used in this work were of analytical grade.

### 2.1. Synthesis of $[\text{Cu}(\text{pn})_2\text{Cl}_2]$

$[\text{Cu}(\text{pn})_2\text{Cl}_2]$  was synthesized by the literature method (Siddiqi et al., 1993) with a slight modification (Scheme 1). To a methanolic ( $25 \text{ cm}^3$ ) solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.66 g, 0.01 mol), 1,3-diaminopropane (1.671 ml, 0.02 mol) was added which slowly dissolved in the same solvent. The navy blue precipitate was formed instantaneously along with some blue precipitate in the same reaction vessel. In excess of solvent navy blue precipitate get dissolved however the blue precipitate remains insoluble and was separated by filtration. Navy blue precipitate

**Table 1** Analytical data and physical properties.

Isomers	M.P. (°C)	Yield (%)	Analysis, % found (Calcd.)				Molar conductance (S <sub>cm</sub> <sup>2</sup> mol <sup>-1</sup> )	
			C	H	N	Cl	DMSO	
Navy blue	200	65	(25.44)	(7.06)	(19.79)	(25.08)	42	
			26.03	6.69	18.75	23.93		
Blue	190	34	(25.44)	(7.06)	(19.79)	(25.08)	41	
			24.79	5.97	18.90	24.79		
Yellow	246	40	(25.44)	(7.06)	(19.79)	(25.08)	44	
			25.88	7.24	17.98	25.21		

**Table 2** Geometrical parameters for **1**, **2** and **3**.

	<b>1</b>	<b>2</b>	<b>3</b>
<i>Bond length (Å)</i>			
Cu–N	2.145	2.144	2.130
Cu–Cl	2.635	2.634	2.732
<i>Bond angle (°)</i>			
N–Cu–N	88.71	88.73	87.72
Cl–Cu–Cl	179.92	179.97	175.53
Cl–Cu–N	93.57	86.43	85.68

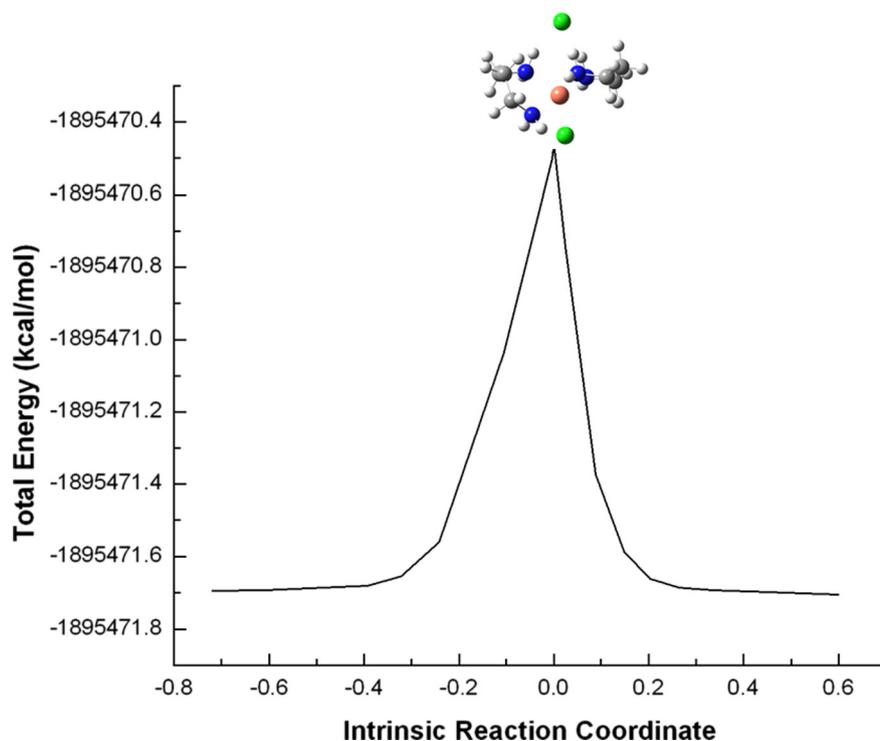
was recovered by slow evaporation of solvent. The precipitates were washed with diethyl ether and dried in vacuum over CaCl<sub>2</sub>. The yellow isomer was prepared by drop wise addition of conc. HCl to navy blue precipitate. It was washed with diethyl ether until no more Cl<sup>-</sup> ions were retained with the precipitate. The presence of chloride ion was monitored by its precipitation with AgNO<sub>3</sub>. Then it was dried in vacuum over CaCl<sub>2</sub>.

## 2.2. Physical measurements

Elemental analysis was carried out with Carlo–Erba 1106. Molar conductance was measured in DMSO on an ELICO Conductivity Bridge model CM 183. The IR spectra (600–4000 cm<sup>-1</sup>) were recorded on an Interspec 2020 FTIR SPECTROLAB, UK as KBr pellet. Far IR (200–500 cm<sup>-1</sup>) 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 with a Mettler Stare SW 8.10 thermal analyzer at CSMCRI-Bhavnagar, India, under nitrogen atmosphere using Al<sub>2</sub>O<sub>3</sub> as reference.

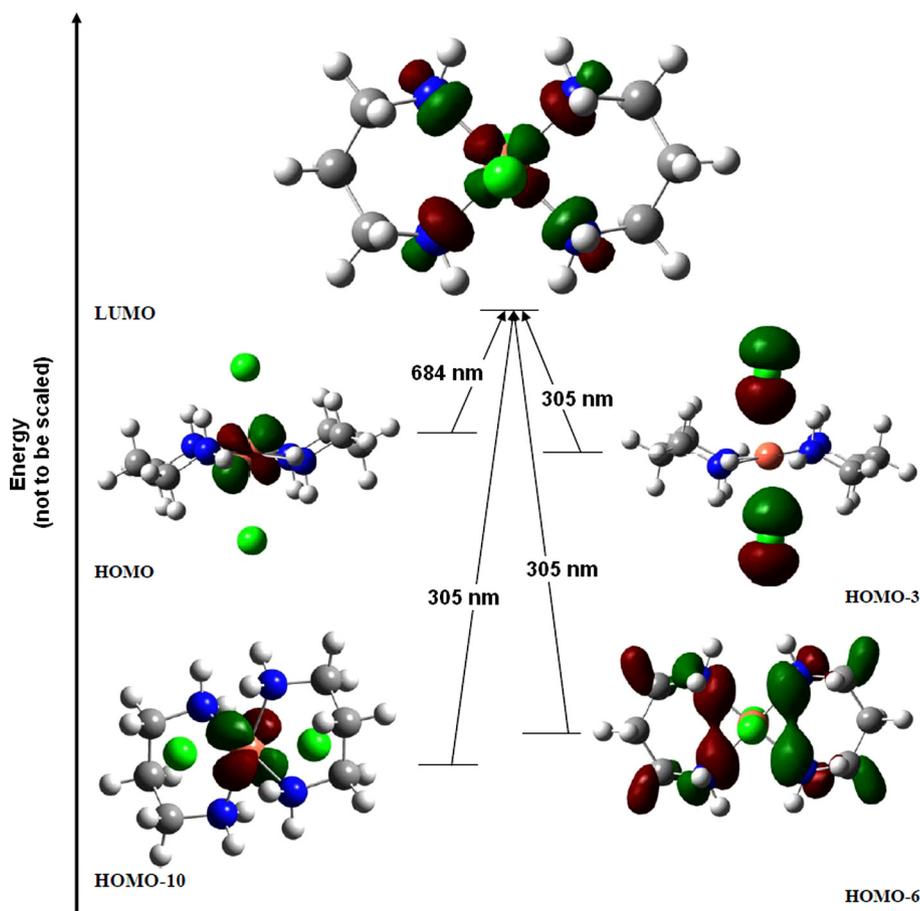
## 2.3. Computational details

Density functional theory (DFT) calculations for all the three complexes, with spin multiplicity 2, were mainly performed with the Gaussian 09 (G09) code (Frisch et al., 2010). Optimized geometries were calculated with the widely adopted U-

**Figure 4** Intrinsic reaction coordinates for the copper complexes.

**Table 3** Electronic spectra.

Isomers	Aqueous medium				DMSO medium			
	UV region		Visible region		UV region		Visible region	
	$\lambda$ (nm)	Abs.						
Navy blue	250	1.442	576	0.156	309	0.118	623	0.202
Blue	240	1.147	585	0.128	308	0.503	687	0.223
Yellow	243	1.316	600	0.635	260	4.000	635	0.072

**Figure 5** Selected orbital transitions for complex **2** (orbital contour value 0.05 a.u.).**Table 4** IR spectra.

Isomer	$\nu(\text{NH}_2)$	$\nu(\text{CH}_2)$	$\nu(\text{CH}_2)_{\text{def.}}$	$\nu(\text{C-N})$	$\nu(\text{Cu-N})$	$\nu(\text{Cu-Cl})$
Navy blue	3256	2919	1580	1172	495	353
	3210	2874				
Blue	3275	2938	1571	1160	501	352
	3225	2883				
Yellow	3068	2900	1576	1183	503	354
	3008	2886				

B3LYP (Lee et al., 1988; Becke, 1993) 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

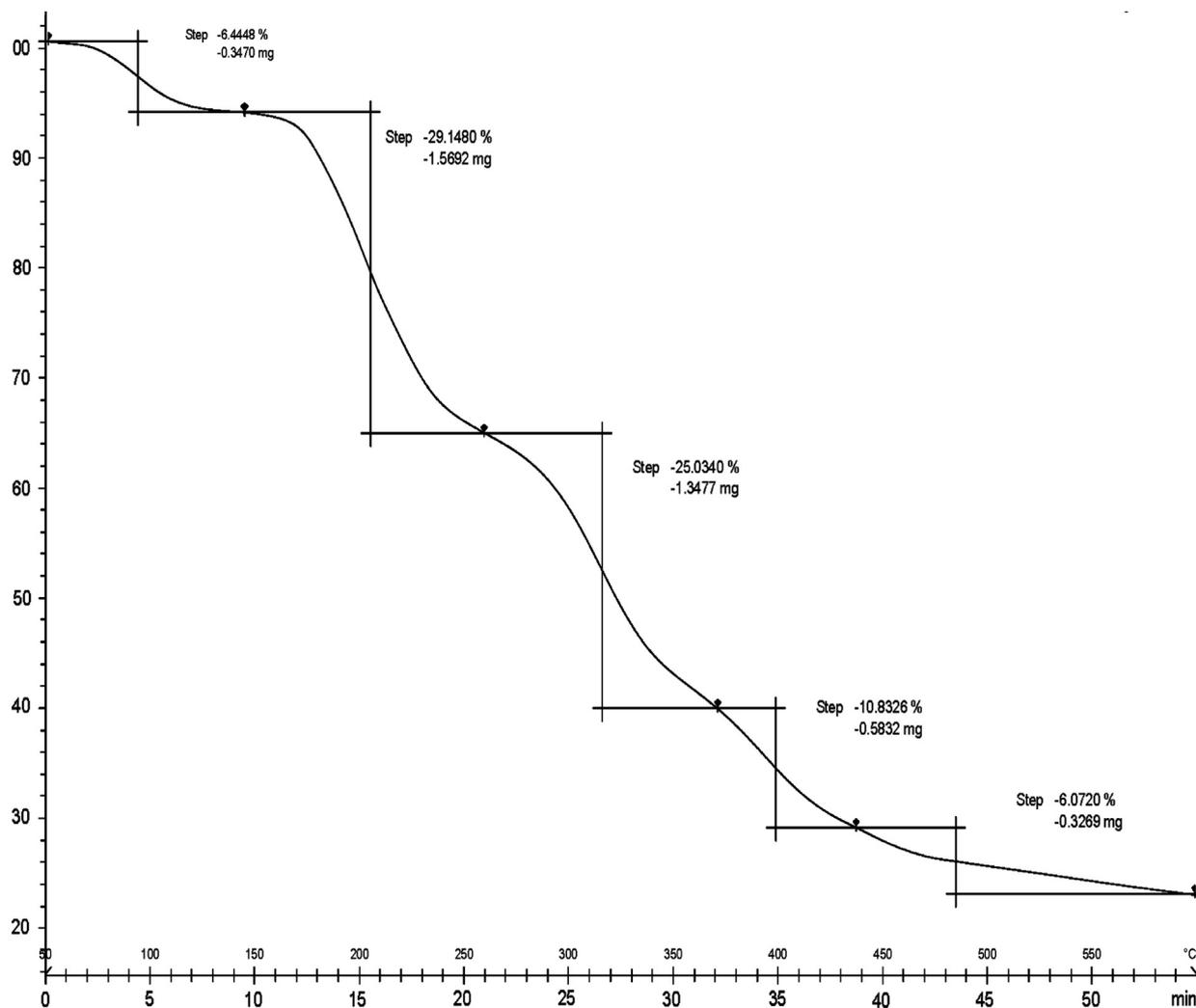


Figure 6a Thermal decomposition pattern. (a) Navy blue isomer. (b) Blue isomer. (c) Yellow isomer.

calculated on the optimized structures both in vacuum and in DMSO using the polarized continuum model (PCM) (Barone et al., 1998) within the Time Dependent-Density Functional Theory (TD-DFT) taking into account the lowest 25 excitations.

### 3. Results and discussion

The Cu(II) in  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$  lies on an inversion center and is pseudo octahedrally (4 + 2) coordinated by four N atoms of two pn and two chloride ions displaying three different spatial conformations namely boat–boat, chair–chair, and chair–boat arrangements (Figs. 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 (Sundberg et al., 1995) than  $90^\circ$ . The concept of distortion isomerism was first introduced by Gazo, 1974; Sundberg, 1994 to describe the distortion in such coordination polyhedral 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 (Wang et al., 2006; Garcia-Orozco et al., 2006; Kupka et al.,

1986). It is observed that the driving force behind this conformational freedom is puckering of the six-membered ring situated at an equatorial position to central Cu(II) ion and hydrogen bonding through the hydrogen of the four amine 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 the solid state (Sundberg and Sillanpaa, 1992; Champouret et al., 2012). Assuming the site symmetry to be  $D_{4h}$  around the central Cu(II) ion, Bersuker and coworkers (Gazo et al., 1976) 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. The yellow isomer is thermally more stable than navy blue and blue ones. All the three conformations of isomers have Cu(II) ion sitting at the center of spatial symmetry and is coordinated with 1,3-diaminopropane ligand forming a six-membered ring in the equatorial position. 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, acidic

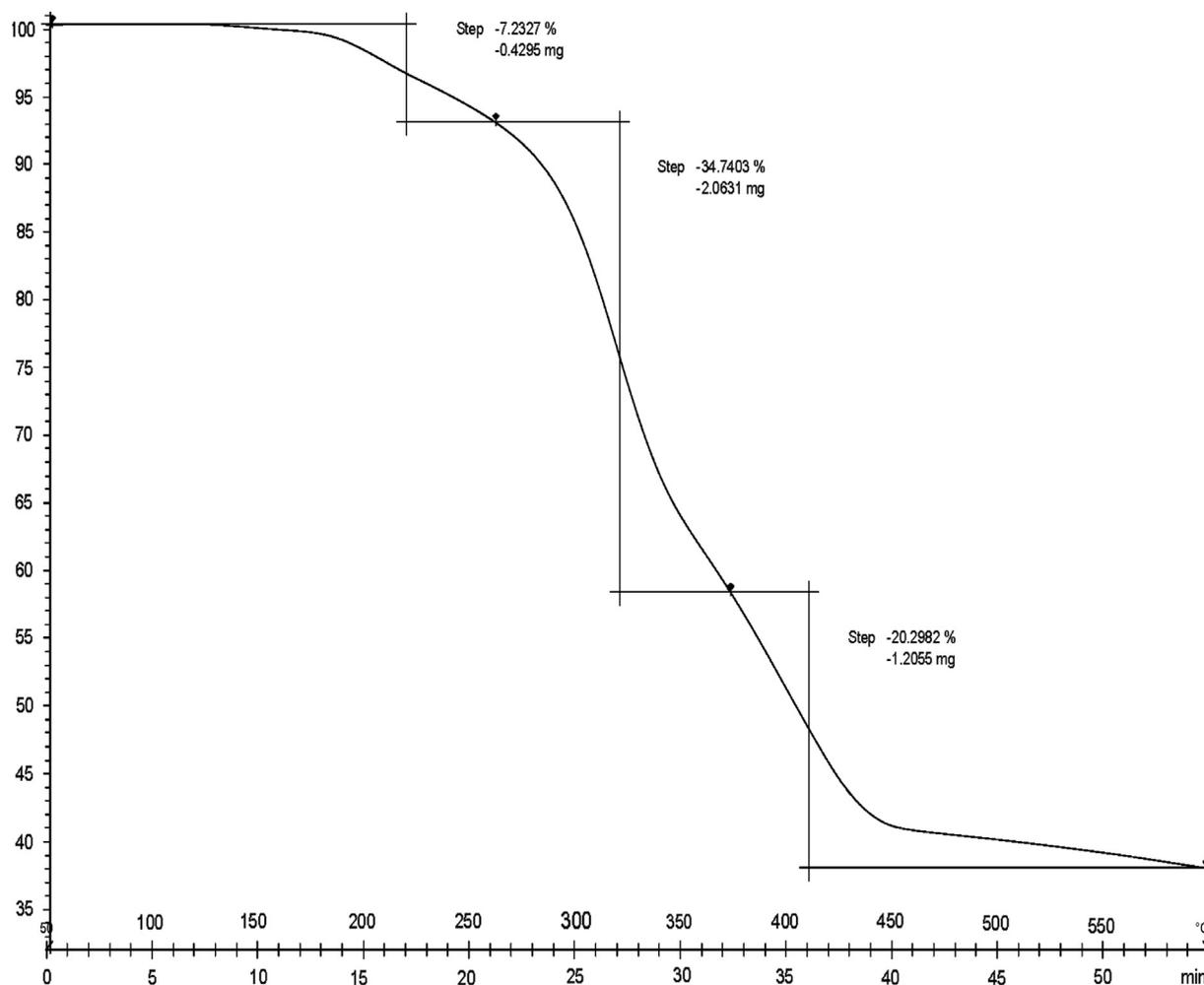


Figure 6b Blue isomer.

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 (pn) 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 (Sundberg et al., 1996, 1998; Sillanpaa et al., 1997).

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. They have different absorption 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 of 40–44  $\text{Scm}^2 \text{mol}^{-1}$  (Geary, 1971).

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 on all the isomers using the hybrid Lee–Yang–Parr (B3LYP) functional. The calculations reveal that the isomer (1) possesses highest energy and thus least stable, whereas the (2) is most stable. The energy difference between isomers (1) and (3) is  $3.12 \text{ kJ mol}^{-1}$ , while those between (1), (2) and (2), (3) are  $11.26$  and  $8.19 \text{ kJ mol}^{-1}$ , respectively. 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 into the mutual transformation of the three conformations, the transition state and intrinsic reaction coordinate calculations were performed (Fig. 4). The calculations indicate that the energy difference between the most stable conformer and the transition state is  $12.22 \text{ kJ mol}^{-1}$ . It indicates that transformation of one conformation to another can be accessible at room temperature in the solution phase. We have experimentally proved that all the isomers in the solution phase turn blue. It is perhaps because of the inversion of pn ring. 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 possesses the chair conformation. The structure of transition state clearly

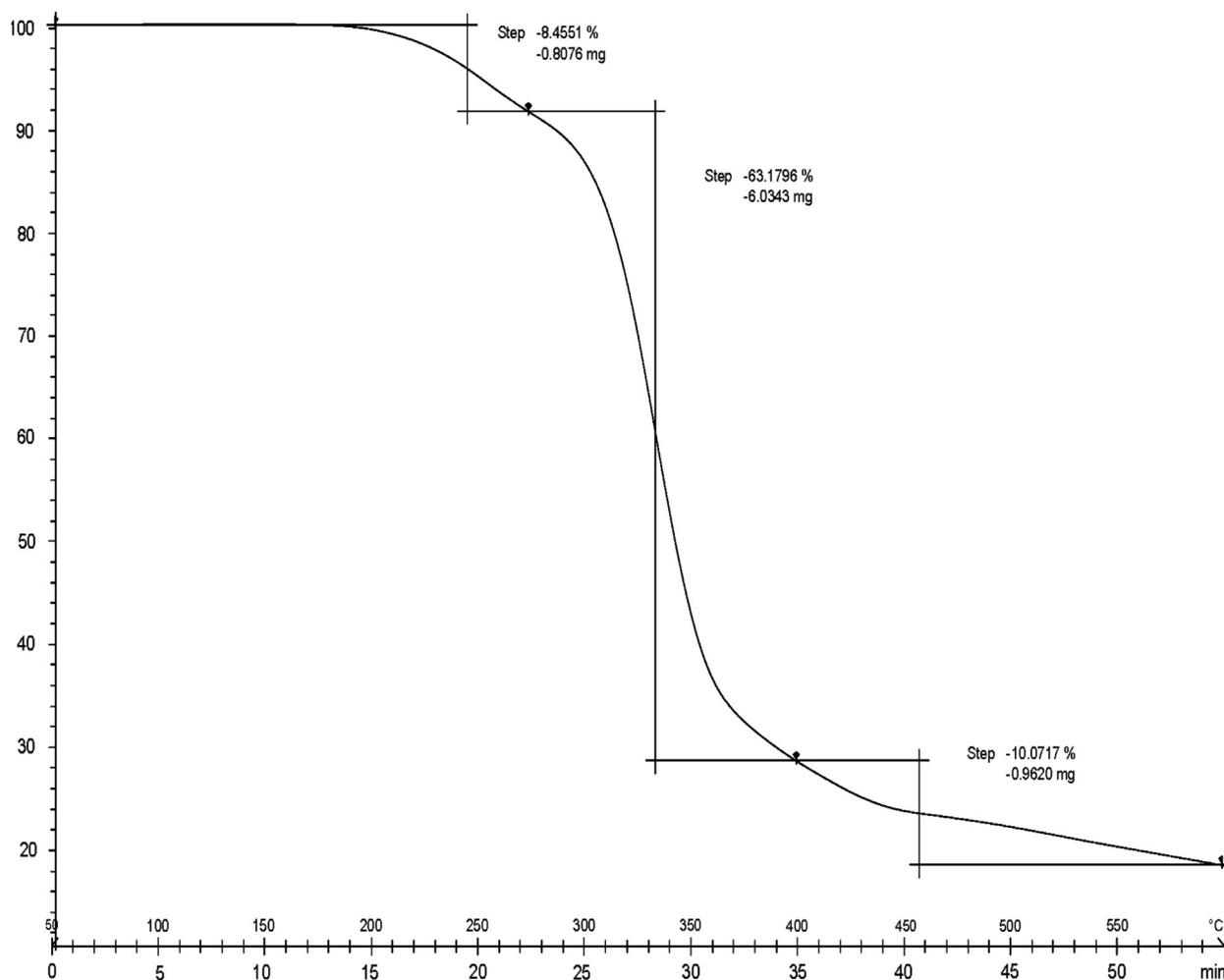


Figure 6c Yellow isomer.

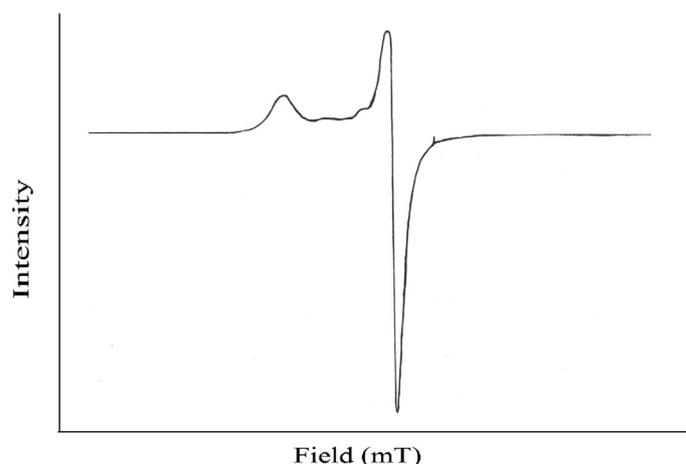
indicates that it can be easily transformed to either more stable structure (2) or relatively less stable structure (1). Obviously the more stable structure dominates and predominantly exists in solution.

### 3.1. Electronic spectra

The electronic spectra of the complexes (Table 3) in DMSO and aqueous medium absorb in 240–310 nm UV region, which may be attributed to ligand to metal charge-transfer (LMCT) corresponding to  $\sigma_N \rightarrow d_x^2 - y^2$  Cu(II),  $\sigma, \pi$  Cl  $\rightarrow d_x^2 - y^2$  Cu(II) transitions. (Zelenak et al., 2006) have 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 the Cl group in an octahedral complex. The M–Cl charge transfer occurs irrespective of the position of the Cl group. In case of chloro bridged complex (Ferrari et al., 1991) the Cl occupies an equatorial position while in a monomeric octahedral (4 + 2) complex Cu–Cl exhibits similar CT although it occupies the 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 the existence of stable isomers. It is concluded that the change in physical properties of  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$  is due to the non planarity of the pn molecule.

An attempt has been made to assign the observed electronic spectra 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  $d_x^2$  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 straightforward. However, approximate assignments can be made, (Chen et al., 2009, 2011; Tommaso and de Leeuw, 2009) although they provide a simplified representation of the transitions. TD-DFT excitations were calculated both in the gas phase and in the solvent using the PCM (water and DMSO). By comparing the calculated spectra, it is evident that calculated 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 spectrum presents a very weak and broad absorption



**Figure 7** EPR spectrum of  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$ .

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  $\sim 305$  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** are presented in Fig. 5.

### 3.2. Infrared spectra

The free pn molecule exhibits two sharp and well-separated narrow bands in the region  $3050\text{--}3350\text{ cm}^{-1}$  arising due to symmetric and asymmetric ( $\text{NH}_2$ ) stretching vibrations (Lever, 1984; Refat et al., 2006). As a consequence of ligation of pn molecule to Cu(II) ion forming a six membered ring, this band shifts to lower wave number ( $3010\text{--}3275\text{ cm}^{-1}$ ) in the solid state (Nami and Siddiqi, 2004). Stretching vibrations of the  $\text{CH}_2$  group of pn are in the range of  $2875\text{--}2960\text{ cm}^{-1}$ . The intensely sharp band in the region  $1570\text{--}1580\text{ cm}^{-1}$  is attributed to deformation vibration of the  $\text{CH}_2$  group (Singh and Kumar, 2006). In addition, a characteristic medium to weak  $\nu(\text{C-N})$  band observed in the range of  $1160\text{--}1183\text{ cm}^{-1}$  is also shifted to lower wave number mainly due to coordination. 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 results  $\nu(\text{Cu-N})$  absorption appears in the region  $450\text{--}600\text{ cm}^{-1}$  as a strong band. In case of  $\text{MX}_2\cdot\text{L}_2$ , where L is a bidentate chelating ligand, X can only occupy the axial position in an octahedral compound. The Cu-Cl stretching frequency in the region  $250\text{--}380\text{ cm}^{-1}$  in our case (Table 4), indicates the presence of chloride ligand at the axial position (Fouda et al., 2008; Kabanos et al., 1992; John et al., 2004). Many other important bands were also observed due to deformation vibration and skeleton vibrations of  $\text{CH}_2$  and  $\text{NH}_2$  groups.

### 3.3. Thermal analysis

TGA profile of all the isomers is essentially identical and consists of well defined stages (Figs. 6Fig. 6a-c). It was realized

while running TGA that these isomers are hygroscopic in nature. They were studied in  $50\text{--}600\text{ }^\circ\text{C}$  temperature range at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . The navy blue isomer is stable up to  $50\text{ }^\circ\text{C}$ . The first decomposition occurs between 50 and  $140\text{ }^\circ\text{C}$  corresponding to the loss of one water molecule. The second step (29 %) corresponds to the 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 pn. The second pn molecule is lost in the subsequent steps. Finally, 22.53% Cu is left as residue at  $600\text{ }^\circ\text{C}$ .

The pyrolysis of blue isomer occurs in three steps. The first decomposition occurs between  $135$  and  $265\text{ }^\circ\text{C}$  indicating a weight loss of  $\sim 8.71\%$  (exp. 7.23%) which corresponds to the  $3/2$  mol of coordinated water. In the second step one mole of pn and chloride ions are lost simultaneously between  $265$  and  $370\text{ }^\circ\text{C}$  exhibiting  $\sim 35.39\%$  of weight loss which is in good agreement with experimental value (34.74 %). The third step indicates a weight loss of  $\sim 19.35\%$  (20.29%) in temperature range of  $370\text{--}600\text{ }^\circ\text{C}$  corresponding to the expulsion of organic moiety  $[(\text{NH}_2)_2(\text{CH}_2)_2]$ . The last step exhibits the loss of  $[\text{CH}_2\text{Cl}]$  in the initial portion of thermogram leaving copper metal at  $600\text{ }^\circ\text{C}$ .

Thermal degradation of yellow isomer also includes three steps. The thermogram shows that the yellow isomer is thermally more stable. The first step of decomposition comprises of a loss of  $\sim 8.71\%$  (exp. 8.45%) corresponding to  $3/2$  mol of coordinated water between  $220$  and  $260\text{ }^\circ\text{C}$ . The second step shows a loss of  $\sim 61.68\%$  (exp. 63.17%) which corresponds to the loss of  $[\text{pn} + \text{Cl}_2 + \text{C}_3\text{H}_{10}]$  moiety between  $260$  and  $400\text{ }^\circ\text{C}$ . The third step includes the loss of  $\text{N}_2$  exhibiting a weight loss of  $\sim 9.03\%$  (exp. 10.07%) between  $400$  and  $600\text{ }^\circ\text{C}$ . In the end Cu metal is left as residue at  $600\text{ }^\circ\text{C}$ .

### 3.4. EPR spectra

The X-band EPR spectrum of one of the isomeric complexes (navy blue) has been 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) center (Fig. 7). The value of  $g_{\parallel}$  and  $g_{\perp}$  has been calculated from the peak position with references to the standard TCNE peak ( $g = 2.0027$ ) at magnetic field 3135 gauss. The tetragonal system provides a

strong evidence for the presence of Jahn–Teller distortion and on the basis of  $g_{\parallel}$  and  $g_{\perp}$  it is proposed that an unpaired electron resides in  $d_{x^2-y^2}$  orbital. The complex does not show hyperfine splitting. The room temperature  $g$  values of  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$  are  $g_{\parallel} = 2.1744$  and  $g_{\perp} = 2.0666$ . It has been reported that for ionic environment  $g_{\parallel} > 2.3$  while for a covalent environment  $g_{\parallel} < 2.3$ , indicating that the present complex exhibits considerable covalent character (Hathaway, 1981). This suggests distortion in the Cu(II) complex from oh symmetry to  $D_{4h}$  symmetry (Emam et al., 2012). The smaller  $g_{\parallel}$  indicates increased delocalization of unpaired electrons away from the metal nucleus which has been interpreted in terms of increased covalency in the metal ligand bond.

#### 4. Conclusion

The reaction of 1,3-diaminopropane with Copper chloride results in the formation of octahedral complex  $[\text{Cu}(\text{pn})_2\text{Cl}_2]$  which exists in three isomeric forms. They are visibly distinct, as they are of three different colors and are stable at room temperature. Their existence has been evidenced by elemental- and thermal analysis, molar 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 in solution because lattice gets ruptured in solution and they attain the most stable structure. The main cause behind existence of these isomers is ring puckering.

#### References

- Allen, F.H., 2002. *Acta Crystallographica Section B* 58, 380.
- Barone, V., Cossi, M., Tomasi, J., 1998. *Journal of Computational Chemistry* 19, 404.
- Becke, A.D., 1993. *Journal of Chemical Physics* 98, 5648.
- Champouret, Y., Gulli, S., Daran, J.C., Poli, R., 2012. *European Journal of Inorganic Chemistry* 10, 1672.
- Chen, Y., Tang, Y.H., Lei, M., 2009. *Journal of the Chemical Society – Dalton Transaction* 13, 2359.
- Chen, H.Y.T., Tommaso, D.D., Hogarth, G., Catlow, C.R.A., 2011. *Journal of the Chemical Society – Dalton Transaction* 40, 402.
- Emam, S.M., AbouEl-Enein, S.A., El-Saied, F.A., Alshater, S.Y., 2012. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 92, 96.
- Feerrari, M.B., Fava, G.G., Lanfranchi, M., Pelizzi, C., Tarasconi, P., 1991. *Journal of the Chemical Society-Dalton Transactions* 8, 1951.
- Fouda, M.F.R., Abd El-Zaher, M.M., Shakdofa, M.M.E., El-Saied, F.A., Ayad, M.I., El- Tabl, A.S., 2008. *Transition Metal Chemistry* 33, 219.
- Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Vreven Jr., T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, W.M., Gonzalez, C., Pople, J.A., 2010. Gaussian Inc., Wallingford, CT.
- Garcia-Orozco, I., Ortega-Alfaro, M.C., Lopez-Cortes, J.G., Toscano, R.A., Alvarez-Toledano, C., 2006. *Inorganic Chemistry* 45, 1766.
- Gazo, J., 1974. *Pure and Applied Chemistry* 38, 279.
- Gazo, J., Bersuker, I.B., Garaj, J., Kabesova, M., Kohout, J., Langfelderova, H., Melnik, M., Serator, M., Valach, F., 1976. *Coordination Chemistry Reviews* 19, 253.
- Geary, W.J., 1971. *Coordination Chemistry Reviews* 7, 81.
- Hathaway, B.J., 1981. *Coordination Chemistry Reviews* 35, 211.
- Hay, R.W., Danby, A., Lightfoot, P., 1997. *Polyhedron* 16, 3261.
- John, R.P., Shreekanth, A., Rajakannan, V., Ajith, T.A., Kurup, M.R.P., 2004. *Polyhedron* 23, 2549.
- Kabanos, T.A., Keramidas, A.D., Mentzafos, D., Russo, U., Terzis, A., Tsangaris, J.M., 1992. *Journal of the Chemical Society – Dalton Transactions* 18, 2729.
- Kupka, H., Degen, J., Urushiyama, A., Angermund, K., Kruger, C., 1986. *Inorganic Chemistry* 25, 3294.
- Lee, C.T., Yang, W.T., Parr, R.G., 1988. *Physical Review B: Condensed Matter and Material Physics* 37, 785.
- Lever, A.B.P., 1984. *Inorganic Electronic Spectroscopy*, second ed. Elsevier, Amsterdam, The Netherlands.
- Luo, J., Zhou, X.G., Weng, L.M., Hou, X.F., 2003. *Acta Crystallographica C* 59, m392.
- Nami, S.A.A., Siddiqi, K.S., 2004. *Synthesis and Reactivity in Inorganic Metal-Organic Chemistry* 34, 1581.
- Navarro, J.A.R., Romero, M.A., Salas, J.M., Molina, J., Tiekink, E.R.T., 1998. *Inorganica Chimica Acta* 274, 53.
- Real, J.A., Gaspar, A.B., Niel, V., Munoz, M.C., 2003. *Coordination Chemistry Reviews* 236, 121.
- Refat, M.S., El-Deen, I.M., Ibrahim, H.K., El-Ghool, S., 2006. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 65, 1208.
- Ribas, J., Escuer, A., Monfort, M., Vicente, R., Cortes, R., Lezama, L., Rojo, T., 1999. *Coordination Chemistry Reviews* 195, 1027.
- Ribas, J., Garcia, A., Costa, R., Monfort, M., Alvarez, S., Zanchini, C., Solans, X., Domenech, M.V., 1991. *Inorganic Chemistry* 30, 84.
- Siddiqi, K.S., Aqra, F.M.A.M., Shah, S.A., Zaidi, S.A.A., Casabo, J., Teixidor, F., 1993a. *Polyhedron* 12, 949.
- Siddiqi, K.S., Aqra, F.M.A.M., Zaidi, S.A.A., 1993b. *Transition Metal Chemistry* 18, 420.
- Siddiqi, K.S., Rafat, F., Kar, S.H., 2004. *Synthesis and Reactivity in Inorganic Metal-Organic Chemistry* 34, 93.
- Sillanpaa, R., Jokela, J., Sundberg, M.R., 1997. *Inorganica Chimica Acta* 258, 221.
- Singh, P.K., Kumar, D.N., 2006. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 64, 853.
- Sundberg, M.R., 1994. *Inorganica Chimica Acta* 218, 151.
- Sundberg, M.R., Kivekas, R., Huovilainen, P., Uggla, R., 2001. *Inorganica Chimica Acta* 324, 212.
- Sundberg, M.R., Koskimies, J.K., Matikainen, J., Tylli, H., 1998. *Inorganica Chimica Acta* 268, 21.
- Sundberg, M.R., Sillanpaa, R., 1992. *Acta Chemica Scandinavica* 46, 34.
- Sundberg, M.R., Sillanpaa, R., Jokela, J., 1996a. *Inorganica Chimica Acta* 248, 1.
- Sundberg, M.R., Sillanpaa, R., Uggla, R., 1996b. *Inorganica Chimica Acta* 245, 35.
- Sundberg, M.R., Uggla, R., 1997. *Inorganica Chimica Acta* 254, 259.
- Sundberg, M.R., Uggala, R., Kivekas, R., 1995. *Inorganica Chimica Acta* 232, 1.
- Thetiot, F., Triki, S., Pala, J.S., Golhen, S., 2003. *Inorganica Chimica Acta* 350, 314.

- Tommaso, D.D., de Leeuw, N.H., 2009. *Geochimica et Cosmochimica Acta* 73, 5394.
- Triki, S., Thetiot, F., Vandavelde, F., Sala-Pala, J., Gomez-Garcia, C., 2005. *Inorganic Chemistry* 44, 4086.
- Wang, G., Zhu, H., Fan, J., Slebodnick, C., Yee, G.T., 2006. *Inorganic Chemistry* 45, 1406.
- Zelenak, V., Orendacova, A., Cisarova, I., Cernak, J., Kravchyna, O.V., Park, J.H., Orendac, M., Anders, A.G., Feher, A., Meisel, M.W., 2006. *Inorganic Chemistry* 45, 1774.