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# Molecular Recognition of Trans-Chiral Schiff Base Metal Complexes for Induced CD

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Additional information is available at the end of the chapter

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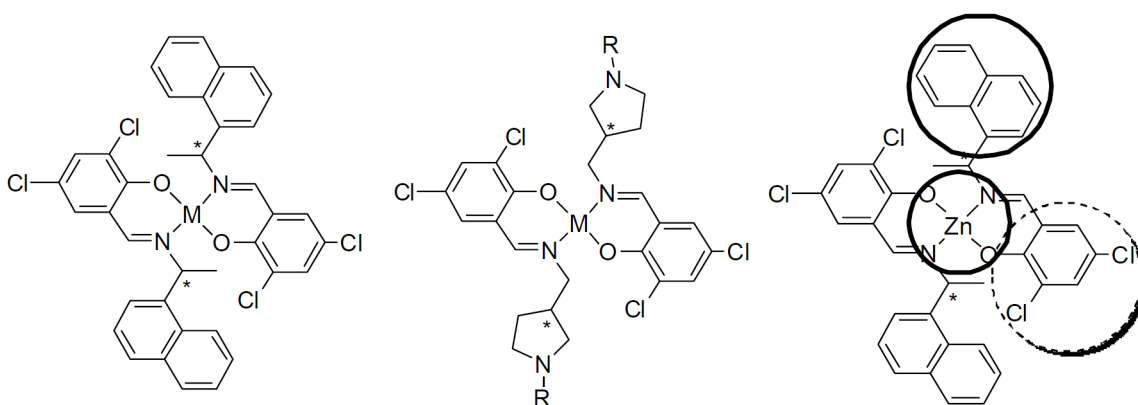
## 1. Introduction

Schiff base is one of the most popular ligands in the field of coordination chemistry [1-5]. Conventionally, transition metal complexes having Schiff base ligands have been investigated about stereochemistry and corresponding electronic properties mainly. For example, solution paramagnetism of Ni(II) complexes, structural phase transition of Cu(II) complexes, chiral catalysts, and some types of molecule-based magnets and other interesting facts about correlation between structures and properties are known and these facts are cooperative effect involving intermolecular interactions and molecular recognition. Because of developing importance as functional chiral materials, many researchers have investigated crystal structures (including thermally-induced structural phase transition and polymorphism by solvents) of *trans*-type chiral Schiff base metal complexes and extract important features of chiral molecular recognition in the solid states.

As mentioned in Abstract section, we have tested observation of some novel phenomena associated with chirality or CD spectroscopy based on intermolecular interactions. Induced CD on various nano-scaled (inorganic) materials from chiral Schiff base metal complexes is one of them and not only electronic and magnetic dipole moments but also molecular recognition between chiral compounds and nano-scaled materials are important factors for these phenomena [6, 7]. For example, we have observed induced CD peaks from chiral Schiff base Ni(II) complexes at d-d region for achiral or chiral Schiff base Cu(II) complexes (without exchanging ligands) [8], at d-d and CT regions for Cu(II)-coordinated metallodendrimers (PAMAM), and surface plasmon region for Cu-clusters prepared in PAMAM by irradiation of UV light for the first time [9, 10]. In this way, we have also reported on induced CD peaks of metal complexes (both achiral and chiral ones), organometallics (ferrocene) [11], metallodendrimers, metal nano-clusters, and nano-particles [9, 10] of metal-semiconductors [12]. Addi-

tionally, we have successfully observed size-dependence of wavelengths of induced CD peaks from chiral Schiff base Zn(II) complexes involving azo-groups at surface plasmon region on colloidal gold particles [13].

As for the induced CD between chiral Schiff base Ni(II) or Zn(II) complexes and Cu-clusters prepared in PAMAM, we have also investigated the role of chiral ligands for molecular recognition. For example, naphthyl groups are appropriate for induced CD, while more flexible groups are not [14] (Figure 1). Therefore, several examples indicated that supramolecular or molecular recognition must be a key reason for specific intermolecular interactions. In this review article, we have summarized several examples of crystal structures and optimized structures (as a model of them in solutions) of *trans*-type chiral Schiff base Ni(II), Cu(II), and Zn(II) complexes. In order to derive important steric factors for molecular recognition, we will point out characteristic features of molecular shapes or their conformational changes *in silico*.



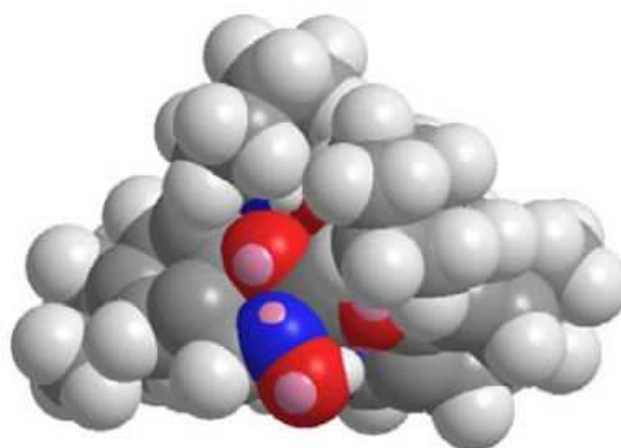
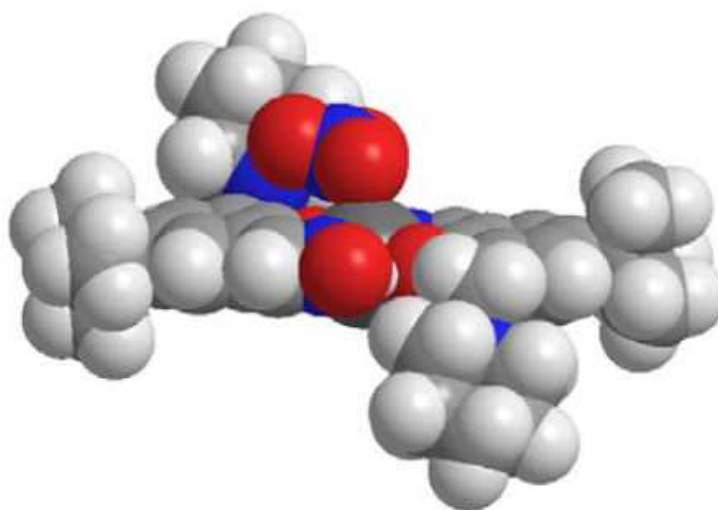
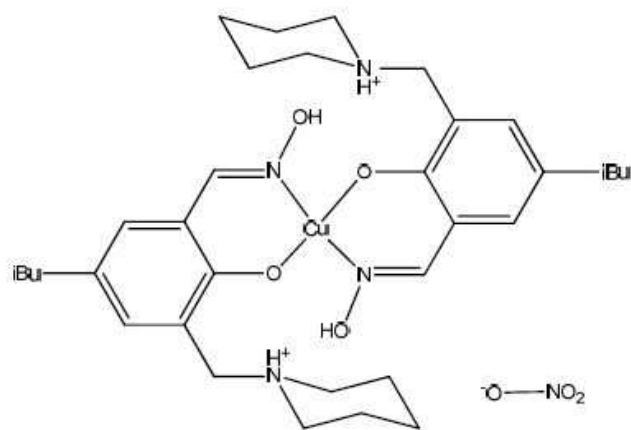
**Figure 1.** Examples of suitable [left] and unsuitable [center] ligands for induced CD based on experiments [9, 10, 14]. [Right] Important (bold circles) and unimportant (broken circle) moieties of ligands for induced CD.

## 2. Computation

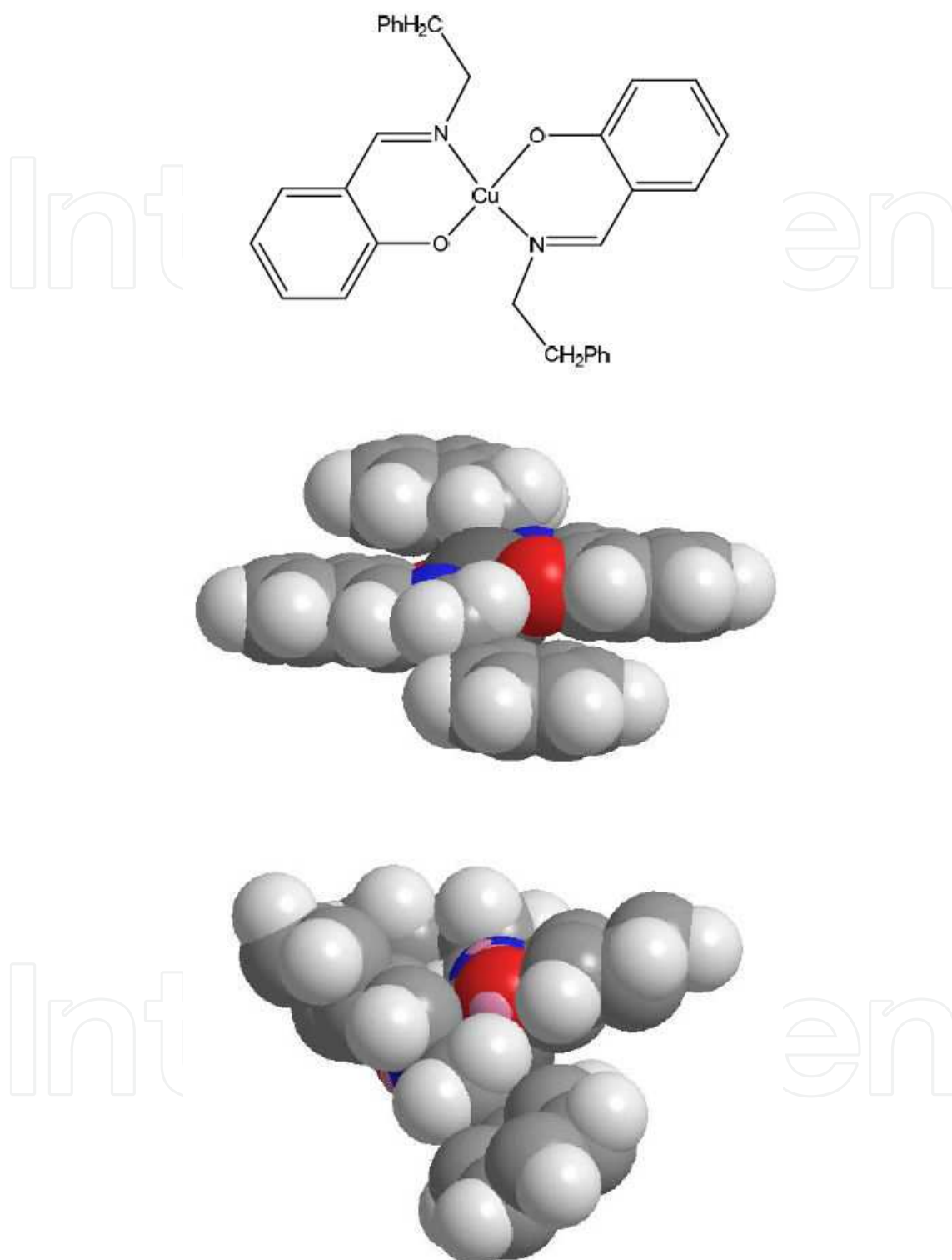
According to a CCDC database [15], we selected some crystal structures of *trans*-type Schiff base metal complexes. As modeling conformational changes in solutions, we obtain optimized structures and their heat of formation by using MM2. We will search appropriate features of molecular shapes for induced CD.

## 3. Results and discussion

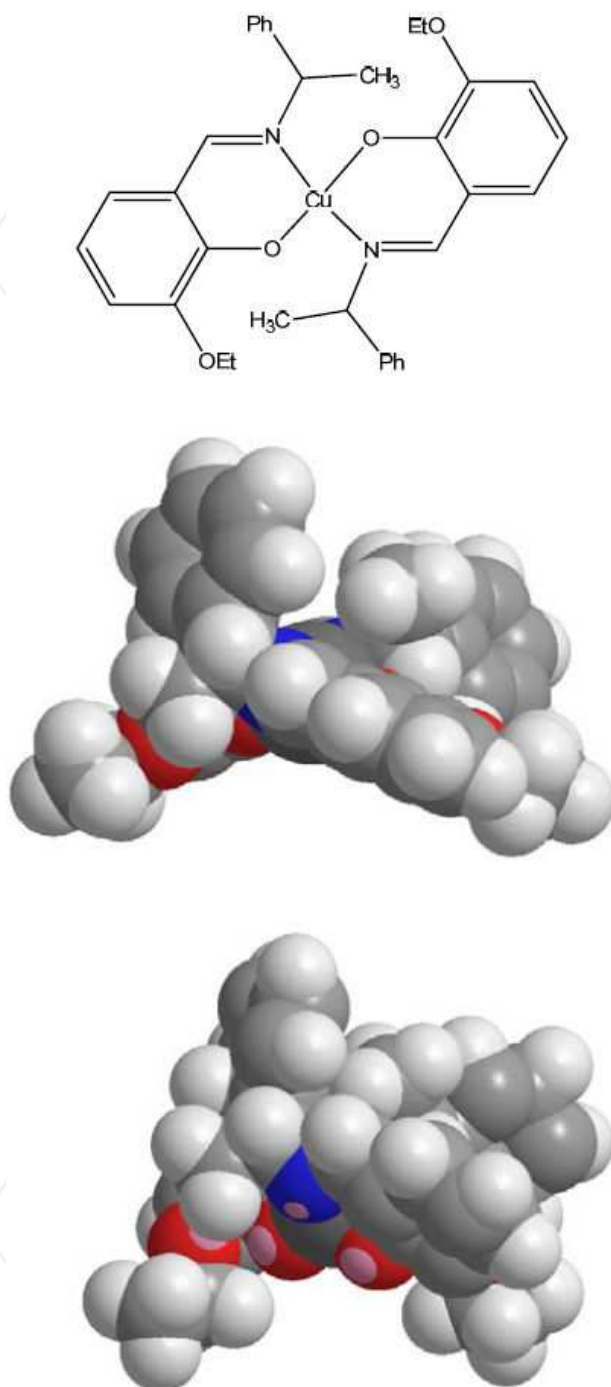
12 examples of *trans*-type Schiff base complexes investigated are mentioned below, molecular structures [top], crystal structures [middle], and optimized structures [bottom] as space-filling models with comments.



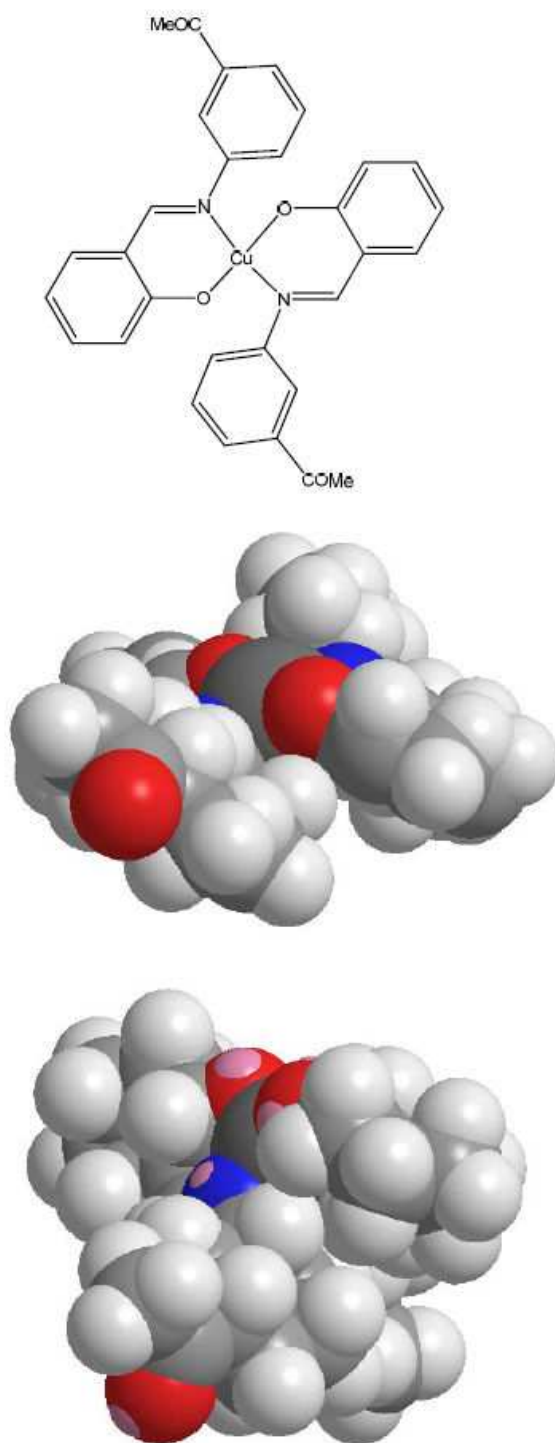
**Figure 2.** CCDC MIMTOS01 [16]. The compound has a formula  $C_{34}H_{52}CuN_4O_4^{2+}, 2(NO_3^-)$ . Novel feature mentioned is that attaching dialkylaminomethyl arms to commercial phenolic oxime copper extractants yields reagents which transport base metal salt very efficiently by forming neutral 1:1 or 1:2 complexes with zwitterionic forms of the ligands. Apparently conformational changes were from a square planar geometry to an umbrella form and twist form (about 45 degree).



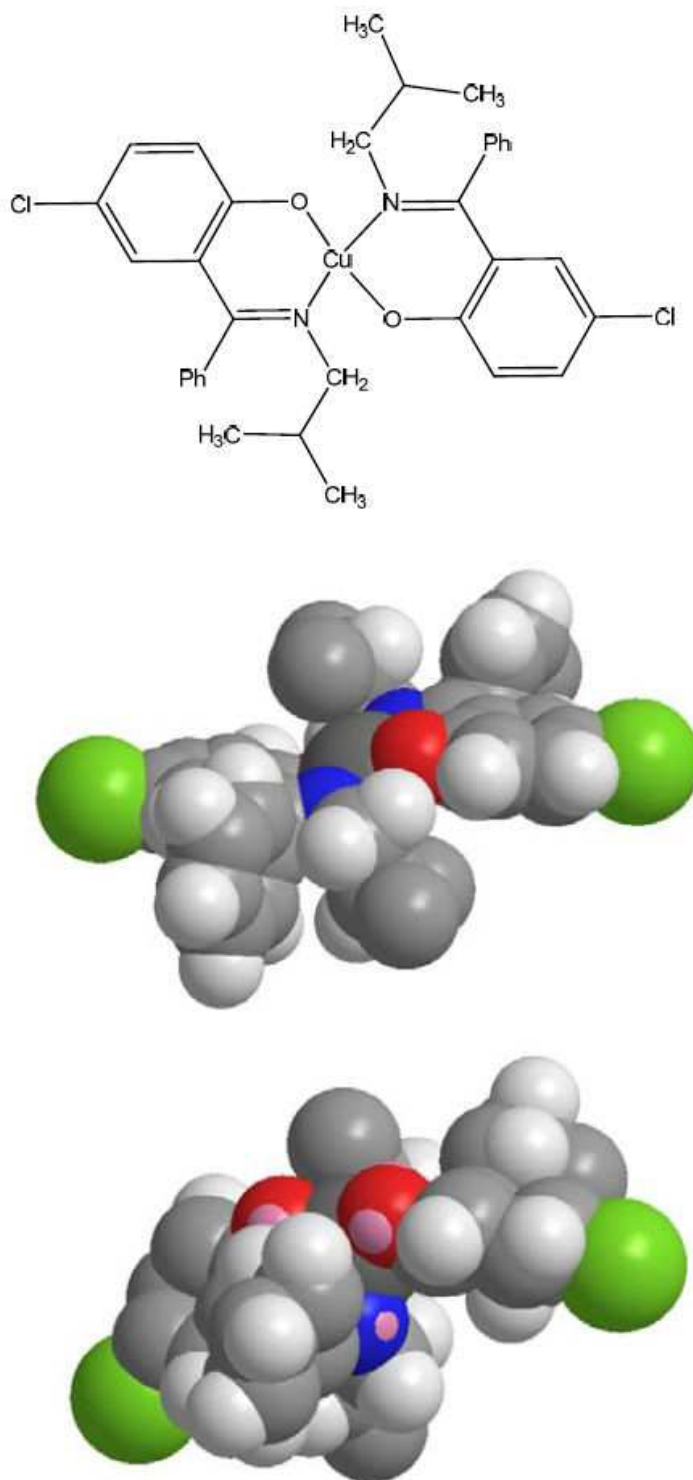
**Figure 3.** CCDC **MAHYEA** [17]. The compound has a formula  $C_{30}H_{28}CuN_2O_2$ . Novel feature mentioned is that it adopts a stepped conformation and displays a square-planar *trans*-[CuN<sub>2</sub>O<sub>2</sub>] coordination geometry. The asymmetric unit contains two independent half molecules and each Cu atom is located on a center of symmetry.



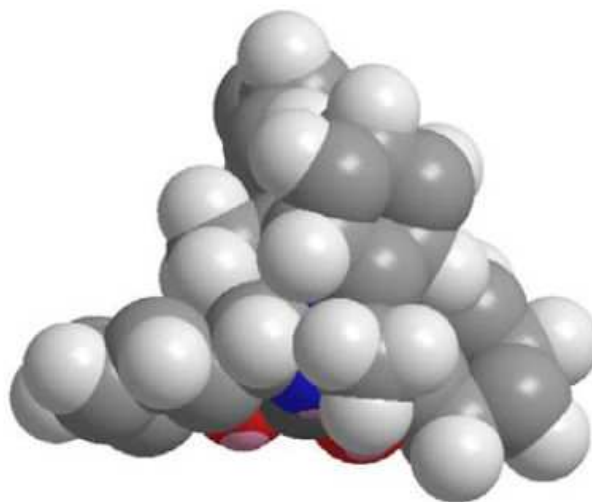
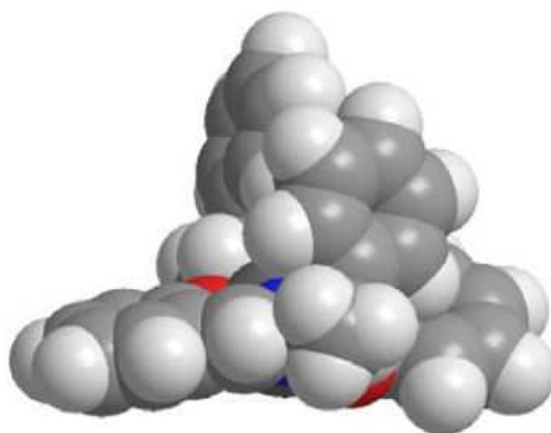
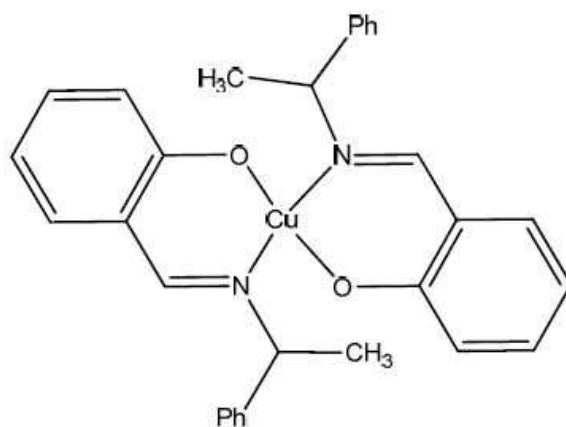
**Figure 4.** CCDC **MAJNIV** [18].The compound has a formula  $C_{34}H_{36}CuN_2O_4$ . Novel feature mentioned is that compressed tetrahedral coordination geometry with an (*R,R*)-absolute configuration. These complexes differ from one another with respect to the 1-phenylethylamine moieties, the direction of the benzene rings being inside and outside of the molecules. Apparently conformational changes were from an umbrella and twist (about 45 degree) form to same and twist (about 90 degree) form. The extended conformation of the phenethylimine pendant groups results in crystal packing formed by weakly aggregated planar molecules. Apparently conformational changes were from a relatively flat step form to a significantly sharp step form.



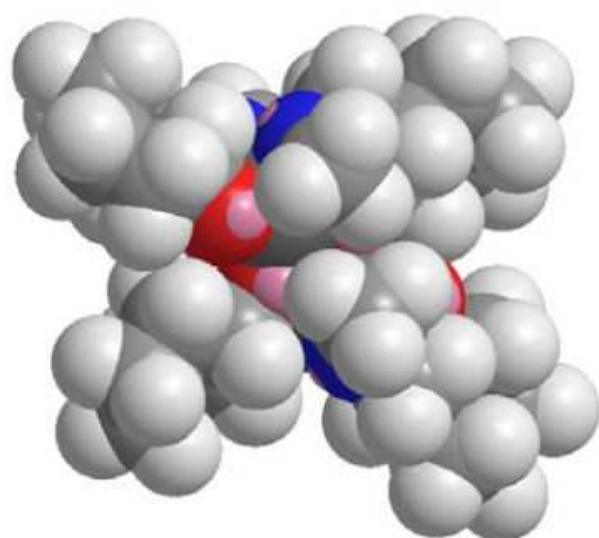
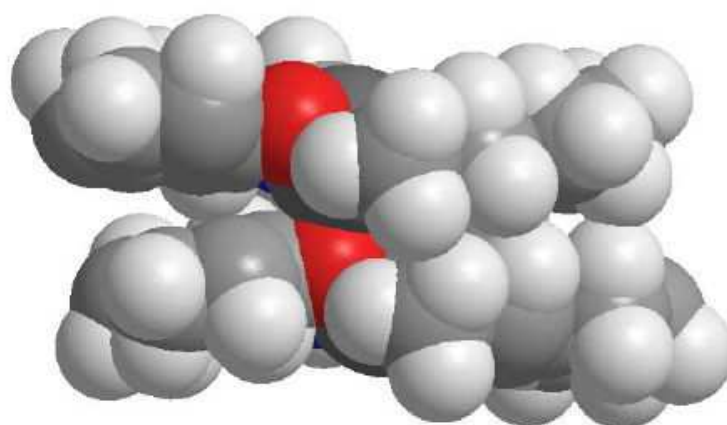
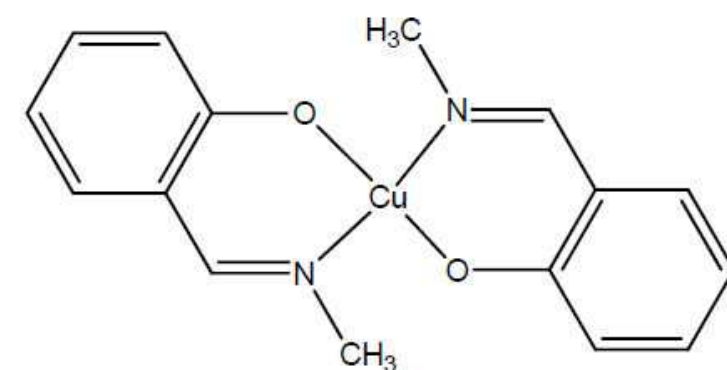
**Figure 5.** CCDC **MIZGIM** [19]. The compound has a formula  $C_{30}H_{24}CuN_2O_4$ . Novel feature mentioned is that the coordination geometry around the copper atom in the complex is intermediate between square-planar and tetrahedral with two salicylidimine ligands in trans arrangement. The molecular chains are linked via additional  $C-H \cdots O$  hydrogen bonds to form a three-dimensional supramolecular network. Apparently conformational changes were from a moderately umbrella and slightly twist form to a twist (about 90 degree) form.



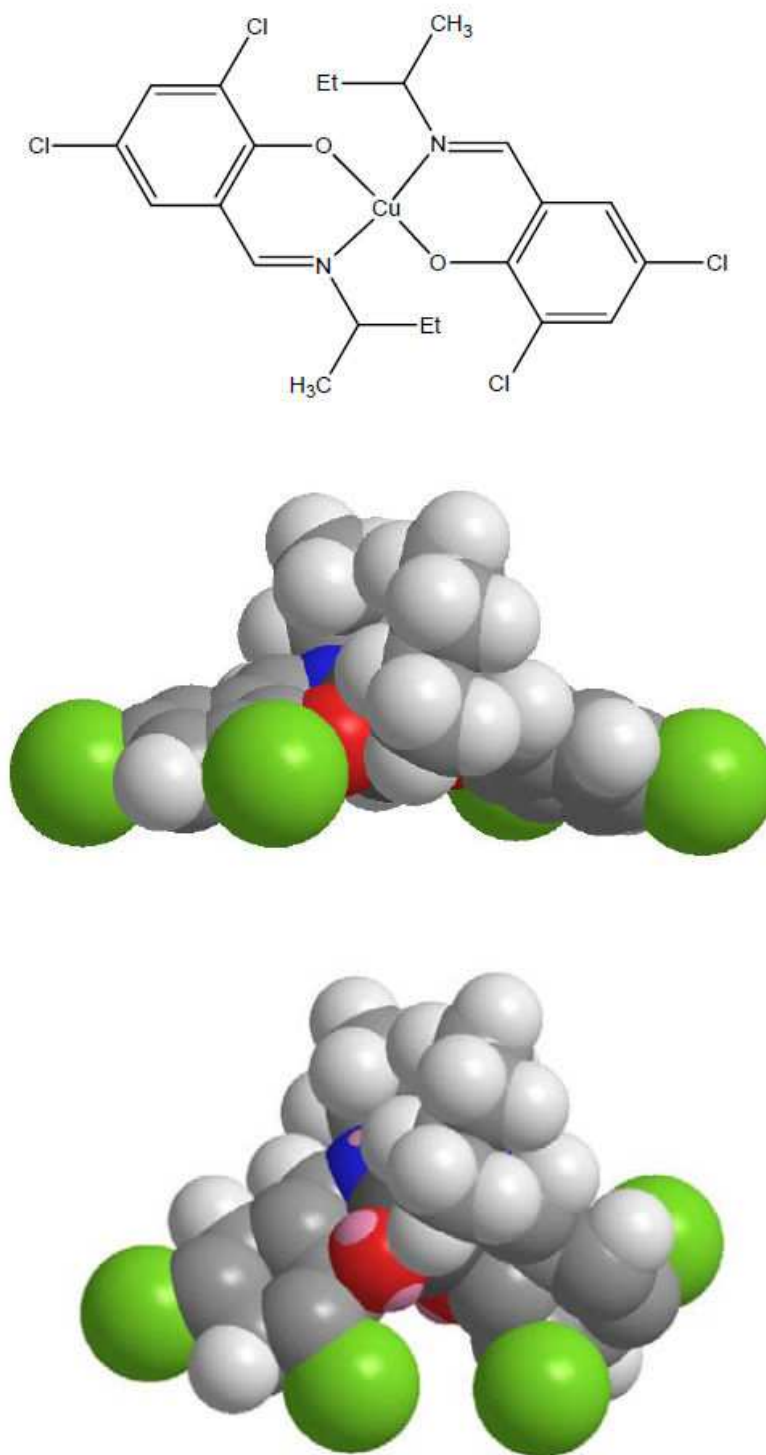
**Figure 6.** CCDC IBHBCU01 [20]. The compound has a formula  $C_{34}H_{34}Cl_2CuN_2O_2$ . Novel feature mentioned is that the isobutyl complex exists in two distinct crystalline forms, green and red. The green isomer has the isobutyl groups pointing to the same side of the approximate  $[CuO_2N_2]$  plane. The red isomer of the isobutyl complex contains two crystallographically independent molecules having the isobutyl groups. Apparently conformational changes were from a step form to an umbrella and twist (about 90 degree) form.



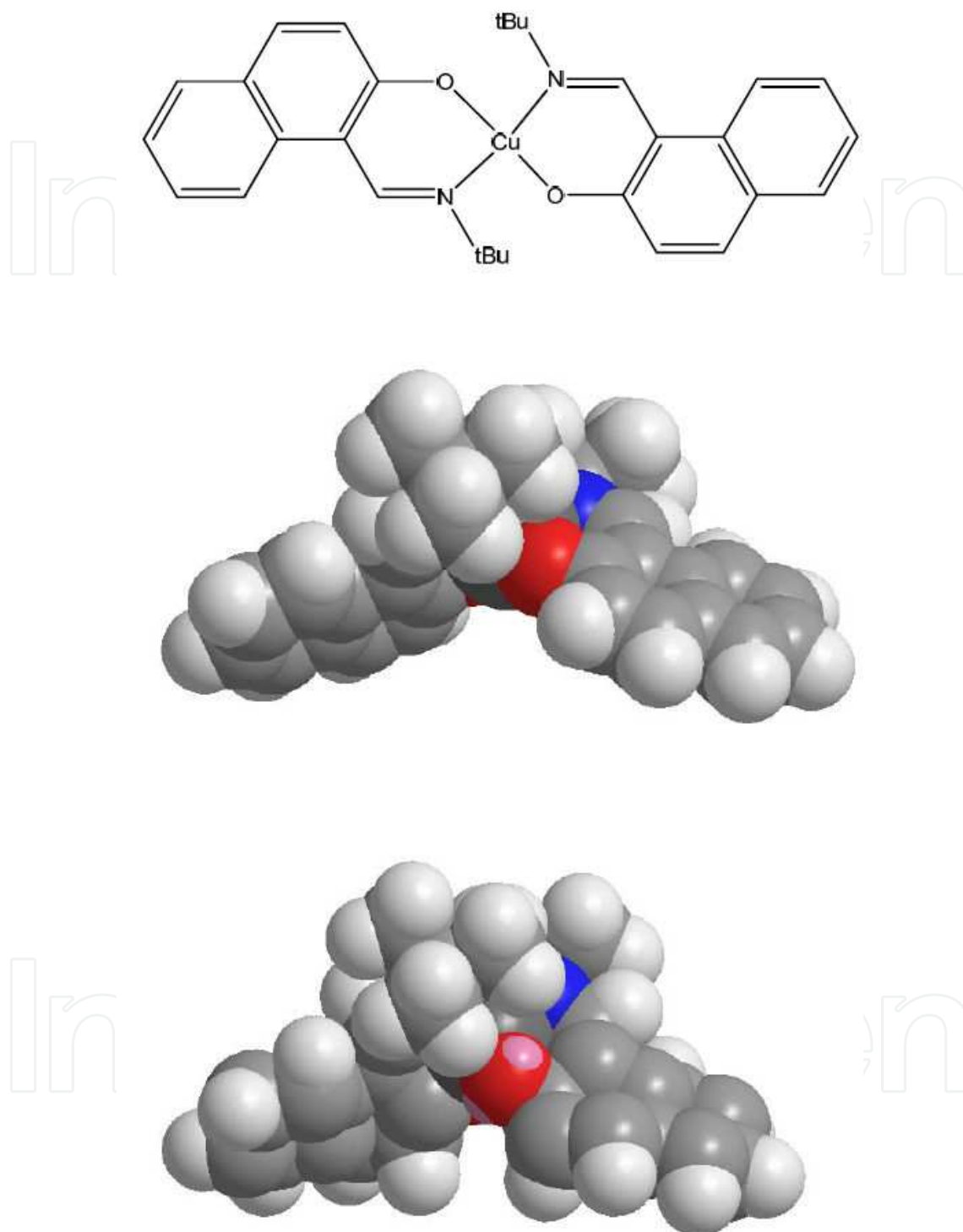
**Figure 7.** CCDC **DPESCU11** [21].The compound has a formula  $C_{30}H_{28}CuN_2O_2$ . Novel feature mentioned is that copper(II) complexes of three chiral enantiomeric pairs of o-hydroxy Schiff bases derived from (R)-(+)-1-phenylethylamine and/or (S)-(-)-1-phenylethylamine, were prepared and characterized. The geometry around the metal atom is distorted square planar. Apparently conformational change was from a twist (about 45 degree) form to a twist (about 90 degree) form.



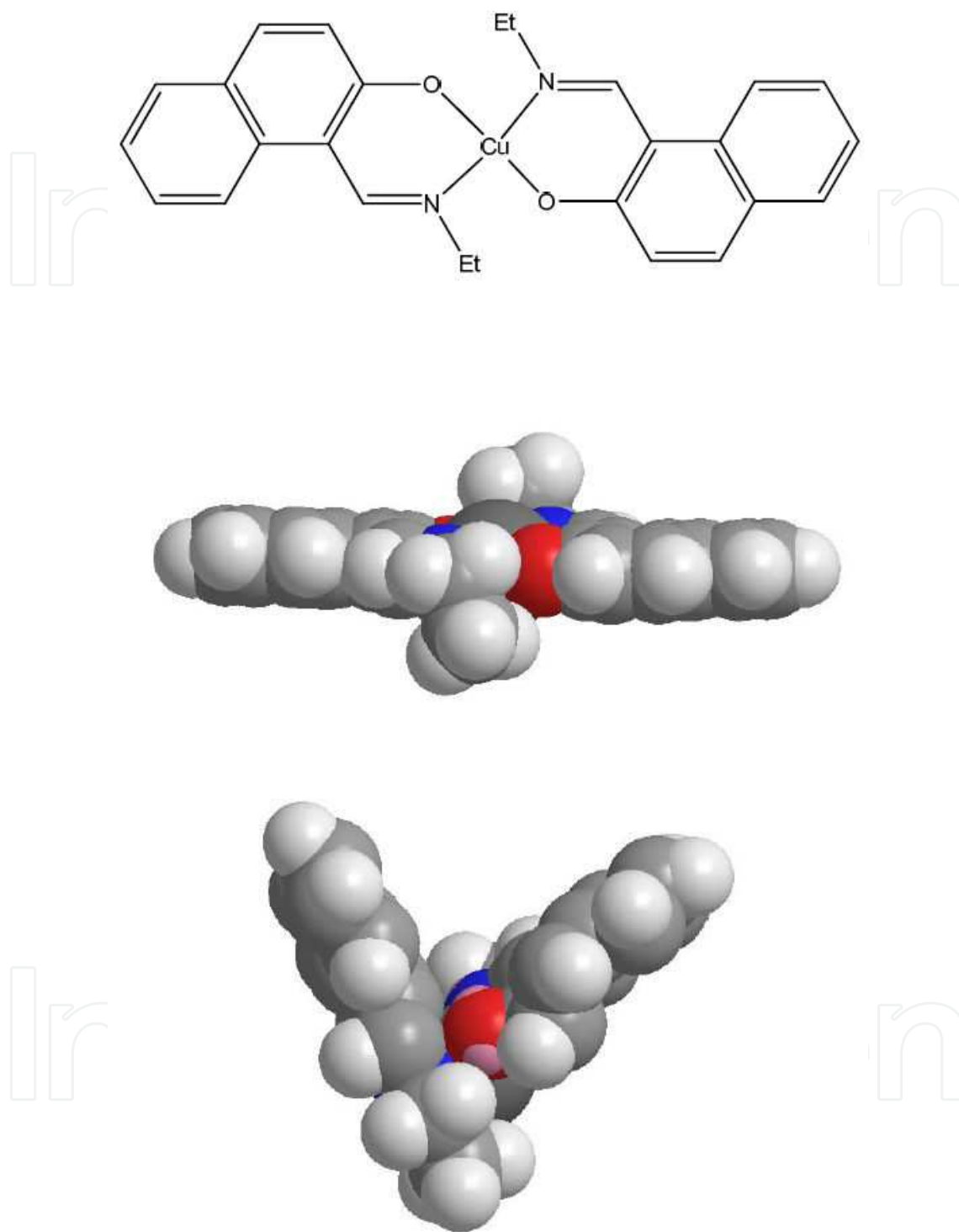
**Figure 8.** CCDC **MSACOP12** [22]. The compound has a formula  $C_{16}H_{16}CuN_2O_2$ . Novel feature mentioned is that a dimeric molecule in which monomeric halves is joined by two Cu-O bonds to complete a square-pyramidal configuration about each copper atom. Distortions in the molecule are evidently due to the close approach of non-bonding regions. It is now seen that this compound displays three different coordination arrangements in its three polymorphic forms. Apparently conformational change was from a step form to an umbrella and twist (about 45 degree) form.



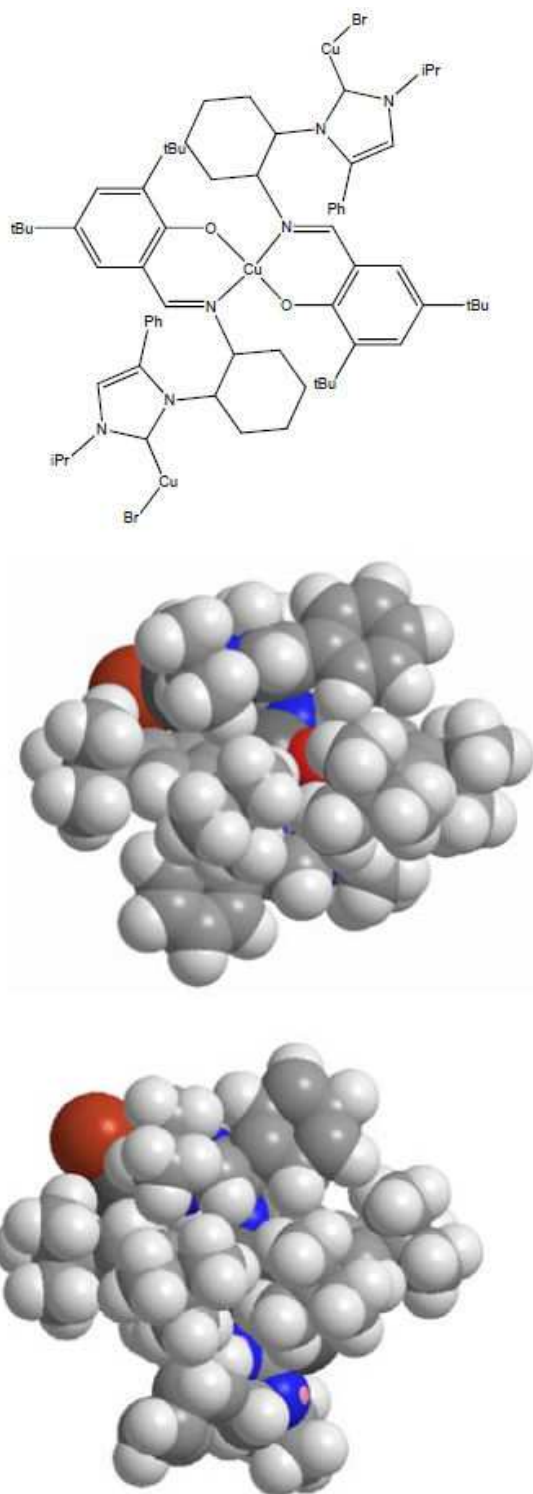
**Figure 9.** CCDC **MAJCUW** [23]. The compound has a formula  $C_{22}H_{24}Cl_4CuN_2O_2$ . Novel feature mentioned is that it has a compressed tetrahedral *trans*- $[CuN_2O_2]$  coordination environment with an umbrella conformation of the overall molecule. The absolute configuration is found to be (*S,S*) for the crystal examined. Molecular recognition for the chiral molecules could not be carried out using hydrogen bonding because of no possible hydrogen bonding sites in the crystal packing. Apparently conformational change was from an umbrella and twist form to a twist (about 45 degree) form.



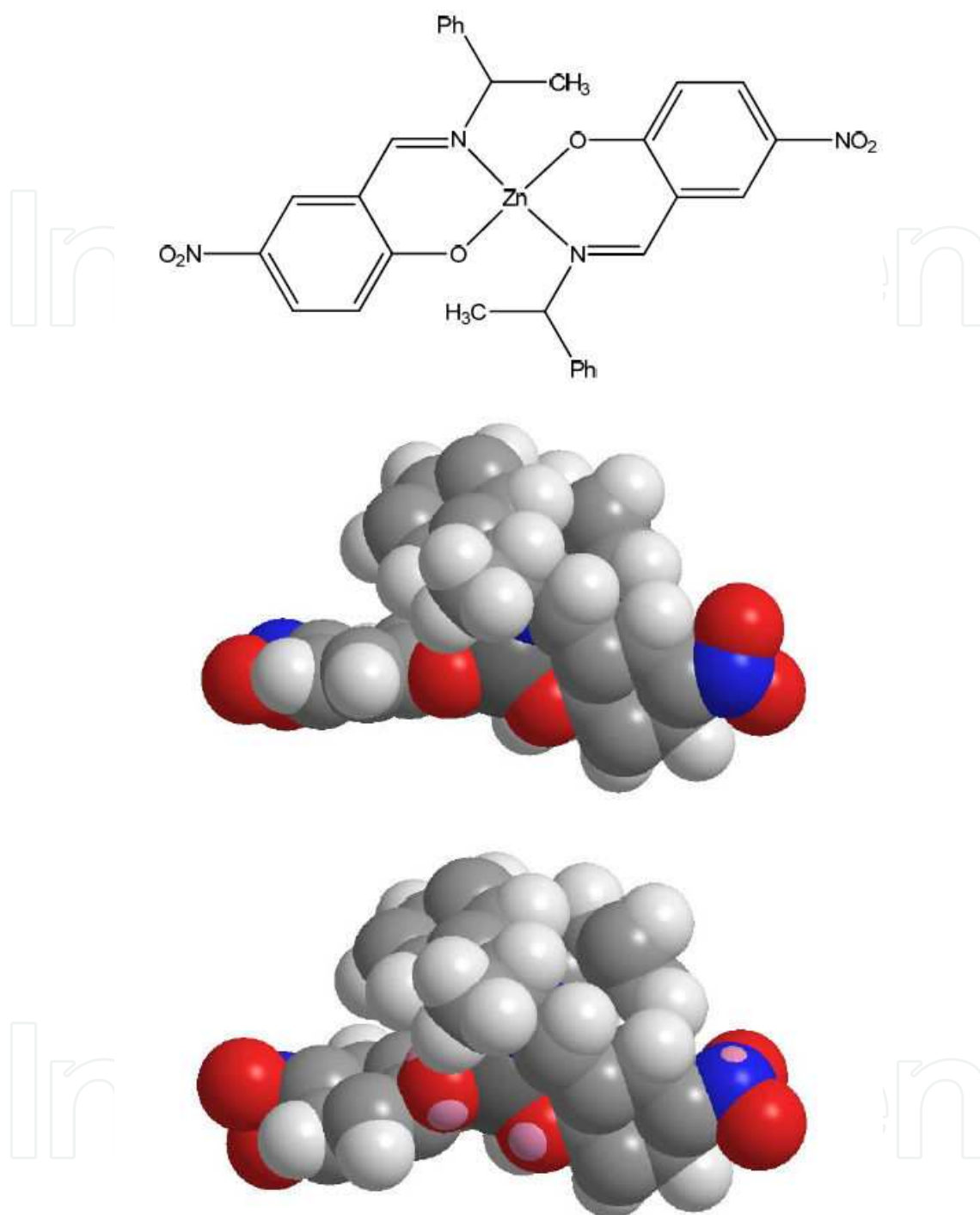
**Figure 10.** CCDC KUPBIH [24].The compound has a formula  $C_{30}H_{32}CuN_2O_2$ . Novel feature mentioned is that correlation between the bulkiness of the imine nitrogensubstituent, deformation of the copper coordination sphere is important and tBu group in the *N*-tBu derivative prevents such dynamic action. In the crystal, this *N*-tBu complex changes upon DFT geometry optimization to a more tetrahedralconfiguration. Apparently conformational change was from an umbrella and slightly twists form to an umbrella and twist (about 90 degree) form.



**Figure 11.** CCDC **KUPBON** [24]. The compound has a formula  $C_{26}H_{24}CuN_2O_2$ . Novel feature mentioned is that the coordination sphere of the N-ethyl derivative has a flat-tetrahedral geometry. The  $N-Cu-N$  and  $O-Cu-O$  angles and the dihedral angle between the planes  $N-Cu-O$  and  $N-Cu-O$  in the solid state found by X-ray diffraction in this study are affected by crystal packing forces according to these DFT calculations. Apparently conformational change was from a flat and square planar form to an umbrella and V-shaped form drastically.



**Figure 12.** CCDC YUBLAJ [23]. The compound has a formula  $C_{66}H_{88}Br_2Cu_3N_6O_2$ . Novel feature mentioned is that it appears that problematic deprotonation of the phenol to give a chelating or bridging ligand is the primary reason for the observed instability based on the stability of related copper NHC–aryl oxide compounds (including mixed valence Cu(I)/Cu(II) centers Cu(I) sites in ligands). Apparently conformational change was from a step and slightly twist form to an umbrella and twist (about 90 degree) form.



**Figure 13.** CCDC **METSUZ** [24]. The compound has a formula  $C_{30}H_{26}N_4O_6Zn$ . Novel feature mentioned is that it crystallizes in the noncentrosymmetric space groups. The geometry around the Zn(II) metalcenter is pseudo-tetrahedral with two oxygen and two nitrogen atoms from the ligands and has the  $\Lambda$  absolute configuration. Apparently conformational change was slight, namely it remained a twist (about 90 degree) from.

In principle, induced CD is caused by non-contact interactions between (electric) dipole moments of chiral additives and achiral materials. Because it is an electromagnetic phenomenon essentially, contact intermolecular interactions, in other words molecular recognition,

may not be an important factor for it. However, the experimental facts that only complexes with specific ligands or metal ions (which determine their coordination geometries) suggested that induced CD appears under appropriate steric (as well as stereochemical) conditions for metal complexes. One of the important factors of steric factors for metal complexes may be distance between (electric) dipole moments at the surface achiral materials which keep their shapes rigidly. The reason for this assumption is that both metallodendrimers metal and nanoparticles have approximately spherical shapes essentially even surrounded in softmaters.

As for biomolecules such as proteins, however, CD spectra are used for monitoring folding or unfolding of peptide chains after binding small molecules of metal complexes [25]. This different phenomenon is not classified into the induced CD mentioned in this article. By including small molecules into proteins with weakly supramolecular forces, molecules of proteins change their molecular conformation, which attributed to shift of strong  $\pi-\pi^*$  bands of C=O moieties electronic or CD spectra. This docking mechanism is directly molecular recognition accompanying with conformational changes of proteins as well as small molecules, which is also confirmed by quenching of fluorescence intensity due to energy transfer.

In contrast, non-contact interactions of (electric) dipole moments for CD spectra have complicated problems. Our preliminary results of CD spectra of chiral Schiff base metal complexes in viscous solutions dissolved a certain protein exhibited concentration dependence of so-called artifact peaks of solid-state CD spectra [26]. The artifact CD peaks are attributed to anisotropic molecular orientation and removed in matrix environment which permits molecular rotation isotropically accompanying with (magnetic) dipole moments of chiral molecules [27]. Therefore, not only CD spectra of chiral molecules in anisotropically oriented matrix such as biomolecules but also induced CD bands involving softmaters is still an open question.

## 4. Conclusion

As summarized in Figure 1[right], according to chemical structures, Zn(II) center and naphthylgroups are suitable factors for induced CD, while 3,5-dichlorosalicylaldehyde moieties are not regardless of common factors. Previous study [11] revealed that in optimized structure, naphthylgroups act as largely spread planar parts outside of a molecular face, which plays an important role in induced CD for this case. In the present study, compounds having identical features were also investigated in view of optimized structures. According to not only 3,5-dichlorosalicylaldehyde moieties (**IBHBCU01** and **MAJCUW**) but also tert-Bu-groups (**MIMTOS01** and **YUBLAJ**), EtO- groups (**MAJNIV**), and NO<sub>2</sub>- groups (**METSUZ**) gave significantly large steric hindrance resulting in steric repulsion between ligands. However, specific geometry could not be induced by bulky groups. Generally, Zn(II) complexes afford a tetrahedral coordination geometry, which prevents from forming flatten planar molecular shapes in view of ligands. Therefore, these two factors may not be definitive factors solely. On the other hand, besides in amine parts (Figure 1), naphthylgroups in aldehyde

parts (**KUPBIH** and **KUPBON**) are also keeping appropriate conditions, namely largely spread planar parts outside of a molecular face. As far as in the sense of molecular recognition, it has advantage for penetrating into inside of dendrimer as well as contacting to the surface of metal nano-particles. Further experimental and/or theoretical investigation including electric factors will be necessary to understand deeply.

## Author details

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