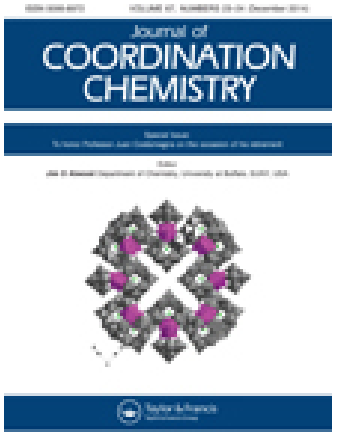

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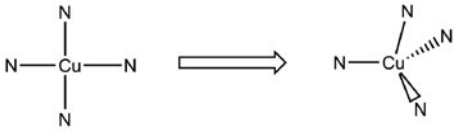

2 N-Cu-N (wide angle) = 130 degrees may favor Cu(II)/Cu(I) electron transfer

The Cambridge Crystallographic Database (CSD) shows $[Cu^{II}L_4]^{2+}$ complexes, L = acyclic amine, fitting well with theoretically calculated structures to describe a planar-to-flat tetrahedral transformation pathway. Statistically, the Cu^{II} "planar" coordination sphere shows two distinct sets of *trans* N–Cu–N bond angles, 180° and near 150°, with the latter somewhat energetically favored according to DFT results. The planar structure is not confirmed theoretically when an example of these molecules in the CSD is geometrically minimized, suggesting that crystallographic or packing forces help to generate the planar structure in the crystal. Results of energy calculations from DFT seem to explain this feature. Less planar and more tetrahedral examples in the CSD are also found and compare well with theoretically converged related molecules. *Trans* N–Cu–N bond angles near 130° seem feasible for both Cu^{I} and Cu^{II} coordination spheres. These copper complexes having the copper coordination sphere in a less tetrahedral geometry are suggested as potential alternative models for blue proteins, and they deserve further exploration.

Keywords: Tetrahedral planar configuration; DFT; Crystal structure; Blue protein; Packing forces

1. Introduction

Copper is an element of major importance in biology. For example, it is essential to all living organisms as a key participant of the respiratory complex, cytochrome c oxidase. In mollusks and crustacea, copper is a constituent of the hemocyanin oxygen transport protein,

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Dedicated to Professor Juan Costamagna who is an inspiration for coordination chemists

which is replaced by the iron-complexed hemoglobin in fish and other vertebrates. Decreased copper levels in *substantia nigra* of Parkinson's patients have been recently shown [1]. In biological electron transport, copper is electronically versatile due to its relatively easy Cu^{I}/Cu^{II} interconversion. This feature is of major importance for blue proteins which deal with long-range electron transport instead of reacting with molecular substrates, as common enzymes do. Therefore, the role of the copper is associated with variable oxidation states, suitable reduction potentials, and fast electron-transfer rates, while defining unusual coordination geometries.

Synthetic models try to mimic the typical distorted tetrahedral structures and reproduce some features observed in plastocyanin, the first blue protein whose structure was determined by X-ray crystallography [2]. The coordination sphere in the type I blue protein, CuN_2S_2, is formed by two histidine imidazoles, a cysteine thiolate and a methionine thioether, as exemplified by phytocyanin [3]. However, some blue proteins do not have the fourth methionine ligand at all, as in fungal laccases, while others, azurins, show an additional interaction from O(carbonyl). Various spectroscopic techniques have been used to describe the electronic structure of the metal center in comparison between model compounds and proteins [4–7] (for an extended list of references, see review by Comba [8]).

The Cu spatial arrangement in Cu proteins has attracted much scientific interest, and chelating ligands for copper are envisioned to model the biological properties of Cu. Research in the Juan Costamagna lab at the University of Santiago, Chile, has focused on the search for chelating ligands tailored for Cu coordination [9–13]. Some of these having Cu geometry in between tetrahedral and square planar [10] may be appropriated as initial models [14] for the blue copper proteins [15]. Characterization of these complexes in the Costamagna lab included determination of their electrochemistry, IR and UV–vis spectroscopy, and X-ray crystallography.

As a result of the wide interest shown by the scientific community on copper, in comparison with other biometals, Cu coordination complexes are among those mostly seen in the Cambridge Crystallographic Database (CSD), and such a large number of compounds allow a reliable statistical analysis to be performed. For many of these complexes, the chelating moiety constrains the metal to exist in an appropriate arrangement mimicking the protein environment [6, 16].

In this work, we wish to extend Prof. Costamagna's interest by attempting to understand the relationship between the structure and the activity of these Cu complexes, in both Cu(I) and Cu(II) oxidation states. To attempt a more extended geometrical investigation of Cu^{II} and Cu^{I} coordination spheres, a different approach is used here.

In this manuscript, we will compare crystallographic geometrical information, obtained from the CSD, with that calculated by us using DFT methods for a set of CuL_4 complexes, where L is an acyclic amine model; NH_3 related models have been used successfully to characterize the reduced state of blue proteins [17]. The advantage of non chelating acyclic donor ligands is the fact that, apart from their volume, they are relatively unhindered and can be useful to study a wide variety of geometries. There are 22 CuN_4 structures in the CSD.

2. Experimental

The theoretical study involved calculations using software programs from Accelrys [18]. Density functional theory code DMol3 was applied to calculate energy, geometry, and frequencies implemented in Materials Studio 7.0 (PC platform) [19]. We employed the double

numerical polarized basis set that includes all the occupied atomic orbitals plus a second set of valence atomic orbitals and polarized d-valence orbitals [20], and correlation generalized gradient approximation was applied in the manner suggested by Perdew–Burke–Ernzerhof [21]. The spin unrestricted approach was exploited with all electrons considered explicitly. The real space cut-off of 6 Å was imposed for numerical integration of the Hamiltonian matrix elements. The self-consistent field convergence criterion was set to the root-mean-square change in the electronic density to be less than 10^{-6} e Å^{-3}. The convergence criteria applied during geometry optimization were 2.72×10^{-4} eV for energy and 0.054 eV Å^{-1} for force.

Safety Note: Since perchlorates are mentioned in this work, we remind the reader that perchlorate salts are quite hazardous and should be handled with extreme care because of potential explosion.

3. Results and discussion

A question that arises when using CSD data is the following: are these solid-state structures *necessarily* equal in the solution state? In the case under study, for some of them, the answer is No. Thus, the triclinic compound tetrakis(S,S-diphenylsulfimide)-copper(II) bis(tetrafluoroborate), refcode BAJZAO, has also a second polymorphic crystal structure (monoclinic form), refcode BAJZAO01 in the CSD [22]. Comparing the two *trans* N–Cu–N bond angles in both structures, one sees a marked difference, 180°, for the triclinic species and 152.2° for the monoclinic one. A related question is: which one of these two solid-state structures is closer to that existing in solution, or is neither?

As mentioned earlier, the Juan Costamagna laboratory has attempted to characterize geometrically and electronically four-coordinate Cu^{II}/Cu^{I} complexes of varied configuration – planar *versus* flat tetrahedral geometry arrangements [10]. The complete transformation pathway between the normally found planar Cu^{II} coordination complexes of these N-chelating ligands and a tetrahedral equivalent Cu^{I} geometry can be described as follows: the *trans* angles N–Cu–N will decrease (range 180°–109.5°) and the N–Cu–N *cis* angles will increase (range 90°–109.5°) consistently. Table 1 shows theoretically calculated results for structures, where both *trans* angles were fixed and equal, along with the 22 related structures found in CSD.

From table 1, a perfect fit between the DFT calculated average *cis* angle and its corresponding experimental X-ray values is seen for decreasing *trans* N–Cu–N bond angles, and this behavior correlates with the transformation of a square-planar configuration to a tetrahedral one. This is associated with decreasing energy and the limit for such behavior is given by $[Cu(NH_3)_4]^{2+}$, with no imposed constraint, which converges to a minimum energy having both *trans* N–Cu–N angles of 157.6° and 157.3°. No structures are found in CSD for *trans* N–Cu–N bond angles lower than 130°. This is consistent with increasing energy of the system as angles approach tetrahedral geometry; for $[Cu(NH_3)_4]^{2+}$ having fixed *trans* N–Cu–N bond angles of 110° and 110°, the ΔE arrives at 6.9 kcal M^{-1}.

Data for both *trans* angles of the 22 structures found in the CSD, already shown in table 1, are depicted in figure 1 and clearly show two population sets, one having *trans* angles of 180° and the other near 150°. The triclinic form of tetrakis(S,S-diphenylsulfimide)-copper(II) bis(tetrafluoroborate), refcode BAJZAO [22] is in the 180° group of structures, while the monoclinic form BAJZAO01 belongs to the 150° group [22].

Table 1. Geometrically optimized structures of $[Cu^{II}(NH_3)_4]^{2+}$ using Dmol3 program intermixed with crystal data from CSD of formula CuL_4, L = acyclic amine ligand. DFT initial geometries have both *trans* angles fixed. They are displayed according to decreasing *trans* angles.

Refcode/DFT	[a]*Cis*1	[a]*Cis*2	[a]*Cis*3	[a]*Cis*4	[b]Fixed *trans*1	[b]Fixed *trans*2	[c]Calcd ΔE	[d]<*cis*>
[e]BAJZAO	91.5	91.5	88.5	88.5	180	180		90
BAJZES	91.4	91.4	88.6	88.6	180	180		90
DAXXEG	92.2	92.2	87.8	87.8	180	180		90
[e]EVUGAD01	90.5	90.5	89.5	89.5	180	180		90
LIQPOQ	92.3	92.3	87.7	87.7	180	180		90
[f]PEGVAZ	91.7	91.7	88.3	88.3	180	180		90
QUBMAB	92.8	92.8	87.2	87.2	180	180		90
RUMPUK	90.0	90.0	90.0	90.0	180	180		90
TIBWUX	91.0	91.0	89.8	89.0	180	180		90
UKIGUR	92.2	92.2	87.8	87.8	180	180		90
XAQTOA	91.1	91.1	88.9	88.9	180	180		90
DFT	**90.1**	**90.1**	**89.9**	**89.9**	**177**	**177**	**0.7**	**90**
DFT	**90.5**	**90.5**	**90.4**	**90.4**	**170**	**170**	**0.3**	**90.4**
DFT	**91.8**	**91.8**	**91.7**	**91.7**	**160**	**160**	**0**	**91.7**
[g]DFT	**93.3**	**92.6**	**91.6**	**91.3**	**157.6**	**157.3**	**0**	**93.0**
PEGVIH	97.4	96.3	89.8	87.4	156.6	152.9		92.7
PEGTOL	96.1	94.0	94.0	89.8	154.9	147.5		93.5
BAJZES	96.2	96.2	89.8	88.9	154.5	154.5		92.8
[f]PEGVAZ	96.2	96.2	89.0	89.8	154.3	154.3		93.0
PEGTUR	97.9	96.9	88.7	88.7	153.4	153.4		93.0
[f]YAKTUA	96.4	96.0	92.7	88.9	153.4	149.1		93.5
EVUFOQ	95.9	95.9	91.3	91.3	152.6	149.2		93.6
COZCOJ	94.2	93.4	93.1	92.7	152.4	151.6		93.4
[e]BAJZAO01	98.7	97.0	88.8	88.8	152.2	152.2		93.3
[e]EVUGAD	97.1	96.3	90.6	89.9	151.6	151.4		93.5
PEGVED	97.3	97.0	91.7	91.2	150.8	145.4		94.3
DFT	**93.9**	**93.9**	**93.8**	**93.8**	**150**	**150**	**0.2**	**93.8**
BAJZIV	97.7	97.6	91.2	90.2	149.6	148		94.2
DFT	**96.7**	**96.7**	**96.6**	**96.6**	**140**	**140**	**1.5**	**96.6**
XOGLUA	100.5	97.3	96.6	94.3	145.3	130.0		97.2
[f]YAKTUA	101.0	97.2	94.1	92.9	142.6	134.0		96.3
DFT	**100.2**	**100.2**	**100.2**	**100.6**	**130**	**130**	**2.1**	**100.3**
DFT	**102.0**	**102.1**	**102.5**	**102.6**	**125**	**125**	**5.3**	**102.3**
DFT	**89.9**	**90.0**	**130.9**	**131.5**	**110**	**110**	**6.9**	**110.6**

Notes: Rows of DFT data are bold face.
[a]DFT calculated *cis* N–Cu–N bond angles, or experimentally found in crystals.
[b]Fixed *trans* N-Cu–N bond angles, or experimentally found in crystals.
[c]DFT calculated delta energy (kcal M^{-1}), referred to the minimum energy found for the *trans* angle 157.6°.
[d]Average *cis* N–Cu–N bond angle.
[e]Two different crystalline cells.
[f]Two independent molecules in the unit cell.
[g]Minimum energy found for the *trans* N–Cu–N bond angle of 157° through no imposed constraints.

Representatives of both populations can occur even in the same crystal as seen in the tetrakis(S,S-diphenylsulfimide)-copper(II) cationic species (refcode PEGVAZ) [23], where the only changes, compared with BAJZAO, are replacing the counterion tetrafluoroborate by perchlorate plus diethyl ether and a monohydrate solvent. Both sets are within a short range of energy variation, about 0.7 kcal M^{-1} from DFT calculations, as shown in table 1. It is surprising that there are no reported crystal complexes between 180° and 156° *trans* angles. A further decrease of the *trans* N–Cu–N bond angle to below 130° becomes difficult as seen by the calculated ΔE increasing greater than 2.1 kcal M^{-1} with respect to the minimum energy for *trans* N–Cu–N bond angles 157° and 157°, as shown in table 1.

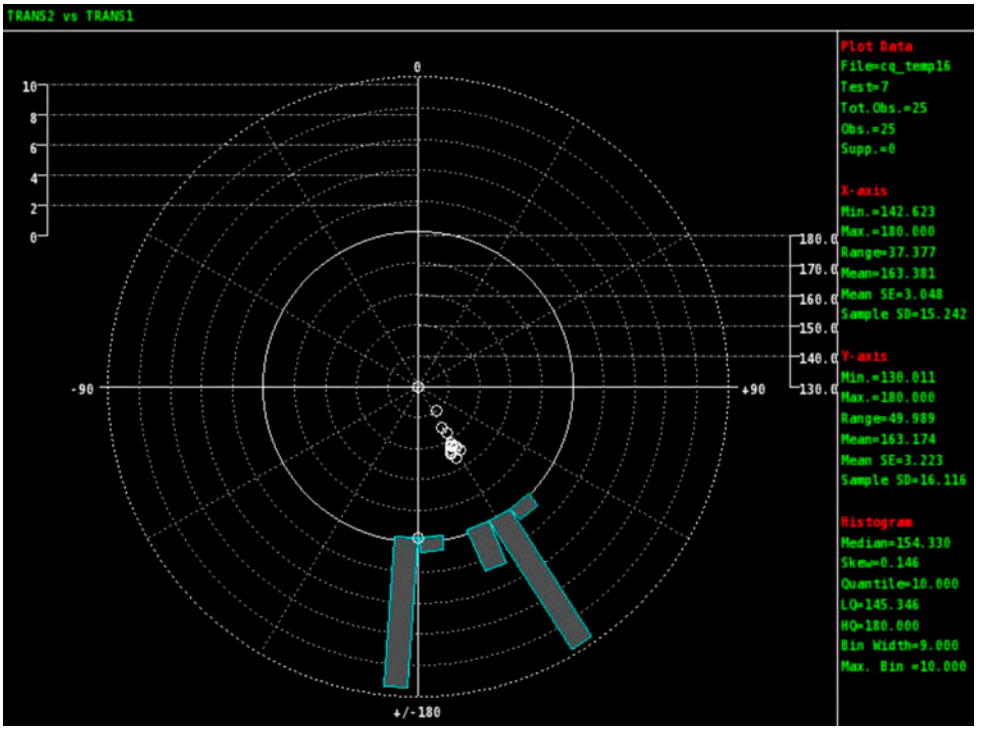


Figure 1. Polar scattergram of trans N–Cu–N bond angles taken from experimental data of 22 CSD crystal structures of table 1. Two populations are clearly distinguished, one having angles of 180° and other near 150°.

Table 2. Geometrically optimized structures of $[Cu^{I}(NH_3)_4]^+$ using Dmol3 program. DFT initial geometries had two N–Cu–N angles fixed, 1st and 2nd columns, except for the first row (*) where no constraints were imposed.

Fixed angle	Fixed angle	Calcd angle	Calcd angle	Calcd angle	Calcd angle	ΔE, kcal M^{-1}
*109.4	*109.8	108.8	109.3	109.7	109.8	0
120	120	103.7	104.1	104.9	105.3	0.6
130	130	100.1	100.2	100.3	100.6	2.1

Geometrical variation in the $[Cu^{I}(NH_3)_4]^+$ reduced coordination sphere is shown in table 2 using DFT methods; scheme 1 is shown for better visualization of the path of geometry transformation. Delta energy in table 2 seems to indicate that angles much wider than 130° are not favored. However, a common area near 130° seems feasible for Cu^{I} and Cu^{II} species. In the crystal structure of the blue protein, phytocyanin [3], the CuN_2S_2 system (two imidazoles, one cysteine, and one methionine in the coordination sphere) has bond angles in the coordination sphere consistent with our calculations in table 2, but seems far removed from the Cu^{II}-related area in table 1. It is well known that there is slight angular variation in bond angles for both, oxidized (blue) and reduced (colorless) blue proteins. Although initial considerations assigned this scarce angular variation to the entatic environment due to the polypeptide chain, later studies showed that the Cu–S(Cys) bond length is considered responsible for blue protein electron transfer features [24–26]. Therefore, our system, which

replaces two S by two N atoms, is unsatisfactory as a model for the conditions found in the blue protein.

The coexistence of both Cu^{II} and Cu^{I} coordination spheres is an important factor for blue proteins, as a slight change in coordination sphere is seen for both oxidized Cu^{II} and reduced Cu^{I} forms. From this study, it seems that the *trans* N–Cu–N angular area near 130° is feasible for both electronic states. Through synthesis of appropriate ligands regulating the coordination sphere geometry, the common *trans* angle area could be reached and facilitate electron transfer.

Furthermore, in trying to answer our original question (which polymorphic structure, the triclinic BAJZAO or the monoclinic BAJZAO01, table 1, resembles that existing in solution?) we used the X-ray coordinates of BAJZAO to run a DFT geometrical optimization. For this square planar triclinic form, the two initial N–Cu–N *trans* angles of 180° were slightly modified and the calculation converged to a structure having both trans angles of 174°. Due to the large number of atoms in BAJZAO, the frequency calculation, necessary to verify if the converged structure was indeed minimum, could not be completed; in other words, a further decrease in the *trans* N–Cu–N angles cannot be excluded. However, the fact that the planar configuration was not stable under this geometry optimization suggests that crystallographic or packing forces are important in determining BAJZAO planarity in the crystal.

We conclude that due to a low variation in energy, as shown in table 1, $[Cu^{II}N_4]^{2+}$ molecules in the crystal may become subject to packing effects which are able to modify the angular parameters in the coordination sphere. A similar analysis applied to $Cu^{II}[N_2S_2]^{+}$ complexes should provide better results than the here studied $Cu[N_4]^{2+}$ system for blue proteins. Unfortunately, there is only one structure catena-(μ_2-(isothiocyanato-S,S)-(bis(2-pyridyl)amine-N,N′)-copper[I]) [27] fulfilling this condition, and thus no statistical data from the CSD can be compared with DFT calculated structures of $Cu[N_2S_2]$ models. A potential explanation for this lack of information is difficult for the synthesis of good coordination sphere models for blue proteins due to the Cu^{II}–S(thiolate) bond tendency to reduce to Cu^{I} with formation of disulfide.

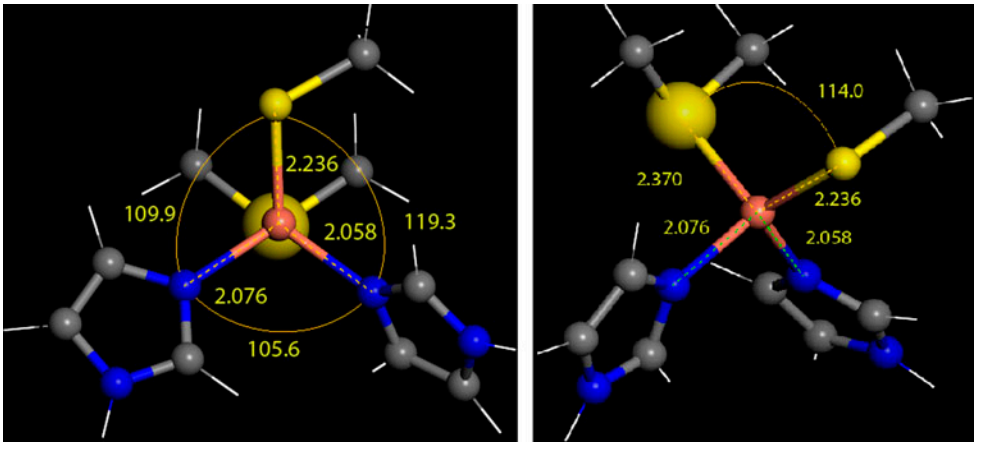
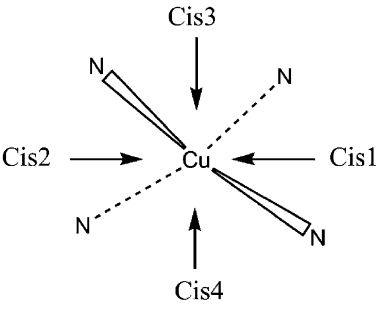


Figure 2. Geometry optimization for a model of the active site of blue proteins {CuII(imidazol)2(CH3S)[(CH3)2S]}$^{+}$ where CH3S and (CH3)2S replace cysteinato and methionine, using initial atomic coordinates from ref. [3]. The left view depicts a projection on the Cu–S(ether) bond, showing a long S(ether) radius for clarity.



Scheme 1. Scheme indicating the six bond angles described in table 1; they are two *trans* angles: N–Cu–N, dashed and perspective lines, and four *cis* angles, *Cis*1, *Cis*2, *Cis*3 and *Cis*4.

Table 3. Cu(imidazole)$_2$(CH_3S)[$(CH_3)_2S$] model of blue proteins in water, first row, compared with phytocyanin (2CBP), 2nd row, and plastocyanin (2Q5B) solved at high resolution.

Cu–N1	Cu–N2	Cu–Sm	Cu–Se	N1–Cu–N2	N1–Cu–Sm	N2–Cu–Sm	Se–Cu–Sm	
2.058	2.076	2.236	2.370	105.6	109.9	101.0	114.0	Mod
1.93	1.95	2.16	2.61	99	110	138	110.6	2CBP
2.08	2.05	2.25	2.61	100	115	126	115	2Q5B

Finally, a geometry optimization was performed using coordinates of the blue protein phytocyanin active site [3], and results shown in figure 2 indicate some increase in Cu–S (mercapto) and both Cu–N bond lengths, along with the contraction of Cu–S(ether), as shown in table 3. However, this calculated coordination sphere shows excellent agreement with the active site of plastocyanin from *Phormidium laminosum* at high resolution [28], as shown in table 3, except for the Cu–S(methionine) bond in the protein which is longer than Cu–S(ether) in our model. In the PDB database, blue proteins show that bond having variable and longer length than Cu–S(Cys) is probably influenced by entatic features, and such a condition cannot be accounted for in a DFT calculation. The nature of metal–thiolate bonding has been recently investigated and discussed [29].

4. Conclusion

Geometry-optimized Cu^{II} complexes, when compared with experimental CSD diffraction data, fit well in the theoretical path of transformation from square-planar to tetrahedral configuration. Statistically, the Cu^{II} coordination sphere has two different sets of N–Cu–N *trans* angles, 180° and near 150°, with the latter slightly favored energetically according to our DFT results. Chelating ligands can mimic spatial conditions for the Cu coordination sphere, but in copper blue proteins, the constraints are not due to chelating ligands, rather the polypeptide chain displaying entatic features from non-chelating amino acid donors. An alternative situation showing the most favored conditions for theoretically studied Cu^{II} and Cu^{I} compounds CuL_4, L = acyclic amine having *trans* N–Cu–N bond angles about 130°, is envisioned. These bond angles seem feasible for both Cu^{I} and Cu^{II} environments and since similar Cu^{I} and Cu^{II} coordination spheres are required for the function of the blue proteins,

they are suggested as a novel option for the geometry needed for electron transfer and worthy of exploration through appropriate chelating ligands. We point out that these angles are wider than those found in the blue proteins.

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