DFT and TD-DFT studies on copper(II) complexes with tripodal tetramine ligands

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Copper(II) complexes, containing aliphatic tripodal tetramine ligand, $[Cu(trpn)(NH_3)]^{2+}$ **(1)**, $[Cu(tren)(NH_3)]^{2+}$ **(2)**, $[Cu(332)(NH_3)]^{2+}$ **(3)** and $[Cu(322)(NH_3)]^{2+}$ **(4)** are optimized at B3LYP/ LANL2DZ and B3LYP/GEN levels of theory in gas phase (where (trpn), (tren), (332) and (322) are $N(CH_2CH_2CH_2NH_2)_3$, $N(CH_2CH_2NH_2)_3$, $N[(CH_2CH_2CH_2NH_2)_2(CH_2CH_2NH_2)]$ and $N[(CH_2CH_2CH_2NH_2)(CH_2CH_2NH_2)_2]$, respectively). The optimization results show that the copper(II) center is trigonal bipyramidal for the studied complexes. Charge distributions on the donor and acceptor atoms are evaluated by natural population analysis. The charge distribution indicates that the ligands transfer their negative charges to copper(II) ions during formation of the complexes. Electronic excitation energies of copper(II) complexes are calculated with time dependent density functional theory in gas phase. It is found that the most intense bands at electronic spectra of complexes stem from $d_{xz}, d_{yz} \rightarrow d_z^2$ or $d_{x^2-y^2}, d_{xy} \rightarrow d_z^2$ transitions.

Iron, zinc and copper ions are the most common transition metal ions in biological systems[1, 2]. Copper has a significant role in biological systems as an essential trace metal or a constituent of complexes. The role of copper in biological systems is well reported[3-5] and the involvement of copper has been described from medical, chemical[6] and biochemical perspective[7], focusing on the molecular physiology of copper transport[8]. A number of binary copper(II) chelate complexes with Schiff base ligand exhibit biological activities such as anticancer[9-12], antibacterial[13-20], anti inflammatory[12], chemical nucleases[14,15] and apoptosis inducer[21,22].

Copper complexes with tripodal tetramine ligand (TT) have been synthesized by Duggan *et al.*[23] and Andreas *et al.*[24] The structures of complexes have been determined by X-ray difraction methods and are reported to have trigonal bipyramidal geometry. It is

reported that copper complexes with TT ligand might lead to very reactive tetrahedral Cu(I) complexes which react rapidly with dioxygen. Copper complexes with TT ligand (Fig. 1) have been used to model the active site in copper proteins containing dicopper center such as hemocyanin[25]. Although the action of copper in biological systems has been intensively investigated, the clinical picture of copper complexes is not always so straightforward, and less is known about the role of copper complexes in medicine.

Compared with the copper complexes containing Schiff base ligands, less is known about the coordination chemistry of copper complexes with TT ligand. The purpose of the present study is to investigate the coordination chemistry of copper complexes with the TT ligands (Fig. 1) by using density functional theory (DFT), and, time dependent density functional theory (TD-DFT) calculations.
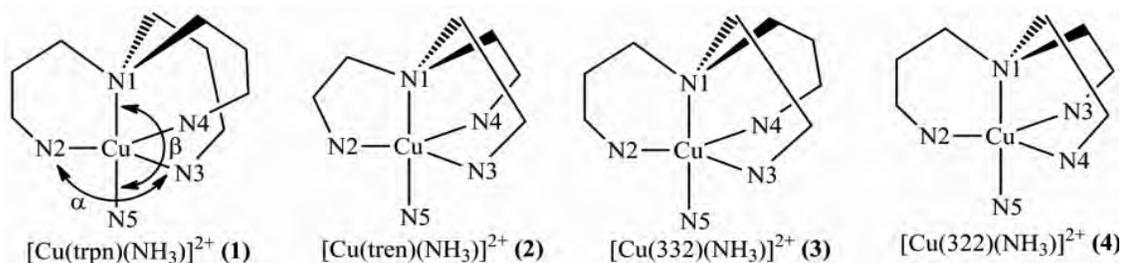

Fig. 1 – Schematic structures of copper(II) complexes.

Molecular geometries for copper(II) complexes with TT ligand have been investigated by using B3LYP method with LANL2DZ and GEN basis sets. NPA atomic charge distributions on complexes and on donor atoms of ligands are calculated at the B3LYP/LANL2DZ level. Electronic excitation energies for mentioned complexes have been obtained by using TD-DFT/B3LYP method with LANL2DZ basis set in gas phase.

Methodology

The input files of the copper(II) complexes were prepared with GaussView 5.0.8[26]. All calculations were made using Gaussian 09 rev. A.02[27] by the DFT/B3LYP method. LANL2DZ and 6-31G(d,p) are the standard basis sets. 6-31G(d,p) is a popular polarized basis set which adds p functions to hydrogen atoms in addition to the d functions on heavy atoms, while LANL2DZ is a basis set for post-third-row atoms. This basis set uses effective core potentials in calculations. In this study, we used a standard basis set and a mix basis set. In the first step, the geometries were fully optimized at the B3LYP/LANL2DZ level for all atoms in the gas phase[28-30]. In the second step, the geometries were fully optimized at the B3LYP/GEN level by using 6-31G(d,p) basis set for H, C, N atoms and LANL2DZ basis set for Cu atom in the gas phase[31]. GEN is a keyword which combines 6-31G(d,p) and LANL2DZ standard basis sets. The analyses of vibrational frequencies indicated that optimized structures of complexes were at stationary points corresponding to local minima without imaginary frequencies. There are different methods for determining the charge distributions of atoms in compounds, one of which is natural population analysis (NPA). The NPA were made at the B3LYP/LANL2DZ level. The electronic spectrum was predicted by calculating the excitation energies between the states. Electronic spectrum calculations of the complexes were made by using time dependent density function theory (TD-DFT)/B3LYP method with LANL2DZ basis set in gas phase[32].

Results and Discussion

Geometry optimization

Copper(II) complexes were optimized at B3LYP/LANL2DZ and B3LYP/GEN levels in gas phase. Figure 2 shows the optimized molecular structures and atomic numbering scheme for complexes **(1)** and **(2)**. Some structural parameters of these complexes are listed in Table 1.

As can be seen from Table 1, acceptable results were obtained by DFT/B3LYP method with LANL2DZ and GEN basis sets for complexes **(1)** and **(2)**. Calculated values of bond angles obtained by using B3LYP/LANL2DZ level are more appropriate than the B3LYP/GEN level. Therefore, DFT/B3LYP/LANL2DZ level was preferred to B3LYP/GEN level for determining the molecular structure. The largest differences of bond angles were taken into account for determining agreement between experimental and theoretical structures. The largest difference between experimental and theoretical values (i.e., 9.5°) is observed for the N3-Cu-N4 bond angle. Molecular geometries can be predicted by calculating valueϵ, from Eq. (1)[33],

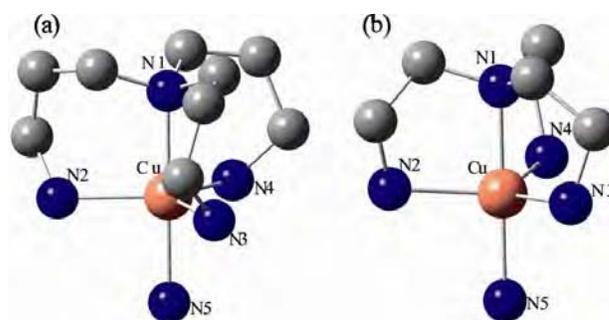$$= \frac{-}{60} \qquad \qquad \ldots(1)$$

Fig. 2 – The optimized structures of (a) complex (**1**) and (b) complex (**2**). [Hydrogen atoms are omited for clarity].

Table 1 — Selected bond lengths (Å) and angles (deg.) for complexes (**1**) and (**2**)

	Complex (**1**)			Complex (**2**)		
	LANL2DZ	GEN	Expt.	LANL2DZ	GEN	Expt.
Bond lengths (Å)						
Cu-N1	2.127	2.139	2.060	2.090	2.105	2.041
Cu-N2	2.179	2.189	2.074	2.168	2.153	2.082
Cu-N3	2.183	2.191	2.117	2.168	2.150	2.082
Cu-N4	2.185	2.189	2.108	2.169	2.151	2.082
Cu-N5	2.142	2.153	2.066	2.081	2.046	2.023
Bond angles (deg.)						
N1-Cu-N2	91.7	91.2	90.7	84.6	83.7	84.9
N1-Cu-N3	91.6	91.2	92.7	84.6	83.8	84.9
N1-Cu-N4	91.7	91.2	90.1	84.6	83.8	84.9
N1-Cu-N5	179.9	179.9	176.6	180.0	179.9	-
N2-Cu-N3	120.1	119.6	122.2	119.1	118.6	119.2
N2-Cu-N4	120.3	119.9	127.9	119.1	118.7	119.2
N2-Cu-N5	88.3	88.8	87.2	95.4	96.3	95.1
N3-Cu-N4	119.3	120.3	109.8	119.1	119.2	119.2
N3-Cu-N5	88.4	88.9	90.6	95.4	96.1	95.1
N4-Cu-N5	88.3	88.7	89.2	95.4	96.2	95.1

Experimental values taken from Refs 23 and 24.

where   and   are the equatorial and axial bond angles, respectively shown in Fig. 1. If the molecular geometry is trigonal bipyramidal,   must be 1. If the geometry is square pyramidal,   must be 0. If   is between 0 and 0.5 the molecular geometry is distorted square pyramidal, while   between 0.5 and 1 indicates that the molecular geometry is distorted trigonal bipyramidal. For complex (1),   (N2-Cu-N3) is equal to 120.1 and   (N1-Cu-N5) is equal to 179.9. From these bond angles,   value was calculated to be 0.996. For complex (2),   (N2-Cu-N3) is 119.1 and   (N1-Cu-N5) is 180.0, giving the   value as 1.01. For complex (1) and (2), the values of   is equal to about 1. These results show that the copper(II) center is trigonal bypiramidal geometry.

The two Cu-N bond lengths, (Cu-N1 and Cu-N5), are shorter than the three Cu-N bond lengths in trigonal bipyramidal complexes. The shorter Cu-N bonds are present in the axial position and the longer Cu-N bonds in the equatorial position. This is contrary to Bent's rule[34]. However, the axial and equatorial bond lengths are interesting in trigonal bipyramidal complexes. In the most of the trigonal bipyramidal complexes, the equatorial bonds are longer than axial linkages[35], which can be explained by hybridization. While trigonal bipyramidal complexes have dsp^3 hybrid orbitals, trigonal bipyramidal compounds of main elements have sp^3d hybrids. The dsp^3 hybrid orbitals occur from $(n-1)$ d, ns and np orbitals whereas the sp^3d hybrid orbitals comprise ns, np and nd orbitals. Since $(n-1)$ d orbitals in trigonal bipyramidal complexes are closer to the nucleus than the nd orbitals, the axial bond distances are shorter than the equatorial bonds. Although the calculated bond distances for complexes (1) and (2) are longer than the experimental values, the calculated results are acceptable, since the differences between theoretical and experimental values of bond lengths are generally less than 0.1 Å.

Figure 3 shows the optimized molecular structure of complexes (3) and (4) with atomic numbering scheme. The selected optimized geometric parameters of the complexes are listed in Table 2.

As can be seen from Table 2, the B3LYP/LANL2DZ level is more appropriate to calculate bond angles and bond distances than the B3LYP/GEN. Therefore, B3LYP/LANL2DZ level was preferred to B3LYP/GEN level. For complex (3), the largest difference between experimental and

theoretical bond angles is for the N3-Cu-N4 bond angle (3.8°). For complex (4), the biggest difference between experimental and theoretical values is for the N2-Cu-N3 bond angle (6.1°). For complex (3),   (N2-Cu-N3) is equal to 106.7° and   (N1-Cu-N5) is equal to 170.9°. From these bond angles,   value was calculated as 1.07. For complex (4),   (N2-Cu-N3) is equal to 107.8° and   (N1-Cu-N5) is equal to 174.1° and   value is calculated as 1.10. For complex (3) and (4), the values of   is equal to ~1.0, indicating that the copper(II) center is trigonal bipyramidal geometry for complexes (3) and (4).

There is no equality in equatorial bond distances and axial bond distances due to asymmetric ligands in complexes (3) and (4). The calculated Cu-N distances are longer than experimental values. For all copper complexes, the central nitrogen atom of the tetramine
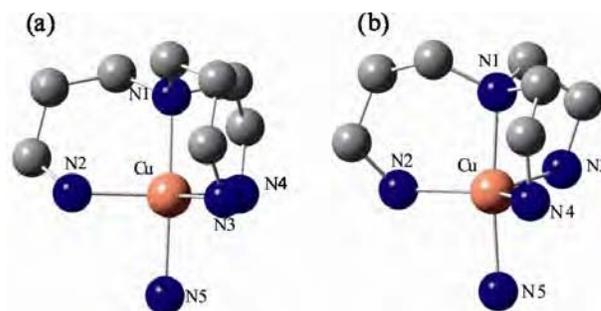

Fig. 3 – The optimized structures of (a) complex (3) and (b) complex (4). [Hydrogen atoms of ligands are omited for clarity].

Table 2 — Selected bond lengths (Å) and angles (deg.) for complexes (3) and (4)

	Complex (3)			Complex (4)		
	LANL2DZ	GEN	Expt.	LANL2DZ	GEN	Expt.
Bond lengths (Å)						
Cu-N1	2.107	2.138	2.078	2.108	2.125	2.064
Cu-N2	2.114	2.116	2.045	2.142	2.145	2.069
Cu-N3	2.246	2.230	2.191	2.226	2.185	2.153
Cu-N4	2.139	2.127	2.047	2.141	2.129	2.037
Cu-N5	2.133	2.090	2.022	2.110	2.071	1.993
Bond angles (deg.)						
N1-Cu-N2	91.1	92.9	90.5	95.3	96.0	92.8
N1-Cu-N3	95.2	94.4	93.1	84.1	83.3	83.9
N1-Cu-N4	84.8	83.9	84.6	84.9	84.3	84.7
N1-Cu-N5	170.9	172.2	171.4	174.1	173.3	175.3
N2-Cu-N3	106.7	108.8	108.0	107.8	111.3	101.7
N2-Cu-N4	148.1	143.7	150.5	134.7	128.3	140.4
N2-Cu-N5	90.0	90.1	89.9	90.6	90.6	91.5
N3-Cu-N4	105.1	107.6	101.3	117.3	120.0	117.2
N3-Cu-N5	93.1	91.4	95.0	93.7	93.0	97.3
N4-Cu-N5	89.4	89.4	90.9	91.2	92.8	90.7

Experimental values taken from Ref. 24.

Table 3 — NPA atomic charge disributions for complexes and donor atoms of free ligands

Atoms	Complex (**1**) Comp.	Lig.	Complex (**2**) Comp.	Lig.	Complex (**3**) Comp.	Lig.	Complex (**4**) Comp.	Lig.
Cu	+0.950	-	+0.914	-	+0.940	-	+0.926	-
N1	–0.554	–0.587	–0.554	–0.579	–0.560	–0.591	–0.556	–0.594
N2	–0.938	–0.949	–0.935	–0.974	–0.922	–0.931	–0.932	–0.931
N3	–0.938	–0.949	–0.935	–0.974	–0.949	–0.951	–0.943	–0.930
N4	–0.938	–0.949	–0.935	–0.973	–0.922	–0.949	–0.931	–0.952
N5	–1.108	–1.168	–1.102	–1.168	–1.108	–1.168	–1.104	–1.168

ligands and ammonia nitrogen atom were located on the axial position and the other nitrogen atoms were located on equatorial position. If there is an agreement between theoretical and experimental bond lengths and angles, it indicates that other properties of mentioned complexes can be explained theoretically. The results show that there is a good agreement between theoretical and experimental structures. Therefore, the atomic charge and electronic spectrum calculations can be made theoretically.

Atomic charge analysis

Atomic charge distributions on donor-acceptor atoms of the studied complexes and donor atoms of free ligands were calculated at B3LYP/LANL2DZ level of theory. Charge distributions between donor atoms of ligands and acceptor atoms of complexes were evaluated by natural population analysis (NPA) in gas phase. The charge distribution results are listed in Table 3.

Comparing the atomic charges in Table 3, it can be seen that the electron density of the donor atoms in the complexes decreased as compared to that in the free ligand, whi_ the electi_.n density __ copper(II) cation increased. For instance, before complexation, the charge on copper is +2, while the charge of the copper in complexes (**1**) is +0.950. This indicates that ligands transfer their negative charges to copper(II) ions during formation of the complexes. In addition, the electron density of copper increases in the order: (**2**) > (**4**) > (**3**) > (**1**). This result shows that the tren ligand has better donor atoms than the other ligands and the increase in number of carbon atoms between the nitrogen atoms in the ligand chain decreases transfer of charge.

Electronic spectra

Electronic excitation energies of the studied complexes were calculated by using TD-DFT/B3LYP method with LANL2DZ basis set in gas phase.

Table 4 — Electronic excitation energies (nm) and the oscillator coefficient of the most intense bands

Complexes	Excitation energy (nm)	Oscillator strength
$[Cu(trpn)(NH_3)]^{2+}$ (**1**)	355.2	0.1223
$[Cu(tren)(NH_3)]^{2+}$ (**2**)	338.3	0.0984
$[Cu(332)(NH_3)]^{2+}$ (**3**)	340.4	0.0902
$[Cu(322)(NH_3)]^{2+}$ (**4**)	341.8	0.1043

Table 5 — The contributions of $3d$-atomic orbitals to 63-67 molecular orbitals

	63	64	65	66	67
d_z^2	0.28620	0.30410	0.58304	–0.08915	–0.39592
$d_{x^2-y^2}$	0.16988	0.17102	0.32814	–0.05659	0.69650
d_{xy}	0.30111	0.64965	–0.41080	0.22647	–0.00098
d_{xz}	0.65430	–0.29982	–0.22007	–0.40820	–0.00805
d_{yz}	0.34303	–0.33688	0.11016	0.66903	0.00136

Electronic excitation energies and the absorption coefficient of the most intense bands are given in Table 4.

The α and β frontier orbitals containing unpaired electrons are present in the complexes. Frontier orbitals of studied complexes are found to be similar. HOMO-1, HOMO, LUMO and LUMO+1 orbital surfaces and energies for complex (**1**) are given in Fig. 4.

A band with large osciclator coefficient for complex (**1**) appears at 355.2 nm. This band comprises the 63 →67 (0.15692) and 64 →67 (0.98053) electronic transitions (coefficients of the wave function for each transition are given in parentheses). The 67 orbital is LUMO, whereas 63 and 64 orbitals are HOMO-3 and HOMO-2, respectively. The contributions of $3d$-atomic orbitals to 63-67 molecular orbitals are given in Table 5.

As can be seen from Table 5, the highest contribution to the 67 orbital is from the $d_{x^2-y^2}$ and d_z^2 orbitals of copper(II) ions, while that to the 63 molecular orbital is from the d_{xz}, d_{yz} and to 64 orbital it is from d_{xy}, d_{yz} orbitals. According to Krishnamurthy and Schaap[36], energy ranking of d-orbitals at trigonal bipyramidal geometry are $d_{xz} = d_{yz} < d_{xy} = d_{x^2-y^2} < d_z^2$. In the present case, the band at 355.2 nm can be said to occur due to the d_{xz}, $d_{yz} \rightarrow d_z^2$ or $d_{x^2-y^2}$ and $d_{xy} \rightarrow d_z^2$ transitions. This prediction is consistent with prediction in the literature[37]. A similar prediction can be made for other studied complexes.
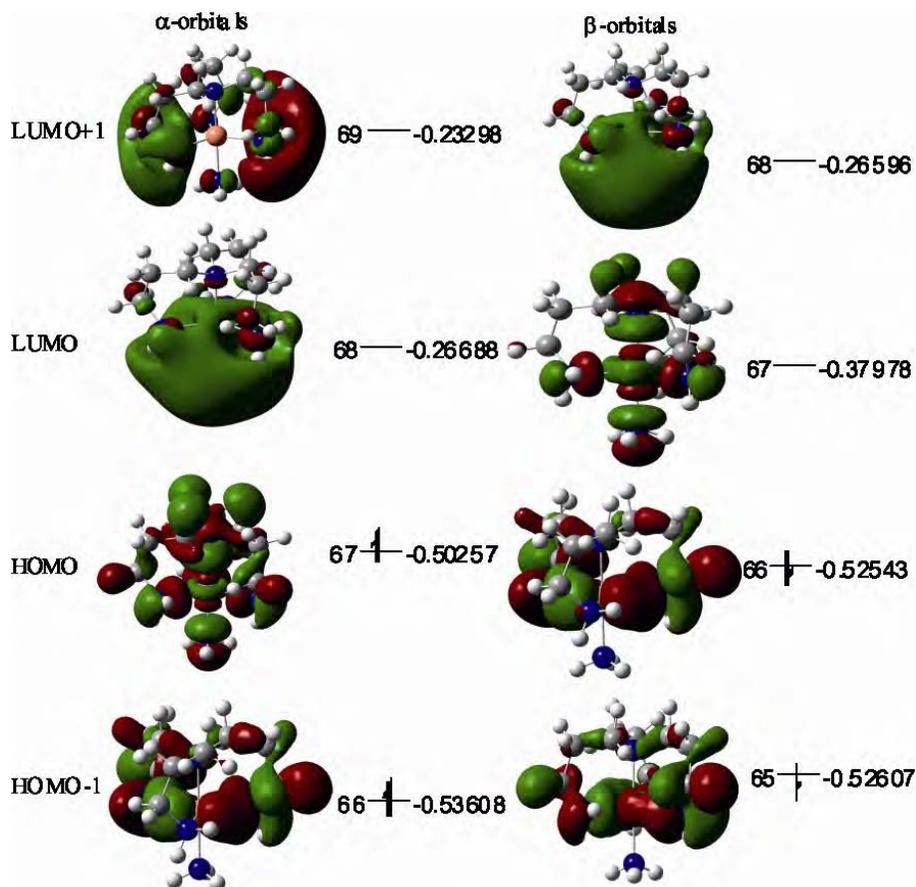
Fig. 4 – HOMO-1, HOMO, LUMO and LUMO+1 orbital surfaces and energies for complex (**1**).

Conclusions

Ab inito calculations were performed on the copper complexes by DFT/B3LYP method with LANL2DZ basis set. Bond lengths and angles were calculated and are in a good agreement with the experimental results. Electronic structures of the complexes were determined using   values calculated for each copper complex. Charge distributions of the complexes were evaluated by using natural population analysis in gas phase. Natural population analysis show that nitrogen atoms in ligand have transferred their electron to the Cu(II) cation during formation of the complexes. Electron density of copper increases in the order: (**2**) > (**4**) > (**3**) > (**1**). Electronic excitation energies of complexes were calculated by TD-DFT/B3LYP method with LANL2DZ basis set in gas phase. It was found that the most intense bands at electronic spectrum of complexes stemmed from d_{xz}, $d_{yz} \rightarrow d_z^2$ or $d_{x^2-y^2}$, and $d_{xy} \rightarrow d_z^2$ transitions.

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