

Research Article

Structural Analysis and Reactivity of Tetramethylcopper(III) Complex towards Nitrogen Donor Ligands by Density Functional Theory

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DFT studies are carried out on some ligand substitution reactions of tetramethylcuprate(III) (TMC) complex with five different nitrogen donor ligands as probe ligands. The geometry optimization of the possible nine model systems and the frequency calculations are carried out at DFT level using LANL2DZ basis set. The selected structural parameters of optimized model systems of Cu(III) complexes are reported and discussed. The change in the M-C bond distance in TMC due to substitution by probe ligands is explained. Natural population analysis (NPA) has been carried out for these complexes to establish the charge of copper in these complexes. A detailed population analysis of valence orbitals of copper complexes supports the existence of d^8 configuration for metal in complexes and there is evidence for the transmission of electrons from the nitrogen donor atom to d_{xy} , $d_{x^2-y^2}$, and 4s orbitals. Bond order calculations have been performed for all the complexes to probe the interaction between Cu(III) and the ligand. The stability of the complexes is ascertained from the computed chemical hardness. In order to understand the nature of Cu(III)-L (L = N donors) and Cu(III)-Me bonds in different complexes, Energy Decomposition Analysis (EDA) has been carried out for all the complexes chosen in the theoretical study. Thermodynamic feasibility of these reactions is investigated in terms of free energy changes of these reactions.

1. Introduction

The coinage metal copper is listed in group 11 in the periodic table and it occurs in a range of oxidation states [Cu(0), Cu(I), Cu(II), Cu(III), and Cu(IV)]. Copper ions in these oxidation states form complexes. Copper complexes in the oxidation states +1, +2, and +3 are more common than complexes of Cu(0) and Cu(IV). The Cu(III)-alkyl complexes are used for the effective C-C bond formation at low temperatures [1–5] and several Cu(III)-alkyl intermediates have also been characterized by Rapid Injection NMR technique [6–11]. Theoretical studies have been carried out to understand the stability and reactivity of Cu(III)-alkyl complexes [12–16]. Bertz et al. reported the efficient preparation of copper(III)

intermediates by using Gilman reagents (Me_2CuLi , LiX where X = Br, I) with 2,3-dichloropropene [17, 18]. Recently, Bertz and Ogle investigated ligand exchange reactions of CuMe_4 with Br^- , CN^- , Ph_2Li , IMH, Cl_2O , and $\text{Li}^+\text{S}^-\text{Ph}$ for selective C-C bond formation [18]. Gärtner et al. studied the ligand exchange reactions of trimethyl copper(III) with I^- , Me^- , MeS^- , Cl^- , and CN^- by DFT method [19]. Some neutral organocopper(III)-alkyl complexes have also been reported by the ligand exchange reaction with PMe_3 , PBu_3 , P(OMe)_3 , PPh_3 , Py, DMAP, MI, MIB, and DBN [13, 19]. The most notable applications of organocopper reagents are the addition to α,β -unsaturated carbonyl compounds and their substitution reactions with organic halides [20–22]. The formation of C-C bond in these reactions was proposed to

be mediated by Cu(III) intermediate and further supported by theoretical studies [12, 15, 16]. However, other reactivity studies such as substitution reactions have not been reported on the ligand substitution reactions of Cu(III)-alkyl complexes with ligands containing different donor atoms. Density functional theory (DFT) calculations showed that the methyl anion is a strong σ -donor ligand that affords the largest stabilization energy in comparison to halides, thiolate and cyanide anions [19]. In this paper, we report the results obtained in the theoretical investigation of some substitution reactions of TMC complex with nitrogen containing ligands being reported and discussed. In the present study the ligands used are all negative ligands (N^{3-} , NH_2^- , $^-\text{NHCH}_2\text{-CH}_2\text{NH}^-$, $^-\text{NHC}_6\text{H}_4\text{NH}^-$, and NH_2^-) so that they are strong enough to substitute methyl group in TMC complex. Natural population analysis and bond order calculations have been performed for all the complexes to establish the charge on the metal atom and understand the metal ion–ligand interactions in these complexes. The feasibility of these ligand substitution reactions is investigated in terms of computed free energy changes.

2. Computational Methods

The geometries of nine complexes (1–9) were fully optimized using the hybrid density functional theory (B3LYP). Carbon, nitrogen, and hydrogen were described using the 6-31G* basis set. Copper atom was described using the LANL2DZ basis set [23–29]. Vibrational frequency analysis has been performed on the optimized structures of the copper complexes to ensure the stationary point and it is to be noted that no negative frequencies were obtained. Natural population analysis (NPA) was performed using the same level of theory and same basis sets. All the computational procedures were used as implemented in the Gaussian-03 package [30]. Energy decomposition analysis was performed at the GGA: PBE/TZ2P level using Amsterdam Density Functional (ADF) program package [31]. Scalar relativistic effects have been considered by using the zero-order regular approximation [32].

3. Results and Discussion

3.1. General Considerations and Optimization of the Complexes. All the cuprate(III) complexes (1–9) have been optimized to the square planar geometry around the Cu(III) center and it may be pointed out that no imaginary frequencies were obtained in the computation. The bond lengths and bond angles of the nine copper(III) complexes are listed in Table 1.

Structure of the nine Cu(III)-methyl complexes 1–9 has been optimized at DFT level using 6-31G* and LANL2DZ basis sets. Complexes 2–9 have generally one non-methyl ligand (which is called probe ligand (L)) out of the four ligands. We have defined the cis/trans-positions in complexes 2–9 with respect to the probe ligand as described in Figure 1. Analysis of data in Table 1 indicates that there is change in the Cu(III)-C bond length as well as Cu-L (L = probe ligand) when the methyl ligand in tetramethylcuprate(III) complex

is replaced by the probe ligand. The Cu-C bond length in complex 1 ($[\text{M}(\text{CH}_3)_4]^{-1}$) is computed and the value is 2.02 Å which is similar to what has been reported by earlier researchers [33, 34]. The bond angle C-Cu-C obtained for complex 1 is close to 180° suggesting that the tetramethylcuprate(III) complex has square planar geometry.

The change in the Cu-C distance in the complexes investigated depends on the probe ligand. When the charge on the anion probe ligand is higher, the change in the metal- C_{trans} bond distance is more. Thus for the nitride (N^{3-}) probe ligand, the Cu- C_{trans} bond length is 2.08 Å and for the imido ligand (NH_2^-) the Cu- C_{trans} bond length is 2.07 Å. In the case of amido (NH_2^-) complex 7, Cu- C_{trans} bond length is 2.02 Å which is the same as in complex 1. However, there is not much change in Cu- C_{cis} distance as the methyl ligand is replaced by probe ligand. It may be mentioned here that the complex $\text{cis}[\text{Cu}(\text{NH})_2(\text{CH}_3)_2]^{3-}$ is not stable and its geometry could not be optimized and only the optimized geometry of trans-isomer was obtained. We found that the Cu-L bond length is also influenced by the probe ligand. It is found that for the nitride probe ligand the Cu-L bond length is shorter while in the case of other probe ligands, the Cu-L bond length is slightly longer. It is also found that Cu-L bond distance is shorter than Cu-C distance in complex 1. The L-Cu-L bond angles presented in Table 1 suggest that there is only slight change in the bond angle due to replacement of alkyl ligand by the probe ligands.

3.2. Charge Distribution in the Cu(III)-Alkyl Complexes. Natural population analysis (NPA) was carried out for complexes 1–9 and the results are given in Table 2. It is observed that cis-methyl carbon atom carries a more negative charge than the trans-methyl carbon of the alkyl group in all complexes 1–9. Both cis- and trans-methyl carbon atoms in complexes 1–9 are negatively charged and establish the anionic nature of the alkyl ligand in all the complexes investigated. It may be noted that the charge on the alkyl carbon atom is not varied significantly when we change the probe ligand. The calculated natural charge on the copper atom in all the complexes is close to +1 and in complexes 2 and 4 small negative charge is obtained. The computed electron population in the central ion in complexes 1–9 is more than the expected value in Cu(III) with d^8 electronic configuration, respectively [31].

The calculated formal charge on the metal ion in the complexes was lower than the formal charge +3, confirming a significant charge donation from the ligands containing nitrogen donor atom. This confirms the electron transmission of donor atoms toward the central metal. This is also supported by the variation in the charge on donor atom of ligand in different complexes.

Cu(III) consequently draws the electron density from the negative ligands surrounding copper center and hence the charge on copper is less than +3 [14, 33–37]. Similar behavior was observed by earlier researchers in Ni(II) complexes with square planar geometry [38].

A detailed population analysis of valence orbitals of copper has been carried out on complexes 1–9 to establish the electronic configuration of the central metal atom in

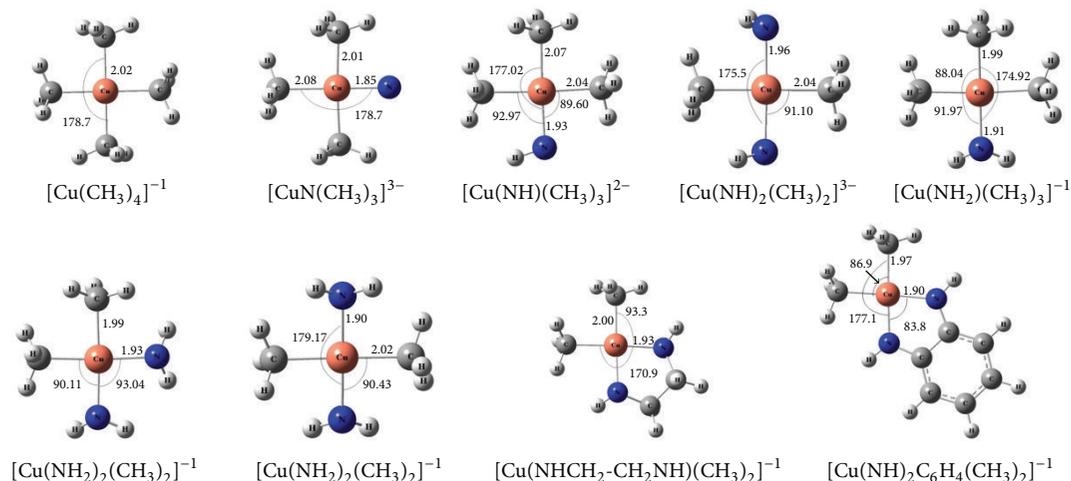


FIGURE 1: Optimized geometries for copper(III) complexes with nitrogen.

TABLE 1: Selected bond lengths (Å) and bond angles (°) of copper III complexes with nitrogen.

Complexes		Bond length (Å)		Bond angle (°)
		Cu-C	Cu-L	L-Cu-L
$[\text{Cu}(\text{CH}_3)_4]^{-1}$	(1)	2.02		
$[\text{CuN}(\text{CH}_3)_3]^{3-}$	(2)	2.01 _{cis} 2.08 _{trans}	1.85 (N)	
$[\text{Cu}(\text{NH})(\text{CH}_3)_3]^{2-}$	(3)	2.04 _{cis} 2.07 _{trans}	1.93 (NH)	
$\text{trans}[\text{Cu}(\text{NH})_2(\text{CH}_3)_2]^{3-}$	(4)	2.04	1.96 (NH)	175.5 (NH)
$[\text{Cu}(\text{NH}_2)(\text{CH}_3)_3]^{-1}$	(5)	1.99	1.91 (NH ₂)	174.92
$\text{cis}[\text{Cu}(\text{NH}_2)_2(\text{CH}_3)_2]^{-1}$	(6)	1.99	1.93 (NH ₂)	93.04
$\text{trans}[\text{Cu}(\text{NH}_2)_2(\text{CH}_3)_2]^{-1}$	(7)	2.02	1.90 (NH ₂)	179.17
$[\text{Cu}(\text{NHCH}_2\text{-CH}_2\text{NH})(\text{CH}_3)_2]^{-1}$	(8)	2.00	1.90 (NH)	85.79
$[\text{Cu}(\text{NH})_2\text{C}_6\text{H}_4(\text{CH}_3)_2]^{-1}$	(9)	1.97	1.90 (NH)	83.81

these complexes and also to identify the extent of electronic transmission from the donor atom of the ligand to the central metal atom and the computational results are presented in Table 3. It may be mentioned here that the electron density in 4p orbital of the metal ion is less than 0.005 in all the complexes and hence these values are not given. The theoretical d-orbital occupation orders for the copper are quite similar, with the lowest population of the $d_{x^2-y^2}$ orbital. The values of the d-orbital populations roughly agree with the occupation order of the d-electron levels for the square planar complexes. The total d-population is about 9 and electron density in 4s is about 0.5. It may be pointed out that the electron density in 3d orbital depends on the strength of the probe ligand. In complexes 6 and 8 the d_{xy} orbital has occupancy of 1.5 while in 2, 3, and 7 the population in $d_{x^2-y^2}$ is about 1.5. This establishes the interaction between these orbitals of metal atom and the orbitals of donor atom of the ligands. It may be suggested here that the pair of electrons from the ligand is transferred mainly to d_{xy} and $d_{x^2-y^2}$ orbitals. This confirms that these complexes are in square planar geometry.

3.3. Wiberg Bond Indices. The Wiberg bond indices (WBI) were calculated for all complexes 1–9. These values are given in Table 4. The WBI of the interaction between Cu(III) and methyl ligand in complex 1 (Cu(III)-Me) is found to be 0.34 and in complexes 8 and 9, the WBI of Cu(III)-L interactions are found to be 0.29 and 0.25, respectively. Thus the interaction between Cu(III) and probe ligands is weaker in these complexes than Cu(III)-Me interaction in TMC complex. In the complexes, $[\text{Cu}(\text{NH}_2)(\text{CH}_3)_3]^{-1}$ (5) $\text{cis}[\text{Cu}(\text{NH}_2)_2(\text{CH}_3)_2]^{-1}$ (6), WBI of the interaction between Cu(III) and probe ligands are less than 0.34 indicating the weaker interaction between the metal ion and probe ligands. However, Cu(III)-Me interactions are stronger in these two complexes as evident from their higher WBI values. The metal-ligand interactions are stronger when the probe ligands are N^{3-} and NH^{2-} . The data in Table 4 also indicate that Cu(III)-Me interactions are influenced by the nature of the probe ligand.

3.4. Chemical Hardness (η). As the Cu(III)-alkyl complexes have been used for the effective C-C bond formation at low

TABLE 2: Computed NPA charge of copper (III) complexes 1–9.

Complexes		Cu	L	Me _{cis}	Me _{trans}
[Cu(CH ₃) ₄] ⁻¹	(1)	0.99			
[CuN(CH ₃) ₃] ³⁻	(2)	-0.36	-1.06 (N)	-1.13	-1.02
[Cu(NH)(CH ₃) ₃] ²⁻	(3)	0.68	-1.30 (NH)	-1.08	-1.10
trans[Cu(NH) ₂ (CH ₃) ₂] ³⁻	(4)	-0.03	-1.20 (NH)	-1.04	
[Cu(NH ₂)(CH ₃) ₃] ⁻¹	(5)	1.03	-1.31 (NH ₂)	-1.05	-0.99
cis[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(6)	1.07	-1.31 (NH ₂)	-0.98	-0.98
trans[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(7)	1.10	-1.26 (NH ₂)	-1.04	-1.04
[Cu(NHCH ₂ -CH ₂ NH)(CH ₃) ₂] ⁻¹	(8)	1.08	-1.07 (N)	-1.01	
[Cu(NH) ₂ C ₆ H ₄ (CH ₃) ₂] ⁻¹	(9)	1.14	-1.01 (N)	-0.96	

TABLE 3: Calculated natural atomic orbital occupancy of copper ion in complexes 1–9.

Complexes		Occupancy of Cu (3d, 4s)					
		d _{xy}	d _{xz}	d _{yz}	d _{z²}	d _{x²-y²}	s
[Cu(CH ₃) ₄] ⁻¹	(1)	1.58	1.99	1.99	1.97	1.99	0.44
[CuN(CH ₃) ₃] ³⁻	(2)	1.98	1.99	1.99	1.97	1.58	0.42
[Cu(NH)(CH ₃) ₃] ²⁻	(3)	1.95	1.99	1.99	1.97	1.60	0.42
trans[Cu(NH) ₂ (CH ₃) ₂] ³⁻	(4)	1.98	1.99	1.98	1.96	1.55	0.41
[Cu(NH ₂)(CH ₃) ₃] ⁻¹	(5)	1.99	1.99	1.99	1.97	1.54	0.41
cis[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(6)	1.51	1.99	1.99	1.97	1.99	0.40
trans[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(7)	1.96	1.99	1.99	1.97	1.52	0.40
[Cu(NHCH ₂ -CH ₂ NH)(CH ₃) ₂] ⁻¹	(8)	1.51	1.99	1.99	1.97	1.99	0.40
[Cu(NH) ₂ C ₆ H ₄ (CH ₃) ₂] ⁻¹	(9)	1.99	1.99	1.47	1.98	1.98	0.39

temperature, several Cu(III)-alkyl intermediates have also been characterized by Rapid Injection NMR technique [6–11] and theoretical studies have been carried out to understand the stability and reactivity of Cu(III)-alkyl complexes in terms of chemical hardness [6, 8, 11, 19]. The experimental observations so far made in these studies indicate clearly that the Cu(III)-alkyl complexes are not stable enough to isolate at room temperature and characterize. In order to understand more about the stability of Cu(III)-alkyl complexes, we computed the total chemical hardness (η) of complexes 1–9 using the energies of HOMO and LUMO. The η value can be from the energy values using the equation [39], $\eta = 1/2(E_{\text{LUMO}} - E_{\text{HOMO}})$. The FMO diagrams for complexes 1–9 are depicted in Figure 2. The calculated chemical hardness for complexes 1–9 is listed in Table 5. According to Pearson’s principle [40], complexes having higher chemical hardness will have more stability than complexes with smaller η values. It is evident from the data in Table 5 that complexes 6–9 have comparable hardness and chemical hardness of these complexes is comparable to that of tetramethylcuprate(III) complex. Thus, these four complexes may have stability comparable to that of complex 1. Relatively smaller chemical hardness values are obtained for complexes 2–5 and hence these four complexes are expected to be less stable than complex 1.

3.5. Energy Decomposition Analysis. Energy decomposition analysis (EDA) is a useful tool to understand the nature of Cu(III)-L (L = probe ligand) and Cu(III)-alkyl bond and also to estimate the intermolecular interaction energies of

metal-ligand systems. Also the separation into the different contributions to this interaction energy gives insight into the nature of the bond. Energy decomposition analysis (EDA) was performed for complexes 1–9 and the results obtained are given in Table 6.

The Pauli repulsive force (ΔE_{pauli}) is slightly more than the electrostatic interaction (ΔE_{elstat}) for complexes 5–9 in which the probe ligands are amido, ethylene diamido, and aryl diamido. Further, in these complexes the electrostatic interaction energy is greater than the orbital overlap energy. These results indicate that the Cu(III)-L interaction is more of ionic in nature in these four complexes. The ionic nature decreases in the order $9 > 8 > 7 > 6$. Baskaran et al. found that interaction of nitrogen containing probe ligands with Cu(III) is ionic in nature [41]. In complexes 2–4, ΔE_{pauli} values for Cu(III)-L interaction are greater than ΔE_{elstat} values. It may be pointed out that orbital interaction energy values are greater than electrostatic contribution suggesting that M-L interaction is less ionic in these three complexes than in complexes 5–9.

EDA analysis can be used to consider the interaction of Me_{cis} with the Cu(III) center. The energy decomposition of Cu(III)-Me_{cis} bond of complexes 2, 3, and 5 containing N ligands is shown in Table 6 and Figure 3(a). The ΔE_{pauli} repulsive force is calculated to be more than ΔE_{elstat} for Cu(III)-Me_{cis} bond in the three complexes. However, the difference between ΔE_{pauli} and ΔE_{elstat} is more for the complexes containing N⁻³ and NH⁻² ligands than amido ligand. Further, ΔE_{orb} for the Cu(III)-Me_{cis} bond is calculated to be less than

TABLE 4: Calculated Wiberg bond indices of different bonds in complexes 1-9.

Complexes		WBI		
		Cu-L	Cu-Me _{cis}	Cu-Me _{trans}
[Cu(CH ₃) ₄] ⁻¹	(1)		0.34	
[CuN(CH ₃) ₃] ³⁻	(2)	1.46 (N)	0.42	0.34
[Cu(NH)(CH ₃) ₃] ²⁻	(3)	0.90 (NH)	0.39	0.34
trans[Cu(NH) ₂ (CH ₃) ₂] ³⁻	(4)	1.03 (NH)	0.47	
[Cu(NH ₂)(CH ₃) ₃] ⁻¹	(5)	0.31 (NH ₂)	0.34	0.40
cis[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(6)	0.31 (NH ₂)	0.41	0.41
trans[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(7)	0.36 (NH ₂)	0.35	0.35
[Cu(NHCH ₂ -CH ₂ NH)(CH ₃) ₂] ⁻¹	(8)	0.29 (NH)	0.39	0.39
[Cu(NH) ₂ C ₆ H ₄ (CH ₃) ₂] ⁻¹	(9)	0.25 (NH)	0.44	0.44

TABLE 5: HOMO, LUMO energies and chemical hardness of complexes 1-9.

Serial number	Complexes		HOMO (hartree)	LUMO (hartree)	$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2 \text{ eV}$
1	[Cu(CH ₃) ₄] ⁻¹	(1)	-0.02871	0.14268	2.33
2	[CuN(CH ₃) ₃] ³⁻	(2)	0.30437	0.35232	0.65
3	[Cu(NH)(CH ₃) ₃] ²⁻	(3)	0.18447	0.25194	0.91
4	trans[Cu(NH) ₂ (CH ₃) ₂] ³⁻	(4)	0.29798	0.35727	0.81
5	[Cu(NH ₂)(CH ₃) ₃] ⁻¹	(5)	-0.01870	0.13911	1.07
6	cis[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(6)	-0.01083	0.12937	1.90
7	trans[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(7)	-0.02691	0.12681	2.09
8	[Cu(NHCH ₂ -CH ₂ NH)(CH ₃) ₂] ⁻¹	(8)	0.27318	0.50635	3.17
9	[Cu(NH) ₂ C ₆ H ₄ (CH ₃) ₂] ⁻¹	(9)	0.22365	0.37096	2.04

TABLE 6: Energy decomposition analysis of copper III complexes with nitrogen.

Serial number	Complexes		Fragment (A)	Fragment (B)	ΔE_{Pauli} kcal mol ⁻¹	ΔE_{elstat}	ΔE_{orb}	ΔE_{int}
1	[Cu(CH ₃) ₄] ⁻¹	(1)	[Cu(CH ₃) ₃]	[CH ₃] ⁻¹	173.51	-183.65	-72.94	-83.08
2	[CuN(CH ₃) ₃] ³⁻	(2)	[Cu(CH ₃) ₃]	N ³⁻	392.19	-318.61	-370.89	-397.31
			[CuN(CH ₃) ₂] ⁻²	trans[CH ₃] ⁻¹	253.46	-8.37	-144.74	100.35
3	[Cu(NH)(CH ₃) ₃] ²⁻	(3)	[CuN(CH ₃) ₂] ⁻²	cis[CH ₃] ⁻¹	262.20	-11.67	-61.07	189.46
			[Cu(CH ₃) ₃]	NH ⁻²	200.43	-179.02	-248.95	-227.54
			[Cu(NH)(CH ₃) ₂] ⁻¹	cis[CH ₃] ⁻¹	179.29	-76.42	-67.28	35.58
4	trans[Cu(NH) ₂ (CH ₃) ₂] ³⁻	(4)	[Cu(NH)(CH ₃) ₂] ⁻¹	trans[CH ₃] ⁻¹	166.34	-76.78	-57.20	32.35
			trans[Cu(NH) ₂ (CH ₃) ₂] ³⁻	[NH] ⁻²	207.11	-12.67	-308.82	-114.38
5	[Cu(NH ₂)(CH ₃) ₃] ⁻¹	(5)	[Cu(NH ₂)(CH ₃) ₂]	[CH ₃] ⁻¹	227.47	4.24	-91.84	139.87
			[Cu(CH ₃) ₃]	[NH ₂] ⁻¹	128.23	-142.92	-66.43	-81.11
			[Cu(NH ₂) ₂ (CH ₃) ₂]	cis[CH ₃] ⁻¹	175.05	-183.85	-73.79	-82.60
6	cis[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(6)	[Cu(NH ₂) ₂ (CH ₃) ₂]	trans[CH ₃] ⁻¹	179.57	-197.60	-81.92	-99.95
			[Cu(NH ₂) ₂ (CH ₃) ₂]	[NH ₂] ⁻¹	124.81	-140.06	-65.21	-80.46
7	trans[Cu(NH ₂) ₂ (CH ₃) ₂] ⁻¹	(7)	[Cu(NH ₂) ₂ (CH ₃) ₂]	[CH ₃] ⁻¹	192.01	-198.92	-87.41	-94.32
			[Cu(NH ₂) ₂ (CH ₃) ₂]	[NH ₂] ⁻¹	130.56	-152.50	-72.74	-94.68
8	[Cu(NHCH ₂ -CH ₂ NH)(CH ₃) ₂] ⁻¹	(8)	[Cu(NHCH ₂ -CH ₂ NH)CH ₃]	[CH ₃] ⁻¹	177.09	-185.29	-75.05	-83.25
			[Cu(NHCH ₂ -CH ₂ NH)(CH ₃) ₂] ⁻¹	[Cu(NHCH ₂ -H ₂ NH)CH ₃]	[CH ₃] ⁻¹	184.15	-196.68	-83.24
9	[Cu(NH) ₂ C ₆ H ₄ (CH ₃) ₂] ⁻¹	(9)	[Cu(NH) ₂ C ₆ H ₄ (CH ₃) ₂] ⁻¹	[CH ₃] ⁻¹	211.58	-231.41	-110.68	-130.51

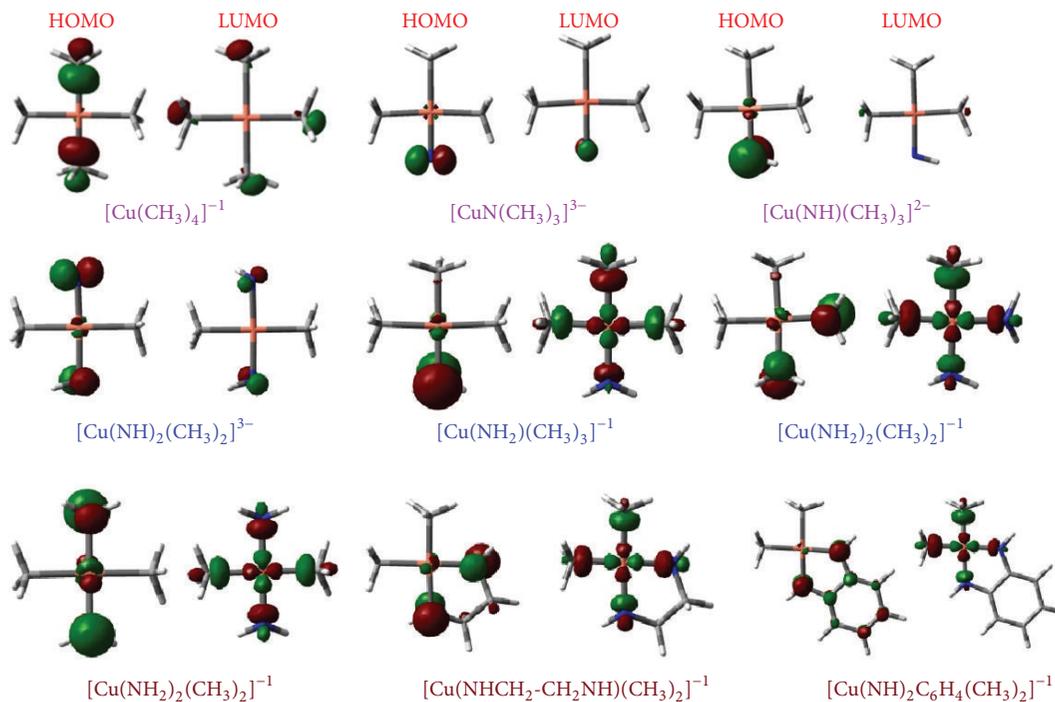


FIGURE 2: FMO of copper(III) complexes (1-9) with methyl and nitrogen donor ligands.

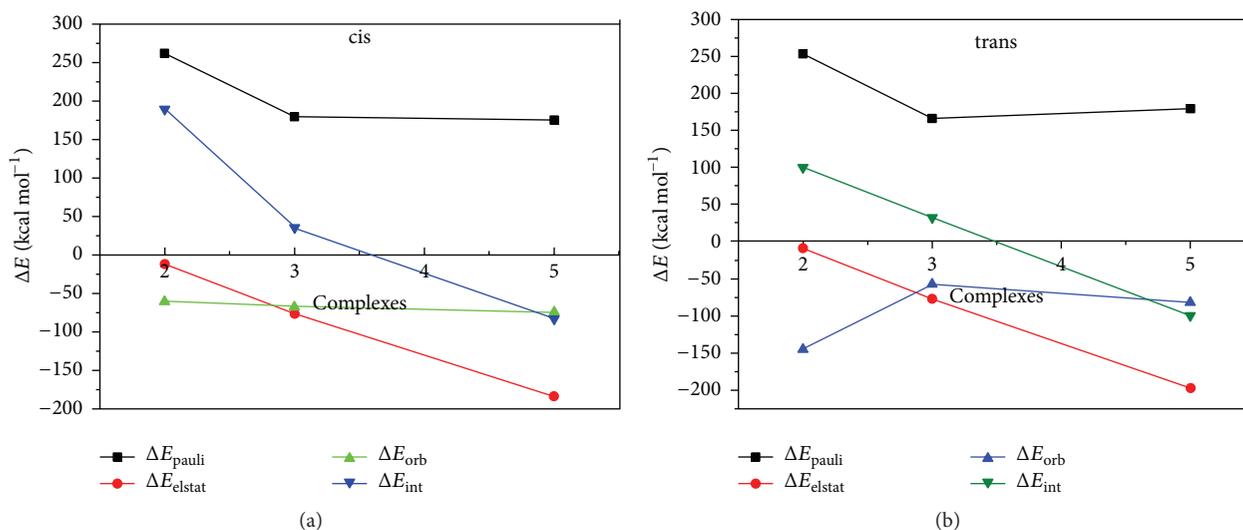


FIGURE 3: EDA for metal center, cis- and trans-methyl group for the three complexes 2, 3, and 5.

ΔE_{elstat} for complexes 3 and 5 and reveals that in these two complexes $M-L_{\text{cis}}$ is more ionic than in complex 2. In the case of other complexes (4, 6-9) Pauli repulsive forces are less and ΔE_{orb} values are less than ΔE_{elstat} values. Thus, Cu(III)-Me interaction is more ionic in these four complexes. The energy decomposition of the Cu(III)-Me_{trans} bond of complexes 2, 3, and 5 is shown in Figure 3(b). It is found that the computed ΔE_{pauli} is calculated to be less than ΔE_{elstat} for complex (5) containing amido ligand as probe ligand indicating that in this complex Cu- Me_{trans} interaction is more ionic which is similar to the trend observed for the Cu(III)-Me_{cis} bond.

However, in the case of complexes 2 and 3 the interaction is ionic but less ionic than in complex 5.

3.6. Free Energy of the Ligand Substitution Reactions. Free energy changes of the nitrogen donor ligand substitution reactions on the Cu(III)-methyl complex are calculated for the eight reactions.

Figure 4 depicts the free energy changes for the seven ligand substitution reactions (except substitution by N^{-3} ligand). ΔG for the substitution of methyl group by N^{-3}

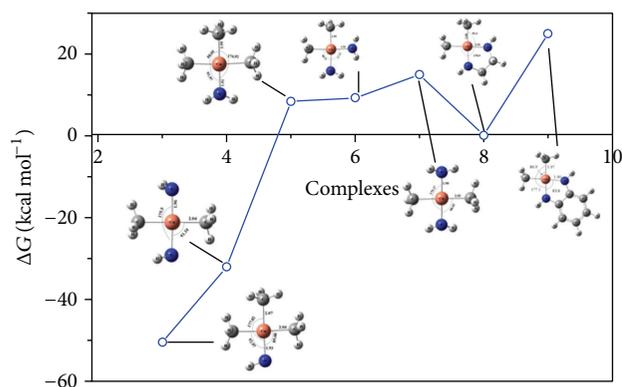


FIGURE 4: Free energy changes of ligand substitution reactions on the Cu(III)-methyl complexes with nitrogen donor ligands.

probe ligand is $-496.47 \text{ kcal mol}^{-1}$ at 298 K in THF solvent. Thus the reaction is thermodynamically feasible. Similarly the values of ΔG for the formation of complexes 3 and 4 from TMC are also negative and these reactions are also feasible thermodynamically at the specified experimental conditions. However, the formation of complexes 4–9 from TMC has positive free energy and hence it may be inferred that these substitution reactions involving amido, ethylene diamido, and aryl diamido probe ligands are thermodynamically not feasible under the specified conditions.

4. Conclusions

DFT studies were performed on eight ligand substitution reactions of tetramethylcuprate(III) (TMC) complex with five different probe ligands containing nitrogen as donor atom. The geometry optimization of the possible nine model systems and the frequency calculations were carried out using LANL2DZ basis set and no imaginary frequencies were obtained. The bond parameters of optimized model systems of Cu(III) complexes are reported and discussed. The change in the Cu(III)-C bond distance in TNC due to substitution by probe ligands is studied. Natural population analysis (NPA) has been carried out for these complexes to establish the charge on copper center in these complexes. A detailed population analysis of valence orbitals of copper complexes supports the existence of d^8 configuration for metal in these complexes and there is evidence for the transmission of electrons from the nitrogen donor atom to d_{xy} , $d_{x^2-y^2}$, and $4s$ orbitals. There is evidence for the interaction between these orbitals ($d_{x^2-y^2}$ and d_{xy}) of metal atom and the orbitals of donor atom of the ligands. It may be suggested here that the pair of electrons from the ligand is transferred mainly to d_{xy} and $d_{x^2-y^2}$ orbitals. This confirms that these complexes are in square planar geometry. It may be pointed out that the electron density in $3d$ orbital depends on the strength of the probe ligand. Bond order calculations have been performed for all the complexes to ascertain the interaction between Cu(III) and the ligand. The stability is determined from the computed chemical hardness of these complexes. Energy decomposition analysis has been carried out for all

the complexes chosen in the theoretical study to understand the nature of Cu(III)-L (L = N donors) and Cu(III)-Me bonds in different complexes. Thermodynamic feasibility of these reactions is investigated in terms of free energy changes of the reactions.

Competing Interests

The authors declare that they have no competing interests.

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