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Ab Initio Studies on the Interaction Between Copper(I) and 5-Nitrotetrazolate Anion

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ABSTRACT

Ab initio molecular orbital calculations on the interaction between Copper(I) and 5-nitrotetrazolate anion were done using different basis sets, at the HF, B3LYP and MP2 levels of theory. Three minima were found to 1A, 1B and IC structures of Cu(I)-5-NTz complex. At the B3LYP/LanL2DZ level, the energy difference between 1A and 1B was computed to be 8.18 kcal/mol, while that between 1A and 1C is 22.76 kcal/mol. The presence of both Cu-N and Cu-O interactions is revealed in 1A structure using both natural bond orbital and atoms-in-molecules analyses, which makes more stable than those of 1B and 1C complexes. The binding energy corrected for both ZPE and BSSE for 1A is found to be -150.59 kcal/mol at the B3LYP/LanL2DZ level. The barrier for the 1B → 1A and 1C → 1B conversion is calculated to be 7.80 kcal/mol and 9.40 kcal/mol, respectively.

Keywords: Cu(I); 5-nitrotetrazolate anion; Ab initio computation; NBO analysis; Cu-X interaction; Transition state

1. INTRODUCTION

Recently, a great deal of interest to generate environmentally less toxic explosives in the energetic materials community. In particular, green primary explosives has been paid to attention in the replacement of lead azide[1-3]. Primary explosives are easily detonated by a physical or electrical stimulus, where these materials has an important in applications in both the military and civilian field. The most common of these materials are heavy metal salts such as lead azide and lead styphnate. It has been known for a long time that the harmful effects of lead to the environment[4]. Hence, the synthesis and characterisation of lead-free primary explosives has an important focus among the current energetic materials research. In the literature, the formation of non-toxic metal complexes containing copper or iron or nickel had been reported instead of toxic heavy lead metal[1-2,5]. It has only been until recent times that metal salts with tetrazole and tetrazolate ligands have been studied as prospective primary explosives[1-2,6]. Tetrazoles[7,8] and tetrazolates[9-10] based compounds are known to be promising with suitable properties such as high density, a positive heat of formation, and a high nitrogen content, these would be suitable candidates as coordinate ligands for the development of new green primary coordination complexes with high explosive performance. Copper tetrazole complexes are suitable materials for the development of new primary explosives[1,6,11-14].

Huynh[1], *et al.* reported metal (iron or copper) complexes of the 5-nitrotetrazolate anion as potential replacements of lead-based primary explosives. Fronabarger[13,14], *et al.* had published Copper(I) 5-nitrotetrazolate (DBX-1) complex as one of the potential candidate for green primary explosive. Using UV-vis and single crystal X-ray analyses, he showed that DBX-1 is a 1:1 complex of copper(I) and 5-nitrotetrazolate. The analysis of structural and electronic properties can greatly facilitate the understanding of physico-chemical properties of DBX-1 as well as its analogue complexes. It is thus important to understand the nature of interaction between Cu(I) cation and 5-nitrotetrazolate (5-NTz) anion which helpful to understand the structural stability of DBX-1 and its decomposition mechanism. DBX-1 has two possible isomers, 1-substiuted tetrazole and 2-substituted tetrazoles. Using semi-empirical calculations, Schroeder & Henry[15] indicated that 1-substiuted tetrazole is more stable than 2-substituted tetrazole. Using B3LYP/aug-cc-pvTZ level, Klapotke[16], *et al.* showed the vibrational frequencies of 5-nitrotetrazolate anion. However, to our knowledge, the detailed theoretical investigations of the interaction between Cu(I) with 5-NTz anion is not available in the literature.

The above discussion indicates that a closer look on the energetic of gas phase (1:1) Cu(I)-5-NTz complex are certainly warranted. In this paper, we have therefore studied (1:1) Cu(I)-5-NTz complex using computational calculations. We have performed ab initio computations on the structures and energies for the various isomers of Cu(I)-5-NTz complex, at the HF, B3LYP and MP2 levels using 6-31G**, 6-311G**, 6-311++G** and LanL2DZ basis sets. To understand the interactions of complexes, natural bond orbital analysis is also done using B3LYP/LanL2DZ level. The computed the energy barrier for the conversion between the isomer is also estimated using B3LYP/LanL2DZ level.

2. COMPUTATIONAL METHODS

Ab initio molecular orbital calculations were done using the Gaussian 03W program[17]. The computational work was

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carried out in DRDO-High Energy Materials Laboratory, Pune. To ascertain the trends in the energetics, the HF, B3LYP and MP2 levels were performed at different basis sets. Geometry optimisations were done both at the HF, B3LYP and MP2 level with analytical gradients, using 6-31G**, 6-311G**, 6-311++G** and LanL2DZ basis sets, to obtain minima corresponding to the various isomers. The methodology adopted to drive the computational parameters of various Cu(I)-5-NTz isomers was generally followed as reported[18]. Structure for 5-nitrotetrazolate (5-NTz) anion was first optimised at the particular level of theory; then this optimised structure was used to optimise the structure of the Cu(I)-5-NTz complex, at the same level of theory. All geometric parameters were allowed to be optimised, and no constraints were imposed on the molecular geometry during the optimisation process. The B3LYP/LanL2DZ level has been taken for further structural, natural bond orbital, charge and vibrational frequencies analyses. To compute the binding energy of the complex formation (ΔE) is given by

$$\Delta E = E_{AB} - E_A - E_B$$

where E_A, E_B and E_{AB} represent the computed energies for *A, B* and *AB,* respectively.

If the value of ΔE is negative, the complex is more stable relative to the precursors. The binding energies of the complexes were corrected separately, for both zero-point energy (ZPE) and basis set superposition error (BSSE) using the counterpoise correction scheme outlined by Boys and Bernardi[19]. Vibrational frequencies were calculated for the optimised geometries to enable us to characterize the nature of the stationary points and ZPE corrections. Frequency calculations were done on the optimised structures of the complexes to ensure minima or saddle point. For anharmonicity correction, the ZPE values were scaled in HF, B3LYP and MP2 calculations. To arrive at the scaling factor, we chose the experimental NO_2 asymmetric stretching mode of DBX-1 (i.e. 1556 cm^{-1})[13] and correlated it with that strongest computed feature of 5-nitrotetrazolate anion in this region. The factor that would bring this computed frequency in agreement with the experimental feature was then calculated and used to scale the ZPE values. The ZPEs after due scaling, were used to calculate the ZPE corrected relative energies for the different isomers. Natural bond orbital (NBO) analysis[20] on the optimised geometries of complexes was carried out to understand the nature of the interactions. To understand the nature of the interactions, Atoms-in-molecules (AIM) analysis[21-23] was carried out on the optimised geometries of complexes. We also computed the transition state structure corresponding to the first order saddle point connecting two isomers. A frequency calculation on transition state structure was done to confirm that this was a first order saddle point and also to obtain the zero-point energy. To get the barrier for isomer interconversion, the energy of the transition structure together with its zero-point energy was used.

3. RESULTS AND DISCUSSION

3.1 Optimised Geometries

The optimised structure of Cu(I)-5-NTz complex at the B3LYP/LanL2DZ level is as shown in Fig. 1. Table 1 gives the selected structural parameters for the optimised Cu(I)-5-NTz complex and 5-nitrotetrazolate (5-NTz) anion at the B3LYP/LanL2DZ level. Isomer **1A** (Fig. 1) shows the structure of a Cu(I)-5-NTz complex in which Cu(I) ion interacts with the lone pairs of N1 atom of 5-NTz anion. The interatomic distances of Cu9-N1 and Cu9-O8 in **1A** complex are 1.953 and 2.160 Å, respectively. The distances of N4-N5, N6-O8, and N3-N4 in

Table 1. Selected structural parameters[a] of three isomers of Cu(I)-5-NTz complex, the transition states, connecting the 1A and 1B minima (TS1), 1B and 1C minima (TS2) and 5-nitrotetrazolate (5-NTz) anion computed at the B3LYP/LanL2DZ level

Parameter	1A	Exp[b]	5-NTz anion	TS1	Parameter	1B	Parameter	1C	TS2
N1-C2	1.317	1.330	1.372	1.352	N1-C2	1.374	N1-C2	1.407	1.394
C2-N3	1.354	1.323	1.372	1.363	C2-N3	1.354	C2-N3	1.407	1.397
N3-N4	1.373	1.354	1.360	1.366	N3-N4	1.361	N3-N4	1.299	1.317
N4-N5	1.389	1.321	1.341	1.368	N4-N5	1.398	N4-N5	1.562	1.504
N1-N5	1.362	1.341	1.360	1.394	N1-N5	1.344	N1-N5	1.299	1.317
C2-N6	1.431	1.448	1.433	1.453	C2-N6	1.454	C2-N6	1.352	1.375
N6-O7	1.258	1.220	1.288	1.272	N6-O7	1.278	N6-O7	1.332	1.367
N6-O8	1.323	1.226	1.288	1.281	N6-O8	1.275	N6-O8	1.332	1.268
Cu9-N1	1.953	1.969		2.069	Cu9-N4	1.878	Cu9-O7	2.117	1.878
Cu9-O8	2.160						Cu9-O8	2.117	
Cu9-N1-C2	112.2	129.9		175.4	Cu9-N4-N5	124.2	Cu9-O7-N6	90.1	125.2
N6C2N1N3	180.0	-178.3	180.0	180.0	N6C2N1N3	180.0	N6C2N1N3	180.0	-177.3
O7N6C2N3	0	-13.5	0.2	-0.6	O7N6C2N3	0.1	O7N6C2N3	0	12.8
O8N6C2N1	0	-12.9	0.2	-0.5	O8N6C2N1	-0.1	O8N6C2N1	0	12.8
Cu9N1C2N5	180.0	-178.3		-10.6	Cu9N4N5N3	-179.9	Cu9O7N6C2	180.0	-106.4

[a] Bond lengths in angstroms and bond angles and dihedral angles in degrees.

[b] The average crystal geometric parameter values of DBX-1 molecular unit are taken from ref.13.

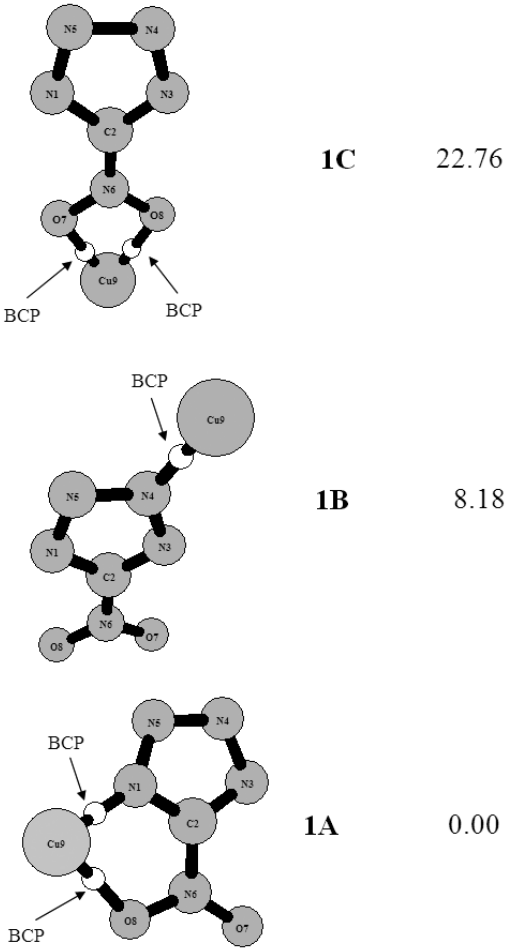

Figure 1. Isomers of Cu(I)-5-NTz complex corresponding to the three minima, 1A, 1B, and 1C, The energy values mentioned against each isomer are relative to the 1A isomer, in kcal/mol. The location of the (3,-1) bond critical point (BCP) for Cu-X bond has been indicated. For clarity, intramolecular bond critical point of 5-NTz in the complex has not been shown.

complex **1A** is lengthened as compared with those of 5-NTz anion (Table 1). On the other hand, the distances of N6-O7, and C2-N3 in complex **1A** is shortened as compared with those of 5-NTz anion. Furthermore, Cu9 and oxygen atoms (O8 and O9) of nitro group of **1A** complex are in plane with the tetrazole ring plane. In **1B** and **1C** complexes, Cu(I) ion interacts with the lone pairs of N4 atom and oxygen (O7 and O8) atoms of 5-NTz anion, respectively. The interatomic distance of Cu9-N4 in **1B** complex is 1.878 Å, which is shorter than those in complex **1A**. The interatomic distance of Cu9-O in **1C** complex is 2.117 Å. The C-NO_2 bond distance of complex **1A** (1.431 Å) is comparable to those of 5-NTz anion (1.433 Å), where it is lengthened in **1B** (1.454 Å) complex and is shortened in **1C** (1.352 Å) complex.

3.2 Natural Bond Orbital and Charge Analyses

NBO analysis was carried out to describe the nature of the interaction. Table 2 gives the stabilisation energy E(2) for the three isomers of Cu(I)-5-NTz at the B3LYP/LanL2DZ level. In Cu(I)-5-NTz isomer, the higher stabilisation energy E(2) between donor and acceptor indicate the stronger Cu-X interaction. As seen from Table 2, the presence of Cu-O interaction along with the Cu-N interaction is well confirmed in isomer **1A** of Cu(I)-5-NTz complex. The analysis of complex **1B** and **1C** shows the Cu-N and Cu-O interactions, respectively. It indicates an important charge transfer between the lone pair of the nitrogen or oxygen atom and the empty lone air of the copper atom for the complexes studied. Further, the Cu-N interaction provides more stabilisation energy than Cu-O interaction. The decreasing order of the stabilisation energies is **1A** > **1B** > **1C** complex (Table 2), which indicates the complex **1A** is the most stable one. This is due to the presence of Cu-N interaction in both **1A** and **1B** complex, where it is absence in **1C** complex. Further, the presence of Cu-O interaction in addition with Cu-N interaction in **1A** than those of **1B** complex resulted an increase in the stabilisation energy of the complex. The strongest stabilisation energies for Cu-N and Cu-O interaction in complex **1A** are 36.99 and 15.73 kcal/mol, respectively, at the B3LYP/LanL2DZ level of theory. Table 3 gives the natural population analysis charges on all the atoms in the complex, with the corresponding values in the uncomplexed 5-NTz anion in parenthesis. An examination of the charges on the different atoms of the complex clearly reveals large changes in charge density, when the complexes were formed between Cu(I) cation and 5-NTz anion. The magnitude of the partial charges at the N1 and O8 sites are markedly increased due to the polarisation caused by the Cu(I) cation in complex **1A**, while at the N3, N4, N5 and O7 sites they are generally decreased. Analogous changes can also be

Table 2. NBO analysis results[a] of three isomers of Cu(I)-5-NTz complex at the B3LYP/LanL2DZ level.

Structure	Donor NBO(i)	Acceptor NBO(j)	E(2)/kcal/mol
1A	LP(1) N1	LP*(6) Cu9	36.99
	LP(1) N1	LP*(7) Cu9	3.86
	LP(1) N1	LP*(9) Cu9	1.67
	LP(2) N1	LP*(8) Cu9	1.18
	LP(2) O8	LP*(6) Cu9	15.73
	LP(2) O8	LP*(7) Cu9	7.73
	LP(1) O8	LP*(7) Cu9	4.95
	LP(1) O8	LP*(6) Cu9	3.29
	LP(3) O8	LP*(8) Cu9	1.45
1B	LP(1) N4	LP*(6) Cu9	48.61
	LP(1) N4	LP*(9) Cu9	1.57
1C	LP(2) O7	LP*(6) Cu9	18.01
	LP(2) O7	LP*(7) Cu9	3.89
	LP(3) O7	LP*(8) Cu9	1.27
	LP(2) O8	LP*(6) Cu9	18.01
	LP(2) O8	LP*(7) Cu9	3.85
	LP(3) O8	LP*(8) Cu9	1.27

[a] LP means lone pair. LP* represents antibond.

Table 3. Partial charges (in e) of three isomers of Cu(I)-5-NTz complex from NPA analysis at the B3LYP/LanL2DZ level

Atom	1A	1B	1C
N1	-0.55(-0.34)[a]	-0.26	-0.23
C2	0.41(0.35)	0.39	0.39
N3	-0.27(-0.34)	-0.26	-0.23
N4	-0.07(-0.15)	-0.39	-0.05
N5	-0.04(-0.15)	-0.06	-0.05
N6	0.43(0.41)	0.42	0.38
O7	-0.25(-0.40)	-0.34	-0.51
O8	-0.50(-0.40)	-0.33	-0.51
Cu9	0.83	0.83	0.81

[a] The partial charges on the atoms for the uncomplexed species are given in parenthesis.

found in the other positions of 5-NTz for complex **1B** and **1C**, when Cu(I) cation associates with them.

3.3 AIM Analysis

In AIM analyses, an interaction between two atoms is manifest through a line of maximum density linking the two nuclei, called an atomic interaction line. For an optimised geometry, the presence of (3, −1) bond critical point indicates a bonding interaction between the two nuclei. Based on the optimised geometry of Cu(I)-5-NTz complexes at the B3LYP/LanL2DZ level, the electron density topography was analysed by using the AIM method. The critical points location of Cu-X (where X = N or O) interaction of Cu(I)-5-NTz complexes are given in Fig. 1. Table 4 gives the Cu-X bond critical point properties of Cu(I)-5-NTz complexes. From Table 4, it is evident that the Laplacian of charge density, $\nabla^2\rho$ and the ratio of eigen values, $|\lambda_1|/\lambda_3$ is positive and less than one, respectively, at the intermolecular (3, -1) bond critical point between the complexes. It clearly indicates the presence of Cu-X interaction in Cu(I)-5-NTz complexes, **1A**, **1B** and **1C**. As seen from Fig. 1 and Table 4, the presence of Cu-O interaction along with the Cu-N interaction is well confirmed in isomer **1A** of Cu(I)-5-NTz complex. This observation is supported by NBO analyses, which indicate a higher stabilisation energy in **1A** is higher than those of **1B** and **1C**.

3.4 Energy Analysis

The relative energies of the isomers at the HF, B3LYP and MP2 levels obtained using 6-31G**, 6-311G**, 6-311++G** and LanL2DZ basis sets are shown in Table 5. At all levels of theory, **1A** isomer is found to be the most stable one. It is at consistent with the report of Schroeder & Henry [15], who indicated the **1A** type isomer is the most stable one. Unsurprisingly, the relative energy value of the different isomers varied with the basis sets and the level of theory employed. At both HF and B3LYP levels, the next higher energy isomer corresponded to a **1B** structure, followed by the **1C** geometry. Interestingly, **1B** isomer did not shown to be a minium at the MP2 level of theory. At MP2/6-311G** level of theory, **1C** isomer did not show a minimum in addition with a **1B** isomer. At the MP2/LanL2DZ level of theory, the energy difference between the **1A** and **1C** was 17.65 kcal/mol, while that was 28.87 kcal/mol at the MP2/6-311++G** level. At the B3LYP/6-311++G** level, the energy difference between **1A** and **1B** is 5.89 kcal/mol, while that between **1A** and **1C** is 23.74 kcal/mol. At the B3LYP/LanL2DZ level, the energy difference between **1A** and **1B** is 8.18 kcal/mol, while that between **1A** and **1C** is 22.76 kcal/mol. Table 5 gives the binding energies corrected for both ZPE and BSSE for the Cu(I)-5-NTz complexes at the HF, B3LYP and MP2 levels obtained using 6-31G**, 6-311G**, 6-311++G** and LanL2DZ basis sets. In general, the more stable the complex (lower relative energy) should be of better binding energy value. At all the levels and larger basis sets, it can be seen in Table 5 that complex **1A** is more strongly bound than other complexes. The ZPE + BSSE corrected binding energy for **1A**, **1B** and **1C** complex is -150.59, -143.18 and -129.02 kcal/mol, respectively, at the B3LYP/LanL2DZ level of theory. The ZPE + BSSE corrected binding energy for **1A** and **1C** complex is -16.57 and -120.80 kcal/mol, respectively, at the MP2/LanL2DZ level of theory. In Cu(I)-5-NTz complexes, the Cu-N interaction was found stronger than Cu-O one. Therefore, the stabilisation energies of the **1A** and **1B** complexes are higher than those of **1C**. Further, the presence of one more Cu-O interaction in addition with Cu-N interaction in **1A** enhances the stability and it results in the stronger complex. At the B3LYP/LanL2DZ level, the calculated dipole moment of **1A**, **1B** and **1C** isomer of Cu(I)-5-NTz complex is 7.54, 10.75 and 11.19 D, respectively. The lowest energy isomer has the lowest dipole moment.

Table 4. Properties of (3, -1) bond critical point in the three isomers of Cu(I)-5-NTz complex computed at the B3LYP/LanL2DZ level

Molecule	$\rho(r_C)$ (eÅ^{-3})	$\nabla^2\rho(r_C)$ (eÅ^{-5})	λ_1 (eÅ^{-5})	λ_2 (eÅ^{-5})	λ_3 (eÅ^{-5})	$\lvert\lambda_1\rvert / \lambda_3$
(a) bond critical points in Cu(I)-5-NTz complex **1A**						
Cu9···O8	0.34	7.9	-1.5	-1.4	10.8	0.1
Cu9···N1	0.60	13.2	-3.1	-2.9	19.1	0.2
(b) bond critical point in Cu(I)-5-NTz complex **1B**						
Cu9···N4	0.73	15.0	-4.0	-3.7	22.7	-0.2
(c) bond critical points in Cu(I)-5-NTz complex **1C**						
Cu9···O7	0.38	8.8	-1.8	-1.7	12.2	-0.1
Cu9···O8	0.38	8.8	-1.8	-1.7	12.2	-0.1

3.5 Transition States

We also performed the computational estimate for barrier to **1A** ↔ **1B** and **1B** ↔ **1C** isomer conversion in Cu(I)-5-NTz complex. The transition state structures were found between the relevant minima at the B3LYP/LanL2DZ level. Frequency calculation was done on the transition state structure to confirm that the structure corresponded to the first-order saddle point and also to obtain zero-point energy. The value of the single imaginary frequency for transition states corresponding to the **1A** ↔ **1B** and **1B**

Table 5. Relative energies[a] and binding energies of three isomers of Cu(I)-5-NTz complex calculated at the HF, B3LYP and MP2 levels using different basis sets.

Basis Set	Isomer	Relative energy			Binding energy		
		HF	B3LYP	MP2	HF	B3LYP	MP2
	1A	0.00	0.00	0.00	-156.75[b]/-156.14[c]/-125.21[d]	-208.34/-207.54/-152.40	-189.75/-189.01/-136.52
6-31G**	**1B**	11.71	14.00	-[e]	-145.40/-144.43/-120.66	-194.73/-193.53/-152.57	-[e]
	1C	28.51	34.55	38.47	-127.69/-127.62/-102.90	-172.94/-172.99/-128.88	-150.69/-150.53/-109.54
	1A	0.00	0.00	0.00	-131.94/-131.15/-121.69	-162.25/-161.27/-145.34	-148.89/-147.99/-132.47
6-311G**	**1B**	5.60	1.58	-[e]	-126.42/-125.55/-117.91	-160.85/-159.69/-145.83	-[e]
	1C	25.18	26.18	-[e]	-105.95/-105.97/-97.74	-135.36/-135.09/-121.73	-[e]
	1A	0.00	0.00	0.00	-131.01/-130.17/-129.10	-153.03/-152.07/-151.05	-149.10/-148.08/-132.56
6-311++G**	**1B**	5.04	5.89	-[e]	-125.20/-124.28/-123.28	-148.16/-147.02/-145.95	-[e]
	1C	22.99	23.74	28.87	-106.41/-106.43/-105.71	-129.29/-129.08/-128.38	-119.91/-119.21/-115.03
	1A	**0.00**	0.00	0.00	-135.71/-134.60/-130.62	-157.52/-156.35/-150.59	-148.56/-147.8/-136.57
LanL2DZ	**1B**	**8.24**	8.18	-[e]	-127.49/-126.36/-123.12	-149.48/-148.17/-143.18	-[e]
	1C	**23.02**	22.76	17.65	-111.44/-111.57/-108.56	-133.57/-133.59/-129.02	-128.42/-130.16/-120.80

[a]Energy relative to the **1A** isomer in kcal/mol. [b]Binding energy not corrected for either ZPE or BSSE. [c]Binding energy corrected for ZPE. The computed ZPE was scaled by 0.8516, 0.8591, 0.8748, 0.9929, 0.9725, 0.9873, 1.0064, 1.1066, 0.8827, 0.8837, 0.8990 and 0.8798 for HF/6-31G**, HF/6-311G**, HF/6-311++G**, HF/LanL2DZ, B3LYP/6-31G**, B3LYP/6-311G**, B3LYP/6-311++G**, B3LYP/LanL2DZ, MP2/6-31G**, MP2/6-311G**, MP2/6-311++G** and MP2/LanL2DZ levels, respectively for the application of the ZPE correction. [d]Binding energy corrected for both ZPE and BSSE. [e]Not shown to be a minimum.

↔ **1C** interconversions are –93 cm^{-1} and –64 cm^{-1}, respectively. The selected structural parameters defining the transition state structure at the B3LYP/LanL2DZ level are given in Table 1 and the structure shown in Fig. 2. Table 6 gives the energy of the three minima, **1A**, **1B**, **1C**, **TS1**, and **TS2** at the B3LYP/LanL2DZ level. After correcting for the zero-point energy, the calculated barrier for the **1B** → **1A** and **1C** → **1B** is to be 7.80 kcal/mol and 9.40 kcal/mol, respectively.

Table 6. Total energies[a] and zero-point energies[a,b] (ZPE) calculated at the B3LYP/LanL2DZ level, for the 1A, 1B and 1C isomers and the transition state structures TS1[c] and TS2[d]

Structure	Total energies	ZPE
1A	-658.2050699	0.035331
1B	-658.1922566	0.035528
1C	-658.1669046	0.033618
TS1[c]	-658.1789649	0.034747
TS2[d]	-658.1521328	0.033807

Barrier height for **1B→1A** conversion = 7.80 kcal/mol
Barrier height for **1C→1B** conversion = 9.40 kcal/mol
[a]Energies are in hartrees.
[b]Zero-point vibrational energy values are unscaled values.
[c]**TS1** is the transition state between **1A** and **1B**.
[d]**TS2** is the transition state between **1B** and **1C**.

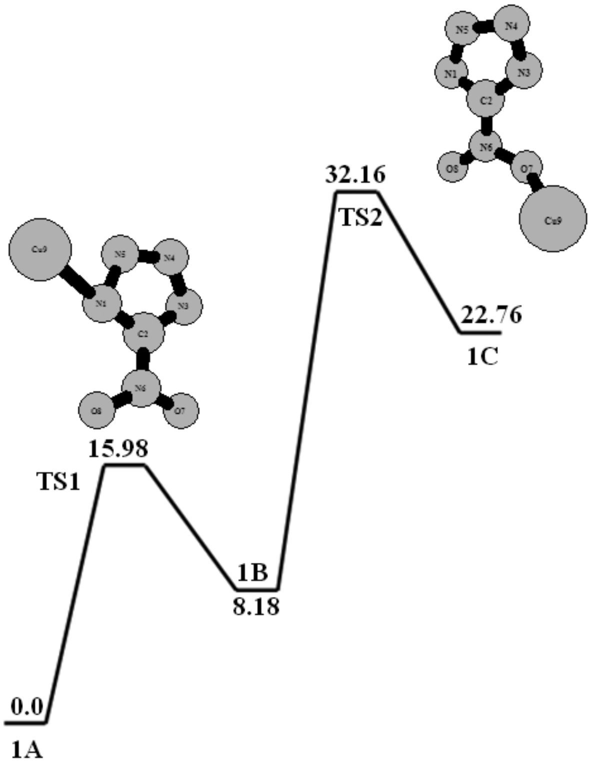

Figure 2. Schematic diagram of the relative energies in kcal/mol of different isomers and the transition states, connecting the 1A isomer and other higher energy isomers.

4. CONCLUSIONS

The (1:1) complexes of copper(I) with 5-nitrotetrazolate anion (5-NTz) were studied using different basis sets, at the HF, B3LYP, and MP2 levels of theory. Three minima were found corresponding to the **1A**, **1B** and **1C** structures of Cu(I)-5-NTz complexes at the B3LYP/LanL2DZ level. At the B3LYP/LanL2DZ level, the energy difference between **1A** and **1B** is 8.18 kcal/mol, while that between **1A** and **1C** is 22.76 kcal/mol. Using both natural bond orbital and atoms-in-molecules analyses, the global minimum **1A** type structure revealed to the presence of both Cu-N and Cu-O interactions. Complex **1B** and **1C** shows the presence of Cu-N and Cu-O interactions, respectively. The Cu-N interaction provides more stabilisation energy than Cu-O interaction. The strongest stabilisation energies for Cu-N and Cu-O interaction in complex **1A** are 36.99 kcal/mol and 15.73 kcal/mol, respectively, at the B3LYP/LanL2DZ level of theory. The value of ZPE + BSSE corrected binding energy for **1A** is found to be -150.59 kcal/mol at the B3LYP/LanL2DZ level. The barrier for the **1B** → **1A** and **1C** → **1B** conversion is calculated to be 7.80 kcal/mol and 9.40 kcal/mol, respectively.

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