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Quantum Chemical Studies on $[Co(ntb)(pic)]^+$ Complex Ion

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Abstract – Tris(2-benzimidazolylmethyl)aminepicolinatocobalt (II), $[Co(ntb)(pic)]^+$, complex were studied theoretically. $[Co(ntb)(pic)]^+$ complex ion were synthesized and geometric parameters, vibration frequencies and UV-VIS spectrum were obtained by Nie et al. in 2010 [1]. In this study, optimized geometric parameters, vibrational spectrum, Molecular Orbital (MO) character analysis, Transition Character (TC) analysis and UV-VIS spectrum were calculated. The correlations between theoretical and experimental results were investigated.

Keywords -
Gaussian 09, DFT method, Tris(2-benzimidazolylmethyl) amine picolinatocobalt (II)

1. Introduction

The imidazole group of histidine has important role in many metalloproteins [2, 3]. Imidazole and benzimidazole are similar group. Tris(2-benzimidazolylmethyl)amine (ntb) was derived from benzimidazole. (ntb) was synthesized by Thompson et al. in 1977 [4]. Structures of (ntb) and picolinato (pic) ligands were presented in Figure 1.

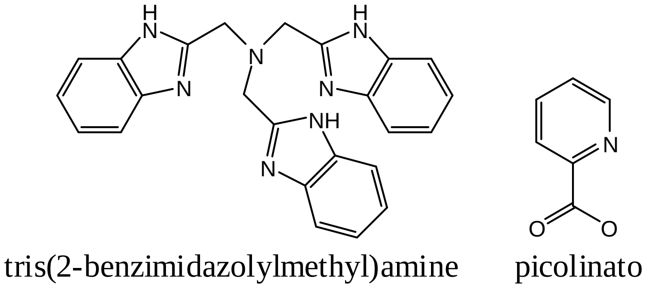

Figure 1. Molecular structures of (ntb) and picolinato ligands

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Properties of chemical species can explain with Quantum Chemical Calculations (QCC). As experimentally, transition state, excited state, transition character of band in UV spectrum cannot be determined clearly. In report of Nie et al., some vibrational frequencies were assigned. The band at 531 nm in UV spectrum was assigned as d → d transition. In this study, the optimized molecular structure of mentioned complex was obtained with DFT method. The more appropriate basis set and phase were selected by comparing experimental and theoretically bond lengths and angles. Vibrational spectrum and UV spectrum were calculated by using more appropriate basis set and phase. The mentioned deficiencies of report of Nie et al. were explained theoretically.

2. Computational Details

The input files of mentioned complex were prepared with GaussView 5.0.8 [5]. All calculations were made by using Gaussian 09 AML64L-Revision-C.01 [6]. The complex ion was performed by using Density Functional Theory (DFT) [7] with LANL2DZ [8 – 10] and 6-31g basis sets. On the other hand, the complex ion were optimized again at B3LYP [8] method with GEN keyword by using 6-31g basis set for O, N, C, H atoms and LANL2DZ basis set for Co atom. All calculations were completed in gas phase and methanol solvent. For solution phase, CPCM, which is model corresponds to Polarized Continuum Model (PCM), was selected for calculation. The vibrational frequency analyses indicate that optimized structures of complex are at stationary points corresponding to local minima without imaginary frequencies. Time Dependent – Density Functional Theory (TD-DFT) [11] method were selected to UV-VIS calculations. UV-VIS spectrum was calculated in n,n-dimethylformamide (DMF) solvent.

3. Result and Discussion

3.1. Optimized Structure

Optimized structures were obtained with B3LYP/LANL2DZ, B3LYP/6-31g and B3LYP/GEN levels. Experimental and theoretical results of bond lengths and angles were compared with each other. For bond lengths and angles, the correlation coefficients (CC) were determined for each level. The CCs were listed in Table 1.

Table 1. The correlation coefficients of bond lengths and angles in gas phase and methanol solvent.

Levels	Bond Length		Bond Angle	
	Gas Phase	Methanol	Gas Phase	Methanol
B3LYP/LANL2DZ	0.773	0.709	0.942	0.943
B3LYP/6-31g	0.773	0.685	0.941	0.943
B3LYP/GEN	0.775	0.666	0.943	0.940

The correlation coefficients of bond lengths and angles indicated that B3LYP/GEN level in gas phase is the best level for mention complex. Optimized molecular structure of mentioned complex was represented in Figure 2 with atomic numbering scheme. The calculated bond lengths and angles in B3LYP/GEN level were listed in Table 2.

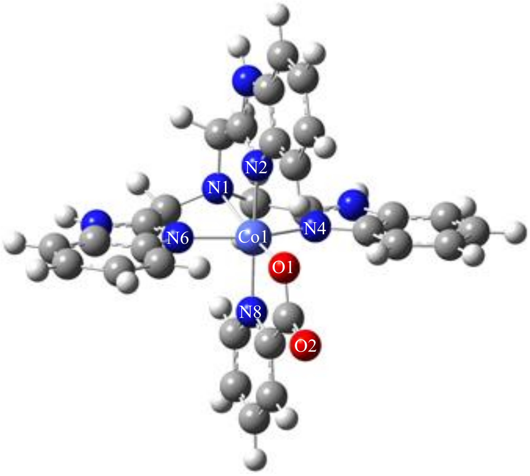


Figure 2. Optimized molecular structure of $[Co(ntb)(pic)]^+$ with atomic numbering scheme at B3LYP/GEN level in gas phase.

Table 2. The selected bond lengths and angles at B3LYP/GEN level in gas phase.

Bond Length	Theoretical	Experimental [1]
Co1 – O1	2.093	2.044
Co1 – N2	1.970	2.091
Co1 – N8	2.007	2.213
Co1 – N4	2.008	2.064
Co1 – N6	2.008	2.092
Co1 – N1	2.545	2.449
Bond Angle	**Theoretical**	**Experimental [1]**
O1 – Co1 – N4	103.38	114.90
O1 – Co1 – N6	103.39	102.07
N4 – Co1 – N6	153.13	136.30
N2 – Co1 – N6	89.93	101.58
N2 – Co1 – N8	175.92	169.10
O1 – Co1 – N1	172.07	166.48
N8 – Co1 – N1	107.13	115.68
N6 – Co1 – N1	76.90	73.88
O1 – Co1 – N2	95.11	93.82
N4 – Co1 – N2	89.93	98.48
O1 – Co1 – N8	80.80	76.24
N4 – Co1 – N8	91.01	82.06
N6 – Co1 – N8	91.01	85.09
N4 – Co1 – N1	76.90	74.63
N2 – Co1 – N1	76.96	74.74

As can be seen from Table 2, the biggest difference between the experimental and theoretical values occurs at bond length of Co1 – N8. For this bond, the predicted value is longer than the experimental value. Their difference is 0.206 Å for B3LYP/GEN in gas phase. Mainly the theoretical bond lengths are shorter than those of experimental values. As for the bond angles, the biggest difference between experimental and theoretical values mainly takes place at N4 – Co1 – N6 bond angle. The predicted value is wider than the experimental value. Their difference is 16.83° for B3LYP/GEN level in gas phase.

The molecular geometry of mentioned complex is distorted octahedral. (ntb) is tetradentate ligand and (pic) is bidentate ligand. (ntb) ligand bonds from four nitrogen atoms with metal ion and (pic) ligand bonds from oxygen and nitrogen atoms.

3.2. Vibrational Spectrum

The vibrational frequencies were calculated at B3LYP/GEN level in gas phase. The calculated stretching frequencies were scaled with 0.9611 [12 – 16] and assigned. These frequencies were represented in Table 3.

Table 3. The selected stretching frequencies (cm^{-1}) of mentioned complex

Assignment	Theo.	Exp.(cm^{-1}) [1]	Assignment	Theo.	Exp.(cm^{-1}) [1]
$\nu_{(-NH)}$	3531	3420	$\nu_{(-C=O)}^{as}$	1611	1595
$\nu_{(-CH)}$	3114	3206	$\nu_{(-C=N)}^{s}$	1436	1474
$\nu_{(-CH)}$	2880	2924	$\nu_{(-C=N)}^{s}$	1429	1454
$\nu_{(-C=O)}^{as}$	1618	1644	$\nu_{(-C=N)}^{as}$	1292	1371
$\nu_{(-C=O)}^{as}$	1614	1621	$\nu_{(-Co-O)}$	685	746

^{s} symmetric stretching, ^{as} anti-symmetric stretching

CC was calculated for vibrational frequencies and this value is 0.9965. According to these results, there is a good agreement between experimental and theoretical stretching frequencies.

3.2. Molecular Orbital Analysis and Electronic Absorption Spectra

Molecular orbital comprises from the linear combinations of atomic orbital. Different atomic orbital contribute to each MO. This contribution can determine with atomic orbital coefficient. In this study, atomic orbital coefficients were calculated at B3LYP/LANL2DZ level for mentioned complex. Percentages of contributions of selected MO were calculated by using atomic orbital coefficient with Eq. (1) [17]

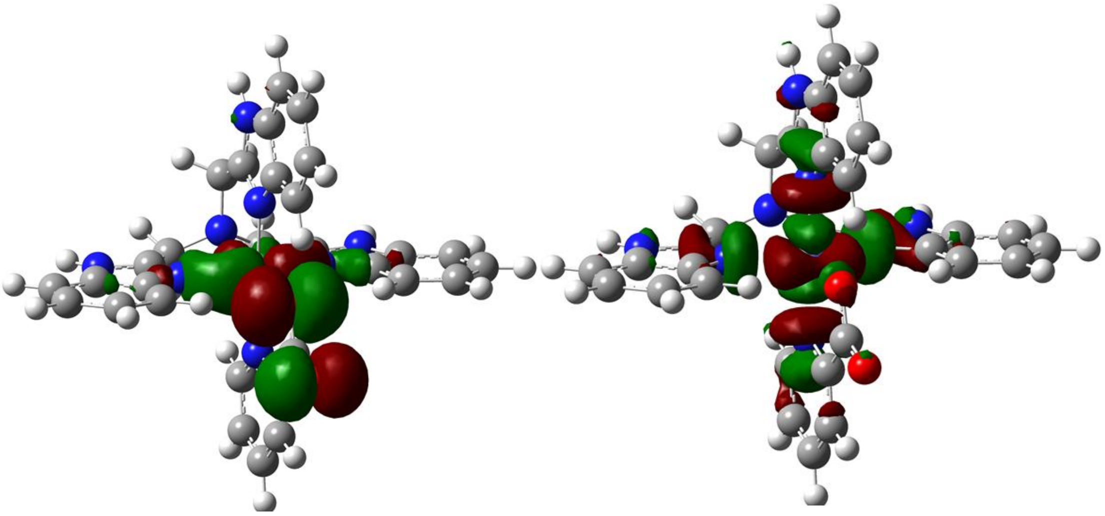
$$\%\text{Contribution}=\frac{n^2}{\Sigma n^2}\text{x}100 \tag{1}$$

Where n is the atomic orbital coefficient and Σn^2 is the sum of the squares of all atomic orbital coefficients in a specific molecular orbital. As experimentally, the band at 531 nm in UV-VIS spectrum was reported and assigned the d → d transition [1]. At calculated UV-

VIS spectrum, there are two bands which are 343.5 and 498.0 nm. TC analysis was calculated with Eq. (2) for 498.0 nm.

$$\%\text{Transition}=\frac{t^2}{\Sigma t^2}\text{x}100 \tag{2}$$

Where t is coefficient of the wavefunction for each excitation and Σt^2 is the sum of the squares of all coefficient of the wavefunction for each excitation in a specific band. The results show that the maximum transition character has been seen from 146β to 152β. The characters of 146β and 152β orbitals are cobalt atom orbitals. Therefore, the band at 498.0 nm was assigned to d → d transition. At UV-VIS spectrum, the wavelength of main band is 343.5 nm. Figure 3 shows the contour diagram of 146β and 152β orbitals. The characters of 146β and 152β orbitals were shown in Figure 3.



146B	152B

Co: %58.7, (ntb): %0.33 (pic): %40.97	Co: %61.49, (ntb): %30.12 (pic): %8.38

Figure 3. The contour diagram and MO character analysis of 146β and 152β.

4. Conclusions

DFT and TD-DFT calculations were performed on the relevant complex, which is $[Co(ntb)(pic)]^+$ by using B3LYP method with LANL2DZ, 6-31g and GEN basis sets. For structure checking, the calculated structural parameters were used to compare with the experimental structure. Theoretical results are in a good agreement with experimental results at B3LYP/GEN level in gas phase. The correlation coefficient of vibrational frequencies was calculated and it is 0.9965 for mentioned complex. Electronic absorption spectrum calculations were calculated with TD-DFT method in DMF solvents. The molecular orbital characters and electronic transition characters were analyzed at B3LYP/GEN level. Two bands were obtained in theoretical electronic absorption spectra. The wavelength of main band is 343.5 nm. MO characters and electronic transition characters show that the band at 498.0 nm can be assigned d → d transitions.

5. Acknowledgments

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