

Quantum Chemical Studies on Molecular Structures of Copper-Pyridine Complexes

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Abstract: The Cu-pyridine and Cu-(pyridine)₂ complexes were studied by quantum chemical calculations. Although pyridine provides both σ - and π -bonding capabilities towards metal atoms and ions, the mono-ligand and di-ligand Cu-pyridine complexes are determined to be σ - structures. In the di-ligand complex, the two pyridine rings prefer the eclipsed to the staggered form. Due to an additional Cu-N σ -bond and stronger ligand π -electron donation, the di-ligand complex possesses a stronger metal ligand interaction than the mono-ligand complex. Upon ionization, the metal-ligand bonding in the di-ligand complex is more strongly enhanced compared to the mono-ligand complex.

Keywords: Copper, Pyridines, Quantum chemical calculations, Metal-ligand bonding

Introduction

Metal-ligand weak interactions are known to play a profound role in supramolecular chemistry, biochemistry, catalysis and environmental science¹⁻⁶. In the last 20 years, supramolecular chemistry has been considered to be a rapid growing branch for developing new materials by assembling various molecular blocks and metal ions. Detailed investigation of the structures and formations of supramolecular systems becomes crucial to make these assemblies suitable for applications as functional materials⁷. Therefore, it can be imagined that metal-ligand interactions are present everywhere in our world and it is valuable to explore how such interactions affect the environment from a chemistry viewpoint.

Copper plays an important role in organisms as one of the so-called “essential” metals. The ubiquitous Cu-organonitrogen complexes and their extensive applications have inspired much interest in the bonding, structures and properties of Cu and nitrogen containing molecules. This research paper presents a systematic quantum chemical study of the metal-ligand binding interaction in Cu-pyridine complexes.

Pyridine (Figure 1), a six-membered cyclic aromatic molecule with σ and π binding capabilities through its nitrogen electron lone pair and π system, respectively, has inspired considerable interests in its bonding with metals over the last ten years. A number of experimental and theoretical investigations have established that most metal-pyridine complexes

are σ complexes⁸⁻¹¹. The bonding of pyridine to copper surfaces has been described by both σ and π interactions¹². In fact, a recent *ab initio* theoretical study by Edmonds and co-workers¹³ suggests that the anionic $[\text{Co-pyridine}]^-$ and $[\text{Co-(pyridine)}_2]^-$ complexes are formed via π bonding. Therefore, it would be interesting to determine the bonding interaction between pyridine and other transition metal atoms such as copper.

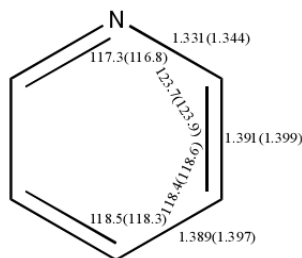


Figure 1. Structure of pyridine from B3P86/6-311+G(d,p) and MP2/6-311+G(d,p) method (in parenthesis: bond lengths, Å, bond angles,^o)

Quantum chemical calculations

With a rapid growth in CPU speed, quantum chemical calculations using available program packages have become increasingly more sophisticated and valuable for predicting, modelling and understanding experimental measurements. Quantum chemical calculations can provide quite reliable results about molecular geometries, energies, electronic states, vibrational frequencies and reaction dynamics. In this research article, theoretical calculations were employed to predict the molecular structures, electronic states, bond strengths and vibrational frequencies of the neutral and ionic metal complexes as well as the AIEs (Adiabatic ionization energies) of the neutral metal complexes.

The Hartree-Fock (HF) method has been widely used to solve problems from small-to medium-sized molecules. However, as HF theory neglects electron correlation, it has been recognized that the HF method is not always reliable for describing many molecular systems. A number of so-called post-Hartree-Fock methods have been devised to improve theoretical results by including electron correlation to the multi-electron wave function. One of these approaches, Møller-Plesset (MP) perturbation theory, treats electron correlation as a perturbation of the HF function. In this theory, the energy of the system is expanded as:

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \dots + \lambda^n E_n$$

Where, E_n is the n th order corrections to the energy. In this research work, the second order MP method (MP2) was used in the theoretical calculations, as it yields good predictions for the Cu-complexes. In addition to the MP2 method, the MP3 and MP4 methods include higher order energy corrections. However, the MP3 method yields little improvement and both MP3 and MP4 methods are much more expensive. Therefore, we mainly used the MP2 method for the theoretical calculations in this work. In this work, all the calculations were carried out with 6-311+G(d,p) basis sets. The geometry optimization by the MP2 method was usually started from an optimized structure obtained from faster density functional theory (DFT) calculations. DFT methods are different from the wavefunction-based *ab initio* methods where the energy of an electronic system is expressed in terms of its electron density. DFT methods have a lower computational cost and a wider range of applications. Although there have been some concerns about the accuracy and reliability of DFT, these calculations have become very popular in modelling various types of molecular systems¹⁴⁻¹⁶ and have yielded reasonable agreement with the experimental results.

Computational strategy and procedure

In this work, both MP2 and DFT calculations were performed with the GAUSSIAN-2003 program package¹⁷. In the DFT calculations, Becke's three parameter hybrid exchange functional (B3) was combined with the gradient-corrected correlation functional of Perdew¹⁸ (P86) or Lee, Yang and Parr (LYP)¹⁹. Pople's triple zeta basis set with polarization and diffuse functions, 6-311+G(*d,p*), was used in most calculations. Electron density maps were generated and vibrational modes were identified with GaussView²⁰ 3.09. AIEs were calculated to be the energy difference between the ionic and neutral complexes, where vibrational zero-point energy corrections were included. Metal-ligand bond dissociation energies were calculated to be the energy difference of the metal atoms and ligands from their complexes.

The theoretical calculations of metal complexes begin from geometry optimization of the free ligand. For ligands with several possible conformations, a systematic local minimum search needs to be performed starting from a number of initial guesses. The global minimum energy structure can be located by comparing the energies of all structures. During this search for the minimum energy structure, weak interactions, such as intramolecular hydrogen bonding, should be considered. Multidimensional FC factors were computed from the theoretical equilibrium geometries, harmonic frequencies and normal modes of the neutral and ionic complexes.

Results and Discussion

Cu-pyridine Complex

In our calculations of the Cu-pyridine complexes, σ and π structures were considered to be formed by Cu binding to the nitrogen atom and to the six-membered π ring, respectively. However, no minimum energy π structure was found for the neutral and ionic species. Table 1 (a&b) lists point groups, electronic states and energies, equilibrium geometries and vibrational frequencies of the Cu-pyridine σ complexes from the B3P86 and MP2 calculations.

Table 1(a). Point groups, electronic states, equilibrium energies (E_e , a.u.), geometries (R, Å, °) and vibrational frequencies (cm^{-1}) of the Cu-pyridine σ complexes from the B3P86 calculations using 6-311+G(*d,p*) basis set

Method	B3P86
Point group	C_{2v}
Electronic state	2A_1
Equilibrium energies (E_e , in a.u.)	1890.2220812
Geometries:	
Cu-N = 2.034, C-N = 1.339, Cu-N-C = 120.9, N-C-C = 122.7, C-C = 1.386, C-C = 1.389	
C-C-C = 118.8	
Frequencies:	
a_1 : 3217, 3195, 3180, 1654, 1235, 1051, 1033, 636, 184; a_2 : 1002, 893, 378;	
b_1 : 1017, 960, 758, 709, 419, 41; b_2 : 3211, 3181, 1631, 1479, 1375, 1324, 1174, 1091, 662, 123.	
Electronic state	1A_1
Equilibrium energies (E_e , in a.u.)	1890.001694
Geometries:	
Cu-N = 1.904, C-N = 1.348,	C-C = 1.386, C-C = 1.389
Cu-N-C = 120.6, N-C-C = 122.0	C-C-C = 119.0
Frequencies:	
a_1 : 3232, 3215, 3308, 1664, 1520, 1246, 1102, 1063, 1046, 667, 271; a_2 : 1004, 891, 392;	
b_1 : 1039, 966, 768, 706, 423, 111; b_2 : 3228, 3212, 1626, 1488, 1387, 1324, 1189, 1106, 658, 168.	

Table 1(b). Point groups, electronic states, equilibrium energies (E_e , a.u.), geometries (R, Å, °) and vibrational frequencies (cm^{-1}) of the Cu-pyridine σ complexes from the MP2 calculations using 6-311+G(d,p) basis set

Method	MP2
Point group	C_{2v}
Electronic state	2A_1
Equilibrium energies (E_e , in a.u.)	-1886.78529
Geometries:	
Cu-N = 2.005, C-N = 1.350, C-C = 1.396, C-C = 1.397 Cu-N-C = 120.9, N-C-C = 122.7, C-C-C = 119.0	
Frequencies:	
a_1 : 3243, 3222, 3213, 1643, 1508, 1241, 1088, 1047, 1027, 630, 186; a_2 : 938, 878, 361; b_1 : 927, 908, 723, 565, 377, 66; b_2 : 3237, 3216, 1615, 1481, 1399, 1381, 1178, 1086, 655, 130	
Electronic state	1A_1
Equilibrium energies (E_e , in a.u.)	-1886.6902916
Geometries:	
Cu-N = 1.899, C-N = 1.358, C-C = 1.393, C-C = 1.397 Cu-N-C = 120.7, N-C-C = 122.1, C-C-C = 119.3	
Frequencies:	
a_1 : 3255, 3239, 3231, 1659, 1517, 1251, 1098, 1063, 1029, 658, 266; a_2 : 943, 878, 368; b_1 : 955, 913, 731, 581, 380, 100; b_2 : 3252, 3234, 1616, 1496, 1399, 1390, 1191, 1099, 652, 166	

Both B3P86 and MP2 calculations predict a configuration in C_{2v} symmetry, where the Cu atom is coplanar to the six-membered π ring. Both methods predict very little geometry change of the pyridine ring upon complexation. The Cu-N distance is predicted to be 0.03 Å longer by the B3P86 method than the MP2 method. Upon ionization, the Cu-N distance is shortened due to reduced repulsion between the Cu $4s^1$ and N lone-pair electrons and additional charge-dipole attraction. The B3P86 method predicts a slightly larger reduction (~ 0.13 Å) of the Cu-N distance than the MP2 method (~ 0.11 Å).

Cu-(pyridine)₂ Complex

The theoretical work of Cu-(pyridine)₂ presented in this paper excludes the π structure, because such a local minimum energy structure was not located for the Cu-pyridine complex. Therefore, the Cu-(pyridine)₂ complex should be formed by Cu atom binding to the nitrogen of each pyridine molecule. The optimized point groups, electronic states, equilibrium energies and geometries and vibrational frequencies predicted by B3P86 and MP2 theories are listed in Table 2 (a&b).

According to the B3P86 calculations, the ground electronic states of the neutral and ionic Cu-(pyridine)₂ complexes are $^2B_{3u}$ and 1A_g under D_{2h} symmetry. The optimized Cu-N distance in the Cu-(pyridine)₂ complex is much shorter than that in the Cu-pyridine complex as seen in Table 3. Accordingly, the pyridine rings in Cu-(pyridine)₂ undergo slightly larger geometry changes than the one in Cu-pyridine upon complexation. Ionization of the $^2B_{3u}$ state will generate the 1A_g state, where the Cu-N distance is slightly elongated and the pyridine rings have nearly the same geometry as that in free ligand. Thus, the metal-ligand bonds are largely enhanced by electron donation from the π clouds of the ligands to the Cu $3p_\pi$ orbital. Such electron donation explains the shorter Cu-N bond length in the neutral species compared to the ions. The Cu-N bond lengths in the ion are slightly longer than those in the neutral complex due to the lack of π electron donation.

Table 2(a). Point groups, electronic states, equilibrium energies (E_e , a.u.), geometries (R , Å,⁰) and vibrational frequencies (cm^{-1}) of the Cu-(pyridine)₂ complexes from the B3P86 calculations using 6-311+G(*d,p*) basis set

Method	B3P86
Point group	D _{2h}
Electronic state	² B _{3u}
Equilibrium energies (E_e , in a.u.)	-2139.3650957
Geometries:	
Cu-N = 1.860, C-N = 1.369, C-C = 1.373, C-C = 1.402 N-Cu-N = 180.0, Cu-N-C = 121.8, N-C-C = 123.1, C-C-C = 120.1, C-N-N-C = 0.0	
Frequencies:	
a _g : 3223, 3206, 3190, 1668, 1488, 1234, 1070, 1051, 1032, 649, 198; b _{1g} : 958, 830, 412; b _{2g} : 956, 838, 710, 666, 375, 107; b _{3g} : 3209, 3190, 1523, 1418, 1362, 1319, 1133, 1085, 658, 147; a _u : 958, 832, 413, 35; b _{1u} : 3223, 3206, 3189, 1609, 1488, 1212, 1073, 1049, 987, 665, 357; b _{2u} : 3209, 3190, 1523, 1416, 1361, 1323, 1132, 1089, 659, 250, 39; b _{3u} : 956, 837, 711, 667, 395, 168, 34	
Electronic state	¹ A _g
Equilibrium energies (E_e , in a.u.)	-2139.1975907
Geometries:	
Cu-N = 1.896, C-N = 1.347, C-C = 1.383, C-C = 1.389 N-Cu-N = 180.0, Cu-N-C = 120.8, N-C-C = 122.5, C-C-C = 119.0, C-N-N-C = 0.0	
Frequencies:	
a _g : 3231, 3213, 3206, 1668, 1522, 1247, 1104, 1067, 1048, 664, 186; b _{1g} : 1004, 894, 393; b _{2g} : 1034, 965, 770, 709, 426, 108; b _{3g} : 3227, 3209, 1628, 1485, 1385, 1323, 1186, 1102, 661, 145; a _u : 1003, 893, 391, 15; b _{1u} : 3231, 3213, 3205, 1668, 1522, 1244, 1104, 1069, 1048, 673, 338; b _{2u} : 3227, 3209, 1630, 1487, 1386, 1325, 1186, 1105, 661, 237, 40; b _{3u} : 1034, 966, 772, 711, 439, 180, 35;	
Point group	D _{2d}
Electronic state	¹ A ₁
Equilibrium energies (E_e , in a.u.)	-2139.1983542
Geometries:	
Cu-N = 1.896, C-N = 1.347, C-C = 1.383, C-C = 1.389 N-Cu-N = 180.0, Cu-N-C = 120.8, N-C-C = 122.4, C-C-C = 119.0, C-N-N-C = 90.0	
Frequencies:	
a ₁ : 3231, 3213, 3206, 1667, 1522, 1246, 1104, 1067, 1047, 664, 187; a ₂ : 1005, 894, 393; b ₁ : 1005, 895, 394, 28; b ₂ : 3231, 3213, 3206, 1667, 1522, 1244, 1104, 1069, 1047, 673, 339; e: 3227, 3209, 1628, 1486, 1385, 1323, 1186, 1103, 1033, 967, 771, 710, 661, 431, 213, 121, 37;	

Table 2(b). Point groups, electronic states, equilibrium energies (E_e , a.u.), geometries (R , Å,⁰) and vibrational frequencies (cm^{-1}) of the Cu-(pyridine)₂ complexes from the MP2 calculations using 6-311+G(*d,p*) basis set

Method	MP2
Point group	D _{2h}
Electronic state	² B _{3u}
Equilibrium energies (E_e , in a.u.)	-2134.483272
Geometries:	

Contd...

Cu-N = 1.838, C-N = 1.358, C-C = 1.355, C-C = 1.393 N-Cu-N = 180.0, Cu-N-C = 121.8, N-C-C = 123.2, C-C-C = 120.0, C-N-N-C = 0.0

Frequencies:

a_g : 3262, 3238, 3217, 1892, 1548, 1285, 1161, 1105, 1060, 667, 209; b_{1g} : 1061, 945, 454; b_{2g} : 1025, 917, 744, 630, 335, 41; b_{3g} : 3243, 3215, 1622, 1446, 1383, 1268, 1160, 1111, 687, 151; a_u : 1063, 947, 458, -27; b_{1u} : 3264, 3243, 3216, 2326, 1550, 1377, 1247, 1096, 1052, 689, 374; b_{2u} : 3243, 3214, 1624, 1443, 1385, 1265, 1163, 1103, 688, 267, 36; b_{3u} : 1027, 919, 748, 628, 377, 218, 15;

Electronic state

1A_g

Equilibrium energies (E_e , in a.u.)

-2134.400602

Geometries:

Cu-N = 1.862, C-N = 1.357, C-C = 1.393, C-C = 1.397 N-Cu-N = 180.0, Cu-N-C = 120.8, N-C-C = 122.2, C-C-C = 119.2, C-N-N-C = 0.0

Frequencies:

a_g : 3255, 3240, 3230, 1659, 1517, 1249, 1103, 1069, 1032, 661, 195; b_{1g} : 940, 879, 367; b_{2g} : 950, 910, 728, 586, 380, 96; b_{3g} : 3251, 3237, 1615, 1493, 1398, 1386, 1189, 10961, 653, 153; a_u : 939, 877, 366, -21; b_{1u} : 3255, 3240, 3230, 1660, 1516, 1247, 1104, 1071, 1031, 673, 354; b_{2u} : 3251, 3236, 1616, 1494, 1388, 1189, 1099, 654, 254, 41; b_{3u} : 950, 911, 729, 583, 395, 178, 34;

Point group

C_1

Electronic state

2A

Equilibrium energies (E_e , in a.u.)

-2134.5007558

Geometries:

Cu-N = 1.863, C-N = 1.355, C-C = 1.394, C-C = 1.397 N-Cu-N = 180.0, Cu-N-C = 120.9, N-C-C = 122.4, C-C-C = 119.2, C-N-N-C = 90.0

Frequencies:

a : 3274, 3253, 3249, 3240, 3236, 3233, 3224, 3208, 1810, 1653, 1615, 1606, 1511, 1487, 1471, 1393, 1382, 1378, 1326, 1258, 1251, 1245, 1182, 1123, 1098, 1093, 1092, 1068, 1049, 1031, 993, 988, 968, 954, 945, 926, 883, 879, 846, 773, 731, 668, 667, 654, 650, 621, 588, 461, 407, 376, 370, 365, 236, 229, 204, 165, 120, 78, 33, 27, 14;

Electronic state

1A_1

Equilibrium energies (E_e , in a.u.)

-2134.4018194

Geometries:

Cu-N = 1.896, C-N = 1.347, C-C = 1.383, C-C = 1.389 N-Cu-N = 180.0, Cu-N-C = 120.8, N-C-C = 122.4, C-C-C = 119.0, C-N-N-C = 90.0

Frequencies:

a_1 : 3240, 3230, 1658, 1516, 1249, 1102, 1069, 1031, 662, 196; a_2 : 954, 884, 373; b_1 : 954, 854, 377, 18; b_2 : 3240, 3230, 1660, 1516, 1247, 1104, 1071, 1031, 674, 354; c : 3255, 3251, 3236, 1615, 1494, 1399, 1387, 1189, 1097, 959, 926, 735, 653, 623, 402, 226, 121, 36;

Table 3. Adiabatic ionization energies (AIE, cm^{-1}), bond dissociation energies (D_0^+ / D_0 kJmol^{-1}) and vibrational frequencies (cm^{-1}) of Cu-pyridine and Cu-(pyridine)₂ from the B3P86 and MP2 calculations using 6-311+G(d,p) basis set

Compounds	Parameters	Symbol	B3P86	MP2
Cu-pyridine	AIE		48623	48623
	D_0^+ / D_0		280.1/45.6	258.7/47.4
	Cu ⁺ /Cu-L stretch	$\nu_{11}^+ / \nu_{11, a_1}$	271/183	266/186

Contd...

Cu-(pyridine) ₂	Cu ⁺ -L o.p.bend	$\nu_{20}^+ / \nu_{20}, b_1$	111/41	100/66
	Pyridine ring distortion	ν_{10}^+, a_1	667	658
	AIE		37713	17211
	D ₀ ⁺ / D ₀		524.6/159.6	517.3/23.5
	L-Cu-L symm.stretch	ν_{11}^+, a_g	186	195
	Pyridine ring distortion	ν_{10}^+, a_g	664	658
	Pyridine ring breath	ν_9^+, a_g	1048	1032
	C-H i.p. bend	ν_7^+, a_g	1104	1103
	C-H i.p. bend	ν_6^+, a_g	1247	1249
	Pyridine rings distortion	ν_4^+, a_g	1668	1659

Conclusion

The Cu-pyridine and Cu-(pyridine)₂ complexes were studied by quantum chemistry calculations. Although pyridine provides both σ and π -bonding capabilities towards metal atoms and ions, the mono-ligand and di-ligand Cu-pyridine complexes are determined to be σ structures. In the di-ligand complex, the two pyridine rings prefer the eclipsed to the staggered form. Due to an additional Cu-N σ bond and stronger ligand π electron donation, the di-ligand complex possesses a stronger metal ligand interaction than the mono-ligand complex. Upon ionization, the metal-ligand bonding in the di-ligand complex is more strongly enhanced compared to the mono-ligand complex. Consequently, the ionization energy of the di-ligand complex is red shifted with respect to the mono-ligand complex.

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