ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 1, pp. 19–24. © Pleiades Publishing, Ltd., 2009.

Crystal Structure and Theoretical Calculation of Copper Complexes with 4,5-Diazafluoren-9-one[1]

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Received October 9, 2007

Abstract—Five copper complexes with 4,5-diazafluoren-9-one have been reported. Some of their structures are determined by single crystal X-ray diffraction. On the basis of experimentation, all the complexes were calculated by DFT-B3LYP/LANL2DZ in Gaussian-98w. By analyzing the experimental and calculated values, it can be concluded, on the one hand, that the experimental results are proved thoroughly by the theoretical calculated results; on the other hand, the theoretical calculated results can deduce the experimental results reasonably well.

DOI: 10.1134/S1070328409010059

INTRODUCTION

More recently, there has been an interest in the photochemical properties of copper complexes of phenanthroline ligands as candidates for the development of photonic devices including sensors, photovoltaic devices, and switches [1]. The photochemical and electrochemical properties of the copper phenanthroline complexes have also been used to study their interaction with biological systems, in particular, DNA intercalation and scission [2, 3]. There have also been numerous studies of these types of complexes in relation to their biomimetic behavior [4]. 4,5-diazafluoren-9-one (**Dafo**), which is a derivative of 1,10-phenanthroline, having an exocyclic keto function [5], has attracted attention of researchers owing, perhaps, to its DNA intercalation [6], catalytic [7], and biological [8] properties. In order to synthesize supramolecular complexes possessing a biological function and materials possessing catalysis and magnetism, our research team has analyzed many literature data in this field. Since 1999, we have synthesized a series of transition metal complexes of Dafo by various methods [9–13]. They have been characterized by element analysis and IR, UV, and fluorescence spectra. The crystal structures of some complexes are also measured. On the basis of experimentation, DFT-B3LYP/LANL2DZ in Gaussian-98w was used to optimize five copper complexes, and the subsequent calculation was continued. The energies of some frontier molecular orbitals and atomic net charge populations of these complexes were researched, and a reasonable structure of one complex was educed in theory.

EXPERIMENTAL

Elemental analysis was performed on a German Vario EL III CHNOS analyzer. IR spectra were measured on a German EQUINOX × 55 analyzer. Crystal structure was obtained on Bruker Smart-1000CCD and RigakuAFC7R diffractometers. The theoretical calculations were carried out with the Gaussian-98w package in the Window operating system on a Legend computer (256 MB, 60 GB). All reagents were of A.R. grade. Dafo was prepared following the method in the literature [11].

The syntheses of complexes $[Cu(Dafo)_2(H_2O)_2](OPA)_2$ (OPA = *o*-phthalic acid, **I**), $[Cu(Dafo)_2(H_2O)_2](ClO_4)_2$ (**II**), and $[Cu(Dafo)_2(H_2O)_2](NO_3)_2$ (**III**) are in the literature ([13], [9], and [10] for **I**, **II**, and **III**, respectively).

Synthesis of complex $[Cu(Dafo)_2Cl_2] \cdot 2H_2O$ (IV). A solution of $CuCl_2 \cdot 2H_2O$ (0.340 g, 2.0 mmol) in 15 ml of water was dropped into a solution of ligand Dafo (0.362 g, 2.0 mmol) in 25 ml of water under stirring. After refluxing for 3 h, a few of crystals of $CuCl_2 \cdot 2H_2O$ (0.100 g) were added to the above solution. The reactants were refluxed for additional 10 h. Later, the reaction solution was left to stand for a day, and heavy green crystals formed. Then the crystals were filtered off, the filtrate was left to stand for

[1] The text was submitted by the authors in English.

4 weeks, and column-like crystals suitable for X-ray diffraction were obtained. Melting point >300°C.

For $C_{22}H_{16}Cl_2CuN_4O_4$

anal. calcd, %:	C, 49.39; H, 2.99; N, 10.47.
Found, %:	C, 48.79; H, 2.85; N, 10.26.

Synthesis of complex [Cu(Dafo)$_2$Br$_2$] (V). To a solution of Dafo (0.363 g, 0.002 mol) in 30 ml of acetone was added $CuBr_2$ (0.345 g, 0.0015 mol) in a mixed solvent of 25 ml of acetone and 5 ml of water. A type of deep green precipitate formed immediately. The precipitate was filtered off, dried thoroughly in air, and the solid of complex **V** was obtained. The yield was 77.6%, melting point >300°C.

For $C_{22}H_{12}Br_2CuN_4O_2$

anal. calcd, %:	C, 44.59; H, 2.02; N, 9.46.
Found, %:	C, 45.01; H, 1.85; N, 9.53.

Crystal structure determination and refinements. The crystal structure analyses of complex **I–III** are depicted in detail in the literature ([13], [9], and [10] for I, **II**, and **III**, respectively).

A single crystal of complex **IV** with dimensions of $0.20 \times 0.18 \times 0.12$ mm was selected for data collection, using a RigakuAFC7R diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71069$ Å). Data were collected by the ω–2θ scan technique. The total reflections collected were 7047. Observed were 2428 unique reflections, and structure analysis was used ($R_{int} = 0.0227$). The structure was solved by direct methods. The positions of all non-H atoms were obtained from successive Fourier syntheses. The positions of all non-H atoms were refined anisotropically with full-matrix least-squares on F^2. In the final difference map, the residuals are 0.592 and –0.449 e/Å^3, respectively. The crystallographic data and analysis parameters are given as follows: monoclinic system, space group $C2/c$ with cell dimensions $a = 7.2306(10)$, $b = 15.364(2)$, $c = 19.290(3)$ Å, $\beta = 98.938(3)°$, $V = 2116.9(5)$ Å^3, $Z = 4$, $F(000) = 1084$, $M = 534.83$, $\rho_{calcd} = 1.678$ g/cm^3, μ(MoK_α) = 1.003 mm^{-1}, $R = 0.0365$, $wR = 0.0509$.

Calculation method. In the calculation, the geometry structures of complexes **I–IV** were constructed according to their crystal structures. The geometric structure of complexes **V** was constructed in Chem3D, and on the basis of this, a reasonable geometric structure was obtained by adjusting the ligand position. Density functional methods (DFT) are very efficient for research. In this paper, the five complexes were optimized and the subsequent calculation was continued by DFT-B3LYP in Gaussian-98w. The transition metal copper was involved in all the calculation systems, so the effective basis set LANL2DZ was used in all the calculation systems.

RESULTS AND DISCUSSION

The crystal structures of complexes **I–IV** are shown in the figure. The selected bond lengths and angles are listed in Table 1.

The conclusion that, in these complexes, the copper atom is in a stretching octahedron can be summed up from the crystal structure data of the complexes. The probable reasons are as follows. (1) There is the Jahn–Teller effect in the copper complexes with Dafo. The orbital energy of e_g and t_{2g} sets split into five initial degenerate d orbitals of the copper atom would give a corresponding change. On the one hand, the energy of e_g splits owing to the decrease in energy of the d_{z2} orbital. On the other hand, the energy of t_{2g} splits owing to the increase in energy of the d_{xy} orbital. Consequently, the degeneracy of both the e_g and t_{2g} orbitals is reduced. The interaction between one nitrogen atom of each Dafo and the central copper atom becomes very weak. Therefore, the stretching octahedron complexes of copper with Dafo are formed. (2) As Dafo itself is concerned, the large N–N bite distance (2.99 Å) enforced by the rigid five-membered central ring leads to unequal binding by the two nitrogen atoms with copper [14]. (3) The steric effect of acid radicals and the reaction media perhaps influence the coordination of Dafo with copper.

By comparison with the coordination bond lengths of complexes **I–IV**, respectively, it is obvious that the interaction between one nitrogen atom of each Dafo and the copper atom is very weak. That is, in detail, the atoms of N(2), N(2*A*) in complex **I**; N(2), N(2*A*) in complex **II**; N(2), N(4) in complex **III**; and N(2), N(2*A*) in complex **IV** have a strong tendency of leaving the central atom. The fact complies with the above conclusion that in these complexes the copper atom is in a stretching octahedron.

Comparing complexes **I–III** with complex **IV**, we can say that the bond lengths of Cu–N(2) and Cu–N(2*A*) in complex **I**, Cu–N(2) and Cu–N(2*A*) in complex **II**, and Cu–N(2) and Cu–N(4) in complex **III** are about 2.6 Å, which is shorter than Cu–N(2) and Cu–N(2*A*) in complex **IV** (about 2.9 Å). The main factor responsible for this behavior is that the coordinative ability of the oxygen atom is stronger than that of the chlorine atom, which results from the fact that the radius of the oxygen atom is shorter than that of the chlorine atom and the electronic density of the former is higher than that of the latter.

Although the crystal of complex **V** was not obtained, its structure can be educed from the calculated results. This will be further discussed in this paper.

The data of selected bonds and angles for the optimized structures **I–V** are shown in Table 1 (the experimental data are in brackets). By comparison with the experimental values of complexes **I–IV**, the average deviation of the calculated value and the experimental value of the main bond lengths and bond angles in the

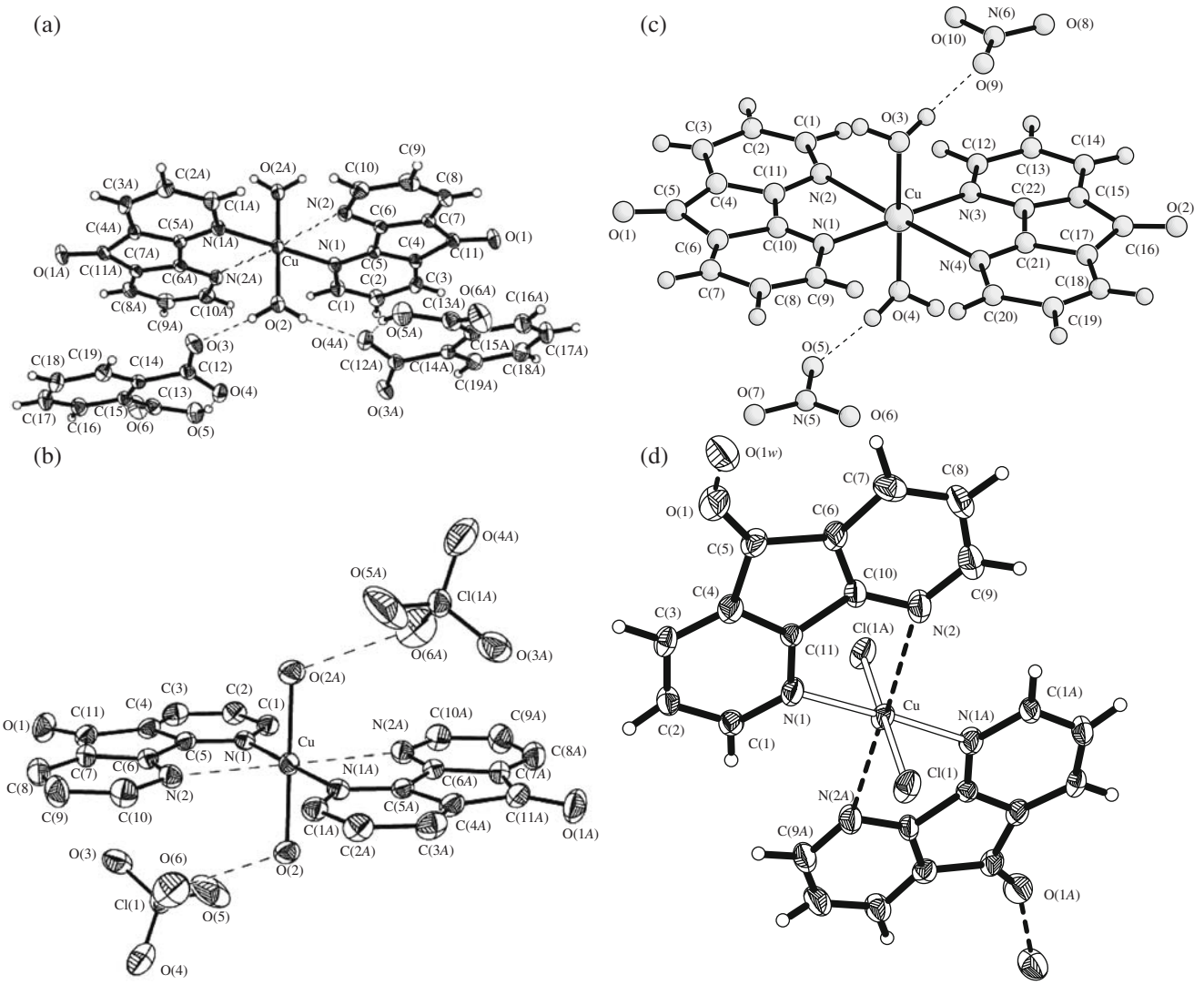

Fig. 1. Structures of compounds: **I** (a), **II** (b), **III** (c), and **IV** (d).

optimized structure is in the range of 1–2% (very little exception). The reasons for the deviation may be as follows: the selection of calculation methods and the approximation of setup groups; the neglect of anionic effect in the course of calculation; the chemical environmental difference of the complex (calculation was based on gas geometry configuration). The deviation can be accepted in a theoretical calculation for a big system.

Complexes **IV** and **V** are both copper complexes with Dafo and halogen, so their structures should be similar. The optimized structures of the two complexes are very close to each other; the calculated value of the main bond lengths and bond angles are very close also (Table 1). The two complexes have similar structures, which is proved by theoretical calculation completely. As complex **IV** is concerned, the optimized structure is according to the crystal structure. Naturally, the optimized structure of complex **V** should also be according to the crystal structure. In complexes **IV** and **V**, the distance of one nitrogen atom of each Dafo and copper is about 2.94 Å, which indicates that the interaction of this nitrogen atom with the copper atom is very weak. So, the conclusion that the copper atom is in a stretching octahedron in complex **V** as complex **IV** is educed in theory.

The calculated value and the experimental value of the IR spectra are listed in Table 2. Comparing the values, the calculated values primarily accord with the experimental values.

The energy of the occupied frontier molecular orbitals is related to the photoelectronic spectra, and the energy D value of E_{HOMO} and E_{LUMO} (ΔE) is related to the UV-Vis spectra. The frontier molecular orbital energy (a.u.) of the complexes obtained from the calculation is shown in Table 3.

Table 1. Selected bond lengths and angles in structures **I–V**, calculated and experimental (in the brackets)

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
I		**II**		**III**		**IV**		**V**	
Cu–N(1)	2.011 (1.983)	Cu–N(1)	2.012 (1.987)	Cu–N(1)	2.011 (1.999)	Cu–N(1)	1.990 (2.008)	Cu–N(1)	1.982
Cu–N(1*A*)	2.011 (1.983)	Cu–N(1*A*)	2.012 (1.987)	Cu–N(2)	2.640 (2.619)	Cu–N(1*A*)	1.990 (2.008)	Cu–N(3)	1.982
Cu–O(2)	2.069 (1.954)	Cu–O(2)	2.088 (1.996)	Cu–N(3)	2.011 (1.987)	Cu–Cl(1)	2.303 (2.371)	Cu–Br(1)	2.565
Cu–O(2*A*)	2.062 (1.954)	Cu–O(2*A*)	2.088 (1.996)	Cu–N(4)	2.640 (2.587)	Cu–Cl(2)	2.303 (2.371)	Cu–Br(2)	2.565
Cu–N(2)	2.642 (2.698)	Cu–N(2)	2.593 (2.604)	Cu–O(3)	2.062 (1.988)	Cu–N(2)	2.953	Cu–N(2)	2.939
Cu–N(2*A*)	2.638 (2.698)	Cu–N(2*A*)	2.593 (2.604)	Cu–O(4)	2.069 (1.966)	Cu–N(2*A*)	2.953	Cu–N(4)	2.939
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
I		N(1)CuO(2)	89.97 (89.85)	O(3)Cu(3)	88.41 (89.92)	N(2)CuN(3)	100.30 (98.92)	Cl(1)CuCl(1*A*)	179.93 (180.0)
N(1)CuN(1*A*)	180.04 (180.00)	N(1)CuO(2*A*)	90.03 (90.15)	O(3)CuN(4)	98.00 (89.72)	N(2)CuN(4)	163.80 (178.32)	**V**	
N(1)CuO(2)	91.61 (90.95)	N(1*A*)CuO(2)	89.98 (90.15)	O(4)CuN(1)	91.61 (90.42)	N(3)Cu(4)	80.10 (79.52)	N(1)CuBr(1)	90.00
N(1)CuO(2*A*)	88.40 (89.05)	N(1*A*)CuO(2*A*)	90.02 (89.85)	O(4)CuN(2)	89.90 (90.72)	**IV**		N(1)CuBr(2)	90.00
N(1*A*)CuO(2)	91.58 (89.05)	O(2)CuO(2*A*)	179.98 (180.0)	O(4)CuN(3)	91.57 (89.32)	N(1)CuCl(1*A*)	90.00 (90.67)	N(1)CuN(3)	180.01
N(1*A*)CuO(2*A*)	88.40 (90.95)	**III**		O(4)CuN(2)	81.90 (89.92)	N(1)CuCl(1)	89.99 (89.33)	N(3)CuBr(1)	90.00
O(2)CuO(2*A*)	179.85 (180.00)	O(3)CuO(4)	179.95 (179.22)	N(1)CuN(2)	80.10 (79.51)	N(1)CuCl(*A*)	180.08 (180.0)	N(3)CuBr(2)	90.00
II		O(3)CuN(1)	88.40 (90.52)	N(1)CuN(3)	179.98 (17.42)	N(1A)CuCl(1*A*)	90.00 (89.33)	Br(1)CuBr(2)	180.00
N(1)CuN(1*A*)	180.00 (180.00)	O(3)CuN(2)	98.10 (89.62)	N(1)CuN(4)	100.40 (102.02)	N(1A)CuCl(1)	90.02 (90.67)		

By comparison with the correlative value, we can obtain the following information. (1) The value of ΔE ($\Delta E = E_{HOMO} - E_{LUMO}$) of complexes **I–III** is higher than that of complexes **IV** and **V**, which proves that complexes **I–III** cannot be excited easily by irradiation. Complexes **I–III** are more stable than complexes **IV** and **V**. (2) The ΔE values of complexes **I–III** are similar to each other. This indicates that complexes **I–III** have similar UV-Vis spectra (experimental values for complexes **I**, **II**, and **III**: $\lambda = 316$, 318, and 317 nm, respectively), which proves that the copper atom has a similar coordination environment in these complexes. The result is in accord with the crystal structures. (3) The ΔE value of complex **IV** is higher than that of complex **V**, which proves that complex **IV** is more stable than complex **V** in irradiation. Probably, the electronegativity of

Table 2. IR spectra of complexes **I–V**

Complex	γ(C=O)		γ(framework)				δ(Ar–H)			
	found	calcd	found		calcd		found		calcd	
I	1735	1723	1596	1353	1610	1340	916	739	913	756
II	1730	1723	1571	1412	1612	1446	915	760	914	756
III	1731	1723	1569	1407	1609	1340	918	761	913	756
IV	1722	1705	1564	1407	1606	1441	916	760	930	798
V	1731	1705	1567	1384	1607	1442	916	755	930	799

chlorine is stronger than that of bromine, and the bonds formed by the former with copper are stronger than those formed by the latter.

The charge layout of copper and its coordination atoms are shown in Table 4 by Mulliken layout analysis and natural population analysis. The results are gained by analyzing the data. (1) The two modes of the analyses indicate the same tendency: the positive charge of the Cu atom is less than its chemical valence (+2); that is, in these complexes, the positive charge of the center is brought down; similarly, the absolute value of the negative charge of the coordination atoms is brought down also. This situation corresponds to Pauling's electric neuter principle [15] and proves the existence of the coordination bonds, which makes possible the charge transfer between the metal ion and the coordination atoms. (2) In the five complexes, the charge of the two nitrogen atoms in the same Dafo is obviously different. This indicates that, in the course of forming coordination bonds, the contribution of one nitrogen atom is bigger than the other. The result is in accord with the above discussion. Dafo is usually unequally bound by the two nitrogen atoms with copper. (3) The net charge difference of complexes **I–III** is tiny, which is related to the similar crystal structures, because the calculation model of complexes **I–III** was constructed according to their crystal structures. In fact, the main coordination bodies of the three complexes are similar and are shown in Figs. 1a–1c. (4) By comparing the halogen atoms of complexes **IV** and **V**, it is easy to find out that the negative charge of the chlorine atom is more than that of the bromine atom. The positive charge of the copper atom in complex **IV** is more than that in complex **V** also. The two aspects determine that complex **IV** is more stable than complex **V**. Thus, the analyses of the two aspects (energies of frontier molecular orbitals and atomic net charge populations) of complexes **IV** and **V** indicate the same results.

Table 3. Energies of some frontier molecular orbitals of complexes **I–V**

Complex	HOMO	LUMO	Δ*E**
I	–0.4794	–0.3271	0.1523
II	–0.4816	–0.3269	0.1521
III	–0.4794	–0.3271	0.1523
IV	–0.2208	–0.1285	0.0923
V	–0.2150	–0.1297	0.0853

* $\Delta E = E_{HOMO} - E_{LUMO}$.

Thus, five copper complexes with 4,5-diazafluoren-9-one were calculated by DFT-B3LYP in Gaussian-98w. The calculated results show the microcosmic characters of the complexes, such as energies of frontier molecular orbitals and atomic net charge populations in theory. The structures of complexes **I–IV** have been determined, and the calculated results are in accord with their structures. However, the structure of complex **V** has not been determined. By analyzing the calculated results of complexes **IV** and **V**, a reasonable structure of complex **V** is educed in theory. In a word, in this paper, the experimental results are proved thoroughly, on the one hand, by the theoretical calculated results, and on the other hand, the theoretically calculated results can deduce the experimental results reasonably well.

Atomic coordinates and details of bond lengths, bond angles, and thermal parameters of complexes **I–IV** and the detailed calculated values for complexes **I–V** are available from the authors on request.

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (nos. 20671076 and 30470408); the National Basic Research Program of China (the 973 Program, no. 2003CB214606); and the Key Laboratory Research and Development Program of Shaanxi Education Section, China (no. 03JS006), for support of this

Table 4. Atomic net charge populations (%) of complexes **I–V**

Complex	Mulliken layout analysis						
I	Cu	O(2)	O(2*A*)	N(1)	N(2)	N(1*A*)	N(2*A*)
	0.6262	–0.7147	–0.7112	–0.2710	–0.0870	–0.2709	–0.0871
II	Cu	O(2)	O(2*A*)	N(1)	N(2)	N(1*A*)	N(2*A*)
	0.6262	–0.7112	–0.7147	–0.2710	–0.0870	–0.2709	–0.0870
III	Cu	O(3)	O(4)	N(1)	N(2)	N(3)	N(4)
	0.6262	–0.7112	–0.7147	–0.2711	–0.0871	–0.2709	–0.0870
IV	Cu	N(1)	N(2)	N(1*A*)	N(2*A*)	Cl(1)	Cl(1*A*)
	0.1482	–0.1896	0.0180	–0.1895	0.0183	–0.3860	–0.3861
V	Cu	N(1)	N(2)	N(3)	N(4)	Br(1)	Br(2)
	0.1052	–0.2013	0.0167	–0.2013	0.0167	–0.3716	–0.3716
Complex	Natural population analysis						
I	Cu	O(2)	O(2*A*)	N(1)	N(2)	N(1*A*)	N(2*A*)
	1.0585	–0.4924	–0.4903	–0.2586	–0.2846	–0.2561	–0.2855
II	Cu	O(2)	O(2A)	N(1)	N(2)	N(1*A*)	N(2*A*)
	1.0713	–0.4878	–0.4879	–0.2587	–0.2919	–0.2588	–0.2941
III	Cu	O(3)	O(4)	N(1)	N(2)	N(3)	N(4)
	1.0531	–0.4868	–0.4885	–0.2553	–0.2890	–0.2592	–0.2867
IV	Cu	N(1)	N(2)	N(1*A*)	N(2*A*)	Cl(1)	Cl(1*A*)
	0.8344	–0.2360	–0.2423	–0.2391	–0.2426	–0.2558	–0.2558
V	Cu	N(1)	N(2)	N(3)	N(4)	Br(1)	Br(2)
	0.5930	–0.2884	–0.2703	–0.2820	–0.2566	–0.1967	–0.1903

work, and we thank Prof. Wen Zhenyi (Northwest University, Modern Physical Research Institute) for supplying the Gaussian-98w software.

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