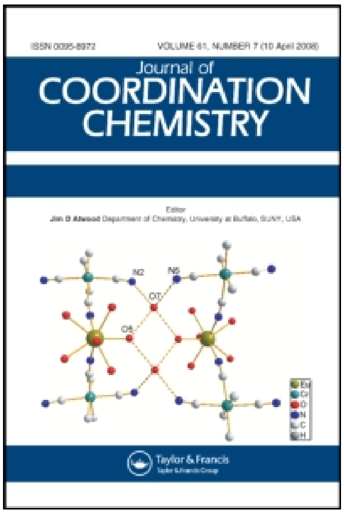

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Experimental and <i>ab initio</i> calculational studies on nitrato[2,4-dichloro-6-((pyridin-2-ylmethylimino)methyl)phenolato]copper(II)

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Experimental and *ab initio* calculational studies on nitrato[2,4-dichloro-6-((pyridin-2-ylmethylimino)methyl)phenolato]copper(II)

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The mononuclear Schiff-base copper(II) compound, $[Cu(C_{13}H_9C_{12}N_2O)(NO_3)]$, has been synthesized and characterized by elemental analysis and X-ray single crystal determination. The compound crystallizes in the orthorhombic, space group $Cmc2_1$ with unit cell dimensions $a = 6.713(1)$, $b = 22.147(3)$, $c = 9.976(1)$ Å, $M_r = 405.67$, $V = 1483.2(3)$ Å^3, $Z = 4$, $R_1 = 0.0568$ and $wR_2 = 0.1331$. X-ray structure determination revealed that the compound possesses crystallographic mirror symmetry. The Cu^{II} ion in the compound is five-coordinate in a distorted trigonal bipyramid with one O and two N atoms of the Schiff-base and by two O atoms of the nitrate anion. In the crystal structure, the molecules are linked via intermoleclular $C-H \cdots O$ non-classical hydrogen bonds, forming a two-dimensional network. Density functional theory (DFT) and Hartree-Fock (HF) calculations of the structure, atomic charge distribution and natural bond orbital analyses have been performed. The calculated results show that the Cu^{II} ion mainly adopts spd^2 hybridization and forms five bonds with the NNO donor set of the Schiff-base ligand and with two O atoms of nitrate from four orientations. The coordinate stabilization energies show that the Schiff-base copper(II) compound is very stable.

Keywords: Copper(II) compound; Schiff-base; Crystal structure; Theoretical calculation

1. Introduction

Investigation of structural stability of compounds by both experimental techniques and theoretical methods has been of great interest. With the development of computational techniques, theoretical modeling of drug design, and functional material design and so on, has become possible. Many important properties, such as dipole moment, vibrational frequencies, reaction pathways, molecular orbitals, electrostatic potentials etc., can be predicted by various computational techniques [1].

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Transition metal and natural base compounds are present in the active sites of several important classes of biological and chemical systems. Study on Schiff-base metal compounds is of great interest in various aspects of biology and chemistry [2–5]. It is helpful to study the biological or chemical behavior of such compounds on the electronic level by investigating the structure characteristics and interactive influence between the metal ions and the Schiff-base ligands. Recently, we reported the structures of a few Schiff-base copper(II) compounds [6–9]. As further study on such compounds, especially at the electronic level, we report herein a Schiff-base copper(II) compound, nitrato[2,4-dichloro-6-((pyridin-2-ylmethylimino)methyl)phenolato]copper(II). The crystal structure of the complex was determined by X-ray diffractive, and other properties (such as the natural bond orbitals (NBOs), electronic density analysis and so on) were made based on electronic levels by theoretical methods.

2. Experimental and computational methods

2.1. *Synthesis of the compound*

All chemicals were obtained from commercial sources and used without further purification. 3,5-dichloro-2-hydroxybenzaldehyde (19.1 mg, 0.1 mmol) and pyridin-2-ylmethylamine (10.8 mg, 0.1 mmol) were dissolved in 15 mL methanol. The mixture was stirred for 30 min to give a yellow solution. To this solution was added an aqueous solution (5 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.1 mmol, 24.2 mg), with stirring. The mixture was stirred at room temperature for an hour and filtered. After allowing the resulting solution to stand in air for nine days, blue block-shaped crystals formed at the bottom of the vessel on slow evaporation of the solvent. C, H and N were analyzed by an Eager-200 element analysis instrument. The copper(II) ions in the complex were leached by heating with a mixture of 6 N CH_3COOH and 6 N HCl (1 : 1). Copper(II) was analyzed iodimetrically by titrating with a standard $Na_2S_2O_3$ solution to the starch end point. Anal. Calcd for $C_{13}H_9Cl_2CuN_3O_4$: C, 38.49; H, 2.24; N, 10.36; Cu, 15.66%. Found: C, 38.39; H, 2.23; N, 10.33; Cu, 15.90%.

2.2. *X-ray single crystal structure determination*

A blue crystal of the compound with approximate dimensions $0.25 \times 0.18 \times 0.10\,\mathrm{mm}^3$ was mounted on a glass fibre. The X-ray single crystal diffraction measurement was carried out at 295(2) K on a Bruker SMART APEX area-detector diffractometer up to a 2θ value of 54.78°. The unit cell parameters and data collections were performed using a Bruker SMART program [10] with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073\,\text{Å}$) by the $\phi - \omega$ scan technique; cell refinement and collected data reduction were performed by the SAINTPLUS program [10], and empirical absorption correction was performed using SADABS program [11]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXTL-97 program [12]. All non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data and experimental details for the structural analysis are summarized in table 1. The fractional atomic coordinates and equivalent isotropic

Table 1. Crystal data and structure refinement parameters for the compound.

Empirical formula	$C_{13}H_9Cl_2CuN_3O_2A$
Formula weight	405.67
Temperature (K)	298(2)
Radiation(Mo-Kα) λ (Å)	0.71073
Crystal shape/color	Block/blue
Crystal size (mm^3)	$0.25 \times 0.18 \times 0.1$
Crystal system	Orthorhombic
Space group	$Cmc2_1$
a (Å)	6.713 (1)
b (Å)	22.147 (3)
c (Å)	9.976 (1)
V (Å^3)	1483.2 (3)
Z	4
D_c (g cm^{-3})	1.817
μ (mm^{-1})	1.86
F(000)	812
θ Range (°)	2.75/27.77
Index range (h, k, l)	$-8/8$, $-27/27$, $-12/12$
Measured reflections	6049
Observed reflections $I \geq 2(I)$	1490
Min. and max. transmission	0.674/0.836
Data/restraints/parameters	1738/6/137
Goodness-of-fit on F^2	1.141
R_1, wR_2 $[I \geq 2\sigma(I)]$	0.0568, 0.1325
R_1, wR_2 (all data)	0.0661, 0.1364
Large diff. Peak and hole (e Å^{-3})	0.55 and -0.73
$(\Delta/\sigma)_{\max}$	<0.0001

$R_1 = \Sigma||F_o| - |F_c||/F_o$, $wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0267P)^2 + 7.3669P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

displacement parameters as well as other supplementary experimental data have been deposited at the Cambridge Crystallographic Data Centre (CCDC 619053).

2.3. *Computational methods*

Two DFT structure optimizations of the compound were performed with the X-ray geometry. The calculations employed the unrestricted Becke's three parameter hybrid functional combined with the Lee–Yang–Parr correction functional (UB3LYP) [13, 14] and the unrestricted Becke's three parameter hybrid functional with Perdew/Wang 91 (UB3PW91) [15–19] density functional theory method. Vibrational frequeny calculations ascertain the structure was stable (no imaginary frequencies). The atomic charges, frontier molecular orbitals (FMOs), natural bond orbitals (NBOs) analyses were performed on the experimental structure by the UB3PW91 method.

To investigate the effects of the intramolecular interactions on the conformation of the molecule, we have performed an optimization of the geometry of the isolated molecule by unrestricted *ab initio* quantum mechanical molecular orbital Hartree–Fock (UHF) calculations [20].

All the calculations were performed at LANL2DZ level with Gaussian 03 software package (version C.02) [21] on a Pentium IV computer, using the default convergence criteria.

3. Results and discussion

3.1. *Structure description of the compound*

The displacement ellipsoid plots with the numbering scheme for the compound are shown in figure 1, and the crystal packing is illustrated in figure 2. Selected bond lengths and angles are listed in table 2. The bond lengths and angles related to the non-classical hydrogen bonding of the compound are listed in table 3.

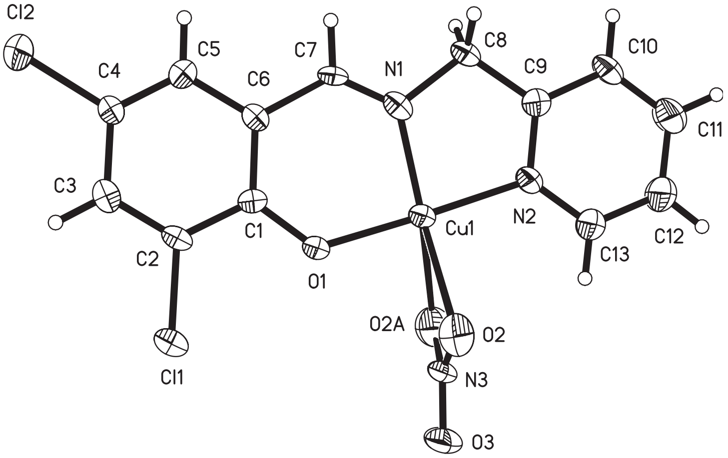


Figure 1. Molecular structure of the compound. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: A $-x$, $1+y$, z.

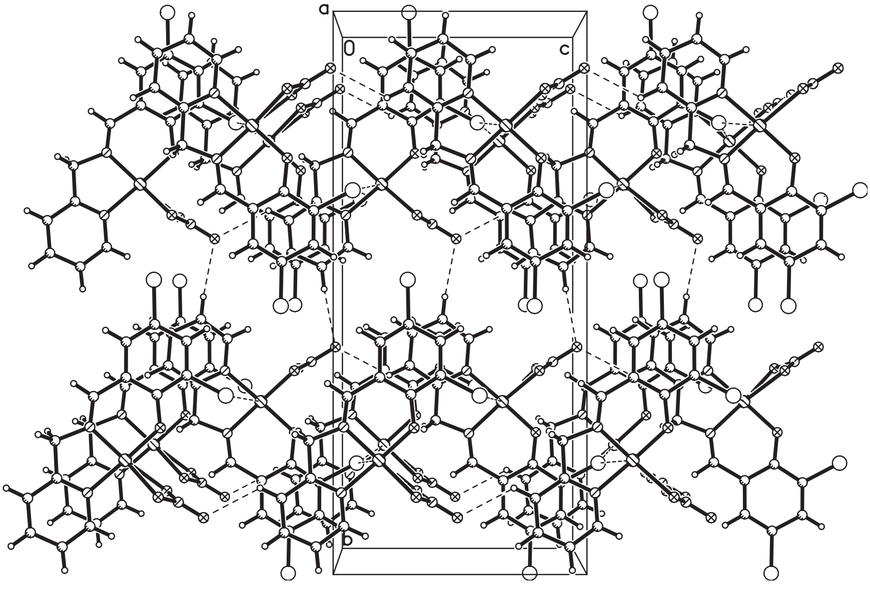


Figure 2. The crystal packing viewed along the *a*-axis. Non-classical hydrogen bonds are shown as dashed lines.

Table 2. Selected geometry structure parameters for the compound.

Experimental Bond lengths (Å)		Calculated			Experimental Bond angles (°)		Calculated		
		B3PW91	B3LYP	HF			B3PW91	B3LYP	HF
Cu1–O1	1.879(6)	1.905	1.912	2.358	O1–Cu1–N1	93.9(3)	92.2	92.1	76.2
Cu1–N1	1.907(10)	1.975	1.986	2.351	O1–Cu1–O2	85.4(3)	91.0	91.3	97.7
Cu1–N2	1.958(8)	2.003	2.015	2.181	N1–Cu1–N2	84.2(4)	82.9	82.8	75.2
Cu1–O2	2.240(7)	2.207	2.215	2.271	N1–Cu1–O2	152.2(2)	149.5	149.4	150.7
O1–C1	1.320(12)	1.310	1.315	1.294	N2–Cu1–O2	96.3(3)	93.3	93.2	107.3
N1–C7	1.208(15)	1.314	1.316	1.321	O2–Cu1–O2A	55.5(4)	60.8	60.9	57.8
N1–C8	1.473(11)	1.471	1.478	1.473	C1–O1–Cu1	127.1(6)	129.7	129.8	137.5
N2–C9	1.333(12)	1.355	1.358	1.331	C7–N1–Cu1	126.6(6)	125.6	125.6	132.2
N2–C13	1.322(14)	1.355	1.359	1.342	C8–N1–Cu1	115.2(7)	115.1	115.1	111.9
O2–N3	1.255(8)	1.330	1.338	1.296	C7–N1–C8	118.2(8)	119.2	119.3	115.9
O3–N3	1.163(10)	1.256	1.262	1.231	C9–N2–Cu1	113.8(7)	115.1	115.1	119.9
C1–C2	1.391(13)	1.436	1.439	1.440	C13–N2–Cu1	126.5(7)	124.4	124.4	119.7
C1–C6	1.393(14)	1.443	1.448	1.458	C13–N2–C9	119.7(8)	120.5	120.5	120.4
C6–C7	1.482(14)	1.432	1.436	1.448	N3–O2–Cu1	95.1(6)	92.1	92.2	93.1
C8–C9	1.480(12)	1.511	1.517	1.516	O2–N3–O2A	112.6(9)	114.1	114.0	115.8
C9–C10	1.389(13)	1.402	1.405	1.397	O3–N3–O2	123.6(5)	122.9	123.0	122.1
C12–C13	1.358(16)	1.397	1.401	1.389	O1–C1–C2	117.4(8)	119.7	119.7	119.7
Cl1–C2	1.730(9)	1.791	1.802	1.778	O1–C1–C6	124.4(9)	124.2	124.1	121.8
C2–C3	1.342(14)	1.384	1.387	1.397	C2–C1–C6	118.3(9)	116.1	116.2	118.5
C5–C6	1.394(11)	1.426	1.430	1.420	N1–C7–C6	127.2(8)	126.6	126.6	127.0
C10–C11	1.355(16)	1.401	1.405	1.391	N1–C8–C9	108.7(8)	110.2	110.2	113.9
C11–C12	1.369(18)	1.405	1.409	1.397	N2–C9–C8	118.1(8)	116.7	116.8	119.2
C3–C4	1.414(15)	1.414	1.417	1.410	N2–C9–C10	120.2(9)	121.0	121.0	121.3
C4–C5	1.318(16)	1.378	1.381	1.400	C10–C9–C8	121.7(8)	122.3	122.2	119.6
Cl2–C4	1.751(9)	1.808	1.819	1.790	N2–C13–C12	122.2(10)	121.3	121.3	121.9
					C1–C2–Cl1	119.5(8)	118.1	118.2	119.0
					C3–C2–C1	122.6(9)	122.7	122.7	122.1
					C3–C2–Cl1	117.9(7)	119.2	119.1	118.9
					C1–C6–C7	120.7(6)	121.7	121.8	125.3
					C1–C6–C5	118.5(12)	120.8	120.7	118.2
					C5–C6–C7	120.8(12)	117.5	117.5	116.5
					C11–C10–C9	119.8(11)	119.0	119.0	118.8
					C13–C12–C11	119.3(11)	118.8	118.8	118.3

(*Continued*)

Table 2. Continued.

Experimental Bond lengths (Å)		Calculated			Experimental Bond angles (°)		Calculated		
		B3PW91	B3LYP	HF			B3PW91	B3LYP	HF
					C2–C3–C4	118.1(9)	119.4	119.3	118.1
					C4–C5–C6	121.9(13)	119.9	119.9	120.8
					C10–C11–C12	118.8(11)	119.3	119.3	119.3
					C5–C4–C3	120.6(9)	121.2	121.3	122.2
					C3–C4–Cl2	118.8(7)	118.6	118.6	118.8
					C5–C4–Cl2	120.5(8)	120.2	120.1	119.0
					O1–Cu1–N2	178.1(4)	175.1	174.8	151.3
					N1–Cu1–O2	152.2(2)	149.5	149.4	150.7
Mean deviation		0.035	0.041	0.074			−0.11	−0.11	−0.74
Mean absolute deviation		0.043	0.047	0.080			1.60	1.62	6.28
Standard deviation		0.051	0.055	0.148			2.05	2.09	6.61

Table 3. Distances (Å) and angles (°) involving non-classical hydrogen bonding of the compound.

D–H···A	D(D–H) (Å)	D(H···A) (Å)	D(D···A) (Å)	Angle(D–H···A) (°)
C10–H10···O3^{i}	0.93	2.51	3.16(1)	127.0
C10–H10···O3^{ii}	0.93	2.51	3.16(1)	127.0
C12–H12···O3^{iii}	0.93	2.44	3.37(1)	175.0
C12–H12···O3^{iv}	0.93	2.44	3.37(1)	175.0

Symmetry code: (i) $x, y, -1+z$; (ii) $1-x, y, -1+z$; (iii) $1-x, 1-y, -1/2+z$; (iv) $x, 1-y, -1/2+z$.

In the mononuclear Schiff-base copper(II) compound, the Cu^{II} ion is five-coordinate in a distorted trigonal bipyramid configuration by one O and two N atoms of the Schiff-base ligand, and by two O atoms of the nitrate. The molecule possesses mirror symmetry, with C1–C13, Cl1, Cl2, O1, O3, N1–N3, H3, H5, H7, and H10–H13 lying on the crystallographic mirror plane. Atom O2 lies 1.0435 Å above the plane defined by the atoms at the mirror plane. The values of the bond angles O2–Cu1–N1 and O2–Cu1–O2A are 152.2(2) and 55.5(4)°, respectively, indicating a distorted trigonal bipyramid geometry (symmetry code: A $-x, 1+y, z$). The bond lengths around the Cu are comparable to the corresponding values observed in similar Schiff-base complexes [6–9].

In the crystal structure, the molecules are linked *via* intermolecular C–H···O non-classical hydrogen bonds, forming a two-dimensional network (more details are given in table 3 and figure 2).

3.2. *Optimized geometry*

Calculated bond lengths and angles of the compound at the LANL2DZ level by DFT and UHF methods are listed in table 2. The bond lengths and angles of the experimental values and the calculated values have been compared by three theoretical methods. Most of the optimized bond lengths are slightly longer than the experimental values, due to the fact that the theoretical calculations are based on the isolated molecules in the gaseous phase, while the experimental results are based on the molecules in the solid state. In general, the values of the compound with DFT methods are more realistic than those with UHF, and the accuracies of the two DFT methods are comparable. Furthermore, the deviations of the experimental and the calculated values are almost equivalent. Based on the above consideration, the calculated result by the B3PW91 method based on LanL2DZ basis set was used to study the properties of the compound.

The differences of the bond lengths and bond angles occur mainly at the Cu1 coordinate environment between the theoretical and experimental data. The biggest deviation of the bond lengths is 0.106 Å at N1–C7 and the biggest deviation of the bond angles is 5.6° at O1–Cu1–O2. The errors of the bond lengths related to the Cu1 atom in the trigonal bipyramid are 0.026 Å (Cu1–O1), 0.068 Å (Cu1–N1), 0.045 Å (Cu1–N2) and −0.033 Å (Cu1–O2) between the experimental and the calculated values. The errors of the bond angles related to the centre Cu1 atom are −1.7, 5.6, −1.3, −2.7, −3.0 and 5.3° at O1–Cu1–N1, O1–Cu1–O2, N1–Cu1–N2, N1–Cu1–O2, N2–Cu1–O2 and O2–Cu1–O2A, respectively. In spite of these differences, the optimized geometry represents a good approximation with the crystal structure and is the basis for

Table 4. Mülliken atom charges and Mülliken spin densities of the compound.

Atom	Mülliken atomic charges	Mülliken spin densities
Cu1	0.6594	0.60375
O1	−0.4344	0.12857
N1	−0.3247	0.11935
N2	−0.3376	0.09124
O2	−0.3022	0.03254
O2A	−0.3022	0.03254
N3	0.2246	−0.00372
C1	0.4178	−0.00942
C7	−0.1155	−0.02221
C8	−0.4593	0.00208
C9	0.3695	−0.00680
C13	−0.1510	−0.00878
O3	−0.2220	−0.00055
C2	−0.2941	0.01191
C6	0.3020	0.00711
C10	−0.2750	0.00594
C12	−0.1808	0.00766
Cl1	−0.0034	−0.00035
C3	−0.1736	−0.00462
C5	−0.2999	−0.00338
C11	−0.1554	−0.00681
C4	−0.1622	0.00040
Cl2	−0.0582	0.00007

calculating other properties, such as natural population analysis (NPA) of the atomic charge distributions, FMOs and NBO analysis, as described below.

3.3. *Atomic charge analysis*

The Mülliken atomic charges and Mülliken atomic spin densities of the non-hydrogen atoms for the compound are listed in table 4.

When comparing the atomic charges in the compound, we found that atomic charge redistribution occurs on all of the atoms. To form [Cu($C_{13}H_9Cl_2N_2O$)(NO_3)], 0.9424e net atomic charges from the Schiff-base ligand and 0.3982e from the nitrate anion were transferred to the copper(II). Total charge density surface is shown in figure 3 by using ChemOffice 2004 software package of version 8.0 [22] based on the UB3PW91/LanL2DZ level calculation. The terminations of the nitrate and the chloro-group of the compound show the negative electronic character, and positive character is shown at the other end. The dipole moment of the compound is 14.5664 Debye. Mülliken atomic spin densities are also redistributed to other atoms, and mainly occur on the donor atoms (O1, N1, N2, O2 and O3) and the acceptor atom Cu1. The spin densities on copper(II) are decreased and the donor atoms have a certain spin densities character.

3.4. *Natural atomic orbital and natural bond orbital analysis*

Selected NBO electronic occupancies and intramolecular natural bond orbitals on alpha and beta electrons interacting at bond critical points for the compound are listed

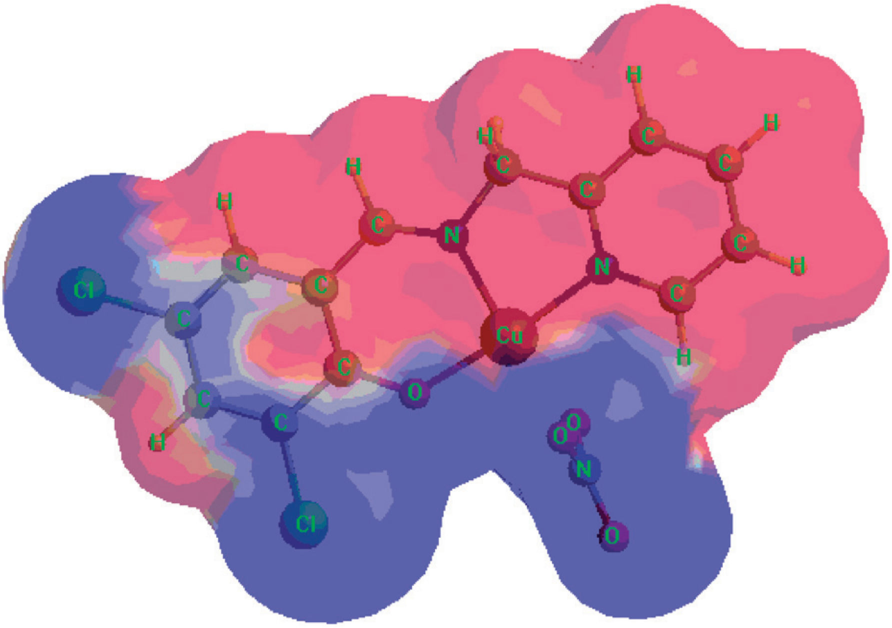


Figure 3. Total charge density surface of the compound.

in tables 5 and 6, which were calculated on natural atomic orbital and bond orbital analysis at UB3PW91/LanL2DZ level based on the experimental structure.

The NBOs analyses revealed the valence electrons on Cu1 adopt lone pair mode including five alpha lone pairs and four beta lone pairs around the Cu1. However, powerful high electron occupancies exist on the LP*(5)Cu1 (0.4054e for beta electrons) with almost s-character and LP*(6)Cu1 (0.1391e and 0.1287e for both alpha and beta electrons) with almost d-character, contributing to the stable coordination compound.

The NBOs analyses for the alpha electrons reveal that the typical single-double arrangements are adopted in the phenyl and pyridyl rings of the Schiff-base ligand, however, for the beta electrons, two double bonds exist in the phenyl ring and the typical single-double arrangement was adopted as the same character of the alpha electrons in the pyridyl ring. There were still higher electronic occupancies at the corresponding antibonds of the double bonds in the phenyl ring and the pyridyl ring, indicating the strong delocalization from the idealized Lewis structure. The double bond (sigma and pi bonds coexist between C7 and N1 atoms) character of the alpha electrons is the same as that of the beta electrons. LP*(1) on C1 and LP(1) on C4 have higher beta electronic occupancies due to the substituent groups of Cl1 and Cl2.

In the nitrate anion, the alpha electronic character is different from that of the beta electrons in the corresponding bond, delocalization of the *p*-electrons exists among O2, O3, O2A and N3 atoms.

To investigate the origin of the electronic interactions deeply, couples of donor and acceptor (donor = donor electrons, acceptor = accept electrons) of NBOs and their interacting stabilization energies for the compound are listed in table 6. The stabilization energies are proportional to the NBO interacting intensities. From the

Table 5. Selected NBOs electron occupancies of the compound.

Alpha electrons		Beta electrons		Alpha electrons		Beta electrons	
BD(1)C1–C2	0.9884	BD(1)C1–C2	0.9836	LP(1)Cu1	0.9987	LP(1)Cu1	0.9986
BD(2)C1–C2	0.7665	BD(1)C2–C3	0.9862	LP(2)Cu1	0.9975	LP(2)Cu1	0.9970
BD*(2)C1–C2	0.2380	BD(2)C2–C3	0.8796	LP(3)Cu1	0.9966	LP(3)Cu1	0.9960
BD(1)C2–C3	0.9865	BD*(2)C2–C3	0.1484	LP(4)Cu1	0.9962	LP(4)Cu1	0.9882
BD(1)C3–C4	0.9851	BD(1)C3–C4	0.9851	LP(5)Cu1	0.9908	LP*(5)Cu1	0.4054
BD(2)C3–C4	0.7937	BD(1)C5–C4	0.9888	LP*(6)Cu1	0.1391	LP*(6)Cu1	0.1487
BD*(2)C3–C4	0.2458	BD(1)C6–C5	0.9797	LP(1)O1	0.9832	LP(1)O1	0.9801
BD(1)C4–C5	0.9889	BD(2)C6–C5	0.8123	LP(2)O1	0.9532	LP(2)O1	0.8488
BD(1)C5–C6	0.9796	BD*(2)C6–C5	0.2516	LP(3)O1	0.8602	LP(3)O1	0.8143
BD(2)C5–C6	0.8109	BD(1)C1–C6	0.9824	LP(1)N1	0.9458	LP(1)N1	0.8440
BD*(2)C5–C6	0.2493	BD(1)O1–C1	0.9913	LP(1)N2	0.9442	LP(1)N2	0.8696
BD(1)C6–C1	0.9846	BD(1)C2–Cl1	0.9893	LP(1)O2	0.9874	LP(1)O2	0.9874
BD(1)O1–C1	0.9940	BD(1)C4–Cl2	0.9906	LP(2)O2	0.9546	LP(2)O2	0.9274
BD(1)C2–Cl1	0.9893	BD(1)C7–C6	0.9784	LP(3)O2	0.8314	LP(3)O2	0.8299
BD(1)C4–Cl2	0.9906	BD(1)N1–C7	0.9920	LP(1)O2A	0.9874	LP(1)O2A	0.9874
BD(1)C6–C7	0.9804	BD(2)N1–C7	0.9837	LP(2)O2A	0.9546	LP(2)O2A	0.9274
BD(1)C7–N1	0.9920	BD*(2)N1–C7	0.1135	LP(3)O2A	0.8314	LP(3)O2A	0.8299
BD(2)C7–N1	0.9840	BD(1)N1–C8	0.9826	LP*(1)N3	0.6030	LP*(1)C1	0.4591
BD*(2)N1–C7	0.1094	BD(1)C8–C9	0.9866	LP(1)O3	0.9895	LP(1)C4	0.5635
BD(1)N1–C8	0.9858	BD(1)C9–C10	0.9871	LP(2)O3	0.9326	LP(1)O3	0.9893
BD(1)C8–C9	0.9867	BD(1)C10–C11	0.9881	LP(3)O3	0.7273	LP(2)O3	0.9329
BD(1)C9–C10	0.9885	BD(2)C10–C11	0.8227	LP(1)Cl1	0.9952	LP(1)Cl1	0.9951
BD(1)C10–C11	0.9881	BD*(2)C10–C11	0.1433	LP(2)Cl1	0.9849	LP(2)Cl1	0.9847
BD(2)C10–C11	0.8217	BD(1)C11–C12	0.9897	LP(3)Cl1	0.9610	LP(3)Cl1	0.9606
BD*(2)C10–C11	0.1425	BD(1)C12–C13	0.9894	LP(1)Cl2	0.9950	LP(1)Cl2	0.9950
BD(1)C11–C12	0.9897	BD(2)C12–C13	0.8119	LP(2)Cl2	0.9868	LP(2)Cl2	0.9868
BD(1)C12–C13	0.9914	BD*(2)C12–C13	0.1265	LP(3)Cl2	0.9711	LP(3)Cl2	0.9711
BD(2)C12–C13	0.8113	BD(1)C13–N2	0.9918				
BD*(2)C12–C13	0.1250	BD(1)N2–C9	0.9923				
BD(1)C13–N2	0.9919	BD(2)N2–C9	0.8841				
BD(1)N2–C9	0.9926	BD*(2)N2–C9	0.2256				
BD(2)N2–C9	0.8859	BD(1)O2–N3	0.9965				
BD*(2)N2–C9	0.2265	BD(1)O2A–N3	0.9965				
BD(1)O2–N3	0.9972	BD(1)N3–O3	0.9969				
BD(1)N3–O3	0.9981	BD(2)N3–O3	0.9958				
BD(1)O2A–N3	0.9972	BD*(1)N3–O3	0.1380				
		BD*(2)N3–O3	0.2240				

BD for 2-center bond, LP for 1-center valence lone pair, and BD* for 2-center antibond, the unstarred and starred labels correspond to Lewis and non-Lewis NBOs, respectively, a serial number (1, 2, ... if there is a single, double, ... bond between the pair of atoms), and the atom(s) to which the NBO is affixed.

Table 6. Selected couples of donor NBOs and acceptor NBOs for the compound.

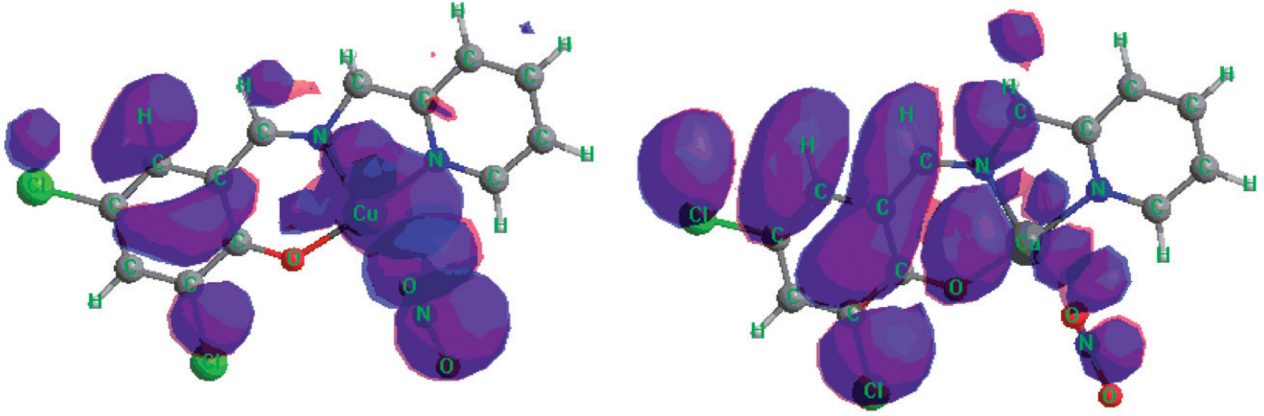
Alpha electrons			Beta electrons		
Donor NBO	Acceptor NBO	kJ mol^{-1}	Donor NBO	Acceptor NBO	kJ mol^{-1}
From Schiff-base ligand to Cu1					
LP(1)O1	LP*(6)Cu1	14.90	LP(1)O1	LP*(6)Cu1	33.89
LP(2)O1	LP*(6)Cu1	85.02	LP(3)O1	LP*(5)Cu1	116.02
LP(1)N1	LP*(6)Cu1	84.73	LP(3)O1	LP*(6)Cu1	83.39
LP(1)N2	LP*(6)Cu1	80.71	LP(1)N1	LP*(5)Cu1	63.55
			LP(1)N1	LP*(6)Cu1	103.43
			LP(1)N2	LP*(5)Cu1	66.90
			LP(1)N2	LP*(6)Cu1	91.84
From nitrate anion to Cu1					
LP(2)O2	LP*(6)Cu1	34.69	LP(2)O2	LP*(5)Cu1	19.75
LP(2)O2A	LP*(6)Cu1	34.69	LP(2)O2	LP*(6)Cu1	35.73
			LP(2)O2A	LP*(5)Cu1	19.75
			LP(2)O2A	LP*(6)Cu1	35.73

LP represents lone pair, LP* represents anti-LP.

Schiff-base ligand to the Cu1, s-p hybridized lone pair electrons of O1, N1 and N2 acting as donor NBOs can easily give electrons to the acceptor NBOs LP*(5)Cu1 and LP*(6)Cu1 (significant powerful conjugative delocalization exists from the O1, N1, N2 to Cu1 and the coordination energies are 333.21, 251.71, 239.45, 90.17 and 90.17 kJ mol^{-1}, respectively), forming the stable coordination structure. From nitrate to Cu1, s-p hybridized lone pair electrons of O2 and O2A acting as donor NBOs co-overlap partly the same orientation of the acceptor NBOs LP*(5)Cu1 and LP*(6)Cu1, so, the conjugative delocalization is not very effective and the stabilization energies are lower than those of other coordinate atoms. According to the result of second order perturbation theory analysis, the lone pairs of Cu1 have no contribution to the coordination of the compound. The sketch maps of the fronter molecular orbitals are shown in figure 4.

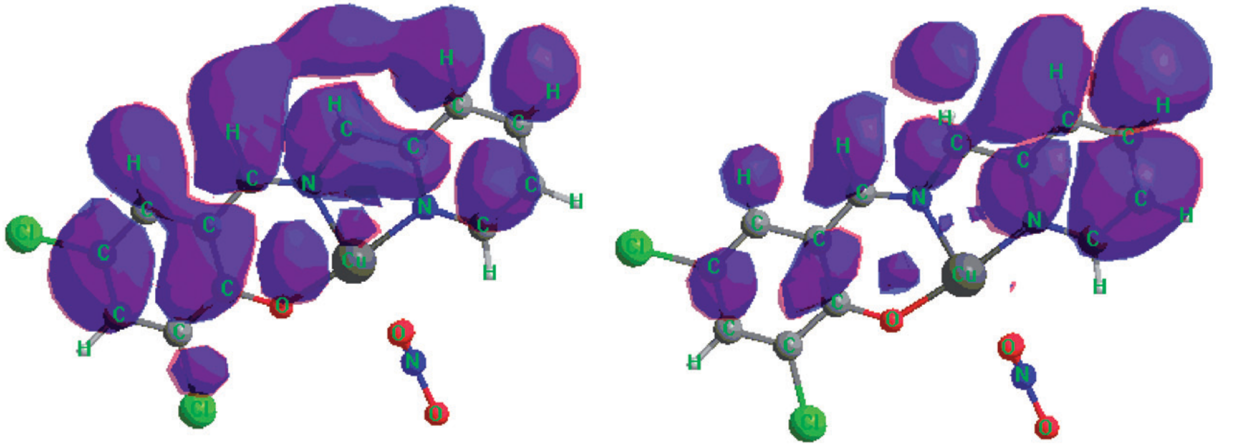
4. Conclusion

In this contribution, one Schiff-base copper(II) compound has been synthesized and characterized by X-ray single crystal diffraction. X-ray structure determination revealed that the compound possesses crystallographic mirror symmetry. The Cu^{II} ion in the compound is five-coordinate in a distorted trigonal bipyramid by one O and two N atoms of the Schiff-base ligand and by two O atoms of the nitrate anion. In the crystal structure, the molecules are linked via intermolecular C–H$\cdots$O non-classical hydrogen bonds, forming a two-dimensional network. *Ab initio* calculational studies on the title compound, gave good correlations between the experimental and calculated structure. The coordination characteristics of the title compound were discussed by studying atomic charges distribution, spin densities and natural bond orbitals in detail.



HOMO-1: -0.2538 hartrees

HOMO: -0.2310 hartrees



LUMO: -0.1034 hartrees

LUMO+1: -0.0927 hartrees

Figure 4. The molecular orbital surfaces and corresponding potential energies of the compound.

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