Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1461-1467

Synthesis and Quantum Chemistry of Two Novel Copper(II) Complexes

QING-LI WEI, SHU-SHENG ZHANG*, JUN GAO and XUE-MEI LI
College of Chemistry and Molecular Engineering
Qingdao University of Science & Technology, Qingdao-266 042, P.R. China
Fax: (86)(532)84023927; Tel: (86)(532)84022750; E-mail: shushzhang@126.com

The reaction of $Cu(NO_3)_2$ with N'-[(2-hydroxyphenyl) methylidene]-2-(4-methyl)acetohydrazide (sal-mphah) led to the formation of a one-dimensional coordination polymer with the empirical formula of $[Cu(sal\text{-}mphah)\cdot H_2O]_n$ $(1\cdot H_2O)$. While, the reaction of $Cu(NO_3)_2$ with salicylidene-[1-(*t*-buty)-5-methyl-1*H*-pyrazole]-formhydrazine (sal-pfh) gave a dinuclear Cu(II) compound $[Cu(sal\text{-}pfh)_2\cdot(\mu\text{-}NO_3)_2]$ (2). The electronic studies of the ligands and their copper(I) complexes have been calculated with density functional theory (DFT/B3LYP) and the coordination character was further discussed.

Key Words: Copper compounds, Quantum chemistry, Density functional theory (DFT/B3LYP)

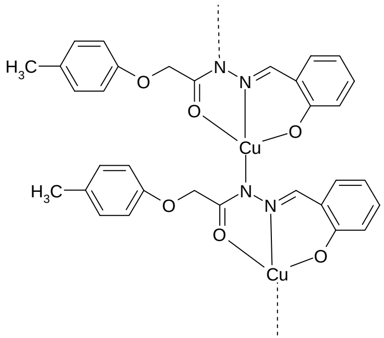
INTRODUCTION

Recently, the crystal engineering of coordination polymers are of considerable interest due to their great potential applications in many areas, such as molecular magnetism[1], heterogeneous catalysis, molecular sieving and non-linear optics[2]. Metal-complexes of Schiff base polymers have been described which exhibit a wide variety of properties such as luminescence or catalytic properties[3]. However, only a few studies have been reported concerning metal-containing ligand complex polymers[4].

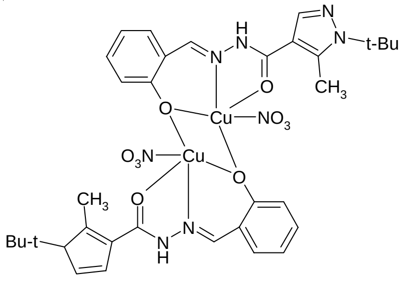
The polymeric copper complex was synthesized from the reaction of salicyledene-*p*-methyl-phenoxy acetylhydrazine with $Cu(NO_3)_2$. While the toluene was substituted with pyrazole moiety, dinuclear copper complex was obtained. We report herein the preparation, crystal structures, characterization of two compounds, $[Cu(sal\text{-}mphah)\cdot H_2O]_n$, $(1\cdot H_2O)$ (**1**) and $[Cu(sal\text{-}pfh)_2\cdot(\mu\text{-}NO_3)_2]$ (**2**). Quantum chemistry study may be used as an analytical instrument in structure elucidation. It has predictive power to assist synthesis and characterization. Because compound **1** is one-dimensional coordination polymer, and each Cu(II) can coordinated with two sal-mphah ligands at the same time, so we have undertaken the quantum chemistry calculation for one unit fragment of **1** (one Cu(II) coordinated to two sal-mphah ligands) in order to investigate the electric structure of **1**. The structures of ligands of compound **1** and **2** are also elucidated.

EXPERIMENTAL

The structures of ligands of compounds **1** and **2** were optimized at the Density functional(DFT) level of theory using Beck 3 hybrid exchange(B3)[5] with Lee. Yang, and Parr correlation (B3LYP)[6]. The 6-31G* basis set was employed in this method.



1



2

Since compound **1** is a one-dimensional coordination polymer and contains metal atom, so its fragment structure was optimized at restricted Hartree Fock (RHF) level with the 3-21G basis set firstly. The optimized results in the first step was secondly optimized at a higher DFT level of B3LYP with the 6-31G* basis set.

RESULTS AND DISCUSSION

Optimized structures parameters of ligand (sal-mphah) and its Cu(II) complex (1): The finally optimized structures parameters of sal-mphah and the fragment of complex **1** were partly summarized in Table-1.

The bond lengths and angles of the fragment calculated by using B3LYP/ 6-31G* do not differ substantially from those obtained with X-ray analysis. The metal coordination bond lengths reported in Table-1 are very close to the crystal data. There are some disparities between the structure parameters of the sal-mphah and those of the fragment of compound **1** obtained with calculation (Table-1). There is significant increase in the O2-C9 bond lengths from 1.242 to 1.255 Å, and in the N1-N2 bond lengths form 1.373 to 1.404 Å. But the N1-C9-O2 bond angle decreases from 125.2 to 120.4°, and the N2-N1-C9 bond angle decreases from 120.2 to 116.2°. These changes are due to coordination between the Cu(II) and the sal-mphah ligand. The N2 and O2 supplied electrons for Cu(II) to form the coordinate bonds, the interaction between N1 and N2, O2 and C9 slow down, so the N1-N2, O2-C9 bond lengths increased relevantly and the decrease of the N1-C9-O2 and the N2-N1-C9 band angle is proportionately to make the N2 and O2 approach to Cu(II) to form coordinate bonds.

TABLE-1
SELECTED BOND LENGTHS AND ANGLES FOR sal-mphah LIGAND AND THE FRAGMENT OF COMPOUND **1** BY CALCULATION

		sal-mphah	Fragment of compound **1**
Bond lengths (Å)	Cu1-N1A	—	1.931
	Cu1-N2	—	1.929
	Cu1-O2	—	1.995
	Cu1-O3	—	1.864
	O2-C9	1.242	1.255
	O3-C16	1.365	1.344
	N1-N2	1.373	1.404
Bond angles (°)	N1A-Cu1-O3	—	94.1
	Cu1-O3-C16	—	125.1
	Cu1-N2-C10	—	129.8
	O2-Cu1-N2	—	82.7
	C9-O2-Cu1	—	110.8
	C16-C11-C10	121.3	119.5
	C11-C10-N2	120.8	122.3
	N1-C9-O2	125.2	120.4
	N2-N1-C9	120.2	116.2

Main atomic electron density populations for sal-mphah ligand: The analysis of Mulliken populations of sal-mphah ligand is based on the optimized geometry[7]. Main atomic electron density populations for sal-mphah ligand are given in Table-2.There are mass negative electric charges on O2, O3, N1 and N2 as listed in Table-2. So all these atoms have the ability to coordinate with metal ion Cu(II). O2, O3 and N2 form a cavity of negative electric charges, implying that they are good tridentate ligand to coordinate with Cu(II) and other metal ions. The analysis of Mulliken population of the fragment of compound **1** shows that the electric charge of Cu(II) is not + 2, but 0.7958, indicating that the electric charges on O2, O3 and N2 have partly transfered to Cu(II) to form the coordination bonds. Because compound **1** is one-dimensional coordination polymer, Cu(II) can contemporarily coordinate with N1A of another sal-mphah ligand beside O2, O3 and N2 and the negative charges on N1A is -0.5156. The conclusion can be drawn that the sal-mpah ligands act as a μ_4-bridge connecting Cu(II) atoms into chains along the c direction, as X-ray analysis.

Main composition and proportion of the frontier orbitals in the fragment of compound 1: In order to investigate the relationship between the characteristic of the frontier orbital and the reactivity of the sal-mphah ligand and the fragment of compound **1**, the atomic orbital populations was calculated based on the optimized geometries. We use the sum of square (SUMSQ) of each atom's orbital coefficients as the contribution of each atom to the molecular orbital, and calculated by nomalization method[8]. Main compositions and proportions of the frontier orbitals and near orbitals in the sal-mphah ligand and the fragment of compound **1** are listed in Table-3 and Table-4. The stereographs of the frontier molecular orbitals (HOMO, LUMO) of the sal-mphah ligand and the fragment of compound **1** are depicted in Figs. 1 and 2.

TABLE-2
MAIN ATOMIC ELECTRON DENSITY POPULATION
FOR sal-mphah LIGAND

	Electric charges		Electric charges
O2(A)	-0.4280	C9(A)	0.5242
O3(A)	-0.6213	C10(A)	0.0755
N1(A)	-0.5156	C11(A)	0.0871
N2(A)	-0.3370	C16(A)	0.2356

TABLE-3
MAIN COMPOSITIONS AND PROPORTIONS OF THE FRONTIER
ORBITALS AND NEAR ORBITALS IN THE sal-mphah LIGAND (%)

	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
N1(A)	13.97	1.05	8.50	0.62	0.40	0.75
N2(A)	8.04	0.13	26.29	9.84	0.21	0.23
O2(A)	6.11	0.90	10.13	6.00	0.30	0.45
O3(A)	5.24	1.13	21.58	3.14	0.01	0.00
C9(A)	0.15	0.01	0.38	7.38	0.52	0.85
C16(A)	0.45	0.21	0.38	6.38	0.02	0.00

TABLE-4
MAIN COMPOSITIONS AND PROPORTIONS OF THE FRONTIER
ORBITALS AND NEAR ORBITALS IN THE FRAGMENT OF
COMPOUND **1** (%)

	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
Cu1	12.10	0.91	1.74	31.72	1.72	1.05
N1	3.02	0.27	0.48	4.06	2.77	12.53
N2	2.96	0.23	0.61	10.64	10.19	6.40
O2	1.32	0.23	0.63	4.73	6.59	6.80
O3	2.64	0.24	0.06	9.34	3.60	0.38
C9	5.79	0.00	0.04	1.17	17.56	19.91
C10	21.08	0.92	1.62	14.40	21.59	1.65
C16	4.24	0.08	0.22	1.77	6.91	1.14
N1A	10.68	10.84	18.72	4.65	0.11	0.00
N2A	11.77	1.51	10.92	1.25	0.08	0.00
O2A	6.56	5.46	8.48	1.04	0.00	0.00
O3A	2.78	15.41	12.32	0.40	0.00	0.00
C10A	1.44	5.84	5.75	0.68	0.00	0.00
C11A	0.58	0.27	10.87	0.12	0.00	0.00
C16A	0.11	3.80	8.46	0.16	0.00	0.00

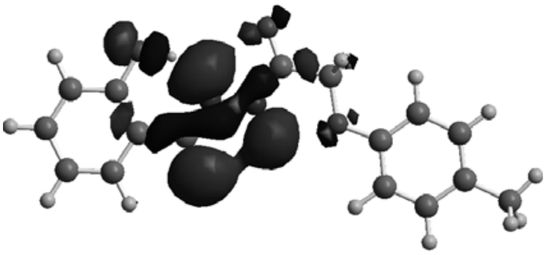


Fig. 1. Stereographs of the frontier molecular orbitals HOMO of the sal-mphah ligand

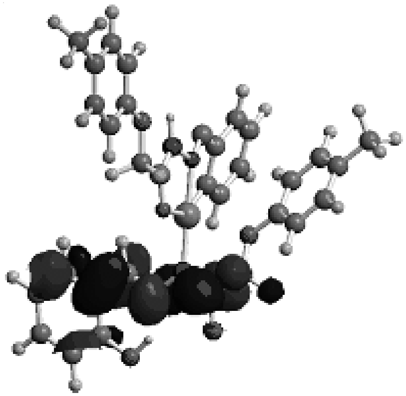


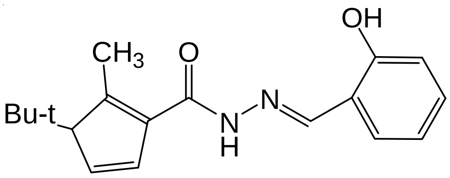
Fig. 2. Stereographs of the frontier molecular orbitals HOMO of the fragment of compound **1**

According to the molecular orbital theory, the frontier molecular orbitals(HOMO, LUMO) and near orbitals have great influence upon the biological activity of compound[9-11]. The reaction between the active molecules mainly happens on the frontier molecular orbitals and near orbitals. The proportions of atoms N2, O2 and O3 in HOMO (26.29, 10.13 and 21.58 %) are higher than other atoms as listed in Table-3 and they form a cavity of electric charges, so that these atoms may provide electrons to coordinate with Cu(II) very easy. The proportion of the atom N1 of another sal-mphah ligand in HOMO is 8.5%, so N1 can also supporting electrons to the Cu(II) to form coordination bond.

At the same time, comparing Fig. 1 with Fig. 2, the stereographs of the frontier molecular orbitals HOMO of the sal-mphah ligand show that the HOMO mainly distribute on N1(A), N2(A), O2(A) and O3(A) atoms; while the stereographs of the frontier molecular orbitals HOMO of the fragment of compound **1** show that HOMO distribution on N2,O2 and O3 of sal-mphah is greatly decreased and ligand sal-pfh still have higher HOMO distribution, so N2A, O2A and O3A of ligand sal-pfh can coordinate with another Cu(II). It may be the important reason why the coordination reaction between sal-mphah ligand and Cu(II) can form a one-dimensional coordination polymer.

On the other hand, the proportion of Cu(II) in LUMO is 31.72%. Cu(II) only coordinate with four atoms in this complex, so Cu(II) should have the ability to keep on reacting with other ligands. It is probably because of steric effect to make other ligand can not approach Cu(II).

Main atomic electron density populations for salicylidene-[1-(t-buty)-5-methyl-1H-pyrazole]-formhydrazine: The optimization of the ligand sal-pfh has been undertaken by DFT(B3LYP) methods. The 6-31G* basis set was employed. The analysis of Mulliken populations of salicylidene-[1-(t-buty)-5-methyl-1H- pyrazole]-formhydrazine is based on the structure optimized with DFT (B3LYP).



Main atomic electron dengsity populations for the ligand sal-pfh are given in Table-5. Mass negative electric charges distribute on the atom O1, O2, N1 and N2 (Table-5). They form a cavity of negative electric charges and they are the main portion of supplying electrons. The negative electric charges on N1 is less than those on N2, but the location of N1 makes it easy approaching Cu(II) to form a 5-membered ring. So O1, O2 and N1 form a tridentate ligand to coordinate with Cu(II).

TABLE-5
MAIN ATOMIC ELECTRON DENSITY POPULATION FOR SALICYLIDENE-[1-(*tert*-BUTYL)-5-METHYL-1H-PYRAZOLE]-FORMHYDRAZINE

	Electric charge		Electric charge
O1	-0.5732	C1	0.2154
O2	-0.4358	C6	0.1568
N1	-0.0950	C7	-0.0238
N2	-0.5700	C8	0.5379

Supplementary material: Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 257712 and 257711 for compounds **1** and **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

ACKNOWLEDGEMENTS

The authors are thankful to the special project of Qingao for generalship of Science and Techonology (No. 05-2-JC-80) and the Outstanding

Adult-young Scientific Research Encouraging Foundation of Shandong Province (No. 2005BS04007) for finanical supporting.

REFERENCES

1. E. Siebel, A.M.A. Ibrahim and R.D. Fischer, *Inorg. Chem.*, **38**, 2530 (1999).
2. S.A. Barnett, A.J. Blake, N.R. Champness and C. Wilson, *Cryst. Eng. Comm.*, 5 (2000).
3. B.B. De, B.B. Lohray, S. Sivaram and P.K. Dhal, *Macromolecules*, **27**, 1291 (1994).
4. A. Wiesemann, R. Zentel and G. Lieser, *Acta Polym.*, **46**, 25 (1995).
5. A.D. Beck, *J. Chem. Phys.*, **98**, 5648 (1993).
6. C. Lee, W. Yang and RG. Parr, *Phys. Rev. B*, **37**, 785 (1988).
7. X.L. Liu, R. Zhao and X.H. Liu, *Acta Chim. Sinica*, **61**, 578 (2003).
8. K.C. Zheng, D.B. Kuang and Y. Shen, *Acta Phys. Chim. Sin.*, **17**, 43 (2001).
9. W.J. Yu, J.Z. Li and G. Li, *Chinese J. Inorg. Chem.*, **15**, 660 (1999).
10. H. Paulus, H. Fuess and P. Baran, *Z. Kristallogr.*, **202**, 134 (1992).
11. T. Narahashi and R.N. Poston, *Science*, **156**, 976 (1967).

(*Received*: 12 January 2006; *Accepted*: 20 September 2006) AJC-5115