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Synthesis and Structures of Two Mononuclear Cu(II) Complexes Derived from 3-Methoxysalicylaldehyde Benzoylhydrazide Ligand

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Reaction of 3-methoxysalicylaldehyde benzoylhydrazide (H_2L) with $Cu(ClO_4)_2·6H_2O$ and heterocycle(imidazole or pyrazol) in methanol results in the formation of two isostructural mononuclear Cu(II) complexes, in which the metal ion is coordinated to the hydrazine-N, carbonyl-O and deprotonated phenolate-O of H_2L and the imine-N atom of the neutral heterocycle, forming a distorted square-planar coordination configuration. In the crystal structure of complexes **1** and **2**, the uncoordinated perchlorate anion is involved in forming intramolecular hydrogen bond. Additionally, complex **2** forms a centrosymmetric dimeric species due to weak apical coordination of the phenolate-O in a reciprocal fashion.

Keywords: Copper complex, Crystal structure, Mononuclear.

INTRODUCTION

The design and synthesis of acylhydrazone ligands and their corresponding metal complexes have received considerable attention[1], as a result of which not only play important roles in the development of coordination chemistry related to magnetism[2], enzymatic reactions[3] and pharmacological applications[4], but also exhibit variety of biological activities[5].

Schiff base ligands formed by reaction between the *o*-vanillin group and benzoylhydrazine (3-methoxysalicylaldehyde benzoylhydrazide, hereafter abbreviated as H_2L) is good candidates to construct metal clusters. The H_2L has O- or N-donors and these donors with suitable relative positions in the ligand can coordinate to metal centers[6,7]. Furthermore, the vanillin group displays a variety of bonding geometries, such as chelating, monodentate bridging, bidentate bridging and chelating bridging, although the coordination ability of the vanillin group is not strong in some cases[8,9].

N-donor heterocycles can react with coordinatively unsaturated copper(II) complexes to give varieties of complexes where the heterocycles molecule is coordinated to the Cu(II) *via* the N-donor[10,11]. Interestingly, the self-assembly patterns of the complexes having the general formula [Cu(L)(hc)] with other monodentate N-donor heterocycles (*L* = acylhy-drazone ligand, hc = pyrazole, imidazole or pyridine) are different[12,13].

Herein, we reported two Cu(II) complexes, [Cu(HL)-(imidazole)]·ClO_4 (**1**) and [Cu(HL)(pyrazol)]·ClO_4 (**2**), using substituted a monodentate N-donor heterocycle. Their crystal structures are also studied.

EXPERIMENTAL

All the reagents and solvents employed were commercially available and used as received without further purification. The 3-methoxysalicylaldehyde benzoylhydrazide ligand (H_2L) was prepared in a similar manner according to the reported procedures[14,15]. Elemental analysis for C, N and H were performed with a Perkin-Elmer 2400 II analyzer.

Caution! Although we did not experience any problem during the work, perchlorate salts in presence of organic materials are potentially explosive. They should be used in small quantities and handled with extreme care.

Preparation of complexes: The complex **1** was synthesized by adding $Cu(ClO_4)_2·6H_2O$ (37 mg, 0.10 mmol) to a solution of H_2L (27.3 mg, 0.1 mmol) in methanol (10 mL). After stirring for 3 h, imidazole (13.6 mg, 0.2 mmol) was added to the resulting solution. Green crystals were isolated from the solution after two weeks. Yield: 37.6 % (based on Cu). Elemental analysis (%) calcd. for $C_{18}H_{17}N_4O_7CuCl$: C, 43.21; H, 3.42; N, 11.20; found C, 43.27; H, 3.40; N, 11.18.

Complex **2** was obtained by a similar procedure to that for **1**, but using pyrazol in place of imidazole. Green crystals formed after two weeks. Yield: 35.9 % (based on Cu). Elemental analysis (%) calcd. for complex **2** $C_{18}H_{17}N_4O_7CuCl$: C, 43.21; H, 3.42; N, 11.20; found C, 43.25; H, 3.40; N, 11.19.

X-Ray crystallography: Crystallographic data were collected on a Bruker Apex II CCD diffractometer with graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å) at a temperature of 185 (± 2) K, for complexes **1** and **2**. Data processing was accomplished with the SAINT processing program. These structures were solved by the direct methods and refined on F^2 by full-matrix least squares using SHELXTL97[16,17]. The location of Cu atom was easily determined and O, N and C atoms were subsequently determined from the difference Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data and refinement details of complexes **1** and **2** are listed in Table-1. CCDC-998370 and CCDC-998371 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: (44) 1223-336033; email: deposit@ccdc.ccam.ac.uk].

RESULTS AND DISCUSSION

Complexes **1** and **2** crystallize in triclinic space group $P\bar{1}$. The structures of the complexes are illustrated in Figs. 1 and 2. The selected bond parameters are listed in Tables 2 and 3. Both complexes have a distorted square-planar geometry. In each complex, the metal ion is coordinated to the hydrazine-N, carbonyl-O and deprotonated phenolate-O of H_2L and the imine-N atom of the neutral heterocycle. The C-O and C-N bond lengths in the amide functionality of the tridentate ligand are within 1.255(5)-1.439(6) and 1.288(6)-1.388(6) Å, respectively. These values are in accord with the enolate form of the amide functionality[18,19]. The Cu-O(phenolate) (1.892(3)-1.910(3) Å) and Cu-N(hydrazine) (1.917(4)-1.923(3) Å) bond lengths are comparable to the bond lengths observed in copper(II) complexes having the same coordinating atoms[20-22]. In addition, the Cu-N(heterocycle) bond lengths of both complexes are in the range of 1.939(3)-1.940(4) Å are unexceptional[18,22]. In each complex, the satisfactory square plane is constructed by a O_2N_2 donor around the Cu(II) metal ion. The Cu(II) metal centers lie 0.067 and 0.075 Å above the O_2N_2 square planes for complexes **1** and **2**, respectively. However,

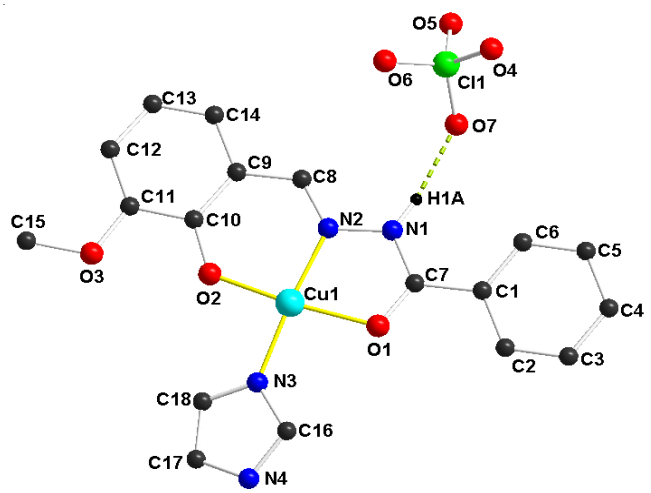

Fig. 1. A view of the complex **1**, showing the atomic numbering scheme

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (º) FOR COMPLEX **1**

Bond lengths			
Cu1-O1	1.985(3)	Cu1-N2	1.917(4)
Cu1-O2	1.892(3)	Cu1-N3	1.940(4)
Bond angles			
O2-Cu1-O1	172.61(14)	O2-Cu1-N2	92.45(15)
N2-Cu1-O1	81.16(15)	O2-Cu1-N3	91.05(15)
N3-Cu1-O1	94.98(15)	N2-Cu1-N3	173.69(17)

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPLEX **1** AND COMPLEX **2**

Complex	[Cu(HL)(imidazole)]·ClO_4 (**1**)	2[Cu(HL)(pyrazol)]·ClO_4 (**2**)
Formula	$C_{18}H_{17}N_4O_7CuCl$	$2C_{18}H_{17}N_4O_7CuCl$
Formula weight	500.35	1000.71
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$\bar{P}$
Colour	Green	Green
a (Å)	9.0657(9)	8.472(3)
b (Å)	10.6278(10)	11.041(3)
c (Å)	11.1888(11)	12.265(3)
α (°)	113.497(2)	68.404(4)
β (°)	92.970(2)	71.303(4)
γ (°)	93.550(2)	68.872(4)
V/(Å^3)	983.28(17)	971.4(5)
Z	2	1
D_{calc} (g cm^{-3})	1.690	1.765
μ (mm^{-1})	1.298	1.321
F(000)	510	526
Range of h, k, l	-9 < = h < = 11, - 11< = k< = 13, -13 < = l < = 12	-9 < = h < = 10, -10 < = k < = 13, -11 < = l < = 15
GOF	1.035	1.097
Data/restraints/parameters	3839/0/269	3780/0/281
R_1, wR_2 [I >2σ(I)][a,b]	R_1 = 0.0576, wR_2 = 0.1370	R_1 = 0.0596 wR_2 = 0.1617
R indices (all data)	R_1 = 0.0896, wR_2 = 0.1544	R_1 = 0.0667, wR_2 = 0.1682
Largest diff. peak and hole (eÅ^{-3})	0.740 and -0.739	1.518 and -1.127

[a]$R = \Sigma \, ||F_o|-|F_c||/\Sigma|F_o|$; [b]$wR_2 = [\Sigma w(F_o^2-F_c^2)^2/ \Sigma w(F_o^2)^2]^{1/2}$

TABLE-4
INTRAMOLECULAR HYDROGEN BOND FOR COMPLEXES **1** AND **2**

	D-H···A	d (D-H)	d (H···A)	d (D···A)	<(DHA)
Complex **1**	N1-H1A···O7	0.88	2.10	2.957(5)	163.4
Complex **2**	N1-H1A···O5	0.88	2.01	2.862(6)	163.4

TABLE-3
SELECTED BOND LENGTHS (Å)
AND ANGLES (°) FOR COMPLEX **2**

Bond lengths			
Cu1-O1	1.982(3)	Cu1-N2	1.923(3)
Cu1-O2	1.910(3)	Cu1-N3	1.939(3)
Bond angles			
O2-Cu1-O1	172.61(11)	O2-Cu1-N2	92.23(13)
N2-Cu1-O1	81.11(13)	O2-Cu1-N3	91.63(13)
N3-Cu1-O1	95.53(13)	N2-Cu1-N3	168.28(14)

none of the two complex molecules as a whole is planar. This is because the twisting of the phenyl ring plane (C1-C6) of the benzoyl fragment in H_2L and that of the heterocycle plane (imidazole and pyrazol) with respect to the plane containing rest of the molecule[12]. In complex **1**, both aromatic rings in each ligand surrounding the copper atoms form a dihedral angle that is 7.34(16)°. Compare to that, the larger dihedral angle found in complex **2** of 30.91(17)° indicates that the twist of H_2L in **1** is significantly smaller than in **2**. The nature of different N-donor heterocycles may result in the different twist of H_2L, although it is difficult to rationalize these outcomes at present[23]. The dihedral angles between the phenyl ring plane and the pyrazol plane are 17.34(17)° and 8.04(18)° for complexes **1** and **2**, respectively. In the crystal structure of complexes **1** and **2**, the uncoordinated perchlorate anion is involved in forming intramolecular hydrogen bonds (Figs. 1 and 2 and Table-4).

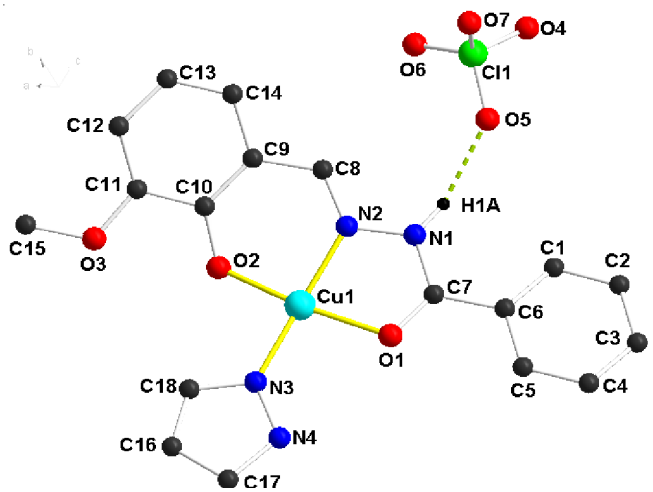

Fig. 2. A view of the complex **2**, showing the atomic numbering scheme

Square-planar Cu(II) complexes are known to form dimeric species containing equatorial-apical bridges due to the involvement of the metal ion in weak interactions with another atom of a neighboring molecule at the apical position[24,25]. Complex **2** forms a centrosymmetric dimeric species due to weak apical coordination of the phenolate-O in a reciprocal fashion (Fig. 3). The Cu1-O2A distance is 2.4343(33) Å. In the Cu_2O_2 core,

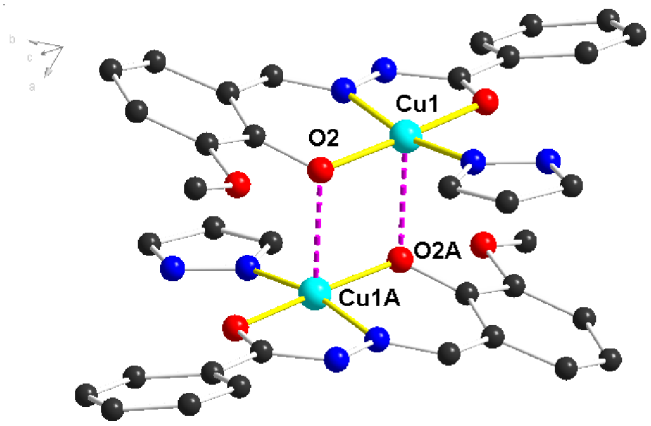

Fig. 3. Dimeric structure of the complex **2**

the Cu1-O2-Cu1A bridge angle and the Cu1···Cu1A distance are 94.765(15)° and 3.2167(13) Å.

Conclusion

To summarize, two novel mononuclear Cu(II) complexes have been prepared by using the Schiff base ligand (H_2L). The both Cu(II) ions adopt a CuN_2O_2 distorted square-planar coordination environment. However, the different N-donor heterocycles of two complex molecules may result in the different twist of H_2L. In addition, complex **2** forms a centrosymmetric dimeric species due to weak apical coordination of the phenolate-O in a reciprocal fashion.

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