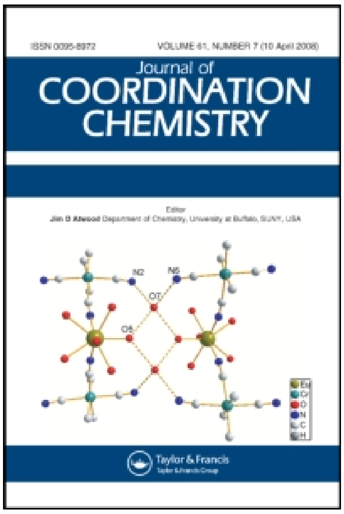

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Ternary copper(II) complexes of aroylhydrazones and mono/bidentate heterocycles with different structures: synthesis, crystal structure and properties

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Ternary copper(II) complexes of aroylhydrazones and mono/bidentate heterocycles with different structures: synthesis, crystal structure and properties

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Two mixed-ligand Cu(II) complexes, $[CuL^1(Himdz] \cdot CH_3OH$ (**1**) and $[CuL^2(phen)] \cdot 0.5DMF$ (**2**), with different structures have been synthesized by using substituted aroylhydrazones, 5-bromo-salicylaldehyde-benzoylhydrazone (H_2L^1) and 5-bromo-salicylaldehyde-3,5-dimeth oxy-benzoylhydrazone (H_2L^2), and mono/bidentate heterocycles, imidazole (Himdz) and 1,10-phenanthroline (phen). Their crystal structures and spectroscopic properties have been studied. X-ray analysis show a distorted square-planar geometry for **1** and a distorted square-pyramidal geometry for **2**, in which the chelating phen ligand displays axial-equatorial bonding. In both structures the ONO tridentate ligand occupies the basal plane. Self-assembly via O–H ··· N, N–H ··· O and C–H ··· O interactions lead to one-dimensional chain arrangement in **1** and **2**.

Keywords: Copper(II) complexes; Crystal structure; Heterocycle; Hydrazone

1. Introduction

The coordination chemistry of aroylhydrazones has received much attention due to their chelating ability and potential pharmacological applications [1–3]. Aroylhydrazones with several coordination sites can act as neutral or monoanionic bidentate or tridentate ligands depending on the substituents and the reaction conditions [4, 5]. Coordination to metals either in keto(I) or enol(I) tautomeric forms make them attractive as ligand [5–14]. Imidazole is a biologically important ligand, monodentate at low pH and bridging at higher pH. The presence of mixed ligands can infer differences in bonding, spectral properties and geometry in coordination complexes [4].

Recently, we reported the self-ssembly of two copper(II) complexes with substituted aroylhydrazones and pyridine and imidazone [15]. Herein, we reported two mixed-ligand Cu(II) complexes, $[CuL^1(Himdz] \cdot CH_3OH$ (**1**) and $[CuL^2(phen)] \cdot 0.5DMF$ (**2**), using substituted aroylhydrazones and a monodentate *N*-donor heterocycle (Himdz) or a bidentate *N*,*N*-donor heterocycle (phen). Their crystal structure and spectroscopic properties are studied.

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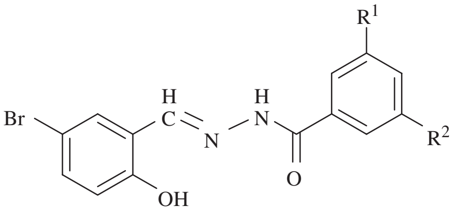

$R^1=R^2=H$ H_2L^1

$R^1=R^2=CH_3O$ H_2L^2

2. Experimental

2.1. *Materials and physical measurements*

C, N and H elemental analyses were carried out with a Varian EL elemental analyzer. IR spectra were recorded on a Bruker Tensor27 FT-IR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Shimadzu 2500PC spectrophotometer. The substituted aroylhydrazones, H_2L^1 and H_2L^2 were prepared by condensation of substituted benzoylhydrazine with 5-bromo-salicylaldehyde in methanol, respectively. All other chemicals and solvents used were of analytical grade available commercially and were used without further purification.

2.2. *Synthesis*

2.2.1. [CuL^1(Himdz]·CH$_3$OH (1). To a mixed solution of methanol (10 cm^3) and DMF (20 cm^3) of H_2L^1 (0.38 g, 1 mmol) and imidazole (0.32 g, 4 mmol), a methanol solution (10 cm^3) of $Cu(O_2CCH_3)_2 \cdot H_2O$ (0.19 g, 1 mmol) was added gradually with stirring. The resulting green solution was further stirred for 2 h and filtered. Greenish brown crystals separated after about one week and were collected. Yield: 60%. M.p. > 300°C. Anal. Calcd for **1** (%): C, 44.96; N, 11.65; H, 3.56. Found: C, 44.76; N, 11.80; H, 3.50.

2.2.2. [CuL^2(phen)]·0.5DMF (2). This complex was prepared by the same method as for **1**, but with H_2L^2 and phen instead of H_2L^1 and imidazole, respectively. Yield: 75%. M.p. > 300°C. Anal. Calcd for the desolvated species $C_{28}H_{21}BrCuN_4O_4$ (%): C, 54.16; N, 9.02; H, 3.41. Found: C, 54.00; N, 8.96; H, 3.45.

2.3. *Crystal structure determination*

Diffraction data of **1** were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Diffraction data of **2** were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å) at 223 (2) K. Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. All hydrogen atoms were located geometrically and refined isotropically. The data collection and refinement details for **1** and **2** are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure*

The molecular structures of **1** and **2** are illustrated in figures 1 and 2 with the atom numbering scheme. Selected bond parameters are listed in tables 2 and 3. The asymmetric unit of **1** contains a complex molecule and a methanol molecule, while the asymmetric unit of **2** contains four complex molecules and two DMF molecules.

The crystal structures of the complexes reveals the presence of a ternary structure consisting of a tridentate ONO-donor hydrazone ligand, a monodentate *N*-donor heterocycle (Himdz) or a bidentate *N*,*N*-donor heterocycle (phen) and the copper(II) in discrete monomeric species. Complex **1** has a distorted square-planar geometry. Complex **2** has a distorted square-pyramidal geometry, in which the *N*,*N*-donor atoms

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{18}H_{17}BrCuN_4O_3$	$C_{29.50}H_{22.75}BrCuN_{4.50}O_{4.50}$
Formula weight	480.81	655.72
Crystal system	Monoclinic	Triclinic
Space group	$P_2(1)/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.821(4)	14.2848(11)
b	8.016(3)	15.6738(9)
c	22.792(7)	25.4401(19)
a	90	77.058(6)
β	102.418(5)	85.540(7)
γ	90	75.374(5)
V (Å^3)	1930.8(11)	5370.0(7)
Z	4	8
D_{Calcd} (Mg m^{-3})	1.654	1.622
Absorption coefficient (mm^{-1})	3.226	2.349
$F(000)$	964	2650
Max. and min. transmission	0.7600/0.3376	0.5392/0.2263
θ range for data collection (°)	1.83–25.01	3.03–25.01
Index ranges	$-12 \le h \le 11$, $-9 \le k \le 9$, $-27 \le l \le 23$	$-16 \le h \le 16$, $-17 \le k \le 18$, $-28 \le l \le 30$
Completeness to $\theta = 25.00°$ (%)	99.5	99.3
Reflection collected	9734	49596
Independent reflection	3380 ($R_{\text{int}} = 0.0736$)	18794 ($R_{\text{int}} = 0.0527$)
Reflections with [$I > 2\sigma$(I)]	2037	13982
Data/restraints/parameters	3380/0/244	18794/5/1457
Goodness-of-fit on F^2	1.001	1.112
Final R indices [$I > 2\sigma$(I)]	$R_1 = 0.0520$, $wR_2 = 0.1174$	$R_1 = 0.0709$, $wR_2 = 0.1351$
R indices (all data)	$R_1 = 0.0990$, $wR_2 = 0.1422$	$R_1 = 0.1004$, $wR_2 = 0.1499$
Largest diff. peak and hole (e Å^{-3})	0.898 and −0.539	1.123 and −0.772

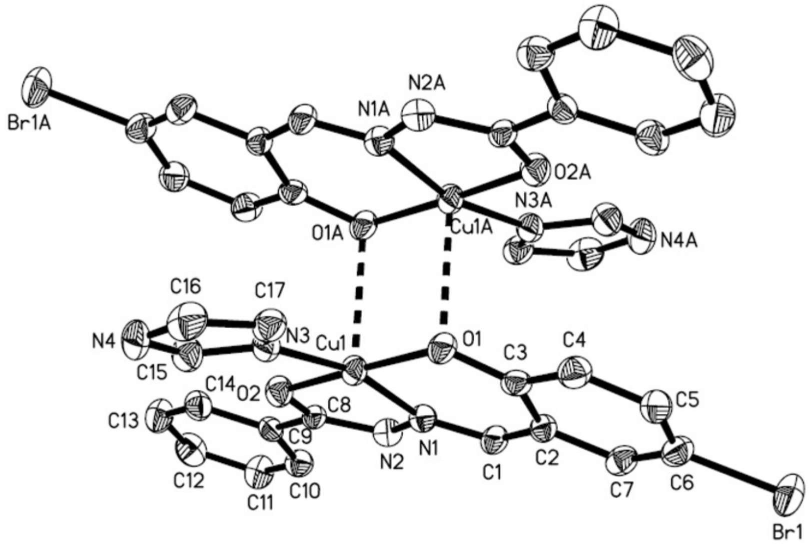

Figure 1. Dimeric structure of $[CuL^1(Himdz)] \cdot CH_3OH$ (**1**) with the atom labeling scheme.

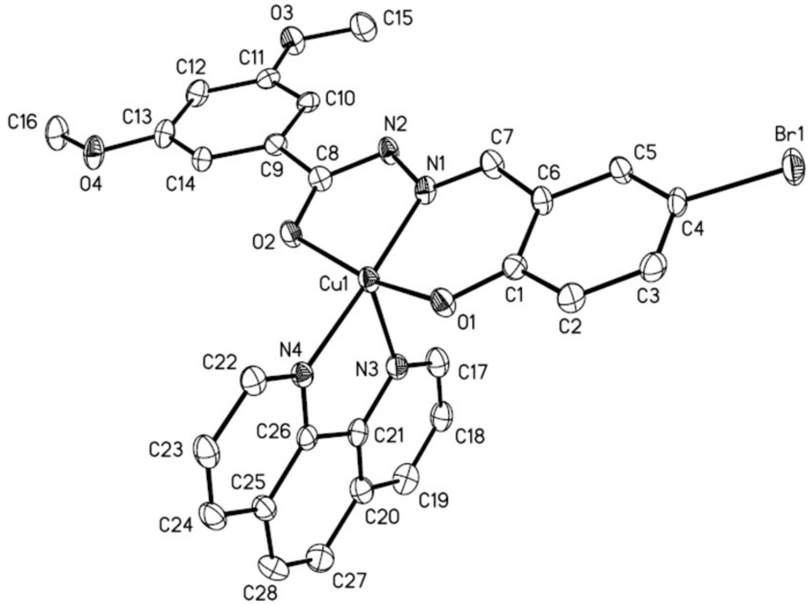

Figure 2. Structure of $[CuL^2(phen)] \cdot 0.5DMF$ (**2**) with the atom labeling scheme.

of phen are axial equatorial. In both structures, ONO-donor hydrazone ligand occupies the basal plane by the phenolate-O, the imine-*N* and the deprotonated amide-O atoms.

The C–O and C–N bond lengths in the amide of the tridentate ligand are 1.277(6)–1.283(6) and 1.328(7)–1.327(7) Å, respectively, consistent with the enolate

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Cu(1)–O(1)	1.917(4)	Cu(1)–N(3)	1.954(5)
Cu(1)–N(1)	1.927(5)	N(2)–C(8)	1.328(7)
Cu(1)–O(2)	1.947(4)	O(2)–C(8)	1.277(6)
O(1)–Cu(1)–N(1)	93.39(17)	O(2)–Cu(1)–N(3)	92.62(18)
O(1)–Cu(1)–O(2)	173.62(17)	C(1)–N(1)–N(2)	118.9(5)
N(1)–Cu(1)–O(2)	80.81(18)	C(1)–N(1)–Cu(1)	126.3(4)
O(1)–Cu(1)–N(3)	93.63(17)	N(2)–N(1)–Cu(1)	114.7(3)
N(1)–Cu(1)–N(3)	165.38(19)	C(8)–N(2)–N(1)	109.1(4)

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Cu(1)–O(1)	1.913(4)	Cu(1)–N(3)	2.316(4)
Cu(1)–N(1)	1.922(4)	N(2)–C(8)	1.328(7)
Cu(1)–O(2)	1.948(4)	O(2)–C(8)	1.282(6)
Cu(1)–N(4)	2.011(4)		
O(1)–Cu(1)–N(1)	93.74(17)	O(2)–Cu(1)–N(4)	94.92(17)
O(1)–Cu(1)–O(2)	163.70(18)	O(1)–Cu(1)–N(3)	105.53(17)
N(1)–Cu(1)–O(2)	81.29(16)	N(1)–Cu(1)–N(3)	101.95(18)
O(1)–Cu(1)–N(4)	90.14(17)	O(2)–Cu(1)–N(3)	90.72(17)
N(1)–Cu(1)–N(4)	176.12(18)	N(4)–Cu(1)–N(3)	77.15(18)

form of the amide [9–15]. The Cu–O(phenolate) (1.917(4), 1.913(4) Å) and Cu–N(imine) (1.927(5), 1.922(4) Å) bond lengths (tables 2 and 3) are comparable to the bond lengths observed in copper(II) complexes having the same coordinating atoms [12, 13]. The Cu–O(amide) distance (1.947(4), 1.949(4) Å) is comparable with distances observed for complexes in which copper(II) is coordinated to a deprotonated amide-O [10, 11, 14, 15]. The Cu–N(heterocycle) bond length is unexceptional [10–13].

In complex **2**, the axial Cu(1)–N(3) (2.316(5) Å) bond length is longer than the equatorial Cu(1)–N(4) (2.011(4) Å) and Cu–N(1) (1.927(5) Å) bond length. The difference of Cu–N bond lengths can be attributed to the difference in π back donating between the phen and hydrazone moieties [16]. The bond angles of O(1)–Cu(1)–N(3) (105.53(17)°), N(1)–Cu(1)–N(3) (101.95(18)°) and N(4)–Cu(1)–N(3) (77.15(18)°) indicate distortion from perfect square-pyramidal geometry. One reason for the deviation from an ideal stereochemistry is the restricted bite angle imposed by hydrazone and phen ligands.

Square-planar copper(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 [14]. Complex **1** forms a centrosymmetric dimeric species due to weak apical coordination of the phenolate-O in a reciprocal fashion (figure 2). The Cu1–O1A distance is 2.5425(6) Å. In the Cu_2O_2 core, the Cu1–O1–Cu1A bridge angle and the Cu1 $\cdots$ Cu1A distance are 93.847(9)° and 3.2854(10) Å.

In the crystal lattice, self-assembly of the dimeric units of **1** and methanol due to hydrogen bonding leads to a one-dimensional array of the solvated species. Each methanol participates in two hydrogen bonds, whereas each dimer participates in four hydrogen bonds and the chain-like arrangement is formed (figure 3). On one side, the O–H of methanol acts is a donor to the uncoordinated and deprotonated amide-N of one dimer with O $\cdots$ N distance and O–H $\cdots$ N angle of 2.782 Å and 164.14°, respectively.

On the other side it acts as an acceptor from the imidazole N–H group of another dimmer. The N···O distance and N–H···O angle are 2.775 Å and 162.85°. Two methanol molecules bridge two dimers in a reciprocal fashion with respect to the donor-acceptor behavior. In **2**, the phenyl ring C–H group of one molecule and the methoxy substituent of an adjacent molecule are involved in hydrogen bonding and a one-dimensional assembly is formed (figure 4). The C···O distance and C–H···O angle are 3.308 Å and 159.9°; solvent molecules are not involved in hydrogen-bonding interactions.

3.2. *IR spectra and electronic spectra*

IR spectrum of **1** displays a strong band at 3135 cm^{-1}, associated with the imidazone N–H group or the solvent O–H group [9]. The spectrum of **2** is devoid of a band in this region. None of the spectra display any band assignable to the C=O group of the amide functionality present in the tridentate Schiff base at ca 1650 cm^{-1}, consistent with deprotonation and the enolate form of the amide in each complex [11, 12]. A strong band attributed to the conjugated C=N–N=C fragment is observed at 1613 cm^{-1} for **1** and 1610 cm^{-1} for **2** [9–15].

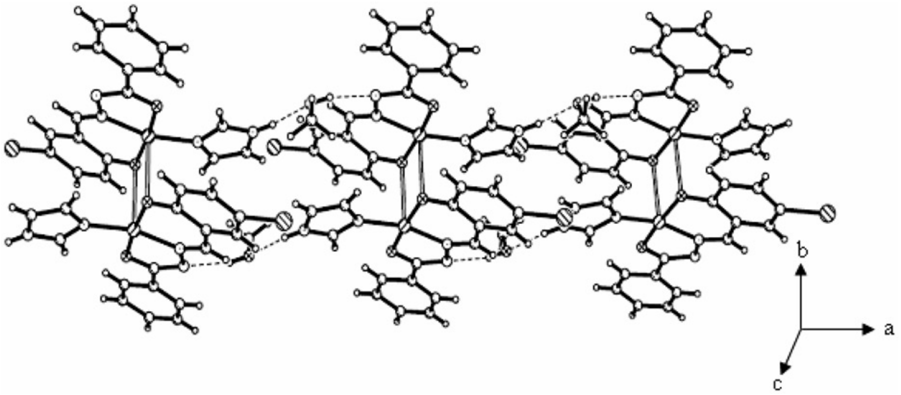

Figure 3. One-dimensional chain arrangement of [CuL^1(Himdz]·CH_3OH (**1**) in the crystal lattice.

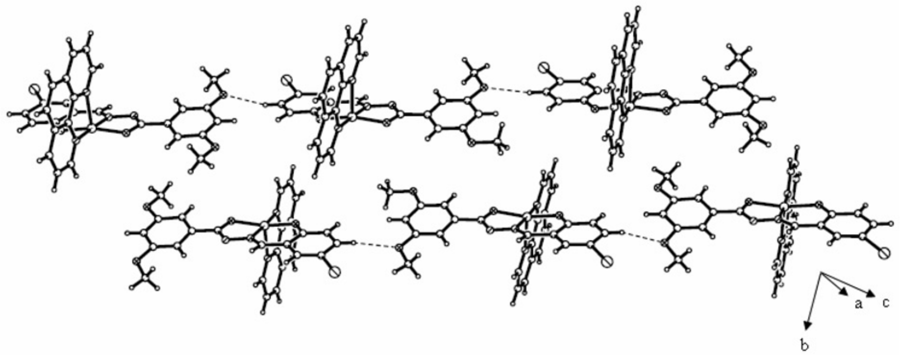

Figure 4. One-dimensional chain arrangement of [CuL^2(phen)]·0.5DMF (**2**) in the crystal lattice.

Electronic spectra of **1** and **2** show intense bands in the range 302–400 nm. Strong absorption peaks between 302 and 336 nm can be assigned to intraligand transitions, and the stronger absorption band at ca 400 nm may correspond to the ligand-to-metal charge transfer [9, 11, 15].

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