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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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## A Crystallographic, Spectroscopic, Thermal, and DFT Investigation of Mixed Ligand Cu(II) Complexes of 2benzoylbenzoate

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## A Crystallographic, Spectroscopic, Thermal, and DFT Investigation of Mixed Ligand Cu(II) Complexes of 2-benzoylbenzoate

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Two mixed ligand complexes of copper(II)-2-benzoylbenzoate (bba) with pyridazine and 4-picoline, namely bis(2-benzoylbenzoate)di(pyridazine)copper(II) 1 and bis(2-benzoylbenzoate)bis(4picoline)copper(II) 2, have been synthesized and characterized by X-ray crystallography. Complexes 1 and 2 crystallize in the monoclinic P2<sub>1</sub>/c space groups. The calculated frequency shifts have shown that the participation of carboxylate groups in coordination to the metal centers in monodentate fashion ( $\Delta$ (OCO) > 200 cm<sup>-1</sup>). The structural features of the complexes have been further studied by DFT/X3LYP extended hybrid functional. The thermal behavior of the complexes was studied by means of simultaneous thermogravimetry, differental thermogravimetry, and differential thermal analysis methods in a static air atmosphere.

Keywords 2-benzoylbenzoate, copper(II) complex, crystal structure, DFT, X3LYP

#### INTRODUCTION

Definite organic compounds containing carboxylates as functional group and/or supramolecular synthon are among the most widely studied ligand classes at present because of providing a good facility for the synthesis of coordination compounds with interesting topologies. Versatile coordination modes are available with carboxylato groups such as monodentate and chelate, different types of CO<sub>2</sub> bridges, and O monoatomic bridges.<sup>[11]</sup> In addition, stable complexes of low coordination numbers are available with flexible and sterically bulk ligands. Metal-carboxylate complexes have diverse structural, physical, and chemical properties, giving rise to versatile practices such as their use in dyes, extractants, drugs, pesticides, catalysts, magnetism, host–guest chemistry,<sup>[2–6]</sup> metal-organic framework materials, and many fields of industry. They also have been utilized by their high surface area, porosity, and attractive adsorptive properties.<sup>[7–9]</sup>

2-benzoylbenzoic acid (Hbba) and its derivatives are used in the synthesis of supramolecular coordination compounds,<sup>[10]</sup> in the preparation of electron-transport materials,<sup>[10]</sup> and in sweeteners.<sup>[11]</sup> But the number of studies with the metal complexes of 2-benzoylbenzoato [bba =  $(C_{14}H_9O_3)^-$ ] is rare in the literature.<sup>[10–19]</sup>

Pyridazine (pdz) as an important heterocycle has two potential N-donor coordination sites and can behave as a monoor bidentate ligand. Pyridazine and derivatives are widely used in pharmaceutical and agrochemical areas.<sup>[20,21]</sup> Their synthesis and applications have been comprehensively reviewed.<sup>[22,23]</sup>

Hbba, pdz, and 4-picoline (4-pic) ligands are shown in Figure 1. In our previous work, we reported the synthesis and structural characterization of transition metal complexes of bba with the coligand 1,10-phenanthroline.<sup>[24,25]</sup>

In the present study, the synthesis, spectral, thermal characterization, DFT/X3LYP analysis, and crystal structures of two new complexes,  $[Cu(bba)_2(pdz)_2]$  **1** and  $[Cu(bba)_2(4-pic)_2]$  **2**, have been represented.

#### **EXPERIMENTAL**

#### Methods of Sample Characterization

All reactions were performed with commercially available reagents and they were used without further purification. The solvents were distilled and dried by standard procedures. IR spectra were recorded on a Bruker Vertex 80V FT-IR spectrophotometer in the range 4000–450 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> using KBr pellet. The C, H, and N content of the complexes were determined with an Elementar Micro Vario CHNS (Germany). Thermal analysis curves (thermogravimetry [TG], differential thermal analysis [DTA], differential thermogravimetry [TG]) were simultaneously obtained on a Perkin-Elmer Diamond thermal analyzer (USA) in a static air atmosphere with a sample of 5–10 mg.

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FIG. 1. Structures of (a) 2-benzoylbenzoic acid, (b) pyridazine, and (c) 4-picoline ligands.

Intensity data for the title compounds were collected using a STOE IPDS-II area detector diffractometer (Germany, MoK $\alpha$  radiation,  $\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods and refined on  $F^2$  with the SHELX-97 program (University of Göttingen, Germany).<sup>[26]</sup> All non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were included using a riding model.

#### Synthesis of [Cu(bba)<sub>2</sub>(pdz)<sub>2</sub>] (1)

Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O (0.006 g, 0.3 mmol) and 2-Hbba (2benzoylbenzoic acid) ligand (0.136 g, 0.6 mmol) were dissolved in 40 mL of ethanol with continuous stirring at 50°C. Then pdz ligand (75  $\mu$ L, 1 mmol) was dropwise added to the solution. X-ray quality blue crystals of [Cu(bba)<sub>2</sub>(pdz)<sub>2</sub>] were obtained by slow evaporation of the solvent at room temperature after one day. Yield: 85%. Anal. Calcd. for C<sub>36</sub>H<sub>26</sub>N<sub>4</sub>O<sub>6</sub>Cu (%): C, 64.14; H, 3.86; N, 8.31. Found (%): C, 64.01; H, 3.90; N, 8.25.

#### Synthesis of [Cu(bba)<sub>2</sub>(4-pic)<sub>2</sub>] (2)

2-Hbba ligand (0.136 g, 0.6 mmol) and Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O (0.006 g, 0.3 mmol) were dissolved in 40 mL of methanolethanol (1:1) mixture with continuous stirring at 50°C. Then a 4-pic ligand (100  $\mu$ L, 1 mmol) was dropwise added to the solution. Dark blue crystals of [Cu(bba)<sub>2</sub>(4-pic)<sub>2</sub>] were obtained by slow evaporation of the solvent at room temperature after one day. Yield: 90%. Anal. Calcd. for C<sub>40</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>Cu (%): C, 68.57; H, 4.57; N, 4.0. Found (%): C, 68.51; H, 4.41; N, 3.91.

#### **RESULTS AND DISCUSSION**

#### **Crystal Structure of 1**

The molecular structure of complex 1 together with the atom numbering scheme is shown in Figure 2 and the crystal packing determined by C-H<sup> $\cdot\cdot\cdot\pi$ </sup> interactions along *b*-axis is given in Figure 3. The detail of data collection, refinement, and crystallographic data for 1 and 2 are summarized in Table 1.

Complex 1 crystallizes in the monoclinic  $P2_1/c$  space group. The monomer complex consists of two bidentate bba and two monodentate pdz ligands. The copper(II) ion is located at the center of inversion and the coordination around the metal ion is distorted octahedral.



FIG. 2. Molecular structure of 1 with ellipsoid probabilities of 50% for Cu and 35% for other atoms (color figure available online).

 TABLE 1

 Crystal data and structure refinement parameters for 1 and 2

	(1)	(2)
Empirical formula	C <sub>36</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> Cu	C <sub>40</sub> H <sub>32</sub> N <sub>2</sub> O <sub>6</sub> Cu
Formula weight	674.15	700.22
Temperature (K)	296	296
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /c
Unit cell dimensions		
<i>a</i> (Å)	13.7177(9)	8.2903(7)
b (Å)	8.3372(4)	20.4904(12)
<i>c</i> (Å)	14.1719(9)	11.3213(9)
$\alpha^{\circ}$	90	90
$oldsymbol{eta}$ $^{\circ}$	103.462(5)	113.697(6)
$\gamma^{\circ}$	90	90
$V (Å)^3$	1576.27(16)	1761.0(2)
Z	2	2
A. coefficient $(mm^{-1})$	0.747	0.669
$D_{calc} (mg m^{-3})$	1.420	1.320
Crystal size (mm)	0.150; 0.317; 0.610	0.270; 0.467; 0.650
Theta range for data collection (°)	1.86; 27.99	1.99; 26.00
Measured reflections	18409	16421
Indepen. reflections	3552	3449
Absorpt. correction <sup>a</sup>	Integration	Integration
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on F <sup>2</sup>
Final <i>R</i> indices $[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0342, wR_2 = 0.0844$ R (all data) = 0.0539, $wR_2 = 0.0905$	$R_1 = 0.0349, wR_2 = 0.0974$ R (all data) = 0.0431, $wR_2 = 0.1014$
Goodness-of-fit on $F^2$	1.022	1.042
Largest difference peak and hole $(e/Å^3)$	-0.354; 0.245	-0.535; 0.230
CCDC number	831085	831086

<sup>a</sup>Stoe and Cie (2002).<sup>[26]</sup>

Cu-O<sub>bba</sub> bond distance is 1.9611(1) Å, which is similar to that reported in [Cu(bba)<sub>2</sub>(benzimidazole)<sub>2</sub>] (1.95(13) Å)<sup>[19]</sup> and in [Cu(bba)<sub>2</sub>(phen)] (1.92(2) and 1.96(2) Å),<sup>[24]</sup> where phen is 1,10-phenanthroline. Relatively long Cu-O2 distance (2.5387(1) Å) and the small C1-O2-Cu1 angle (77.718°(3)) denotes the

TABLE 2Selected hydrogen bonds (°) for 1					
D—H· · ·A	D—H D—H (Å)	H· · ·A (Å)	D· · ·A (Å)	$\begin{array}{c} D - H \cdots A \\ (^{\circ}) \end{array}$	
(1)					
С3—Н3…О3	0.93	2.44	3.180 (3)	137	
C18—H18…O2	0.93	2.41	3.309 (3)	163	

weak coordination of O2 atom to the metal ion and hereby, a pseudodistorted octahedral geometry around copper(II) center is provoked rather than a square-planar geometry in contrast to that IR results suggest. Selected hydrogen bonds are given in Table 2.

As shown in Table 3, there are intermolecular hydrogen bonds between bba ligand and carbonyl O atom of the bba ligand (C3-H3…O3; 2.437 Å) and between pdz and carboxylato O atom of the bba ligands (C18-H18…O2; 2.407 Å). The chains are cross-linked by C-H… $\pi$  and  $\pi$ … $\pi$  stacking interactions (C11-H11…Cg2 (C2-C7) 2.908 Å, C15-H15…Cg3 (C9-C14) 2.793 Å, and Cg1-Cg1 4.2788(13) Å) arranged by free rotation of benzoyl synthons of flexible bba ligands, and these weak interactions together with partially effective aforementioned H-bonds are primarily responsible for self-assembling of **1** leading to the lattice formation.



FIG. 3. Crystal packing of 1 along *b*-axis, C-H… $\pi$  interactions (dotted lines), and coordination polyhedra around central atoms (color figure available online).

#### **Crystal Structure of 2**

Structure analysis of **2** shows that complex crystallizes in monoclinic  $P2_1/c$  space group. The symmetric unit consists of two bba and two 4-pic ligands. As depicted in Figure 4, each Cu(II) is coordinated by four oxygen each from two bba ligands and by two nitrogen from two 4-pic ligands, resulting in a distorted octahedral geometry analogous to **1**. Crystal packing determined by C17-H17<sup>••</sup> Cg2 interactions along a-axis is given in Figure 5.

Cu-O<sub>bba</sub> bond distance is 1.956(12) Å similar with the corresponding one in [Cu(bba)<sub>2</sub>(benzimidazole)<sub>2</sub>] (1.95(13) Å)<sup>[19]</sup> and [Cu(bba)<sub>2</sub>(phen)] (1.92(2) and 1.96(2).<sup>[24]</sup> Cu-N<sub>4-pic</sub> bond distance is 1.997(15) Å, which is slightly longer than the corresponding one in [Cu(dipic)(4-picoline)]<sub>n</sub> (1.920(15) and 1.890(11) Å),<sup>[27]</sup> [Cu(pmpa)(4-methylpyridine)(H<sub>2</sub>O)]-(H<sub>2</sub>O)(ClO<sub>4</sub>) (1.986(4) Å).<sup>[28]</sup> But Cu-N<sub>4-pic</sub> bond distance is slightly shorter than in (PEPA)(4-methylpyridine)(H<sub>2</sub>O)](ClO<sub>4</sub>)

The intermolecular C17-H17 $\cdots$ Cg2 (C8-C13) (2.9077 Å) and C5-H5 $\cdots$ Cg3 (C15-C20) (3.0134 Å) interactions between bba ligands are only responsible for self-assembling of **2** and leads to the crystal packing because none of intra- or intermolecular H-bonds were detected from Platon analysis of the structure.

In previously reported Co(II) and Ni(II) counterparts of 1 and 2 with coligand 3-picoline, bba acted as monodentate and two aqua ligands participated to the coordination in coplanar

TABLE 3

Assignment	1			2		
	Calc.	Exp.	Int.	Calc.	Exp.	Int.
v(CH) <sub>4-pic</sub>				3114	3062w	38.92
$v(CH)_{pdz}$	3124	3067w	15.82	_	_	
$v(CH)_{phenyl}$	3087	3020w	11.59	3080	3017w	54.12
v(CH) <sub>aliph.</sub>	_	_	_	2929	2918w	30.14
v(C=0)	1704	1673s	292.59	1688	1668s	363.63
$v(OCO)_{asym}$	1622	1586s	292.36	1635	1591s	323.58
$v(OCO)_{sym}$	1350	1379vs	1155.84	1336	1372vs	1050.84
v(C=N)	—	—	—	1610	1557w	189.26

Selected calculated and experimental vibrational frequencies of 1 and 2 in  $cm^{-1}$  and calculated intensities in km/mol

*Note.* s = strong; w = weak; vs = very strong.



FIG. 4. Molecular structure of 2 with ellipsoid probabilities of 50% for Cu and 30% for other atoms (color figure available online).

position with bba ligands, and more ordered octahedral complexes were resulted than 1 and 2.<sup>[32]</sup> This is because Co(II) and Ni(II) are not as prone as Cu(II) to form highly distorted octahedral complexes as 1 and 2. Therefore, the difference on the coordination behaviors of bba ligands in corresponding Cu(II) complexes here not only comes from versatility of bba ligands but also from tendency of Cu(II) ion. This is because copper(II) forms a larger variety of complexes with different coordination geometries as compared with other transition metal(II) ions.

#### **IR Spectra**

Some characteristic experimental and calculated gas-phase vibrational stretching frequencies scaled with 0.96, previously obtained value in the literature for B3LYP/6–31g(d,p) level,<sup>[33]</sup>

are listed in Table 3. The experimental and calculated IR spectra of **1** and **2** are given in Figure 6. Even with scaling, the overestimation of calculated vibrations is caused by the negligence of anharmonic effects, appears in the solid state, by DFT. However, for qualitative assignment of observed frequencies, it is very practical and useful that the comparison of experimental values with calculated vibration modes. In the observed spectra, the characteristic  $v(OCO)_{asym}$  values are 1586 and 1590 cm<sup>-1</sup>,  $v(OCO)_{sym}$  values are 1379 and 1372 cm<sup>-1</sup>, and the calculated  $\Delta(OCO)$  values { $v(OCO)_{asym} - v(OCO)_{sym}$ } are 207 cm<sup>-1</sup> and 218 cm<sup>-1</sup> for **1** and **2**, respectively. These  $\Delta(OCO)$  values are in accordance with monodentate ( $\Delta > 200$  cm<sup>-1</sup>) coordination modes of carboxylate ligands.<sup>[34]</sup> Besides medium intensity bands around 1604–1614 cm<sup>-1</sup> may be assigned to v(C-N) of the aromatic ring of the Lewis base, confirming their presence in adducts.<sup>[35]</sup>

#### Thermal Analysis

Thermal analysis plots of **1** and **2** are given in Figures 7 and 8, respectively. The thermal behavior of **1** was followed up to 900°C in a static air atmosphere. **1** decomposes in two stages. The first stage between 161 and 258°C corresponds to the endothermic removal of the two pdz and one bba ligand with a mass loss of 57.16% (calcd. mass loss 57.50%; DTG<sub>max</sub> = 235°C). Decomposition of the one bba ligand occurs in the second stage (258–490°C) with a mass loss of 34.36% (calcd. mass loss 33.40%). The last decomposition step of the complex seems vigorously exothermic (DTA at 449°C) and is related to the burning of organic residue. The total mass loss of all decomposition process is 91.52% (calcd. 90.90%) and suggests that CuO is the end product.

Complex 2 shows a three-stage decomposition process. In the first stage, endothermic degradation of one 4-pic occurs between  $134-188^{\circ}$ C with an experimental mass loss of 12.93%



FIG. 5. Crystal packing of 2 along b-axis, C-H...  $\pi$  interactions (dotted lines), and coordination polyhedra around central atoms (color figure available online).







FIG. 7. Simultaneous thermal analysis plots of 1. TG = thermogravimetry; DTG = differential thermogravimetry; DTA = differential thermal analysis (color figure available online).



FIG. 8. Simultaneous thermal analysis plots of 2. TG = thermogravimetry; DTG = differential thermogravimetry; DTA = differential thermal analysis (color figure available online).

(calcd. mass loss 13.28%; DTG<sub>max</sub> = 175°C). The second stage (188–310°C) is related to degradation of one 4-pic and one bba ligand, giving an exothermic peak (found = 44.58, calcd. = 45.42%). In the last stage, which is extremely exothermic in the 310–535°C range, one bba ligand abruptly burned (DTA = 410, 455, and 471°C). The total mass loss of complete decomposition process is 90.95% (calcd. 90.84%) and suggests that CuO is the end product.

#### **Computational Procedure**

All computations in this study were executed by using the Gaussian 03W Revision  $E.01^{[36]}$  program suite and applying unrestricted formalism for all complexes. The extended density hybrid functional X3LYP was used throughout the calculations. The basis sets LANL2DZ, in geometry optimizations, and 6–311 + G(d,p), in single-point energy (SPE) calculations, were applied for the Cu atom, while only 6–31g(d,p) was



FIG. 9. Superimpositions of optimized (blue) and X-ray (orange) geometries of 1 (a) and 2 (b) (color figure available online).

Bond lengths (Å)				Bond angles (°)			
		Calc.				Calc.	
Bond	Exp.	X3LYP	B3LYP	Angle	Exp.	X3LYP	B3LYP
(1)							
Cu1-N1	2.0133(16)	2.061	1.983	O1 <sup>i</sup> -Cu1-N1 <sup>i</sup>	91.11(6)	90.866	91.021
Cu1-O1	1.9611(13)	1.976	2.049	O1-Cu1-N1 <sup>i</sup>	88.89(6)	89.134	88.981
Cu1-O2	2.5387(1)	2.593	2.552	O1-Cu-O2	56.849(2)	56.546	57.174
(2)							
Cu1-O1	1.9560(12)	1.978	1.984	01-Cu1-N1	89.39(6)	89.510	89.546
Cu1-N1	1.9970(15)	2.066	2.054	O1-Cu1-N1 <sup>i</sup>	90.61(6)	90.492	90.453
Cu1-O2	2.5857(1)	2.657	2.618	O1-Cu-O2	55.961(2)	55.374	56.045

 TABLE 4

 Selected distances and angles of the optimized and X-ray geometries of 1 and 2

applied for non-metal atoms. The initial guess structures for geometry optimizations were taken from experimental X-ray geometries and the succeeding calculations were carried out based on the optimized geometries. Harmonic vibrational frequency analyses of the optimized structures were performed to check whether they are the true global minima with no imaginary frequency. Calculated spectra were simulated by using the Swizard Program.<sup>[37]</sup>

#### Geometry Optimizations and NBO Analysis

The main geometrical parameters related to X-ray and optimized geometries of **1** and **2** are given in Table 4 and superimpositions of X-ray and optimized structures of **1** and **2** are presented in Figure 9. Also the results obtained by the most popular all-purpose B3LYP functional are additionally given for comparison in the Table 4. Though the results obtained both from X3LYP and B3LYP calculations are in perfect agreement with the experiment, X3LYP values are slightly better agreement with the X-ray geometries than B3LYP ones. In addition, the root mean square error values of overall X3LYP-optimized structures of **1** and **2** are 0.333 Å and 0.466 Å while those of B3LYP ones are 0.333 Å and 0.476 Å, respectively. Based on the results, The X3LYP method was essentially preferred

 TABLE 5

 Major second order energies from NBO analysis

1			2		
Donor	Acceptor	E2 (kcal/ mol)	Donor	Acceptor	E2 (kcal/ mol)
O1(LP) O2(LP) N1LP)	Cu1(LP*) Cu1(LP*) Cu1(LP*)	16.01 3.03 14.9	O1(LP) O2(LP) N1LP)	Cu1(LP*) Cu1(LP*) Cu1(LP*)	15.26 2.31 15.19

*Note*. LP = a lone pair valence orbital;  $LP^* = empty$  valence orbital.

for the calculative procedure in this study, owing to the fact that optimized geometries are essential for all other calculations in theoretical insight. In both functional, the calculated Cu1-O2 distances in both 1 and 2 more deviated from experimental values compared with the Cu1-N1 and Cu1-O1 distances. Therefore, the calculated structures of 1 and 2 favor the square-planar geometry. The Natural Bond Orbital (NBO) analysis of intraunits of 1 fairly manifests electron populations of d-orbitals within octahedral copper(II) center whereas electron population between  $dz^2$  and  $dx^2-y^2$  orbitals seems to be interfused to some extent in 2. Second-order perturbation theory analysis of Fock matrix in 1 and 2 specifies the strongest noncovalent intramolecular interactions take place between donor atoms and central copper(II) ions. Selected, considerably high, second-order energies in Table 5 point out that tremendoulsy weak covalent character of the related interactions. As seen, the interactions between O2 and central atoms in 1 (3.03 kcal/mol) and 2 (2.31 kcal/mol) are not as significant as these between O1 and central atoms. Accordingly, the weak interactions of these donors to the metal centers are not to be considered as a coordination bond by theoretical insight. Besides none of natural bond orbitals was detected between donor atoms and central ions.

#### **CONCLUSIONS**

The newly synthesized Cu(II) complexes have been characterized by elemental analyses, FT-IR, thermal analysis, and Xray single-crystal diffractometry. The crystal structure analysis showed that compounds 1 and 2 consist of neutral monomeric units and all complexes exhibit pseudo-octahedral geometry. Conversely, both experimental IR spectroscopic and calculated data present the monodentate coordination behavior of the bba ligands to the metal centers and suggest square-planar geometry. Consequently, combining the whole findings we have concluded that the geometry around metal ions distorted from square-planar toward octahedral geometry by weak coordination of O2 atoms. The chains in the complexes are cross-linked by C-H·· $\pi$  and  $\pi$ ·· $\pi$  stacking interactions. It has been also shown that X3LYP geometries of **1** and **2** are slightly better agreement with X-ray geometries than these obtained by the most popular B3LYP method. Accordingly the general trends observed in experimental studies have been well represented by the calculated data. TG analyses show that **1** and **2** are thermally stable (T<sub>decomp.</sub> > 175°C).

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#### 1458

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