

# Synthesis, Crystal Structure and Magnetic Properties of a Copper(II) *p*-Formylbenzoate Complex

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A new Cu(II) complex was prepared at room temperature from the reaction of *p*-formylbenzoic acid, phenanthroline, CuCl<sub>2</sub>·2H<sub>2</sub>O, and NaOH under ethanolic aqueous conditions. The complex has been characterized by X-ray diffraction, IR spectroscopy, TG-DTA analyses, and magnetic measurements. Single-crystal X-ray diffraction analysis indicated that the complex crystallizes in the triclinic space group *P* $\bar{1}$  with the cell dimensions  $a = 7.875(2)$ ,  $b = 10.724(2)$ ,  $c = 15.317(3)$  Å,  $\alpha = 102.65(3)$ ,  $\beta = 93.71(3)$ ,  $\gamma = 107.64(3)^\circ$ . The Cu atoms are in the environment of distorted CuN<sub>2</sub>O<sub>3</sub> tetragonal pyramids. These discrete complex molecules are packed through intermolecular  $\pi \cdots \pi$ -stacking interactions and C–H $\cdots$ O hydrogen bonds forming a supramolecular structure. The title complex obeys the Curie-Weiss law with a Curie constant  $C = 0.53 \text{ cm}^3 \text{ K mol}^{-1}$  and a Weiss constant  $\theta = -0.27 \text{ K}$ . The shape of the  $\chi_m T$  curve is characteristic of weak ferromagnetic interactions between the Cu(II) centers from 300 to 7 K, while there are weak antiferromagnetic interactions below 7 K.

**Key words:** Synthesis, Crystal Structure, Infrared Spectrum, Thermal Analysis, Magnetic Properties

## Introduction

Design and syntheses of copper complexes are of great interest due to their intriguing network architecture and packing motifs [1–4], as well as their potential applications in catalysts, magnetic materials or molecular sensors [5–8].

As evidenced by many papers [9, 10], bidentate phenanthrolines (phen) chelate metallic ions to form mononuclear complexes, while  $\pi \cdots \pi$  stacking interactions between the aromatic rings in phens can contribute to form supramolecular systems. A large number of coordination polymers of different dimensionality have been prepared using a variety of carboxylic acids. Of the many compounds investigated, those containing benzene-core carboxylic acids make up an important family rich in coordination modes. Benzoic acid and its derivatives also form low-dimensional supramolecular architectures functioning as hydrogen bond acceptors as well as donors in assembling supramolecular complexes [11, 12]. The Cu(II) ion is widely and successfully used in the field of supramolecular coordination chemistry due to its mag-

netic properties and biological activities. Cu is an essential microelement in the human body which takes part in hematopoiesis, melanin formation, connective tissue synthesis, and respiration [13].

To date many Cu(II) complexes containing derivatives of benzoic acid have been reported, where the substituents were halogen, nitro and cyano groups [14–17]. However, only two derivatives substituted by a formyl group are known so far, both based on *p*-formylbenzoic acid (Hfba) [18, 19], Cu(phen)(H<sub>2</sub>O)(fba)(NO<sub>3</sub>) and [Cu(H<sub>2</sub>O)<sub>2</sub>(fba)<sub>2</sub>]·2H<sub>2</sub>O. We now have synthesized a new Cu(II) complex Cu(phen)(H<sub>2</sub>O)(fba)<sub>2</sub>. Its IR spectrum, thermal analysis data, powder X-ray diffraction pattern, crystal structure, and magnetic properties are described in detail in this paper.

## Results and Discussion

### Syntheses

Under alkaline conditions, the reaction of *p*-formylbenzoic acid, phenanthroline and CuCl<sub>2</sub>·2H<sub>2</sub>O

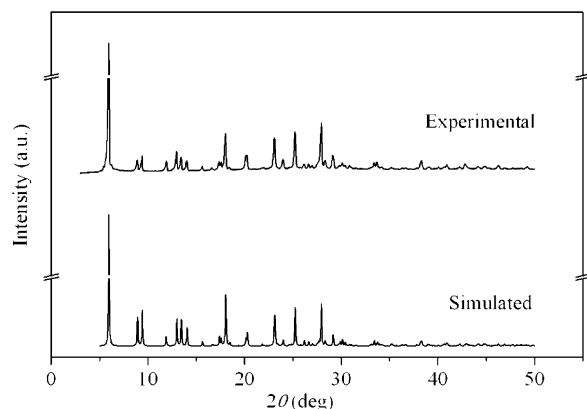
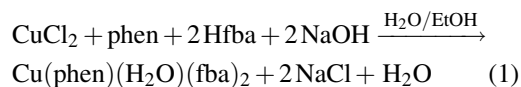


Fig. 1. Experimental and simulated PXRD patterns of the title compound.

in an ethanolic aqueous solution yielded  $\text{Cu}(\text{phen})(\text{H}_2\text{O})(\text{fba})_2$ . Slow evaporation of the resulting solution led to the crystallization of the title compound. The phase purity of the crystalline product and the filter residue were confirmed by comparing the experimental powder X-ray diffraction (PXRD) pattern with the one simulated on the basis of the single-crystal data (Fig. 1). The above synthetic reaction can be expressed by the following equation:



The title compound was found to be stable in air and insoluble in common solvents such as water, ethanol and acetone.

#### Description of the crystal structure

The asymmetric unit contains a Cu(II) ion, a phenanthroline molecule, two *p*-formylbenzoate ions and one water molecule. Both crystallographically distinct *p*-formylbenzoate anions function as a monodentate ligand to bind one  $\text{Cu}^{2+}$  ion. The metal atoms are each coordinated by one phen ligand, two crystallographically independent *p*-formylbenzoate anions and one water molecule to form  $\text{Cu}(\text{phen})(\text{H}_2\text{O})(\text{fba})_2$  complex molecules (Fig. 2). The ligating atoms around each Cu atom build up a square-pyramidal  $\text{CuN}_2\text{O}_3$  coordination environment with one carboxylate O1 atom at the apical position and the two pyridyl N

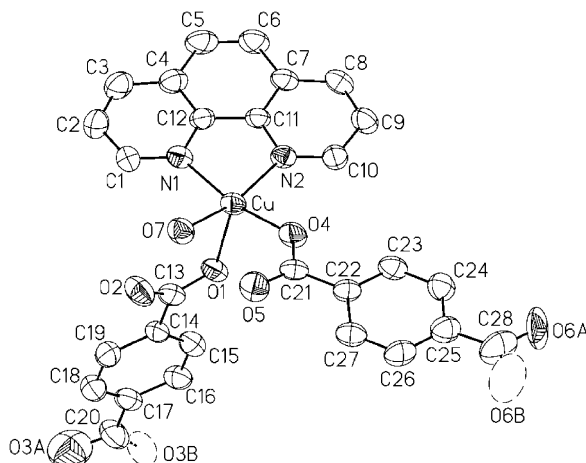


Fig. 2. ORTEP view of the molecular structure of  $\text{Cu}(\text{phen})(\text{H}_2\text{O})(\text{fba})_2$  with displacement ellipsoids at the 45% probability level and atom labeling. The formyl oxygen atoms were found to be twofold disordered.

atoms, the aqua O7 atom and the second carboxylate O4 atom at the corners of the basal plane. The Cu–O bond lengths to the basal O atoms are 1.942(5) and 1.974(4) Å, slightly shorter than the Cu–N bond lengths (2.009(5), 2.025(5) Å), and the axial Cu–O bond length is 2.305(4) Å. The *cisoid* bond angles fall in the range 82.0(1)–104.5(1)°, and the *transoid* ones are 162.9(1) and 167.5(1)°, exhibiting substantial deviations from 90 and 180° for an ideal square pyramid. In comparison with literature data, the above bonding values are normal [20]. Towards the apical carboxylate O1 atom, the Cu atom is shifted by 0.225(2) Å from the basal plane. According to Addison's definition [21], the  $\tau$  value for the Cu atom is 0.08 ( $\tau=0$  and 1 for a regular square pyramid and a regular trigonal bipyramid, respectively). The above observation indicates that the coordination geometry is a slightly distorted square pyramid of a 4 + 1 type. The complex molecules display significant intramolecular hydrogen bonds from the aqua ligand to the uncoordinating carboxylate O atoms (O2, O5) with  $d(\text{O} \cdots \text{O}) = 2.554$ , 2.620 Å and  $\angle(\text{O} - \text{H} \cdots \text{O}) = 150$ , 157° (Table 1). Such intramolecular hydrogen bonding interactions may be the reason why the distal carboxylate and formyl groups of the *p*-formylbenzoate ligand are no longer coplanar with the central benzene ring, but the dihedral angles are small at 7.89° and 9.68°.

Along the crystallographic *a* axis, the complex molecules are arranged in such a way that the neigh-

Table 1. Selected bond lengths (Å) and angles (deg) for Cu(phen)(H<sub>2</sub>O)(fba)<sub>2</sub> with estimated standard deviations in parentheses.<sup>a</sup>

Distances				
Cu–N1	2.025(5)	Cu–O4	1.942(5)	
Cu–N2	2.009(5)	Cu–O7	1.977(4)	
Cu–O1	2.305(4)			
Angles				
N1–Cu–N2	82.0(1)	N2–Cu–O4	167.5(1)	
N1–Cu–O1	104.5(1)	N2–Cu–O7	92.0(1)	
N1–Cu–O4	88.7(1)	O1–Cu–O4	99.7(1)	
N1–Cu–O7	162.9(1)	O1–Cu–O7	91.4(1)	
N2–Cu–O1	90.6(1)	O4–Cu–O7	94.3(1)	
Hydrogen bonding contacts				
D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D–H...A)	∠(D–H...A)
O7–H71...O2	0.84	1.78	2.548	150
O7–H72...O5	0.85	1.81	2.611	157
C8–H8...O5 <sup>#1</sup>	0.93	2.38	3.302	146

<sup>a</sup> Symmetry transformation: #1 *x*, *y* + 1, *z*.

bors are centrosymmetrically related, so that the phen ligand of one complex molecule is nearly parallel to one *p*-formylbenzoato ligand of the neighboring molecule. In other words, the parallel orientated phen and *p*-formylbenzoato ligands are stacked alternately with the close interplanar distance of 3.40(1) Å, suggesting considerable  $\pi\cdots\pi$  stacking interactions, which are responsible for the assembly of the complex molecules into supramolecular chains (Fig. 3a). The *p*-formylbenzoato ligands which are not engaged in  $\pi\cdots\pi$ -stacking interactions are arranged on both sides of the chains. Owing to weak C8–H8...O5<sup>#1</sup> hydrogen bonds (symmetry operation: #1 *x*, *y* + 1, *z*), the chains are further assembled to generate supramolecular layers parallel to (010) as shown in Fig. 3b. Along the crystallographic *c* axis, the resulting layers are stacked in a sequence ...AAAA... to meet the requirements for close-packing.

#### Infrared spectrum

Fig. 4 shows the IR spectrum of the title complex. The broad bands centered at 3475 cm<sup>−1</sup> are due to the O–H stretching vibrations of the coordinated water molecules. The strong band at 1689 cm<sup>−1</sup> is attributed to the C=O stretching of the formyl group. The bands around 1595 and 1380 cm<sup>−1</sup> correspond to the asymmetric ( $\nu_{as}$ ) and symmetric ( $\nu_s$ ) stretching vibrations of the carboxylate groups, respectively. Furthermore, the value of ( $\nu_{as} - \nu_s$ ) = 215 cm<sup>−1</sup> clearly indicates the monodentate coordination mode of car-

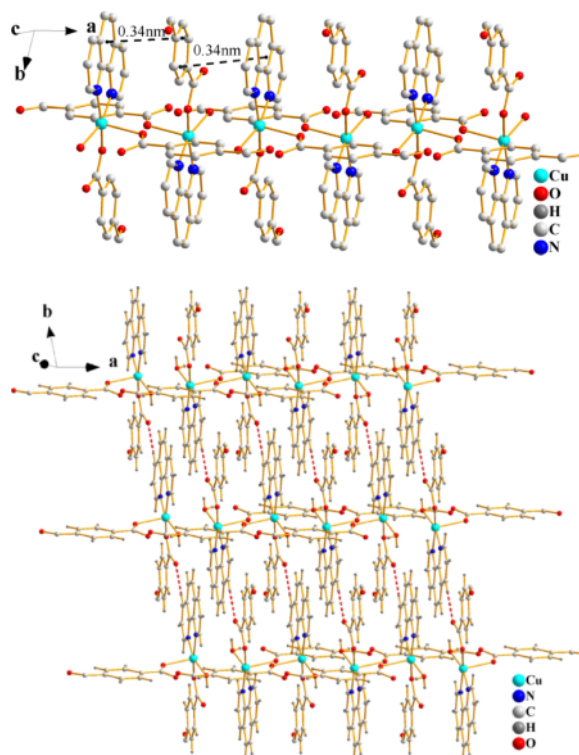


Fig. 3. (top) The chain generated from  $\pi\cdots\pi$ -stacking interactions in the title compound; (bottom) the layer formed by weak C8–H8...O5<sup>#1</sup> (#1 = *x*, *y* + 1, *z*) hydrogen bonds of the title compound.

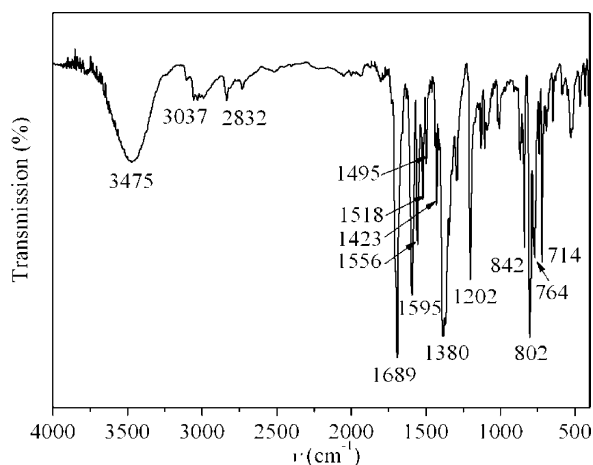


Fig. 4. Infrared spectrum of the title compound.

boxylic groups [22], which is consistent with the single-crystal X-ray diffraction. The middle-intensity and narrow bands in the range of 1423–1595 cm<sup>−1</sup> are attributed to C=C and C=N vibrations of the fba

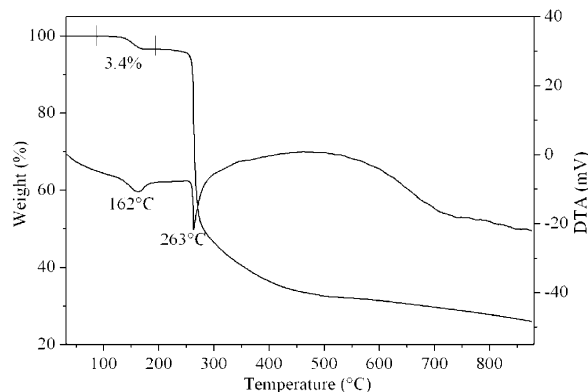


Fig. 5. The TG-DTA curve of the title compound.

and phen ligands. The =C–H bending vibration out-of-plane on the aromatic ring of fba at 842 and 764  $\text{cm}^{-1}$  correspond to a *para*-substitution, and two middle-intensity peaks at 714 and 842  $\text{cm}^{-1}$  belong to phen. The absence of a strong band at 1723  $\text{cm}^{-1}$  demonstrates that all ligands are deprotonated.

#### Thermal analysis

The thermal behavior of the title compound  $\text{Cu}(\text{phen})(\text{H}_2\text{O})(\text{fba})_2$  is depicted in Fig. 5. The DTA curve shows two endothermic peaks centered at 143 and 252 °C. The sample is found to be stable below 130 °C. The first weight loss of 3.4% between 130 and 170 °C with an endothermic peak corresponds to the removal of a coordinated water molecule (*ca.* 3.21 %). The residue  $\text{Cu}(\text{phen})(\text{fba})_2$  remains stable up to 233 °C. Upon further heating, it shows a framework collapse with the removal of one phen molecule and further decomposition. A residue of 25.2 % is collected at 900 °C.

#### Magnetic properties

The magnetic behavior of  $\text{Cu}(\text{phen})(\text{H}_2\text{O})(\text{fba})_2$  in the form of  $\chi_m$  and  $\chi_m T$  versus  $T$  plots in the temperature range 2–300 K is shown in Fig. 6. The  $\mu_{\text{eff}}$  value of  $1.77 \mu_B$  at room temperature is somewhat larger than the spin-only value of  $1.73 \mu_B$  for a ground-state  $\text{Cu}^{2+}$  ion, indicating no magnetic ordering between adjacent  $\text{Cu}^{2+}$  ions. The room temperature  $\chi_m T$  value is  $0.31 \text{ cm}^3 \text{ K mol}^{-1}$ , slightly smaller than the spin-only value of  $0.37 \text{ cm}^3 \text{ K mol}^{-1}$ . Upon lowering the temperature, the  $\chi_m T$  value increases linearly ap-

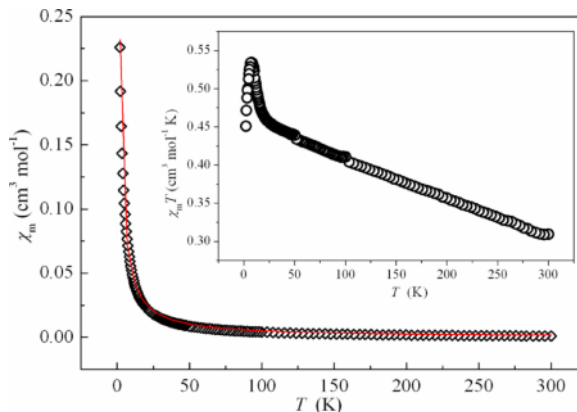


Fig. 6. Temperature dependence of the magnetic susceptibility of the title compound. Solid lines represent the best fit.

proaching a knee point at 20 K, and then increases sharply to the maximum of  $0.53 \text{ cm}^3 \text{ K mol}^{-1}$  at 7 K. Afterwards it decreases radically to  $0.45 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. This behavior indicates weak ferromagnetic and antiferromagnetic interactions between  $\text{Cu}^{2+}$  ions from room temperature to 7 K and from 7 K to 2 K, respectively. The  $\chi_m$  data can be fitted well to the Curie-Weiss equation  $\chi_m = C/(T - \theta)$ , with the Curie constant  $C = 0.53 \text{ cm}^3 \text{ K mol}^{-1}$  and a Weiss constant  $\theta = -0.27 \text{ K}$ .

## Experimental Section

#### Materials

All chemicals were commercially available in reagent grade and were used without further purification.

#### Physical methods

Powder X-ray diffraction was carried out with a Bruker D8 Focus X-ray diffractometer using a Cu target ( $\lambda = 1.54056 \text{ \AA}$ ) and a Ni filter at room temperature with the range of  $2\theta$  between 5 and  $50^\circ$ . Single-crystal data were collected with a Rigaku R-Axis Rapid IP X-ray diffractometer using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The infrared spectra were recorded in the range  $4000\text{--}400 \text{ cm}^{-1}$  using KBr pellets with an FTIR 8900 spectrometer. The thermogravimetric measurement was performed under a flow of nitrogen gas from room temperature to 900 °C at a heating rate of  $10^\circ \text{C min}^{-1}$  by using a Seiko TG/DTA 6300 apparatus. The temperature-dependent magnetic susceptibility was determined with a Quantum Design SQUID magnetometer (Quantum Design Model MPMS-7) in the temperature range 2–300 K.

*Synthesis of Cu(phen)(H<sub>2</sub>O)(fba)<sub>2</sub>*

To a stirred mixed solvent consisting of 5.0 mL H<sub>2</sub>O and 5.0 mL EtOH was successively added 0.1501 g (1.0 mmol) Hfba and 1 mL 1 M NaOH, leading to a yellow solution. 0.0852 g (0.5 mmol) CuCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in another mixed solvent consisting of 5.0 mL H<sub>2</sub>O and 5.0 mL EtOH to yield a blue solution, which was then dropwise added to the above yellow solution to produce a blue precipitate. After stirring for about 15 min, a blue suspension was formed. To the resulting suspension was added an ethanolic aqueous solution of 0.0958 g (0.5 mmol) phenanthroline monohydrate in 5.0 mL H<sub>2</sub>O and 5.0 mL EtOH, the mixture being dark in color. After stirring for one hour, a solid was filtered off, and the dark filtrate (pH = 4.33) was allowed to

stand at room temperature for slow evaporation. Blue plate-shaped crystals of Cu(phen)(H<sub>2</sub>O)(fba)<sub>2</sub> were formed in 3 d. No deterioration was observed when the crystals were exposed to air. Finally, 180.5 mg product was collected (yield: *ca.* 65% based on the initial CuCl<sub>2</sub>·2H<sub>2</sub>O input). – PXRD (Cu K $\alpha$  radiation,  $\lambda$  = 1.54056 Å)  $2\theta/I$ : 6.0/100, 8.9/3, 9.4/4, 11.9/3, 13.0/5, 15.6/4, 14.0/3, 18.0/9, 20.2/4, 23.0/8, 24.0/4, 25.2/10, 27.9/12, 29.1/4 (Fig. 1). – IR data (cm<sup>−1</sup>, KBr):  $\nu$  = 3475m(br), 1689vs(sp), 1595s(sp), 1556s, 1518m, 1495m, 1423m(sh), 1380s, 1294m(sh), 1202s, 842s, 802vs, 764s, 714s (Fig. 4).

*X-Ray structure determination*

A suitable crystal of Cu(phen)(H<sub>2</sub>O)L<sub>2</sub> was selected under a polarizing microscope and fixed with epoxy cement on a fine glass fiber which was then mounted on the diffractometer for cell determination and subsequent data collection using the  $\omega$ -scan technique in the range of  $2 \leq 2\theta \leq 55^\circ$ . The data were corrected for Lp effects and empirically for absorption. The structure was solved by Direct Methods using the program SHELXS-97 [23, 24] and refined through difference Fourier synthesis with the SHELXL-97 program [25, 26]. All non-hydrogen atoms were refined anisotropically on  $F^2$  by full-matrix least-squares methods. The O atoms of the formyl groups were found to be disordered and were refined in a 50:50 split-atom model (O3A, O3B and O6A, O6B, respectively). The hydrogen atoms were placed in calculated positions and assigned a fixed isotropic displacement parameter of 1.2 times the equivalent isotropic  $U$  of the atoms to which they were attached, and allowed to ride on their respective parent atoms, with 100% occupancy, except for atoms H20A, H20B, H28A, H28B of the formyl groups which had 50% occupancy each. The hydrogen atoms of water molecules were found in a difference Fourier map. A summary of the key crystallographic information is given in Table 2 and important bond lengths and bond angles are summarized in Table 1.

*Acknowledgement*

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Table 2. Crystal structure data for Cu(phen)(H<sub>2</sub>O)(fba)<sub>2</sub>.

Formula	C <sub>28</sub> H <sub>20</sub> CuN <sub>2</sub> O <sub>7</sub>
$M_r$	560.01
Crystal size, mm <sup>3</sup>	0.112 × 0.131 × 0.105
Crystal system	triclinic
Space group	$P\bar{1}$
$a$ , Å	7.875(2)
$b$ , Å	10.724(2)
$c$ , Å	15.317(1)
$\alpha$ , deg	102.65(2)
$\beta$ , deg	93.71(2)
$\gamma$ , deg	107.64(2)
$V$ , Å <sup>3</sup>	1190.8(1)
$Z$	2
$D_{\text{calcd}}$ , g cm <sup>−3</sup>	1.56
$\mu$ (Mo K $\alpha$ ), mm <sup>−1</sup>	1.0
$F(000)$ , e	574
$hkl$ range	−9 → +10, ±13, ±19
$((\sin \theta)/\lambda)_{\text{max}}$ , Å <sup>−1</sup>	0.648
Refl. measured/unique/ $R_{\text{int}}$	11 729/5439/0.0442
Restraints/ref. parameters	28/361
$R(F)/wR(F^2)^{a,b}$ (all refl.)	0.1329/0.1939
Weighting scheme A/B <sup>b</sup>	0.0645/2.0644
GoF ( $F^2$ ) <sup>c</sup>	1.141
$\Delta\rho_{\text{fin}}$ (max/min), e Å <sup>−3</sup>	0.99/−1.66

<sup>a</sup>  $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ; <sup>b</sup>  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ ; <sup>c</sup>  $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$ .

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