

# Synthesis and Crystal Structure of Two One-dimensional Chain Copper Complexes [Cu(TTA)<sub>2</sub>(4,4'-azpy)] and [Cu(TTA)<sub>2</sub>(3,3'-azpy)]

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Two copper complexes [Cu(TTA)<sub>2</sub>(4,4'-azpy)] (1) and [Cu(TTA)<sub>2</sub>(3,3'-azpy)] (2) (HTTA = 1,1,1-trifluoro-3-(2-thenoyl)-acetone, 4,4'-azpy = 4,4'-azobispyridine, 3,3'-azpy = 3,3'-azobispyridine) were synthesized and characterized. The crystal structures were determined by X-ray diffraction analysis. The crystal 1 belongs to triclinic with space group  $P\bar{1}$ ,  $a = 0.8515(2)$  nm,  $b = 0.9259(2)$  nm,  $c = 0.9468(2)$  nm,  $\alpha = 66.126(9)^\circ$ ,  $\beta = 79.667(9)^\circ$ ,  $\gamma = 90.13(1)^\circ$ ,  $Z = 1$ ,  $V = 0.6692(2)$  nm<sup>3</sup>,  $D_c = 3.425$  g/cm<sup>3</sup>,  $\mu = 2.113$  mm<sup>-1</sup>,  $F(000) = 694$ ,  $R_1 = 0.0594$ ,  $wR_2 = 0.1499$ . The crystal 2 belongs to monoclinic with space group  $P2_1/c$ ,  $a = 1.0661(2)$  nm,  $b = 1.4296(3)$  nm,  $c = 1.0041(3)$  nm,  $\beta = 114.50(3)^\circ$ ,  $V = 1.3926(5)$  nm<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.646$  g/cm<sup>3</sup>,  $\mu = 1.015$  mm<sup>-1</sup>,  $F(000) = 694$ ,  $R_1 = 0.0535$ ,  $wR_2 = 0.1113$ . In the crystals of complexes 1 and 2, the copper atoms have distorted octahedral symmetry. The two compounds possess very similar one-dimensional linear chains linked through the rod-like 4,4'-azpy ligands or 3,3'-azpy ligands.

**Keywords** crystal structure, one-dimensional chain, copper complex, azobispyridine

## Introduction

Self-assembly of coordination polymers from the basic building blocks is of considerable interest due to their intriguing diverse architectures and potential applications in catalysis and advanced materials such as magnetic, optic, and electronic materials.<sup>1-4</sup> The architectures of coordination polymers can be reliably predicted, since previously known metal coordination environments are propagated into one-, two-, and three-dimensional motifs with rigid multitopic organic "spacer" ligands. The reaction of a metal complex exhibiting two vacant or substitutable coordination sites with a bridging ligand is the most common and effective synthetic method for one-dimensional chain compounds. The bridging ligands such as 4,4'-azobispyridine and 3,3'-azobispyridine have been used to link metal ions to form infinite configurations.<sup>5-8</sup>

Many  $\beta$ -diketons such as 1,1,1-trifluoro-3-(2-thenoyl)-acetone, acetylacetone, hexafluoroacetylacetone complexes have been reported.<sup>9-16</sup> In the present work, by using a  $\beta$ -diketon ligand 1,1,1-trifluoro-3-(2-thenoyl)acetone (HTTA) and bridging ligand 4,4'-azobispyridine (4,4'-azpy) or 3,3'-azobispyridine (3,3'-azpy) as a mixed ligand system, two copper complexes [Cu(TTA)<sub>2</sub>(4,4'-azpy)] (1) and [Cu(TTA)<sub>2</sub>(3,3'-azpy)] (2) were synthesized and characterized.

## Experimental

### Instruments and materials

All reagents were of A. R. grade and used without further purification. 4,4'-Azobispyridine (4,4'-azpy) and 3,3'-azobispyridine (3,3'-azpy) were prepared following the reported method.<sup>17</sup> Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. ESR spectrum was recorded in solid state on an Er2000-SRC instrument. Magnetic susceptibilities were measured in the solid state using a CAHN-2000 Faraday balance with [Ni(en)<sub>2</sub>]S<sub>2</sub>O<sub>3</sub> as a standard at 6000 G magnetic field.

### Synthesis of [Cu(TTA)<sub>2</sub>(4,4'-azpy)] (1)

The complex 1 was prepared by mixing a solution of 1,1,1-trifluoro-3-(2-thenoyl)acetone (HTTA) (0.222 g, 0.1 mmol) and 4,4'-azpy (0.184 g, 0.1 mmol) in 60 mL of EtOH/DMF (2:1, V/V) with powdered Cu (0.192 g, 3 mmol). The mixture was stirred for 10 h at 70 °C and the resulting solution was allowed to stand at room temperature under the air. After three weeks, the brown platelet single crystals [Cu(TTA)<sub>2</sub>(4,4'-azpy)] (1) suitable for X-ray diffraction were obtained. Yield 0.178 g. Elemental analysis con-

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firmed the organic content. Anal. calcd for  $C_{26}H_{16}CuF_6N_4O_4S_2$ : C 45.25, H 2.34, N 8.12, found C 45.34, H 2.26, N 8.01.

#### Synthesis of $[Cu(TTA)_2(3,3'-azpy)]$ (**2**)

$[Cu(TTA)_2(3,3'-azpy)]$  was prepared from  $Cu(TTA)_2$  and 3,3'-azpy.  $CuSO_4 \cdot 5H_2O$  (1.000 g, 4 mmol) was dissolved in 20 mL of boiling water, and 20 mL of ethanol solution of 1,1,1-trifluoro-3-(2-thenoyl)acetone (HTTA) (1.778 g, 8 mmol) was added with vigorous stirring for 0.5 h. After cooling the solution to room temperature, the precipitate was filtered off and dried. Yield of  $Cu(TTA)_2$  was 1.742 g. Then 20 mL of ethanol solution of 3,3'-azpy (0.184 g, 1 mmol) and 10 mL of DMF solution of  $[Cu(TTA)_2]$  (0.506 g, 1 mmol) were mixed and stirred for 10 min, and the resulting solution was allowed to stand at room temperature. After two weeks, green prism crystals  $[Cu(TTA)_2(3,3'-azpy)]$  suitable for X-ray diffraction were obtained. Yield 0.586 g. Elemental analysis confirmed the organic content. Anal. calcd for  $C_{26}H_{16}CuF_6N_4O_4S_2$ : C 45.25, H 2.34, N 8.12, found C 45.04, H 2.27 N 7.93.

#### X-Ray structure determination

Single crystals with dimensions 0.23 mm  $\times$  0.12 mm  $\times$  0.04 mm for **1** and 0.23 mm  $\times$  0.21 mm  $\times$  0.20 mm for **2** were selected for data collection at 193.1 K, using a RIGAKU CrystalClear with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.071073$  nm). Data were collected by  $\omega$  scan technique. The structure was solved by direct methods using SHELX-97 program package<sup>18</sup> and refined with full-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms. The positions of hydrogen atoms for **1** were calculated using idealized geometry, while the positions of hydrogen atoms for **2** were obtained from successive Fourier syntheses. The refinement gave final  $R_1 = 0.0594$ ,  $wR_2 = 0.1499$  with  $w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 1.9590P]$ , where  $P = (F_o^2 + 2F_c^2)/3$  for **1** and  $R_1 = 0.0535$ ,  $wR_2 = 0.1113$  with  $w = 1/[(2(F_o^2) + (0.0462P)^2 + 1.5486P)]$ , where  $P = (F_o^2 + 2F_c^2)/3$  for **2**. The maximum shifts  $(\Delta/\sigma)_{max}$  are 0.000 and 0.000 and the goodness of fit  $S = 1.080$  and 1.167 for **1** and **2**, respectively. The maximum and minimum peaks on the final difference Fourier map corresponded to 1645  $e \cdot nm^{-3}$  and  $-789 e \cdot nm^{-3}$ , respectively for **1** and 336  $e \cdot nm^{-3}$  and  $-493 e \cdot nm^{-3}$ , respectively for **2**.

## Results and discussion

#### Crystal structure

The two compounds have similar linear chain structures, which are formed by bridging 4,4'-azpy or 3,3'-azpy ligands connecting the  $Cu(TTA)_2$  units.

The crystallographic data and the selected bond lengths and angles of the complexes **1** and **2** are listed in Tables 1 and 2, respectively. Part of the structure of the complex **1** is shown in Fig. 1. The complex molecule displays center symmetry, and the Cu atom locates at the center position. The Cu atom is in a greatly distorted octahedral environment with four shorter and two longer bonds. The shorter bonds [Cu(1)—O(1) 0.1958(2) nm and Cu(1)—O(2) 0.1971(3) nm] are formed by four oxygen atoms of two symmetry-related TTA ligands. These bonds form a square-planar arrangement. Some coordination bond distances found in relevant copper and nickel complexes are summarized in Table 3. The Cu—O bond lengths in **1** are consistent with those in copper complexes  $Cu(TTA)_2(4,4'-bipy)$  [0.1983(4)—0.2096(5) nm],<sup>9</sup>  $Cu(TTA)_2(py_2)$  [0.1945(3)—0.1970(3) nm],<sup>10</sup>  $[Cu(TTA)_2](btr_2)$  [0.1936(2)—0.1950(2) nm],<sup>11</sup>  $Cu(acac)_2(4,4'-bipy)$  [0.1948(3)—0.1965(3) nm],<sup>14</sup>  $Cu(hfac)_2(py_2)$  [0.1924(7)—0.2004(7) nm],<sup>15</sup> and in nickel complexes  $[Ni(TTA)_2(3-mepy)_2]$  [0.2024(5)—0.2045(5) nm],<sup>12</sup>  $[Ni(TTA)_2(4-mepy)_2]$  [0.2022(3)—0.2058(4) nm],<sup>13</sup> and shorter than those in  $[Cu(hfac)_2(mpydz)_2]$  [0.2009(3)—0.2228(4) nm].<sup>16</sup> The bond angle of O(1)—Cu(1)—O(2) is 92.28(11) $^\circ$  and  $O_4$  planes is ideally planar. Two longer Cu(1)—N(1) bonds for Cu to nitrogen atoms of bridging ligand 4,4'-azpy are 0.2428(3) nm. The Cu—N bond lengths are consistent with those in copper complexes  $Cu(acac)_2(4,4'-bipy)$  [0.2449(3)—0.2452(3) nm],<sup>14</sup>  $Cu(hfac)_2(py_2)$  [0.2529(9) nm],<sup>15</sup> and longer than in  $Cu(TTA)_2(4,4'-bipy)$  [0.2201(8) nm],<sup>9</sup>  $Cu(TTA)_2(py_2)$  [0.2340(1) nm],<sup>10</sup>  $[Cu(TTA)_2](btr_2)$  [0.2290(3) nm],<sup>11</sup>  $[Cu(hfac)_2(mpydz)_2]$  [0.2043(4) nm],<sup>16</sup> and nickel complexes  $[Ni(TTA)_2(3-mepy)_2]$  [0.2090(6)—0.2104(6) nm],<sup>12</sup>  $[Ni(TTA)_2(4-mepy)_2]$  [0.2097(4) nm].<sup>13</sup> 4,4'-Azpy ligand molecule exhibits a *trans* fashion in the complex **1**. The dihedral angle between two pyridyl groups of the 4,4'-azpy ligand is 0.00 $^\circ$ . The Cu atoms are bridged by 4,4'-azpy ligand with the nearest Cu—Cu separation 1.3823 nm within

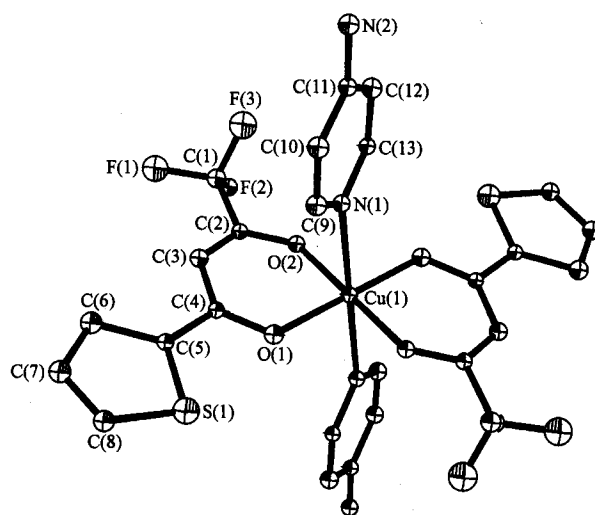


Fig. 1 Local coordination of Cu in **1** with 30% thermal ellipsoids.

**Table 1** Crystallographic data for the complexes **1** and **2**

	[Cu(TTA) <sub>2</sub> (4,4'-azpy)] (1)	[Cu(TTA) <sub>2</sub> (3,3'-azpy)] (2)
Formula	C <sub>26</sub> H <sub>16</sub> CuN <sub>4</sub> O <sub>4</sub> F <sub>6</sub> S <sub>2</sub>	C <sub>26</sub> H <sub>16</sub> CuN <sub>4</sub> O <sub>4</sub> F <sub>6</sub> S <sub>2</sub>
<i>M<sub>r</sub></i>	690.09	690.09
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (nm)	0.8515(2)	1.0661(2)
<i>b</i> (nm)	0.9259(2)	1.4296(3)
<i>c</i> (nm)	0.9468(2)	1.0041(3)
$\alpha$ (°)	66.126(9)	90.00
$\beta$ (°)	79.667(9)	114.50(3)
$\gamma$ (°)	90.13(1)	90.00
<i>V</i> (nm <sup>3</sup> )	0.6692(2)	1.3926(5)
<i>Z</i>	2	2
<i>D</i> <sub>calc.</sub> (g/cm <sup>3</sup> )	3.425	1.646
Absorption coefficient (mm <sup>-1</sup> )	2.113	1.015
Absorption correction	Empirical	Empirical
<i>T</i> <sub>min</sub>	0.61	0.67
<i>T</i> <sub>max</sub>	0.81	0.82
<i>F</i> (000)	694	694
2 $\theta$ Range (°)	7.14–54.96	7.08–54.96
Index ranges	-11 ≤ <i>h</i> ≤ 9, -12 ≤ <i>k</i> ≤ 11, -12 ≤ <i>l</i> ≤ 12	-13 ≤ <i>h</i> ≤ 13, -17 ≤ <i>k</i> ≤ 18, -13 ≤ <i>l</i> ≤ 11
Reflection collections	7352	15087
Independent reflections	2980	3183
Data/restraints/parameters	2980/0/195	3183/0/228
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.080	1.167
Final [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] indices	<i>R</i> <sub>1</sub> = 0.0594, <i>wR</i> <sub>2</sub> = 0.1499	<i>R</i> <sub>1</sub> = 0.0535, <i>wR</i> <sub>2</sub> = 0.1113
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0679, <i>wR</i> <sub>2</sub> = 0.1552	<i>R</i> <sub>1</sub> = 0.0652, <i>wR</i> <sub>2</sub> = 0.1156
Largest diff. peak and hole (e <sup>-</sup> nm <sup>-3</sup> )	1645 and -789	336 and -493

**Table 2** Selected bond lengths (nm) and angles (°) for the complexes **1** and **2**

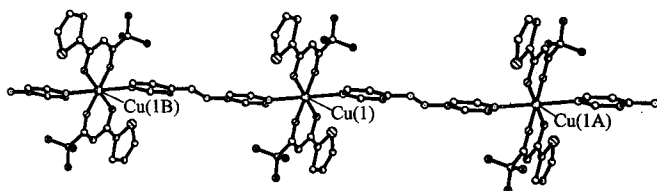
Complex 1			
Cu(1)—O(1)	0.1958(2)	Cu(1)—O(2)	0.1971(3)
Cu(1)—N(1)	0.2428(3)		
O(1)-Cu(1)-O(1A)	180.00(14)	O(1)-Cu(1)-O(2)	92.34
O(2)-Cu(1)-O(1A)	87.66(11)	O(2)-Cu(1)-O(2A)	180.0
O(1)-Cu(1)-N(1)	88.66(11)	O(2)-Cu(1)-N(1)	85.09(11)
O(1A)-Cu(1)-N(1)	91.34(11)	O(2A)-Cu(1)-N(1)	94.91(11)
N(1)-Cu(1)-N(1A)	180.0		
Complex 2			
Cu(1)—O(1)	0.2181(2)	Cu(1)—O(2)	0.2048(2)
Cu(1)—N(1)	0.2016(3)		
O(1)-Cu(1)-O(1A)	180.00(5)	O(1)-Cu(1)-O(2)	85.45(8)
O(2)-Cu(1)-O(1A)	94.55(8)	O(2)-Cu(1)-O(2A)	180.00(11)
O(1)-Cu(1)-N(1)	91.08(8)	O(2)-Cu(1)-N(1)	88.60(8)
O(1A)-Cu(1)-N(1)	88.92(8)	O(2A)-Cu(1)-N(1)	91.40(8)
N(1)-Cu(1)-N(1A)	180.0		

Symmetry code: A - *x*, - *y*, - *z* + 1.

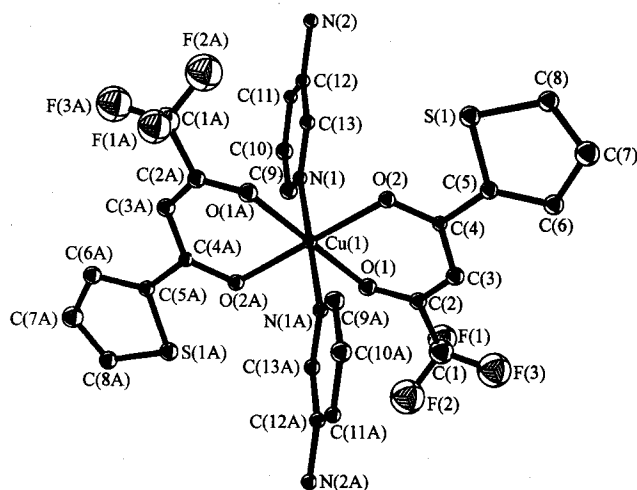
**Table 3** Comparison of coordination bond distances (nm)

Complex	Cu-O in equatorial plane	Cu-N in axial direction	Ref.
Cu(TTA) <sub>2</sub> (4,4'-bipy)	0.1983(4)—0.2096(5)	0.2201(8)	9
Cu(TTA) <sub>2</sub> (pyz)	0.1945(3)—0.1970(3)	0.2340(1)	10
{[Cu(TTA) <sub>2</sub> ](btrz)}	0.1936(2)—0.1950(2)	0.2290(3)	11
[Ni(TTA) <sub>2</sub> (3-mepy) <sub>2</sub> ]	0.2024(5)—0.2045(5)	0.2090(6)—0.2104(6)	12
[Ni(TTA) <sub>2</sub> (4-mepy) <sub>2</sub> ]	0.2022(3)—0.2058(4)	0.2097(4)	13
Cu(acac) <sub>2</sub> (4,4'-bipy)	0.1948(3)—0.1965(3)	2.449(3)—2.452(3)	14
Cu(hfac) <sub>2</sub> (pyz)	0.1924(7)—0.2004(7)	0.2529(9)	15
[Cu(hfac) <sub>2</sub> (mpydz) <sub>2</sub> ]	0.2009(3)—0.2228(4)	0.2043(4)	16
[Cu(TTA) <sub>2</sub> (4,4'-azpy)]	0.1958(2)—0.1971(3)	0.2428(3)	This work
[Cu(TTA) <sub>2</sub> (3,3'-azpy)]	0.2048(2)—0.2181(2)	0.2016(3)	This work

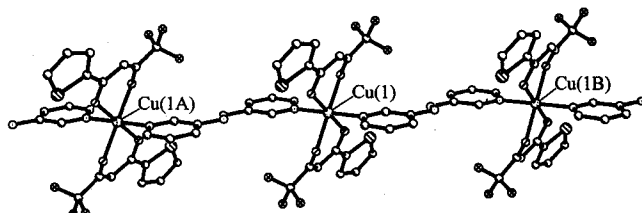
the chain (Fig. 2). The separations of metal ions between the two neighboring chains are 0.8515 and 0.9259 nm, respectively.

**Fig. 2** View of the one-dimensional chain in the *a* direction in 1.

Part of the structure of the complex 2 is shown in Fig. 3. Cu atom has an elongated octahedral geometry. The equatorial plane is defined by four O atoms from two symmetry-related chelated TTA ligands, while the axial positions being occupied by two N atoms from two different 3,3'-azpy ligands in *trans* fashion. The Cu—O bond lengths [0.2048(2)—0.2181(2) nm] are slightly longer than the distances [0.1958(2)—0.1971(3) nm] found in 1. The Cu—N bond lengths [0.2016(3) nm] are consistent with those in [Cu(hfac)<sub>2</sub>(mpydz)<sub>2</sub>] [0.2043(4) nm],<sup>16</sup> [Ni(TTA)<sub>2</sub>(3-mepy)<sub>2</sub>] [0.2090(6)—0.2104(6) nm]<sup>12</sup> and [Ni(TTA)<sub>2</sub>(

**Fig. 3** Local coordination of Cu in 2 with 30% thermal ellipsoids.

(4-mepy)<sub>2</sub>] [0.2097(4) nm],<sup>13</sup> but obviously shorter than those in 1 [0.2428(3) nm] and other copper complexes [0.2201(4)—0.2529(9) nm].<sup>9-11,14,15</sup> The dihedral angle between two pyridyl groups of the 3,3'-azpy ligand is 0.00°. The Cu atoms are bridged by the 3,3'-azpy ligands with the closest Cu—Cu intra-chain separation 1.0661 nm (Fig. 4). Each chain is surrounded by four identical chains. The neighboring inter-chain Cu—Cu distances are 0.8735 nm.

**Fig. 4** View of the one-dimensional chain in the *c* direction in 2.

The two compounds possess very similar one-dimensional linear chains linked through the rod-like 4,4'-azpy ligands or 3,3'-azpy ligands. One unexpected feature is that no solvent or guest molecules are included in the void between chains and no hydrogen-bonding interaction is observed. Both compounds may be regarded as essentially one-dimensional chain compounds.

#### Electronic spin resonance spectrum and magnetic properties

The ESR spectrum of the complex 1 in solid state shows a symmetric feature with the *g* values,  $g_{\parallel} = 2.356$  and  $g_{\perp} = 2.084$ . The ESR spectrum of the complex is typically the same as the copper(II) ion, and the data suggest elongated octahedron geometry with  $g_{\parallel} > g_{\perp} > g_e$ , and the unpaired electron occupies the  $d(x^2 - y^2)$  orbital,<sup>19</sup> which is consistent with the crystal structure. The ESR spectrum of the complex 2 in solid state shows  $g_{\text{iso}} = 2.144$ . The magnetic moments at 300 K are 1.93 B. M. and 1.94 B. M. for the complexes 1 and 2, respectively. The values are close to the spin-only value 1.73 B. M. for one local  $S = 1/2$  spin. The magnetic moments exhibit continuous decrease upon cooling to

1.88 B.M. and 1.84 B.M. at 76 K for **1** and for **2**, respectively. Variable-temperature magnetic susceptibility studies in the temperature range of 75–300 K, show that the complexes obey the Curie-Weiss law,  $\chi_m = C/(T - \theta)$ , with values of  $\theta = -8.67$  K,  $C = 0.479$  emu · K · mol<sup>-1</sup> for **1** and  $\theta = -10.97$  K,  $C = 0.490$  emu · K · mol<sup>-1</sup> for **2**.<sup>20</sup> It indicates that the complexes **1** and **2** belong to the “Curie-Weiss” paramagnetic compounds.

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