

## Notes

## Synthesis and X-ray Structural Study of a 6-Coordinate Copper(II) Complex with *N,N,N',N'*-Tetrakis(2-pyridylmethyl)-1,2-ethanediamine

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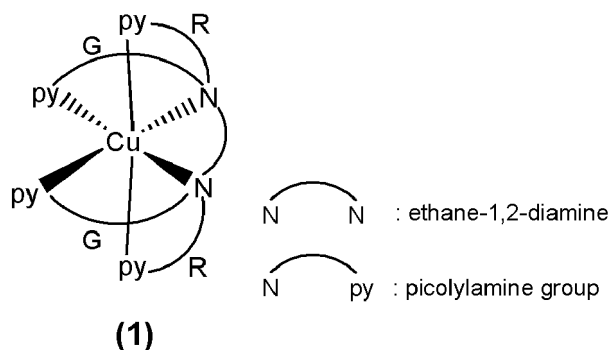
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Many transition metal ions coordinate to *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (*tpen*) with a coordination number of 6. Such 6-coordinate  $[M(tpen)]^{n+}$  complexes are well known for M = Fe(II), Fe(III), Cr(III), and Co(III).<sup>1,4</sup> In spite of the steric crowding<sup>3</sup> of the *tpen*, the structures of these metal complexes are typically mononuclear octahedron with the *tpen* ligand coordinated in a hexadentate manner. In contrast, when the *tpen* ligand is coordinated to the copper(II), a variety of geometries can be formed due to the various bonding modes of the *tpen* and the  $d^9$  configuration of the copper(II).<sup>5,6</sup>

Recently, a 5-coordinate  $[Cu(tpen)]^{2+}$  complex having one uncoordinated pyridine N atom was obtained by reacting the *tpen* with copper(II) perchlorate.<sup>7</sup> In this reaction, we did not find a 6-coordinate  $[Cu(tpen)]^{2+}$  complex. However, in the present paper, a 6-coordinate complex,  $[Cu(tpen)](ClO_4)_2 \cdot 2/3H_2O$  (**1**), is synthesized, and its structural characterization is reported.



### Experimental Section

**Materials and instruments.** All chemicals were purchased from commercial sources and used without further purification. The solid-state electronic spectrum by the diffuse reflectance method was measured using VARIAN

CARY-100 Conc UV-vis spectrophotometer. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a FISON EA1108 elemental analyzer.

**Synthesis of  $[Cu(tpen)](ClO_4)_2 \cdot 2/3H_2O$  (**1**).** The *tpen* ligand was prepared as previously reported in the literature.<sup>8,9</sup> Copper(II) perchlorate hexahydrate (1.1 g, 3.0 mmol) and *L*-proline (0.7 g, 6.1 mmol) were dissolved at room temperature in 15 and 30 cm<sup>3</sup> of methanol, respectively. These solutions were mixed and stirred for 10 min. Into this solution, the *tpen* (1.3 g, 3.1 mmol) dissolved in 20 cm<sup>3</sup> of methanol was added and mixed. Immediately after mixing, a small amount of the precipitate formed and the mixture was stirred for 3 h at room temperature. This precipitate was filtered and removed. The removed precipitate was a 5-coordinate  $[Cu(tpen)]^{2+}$  complex.<sup>7</sup> The filtrate was left for a few days to obtain a blue crystalline product, which was filtered and washed with cold water. Yield: 1.2 g (57.1%). Analysis calculated for **1**: C 44.67, H 4.23, N 12.02%; and found: C 44.45, H 4.05, N 12.04%.  $\lambda$ /nm: 687 and 403 in the solid state.

**Caution!** Because the perchlorate salt of **1** is potentially explosive, only a small amount of material should be prepared, and it should be handled with care.

**X-ray crystallography.** A crystal of dimensions 0.40 × 0.10 × 0.10 mm<sup>3</sup> for **1** was selected for X-ray data collection. The data were collected using a Bruker SMART diffractometer equipped with Mo-K<sub>α</sub> radiation (= 0.71073 Å) in the  $\pi$  and  $\omega$  scan mode at 173(2) K. Absorption correction was not applied. Structure analysis and refinement calculations were carried out with X-STEP programs<sup>10</sup> package. The structures were solved by the direct method. The crystallographic data for **1** are summarized in Table 1.

All H atoms bonded to C atoms were included in the structure-factor calculation at idealized positions, and were allowed to ride on their parent atoms with relative isotropic displacement parameters [ $U_{iso}(H) = 1.2U_{eq}(C)$ ] and [ $U_{iso}(H) = 1.5U_{eq}(O)$ ].

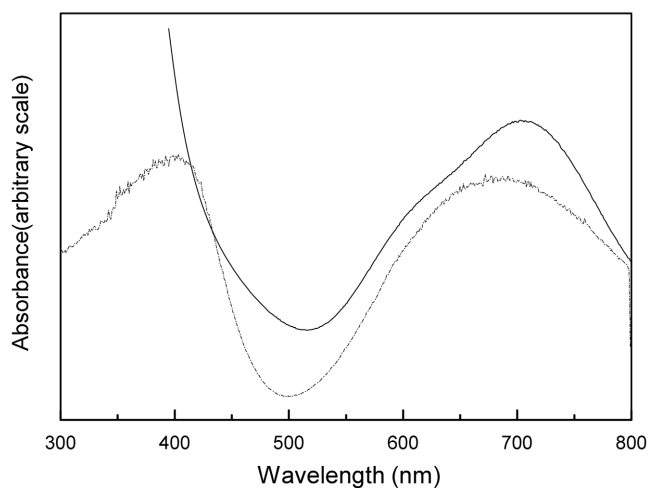
**Table 1.** Crystallographic data for **1**

Formula	C <sub>26</sub> H <sub>29.33</sub> Cl <sub>2</sub> Cu N <sub>6</sub> O <sub>8.67</sub>
FW	698.99
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	41.464(2)
<i>b</i> , Å	9.3651(3)
<i>c</i> , Å	23.7188(9)
$\beta$ , deg	107.652(1)
<i>Z</i>	12
<i>V</i> , Å <sup>3</sup>	8776.7(6)
$\rho_{\text{calc}}$ , Mg/m <sup>3</sup>	1.587
$\theta$ range, deg.	1.03–28.26
Measured reflections	10206
<i>I</i> > 2	4316
GOF	1.364
$\mu$ , mm <sup>-1</sup>	0.992
<i>R</i> 1 ( <i>I</i> > 2 ( <i>I</i> ))	0.0527
<i>R</i> w ( <i>I</i> > 2 ( <i>I</i> ))	0.1125
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ , e Å <sup>-3</sup>	0.683 and –0.715

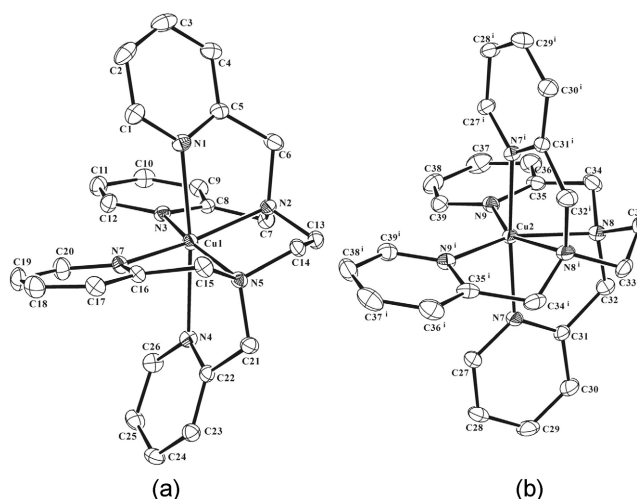
## Results and Discussion

Figure 1 shows the solid-state electronic spectrum of **1** and the published spectrum<sup>7</sup> of a 5-coordinate [Cu(*tpen*)]<sup>2+</sup> complex for comparison. The former spectrum (dotted curve) shows two absorption bands with the maxima at 687 and 403 nm in the visible region, whereas the latter spectrum (the solid curve) shows a band maximum at 704 nm and a shoulder at ~606 nm. These differences indicate that complex **1** obtained in the present work is not a 5-coordinate [Cu(*tpen*)]<sup>2+</sup> complex having one uncoordinated pyridine N atom.

**Structure and geometry of 1.** The ORTEP<sup>11</sup> and packing views are depicted in Figures 2 and 3, respectively. Crystallographically, the [Cu(*tpen*)]<sup>2+</sup> cation occupies two different sites (hereinafter referred to as Site A and Site B) in



**Figure 1.** Solid-state electronic spectra of complex **1** (dotted curve) and a 5-coordinate [Cu(*tpen*)](ClO<sub>4</sub>)<sub>2</sub> complex (solid curve)<sup>7</sup>.

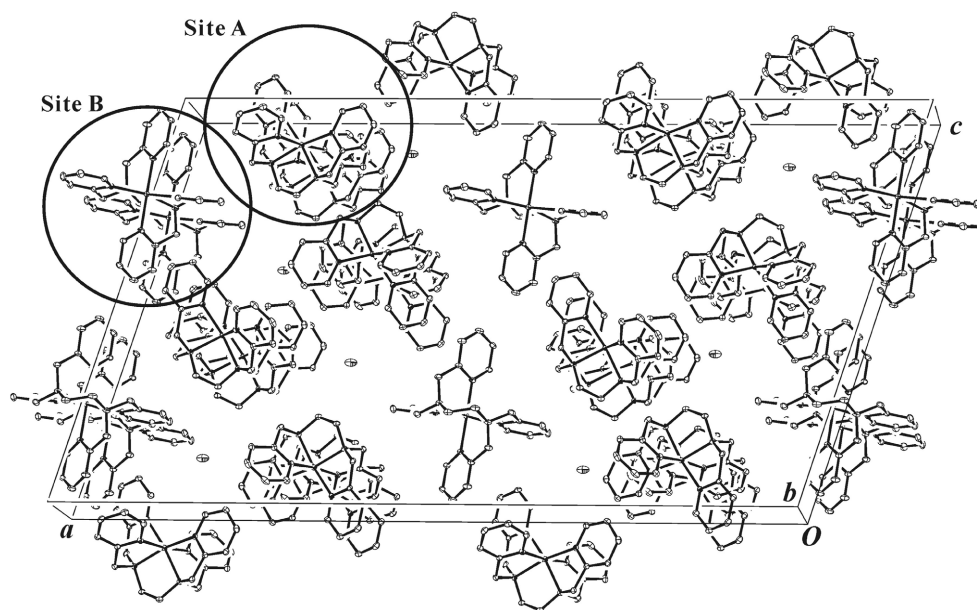


**Figure 2.** An ORTEP drawing for Site A (a) and Site B (b) of **1** with the atom numbering; displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity [Symmetry code: (i) 1-*x*, *y*, 1/2-*z*].

a 2 to 1 ratio of Site A to Site B in the unit cell. The two molecular types, in addition to their different crystallographic positions, exhibit slightly different structural characteristics. As shown in Figure 2, the copper(II) in both Site A and Site B of **1** take a coordination number of six and have distorted octahedral geometry with two amine N atoms and four pyridine N atoms. There is no obvious difference in the intermolecular contacts for cations of Site A and those for cations of Site B, as can be seen from the packing diagram in Figure 3. However, it shows that the influence of water on the intermolecular contacts is different for the two different sites in the unit cell.

**Selected bond lengths and angles for Site A and Site B (Table 2).** The Cu-N<sub>aliph</sub> (N2 and N5) distances at Site A are 2.045(2) and 2.055(2) Å, respectively. In Site A the two equatorial Cu-N<sub>py</sub> distances (N3 and N6) are 2.037(2) and 2.049(3) Å, while the two axial Cu-N<sub>py</sub> distances (N1 and N4) are 2.377(3) and 2.308(2) Å, respectively. The two equatorial Cu-N<sub>py</sub> distances at Site A are slightly shorter than the Cu-N<sub>aliph</sub> distances or similar with the Cu-N<sub>aliph</sub> distances, but the two axial Cu-N<sub>py</sub> distances are considerably longer than the Cu-N<sub>aliph</sub> distances. However, the Cu-N<sub>aliph</sub> (N8 and N8') distances at Site B are same, 2.238(3) Å. In Site B, four Cu-N<sub>py</sub> distances (N7, N7', N9 and N9') are in the range of 2.044(3) ~ 2.118(2) Å. Namely, the Cu-N<sub>py</sub> distances at Site B are significantly shorter than the Cu-N<sub>aliph</sub> distances. All the aforementioned differences in the bond lengths of the A and B Sites indicate that the structural characteristics of the A and B Sites are different.

The N<sub>G</sub>-Cu-N<sub>G</sub> (in the plane of the ethane-1,2-diamine ring) angles (N2-Cu1-N3 and N5-Cu1-N6) for the picolylamine units at Site A are 82.1(1) and 82.6(1)°, respectively. In contrast, the N<sub>G</sub>-Cu-N<sub>G</sub> angles (N8-Cu2-N9 and N8'-Cu2-N9') for the picolylamine units at Site B are same, 78.0(1)°. The N<sub>G</sub>-Cu-N<sub>G</sub> angles at Site A and Site B are smaller than the N<sub>aliph</sub>-Cu-N<sub>aliph</sub> angles for the ethane-1,2-diamine unit

Figure 3. Unit cell of **1**.Table 2. Selected bond distances (Å) and angles (deg) for **1**

Site A		Distances	
Cu(1)-N(1)	2.377(3)	Cu(1)-N(4)	2.308(2)
Cu(1)-N(2)	2.045(2)	Cu(1)-N(5)	2.055(2)
Cu(1)-N(3)	2.037(2)	Cu(1)-N(6)	2.049(3)
Angles			
N(3)-Cu(1)-N(6)	111.2(1)	N(3)-Cu(1)-N(2)	82.1(1)
N(6)-Cu(1)-N(2)	161.8(1)	N(3)-Cu(1)-N(5)	163.9(1)
N(6)-Cu(1)-N(5)	82.6(1)	N(2)-Cu(1)-N(5)	86.4(1)
N(3)-Cu(1)-N(4)	92.2(1)	N(6)-Cu(1)-N(4)	85.3(1)
N(2)-Cu(1)-N(4)	107.2(1)	N(5)-Cu(1)-N(4)	80.4(1)
N(3)-Cu(1)-N(1)	88.8(1)	N(6)-Cu(1)-N(1)	88.2(1)
N(2)-Cu(1)-N(1)	79.4(1)	N(5)-Cu(1)-N(1)	100.2(1)
N(4)-Cu(1)-N(1)	173.4(1)		
Site B		Distances	
Cu(2)-N(7)	2.044(3)	Cu(2)-N(8')	2.238(3)
Cu(2)-N(7')	2.044(3)	Cu(2)-N(9)	2.118(2)
Cu(2)-N(8)	2.238(3)	Cu(2)-N(9')	2.118(2)
Angles			
N(7)-Cu(2)-N(7')	175.5(2)	N(7)-Cu(2)-N(9)	90.3(1)
N(7')-Cu(2)-N(9)	91.8(1)	N(7)-Cu(2)-N(9')	91.8(1)
N(7')-Cu(2)-N(9')	90.3(1)	N(9)-Cu(2)-N(9)	124.8(1)
N(7)-Cu(2)-N(8)	80.2(1)	N(7')-Cu(2)-N(8)	96.4(1)
N(9)-Cu(2)-N(8)	78.0(1)	N(9')-Cu(2)-N(8)	156.2(1)
N(7)-Cu(2)-N(8')	96.4(1)	N(7')-Cu(2)-N(8')	80.2(1)
N(9)-Cu(2)-N(8')	156.2(1)	N(9')-Cu(2)-N(8')	78.0(1)
N(8)-Cu(2)-N(8')	80.6(1)		

(86.4(1)° for Site A and 80.6(1)° for Site B). This may be attributed to rigid *tpen*. Also, due to the puckering of the ethane-1,2-diamine ring, the  $N_{\text{aliph}}\text{-Cu-N}_{\text{aliph}}$  angles at Site A and Site B are closer to the ideal angle of 90° than those of the  $N_{\text{G}}\text{-Cu-N}_{\text{G}}$ .

Table 3. Ring angle sum deviations from ideal ring angle sum for **1**

Ring	Site A	Site B
R <sub>1</sub>	17.1 (N1-N2)	10.4 (N7-N8)
R <sub>2</sub>	16.7 (N4-N5)	10.4 (N7'-N8')
G <sub>1</sub>	27.7 (N2-N3)	26.7 (N8-N9)
G <sub>2</sub>	24.0 (N5-N6)	26.7 (N8'-N9')

A measure of the overall strain for **1** can be obtained by examining the equatorial valency angle.<sup>12</sup> As shown in Table 2, the equatorial  $N_{\text{py}}\text{-Cu-N}_{\text{py}}$  valency angle at Site A and Site B are 111.2(1) and 124.8(1)°, respectively. These values are much larger than the 90° expected for a regular octahedron, indicating that both A and B Sites are highly strained structurally.

**Ring strains.** Ring strain is quantitatively estimated using the difference in the ideal sum and the actual sum of the bond angles of a five-membered picolylamine ring.<sup>12</sup> The difference in ring angle sums,  $\Delta$ , is a measure of ring strain. As can be seen in Table 3, the ring angle sums of both R (out of the plane of the ethane-1,2-diamine ring) and G rings in Site A and Site B deviate from those of ideal rings. In particular, the  $\Delta$  values of the G rings in Site A and Site B are larger than those of the R rings. This indicates that the G rings in both Site A and Site B are significantly more strained than the R rings.

## Conclusion

Reacting *tpen* with copper(II) perchlorate as a starting material produced a new 6-coordinate  $[\text{Cu}(\textit{tpen})]^{2+}$  complex,  $[\text{Cu}(\textit{tpen})](\text{ClO}_4)_2 \cdot 2/3\text{H}_2\text{O}$ . It has two slightly different structures in the unit cell. They are structurally unstable and distorted octahedral.

**Supplementary material.** Crystallographic data for the structure reported here have been deposited with the *Cambridge Crystallographic Data Center* (Deposition No. CCDC-264156). The data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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