

## Synthesis and Structure of Dicopper (II) Complex of 1,4-bis[N,N-bis(2-picoly)amino]butane

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**Abstract:** 1,4-bis[N,N-bis(2-picoly)amino]butane [**BPAB**] and its binuclear Cu(II) complex have been synthesised and characterised using IR, UV, AA, <sup>1</sup>H-NMR and X ray diffraction. The reaction of **BPAB** with two equivalents of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O gave a binuclear Cu(II) complex [Cu<sub>2</sub>(**BPAB**)(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>·4H<sub>2</sub>O. The two chelating bispicolyamine arms in **BPAB** are tethered by a butyl group with each Cu<sup>2+</sup> ion in [Cu<sub>2</sub>(**BPAB**)(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>·4H<sub>2</sub>O coordinating in a slightly distorted square planar geometry. The crystal data for [Cu<sub>2</sub>(**BPAB**)(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>·4H<sub>2</sub>O: monoclinic, space group *P*2<sub>1</sub>/*n* with cell dimensions of *a* = 13.948 (3) Å, *b* = 10.881 (3) Å, *c* = 15.244 (3) Å, β = 113.49 (2)°, *V* = 2121.6 (9) Å<sup>3</sup>, ρ<sub>calc</sub> = 1.680 g cm<sup>-3</sup> for *Z* = 4, μ = 13.4 cm<sup>-1</sup>. [The Journal of American Science. 2009;5(1):45-49]. (ISSN: 1545-1003).

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### 1. Introduction

Several divalent metal ions have been examined in the search for model enzymes that could mimic the chemistry taking place at the active sites of metalloenzymes [1-5]. In most such studies nitrogen donor ligands have been a logical choice since most of these ligands, e.g. pyridine [6] and pyrazole [7], have pK<sub>a</sub> values that are close to those found in histidyl moieties in several enzymes. Of particular interest are binuclear copper complexes which could be used as models for protein-metal binding sites in bio-processes. Examples of copper-containing proteins with binuclear Cu(II) centres in their active sites are hemocyanin for O<sub>2</sub> transport, tyrosinase for the hydroxylation of monophenols and oxidation of catechols as well as catechol oxidase for the oxidation of catechols [8-10]. In one study Karlin et al.[11] were able to demonstrate that the binuclear Cu(I) complex of *m*-xylpy (py = 2-pyridyl) acts as a good model for the deoxy-sites in the proteins. Selmececi et al.[12] were also able to demonstrate the ability of binuclear copper complexes of 1,3-bis[N,N-bis(2{2-pyridyl}ethyl)amino]propane and 1,3-bis[N,N-bis(2{2-pyridyl}ethyl)amino]-2-hydroxypropane to catalyze the oxidation of 3,5-di-*tert*-butylcatechol. The fundamental structure-reactivity relationships were also highlighted in the above study. In this paper we report the synthesis and characterisation of a binuclear copper complex of **BPAB** with a view to understanding the coordination behaviour of the binucleating tridentate N-donor ligand. Previously we reported the synthesis and structure of a binuclear Cu(II) complex of 1,3-bis[N,N-bis(2-picoly)amino]propan-2-ol which has the two chelating bispicolyamine arms tethered by a 2-hydroxypropyl group with each Cu<sup>2+</sup> ion coordinated to three bispicolyamine nitrogen atoms, a H<sub>2</sub>O molecule on one arm and a Cl ligand on the other arm [13].

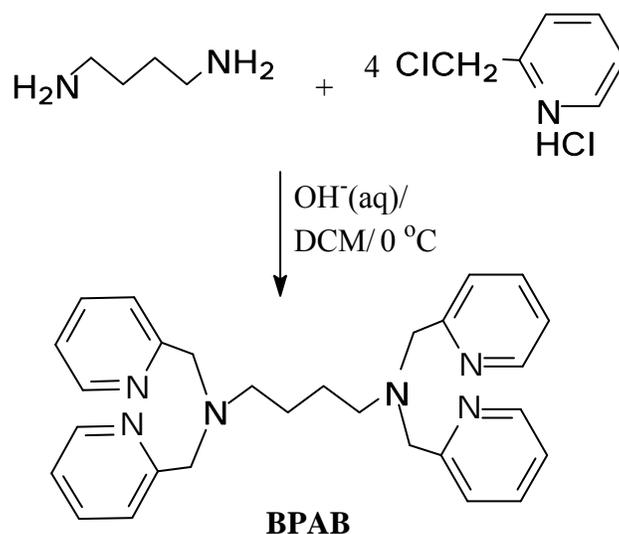
### 2. Experimental

#### 2.1 Materials

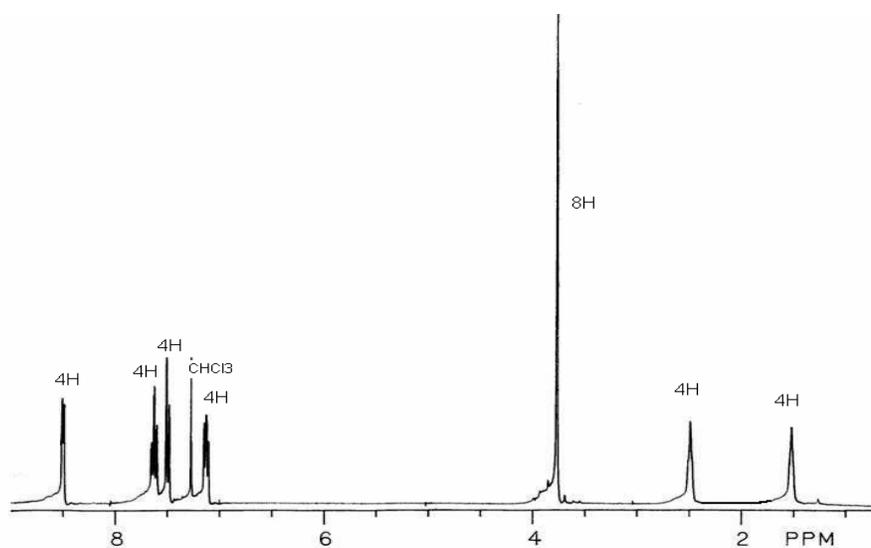
Methanol, dichloromethane (DCM), acetonitrile, Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2-picolychloride·HCl, 1,4-diaminobutane and NaOH were reagent grade and were used as purchased from Aldrich. The ligand **BPAB** was synthesized by a modification of literature method and characterized by spectroscopic methods. <sup>1</sup>H-NMR spectra were run in CDCl<sub>3</sub> with internal TMS standard on a GE 300 MHz spectrometer. IR spectra were collected on a Perkin-Elmer FT-IR model 1600. UV-Vis spectra were collected on a Perkin-Elmer Lambda 2 spectrometer using 1-cm quartz cuvettes. The %Cu in a complex was determined using Perkin-Elmer AAS (model 2380) equipped with a hollow cathode source and employing air/acetylene flame.

#### 2.2 Synthesis of 1,4-bis[N,N-bis(2-picoly)amino]butane

**BPAB** was synthesised by a slight modification of the literature method [14] in accordance with reaction scheme 1. An aqueous solution of NaOH (0.0975 mol in 35 cm<sup>3</sup> water) was added dropwise to an aqueous solution of 2-picolychloride·HCl prepared by adding 16.0 g of 2-picolychloride·HCl (0.0975 moles) to 40 cm<sup>3</sup> of distilled water at 0 °C. An aqueous solution of 1,4-diaminobutane (2.15 g in 40 cm<sup>3</sup> water), also maintained at 0 °C, was added dropwise to the vigorously stirred reaction mixture. The mixture was stirred for 20 min after which 100 cm<sup>3</sup> of DCM was added. The reaction mixture, maintained at pH 9-10, was left to stir for 2 days at 0 °C and for 4 more days at room temperature. The product, **BPAB**, was then filtered out as a beige precipitate and recrystallized in acetonitrile. The yield was 6.0 g (55%). IR (Nujol) spectrum:ν (cm<sup>-1</sup>): 1588 (py stretch). <sup>1</sup>H NMR (CDCl<sub>3</sub>-TMS): δ (ppm): 1.51 (4H), 2.49 (4H), 3.76 (s, 8H), 7.12 (m, 4H), 7.27 (CHCl<sub>3</sub> impurity in CDCl<sub>3</sub>), 7.51 (m, 4H), 7.62 (m, 4H), 8.49 (m, 4H). Figure 1 shows the <sup>1</sup>H-NMR spectrum of **BPAB**.



**Scheme 1.** Synthesis of 1,4-bis[N,N-bis(2-picoly)amino]butane (**BPAB**)



**Figure 1.**  $^1\text{H-NMR}$  spectrum of **BPAB**

### 2.3 Synthesis of $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$

To a solution of **BPAB** in methanol (2.2 mmol in  $75 \text{ cm}^3$ ) was added 1.63g (4.4 mmol) of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The mixture was allowed to stir at room temperature for 24 h. The resulting blue precipitate was filtered off and dried in air. The remaining solution was left to evaporate slowly at room temperature yielding blue crystals of  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  complex. IR (Nujol) spectrum,  $\nu$  ( $\text{cm}^{-1}$ ): 3500 (OH stretch), 1611 (NH stretch), 1574 (py stretch), 1049 ( $\text{ClO}_4^-$ ), UV-Vis:  $\lambda_{\text{max}}(\text{nm}) = 654$ ,  $\epsilon_{\text{max}}(\text{M}^{-1} \text{ cm}^{-1}) = 227$ , %Cu: Found = 11.69, calc = 11.71.

### 2.4 Crystallographic structure determination

A crystal of  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  complex was mounted in a random orientation on the end of a glass fiber using 5 min epoxy cement and transferred to a goniometer head. Preliminary crystal parameters and reflection data were obtained at room temperature and processed by standard methods [15,16] on a Rigaku AFC6S X-ray diffractometer with graphite monochromated  $\text{Mo K}\alpha$  radiation and 12 kW rotating anode generator. Details of the crystal data collection are given in Table 1. The structure was solved by direct methods [17] as implemented in the

SHELXTLPC system of computer programmes and refined to convergence by full matrix least-squares methods. All hydrogens were found and their positional parameters refined. Atomic scattering factors used were those from the International Table for X-ray crystallography [18].

**Table 1.** Crystallographic data for  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$

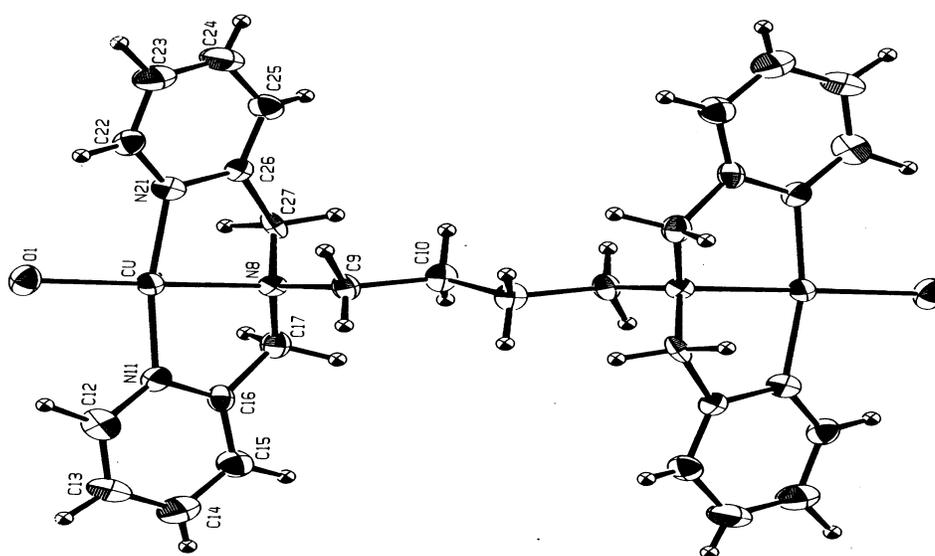
Chemical formula	$\text{C}_{28}\text{H}_{44}\text{N}_6\text{O}_{22}\text{Cl}_4\text{Cu}_2$	$\beta(^{\circ})$	113.49(2)
Formula weight	1085.50	$V(\text{\AA}^3)$	2121.6(9)
Crystal colour, habit	Blue, prism	$Z$	4
Crystal system	Monoclinic	$\rho_{\text{calc}}(\text{g cm}^{-3})$	1.680
Crystal dimensions	0.200x0.150x0.300	$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	13.4
Space group	$P2_1/n$	No unique reflections	3281
$a(\text{\AA})$	13.948(3)	No of observations	1567
$b(\text{\AA})$	10.881(3)	$R$	0.062
$c(\text{\AA})$	15.244(3)	$R_w$	0.066

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad R_w = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2} \right]^{1/2}$$

**Table 2.** Selected bond distances and bond angles in  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2]^{4+}$

Bond distance ( $\text{\AA}$ )	
Cu–O1	1.990 (8)
Cu–N8	2.017 (9)
Cu–N11	1.970 (1)
Cu–N21	1.970 (1)
Bond angles ( $^{\circ}$ )	
O1–Cu–N8	174.3 (4)
O1–Cu–N11	97.6 (4)
O1–Cu–N21	95.3 (4)
N8–Cu–N11	82.9 (4)
N8–Cu–N21	83.9 (4)
N11–Cu–N21	166.3 (4)

Estimated standard deviations in the least significant figure are given in parentheses



**Figure 2.** ORTEP drawing of the crystal structure of  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2]^{4+}$

### 3. Results and Discussion

The reaction of **BPAB** with two equivalents of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  gave a binuclear complex  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ . A summary of the crystallographic data and structure parameters for  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  is provided in Table 1. A list of selected bond distances and bond angles is given in Table 2. The ORTEP drawing of the crystal structure for  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2]^{4+}$ , the cation of complex  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ , is shown in Figure 2. The two chelating bispicolylamine arms are tethered by a butyl group and each  $\text{Cu}^{2+}$  ion coordinates to three bispicolylamine nitrogen atoms and a  $\text{H}_2\text{O}$  molecule. In the outer coordination sphere are four perchlorate anions and four  $\text{H}_2\text{O}$  molecules. The bonds O-Cu-N8 ( $174.3^\circ$ ) and N11-Cu-N21 ( $166.3^\circ$ ) are almost linear whilst bond angles O-Cu-N21 ( $95.3^\circ$ ), O-Cu-N11 ( $97.6^\circ$ ), N8-Cu-N11 ( $82.9^\circ$ ), and N8-Cu-N21 ( $83.9^\circ$ ) are close to  $90^\circ$ . This suggests a slightly distorted square planar geometry around each Cu (II) ion. The bispicolylamine arm chelates to the  $\text{Cu}^{2+}$  centre with Cu-N bond distances of 2.017(9)Å, 1.97(1)Å and 1.97(1)Å and Cu-O bond distance of 1.990 (8)Å. The Cu-N and Cu-O bond distances in  $[\text{Cu}_2(\text{BPAB})(\text{OH}_2)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  are typical and compares closely to those in dicopper complexes of 1,3-bis[N,N-bis(2-picolyl)amino]propan-2-ol [13] and 1,3-bis[N,N-bis(2-picolyl)amino]propane [12]. The latter has been shown to catalyse the oxidation of 3,5-ditert-butylcatechol to the corresponding *o*-quinone and hydrogen peroxide [12].

The synthesis of a binucleating ligand, 1,4-bis[N,N-bis(2-picolyl)amino]butane, and its dimeric Cu(II) complex derives its significance from our interest in developing transition metal complexes that can mimic protein-metal binding sites in bio-processes; for example, hemocyanin for  $\text{O}_2$  transport, tyrosinase for the hydroxylation of monophenols and catechol oxidase for the oxidation of catechols. We report here the synthesis and structure of Cu(II) complex of 1,4-bis[N,N-bis(2-picolyl)amino]butane. Methods used for structure elucidation include IR, UV, AA,  $^1\text{H-NMR}$  and X ray diffraction. The contribution made will definitely draw interest to researchers in fields of organometallic and bioinorganic chemistry as well as biocatalysis.

### 4. Conclusions

A binucleating 1,4-bis[N,N-bis(2-picolyl)amino]butane and its dimeric Cu(II) complex were prepared and characterised using IR, UV, AA,  $^1\text{H-NMR}$  and X ray diffraction. The two chelating bispicolylamine arms are tethered by a butyl group with each  $\text{Cu}^{2+}$  ion coordinated to three bispicolylamine nitrogen donor atoms and to  $\text{H}_2\text{O}$ , through its oxygen donor atom, in a slightly distorted square planar geometry. Four perchlorate ions and four  $\text{H}_2\text{O}$  molecules form the outer coordination sphere.

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