

## A Unique Example of a Self-assembled Hydrogen-Bonded Polynuclear Sheet in the Solid-State Structure of a Retrobispeptide–Copper(II) Complex

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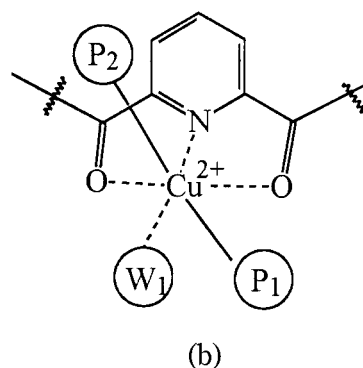
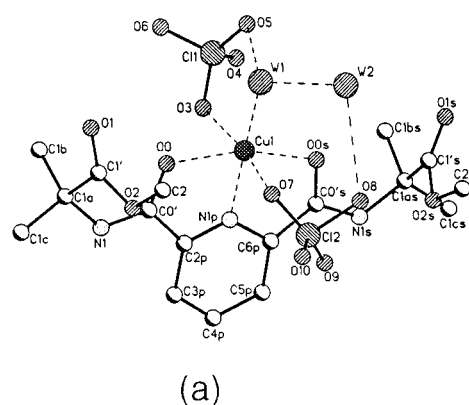
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In recent years considerable interest has been shown in the design and synthesis of polynuclear self-assemblies from transition metal ions and organic ligands.<sup>1a–11</sup> Of particular interest in the metal-ion-directed self-assemblies is the generation of huge polynuclear clusters that may not only provide an approach toward the generation of supramolecular metals with interesting metallic properties but also have bioinorganic significance as metallo-enzyme mimics. Although several examples of discrete metal complexes are known in the biological world,<sup>2</sup> there are hardly any reports of extended polynuclear self-assemblies created by metal ions.<sup>3</sup>

Among the factors that induce the self-assembly processes, design of the ligand plays a crucial role in deciding between discrete vs extended structures of the metal complexes. One of the popular strategies to fabricate extended coordination networks is to not allow the ligand to utilize all its coordination sites in binding to the same metal center.<sup>4</sup> This can be achieved by using appropriate spacers in the ligand building blocks. Using this approach a large variety of extended polynuclear self-assemblies have been created from organic ligands and transition metal ions.<sup>1,5</sup>

An attractive concept would be to use a combination of coordinative and hydrogen bonding interactions to engineer polynuclear assemblies that may have direct relevance to developing bioactive materials and may be more useful as chemical

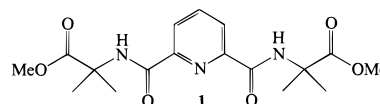


**Figure 1.** (a) Crystal structure of the repeating block of Cu(II) complex **2**. Three of the four equatorial positions on the Cu(II) center are occupied by the ligand **1** while the fourth one is occupied by an H<sub>2</sub>O (W1) molecule. The axial positions are occupied by the coordinated perchlorate ions (P<sub>1</sub> and P<sub>2</sub>). The distances between Cu(II) and its coordinated ligands are Cu–N1p (1.940), Cu–O(00) (2.055), Cu–O(00s) (2.065), Cu–W1 (1.886), Cu–O3(ClO<sub>4</sub><sup>-</sup>) (2.460), and Cu–O7(ClO<sub>4</sub><sup>-</sup>) (2.380). (b) A chemical representation of the Cu(II) module.

models for mimicking biological processes. Appropriately modified peptide ligands were considered by us an exciting possibility to generate such structures.

In this paper, we provide the first example of such a concept and report on the use of pyridine-linked retrobispeptide as an efficient ligand for the creation of hydrogen-bonded polynuclear sheets of Cu(II) ions. The choice of a pyridine spacer was based on the consideration that, apart from providing an additional coordination site, this unit is known to have an affinity for water.<sup>6</sup>

The tridentate bispeptide ligand **1**<sup>7</sup> was readily prepared by the reaction of  $\alpha$ -aminoisobutyric acid methyl ester with 2,6-pyridine dicarbonyldichloride in dry dichloromethane in the presence of triethylamine. The ligand **1** was treated with equimolar amounts of cupric perchlorate in acetonitrile to give the coordination complex **2** as pale blue crystals.<sup>8</sup>



The crystal structure<sup>9</sup> of **2** (Figure 1) revealed a mononuclear

(6) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature (London)* **1998**, *393*, 671.

(7) Selected data for **1**: Yield 90%; mp 109–110 °C; IR (KBr) 3417, 3376, 3003, 2960, 1758, 1737, 1696, 1677, 1533, 1463, 1445, 1389 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  1.33 (s, 12H), 3.76 (s, 6H), 7.95 (t,  $J$  = 7.7 Hz, 1H), 8.26 (d,  $J$  = 7.8 Hz, 2H), 8.57 (s, 2H); FAB MS (%) 366 (M + H)<sup>+</sup> (100).

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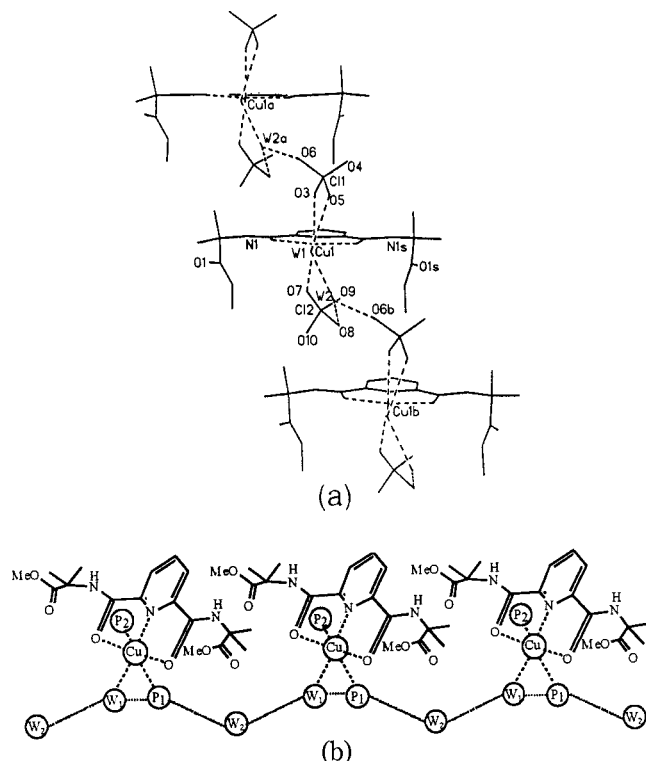
(1) (a) Robson, R. In *Comprehensive Supramolecular Chemistry*, Vol. 6; MacNicol, D. D., Toda, F., Bishop, R., eds.; Pergamon: Oxford, 1996. (b) Constable, E. C. In *Comprehensive Supramolecular Chemistry*, Vol. 9, Sauvage, J.-P., Hosseini, M. W., Eds.; Pergamon: Oxford, 1996. (c) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, 1995. (d) Piguat, C.; Bernardinelli, G.; Bocquet, B.; Schaad, O.; Williams, A. F. *Inorg. Chem.* **1994**, *33*, 4112. (e) Stumpf, H. O.; Pei, Y.; Kahn, O.; Sletten, J.; Renard, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 6738, and references therein. (f) Gelling, O. J.; van Bolhuis, F.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1991**, 917. (g) Dai, Y.; Katz, T. J.; Nichols, D. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2109. (h) Wu, B.; Zhang, W.-J.; Yu, S.-Y.; Wu, X.-T. *Chem. Commun.* **1997**, 1795. (i) Tilley, T. D.; Liu, F.-Q. *Chem. Commun.* **1998**, 103. (j) Kaes, C.; Hosseini, M. W.; Rickard, C. E. F.; Skelton, B. W.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 920. (k) Funeriu, D. P.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.-Eur. J.* **1997**, *3*, 99. (l) Mamula, O.; Zelewsky, A.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 290.

(2) *Metal Ions in Biological Systems*, Vol. 1–9, Sigel, H., Ed.; Marcel Dekker: New York, 1979.

(3) To our knowledge, in the Zn-finger protein, the transcription factor TF III A (required for RNA polymerase III to transcribe 5S RNA genes) with a series of 9 fingers organized as tandem repeats provides the only known example of a polynuclear extended self-assembly in nature (Lewin, B., Ed. *Genes V*; Oxford University Press: New York, 1994; p 890).

(4) Carina, R. F.; Bernardinelli, G.; Williams, A. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1463.

(5) (a) Ranganathan, D.; Vaish, N. K.; Chandramouli, G. V. R.; Varghese, B.; Muthukumar, R. B.; Manoharan, P. T. *J. Am. Chem. Soc.* **1995**, *117*, 1643. (b) Karle, I. L.; Ranganathan, D.; Haridas, V. *J. Am. Chem. Soc.* **1997**, *119*, 2777.

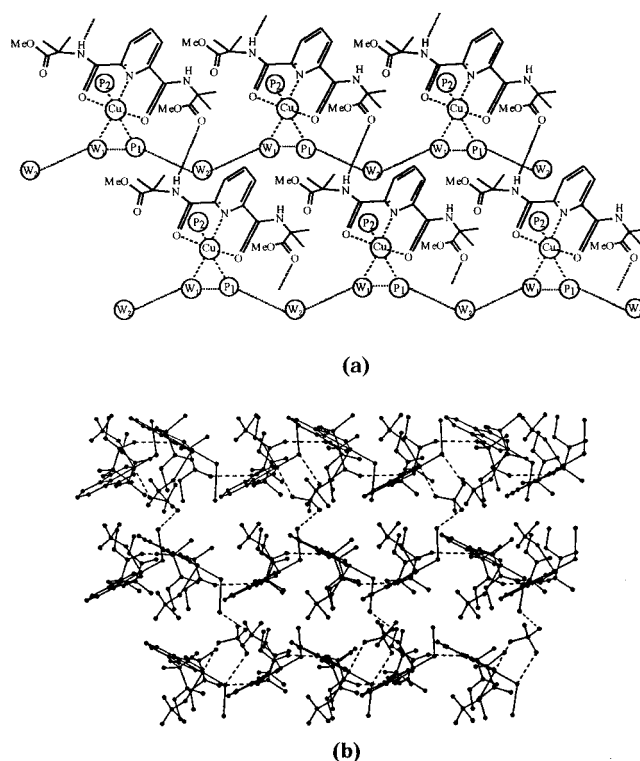


**Figure 2.** (a) Polynuclear string assembly formed by stitching of mononuclear modules by water ( $W_2$ ) molecules. The string shows three modules linked by  $W_2$ --O6 ( $P_1$ ) (O--O = 2.96 Å) hydrogen bonds. (b) Another view of the string assembly in a schematic picture. The mononuclear modules are stitched as pendants on the hydrogen-bonded backbone of  $(W_2$ -- $W_1$ -- $P_1$ ) $_n$  repeats. The hydrogen bond between  $W_2$  and  $P_2$  is not shown.  $W_1 = W_2 = H_2O$ ;  $P_1 = P_2 = ClO_4^-$ .

complex in which the  $Cu^{2+}$  ion is octahedrally coordinated. Three coordination sites are provided by the ligand and the remaining three by two coordinating perchlorate ions ( $P_1$ ,  $P_2$ ) and one water molecule ( $W_1$ ) in the complex. The crystal structure further showed that the mononuclear blocks are linked by water ( $W_2$ ) molecules, which act as hydrogen-bonding bridges, into an infinite polynuclear string with an internuclear Cu--Cu distance of 8.48 Å. Figure 2 shows three complexes in a string assembly linked by  $W_2$ --O6 ( $P_1$ ) hydrogen bonds (O--O = 2.96 Å).

(8) Selected data for copper complex **2**: The copper complex (mp 196–200 °C, dec; IR(KBr) 3438, 3206, 3091, 3016, 2958, 1749, 1739, 1632, 1623, 1599, 1548, 1468, 628  $cm^{-1}$ ) showed a pseudoaxial symmetry in an electron paramagnetic resonance EPR spectrum (solid, room temp.,  $g^{\circ} = 2.332$ ;  $g_{\perp} = 2.093$  A $^{\circ} = 105$  G). The observation of axial signal is noteworthy in view of the orthorhombic distortion of the  $CuNO_3$  coordination sphere (X-ray structure). A careful examination of the spectrum reveals that a rhombic component is superimposed on an axial component. Similar results were obtained in  $CH_3CN$  and  $MeOH$  solvents with  $g^{\circ}$  values of 2.158 and 2.170, respectively. The UV–vis absorption spectrum of the complex in solution exhibits a broad absorption maximum at  $\sim 800$  nm, consistent with pseudo octahedral geometry for Cu(II). (Ang, H. G.; Kwik, W. L.; Honson, G. R.; Crowther, J. A.; McPartlin, M.; Choi, N. *J. Chem. Soc., Dalton Trans.* **1991**, 3193.)

(9) X-ray diffraction analysis of **2**: X-ray data were collected at 20 °C on an automated diffractometer with Mo radiation ( $\lambda = 0.71073$  Å). Three-check reflections were monitored after every 97 measurements. Absorption corrections were applied to the data. Full-matrix anisotropic least-squares analysis on  $F^2$  data was performed with the hydrogen atoms placed in ideal positions and allowed to ride on the C or N atoms to which each was bonded. Anomalous dispersion corrections were applied to the Cu and Cl atoms in the least-squares calculations.  $C_{17}H_{23}N_3O_6 \cdot Cu(ClO_4)_2 \cdot 2H_2O$ , space group  $P2_1$  with  $a = 8.483$ -(3) Å,  $b = 10.536$ (5) Å,  $c = 15.923$ (5) Å,  $\beta = 91.39$ (3) $^{\circ}$ ,  $V = 1422.7$  Å $^3$ ,  $Z = 2$ ,  $d_{calc} = 1.540$  g/cm $^3$ , blue prism,  $R_1 = 8.65\%$  for 2225 data.



**Figure 3.** (a) A chemical representation of the polynuclear sheet assembly of copper complex **2** formed by connecting strings through N-H...O=C (N...O = 2.92 Å) hydrogen bonds.  $W_2$ -- $P_2$  hydrogen bonds are not shown. (b) A schematic view showing the 3-D assembly of the polynuclear sheets. The horizontal dashed lines represent all NH...O=C hydrogen bonds. The skewed dashed lines represent hydrogen bonds between water molecules and perchlorate oxygens.

A noteworthy feature of the string assembly is the presence of unutilized NH and CO groups on the modules which further connect the strings into a hydrogen-bonded polynuclear sheet via intermolecular NH...O=C (N...O = 2.92 Å) hydrogen bonds (Figure 3a–b). The sheet is corrugated because N1s...O1s hydrogen bonds are formed to a parallel string that overlaps the bottom string.

In summary, we have shown that appropriately designed peptide ligands can lead to hydrogen-bonded 2-D or 3-D coordination polymers that may have interesting solid-state properties. A novel feature of the Cu(II) assembly described here is the participation of water molecules as hydrogen-bonding bridges connecting the mononuclear modules into a polynuclear string. The complementary hydrogen bonding of NH and CO groups of the peptide ligand then connect the strings into a hydrogen-bonded polynuclear sheet. Functional properties of the present complex are under study.

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**Supporting Information Available:** EPR spectra of copper complex **2** in solid state,  $CH_3OH$  and  $CH_3CN$  (PDF); UV–vis of **2** in  $CH_3OH$  and  $CH_3CN$  (PDF). Coordinates, bond lengths, bond angles, hydrogen atoms and anisotropic thermal parameters for crystal structure of **2** (PDF).

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