

## Novel Silver(I) and Copper(II) Complexes of Tetrakis(2-pyridyl)methane

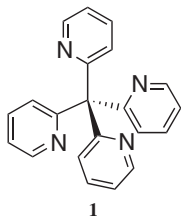
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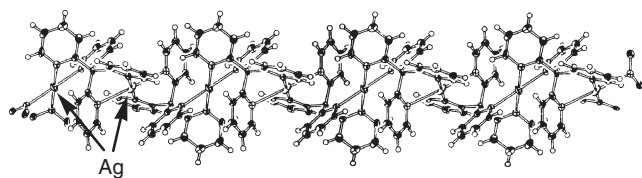
Tetrakis(2-pyridyl)methane forms a novel one dimensional coordination polymer complex with Ag(I) ion and two kinds of complexes different in coordination modes with Cu(II) ion, indicating its versatile ability as a symmetric tetradentate ligand.

Tetraphenylmethane and its derivatives have attracted considerable attention in relation to crystal engineering<sup>1</sup> and three-dimensionally extended  $\pi$ -electron systems.<sup>2</sup> The synthesis of some transition metal complexes of tetraphenylmethanes and their interesting aspects including the unique network of crystal structure and electrochemical properties have also been reported.<sup>3</sup> Tetrapyridylmethanes would be interesting molecules as tetrahedral tetradentate ligands because of the high ability of pyridine to form complexes with transition metals. We have recently reported the synthesis of tetrakis(2-pyridyl)methane **1** as the first member of fifteen possible tetrapyridylmethanes.<sup>4</sup> Here we report the syntheses and structures of novel metal complexes of **1** with Ag(I) and Cu(II) ions, among them the Ag(I) complex having an infinite polycationic rod-shaped structure.



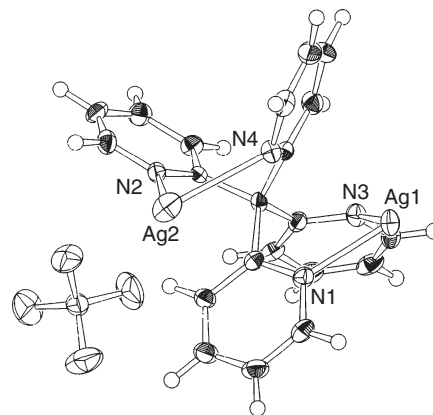
Addition of one equivalent of silver perchlorate in methanol to a chloroform solution of **1** smoothly precipitated a silver complex, **1**·AgClO<sub>4</sub>, as air-stable, colorless powder in 70% yield.<sup>5</sup> Recrystallization of the precipitates from acetonitrile–ether afforded a single crystal suitable for X-ray structure analysis.<sup>6</sup> The most remarkable structural feature of the complex thus revealed is that it has an infinite polycationic rod-shaped structure bridged by silver ions (Figure 1): one silver ion is coordinated by two nitrogen atoms of one molecule of **1** and two nitrogen atoms of another molecule, thus linearly bridging the highly symmetric tetradentate ligand. To our knowledge, this is the first example of coordination polymer constructed by tetragonal Ag(I) ion and a tetradentate ligand.

Figure 2 shows the structure of **1** coordinated to Ag(I) ions in more detail. The two Ag(I)–N bonds are different in the



**Figure 1.** Infinite polycationic coordination rod of  $\{[\text{Ag} \cdot \mathbf{1}] \cdot (\text{ClO}_4)\}_\infty$  complex (Perchlorate ions are omitted for clarity).

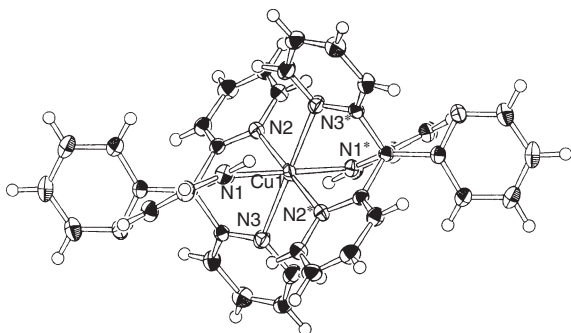
length. One (Ag1...N3 2.54 Å, Ag2...N4 2.69 Å) is considerably longer than the other (Ag1–N1; 2.32 Å, Ag2–N2; 2.22 Å), and the shorter ones are similar to the bond lengths commonly observed for Ag(I) complexes coordinated by  $sp^2$  nitrogen. Thus, the Ag(I) ions in the coordination polymer take a (formally) rectangular coordination geometry<sup>7</sup> differing from usual tetrahedral coordination geometry and are aligned alternately with **1** along *a* axis. The intra-rod distance between Ag(I) ions is 5.18 Å and the closest inter-rod distance between Ag(I) ions is 9.98 Å. The dihedral angle between the two rectangular coordination planes is 11.1°.



**Figure 2.** ORTEP drawing of asymmetric unit of  $\{[\text{Ag} \cdot \mathbf{1}] \cdot (\text{ClO}_4)\}_\infty$  (50% probability). Selected bond lengths (Å) and angles (°): Ag1–N1 2.315(4), Ag1...N3 2.538(4), Ag2–N2 2.224(4), Ag2...N4 2.685(4), N1–Ag1–N3 79.7(1), N1–Ag1–N3<sup>1)</sup> 100.3(1), N2–Ag2–N4 76.8(1), N2–Ag2–N4<sup>2)</sup> 103.2(1). Symmetry operations; 1)  $-x + 1, -y, -z$ . 2)  $-x + 2, -y, -z$ .

On the other hand, methane **1** formed two kinds of single crystals by slow crystallization from an equimolar mixture of **1** and copper(II) perchlorate in acetonitrile–ether: one is purple and the other is brown in appearance. Both the complexes have the same 1:2 composition with respect to Cu(II) and **1**, but the brown crystal includes two molecules of acetonitrile per one molecule of the complex. The brown crystals were liable to turn purple in a few minutes upon standing in air at room temperature probably due to escape of included acetonitrile.

Figure 3 shows the X-ray structure of the purple complex,  $[\text{Cu} \cdot \mathbf{1}_2] \cdot (\text{ClO}_4)_2$ .<sup>8</sup> The Cu(II) ion adopts a tetragonally distorted octahedral coordination geometry (Cu1–N1 1.99 Å, Cu1–N2 2.04 Å, Cu1...N3 2.38 Å); thus, one of the four 2-pyridyl groups in **1** is free from the coordination. The average coordination bond length (2.14 Å) is slightly longer than that in the Cu(II) complex of tris(2-pyridyl)methane (2.10 Å),<sup>9</sup> where Cu(II) ion adopts an undistorted octahedral coordination geometry. The distortion of the coordination environment of  $\text{Cu} \cdot \mathbf{1}_2$  may be ascribed to the tetra-substituted methane structure of **1** that increases rigidity of the molecule and prevents taking a conformation

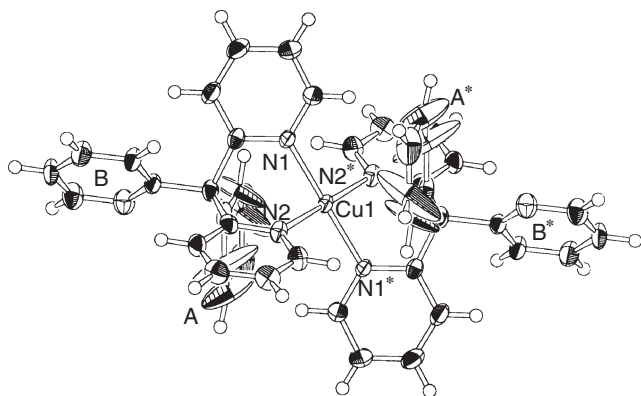


**Figure 3.** ORTEP drawing of the purple complex  $[\text{Cu}\cdot\mathbf{1}_2]\cdot(\text{ClO}_4)_2$  (50% probability). Perchlorate ions are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Cu1-N1}$  1.991(2),  $\text{Cu1-N2}$  2.039(2),  $\text{Cu1}\cdots\text{N3}$  2.375(2),  $\text{N1-Cu1-N2}$  86.23(6),  $\text{N1-Cu1-N2}^*$  93.77(6),  $\text{N1-Cu1-N3}$  83.59(7),  $\text{N1-Cu1-N3}^*$  96.41(7),  $\text{N2-Cu1-N3}$  86.98(6),  $\text{N2-Cu1-N3}^*$  93.02(6).

for an ideal tripodal ligand.

Figure 4 shows the molecular structure of the brown complex,  $[\text{Cu}\cdot\mathbf{1}_2]\cdot(\text{ClO}_4)_2\cdot(\text{CH}_3\text{CN})_2$ .<sup>10</sup> Differing from the octahedral coordination geometry in the purple complex, the Cu(II) ion in this complex adopts a tetragonal geometry, leaving two of the four pyridyl groups of **1** uncomplexed. The included acetonitrile molecules occupy the side of two uncoordinated pyridyl groups A and A\*, eventually preventing these and the other two uncoordinated 2-pyridyl groups B and B\* from coordination to the Cu(II) ion.<sup>11</sup> There seems no particular interaction between the cyano group of acetonitrile molecule and the Cu(II) ion, and therefore the acetonitrile molecules can escape fairly easily. Although a number of the crystal structures of the transition metal complexes of tris(2-pyridyl)methane have been reported,<sup>12</sup> no complexes of the dipodal coordination mode like the present brown complex of **1** have been found.

In summary, the highly symmetric tetradentate ligand **1** can take various metal-binding patterns such as two-fold dipodal as observed in the Ag(I) complex, tripodal or dipodal as observed in the Cu(II) complexes. These results suggest a further rich coordination chemistry of **1** and the formation of its complexes with other transition metal ions is under progress.



**Figure 4.** ORTEP drawing of the brown complex  $[\text{Cu}\cdot\mathbf{1}_2]\cdot(\text{ClO}_4)_2\cdot(\text{CH}_3\text{CN})_2$  (50% probability). Perchlorate ions and acetonitrile molecules are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Cu1-N1}$  1.991(6),  $\text{Cu1-N2}$  1.984(4),  $\text{N1-Cu1-N2}$  86.1(2),  $\text{N1-Cu1-N2}^*$  93.9(2).

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- $\mathbf{1}\cdot\text{AgClO}_4$ : mp > 350  $^\circ\text{C}$ ,  $^1\text{H NMR}$  (270 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  7.23 (ddd,  $J = 7.8, 4.9, 1.0$  Hz, 4H, Py-5H), 7.52 (dt,  $J = 7.8, 1.0$  Hz, 4H, Py-3H), 7.72 (td,  $J = 7.8, 1.9$  Hz, 4H, Py-4H), 8.36 (ddd,  $J = 4.9, 1.9, 1.0$  Hz, 4H, Py-6H); Anal. Calcd for  $\text{C}_{21}\text{H}_{16}\text{AgClN}_4\text{O}_4$ : C, 47.44; H, 3.03; N, 10.54. Found: C, 47.44; H, 3.02; N, 10.61%.
- Crystal data for  $\{[\text{Ag}\cdot\mathbf{1}]\cdot(\text{ClO}_4)\}_\infty$ :  $\text{C}_{21}\text{H}_{16}\text{AgClN}_4\text{O}_4$ ,  $M = 531.70$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 10.351(4)$ ,  $b = 12.375(4)$ ,  $c = 15.670(5)$   $\text{\AA}$ ,  $\beta = 92.15(2)^\circ$ ,  $V = 2005(1)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.761$   $\text{g cm}^{-3}$ ,  $T = 200$  K. Of the 20416 reflections which were collected, 4557 were unique ( $R_{\text{int}} = 0.060$ ) used in refinement.  $R = 0.081$  (3252 data,  $I > 2\sigma(I)$ ),  $wR_2 = 0.102$  (all data), GOF = 1.24.
- It is probable that the Ag(I) ion is diagonally coordinated in reality and undergoing rapid switching of coordination with the nearby free  $\text{sp}^2$  nitrogens in the crystal. For swift switching of diagonal coordination in the Ag(I) complex in solution, see Q.-Y. Zhu, Y. Zhang, J. Dai, G.-Q. Bian, D.-X. Jia, J.-S. Zhang, and L. Guo, *Chem. Lett.*, **32**, 762 (2003).
- Crystal data for the purple complex  $[\text{Cu}\cdot\mathbf{1}_2]\cdot(\text{ClO}_4)_2$ :  $\text{C}_{42}\text{H}_{32}\text{Cl}_2\text{CuN}_8\text{O}_8$ ,  $M = 911.22$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 9.90(1)$ ,  $b = 15.75(1)$ ,  $c = 12.58(1)$   $\text{\AA}$ ,  $\beta = 101.73(3)^\circ$ ,  $V = 1921(12)$   $\text{\AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.575$   $\text{g cm}^{-3}$ ,  $T = 200$  K. Of the 16858 reflections which were collected, 4365 were unique ( $R_{\text{int}} = 0.032$ ) used in refinement.  $R = 0.034$  (3919 data,  $I > 2\sigma(I)$ ),  $wR_2 = 0.111$  (all data), GOF = 1.10.
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- Crystal data for the brown complex  $[\text{Cu}\cdot\mathbf{1}_2]\cdot(\text{ClO}_4)_2\cdot(\text{CH}_3\text{CN})_2$ :  $\text{C}_{46}\text{H}_{38}\text{Cl}_2\text{CuN}_{10}\text{O}_8$ ,  $M = 993.32$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 10.564(5)$ ,  $b = 11.063(5)$ ,  $c = 11.008(4)$   $\text{\AA}$ ,  $\alpha = 66.91(4)$ ,  $\beta = 77.60(4)$ ,  $\gamma = 67.21(3)^\circ$ ,  $V = 1088(3)$   $\text{\AA}^3$ ,  $Z = 1$ ,  $D_{\text{calc}} = 1.516$   $\text{g cm}^{-3}$ ,  $T = 200$  K. Of the 9814 reflections which were collected, 4572 were unique ( $R_{\text{int}} = 0.047$ ) used in refinement.  $R = 0.076$  (3212 data,  $I > 2\sigma(I)$ ),  $wR_2 = 0.271$  (all data), GOF = 1.12.
- Some atoms around A and A\* show considerably large thermal ellipsoids, which seems to be associated with loosely included acetonitrile molecules also showing large thermal ellipsoids.
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