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Tetrakis(4-pyridyl)methane: Synthesis, Properties, and a Diamondoid Network Structure of Its Silver(I) Complex

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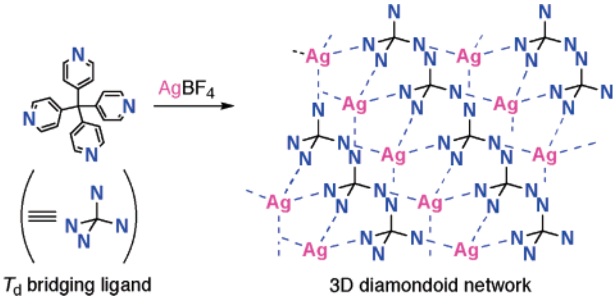
ABSTRACT



The title compound, which has the highest symmetry among tetrapyridylmethane isomers, has been synthesized from tris(4-pyridyl)methane and 4-chloropyridine. The silver(I) complex of the title compound forms a three-dimensional, non-interpenetrated diamondoid network in a crystal.

Due to their fascinating properties, such as a porous function, spontaneous magnetization, and high conductivity, coordination polymers have attracted considerable attention in the last two decades.[1] In particular, coordination polymers with a three-dimensional diamondoid network structure[2] have been intensively studied for potential application to nonlinear optic (NLO) materials.[3] Recently, we reported the synthesis and properties of tetrakis(2-pyridyl)methane (**1**)[4] and the crystal structures of the metal complexes of **1**.[5] For the construction of the coordination polymer with a diamondoid network structure, tetrakis(4-pyridyl)methane (**2**) is one of the most intriguing molecules because the four nitrogen atoms are fixed at the vertexes of the tetrahedron regardless of the rotation of the pyridyl group. According to the PM3 calculation for **2**, the distance between two nitrogen atoms is approximately 7.1 Å. Here, we report the synthesis and properties of **2** as well as the crystal structure of its silver(I) complex. To our knowledge, the coordination polymer featured by a diamondoid network structure constructed by the combination of a T_d ligand and T_d metal ion is still rare.[6]

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[1] (a) Janiak, C. *Dalton Trans.* **2003**, 2781. (b) Kitagawa, S.; Noro, S. In *Comprehensive Coordination Chemistry II*; MeCleverty, J. A., Meyer, T. J., Eds; Elsevier: Oxford, England, 2004; Vol. 7, p 231. (c) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109.

[2] (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Zhang, J.; Lin, W.; Chen, Z.-F.; Xiong, R.-G.; Abrahams, B. F.; Fun, H.-K. *J. Chem. Soc., Dalton Trans.* **2001**, 1806. (c) Ferlay, S.; Koenig, S.; Hosseini, M. W.; Pansanel, J.; Cian, A. D; Kyritsakas, N. *Chem. Commun.* **2002**, 218. (d) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *Chem.—Eur. J.* **2002**, *8*, 1519. (e) Liu, Y.-H.; Wu, H.-C.; Lin, H.-M.; Hou, W.-H.; Lu, K.-L. *Chem. Commun.* **2003**, 60. (f) Westcott, A.; Whitford, N.; Hardie, M. J. *Inorg. Chem.* **2004**, *43*, 3663. (g) Natarajan, R.; Savitha, G.; Dominiak, P.; Wozniak, K.; Moorthy, J. N. *Angew. Chem., Int. Ed.* **2005**, *44*, 2115. (h) Zhang, L.; Lü, X.-Q.; Chen, C.-L.; Tan, H.-Y.; Zhang, H.-X.; Kang, B.-S. *Cryst. Growth Des.* **2005**, *5*, 283.

[3] (a) Evans, O. R.; Xiong, R.-G.; Wang, Z.; Wong, G. K.; Lin, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 536. (b) Lin, W.; Ma, L.; Evans, O. R. *Chem. Commun.* **2000**, 2263. (c) Evans, O. R.; Lin, W. *Chem. Mater.* **2001**, *13*, 2705. (d) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511.

[4] Matsumoto, K.; Kannami, M.; Oda, M. *Tetrahedron Lett.* **2003**, *44*, 2861.

[5] (a) Matsumoto, K.; Kannami, M.; Oda, M. *Chem. Lett.* **2004**, *33*, 1096. See also: (b) Okazawa, A.; Ishida, T.; Nogami, T. *Chem. Lett.* **2004**, *33*, 1478. (c) Okazawa, A.; Ishida, T.; Nogami, T. *Polyhedron* **2005**, *24*, 2584.

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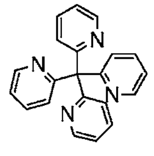

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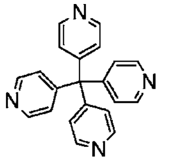
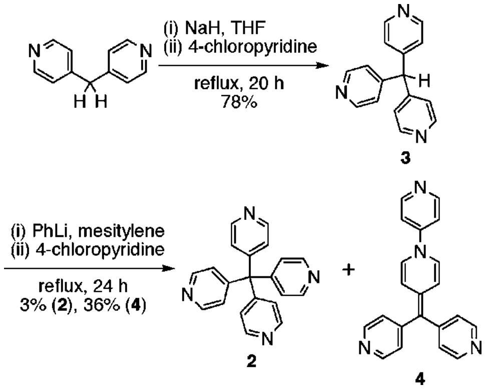


2

The synthesis of **2** is shown in Scheme 1. Tris(4-pyridyl)methane (**3**), the precursor of **2**, was prepared from bis(4-pyridyl)methane[7] and 4-chloropyridine in 78% yield. In contrast to the synthesis of **1**, the desired compound **2**[8] could be obtained only in 3% yield under similar conditions used for **1**. The main product in this reaction was the 1,4-dihydropyridine derivative **4** (36%) with the recovery of **3** (14%). Compound **4** was formed by the reaction of the tris(4-pyridyl)methyl anion with 4-chloropyridine at the nitrogen atom. The yield of **2** was not improved by the replacement of the solvent with diglyme (5%). Neither the prolonged reaction time nor the increased amounts of 4-chloropyridine affected the yield of **2**. The related reaction of tris(2-pyridyl)methyl anion with 4-chloropyridine gave tris(2-pyridyl)(4-pyridyl)methane (**5**) but only in a poor yield (5%) with the recovery of **3** (59%). In this reaction, the dihydropyridine derivative related to **4** was not obtained. This result suggested that 4-chloropyridine hardly reacted with the tris(2-pyridyl)methyl anion because of the steric congestion around the central carbon of the anion. Therefore, the low yield of **2** could be attributed not only to high reactivity at the nitrogen atom in the tris(4-pyridyl)methyl anion but also to the low reactivity of 4-chloropyridine with the aromatic nucleophilic substituent because of the steric effect.

Scheme 1. Synthesis of **2**



The purification of **2** was somewhat difficult and tedious because of the high affinity of **2** for water and the difficulty in separating it from the other compounds; repeated extraction, column chromatography on alumina, and gel permeation chromatography were needed for obtaining the pure material of **2** (see Supporting Information). Compound **2** is a stable, colorless crystalline substance, and is soluble in chloroform and dichloromethane, less soluble in methanol, acetone, ethyl acetate, and sparingly soluble in ether and hexane.

Consistent with its high symmetry, **2** shows only two signals in its ^{1}H NMR spectrum and four signals in its ^{13}C NMR spectrum (Table 1). The chemical shift of the central carbon atom (Cα) of **2** is observed at δ 63.6. Compared to that of tetraphenylmethane (δ 64.9), the slightly higher field shift is observed. Since this trend is commonly observed in the series of 4-pyridylmethanes compared with phenylmethanes, the high field shift of Cα would be simply due to the substituent effect of 4-pyridyl group. The chemical shift of Cα of **1** is observed at a lower field (δ 72.4) than that of **2**, exhibiting the inductive effect of the nitrogen atom. As observed in the series of 2-pyridylmethanes, (2-Py)$_n$CH$_{(4-n)}$, the longest absorption maximum of **2** exhibits a slightly red shift compared to **3** and other 4-pyridylmethanes. In both cases, intramolecular interaction between the pyridyl groups, sometimes referred to as homoconjugation,[9] is still not evident.

The molecular structure of **2** was confirmed by X-ray crystallographic analysis (Figure 1).[10] The average bond length of C1−C*ipso* (1.534 Å) is slightly shorter than that in **1** (1.545 Å)[11] and tetraphenylmethane (1.553 Å).[12] The shorter bond length in **2** would be due to the small interior angle at the *ipso*-carbons in **2** derived from the fact that pyridine has an intrinsic small interior angle at the 4-position.

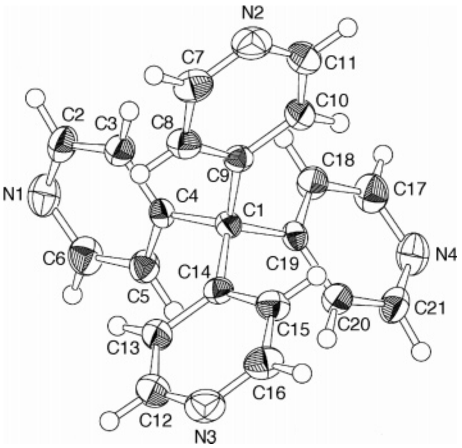


Figure 1. ORTEP drawing of **2** along the *a*-axis (50% probability).

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(6) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1989**, *111*, 5962. (b) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (c) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239. See also: (d) Venkataraman, D.; Lee, S.; Moore, J. S.; Zhang, P.; Hirsch, K. A.; Gardner, G. B.; Covey, A. C.; Prentice, C. L. *Chem. Mater.* **1996**, *8*, 2030.

(7) Gaus, P. L.; Haim, A.; Johnson, F. *J. Org. Chem.* **1977**, *42*, 564.

(8) Spectroscopic data for **2**: mp 293−294 °C; MS (EI) *m/z* (rel intensity) 324 (M^+, 60), 246 ($[M - C_5H_4N]^+$, 100), 168 ($[M - 2(C_5H_4N)]^+$, 14); ^{1}H NMR (270 MHz, CDCl$_3$) δ/ppm 8.61 (dd, $J = 4.6$, 1.6 Hz, 8H), 7.08 (dd, $J = 4.6$, 1.6 Hz, 8H); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ/ppm 150.9, 150.0, 124.9, 63.6. Anal. Calcd for $C_{21}H_{16}N_4$: C, 77.76; H, 4.97; N, 17.27. Found: C, 77.39; H, 4.97; N, 17.17.

(9) (a) Oldham, W. J., Jr.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 2987. (b) Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695. (c) Sengupta, S.; Sadhukhan, S. K.; Muhuri, S. *Tetrahedron Lett.* **2002**, *43*, 3521. (d) Sengupta, S.; Pal, N. *Tetrahedron Lett.* **2002**, *43*, 3517.

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts^{a} and the Longest Absorption Maxima^{b} of 4-Pyridylmethanes $(4\text{-Py})_n\mathrm{CH}_{(4-n)}$ ($n = 1-4$)

	^{1}H NMR Chemical Shifts (ppm)			^{13}C NMR Chemical Shifts (ppm)				UV−Vis Absorption	
compound	Cα-H	H-2,6	H-3,5	Cα	C-2,6	C-3,5	C-4	$\lambda_{\max}$ (nm)	log ϵ
(4-Py)CH_3	2.26	8.42	7.02	20.0	148.4	123.5	145.8	256	3.17
$(4\text{-Py})_2CH_2$	3.96	8.53	7.09	40.2	149.7	123.8	147.3	257	3.57
3	5.43	8.59	7.02	54.8	150.2	124.0	148.8	259	3.76
2		8.61	7.08	63.6	150.0	124.9	150.9	262	3.88

^{a} In $CDCl_3$ at 30 °C. ^{b} In CH_2Cl_2.

Single crystals of the silver(I) complex of **2** suitable for X-ray crystallographic analysis were obtained from a DMSO solution containing an equimolar mixture of **2** and silver(I) tetrafluoroborate by slow vapor diffusion with methanol (Figure 2).[13] It should be noted that the silver(I) ion and **2** produced a three-dimensional diamondoid coordination network (Figure 3) as we expected. The characteristic features of the network are as follows: (1) Viewing along the crystallographic (110) and (−110) directions, a porous, honeycomb structure is observed (Figure 4), and the hexagonal channel is the size of 6.6 × 6.6 × 4.4 Å; (2) no interpenetration is observed, and the distance between the silver(I) ion and the central carbon atom of **2** is approximately 6.6 Å (in the range of 6.57−6.63 Å), which is too short for interpenetration; and (3) because of the porous network, the positions of the tetrafluoroborate ion and solvent molecules, which might be present somewhere, cannot be determined.

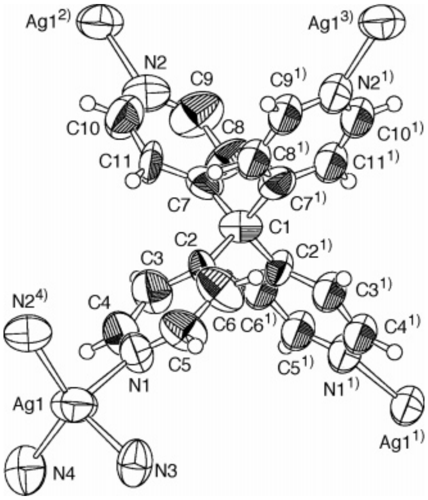

Figure 2. ORTEP drawing of the silver(I) complex of **2** along the a-axis (50% probability). Although there are two crystallographic independent molecules of **2**, only one molecule is shown. BF_4 ions are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1−N1 2.31(1), Ag1−N2$^{4)}$ 2.22(1), Ag1−N3 2.28(1), Ag1−N4 2.23(1), N1−Ag1−N2$^{4)}$ 101.1(5), N1−Ag1−N3 104.7(4), N1−Ag1−N4 109.0(4), N2$^{4)}$−Ag1−N3 116.9(5), N2$^{4)}$−Ag1−N4 121.6(5), N3−Ag1−N4 102.2(5). Symmetry operations: (1) $-x, -y + 1, z$; (2) $x - 1/2, -y + 1, -z + 1$; (3) $-x + 1/2, -y + 1, -z + 1$; (4) $x + 1/2, -y + 1/2, -z + 1$.

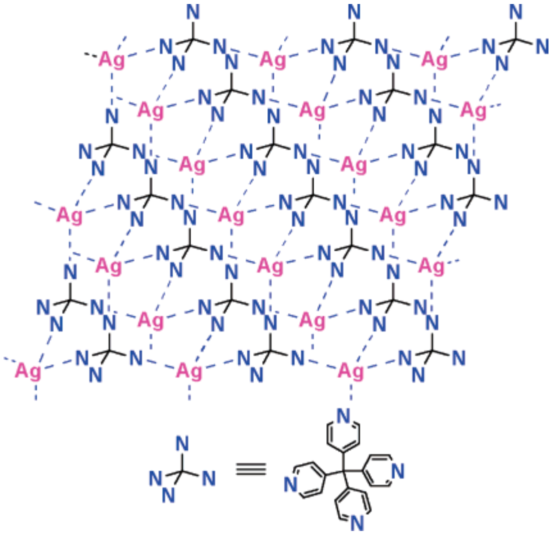

Figure 3. Schematic diagram of three-dimensional diamondoid coordination network of silver(I) of **2**. Blue broken lines show coordination bonds between silver and nitrogen.

The colorless crystals of the complex tend to effloresce within a few minutes upon standing in air. Similar to the silver(I) complex of pyridine,[14] the silver(I) ion takes a distorted tetrahedral coordination geometry and binds four neighboring molecules of **2**. The bond lengths of the

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(10) Crystallographic data for **2**: $C_{21}H_{16}N_4$, $FW = 324.38$, triclinic, space group $P\bar{1}$, $a = 7.113(7)$, $b = 8.547(9)$, $c = 14.99(1)$ Å, $\alpha = 78.64(8)$, $\beta = 76.36(8)$, $\gamma = 65.54(8)$°, $V = 801(5)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.344$ g·cm^{-3}, $T = 200$ K, of the 7980 reflections which were collected, 3661 were unique used in refinement. $R1 = 0.044$ (2418 data, $I > 2\sigma(I)$), $wR2 = 0.122$ (all data), GOF = 0.90.

(11) We obtained a single crystal of **1**, which showed the higher crystal system (tetragonal) than that reported in ref 3 after we published it. This bond length is referred to the data of the tetragonal crystal of **1**.

(12) Robbins, A.; Jeffrey, G. A.; Chesick, J. P.; Donohue, J.; Cotton, F. A.; Frenz, B. A.; Murillo, C. A. *Acta Crystallogr.* **1975**, *B31*, 2395.

(13) Crystallographic data for silver(I) complex of **2**: $C_{21}H_{16}N_4AgBF_4$, $FW = 519.06$, orthorhombic, space group $P2_12_12$, $a = 13.871(6)$, $b = 13.979(5)$, $c = 17.520(6)$ Å, $V = 3397(8)$, $Z = 4$, $D_{\mathrm{calcd}} = 1.015$ g·cm^{-3}, $T = 200$ K, of the 31 541 reflections which were collected, 7735 were unique used in refinement. $R1 = 0.132$ (7735 data, $I > 2\sigma(I)$), $wR2 = 0.400$ (all data), GOF = 1.08.

(14) Nilsson, K.; Oskarsson, Å. *Acta Chem. Scand.* **1982**, *A36*, 605.

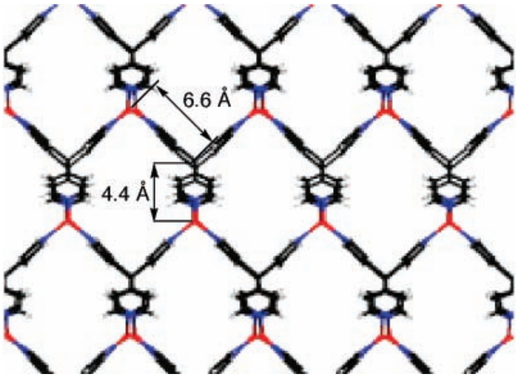

Figure 4. Honeycomb structure of silver(I) complex of **2**. Red, silver; blue, nitrogen; black, carbon; and white, hydrogen.

coordination bonds are in the range of 2.2−2.3 Å. Although there are two crystallographically independent molecules of **2**, their molecular structures are similar. The geometry of **2** is also distorted from the ideal tetrahedral structure; the distance between two nitrogen atoms of **2** is in the range of 6.3−7.5 Å (N1···N1* 6.48 Å, N1···N2 7.44 Å, N2···N2* 6.26 Å).

In summary, we have synthesized tetrakis(4-pyridyl)-methane (**2**), as an ideal T_d bridging ligand. As expected, the silver(I) complex of **2** forms a three-dimensional diamondoid coordination polymer. The improved synthesis of **2** and the construction of other metal complexes of **2** are now under investigation.

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Supporting Information Available: Experimental procedures and product characterization for all new compounds, and the X-ray crystallographic data for compound **2** and its silver(I) complex are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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