Silver(I) Complex Crystals Switched by a Water Molecule

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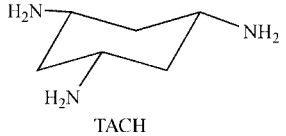
The reaction of $AgPF_6$ and *cis*,*cis*-1,3,5-triaminocyclohexane (TACH) in a 1:1 ratio in methanol solution gave two different coordination polymer crystals depending on the presence/absence of water. The crystal structure in the absence of water is a one-dimensional, tube-like polymer with formula $\{[Ag^{I}(TACH)]PF_6\}_n$, while in the presence of water the structure is a three-dimensionally expanded complex network built up from cage units containing a water molecule, $\{[Ag^{I}_3(TACH)_4](PF_6)_3{\cdot}H_2O\}_{ni}$ this structure is induced even by a trace amount of water.

Introduction

Molecular regulation at the nanometer-scale level is very important and interesting from the viewpoint of the design and synthesis of nanoporous materials. The investigation of nanoporous compounds prepared by the self-assembly of metal ions and organic compounds has been investigated extensively.[1] Metal ions are often used as a junction between organic molecules as their characteristic geometries — such as trigonal planar, tetragonal planar, tetrahedral, and octahedral — allow the construction of higher-dimensional structures. Recently, some interesting compounds based on non-covalent interactions have been reported. Catenanes are formed by only a π-π interaction between aromatic rings,[2,3] and Aoyama et al. have succeeded in preparing organic zeolites linked by a hydrogen bond.[4]

The hydrogen bond is one of the most important non-covalent interactions in biological systems, and it plays an important role in the stabilization of DNA-protein structures and in mutual recognition between proteins.[5] Such non-covalent interactions contribute significantly to the formation of high-dimensional structures in DNA and/or proteins, even in water. The hydrogen bond participates clearly in such structure maintenance and recognition.[6] However, it is difficult for small molecules to interact intermolecularly in water through hydrogen bonding as the water behaves as an inhibitor. These facts imply that the water molecule is one of the essential factors in the steric interaction of DNA-proteins, although it functions as an inhibitor, too. Recently we prepared a new nanoporous material from the reaction of Cu^{I} ion and *cis*,*cis*-1,3,5-triaminocyclohexane (TACH),[7] in which we used the characteristics of the Cu^{I} ion and TACH ligand: the former prefers two-coordinate linear, three-coordinate trigonal-planar, or four-coordinate tetrahedral structures and the latter has C_{3v} symmetry. In this study, using the Ag^{I} ion instead of Cu^{I}, the reaction of $AgPF_6$ with TACH at 1:1 was carried out. Interestingly, two different complex crystals were prepared in absolute methanol and in methanol/water solutions, indicating that the formation of these silver complex crystals was discriminatively switched by the presence of a water molecule. This water-induced transformation of supramolecular structures in the crystalline state is quite novel, although it has been reported that the supramolecular structures of silver(I)-polynitrile complexes are transformed into each other by a similar anion exchange in the crystalline state.[8] Here we describe the preparation and structural characterization of their complexes in detail.



TACH

Results and Discussion

A methanol solution of TACH was added to an absolute methanol solution of $AgPF_6$ in a 1:1 ratio. Allowing the reaction solution to stand for a few hours afforded a colorless crystal suitable for an X-ray diffraction measurement, which was identified as $\{[Ag^{I}(TACH)]PF_6\}_n$ (**1**) from the elemental analysis. Complex **1** crystallizes in the monoclinic system with space group $P2_1/n$. It contains one Ag^{I} ion, one

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TACH molecule, and one PF_6^- ion as crystallographically independent components of the unit cell. The Ag^I ion has a trigonal planar geometry, with coordination of three primary amine nitrogens from three TACH molecules, and the TACH molecule has a chair-form with the three amino groups oriented in the equatorial direction as expected from its *cis*,*cis*-conformation. The Ag^I and TACH units are linearly linked to each other to form a tube-like structure with a small pore of ca. 4×4 Å^2, as shown in Figure 1B, which is a one-dimensional infinite coordination polymer related by a crystallographic screw axis. The tube-like coordination polymers are weakly linked to each other by PF_6^- anions, as shown in Figure 1A. The tube-like coordination polymer may best be described by the formula $\{[Ag^I(TACH)]PF_6\}_n$. The Ag−N bond lengths agree well with those found in analogous Ag^I complexes reported hitherto (2.2−2.4 Å).[9] The nearest Ag−Ag distance is 5.689(3) Å.

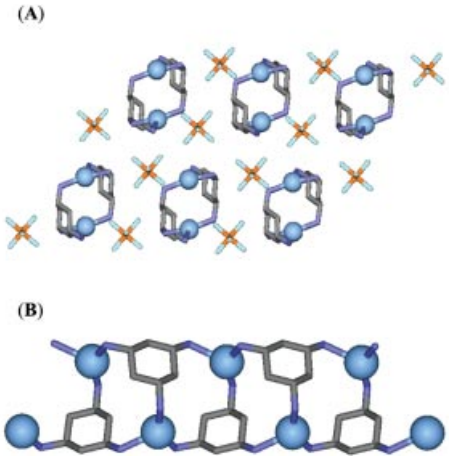

Figure 1. Wire models of the one-dimensional infinite structures of **1** viewed along the crystallographic *ac* (**A**) and *ab* planes (**B**); the blue and gray colored atoms denote nitrogen and carbon atoms, respectively; the large blue-colored atom is a silver(I) ion; hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°): Ag(1)−N(1) 2.228(9), Ag(1)−N(2) 2.251(8), Ag(1)−N(3) 2.398(8); N(1)−Ag(1)−N(2) 148.4(3), N(1)−Ag(1)−N(3) 111.5(3), N(2)−Ag(1)−N(3) 100.1(3)

The addition of a methanol/water (20:1 v/v%) solution of TACH to a methanol solution of $AgPF_6$ in a 1:1 ratio and allowing the reaction solution to stand for a few hours afforded a colorless crystal suitable for an X-ray diffraction measurement. The complex was identified as $\{[Ag^I_3(TACH)_4](PF_6)_3 \cdot H_2O\}_n$ (**2**) from the elemental analysis. Complex **2** crystallizes in the cubic system with space group $I2_13$, and contains half an Ag^I ion, two units of one-third parts of TACH molecule, half a PF_6^- ion, and six units of one-sixth parts of disordered water molecules as the independent atoms in the unit cell. In spite of the same reaction conditions as for the synthesis of **1**, except for the presence of water, the crystal structure of **2** is quite different from that of **1**. The geometry around the Ag^I ion is tetrahedral, with four primary amine nitrogens from four TACH molecules, although the conformation of the cyclohexane ring and the orientation of three amino groups are the same

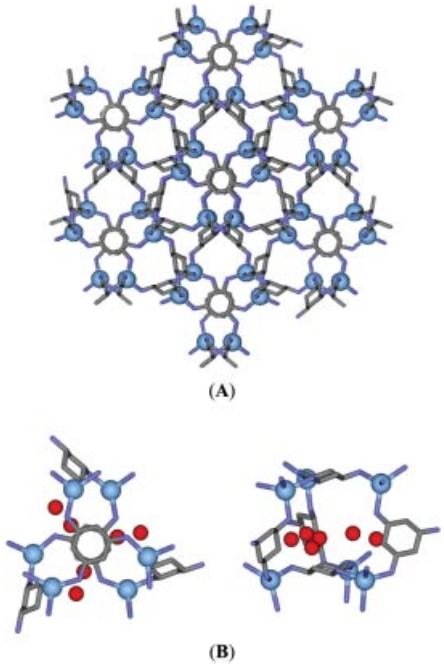

Figure 2. Wire models of the three-dimensionally expanded structure of **2** viewed along the apex of the unit cell (**A**), and top (left) and side (right) views of the cage structure (**B**) of **2** consisting of six Ag^I ions and five TACH molecules; the large blue- and red-colored atoms denote a silver ion and a disordered water molecule, respectively; the counteranions and hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°): Ag(1)−N(1) 2.383(7), Ag(1)−N(2) 2.356(7); N(1)−Ag(1)−N(2) 100.9(2), N(1)−Ag(1)−N(1*) 128.8(4), N(1)−Ag(1)−N(2*) 101.0(2) (atoms with and without an asterisk are related by a crystallographic threefold axis)

as those of **1**. The dihedral angle of the two planes defined by three atoms, N(1)−Ag(1)−N(2) and N(1*)−Ag(1)−N(2*), is 69°. Judging from the bond angles (denoted in the caption of Figure 2) and the dihedral angle, the Ag^I ion is distorted from a regular tetrahedron.

As is clear from the crystal structure of **2** viewed through the apex of the unit cell (the crystallographic threefold axis), the Ag^+ ions and TACH ligands form three-dimensionally expanded networks (Figure 2). The network is made up of cage units consisting of six silver(I) ions and five TACH molecules (Figure 2B). As shown in the left and right figures of Figure 2B, exhibiting the top and side views of the cage structure, respectively, the center of the TACH molecule lies on the threefold axis and the two cyclohexane rings of the top and bottom TACHs of the cage are twisted with a rotation angle of about 30°. The cage unit is surrounded by six PF_6^- counteranions that are related by threefold axis symmetry; the inner space of the cage is occupied by disordered water molecules, which are incorporated by a hydrophilicity inside the cage. The cage contains pores with a height of about 6 Å and an inner diameter of about 4 Å based on the van der Waals radius of the atoms.[10] The existence of this porosity is also obvious from the lower density of **2** ($\rho = 1.810$ g·cm^{-3}) compared with that of **1** ($\rho = 2.054$ g·cm^{-3}).

Although **1** and **2** were prepared under the same conditions except for the absence/presence of water, respec-

tively, **1** has a one-dimensional infinite tube-like structure, while **2** exhibits a three-dimensionally expanded network structure constructed from cage units. Both **1** and **2** were obtained from the same starting materials in the same ratio ($AgPF_6$:TACH = 1:1), and **2** was isolated even in the presence of a trace amount of water. Interestingly, a crystal obtained from a suspended solution of **1** in water showed the same X-ray diffraction pattern as the simulation pattern estimated from the single crystal X-ray diffraction measurements of **2** (Figure S1; Supporting Information, see footnote on the first page of this article). A single crystal obtained from the suspended solution also exhibited the same lattice parameters as those of **2**. It is therefore clear that water promotes such a large difference in the coordination structure and the dimensionality.[11] This may be induced by the strong hydrogen bonding ability of water and the difference in the polarity or permittivity of the solvents [H_2O (ε_r = 78.3) and CH_3OH (ε_r = 32.6) at 25 °C].[12] The difference in their formula may be due to the different coordination of TACH molecules to the Ag^I ion: **1** is three-coordinate trigonal-planar and **2** is four-coordinate tetrahedral. The above facts suggest that the water raises the Lewis acidity of the Ag^I ion and assists the linkage of the TACH ligand to the Ag^+ ion. Also, based on the O···(H)N distance of about 2.9 Å, the cage structure could be derived from the hydrogen bonding interaction between the water molecule and the hydrophilic primary amine of the TACH ligands.

In conclusion, we succeeded in the discriminative preparation and structural characterization of two kinds of Ag^I coordination polymers, which gave one- and three-dimensional infinite structures from absolute methanol and from methanol/water, respectively. These structures are switched by the presence of a water molecule.

Experimental Section

$\{[Ag^I(TACH)]PF_6\}_n$ (1): A mixture of TACH (12.9 mg, 0.100 mmol) in methanol (4 mL) was added to an absolute methanol solution (4 mL) of $AgPF_6$ (25.3 mg, 0.100 mmol). After removal of an insoluble material by filtration, allowing the reaction solution to stand for a few hours gave colorless crystals of the title compound (38 mg, 25%). $C_6H_{15}AgF_6N_3P$ (382.04): calcd. C 18.86, H 3.96, N 11.00; found C 19.05, H 3.89, N 11.08.

Crystal Data: $C_6H_{15}AgF_6N_3P$, M = 382.04, monoclinic, space group $P2_1/n$ (no. 14), a = 9.608(8), b = 7.725(6), c = 17.18(1) Å, β = 104.44(1)°, V = 1235(1) Å^3, Z = 4, $\rho_{calcd.}$ = 2.054 g cm^{-3}, μ = 18.14 cm^{-1}, $2\theta_{max}$ = 55.0 °, Mo-K_α radiation (λ = 0.71070 Å), T = 173 K, R = 0.090, Rw = 0.215 (for all reflection data), and GOF = 1.30 for 2814 independent reflections with $I > 2\sigma(I)$ and 154 variables.

$\{[Ag^I_3(TACH)_4](PF_6)_3\cdot H_2O\}_n$ (2): A mixture of TACH (12.9 mg, 0.100 mmol) in methanol (4 mL) and water (0.2 mL) was added to a methanol solution (4 mL) of $AgPF_6$ (25.3 mg, 0.100 mmol). After removal of an insoluble material by filtration, allowing the reaction solution to stand for a few hours gave colorless crystals of the title compound. $C_{24}H_{62}Ag_3F_{18}N_{12}OP_3$ (1293.33): calcd. C 22.29, H 4.83, N 13.00; found C 22.68, H 4.69, N 12.86.

Crystal Data: $C_{24}H_{62}Ag_3F_{18}N_{12}OP_3$, M = 1293.33, cubic, space group $I2_13$ (no. 199), a = 16.8048(7) Å, V = 4745.7(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.810 g cm^{-3}, μ = 14.31 cm^{-1}, $2\theta_{max}$ = 54.8°, Mo-K_α radiation (λ = 0.71070 Å), T = 173 K, R = 0.066, Rw = 0.176 (for all reflection data), and GOF = 1.36 for 911 independent reflections with $I > 2\sigma(I)$ and 102 variables.

Conversion of 1 to 2: Suspension of a crystal of **1** (10 mg) in water for four days gave colorless crystals that exhibit almost the same X-ray powder diffraction pattern as that of **2** estimated from the single-crystal X-ray diffraction measurements. The single crystal obtained has the same lattice parameters as the crystal of **2**.

CCDC-212323 (**1**) and -212322 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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