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Inorganic Chemistry Communications 9 (2006) 60–63

INORGANIC CHEMISTRY COMMUNICATIONS

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Solid channel structure and nanoscale drum-like Ag_6 cluster constructed with pentafluorobenzenethiolate and triphenylphosphine ligands: The use of water-soluble silver(I) carboxylate as silver(I) source

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Received 26 August 2005; accepted 2 October 2005
Available online 15 November 2005

Abstract

A nanoscale drum-like hexanuclear silver(I) cluster $[Ag(pfbt)(PPh_3)]_6$ **1** (Hpfbt = pentafluorobenzenethiol), which showed the arrays of channels based on its self-assembly in the solid, was obtained by the 1:1 molar-ratio reaction of the insoluble polymeric precursor $_\infty[Ag(pfbt)]$ **2** and PPh_3 in chloroform. Synthetic yield and purity of **1** were strongly dependent on the purity of **2**. Compound **2** with higher purity was prepared in good yield using light-stable and water-soluble silver(I) carboxylate $[Ag(Hpyrrld)]_2$ ($H_2pyrrld$ = 2-pyrrolidone-5-carboxylic acid) as the silver(I) source.

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Keywords: Nanoscale hexanuclear silver(I) cluster; Solid channel structure; Pentafluorobenzenethiol; Triphenylphosphine; 2-Pyrrolidone-5-carboxylic acid

There is currently considerable interest in the coordination chemistry of coinage metals such as silver(I) and gold(I) with biological and/or medicinal activities [1–3]. In the structural viewpoint, silver(I) complexes with thiol ligands have shown a tendency to form cluster and polymer structures [1,4], whereas the corresponding gold(I) complexes have shown supramolecular arrangements of 2-coordinate linear units [1,5–7].

It is known that the cooperation with electron-deficient fluorinated aromatics and electron-rich aromatics can induce electrostatic quadrupole stacking interaction and contribute to the architecture of extended structures in the crystal [8–13]. For example, the supramolecular dimer of the triphenylphosphinegold(I) complex $[Au(pfbt)(PPh_3)]_2$ (Hpfbt = pentafluorobenzenethiol; Chart 1) through intermolecular quadrupole interactions between the fluorinated phenyl ring ($pfbt^-$) and the phenyl ring of the neighboring PPh_3 molecule was realized in the solid state and in solution, the molecular structure of which contained intramolecular Au$\cdots$F and H(phenyl of PPh_3)$\cdots$F interactions as well as 2-coordinate P–Au–S bonding [14]. The related gold(I) complex $[Au(SPh)(PPh_3)]$ with the unfluorinated aromatic thiolate has shown a dimeric arrangement through the aurophilic interaction [15]. On the other hand, the triphenylphosphinesilver(I) complex with flurorine-free aromatic ligand, $[Ag(SPh)(PPh_3)]_4$ (SPh^- = benzenethiolate), has been reported as a tetranuclear silver(I) cluster with highly distorted chair structure [16]. However, the structure of the $pfbt^-$ analogs of triphenylphosphinesilver(I) complex has not been reported so far. Thus, we have aimed at preparing such a complex and examining the effect of fluorinated and unfluorinated aromatic thiolate ligands on the molecular structure of the triphenylphosphinesilver(I) complexes.

Recently, we have found that the chiral and achiral silver(I) carboxylates, $[Ag(R\text{- or }S\text{-Hpyrrld})]_2$ and $[Ag(R,S\text{-Hpyrrld})]_2$ ($H_2pyrrld$ = 2-pyrrolidone-5-carboxylic acid) [17,18] are light-stable and water-soluble Ag–O bonding

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doi:10.1016/j.inoche.2005.10.003

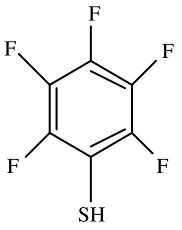

Chart 1. Hpfbt (pentafluorobenzenethiol).

complexes. Their triphenylphosphine derivatives, e.g., $[\mathrm{Ag}_2(R\text{- or }S\text{-Hpyrrld})_2(\mathrm{H_2O})(\mathrm{PPh_3})_2]\cdot\mathrm{H_2O}$, $[\mathrm{Ag}(R\text{- or }S\text{-Hpyrrld})(\mathrm{PPh_3})_2]_2$, $[\mathrm{Ag}(R,S\text{-Hpyrrld})(\mathrm{PPh_3})]_2$ and $[\mathrm{Ag}(R,S\text{-Hpyrrld})(\mathrm{PPh_3})_2]$, showed different Ag–O bonding modes depending on the number of $\mathrm{PPh_3}$ ligands and the chirality of the $\mathrm{Hpyrrld}^-$ ligand [19]. The Ag–O bonding complexes and the triphenylphosphinesilver(I) derivatives have been recently used as useful precursors for formation of novel silver(I) clusters such as $[\mathrm{Ag(2\text{-}Hmba)(PPh_3)}]_4$ ($2\text{-H}_2\mathrm{mba}$ = 2- mercaptobenzoic acid) with a three-leaves propeller (C_3 symmetry) [20] and $[\mathrm{Ag_2(Himdc)(PPh_3)_2}]_2$ ($\mathrm{H_3imdc}$ = imidazole-4,5-dicarboxylic acid) with a "bivalve"-like skeleton [21].

In this work, a nanoscale, S_6 symmetry drum-like hexanuclear silver(I) cluster $[\mathrm{Ag(pfbt)(PPh_3)}]_6$ **1** was successfully obtained in the 1:1 molar-ratio reaction of the insoluble polymeric precursor ${}_{\infty}[\mathrm{Ag(pfbt)}]$ **2** and $\mathrm{PPh_3}$ in chloroform [22,23]. Complex **1** showed the arrays of channels resulting from its self-assembly in the solid state. The water-soluble silver(I) carboxylate $[\mathrm{Ag(Hpyrrld)}]_2$ was used as the silver(I) source for preparation of **2** with higher purity. Herein, we report the synthesis of **1** and **2**, and the unequivocal characterization of **1** with elemental analysis, TG/DTA, FTIR, solution (^{1}H and ^{31}P) NMR and solid-state ^{31}P CPMAS NMR, and single-crystal X-ray crystallography.

Compound **1** as colorless plate crystals was obtained in 79.0% (0.45 g scale) yield by the 1:1 molar-ratio reaction of **2** and $\mathrm{PPh_3}$ in chloroform. Pale yellow powder of **2** was obtained in 95.3% (1.17 g scale) yield by the 1:2 molar-ratio reaction of $[\mathrm{Ag}(R,S\text{-Hpyrrld})]_2$ and Hpfbt in a 1:1 mixed $\mathrm{H_2O}$/EtOH solvent. Instead of $[\mathrm{Ag}(R,S\text{-Hpyrrld})]_2$, the silver(I) sources such as $\mathrm{Ag_2O}$ and $\mathrm{AgNO_3}$ gave the impure solid **2** contaminated with unreacted $\mathrm{Ag_2O}$ and $\mathrm{NO_3^-}$ ion [22]. The synthetic reactions of **2** and **1** are shown in Eqs. (1) and (2):

$$1/2[\mathrm{Ag}(R,S\text{-Hpyrrld})]_2 + \mathrm{Hpfbt} \rightarrow {}_{\infty}[\mathrm{Ag(pfbt)}]\mathbf{2} + R,S\text{-H}_2\mathrm{pyrrld} \qquad (1)$$

$$6_{\infty}[\mathrm{Ag(pfbt)}]\mathbf{2} + 6\mathrm{PPh_3} \rightarrow [\mathrm{Ag(pfbt)(PPh_3)}]_6\mathbf{1} \qquad (2)$$

The composition and molecular formula of **1** were consistent with elemental analysis, TG/DTA, FTIR, solution (^{1}H and ^{31}P) NMR and solid-state ^{31}P CPMAS NMR.

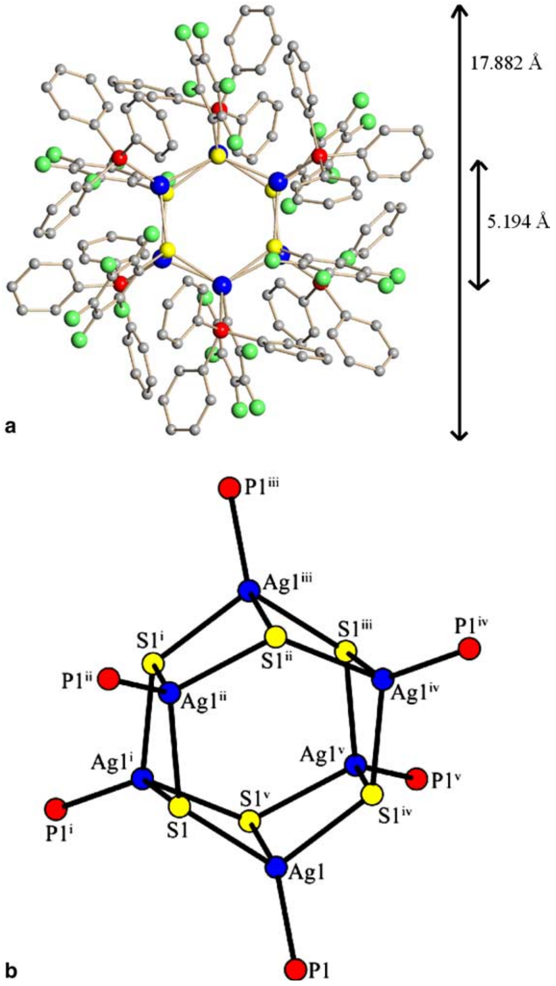

Fig. 1. (a) Molecular structure of **1** (symmetry operation $\mathrm{i} = y+2, -x+y+1, -z+2$; $\mathrm{ii} = -x+y+2, -x+1, z$; $\mathrm{iii} = -x+2, -y, -z+2$; $\mathrm{iv} = -y+1, x-y-1, z$; $\mathrm{v} = x-y, x-1, -z+2$) and (b) its skeleton representation with Ag, S, and P atoms. Selected interatomic distances (Å) and angles (°): Ag1–P1 2.4137(5), Ag1–S1 2.6062(5), Ag1–$\mathrm{S1^{iv}}$ 2.6084(5), Ag1–$\mathrm{S1^{v}}$ 2.6930(5), Ag1···$\mathrm{Ag1^{i}}$ separation 3.875 Å; P1–Ag1–S1 119.564(16), P1–Ag1–$\mathrm{S1^{iv}}$ 115.210(16), S1–Ag1–$\mathrm{S1^{iv}}$ 109.92(2), P1–Ag1–$\mathrm{S1^{v}}$ 134.069(17), S1–Ag1–$\mathrm{S1^{v}}$ 85.798(15), $\mathrm{S1^{iv}}$–Ag1–$\mathrm{S1^{v}}$ 85.751(15)°.

The solid-state ^{31}P CPMAS NMR spectra of **1** showed phosphorus resonance of doublet peaks (two lines) due to ^1J(Ag–P) coupling for the $\mathrm{PPh_3}$ ligand coordinating to the six equivalent silver(I) atoms. The solid-state ^{31}P NMR are consistent with the solid-state structure revealed by X-ray crystallography.

Solution ^{31}P NMR in $\mathrm{CDCl_3}$ of **1** showed one ^{31}P resonance at 9.30 ppm on the basis of coordination to the six equivalent silver(I) atoms. The ^{1}H NMR spectra of **1** showed multiplet peaks for aryl protons of the $\mathrm{PPh_3}$ ligand.

X-ray structure analysis revealed that an S_6 symmetry hexanuclear silver(I) cluster **1** was a micelle-like nanoscale object with an external diameter ca. 18 Å and an internal diameter ca. 5 Å (Fig. 1(a) and (b)), and it constructed nanoporous channel structures based on its self-assembly in the solid state (Fig. 2) [24].

The molecular structure of **1**, constructed with six 4-coordinated $\mathrm{Ag}(\mu_3\text{-S})_3\mathrm{P}$ units (Ag1, $\mathrm{Ag1^{i}}$, $\mathrm{Ag1^{ii}}$, $\mathrm{Ag1^{iii}}$, $\mathrm{Ag1^{iv}}$ and $\mathrm{Ag1^{v}}$), was stabilized with many Ag–(μ_3–S) and Ag–P bondings as well as several non-covalent, weak

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