Synthesis and Structure of a Molecular Metal Propeller with Three Leaves, a Tetranuclear Silver(I) Cluster Formed by 2-Mercaptobenzoate and Triphenylphosphine Ligands

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A tetranuclear silver(I) cluster, $[Ag(2\text{-}Hmba)(PPh_3)]_4 \cdot 0.5CHCl_3 \cdot 0.5C_2H_5OH$ **1** ($2\text{-}H_2mba$ = 2-mercaptobenzoic acid), was prepared using the silver(I)–oxygen bonding precursor $[Ag_2(R\text{-}Hpyrrld)(S\text{-}Hpyrrld)]$ ($H_2pyrrld$ = 2-pyrrolidone-5-carboxylic acid), PPh_3 and $2\text{-}H_2mba$ in an organic solvent. The crystal structure of **1** was composed of a racemic mixture of a propeller cluster having three "leaves" constructed with three $Ag(\mu_3\text{-}S)(\mu_2\text{-}S)P$ units and one $Ag(\mu_2\text{-}S)_3P$ unit. The $Hpyrrld^-$ ligand in the precursor plays an important role in the formation of **1**, although this ligand disappeared from the product.

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] In the structural viewpoint, silver(I) complexes with thiol ligands have shown a tendency to form cluster and polymer structures, whereas the corresponding gold(I) complexes have shown supramolecular arrangements of 2-coordinate linear units.[1,2]

In fact, we have recently found some light- and thermally stable silver(I)–sulfur bonding clusters with architectural beauty, e.g., an octanuclear cluster $K_{12}[Ag_8(2\text{-}mba)_{10}] \cdot 12H_2O$,[2a] a wheel-type octanuclear cluster $[H_4Ag_8(2\text{-}mpa)_6(PPh_3)_6] \cdot EtOH$ ($2\text{-}H_2mpa$ = a racemic form of 2-mercaptopropionic acid)[2b] and a "cyclohexane-chair"-type hexanuclear cluster $Na_4(Tris)_2\text{-}[Ag(mna)]_6 \cdot 10H_2O$ (H_2mna = 2-mercaptonicotinic acid, $Tris^+$ = tris(hydroxymethyl)methylammonium).[2c,d]

As to the Ag–O bonding precursors, we have recently synthesized right- and left-handed chiral helical polymers in the solid state formed by self-assembly of bis(carboxylato-*O*,*O′*) disilver(I) unit $[Ag(R\text{-}Hpyrrld)]_2$ and $[Ag(S\text{-}Hpyrrld)]_2$, respectively, and an achiral polymer sheet by self-assembly of the meso-form precursor $[Ag_2(R\text{-}Hpyrrld)(S\text{-}Hpyrrld)]$, and determined their crystal and molecular structures.[2e,f]

In the reaction of $[Ag_2(R\text{-}Hpyrrld)(S\text{-}Hpyrrld)]$ with thiol and phosphine ligands, an inorganic molecule of high nuclearity, symmetry and architectural beauty was unexpectedly found as a novel tetranuclear silver(I) cluster $[Ag(2\text{-}Hmba)(PPh_3)]_4 \cdot 0.5CHCl_3 \cdot 0.5C_2H_5OH$ **1** with a three-leaves propeller. Herein, we report synthesis and structural characterization of **1**.

Compound **1** was formed in the 1:2:2 molar-ratio reaction of $[Ag_2(R\text{-}Hpyrrld)(S\text{-}Hpyrrld)]$, PPh_3 and $2\text{-}H_2mba$ in a 1:4 mixed $CHCl_3$/EtOH solvent, and yellow plate crystals of **1** were obtained in 81.0% (0.88-g scale) yield by slow evaporation of the reaction solution at room temperature. The composition and molecular formula of **1** were consistent with elemental analysis, TG/DTA, FTIR, solution (^1H, ^{13}C, ^{31}P, and ^{109}Ag) NMR, UV–vis absorption, solid state ^{31}P CPMAS NMR and X-ray crystallography.[3,4] Synthetic reaction of **1** is shown in eq 1.

$$2\,[Ag_2(R\text{-}Hpyrrld)(S\text{-}Hpyrrld)] + 4\,PPh_3 + 4\ 2\text{-}H_2mba \rightarrow [Ag(2\text{-}Hmba)(PPh_3)]_4 + 4\ R,S\text{-}H_2pyrrld \quad (1)$$

X-ray structure analysis[4] revealed the tetranuclear silver(I) cluster (Figure 1a). The skeleton representation with Ag, S, and P atoms and the view of the skeleton through a C_3 axis of $Ag4 \cdots \mu_3\text{-}S1$ are shown in Figures 1b and 1c, respectively. The molecular structure of **1** was a propeller-type Ag_4 cluster with C_3 symmetry, in which the coordination environment around each silver(I) atom comprised three $Ag(\mu_3\text{-}S)(\mu_2\text{-}S)P$ units (Ag1, Ag2, Ag3) and one $Ag(\mu_2\text{-}S)_3P$ unit (Ag4). The molecular silver(I) propeller exhibited three "leaves" formed by three $Ag(\mu_3\text{-}S)(\mu_2\text{-}S)P$ units around the $Ag4 \cdots \mu_3\text{-}S1$ (C_3) axis. In the unit cell, a combination of four right-handed propellers and four left-handed propellers ($Z = 8$), i.e. racemic mixtures were contained. In **1**, two unequivalent silver(I) atoms, based on three trigonal pyramids of an AgS_2P core and one distorted

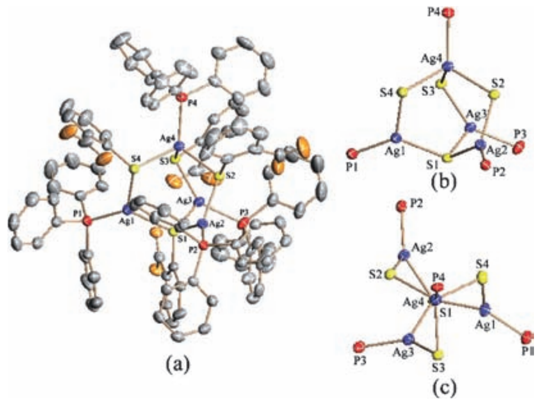

Figure 1. (a) Molecular structure of **1** and (b) its skeleton representation with Ag, S, and P atoms. Selected interatomic distances (Å) and angles (°): Ag1–S1 2.4926(15), Ag1–S4 2.5134(17), Ag2–S1 2.4881(15), Ag2–S2 2.5277(15), Ag3–S1 2.5558(16), Ag3–S3 2.4587(15), Ag4–S2 2.6514(15), Ag4–S3 2.6209(15), Ag4–S4 2.6281(17), Ag1–P1 2.3902(17), Ag2–P2 2.3908(16), Ag3–P3 2.4015(16), Ag4–P4 2.4723(16) Å; S1–Ag1–S4 97.42(5), S1–Ag2–S2 94.75(5), S3–Ag3–S1 113.74(5), S3–Ag4–S4 101.06(5), S3–Ag4–S2 107.87(5), S4–Ag4–S2 103.53(5), P1–Ag1–S1 135.52(6), P1–Ag1–S4 127.01(5), P2–Ag2–S1 132.24(5), P2–Ag2–S2 130.55(5), P3–Ag3–S1 108.72(6), P3–Ag3–S3 137.08(6), P4–Ag4–S3 119.67(5), P4–Ag4–S4 110.58(5), P4–Ag4–S2 112.43(5)°. (c) View of the skeleton through the C_3 axis. A propeller is constructed with an axis of $Ag4 \cdots \mu_3\text{-}S1$ (C_3 axis) and three leaves of $Ag(\mu_3\text{-}S)(\mu_2\text{-}S)P$ units around the axis.

tetrahedron of an AgS_3P core, were contained.

Solid-state ^{31}P CPMAS NMR of **1** showed two signals at 3.5 and 11.8 ppm due to two unequivalent P atoms, being consistent with X-ray crystallography. On the other hand, ^{31}P NMR of **1** in DMSO-d_6 at 22.9 °C showed a single peak at 9.3 ppm, suggesting that **1** in solution is under rapid motion in the NMR time scale. Correspondingly, ^{109}Ag NMR of **1** in DMSO-d_6 at 22.9 °C also showed only one signal at 993.7 ppm with reference to an external saturated $AgNO_3$ in D_2O. In the ^{31}P NMR of **1** in DMF at −50.2 °C, a shoulder peak appeared at 8.2 ppm as well as a main peak at 12.8 ppm. This fact is attributable to the restricted motion of **1** in solution at lower temperature.

As to eq 1, the $Hpyrrld^-$ ligand in the precursor plays an important role in the formation of **1**, although it disappeard from **1**. The molecular structure of **1** is in contrast to that of the previously reported monomeric tetrahedral silver(I) complex $[Ag(2\text{-}Hmba)(PPh_3)_3]$ **2**,[2g,5] which was prepared by a reaction of $[AgCl(PPh_3)_3]$ with 2-H_2mba in the presence of NaOH and, also, by the reaction of $[Ag(2\text{-}Hmba)]_n$ and PPh_3. Yellow plate crystals of **1** were also obtained in 57.9% (0.36-g scale) yield from the 1:2 molar-ratio reaction of the separately prepared intermediate $[Ag(R,S\text{-}Hpyrrld)(PPh_3)]_2$ with 2-H_2mba, suggesting that the reaction (1) proceeds via formation of this intermediate. The enantiomeric precursors $[Ag(R\text{-}Hpyrrld)]_2$ and $[Ag(S\text{-}Hpyrrld)]_2$, used instead of $[Ag_2(R\text{-}Hpyrrld)(S\text{-}Hpyrrld)]$, also gave racemic mixtures of **1**.

By changing the amounts of PPh_3 used in eq 1, the products were changed: the 1:4:2 molar-ratio reaction of $[Ag_2(R\text{-}Hpyrrld)(S\text{-}Hpyrrld)]$, PPh_3 and 2-H_2mba gave **2** as well as **1** (1.20-g scale combined yield of **1** + **2**) and the 1:6:2 molar-ratio reaction gave only **2** as colorless prism crystals in 64.5% (1.46-g scale) yield.

Unique compound **1** can be compared with the previously reported tetranuclear silver(I) clusters, e.g., $[Ag_4(SPh)_4(PPh_3)_4]$ (SPh^- = benzenethiolate) with a highly distorted chair structure,[6a] $[\{AgI[P(C_6H_{11})_3]\}_4]$ with a standard cubane tetramer,[6b] $[Ag_4(\mu\text{-dppm})_4(\mu\text{-i-mnt})_2]$ (i-mnt^{2-} = 2,2-dicyano-1,1-ethylenedithiolate; dppm = bis(diphenylphosphino)methane) with a distorted square planar structure,[6c] $[Ag_4(dppm)_4(NO_3)_2](PF_6)_2$ consisting of two $[Ag_2(dppm)_2]^{2+}$ subunits bound together by two bridging nitrate anions,[6d] $[Ag_4Cl_4(dppm)_2]$ consisting of discrete neutral tetranuclear units with a center of symmetry coinciding with a crystallographic center[6e] and $[(AgPPh_3)_4(\mu\text{-SC}\{O\}R)_4]$ (R = Me or Ph) consisting of eight-membered Ag_4S_4 rings.[6f]

In summary, the tetranuclear silver(I) cluster **1** with a three-leaves propeller was isolated, and its crystal and molecular structures determined. The present reaction would be applicable for construction of novel silver(I) clusters using some aromatic and aliphatic thiol ligands, instead of 2-H_2mba.

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3 **1**: To 0.472 g (1.00 mmol) of $[Ag_2(R\text{-}Hpyrrld)(S\text{-}Hpyrrld)]$[2e] suspended in 50 mL of 1:4 mixed $CHCl_3$/EtOH was added 0.525 g (2.00 mmol) of PPh_3, followed by stirring for 1 h. To the solution was added 0.308 g (2.00 mmol) of 2-H_2mba, followed by stirring for 5 min. After filtering the yellow solution through a folded filter paper (Whatman #5), the filtrate was slowly evaporated at room temperature. After one day yellow plate crystals were formed, which were collected on a membrane filter (JG 0.2 μm), washed with water (50 mL times 2), EtOH (50 mL times 2) and ether (50 mL times 2), and thoroughly dried in vacuo for 2 h. The pale yellow powder obtained in 0.88 g (81.0%) yield was soluble in DMF and DMSO, and insoluble in water, EtOH and ether. Complex **1** in $CHCl_3$ and CH_2Cl_2 was unstable and the PPh_3 ligand readily dissociated to precipitate a solid of $[Ag(2\text{-}Hmba)]_n$. Anal. Found: C, 56.12; H, 3.66%. Calcd for $C_{101.5}H_{83.5}O_{8.5}S_4P_4Ag_4Cl_{1.5}$ or $[Ag(2\text{-}Hmba)(PPh_3)]_4 \cdot 0.5CHCl_3 \cdot 0.5C_2H_5OH$: C, 56.02; H, 3.87%. TG/DTA data: decomposition began around 170 °C with an exothermic peak at 272 °C and endothermic peaks at 76, 248, and 294 °C. Prominent IR bands at 1800–400 cm^{-1} region (KBr disk): 1711vs, 1585m, 1552w, 1479m (PPh_3), 1450w, 1433vs (PPh_3), 1385m, 1271m, 1223w, 1095m (PPh_3), 1036m, 997w, 741vs (PPh_3), 692vs (PPh_3), 642w, 517s (PPh_3), 503m cm^{-1}. ^1H NMR (DMSO-d_6, 24.0 °C): δ 1.07 (EtOH), 3.46 (EtOH), 6.52 (1H, t, H14), 6.82 (1H, t, H15), 7.13–7.40 (15H, m, Aryl and $CHCl_3$), 7.49 (1H, d, H13), 7.58 (1H, d, H16). ^{13}C NMR (DMSO-d_6, 24.2 °C): δ 18.4 (EtOH), 55.9 (EtOH), 79.0 ($CHCl_3$), 122.6 (C15), 128.5 ($^3J_{CP}$ 9.1 Hz, PPh_3), 129.5 (C11), 129.8 (C14), 130.0 (s, PPh_3), 131.5 ($^1J_{CP}$ 26.5 Hz, PPh_3), 132.2 (C16), 133.0 ($^2J_{CP}$ 16.6 Hz, PPh_3), 136.7 (C13), 143.8 (C12), 168.9 (C17). ^{31}P NMR (DMSO-d_6, 22.9 °C): δ 9.3. ^{31}P NMR (DMF, −50.2 °C): δ 8.2 (shoulder), 12.8 (main). ^{109}Ag NMR (DMSO-d_6, 22.9 °C): δ 993.7. ^{31}P CPMAS NMR (25.0 °C): δ 3.5 ($J_{Ag\text{-}P}$ 476.4 Hz), 11.8 ($J_{Ag\text{-}P}$ 297.7 Hz). UV–vis (DMSO): 264 nm (ε 1.42×10^5).

4 The intensity data were collected at 90 K on a Bruker SMART/APEX CCD diffractometer. The structure was solved by direct methods (SHELXTL version 5.10), and refined by a full-matrix least-squares on F^2. Crystal data for **1**: $C_{102}H_{86}O_9S_4P_4Ag_4$, $M_r = 2193.31$, monoclinic, space group $C2/c$, $a = 37.626(8)$, $b = 29.464(6)$, $c = 25.400(5)$ Å, $\beta = 132.258(3)°$, $V = 20841(8)$ Å^3, $Z = 8$, $D_{calcd} = 1.364$ $g cm^{-3}$, $\mu = 0.934$ mm^{-1}, 124968 reflections collected, 26002 independent ($R_{int} = 0.0760$), $R_1 = 0.0629$, $wR_2 = 0.2177$ for $I > 2\sigma(I)$, $R_1 = 0.0893$, $wR_2 = 0.2362$, GOF = 1.041 for all data. The solvated EtOH was highly disordered. The details of the crystal data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 259303.

5 **2**: ^{31}P CPMAS NMR (25.0 °C): δ 3.9 ($J_{Ag\text{-}P}$ 478.5 Hz, $J_{P\text{-}P}$ 59.6 Hz). UV–vis ($CHCl_3$): 231 nm (ε 1.12×10^5), 245 nm (ε 7.52×10^4), 252 nm (ε 7.85×10^4), 258 nm (ε 7.31×10^4). Other data are shown in Ref. 2g.

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