Synthesis and Structure of a Molecular Metal Wheel, an Octanuclear Silver(I) Cluster Formed by Racemic 2-Mercaptopropionic Acid and Triphenylphosphine Ligands

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The molecular structure of $[H_4Ag_8(2\text{-mpa})_6(PPh_3)_6]\cdot EtOH$ **1** (2-H_2mpa=a racemic form of 2-mercaptopropionic acid), prepared by a 1 : 5 molar-ratio reaction of polymeric $[Ag(2\text{-Hmpa})]_n$ **2** suspended in EtOH with PPh_3 in $CHCl_3$, was a wheel-type octanuclear silver(I) cluster; the rim of the wheel was constructed with the outside six $Ag(\mu_3\text{-}S)_2P$ units and the axle was formed by the central two $Ag(\mu_3\text{-}S)_3$ units with Ag–Ag separation, 3.122 Å.

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 structures, whereas the corresponding gold(I) complexes have shown supramolecular arrangements.[2] In this work, a molecule of high nuclearity, symmetry, and architectural beauty was found in the novel silver(I) complex $[H_4Ag_8(2\text{-mpa})_6(PPh_3)_6]\cdot EtOH$ **1** formed with racemic 2-mercaptopropionic acid (2-H_2mpa) and PPh_3 ligands.

Compound **1** was prepared by a 5 : 1 molar-ratio reaction in a 1 : 1 mixed EtOH/$CHCl_3$ solvent of PPh_3 with the precursor $[Ag(2\text{-Hmpa})]_n$ **2**,[3] which was obtained from a stoichiometric reaction in aqueous media of Ag_2O and 2-H_2mpa in the presence of aqueous NaOH. Pale yellow block crystals of **1**, sparingly soluble in DMSO and DMF, and insoluble in water and most organic solvents, were obtained in 76.3% (0.30 g scale) yield by vapor diffusion of the mixed EtOH/$CHCl_3$ solution with external ether in a sealed flask. The same crystals were also obtained using a mixed EtOH/CH_2Cl_2 solution.

The composition and molecular formula of **1** were consistent with elemental analysis, TG/DTA, FTIR, ^1H and ^{31}P NMR, and solid state ^{31}P CPMAS NMR.[4] Synthetic reactions of **1** are shown in eqs. (1) and (2).

$$4Ag_2O + 8\ 2\text{-}H_2mpa \rightarrow 8/n[Ag(2\text{-Hmpa})]_n + 4\ H_2O \quad (1)$$

$$8/n[Ag(2\text{-Hmpa})]_n + 6\ PPh_3 \rightarrow [H_4Ag_8(2\text{-mpa})_6(PPh_3)_6] + 2\ 2\text{-}H_2mpa \quad (2)$$

The solid FTIR spectrum of **1** showed the disappearance of the S–H stretching band around 2560 cm^{-1} due to the SH group in the free ligand, suggesting the metal–S bond formation. Broad bands around 1719 cm^{-1} and multiple weak bands in the 3000–2500 cm^{-1} region are attributed to the presence of protonated carboxyl groups. The 2-mpa^{2-} and PPh_3 ligands coordinating to the silver(I) center were also confirmed with ^1H and ^{31}P NMR, respectively. The four protons in **1** were not exchanged with other cations such as R_4N^+ (R = Bu, Et, Me).

X-ray structure analysis[5] revealed the octanuclear silver(I) cluster depicted in Figure 1(a). The crystals of **1** contained one solvated EtOH molecule per one Ag_8 cluster molecule. The methyl, methyne and carboxyl groups of the 2-mpa^{2-} ligand and the solvated EtOH were disordered and, thus, the structure was refined based on 50–50% occupancies. The position of the four protons in **1** and the hydrogen bonding interaction among the clusters were not confirmed due to the disordered state of the 2-mpa^{2-} ligand.

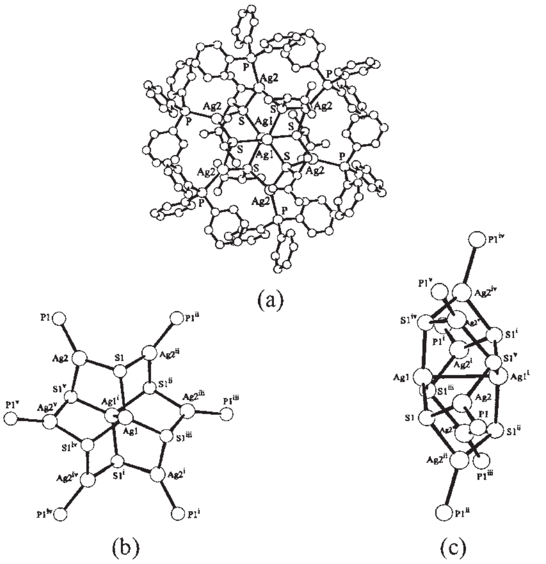

Figure 1. (a) Top view of molecular structure of **1** and (b) its skeleton representation with Ag, S and P atoms (symmetry operations i; $-x+2/3,\ -y+4/3,\ -z+1/3$, ii; $x-y+2/3,\ x+1/3,\ -z+1/3$, iii; $-y+1,\ x-y+1,\ z$, iv; $-x+y,\ -x+1,\ z$, v; $y-1/3,\ -x+y+1/3,\ -z+1/3$). Selected interatomic distances (Å) and angles (°): Ag1–Ag1^{i} 3.122(1), Ag1–S1 2.487(1), Ag2–S1 2.497(1), Ag2–S1^{v} 2.460(1), Ag2–P1 2.392(1) Å; Ag1^{i}–Ag1–S1 86.47(3), Ag1–S1–Ag2 108.30(4), Ag1–S1–Ag2^{ii} 112.33(5), Ag2–S1–Ag2^{ii} 98.91(4), S1–Ag2–S1^{v} 98.43(5), S1–Ag1–S1^{iii} 119.625(6), S1–Ag2–P1 124.28(4), S1^{v}–Ag2–P1 134.57(4)°. (c) Side view of the skeleton representation. Six Ag atoms of the rim are arrayed on a vertical plane across the center of the Ag1–Ag1^{i} axis.

The molecular structure of **1** was a wheel-type cluster $[H_4Ag_8(2\text{-mpa})_6(PPh_3)_6]$, in which the coordination environment around each silver(I) atom comprised six $Ag(\mu_3\text{-}S)_2P$ units (Ag2, Ag2^{i}, Ag2^{ii}, Ag2^{iii}, Ag2^{iv}, Ag2^{v}) and two $Ag(\mu_3\text{-}S)_3$ units (Ag1, Ag1^{i}). The molecular silver wheel was composed of a rim formed by six $Ag(\mu_3\text{-}S)_2P$ units [Ag2–S1 2.497(1) Å, Ag2–S1^{v} 2.460(1) Å, Ag2–P1 2.392(1) Å] and an axle formed by two

Ag(μ_3-S)$_3$ units [Ag1–S1 2.487(1) Å, Ag1–S1^{iii} 2.487(1) Å, Ag1–S1^{iv} 2.487(1) Å]. The octanuclear unit in the solid state is centrosymmetric and the skeleton with Ag, S and P atoms has idealized S_6 symmetry (Figure 1(b)). The rim of the wheel has a diameter of approximately 7.5 Å. Six Ag atoms of the rim are arrayed on a vertical plane across the center of the Ag1–Ag1^{i} axis (Figure 1(c)); on the left (Ag1) side of the vertical plane, three 2-mpa^{2-} ligands were arranged with the *R*-forms, while on the right (Ag1^{i}) side the other three ligands were arranged with the *S*-forms. Since the *R*- and *S*-forms of the 2-mpa^{2-} ligand in **1** are alternately arrayed, this structure will not be formed with only the chiral ligands.

Two silver centers Ag2 and Ag2^{ii} in the rim are linked by μ_3-S1 atom [Ag2–S1–Ag2^{ii} angle 98.91(4)°], which was also connected to the Ag1 atom of the axle [Ag1^{i}–Ag1–S1 angle 86.47(3)°]. The Ag1–Ag1^{i} separation in the axle was 3.122(1) Å, which is intermediate between the Ag–Ag separation found in the metallic silver (2.88 Å)[6a] and twice the van der Waals radii for silver (3.44 Å),[6b] suggesting an existence of weak metal-metal interactions.[7] In the Ag(μ_3-S)$_2$P unit, four atoms (Ag2, S1, S1^{v}, P1) are almost coplanar [S1–Ag2–S1^{v} 98.43(5)°, S1–Ag2–P1 124.28(4)°, S1^{v}–Ag2–P1 134.57(4)°; their sum 357.3°] and in the central Ag(μ_3-S)$_3$ unit, four atoms (S1, S1^{iii}, S1^{iv}, Ag1) are coplanar [S1–Ag1–S1^{iii} angle 119.625(6)°, S1–Ag1–S1^{iv} 119.625(6)°, S1^{iv}–Ag1–S1^{iii} 119.625(6)°; their sum 358.9°].

The molecular silver(I) wheel **1** with PPh$_3$ ligand is unique and quite different from the recent octanuclear metal clusters with sulfur donor atom and without the phosphine ligand; e.g., $K_{12}[Ag_8(2\text{-mba})_{10}]\cdot 12H_2O$(2-H$_2$mba = 2-mercaptobenzoic acid) consisting of two butterfly-type Ag$_4$S$_4$ subunits bridged by two μ_3-S atoms,[2c] and $[\{Ag_8(\mu_4\text{-}SC_2H_4NH_3)_6Cl_6\}Cl_2]_n$ with a one-dimensional chain structure[8a] and $[\{Cu_8Cl_6(SC_2H_4NH_3)_6\}Cl_2]_n$,[8b] both with an M$_4$($\mu_4$-S) bridge coordination mode. As a molecular metal wheel, but without the axle, a molecular ferric wheel $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$ of ~12 Å in diameter[9a] and a golden wheel $[\{CSAu(PPh_3)\}_6]$ formed on benzenehexathiol[9b] have been known.

Complex **1** is also in marked contrast to the previously found silver(I) complexes with the aromatic thiols and PPh$_3$ ligands, e.g., [Ag(2-Hmba)(PPh$_3$)$_3$][2e] and [Ag(2-Hmna)(PPh$_3$)$_n$] (2-H$_2$mna = 2-mercaptonicotinic acid; $n = 2$ and 3)[2f], which are monomeric silver(I) complexes with distorted tetrahedral geometries without any intermolecular interactions.

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3 **2:** The relatively light-unstable yellow powder obtained in 4.09 g (95.9%) yield was soluble in DMSO and DMF, but insoluble in water and most organic solvents. Anal. Found: C, 16.85; H, 2.16%. Calcd for C$_3$H$_5$O$_2$SAg or [Ag(2-Hmpa)]: C, 16.92; H, 2.37%. TG/DTA data: no weight loss was observed before decomposition; decomposition began around 161 °C with endothermic peaks at 206 and 215 °C. Prominent IR bands at 1800–400 cm^{-1} region (KBr disk): 1686 vs, 1558 m, 1446 s, 1372 s, 1322 s, 1237 s, 1178 s, 1068 m, 989 m, 851 m, 779 m, 661 m, 506 m cm^{-1}. ^{1}H NMR (DMSO-d_6, 22.6 °C): δ 1.51 (3H, d, J 6.9 Hz, CH$_3$), 3.74 (1H, q, J 6.9 Hz, CH), 12.42 (1H, br, CO$_2$H). ^{13}C NMR (DMSO-d_6, 26.8 °C): δ 26.2 (CH$_3$), 40.6 (CH), 177.1 (CO$_2$H). ^{109}Ag NMR (DMSO-d_6, 23.3 °C, referenced to an external AgNO$_3$ aqueous solution): δ 896.6.

4 a) **1:** To 0.21 g (1.00 mmol) of [Ag(2-Hmpa)]$_n$ suspended in 10 mL EtOH was added a colorless solution of 1.33 g (5.00 mmol) of PPh$_3$ dissolved in 10 mL CHCl$_3$, followed by stirring for 2 h. After filtering the pale yellow solution through a folded filter paper (Whatman No. 2), a vapor diffusion using the filtrate as an inner solution and ether as an external solvent was performed at room temperature. Pale yellow block crystals were collected on a membrane filter (JG 0.2 μm), washed with ether (50 mL × 2), thoroughly dried by suction and then dried in vacuo for 2 h. The pale yellow powder obtained in 0.30 g (76.3%) yield was sparingly soluble in DMSO and DMF, and insoluble in water and most organic solvents. Anal. Found: C, 49.22; H, 3.86%. Calcd for $C_{128}H_{124}O_{13}P_6S_6Ag_8$ or $[H_4Ag_8(mpa)_6(PPh_3)_6]\cdot EtOH$: C, 49.41; H, 4.02%. TG/DTA data: decomposition began around 174 °C with exothermic peaks at 183, 201 and 299 °C and endothermic peaks at 193 °C. Prominent IR bands at 1800–400 cm^{-1} region (KBr disk): 1719 m, 1637 m, 1617 m, 1571 m, 1479 m (PPh$_3$), 1435 vs (PPh$_3$), 1390 m, 1365 m, 1308 m, 1217 m, 1161 m, 1119 m, 1096 s (PPh$_3$), 1070 m, 1027 m, 997 m, 847 m, 744 vs (PPh$_3$), 694 vs (PPh$_3$), 519 vs (PPh$_3$), 501 s (PPh$_3$), 434 m cm^{-1}. ^{1}H NMR (DMSO-d_6, 21.7 °C): δ 1.27 (3H, br, CH$_3$), 3.73 (1H, br, CH), 7.32–7.46 (15H, m, Ph). ^{31}P NMR (DMSO-d_6, 22.6 °C): δ 5.69 (br). Solid state ^{31}P CPMAS NMR (23.4 °C, referenced to (NH$_4$)$_2$HPO$_4$ δ 1.60): δ 9.80, 13.35 (splitting due to ^{1}J(Ag–P) coupling[4b]). ^{13}C and ^{109}Ag NMR measurements were unsuccessful due to insufficient concentration. b) G. A. Bowmaker, E. N. de Silva, P. C. Healy, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, **1999**, 901.

5 The intensity data were collected at 103 K on a Rigaku RAXIS-RAPID Imaging Plate diffractometer. The structures were solved by direct methods followed by subsequent difference Fourier calculation and refined by a full-matrix least-squares procedure using TEXSAN package.[10] Crystal data: $C_{128}H_{124}O_{13}S_6P_6Ag_8$, $M = 3111.53$, trigonal, R-3 (No. 148), $a = 18.9819(5)$ Å, $c = 29.9327(4)$ Å, $V = 9340.2(4)$ Å^3, $Z = 3$, $D_{calc} = 1.659$ g cm^{-3}, $\mu = 14.64$ cm^{-1}, λ(Mo Kα) = 0.71069 Å, $F(000) = 4674.00$. Refinement on 6044 data with $I > -3.0\sigma(I)$, $2\theta < 60.03°$ gave $R_{int} = 0.028$, $R = 0.072$, $R_w = 0.158$, $R1 = 0.056$ ($I > 2.0\sigma(I)$) and GOF = 1.44.

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10 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation 1985 & 1999.