Synthesis and Crystal Structure of a Water-soluble, Anionic Octanuclear Silver(I) Cluster Formed by 2-Mercaptobenzoic Acid (H_2mba); $K_{12}[Ag_8(mba)_{10}]\cdot 12H_2O$

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We have prepared a novel water-soluble silver(I) complex showing effective antibacterial activities $K_{12}[Ag_8(mba)_{10}]\cdot 12H_2O$ (**1a**, H_2mba = 2-mercaptobenzoic acid) from the Ag_2O : H_2mba : KOH = 1 : 4 : 8 molar ratio reaction in aqueous media and determined its crystal structure. The X-ray crystallography revealed that **1a** was a discrete, anionic octanuclear silver(I) cluster consisting of two butterfly-type Ag_4S_4 subunits bridged by two μ_3-S atoms.

In the medicinally or pharmaceutically active compounds of silver(I) and gold(I), most of the complexes formed by thiol ligands are harder to crystallize and are believed to be polymeric.[1] We have so far synthesized and characterized a class of silver(I) and gold(I) complexes with thiol ligands, i.e., 2-mercaptobenzoic acid (H_2mba) and thiomalic acid (H_3tma), such as $\{M[Ag(mba)]\cdot nH_2O\}_n$ (**2a**, M = H, n = 0; **2b**, M = Na, n = 1; **2c**, M = K, n = 2),[2a] $\{Na[Ag(Htma)]\cdot 0.5H_2O\}_n$ **3**,[2b,2c] $\{Na_2[Au(tma)]\cdot 1.75\ H_2O\}_n$ **4**,[1,2d,2f,3] and $Na_3[Au(mba)_2]\cdot 5H_2O$ **5**.[2e,2f] The polymeric or oligomeric silver(I) complexes **2a**, **2b**, **2c** and **3** have displayed effective antimicrobial activities against selected bacteria, yeast and mold.[2a,2b] The water-soluble salt **2b** has been commercialized as an antimicrobial agent.[2g] Except **5**, all of the compounds were difficult to crystallize.

Since our first report in 1995,[2a] considerable efforts have been made to get crystals of the water-soluble silver(I) complex **2b**, prepared from a reaction of the $AgNO_3$: H_2mba : NaOH = 1 : 1 : 2 molar ratio. In this work, we found that the potassium and sodium salts of silver(I) 2-mercaptobenzoate $M_{12}[Ag_8(mba)_{10}]\cdot nH_2O\cdot m$MeOH (**1a**, M = K, n = 12, m = 0; **1b**, M = Na, n = 5, m = 2), obtained from reactions of Ag_2O : H_2mba : MOH = 1 : 4 : 8 molar ratio in aqueous solution, were crystallized from a solvent mixture of water/methanol in a sealed flask. The compounds **1a** and **1b** also showed effective antibacterial activities similar to those of **2a** and **2b**,[2h] and the complexes **1a** and **1b** had a tendency to transformation via **2a** to **2b** and **2c**, respectively, by treatment with aqueous H_2SO_4 and then aqueous MOH. Although crystallization of the original complexes **2a**, **2b** and **2c** themselves is still difficult, we were successful for X-ray analysis of **1a** with an unexpected composition and a novel cluster structure. Herein, we report the synthesis and structure of **1a**.

The molecular formula of **1a** with 12 hydrated water isolated in 84.2% (6.01 g) yield was consistent with all data of elemental analysis, TG/DTA, FT-IR and ^{1}H, ^{13}C and ^{109}Ag NMR spectroscopies.[4,5] The formation of **1a** is shown in Eq 1.

$$4\ Ag_2O + 10\ H_2mba + 12\ KOH \rightarrow K_{12}[Ag_8(mba)_{10}] + 16\ H_2O \qquad (1)$$

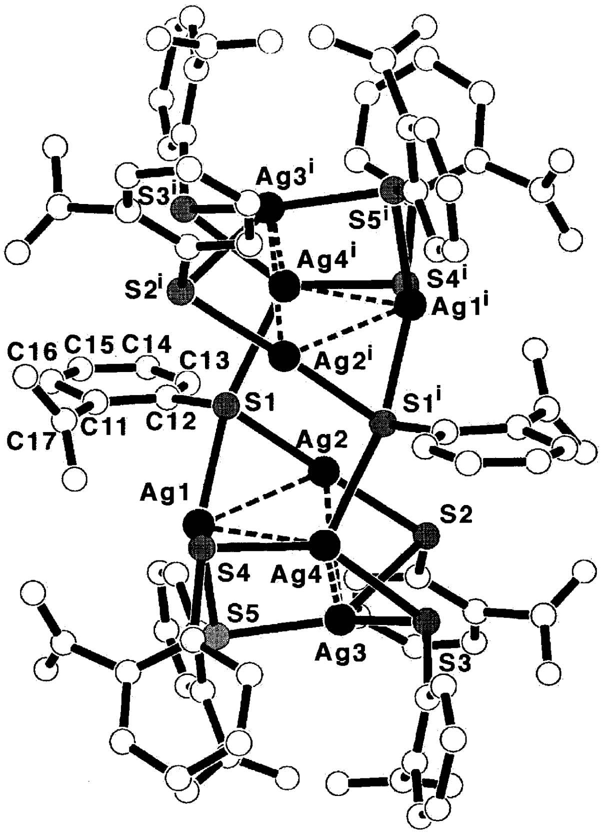

Figure 1. Molecular structure of complex **1a** (symmetry operation i; -x, -y, -z). Potassium ions, H_2O molecules and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): S1-Ag1 2.569(7), S1-Ag2 2.385(7), S1-Ag4^i 2.685(7), Ag1···Ag2 3.155(4), Ag1-S4 2.549(8), S4-Ag4 2.447(7), Ag1···Ag4 2.974(4), Ag4···Ag3 2.875(4), Ag4-S3 2.491(8), Ag3-S3 2.489(8), Ag2···Ag3 3.048(4), S5-Ag3 2.451(8), Ag1-S5 2.503(7), Ag2-S2 2.376(9), Ag3-S2 2.77(1), S1-Ag1-S4 122.6(2), S1-Ag1-S5 122.5(3), S4-Ag1-S5 110.4(3), S1-Ag2-S2 173.2(3), S2-Ag3-S3 91.4(3), S2-Ag3-S5 123.0(3), S3-Ag3-S5 142.3(3), S1^i-Ag4-S3 97.1(2), S1^i-Ag4-S4 119.6(2), S3-Ag4-S4 143.2(3).

The solid FT-IR measurements showed (1) an appearance of a strong broad band at ~ 3450 cm^{-1} due to the vibrations of hydrated water, (2) a disappearance of the S-H stretching band at ~ 2560 cm^{-1} due to the SH group in the free H_2mba, suggesting the Ag-S bond formation, and (3) a shift to splitting bands at ~ 1563 cm^{-1} from one very strong carbonyl stretching band at ~ 1680 cm^{-1} for the free H_2mba, upon the complexation. The ^{109}Ag NMR of **1a** measured in D_2O showed two resonances at 508.7 and 927.8 ppm as sharp and broad signals, respectively, with reference to an external saturated $AgNO_3$ in D_2O by the substitution method, indicating the presence of two unequivalent silver(I) atoms.

The molecular structure of **1a** (Figure 1) was determined with single-crystal X-ray diffraction analysis.[6] The complex **1a** was a discrete monomer consisting of an anionic, octanuclear cluster $[Ag_8(mba)_{10}]^{12-}$, which was composed of two butterfly-type Ag_4S_4 cores. The octanuclear unit in the solid-state was centrosymmetric. The Ag-Ag separations in the Ag_4S_4 cores ranged from 2.875(4) to 3.155(4) Å, which are intermediate between the Ag-Ag separation found in the metallic silver (2.88 Å)[7a] and twice the van der Waals radii for silver (3.44 Å),[7b] suggesting an existence of weak metal-metal interactions.[8] In the butterfly Ag_4S_4 core, the four μ_2-S atoms (S2, S3, S4, S5) of the four ligands were bridged between two silver(I) atoms. The two Ag_4S_4 butterfly cores were linked by two μ_3-S atoms (S1, S1^i) of the two mba^{2-} ligands. None of the carboxyl groups participated in the coordination to silver(I) centers. Six potassium ions in the half-unit were observed. The coordination environment around each silver(I) atom comprised three 3-coordinate (Ag1, Ag3, Ag4) and one 2-coordinate (Ag2) silver(I) geometries. The molecular structure of **1a** is novel and quite different from those of the recent polymeric octanuclear metal clusters with sulfur donor atoms; e.g., $[\{Ag_8(\mu_4\text{-}SC_2H_4NH_3)_6Cl_6\}Cl_2]_n$ with one dimensional chain structure [9a] and $[\{Cu_8Cl_6(SC_2H_4NH_3)_6\}Cl_2]_n$,[9b] both with an $M_4(\mu_4\text{-}S)$ bridge coordination mode.

References and Notes

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4 Synthesis of **1a**: To a stirred suspension of 6.17 g (40.0 mmol) of H_2mba ligand in 20 mL water was added 80.0 mL of 1.0 M aqueous KOH solution (80.0 mmol), followed by adding 2.32 g (10.0 mmol) of solid Ag_2O. The black suspension was stirred overnight at room temperature to give a clear yellow solution. The yellow filtrate, obtained by passing through a membrane filter (JV 0.1 μm), was added dropwise to 300 mL of 1 : 2 mixed solution of ethanol/diethyl ether, giving a yellow oil, which was rinsed three times with 150 mL of the 1 : 2 mixed solution of ethanol/diethyl ether. The yellow oil was dissolved in 5 mL water, followed by adding 500 mL methanol. After filtration of the yellow solution through a membrane filter (JV 0.1 μm), the filtrate in a sealed flask was allowed to stand for 10 days at room temperature. After one day, pale yellow needle crystals began to form. After 10 days, the crystals collected on a membrane filter (JG 0.2 μm) were washed with (50 mL x 2) methanol and (50 mL x 2) diethyl ether, thoroughly dried by suction and then dried in vacuo for 2 h. The light- and thermally-stable yellow powder of **1a** obtained in 6.01 g (84.2%) yield was hygroscopic and soluble in water, but insoluble in most organic solvents. From similar work-up, the sodium salt **1b** was obtained in 3.45 g (49.0%) yield.

5 **1a**: Anal. Found: C, 27.54; H, 2.37%. Calcd for $C_{70}H_{64}O_{32}S_{10}Ag_8K_{12}$ or $K_{12}[Ag_8(mba)_{10}]\cdot 12H_2O$: C, 27.39; H, 2.10%. TG/DTA data: weight loss of 6.98% was observed below 264 ˚C with an endothermic peak at 46 ˚C (calcd for 12 hydrated water, 7.04%); decomposition began around 306 ˚C with exothermic peaks at 306 and 390 ˚C. IR (KBr disk): 1563vs, 1462m, 1427s, 1398s, 1253w, 1150w, 1121w, 1054m, 1032w, 842w, 755m, 709m, 652w, 452w cm^{-1}. ^{1}H NMR (399.65 MHz, 25˚ C, D_2O): δ 6.74 (1H, dd, H14, *J* 7.57 Hz), 6.98 (1H, dd, H15, *J* 7.45 Hz), 7.09 (1H, d, H16, *J* 7.57 Hz), 7.44 (1H, d, H13, *J* 7.81 Hz) ppm. ^{13}C NMR (100.40 MHz, 25 ˚C, D_2O): δ 126.4 (C15), 128.0 (C16), 130.3 (C14), 137.0 (C12), 138.4 (C13), 145.5 (C11), 181.1 (C17) ppm. ^{109}Ag NMR (18.45 MHz, 25 ˚C, D_2O): δ 508.7, 927.8 ppm. Numbering of ^{1}H and ^{13}C NMR resonances is designated to Figure 1.

6 Crystal data for **1a:** $C_{70}H_{40}O_{20}S_{10}K_{12}Ag_8$. M = 2853.8, triclinic, a = 13.178(9) Å, b = 17.422(9) Å, c = 13.125(5) Å, α = 103.08(4)˚, β = 95.43(6)˚, γ = 68.88(5)˚, V = 2738(3) Å^3, space group $P\bar{1}$(#2), Z = 1, $F(000)$ = 1728.0, Mo-Kα radiation, room temperature. D_{cal} = 2.18 g cm^{-3}. μ = 28.39 cm^{-1}. A pale yellow needle crystal of **1a** (0.3 x 0.1 x 0.1 mm^3) was sealed in a glass capillary. All crystallographic measurements were made using RIGAKU AFC5S diffractometer. The number of solvated molecules was determined with elemental analysis and TG/DTA. The solvated water was highly disordered. The structure was solved by the heavy atom Patterson method and refined by full-matrix least-squares using TEXSAN software package.[10] The R and R_w factors after refinement using 2825 observed reflections ($I > 2\sigma(I)$) among 12557 unique reflections were 0.072 and 0.086, respectively. Only Ag, K and S atoms were refined with anisotropic thermal factors. All other atoms were refined with isotropic temperature factor.

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10 TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation 1985 and 1992.