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# Two birds with one stone: Anion templated ball-shaped $Ag_{56}$ and disc-like $Ag_{20}$ clusters

**Di Sun,*[a] Hua Wang,[a] Hai-Feng Lu,[a] Sheng-Yu Feng,[a] Zhen-Wei Zhang,[b] Guo-Xin Sun,[b] Dao-Feng Sun[a]**

[a] *Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China. E-mail: dsun@sdu.edu.cn. Fax: +86-531-88364218.*

[b]*School of Chemistry and Chemical Engineering, University of Jinan, 106 Jiwei Road, 250022 Jinan, PR China.*

## (1) Experiment details

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were recorded on a Nicolet AVATAT FT-IR360 spectrometer as KBr pellets in the frequency range of 4000-400 $cm^{-1}$. The elemental analyses (C, H, N, S contents) were determined on a Vario EL □ analyzer. Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with Cu $K_{\alpha}$ radiation equipped with an X'Celerator detector. Photoluminescence spectra were measured on a Hitachi F-7000 Fluorescence Spectrophotometer equipped with dewar flask with a Suprasil quartz cold finger.

**(2) Synthesis of 1 and 2**

Reaction of $AgSBu^t$ (59 mg, 0.3 mmol) and AgOAc (50 mg, 0.3 mmol) in methanol-ethanol-DMF (v:v:v = 2:4:3, 9 mL) under the ultrasonic condition (160W, 40 KHz, 40 min, room temperature) initially produced a great deal of white precipitation, after 20 min ultrasonication, the white precipitation became pale yellow cloudy solution, which gradually became clear red soultion after another 20 min ultrasonication. The red solution was filtered and the filtrate was evaporated slowly in air at room temperature. The red crystals **1** and colorless **2** were manually isolated one by one and washed with methanol and dried at room temperature. Yield: 37 % for **1** and < 5% for **2**. Anal. Calcd for **1**: $C_{121}H_{256}Ag_{56}S_{33}N_6O_{27}$: C, 15.58; H, 2.77; N, 0.90; S, 11.35. Found: C, 15.11; H, 3.24; N, 1.35; S, 10.65. Selected IR peaks ($cm^{-1}$): $\nu_{as}$ 1562 (C=O of $OAc^-$) and $\nu_s$ 1411 (C=O of $OAc^-$).

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## (3) X-ray Crystallography

Single crystal of the clusters **1** and **2** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for **1** and **2** were collected on a Bruker-AXS CCD single-crystal diffractometer with graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 20 frames each, each frame corresponds to a 0.3° scan in 5 s, followed by spot integration and least-squares refinement. Data were measured using ω scans of 0.3° per frame for 40 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.[1] Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[1] The highest possible space group was chosen for **1** and **2**. Using Olex2,[2] the structure was solved with the Superflip[3] structure solution program using Charge Flipping and refined with the XL[4] refinement package using Least Squares minimisation. All structures were examined using the Addsym subroutine of PLATON[5] to assure that no additional symmetry could be applied to the models.

For **1**, the relatively high R1 and wR2 values in this structure are partially due to the total instability of the crystals towards loss of initially accumulated solvent and weak diffraction, and in part due to disordering of Ag atoms as well as the solvents and anions. It was not possible to improve present convergence, although more then eight different datasets were collected in total (and more then 20 crystals were examined) under different conditions, using either SMART Apex II CCD and Xcalibur, Eos, Gemin, varying the crystal size, exposition and data reduction parameters.

Nine Ag atoms (Ag1-Ag9) were disordered and refined with splitting mode. The occupancy factors of the disordered Ag atoms as follows:

Ag1A:Ag1B 0.95:0.05;

Ag2A:Ag2B 0.75:0.25;

Ag3A:Ag3B:Ag3C:Ag3D 0.40:0.15:0.05:0.40;

Ag4A:Ag4B 0.10:0.90;

Ag5A:Ag5B:Ag5C:Ag5D 0.15:0.60:0.20:0.05;

Ag6A:Ag6B:Ag6C 0.10:0.70:0.20;

Ag7A:Ag7B:Ag7C:Ag7D 0.20:0.55:0.15:0.10;

Ag8A:Ag8B:Ag8C:Ag8D 0.50:0.30:0.15:0.05;

Ag9A:Ag9B:Ag9C:Ag9D 0.40:0.40:0.10:0.10;

To assist the refinement of **1**, several restraints were applied: (1) some C-C and C-S bonds restrained to be similar (DFIX); (2) thermal parameters on adjacent atoms in disordered moieties were restrained to be similar (DELU, SIMU and ISOR).

For **2**, due to relatively large thermal motion of the tert-butyl groups (C6-C8), the *U*eq of C atoms on this tert-butyl group were restrained by using the command SIMU. Ag9 atom was disordered and refined with splitting mode. The occupancy factor of the disordered Ag atoms is Ag9:Ag9' 0.70:0.30.

1. Bruker. *SMART, SAINT and SADABS.* Bruker AXS Inc., Madison, Wisconsin, USA, 1998.

2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.

3. J. Appl. Cryst. (2007) 40, 786-790

4. XL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122.

5. A. L. Spek, Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.

## (4) Table S1 Crystal data and structure refinement for 1 and 2.

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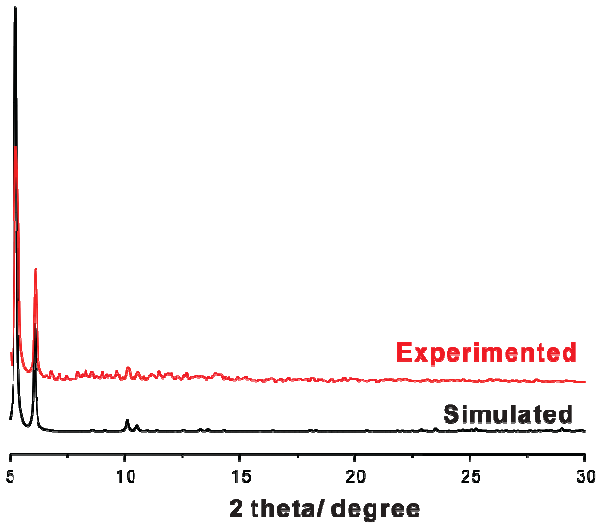
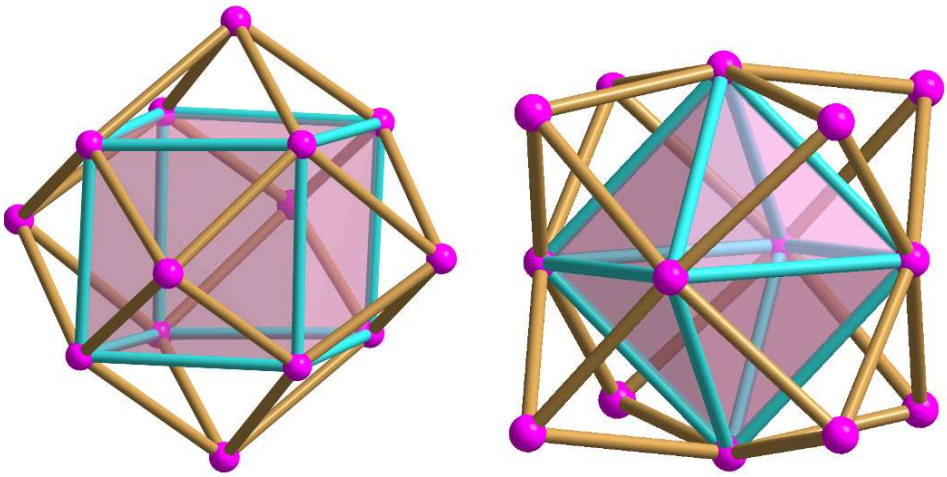
|---|---|---|
| Empirical formula | $C_{80}H_{180}Ag_{56}S_{33}$ | $C_{69}H_{142}Ag_{20}N_4O_{23}S_{10}$ |
| Formula weight | 8240.94 | 3873.97 |
| Temperature/K | 100(2) | 173(2) |
| Crystal system | cubic | monoclinic |
| Space group | Pa-3 | $P2_1/n$ |
| a/Å | 29.022(6) | 11.887(2) |
| b/Å | 29.022(6) | 19.864(4) |
| c/Å | 29.022(6) | 25.881(5) |
| α/° | 90.00 | 90.00 |
| β/° | 90.00 | 91.49(3) |
| γ/° | 90.00 | 90.00 |
| Volume/$Å^3$ | 24444(8) | 6109(2) |
| Z | 4 | 2 |
| $\rho_{calc}mg/mm^3$ | 2.239 | 2.106 |
| $m/mm^{-1}$ | 4.666 | 3.347 |
| F(000) | 15280.0 | 3736.0 |
| Crystal size/$mm^3$ | 0.20 × 0.15 × 0.15 | 0.15 × 0.15 × 0.1 |
| 2Θ range for data collection | 5.26 to 49.98° | 6.12 to 50° |
| Index ranges | $-34 \le h \le 19$, $-33 \le k \le 15$, $-30 \le l \le 34$ | $-14 \le h \le 14$, $-23 \le k \le 23$, $-27 \le l \le 30$ |
| Reflections collected | 26664 | 38879 |
| Independent reflections | 7126[R(int) = 0.0489] | 10716[R(int) = 0.0577] |
| Data/restraints/parameters | 7126/244/435 | 10716/24/628 |
| Goodness-of-fit on $F^2$ | 1.069 | 1.015 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0829$, $wR_2 = 0.2422$ | $R_1 = 0.0485$, $wR_2 = 0.1179$ |
| Final R indexes [all data] | $R_1 = 0.1056$, $wR_2 = 0.2648$ | $R_1 = 0.0560$, $wR_2 = 0.1223$ |

**(5) Fig. S1: XRD pattern of 1**



**(6) Fig. S2: Structure comparison for $Ag_{14}$ cores of 1 (left) and $[Ag_{62}S_{13}(SBu^t)_{32}](BF_4)_4$ (right)**



**(7) Fig. S3: The UV-Vis absorption (reflectance) spectra of solid state sample of complex 1**