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Synthesis and crystal structure of a novel decanuclear silver cluster complex $[\mathrm{Ag(SC_6H_2Pr^i_3}\text{-}2,4,6)]_{10}\cdot 2\mathrm{CHCl_3}\cdot\mathrm{C_2H_5OH}$

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The cluster $[\mathrm{Ag(SC_6H_2Pr^i_3}\text{-}2,4,6)]_{10}$ (1) contains a 20-membered ring of alternating silver and sulfur atoms, which is compactly folded; the sulfur atoms are doubly bridging and each silver atom exhibits linear two-coordination in the primary Ag–S interactions.

The study of metal chalcogenide complexes attracts wide interest not only because of their diversity of bonding modes and structural motifs,[1] but also for their potential use as precursors for materials[2] and relevance as models for the active site of metalloproteins.[3] There are a remarkably large number of silver(I) and copper(I) thiolate[4] and selenolate[5] complexes reported. A series of Ag(I) and Cu(I) complexes with sterically hindered thiolate and selenolate ligands have been synthesized and structurally characterized by us.[6,7] The insertion reaction of $\mathrm{CS_2}$ into M–S bonds (M = Ag, Cu, Cd) and its application in the synthesis of clusters has been reviewed.[8] We also measured the optical limiting property of some Ag(I) and Cu(I) complexes with thiolate or selenolate ligands,[7] and the relationship between structure and the non-linear optical property of homoleptic metal chalcogenolate clusters is being explored.

In 1989, we reported that the reaction of silver nitrate with the sterically hindered arylthiol 2,4,6-$\mathrm{Pr^i_3C_6H_2SH}$ resulted in a polymeric complex $[(\mathrm{AgSC_6H_2Pr^i_3}\text{-}2,4,6)_4\cdot\mathrm{CHCl_3}]_n$ (**2**),[9] which consists of one-dimensional double $(\mathrm{Ag{-}SR})_n$ strand belts. The polymeric complex (**2**) (150 mg) reacted readily with a small amount (3 drops) of $\mathrm{CS_2}$ in chloroform (5 ml) to give pale-yellow crystals $\{[\mathrm{AgS_2CSC_6H_2Pr^i_3}\text{-}2,4,6]_2[\mathrm{AgSC_6H_2Pr^i_3}\text{-}2,4,6]_6\}\cdot 8\mathrm{CHCl_3}$ (**3**),[9] the molecular structure of which consists of eight coplanar silver atoms linked through arylthiolate (RS) and aryltrithiocarbonate ($\mathrm{RSCS_2}$) ligands, involving insertion of $\mathrm{CS_2}$ into one-quarter of the Ag–S bonds of $[\mathrm{AgSR}]_n$. However, recently we found that the polymeric complex (**2**) (150 mg) reacted with a little more (0.5 ml) $\mathrm{CS_2}$ in chloroform (5 ml), then recrystallized in the $\mathrm{CHCl_3{-}CS_2{-}C_2H_5OH}$ mixed solvent system to form orange-red crystals, unexpectedly the structure of which is a novel decanuclear silver cluster complex $[\mathrm{Ag(SC_6H_2Pr^i_3}\text{-}2,4,6)]_{10}\cdot 2\mathrm{CHCl_3}\cdot\mathrm{C_2H_5OH}$ (**1**), not involving insertion of $\mathrm{CS_2}$. We present herein the synthesis, crystal structure and optical limiting property of this new complex.

Carbon disulfide (0.5 ml) was added to a colorless solution of $(\mathrm{AgSC_6H_2Pr^i_3}\text{-}2,4,6)_n$ (**2**)[9] (150 mg) in $\mathrm{CHCl_3}$ (5 ml), and the solution turned yellow in several min. The yellow solution was evaporated slowly at room temperature (18–20 °C) for several days to reach dryness resulting in an orange powder, which was dissolved in $\mathrm{CHCl_3}$ (5 ml) again. The solution was filtered and 3–4 drops of $\mathrm{CS_2}$ and 1 ml absolute ethanol were added. The red solution was evaporated slowly at room temperature for several days, then orange-red block crystals (**1**) formed with a few pale-yellow prismatic crystals of (**3**). The crystals (**1**) and (**3**) could be separated by handpicking, because they have quite different colors and the amount of crystals (**3**) was very small. The crystals (**1**) effloresced and turned into a pale-yellow powder in air. The powder melted at 187.5–189.6 °C. Anal. for (**1**) (unsolvated): Found: C, 52.16; H, 6.68. Calc. for $\mathrm{C_{150}H_{230}Ag_{10}S_{10}}$: C, 52.48; H, 6.75%. IR (KBr): 3048w, 2959vs, 2934sh, 2869m, 1629m, 1459m, 1426m, 1383w, 1308m, 1260m, 1158w, 1103w, 1057w, 1027w, 875w, 564w, 474w $\mathrm{cm^{-1}}$.

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The X-ray crystal structure determination[10] indicates that the complex (**1**) is a neutral cluster, which consists of ten silver atoms linked through ten aryl thiolate ligands. Figs. 1 and 2 give the molecular configuration and the structure of the $\mathrm{Ag_{10}S_{10}}$ core, respectively. The core is a 20-membered ring of alternating silver and sulfur atoms, which is compactly folded. To our knowledge, this is the first example of a silver thiolate complex of cyclo-$(\mu\text{-SR})_{10}\mathrm{M}_{10}$ type, although there are complexes of the cyclo-$(\mu\text{-SR})_x\mathrm{M}_x$ type (M = Ag or Cu, x = 3, 4, 8, 12, 14) found in the literature.[4,11–13] Fenske *et al.* reported a silver tellurate polymeric complex $[\mathrm{Ag_{10}(TePh)_{10}(PMe_3)_2}]_\infty$, in which all the PhTe ligands function as μ_3-bridges, the structure of the $\mathrm{Ag_{10}Te_{10}}$ core in the molecular repeat unit is not a cycle of alternating silver and tellurium atoms.[14] In the 20-membered

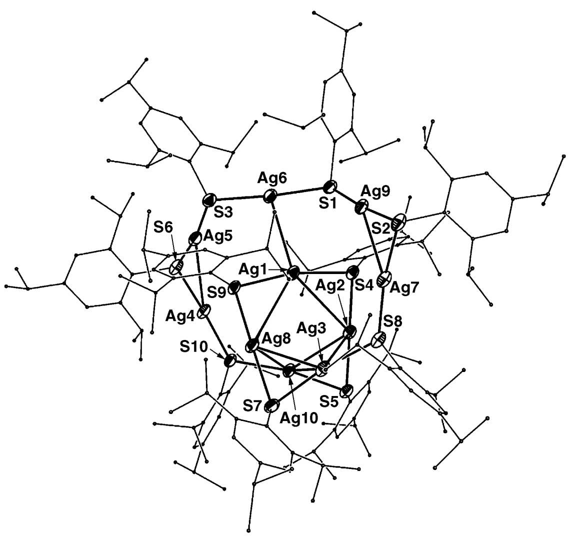

Fig. 1 Perspective view of the molecular structure of $[\mathrm{Ag(SC_6H_2Pr^i_3)}]_{10}$ (**1**).

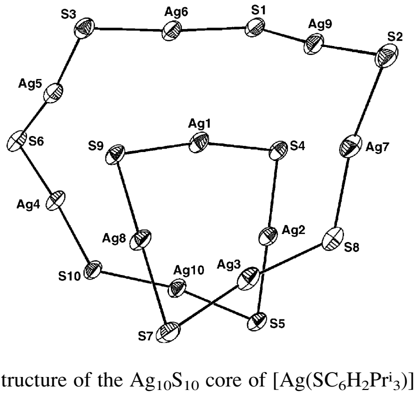

Fig. 2 Structure of the $\mathrm{Ag_{10}S_{10}}$ core of $[\mathrm{Ag(SC_6H_2Pr^i_3)}]_{10}$ (**1**).

ring of complex (**1**), each of the ten silver atoms is almost linearly coordinated, S–Ag–S mean angle 172.18° (166.62–179.44°). The intra-cycle distances of Ag–S bonds average 2.389 Å (2.361–2.428 Å), which is longer than the average Ag–S distance of 2.358 Å (2.320–2.387 Å) in the starting material (**2**) and 2.370 Å (2.352–2.387 Å) in its insertion product with CS_2 (**3**),[9] but shorter than the intra-cycle average Ag–S distance of 2.45 Å (2.40–2.50 Å) in cyclo-$(\mu\text{-}SC_6H_{11})_{12}Ag_{12}$.[13] As a consequence of the folding of the 20-membered ring, **1** exhibits secondary Ag···S interactions between the 'big' and 'small' rings in the molecule. These Ag···S distances average 3.236 Å (2.968–3.431 Å), which is longer than the average contra-cycle and inter-cycle Ag···S distance in $[(AgSC_6H_{11})_{12}]_n$ (ave. 2.71 Å),[13] but slightly shorter than the average inter-cycle Ag···S distance in $[AgSCH(SiMe_3)_2]_8$ (ave. 3.270 Å).[11] The cyclic structure of a molecule of (**1**) could be stabilized by these secondary interactions.

The array of Ag atoms might be considered as a bridged butterfly (see Fig. 3). The Ag–Ag contacts vary between 2.899–4.313 Å, which fall into three categories. The Ag–Ag distances bridged by S atoms forming acute angles (Ag–S–Ag angles average 78.74°) have a mean value of 3.127 Å (2.899–3.358 Å), which is shorter than the sum of the van der Waals radii of two Ag atoms (3.44 Å), and longer than the Ag–Ag distance in metallic Ag (2.886 Å), and may suggest they are related by so-called agentophilicity.[15] The Ag···Ag distances corresponding to the Ag–S–Ag obtuse angles (ave. 114.56°) average 4.065 Å (3.808–4.313 Å), which indicates that they are non-bonding and involved in very weak interactions. However, the distance between Ag3 and Ag10, unbridged by S, is rather shorter, 3.427 Å, which may be a feature of this ring structure of complex (**1**).

There is a pseudo two fold rotation axis along the Ag1–Ag6 bonding direction in the $Ag_{10}S_{10}$ core, but it departs from C_2 symmetry due to the bulky sterically hindered ligands $(2,4,6\text{-}Pr^i{}_3C_6H_2S^-)$. Also the steric hindrance of the ligands with bulky substituents prevents the neighboring cycles from close approach to form a polymeric structure. However, the use of a less bulky ligand $C_6H_{11}SH$ gives a one-dimensional polymeric complex $[(AgSC_6H_{11})_{12}]_n$,[13] in which the 24-membered cycles overlap with secondary Ag···S interactions between cycles.

As to the formation mechanism of the complex (**1**), it is suggested that the starting material (**2**) reacted with CS_2 first, then the insertion product, activated by the insertion of CS_2 into Ag–S bonds, dissociated into various 'active fragments' under the attack of solvents. The new product was formed by the optimum "self-assembly" of these active fragments, which crystallized from the solution. This mechanism is similar to that of the formation of complexes $Ag_{14}(\mu_6\text{-}S)(SPh)_{12}(PPh_3)_8$, $Cu_{14}(\mu_2\text{-}S)(SPh)_{12}(PPh_3)_6$, $(Ag_5I_6)_n(PPh_3CH_2I)$ *etc*., which has been discussed previously.[8]

The optical limiting property, which refers to the decrease in transmittance of a material with increments in the input light fluence or intensity, was measured for complexes (**1**) and (**3**). The pure complex (**1**) dissolved in chloroform was studied using 10 ns laser pulses at wavelengths of 532 nm and 1064 nm. The experimental setup was similar to that used in our previous work.[16] At a concentration of 1×10^{-3} M, the linear transmissibility of the sample in a 1 cm thick glass cell was measured to be 84 and 97% at 532 nm and 1064 nm respectively. At 532 nm, the obvious optical limiting effect was occurring and the limiting threshold was measured to be about 2.6 J cm^{-2}. The optical limiting capability of complex (**3**) is weaker than that of (**1**) under the same conditions. However, the optical limiting behavior of both (**1**) and (**3**) is much weaker than that of the cluster complex $[Ag_8(2,4,6\text{-}Pr_3{}^iC_6H_2Se)_8]$,[7] the structure of the Ag_8Se_8 core of which consists of a compressed distorted Ag_8 hexagonal bipyramid embedded in a distorted rhombohedron formed by eight selenium atoms of the aryl-selenolate ligands. In addition, with increasing input fluence, the output fluence increased linearly and no optical limiting response was observed at 1064 nm for complexes (**1**) and (**3**). In order to design new materials with better optical limiting performance, a systematic study on the structure–property relationship is necessary.

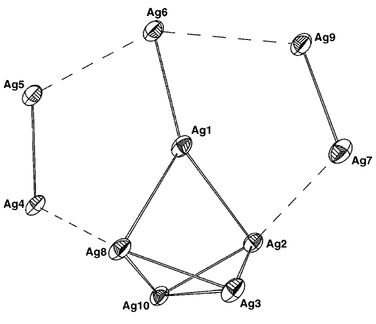

Fig. 3 Arrangement of the Ag_{10} bridged butterfly hung on an outer bridge of Ag atoms. Ag–Ag distances are shown as solid lines (< 3.44 Å) and dash lines (> 3.44 Å), respectively.

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10 *Crystal data* for **1**: $C_{154}H_{238}Ag_{10}Cl_6OS_{10}$, M = 3717.44, triclinic, space group $P\bar{1}$, a = 20.0290(4), b = 22.5472(6), c = 19.2607(5) Å, α = 102.681(1), β = 91.705(1), γ = 78.222(2)°, V = 8306.3(4) Å^3, D_c = 1.486 g cm^{-3}, Z = 2, T = 123(2) K, μ(MoKα) = 1.419 mm^{-1}, 69088 reflections collected, 28144 unique (R_{int} = 0.0371), final R indices [$I > 2\sigma(I)$], R_1 = 0.0524, wR_2 = 0.1356; R indices (all data), R_1 = 0.0944, wR_2 = 0.1492. Data collected on a Rigaku R-AXIS RAPID image plate diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) operating at 50 KV and 40 mA. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program (T. Higashi, Rigaku Corporation, Tokyo, Japan, 1995). The structure was solved by direct methods and successive difference maps (SHELX-97) and refined by full-matrix least-squares on F^2 using all unique data (SHELXL-97). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in their calculated positions with geometrical constraint and refined in the riding model. There are four large difference Fourier unknown peaks (1.13, 1.15, 1.65, 1.66 e Å^{-3}) near the $CHCl_3$ solvent molecules. CCDC reference number 175021. See http://www.rsc.org/suppdata/cc/b1/b110900f/ for crystallographic data in CIF or other electronic format.
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