

## Synthesis and Crystal Structure of a Decanuclear Silver(I)-thiolate Compound $\text{Ag}_{10}\text{S}[\text{S}_2\text{P}(\text{OEt})_2]_8$

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A new decanuclear silver(I) compound  $\text{Ag}_{10}(\mu_8\text{-S})(\text{dtp})_8$  [ $\text{dtp}=\text{S}_2\text{P}(\text{OEt})_2$ ] was isolated from a reaction mixture containing  $\text{W}_2\text{S}_4(\text{dtp})_2$  and  $\text{AgNO}_3$ , and its solid-state molecular structure was determined by X-ray crystallography. The crystallographic study revealed that the compound contains a distorted mono-capped quasi-prism [ $\text{Ag}_{10}$ ] with an octal-bridging S atom at the center of the prism. The compound ( $\text{C}_{32}\text{H}_{80}\text{Ag}_{10}\text{O}_{16}\text{P}_8\text{S}_{17}$ ,  $M_r=2592.46$ ) crystallizes in the monoclinic  $P2_1/n$  space group, with  $a=1.5111(5)$  nm,  $b=2.3656(8)$  nm,  $c=2.284(1)$  nm,  $\beta=96.88(3)^\circ$ ,  $V=8.107(5)$  nm<sup>3</sup>,  $Z=4$  and  $D_c=2.12$  g · cm<sup>-3</sup>. The solution using direct method and full-matrix least-squares refinement led to  $R=0.066$ ,  $R_w=0.078$  for 3928 reflections with  $I>3\sigma(I)$ .

**Keywords** silver(I)-thiolate complex, diethyldithiophosphate ligand, synthesis, crystal structure

### Introduction

Polynuclear Ag(I)-thiolate compounds are of interests due to their unique molecular structures and metal-metal interactions. There were some such compounds reported in literatures, including  $\text{Ag}_8(\mu_6\text{-S})(\text{dtp})_6$  [ $\text{dtp}=\text{S}_2\text{P}(\text{OEt})_2$ ] with [ $\text{Ag}_8$ ] cube,<sup>1</sup>  $\{\text{Ag}[\text{S}_2\text{P}(\text{OC}_3\text{H}_7)_2]\}_6$  with a [ $\text{Ag}_6$ ] distorted octahedron,<sup>2</sup>  $\text{Ag}_{11}\text{S}(\text{Et}_2\text{dte})_9$  [ $\text{Et}_2\text{dte}=\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$ ] with a [ $\text{Ag}_{11}$ ] cage of a 3-fold axis,<sup>3</sup> and  $\text{Ag}_{14}(\mu_6\text{-S})(\text{SPh})_{12}(\text{PPh}_3)_8 \cdot 4\text{CH}_3\text{OH} \cdot 13\text{H}_2\text{O}$  with a [ $\text{Ag}_{14}\text{S}_{12}$ ] cage composed of a staggered [ $\text{Ag}_6$ ] octahedron, a [ $\text{Ag}_8$ ] cube and a [ $\text{S}_{12}$ ] icosahedron.<sup>4</sup> More recently, two decanuclear Ag(I) compounds, [ $\text{Ag}(\text{SC}_6\text{H}_2\text{Pr}_3^-2,4,6)_{10} \cdot 2\text{CHCl}_3 \cdot \text{C}_2\text{H}_5\text{OH}$ ]<sup>5</sup> and  $\text{Ag}_{10}(\mu_{10}\text{-Se})[\text{Se}_2\text{P}(\text{OEt})_2]_8$ <sup>6</sup> were reported. In the course of our study on the reactions of binuclear compounds [ $\text{M}_2\text{O}_n\text{S}_{4-n}\text{L}_2$ ] ( $\text{M}=\text{Mo}, \text{W}$ ;  $\text{L}=\text{dtp}$  or  $\text{Et}_2\text{dte}$ ;  $n=0, 1, 2$ ) with other transition metal compounds such as  $\text{CuI}$  and  $\text{NiCl}_2$ ,<sup>7</sup> it was revealed that the transfer of dtp or  $\text{Et}_2\text{dte}$  ligand from [ $\text{M}_2\text{O}_n\text{S}_{4-n}\text{L}_2$ ] compounds to other transition metal occurs, leading to formation of new complex or polynuclear compounds, for instance  $\text{Cu}(\text{Et}_2\text{dte})_2$ <sup>7</sup> and  $\text{Cu}_8\text{S}(\text{dtp})_6$ .<sup>8,9</sup> In this paper, we report the preparation and crystal structure of a new decanuclear compound  $\text{Ag}_{10}\text{S}[\text{S}_2\text{P}(\text{OEt})_2]_8$ , which was formed by the transfer of dtp ligand from  $\text{W}_2\text{S}_4(\text{dtp})_2$  to Ag(I).

### Experimental

#### Preparation

$\text{W}_2\text{S}_4(\text{dtp})_2$  [ $\text{dtp}=\text{S}_2\text{P}(\text{OEt})_2$ ]<sup>10</sup> (0.18 g, 0.21 mmol)

was added to a solution of  $\text{K}_2(i\text{-mnt})$  [ $i\text{-mnt}=\text{S}_2\text{C}=\text{C}(\text{CN})_2$ ] (0.11 g, 0.5 mmol) in mixed ethanol/acetone (20 mL, 1/1 in V/V). After the reaction mixture was stirred at room temperature for 30 min,  $\text{AgNO}_3$  (0.085 g, 0.5 mmol) was added, resulting in a black precipitate immediately. A solution of  $\text{PPh}_3$  (0.22 g, 0.83 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was then added slowly while stirring, and the mixture was stirred for 50 min after addition. The reaction mixture was then filtered through filter paper to provide a yellow filtrate. The filtrate was set open in the air for one month, affording yellow crystals of the compound  $\text{Ag}_{10}\text{S}(\text{dtp})_8$ .

#### Structure determination

The X-ray diffraction data of a yellow crystal with dimension of 0.3 mm × 0.2 mm × 0.2 mm were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo  $\text{K}\alpha$  radiation ( $\lambda=0.071073$  nm). The crystal was stuck to the end of glass fiber by neutral jelly and mounted onto the diffractometer. The unit cell parameters were determined and refined by a least-squares treatment of the setting angles of 25 automatically centered reflections ( $7.22^\circ < \theta < 10.79^\circ$ ). The intensity data were collected by using  $\omega$ - $2\theta$  scan mode in the range of  $1^\circ < \theta < 25^\circ$  ( $h, 0-18$ ;  $k, 0-28$ ;  $l, -27-27$ ) and a variable scan speed was used (max. 16 ( $^\circ$ )/min) with the scan width of  $0.892 + 0.35 \tan \theta$  ( $^\circ$ ). The reflections measured were corrected for  $\text{Lp}$  effects and the absorption using  $\psi$  scan technique ( $T_{\text{max.}}=1$  and  $T_{\text{min.}}=0.7616$ ). A total of 14663 inde-

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Received December 1, 2003; revised and accepted March 30, 2004.

Project supported by the National Natural Science Foundation of China (Nos. 29673046 and 29733090), the Natural Science Foundation of Fujian Province (No. B96018) and the State Key Laboratory of Structural Chemistry.

pendent intensity data were obtained, of which 3928 with intensity  $I \geq 3\sigma(I)$  were used in the structure solution and refinements. The molecular structure was solved by a combination of direct method (MITHRIL) and difference Fourier syntheses. Anisotropic thermal parameters were refined only for Mo, S and P atoms while isotropic vibrations were assumed for O and C atoms. The hydrogen atoms were not located in the refinement. The full matrix least-squares refinement was based on  $F$  and the number of refined parameters was

512, leading to the final residuals being  $R=0.066$ ,  $R_w=0.078$ . GOF (goodness of fit indicator)=1.79, max. shift/error on final LS cycle  $\Delta/\sigma=0.62$ , and the max. and min. residual densities are 1130 and  $-890 \text{ e/nm}^{-3}$ , respectively. All the calculations were carried out on a MICRO-VAX3100 computer using the TEXSAN program.<sup>11</sup> The fractional coordinates and equivalent isotropic thermal parameters for all the nonhydrogen atoms are listed in Table 1.

**Table 1** Positional and equivalent isotropic thermal parameters ( $\times 10^{-2} \text{ nm}^2$ ) for  $\text{Ag}_{10}\text{S}(\text{dtp})_8^a$

Atom	$x$	$y$	$z$	$B_{\text{eq}}$	Atom	$x$	$y$	$z$	$B_{\text{eq}}$
Ag(1)	0.3957(2)	0.3362(1)	0.5278(1)	6.9(1)	O(8)	0.472(1)	0.4010(7)	0.6799(7)	5.3(4)
Ag(2)	0.3970(2)	0.2455(1)	0.6255(1)	7.3(2)	O(9)	-0.018(1)	0.2351(8)	0.7462(9)	7.8(5)
Ag(3)	0.3208(2)	0.2239(1)	0.4589(1)	8.3(2)	O(10)	0.058(2)	0.144(1)	0.784(1)	10.0(7)
Ag(4)	0.4201(2)	0.1397(1)	0.5474(1)	7.7(2)	O(11)	0.411(2)	0.142(1)	0.761(1)	14(1)
Ag(5)	0.2007(2)	0.3524(1)	0.5428(1)	7.1(2)	O(12)	0.467(2)	0.045(1)	0.716(1)	9.9(7)
Ag(6)	0.1598(2)	0.2928(1)	0.6537(1)	8.1(2)	O(13)	0.441(2)	0.0798(9)	0.3979(9)	8.5(6)
Ag(7)	0.1139(2)	0.2594(1)	0.4583(1)	8.2(2)	O(14)	0.302(2)	0.028(1)	0.374(1)	9.9(7)
Ag(8)	0.0482(2)	0.2058(1)	0.5694(1)	8.3(2)	O(15)	-0.014(1)	0.081(1)	0.381(1)	9.4(6)
Ag(9)	0.2280(2)	0.1694(1)	0.6352(1)	7.7(2)	O(16)	-0.108(1)	0.1553(8)	0.4259(8)	6.8(5)
Ag(10)	0.1991(2)	0.1367(1)	0.5014(1)	8.5(2)	C(1)	0.627(3)	0.316(2)	0.454(2)	12(1)
S	0.2408(5)	0.2374(3)	0.5519(3)	5.0(4)	C(2)	0.692(4)	0.357(2)	0.450(2)	20(2)
S(1)	0.5330(5)	0.2976(3)	0.5861(3)	5.8(4)	C(3)	0.693(4)	0.141(3)	0.553(3)	19(2)
S(2)	0.5030(5)	0.1966(3)	0.4764(3)	6.3(5)	C(4)	0.770(4)	0.154(2)	0.561(2)	18(2)
S(3)	0.3614(5)	0.3234(3)	0.4188(3)	6.2(5)	C(5)	0.205(3)	0.309(2)	0.298(2)	14(2)
S(4)	0.1472(5)	0.3646(3)	0.4336(3)	5.8(4)	C(6)	0.214(3)	0.306(2)	0.244(2)	18(2)
S(5)	0.0770(5)	0.3747(3)	0.6084(4)	6.8(5)	C(7)	0.351(5)	0.466(3)	0.410(3)	21(3)
S(6)	-0.0392(5)	0.2812(3)	0.5113(3)	6.3(5)	C(8)	0.345(4)	0.521(3)	0.416(3)	19(2)
S(7)	0.3334(5)	0.4160(3)	0.5829(3)	5.5(4)	C(9)	-0.091(5)	0.450(3)	0.523(3)	25(3)
S(8)	0.3339(5)	0.3173(3)	0.6943(3)	5.6(4)	C(10)	-0.137(3)	0.479(2)	0.477(2)	11(1)
S(9)	0.1748(6)	0.2226(4)	0.7340(4)	7.4(5)	C(11)	-0.168(4)	0.305(2)	0.623(2)	17(2)
S(10)	0.0047(7)	0.1540(4)	0.6554(4)	9.6(6)	C(12)	-0.214(3)	0.329(2)	0.665(2)	14(1)
S(11)	0.4825(5)	0.1522(3)	0.6519(3)	6.5(5)	C(13)	0.240(3)	0.466(2)	0.699(2)	14(1)
S(12)	0.2911(6)	0.0772(3)	0.6642(4)	7.4(5)	C(14)	0.207(3)	0.434(2)	0.741(2)	15(2)
S(13)	0.2887(6)	0.1519(4)	0.3762(4)	8.4(6)	C(15)	0.525(2)	0.386(1)	0.736(1)	7.0(8)
S(14)	0.3262(6)	0.0645(3)	0.4957(4)	7.5(5)	C(16)	0.615(3)	0.386(2)	0.731(2)	11(1)
S(15)	0.0393(6)	0.1127(3)	0.5046(4)	7.0(5)	C(17)	-0.003(2)	0.264(1)	0.805(1)	8.0(9)
S(16)	0.0578(6)	0.1921(4)	0.3805(4)	8.1(6)	C(18)	0.002(2)	0.321(2)	0.789(2)	10(1)
P(1)	0.5837(6)	0.2439(4)	0.5305(4)	6.6(5)	C(19)	0.023(5)	0.098(4)	0.785(4)	26(4)
P(2)	0.2553(6)	0.3723(3)	0.3944(4)	5.9(5)	C(20)	0.035(4)	0.060(2)	0.816(3)	18(2)
P(3)	-0.0385(6)	0.3470(4)	0.5651(4)	6.7(5)	C(21)	0.365(5)	0.131(3)	0.798(3)	24(3)
P(4)	0.3683(5)	0.3929(3)	0.6678(3)	5.0(4)	C(22)	0.392(3)	0.164(2)	0.850(2)	16(2)
P(5)	0.0513(6)	0.1891(4)	0.7289(4)	6.5(5)	C(23)	0.557(3)	0.048(2)	0.743(2)	11(1)
P(6)	0.4107(6)	0.1031(4)	0.6995(4)	6.2(5)	C(24)	0.574(3)	-0.006(2)	0.772(2)	12(1)

continued

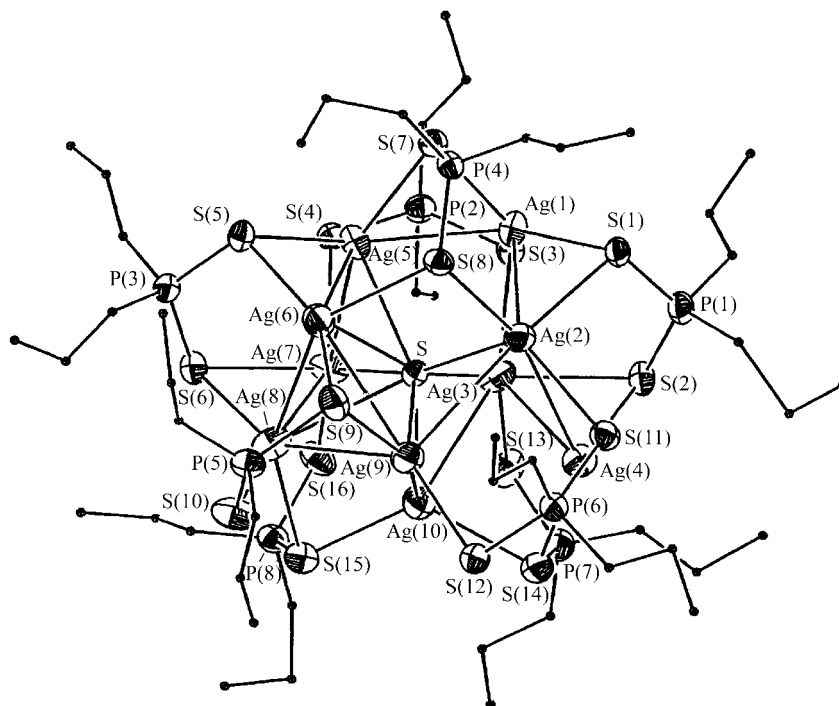
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
P(7)	0.3396(6)	0.0810(4)	0.4107(4)	7.4(6)	C(25)	0.507(2)	0.036(1)	0.422(1)	8.2(9)
P(8)	-0.0098(6)	0.1352(3)	0.4224(4)	6.1(5)	C(26)	0.594(2)	0.054(1)	0.406(1)	8(1)
O(1)	0.653(2)	0.278(1)	0.495(1)	10.2(7)	C(27)	0.207(3)	0.014(2)	0.370(2)	11(1)
O(2)	0.655(2)	0.206(1)	0.571(1)	9.9(7)	C(28)	0.191(2)	-0.030(2)	0.319(2)	11(1)
O(3)	0.233(1)	0.366(1)	0.325(1)	9.2(6)	C(29)	-0.029(3)	0.022(2)	0.401(2)	14(2)
O(4)	0.282(2)	0.438(1)	0.400(1)	11.6(8)	C(30)	-0.073(4)	-0.007(3)	0.361(3)	8(2)
O(5)	-0.087(2)	0.397(1)	0.523(1)	13.1(9)	C(30')	-0.114(5)	0.028(3)	0.399(3)	8(2)
O(6)	-0.099(2)	0.336(1)	0.618(1)	14(1)	C(31)	-0.159(3)	0.173(2)	0.372(2)	11(1)
O(7)	0.333(1)	0.4404(8)	0.7103(8)	6.9(5)	C(32)	-0.246(3)	0.190(2)	0.384(2)	16(2)

$$^a B_{\text{eq}} = 4/3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + abc\cos\gamma\beta(1,2) + accos\beta\beta(1,3) + bccos\alpha\beta(2,3)].$$

## Results and discussion

The molecular structure of the compound  $\text{Ag}_{10}\text{S}[\text{S}_2\text{P}(\text{OEt})_2]_8$  is depicted in Figure 1, and its irregular  $[\text{Ag}_{10}]$  polyhedron shown in Figure 2 along with the Ag—Ag distances. Selected bond distances and angles are listed in Table 2. As illustrated in Figure 2, the geometry of the  $[\text{Ag}_{10}]$  polyhedron can be described as a highly distorted monocapped quasi-prism, of which the upper and bottom planes are defined by Ag(6)-Ag(5)-Ag(7)-Ag(8) and Ag(2)-Ag(1)-Ag(3)-Ag(10)-Ag(9), respectively, with the remaining Ag(4) as a capping atom. The Ag—Ag distances ranging from 0.3001(4) to 0.3379(4) nm, with an average distance  $d_{\text{ave}}$

of 0.3149 nm, are all shorter than the sum of the Van der Waals radii (0.344 nm), indicating considerable Ag(I)—Ag(I) argentophilic interaction.<sup>12-14</sup> Meanwhile the average Ag(I)—Ag(I) distance is shorter than those observed in  $\text{Ag}_8(\mu_6\text{-S})(\text{dtp})_6$  (0.3229 and 0.3494 nm) with  $d_{\text{ave}} = 0.3362$  nm,  $\{\text{Ag}[\text{S}_2\text{P}(\text{OC}_3\text{H}_7)_2]_6\}_6$  (0.31551—0.4128 nm) with  $d_{\text{ave}} = 0.3371$  nm,  $\text{Ag}_{14}(\mu_6\text{-S})(\text{SPh})_{12}(\text{PPh}_3)_8 \cdot 4\text{CH}_3\text{OH} \cdot 13\text{H}_2\text{O}$  (0.3894—0.4264 nm) with  $d_{\text{ave}} = 0.4111$  nm and  $[\text{Ag}(\text{SC}_6\text{H}_2\text{Pr}_3^i-2,4,6)]_{10}$  (0.2899—0.4313 nm) with  $d_{\text{ave}} = 0.3596$  nm, but slightly longer than that of  $\text{Ag}_{10}\text{Se}[\text{Se}_2\text{P}(\text{OEt})_2]_8$  (0.2956—0.3378 nm) with  $d_{\text{ave}} = 0.3067$  nm.



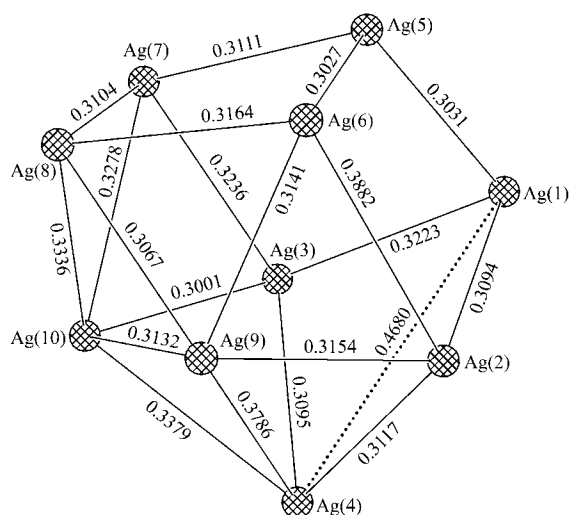
**Figure 1** An ORTEP drawing of  $\text{Ag}_{10}\text{S}(\text{dtp})_8$ . The  $(\text{OC}_2\text{H}_5)$  groups are represented by small balls and rods for clarity.

**Table 2** Selected bond distances (nm) and angles (°)

Ag(1)—Ag(5)	0.3031(4)	Ag(1)—S(1)	0.2499(8)	Ag(6)—S(9)	0.2465(9)	S(1)—P(1)	0.201(1)
Ag(1)—Ag(2)	0.3095(4)	Ag(1)—S(3)	0.2502(8)	Ag(6)—S(5)	0.2467(9)	S(2)—P(1)	0.197(1)
Ag(1)—Ag(3)	0.3224(4)	Ag(1)—S(7)	0.2514(8)	Ag(6)—S(8)	0.2744(8)	S(3)—P(2)	0.200(1)
Ag(2)—Ag(4)	0.3117(4)	Ag(2)—S(8)	0.2573(8)	Ag(6)—S	0.3049(8)	S(4)—P(2)	0.196(1)
Ag(2)—Ag(9)	0.3153(4)	Ag(2)—S(11)	0.2592(8)	Ag(7)—S(16)	0.2459(8)	S(5)—P(3)	0.201(1)
Ag(3)—Ag(10)	0.3001(4)	Ag(2)—S(1)	0.2646(8)	Ag(7)—S(4)	0.2614(8)	S(6)—P(3)	0.198(1)
Ag(3)—Ag(4)	0.3094(4)	Ag(2)—S	0.2736(8)	Ag(7)—S	0.2746(8)	S(7)—P(4)	0.202(1)
Ag(3)—Ag(7)	0.3236(4)	Ag(3)—S(13)	0.2546(9)	Ag(7)—S(6)	0.2786(8)	S(8)—P(4)	0.198(1)
Ag(4)—Ag(10)	0.3379(4)	Ag(3)—S	0.2588(8)	Ag(8)—S(10)	0.247(1)	S(9)—P(5)	0.202(1)
Ag(5)—Ag(6)	0.3026(4)	Ag(3)—S(3)	0.2626(8)	Ag(8)—S(6)	0.2504(8)	S(10)—P(5)	0.193(1)
Ag(5)—Ag(7)	0.3112(4)	Ag(3)—S(2)	0.2810(8)	Ag(8)—S(15)	0.2647(9)	S(11)—P(6)	0.200(1)
Ag(6)—Ag(9)	0.3140(4)	Ag(4)—S(11)	0.2478(8)	Ag(8)—S	0.3076(8)	S(12)—P(6)	0.199(1)
Ag(6)—Ag(8)	0.3164(4)	Ag(4)—S(14)	0.2484(9)	Ag(9)—S(12)	0.2441(8)	S(13)—P(7)	0.197(1)
Ag(7)—Ag(8)	0.3104(4)	Ag(4)—S(2)	0.2548(9)	Ag(9)—S	0.2516(7)	S(14)—P(7)	0.201(1)
Ag(7)—Ag(10)	0.3279(4)	Ag(5)—S(4)	0.2546(8)	Ag(9)—S(9)	0.279(1)	S(15)—P(8)	0.201(1)
Ag(8)—Ag(9)	0.3066(4)	Ag(5)—S(5)	0.2586(8)	Ag(10)—S(15)	0.249(1)	S(16)—P(8)	0.200(1)
Ag(8)—Ag(10)	0.3337(4)	Ag(5)—S(7)	0.2586(8)	Ag(10)—S	0.2690(7)		
Ag(9)—Ag(10)	0.3131(4)	Ag(5)—S	0.2788(7)	Ag(10)—S(14)	0.2585(9)		
Ag(2)-Ag(1)-Ag(3)	75.6(1)	S(4)-Ag(5)-S(5)	112.2(3)	S(8)-Ag(2)-S(11)	129.1(3)	S(4)-Ag(7)-S	102.3(2)
Ag(1)-Ag(2)-Ag(9)	120.7(1)	S(4)-Ag(5)-S(7)	115.0(3)	S(8)-Ag(2)-S(1)	105.1(2)	S(4)-Ag(7)-S(6)	96.2(3)
Ag(10)-Ag(3)-Ag(1)	127.0(1)	S(4)-Ag(5)-S	103.0(2)	S(8)-Ag(2)-S	93.8(2)	S-Ag(7)-S(6)	103.6(2)
Ag(3)-Ag(4)-Ag(2)	77.2(1)	S(5)-Ag(5)-S(7)	105.0(3)	S(11)-Ag(2)-S(1)	95.2(3)	S(10)-Ag(8)-S(6)	126.9(3)
Ag(3)-Ag(4)-Ag(10)	55.04(9)	S(5)-Ag(5)-S	108.8(3)	S(11)-Ag(2)-S	116.9(2)	S(10)-Ag(8)-S(15)	91.8(3)
Ag(2)-Ag(4)-Ag(10)	91.2(1)	S(7)-Ag(5)-S	112.9(2)	S(1)-Ag(2)-S	118.1(2)	S(10)-Ag(8)-S	124.7(3)
Ag(6)-Ag(5)-Ag(7)	94.4(1)	S(9)-Ag(6)-S(5)	147.0(3)	S(13)-Ag(3)-S	128.8(3)	S(6)-Ag(8)-S(15)	108.0(3)
Ag(5)-Ag(6)-Ag(8)	86.6(1)	S(9)-Ag(6)-S(8)	83.8(3)	S(13)-Ag(3)-S(3)	111.8(3)	S(6)-Ag(8)-S	101.8(2)
Ag(8)-Ag(7)-Ag(5)	86.2(1)	S(9)-Ag(6)-S	105.6(3)	S(13)-Ag(3)-S(2)	92.8(3)	S(15)-Ag(8)-S	96.6(2)
Ag(7)-Ag(8)-Ag(6)	91.9(1)	S(5)-Ag(6)-S(8)	113.2(3)	S-Ag(3)-S(3)	109.1(2)	S(12)-Ag(9)-S	135.6(3)
Ag(10)-Ag(9)-Ag(2)	95.3(1)	S(5)-Ag(6)-S	104.3(2)	S-Ag(3)-S(2)	117.2(2)	S(12)-Ag(9)-S(9)	108.9(3)
Ag(3)-Ag(10)-Ag(9)	97.3(1)	S(8)-Ag(6)-S	83.8(2)	S(3)-Ag(3)-S(2)	89.4(3)	S-Ag(9)-S(9)	112.3(3)
S(1)-Ag(1)-S(3)	123.1(3)	S(16)-Ag(7)-S(4)	121.3(3)	S(11)-Ag(4)-S(14)	132.3(3)	S(15)-Ag(10)-S(14)	125.5(3)
S(1)-Ag(1)-S(7)	110.2(3)	S(16)-Ag(7)-S	126.0(3)	S(11)-Ag(4)-S(2)	113.0(3)	S(15)-Ag(10)-S	111.5(3)
S(3)-Ag(1)-S(7)	122.9(3)	S(16)-Ag(7)-S(6)	101.7(3)	S(14)-Ag(4)-S(2)	111.9(3)	S(14)-Ag(10)-S	118.0(3)

The second interesting structural feature of the current compounds is the presence of an octat-bridging S atom at the center of the  $[\text{Ag}_{10}\text{S}]$  prism with the distances of  $\text{Ag}(2)\text{—S} = 0.2736(8)$  nm,  $\text{Ag}(3)\text{—S} = 0.2588(8)$  nm,  $\text{Ag}(5)\text{—S} = 0.2788(7)$  nm,  $\text{Ag}(6)\text{—S} = 0.3049(8)$  nm,  $\text{Ag}(7)\text{—S} = 0.2746(8)$  nm,  $\text{Ag}(8)\text{—S} = 0.3076(8)$  nm,  $\text{Ag}(9)\text{—S} = 0.2516(7)$  nm,  $\text{Ag}(10)\text{—S} = 0.2690(7)$  nm, indicating bonding interactions. The mean  $\text{Ag}\text{—S}$  value (0.2774 nm) is slightly shorter than the corresponding  $\text{Ag}\text{—}(\mu_8\text{-Se})$  distance (0.28675 nm) in compound  $\text{Ag}_8(\mu_8\text{-Se})[\text{Se}_2\text{P}(\text{OPr}^i)_2]_6$ <sup>15</sup> and the  $\text{Ag}\text{—}(\mu_6\text{-S})$  distance (0.2782 nm) in compound  $\text{Ag}_8(\mu_6\text{-S})(\text{dtp})_6$ .<sup>1</sup> No such interactions were observed

between the S atom and Ag(1) or Ag(4) [0.3399 nm for  $\text{Ag}(1)\text{—S}$  and 0.3572 nm for  $\text{Ag}(4)\text{—S}$ ]. Unlike  $\text{Ag}_{10}(\mu_{10}\text{-Se})[\text{Se}_2\text{P}(\text{OEt})_2]_8$ , of which the central Se atom is bonded to all ten Ag(I) atoms, the compound  $\text{Ag}_{10}(\mu_8\text{-S})[\text{S}_2\text{P}(\text{OEt})_2]_8$  possesses a central S atom coordinated only to eight of its ten Ag(I) atoms, probably as a result of the smaller size of sulfur. The present compound is the first example for decanuclear silver(I) thiolate complex containing a  $\mu_8\text{-S}$  atom. A shorter average  $\text{Ag}\text{—Ag}$  distance in  $\text{Ag}_{10}\text{S}[\text{S}_2\text{P}(\text{OEt})_2]_8$  compared with  $[\text{Ag}(\text{SC}_6\text{H}_2\text{Pr}_3^i\text{-}2,4,6)]_{10}$  is likely due to the presence of the  $\mu_8\text{-S}$  atom, which pulls the Ag atoms close to each other to result in strong  $\text{Ag}\text{—Ag}$  argentophilic



**Figure 2** Structure of [Ag<sub>10</sub>] polyhedron showing Ag—Ag distances (nm).

interactions. A similar effect was also observed in Ag<sub>10</sub>(μ<sub>10</sub>-Se)[Se<sub>2</sub>P(OEt)<sub>2</sub>]<sub>8</sub>.

The third interesting feature of the current compound is the existence of two different bridging patterns of the dtp ligands. As depicted in the Figure 1, four dtp ligands which contain P(1), P(2), P(3), P(4) respectively are located on the four uncapped [Ag<sub>4</sub>] planes with a tetra-connective bridging (μ<sub>2</sub>, μ<sub>2</sub>) pattern. The other four dtp ligands are situated on four triangular faces with a trimetallic triconnective (μ<sub>1</sub>-S, μ<sub>2</sub>-S) pattern. The triangular faces are defined by Ag(6)-Ag(8)-Ag(9), Ag(2)-Ag(4)-Ag(9), Ag(3)-Ag(4)-Ag(10) and Ag(7)-Ag(8)-Ag(10), respectively. Accordingly, the ten Ag(I) atoms have two different coordination geometries with sulfur atoms. Six of the Ag(I) atoms [Ag(2), Ag(3), Ag(5), Ag(6), Ag(7), Ag(8)] are coordinated with four S atoms in a distorted tetrahedron, and the remaining four [Ag(1), Ag(4), Ag(9), Ag(10)] are bonded to only three S atoms, likely due to the steric hindrance of the bulky dtp ligands.

The formation of this compound shows that the starting binuclear cluster W<sub>2</sub>S<sub>4</sub>(dtp)<sub>2</sub> is disrupted during

the reaction and then some dtp are captured by Ag(I). The central S might come from *i*-mnt ligand or from the bridging S or W=S due to the decomposition of W<sub>2</sub>S<sub>4</sub>(dtp)<sub>2</sub>. The present compound provides insight into the reactivity of M<sub>2</sub>S<sub>4</sub>(dtp)<sub>2</sub> cluster again and this results in the discovery of the new Ag(I)-thiolate compound with a novel structure.

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