Communications

A Novel Octahedral Hexasilver(I) Cluster: $Ag_6[SSCN(n\text{-}C_4H_9)_2]_6$

ZHANG, Wei-Guang[*,a,b](章伟光) **ZHONG, Yun**[b](钟昀) **TAN, Min-Yu**[*,a](谭民裕)
LIU, Wei-Sheng[a](刘伟生) **SU, Cheng-Yong**[c](苏成勇)
[a]*Department of Chemistry, Lanzhou University, Lanzhou, Gansu 730000, China*
[b]*Department of Chemistry, South China Normal University, Guangzhou, Guangdong 510631, China*
[c]*School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, Guangdong 510275, China*

The first crystal structural report of a AgDTC complex (DTC = dialkyldithiocarbamate, R = *n*-butyl) presented in this paper shows that it is a hexanuclear species. The structural arrangement for the DDP (dialkyldithiophosphate) ligands is different from that of $Cu_6(DDP)_6$, but is the same as that of $Ag_6[SSP(O\text{-}i\text{-}Pr)_2]_6$.

Keywords X-ray crystal structure, cluster, silver *n*-dibutyldithiocarbamate complex

Compounds formed from Cu, Ag and Au with dithiolate ligands, such as the dialkyldithiocarbamate (DTC), mercaptothiazoline (HMT) and dialkyldithiophosphates (DDP), have played an important role in technology.[1] Cu(I)-S clusters also have been implicated in biology as anti-oxidants.[2]

The cubane Ag cluster of the maleonitriledithiolate (*i*-MNT) ligand was synthesized and characterized by Dietrich[3] and Liu.[4] The clusters of Ag with 2-mercaptothiazoline (MT) were synthesized and structurally characterized by Lopez.[5] Recently, other clusters of silver with a crown-ether ligand,[6] an aryl selenolate ligand[7] and thiocarboxylates ligand[8] have been reported. However, no examples have been reported about the polynuclear silver clusters with DTC ligands, except $Ag_{11}(\mu_5\text{-}S)[SSCNEt_2]_9$[9] and $Ag_6[SSCNEt_2]_6$.[10]

We describe here the synthesis and structure of a AgDTC complex (R = *n*-butyl). Although the crystal structures of $Ag_{11}(\mu_5\text{-}S)[SSCNEt_2]_9$[9] and $Ag_6[SSCNEt_2]_6$[10] have been described, the structure of a AgDTC complex (R = *n*-butyl) presented in this paper shows that it is one of hexanuclear species. The structural arrangement is different from that of $Cu_6(DDP)_6$ [Fig. 1a], but is the same as that of $Ag_6[SSP(O\text{-}i\text{-}Pr)_2]_6$ [Fig. 1b].[11]

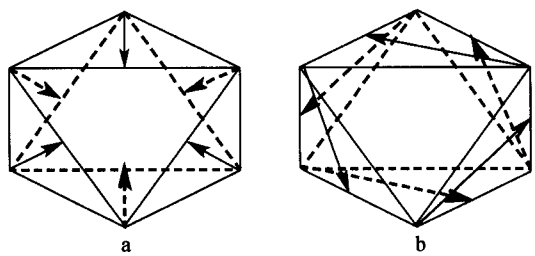

Fig. 1 Drawings of D_{3d} octahedral (a) and S_6 octahedral (b). Arrow represent the μ_2-S atoms of the ligands with tails being unsaturated with μ_1-S atoms.

To a solution of 0.04 mol of di-*n*-butylamine and 0.04 mol of sodium hydroxide dissolved in 20 mL of water was added 0.04 mol of carbonyl disulfide slowly at 0 ℃. The mixture was stired for 1 h at room temperature. Then a stoichiomitric amount of silver nitrate in 20 mL of water was added with stirring for extra 9 h. Extracting with toluene, washing with water three times the colorless crys-

* E-mail: wgzhang@scnu.edu.cn
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tal was obtained after 50 d suitable for X-ray analysis.

Selected spectroscopic data. IR (KBr): ν(C—N) 1480, ν(CSS) 945, ν(N—H) 2931 cm^{-1}. XPS (PHI-5702 Multi-functional X-ray Photoelectron Spectrometer, Mg Kα radiation as the excitation source): Ag(3d)$_{5/2}$ 368.1, C(1s) 284.6, N(1s) 339.8, S(2p) 162.1 eV.

A colorless single crystal of $Ag_6[SSCN(n\text{-}C_4H_9)_2]_6$ with the dimensions 0.44 mm × 0.20 mm × 0.20 mm was mounted on glass fibers and data collections were performed on an CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.071073 nm) at 296 K, using the $\omega/2\theta$ scan technique. The reflections were corrected for absorption by the Gaussian integration method, for Lorentz polarization and secondary extinction effects. The structure was solved by the Patterson method and subsequent difference Fourier techniques, and was refined by full-matrix least-squares methods with anisotropic thermal factors for all non-hydrogen atoms; a number of the hydrogen atoms were placed in calculated positions. All calculations were performed using the SHELXTL system of computer programs. The final values $R_1 = 0.0408$, $wR_2 = 0.1010$ were obtained.

Crystal data: $C_{54}H_{108}Ag_6N_6S_{12}$, $M_r = 1873.4$, triclinic, space group P-1, $a = 1.1520(2)$ nm, $b = 1.2401(3)$ nm, $c = 1.3314(3)$ nm, $\alpha = 91.560(4)°$, $\beta = 95.926(4)°$, $\gamma = 98.145(4)°$, $V = 1.8713(7)$ nm^3, $Z = 1$, $D_c = 3.325$ Mg/m^3, $F(000) = 1896$.

The molecular structure of $Ag_6[SSCN(n\text{-}C_4H_9)_2]_6$ is shown in Fig. 2 (the n-butyl groups are omitted for clarity). The selected bond lengths and bond angles are shown in Table 1.

Table 1 Selected bond lengths [nm] and angles [deg.][a]

Ag(1)—S(4)	0.24478(13)	S(1)—C(1)	0.1752(4)
Ag(1)—S(6)	0.25238(11)	S(1)—Ag(3) # 1	0.25418(12)
Ag(1)—S(1)	0.25444(12)	S(2)—C(1)	0.1705(4)
Ag(1)—Ag(3)	0.29610(7)	S(3)—C(10)	0.1745(4)
Ag(1)—Ag(2)	0.29657(7)	S(4)—C(10)	0.1709(4)
Ag(2)—S(2)	0.24957(12)	S(5)—C(19)	0.1695(4)
Ag(2)—S(3)	0.25338(12)	S(6)—C(19)	0.1766(4)
Ag(2)—S(6) # 1	0.25532(12)	S(6)—Ag(2) # 1	0.25532(11)
Ag(2)—Ag(3) # 1	0.31943(7)	N(1)—C(1)	0.1330(5)
Ag(3)—S(5)	0.24814(14)	N(2)—C(10)	0.1336(5)
Ag(3)—S(3)	0.25001(11)	N(3)—C(19)	0.1322(5)
Ag(3)—S(1) # 1	0.25418(12)		
S(4)-Ag(1)-S(6)	139.14(5)	S(5)-Ag(3)-Ag(1)	95.55(3)
S(4)-Ag(1)-S(1)	127.96(4)	S(3)-Ag(3)-Ag(1)	74.52(3)
S(6)-Ag(1)-S(1)	90.83(4)	S(1) # 1-Ag(3)-Ag(1)	130.21(3)
S(4)-Ag(1)-Ag(3)	95.33(3)	S(5)-Ag(3)-Ag(2) # 1	86.40(4)
S(6)-Ag(1)-Ag(3)	70.02(3)	S(3)-Ag(3)-Ag(2) # 1	132.73(3)
S(1)-Ag(1)-Ag(3)	120.59(3)	S(1) # 1-Ag(3)-Ag(2) # 1	66.55(3)
S(4)-Ag(1)-Ag(2)	88.26(4)	Ag(1)-Ag(3)-Ag(2) # 1	80.732(14)
S(6)-Ag(1)-Ag(2)	120.72(3)	C(1)-S(1)-Ag(3) # 1	102.71(14)
S(1)-Ag(1)-Ag(2)	70.38(3)	C(1)-S(1)-Ag(1)	107.74(14)
Ag(3)-Ag(1)-Ag(2)	73.135(13)	Ag(3) # 1-S(1)-Ag(1)	108.71(4)
S(2)-Ag(2)-S(3)	126.33(4)	C(1)-S(2)-Ag(2)	100.05(14)
S(2)-Ag(2)-S(6) # 1	120.48(4)	C(10)-S(3)-Ag(3)	109.11(14)
S(3)-Ag(2)-S(6) # 1	106.41(4)	C(10)-S(3)-Ag(2)	108.16(14)

Continued

S(2)-Ag(2)-Ag(1)	88.27(3)	Ag(3)-S(3)-Ag(2)	89.08(3)
S(3)-Ag(2)-Ag(1)	73.97(3)	C(10)-S(4)-Ag(1)	102.29(14)
S(6) # 1-Ag(2)-Ag(1)	135.64(3)	C(19)-S(5)-Ag(3)	99.93(14)
S(2)-Ag(2)-Ag(3) # 1	87.78(3)	C(19)-S(6)-Ag(1)	113.58(14)
S(3)-Ag(2)-Ag(3) # 1	137.67(3)	C(19)-S(6)-Ag(2) # 1	103.44(14)
S(6) # 1-Ag(2)-Ag(3) # 1	65.78(3)	Ag(1)-S(6)-Ag(2) # 1	103.63(4)
Ag(1)-Ag(2)-Ag(3) # 1	84.196(18)	S(2)-C(1)-S(1)	120.6(2)
S(5)-Ag(3)-S(3)	134.99(5)	S(4)-C(10)-S(3)	122.5(2)
S(5)-Ag(3)-S(1) # 1	117.54(4)	S(5)-C(19)-S(6)	120.8(2)
S(3)-Ag(3)-S(1) # 1	100.74(4)		

[a]Symmetry transformations used to generate equivalent atoms: # 1 $-x+1$, $-y+1$, $-z+1$

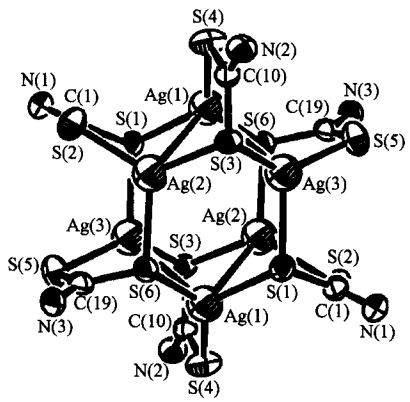

Fig. 2 Thermal ellipsoid drawing (50% probability) of $Ag_6[SSCN(n\text{-}C_4H_9)_2]_6$. The *n*-butyl groups were omitted for clarity.

There is an ideal three-fold symmetry axis through the two opposite unoccupied Ag_3 triangles of the distorted octahedron. There are three two-fold symmetry axes. Each bisects the whole molecule perpendicular to the three-fold axis. The point group symmetry is D_{3d}, although there is no molecular symmetry other than the inversion center for the complex in the solid state.

The silver atoms, each of which is coordinated to three sulfur atoms of the dibutyldithiocarbamate ligands, are located at the vertices of a distorted octahedron. The displacements of the silver atoms from the plane through the sulfur atoms range from 0.0210(4) to 0.02804(8) nm. The Ag—S distances range from 0.2448 to 0.2966 nm. The ligands are tridentate (μ_2-S; μ_1-S) and bridge across the Ag_3 triangles with bridging S atoms occupying all three edges of these trans-oriented triangles. The other six sulfur atoms [S(1), S(3), S(5), S(1) # 1, S(3) # 1, S(5) # 1] of the ligands are terminally coordinated to only one silver atom. The Ag(1)—Ag(3) and Ag(1)—Ag(2) distances are 0.29610(7) and 0.29657(7) nm, respectively. It indicates the formation of Ag—Ag bond. The Ag—Ag distances within the Ag_3 triangles, which have only one edge bridged by S, are in the range of 0.29610—0.31943 nm. The average Ag—Ag distance within the two Ag_3 triangles having each edge occupied by the bridging S atoms is 0.30221 nm. The mean distance between these two Ag_3 triangles through which the pseudo three-fold axis passes is 0.31943 nm.

Crystal data for the title complex is available from the Cambridge Crystallographic Data Center (CCDC No. 160050).

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