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研究简报

双核银化合物：六乙烯基硫脲二高氯酸合银的合成和晶体结构

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Synthesis and Crystal Structure of Dimeric Silver (I) Complex: Hexaethylene Thiourea Bispercholate Disilver (I), $[Ag_2(ETU)_6]\cdot(ClO_4)_2$

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The crystal and molecular structure of $[Ag_2(ETU)_6]\cdot(ClO_4)_2$ has been determined by X-ray crystallography. It crystallizes in the monoclinic, space group $P2_1/c$, with lattice parameters $a=0.63270(9)$ nm, $b=2.4264(2)$ nm, $c=1.2128(1)$ nm, $\beta=92.721(9)°$, $V=1.8597(3)$ nm^3, $Z=4$, $D_c=1.835$ Mg·m^{-3}, $F(000)=1032$, $\mu=1.591$ mm^{-1}. The molecule is built up of centro-symmetric dimeric entities, in which the four-membered Ag_2S_2 ring is planar and the angle of S(3)-Ag(1)-S(3A) is 107.70(2)° for symmetry requirements. The silver atoms have slightly distorted tetrahedral coordination environment, and the sulfur atoms of the ETU group occupy four coordination sites. The two percholate anions in general position balance the charge. In the solid state, the title compound forms three dimensional network structures through hydrogen bonds. The intermolecular hydrogen bonds and extensive intermolecular interaction connect the $[Ag_2(ETU)_6]^{2+}$ ion and two ClO_4^- anions to contribute to the stability of the structure. CCDC: 208731.

Keywords: crystal structure disilver complex ethylene thiourea

0 Introduction

Fungicides of the ethylenebisdithiocarbamate (EBDC) group have been widely used in the cultivation of potatoes, vegetables and berries. Ethylene thiourea (ETU) is present as an impurity (up to 10%) in fungicides of the EBDC group[1], and it is also an important metabolite from the biotic degradation of the fungicides. It has been proved that ETU have thyreotoxic, teratogenic, and carcinogenic effects on test animals[2]. Recently, ETU was found to induce DNA damage to liver, kidney, lung, and spleen in mice[3]. Industrially, ETU is commonly used as an additive in the production of rubber. ETU is a polar compound with a high water solubility and it is known to be mutagenic and teratogenic in rats[4], for which

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reason most studies on degradation of EBDC fungicides focus on the formation of ETU[5,6]. However, the chemistry of metal complexes with ETU ligands has scarcely been explored. ETU can coordinate to metal easily because of its multifunctional coordination modes (unidentate-N, unidentate-S or bidentate-N: S)[7]. For these reasons, our group began to synthesize various metal coordination compounds with ETU and study their chemical properties. Ag (I) systems were selected for our studies because of evidence that Ag (I) has a distinct preference for bonding to S atom. When we chose ETU reacted with $AgClO_4$ in EtOH, $[Ag_2(ETU)_6] \cdot (ClO_4)_2$ was obtained. Herein we report the crystal structure of hexa(ethylene thiourea) bispercholate disilver (I), $[Ag_2(ETU)_6] \cdot (ClO_4)_2$.

1 Experimental

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

1.1 Synthesis

To a hot EtOH solution of ETU ($C_3H_6N_2S$ 8.2g, 0.08mol), an EtOH solution of silver (I) perchlorate hydrate ($AgClO_4 \cdot H_2O$ 2.25g, 0.01mol) was added and refluxed for 5h. The colorless solution was filtered and the filtrate was left to stand undisturbed. The colorless prisms of the title complex were obtained by slow evaporation of EtOH at room temperature for one week. The C, H and N contents were determined by elemental analysis(Found(%): C, 20.93; H, 3.48; N, 16.08. Calc. (%) for $C_9H_{18}AgClN_6O_4S_3$: C, 21.04; H, 3.53; N, 16.36). Yield(%): ~94.

1.2 Crystallographic Data Collection and Structure Determination

A summary of the key crystallographic information is given in Table 1. The selected crystal of the complex with suitable dimensions was mounted on a SMART CCD diffractometer. The data collection was performed at room temperature (20℃) by $\omega/2\theta$ scan technique with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.071073nm). Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction was carried out by using SADABS[8] program. The structure were solved by direct methods using SHELXS-97[9]. All the nonhydrogen atoms were refined on F^2 anistropically by full-matrix least squares method[10]. Hydrogen atoms were located from the difference Fourier map and added to the structure calculations, but their positions were not refined. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave $R = 0.0343$, $wR = 0.0990$ for 3669 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[(2(F_o^2) + (0.0570P)^2 + 1.1003P]$, where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray Crystallography[11].

CCDC: 208731.

Table 1 Crystal Data and Structure Refinement for the Title Compound

empirical formula	$C_9H_{18}AgClN_6O_4S_3$
formula weight	513.79
temperature/K	293(2)
wavelength/nm	0.071073
crystal system, space group	monoclinic, $P2_1/c$
a/nm	0.63270(9)
b/nm	2.42637(17)
c/nm	1.21280(11)
β/(°)	92.721(9)
volume/nm^3	1.8597(3)
Z	4
calculated density/(Mg · m^{-3})	1.835
absorption coefficient/mm^{-1}	1.591
F(000)	1032
crystal size/mm^3	0.2×0.3×0.2
theta range for data collection/(°)	1.68 to 27.50
limiting indices	$-1 \leq h \leq 8$
	$-1 \leq k \leq 31$
	$-15 \leq l \leq 15$
reflections collected/unique	5627/4256[R(int) = 0.0241]
completeness to θ = 27.50	99.5%
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	4256/0/218
goodness-of-fit on F^2	1.056
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0343, wR_2 = 0.0990
R indices (all data)	R_1 = 0.0412, wR_2 = 0.1043
extinction coefficient	0.0090(6)
largest diff. peak and hole/(e · nm^{-3})	574 and −714

2 Result and Discussion

The crystal structure of the title complex, $[Ag_2(ETU)_6] \cdot (ClO_4)_2$, consists of discrete $[Ag_2(ETU)_6]^{2+}$ dication and two ClO_4^- anions. The silver

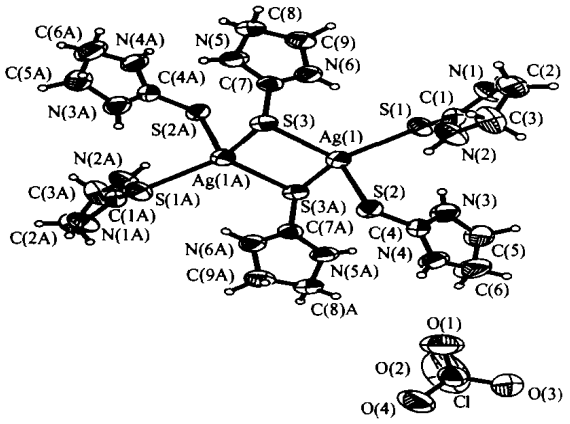

Fig. 1　Structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme

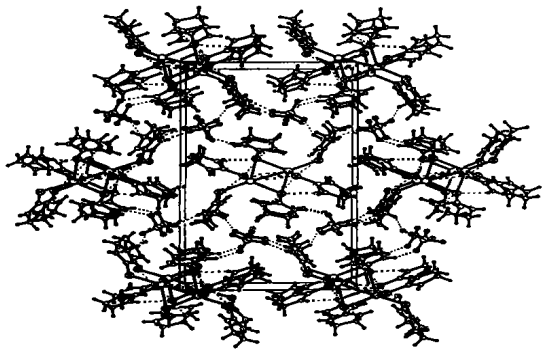

Fig. 2　A view of the crystal packing down the *a* axis for $[Ag_2(ETU)_6]\cdot(ClO_4)_2$

(I) ion is situated on a crystallographic inversion center and has a tetrahedral coordination environment. Fig. 1 and 2 show a perspective view of the title compound with atomic numbering scheme and a perspective view of the crystal packing in the unit cell, respectively. Selected bond lengths(nm) and angles(°) are presented in Table 2.

The polyhedron about silver can be described as tetrahedron with four S atoms from four neutral ETU ligands. Four ETU molecules through the S atoms are coordinated to each Ag(I) ion, and two percholate anions in general position balances the charge. The bridging mode is constructed two S atoms of the two ETU ligands, and to form a four-membered Ag_2S_2 ring. The Ag(1A)-S-Ag(1) angle is 72.30(2)°. The S-Ag-S angles in the title complex are in the range of 102.83(3)°~115.28(3)° (average 109.35°), quite close to the ideal tetrahedral angle. The Ag···Ag distance [0.30968(5) nm] is shorter than that of other disilver (I) compounds[12,13].

The four Ag-S bonds around an Ag (I) ion are non-equivalent. The bridging bonds [0.26007(8) nm and 0.26807(8) nm, respectively] are significantly longer than the other two Ag-S bonds [0.25565(8) nm and 0.25664(8) nm, respectively]. No significant difference of the Ag-S bond lengths is observed compared with those of similar tetrahedral structure [0.2507~0.2644nm], which were found in other silver(I) complexes[7,12,14].

The three ethylene thiourea rings with the conjunction sulfer atom are close to planar, the maximum deviation from the least squares plane through the ring atoms are 0.0027(3) nm, 0.0045(3) nm and 0.0308(3) nm, respectively. The dihedral angles between three ethylene thiourea rings are 10.90(2)°, 80.84(2)° and 88.69(2)°, respectively.

The most interesting structural feature of the complex is the intramolecular and intermolecular hydrogen bonds, potentially weak (C-H···Y hydrogen bonds, Y=O, N and S) intermolecular interactions and π-π stacking interactions between the molecules. In the solid state of $[Ag_2(ETU)_6]\cdot(ClO_4)_2$, the secondary amine nitrogen atoms are involved in three intramolecular hydrogen bonds with the thiono sulfur atoms having the contact distances of 0.34746(1) nm, 0.35127(1) nm and 0.35514(1) nm for N(2)···S(2), N(3)···S(1) and N(6)···S(1), respectively. There are two O···H-N and one S···H-N intermolecular

Table 2　Selected Bond Lengths(nm) and Angles(°)

Ag(1)-S(2)	0.25565(8)	Ag(1)-S(3)	0.25664(8)	Ag(1)-S(1)	0.26007(8)
Ag(1)-S(3A)	0.26807(8)	Ag(1A)-S(3)	0.26807(8)	Ag(1)-Ag(1A)	0.30968(5)
S(2)-Ag(1)-S(3)	111.18(3)	S(2)-Ag(1)-S(1)	109.21(3)	S(1)-Ag(1)-S(3)	115.28(3)
S(2)-Ag(1)-S(3A)	102.83(3)	S(3)-Ag(1)-S(3A)	107.70(2)	S(1)-Ag(1)-S(3A)	109.91(3)
Ag(1)-S(3)-Ag(1A)	72.30(2)				

Table 3 Intermolecular Interaction Distances(nm) of the Title Compound

D	H	A	symm	D-H	H…A	D…A	D-H…A
N(1)	H(1B)	O(3)	$-1+x,\ 1/2-y,\ 1/2+z$	0.08600	0.21754	0.29596	151.47
N(4)	H(4B)	S(3)	$1-x,\ -y,\ -z$	0.08600	0.26966	0.34439	146.10
N(5)	H(5A)	O(1)	$-1+x,\ 1/2-y,\ -1/2+z$	0.08600	0.22228	0.30195	154.02
C(3)	H(3D)	O(4)	$-1+x,\ -1+y,\ z$	0.09700	0.25429	0.34069	148.36
C(9)	H(9A)	S(3)	$-1+x,\ y,\ z$	0.09700	0.28726	0.37557	151.82

D: Donor; A: Acceptor; symm: Symmetry applied in acceptor.

hydrogen bonds in the structure. The donor and acceptor distances are N(2)…O(3) $(-1+x,\ 1/2-y,\ 1/2+z)$ 0.29596(4) nm, N(5) …O(1) $(-1+x,\ 1/2-y,\ -1/2+z)$ 0.30195(5) nm and N(4) …S(3) $(1-x,\ -y,\ -z)$ 0.34439(4) nm, respectively. The O(4) and S(3) with C atoms in alkyl form potentially weak C-H…Y (Y = O, S) intermolecular interactions, the donor and acceptor distances are C(3) …O(4) 0.34069nm [symmetry code: $x,\ y,\ z$] and C(9) …S(3) 0.37557nm [symmetry code: $-1+x,\ y,\ z$], respectively (See Table 3).

There are some π-π stacking interactions between the molecules in the crystal. There are two types of strong π-π stacking interactions; Ag_2S_2 ring-ethylene thiourea ring$(-x,\ -y,\ -z)$ and ethylene thiourea ring - ethylene thiourea ring $(-x,\ -y,\ -z)$. The center-to-center distances are 0.4045nm and 0.4279nm, respectively. The shortest interplanar distances above are 0.2744nm and 0.3213nm, respectively. It is obvious that they form the slightly stronger π-π stacking interaction[15, 16]. All above intermolecular hydrogen bonds and extensive intermolecular interaction link the $[Ag_2(ETU)_6]^{2+}$ and perchlorate anions forming three-dimensional network which stabilizes the structure.

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