A Novel Chiral Silver(I) Complex from the Reaction of Thiazolidinethione with AgOAc

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Keywords: Silver / Cluster compounds / S ligands / Structure elucidation

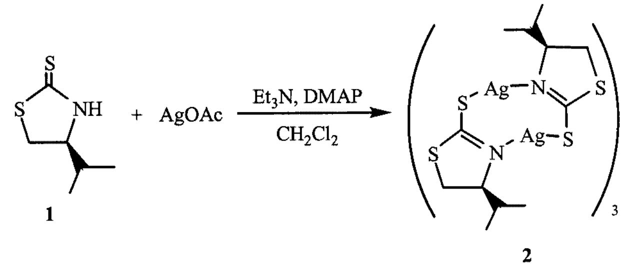
A novel chiral silver(I) complex was successfully synthesized from the reaction of chiral (*S*)-4-isopropylthiazolidine-2-thione ligand (**1**) with AgOAc in dichloromethane in the presence of Et_3N and DMAP at room temperature. Its unique crystal structure was unambiguously disclosed by X-ray analysis. The six silver atoms and six (*S*)-4-isopropylthiazolidine-2-thione ligands present in the complex are connected through the S and N atoms to form a cluster containing a silver octahedron with six faces of the octahedron capped by ligands.

Introduction

Historically, the chemistry of metal-sulfur-nitrogen cluster complexes has been a very active field for organometallic chemists because of the novelty and versatility of the structures and reactivities of such clusters, as well as their potential applications as models for the active site in non-heme proteins such as the ferredoxins.[1] In addition, many cluster complexes bearing chiral ligands can be used as catalysts in asymmetric reactions.[2] Recently, during our investigations on the utilization of thiazolidine-2-thione as a chiral auxiliary, we found that the nitrogen atom and sulfur atom of the thiocarbonyl group of thiazolidine-2-thione can readily coordinate to a metal center to afford the corresponding chiral metal complex. In particular, with AgOAc as the metal source we found that a very unusual chiral metal cluster was formed under very mild reaction conditions. This novel cluster has a silver octahedron with six faces of the octahedron capped by chiral ligands. Herein, we wish to report the synthesis and crystal structure of this novel chiral Ag^I cluster complex.

Results and Discussion

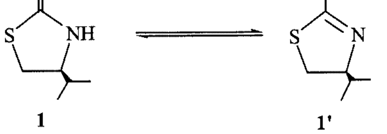
The chiral ligand (*S*)-4-isopropylthiazolidine-2-thione (**1**) was prepared according to a literature procedure.[3] The reaction of **1** with AgOAc gave a novel Ag^I complex **2** in the presence of Et_3N and DMAP in dichloromethane under very mild reaction conditions (Scheme 1). The structure of **2** was established by spectroscopic data and microanalysis.



Scheme 1

We believe that the formation of **2** is caused by the fact that (*S*)-4-isopropylthiazolidine-2-thione (**1**) is in equilibrium with its tautomer **1′**, which reacts directly with AgOAc to give the corresponding Ag^I complex **2** (Scheme 2).[4] In order to clarify the crystal structure of **2** by X-ray analysis, we recrystallized **2** from dichloromethane and petroleum ether (1:5) to obtain a yellowish single crystal of **2** in which one molecule of CH_2Cl_2 was included (see the microanalysis data of **2** in the Exp. Section). The crystal structure is shown in Figure 1. Selected bond lengths and bond angles are shown in Table 1 and the crystal data of **2** are summarized in Table 2.

The chiral Ag^I complex **2** is an air- and moisture-stable solid which crystallizes in the space group *P*2(1)3. Six (*S*)-4-isopropylthiazolidine-2-thione (**1**) ligands and six Ag^I atoms form a cluster possessing a silver octahedron with six faces of the octahedron capped by ligands that alternate in



Scheme 2

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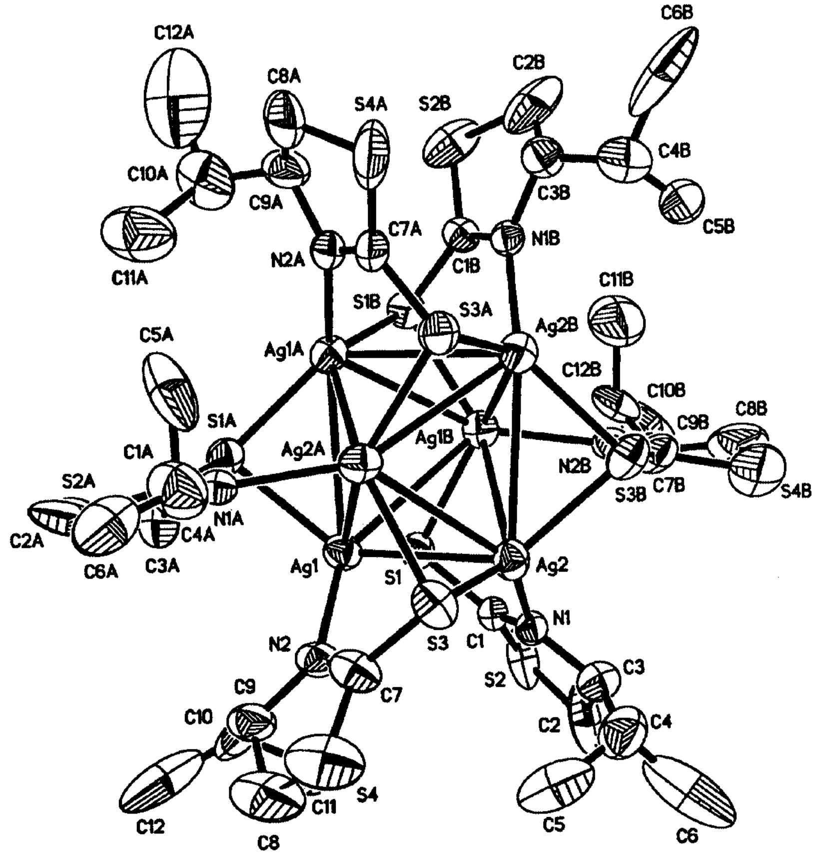


Figure 1. The X-ray crystal structure of **2**

Table 1. Selected bond lengths [Å] and angles [deg] for **2**

Ag(1)−N(2)	2.250(5)	Ag(1)−S(1)	2.4511(16)
Ag(1)−S(1)#1	2.5117(17)	Ag(1)−Ag(2)	2.9812(6)
Ag(1)−Ag(2)#1	3.2076(6)	Ag(1)−Ag(1)#2	3.3260(8)
Ag(1)−Ag(1)#1	3.3260(8)	Ag(2)−N(1)	2.261(5)
Ag(2)−S(3)	2.4582(18)	Ag(2)−S(3)#2	2.5139(19)
Ag(2)−Ag(1)#2	3.2076(6)	S(1)−Ag(1)#2	2.5117(17)
N(2)−Ag(1)−S(1)	128.03(14)	N(1)−Ag(2)−S(3)	129.07(13)
N(2)−Ag(1)−S(1)#1	108.60(13)	N(1)−Ag(2)−S(3)#2	108.65(12)
S(1)−Ag(1)−S(1)#1	116.67(8)	S(3)−Ag(2)−S(3)#2	116.77(9)
N(2)−Ag(1)−Ag(2)	83.41(15)	N(1)−Ag(2)−Ag(1)	83.63(12)
S(1)−Ag(1)−Ag(2)	80.93(4)	S(3)−Ag(2)−Ag(1)	80.46(4)
S(1)#1−Ag(1)−Ag(2)	136.62(4)	S(3)#2−Ag(2)−Ag(1)	134.88(5)
N(2)−Ag(1)−Ag(2)#1	78.21(14)	N(1)−Ag(2)−Ag(1)#2	78.05(13)
S(1)−Ag(1)−Ag(2)#1	135.74(4)	S(3)−Ag(2)−Ag(1)#2	133.90(4)
S(1)#1−Ag(1)−Ag(2)#1	75.60(4)	S(3)#2−Ag(2)−Ag(1)#2	75.24(4)
Ag(2)−Ag(1)−Ag(2)#1	66.131(19)	Ag(1)−Ag(2)−Ag(1)#2	64.898(19)
N(2)−Ag(1)−Ag(1)#2	144.19(15)	C(1)−S(1)−Ag(1)	105.9(2)
S(1)−Ag(1)−Ag(1)#2	48.70(4)	C(1)−S(1)−Ag(1)#2	98.75(19)
S(1)#1−Ag(1)−Ag(1)#2	99.77(4)	Ag(1)−S(1)−Ag(1)#2	84.15(5)
Ag(2)−Ag(1)−Ag(1)#2	60.844(17)	C(7)−S(3)−Ag(2)	104.5(2)
Ag(2)#1−Ag(1)−Ag(1)#2	88.441(13)	C(7)−S(3)−Ag(2)#1	99.7(2)
N(2)−Ag(1)−Ag(1)#1	128.88(13)	Ag(2)-S(3)−Ag(2)#1	85.71(6)
S(1)−Ag(1)−Ag(1)#1	101.09(4)	C(1)−N(1)−Ag(2)	122.3(4)
S(1)#1−Ag(1)−Ag(1)#1	47.15(4)	C(3)−N(1)−Ag(2)	124.9(4)
Ag(2)−Ag(1)−Ag(1)#1	92.372(15)	C(7)−N(2)−Ag(1)	122.5(5)
Ag(2)#1−Ag(1)−Ag(1)#1	54.258(15)	C(9)−N(2)−Ag(1)	125.5(5)
Ag(1)#2−Ag(1)−Ag(1)#1	60.0		

Table 2. Crystal data and structure refinement of **2**

Empirical formula	$C_{37}H_{62}Ag_6Cl_2N_6S_{12}$
Formula weight	1693.77
Temperature	293(2) K
Crystal system	cubic
Lattice type	primitive
a [Å]	18.2009(4)
b [Å]	18.2009(4)
c [Å]	18.2009(4)
α	90°
β	90°
γ	90°
V [Å^3]	6029.5(2)
Space group	*P*2(1)3
Z	4
$D_{calcd.}$ [g/cm^3]	1.866
F(000)	3336
θ range for data collection	1.58 to 28.31°
Reflections collected/unique	37226/4896 [*R*(int) = 0.0947]
Completeness to θ = 28.32	98.2%
Absorption correction	Sadabs
Max. and min. transmission	1.0000 and 0.7809
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4896/2/222
Goodness-of-fit on F^2	0.738
Final *R* indices [$I > \sigma(I)$]	$R_1 = 0.0329$, $wR_2 = 0.0655$
R indices (all data)	$R_1 = 0.0801$, $wR_2 = 0.0688$
Absolute structure parameter	−0.02(4)
Extinction coefficient	0.000 085(18)
Largest diff. peak and hole [e·Å^{-3}]	0.609 and −0.386

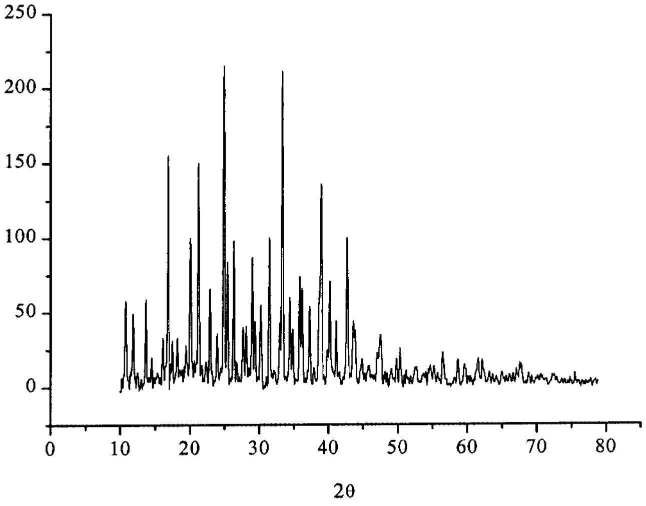


Figure 2. The powder XRD spectrum of **2** obtained directly by column chromatography

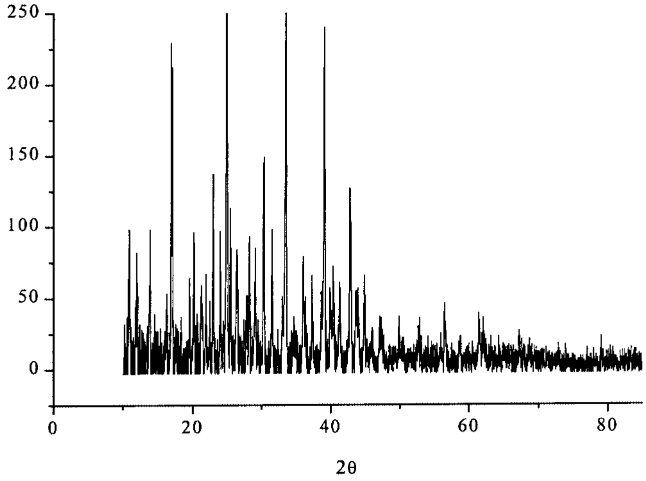


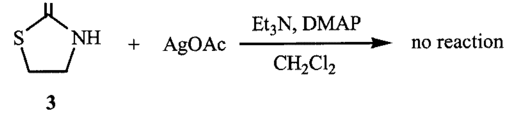
Figure 3. The powder XRD spectrum of **2** obtained after recrystallization

their orientation (Figure 1): two adjacent ligands take an anti-parallel direction using their S and N atoms to coordinate to the Ag center forming the Ag/S,N core network. Each Ag atom is coordinated by two sulfur atoms with bond lengths of 2.4527(16) and 2.5121(16) Å and a nitrogen atom with a bond length of 2.247(5) Å. In addition, the Ag^I-Ag^I distances are 2.9811(6), 3.2071(6), 3.3269(8), and 3.2071(6) Å. This distance is within the sum of the van der Waals radii of Ag of 3.44 Å (Ag = 1.72 Å[5]). The six silver atoms and six sulfur atoms present in complex **2** are connected with S and N atoms with the bond angles shown in Table 2. The Ag/S,N core forms a six-silver network. Two faces located at opposite sites of the cluster **2** are open. Based on a powder XRD analysis of the **2** obtained directly from the solvent after column chromatography (Figure 2) and of a single crystal of **2** obtained after recrystallization from dichloromethane and petroleum ether (1:5) (Figure 3), we can conclude that both samples are essentially the same. It is impossible to form by-products such as clusters of different nuclearity or coordination polymers from solution.

Compared to the metal-metal distances in the open-shell metallic silver in cluster **2** as well as to the rather underestimated sum of van der Waals radii (Ag−Ag = 3.44), we believe that a closed-shell d^{10}-d^{10} metallophilic interaction (argentophilic interaction) may exist in the above clusters[6] as the Ag−Ag distance is close to the upper van der Waals limit.[7] Assignment of these metal-metal contacts to crystal packing forces is unwarranted since the M−M vectors have a specific directionality. In addition, the M−M interactions do not seen to be dictated by ligand-packing effects. No π-stacking or hydrogen-bonding interactions are apparent in the crystal structures of **2**.

It should be emphasized here that when using the simplest thiazolidine-2-thione **3** as the substrate under the same reaction conditions, no reaction occurred (Scheme 3). We believe that this may be due to the fact that the tautomer of **3** is very unstable and the equilibrium between **3** and its tautomer lies almost completely in the direction of **3**.

Yamamoto and co-workers have reported many catalytic enantioselective reactions using chiral phosphane ligand·Ag^I complexes as the catalyst, although they did not disclose the nature of the active species.[8] Therefore, we also



Scheme 3

tried to use this novel chiral cluster in some catalytic asymmetric reactions. Unfortunately we found that these reactions are very sluggish. We are now looking for suitable reaction conditions for these catalytic asymmetric reactions.

In conclusion, we have isolated a novel Ag^I/S,N metal cluster from the reaction of (*S*)-4-isopropylthiazolidine-2-thione (**1**) with AgOAc and determined its structure by X-ray analysis. This result also confirms that silver(I) can easily form an unexpected polymeric metal cluster with an S,N ligand. Such a chiral metal cluster should be very interesting in the synthesis of novel metal complexes for asymmetric catalysis. Work in this direction is currently in progress.

Experimental Section

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined in a solution of $CHCl_3$ or methanol at 20 °C by using a Perkin−Elmer-241 MC digital polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg·cm^2·g^{-1}. ^{1}H NMR spectra were determined for solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard on a Bruker AMX-300 spectrometer; *J* values are in Hz. IR spectra were determined on a Perkin−Elmer 983 spectrometer. Mass spectra were recorded with an HP-5989 instrument. All solid compounds reported in this paper gave satisfactory CHN microanalyses. The chiral starting materials (*S*)-4-isopropylthiazolidine-2-thione (**1**) and thiazolidine-2-thione (**3**) were prepared according to literature procedures.[3]

(*S*)-4-Isopropylthiazolidine-2-thione (1): Yield 300 mg, 96%; mp: 66−67 °C; $[\alpha]_D^{20} = -35.4$ ($c = 0.96$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 1.0$ (d, $J = 7.2$ Hz, 3 H, CH_3), 1.03 (d, $J = 7.2$ Hz, 3 H, CH_3), 1.96 (quintet, $J = 7.2$ Hz, 1 H, CH), 3.33 (dd, $J = 11.2$, 8.5 Hz, 1 H, CH), 3.52 (dd, $J = 11.2$, 5.5 Hz, 1 H, CH), 4.0−4.10 (m, 1 H, CH), 7.62 (s, 1 H, NH) ppm. The physical data and ^{1}H NMR spectroscopic data are consistent with those reported in the literature.[3c]

Thiazolidine-2-thione (3): Yield 450 mg, 95%. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 3.58$ (t, J = 7.6 Hz, 2 H, CH_2), 4.01 (t, J = 7.6 Hz, 2 H, CH_2), 8.27 (s, 1 H, NH) ppm. The physical data and ^{1}H NMR spectroscopic data are consistent with those reported in the literature.[3c]

Preparation of Chiral Silver(I) Complex 2: (*S*)-4-isopropylthiazolidine-2-thione (**1**) (65 mg, 0.5 mmol), AgOAc (84 mg, 0.5 mmol) and DMAP (6.0 mg, 0.05 mmol) were added to a Schlenk tube under argon atmosphere. CH_2Cl_2 (5.0 mL) and Et_3N (61 mg, 0.6 mmol) were added successively and the reaction mixture was stirred at room temperature for 24 h. After filtration, the filtrate was washed with water (10 mL) and the organic layer was dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (length: 20 cm, φ: 2 cm) to give the complex **2** as a yellowish solid (eluent: EtOAc/petroleum ether, 1:4). 120 mg, 83%; m.p. 158−160 °C (dec.); $[\alpha]_D^{20} = +251$ ($c = 0.11$, $CHCl_3$). IR (KBr): $\tilde{\nu} = 1265$, 1421, 1541 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 0.94$ (d, $J = 6.7$ Hz, 3 H, CH_3), 0.97 (d, $J = 6.7$ Hz, 3 H, CH_3), 2.22−2.40 (m, 1 H, CH), 3.30 (d, $J = 9.7$ Hz, 2 H, CH_2), 4.20−4.32 (m, 1 H, CH) ppm. ESI-MS: $m/z = 1259$ [M^+] (acetone/acetonitrile, 2:1) $C_{36}H_{60}Ag_2N_6S_{12}\cdot CH_2Cl_2$ (1693.77): calcd. C 26.24, H 3.69, N 4.96; found C 26.45, H 3.64, N 4.94.

X-ray Crystallography: A suitable crystal was mounted on the top of a glass capillary. Crystal data and details of data collection and structure refinement are given in Table 2. Data were collected on a CCD area detector with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) using the ω-2θ technique at 20 °C. A total of 4896 unique reflections was collected. The data were collected for Lorentz polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares. All hydrogen atoms were included in their calculated positions. All calculations were performed using the SHELXS-97 (Sheldrick, 1990) crystallographic software package. Final *R* and R_w values were 0.0329 and 0.0655. CCDC-177953 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the Inoue Photochirogenesis Project for chemical reagents, the State Key Project of Basic Research (Project 973) (No. G2000048007) and the National Natural Science Foundation of China (20025206) for financial support.

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[1] For comprehensive reviews, see: [1a] R. D. Adams, M. Tsai, *J. Cluster Sci.* **1979**, *1*, 249−267. [1b] L. Marko', B. Marko'-Monostory, in *The Organic Chemistry of Iron* (Eds.: E. A. K. von Gustorf, F.-W. Grevels, I. Fischer); Academic Press: New York, **1981**; p. 283. [1c] H. Ogino, S. Inomata, H. Tobita, *Chem. Rev.* **1998**, *98*, 2093−2121.

[2] *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima); VCH Publishers: Cambridge, **1993**.

[3] [3a] C. Agami, F. Couty, B. Prince, O. Vehier, *Tetrahedron Lett.* **1993**, *34*, 7061−7062. [3b] I. Ryu, S. Murai, N. Sonoda, *J. Org. Chem.* **1986**, *51*, 2391−2393. [3c] D. Delaunay, L. Toupet, M. L. Corre, *J. Org. Chem.* **1995**, *60*, 6604−6607.

[4] S. Jasmin, D. R. Dalton, *J. Heterocycl. Chem.* **1994**, *31*, 1079−1081.

[5] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451.

[6] For closed-shell d^{10}-d^{10} interaction in inorganic chemistry see: P. Pyykko, *Chem. Rev.* **1997**, *97*, 597−636.

[7] For ligand-unsupported metal-metal (M = Cu, Ag) interactions see: [7a] K. Singh, J. R. Long, P. Stavropoulos, *J. Am. Chem. Soc.* **1997**, *119*, 2942−2943. [7b] C.-M. Che, M.-C. Tse, M. C. W. Chan, K. K. Cheung, D. L. Phillips, K.-H. Leung, *J. Am. Chem. Soc.* **2000**, *122*, 2464−2468.

[8] [8a] A. Yanagisawa, H. Nakashima, A. Ishiba, H. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 4723−4724. [8b] A. Yanagisawa, Y. Nakatsuka, H. Nakashima, H. Yamamoto, *Synlett* **1997**, 933−934. [8c] A. Yanagisawa, A. Ishiba, H. Nakashima, H. Yamamoto, *Synlett* **1997**, 88−90. [8d] A. Yanagisawa, Y. Nakatsuka, K. Asakawa, H. Kageyama, H. Yamamoto, *Synlett* **2001**, 69−72. [8e] M. Shi, W.-S. Sui, *Tetrahedron: Asymmetry* **2000**, *11*, 773−779.

Received May 24, 2002
[I02288]