

Formation and X-ray Structure of a Silver Iodide Based Polymeric Complex (Ag₅I₆)_n(Ph₃PCH₂I)_n

Xianglin Jin*, Kaluo Tang, Weidong Liu, and Youqi Tang

Institute of Physical Chemistry, Peking University, Beijing 100871, People's Republic of China

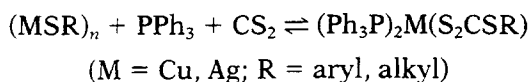
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ABSTRACT

Compounds [(Ph₃P)₂AgS₂CSR (R = Bu', TIPT(2,4,6-triisopropylthiophenolato))], formed by inserting CS₂ into the Ag-S bond in AgSR in the presence of PPh₃, react with CH₂I₂ to give pale yellow crystals of (Ag₅I₆)_n(Ph₃PCH₂I)_n, which consist of the polymeric anion (Ag₅I₆)_n⁻ and the cation (Ph₃PCH₂I)_n⁺. The poly-anion (Ag₅I₆)_n⁻ is composed of alternate I₅-pentagons and Ag₅-pentagons that are connected by Ag-I bonds along the C axis to form a layered "pagoda" structure, in which there exists an unusual stereochemistry of iodine. Crystal data: monoclinic, space group P2₁/c, a = 15.004(12) Å, b = 27.19(2) Å, c = 7.898 Å, β = 97.18(5)°, V = 3205(4) Å³, Z = 4, R = 0.0673 for 2726 observed reflections.

INTRODUCTION

In recent years, we have found that silver or copper thiolate complexes can react readily with CS₂ in the presence of PPh₃ to give almost the same structure of mononuclear insertion products [1-4]



This is a reversible reaction. Further investigation showed that some insertion products of this kind can also react easily with various solvents to

form unexpected metal cluster complexes. By applying this method, we have synthesized a series of cluster complexes with amazing structures, including [Ag₁₄(SPh)₁₂(PPh₃)₈(μ₆-Cl)] Cl [5], Cu₁₄(μ₂-S)(SPh)₁₂(PPh₃)₆ [6], and so on. Recently, a silver iodide based polymeric complex (Ag₅I₆)_n(Ph₃PCH₂I)_n was obtained by the reaction of the insertion products (Ph₃P)₂AgS₂CSR (R = Bu', TIPT (2,4,6-triisopropylthiophenolato)) with CH₂I₂. The silver iodide based complex has been studied extensively because of interest in the bonding mechanisms, whereby silver iodide complexes may act as potential ice nucleants or solid electrolytes [7]. The method we reported may provide the basis for a new route for the synthesis of novel silver iodide based complexes. Here, we present the synthesis and crystal structure of a novel complex.

EXPERIMENTAL

The title compound was obtained as follows. The yellow crystals of the compounds [(Ph₃P)₂AgS₂CSR] (R = Bu', TIPT) were synthesized according to the previously reported method [1,2]. When compounds [(Ph₃P)₂AgS₂CSR] (R = Bu', TIPT) (30 mg) were dissolved in CH₂I₂ (5 cm³), the initial red color of the solvent changed into yellow abruptly. Pale yellow block crystals formed by slow diffusion of acetone into the CH₂I₂ solution over 2 months. The crystals are stable in the air, mp 202-206°C.

X-ray Crystal Structure Determination of the Title Complex

The crystal data for this complex are summarized in Table 1, together with some details. The diffraction intensities were collected at room temperature on a Siemens R3 diffractometer with Mo

Dedicated to Professor Shigeru Oae on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

TABLE 1 Summary of Crystal Data and Experimental Details for Title Complex

Formula	$C_{19}H_{17}Ag_5I_7P$
M	1703.9
Space group	$P2_1/c$
Color/Habit	pale yellow block
Crystal system	monoclinic
$a/\text{\AA}$	15.004(12)
$b/\text{\AA}$	27.19(2)
$c/\text{\AA}$	7.898(4)
$\beta/^\circ$	97.18(5)
$V/\text{\AA}^3$	3205(4)
Z	4
$D_c/g\text{ cm}^{-3}$	3.531
$\lambda(\text{Mo } K_\alpha)/\text{\AA}$	0.71073
$F(000)$	3008
Crystal dimension/ mm^3	$0.4 \times 0.2 \times 0.2$
Scan mode	$2\theta-\theta$
2θ range	$3.0 < 2\theta < 45.0$
Scan rate/ min^{-1}	4.88–29.30
Scan range/ $^\circ$	1.0
Number of reflections measured	4719
Number observed [$F > 5.0 \sigma(F)$]	2726
R	0.0673
R_w	0.0777

K_α ($\lambda = 0.71073 \text{ \AA}$) radiation. The structure was solved by a direct method with the SHELXTL PLUS program. Blocked full-matrix least-squares refinement of all positional parameters and anisotropic thermal parameters for all the nonhydrogen atoms in the ligands were obtained. The atomic coordinates for the nonhydrogen atoms of the title complex are presented in Table 2. Additional material available from the author comprises thermal parameters, bond lengths, and angles.

RESULTS AND DISCUSSION

The crystal structure determination indicates that the title complex consists of the polymeric anion $(\text{Ag}_5\text{I}_6)_n^-$ and the $(\text{Ph}_3\text{PCH}_2\text{I})^+$ cation. The cations are distributed over interstitial positions among the anions. An ORTEP view of a part of the polyanion $(\text{Ag}_5\text{I}_6)_n^-$ is displayed in Figure 1. The packing diagram of the unit cell along the c -axis is shown in Figure 2. The polyanion is arranged to form a layered polymeric "pagoda" structure, which is composed of alternate I_5 -pentagons and Ag_5 -pentagons and connected by Ag–I bonds. Each "story" of the pagoda is built up with an I_5 -pentagon "floor" and an Ag_5 -pentagon "ceiling," between which there lies an I^* atom. The I^* atom is 1.07 \AA above the I_5 -pentagon plane and 1.47 \AA below the Ag_5 -pentagon plane. Neighbored stories, between which there is no I atom, are placed in a staggered manner. The $\text{Ag} \cdots \text{Ag}$ distances in the Ag_5 -pentagon and the $\text{I} \cdots \text{I}$ distances in the I_5 -pentagon average 4.73 \AA (4.629–

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	U(eq)
Ag(1)	4001(2)	2999(1)	4907(3)	30(1)
Ag(2)	1460(2)	4055(1)	4339(3)	36(1)
Ag(3)	–1052(2)	2999(1)	3764(3)	33(1)
Ag(4)	–183(2)	1314(1)	3875(3)	28(1)
Ag(5)	3036(2)	1274(1)	4653(3)	30(1)
I(1)	3242(2)	2813(1)	8013(4)	80(1)
I(2)	1440(2)	3521(1)	7449(4)	78(1)
I(3)	–252(2)	2772(1)	7142(5)	79(1)
I(4)	423(2)	1632(2)	7261(5)	86(1)
I(5)	2517(2)	1626(1)	7779(5)	84(1)
I(6)	1494(2)	2488(1)	6176(3)	35(1)
I(7)	6545(2)	1394(1)	–330(4)	56(1)
P(1)	6828(6)	841(3)	3365(12)	35(3)
C(11)	6538(24)	1379(12)	4334(43)	37(12)
C(12)	7177(22)	1787(12)	4506(49)	42(13)
C(13)	6964(28)	2208(14)	5396(57)	60(17)
C(14)	6158(24)	2257(12)	6060(40)	36(12)
C(15)	5531(22)	1884(10)	5906(43)	36(12)
C(16)	5746(22)	1435(13)	5033(49)	44(13)
C(21)	5820(23)	487(13)	2815(41)	38(12)
C(22)	5043(25)	696(14)	2011(48)	46(14)
C(23)	4301(29)	416(17)	1646(56)	65(18)
C(24)	4299(32)	–67(17)	1950(59)	68(19)
C(25)	5045(39)	–289(18)	2653(56)	77(21)
C(26)	5822(27)	–32(15)	3092(56)	61(17)
C(31)	7661(24)	525(13)	4785(48)	44(14)
C(32)	7933(22)	672(14)	6341(43)	39(13)
C(33)	8600(33)	434(18)	7378(69)	82(21)
C(34)	9022(30)	50(17)	6769(66)	70(20)
C(35)	8781(27)	–124(14)	5306(76)	72(21)
C(36)	8096(26)	123(15)	4142(58)	57(16)
C(1)	7376(28)	954(15)	1491(51)	61(16)

Note: Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_i tensor.

4.805 \AA) and 3.27 \AA (3.126–3.405 \AA), respectively. The Ag atoms deviate only about 0.01 \AA (mean) from the Ag_5 -pentagon plane, and the I atoms have a deviation of 0.03 \AA (mean) from the I_5 -pentagon plane, which indicates that both I_5 -pentagons and Ag_5 -pentagons are planar. Each Ag atom is bonded by three I atoms, while each I atom in the I_5 -pentagon is tetrahedral-coordinated by three triply bridging Ag atoms and one I^* atom. The I^* atom is bonded by five I atoms of the I_5 -pentagon, and these six I atoms form an uncommon I_6 pentagonal pyramidal structure. To our knowledge, the stereochemistry of iodine is generally consistent with the arrangements of 4, 5, 6, and 7 pairs of valence electrons, tetrahedral, trigonal bipyramidal, octahedral, and pentagonal bipyramidal, on the assumption that lone pairs occupy bond positions. But the I^* atom in $(\text{Ag}_5\text{I}_6)_n^-$ displays an unusual coordination type. Peters et al. reported two compounds $\text{HAg}_5\text{I}_6 \cdot 2\text{L}$ (L-N,N-diethyl-acetamide or N-methyl-2-pyrrolidinone) with the same polyanion $[\text{Ag}_5\text{I}_6]_n^-$ [8], but the synthetic method they used and

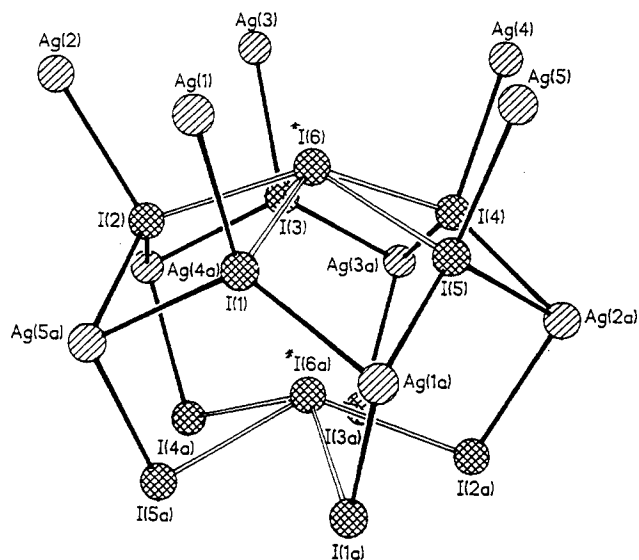


FIGURE 1 The structure of a part of the polymeric anion $(Ag_5I_6)_n^-$.

the cations are different from ours. In comparison with the structures of the polyanion $[Ag_5I_6]_n^-$ in the two compounds, the central I^* atom in the title compound is close to the I_5 -pentagon plane, and the distances between I^* and five I atoms of the I_5 -pentagon are within bonding distance (av 2.963 Å). It is far from the Ag_5 -pentagon plane. The distances between I^* and Ag atoms average 4.332 Å. In contrast, the central I^* atom in the two compounds reported by Peters is close to the Ag_5 -pen-

tagon plane. The distances between I^* and five Ag atoms average 2.842 Å, and the distances between I^* and I atoms of the I_5 -pentagon are at a non-bonding distance. The Ag atoms in the two compounds are tetrahedral-coordinated by four I atoms, while the coordination numbers of Ag atoms in the title compound are three. However, the distances between Ag and the peripheral I atoms, averaging 2.837 Å in the title compounds, are similar to the values found in the two compounds (av 2.842 Å) and in other silver iodide complexes [7]. The I–Ag–I angles formed by I atoms from different I_5 -pentagons average 98.6°(95.7–102.0°), which are much larger than those (mean 70.6°(67.2–74.3°)) formed by I atoms from the same I_5 -pentagon. Contrarily, the Ag–I–Ag angles with Ag atoms from different Ag_5 -pentagons (mean 111.2°(104.4–115.7°)) are smaller than those with Ag atoms from the same Ag_5 -pentagon (mean 115.8°(111.3–120.2°)). The $I^*–I$ angles average 66.5° (62.7–69.5°).

As to the formation mechanism of this complex, it is suggested that the insertion product $(Ph_3P)_2AgCS_2SR$, which was activated by the insertion of CS_2 into Ag–S bonds, dissociated into various "active moieties" under the attack of CH_2I_2 , and the cation $(Ph_3PCH_2I)^+$ might be the result of a nucleophilic displacement reaction of Ph_3P with CH_2I_2 ($Ph_3P + CH_2I_2 \rightarrow Ph_3PCH_2I^+ + I^-$), [9] while the polymeric anions $(Ag_5I_6)_n^-$ arise from the optimum "self-assembly" of Ag^+ and I^- . However, further investigation is needed.

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REFERENCES

- [1] K. Tang, Q. Xing, J. Yang, Q. Yang, Y. Tang, *Acta Chim Sinica*, 48(3), 1990, 242.
- [2] K. Tang, D. Wu, X. Jin, Y. Tang, *Acta Sci. Nature Univ. Peking*, 28, 1992, 446.
- [3] P. G. Eller, R. R. Ryan, *Acta Cryst.*, B33, 1977, 619.
- [4] A. Avdeff, J. P. Fackler, Jr., *J. Coord. Chem.* 4, 1975, 211.
- [5] X. Jin, W. Liu, K. Tang, Y. Tang, *The Abstracts of 2nd National Conference on Coordination Chemistry*, Nanjing China, Oct. 1993, p. 145.
- [6] K. Tang, T. Xia, X. Jin, Y. Tang, *Polyhedron*, 12(23), 1993, 2895–2898.
- [7] Gerald B. Ansell, *J. Chem. Soc., Perkin Trans., II*, 1975, 104–106.
- [8] Karl Peters, Walter Ott, Hans Georg von Schnening, *Angew. Chem. Int. Ed. Engl.*, 21, 1982, 697.
- [9] David W. Allen, Ian T. Miller, *Tetrahedron Lett.*, 6, 1968, 745–50.

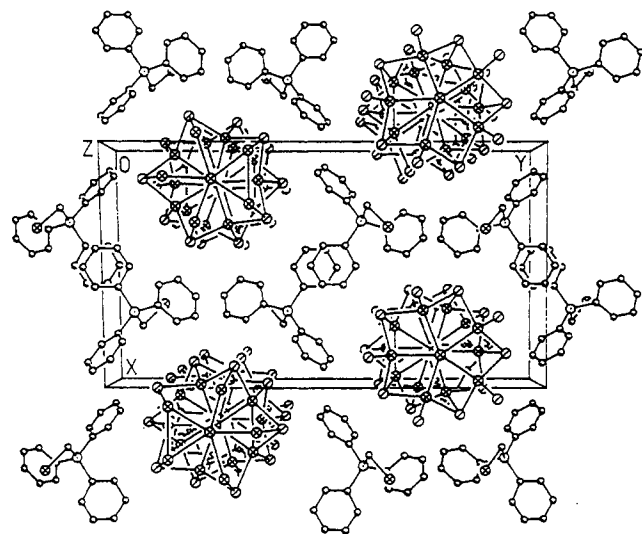


FIGURE 2 The packing diagram of the unit cell of $(Ag_5I_6)_n(Ph_3PCH_2I)_n$.