



一种新颖有机/无机杂化配位聚合物 $[(C_7H_{18}N)(Ag_2I_3)]_n$ 的合成、结构及量子化学计算

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Novel Inorganic-Organic Hybrid Coordination Polymer $[(C_7H_{18}N)(Ag_2I_3)]_n$: Synthesis, Crystallographic Structure and Quantum Chemistry Calculation

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Abstract: A one dimensional coordination polymer, $[(C_7H_{18}N)(Ag_2I_3)]_n$ ($(C_7H_{18}N)^+$ =Methyltriethylammonium) has been successfully synthesized and characterized by X-ray single-crystal diffraction method. Structure analysis shows that the compound consists of organic cations(Methyltriethylammonium) and inorganic anion chains $(Ag_2I_3)_n^-$. The inorganic moiety consists of AgI_4 tetrahedron, which shares the same edges with adjacent AgI_4 tetrahedrons to form one-dimensional infinite double chains along a -axis. There exists weak interaction among $Ag \cdots Ag$ atoms in the crystal. Anion chains are surrounded by Methyltriethylammonium cations. Anion chains and cations are in combination with each other by static attracting forces in the crystal to form so-called organic-inorganic hybrid structure. According to the crystal structure data, quantum chemistry calculation with DFT on B3LYP level was used to reveal the electronic structure of title compound. CCDC: 254288.

Key words: organic-inorganic hybrid; template synthesis; silve(I) iodide; quantum chemistry calculation

0 Introduction

Organic-inorganic hybrid metal halides have received extensive attention in recent years owing to their great fundamental and practical interest and represents new directions in solid-state chemistry^[1,2].

The architectures of metal halides can be tuned at the molecular level so as to possess unusual electronic properties, various components and potential applications in areas of molecular absorption, catalysis, electromagnetism, and photochemistry^[3-7]. It is therefore vital to design and synthesize novel organic-inorganic

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hybrid metal halides to explore their various properties.

A recent advance in this system is to design the coordination frameworks of silver(I) halides by the incorporation of various organic structure-directing agents(SDA). A series of complexes have been reported, such as $\text{Bu}_4\text{N}[\text{Ag}_3\text{I}_4]^{[8]}$, $\{[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Ag}_{4.95}\text{Cu}(\text{I})_{1.0518}\}_n^{[9]}$, $[\text{C}_6\text{H}_{14}\text{NO}_2][\text{Ag}_5\text{Br}_8]^{[10]}$, $\{(\text{C}_{12}\text{H}_{14}\text{N}_2)[\text{Ag}_2\text{I}_4]\}_n^{[11]}$. It is noteworthy that the introduction of new organic template agents always leads to the dramatic structural change of the basic inorganic phases^[12]. It seems that the structure of inorganic moiety incline to complication when the space volume of SDA increases. Furthermore, even under the same SDA, the inorganic structure could be different. So the coordination chemistry of silver halide is versatile and the study about this is just in the ascendant. We aim at probing into the impact of organic quaternary ammonium cations in the structure of inorganic chain. We now wish to report the successful preparation and structural characterization of a novel coordination polymer $[(\text{C}_7\text{H}_{15}\text{N})(\text{Ag}_2\text{I}_3)]_n$.

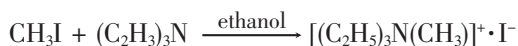
1 Experimental

1.1 Materials and instrumentation

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. IR spectra were carried out on a Nicolet Co. Magna-IR 750 spectrometer with KBr pellets in the $4\,000\sim 400\text{ cm}^{-1}$ regions. Quantum chemistry calculation was carried on a Pentium IV computer with G03 program.

1.2 Preparation of the title compound

$\text{C}_7\text{H}_{15}\text{I}$ was prepared as reported in literature^[13]:



The title compound $[(\text{C}_7\text{H}_{15}\text{N})(\text{Ag}_2\text{I}_3)]_n$ was prepared by self-assembling reaction of AgI with $\text{C}_7\text{H}_{15}\text{NI}$. AgI (0.469 5 g, 2.0 mmol) and $\text{C}_7\text{H}_{15}\text{NI}$ (0.192 0 g, 0.8 mmol) were dissolved in 7 mL DMF. After that, the mixed solution was stirred till it became colorless clear, with the pH value being adjusted to 6.5 by the addition of 10% NaOH/DMF solution, and then filtered. The resulting solution was kept at room temperature for three days to obtain colorless needle single crystals. The IR spectra were recorded in the $4\,000\sim 400\text{ cm}^{-1}$ region by using KBr pellets and Nicolet Co. Magna-IR 750 spectrometer. Quaternary ammonium (cm^{-1}): $\nu_{\text{-CH}_2}^{\text{as}}=1\,450.89$; $\nu_{\text{-CH}_3}=1\,380.56$; $\nu_{\text{C-N}}=1\,191.46$; $\nu_{\text{C-C}}=1\,580.23$.

1.3 Data collection, structure solution, and refinement

A colorless needle single crystal with dimensions of $0.30\text{ mm} \times 0.20\text{ mm} \times 0.20\text{ mm}$ was selected and the measurement of the crystal was carried out on Rigaku Weissenberg IP diffractometer with Mo $K\alpha$ ($\lambda=0.071\,069\text{ nm}$) for the data collection. A total of 12 272 reflections were collected, of which 1 782 are independent in the range of $2.01^\circ < \theta < 27.48^\circ$ at 298 K and 1 179 are observed reflections with $I > 2.000\sigma(I)$. The corrections of Lp factor and Multi-scan absorption correction were applied. All the collected reflections were used in the structure analysis. Heavy atoms were dissolved by direct method, and other non-hydrogen

Table 1 Crystal data and structure refinement parameters for $[(\text{C}_7\text{H}_{15}\text{N})(\text{Ag}_2\text{I}_3)]_n$

Formula	$\text{C}_7\text{H}_{15}\text{NAg}_2\text{I}_3$	$F(000)$	1 280
Molecular weight	1 560.4(2)	θ range / $^\circ$	2.01 to 27.48.
Crystal size / mm	$0.30 \times 0.20 \times 0.20$	Index ranges	$0 \leq h \leq 9, 0 \leq k \leq 16, 1 \leq l \leq 22$
Crystal system	Orthorhombic	Reflections collected:total,	12 272
Space group	$Pnma$	Independent reflections	1 782
a / nm	0.720 99(5)	Reflections observed ($>2\sigma$)	1 179
b / nm	1.239 22(9)	R_{int}	0.061 807
c / nm	1.746 48(15)	Data / restraints / parameters	1 782 / 0 / 69
V / nm^3	1.560 4(2)	Goodness-of-fit S on F^2	0.958
Z	4	Final R_1 wR_2 [$I > 2\sigma(I)$]	0.039 4, 0.111 0
D_c / ($\text{g}\cdot\text{cm}^{-3}$)	3.034	All data	0.060 3, 0.135 3
μ / (mm^{-1})	8.414	Largest peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	1 415, -2 050

atoms were determined with successive difference Fourier syntheses. The hydrogen atoms were located at the calculated positions. The anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-squares on F^2 for 69 parameters. All calculations were performed on a computer with

SHELX 97 program package^[14,15]. Space group, lattice parameters, and other relevant information are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

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Table 2 Selected bond lengths (nm) and bond angles ($^\circ$)

I(1)-Ag(1)	0.294 07(9)	I(1)-Ag(1)a	0.294 07(9)	I(1)-Ag(1)b	0.295 18(10)
I(1)-Ag(1)c	0.295 18(10)	I(2)-Ag(1)	0.280 35(8)	I(2)-Ag(1)d	0.280 54(9)
Ag(1)-I(2)c	0.280 54(9)	Ag(1)-I(1)d	0.295 18(10)	Ag(1)-Ag(1)a	0.317 86(13)
N(1)-C(1)	0.144 0(17)	N(1)-C(3)	0.150 7(8)	N(1)-C(3)e	0.150 7(8)
N(1)-C(5)	0.159 9(16)	C(1)-C(2)	0.154(2)	C(3)-C(4)	0.151 3(10)
Ag(1)-I(1)-Ag(1)a	65.43(3)	Ag(1)-I(1)-Ag(1)b	109.32(3)	Ag(1)a-I(1)-Ag(1)b	75.453(18)
Ag(1)-I(1)-Ag(1)c	75.453(18)	Ag(1)a-I(1)-Ag(1)c	109.32(3)	Ag(1)b-I(1)-Ag(1)c	65.15(3)
Ag(1)-I(2)-Ag(1)d	80.006(19)	I(2)-Ag(1)-I(2)c	117.44(3)	I(2)-Ag(1)-I(1)	111.89(3)
I(2)c-Ag(1)-I(1)	102.39(3)	I(2)-Ag(1)-I(1)d	102.15(3)	I(2)c-Ag(1)-I(1)d	108.78(3)
I(1)-Ag(1)-I(1)d	114.69(2)	I(2)-Ag(1)-Ag(1)a	121.278(17)	I(2)c-Ag(1)-Ag(1)a	121.254(16)
I(1)-Ag(1)-Ag(1)a	57.286(16)	I(1)d-Ag(1)-Ag(1)a	57.424(15)	C(1)-N(1)-C(3)	115.3(6)
C(1)-N(1)-C(3)e	115.3(6)	C(3)-N(1)-C(3)e	107.2(8)	C(1)-N(1)-C(5)	103.9(10)
C(3)-N(1)-C(5)	107.3(6)	C(3)e-N(1)-C(5)	107.3(6)	N(1)-C(1)-C(2)	108.5(11)
N(1)-C(3)-C(4)	115.6(6)				

Symmetry transformations used to generate equivalent atoms: a: $x, -y+1/2, z$; b: $x+1/2, -y+1/2, -z+1/2$; c: $x+1/2, y, -z+1/2$; d: $x-1/2, y, -z+1/2$; e: $x, -y-1/2, z$.

2 Results and discussion

2.1 Crystal structure

The structure of $[Ag_2I_3]^-_n$ chain is shown in Fig.1, the crystal packing diagram of the title compound is revealed in Fig.2.

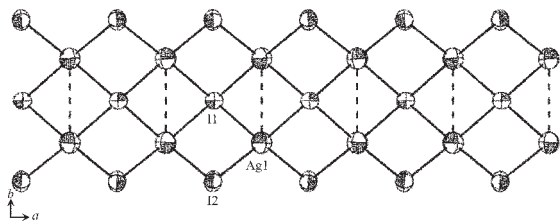


Fig.1 Structure of $[Ag_2I_3]^-_n$ chain

As shown in Fig.2, the whole crystal structure of polymer $[(C_7H_{18}N)(Ag_2I_3)]_n$ consists of organic moiety $(C_7H_{18}N)^+$ ($(C_7H_{18}N)^+$ =methyltriethylammonium) and inorganic moiety(chain-like $(Ag_2I_3)^-$). In other words, this structure is a one-dimensional infinite polymeric anion accompanied by discrete cations. The one-dimensional $(Ag_2I_3)^-$ chain has previously been observed^[16] and consists of a double chain of edge-sharing AgI_4 tetrahedra running parallel to the a axis (Fig.1). As a re-

sult, two distinct types of iodine atom are found: peripheral iodine atoms which are two-coordinate and make up the edges of the polymeric string, and four-coordinate central iodine atoms, these central iodine

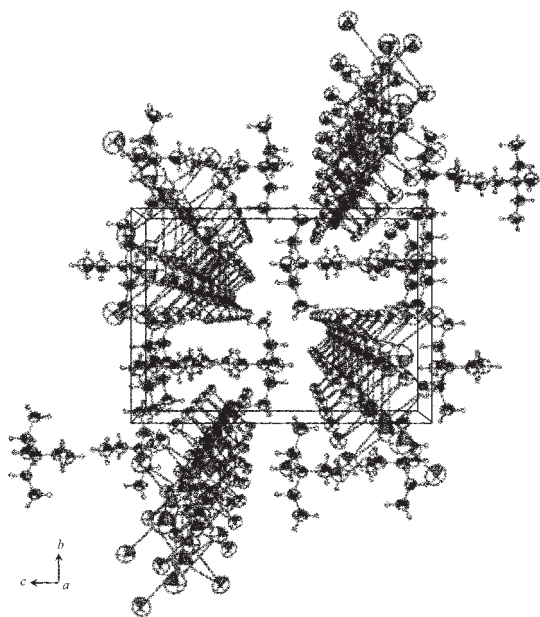


Fig.2 Packing diagram of title compound

atoms lie on a mirror plane which is normal to the polymeric axis.

The polymeric anion, interestingly, is different in structure to that of $[\text{Cu}_2\text{I}_3]_n^-$, which has been subject of several independent determination^[17]. In the present structure, the metal atoms are four-coordinate and the iodine atoms two- and four-coordinate; in the copper(I) analogue the copper atoms are also four-coordinate, which the iodine atoms are three-coordinate.

Because the iodine atoms are of a bridging nature, the silver atom environment is distorted from that of a perfect tetrahedron. From the table, the AgI_4 tetrahedra are highly distorted, with Ag-I bond distances ranging between 0.280 35(8) and 0.295 18(10) nm and tetrahedral bond angles varying from 57.424(15) to 121.278(17)°. There are one independent Ag atoms in each unit cell. The bond distances of Ag-I range from 0.280 35(8) to 0.295 18(10) nm, with the average value of 0.287 54(1) nm. These values are slightly shorter than that of 0.293 77(9) nm in $(\text{Et}_4\text{N})_6(\text{Ag}_6\text{I}_{11})\text{I}$ ^[18]. The Ag...Ag distance is 0.317 86(13) nm, which is slightly shorter than $(\text{Et}_4\text{N})_6(\text{Ag}_6\text{I}_{11})\text{I}$ (0.320 05(14) nm) but much shorter than Van der Waals radius of silver (0.344 nm). This shows that there exists weak interaction in the polyanions, which can be potential used in anti-bacterium reagent^[19]. We can also conclude from the value of Ag...Ag distance that there exists argentaffin interaction between Ag atoms^[20], which lead to shorter M...M distances.

As shown in Fig.2., the neighboring $[\text{Ag}_2\text{I}_3]_n^-$ polyanion chains act as channels wherein organic cations lie sandwiched between two adjacent chains. Organic groups don't participate in coordination, they connect with inorganic moiety by non-covalent interaction-static attracting forces. Organic moiety and inorganic moiety alternate to form so-called organic-inorganic hybrid structure. Previous studies show that organic cations act as a template and control the synthesis of the whole structure. These provide additional fine variables in tuning the structure and electronic properties of organic-inorganic hybrid material. And furthermore, alkyl ammonium molecular can play the role of a barrier layer with low dielectric constant and a large gap, in contrast to the upstanding conductivity of metal halide. So the title compound can be used as organic/inorganic quantum-well material.

2.2 Electronic structure study of title compound

We adopt Gaussian03 program and B3LYP method^[21,22] which brought forward by Becke to investigate the electronic structure of the title compound. A snippet of $[\text{Ag}_6\text{I}_{12}]$ was chosen as studied system. Iodine atoms were blocked out with Hydrogen atoms. Cep-4g basis sets is used for Ag and I atoms. H atoms adopt 6-31g(d) basis sets, Multiplicity is set as 1 and BNO method is used. 290 basis functions, 628 primitive gaussians, 102 α electrons and 102 β electrons is involved in the calculation. The Mulliken atomic charges and natural electron configuration of compound is shown in Table 3. FMO of title compound are shown in Fig.3.

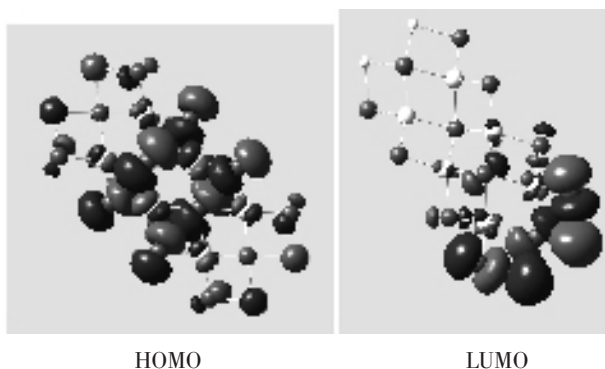


Fig.3 FMO of title compound

The energy of title compound is -1 017.887 932 84 a.u. after 14 cycles of calculation. HOMO (Fig.3) energy of crystal orbit is -0.059 31 a.u., and LUMO (Fig.3) energy is -0.030 74 a.u., the band gap is 0.028 57 a.u. (0.777 429 698 eV). Dipole moment of compound is 0.186 4 Debye, indicating the compound is polarized.

The result of quantum chemistry calculation (Table 3) shows that the net charge of Ag range from 0.085 067 to 0.126 821, deviating from +1. The net charges of I atoms range from -0.078 070 to -0.306 366. These indicate that part electrons of I atoms have transferred from I atoms to Ag atoms and come into being coordinate bonds. As shown in Table 3, we can see the electron number of Ag 4d orbits range from 9.94 to 9.96 (approaching to 10) and 5s orbits range from 0.41 to 0.42 (6s electron were too small to be omitted). From the above we can conclude that the Ag atom form coordinate bond with I atoms with 5s. The electron number of I 5s orbit range from 1.93 to 1.97 (approached to 10 and can be treated as lone pair

Table 3 Mulliken atomic charges and natural electron configuration of part atoms

Atoms	Net charge	Electron Configuration
I1a	-0.141 876	[core]5s(1.96)5p(5.38)
I1b	-0.075 719	[core]5s(1.93)5p(5.64)6S(0.01)
I1c	-0.078 070	[core]5s(1.93)5p(5.64)6S(0.01)
I1d	-0.154 151	[core]5s(1.97)5p(5.42)
I2a	-0.269 681	[core]5s(1.97)5p(5.42)
I2b	-0.269 681	[core]5s(1.97)5p(5.42)
I2c	-0.306 366	[core]5s(1.94)5p(5.69)
I2d	-0.305 864	[core]5s(1.94)5p(5.69)
I2e	-0.305 864	[core]5s(1.94)5p(5.69)
I2f	-0.306 366	[core]5s(1.94)5p(5.69)
I2g	-0.259 172	[core]5s(1.97)5p(5.41)
I2h	-0.259 172	[core]5s(1.97)5p(5.41)
Ag1a	0.086 940	[core]5s(0.41)4d(9.94)5p(0.03)6S(0.01)
Ag1b	0.086 940	[core]5s(0.41)4d(9.94)5p(0.03)6S(0.01)
Ag1c	0.126 821	[core]5s(0.40)4d(9.96)5p(0.03)6S(0.01)
Ag1d	0.085 067	[core]5s(0.41)4d(9.94)5p(0.03)6S(0.01)
Ag1e	0.085 067	[core]5s(0.41)4d(9.94)5p(0.03)6S(0.01)
Ag1f	0.126 821	[core]5s(0.40)4d(9.96)5p(0.03)6S(0.01)

electrons) and 5p orbit range from 5.38 to 5.64. So we can conclude that the I atoms form coordinate bond with Ag atoms with 5p (mainly from 5p_x orbit indicated by NBO orbit analysis). Crystal orbit overlap population show that the overlap population number of Ag1a and Ag1b, Ag1c and Ag1f, Ag1d and Ag1e are 0.001 681, 0.008 008 and 0.003 148 respectively. These indicate that weak interaction between Ag atoms exist, which is consistent with the structure determination that there exists argentaffin interaction between Ag atoms.

Reference:

- [1] Ouahab L. *Chem. Master.*, **1997**,**9**:1909~1926
- [2] Garder G B, Kiang Y H, Lee S, et al. *J. Am. Chem. Soc.*, **1996**,**118**:6946~6953
- [3] Mitzi D B, Wang S, Chess C A, et al. *Science*, **1995**,**267**: 1473~1746
- [4] Lacroix P G, Clement R, Nakatani K, et al. *Science*, **1994**, **263**:658~660
- [5] Mitzi D B, Wang S, Field C A, et al. *Nature*, **1994**,**369**:467~469
- [6] Mitzi D B. *Prog. Inorg. Chem.*, **1999**,**48**:1~8
- [7] Mitzi D B, Liang K, Wang S. *Inorg. Chem.*, **1998**:321~327
- [8] Gilmore C J, Tucker P A, Woodward P. *J. Chem. Soc. (A)*, **1971**:1337~1341
- [9] Chen Z R, Huang C C, Chen J H, et al. *Chinese J. Struct. Chem.*, **2003**,**22**:114~118
- [10] John D K, Allan H W. *Inorg. Chem.*, **1984**,**23**:3825~3827
- [11] LI H H, Chen Z R, Huang C C, et al. *Chinese J. Struct. Chem.*, **2004**,**23**:288~291
- [12] Chestnut D J, Kusnetzow A, Birge R R, et al. *Inorg. Chem.*, **1999**,**38**:2663~2671
- [13] Huang S, Xie R G. *Preparation Manual of Organic Synthesis Reagent*, Sichuan University Press, **1988**.
- [14] Sheldrick G M. *SHELX97, Program for Crystal Structure Solution*. University of Gottingen, Germany, **1997**.
- [15] Sheldrick G M. *SHELX97, Program for Crystal Structure Refinement*. University of Gottingen, Germany, **1997**.
- [16] Coetzer J. *Acta Crystallog.*, **1975**,**B31**:2115~2117
- [17] Andersson S, Jagner S. *Acta Chem. Scand., Sect. A*, **1985**, **39**:181~185
- [18] Zhao Y, Su W, Cao R, et al. *Acta Cryst.*, **1999**,**B31**:9900122
- [19] Nomiya K, Takahashi S, Noguchi R. *J. Chem. Soc., Dalton Trans.*, **2000**:2091~2097
- [20] Che C M, Tse M C, Leung K H. *J. Am. Chem. Soc.*, **2000**, **122**:2464~2468
- [21] Parr R G, Yang W T. *Density-functional Theory of Atoms and Molecules* [M]. USA: Oxford Univ Press, **1989**.
- [22] Liao M Z, Wu G S, Liu H L. *Ab Initio Calculation Method of Quantum Chemistry* [M], Beijing: Tsinghua University Press, **1984**.1769