



Synthesis, Crystal Structure of Poly-catena-[(1-ethyl-3-isopropyl-imidazolium)hexa-iodo-tetra silver(I)]

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The complex $[(\text{CH}_3)_2\text{CH}\{\text{CH}(\text{NCHCHN})\text{CH}_2\text{CH}_3\}^+]_{2n}[(\text{Ag}_4\text{I}_6)^{2-}]_n$ has been synthesized by the reaction of Ag_2O with $[(\text{CH}_3)_2\text{CH}\{\text{CH}(\text{NCHCHN})\text{CH}_2\text{CH}_3\}^+]^+$ I in a 1:3 molar ratio at 173 °C in DMSO and characterized by elemental analysis, ^1H NMR and single-crystal X-ray diffraction analysis. It crystallizes in orthorhombic, space group Pca21 with $a = 21.315(9)$, $b = 7.202(3)$, $c = 21.380(10)$ Å, $\beta = 90^\circ$ $V = 3282(2)$ Å³, $M_r = 1471.32$, $Z = 4$, $D_c = 2.978$ g/cm³, $\mu(\text{MoK}\alpha) = 8.01$ mm⁻¹ and $F(000) = 2640$. The structure was refined to $R = 0.0303$ and $wR = 0.061$ for 2758 observed reflections with $I > 2\sigma(I)$. The asymmetric unit of the title complex $[(\text{CH}_3)_2\text{CH}\{\text{CH}(\text{NCHCHN})\text{CH}_2\text{CH}_3\}^+]_{2n}[(\text{Ag}_4\text{I}_6)^{2-}]_n$ is a ionic coordination polymer, consisting of two substituted imidazolium cation and an infinite anionic $[\text{Ag}_4\text{I}_6]^{2-}$ chain. Within the chain the Ag(I) ions have distorted tetrahedral geometry when the Ag-Ag interactions are not taken into account, which are coordinated by four iodide ions. Meanwhile the iodide ions link four neighboring Ag atoms, whereas iodide acts as a bridge between two Ag atoms. A four-membered ring system is formed by corner sharing of the AgI_4 tetrahedra.

Keywords: Polymeric, Silver, Crystal structure, Imidazolium.

INTRODUCTION

Silver and other transition metal N-heterocyclic carbene complexes have been played important role in the development of metal carbene systems for transmetalation. To data, a variety of structures of N-heterocyclic carbene silver complexes have been reported, which include mono-N-heterocyclic complexes of silver, multi-N-heterocyclic complexes of silver and silver clusters stabilized by N-heterocyclic carbenes ($\text{C-Ag}_{\text{cluster}}$)¹⁻⁹. The ionic coordination polymer $[\text{Ag}(\text{carbene})_2][\text{Ag}_2\text{I}_6]$ have been synthesized by the reaction of 1,3-dimethylimidazolium iodide with silver oxide in dichloromethane by Chen *et al.*¹⁰. However, an attempt to synthesize the ionic coordination polymer of carbene silver by the reaction of 1-ethyl-3-isopropyl-imidazolium iodide with silver in DMSO at refluxing failed and the poly-catena-[(1-ethyl-3-isopropyl-imidazolium)hexa-iodo-tetra silver(I)] were isolated. Here, we report the preliminary results.

EXPERIMENTAL

The melting point was determined in a sealed argon filled capillary tube and uncorrected. The elemental analyses of C, H and N were performed by the direct combustion on a Carlo-Erba EA-1110 instrument, ^1H NMR spectra were obtained in C_6D_6 (400MHz).

Synthesis of $[(\text{CH}_3)_2\text{CH}\{\text{CH}(\text{NCHCHN})\text{CH}_2\text{CH}_3\}^+]_{2n}[(\text{Ag}_4\text{I}_6)^{2-}]_n$: Silver oxide (0.696 g, 3 mmol) was added to a

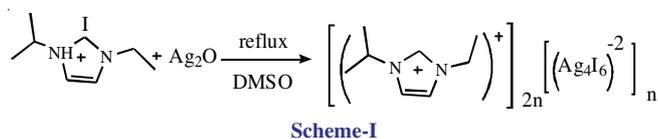
solution of 1-ethyl-3-isopropyl-imidazolium iodide (1.596 g, 6 mmol) in DMSO (50 mL). The mixture was refluxed for 4 h under stirring, resulting in a clean solution. When the solvent was removed, the residue was extracted with acetonitrile. The remaining residue was separated by centrifugation and the resulting solution was kept at the room temperature. Colourless crystals of the title compound were obtained after slow evaporation (1.64 g, 75 %) m.p.: 426 K (decomp.). ^1H NMR (CDCl_3): 9.43 (m, 1H, NCHN), 6.84 (s, 1H, CH), 6.86 (s, 1H, CH), 4.05 (m, 1H, CH), 3.78 (m, 2H, CH), 1.52 (m, 3H, CH_3), 1.57 (m, 6H, CH_3) ppm. Anal. Calcd.: C, 13.04; H, 2.03; N, 3.80; found: C, 13.21; H, 1.98; N, 3.78 %.

Structure determination: A colourless crystal with dimensions of 0.18 mm × 0.14 mm × 0.13 mm was sealed in a thin-walled glass capillary for X-ray diffraction studies. Intensity data were collected on a Rigaku Mercury CCD area detector equipped with a graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ nm). The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. A total of 15439 reflections were collected in the range of $1.91 \leq \theta \leq 25.01$ by using an ω scan mode at 296 K, of which 2970 ($R_{\text{int}} = 0.0614$) were independent. 2758 observed reflections with $I > 2\sigma(I)$ were used in the structure refinement. The structure was solved by direct methods. Non-hydrogen atoms were determined with successive difference Fourier syntheses. The hydrogen atoms were located at the calculated positions. The anisotropic thermal parameters for

the non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 . The final refinement converged to $R = 0.027$ and $wR = 0.065$ ($w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 2.9503P]$, where $P = (F_o^2 + 2F_c^2)/3$, $(\Delta/\sigma)_{\max} = 0.001$, $S = 1.09$, $(\Delta\rho)_{\max} = 0.96$ and $(\Delta\rho)_{\min} = -1.42 \text{ e}/\text{\AA}^{-3}$. The programs for structure solution and refinement are SHELXS-97¹¹ (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997)¹², respectively.

RESULTS AND DISCUSSION

Crystal structure of the title complex: Reaction of Ag_2O with 2 equiv of 1-ethyl-3-isopropyl-imidazolium iodide in DMSO at refluxing gave a light brown solution. After workup, the title complex was isolated as colourless crystal in 75 % yield (**Scheme-I**). The composition of the title complex was confirmed by elemental analysis and $^1\text{H NMR}$ and its definitive structure was determined by X-ray diffraction.



The molecular structure of the title complex is shown in Fig. 1, the molecular structure of the polymeric anion $[(\text{Ag}_4\text{I}_6)^{-2}]_n$ is shown in Fig. 2, The crystallographic data were collected in Table-1, The selected bond angles are given in Table-2, The select bond lengths for the title compound are given in Table-3.

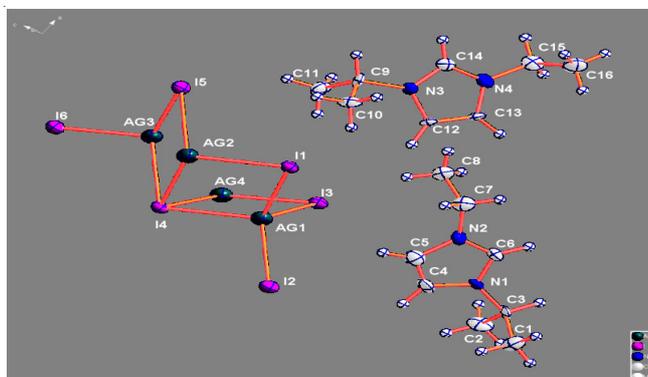


Fig. 1. Crystal structure of title complex

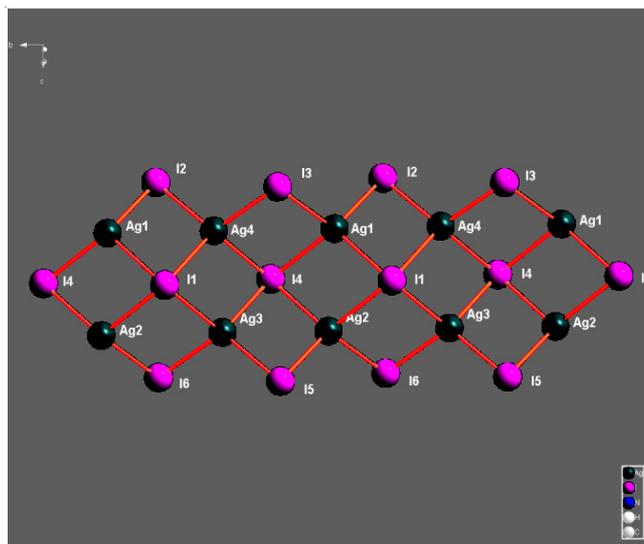


Fig. 2. Molecular structure of the polymeric anion $[(\text{Ag}_4\text{I}_6)^{-2}]_n$

The reaction of Ag_2O with imidazolium is strongly influenced by the reaction conditions imidazolium salt used. The silver N-heterocyclic carbene complexes are usually synthesized by reaction of Ag_2O with imidazolium at the room temperature in CH_2Cl_2 , 1,2-dichloroethane, DMSO, DMF, acetone, methanol, acetonitrile and water. Only the silver oxide reactions with bulky imidazolium salts require refluxing. But there is no report about the reaction of Ag_2O with small volume of imidazolium salts at refluxing in DMSO. The result indicates the reaction doesn't give the silver N-heterocyclic carbene complex instead of silver polymer with imidazolium. This suggests the high temperature affects the ability of silver to effectively deprotonate the imidazolium salt.

The title complex $[(\text{CH}_3)_2\text{CH}\{\text{CH}(\text{NCHCHN})\text{CH}_2\text{CH}_3\}^+]_{2n}[(\text{Ag}_4\text{I}_6)^{-2}]_n$ is a ionic coordination polymer, consisting of two substituted imidazolium cation and an infinite anionic $[(\text{Ag}_4\text{I}_6)^{-2}]_n$ chain.

Although the $[(\text{Ag}_4\text{I}_6)^{-2}]_n$ structure has been recently found the silver N-heterocyclic carbene complexes for Ag (carbene)₂[Ag_4I_6]¹³, Its structural feature is different from the title complex.

In $\text{Ag}(\text{carbene})_2[\text{Ag}_4\text{I}_6]$ published¹³, the cation has a typical linear conformation of $\text{Ag}(\text{carbene})_2^+$ and the building $[(\text{Ag}_4\text{I}_6)^{-2}]_n$ is linked by two Ag-I bonds, the I(1) and I(2) ions link three neighboring Ag atoms, whereas the I(3) acts as a

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT PARAMETERS FOR TITLE COMPLEX

Empirical formula	$\text{C}_{16}\text{H}_{30}\text{N}_4\text{Ag}_4\text{I}_6$	F(000)	2640
Formula weight	1471.3	Calculated density (g cm^{-3})	2.978
Temperature (K)	446 ± 2	Absorption coefficient (mm^{-1})	8.007
Wavelength (nm)	0.71073	Θ Range for data collection ($^\circ$)	1.91-25.01
Crystal system	Orthorhombic	Limiting indices	$-25 \leq h \leq 18, -8 \leq k \leq 8, -25 \leq l \leq 25$
Space group	Pca21	Observed reflections ($I > 2\sigma(I)$)	2758
A (nm)	2.1315(9)	Reflections collected/unique	15439/2970
b (nm)	0.7202(3)	Refinement method	Full-matrix least-squares techniques on F^2
c (nm)	2.1380(10)	Data/restraints/parameters	2970 / 13 / 277
β ($^\circ$)	90.00	Goodness-of-fit on F^2	1.087
Volume (nm^3)	3282(2)	Final R indices	$R_1 = 0.0271, wR_2 = 0.0610$
Z	4	R indices (all data)	$R_1 = 0.0303, wR_2 = 0.0652$

TABLE-2
SELECTED BOND LENGTHS (Å) FOR THE PRESENT COMPOUND

Bond	Dist	Bond	Dist
Ag(1)-I(1)	2.9035(15)	Ag(1)-I(4)	2.9616(16)
Ag(1)-Ag(2)	3.2073(17)	Ag(1)-Ag(4)#1	3.3690(18)
Ag(2)-I(5)	2.8279(15)	Ag(2)-I(6)#1	2.8382(15)
Ag(2)-I(4)	2.9218(15)	Ag(2)-I(1)	2.9552(16)
Ag(2)-Ag(3)	3.3612(18)	Ag(3)-I(5)	2.8467(15)
I(1)-Ag(4)#1	2.9333(15)	I(1)-Ag(3)#1	2.9609(15)
I(2)-Ag(4)#1	2.8400(15)	I(6)-Ag(2)#2	2.8383(15)
N(1)-C(6)	1.319(16)	N(1)-C(4)	1.38(2)
N(2)-C(5)	1.392(17)	N(3)-C(12)	1.418(18)

Symmetry codes: (i) x, y-1, z; (ii) x, y + 1, z

TABLE-3
SELECTED BOND LENGTHS (Å) FOR THE PRESENT COMPOUND

Angles	(°)	Angles	(°)
I(2)-Ag(1)-I(3)	118.67(5)	I(2)-Ag(1)-I(4)	110.17(5)
I(2)-Ag(1)-I(1)	108.80(4)	I(2)-Ag(1)-Ag(2)	127.60(4)
I(4)-Ag(1)-Ag(2)	56.37(4)	I(3)-Ag(1)-Ag(4)#1	131.75(4)
Ag(2)-Ag(1)-Ag(4)#1	94.75(3)	I(5)-Ag(2)-I(6)#1	118.41(5)
I(5)-Ag(2)-Ag(1)	127.28(4)	I(4)-Ag(2)-Ag(1)	57.56(3)
I(5)-Ag(3)-I(1)#2	109.49(5)	I(2)#2-Ag(4)-Ag(3)	126.35(4)
C(6)-N(1)-C(4)	108.2(12)	C(3)-C(1)-H(1A)	109.5
H(15A)-C(15)-H(15B)	107.9	N(4)-C(15)-H(15B)	109.2

bridge between two Ag atoms. But in title complex, the cation is a simple substituted imidazolium, the building $[\text{Ag}_4\text{I}_6]^{2-}$ consists of the four-membered rings formed by iodine and silver ions. Within the anionic $[\text{Ag}_4\text{I}_6]^{2-}$ chain both of the Ag(I) and the iodide ions have tetrahedral geometry and each silver atom is coordinated by four iodine atoms and each iodine atom is bound to four silver atoms. The angles of I(2)-Ag(1)-I(3), I(2)-Ag(1)-I(1), I(3)-Ag(1)-I(1), I(2)-Ag(1)-I(4), I(5)-Ag(2)-Ag(1), I(2ii)-Ag(4)-I(3), 118.67 (5), 108.80 (4), 107.82 (5), 110.17 (5), 127.28 (4), 118.74 (5) are, for 4, respectively, which deviate from the ideal angle of 109.5. A system of four-membered rings is formed by edge sharing of the AgI_4 tetrahedron. The I(2)-Ag(1)-Ag(2)-I(5) atoms lie in the same plane and the Ag(1)-Ag(2) atoms with I(3) and I(6i) atoms form another plane.

It was known that the type of anionic complexes $[\text{Ag}_m\text{I}_n]^{(n-m)-}$ formed is strongly influenced by the counter cation and the nature of the halide¹³. In the case of iodide, the ions $[\text{AgI}_3]^{2-}$, $[\text{Ag}_2\text{I}_4]^{2-}$, $[\text{Ag}_4\text{I}_8]^{4-}$, $[\text{Ag}_4\text{I}_6]^{2-}$ have been reported, which all are independent anionic forms, but the $[(\text{Ag}_4\text{I}_6)^{2-}]_n$ is a new anionic polymeric form and exists as an three dimensional polymer.

The Ag-I bond distances range between 2.8279(15) and 2.9616(16) Å. The Ag(1)-Ag(2), Ag(2)-Ag(3), Ag(1)-Ag(4)#1 bond distances within the building unit $[(\text{Ag}_4\text{I}_6)^{2-}]_n$ are 3.2073(17), 3.3612(18), 3.3690(18) Å, respectively and the average length is 3.3125 Å.

It is noted that 1,3-dimethylimidazolium chloride and 1,3-dimethylimidazolium bromide reacted with Ag_2O to afford one-dimensional polymers, which are composed of alternating $[\text{Ag}(\text{carbene})_2]^-$ and $[\text{AgX}_2]^+$ associated through Ag-Ag interactions⁸ at a distance of about 3.19 Å, meanwhile, the 1,3-dimethylimidazolium iodide reacted with Ag_2O in dichloromethane at room temperature gives a coordination polymer $[\text{Ag}(\text{carbene})_2]_2[\text{Ag}_4\text{I}_6]$, but 1-ethyl-3-isopropyl-imidazolium

iodide with silver in DMSO at refluxing afford ring structural polymer $[(\text{CH}_3)_2\text{CH}\{\text{CH}(\text{NCH}_2\text{CHN})-\text{CH}_2\text{CH}_3\}^+]_{2n}[(\text{Ag}_4\text{I}_6)^{2-}]_n$, these results further indicate the reaction conditions and the imidazolium salt used have a great influence on the products and the product structures and the high temperature affects the ability of silver to effectively deprotonate the imidazolium salt.

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