

Synthesis, crystal structure of poly[3,3'-dimethyl-1,1'-(ethane-1,2-diyl)diimidazolium[tetra- μ -bromido-silver(I)]]

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Abstract : The title complex $[(CH_3\{CH(NCHCHN)\}CH_2)_2]_n^{2+}[(Ag_2Br_4)^{2-}]_n$ has been synthesized by the reaction of Ag_2O with $[(CH_3\{CH(NCHCHN)\}CH_2)_2]^{2+} Br_2^-$ in a 1 : 3 molar ratio at 189 °C in DMSO and characterized by elemental analysis, 1H NMR and single-crystal X-ray diffraction analysis. It crystallizes in monoclinic, space group P21/c with $a = 9.1402$ (10) Å, $b = 12.5548$ (13) Å, $c = 8.2710$ (9) Å, $\beta = 104.696$ (2)°, $V = 918.07$ (17) Å³, $M_r = 363.82$, $Z = 4$, $D_c = 2.632$ g/cm³, $\mu(MoK\alpha) = 10.83$ mm⁻¹ and $F(000) = 676$. The structure was refined to $R = 0.028$ and $wR = 0.071$ for 1466 observed reflections with $I > 2\sigma(I)$. The asymmetric unit of the title salt, $[(CH_3\{CH(NCHCHN)\}CH_2)_2]_n^{2+}[(Ag_2Br_4)^{2-}]_n$, contains one-half of a substituted imidazolium cation, one Ag^+ and two Br^- ions. The cation is completed by crystallographic inversion symmetry. The crystal structure is made up from polymeric sheets of $\{[AgBr_2]^- \}_n$ anions. The basic building unit of the anion is a slightly distorted $AgBr_4$ tetrahedron. A four- and twelve-membered ring system is formed by corner sharing of the $AgBr_4$ tetrahedra. The imidazolium cations are located between the anionic sheets and partly protrude into the voids defined by the twelve-membered rings.

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 transmetallation reactions. The silver oxide is the most commonly used metal base for this purposes. Recent review dealing with silver N-heterocyclic carbenes were published by Arnold¹, Lin and Vasam². The product molecular structure differs depending upon reaction conditions and the imidazolium salt used. To date, a variety of structures of N-heterocyclic carbene silver complexes have been reported, which include mononuclear complexes with one or two carbenes coordinated to Ag^I , halide-bridged dinuclear complexes, multinuclear and polymeric N-heterocyclic carbene silver complexes, etc.³⁻¹⁰. In 2003, the silver carbene $[Ag_2(Me_2-edimy)Cl_2]$ has been successfully synthesized by the reaction of $[Me_2-edimyH_2][PF_6]_2$ with Ag_2O in CH_3CN and $[NMe_4]Cl$ ⁸. However, the reaction of $[(CH_3\{CH(NCHCHN)\}CH_2)_2]^{2+} Br_2^-$ with silver oxide in DMSO at refluxing gives poly[3,3'-dimethyl-1,1'-(ethane-1,2-diyl)diimidazolium[tetra- μ -bromido-silver(I)]].

Synthesis and crystal structure are reported in this article.

Experimental

General procedures :

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 $CDCl_3$ (400 MHz).

Synthesis of $[(CH_3\{CH(NCHCHN)\}CH_2)_2]_n^{2+}[(Ag_2Br_4)^{2-}]_n$:

Ag_2O (1.16 g, 5 mmol) was added to a solution of 1*H*-imidazolium, 1,1'-(1,2-ethanediyl)bis(3-methyl) dibromide (3.52 g, 10 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. Colorless crystals of the title compound were obtained after slow evapora-

tion (2.1 g, 58%) m.p. : 442 K (dec); ^1H NMR (CDCl_3) : 9.36 (1H, m, NCHN), 9.43 (1H, m, NCHN), 6.85 (2H, s, CH), 6.88 (2H, s, CH), 4.47 (4H, s, CH_2), 3.87 (6H, s, CH_3) ppm; Anal. Calcd. : C, 16.49; H, 2.19; N, 7.69; Found : C, 16.33; H, 2.04; N, 7.35%.

Structure determination :

A colorless crystal with dimensions of 0.23 mm \times 0.20 mm \times 0.19 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 ($\lambda = 0.71073 \text{ \AA}$). The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. A total of 4540 reflections were collected in the range of $2.8 \leq \theta \leq 227.6$ by using an ω scan mode at 296 K, of which 1605 ($R_{\text{int}} = 0.028$) were independent. 1466 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

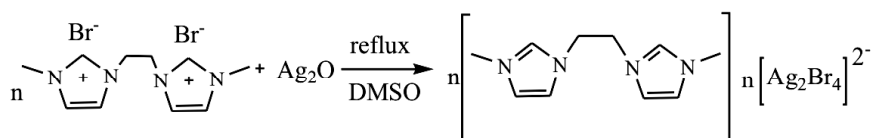
techniques on F^2 . The final refinement converged to $R = 0.028$ and $wR = 0.071$ ($w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.09165P]$, where $P = (F_o^2 + 2F_c^2)/3$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $S = 1.02$, $(\Delta\rho)_{\text{max}} = 0.71$ and $(\Delta\rho)_{\text{min}} = -0.76 \text{ e/\AA}^3$). The programs for structure solution and refinement are SHELXS-97¹¹ and SHELXL-97¹², respectively.

Results and discussion

Crystal structure of the title complex :

Reaction of Ag_2O with 2 equiv. of $[(\text{CH}_3\{\text{CH}(\text{NCHCHN})\}\text{CH}_2)_2]^{2+} \text{Br}_2^{2-}$ in DMSO at refluxing gave a light brown solution. After workup, the title complex was isolated as colorless crystals in 58% yield (Scheme 1). The composition of the title complex was confirmed by elemental analysis and ^1H 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 $[(\text{Ag}_2\text{Br}_4)^{2-}]_n$ is shown in Fig. 2, the packing diagram of the title complex is shown in Fig. 3. The details crystallographic data were collected in Table 1. The selected bond lengths are given in Table 2. The selected bond angles for the title compound are given Table 3.



Scheme 1

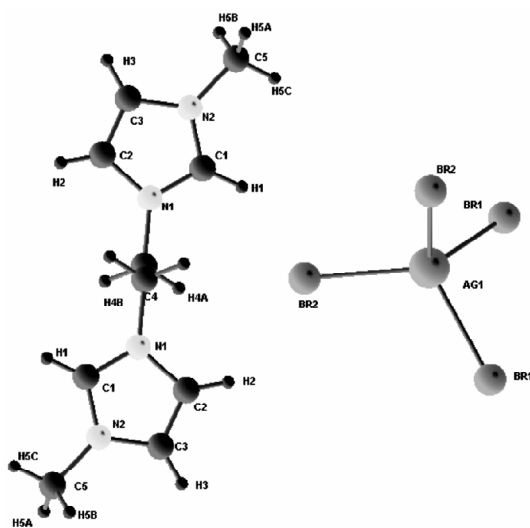


Fig. 1. Molecular structure of title complex (30% probability level).

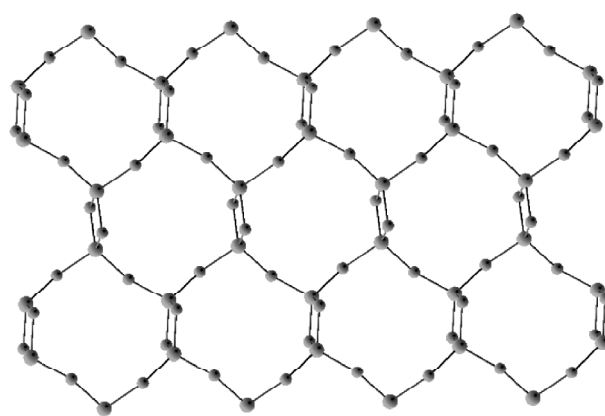
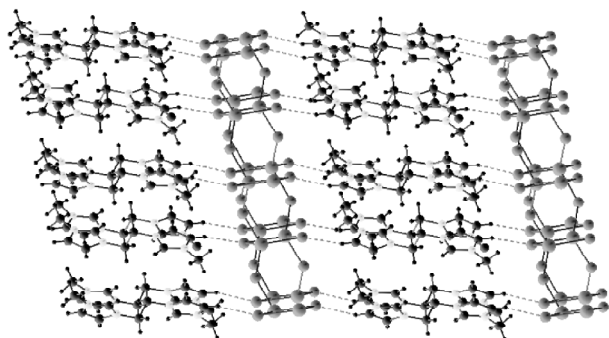


Fig. 2. Molecular structure of the polymeric anion $\{[\text{Ag}_2\text{Br}_4]^{2-}\}_n$.

Although the reaction of $[\text{Me}_2\text{-edimyH}_2][\text{PF}_6]_2$ with silver oxide in dichloromethane CH_3CN and $[\text{NMe}_4]\text{Cl}^8$.

**Fig. 3.** The packing diagram of the title complex.

anion forms polymeric sheets. The cations are located between the sheets and partly reach through the voids of the anions. A characteristic feature of the polymeric $\{[\text{Ag}_2\text{Br}_4]^{2-}\}_n$ anion is the construction of rings built up from corner-sharing of slightly distorted Ag_2Br_4 tetrahedra. A large twelve-membered ring is formed by six alternating bromine and six silver atoms; another four-membered ring completes the building units of the polymeric anion (Fig. 2). The four-membered ring is very similar to that in the complex anion $[\text{Ag}_4\text{Br}_8]^{4-}$ ¹³, these anions

Table 1. Crystallographic data and structure refinement parameters for title complex

Empirical formula	$\text{C}_5\text{H}_8\text{AgBr}_2\text{N}_2$	$F(000)$	676
Formula weight	363.82	Calculated density (g cm^{-3})	2.632
Temperature (K)	296	Absorption coefficient (mm^{-1})	10.83
Wavelength (nm)	0.71073 Å	Θ range for data collection ($^\circ$)	2.8–27.6°
Crystal system	Monoclinic	Limiting indices	$-10 \leq h \leq 10$, $-13 \leq k \leq 14$, $-9 \leq l \leq 5$
Space group	P21/c	Observed reflections ($I > 2\sigma(I)$)	1466
a (nm)	0.91402 (10)	Reflections collected/unique	4540/1605
b (nm)	1.25548 (13)	Refinement method	Full-matrix least-squares techniques on F^2
c (nm)	0.82710 (9)	Data/restraints/parameters	1065/0/93
β ($^\circ$)	104.696 (2)°	Goodness-of-fit on F^2	1.020
Volume (nm^3)	918.07 (17) Å ³	Final R indices	0.0308
Z	4	R indices (all data)	0.0279

Table 2. Selected bond lengths (Å) for the title compound

Bond	Dist.	Bond	Dist.
Ag(1)–Br(2)	2.6864(6)	N(1)–C(2)	1.370(5)
Ag(1)–Br(2i)	2.7041(6)	N(1)–C(4)	1.466(5)
Ag(1)–Br(1)	2.7072(6)	N(2)–C(1)	1.324(5)
Ag(1)–Br(1ii)	2.7080(6)	N(2)–C(3)	1.355(6)
Br(1)–Ag(1ii)	2.7080(6)	N(2)–C(5)	1.466(6)
Br(2)–Ag(1iii)	2.7041(6)	N(1)–C(1)	1.322(5)

Symmetry codes : (i) $x, -y + 1/2, z + 1/2$; (ii) $-x, -y, -z + 2$; (iii) $x, -y + 1/2, z - 1/2$; (iv) $-x, -y + 2, -z + 1$.

The product molecular is a silver carbene $[\text{Ag}_2(\text{Me}_2\text{-edimy})\text{Cl}_2]$, which is different from that of the title complex. The reaction of $[(\text{CH}_3\{\text{CH}(\text{NCHCHN})\}\text{CH}_2)_2]^{2+} \text{Br}_2^{2-}$ with silver oxide in DMSO at refluxing gives the title compound $[(\text{CH}_3\{\text{CH}(\text{NCHCHN})\}\text{CH}_2)_2]_n^{2+} [(\text{Ag}_2\text{Br}_4)^{2-}]_n$. As shown in Fig. 1, the crystal structure of the title complex is composed of $[(\text{CH}_3\{\text{CH}(\text{NCHCHN})\}\text{CH}_2)_2]^{2+}$ cations and $[\text{Ag}_2\text{Br}_4]^{2-}$ anions. The

contain tetrahedrally coordinated Ag^+ atoms, whereas $[\text{Ag}_4\text{Br}_8]^{4-}$ ion, isolated as the tetraphenylphosphonium and tetraphenylarsonium salts, contains three-coordinated and four-coordinated Ag^{+14} .

The angles of Br(2)–Ag(1)–Br(1), Br(2i)–Ag(1)–Br(1), Br(2)–Ag(1)–Br(1ii), Br(2)–Ag(1)–Br(2i), are 119.92(2), 116.17(2), 114.459(19), 100.636(15) for the title complex, respectively, which deviate from the ideal angle of 109.5. The bond distances of Ag(1)–Br(2), Ag(1)–Br(2i), Ag(1)–Br(1), Ag(1)–Br(1ii), are 2.6864(6), 2.7041(6), 2.7072(6), 2.7080(6) for the title complex, respectively and the average Ag–Br distance in the title compound is 2.7014 Å, which are considerably longer than for the $[\text{Ag}_2\text{Br}_4]^{2-}$ dimer (2.518 Å)¹⁴. This values are comparable to other tetrahedral AgBr_4^{15} . The Br(1ii)–Ag(1)–Br(1)–Ag(1ii) atoms lie in the same plane.

It is noted that most of the metallation reactions involving imidazolium salts and silver oxide proceed at

Table 3. Selected bond angles (°) for the title compound

Angle	(°)	Angle	(°)
Br(2)-Ag(1)-Br(2i)	100.636(15)	Ag(1)-Br(2)-Ag(1iii)	145.64(2)
Br(2)-Ag(1)-Br(1)	119.92(2)	C(1)-N(1)-C(2)	108.4(3)
Br(2i)-Ag(1)-Br(1)	108.758(18)	C(1)-N(1)-C(4)	126.0(3)
Br(2)-Ag(1)-Br(1ii)	114.459(19)	C(2)-N(1)-C(4)	125.6(4)
Br(2i)-Ag(1)-Br(1ii)	116.17(2)	C(1)-N(2)-C(3)	108.0(4)
Br(1)-Ag(1)-Br(1ii)	97.736(17)	Br(1ii)-Ag(1)-Br(1)-Ag(1ii)	0.0
Ag(1)-Br(1)-Ag(1ii)	82.263(17)	C(4)-N(1)-C(1)-N(2)	-180.0(4)
C(4)-N(1)-C(2)-C(3)	179.1(5)	C(5)-N(2)-C(1)-N(1)	178.7(4)
C(5)-N(2)-C(3)-C(2)	-178.9(5)	Br(1ii)-Ag(1)-Br(2)-Ag(1iii)	-1.73(4)
C(1)-N(1)-C(2)-C(3)	-0.4(7)		

room temperature, Tulloch and co-workers found that silver oxide reactions with bulky imidazolium salts often require refluxing⁹. The need for refluxing suggests that steric bulk around the imidazolium cation affects the ability of the silver oxide to effectively deprotonate the imidazolium salt. Meanwhile moieties with one imidazolium ring have been observed to react faster with silver oxide than those ligands that possess two or more imidazolium cations⁹. But silver N-heterocyclic carbene complexes with two imidazolium rings¹⁶ and three imidazolium rings¹⁷ have been synthesized at room temperature in water and at 75 °C in DMSO solution. To our surprising, the reaction of silver oxide with ligand with two imidazolium rings in DMSO at refluxing can't afford the silver N-heterocyclic carbene complex, but a silver imidazolium ionic complex $[(CH_3\{CH(NCHCHN)\}CH_2)_2]_n^{2+}[(Ag_2Br_4)^{2-}]_n$ instead. The reason for the difference observed between this system and those reported in Ref.^{16,17} may be due to difference in the anion of imidazolium employed and solvent and the imidazolium in the system reported in in Ref.^{16,17} have strong acidity.

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