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Synthesis and characterization of oligomeric and polymeric silver-imidazol-2-ylidene iodide complexes

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Abstract

Reaction of N,N'-dimethylimidazolium iodide with Ag_2O in CH_2Cl_2 leads to the coordination polymer $[Ag(carbene)_2]_2[Ag_4I_6]$ (**2**), which consists of the cation $[Ag(carbene)_2]^+$ and anionic infinite one-dimensional $[Ag_4I_6]^{2-}$ chain. The cations and anionic chains are connected into two-dimensional network structure. Treatment of N-allyl-N'-methylimidazolium iodide with Ag_2O yielded a tetranuclear N-heterocyclic carbene silver complex $[Ag(carbene)_2]_2[Ag_2I_4]$ (**3**). The polymeric $[Ag(carbene)][AgI_2]$ (**4**) was isolated when the tetranuclear complex **3** was heated at 80 °C. The monocarbene complex **4** adopts infinite one-dimensional ribbon stair structure in which the silver atoms are held together by multiple iodide bridges and weak Ag···Ag interaction. The compounds have been fully characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography.

Keywords: Imidazol-2-ylidenes; Silver complexes; Silver–silver interaction; Coordination polymer; X-ray diffraction

1. Introduction

The organometallic chemistry of imidazol-2-ylidenes has been receiving considerable attention since Arduengo et al. isolated the first stable imidazol-2-ylidene in its free state in 1991 [1]. These N-heteocyclic carbenes act as σ donating ligands without significant back donation and form stable metal–carbene complexes with many transition metals [2]. N-Heterocyclic carbenes are more comparable to P-, N- and O-donating ligands rather than classical carbenes. The imidazol-2-ylidene complexes of late transition metals have been demonstrated to be efficient catalysts for some organic transformation processes, such as carbon–carbon coupling reactions [3,4], CO–ethylene co-polymerization [5], olefin metathesis [6], hydrosilation, and hydroformation reactions of olefins [7,8]. However, it is not always convenient to synthesize complexes from free carbenes and transition metals. An alternative route is the use of silver–carbene complexes as carbene transfer reagents, which was described by Wang and Lin in 1998 [9]. The silver–carbene complexes may be obtained by treatment of Ag_2O with corresponding N,N'-dialkylimidazolium salts. So far, a number of silver–ylidene complexes have been prepared and characterized [10–17], revealing mononuclear complexes with one or two carbenes coordinated to Ag(I), or halide-bridged dinuclear complexes. However, few multinuclear and polymeric silver complexes have been reported [14].

In this paper we report the preparation and structural characterization of one-dimensional polymeric complexes $[Ag(carbene)_2]_2[Ag_4I_6]$ and $[Ag(carbene)][AgI_2]$, and the oligomeric silver–carbene complex $[Ag(carbene)_2]_2[Ag_2I_4]$.

2. Results and discussion

2.1. Synthesis and NMR characterization

N-Methylimidazole was alkylated with methyl iodide and allyl iodide to afford yellow solids of N,N'-dimethylimidazolium iodide and N-allyl-N'-methylimidazolium iodide (**1**) in excellent yields, respectively. N,N'-dimethylimidazolium iodide reacts readily with Ag_2O in CH_2Cl_2 to give a white solid [Ag(carbe-

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ne)$_2$]$_2$[Ag$_4$I$_6$] (**2**), which was purified by recrystallization from hot DMSO. The tetranuclear complex [Ag(carbene)$_2$]$_2$[Ag$_2$I$_4$] (**3**) was obtained similarly from the reaction of *N*-allyl-*N′*-methylimidazolium iodide with Ag$_2$O, and isolated directly from its CH$_2$Cl$_2$ solution. Both **2** and **3** are poorly soluble in common organic solvents once they were isolated, but they can dissolve in hot DMSO. When a suspension of **3** in DMSO was heated at 80 °C for a few hours, a new coordination polymer **4** with the formula [Ag(carbene)][AgI$_2$] was afforded. Complex **4** does not dissolve in any solvent once it was crystallized from hot DMSO.

These silver–carbene complexes were fully characterized by elemental analysis and ^{1}H-NMR spectroscopy. In the ^{1}H-NMR spectrum of **1**, a peak at low field (9.80 ppm) indicates the presence of an acidic CH proton. ^{1}H-NMR spectra of **2** and **3** in DMSO-d_6 showed the complete disappearance of the acidic 2H-imidazolium protons, indicating the formation of silver–carbene complexes. Because of the poor solubility in DMSO at room temperature, ^{13}C-NMR spectra of **2**–**4** were not recorded. The structures of complexes **2**–**4** were determined by X-ray diffraction analysis.

2.2. Molecular structure of 2

The structure of **2** is shown in Fig. 1. Complex **2** is a ionic coordination polymer, consisting of the cation [Ag(carbene)$_2$]$^+$ and one-dimensional infinite anionic [Ag$_4$I$_6$]$^{2-}$ chain. Selected bond distances and angles are given in Table 1. The cation has a typical linear conformation of [Ag(carbene)$_2$]$^+$ with a C–Ag–C angle of 170.6(3)°, comparable with other examples of linear [Ag(carbene)$_2$]$^+$ complexes. The Ag–C bond distances [2.091(7) and 2.088(7) Å] are consistent with other reported silver–carbene complexes [10–17]. The building unit [Ag$_4$I$_6$]$^{2-}$ is linked by two Ag–I bonds. 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. The I(1) and I(2) ions link three neighboring Ag atoms, whereas I(3) acts as a bridge between two Ag atoms. The Ag–I bond distances range between 2.7959(9) and 2.9488(9) Å. The Ag–Ag bond distances within the building unit [Ag$_4$I$_6$]$^{2-}$ are around 3.0 Å, which are shorter than the sum of the van der Waals radii, suggesting some metal–metal interaction. Furthermore, the cations and anionic chains are connected each other via Ag(3)–I(3) interaction forming two-dimensional network structure (Fig. 2). The Ag(3)–I(3) separation (3.757 Å) is relatively long when compared to the corresponding values of [Ag$_4$I$_6$]$^{2-}$, showing weak interaction between the cations and anionic chain. It was known that the type of anionic complexes [Ag$_l$X$_k$]$^{(k-1)-}$ formed is strongly influenced by the countercation and the nature of the halide [18]. In the case of iodide, the ions [AgI$_3$]$^{2-}$, [Ag$_2$I$_4$]$^{2-}$, and [Ag$_4$I$_8$]$^{4-}$ have been reported. Thus [Ag$_4$I$_6$]$^{2-}$ is a new anionic [Ag$_l$X$_k$]$^{(k-l)-}$ complex form and exists as an one-dimensional polymer.

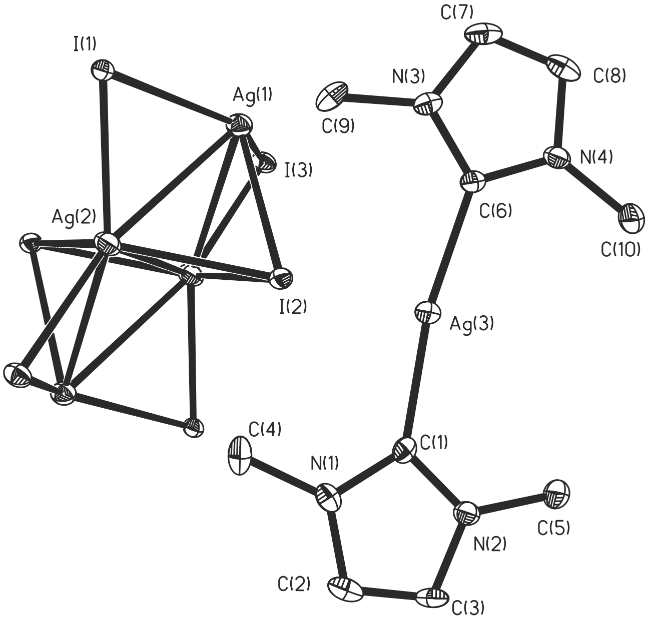

Fig. 1. ORTEP diagram of **2** in the crystal state with 50% probability ellipsoids.

It is noted that *N*,*N′*-dimethylimidazolium chloride and *N*,*N′*-dimethylimidazolium bromide reacted with Ag$_2$O to afforded one-dimensional polymers, which are composed of alternating [Ag(carbene)$_2$]$^+$ and [AgX$_2$]$^-$ associated through Ag–Ag interactions at a distance of ca. 3.19 Å [15].

2.3. Molecular structure of 3

Crystals suitable for X-ray crystallography of **3** were obtained by slow cooling of a hot DMSO solution of the complex. As has been revealed by X-ray diffraction analysis, complex **3** crystallizes as a tetranuclear compound of the formula [Ag(carbene)$_2$]$_2$[Ag$_2$I$_4$] that is symmetric about an inversion center. One half of the molecule comprises the asymmetric unit of the structure. The structure of the silver–carbene complex of **3** is shown in Fig. 3 and selected bond distances and angles are listed in Table 2. The complex consists of two [Ag(carbene)$_2$]$^+$ and one [Ag$_2$I$_4$]$^{2-}$ units, which are held together by Ag–Ag interactions. The geometry at the Ag(1) atom is nearly linear or T-shaped when the Ag(1)–Ag(2) interaction is taken into consideration, which is bi-coordinated by two carbene carbon atoms with a C–Ag–C angle of 172.8(3)°. The Ag–C bond lengths are 2.103(9) and 2.081(9) Å, which are slightly longer than those values in complex **2**. These values are quite normal when compared to the same values reported for other [Ag(carbene)$_2$]$^+$ complexes [10–14].

Table 1
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Ag(1)–I(1)	2.8731(9)	Ag(1)–I(2)	2.9488(9)
Ag(1)–I(3)	2.8204(10)	Ag(1)–I(1)#1	2.9229(10)
Ag(2)–I(1)	2.8469(10)	Ag(2)–I(2)	2.9037(11)
Ag(2)–I(2)#2	3.0489(9)	Ag(2)–I(3)#2	2.7959(9)
Ag(1)–Ag(2)	3.1792(10)	Ag(1)–Ag(2)#2	3.0718(11)
Ag(2)–Ag(1)#2	3.0718(11)	Ag(2)–Ag(2)#2	2.9167(13)
Ag(3)–C(1)	2.091(7)	Ag(3)–C(6)	2.088(7)
Bond angles			
I(3)–Ag(1)–I(1)	137.86(3)	I(3)–Ag(1)–I(1)#1	106.55(2)
I(1)–Ag(1)–I(1)#1	94.25(2)	I(3)–Ag(1)–I(2)	101.69(3)
I(1)#1–Ag(1)–I(2)	118.35(3)	I(1)–Ag(1)–I(2)	99.74(3)
I(3)–Ag(1)–Ag(2)#2	56.461(18)	I(1)–Ag(1)–Ag(2)#2	106.13(2)
I(1)#1–Ag(1)–Ag(2)#2	159.52(3)	I(2)–Ag(1)–Ag(2)#2	60.81(2)
Ag(1)–I(1)–Ag(1)#1	85.75(2)	Ag(2)–I(2)–Ag(1)	65.80(2)
Ag(2)–I(2)–Ag(2)#2	58.62(2)	Ag(1)–I(2)–Ag(2)#2	61.59(2)
Ag(2)#2–I(3)–Ag(1)	66.31(3)		
I(3)–Ag(1)–Ag(2)	110.04(3)	I(1)–Ag(1)–Ag(2)	55.84(2)
I(1)#1–Ag(1)–Ag(2)	143.30(3)	I(2)–Ag(1)–Ag(2)	56.42(2)
Ag(2)–I(1)–Ag(1)	67.53(2)	Ag(2)–I(1)–Ag(1)#1	145.14(3)
Ag(2)#2–Ag(1)–Ag(2)	55.60(3)	I(3)#2–Ag(2)–I(1)	129.23(3)
I(3)#2–Ag(2)–I(2)	107.85(2)	I(1)–Ag(2)–I(2)	101.45(2)
I(3)#2–Ag(2)–Ag(2)#2	118.90(3)	I(1)–Ag(2)–Ag(2)#2	111.12(3)
I(2)–Ag(2)–Ag(2)#2	63.18(2)	I(3)#2–Ag(2)–I(2)#2	99.81(3)
I(1)–Ag(2)–I(2)#2	98.96(2)	I(2)–Ag(2)–I(2)#2	121.38(2)
Ag(2)#2–Ag(2)–I(2)#2	58.20(3)	I(3)#2–Ag(2)–Ag(1)#2	57.23(2)
I(1)–Ag(2)–Ag(1)#2	155.70(3)	I(2)–Ag(2)–Ag(1)#2	97.09(2)
Ag(2)#2–Ag(2)–Ag(1)#2	64.07(2)	I(2)#2–Ag(2)–Ag(1)#2	57.601(18)
I(3)#2–Ag(2)–Ag(1)	165.12(3)	I(1)–Ag(2)–Ag(1)	56.63(2)
I(2)–Ag(2)–Ag(1)	57.782(18)	Ag(2)#2–Ag(2)–Ag(1)	60.34(3)
I(2)#2–Ag(2)–Ag(1)	91.97(3)	Ag(1)#2–Ag(2)–Ag(1)	124.40(3)
C(6)–Ag(3)–C(1)	170.6(3)	N(1)–C(1)–Ag(3)	130.4(5)
N(3)–C(6)–Ag(3)	130.2(5)	N(4)–C(6)–Ag(3)	125.5(5)

Symmetry transformations used to generate equivalent atoms: (#1) $-x, -y+1, -z+1$; (#2) $-x+1, -y+1, -z+1$.

The Ag(2) atom adopts tetrahedral geometry. The Ag–I(terminal) bond distance [2.7201(11) Å] is relatively shorter than those of Ag–I(bridging) bonds [2.8313(15) and 2.7839(15) Å]. There is no important interaction between silver ions and the allyl groups. The Ag(1)–Ag(2) bond distance [3.0424(14) Å] between the $[Ag(carbene)_2]^-$ and $[Ag_2I_4]^{2-}$ and the Ag(2)–Ag(2A) bond distance [2.9643(16) Å] within the anion $[Ag_2I_4]^{2-}$ do not show significant difference. The Ag–Ag interactions have been found in many silver complexes. The term *argentophilicity* has been adopted to describe this metal–metal interaction. The attraction between d^{10}–d^{10} closed-shell metals promotes the aggregation of silver(I) centers, which has been supported by spectroscopic and structural evidence.

2.4. Crystal structure of **4**

Single crystals of **4** obtained from DMSO when subjected to an X-ray diffraction experiment were shown to have a step structure, which aggregate into an infinite ribbon stair structure (Figs. 4 and 5). Selected bond distances and angles are summarized in Table 4. The complex may be viewed as an aggregated 1:1 adduct of [Ag(carbene)I] and AgI, which are held together by triple and quadruple halide bridges and Ag···Ag interaction. There are two independent silver atoms in the crystal structure of **4**. Ag(1) is coordinated by a carbene carbon atom, two triple-bridging iodide, and one quadruple-bridging iodide ions, and Ag(2) is surrounded by one triple-bridging and three quadruple-bridging iodide ions. The Ag–C bond distance of the monocarbene silver complex is longer than those of the biscarbene–silver complexes **2** and **3**, arising from the variation of coordination environment of silver atoms. The Ag–I bond distances are in the wide range of 2.799(2)–3.233(3) Å, which are comparable to the corresponding values in **2** and **3**. The relatively long Ag–Ag separations [3.103(3) and 3.217(2) Å] also show that the Ag–Ag interactions are very weak, and the ribbon stair structure is mainly stabilized by the multiple bridging iodides.

The metal complexes of the *N*-heterocyclic carbenes usually show high thermal stability and hydrolytic

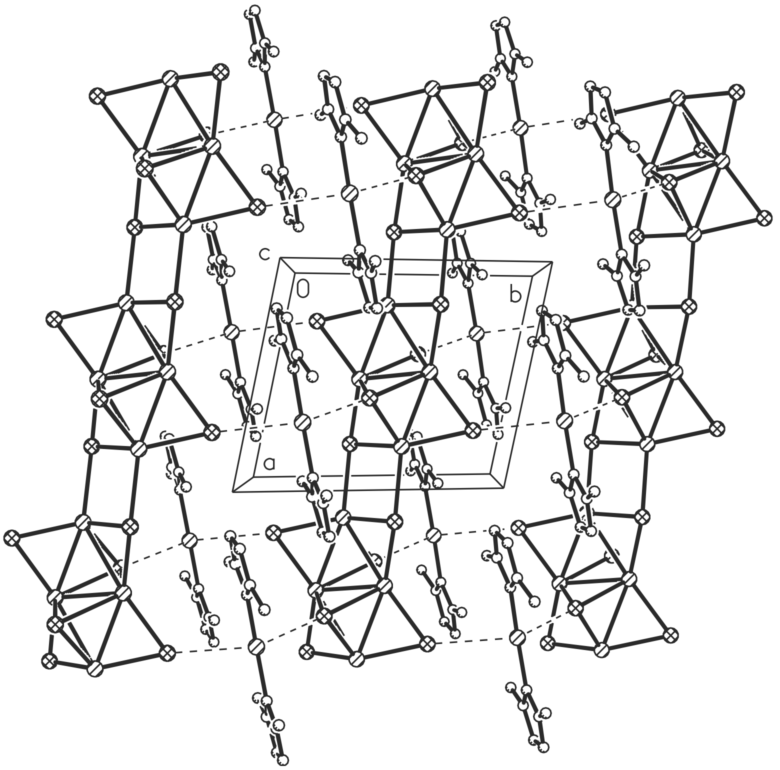

Fig. 2. Polymeric chain structure of **2**, showing Ag···I interaction between the cation $[Ag(carbene)_2]^+$ and the anionic chains.

durability because of the strong metal–carbon bonds. The M–C bond in transition metal complexes is generally considered to be extremely robust and kinetically inert to substitution [19], although in the case of $[Ag(carbene)_2][AgBr_2]$, the transfer of a carbene and a bromide bridge to form [Ag(carbene)Br] may occur in solution [9]. The thermal arrangement of $[Ag(carbene)_2]$ unit in **3** is remarkable, since one of the Ag–C bonds must be cleaved and subsequently the released carbene must react with another silver atom to form the final mono(carbene)silver complex.

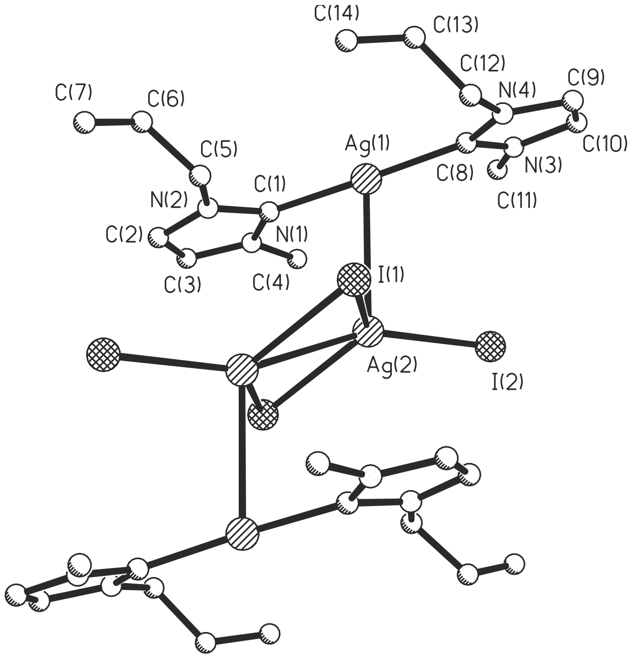

Fig. 3. Molecular structure of complex **3** showing the atom-numbering scheme. All H atoms have been omitted for clarity.

In summary, we have synthesized new silver-imidazol-2-ylidene complexes, and the structures of these tetranuclear and polymeric silver complexes are described. It

Table 2
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Ag(1)–C(1)	2.086(9)	Ag(1)–C(8)	2.079(9)
Ag(1)–Ag(2)	3.0421(14)	Ag(2)–I(2)	2.7200(12)
Ag(2)–I(1)	2.7846(15)	Ag(2)–I(1)#1	2.8310(15)
Ag(2)–Ag(2)#1	3.042(14)		
Bond angles			
C(8)–Ag(1)–C(1)	172.4(3)	C(8)–Ag(1)–Ag(2)	106.9(3)
C(1)–Ag(1)–Ag(2)	76.5(3)	I(2)–Ag(2)–I(1)#1	122.06(4)
I(2)–Ag(2)–I(1)	116.49(4)	I(1)#1–Ag(2)–I(1)	116.28(3)
I(2)–Ag(2)–Ag(2)#1	157.67(5)	I(1)#1–Ag(2)–Ag(2)#1	58.92(4)
I(1)–Ag(2)–Ag(2)#1	57.40(4)	I(2)–Ag(2)–Ag(1)	92.45(5)
I(1)#1–Ag(2)–Ag(1)	80.51(3)	I(1)–Ag(2)–Ag(1)	120.39(4)
Ag(2)#1–Ag(2)–Ag(1)	109.17(5)	N(2)–C(1)–Ag(1)	129.5(7)
N(1)–C(1)–Ag(1)	126.7(6)	N(4)–C(8)–Ag(1)	129.5(7)
N(3)–C(8)–Ag(1)	129.5(6)	Ag(2)#1–I(1)–Ag(2)	63.68(3)

Symmetry transformations used to generate equivalent atoms: (#1) $-x+1$, $-y$, $-z+1$.

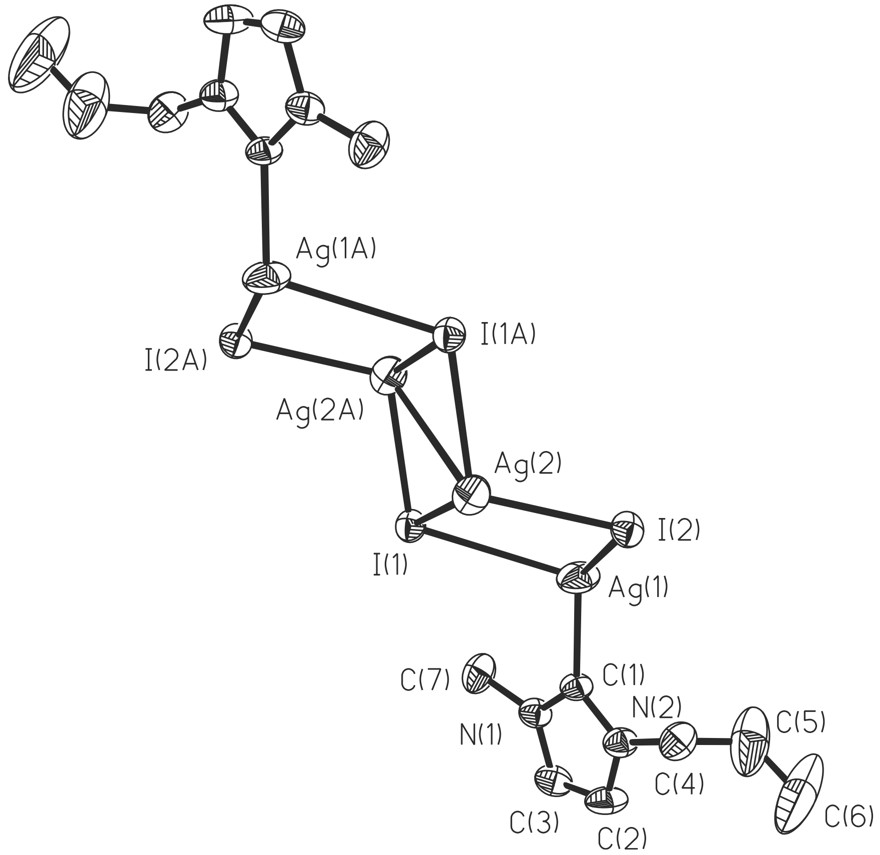

Fig. 4. Perspective view of complex **4** with thermal ellipsoids at 30% probability level.

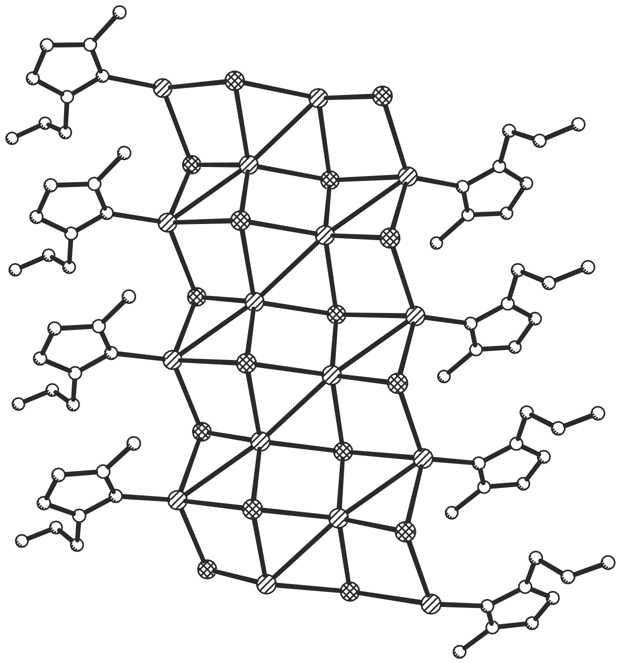

Fig. 5. A section of the one-dimensional infinite stair structure of complex **4**.

has been illustrated that which structure a silver halide complex adopts depends on the sizes of the metal and halide atoms, on the steric bulk of the ligand, and on the solvents from which it crystallized [18]. The silver carbene complexes ($X = Cl^-$ and Br^-) usually adopt linear [Ag(carbene)X] or $[Ag(carbene)_2][AgX_2]$ structures [3–13]. The results presented here illustrate that silver iodide complexes of *N*-heterocyclic carbenes tend to aggregate into oligomeric or polymeric chain materials. At present it is not clear how the solvents influence the crystallization. The poor solubility of these complexes prevents a detailed study on the role of the solvents and other crystallization conditions. These three *N*-heterocyclic carbene complexes are very stable toward light and air at room temperature, which may offer convenient carbene precursors for the preparation of other transition metal complexes.

3. Experimental

All solvents and chemicals were analytical reagent grade and were used without further purification. Elemental analysis was carried out on a Perkin–Elmer 240 microanalyzer. ^{1}H-NMR data were recorded on Bruker AMX-300 spectrometers. The spectra were referenced internally using the signal from the residual

Table 3
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
Ag(1)–C(1)	2.161(9)	Ag(1)–I(2)	2.872(2)
Ag(1)–I(1)	3.233(3)	Ag(1)–I(2)#1	2.922(2)
Ag(2)–I(1)	2.946(2)	Ag(2)–I(2)	2.799(2)
Ag(2)–I(1)#2	2.864(2)	Ag(1)–Ag(2)#1	3.217(2)
Ag(2)–I(1)#3	2.905(2)	Ag(2)–Ag(2)#3	3.103(3)
Bond angles			
C(1)–Ag(1)–I(2)	126.1(3)	C(1)–Ag(1)–I(2)#1	117.5(3)
I(2)–Ag(1)–I(2)#1	101.24(7)	C(1)–Ag(1)–Ag(2)#1	129.0(3)
I(2)–Ag(1)–Ag(2)#1	103.63(5)	I(2)#1–Ag(1)–Ag(2)#1	54.00(4)
C(1)–Ag(1)–I(1)	107.8(3)	I(2)–Ag(1)–I(1)	93.87(4)
I(2)#1–Ag(1)–I(1)	106.71(4)	I(2)–Ag(2)–I(1)#2	121.53(4)
Ag(2)#1–Ag(1)–I(1)	52.72(5)	I(2)–Ag(2)–I(1)#3	111.63(6)
I(1)#2–Ag(2)–I(1)#3	104.93(5)	I(2)–Ag(2)–I(1)	102.03(5)
I(1)#2–Ag(2)–I(1)	100.85(7)	I(1)#3–Ag(2)–I(1)	115.95(5)
I(2)–Ag(2)–Ag(2)#3	122.89(7)	I(1)#2–Ag(2)–Ag(2)#3	114.84(7)
I(1)#3–Ag(2)–Ag(2)#3	58.61(5)	I(1)–Ag(2)–Ag(2)#3	57.34(5)
I(2)–Ag(2)–Ag(1)#2	57.61(6)	I(1)#2–Ag(2)–Ag(1)#2	63.93(5)
I(1)#3–Ag(2)–Ag(1)#2	131.36(5)	I(1)–Ag(2)–Ag(1)#2	112.67(5)
Ag(2)#3–Ag(2)–Ag(1)#2	169.95(6)	Ag(2)#1–I(1)–Ag(2)	100.85(7)
Ag(2)#1–I(1)–Ag(2)#3	75.07(5)	Ag(2)#3–I(1)–Ag(2)	64.05(5)
Ag(2)#1–I(1)–Ag(1)	63.35(3)	Ag(2)#3–I(1)–Ag(1)	115.42(6)
Ag(2)–I(1)–Ag(1)	77.49(4)	Ag(2)–I(2)–Ag(1)	86.14(4)
Ag(2)–I(2)–Ag(1)#2	68.38(4)	Ag(1)–I(2)–Ag(1)#2	101.24(7)

Symmetry transformations used to generate equivalent atoms: (#1) $x-1, y, z$; (#2) $x+1, y, z$; (#3) $-x+1, -y+1, -z$.

solvent (^{1}H). *N*,*N*′-Dimethylimidazolium iodide was prepared according to the reported procedure [20].

3.1. Preparations of 1-allyl-3-methylimidazolium iodide (1)

A solution of *N*-methylimidazole (1.64 g, 20 mmol) and allyl iodide (3.7 g, 22 mmol) in toluene (20 ml) was stirred for 2 h at room temperature. The solvent was removed and the resulted yellow solid was washed with ether. Yield: 4.5 g (89%). Anal. Calc. for $C_7H_{11}IN_2$: C, 33.62; H, 4.43; N, 11.20%. Found: C, 33.19; H, 4.58; N, 11.42%. ^{1}H-NMR ($CDCl_3$): 9.80 (s, NCHN, 2H), 7.65, 7.55 (both d, $J_{HH} = 16.2$ Hz, NCHCHN), 6.04 (m, C*H*=CH$_2$, 1H), 5.50 (m, CH=C*H*$_2$, 2H), 4.99 (d, $J_{HH} = 6.0$ Hz, NCH$_2$, 2H), 4.08 (s, CH$_3$, 3H).

3.2. Preparation of 1,3-dimethylimidazol-2-ylidene silver iodide (2)

Silver oxide (0.23 g, 1.0 mmol) was added to a solution of 1,3-methylimidazolium iodide (0.44 g, 2.0 mmol) in dichloromethane (20 ml), and the suspension was stirred overnight. The resulted white solid was filtered and washed with diethyl ether. Recrystallization from hot DMSO gave colorless crystals. Yield: 44%. Anal. Calc. for $C_{10}H_{32}Ag_3I_3N_4$: C, 13.40; H, 1.80; N, 6.25%. Found: C, 13.52; H, 1.69; N, 6.07%. ^{1}H-NMR (DMSO-*d*^{6}): 7.48 (s, CH, 2H), 3.90 (s, CH$_3$, 6H).

3.3. Preparation of 1-allyl-3-methylimidazol-2-ylidene silver iodide (3)

Silver oxide (0.23 g, 1 mmol) was added to a solution of 1-allyl-3-methylimidazolium iodide (0.5 g, 2 mmol) in dichloromethane (20 ml), and the suspension was stirred overnight. The resulted solution was filtered, and the filtrate was condensed to 8 ml. Colorless crystals were obtained on standing and slow evaporation of the solution. Yield: 26%. Anal. Calc. for $C_{28}H_{40}Ag_4I_4N_8$: C, 23.55; H, 2.82; N, 7.85%. Found: C, 23.58; H, 2.65; N, 7.24%. ^{1}H-NMR (DMSO-*d*^{6}): 7.52, 7.49 (both d, $J_{HH} = 16.0$ Hz, NCHCHN), 6.13 (m, C*H*=CH$_2$, 1H), 5.28 (m, CH=C*H*$_2$, 2H), 4.89 (d, $J_{HH} = 6.0$ Hz, NCH$_2$, 2H), 3.93 (s, CH$_3$, 3H).

3.4. Preparation of 1-allyl-3-methylimidazol-2-ylidene silver iodide (4)

A suspension of complex **3** in DMSO was heated in dark at 80 °C overnight. The resulted colorless solution was filtered. Colorless crystals of **4** were grown after cooling and standing for a few days. Yield: ca. 15%. Anal. Calc. for $C_7H_{10}Ag_2I_2N_2$: C, 14.21; H, 1.70; N, 4.73%. Found: C, 13.97; H, 1.68; N, 4.82%.

3.5. X-ray crystal structure determination

Suitable crystals of **2**–**4** were mounted on a glass fibre on a Bruker SMART 1000 CCD diffractometer operating

Table 4
Crystal data and structure refinement parameters for **2**–**4**

Compound	**2**	**3**	**4**
Empirical formula	$C_{20}H_{32}Ag_6I_6N_8$	$C_{28}H_{40}Ag_4I_4N_8$	$C_7H_{10}Ag_2I_2N_2$
Formula weight	1793.16	1427.76	591.71
Temperature (K)	173(2)	123(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions			
a (Å)	8.515(2)	8.469(4)	4.478(4)
b (Å)	10.197(3)	11.653(5)	16.714(14)
c (Å)	11.823(3)	11.823(5)	17.834(15)
α (°)	106.341(3)	60.779(5)	90
β (°)	95.614(3)	81.232(6)	95.922(10)
γ (°)	99.685(4)	87.271(5)	90
V (Å^3)	959.5(5)	1005.9(8)	1327.7(19)
Z	1	1	4
Calculated density (Mg m^{-3})	3.103	2.357	2.960
Absorption coefficient (mm^{-1})	7.852	5.017	7.564
$F(0\,0\,0)$	808	664	1064
Crystal size (mm)	0.10 × 0.10 × 0.15	0.06 × 0.19 × 0.28	0.10 × 0.12 × 0.36
θ range for data collection	4.74–23.96	4.98–23.86	4.76–23.64
Limiting indices	$-9 \le h \le 9$, $-9 \le k \le 11$, $-13 \le l \le 13$	$-9 \le h \le 8$, $-12 \le k \le 11$, $-10 \le l \le 12$	$-5 \le h \le 4$, $-14 \le k \le 18$, $-19 \le l \le 19$
Reflections collected	2990	3175	3423
Reflections unique	2405 [$R_{int} = 0.0182$]	2475 [$R_{int} = 0.0272$]	1733 [$R_{int} = 0.0342$]
Data/restraints/parameters	2405/0/186	2475/0/201	1733/0/119
Goodness-of-fit on F^2	1.022	1.082	1.105
Final R indices [$I > 2\sigma(I)$]	0.0256, 0.0581	0.0639, 0.1690	0.0430, 0.1053
R indices (all data)	0.0301, 0.0598	0.0656, 0.1717	0.0465, 0.1079
Largest difference peak and hole, (e Å^{-3})	0.722 and −0.729	2.375 and −3.553	0.897 and −1.549

at 50 kV and 40 mA using Mo–K radiation (0.71073 Å). Data collection and reduction were performed using the SMART and SAINT software. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using SHELXTXL package [21]. The hydrogen atoms were generated geometrically and included in structure factor calculations. The selected bond lengths and angles for **2**–**4** were summarized in Tables 1–3, respectively. Crystal data and refinement details of the three silver carbene complexes are given in Table 4.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 203039 (**2**), 203040 (**3**) and 205653 (**4**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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