



New structural motifs of silver and gold complexes of pyridine-functionalized benzimidazolyliene ligands

Xiaoming Zhang, Shaojin Gu, Qinqin Xia, Wanzhi Chen*

Department of Chemistry, Zhejiang University, Xixi Campus, Hangzhou 310028, PR China

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ABSTRACT

Reaction of 1,3-bis(picoyl)benzimidazolium chloride ([HL1]Cl) with Ag_2O yields mononuclear complex $[\text{Ag}(\text{L1})\text{Cl}]$ (**2**), further reaction of **2** with $\text{Au}(\text{Et}_2\text{S})\text{Cl}$ afforded $[\text{Au}(\text{L1})\text{Cl}]$ (**3**). Treatment of **2** with AgBF_4 gave the trinuclear silver cluster $[\text{Ag}_3(\text{L1})_3](\text{BF}_4)_3$ (**4**), whereas the digold complex $[\text{Au}_2(\text{L1})_2](\text{BF}_4)_2$ (**5**) can be easily obtained from the carbene transfer reaction of **4** with $\text{Au}(\text{Et}_2\text{S})\text{Cl}$. A one-dimensional coordination polymer $[\text{Ag}(\text{L2})](\text{BF}_4) \cdot \text{CH}_3\text{CN}$ (**8**) was isolated from the reaction of $[\text{Ag}(\text{L2})\text{Cl}]$ (**7**, $\text{L2} = 1$ -benzyl-3-picoylbenzimidazolyliene) with additional Ag^+ in good yield. The dinuclear $[\text{Ag}_2(\text{L3})_2](\text{PF}_6)_2$ (**12**, $\text{L3} = 1,4$ -di(*N*-benzylbenzimidazolyliene)but-2-yne) is a 18-membered macrocycle. All these complexes have been structurally characterized. Complex **2** shows a dimeric structure because of intermolecular $\text{Ag} \cdots \text{Cl}$ interactions. Complex **4** consists of a triangular Ag_3 ring with very short $\text{Ag}–\text{Ag}$ contacts 2.777(1) Å, the $\text{Au}–\text{Au}$ distance in **5** is 3.206(2) Å showing very weak $\text{Au}–\text{Au}$ interaction and the macrocyclic cations in **12** are aligned one above another to form channels filled with hexafluorophosphate anions. The complexes **2–5**, **8**, and **12** are intensely luminescent upon irradiation of uv light, and their emission properties are briefly described.

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1. Introduction

The organometallic chemistry of *N*-heterocyclic carbene (NHCs) has been extensively studied in the recent decade [1–7]. The metal–NHC complexes exhibit excellent catalytic activity for many practically useful organic transformation especially for olefin metathesis [8–13], C–C [14–19], and C–N [20–24] bond formation reactions. Although metal NHC complexes can be prepared via various procedures, the use of silver carbene complexes as carbene transfer reagent for the synthesis of other metal complexes is one of most convenient way [25–30]. Such a route overcomes the difficulties arising from the isolation of unstable free heterocyclic carbenes and avoids the hard conditions when azolium salts react directly with metal salts.

A large number of silver complexes of *N*-heterocyclic carbenes have been synthesized and structurally characterized, and their potential uses as catalysts, medicine, and luminescent materials have also been studied. The achievement such as their synthetic routes, structural features, and applications of $\text{Ag}–\text{NHC}$ complexes has been summarized by Youngs and coworkers [31,32] and Lin et al. [33–35], respectively. These complexes are normally prepared according to three different procedures: (1) reaction of free NHC with silver salts [36]; (2) reaction of azolium salts with silver bases such Ag_2O , Ag_2CO_3 , and AgOAc [35,37–39]; (3) reaction of

azolium salts with silver salts under basic phase transfer conditions [33–35]. Among these approaches, route (2) is more convenient and most frequently used. So far, most of the known silver–NHC complexes are reported to be prepared by treatment of Ag_2O with the corresponding imidazolium salts. Benzimidazolin-2-ylidenes as a class of NHC ligands are easily accessible from commercially available benzimidazole or *o*-phenylenediamine [40,41]. The preparation, structures, and reactions of benzannulated NHCs have been well studied by Hahn's group [42–52], however, compared to their imidazolyliene analogues, benzimidazolin-2-ylidenes complexes are less studied both in structural diversity and homogeneous catalysis [53–57]. Free benzimidazolin-2-ylidene usually forms dimeric complexes, thus the preparation of metal–benzimidazolin-2-ylidene complexes through $\text{Ag}–\text{benzimidazolin-2-ylidene}$ transmetallation approach is convenient and practical. The $\pi–\pi$ interaction between the benzimidazolyliene rings might provide structural diversity to form 1D, 2D, and 3D structures.

Our recent research focuses on the design and preparation of multinuclear metal complexes or coordination polymers containing direct metal–metal interactions, and a number of metal complexes having short Pt–Ag, Pt–Ti, Pt–Pt, Pt–Pd, Ag–Ag, and Cu–Cu contacts have been characterized [58–62]. Heteroarene functionalized *N*-heterocyclic carbene ligands have proven to be good donating ligands for the assemblage of new metal clusters [63–70]. As a continuation, we report here the preparation and characterization of new silver and gold–carbene complexes, $[\text{Ag}(\text{L1})\text{Cl}]$, $[\text{Au}(\text{L1})\text{Cl}]$,

* Corresponding author. Fax: +86 571 88273314.

E-mail address: chenwzz@zju.edu.cn (W. Chen).

[Ag₃(L1)₃](BF₄)₃, [Au₂(L1)₂](BF₄)₂, [Ag(L2)Cl], {[Ag(L2)](BF₄) ? CH₃CN}_n, and [Ag₂(L3)₂](PF₆)₂, (L1 = 1,3-bis(picoly)benzimidazolylidene, L2 = 1-benzyl-3-picolybenzimidazolylidene, L3 = 1,4-di(*N*-benzylbenzimidazoliumyl)but-2-yne) containing bidentate or tridentate functionalized benzimidazolin-2-ylidene ligands. Seven silver and gold complexes were analyzed by X-ray single-crystal diffraction. The emission properties of these complexes in acetonitrile solution were also briefly described.

2. Experimental

2.1. General procedures

All the chemicals were obtained from commercial suppliers and used without further purification. *N*-picolybenzimidazole [71] and Au(Et₂S)Cl [72] were prepared according to the known procedures. The C, H, and N elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. ¹H and ¹³C NMR spectra were recorded on Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield to TMS at δ = 0 ppm and coupling constants (*J*) are expressed in Hz. The photoluminescence study was carried out in the solution of acetonitrile at room temperature using a Hitachi 850 spectrometer.

2.2. Synthesis of imidazolium salts and metal complexes

2.2.1. 1,3-Bis(picoly)benzimidazolium chloride hydrate (1)

A mixture of NaHCO₃ (8.4 g, 0.1 mol), picoly chloride hydrochloride (8.15 g, 50 mmol) and benzimidazole (2.95 g, 25 mmol) in 100 mL of EtOH was refluxed for 2 days and cooled to room temperature. The solvent was removed and the resulted viscous brown liquid was dissolved in CH₂Cl₂ (150 mL). After filtration, the filtrate was dried with anhydrous MgSO₄. The solvent was removed and the brown solid was washed with THF and dried to give a light brown powder. Yield: 6.1 g (69%). ¹H NMR (400 MHz, CDCl₃): δ 11.82 (s, NCHN, 1H), 8.50 (d, *J* = 4.0 Hz, pyridine, 2H), 7.85 (m, pyridine and benzimidazole, 4H), 7.74 (t, *J* = 7.2 Hz, pyridine, 2H), 7.53 (m, benzimidazole, 2H), 7.26 (m, pyridine, 2H), 6.01 (s, CH₂, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 152.0, 149.2, 143.6, 137.3, 131.2, 126.5, 123.5, 123.3, 113.8, 52.2. Anal. Calc. for C₁₉H₁₉N₄ClO: C, 64.31; H, 5.40; N, 15.79. Found: C, 64.11; H, 5.71; N, 15.48%.

2.2.2. Synthesis of [Ag(L1)Cl] (2)

A suspension of Ag₂O (128 mg, 0.55 mmol) in 20 mL of CH₂Cl₂ was treated with 1,3-bis(picoly)benzimidazolium chloride hydrate (1) (355 mg, 1.0 mmol). The mixture was stirred for 5 h with exclusion of light at room temperature. The resulted mixture was then filtered through Celite, and the filtrate was concentrated to about 2 mL under vacuum. A light brown solid was obtained by adding 20 mL of Et₂O. Yield: 364 mg (82%). ¹H NMR (400 MHz, CDCl₃): δ 8.59 (d, *J* = 4.8 Hz, pyridine, 2H), 7.67 (m, pyridine, 2H), 7.53 (m, benzimidazolylidene, 2H), 7.33 (m, benzimidazolylidene, 2H), 7.28 (d, *J* = 8.0 Hz, pyridine, 2H), 7.24 (m, pyridine, 2H), 5.75 (s, CH₂, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 190.9 (Ag-C), 155.7, 149.9, 137.7, 134.1, 124.4, 123.6, 122.5, 112.7, 53.8. Anal. Calc. for C₁₉H₁₆N₄ClAg: C, 51.43; H, 3.63; N, 12.63. Found: C, 51.49; H, 3.83; N, 12.75%.

2.2.3. Synthesis of [Au(L1)Cl] (3)

Au(Et₂S)Cl (70 mg, 0.22 mmol) was added to the colorless solution of 2 (88 mg, 0.2 mmol) in 20 mL of CH₂Cl₂. The mixture was protected from light and stirred at room temperature overnight. The resulted mixture was filtered through Celite to remove AgCl, and the filtrate was reduced to about 2 mL. After addition of 20 mL of Et₂O, a white precipitate was obtained. Yield: 72 mg

(68%). ¹H NMR (400 MHz, CDCl₃): δ 8.57 (d, *J* = 4.8 Hz, pyridine, 2H), 7.70 (m, pyridine, 2H), 7.58 (m, benzimidazolylidene, 2H), 7.34 (m, benzimidazolylidene, 2H), 7.47 (d, *J* = 7.2 Hz, pyridine, 2H), 7.28–7.25 (m, pyridine, 2H), 5.87 (s, CH₂, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 179.2 (Au-C), 154.2, 149.4, 137.5, 133.4, 124.8, 123.5, 122.4, 112.6, 54.4. Anal. Calc. for C₁₉H₁₆N₄ClAu: C, 42.83; H, 3.03; N, 10.52. Found: C, 42.50; H, 3.27; N, 10.36%.

2.2.4. Synthesis of [Ag₃(L1)₃](BF₄)₃ ? 2CH₃CN (4)

To a solution of 2 (134 mg, 0.3 mmol) in 10 mL of acetonitrile was added AgBF₄ (160 mg, 0.81 mmol). A white precipitate was produced immediately. The mixture was protected from light and stirred overnight. The filtrate was reduced to a minimum volume and addition of Et₂O (20 mL) afforded a white powder. Yield: 108 mg (73%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.10–8.02 (m, 18H), 7.52 (d, *J* = 2.8 Hz, 6H), 7.32 (t, *J* = 5.6 Hz, 12H), 5.81 (br, CH₂, 12H). No satisfactory elemental analysis was obtained due to its sensitivity towards light and partial loss of the solvent molecules.

2.2.5. Synthesis of [Au₂(L1)₂](BF₄)₂ (5)

The compound was prepared as described for 3 from 4 (44 mg, 0.089 mmol) and Au(Et₂S)Cl (36 mg, 0.11 mmol) in 10 mL of acetonitrile. The compound was isolated as a white solid. Yield 38 mg (61%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.60 (br, 8H), 7.80 (s, 8H), 7.49 (m, 8H), 5.94 (br, CH₂, 8H). Anal. Calc. for C₃₈H₃₂N₈B₂F₈Au₂: C, 39.07; H, 2.76; N, 9.59. Found: C, 38.85; H, 2.96; N, 9.46%.

2.2.6. Synthesis of 1-benzyl-3-picolybenzimidazolium chloride hydrate (6)

N-picolybenzimidazole (2.1 g, 10 mmol) and benzyl chloride (5.0 g, 40 mmol) were mixed together in 100 mL of toluene. The mixture was refluxed overnight, then the white solid was isolated and washed with several portions of toluene (2 × 10 mL) and Et₂O (2 × 10 mL). Yield: 2.7 g (77%). ¹H NMR (400 MHz, CDCl₃): δ 12.04 (s, NCHN, 1H), 8.49 (d, *J* = 4.8 Hz, pyridine, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.75 (m, 1H), 7.56–7.47 (m, 5H), 7.40–7.35 (m, 3H), 7.27–7.24 (m, 1H), 6.07 (s, CH₂, 2H), 5.83 (s, CH₂, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 152.1, 149.2, 143.6, 137.3, 132.1, 131.5, 130.7, 129.0, 128.8, 127.9, 127.8, 126.6, 123.5, 123.4, 114.2, 112.9, 52.1, 51.2. Anal. Calc. for C₂₀H₁₈N₃ClO: C, 67.89; H, 5.70; N, 11.88. Found: C, 67.68; H, 5.96; N, 11.73%.

2.2.7. Synthesis of [Ag(L2)Cl] (7)

The product was prepared as described for 2 employing 6 (177 mg, 0.50 mmol) and Ag₂O (64 mg, 0.28 mmol) in 20 mL of CH₂Cl₂. Yield: 178 mg (80%), colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 8.59 (d, *J* = 4.8 Hz, pyridine, 1H), 7.55–7.52 (m, 1H), 7.69–7.65 (m, 1H), 7.36–7.24 (m, 10H), 5.75 (s, 2H), 5.65 (s, 2H). ¹³C NMR (CDCl₃) δ 155.7, 149.9, 137.8, 136.7, 134.3, 133.7, 129.2, 128.5, 127.7, 124.6, 124.5, 123.7, 122.6, 112.9, 112.8, 53.9, 52.4. Anal. Calc. for C₂₀H₁₇ClN₃Ag: C, 54.26; H, 3.87; N, 9.49. Found: C, 54.35; H, 4.09; N, 9.38%.

2.2.8. Synthesis of {[Ag(L2)](BF₄) · CH₃CN}_n (8)

The compound was prepared as described for 4 by starting from 7 (88 mg, 0.2 mmol) and AgBF₄ (103 mg, 0.52 mmol) in 15 mL of CH₃CN. Yield: 72 mg (82%), a white powder. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.66 (s, pyridine, 1H), 8.09–8.06, 7.99–7.95 (both m, pyridine, each 1H), 7.77–7.75, 7.69–7.67 (both m, benzimidazolylidene, each 1H), 7.55–7.56 (m, 1H), 7.43–7.39 (m, 4H), 7.32–7.26 (m, 3H), 6.03 (s, CH₂, 2H), 5.74 (s, 2H), 2.07 (s, CH₃CN, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 188.7 (Ag-C), 154.7, 151.9, 139.7, 136.5, 134.5, 134.0, 129.1, 128.4, 127.9, 125.4, 124.8, 124.7, 124.6, 118.5 (CH₃CN), 113.0, 112.8, 54.71, 52.29, 1.52 (CH₃CN).

Anal. Calc. for $C_{22}H_{20}N_4BF_4Ag$: C, 49.38; H, 3.77; N, 10.47. Found: C, 49.07; H, 3.92; N, 10.23%.

2.2.9. Synthesis of $[H(L2)](PF_6)$ (**9**)

To the aqueous solution of **6** (1.06 g, 3 mmol) was added an excess of NH_4PF_6 (1.2 g, 7.3 mmol) led to an immediate white precipitate. The white solid was collected and wash with water and Et_2O . Yield: 1.25 g (94%). 1H NMR (400 MHz, $DMSO-d_6$): δ 10.09 (s, NCHN, 1H), 8.49 (d, $J = 4.0$ Hz, pyridine, 1H), 8.00–7.90 (m, 3H), 7.70–7.63 (m, 3H), 7.54–7.52 (m, 2H), 7.47–7.37 (m, 4H), 5.96 (s, CH_2 , 2H), 5.86 (s, CH_2 , 2H). ^{13}C NMR (100 MHz, $DMSO-d_6$): δ 153.3, 150.0, 143.9, 138.0, 134.4, 131.9, 131.2, 129.5, 129.2, 129.1, 128.6, 127.3, 127.2, 124.2, 123.2, 114.3, 51.31, 50.35. Anal. Calc. for $C_{20}H_{18}N_3PF_6$: C, 53.94; H, 4.07; N, 9.44. Found: C, 53.66; H, 4.33; N, 9.17%.

2.2.10. Synthesis of $[Ag(L2)](PF_6)$ (**10**)

The compound was prepared as described for **2** employing **9** (134 mg, 0.3 mmol) and Ag_2O (38 mg, 0.165 mmol) in 10 mL of CH_3CN . Workup gave a white powder. Yield: 120 mg (93%), 1H NMR (400 MHz, $DMSO-d_6$): δ 8.54 (d, $J = 4.0$ Hz, pyridine, 1H), 7.90 (m, 1H), 7.75 (m, 1H), 7.71 (m, 2H), 7.43–7.37 (m, 5H), 7.31–7.26 (m, 3H), 5.96 (s, CH_2 , 2H), 5.77 (s, CH_2 , 2H). ^{13}C NMR (100 MHz, $DMSO-d_6$): δ 155.5, 149.9, 137.7, 136.7, 134.3, 133.7, 129.2, 129.1, 128.4, 127.7, 124.7, 124.6, 123.7, 122.7, 112.8, 53.7, 52.3. Anal. Calc. for $C_{40}H_{34}N_6PF_6Ag$: C, 56.42; H, 4.02; N, 9.87. Found: C, 56.42; H, 4.07; N, 9.69%.

2.2.11. Synthesis of 1,4-di(*N*-benzylbenzimidazoliumyl)but-2-yne hexafluorophosphate $[H_2(L3)](PF_6)_2$ (**11**)

Addition of 1,4-dibromobut-2-yne (2.1 g, 10 mmol) to a solution of *N*-benzylbenzimidazole (5.2 g, 25 mmol) in 20 mL of toluene. The mixture was refluxed overnight. After the solvent was decanted, the resulting precipitate was dissolved into 20 mL of water. To the aqueous solution an excess of NH_4PF_6 (30 mmol) in 10 mL of H_2O was added affording a white precipitate, which was collected by filtration. Yield: 4.9 g, (65%). 1H NMR (400 MHz, $DMSO-d_6$): 9.96 (s, NCHN, 2H), 8.00 (s, benzimidazole, 4H), 7.66 (d, $J = 8.8$ Hz, benzyl, 4H), 7.51 (s, benzimidazole, 4H), 7.41 (s, benzyl, 6H), 5.80 (s, CH_2 , 4H), 5.64 (s, CH_2 , 4H). ^{13}C NMR (100 MHz, $DMSO-d_6$): δ 142.8, 134.1, 131.3, 131.1, 129.4, 129.2, 128.7, 127.5, 127.3, 114.5, 114.3, 79.9, 50.4, 37.4. Anal. Calc. for

$C_{32}H_{28}N_4P_2F_{12}$: C, 50.67; H, 3.72; N, 7.39. Found: C, 50.53; H, 3.88; N, 7.20%.

2.2.12. Synthesis of $[Ag_2(L3)_2](PF_6)_2$ (**12**)

The compound was prepared as described for **2** employing **11** (227 mg, 0.3 mmol) and Ag_2O (76 mg, 0.33 mmol) in 10 mL of CH_3CN . Workup gave compound **12** as a white solid. Yield: 125 mg (58%). 1H NMR (400 MHz, $DMSO-d_6$): δ 7.94 (s, 2H), 7.79 (s, 4H), 7.52–7.43 (m, 14H), 7.27–7.13 (m, 16H), 5.85 (s, CH_2 , 4H), 5.58 (s, CH_2 , 8H), 5.37 (s, CH_2 , 4H). Anal. Calc. for $C_{64}H_{52}N_8P_2F_{12}Ag_2$: C, 53.42; H, 3.64; N, 7.79. Found: C, 53.41; H, 3.73; N, 7.66%.

For all complexes, X-ray quality crystals were obtained by slow diffusion of Et_2O into their CH_3CN solution at room temperature.

2.3. X-ray structural determination

Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with a Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) by using an ω - 2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software [73]. 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 SHELXTL package [74]. Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C–H distances of 0.93–0.97 Å and $U_{iso}(H) = -1.2 - 1.5U_{eq}(C)$. Further details of the structural analyses are summarized in Tables 1 and 2.

3. Results and discussion

3.1. Synthesis and spectral characterization

According to the procedure developed by Lin et al. [35,37–39], the direct reaction of Ag_2O and 1,3-bis(picoly)benzimidazolium chloride afforded $[Ag(L1)Cl]$ (**2**) as a colorless crystalline solid (Scheme 1). The analogous gold compound $[Au(L1)Cl]$ (**3**) could be easily obtained via carbene transfer reaction of **2** with one equivalent of $Au(SEt_2)Cl$. Their 1H and ^{13}C NMR spectra are consistent with the proposed formula. ^{13}C NMR spectra exhibit singlets at 190.9 and 179.2 ppm for **2** and **3**, respectively, characteristic of the carbenic carbon resonances. In the ESI spectrum of **2** in acetonitrile,

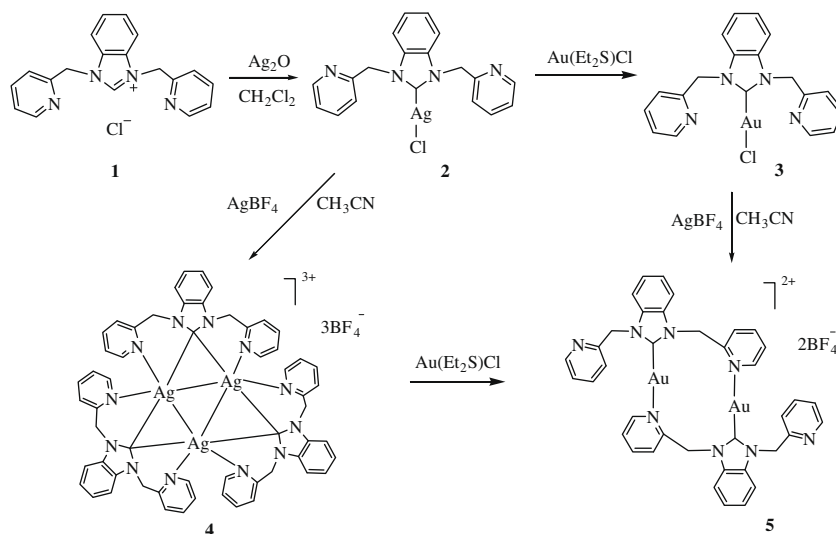
Table 1
Summary of X-ray crystallographic data for complexes **2–5**.

	2	3	4	5
Formula	$C_{19}H_{16}AgClN_4$	$C_{19}H_{16}AuClN_4$	$C_{61}H_{54}Ag_3B_3F_{12}N_{14}$	$C_{38}H_{32}Au_2B_2F_8N_8$
Formula weight	443.68	532.77	1567.22	1168.27
Crystal system	Triclinic	Triclinic	Hexagonal	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P-62c$	$P2_1/n$
<i>a</i> (Å)	8.087(2)	9.6903(14)	13.3009(11)	8.1923(14)
<i>b</i> (Å)	10.965(3)	9.7451(15)	13.3009(11)	21.338(2)
<i>c</i> (Å)	11.025(3)	9.9664(15)	22.4938(19)	23.013(2)
α (°)	67.299(2)	85.913(3)		
β (°)	89.359(3)	84.206(3)		92.014(2)
γ (°)	79.213(3)	76.512(2)		
<i>V</i> (Å ³)	884.0(4)	909.4(2)	3446.3(5)	4020.4(9)
<i>Z</i>	2	2	2	4
<i>D</i> _{calc} (Mg/m ³)	1.667	1.946	1.475	1.930
μ (mm ⁻¹)	1.300	8.244	0.922	7.366
<i>F</i> (000)	444	508	1518	2224
Reflections collected	4433	4782	14 558	15 370
Reflections unique, <i>R</i> _{int}	3048, 0.0110	3152, 0.0279	2088, 0.0848	6751, 0.0942
Goodness-of-fit on <i>F</i> ²	1.005	1.037	1.107	1.100
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0260, 0.0606	0.0280, 0.0639	0.0503, 0.1277	0.1089, 0.2679
<i>R</i> (all data)	0.0334, 0.0647	0.0345, 0.0674	0.0681, 0.1387	0.1719, 0.3049
Largest difference in peak and hole (e Å ⁻³)	0.522, -0.361	0.673, -1.107	0.530, -0.485	1.543, -3.625

Table 2
Summary of X-ray crystallographic data for complexes **8**, **10**, and **12**.

	8	10	12
Formula	C ₂₂ H ₂₀ AgBF ₄ N ₄	C ₄₀ H ₃₄ AgF ₆ N ₆ P	C ₆₄ H ₅₂ Ag ₂ F ₁₂ N ₈ P ₂
Formula weight	535.10	851.57	1438.82
Crystal system	Monoclinic	Triclinic	Tetragonal
Space group	<i>Pn</i>	<i>P</i> $\bar{1}$	<i>P</i> ₄ <i>2</i> / <i>nbc</i>
<i>a</i> (Å)	5.597(9)	8.292(3)	17.549(2)
<i>b</i> (Å)	9.4250(14)	10.812(4)	17.549(2)
<i>c</i> (Å)	20.540(2)	11.763(5)	19.994(3)
α (°)		70.289(5)	
β (°)	97.234(2)	87.961(4)	
γ (°)		69.055(4)	
<i>V</i> (Å ³)	1074.9(17)	922.9(6)	6157.8(14)
<i>Z</i>	2	1	4
<i>D</i> _{calc} (Mg/m ³)	1.653	1.532	1.552
Reflections collected	5037	4764	24846
Reflections unique, <i>R</i> _{int}	3297, 0.0189	3185, 0.0155	2714, 0.0683
Goodness-of-fit on <i>F</i> ²	1.045	1.045	1.302
<i>R</i> [<i>I</i> > 2 σ]	0.0403, 0.0990	0.0326, 0.0741	0.0887, 0.1665
<i>R</i> (all data)	0.0452, 0.1028	0.0424, 0.0825	0.1269, 0.1801
Largest difference in peak and hole (e Å ⁻³)	0.735, -0.421	0.297, -0.238	0.554, -0.583

the most intense peaks were observed at 850.23 and 442.53 amu corresponding to [Ag₂(L1)₂Cl]⁺ (calc. 849.05 amu) and [Ag(L1)Cl]⁺ (calc. 442.01 amu). The ESI spectrum of **3** shows the most intense peaks at 1029.07 amu due to [Au₂(L1)₂Cl]⁺ (calc. 1029.18 amu), whereas the peak at 797.36 amu can be assigned to [Au(L1)₂]⁺ (calc. 797.24 amu). Treatment of **2** with an excess of AgBF₄ gave the trinuclear complex [Ag₃(L1)₃]³⁺ (**4**) after removal of the resulting AgCl precipitate. However, reaction of **4** with 3 equiv. of Au(SEt₂)Cl did not afford the expected [Au₃(L1)₃]³⁺, instead, a digold complex **5** with a formula of [Au₂(L1)₂]²⁺ was obtained. Compound **5** could also be obtained from the reaction of **3** with an excess of AgBF₄. An ESI spectrum of **4** in acetonitrile displays the most intense peaks at 1396.54, 902.71, and 407.29 amu due to [Ag₃(L1)₃(BF₄)₂]⁺ (calc. 1395.16 amu), [Ag₂(L1)₂(BF₄)]⁺ (calc. 901.09 amu), and [Ag(L1)]⁺ (calc. 407.04 amu). The peaks at 1080.65, 797.34, and 497.58 amu are seen for **5**, arising from the fragments [Au₂(L1)₂(BF₄)]⁺ (calc. 1081.21 amu), [Au(L1)₂]⁺ (calc. 797.24 amu), and [Au(L1)]⁺ (calc. 497.10 amu). Compound **4** is not stable in solution and also light sensitive, and thus no satisfactory ¹³C NMR spectrum and elemental analysis were obtained.



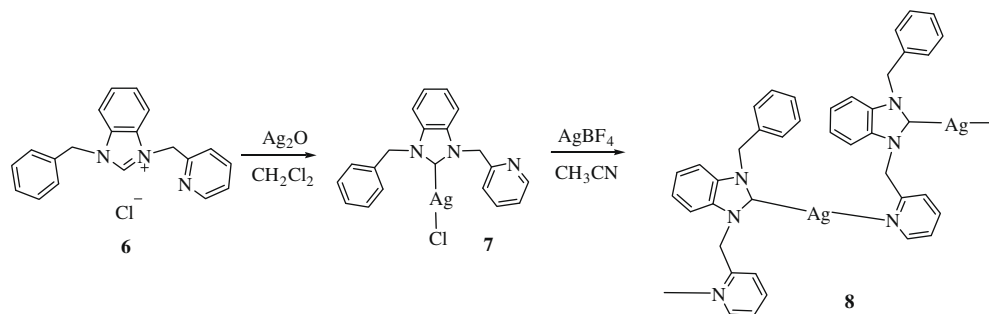
Scheme 1. Synthesis of complexes **2**–**5**.

[Ag(L2)Cl] (**7**), generated from the reaction of 1-benzyl-3-picolylbenzimidazolium chloride and Ag₂O, reacted with AgBF₄ led to isolation of the coordination polymer **8** (Scheme 2). The compound shows a singlet at 188.7 ppm in its ¹³C NMR spectrum assignable to the carbene carbon atom, and the chemical shift is well consistent with those of the known silver–NHC complexes in the range of 213.7–163.2 ppm [59–61]. The ESI spectrum of **8** displays peaks at 852.86, 706.20, and 406.19 amu which can be assigned to [Ag₂(L2)₂CH₃CN]⁺ (calc. 853.12 amu), [Ag(L2)₂]⁺ (calc. 705.19 amu), and [Ag(L2)]⁺ (calc. 406.05 amu). As expected, the deprotonation of 1-benzyl-3-picolylbenzimidazolium hexafluorophosphate with Ag₂O yielded the [Ag(NHC)₂]⁺ compound (**10**), shown in Scheme 3. Compounds **7** and **10** did not show the resonance signals of carbenic carbons in their ¹³C NMR spectra. The reason is not clear, probably because of the dynamic behaviour of the complexes arising from the dissociation and association processes in solution. The ESI spectra of **10** shows peaks at 705.22 and 300.39 amu which can be assigned to [Ag(L2)₂]⁺ (calc. 705.19 amu), and [L2]⁺ (calc. 299.14 amu).

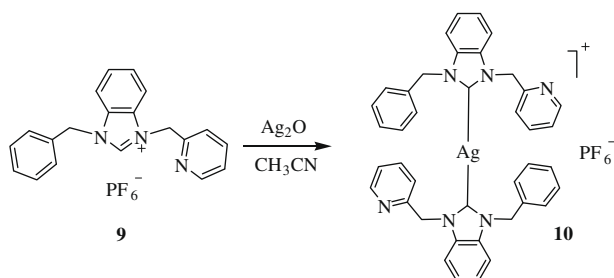
[H₂(L3)](PF₆)₂ (**11**) is a diimidazolium salt with two N-benzylbenzimidazolium bridged by a rigid –CH₂–C≡C–CH₂– linker. As shown in Scheme 4, reaction of **11** with Ag₂O afforded a macrocyclic complex [Ag₂(L3)₂](PF₆)₂ (**12**). The disappearance of downfield carbene proton signal in its precursor **11** clearly demonstrates the formation of Ag–carbene complex. However, the signals in ¹H NMR spectra of **12** are broad and no satisfactory ¹³C NMR spectra could be obtained though the data were repeatedly collected. ESI of complex **12** shows peaks at 1292.53 and 573.16 amu corresponding to [Ag₂(L3)₂(PF₆)₂]⁺ (calc. 1291.20 amu), and [Ag(L3)]⁺ (calc. 573.12 amu).

3.2. X-ray structural description

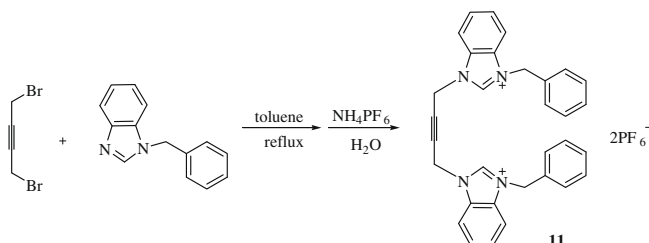
The structures of **2** and **3** are shown in Figs. 1 and 2, respectively. The two compounds are isostructural and crystallize in the same space group. Both metal atoms are bicoordinated by chloride and 1,3-bis(picolyl)benzimidazolylidene ligands. The pyridine groups do not interact with the central metal atoms. The silver atom is bicoordinated with a carbene carbon atom and a chloride ion, with the Ag–C and Ag–Cl bond distances of 2.088(3) and 2.353(1) Å. These bond distances are consistent with those of the known silver–NHC complexes having C–Ag–Cl motif [75,76]. Interestingly, the X-ray diffraction analysis showed that complex



Scheme 2. Synthesis of complexes 7 and 8.

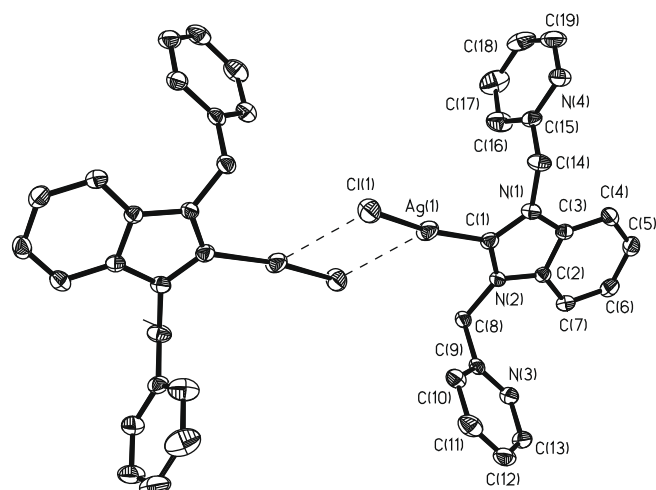
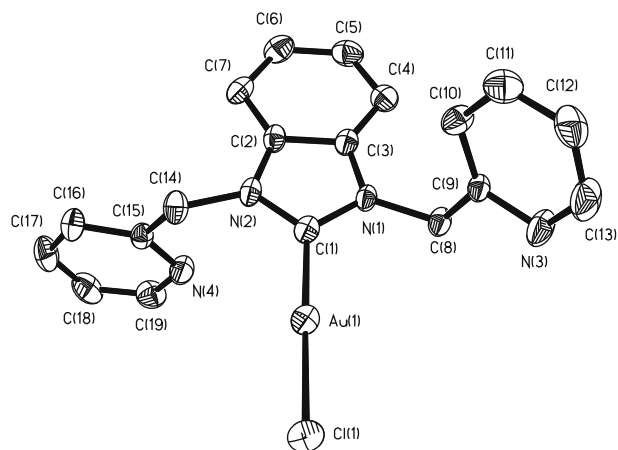


Scheme 3. Synthesis of complex 10.



Scheme 4. Synthesis of complex 12.

2 associates via weak Ag \cdots Cl interaction to give a dimeric structure. The intermolecular Ag–Cl distance is 3.071 Å, whereas the intermolecular Ag \cdots Ag contact is 3.993 Å, illustrating that there is no Ag–Ag interaction. The C–Ag–Cl is more bent than those of other Ag(NHC)Cl complexes that is obviously resulted from the dimerization. Unlike **2**, the gold complex **3** does not associate, which is evidenced by the quite long intermolecular Au \cdots Cl distances of 4.766 Å. It should be noted that both Au–Cl and Au–C bond distances of **3** are shorter than those of its silver analogous. Another feature of the gold complex is that the Cl–Au–C axis (177.89(14)°) is much more linear than C–Ag–Cl (164.93(8)°). The two pyridine rings are located below and up the coordination plane defined by benzimidazolylene ring and MCl, and the dihedral angles are 87.04 and 82.57° for **2** and **3**, respectively. Mononu-

Fig. 1. Molecular structure of **2**. Selected bond distances (Å) and angles (°): Ag(1)–Cl(1) 2.088(3), Ag(1)–Cl(1) 2.353(1), C(1)–Ag(1)–Cl(1) 164.93(8).Fig. 2. Molecular structure of **3**. Selected bond distances (Å) and angles (°): Au(1)–Cl(1) 1.982(5), Au(1)–Cl(1) 2.278(2), C(1)–Au(1)–Cl(1) 177.89(14).

clear gold–NHC complexes often show intermolecular gold–gold interactions [77]. The closest intermolecular Au \cdots Au distance is 3.593 Å for **3** showing very weak auriphilic interaction.

Complex [Ag(L2)₂](PF₆) (**10**) is also mononuclear crystallizing in a space group *P*1̄. The silver atom is coordinated by two 1-benzyl-3-picolylimidazolylene ligands in perfectly linear C–Ag–C coordination geometry. The Ag–C bond distances are the same as that of **2**. As shown in Fig. 3, the phenyl and pyridyl rings of the same 1-benzyl-3-picolylbenzimidazolylene are directed towards the

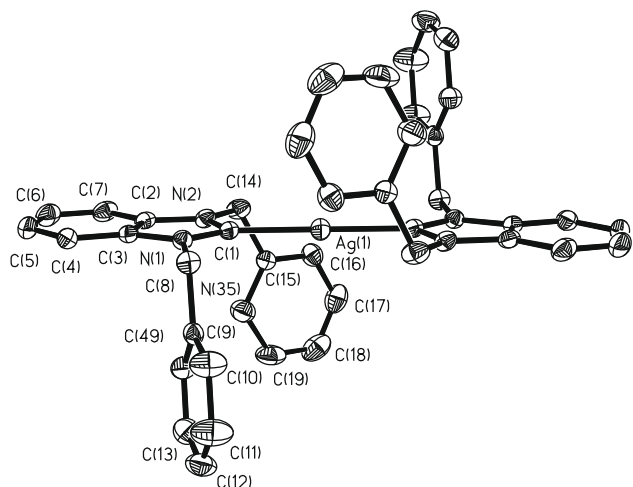


Fig. 3. Molecular structure of the cation of **10**. Selected bond distances (Å) and angles (°): Ag(1)–C(1) 2.086(3), C(1)#1–Ag(1)–C(1) 180.0. Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+2, -z+1$.

same side of the silver coordination plane. The two benzimidazolylidene rings are coplanar, quite different from most of the $[\text{Ag}(\text{NHC})_2]^+$ complexes in which the two NHC rings are normally bisected [78–80].

Reaction of **2** with Ag^+ in acetonitrile yielded **4** as a trinuclear silver complex which contains a triangular Ag_3 ring. The asymmetric unit consists of one third of the molecule with a threefold axis passing through the center of the Ag_3 ring. As shown in Fig. 4, the silver atom is coordinated by two pyridine and two benzimidazolylidene ligands in severely distorted tetrahedron geometry. Each side of the Ag_3 ring is capped by a benzimidazolylidene acting as a bridging ligand. This unusual coordination mode of imidazolylidene was only observed in a few silver(I) [81–83] and copper(I) [84] complexes. This bonding situation of Ag_2C ring can be best viewed as $3c2e$ bonding. As a result of this bridging fashion, the Ag–C (av. 2.26 Å) distances become exceptionally long, remarkably longer than those found for **2** and **10**. The Ag–N (2.40 Å) distances of **4**

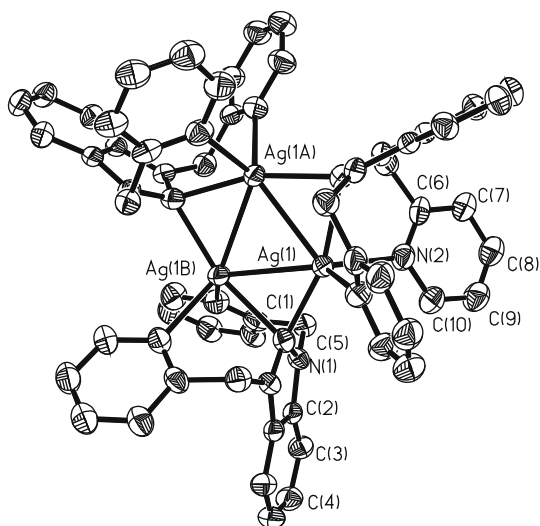


Fig. 4. Molecular structure of the cation of **4**. Selected bond distances (Å) and angles (°): Ag(1)–Ag(1)#1 2.777(1), Ag(1)–C(1) 2.230(11), Ag(1)–C(1)#1 2.301(10), Ag(1)–N(2)#2 2.399(7), Ag(1)–N(2) 2.399(7), C(1)–Ag(1)–C(1)#1 164.4(3), C(1)#1–Ag(1)–N(2) 85.1(2), N(2)#2–Ag(1)–N(2) 102.7(3), Ag(1)#1–Ag(1)–Ag(1)#3 60.0. Symmetry transformations used to generate equivalent atoms: #1 $-y+1, x-y, z$; #2 $x, y, -z+3/2$; #3 $-x+y+1, -x+1, z$.

are also quit long. The three benzimidazolylidene rings are perfectly perpendicular to the Ag_3 plane as evidenced by the dihedral angles of 90° .

Another structural feature of **4** is the very short Ag–Ag distances (2.777(1) Å), remarkably shorter than those found in our previously reported linear chain Ag_4 , square-planar Ag_4 clusters [63,64]. Although a large number of silver–NHC complexes have been reported, silver clusters with short Ag–Ag contacts supported by NHC ligands are still rare [31–37]. The Ag–Ag contacts are similar to the trimetallic Ag(I) complex stabilized by bridging NHC ligands [82].

The molecular structure of **5** established by an X-ray diffraction study is depicted in Fig. 5. The digold complex crystallizes in monoclinic space group $P2_1/n$. Its asymmetric unit consists of two independent gold atoms which are bonded together by two 1,3-bis(picoyl)benzimidazolylidene ligands. Each benzimidazolylidene links two gold atoms in a bidentate mode, and only one pyridine is coordinated. The two gold atoms are both bicoordinated by a pyridine and an benzimidazolylidene ligands in nearly linear geometry with C–Au–N angles of 175.2° . The Au–C and Au–N bond distances are normal and consistent with those of the known Au–NHC complexes. The Au–Au distance is 3.206(2) Å showing weak gold–gold interaction. No intermolecular Au–Au interaction is observed due to steric hindrance of the ligand.

Gold–NHC complexes have proven their potential applications in pharmaceuticals, chemical vapour depositions, liquid crystals, and optical devices. The Au(I)–NHC chemistry has been reviewed by Lin et al. in 2005 [34]. The reported gold–NHC complexes are normally have linear $[\text{Au}(\text{NHC})_2]^+$ or $\text{Au}(\text{NHC})\text{X}$ (X = halogen ions) structural motifs, few $\text{Au}(\text{NHC})\text{X}$ (X = N, O ligands) have been prepared and structurally characterized. Complex **5** represents one of the rare examples having $\text{Au}(\text{NHC})\text{X}$.

The complex **8** is a one-dimensional chain polymer (Fig. 6). The X-ray structural analysis revealed that the asymmetric unit contains one silver atom and one 1-benzyl-3-picoylbenzimidazolylidene. Each silver atom is bonded to an benzimidazolylidene and a pyridine group forming 1D chain structure. The Ag–C (2.104(7) Å) distance is slightly longer than those found in **2** and **10**. The Ag–N (2.182(6) Å) distance is much shorter than those of the trinuclear complex **4** presented above. These Ag–C and Ag–N bond distances

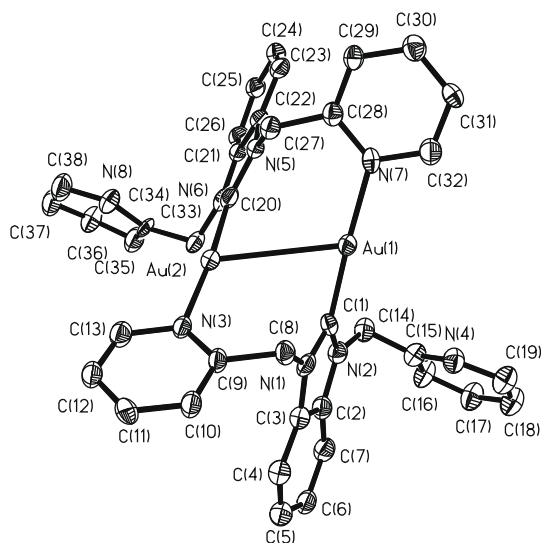


Fig. 5. Molecular structure of the cation of **5**. Selected bond distances (Å) and angles (°): Au(1)–C(1) 1.93(3), Au(1)–N(7) 2.06(2), Au(2)–C(20) 2.00(3), Au(2)–N(3) 2.057(19), Au(1)–Au(2) 3.206(2), C(1)–Au(1)–N(7) $175.2(10)$, C(20)–Au(2)–N(3) $175.2(9)$.

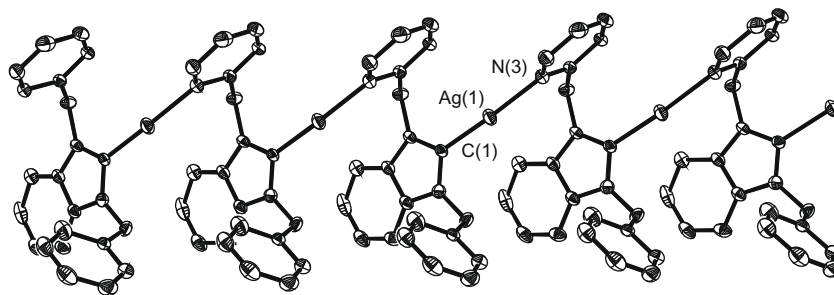


Fig. 6. Molecular structure of the cation of **8**. Selected bond distances (Å) and angles (°): Ag(1)–C(1) 2.104(7), Ag(1)–N(3) 2.182(6), C(1)–Ag(1)–N(3) 168.7(2).

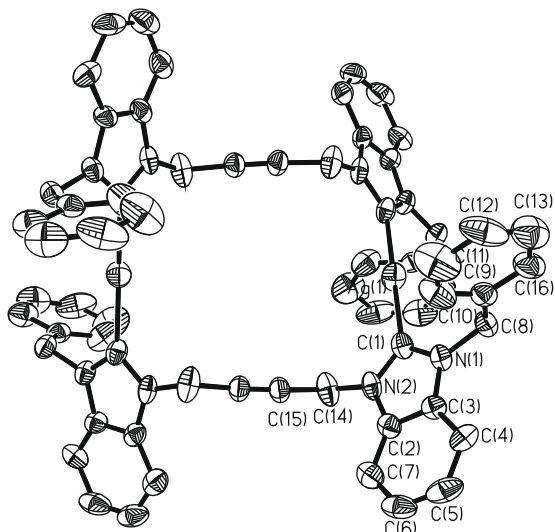


Fig. 7. Molecular structure of the cation of **12**. Selected bond distances (Å) and angles (°): Ag(1)–C(1) 2.111(11), C(1)#1–Ag(1)–C(1) 179.8(5). Symmetry code: #1 $-y + 1, x - y, z$.

are approximately consistent with those of our previously reported multinuclear silver complexes containing NHC ligands. The dihedral angles between the benzimidazolylene ring, phenyl and pyridyl rings are 89.50 and 86.28°, respectively, and the two six-membered rings are located at the same side of the coordination plane of silver. This arrangement prohibits any possible silver–silver interaction along the chain. Furthermore, the silver atoms are perfectly arranged into a linear chain along the crystallographic *a* axis with Ag...Ag...Ag angles being 180°. The 1D chain structure supported by NHC ligands is rare. The successful isolation and characterization of **8** illustrates that it is possible to construct coordination polymers using bifunctional NHC ligands as building blocks [85].

X-ray diffraction analysis revealed that complex **12** is a disilver complex displaying twisted square conformation. The molecular structure of **12** is shown in Fig. 7. The asymmetric unit of **12** contains one fourth of the molecule and there is a fourfold axis passing through the center of the molecule. Two silver ions are linked by two 1,4-di(*N*-benzylbenzimidazolylidene)but-2-yne ligands forming a molecular square. Both silver ions show linear C–Ag–C geometry with C–Ag–C angles of 179.8(5)°. The Ag–C bond distance of **12** is longer than that of **10** having the same coordination environ-

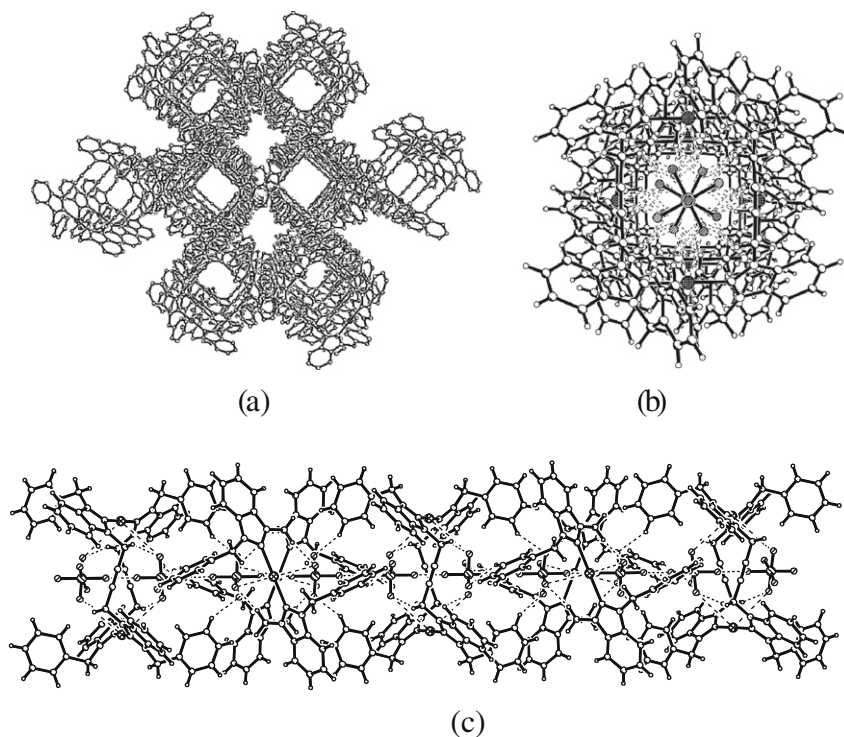


Fig. 8. (a) Stack diagram of **12** showing one-dimensional channel in its solid state. (b) and (c) Channels filled with hexafluorophosphate anions showing weak interactions of cations and anions.

ment. The two benzimidazolylidene rings coordinated to the same silver ions are nearly perpendicular with a dihedral angle of 87.01° .

The macrocyclic cations are aligned one above another to form one-dimensional channels filled with hexafluorophosphate anions (Fig. 8). Weak Ag...F and H...F interactions can be observed. Every four channels assemble together through π - π interactions between the adjacent benzimidazolylidene rings to form another channel which is also filled with hexafluorophosphate anions. Cationic channels formed in crystals of metal complexes of crown ethers are known [86,87], however, to the best of our knowledge, this is the first example of receptor and guest channel complex supported by NHC ligands.

3.3. Luminescence properties

The photoluminescent properties of complexes **2–5**, **8**, and **12** in acetonitrile at room temperature have been studied. The emission spectra are given in Figs. 9 and 10. Complex **2** displays strong

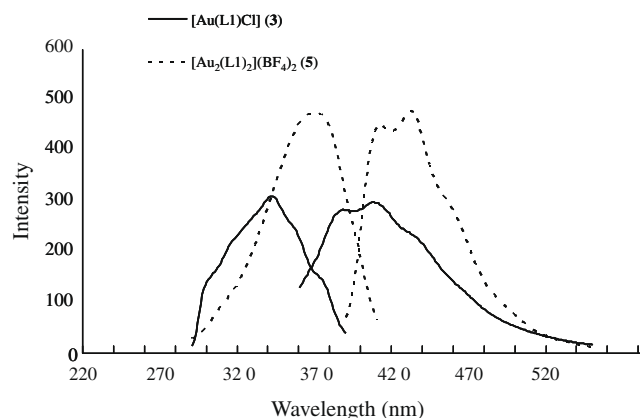


Fig. 9. Emission (right) and excitation (left) spectra of $[\text{Au}(\text{L}1)\text{Cl}]$ (**3**) (solid line, $c = 9.30 \times 10^{-5} \text{ M}$) and $[\text{Au}_2(\text{L}1)_2](\text{BF}_4)_2$ (**5**) (dashed line, $c = 9.67 \times 10^{-5} \text{ M}$) in acetonitrile.

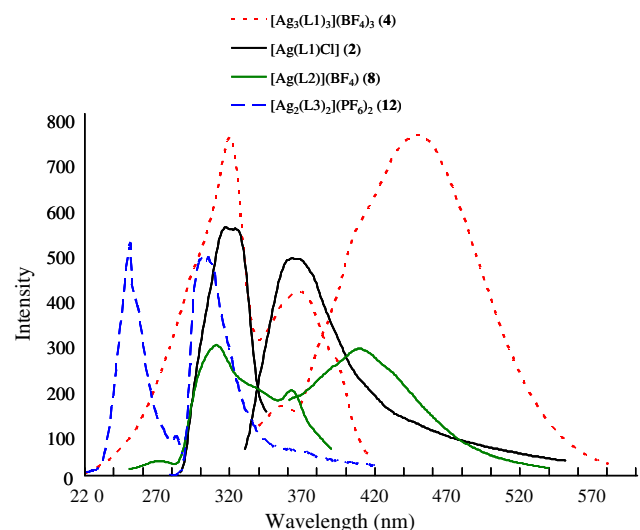


Fig. 10. Emission (right) and excitation (left) spectra of $[\text{Ag}(\text{L}1)\text{Cl}]$ (**2**) (black, $c = 1.02 \times 10^{-4} \text{ M}$), $[\text{Ag}_3(\text{L}1)_3](\text{BF}_4)_3$ (**4**) (red, $c = 9.47 \times 10^{-5} \text{ M}$), $[\text{Ag}(\text{L}2)](\text{BF}_4)$ (**8**) (green, $c = 9.55 \times 10^{-5} \text{ M}$), and $[\text{Ag}_2(\text{L}3)_2](\text{PF}_6)_2$ (**12**) (blue, $c = 9.69 \times 10^{-5} \text{ M}$) in acetonitrile. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

broad emission band at 362 nm upon excitation at 323 nm. Although complex **3** has the same structure as **2**, complex **3** shows a high-energy emission band at 388 nm and a low-energy band at 407 nm when irradiated at 342 nm. For comparison, $[\text{Au}(\text{Me}_2\text{bimy})\text{Cl}]$ ($\text{Me}_2\text{bimy} = N,N$ -dimethylbenzimidazolylidene) displays two emission bands at 420 nm and 620 nm, and the large red shifts could be ascribed to the existence of intermolecular $\text{Au}^{\text{I}}-\text{Au}^{\text{I}}$ and ring π - π interactions.

The digold complex has a C–Au–N structural motif showing quite different emission properties from the mononuclear complex **3**. At room temperature, the emission spectrum of **5** in acetonitrile shows two emission bands at 412, 431 nm with nearly the same intensities, and a less intensive shoulder peak at 465 nm upon excitation at 371 nm. The emission spectrum of the Ag_3 complex only shows one broad band at 450 nm in acetonitrile, very similar to that of the previously reported Ag_3 cluster also supported by NHC ligand. For the polymeric complex **8**, only a very broad band at 410 nm was observed upon excitation at 310 nm. Complex **12** in acetonitrile exhibits its emission band at 305 nm. The luminescence of these complexes may be originated from the mixed excitation states. Either intraligand or metal-centered electronic transfer processes can be possible. Further work is required to clarify the nature of the emission properties.

4. Conclusions

In summary, we have successfully prepared and structurally characterized a few mono-, di-, trinuclear, and polymeric silver and gold complexes containing pyridine-functionalized imidazolylidene. These ligands show diverse coordination abilities and coordination modes leading to unexpected structural motifs of silver–NHC complexes. The complexes **2–5**, **8**, and **12** are intensely luminescent in their acetonitrile solution at room temperature. It implies that coinage complexes with novel structures and unique optical properties may be obtained by using rationally designed N,C-mixed NHC ligands.

Acknowledgements

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Appendix A. Supplementary material

CCDC 663000, 663001–663005 and 726622 contain the supplementary crystallographic data for **2–5**, **8**, **10**, and **12**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.031.

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