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FULL PAPER

Structural diversity of N-heterocyclic carbene complexes of silver(I)

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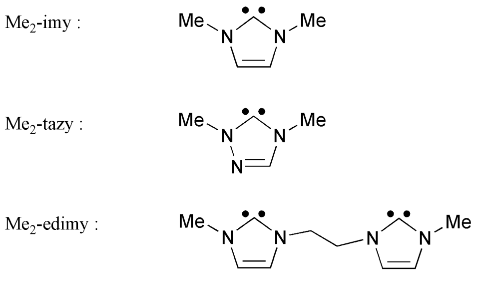
Seven N-heterocyclic carbene complexes of silver(I) have been synthesized, five of which were structurally characterized. Polymeric Ag^I-carbene complexes with a diverse range of structures are formed through extended Ag^I–Ag^I interactions, Ag^I-bridging halides, Ag^I-bridging dicarbenes, and ring π–π interactions. Compounds having extended Ag^I–Ag^I-centered interactions exhibit low energy emission bands at $\lambda_{max} \approx$ 540 nm. These bands are assigned to metal-centered transitions involving extended Ag^I–Ag^I interactions.

Recently, N-heterocyclic carbenes have become a very important class of ligands in the chemistry of transition metal complexes.[1] One reason for this is that these imidazol-2-ylidene (imy) carbenes are readily accessible through deprotonation of N,N′-disubstituted imidazolium salts, which can be easily derivatized. Furthermore, the strong σ-donor ability of these N-heterocyclic carbenes leads to the formation of many stable metal-carbene complexes, which are good catalysts in numerous chemical transformations[2] and are promising candidates for metal-organic materials.[3] Since the first isolation of a homoleptic Ag^I-carbene complex,[4] only a few reports on the imidazol-2-ylidene complexes of Ag^I have appeared.[5,6] We have also described a simple method for the synthesis of Ag^I-carbene complexes and their uses as carbene transfer agents.[6] Recently, in an attempt to synthesize liquid crystalline Ag^I and Au^I-carbene complexes, unexpected tetranuclear Ag_4 and Au_2Ag_2 complexes of imidazol-2-ylidenes were isolated.[7] Our continuing study shows that the diversity of the crystal structures may lead to interesting properties, such as luminescence, and thus may be used in the design of supramolecular architectures and materials with special properties. In this work, we report the isolation and characterization of some simple N-substituted Ag^I-carbene complexes. Despite the simplicity of their formulae, polymeric structures constructed through extended metal–metal interactions, metal-bridging halides and carbenes, and π–π interactions are observed.

Results and discussion

Synthesis

Abbreviations for the carbenes with representative drawings and the numbering of the compounds are shown in Scheme 1. The Ag^I-imy carbene complex **2** was prepared using the method developed by us,[6] in which the imidazolium bromide is treated with Ag_2O. Because the chloride salts, $[Me_2\text{-imyH}]Cl$, $[Me_2\text{-tazyH}]Cl$, and $[Me_2\text{-edimyH}_2]Cl_2$ are difficult to synthesize, the complexes **1**, **4** and **7** were prepared indirectly from the imidazolium and triazolium BPh_4 or PF_6 salts in the presence of $[Me_4N]Cl$. Since $[Me_2\text{-tazyH}]Br$ is very hydroscopic, compound **5** was obtained by following the same preparative method as for **4**, but using $[NMe_4]Br$ instead of $[NMe_4]Cl$. Attempts to prepare analogous iodo compounds in CH_2Cl_2, lead to the isolation of chloro compounds. The source of chloride in this preparation method is likely the CH_2Cl_2 solvent. Exchange of bromide for chloride was reported[5] when the reaction of N-functionalized imidazolium bromide and Ag_2O was carried out in chlorinated solvents under reflux. In our preparative method, reactions were carried out at room temperature. During the reactions, the exchange of iodide for chloride was observed, but not bromide for chloride. This result indicates a lower activation energy of exchange of iodide for chloride than that of bromide for chloride. The nitrate salts, **3** and **6**, were prepared by the addition of equimolar amounts of aqueous $AgNO_3$ to acetonitrile solutions of **1** and **4**, respectively. The solid samples of these silver carbene complexes are stable toward light and air at room temperature.



$[Ag(Me_2\text{-imy})_2][AgCl_2]$, **1**
$[Ag(Me_2\text{-tazy})Cl]_2$, **4**
$[Ag(Me_2\text{-imy})_2][AgBr_2]$, **2**
$[Ag(Me_2\text{-tazy})Br]_2$, **5**
$[Ag(Me_2\text{-imy})_2][NO_3]$, **3**
$[Ag(Me_2\text{-tazy})_2][NO_3]$, **6**
$[Ag_2(Me_2\text{-edimy})Cl_2]$, **7**

Scheme 1 Representative drawings of the various carbenes, abbreviations for the compounds and their numbering.

Molecular structures

Crystal data and experimental details for **1**, **2** and **5**–**7** are given in Table 2. An ORTEP drawing of **1**, is shown in Fig. 1(a). Selected bond distances and angles are given in the figure caption. This compound exhibits a one-dimensional polymeric structure [Fig. 1(b)]. Each polymer chain is composed of alternating cations and anions associated through Ag^I–Ag^I interactions at a distance of 3.189 Å. This distance is less than the sum of the van der Waals radii of 3.44 Å for silver, but is at the lower end of the range observed for ligand-unsupported Ag^I–

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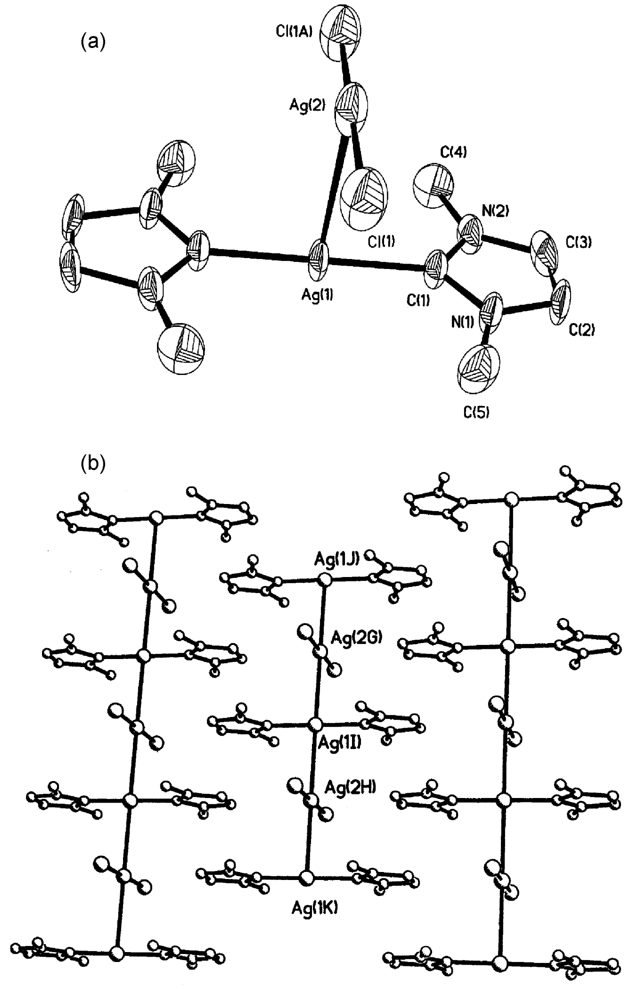

Fig. 1 (a) ORTEP diagram of **1** in the crystalline state with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ag(1)–Ag(2) = 3.189(4), Ag(1)–C(1) = 2.096(6), Ag(2)–Cl(1) = 2.335(2); C(1)–Ag(1)–C(1′) = 180(4), Cl(1)–Ag(2)–Cl(1′) = 180.00(12), C(1)–Ag(1)–Ag(2) = 90.0, Cl(1)–Ag(2)–Ag(1) = 90.0. (b) Packing diagram of **1** showing the infinite 1-D linear motif.

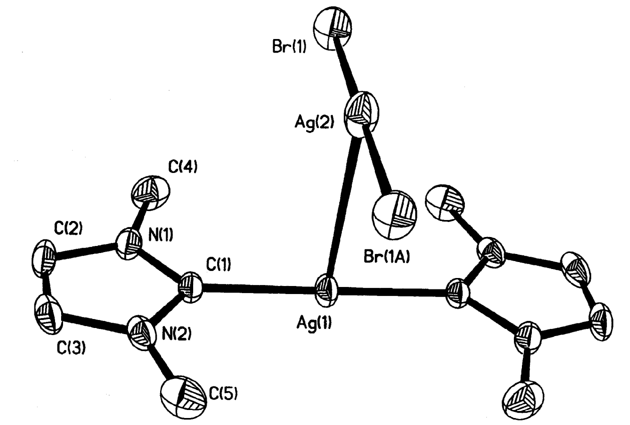

Fig. 2 ORTEP diagram of **2** in the crystalline state with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ag(1)–Ag(2) = 3.2082(4), Ag(1)–C(1) = 2.084(5), Ag(2)–Br(1) = 2.4390(7), C(1)–Ag(1)–C(1′) = 180, Br(1)–Ag(2)–Br(1′) = 180, C(1)–Ag(1)–Ag(2) = 90.0, Br(1)–Ag(2)–Ag(1) = 90.0.

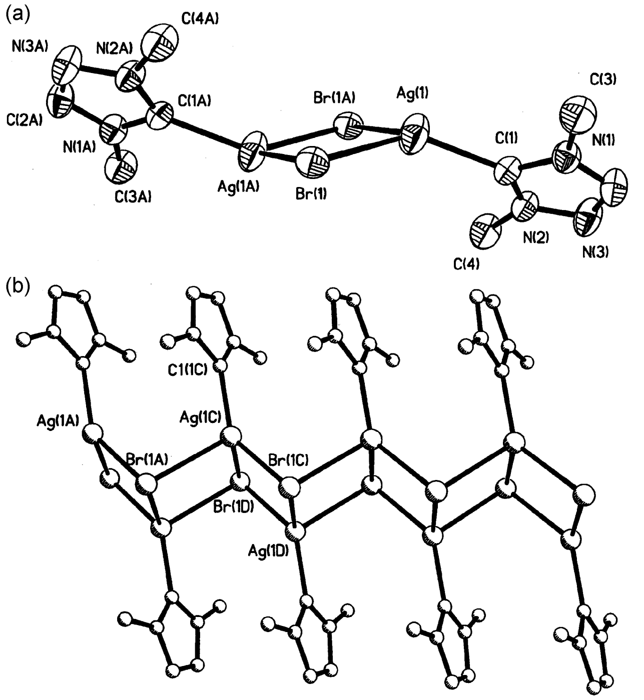

Fig. 3 (a) ORTEP diagram of **5** in the crystalline state with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ag(1C)–C1(1C) = 2.131(5), Ag(1C)–Br(1C) = 2.6581(8), Ag(1C)–Br(1D) = 2.8658(8), Ag(1C)–Br(1A) = 2.8467(8); C1(1C)–Ag(1C)–Br(1C) = 134.99(14), C1(1C)–Ag(1C)–Br(1D) = 112.9(4), C1(1C)–Ag(1C)–Br(1A) = 111.48(14), Br(1C)–Ag(1C)–Br(1D) = 95.20(2), Br(1C)–Ag(1C)–Br(1A) = 99.32(2), Br(1D)–Ag(1C)–Br(1D) = 95.42(2), Ag(1C)–Br(1C)–Ag(1D) = 80.68(2). (b) Packing diagram of **5** showing the staircase motif.

Ag^I distances (2.80 to 3.30 Å).[8] The $[Ag(Me_2\text{-imy})_2]^+$ cation has two imy carbenes linearly coordinated to Ag^I, such that the C(1)–Ag(1)–C(1B) angle is 180°. The two imy ring planes are essentially coplanar. The Ag–C bond distances [2.09(6) Å] are comparable to those found in other silver(I) carbene complexes.[4,5] The linear $[AgCl_2]^-$ anion has a Cl(1)–Ag(2)–Cl(2) angle of 180°. The average Ag–Cl bond distance of 2.33(5) Å in **1** is comparable to that in $[AgCl_2]^-$.[9] To avoid steric congestion, the linear cations and anions are stacked in a staggered fashion. Interactions between neighboring polymeric chains through head-to-tail stacking (3.1879 Å) of the imy rings are observed. Among the majority of halogenoargentates, only a few examples of discrete $[Ag(halide)_2]^-$ ions have been structurally characterized.[9] To the best of our knowledge, this is the first example of an Ag^I–Ag^I-bonded polymeric structure consisting of discrete $Ag(ligand)_2$ cations and $Ag(halide)_2$ anions. Interestingly, a seemingly analogous complex, $[Ag(Et_2\text{-bimy})_2][AgBr_2]$ (bimy = 1,3-diethylbenzimidazol-2-ylidene), only forms a Ag^I–Ag^I bonded ion pair.[6] Examples of polymeric Ag^I complexes having alternating cations and anions forming zigzag Ag^I chains, such as $[Ag(PMe_3)_2][Ag(CCPh)_2]$[10] and $[Ag(PMe_3)_2]$-$[Ag(CCSiMe_3)]$, are known.[11]

The crystal structure of **2** is very similar to that of complex **1**. An ORTEP drawing of **2** is presented in Fig. 2. Selected bond distances and angles are given in the caption.

The crystal structure of **5** reveals a polymeric 'staircase' of 'AgBr' (Fig. 3). Each tetrahedrally coordinated Ag^I atom is bridged by three μ_3-Br ligands and is coordinated by a tazy carbene to generate an infinite 1-D motif. The three Ag–Br distances of 2.6581(8), 2.8658(8) and 2.8467(8) Å are comparable to other tetrahedrally bonded Ag–Br bonds.[12] The Ag–C bond of 2.13(1) Å is slightly longer than those in complexes **1** and **2**. The tazy rings, which protrude outward along the polymeric AgBr chain, are stacked with a relatively long ring–ring distance (3.62 Å). Similar staircase structures have been found in other pyridyl or phosphinyl Ag halide architectures.[12]

Compound **6**, consists of a dicarbene $[Ag(Me_2\text{-tazy})_2]^+$ cation and an NO_3^- anion (Fig. 4). In the cation, the Ag^I has two linearly bonded tazy carbenes, and the two ring planes are twisted at an angle of 11.4° relative to each other. The two Ag–C bonds of 2.089(3) and 2.092(3) Å are comparable to those in the the known Ag^I-imy complexes. The nitrate anion does not

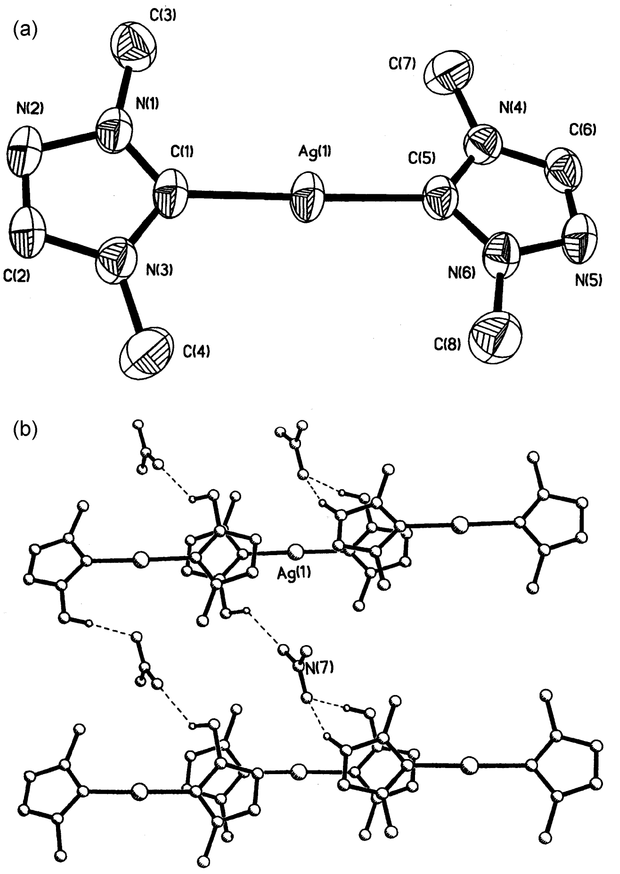

Fig. 4 (a) ORTEP diagram of **6** in the crystalline state with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ag(1)–C(1) = 2.089(3), Ag(1)–C(5) = 2.092(3); C(1)–Ag(1)–C(5) = 176.54(10). (b) Packing diagram of **6** showing the π–π interactions and C–H ··· O hydrogen bonds between NO_3^- and the cations.

bond to the silver atom, but rather, forms four C–H ··· O hydrogen bonds (2.359–2.496 Å). Of the four C–H proton donors, one is from a tazy ring and three are from different methyl groups. It appears that in this C–H hydrogen bonding donor rich environment, the nitrate anion energitically prefers to form four C–H ··· O hydrogen bonds rather than to coordinate to the silver(I). The packing diagrams of this compound show that the two tazy rings interact with neighboring cations through π–π interactions (ring–ring distance 3.42 Å) to form a 1-D polymer. Each polymer chain is further linked together through bridging nitrates.

An ORTEP drawing of compound **7** together with selected bond distances and bond angles is shown in Fig. 5. In compound **7**, the dicarbene ligand arranges in an antiparallel fashion and coordinates to two different Ag^I ions. Each Ag^I center is coordinated to a carbene and two bridging chloride ligands to adopt a distorted trigonal planar geometry. The Ag^I ions are thus connected through a bridging dicarbene and two bridging chlorides to form an extended 1-D ladder polymer. The silver–carbene carbon bond distance of 2.113(1) Å is slightly longer than those in other Ag^I-imy compounds,[5,6] but shorter than that of compound **6**.

The metal-containing network of complexes **1**, **2** and **5**–**7** are formed from different discrete building blocks. The 1-D linear structures of complexes **1** and **2** are composed of alternating $[Ag(carbene)_2]^+$ cations and $[Ag(halide)_2]^-$ anions to form an infinite linear chain of Ag–Ag metal bonds. While the 1-D structure of complex **5** is a polymeric staircase with Ag–Br bonds, the 2-D layer structure of complex **6** is formed by non-covalent bonds, including tazy ring–ring interactions and C–H ··· O hydrogen bonds. In compound **7**, each Ag^I ion is bridged by a dicarbene and two chloride ligands to form a 1-D polymer. The ease with which the carbene is derivatized and the structural diversity of these silver carbene complexes suggest they may have potential applications in the crystal engineering of inorganic–organic hybrid materials.

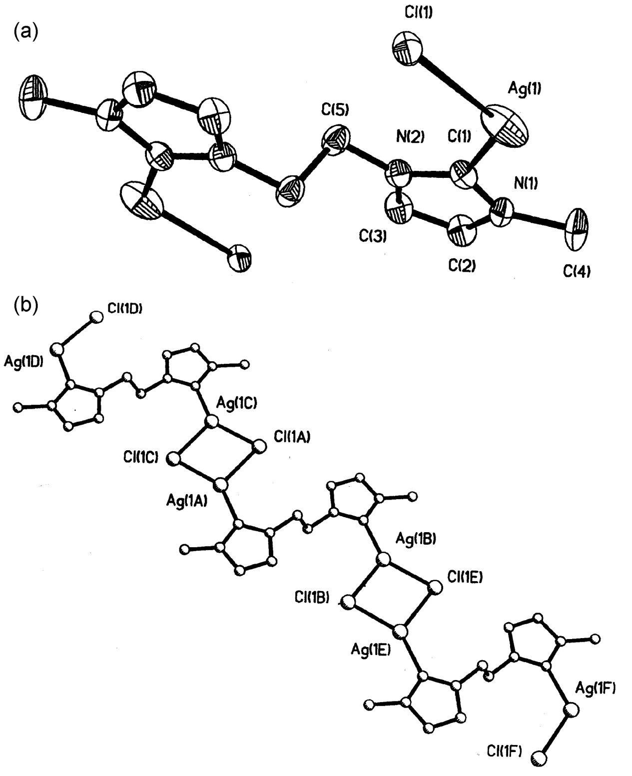

Fig. 5 (a) ORTEP diagram of **7** in the crystalline state with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ag(1)–C(1) = 2.113(1), Ag(1)–Cl(1) = 2.481(3); C(1)–Ag(1)–Cl(1) = 122.8 (3). (b) Packing diagram of **7** showing the polymeric structure.

^{13}C NMR, electronic absorption and emission spectroscopies

The lability of Ag–carbene bonds in solution is demonstrated by the ^{13}C NMR spectroscopic studies. The ^{13}C NMR spectra of **1**–**6** in DMSO-d_6 show that the carbene carbons give only sharp signals at 179.4, 181.6 and 180.7, 182.6, 182.6, and 182.2 ppm, respectively. No $^{107,109}Ag$–^{13}C couplings were observed. These results can be interpreted in terms of fluxional behavior and have been observed in other Ag^I-carbene complexes.[5]

The electronic absorption spectra of these Ag^I-carbene complexes in acetonitrile display intense absorption bands at $\lambda_{max} \approx$ 220 nm with absorption coefficients of the order of 10^4 dm^3 mol^{-1} cm^{-1} (Table 1). These bands are very similar to those found for the carbene precursors in terms of position and band shape. Therefore, these bands are assigned to an intraligand (IL) transition of the carbene ligands. Although these Ag^I-carbene compounds aggregate in the solid state, we have been unable to observe the aggregation in solution; the ε values of the bands are concentration independent in the range 4×10^{-3}–10^{-4} M.

All these Ag^I-carbene compounds are luminous in the solid state, and the photophysical data are given in Table 1. Crystalline compounds of **1** and **2** each display two emission maxima. For the two compounds, the high energy emission maxima occur at λ_{max} = 392 and 390 nm, corresponding to excitations at λ_{max} = 330 and 340 nm, respectively. The low energy emission bands occur at λ_{max} = 544 and 538 nm, with excitations at λ_{max} = 316 and 324 nm, respectively. For crystalline compounds **3** and **7**, only high energy emission bands appear, λ_{max} = 395 and 413 nm, respectively. All the Ag^I-tazy complexes (**4**–**6**) also exhibit high energy emission bands (λ_{max} in the range 400 to 420 nm). All these compounds (**1**–**7**) thus possess high energy emissions at ~400 nm, which have also been observed for the carbene precursors. We therefore assign the high energy

Table 1 Photophysical data for compounds **1**–**7**

Compound	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1}) in CH_3CN	λ_{em}/nm (lifetime/μs)	λ_{ex}/nm
1	217 (22 900)	392 (23)	330
		544 (24)	316
2	220 (27 100)	390 (25)	340
		538 (23)	324
3	222 (15 700)	395 (31)	340
4	220 (9300)	420 (30)	300
5	220 (13 000)	420 (29)	300
6	224 (12 700)	402 (25)	302
7		413 (49)	295

emissions to silver(I)-perturbed intraligand transitions. When solid samples of **1** and **2** were obtained by dissolving the crystalline samples in CH_2Cl_2, followed by rapid precipitation through the addition of hexane, the low energy bands decreased in intensity (Fig. 6). Because, among the compounds studied, only crystalline compounds **1** and **2** possess extended Ag–Ag interactions, the additional low energy bands must arise from metal-centered electronic transitions involving polymeric Ag^I chains. The large Stokes' shifts and the long emission lifetimes suggest that the low energy emissions are phosphorescent in nature.

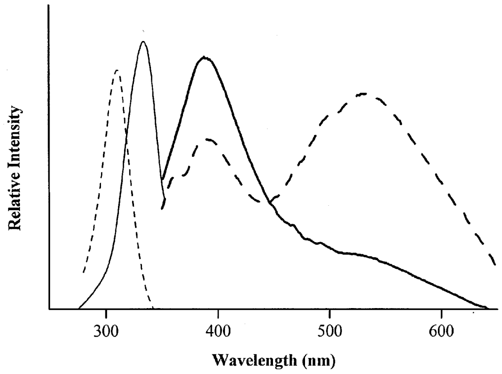

Fig. 6 Excitation and emission spectra of [Ag(Me$_2$-im)$_2$][AgCl$_2$] (**2**) in the solid state; (a) crystalline sample (dashed line), (b) powder sample obtained by rapid precipitation from solution (solid line).

Experimental

Imidazolium and triazolium halides were prepared using literature methods.[13] The BPh_4^- and PF_6^- salts were obtained by simple displacement reactions from the halide salts in H_2O. The ^1H NMR spectra were recorded on a Bruker AC-F300 spectrometer at 300 MHz. Chemical shifts, δ, are reported relative to the internal standard TMS for both ^1H and ^{13}C NMR. Absorption spectra were obtained on a Shimadzu UV-2101 PC spectrophotometer. Emission, excitation and lifetime spectra were obtained with an Aminco Bowman AD2 luminescent spectrofluorometer. Microanalyses were performed by the Taiwan Instrumentation Center.

Synthesis

[Ag(Me$_2$-imy)$_2$][AgCl$_2$] (1). Ag_2O (58.3 mg, 0.25 mmol) was added to a solution of [Me$_2$-imyH]BPh$_4$ (210 mg, 0.50 mmol) and tetramethylammonium chloride (55.1 mg, 0.50 mmol) in 60 mL CH_2Cl_2–CH_3CN (1 : 1). This suspension became a clear solution after stirring for 12 h at room temperature. The volume of the solution was reduced to 10 mL under vacuum and 20 mL of hexane was then added to produce a white solid. The solid was filtered off and recrystallized from CH_2Cl_2–hexane to produce a colorless crystalline product in 91% yield. An identical product was obtained when [Me$_2$-imyH]I was used. Mp: 198 °C (dec). ^1H NMR (DMSO-*d*$_6$): 7.40 (s, 4H, CH), 3.75 (s,12H, CH_3) ppm. Anal. calcd. for $C_{10}H_{16}N_4Ag_2Cl_2$: C, 25.08; H, 3.37; N, 11.70; found: C, 24.88; H, 3.52; N, 11.65%.

[Ag(Me$_2$-imy)$_2$][AgBr$_2$] (2). Ag_2O (166 mg, 0.71 mmol) was added to a solution of [Me$_2$-imyH]Br (253 mg, 1.43 mmol) in CH_2Cl_2 (30 mL). This suspended solution became clear after stirring for 2 h at room temperature. The volume of the solution was reduced to 10 mL under vacuum and 20 of mL hexane was then added to a produce a white solid. The solid was filtered and recrystallized from CH_2Cl_2–hexane to give a colorless crystalline product in an 89% yield. Mp: 214 °C (dec). ^1H NMR (DMSO-*d*$_6$): 7.41 (s, 4H, CH), 3.77 (s,12H, CH_3) ppm. Anal. calcd. for $C_{10}H_{16}N_4Ag_2Br_2$: C, 21.15; H, 2.84; N, 9.87; found: C, 21.10; H, 2.72; N, 9.54%.

[Ag(Me$_2$-imy)$_2$][NO$_3$] (3). Aqueous $AgNO_3$ (105 mg, 0.62 mmol, in 5 mL H_2O) was added to **1** (295 mg, 0.62 mmol) in 50 mL of CH_3CN. The resultant solution was stirred for 1 h. After which, the AgCl precipitate was filtered off and the filtrate was dried under vacuum. The white solid was then recrystallized from CH_2Cl_2–hexane to produce a colorless crystalline product in an 81% yield.Mp: 188 °C (dec). ^1H NMR (DMSO-*d*$_6$): 7.44 (s, 4H, CH), 3.82 (s,12H, CH_3) ppm. Anal. calcd. for $C_{10}H_{16}N_5AgO_3$: C, 33.17; H, 4.45; N, 19.34; found: C, 32.08; H, 4.60; N, 18.78%. The small deviation in the elemental analysis is due to slight contamination with $[AgCl_2]^-$. The following three Ag-tazy compounds were prepared using methods similar to those described for the Ag-imy complexes; yields of ~80% were obtained.

[Ag(Me$_2$-tazy)Cl] (4). Mp: 182 °C (dec). ^1H NMR (DMSO-*d*$_6$): 8.74 (s, 1H, CH), 4.00 (s,3H, CH_3), 3.83 (s,3H, CH_3) ppm. Anal. calcd. for $C_4H_7N_3AgCl$: C, 19.98; H, 2.93; N, 17.48; found: C, 19.90; H, 3.01; N, 17.44%.

[Ag(Me$_2$-tazy)Br] (5). Using a mixture of [Me$_2$-tazyH]BPh$_4$ and [NMe$_4$]Br as a source of bromide is easier to handle. Mp: 172 °C (dec). ^1H NMR (DMSO-*d*$_6$): 8.75 (s, 1H, CH), 3.99 (s, 3H, CH_3), 3.82 (s, 3H, CH_3). Anal. calcd. for $C_4H_7N_3AgBr$: C, 16.86; H, 2.48; N 14.75; found: C, 16.77; H, 2.44; N, 14.58%.

[Ag(Me$_2$-tazy)$_2$][NO$_3$] (6). Mp: 174·(dec). ^1H NMR (DMSO-*d*$_6$): 8.81(s, 2H, CH), 4.05 (s, 6H, CH_3), 3.89 (s, 6H, CH_3) ppm. Anal. calcd. for $C_8H_{14}N_7AgO_3$: C, 26.39; H, 3.88; N, 26.93; found: C, 26.15; H, 3.85; N, 26.86%.

[Ag$_2$(Me$_2$-edimy)Cl$_2$] (7). [Me$_2$-edimyH$_2$][PF$_6$]$_2$ (412 mg, 0.95 mmol) in 20 mL of CH_3CN and [NM$_4$]Cl (187 mg, 1.70 mmol) in 20 mL of CH_2Cl_2 were mixed. To this mixture, Ag_2O (434 mg, 0.85 mmol) was added, and was stirred for 1 d. The white precipitate thus formed was filtered off and the filtrate was dried to give a white solid product. Recrystallization from CH_2Cl_2 produced a white crystalline compound in ~80% yield. Mp: 148 °C (dec). ^1H NMR (DMSO-*d*$_6$): 7.39 (s, 2H, CH), 7.34 (s, 2H, CH), 4.66 (s, 4H, CH_2), 3.75 (s, 6H, CH_3) ppm. Anal. calcd. for $C_{10}H_{14}N_4Ag_2Cl_2$: C, 25.19 H, 2.96; N, 11.75; found: C, 24.76; H, 3.00; N, 11.38%.

Table 2 Crystal data and structure refinement for **1**, **2**, **5**–**7**

	1	**2**	**5**	**6**	**7**
Empirical formula	$C_{10}H_{16}Ag_2Cl_2N_4$	$C_{10}H_{16}Ag_2Br_2N_4$	$C_4H_7AgBrN_3$	$C_8H_{14}AgN_5O_3$	$C_{10}H_{10}Ag_2Cl_2N_4$
M	478.91	567.83	284.89	336.11	472.81
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$C2/m$	$C2/m$	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$
a/Å	15.568(6)	15.6963(14)	4.0669(3)	7.776(2)	6.1651(8)
b/Å	6.376(2)	6.4163(7)	12.2600(12)	8.557(2)	7.5411(10)
c/Å	8.206(2)	8.2982(8)	15.2481(14)	10.420(2)	15.646(2)
a/°	90	90	90	85.26(3)	90
β/°	111.45(4)	110.656(6)	95.673(6)	77.74(3)	94.125(3)
γ/°	90	90	90	79.41(3)	90
U/Å^3	758.1(4)	782.00(13)	756.55(12)	665.3(2)	725.55(16)
Z	2	2	4	2	2
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
μ/mm^{-1}	2.923	7.602	7.862	1.520	3.053
Reflections collected	1690	780	1528	2335	1965
Independent reflections	721	751	1327	2335	1002
Final R_1 [$I > 2\sigma(I)$]	0.0710	0.0260	0.0323	0.0285	0.0763
wR_2 (all data)	0.1733	0.0701	0.0862	0.0757	0.1946

X-Ray structure determinations

Single crystal X-ray data for **1**, **2** and **5**–**7** were collected on a Bruker P4 diffractometer equipped with a graphite monochromator using a Mo-Kα radiation ($\lambda = 0.71073$ Å). Details of crystal parameters, data collection and structure refinements are summarized in Table 2. All structures were solved and refined using SHELX 97.[14] All non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms.

CCDC reference numbers 180229–180233.

See http://www.rsc.org/suppdata/dt/b2/b201957d/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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