



Synthesis and structures of polymeric silver and mercury complexes with amido-functionalized N-heterocyclic carbenes

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ARTICLE INFO

Article history:

Received 25 November 2008

Received in revised form 5 March 2009

Accepted 9 March 2009

Available online 18 March 2009

Keywords:

Silver carbene
Mercury carbene
Acetamide
Hydrogen bond
Amide
Amido

ABSTRACT

Four amido-functionalized N-heterocyclic silver(I) and mercury(II) carbene complexes, $[(\text{CH}_3\text{-imy-CH}_2\text{CONH}_2)_2\text{Ag}_2\text{Br}_2]$ (**3**), $[\text{Ag}(\text{CH}_3\text{-bimy-CH}_2\text{CONH}_2)_2]_4[\text{Ag}_4\text{Br}_8]$ (**4**), $[\text{Hg}(\text{CH}_3\text{-imy-CH}_2\text{CONH}_2)_2][\text{HgBr}_4]$ (**5**), and $[\text{Hg}(\text{CH}_3\text{-bimy-CH}_2\text{CONH}_2)_2][\text{HgBr}_4]$ (**6**), have been synthesized and structurally characterized. Crystal packing revealed a 2D polymeric structure of complex **3**. In addition to a repeated interaction between the Ag_2Br_2 units responsible for the 1D polymeric ladder structure, a pair of hydrogen bonding interactions between the amido groups of the adjacent molecules provided a basis for the other dimension of the polymeric chain. Complex **4** is comprised of a unique oligomeric anion $[\text{Ag}_4\text{Br}_8]^{4-}$ and four $[\text{Ag}(\text{CH}_3\text{-bimy-CH}_2\text{CONH}_2)_2]^+$ cations. Crystal packing of **4** revealed a one-dimensional polymeric structure in which the cations are connected to each other through a pair of hydrogen bonding interactions between the adjacent amido groups. Compounds **5** and **6** are both ionic consisting of a mercury carbene cation and $[\text{HgBr}_4]^{2-}$ anion. An intramolecular interaction of the amido oxygen with the mercury atom of the cation was observed in these two complexes. The interaction between the mercury of the cation and a bromide of the anion, along with the hydrogen bonding interaction of the adjacent amido groups, is responsible for the 2D polymeric structures of these two complexes in the solid state.

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1. Introduction

Since N-heterocyclic carbene (NHCs) complexes had been independently prepared by Öfele [1] and Wanzlick and Schönherr [2–4] and the first synthesis of a stable N-heterocyclic carbene by Arduengo et al. in 1991 [5], the chemistry of imidazole-2-ylidene (imy) and benzimidazole-2-ylidene (bimy) have received considerable attention. NHC carbene, a strong σ -donor and a weak π -acceptor, strongly interacts with different transition metals in various oxidation states [6–9]. This electronic property combined with the steric effect of the substituents on the nitrogen atoms next to the carbene carbon atom provide a basis for the increased catalytic activity and selectivity of these carbene complexes [10–13]. Thus, extensive catalytic studies in the field of application to organic synthesis have been reported [14–19]. Furthermore, the diversity of their structures resulting from, for example, extended metal–metal interactions, metal-bridging halides and carbenes, intermolecular hydrogen bonds and π - π interactions, may lead to interesting structural motifs, such as supramolecular architectures, as well as to inorganic–organic hybrid materials [20–25]. Our interest has been the influence of a carbene functionalized sidearm on

the structural diversity of the related metal carbene complexes. We have reported the acetamide functionalized carbene complexes $[\text{Hg}(2\text{-pyrazinyl-imy-CH}_2\text{CONH}_2)_2]\text{X}$ ($\text{X} = \text{PF}_6, \text{BF}_4$) and $[\text{Hg}(2\text{-pyrimidyl-imy-CH}_2\text{CONH}_2)_2]\text{X}$ ($\text{X} = \text{BF}_4$) [26], in which the amido groups are located on the same side. Intermolecular hydrogen bonding interaction between the amido groups of the adjacent molecules leads to a rectangular architecture. Recently, several structurally diverse acetamide functionalized carbene complexes have been also published by Ghosh and co-workers [27,28]. Here the results of our recent studies of the silver and mercury complexes with amido-functionalized N-heterocyclic carbene are reported. Due to the intermolecular hydrogen bonding interactions and the interaction between the packing units, 1D and 2D supramolecular architectures have been obtained.

2. Experimental

2.1. General procedures

All solvents and chemicals were of the analytical reagent grade and used as received from the commercial suppliers. Elemental analysis was carried out on a Perkin–Elmer CHN-2400 microanalyzer. Proton spectra ($\delta(\text{TMS}) = 0.00$ ppm) were recorded either on a Bruker Avance DPX300 or a Bruker Avance II 400 spectrometer

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Table 1

Crystallographic data for 1-methylacetamido-3-methylbenzimidazolium bromide (**1**) and 1-methylacetamido-3-methylbenzimidazolium bromide (**2**).

Empirical formula	C ₆ H ₁₀ BrN ₃ O	C ₁₀ H ₁₂ BrN ₃ O
Formula weight	220.08	270.14
T (K)	150(1)	298(2)
Crystal system	monoclinic	monoclinic
Space group	P2(1)/c	P2(1)/c
a (Å)	9.2125(8)	11.7618(10)
b (Å)	12.3382(10)	10.8773(9)
c (Å)	8.3641(7)	9.2222(8)
α (°)		
β (°)	113.215(2)	108.489(2)
γ (°)		
V (Å ³)	873.73(13)	1118.96(16)
Z	4	4
ρ _{calc} (g/cm ³)	1.673	1.604
Crystal size (mm ³)	0.25 × 0.20 × 0.20	0.35 × 0.35 × 0.25
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
θ limits (°)	2.41–27.50	1.83–27.49
Index ranges	−8 ≤ h ≤ 11 −15 ≤ k ≤ 16 −10 ≤ l ≤ 10	−14 ≤ h ≤ 15 −14 ≤ k ≤ 14 −11 ≤ l ≤ 11
Reflections collected	5508	10619
Unique reflections	1992	2563
F(000)	440	544
Completeness to θ (%)	99.9	99.9
μ (mm ^{−1})	4.654	3.651
Data/restraints/parameters	1992/0/101	2563/0/137
R ₁ ^a [I > 2.0σ(I)]	0.0309	0.0333
wR ₂ ^b (all data)	0.0773	0.0831
R _{int}	0.0289	0.0325
Goodness-of-fit on F ²	1.011	1.011

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$.

operating at 300.130 MHz and 400.132 MHz, respectively. Infrared spectra were recorded on a Jasco FT/IR-460 Plus spectrometer with 2 cm^{−1} resolution.

2.2. X-ray structure determination

Crystallographic data collections were carried out on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150(2) or 298(2) K. Unit cell parameters were retrieved and refined using DENZO-SMN [29] software on all reflections. Data reduction was performed with the DENZO-SMN [29] software. An empirical absorption was based on the symmetry-equivalent reflections and was applied to the data using SORTAV [30,31] program. The structure was solved using the SHELXS-97 [32] program and refined using SHELXL-97 [33] program by full-matrix least-squares on F² values. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were fixed at calculated positions and refined using a riding mode. Crystallographic data of **3–6** are summarized in Table 1.

2.3. Preparation of complexes

2.3.1. 1-Methylacetamido-3-methylimidazolium bromide (**1**)

1-Methylimidazole (84.2 mg, 1.0 mmol), 2-bromoacetamide (139.8 mg, 1.0 mmol) and about 15 mL of acetonitrile were placed into a 50 mL flask. The flask was heated to reflux under nitrogen causing a formation of a white precipitate. After refluxing for 8 h, the solvent was removed, and the solid was washed with 20 mL of CH₂Cl₂. The resulting white solid was dissolved in methanol and kept at 0 °C for crystallization. Colorless crystals were obtained (94.3 mg, 42% yield). *Anal. Calc.* for C₆H₁₀BrN₃O: C, 32.75; H, 4.58; N, 19.09. *Found:* C, 32.63; H, 4.52; N, 19.01%. ¹H NMR (DMSO-*d*₆): δ 9.08 (s, 1H, NCHN), 7.86 (s, 1H, NH₂), 7.68 (s, 2H, CH=CH), 7.51 (s, 1H, NH₂), 4.96 (s, 2H, CH₂), and 3.88 ppm (s, 3H, CH₃). ¹³C NMR

(DMSO-*d*₆): δ 167.22 (CO), 138.14 (NCN), 124.21 (CH=CH), 123.38 (CH=CH), 50.92 (CH₂), and 36.30 ppm (CH₃). IR (KBr): 3373(vw), 3288(m), 3168(s), 2993(vw), 2928(vw), 2851(vw), 2797(vw), 2732(vw), 1687(vs), 1626(w), 1572(w), 1560(w), 1438 (vw), 1396(vw), 1342(m), 1304(m), 1263(vw), 1174(m), 1125 (vw), 1091(vw), 1036(w), 1018(vw), 972(vw), 864(vw), 843(vw), 787(vw), 756(vw), 675(w), 651(w), 623(m), 598(w), and 551(vw) cm^{−1}.

2.3.2. 1-Methylacetamido-3-methylbenzimidazolium bromide (**2**)

The preparation of [CH₃-Bim-CH₂CONH₂]Br was similar to that of compound **1**. From 132.1 mg of 1-methylbenzimidazole (1.0 mmol) and 139.6 mg of 2-bromoacetamide (1.0 mmol), 189.0 mg of colorless crystals were obtained (70.0% yield). *Anal. Calc.* for C₁₀H₁₂BrN₃O: C, 44.46; H, 4.48; N, 15.56. *Found:* C, 44.44; H, 4.49; N, 15.51%. ¹H NMR (DMSO-*d*₆): δ 9.79 (s, 1H, NCHN), 8.03 (m, 2H, C₆H₄, NH₂), 7.94 (m, 1H, C₆H₄), 7.68 (m, 3H, C₆H₄, NH₂), 5.33 (s, 2H, CH₂), and 4.13 ppm (s, 3H, CH₃). ¹³C NMR (DMSO-*d*₆): δ 167.00 (CO), 144.15 (NCN), 131.97, 131.92, 127.16, 126.92, 114.11, 113.92 (C₆H₄), 48.79 (CH₂), and 33.88 ppm (CH₃). IR (KBr): 3305(vw), 3236(vw), 3138(s), 3033(vw), 2979(vw), 2942 (vw), 1793(vw), 1691(vs), 1680(vs), 1612(w), 1568(m), 1487(vw), 1460(w), 1444(w), 1414(vw), 1387(m), 1367(vw), 1346(vw), 1292(m), 1279(w), 1215(w), 1203(w), 1165(vw), 1142(vw), 1128 (vw), 1111(vw), 1090(vw), 1030(vw), 1012(vw), 980(vw), 941 (vw), 902(vw), 845(vw), 804(vw), 767(m), 756(m), 652(vw), 617(vw), 595(vw), 569(w), 534(vw), 507(vw), and 426(w) cm^{−1}.

2.3.3. 1-Methylacetamido-3-methylimidazol-2-ylidene silver bromide (**3**)

1-Acetamido-3-methylimidazolium bromide (0.4413 g, 2.0 mmol) and silver oxide (232.1 mg, 1.0 mmol) were placed into a 50 mL flask. The flask was covered with aluminium foil followed by a transfer of about 20 mL of CH₂Cl₂ into the flask. After stirring for 1 day, the solution was removed by filtration and the resulting white solid was washed with CH₂Cl₂ several times. The resulting white solid was dissolved in DMSO for crystallization. Colorless crystals were obtained (241.9 mg, 37% yield). *Anal. Calc.* for C₁₂H₁₈Ag₂Br₂N₆O₂: C, 22.04; H, 2.77; N, 12.85. *Found:* C, 22.07; H, 2.90; N, 12.78%. ¹H NMR (DMSO-*d*₆): δ 7.63 (s, 1H, NH₂), 7.37 (s, 2H, CH=CH), 7.31 (s, 1H, NH₂), 4.75 (s, 2H, CH₂), and 3.77 ppm (s, 3H, CH₃). ¹³C NMR (DMSO-*d*₆): δ 181.65 (NCN), 169.06 (CO), 123.87 (CH=CH), 122.87 (CH=CH), 53.21 (CH₂), and 38.54 ppm (CH₃). IR (KBr, cm^{−1}): 3398(m), 3306(vw), 3237(vw), 3184(w), 3138(vw), 3107(vw), 2935(vw), 1683(s), 1621(w), 1568(vw), 1549(vw), 1471(vw), 1449(vw), 1430(vw), 1401(vw), 1391(w), 1357(vw), 1341(vw), 1308(w), 1230(w), 1193(vw), 1139(vw), 1100(vw), 1081(vw), 1032(vw), 962(vw), 875(vw), 824(vw), 801(vw), 760(vw), 717(w), 702(vw), 622(vw), 610(vw), 553(vw), and 496(w).

2.3.4. [1-(Methylacetamido)-3-(methylbenzimidazol-2-ylidene)]₂ Ag₄[Ag₄Br₈] (**4**)

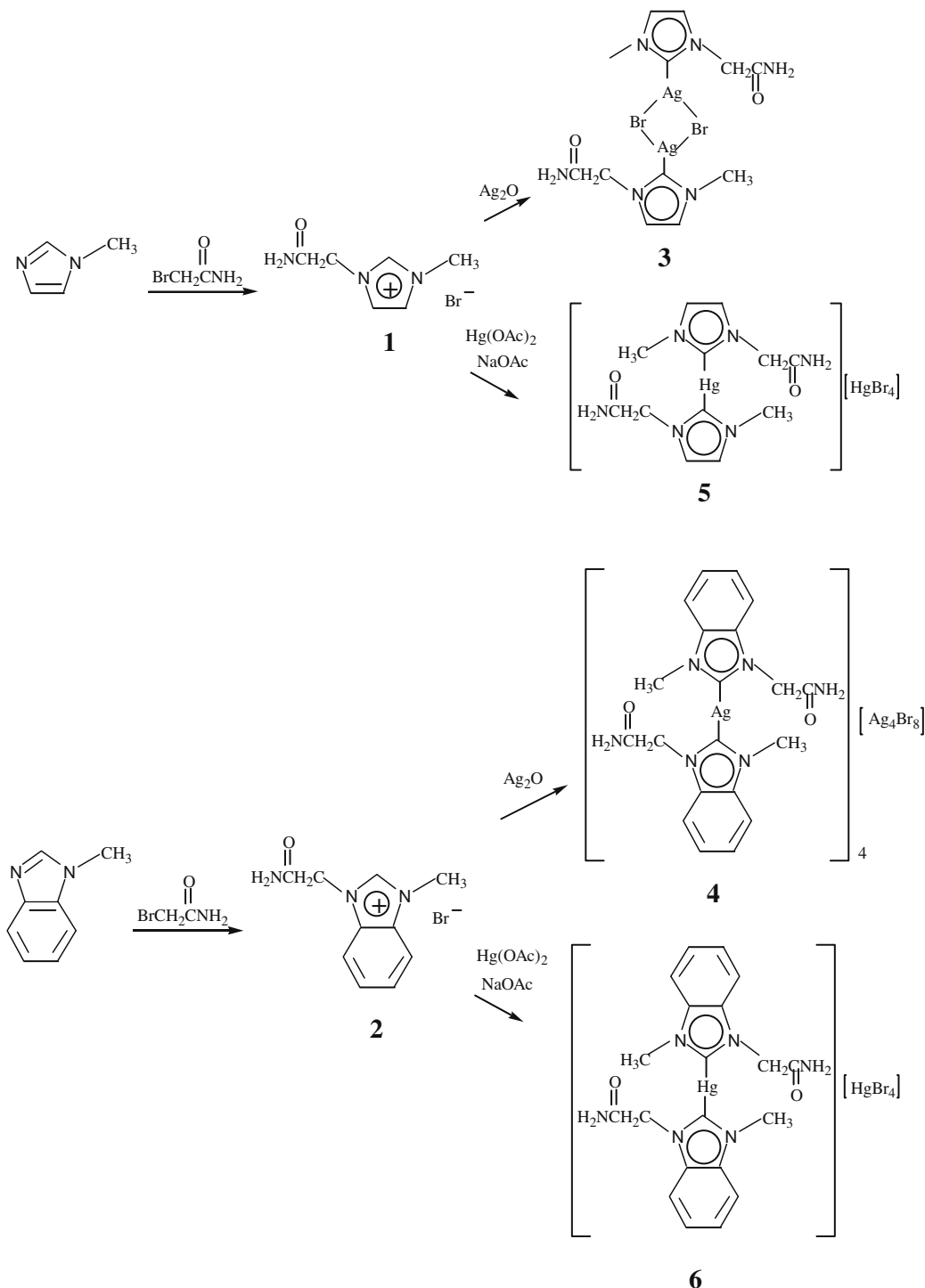
The preparation was similar to that of **3**. From 541.2 mg (2.0 mmol) of 1-acetamido-3-methylbenzimidazolium bromide and 230.5 mg (1.0 mmol) of silver oxide, 750.4 mg (98%) of **4** · 2H₂O was isolated after washing with CH₂Cl₂. A crystal suitable for X-ray diffraction analysis was isolated from DMSO solution. *Anal. Calc.* for C₈₀H₈₈Ag₈Br₈N₂₄O₈ · 2H₂O: C, 31.48; H, 3.04; N, 11.01. *Found:* C, 31.33; H, 3.07; N, 11.07%. ¹H NMR (DMSO-*d*₆): δ 7.76 (m, 2H, C₆H₄, NH₂), 7.64 (m, 1H, C₆H₄), 7.44 (m, 3H, C₆H₄, NH₂), 5.12 (s, 2H, CH₂), and 4.05 ppm (s, 3H, CH₃). ¹³C NMR (DMSO-*d*₆): δ 192.31 (NCN), 168.69 (CO), 134.42, 134.25, 124.44, 124.29, 112.38 (C₆H₄), 50.99 (CH₂), and 36.00 ppm (CH₃). IR (KBr): 3332(m), 3318(m), 3161(m), 3034(vw), 2993(vw), 2977 (vw), 2935(w), 2918(w), 2912(w), 2831(vw), 2786(vw), 2360

(vw), 2338(vw), 1686(vs), 1641(vw), 1610(vw), 1480(vw), 1465(vw), 1438(s), 1392(s), 1346(vw), 1311(s), 1269(vw), 1204(w), 1173(vw), 1131(vw), 1104(vw), 1033(vw), 1026(s), 978(vw), 951(vw), 932(vw), 867(vw), 821(vw), 792(vw), 764(s), 740(s), 710(vw), 618(m), 606(m), 580(m), 508(vw), and 434(w) cm^{-1} .

2.3.5. $[1-(\text{Methylacetamido})-3-(\text{methylimidazol-2-ylidene})]_2\text{Hg}[\text{HgBr}_4]$ (**5**)

1-Acetamido-3-methylimidazolium bromide (110.7 mg, 0.5 mmol) and mercury acetate (81.0 mg, 0.25 mmol) were placed into a 50 mL flask followed by a transfer of about 20 mL of CH_3CN into

the flask. After refluxing for 1 day, the solution was removed by filtration, and the resulting white solid was washed with CH_3CN several times. A white solid was obtained (99.3 mg, 39.8% yield). *Anal. Calc.* for $\text{C}_{12}\text{H}_{18}\text{Br}_4\text{Hg}_2\text{N}_6\text{O}_2$: C, 14.43; H, 1.82; N, 8.41. *Found:* C, 14.3382; H, 1.90; N, 8.49%. $^1\text{H NMR}$ ($\text{DMSO}-d_6$): δ 7.84 (s, 1H, NH_2), 7.64 (s, 1H, $\text{CH}=\text{CH}$), 7.63 (s, 1H, $\text{CH}=\text{CH}$), 7.46 (s, 1H, NH_2), 5.17 (s, 2H, CH_2), and 3.98 ppm (s, 3H, CH_3). $^{13}\text{C NMR}$ ($\text{DMSO}-d_6$): δ 177.66 (NCN), 168.74 (CO), 124.96 ($\text{CH}=\text{CH}$), 124.36 ($\text{CH}=\text{CH}$), 52.46 (CH_2), and 38.22 ppm (CH_3). IR (KBr): 3353(m), 3279(s), 3149(s), 3122(s), 2965(vw), 2924(vw), 2801(vw), 2755(vw), 2357(vw), 2287(vw), 2219(vw), 1943(vw),



Scheme 1.

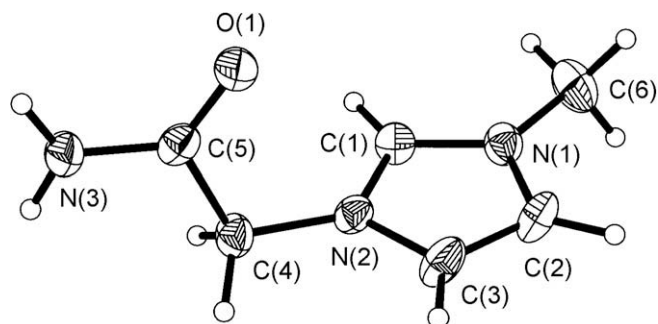


Fig. 1. Molecular structure of the cation in **1** showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): C(1)–N(1): 1.322(3); C(1)–N(2): 1.331(3); C(5)–O(1): 1.222(3); C(5)–N(3): 1.326(3); C(5)–N(3): 1.326(3); N(1)–C(1)–N(2): 108.7(2).

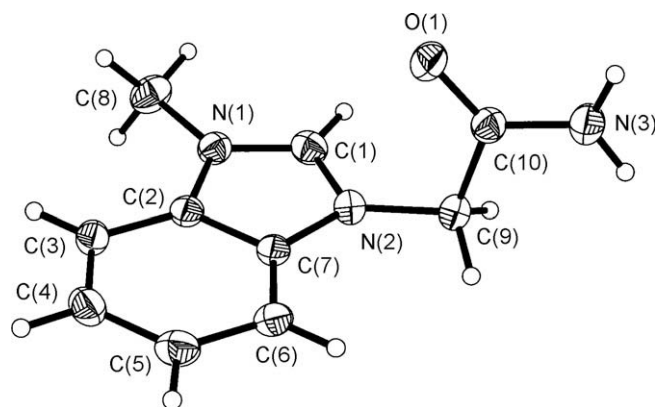


Fig. 2. Molecular structure of the cation in **2** showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): C(1)–N(1): 1.320(3); C(1)–N(2): 1.334(3); C(10)–O(1): 1.220(3); C(10)–N(3): 1.319(3); N(1)–C(1)–N(2): 110.8(2).

1683(vs), 1621(w), 1568(vw), 1479(w), 1442(w), 1421(vw), 1410(vw), 1391(m), 1257(w), 1203(w), 1162(vw), 1139(vw), 1085(vw), 1062(vw), 1020(vw), 970(vw), 890(vw), 863(vw), 813(w), 797(vw), 764(s), 687(m), 656(m), 626(w), and 453(vw) cm^{-1} .

2.3.6. $[[1-(\text{Methylacetamido})-3-(\text{methylimidazol-2-ylidene})]_2\text{Hg}][\text{HgBr}_4]$ (**6**)

The preparation was similar to that of **5**, except that 135.3 mg (0.5 mmol) of 1-acetamido-3-methylbenzimidazolium bromide, 81.0 mg (0.25 mmol) of mercury acetate and 43.0 mg (0.25 mmol) of sodium acetate were used. A white solid was obtained (120.8 mg, 44% yield). *Anal. Calc.* for $\text{C}_{20}\text{H}_{22}\text{Br}_4\text{Hg}_2\text{N}_6\text{O}_2$: C, 21.86; H, 2.02; N, 7.65. *Found*: C, 21.67; H, 2.09; N, 7.71%. $^1\text{H NMR}$ ($\text{DMSO}-d_6$): δ 7.96 (m, 2H, C_6H_4 , NH_2), 7.82 (m, 1H, C_6H_4), 7.67 (m, 3H, C_6H_4 , NH_2), 5.54 (s, 2H, CH_2), and 4.28 ppm (s, 3H, CH_3). $^{13}\text{C NMR}$ ($\text{DMSO}-d_6$): δ 184.64 (NCN), 168.24 (CO), 133.70, 126.25, 126.07, 113.42, 112.97 (C_6H_4), 50.08 (CH_2) and 35.83 ppm (CH_3). IR (KBr): 3348(w), 3328(w), 3304(w), 3249(vw), 3165(m), 3046(vw), 2916(vw), 2360(vw), 2337(vw), 1675(vs), 1609(w), 1568(vw), 1487(vw), 1461(s), 1418(w), 1403(m), 1362(w), 1351(vw), 1327(w), 1277(vw), 1261(vw), 1215(w), 1181(vw), 1139(vw), 1112(vw), 1028(vw), 974(vw), 939(vw), 886(vw), 836(vw), 794(w), 756(vw), 663(s), 652(w), 626(w), 614(w), and 576(w) cm^{-1} .

3. Results and discussion

N-methylimidazole and *N*-methylbenzimidazole were alkylated with 2-bromoacetamide to afford 1-methylacetamido-3-methylimidazolium bromide (**1**) and 1-methylacetamido-3-methylbenzimidazolium bromide (**2**) (Scheme 1), respectively, in good yields. Analogous alkylation procedures have been used by Burgess and co-workers [34] and Ghosh and co-workers [35–37] in the prepara-

Table 2
Crystallographic data for $[(\text{CH}_3\text{-imy-CH}_2\text{CONH}_2)_2\text{Ag}_2\text{Br}_2]$ (**3**), $[\text{Ag}(\text{CH}_3\text{-bimy-CH}_2\text{CONH}_2)_2]_2[\text{Ag}_2\text{Br}_4] \cdot 2(\text{CH}_3)_2\text{SO}$ (**4**), $[\text{Hg}(\text{CH}_3\text{-imy-CH}_2\text{CONH}_2)]_2[\text{HgBr}_4]$ (**5**), and $[\text{Hg}(\text{CH}_3\text{-bimy-CH}_2\text{CONH}_2)]_2[\text{HgBr}_4] \cdot (\text{CH}_3)_2\text{SO}$ (**6**).

Empirical formula	$\text{C}_{12}\text{H}_{18}\text{Ag}_2\text{Br}_2\text{N}_6\text{O}_2$	$\text{C}_{44}\text{H}_{56}\text{Ag}_4\text{Br}_4\text{N}_{12}\text{O}_6\text{S}_2$	$\text{C}_{12}\text{H}_{18}\text{Br}_4\text{Hg}_2\text{N}_6\text{O}_2$	$\text{C}_{22}\text{H}_{28}\text{Br}_4\text{Hg}_2\text{N}_6\text{O}_3\text{S}$
Formula weight	653.88	1664.25	999.15	1177.38
<i>T</i> (K)	150(1)	150(1)	298(2)	150(2)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
<i>a</i> (Å)	4.3489(1)	12.7840(5)	8.1852(4)	9.0753(4)
<i>b</i> (Å)	17.3223(5)	15.0755(6)	18.4391(8)	10.6715(5)
<i>c</i> (Å)	11.7995(3)	15.9313(6)	15.2104(7)	17.5450(8)
α (°)		108.820(1)		84.435(1)
β (°)	91.0179(14)	93.416(1)	93.8540(10)	88.251(1)
γ (°)		106.007(1)		65.792(1)
<i>V</i> (Å ³)	888.75(4)	2756.05(19)	2290.48(18)	1542.38(12)
<i>Z</i>	2	2	2	2
ρ_{calc} (g/cm^3)	2.443	2.005	2.897	2.535
Crystal size (mm^3)	$0.40 \times 0.06 \times 0.02$	$0.15 \times 0.10 \times 0.05$	$0.1 \times 0.05 \times 0.03$	$0.20 \times 0.15 \times 0.10$
Radiation (λ , Å)	Mo $\text{K}\alpha$ (0.71073)	Mo $\text{K}\alpha$ (0.71073)	Mo $\text{K}\alpha$ (0.71073)	Mo $\text{K}\alpha$ (0.71073)
θ limits (°)	2.09–27.50	1.37–25.00	1.74–25.05	1.17–27.50
Index ranges	$-5 \leq h \leq 5$ $-21 \leq k \leq 22$ $-15 \leq l \leq 15$	$-15 \leq h \leq 15$ $-17 \leq k \leq 17$ $-18 \leq l \leq 18$	$-9 \leq h \leq 9$ $-21 \leq k \leq 21$ $-18 \leq l \leq 15$	$-11 \leq h \leq 11$ $-13 \leq k \leq 13$ $-22 \leq l \leq 22$
Reflections collected	8550	30345	12206	24848
Unique reflections	2046	9698	4019	13978
<i>F</i> (000)	624	1624	1792	1084
Completeness to θ (%)	99.9	100.0	99.1	99.9
μ (mm^{-1})	6.718	4.432	20.386	15.226
Max./min. transmission	0.882, 0.709	0.8088, 0.5561	1, 0.615917	0.3113, 0.1507
Data/restraints/parameters	2046/0/110	9698/0/650	4019/0/238	13978/3/664
R_1^a [$I > 2.0\sigma(I)$]	0.0307	0.0697	0.0333	0.0598
wR_2^b (all data)	0.0799	0.1491	0.0656	0.1393
R_{int}	0.0427	0.0526	0.0286	0.0501
Goodness-of-fit on F^2	1.012	1.309	1.042	1.016

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$.

ration of their amido-functionalized N-heterocyclic carbene ligand precursors. In the ^1H NMR spectra in deuterated DMSO, the diagnostic acidic 2H-imidazolium protons appear at 9.08 ppm for **1** and 9.79 ppm for **2**. The amide protons of **1** (7.51 and 7.86 ppm) and **2** (7.68 and 8.03 ppm) are not equivalent due to a partial double bond character of the C(O)–NH₂ bond. These chemical shifts are slightly downfield compared with those of 2-bromoacetamide (7.25 and 7.62 ppm), thereby suggesting the presence of a Br \cdots H–N type hydrogen bonding in solution between the Br $^-$ anion and the amide protons of the cation. Similar hydrogen bonding interactions have been found, for examples, in compound [1-(R)-3-[N-(*t*-butylacetamido)imidazol-2-ylidene]]₂AgCl (R = *t*-Bu, *i*-Pr [27,28] and compound [N-(2,6-diisopropylphenyl)-3-[bis(2-pyridylmethyl)amino]propanamide]CuCl [38]. The ^1H NMR spectra of **1** and **2** taken at 60 °C both display their amide signals merged into singlets at 7.37 and 7.56 ppm, respectively.

Crystals of **1** and **2** suitable for single crystal X-ray diffraction analyses were grown from methanol solution at 0 °C. The solid state molecular structures of **1** and **2** (Table 1, Figs. 1 and 2) provide evidence for the partial double bond character of the C(O)–NH₂ bond and the hydrogen bonding between the bromide anion and the amide protons. The C(O)–NH₂ bond distances are 1.326(3) Å in **1** and 1.319(3) Å in **2**, which are shorter than the sum of the individual single bond covalent radii of C (0.772 Å) and N (0.70 Å) [39]. The closest Br \cdots N distances, 3.361 Å in **1** and 3.372 Å in **2**, are within the value of the sum of the van der Waals radii of Br and N (3.35–3.55 Å) [40].

Upon reaction with Ag₂O, **1** and **2** produced the silver–carbene complexes [(CH₃-imy-CH₂CONH₂)₂Ag₂Br₂] (**3**) and [Ag(CH₃-bimy-CH₂CONH₂)₂]₄[Ag₄Br₈] (**4**) (Scheme 1), respectively. With mercury

acetate, **1** and **2** afforded the mercury–carbene complexes [Hg(CH₃-imy-CH₂CONH₂)₂][HgBr₄] (**5**) and [Hg(CH₃-bimy-CH₂CONH₂)₂][HgBr₄] (**6**) (Scheme 1), respectively. At room temperature these N-heterocyclic carbene metal complexes are neither air nor light-sensitive.

Formation of the metal carbene complexes is corroborated by the absence of the 2H-imidazolium proton signals in their ^1H NMR spectra. For each metal carbene complex the nonequivalent amide protons appear as a pair of singlets (7.31 and 7.63 ppm (**3**); 7.44 and 7.76 ppm (**4**); 7.46 and 7.84 ppm (**5**); 7.67 and 7.96 ppm (**6**)). These chemical shifts are also slightly downfield from those of 2-bromoacetamide, which was attributed to the effect of the hydrogen bonding in solution. In the ^{13}C spectra of the above complexes the carbene signals appear as sharp singlets at about 40 ppm downfield from that of the (benz)imidazolium salt. The $^{107,109}\text{Ag}$ – ^{13}C coupling in **3** and **4** or the ^{199}Hg – ^{13}C coupling in **5** and **6** is not observed, which could be attributed to the fluxional behavior of the labile metal–carbene bonds [23,41–44].

Crystals of **3–6** suitable for X-ray diffraction analyses were obtained through slow evaporation of their DMSO solutions at room temperature. The unit cell of **4** contains two DMSO solvent molecules and the unit cell of **6** contains one DMSO solvent molecule. The crystal data for **3–6** are provided in Table 2. The molecular structures of **3–6** are shown in Figs. 3–6, and the selected bond distances and angles are given in the figure captions. Due to the presence of inversion centers the asymmetric units for **3** and **5** are comprised of half of the molecule in both cases.

An important feature of the silver carbene complexes is their structural diversity in the solid state, which ranges from a simple monomer to different types of polymeric structures [45–48]. Com-

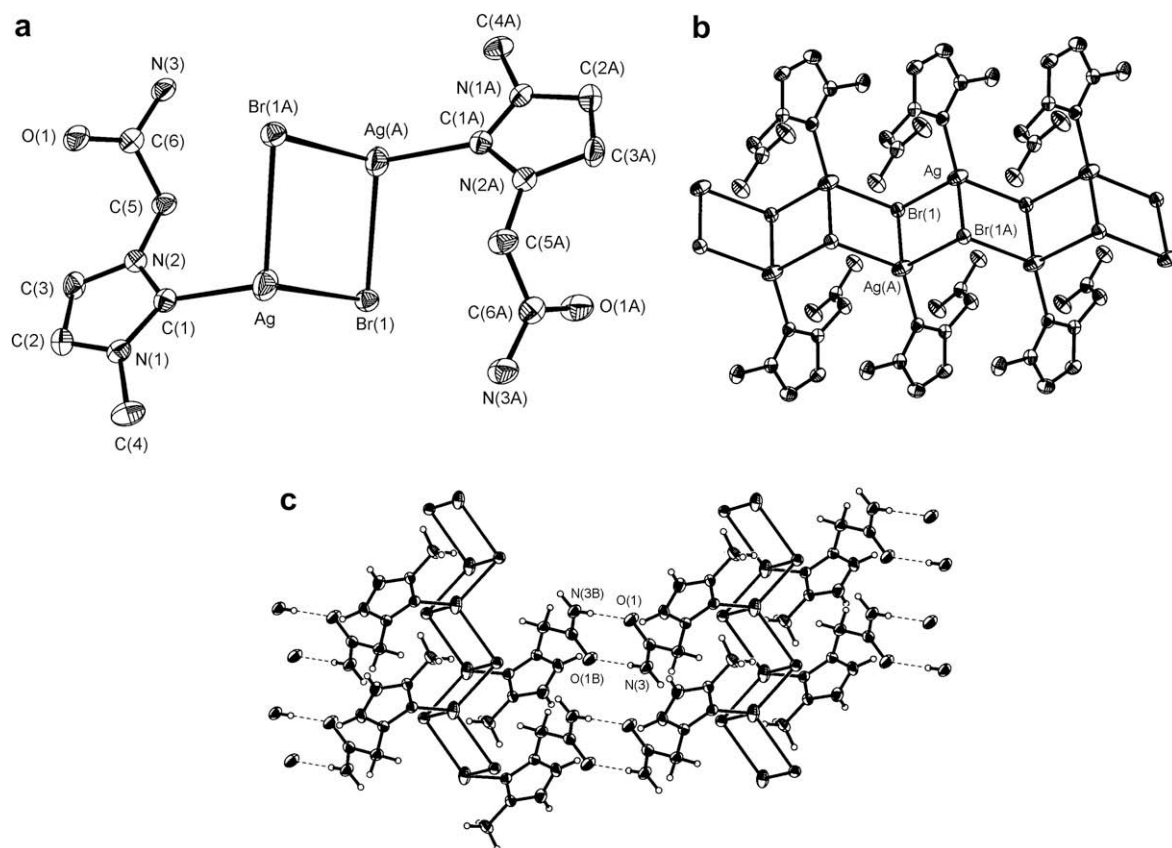


Fig. 3. Molecular structure of **3** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag–C(1): 2.155(3); Ag–Br(1A): 2.6961(5); Ag–Br(1): 2.8211(4); Ag–Br(1B): 2.9215(5); C(1)–Ag–Br(1A): 130.94(9); C(1)–Ag–Br(1): 114.12(8); Br(1A)–Ag–Br(1): 104.021(15); C(1)–Ag–Br(1B): 106.65(9); Br(1A)–Ag–Br(1B): 91.804(13); Br(1)–Ag–Br(1B): 104.325(14); Ag(B)–Br(1)–Ag: 104.021(15); Ag(B)–Br(1)–Ag(A): 88.196(13); Ag–Br(1)–Ag(A): 75.675(14); N(1)–C(1)–N(2): 104.4(3).

plex **3** is a neutral species composed of $(\text{CH}_3\text{-imy-CH}_2\text{CONH}_2)\text{AgBr}$ repeating units. Two of such units are held together by two bridging bromine atoms to form a dimeric structure (Fig. 3a). The crystal packing revealed the 2D polymeric structure of **3**. A one-dimensional staircase polymer chain is formed through an extended Ag–Br interaction of the Ag_2Br_2 rhombic structure (Fig. 3b). Each Ag atom coordinated to a carbene carbon and three u_3 -bridging Br ligands is in a tetrahedral environment. The Ag–C_{carb} bond distance of 2.155(3) Å is longer than the sum of individual covalent radii of Ag and C (2.11 Å) [39], but slightly shorter than that found in $[(\text{allyl-imy-CH}_3)\text{Ag}][\text{AgI}_2]$ (2.161(9) Å) [49,50]. The Ag–Br distances of 2.6961(5), 2.8211(4), and 2.9215(5) Å are comparable to other Ag–Br bonds characteristic for tetrahedral coordination [23,51,52]. Within the Ag_2Br_2 rhombic structure, the Br(1)–Ag–Br(1B) angle (104.325(14)°) is larger than the Ag–Br(1)–Ag(A) (75.675(14)°). The Ag–Ag distance is 3.524 Å, which is slightly longer than the sum of the van der Waals radii for two silver atoms [40].

In addition to the extended Ag–Br interaction, an intermolecular hydrogen bonding interaction between the amide NH_2 protons and the adjacent amide oxygen atom was also found. As shown in Fig. 3c, each amido group of the repeating unit of the one-dimensional polymer is hydrogen bonded to the adjacent amido group of the repeating unit forming a 2D supramolecular architecture. The N...O distance of 2.936 Å is smaller than the sum of the van der Waals radii of N and O atoms (3.05 Å) [40]. Indeed, the same type of the dimer structure is also found for the amido-functionalized metal carbene complexes **4–6**.

The molecular structure of complex **4** is shown in Fig. 4. Complex **4** being ionic, the unit cell consists of two $[\text{Ag}(\text{CH}_3\text{-Bim-CH}_2\text{CONH}_2)_2]^+$ cations (Fig. 4a) and one half of the oligomeric $[\text{Ag}_4\text{Br}_8]^{4-}$ anion (Fig. 4b). The cations C–Ag–C angles are 170.6(3) and 169.6(3)°, which is consistent with other linear $[\text{Ag}(\text{carbene})_2]^+$ complexes [49,50]. The Ag–C distances are 2.096(9), 2.097(8), 2.103(8) and 2.113(8) Å. Although these bond distances are shorter than those found in **3**, they fall in the range of Ag–C bond distances (2.074(5)–2.131(5) Å) generally found in other Ag–NHC complexes [15–19,23,35,53]. The crystal packing reveals the 1D polymeric structure of the cations through the hydrogen bonding between the amido groups of the adjacent cations. The N...O distances are 2.912 and 2.956 Å. Hydrogen bonding was also found between the amido group and the DMSO solvent molecule. The closest distances between the amido nitrogen and the oxygen atom of $(\text{CH}_3)_2\text{SO}$ are 2.837 and 2.873 Å.

The unique oligomeric $[\text{Ag}_4\text{Br}_8]^{4-}$ anion is formed by four Ag atoms and eight bromine atoms. The Ag atoms are either in the distorted trigonal or tetrahedral environments, and three four-membered rings can be observed. Atoms Ag(3), Br(1), Ag(3A), and Br(1A) form an almost perfect square with 90.97(3)° and 89.03(3)° angles. The Ag–Br distance for a terminal bromide is 2.5395(12) Å. The Ag–Br distances for the bridging bromides are longer falling in the range of 2.6454(13)–2.7941(12) Å. The Ag...Ag distances are 3.504 and 3.828 Å suggesting no Ag–Ag interaction within the anion. To our knowledge, $[\text{K}(\text{crypt-2,2,2})_4][\text{Ag}_4\text{Br}_8]$ is the only example of a compound containing oligomeric $[\text{Ag}_4\text{Br}_8]^{4-}$ anion that has been reported in literature [54]. However, the bond distances and angles of $[\text{Ag}_4\text{Br}_8]^{4-}$ in $[\text{K}(\text{crypt-2,2,2})_4][\text{Ag}_4\text{Br}_8]$ are different from those found in **4**. In $[\text{K}(\text{crypt-2,2,2})_4][\text{Ag}_4\text{Br}_8]$, the terminal Ag–Br distances are shorter (2.518(2) Å) and the bridging Ag–Br distances are falling in a wider range (2.631(2)–2.799(2) Å), and the Ag...Ag distances are 3.562(1) and 3.595(2) Å. The angles of the “square” formed by the Ag(3), Br(1), Ag(3A) and Br(1A) atoms in $[\text{K}(\text{crypt-2,2,2})_4][\text{Ag}_4\text{Br}_8]$ are 96.87(4)° and 83.13(4)° [54]. Different cations in these two compounds resulting in different crystal packing forces could account for such a difference in the bond distances and angles of the anions.

For complex **5**, an ionic compound, two $[\text{Hg}(\text{CH}_3\text{-imy-CH}_2\text{CONH}_2)_2]^{2+}$ cations and two $[\text{HgBr}_4]^{2-}$ anions with slightly different bond distances and angles are found in the unit cell. The C–Hg–C angle values found for each cation (179.999(2)° and 179.999(3)°) are consistent with those found for 1,3-diphenylimidazol-2-ylidene mercury perchlorate (180°) [2,4]. The Hg–C bond distances are 2.078(9) and 2.051(9) Å. The previously reported mercury carbene Hg–C bond distances fall into the range of 1.97(2)–2.22(3) Å [2,4,53,55,56]. Unlike the silver complexes **3** and **4**, the mercury complex is characterized by an interaction between an amide oxygen and the mercury atom. The Hg...O distances of 2.794 and 2.802 Å are shorter than the sum of the van der Waals radii of O and Hg atoms (3.0 Å) [40], suggesting a weak interaction of the amide group with the Hg atom, which may be resulted from the higher oxidation state of the mercury ion compared with that of the Ag(I) in the silver carbene complexes. The Hg–Br distances of the anions are falling in the range of 2.5796(11)–2.6351(11) Å. Crystal packing revealed a 2D polymeric structure of complex **5**. One dimension of the polymer chain is forged by the Hg...Br interaction between the anion and the cation. The Hg(1)...Br(2) and Hg(2)...Br(1) distances are 3.227 and 3.386 Å, respectively. These distances are within the sum of the van der Waals radii of Br and Hg atoms (3.3–3.5 Å) [40]. The hydrogen bonds between the amido groups of the adjacent cations constitute the other dimension of the polymer chain. The N...O distance for the adjacent amido groups is 2.901 Å.

Previously we have prepared the mercury amido-functionalized carbene complexes $[\text{Hg}(\text{2-pyrazinyl-imy-CH}_2\text{CONH}_2)_2]\text{X}$ (X = PF₆, BF₄) and $[\text{Hg}(\text{2-pyrimidyl-imy-CH}_2\text{CONH}_2)_2]\text{X}$ (X = BF₄) [26]. The interaction between mercury and nitrogen atoms of the pyrazinyl

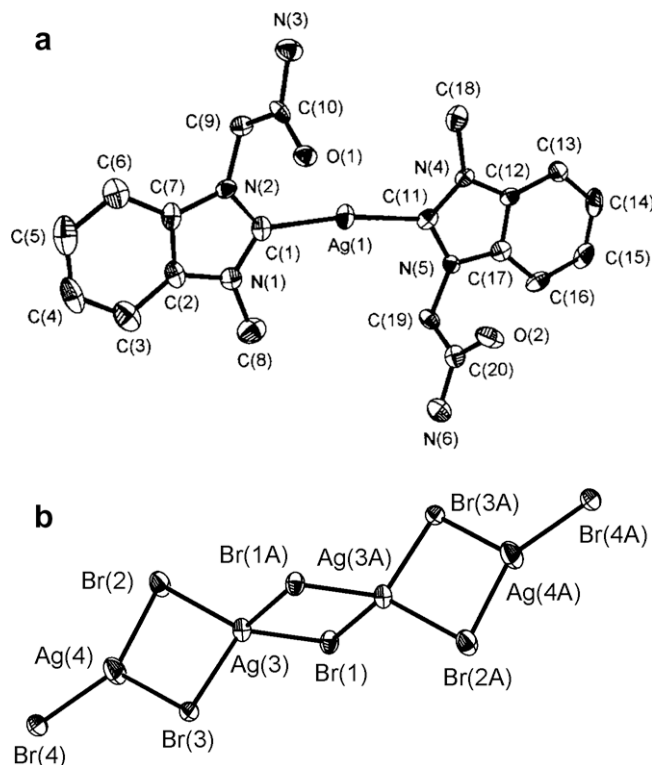


Fig. 4. Molecular structure of **4** showing 50% probability thermal ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–C(1): 2.097(8); Ag(1)–C(11): 2.096(9); Ag(2)–C(21): 2.103(8); Ag(2)–C(31): 2.113(8); C(11)–Ag(1)–C(1): 170.6(3); C(21)–Ag(2)–C(31): 169.6(3); N(1)–C(1)–N(2): 106.3(7); N(4)–C(11)–N(5): 105.7(7); N(7)–C(21)–N(8): 105.3(7); N(10)–C(31)–N(11): 105.9(7); Br(1)–Ag(3)–Br(1A): 90.97(3); Ag(3)–Br(1)–Ag(3A): 89.03(3)°.

(pyrimidyl) substitute produced a skewed Hg–carbene core conformation that forced the two amido groups to be on the same side and formed a U-shaped building block. In the crystal packing, the intermolecular hydrogen bonding interaction between the adjacent amido groups connects the U-shaped building blocks leading to a rectangular architecture. In the alkyl- substituted analog of complex **5** lacking the Hg–N interaction found in complexes $[\text{Hg}(2\text{-pyrazinyl-imy-CH}_2\text{CONH}_2)_2]\text{X}$ ($\text{X} = \text{PF}_6, \text{BF}_4$) and $[\text{Hg}(2\text{-pyrimidyl-imy-CH}_2\text{CONH}_2)_2]\text{X}$ ($\text{X} = \text{BF}_4$), a *trans-anti* conformation precluded the U-shaped conformations of the amido groups and the resulting rectangular architecture. It is noteworthy that without the Hg–N interaction, a weak interaction between the amido oxygen and the mercury atom was observed.

Complex **6** is also an ionic compound, containing two $[\text{Hg}(\text{CH}_3\text{-bimy-CH}_2\text{CONH}_2)_2]^{2+}$ cations and two $[\text{HgBr}_4]^{2-}$ anions in the unit cell. The C–Hg–C angles of the two cations are $174.8(6)^\circ$ and $176.5(6)^\circ$. The Hg–C bond distances are 2.070(15), 2.089(15), 2.064(16) and 2.121(15) Å. The Hg–Br bond distances of the anions are falling in the range of 2.5501(19)–2.6753(18) Å. The weak interactions and the 2D polymeric structure observed for complex **5** are also found in complex **6**. The Hg...O distances between mercury and oxygen atoms of the amido group are 2.802 and 2.827 Å

for Hg(1) and 2.780 and 3.040 Å for Hg(2). The Hg...Br distances between the cation and the anion are in the range of 3.193–3.483 Å. The N...O distances for the adjacent amido group of the cations are determined to be 2.880, 2.960, 2.847 and 2.922 Å. Hydrogen bonds between the amido group and the solvent molecule are also found in **6**. The closest $(\text{CH}_3)_2\text{SO}\cdots\text{N}$ distances between the amido nitrogen and oxygen of DMSO are 2.894 and 3.352 Å. It is noteworthy that many carbene complexes containing benzimidazole-2-ylidene display a π – π stacking interactions between the aromatic rings of the adjacent molecules [19,57]. This type of interaction was not found in complexes **4** and **6**, possibly due to the stronger hydrogen bonding interaction between the amido groups of the adjacent molecules.

In summary, the amido-functionalized carbene ligand precursors and corresponding silver and mercury carbene complexes have been prepared and characterized. While **3** is a neutral compound, **4–6** are ionic. In addition to the metal–carbene interaction, a weak interaction between the amide oxygen and the mercury atom were also found in complexes **5** and **6**, possibly due to the higher oxidation state of mercury. A hydrogen bonding interaction of the amido groups of the adjacent cations is responsible for the one-dimensional polymeric structure found in **4**. In addition to

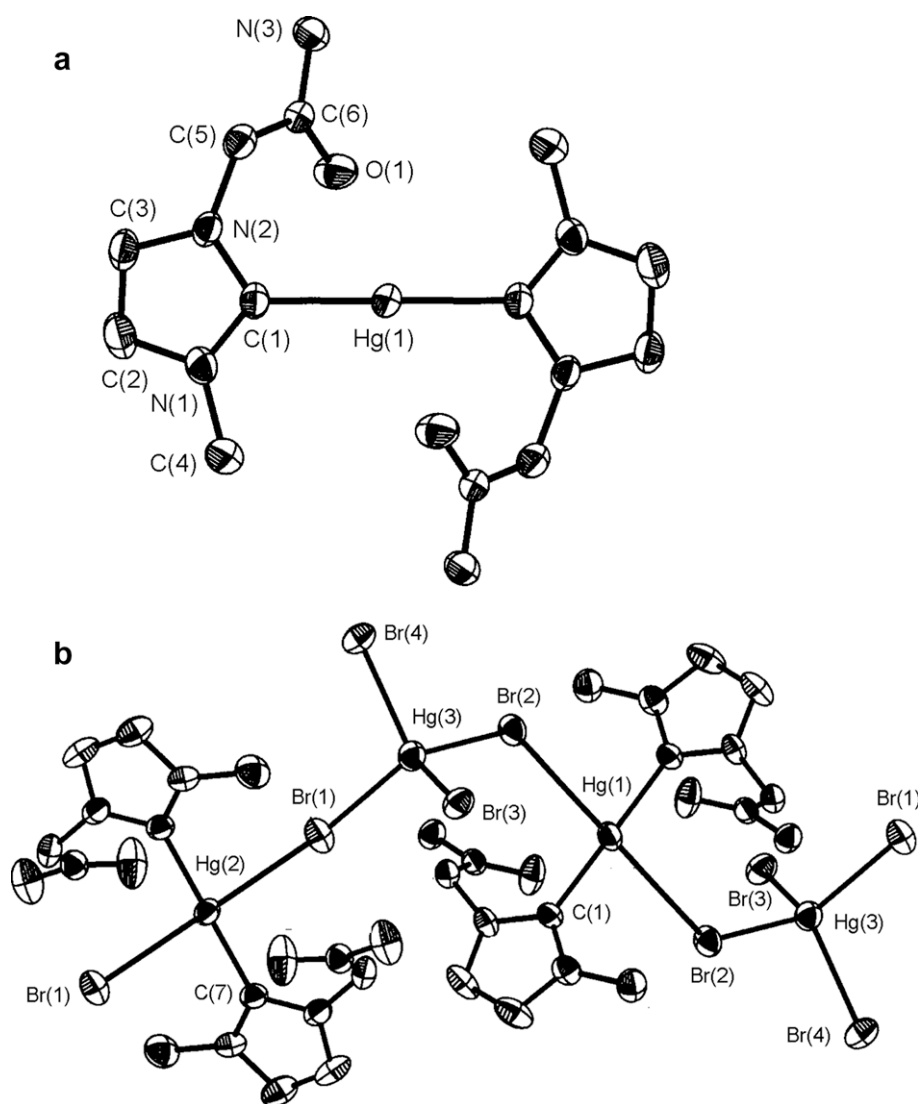


Fig. 5. Molecular structure of **5** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Hg(1)–C(1): 2.078(9); Hg(2)–C(7): 2.051(9); C(1)–Hg(1)–C(1A): 179.999(2); C(7)–Hg(2)–C(7B): 179.999(3); N(1)–C(1)–N(2): 106.5(8); N(4)–C(7)–N(5): 106.3(8).

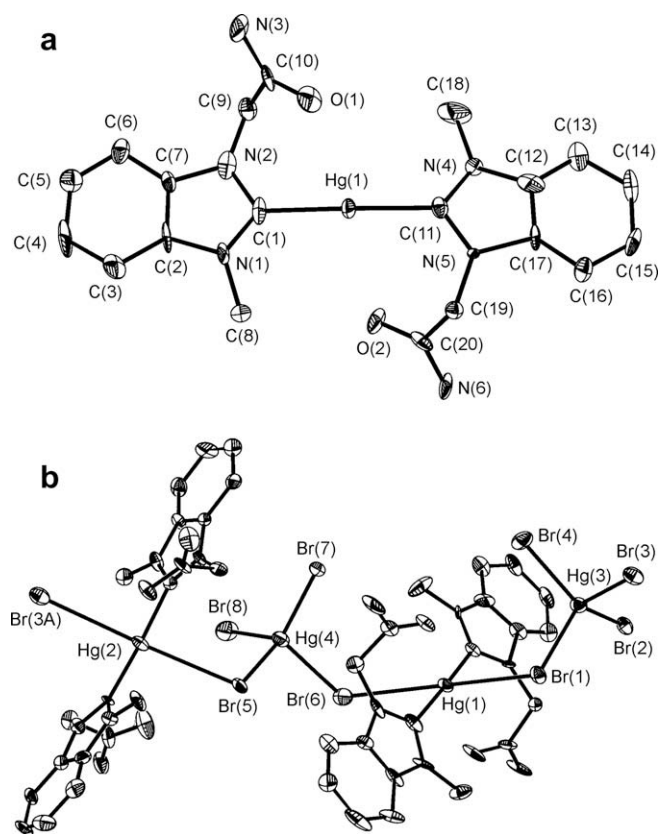


Fig. 6. Molecular structure of **6** showing 50% probability thermal ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): Hg(1)–C(1): 2.070(15); Hg(1)–C(11): 2.089(15); Hg(2)–C(21): 2.064(16); Hg(2)–C(31): 2.121(15); C(1)–Hg(1)–C(11): 174.8(6); N(1)–C(1)–N(2): 106.7(14); N(4)–C(11)–N(5): 108.1(13); C(21)–Hg(2)–C(31): 176.5(6); N(7)–C(21)–N(8): 105.6(13); N(10)–C(31)–N(11): 111.0(14).

the hydrogen bonding, an extended Ag–Br interaction in **3** and the interaction between the cation and the anion in **5** and **6** constitute another dimension of the polymeric structure resulting in a two-dimensional supramolecular architecture.

Acknowledgment

This work was financially supported by the National Science Council of the ROC through Grant NSC 96-2113-M-259-014.

Appendix A. Supplementary material

CCDC 698275, 698276, 698277, 698278, 698279 and 698280 contains the supplementary crystallographic data for this paper. 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.ica.2009.03.014.

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