



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)]₂Ag₄[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

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