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Syntheses and characterization of neutral and cationic cyclic (alkyl)(amino)carbene mercury [cAAC-Hg(II)] complexes

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ABSTRACT

Reactions of cyclic (alkyl)(amino)carbenes, $cAAC^{Me}$ and $cAAC^{cy}$ with equimolar quantity of HgX_2 salts afforded their corresponding halide bridged dimeric complexes, $[cAAC^{Me}HgCl(\mu\text{-}Cl)]_2$ (**1**), $[cAAC^{cy}\cdot HgCl(\mu\text{-}Cl)]_2$ (**2**), $[cAAC^{Me}\cdot HgI(\mu\text{-}I)]_2$ (**3**) and $[cAAC^{cy}\cdot HgI(\mu\text{-}I)]_2$ (**4**) (Me = methyl and cy = cyclohexyl). It has been possible to perform stepwise substitution of Br^- in $[cAAC^{cy}\cdot HgBr(\mu\text{-}Br)]_2$ with NO_3^- leading to the isolation and characterization of the mononitrate species, $cAAC^{cy}\cdot HgBr(NO_3)$ (**5**) and the dinitrate compound $[cAAC^{cy}\cdot Hg(NO_3)(\mu\text{-}NO_3)]_2$ (**6**). The cationic mercury species, $[(cAAC^{Me})_2Hg(NO_3)]^+[NO_3]^-$ (**7**) has also been synthesized by the reaction of adduct, $[cAAC^{Me}\cdot HgBr(\mu\text{-}Br)]_2$ with 2 eq. of $AgNO_3$. On reaction of $[cAAC^{cy}\cdot HgCl(\mu\text{-}Cl)]_2$ (**2**) with $AgClO_4$, only one chlorine could be substituted by perchlorate resulting in the formation of chlorine bridged dimeric complex, $[cAAC^{cy}\cdot Hg(ClO_4)(\mu\text{-}Cl)]_2$ (**8**). On performing the reaction between $cAAC^{cy}$ and $HgCl_2$ in 2:3 relative stoichiometry, a dicationic mercury species $[(cAAC^{yc})_2Hg]^{2+}[Hg_2Cl_6]^{2-}$ (**9**) was isolated in moderate yield.

1. Introduction

The facile synthesis of N-heterocyclic carbenes (NHCs), bis(amino)cyclopropenylidenes (BACs), and cyclic (alkyl)(amino)carbenes (cAACs) have led to enormous development in the area of metal carbene chemistry [1]. The first metal N-heterocyclic carbene complex reported [2], $(Ph_2\text{-}NHC)_2Hg]^{2+}2[ClO_4]^-$ was of an element from group 12 and subsequently a rapid development with adducts of carbenes with metals from other groups of the periodic table was witnessed. Among the elements from group 12, the nontoxic Zn has gained some attention whereas, the carbene adducts of heavier elements, Cd and Hg are less developed perhaps due to toxicity associated with these elements [3]. In this context, Roesky and coworkers (2012) demonstrated the use of cAACs as a potential ligand to stabilize Zn complexes such as the adduct $(cAAC)ZnCl_2$, a singlet biradicaloid $(cAAC)_2Zn$ and the hydrogenated complex $(cAACH)_2Zn$ (Fig. 1) [4]. Synthesis and characterization of neutral and cationic cAAC-Hg(II) adducts (Fig. 1) and their application in intermolecular hydroamination between phenylacetylenes and anilines [5] prompted us to investigate this area further. In this endeavor, we noticed that the routes for the synthesis of NHC–Hg(II) complexes needed subtle modifications when applied to the synthesis of cAAC-Hg(II) complexes [6]. Therefore, the strategy used to synthesize neutral (HgO route) and cationic complexes ($Hg(OAc)_2$ route) of NHC–Hg(II) could not be applied to synthesize similar cAAC adducts of Hg(II) [5,6]. These cAAC-Hg(II) adducts are obtained by the treatment of *in-situ* generated carbene with the HgX_2 salts. To extend the chemistry of neutral and cationic cAAC-Hg(II) adducts herein we report on the syntheses and characterization of several new cAAC complexes, $[cAAC^{Me}\cdot HgCl(\mu\text{-}Cl)]_2$ **(1)**, $[cAAC^{cy}\cdot HgCl(\mu\text{-}Cl)]_2$ **(2)**, $[cAAC^{Me}\cdot HgI(\mu\text{-}I)]_2$ **(3)** and $[cAAC^{cy}\cdot HgI(\mu\text{-}I)]_2$ **(4)**, $cAAC^{cy}\cdot HgBr(NO_3)$ (**5**), $[cAAC^{cy}\cdot Hg(NO_3)(\mu\text{-}NO_3)]_2$ (**6**), $[(cAAC^{Me})_2Hg(NO_3)]^+[NO_3]^-$ (**7**), $[cAAC^{cy}\cdot Hg(ClO_4)(\mu\text{-}Cl)]_2$ (**8**) and $[(cAAC^{cy})_2Hg]^{2+}[Hg_2Cl_6]^{2-}$ (**9**). **Caution!** Organomercury compounds are highly toxic. All necessary care in handling mercury compounds must be exercised.

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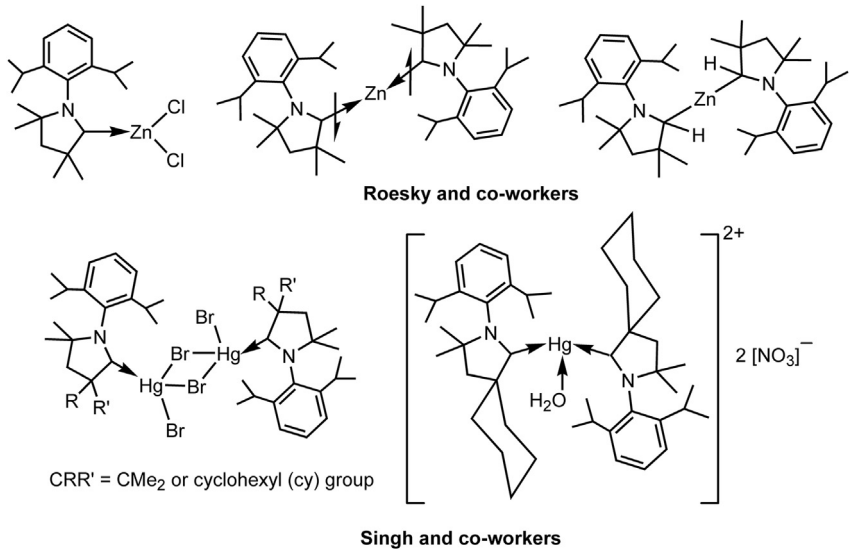


Fig. 1. Known complexes of cAACs with group 12 elements.

2. Experimental section

2.1. General consideration

All manipulations were performed under nitrogen/argon atmosphere using Schlenk line or glove box. All chemicals were purchased from Sigma-Aldrich and used without further purification. Cyclic (alkyl)(amino)carbenes, $cAAC^{Me}$ and $cAAC^{cy}$ were prepared using reported procedure [7]. FT-IR spectra of complexes **1**–**9** were recorded (in the range 4000–400 cm^{-1}) with a Perkin–Elmer Lambda 35-spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer with TMS as external reference; chemical shift values are reported in ppm. High-resolution mass spectrometry was performed with Waters SYNAPT G2-S.

Caution: Organomercury compounds are highly toxic. While handling these compounds, protective neoprene gloves should be worn and an efficient hood must be used. Residues and wastes containing mercury should be disposed off according to local regulations.

2.2. Syntheses

2.2.1. Synthesis of $[cAAC^{Me}{\cdot}HgCl(\mu\text{–}Cl)]_2$ (1)

A mixture of $[cAAC^{Me}H]^{+}Cl^{-}$ (0.44 g, 1.38 mmol) and K $[N(SiMe_3)_2]$ (0.28 g, 1.40 mmol) was taken in THF (25 mL). The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to a suspension of $HgCl_2$ (0.37 g, 1.38 mmol) in THF (5 mL). The mixture was stirred at room temperature for 3 h followed by filtration to obtain a white solid. This solid was further washed with THF (10 mL) to afford **1** as a white solid. Colorless crystals of **1** were grown from acetonitrile at room temperature. Yield: 0.55 g, 71.5%. Mp: 234–236 °C. IR (KBr, cm^{-1}) $\tilde{\nu}$: 2967, 2868, 1634, 1555, 1463, 1388, 1371,1320, 1203, 1125, 1050, 807, 776, 564.[1] H NMR (400 MHz, DMSO-d_6): $\delta = 7.50$ (t, 2H, *p*Ar-H, $^{3}J_{H-H} = 8$ Hz), 7.38 (d, 4H, *m*Ar-H, $^{3}J_{H-H} = 8$ Hz), 2.67 (sept, 4H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz), 2.24 (s, 4H, CH_2), 1.59 (s, 12H, CH_3), 1.41 (s, 12H, CH_3), 1.26 (d, 12H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz) 1.21 (d, 12H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 245.5$, 144.5, 132.8, 130.6, 125.5, 123.7, 84.4, 54.7, 48.2, 28.6, 28.4, 27.3, 26.5, 23.5. HRMS (ES^{+}): *m/z* calcd for $C_{40}H_{62}N_2Hg_2Cl_3$: 1079.3512: $[M - Cl]^{+}$; found: 1079.3481.

2.2.2. Synthesis of $[cAAC^{cy}{\cdot}HgCl(\mu\text{-}Cl)]_2$ (2)

A mixture of $[cAAC^{cy}H]^{+}Cl^{-}$ (0.49 g, 1.38 mmol) and K $[N(SiMe_3)_2]$ (0.28 g, 1.40 mmol) was taken in THF (25 mL). The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to a suspension of $HgCl_2$ (0.37 g, 1.38 mmol) in THF (5 mL). The mixture was stirred at room temperature for 3 h followed by filtration to obtain a white solid. This solid was further washed with THF (10 mL) to afford **2** as a white solid. Colorless crystals of **2** were grown from acetonitrile at room temperature. Yield: 0.56 g, 67.9%. Mp: 268–271 °C. IR (KBr, cm^{-1}) $\tilde{\nu}$: 2972, 2931, 2863, 1595, 1462, 1445, 1387, 1264, 1138, 1110, 1049, 933, 810, 776.[1] H NMR (400 MHz, DMSO-d_6): $\delta = 7.51$ (t, 2H, *p*Ar-H, $^{3}J_{H-H} = 8$ Hz), 7.40 (d, 4H, *m*Ar-H, $^{3}J_{H-H} = 8$ Hz), 2.69 (sept, 4H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz), 2.33 (s, 4H, CH_2), 1.50–2.0 (m, 10H, cy), 1.42 (s, 12H, CH_3), 1.25 (d, 12H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz) 1.19 (d, 12H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 245.0$, 145.2, 132.6, 131.1, 126.4, 86.5, 58.9, 43.7, 35.7, 29.0, 28.4, 26.4, 24.9, 23.2, 21.0. HRMS (AP^{+}): *m/z* calcd for $C_{46}H_{70}N_2Hg_2Cl_3$: 1159.3993: $[M - Cl]^{+}$; found: 1159.3987.

2.2.3. Synthesis of $[cAAC^{Me}{\cdot}HgI(\mu\text{–}I)]_2$ (3)

Synthesis of **3** was performed in a manner similar to that for **1**. Quantity of reagents used were $[cAAC^{Me}H]^{+}Cl^{-}$ (0.44 g, 1.38 mmol), $K[N(SiMe_3)_2]$ (0.28 g, 1.40 mmol) and HgI_2 (0.63 g, 1.38 mmol). Colorless crystals of **3** were grown from acetonitrile at room temperature. Yield: 0.59 g, 72.5%. Mp: 260–263 °C. IR (KBr, cm^{-1}) $\tilde{\nu}$: 2968, 2928, 2872, 1550, 1458, 1390, 1370, 1321, 1205, 1125, 803, 775, 562. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.51$ (t, 2H, *p*Ar-H, $^{3}J_{H-H} = 8$ Hz), 7.40 (d, 4H, *m*Ar–H, $^{3}J_{H-H} = 8$ Hz), 2.68 (sept, 4H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz), 2.26 (s, 4H, CH_2), 1.59 (s, 12H, CH_3), 1.43 (d, 12H, CH_3), 1.27 (d, 12H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz), 1.23 (d, 12H, $CH(CH_3)_2$, $^{3}J_{H-H} = 8$ Hz). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 144.5$, 132.8, 130.7, 125.7, 84.6, 54.7, 48.4, 28.6, 28.4, 27.2, 26.5, 23.5. HRMS (ES^{+}): *m/z* calcd for $C_{40}H_{62}Hg_2N_2I_3$: 1353.1450: $[M - I]^{+}$; found: 1353.1472.

2.2.4. Synthesis of $[cAAC^{cy}{\cdot}HgI(\mu\text{–}I)]_2$ (4)

Synthesis of **4** was performed in a manner similar to that for **2**. Quantity of reagents used were $[cAAC^{cy}H]^{+}Cl^{-}$ (0.49 g, 1.38 mmol),

$K[N(SiMe_3)_2]$ (0.28 g, 1.40 mmol) and HgI_2 (0.63 g, 1.38 mmol). Colorless crystals of **4** were grown from acetonitrile at room temperature. Yield: 0.78 g, 72.4%. Mp: 263–265 °C. IR (KBr, cm^{-1}) $\tilde{\nu}$: 2972, 2931, 2859, 1548, 1462, 1445, 1391, 1370, 1264, 1141, 1107, 1052, 933, 806, 772.[1] H NMR (400 MHz, DMSO-d_6): $\delta = 7.50$ (t, 2H, *p*Ar-H, $^3J_{H-H} = 8$ Hz), 7.40 (d, 4H, *m*Ar-H, $^3J_{H-H} = 8$ Hz), 2.69 (sept, 4H, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 2.32 (s, 4H, CH_2), 1.47–1.55 (m, cy), 1.63 (s, 6H, CH_3), 1.44 (s, 12H, CH_3), 1.25–1.23 (overlapped d, 24H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 144.3$, 132.9, 130.6, 125.7, 83.8, 60.1, 44.1, 33.4, 29.1, 28.3, 26.9, 24.5, 23.8, 21.2. HRMS (ES^+): *m/z* calcd for $C_{46}H_{70}N_2Hg_2I_3$: 1433.2078: $[M-I]^+$; found: 1433.2101.

2.2.5. Synthesis of $cAAC^{cy}{\cdot}HgBr(NO_3)$ (**5**) and $[cAAC^{cy}{\cdot}Hg(NO_3)(\mu\text{-}NO_3)]_2$ (**6**)

A mixture of $[cAAC^{cy}{\cdot}HgBr(\mu\text{-}Br)]_2$ (0.69 g, 1.00 mmol) and $AgNO_3$ (0.34 g, 2.00 mmol) was taken in THF (30 mL). The resulting suspension was stirred at room temperature for 2 h. The mixture was filtered, and the clear filtrate was concentrated (15 mL) and kept at room temperature for crystallization to afford mixture of colorless crystals of **5** and **6**. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (m, *p*Ar–H, $^3J_{H-H} = 8$ Hz), 7.43 (d, *m*Ar–H, $^3J_{H-H} = 8$ Hz), 7.36 (d, *m*Ar–H, $^3J_{H-H} = 8$ Hz), 2.80 (sept, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 2.69 (sept, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 2.43 (s, CH_2), 2.32 (s, CH_2), 2.00–1.30 (m, cy), 1.58 (s, CH_3), 1.53 (s, CH_3), 1.35 (d, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 1.30 (d, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 1.27 (d, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 1.09 (d, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 241.7$, 145.9, 144.8, 133.1, 132.7, 132.0, 131.9, 126.7, 126.3, 86.9, 84.9, 59.7, 59.3, 36.4, 33.7, 30.0, 29.7, 29.4, 29.3, 21.2, 27.1, 23.6, 21.4, 21.4. HRMS (ES^+): *m/z* calcd for **5**: $C_{23}H_{35}BrHgN$: 606.1644 $[M\text{-}NO_3^-]^+$; found: 606.1661; *m/z* calcd for **6**: $C_{46}H_{69}Hg_2N_5O_9$: 1237.4501 $[M\text{-}H\text{–}NO_3^-]^+$; found: 1237.4539.

2.2.6. Synthesis of $[(cAAC^{Me})_2Hg(NO_3)]^+[NO_3]^-$ (**7**)

A mixture of $[cAAC^{Me}{\cdot}HgBr(\mu\text{-}Br)]_2$ (0.65 g, 1.00 mmol) and $AgNO_3$ (0.34 g, 2.00 mmol) was taken in THF (30 mL). The resulting suspension was stirred at room temperature for overnight. The mixture was filtered, and the clear filtrate was concentrated (10 mL) and kept at room temperature for crystallization to afford colorless crystals of **7**. Yield: 0.11 g, 24.6%. Mp: 237–240 °C. IR (KBr, cm^{-1}) $\tilde{\nu}$: 2971, 1509, 1461, 1385, 1273, 1205, 1131, 1023, 978, 809, 777.[1] H NMR (400 MHz, DMSO-d_6): $\delta = 7.59$ (t, 2H, *p*Ar-H, $^3J_{H-H} = 8$ Hz), 7.48 (d, 4H, *m*Ar-H, $^3J_{H-H} = 8$ Hz), 2.71 (sept, 4H, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 2.35 (s, 4H, CH_2), 1.55 (s, 12H, CH_3), 1.46 (s, 12H, CH_3), 1.27 (d, 12H, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 1.18 (d, 12H, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 144.5$, 132.7, 131.4, 126.1, 85.7, 67.1, 54.0, 39.5, 28.5, 26.5, 23.4, 23.2. HRMS (ES^+): *m/z* calcd for $C_{40}H_{63}HgN_4O_6$: 897.4462 $[M+H]^+$; found: 897.4433.

2.2.7. Synthesis of $[cAAC^{cy}{\cdot}Hg(ClO_4)(\mu\text{–}Cl)]_2$ (**8**)

A mixture of $[cAAC^{cy}{\cdot}HgCl(\mu\text{–}Cl)]_2$ (**2**) (0.59 g, 1.00 mmol) and $AgClO_4$ (0.20 g, 1.00 mmol) was taken in THF (30 mL). The resulting suspension was stirred at room temperature for overnight. The mixture was filtered, and the residue was dissolved in acetonitrile for crystallization. Colorless crystals of **8** were obtained from acetonitrile at room temperature after 3 days. Yield: 0.38 g, 57.48%. Mp: 292–294 °C. IR (KBr, cm^{-1}) $\tilde{\nu}$: 2969, 2932, 2862, 1594, 1456, 1145, 1093, 931, 809, 626.[1] H NMR (400 MHz, DMSO–d_6): $\delta = 7.61$ (t, 2H, *p*Ar–H, $^3J_{H-H} = 8$ Hz), 7.49 (d, 4H, *m*Ar–H, $^3J_{H-H} = 8$ Hz), 2.71 (sept, 4H, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 2.41 (s, 4H, CH_2), 1.56–2.29 (m, 10H, cy), 1.46 (s, 12H, CH_3), 1.29 (d, 12H, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 1.19 (d, 12H, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz). ^{13}C NMR (100 MHz, DMSO–d_6): $\delta = 252.2$, 161.9, 150.2, 148.9, 143.4, 102.4, 84.5, 76.2, 60.8, 50.0, 46.4, 45.7, 43.8, 41.8, 40.6, 38.3. HRMS (ES^+): *m/z* calcd for $C_{23}H_{35}NHgCl$: 562.2158: $[M\text{–}ClO_4]^{2+}$; found: 562.2134. Attempts to substitute all chlorines in **2** with perchlorate using higher equivalents of $AgClO_4$ afforded compound **8** only.

2.2.8. Synthesis of $[(cAAC^{cy})_2Hg]^{2+}[Hg_2Cl_6]^{2-}$ (**9**)

A mixture of $[cAAC^{cy}H]^+Cl^-$ (0.18 g, 0.50 mmol) and $K[N(SiMe_3)_2]$ (0.10 g, 0.50 mmol) was taken in THF (15 mL). The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to a suspension of $HgCl_2$ (0.20 g, 0.75 mmol) in THF (5 mL). The mixture was stirred at room temperature for 3 h followed by filtration to obtain a white solid. This solid was further washed with THF (10 mL) to afford **9** as a white solid. Colorless crystals of **9** were grown from acetonitrile at room temperature. Yield: 0.40 g, 54.6%. Mp: 257–260 °C. IR (KBr, cm^{-1}) $\tilde{\nu}$: 2973, 2836, 2862, 1596, 1450, 1385, 1321, 1267, 1135, 1047, 938, 811, 778, 593, 558. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.63$ (t, 2H, *p*Ar-H, $^3J_{H-H} = 8$ Hz), 7.57 (d, 4H, *m*Ar-H, $^3J_{H-H} = 8$ Hz), 2.75 (sept, 4H, $CH(CH_3)_2$, $^3J_{H-H} = 8$ Hz), 2.33 (s, 4H, CH_2), 1.69–1.49 (m, 12H, cy), 1.45 (s, 12H, CH_3), 1.26-1.23 (m, 24H, $CH(CH_3)_2$), 1.11–1.06 (m, 6H, cy), 0.82–0.73 (m, 2H, cy). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 243.5$, 145.0, 132.5, 131.3, 126.4, 86.8, 67.0, 58.7, 43.5, 35.4, 28.9, 28.3, 28.2, 25.1, 24.6, 24.2, 20.8. HRMS (ES^-): *m/z* calcd for $HgCl_3$: 306.8745: $[Hg_2Cl_6]^{2-}$; found: 306.8730; (ES^+): *m/z* calcd for $C_{46}H_{70}HgN_2Cl$: 887.4932: $[M - Hg_2Cl_5]^+$; found: 887.4891.

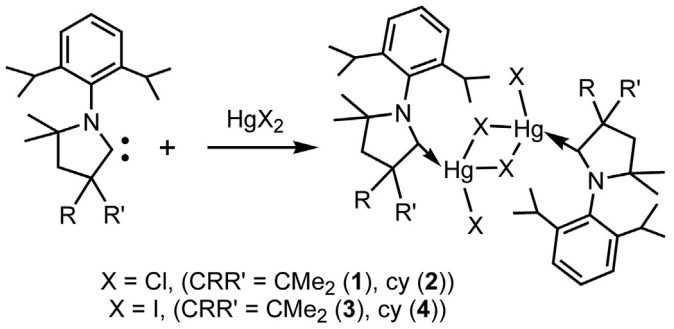
2.3. Single crystal X-ray structural characterization of compounds **1**–**9**

Single crystal X-ray diffraction data of **1, 3, 4, 6** and **8** were collected on a Bruker AXS KAPPA APEX-II CCD diffractometer with MoKα radiation using omega scans equipped with Oxford Cryosystem 700 plus with a sample to detector distance of 6 cm with variable position of the detector. Unit cell determination and refinement and data collection were done using the Bruker APPEX-II suite [8], data reduction and integration were performed using SAINT v8.34 A (Bruker, 2013) [9] and absorption corrections and scaling were done using SADABS-2014/5 (Bruker, 2014/5) [10]. Single crystal X-ray diffraction data of **2**, **5, 7** and **9** were collected using a Rigaku XtaLAB mini diffractometer equipped with Mercury375 M CCD detector. The data were collected with MoKα radiation (λ = 0.71073 Å) using omega scans. During the data collection, the detector distance was 49.9 mm (constant) and the detector was placed at 2θ = 29.85° (fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite [11]. All the crystal structures were solved through OLEX2 [12] package using XT [13] and the structures were refined using XL [13]. All non-hydrogen atoms were refined anisotropically. All figures were generated using Mercury. One of the two isopropyl groups, five membered carbene ring and nitrate groups in **7** were found to be disordered. These disordered atoms were refined with appropriate use of PART and EADP commands. The geometric data reported here are taken from the CIF.

3. Results and discussion

3.1. Synthesis and characterization of complexes **1**–**9**

To highlight any resemblance or disparity in the synthesis, structure and properties of NHC–Hg(II)X_2 complexes (X = Cl and I), with that of cAAC-Hg(II)X_2 complexes, we have prepared the complexes, $[cAAC^{Me}HgCl(\mu\text{-}Cl)]_2$ (**1**), $[cAAC^{cy}{\cdot}HgCl(\mu\text{-}Cl)]_2$ (**2**), $[cAAC^{Me}{\cdot}HgI(\mu\text{-}I)]_2$ (**3**) and $[cAAC^{cy}{\cdot}HgI(\mu\text{-}I)]_2$ (**4**) based on carbenes $cAAC^{Me}$ and $cAAC^{cy}$ (Me = methyl and cy = cyclohexyl) and these complexes were found to be halide bridged dimers in the



Scheme 1. Syntheses of $[cAAC^{Me/cy}{\cdot}HgX(\mu\text{-}X)]_2$ adducts (**1**–**4**).

solid state. Complexes **1**–**4** were synthesized by the reaction of *in-situ* generated $cAAC^{Me}$ and $cAAC^{cy}$ carbenes with an equimolar amount of HgX_2 salts (X = Cl and I) (Scheme 1). The formation of these complexes was apparent by downfield shifted signal for the carbene carbon in ^{13}C NMR spectra for **1** and **2** (≈245 ppm) when compared to the free carbenes (312 ppm for $cAAC^{Me}$ and 316 ppm for $cAAC^{cy}$), the corresponding signals for **3** and **4** were not observed.

The features in the ^{1}H NMR spectra of **1**–**4** were in accordance with the expected adducts. The HRMS spectra of these complexes revealed their dimeric nature due to signals at *m/z* = 1079.3481 (calcd. 1079.3512 for $[M - Cl]^+$) (**1**), 1159.3987 (calcd. 1159.3993 for $[M - Cl]^+$) (**2**), 1353.1472 (calcd. 1353.1450 for $[M - I]^+$) (**3**) and 1433.2101 (calcd. 1433.2078 for $[M - I]^+$) (**4**).

The unambiguous composition of compounds **1**–**4** have been confirmed by single crystal X-ray structural analysis (Fig. 2, Table S1 in ESI). Crystals suitable for X-ray diffraction of complexes **1**–**4** were grown from acetonitrile at room temperature and these complexes were found to crystallize in monoclinic system with $P2_1/n$ ($P2_1/c$ for **2**) space group. All these complexes formed halide bridged dihalomercury(II) structures, $[cAAC^{Me/cy}{\cdot}HgX(\mu\text{-}X)]_2$ (X = Cl (**1** & **2**) and I (**3** & **4**)) in their solid state (Fig. 2). Mercury atoms in these complexes adopt distorted tetrahedral geometry consisting of one cAAC unit, a terminal and two bridged halides X. The C—Hg bond distances (2.1205(5) (**1**), 2.120(5) (**2**), 2.162(4) (**3**), 2.170(5) Å (**4**)) for these complexes were comparable to their bromide analogs, $[cAAC^{Me}{\cdot}HgBr(\mu\text{-}Br)]_2$ (2.163(7) Å) and $[cAAC^{cy}{\cdot}HgBr(\mu\text{-}Br)]_2$ (2.144(3) Å) complexes [5]. In all these complexes, the bridging Hg–X distances (2.6936(13) (**1**), 2.7128(13) (**2**), 2.9347(3) (**3**) and 2.9525(4) Å (**4**)) were, as expected, longer than the terminal Hg-X distances (2.3829(14) (**1**), 2.3793(13) (**2**), 2.6849(4) (**3**) and 2.6960(4) Å (**4**)). It has been previously observed that NHCs form mononuclear $NHC{\cdot}Hg(II)Cl_2$ and dimeric $[NHC{\cdot}HgI(\mu\text{-}I)]_2$ complexes [6] whereas with cAACs, the HgX_2 salts (X = Cl, Br and I) formed dimers $[cAAC^{Me/cy}{\cdot}HgX(\mu\text{-}X)]_2$. NHCs are predicted to be less electrophilic than cAACs, the dimeric nature of $Hg(II)Cl_2$ complexes **1** and **2** indicate relatively weaker donation from cAAC allowing Hg(II) to increase its coordination number to satisfy its electronic demand. The dimeric nature of $Hg(II)I_2$ complexes with cAAC, **3** and **4** were similar to those found for Hg(II)—NHC complexes [6].

Recently, we showed the reaction of $[cAAC^{cy}{\cdot}HgBr(\mu\text{-}Br)]_2$ with $AgNO_3$ affords a dicationic Hg(II) complex, $[(cAAC^{cy})_2Hg(H_2O)]^{2+}2[NO_3]^-$ [5]. On further elaboration of this work, it was observed that the reaction proceeds through the formation of mercury mononitrate, $cAAC^{cy}{\cdot}HgBr(NO_3)$ (**5**) and dinitrate complex, $[cAAC^{cy}{\cdot}Hg(NO_3)(\mu\text{-}NO_3)]_2$ (**6**) (Scheme 2). Complexes **5** and **6** were obtained as a mixture that could not be separated. The ^{1}H NMR spectrum of this mixture showed two doublets and a merged triplet in aromatic region whereas the aliphatic region clearly showed two septets and their corresponding doublets (for isopropyl groups on cAAC) indicating the presence of two complexes. Continuing the reaction for a longer period (nearly 14 h) led to the isolation of reported dicationic species, $[(cAAC^{cy})_2Hg(H_2O)]^{2+}2[NO_3]^-$ [5]. The formation of **5** and **6** was also seen by HRMS spectra with signal *at m/z* 606.1661 (calcd. 606.1644 for $[M - NO_3]^+$) (**5**) and 1237.4539 (calcd. 1237.4501 for $[M\text{-}H\text{—}NO_3]^+$) (**6**) due to the loss of one nitrate ion from each.

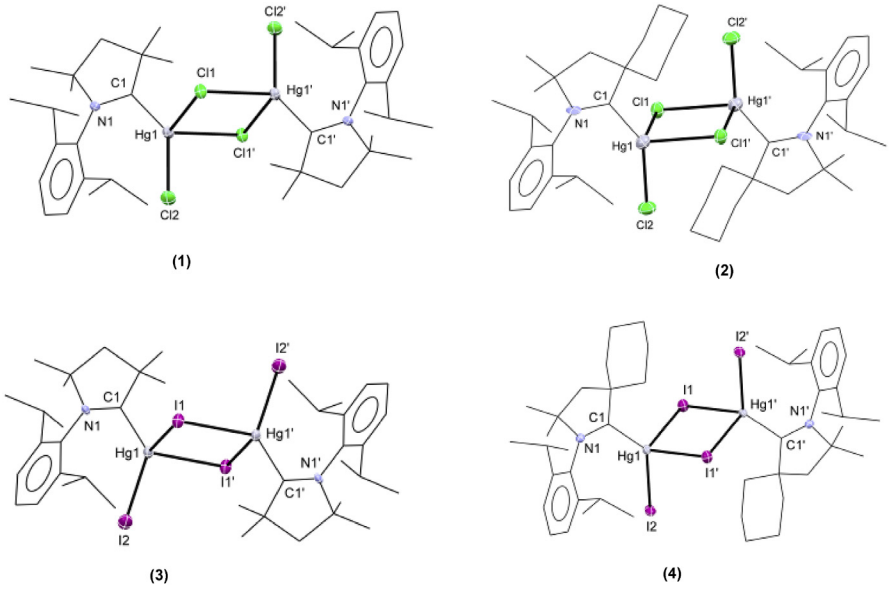
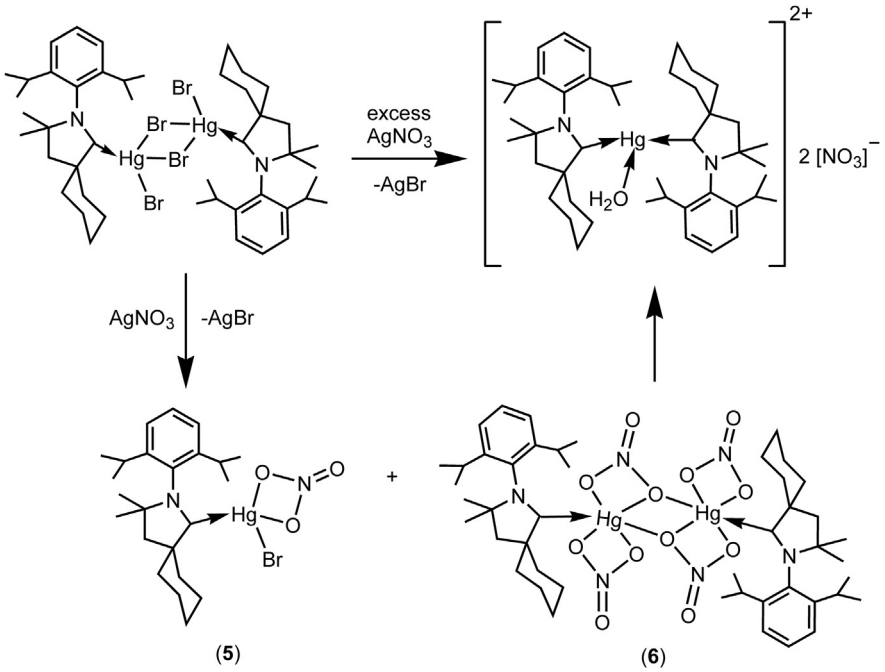


Fig. 2. Single crystal X–ray structures of $[cAAC^{Me}{\cdot}HgCl(\mu\text{-}Cl)]_2$ (**1**), $[cAAC^{cy}{\cdot}HgCl(\mu\text{-}Cl)]_2$ (**2**), $[cAAC^{Me}{\cdot}HgI(\mu\text{-}I)]_2$ (**3**) and $[cAAC^{cy}{\cdot}HgI(\mu\text{-}I)]_2$ (**4**). Ellipsoids are shown at 50% probability levels. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: for **1**: Hg1—Cl1 2.6936(13), Hg1—Cl2 2.3829(14), Hg1—C1 2.120(5); Cl1—Hg1—Cl1′ 87.85(4), Hg1—Cl1—Hg1′ 92.15(4), Cl1—Hg1—Cl2 98.09(5), C1—Hg1—Cl1 111.00(12), C1—Hg1—Cl2 140.18(13); for **2**: Hg1—Cl1 2.7128(13), Hg1—Cl2 2.3793(14), Hg1—C1 2.120(5); Cl1—Hg1—Cl1′ 84.29(4), Hg1—Cl1—Hg1′ 95.71(4), Cl1—Hg1—Cl2 97.68(5), C1—Hg1—Cl1 113.12(13), C1—Hg1—Cl2 141.57(13); for **3**: Hg1—I1 2.9347(3), Hg1—I2 2.6849(4), Hg1—C1 2.162(4); I1—Hg1—I1′ 91.303(9), Hg1—I1—Hg1′ 88.697(9), I1—Hg1—I2 100.513(11), C1—Hg1—I1 111.39(10), C1—Hg1—I2 132.94(11); for **4**: Hg1—I1 2.9525(4), Hg1—I2 2.6960(4), Hg1—C1 2.170(5); I1—Hg1—I1′ 91.210(11), Hg1—I1—Hg1′ 88.790(11), I1—Hg1—I2 100.058(13), C1—Hg1—I1 111.38(11), C1—Hg1—I2 134.50(13).



Scheme 2. Syntheses of cAAC^{cy}·HgBr(NO_3) (**5**) and [cAAC^{cy}·Hg(NO_3)(μ-NO_3)]$_2$ (**6**).

The X-ray quality crystals of complexes **5** and **6** were grown from THF at room temperature. Complexes **5** and **6** were found to crystallize in orthorhombic and triclinic system with $P2_12_12_1$ and $P\bar{1}$ space group, respectively (Table S2 in ESI). The structure of complex **5** in the solid state shows that mercury is tetracoordinated and connected to a cAAC^{cy} unit, a bromide and a bidentate nitrate group (Fig. 3). The structure of complex **6** was observed as a dimer containing two hexacoordinated mercury centers bridged by two nitrate groups (Fig. 4). The C–Hg bond distances for complex **5** (2.080(11) and **6** (2.068(4) Å) are similar to that reported for dicationic species, [(cAAC^{cy})$_2$Hg(H_2O)]$^{2+}$2[NO_3]$^-$ (2.072(4) Å) and [(NHC)$_2$Hg]$^{2+}$ 2.073(6) Å, whereas, slightly shorter than that reported for complexes, [cAAC^{cy}·HgBr(μ-Br)]$_2$ (2.144(3) Å) [5,14,15] and **1**–**4**.

In view of limited methods available to synthesize dicationic bis(NHC) mercury salts, [(NHC)$_2$Hg]$^{2+}$ we were prompted to explore the syntheses and properties of similar dications using cAACs (see Scheme 2). Known procedures in such transformations involve either the reaction of mercury acetate with an imidazolium salt or a free NHC with a mercury(II) salt [2a,b,14,15]. Recently, we found that the mercury acetate route could not afford the bis(cAAC) salts, [(cAAC)$_2$Hg]$^{2+}$ therefore we adopted an alternate salt metathesis route to synthesize three coordinated dicationic species [(cAAC^{cy})$_2$Hg(H_2O)]$^{2+}$2[NO_3]$^-$ by reacting the adduct [cAAC^{cy}·HgBr(μ-Br)]$_2$ with $AgNO_3$ in THF. Following our work in this area we treated the adduct [cAAC^{Me}·HgBr(μ-Br)]$_2$ with $AgNO_3$ in THF to afford a cationic Hg(II) species, [(cAAC^{Me})$_2$Hg(NO_3)]$^+$[NO_3]$^-$ (**7**) (Scheme 3).

Formation of AgBr was observed in this route and upon filtration and concentration of the mother liquor colorless crystals of the cationic complex [(cAAC^{Me})$_2$Hg(NO_3)]$^+$[NO_3]$^-$ (**7**) were obtained. The ^{1}H NMR and ^{13}C NMR spectra of **7** in DMSO-d_6 showed the expected signals for cAAC^{Me} however, the carbene carbon signal could not be observed in its ^{13}C NMR spectrum. The HRMS spectrum for **7** showed a fragment for the cation at *m/z* 897.4433 (calcd. 897.4462 for [M+H]$^+$).

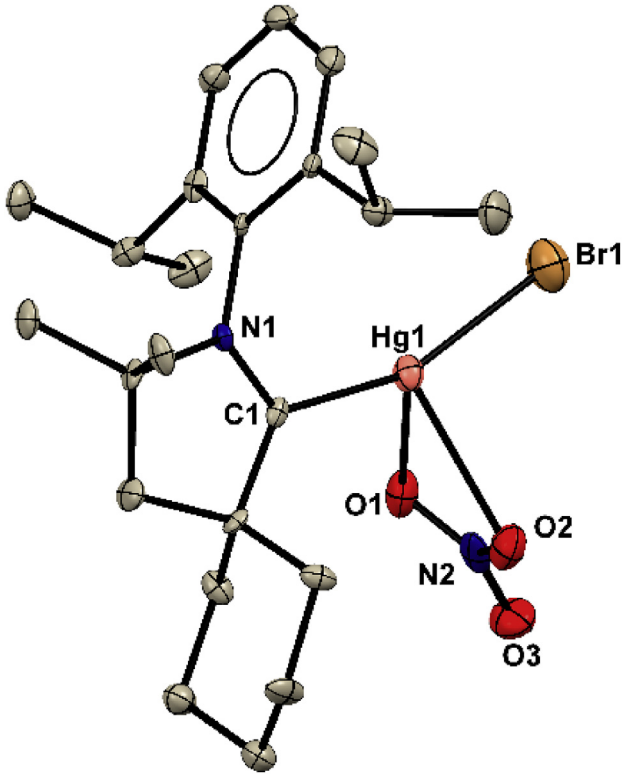


Fig. 3. Single crystal X–ray structure of cAAC^{cy}·HgBr(NO_3) (**5**). Ellipsoids are shown at 50% probability levels. THF molecule present in the lattice and all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg1–Br1 2.4341(14), Hg1–C1 2.080(11), Hg1–O1 2.556(9), Hg1–O2 2.568(8); C1–Hg1–Br1 159.0(3), O1–Hg1–O2 49.2(3), Br1–Hg1–O1 91.13(19), Br1–Hg1–O2 92.14(19), C1–Hg1–O1 107.1(3), C1–Hg1–O2 107.7(3).

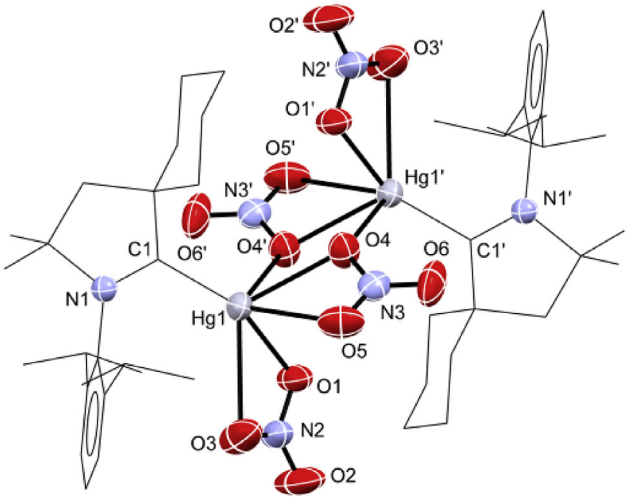


Fig. 4. Single crystal X–ray structure of $[cAAC^{cy}\cdot Hg(NO_3)(\mu\text{-}NO_3)]_2$ (**6**). Ellipsoids are shown at 50% probability levels. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg1–O1 2.143(3), Hg1–O4 2.518(3), Hg1–C1 2.068(4), O1–N2 1.312(5), O2–N2 1.212(6), O3–N2 1.201(6), O4–N3 1.272(5), O5–N3 1.240(6), O6–N3 1.214(5); O1–Hg1–O4 84.30(13), O1–Hg1–O4′ 75.59(12), O4–Hg1–O4′ 63.70(12), C1–Hg1–O1 157.98(16), C1–Hg1–O4 110.08(13), C1–Hg1–O4′ 117.50(14), N2–O1–Hg1 109.1(3), Hg1–O4–Hg1′ 116.30(11), N3–O4–Hg1 127.3(3).

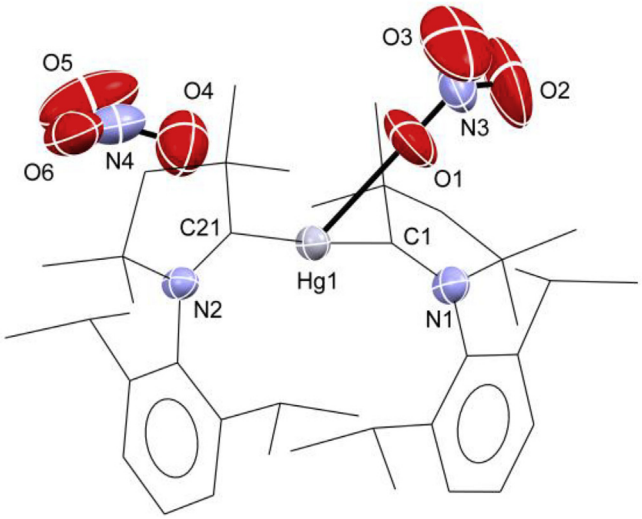
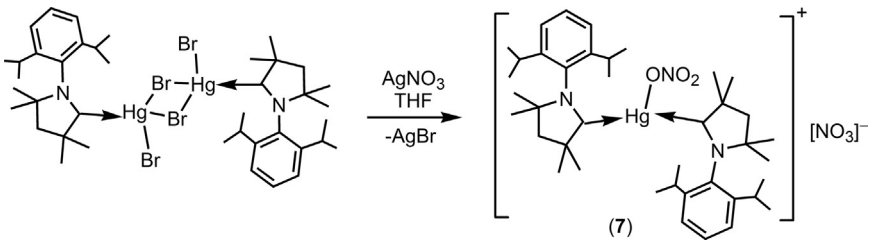


Fig. 5. Single X–ray crystal structure of $[(cAAC^{Me})_2Hg(NO_3)]^+[NO_3]^-$ (**7**). Ellipsoids have been shown at 50% probability levels. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg1–C1 2.087(5), Hg1–C21 2.100(4), Hg1–O1 2.637(5); C1–Hg1–C21 174.69(18), C1–Hg1–O1 79.6(2), C21–Hg1–O1 98.7(2). Only the major component of the disordered parts of the molecule are depicted here.

Crystals suitable for X-ray diffraction of complex **7** were grown from THF at room temperature. Crystal data for **7** were collected at 298 K and was found to crystallize in monoclinic system with $P2_1/c$ space group (Table S2 in ESI). The crystal structure of **7** indicated the formation of a cationic three coordinated Hg(II) complex with one NO_3^- connected to Hg(II) and other as a counter anion. The Hg(II) centre was coordinated with two $cAAC^{Me}$ units in an almost linear fashion (Fig. 5) with the C1–Hg1–C21 bond angle (174.69(18)°) that compares well with the known cationic NHC–Hg(II) complexes [14c,14e,15d]. The C–Hg bond lengths in **7** are slightly shorter (2.087(5) Å) than that of precursor $[cAAC^{Me}\cdot HgBr(\mu\text{-}Br)]_2$ (2.163(7) Å) but similar to that reported for cationic NHC–Hg(II) complexes [14c,14e,15d]. The Hg1–O1 distance of 2.637(5) Å is longer than that known for Hg–O covalent bonds (2.0–2.4 Å) [16] and can be attributed as secondary bonding interactions in view of the sums of the van der Waals radii (Hg···O, 3.05 Å) [16].

In further attempts to prepare cationic Hg complexes *via* the substitution of Cl^- with weakly coordinating anions such as BF_4^- or ClO_4^-, the reaction between $[cAAC^{cy}\cdot HgCl(\mu\text{-}Cl)]_2$ (**2**) and $NaBF_4$ did not occur. However, the reaction between **2** and $AgClO_4$ was carried out that smoothly afforded a product that was characterized to be $[cAAC^{cy}\cdot Hg(ClO_4)(\mu\text{-}Cl)]_2$ (**8**). The ^{13}C NMR spectrum of this product showed the signal for carbene carbon at 252.2 ppm compared to that observed in **2** (245.0 ppm). Other signals in the ^1H and ^{13}C NMR spectra of this product were consistent with the carbene bound to Hg centre. The HRMS spectrum of this product showed the signal at *m/z* 562.2134 (calcd. 562.2158 for $[M - ClO_4]^{2+}$ corresponding to $[cAAC^{cy}\cdot HgCl)]_2$). The unambiguous composition of compound **8** was confirmed by single crystal X-ray structural analysis (Table S3 in ESI). Crystals suitable for X-ray diffraction of complex **8** were grown from acetonitrile at room temperature. Complex **8** was found to crystallize in the monoclinic system with $P2_1/c$ space group. Complex **8** formed chlorine bridged dimeric structure, $[cAAC^{cy}\cdot HgClO_4(\mu\text{-}Cl)]_2$ in the solid state (Fig. 6). Mercury atoms in this complex are tetracoordinated by connecting with one $cAAC^{cy}$ unit, an O-connected ClO_4^- and two bridged Cl^- groups. The C–Hg bond distances for complex **8** (2.068(6) Å) are comparable to that reported for dicationic species, $[(cAAC^{cy})_2Hg(H_2O)]^{2+}2[NO_3]^-$ (2.072(4) Å) and $[(NHC)Hg]^{2+}$ 2.073(6) Å, whereas, slightly shorter than that found in $[cAAC^{cy}\cdot HgBr(\mu\text{-}Br)]_2$ (2.144(3) Å) [5,14,15] and complexes **1**–**4**. The Hg–O distances found in **8** are 2.706(2) Å) which are much longer than the Hg–O covalent bonds and are better described as secondary bonding interactions in view of the sums of the van der Waals radii (Hg···O, 3.05 Å) [16].

The formation of HgX_4^{2-} or $Hg_2X_6^{2-}$ anions are common in the synthesis of complexes of HgX_2 salts particularly when the HgX_2 salts are used in excess [17]. In view of this, we thought of exploiting this approach to prepare cationic Hg(II) complexes by using more than one equivalents of $HgCl_2$ with an anticipation that



Scheme 3. Syntheses of $[(cAAC^{Me})_2Hg(NO_3)]^+[NO_3]^-$ **(7)**.

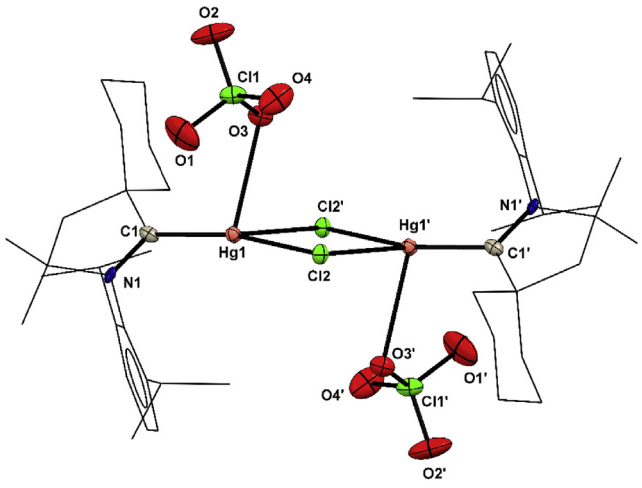


Fig. 6. Single crystal X–ray structure of $[cAAC^{cy}\cdot Hg(ClO_4)(\mu\text{-}Cl)]_2$ (**8**). Ellipsoids are shown at 50% probability levels. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg1–Cl2 2.3052(14), Hg1–Cl2′ 3.068(2), Hg1–C1 2.068(6), Hg1–O3 2.706(2); C1–Hg1–Cl2 167.64(15), Cl2–Hg1–Cl2′ 82.97(4), Hg1–Cl2–Hg1′ 97.03(3), Cl1–Hg1–O3 86.90(5), C1–Hg1–Cl2′ 104.22(1), C1–Hg1–O3 103.74(2).

chloride migration from the carbene bonded Hg(II) will facilitate the formation of ions such as $HgCl_4^{2-}$ or $Hg_2Cl_6^{2-}$. In this endeavour, on performing a reaction in 2:3 stoichiometry between $cAAC^{cy}$ and $HgCl_2$, we isolated complex $[(cAAC^{cy})_2Hg]^{2+}[Hg_2Cl_6]^{2-}$ (**9**) in moderate yield. The ^1H NMR spectrum of **9** showed the pattern expected for $cAAC^{cy}$ and the ^{13}C NMR spectrum of **9** showed the carbene carbon at 243.5 ppm. The ESI^- spectrum of **9** showed the signal for dianion at *m/z* 306.8730 (calcd. 306.8745) for $[Hg_2Cl_6]^{2-}$ later confirmed by X-ray structure. The ESI^+ spectrum of **9** showed the signal at *m/z* 887.4891 (calcd. 887.4932 for $[M - Hg_2Cl_5]^+$. Crystals suitable for X-ray diffraction of complex **9** were grown from acetonitrile at room temperature. Crystal data for **9** were collected at 100.0(2) K and it was found to crystallize in the orthorhombic system with $P2_12_12_1$ space group (Table S3 in ESI). The crystal structure of **9** confirmed its composition as $[(cAAC^{cy})_2Hg]^{2+}[Hg_2Cl_6]^{2-}$ in agreement with the data obtained from HRMS. The mercury atom in the dicationic moiety $[(cAAC^{cy})_2Hg]^{2+}$ was coordinated with two $cAAC^{cy}$ units in a nearly linear geometry with the C1–Hg1–C1' bond angle of 178.0(10)° (Fig. 7) and the C–Hg bond distances are 2.079(7) Å. The counter ion $[Hg_2Cl_6]^{2-}$ adopts an overall edge shared bi-tetrahedral structure [17].

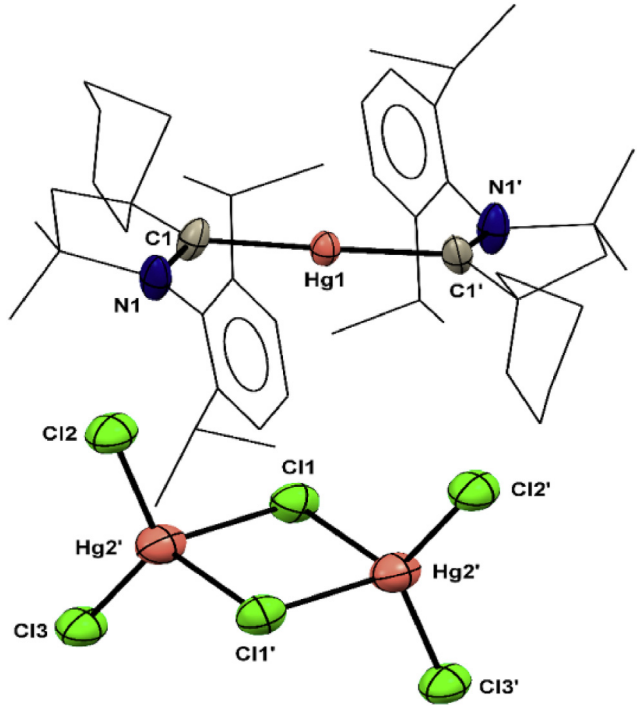


Fig. 7. Single crystal X–ray crystal structure of $[(cAAC^{cy})_2Hg]^{2+}[Hg_2Cl_6]^{2-}$ (**9**). Ellipsoids have been shown at 50% probability levels. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg1–C1 2.079(7), Hg2–Cl3 2.390(3), Hg2–Cl1′ 2.569(2), Hg2–Cl1 2.708(3), Hg2–Cl2 2.381(4), Cl1–Hg2 2.708(3); C1–Hg1–C1′ 178.0(10), Cl3–Hg2–Cl1 104.27(15), Cl3–Hg2–Cl1 111.13(15), Cl1–Hg2–Cl1 90.71(7), Cl2–Hg2–Cl3 127.48(10), Cl2–Hg2–Cl1 104.31(15), Cl2–Hg2–Cl1 111.58(15), Hg2–Cl1–Hg2 89.29(7).

4. Conclusions

In conclusion, the new derivatives of cAAC-Hg(II) complexes, $[cAAC^{Me}\cdot HgCl(\mu\text{-}Cl)]_2$ (**1**), $[cAAC^{cy}\cdot HgCl(\mu\text{-}Cl)]_2$ (**2**), $[cAAC^{Me}\cdot HgI(\mu\text{-}I)]_2$ (**3**) and $[cAAC^{cy}\cdot HgI(\mu\text{-}I)]_2$ (**4**) have been synthesized. In order to gain insights on the formation of previously reported Hg cation, *via* the reaction of $[cAAC^{cy}\cdot HgBr(\mu\text{-}Br)]_2$ with $AgNO_3$, led to the successful isolation of $cAAC^{cy}\cdot HgBr(NO_3)$ (**5**) and a dinitrate, $[cAAC^{cy}\cdot HgNO_3(\mu\text{-}NO_3)]_2$ (**6**) complex. Additionally, the cationic mercury species, $[(cAAC^{Me})_2Hg(NO_3)]^+[NO_3]^-$ (**7**) has also been synthesized by the reaction of $[cAAC^{Me}\cdot HgBr(\mu\text{-}Br)]_2$ with $AgNO_3$. Interestingly, only one chlorine in **2** could be substituted with perchlorate leading to the formation of a dimeric complex, $[cAAC^{cy}\cdot Hg(ClO_4)(\mu\text{-}Cl)]_2$ (**8**). It has also been possible to prepare two coordinated dicationic Hg(II) complex, $[(cAAC^{cy})_2Hg]^{2+}[Hg_2Cl_6]^{2-}$ (**9**) from a 2:3 stoichiometric reaction of $cAAC^{cy}$ and $HgCl_2$.

Caution

Organomercury compounds are highly toxic. While handling these compounds protective neoprene gloves should be worn and an efficient hood must be used. Residues and wastes containing mercury should be disposed off according to local regulations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.11.005.

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