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Mercury(II), copper(II) and silver(I) complexes with ether or diether functionalized bis-NHC ligands: synthesis and structural studies[†]

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The oligoether-linked dibenzimidazolium (or diimidazolium) salts, bis[2-(3-ethylbenzimidazolium-1-yl) ethyl]ether diiodide (1), bis[2-(3-"butylbenzimidazolium-1-yl)ethyl]ether diiodide (2), 1,1'-[1,2ethanediyl-bis(oxy-1.2-ethanediyl)]-bis(3-benzylbenzimidazolium-1-yl) diiodide (3), 1,1'-[1.2ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-ethylbenzimidazolium-1-yl) di-hexafluorophosphate (4), 1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-benzylimidazolium-1-yl) diiodide (5), and their five mercury(II), copper(II) and silver(I) complexes with ether or diether linkers mercury- $\{C, C'-bis[2-(3-(3-bis[2-(3-(3-(3-(3-)))))))))$ ethylimidazolin-2-yliden-1-yl)ethyl]ether} tetraiodomercurate (7), copper-{C,C'-bis[2- $(3-nbutylimidazolin-2-yliden-1-yl)ethyl]ether}$ tetraiodomercurate (8), mercury-{C,C'-1,1'-[1,2ethanediylbis(oxy-1,2-ethanediyl)]-bis(3-benzylbenzimidazolin-2-yliden-1-yl)} triiodomercurate acetate (9), silver-{C,C'-1,1'-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]-bis(3-ethylbenzimidazolin-2yliden-1-yl)} hexafluorophosphate (10) and mercury-{C,C'-1,1'-[1,2-ethanediylbis(oxy-1,2ethanediyl]]-bis(3-benzylimidazolin-2-yliden-1-yl)} tetraiodomercurate (11), as well as one anionic complex bis[2-(3-"butylbenzimidazolium-1-yl)ethyl]ether di- μ -iodo-bis(diiodomercurate) (6) were prepared and characterized. Each of N-heterocyclic carbene metal complexes 7-11 possesses a macrometallocycle, respectively, formed by one metal atom and one bidentate chelate carbene ligand. In the crystal packing of complexes 6–11, 2D supramolecular layers are formed *via* intermolecular weak interactions, including π - π interactions, hydrogen bonds, C-H··· π contacts and weak Hg···I bonds.

Introduction

The transition metal complexes of N-heterocyclic carbenes (NHCs) have attracted considerable interest over the past two decades due to their structural variety and easy access through deprotonation of N,N'-disubstituted benzimidazolium (or imidazolium) salts.¹ The strong σ -donating ability of N-heterocyclic carbenes lead to high stability of their metal complexes toward heat, moisture and air. More recently, much effort has also been devoted to the synthesis of functionalized NHC ligands and their metal complexes.² Among N-heterocyclic carbene ligands, some bis-NHC ligands with bridging linkers (such as alkyl,³ aryl,⁴ pyridyl and lutidinyl⁵) have been reported, and their metal complexes have also been investigated.

As ancillary ligands, N-heterocyclic carbenes are attractive alternative to the widely utilized phosphine ligands in organometallic catalysis. The NHC silver(I) and mercury(II) complexes have played important roles in the development of the Nheterocyclic carbene chemistry.⁶ Particularly, N-heterocyclic carbene silver(i) complexes can be used as carbene transfer reagents to make other NHC metal complexes.⁷ In contrast, few examples of the NHC copper(ii) complexes have been reported so far.⁸ Recently, some silver(i) and mercury(ii) complexes containing bidentate bis-NHC ligands with alkyl and durene linkers have been published by us.⁹ As a continuation, we reported herein the synthesis, structures and fluorescent emission spectra of five NHC mercury(ii), copper(ii) and silver(i) complexes 7–11 with ether or diether linkers, as well as one anionic complex 6.

Results and discussion

Synthesis and general characterization of precursors 1–5 and complexes 6–11

The dibenzimidazolium (or diimidazolium) salts, 1-3 and 5 were prepared from benzimidazole (or imidazole) by stepwise alkylation with 1-iodoalkane in the presence of NaH in THF at 60 °C for 48 h, followed by quarterization with 2,2'-diiododiethyl ether or 1,2-bis(2-iodoethoxy)ethane in sequence (Scheme 1). The precursor 4 was obtained by two steps. The first step is in a manner analogous to that for 1, and the second step is through

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Scheme 1 Preparation of precursors 1-5.

an anionic exchange with ammonium hexafluorophosphate in methanol (method 2 in Scheme 1(1)). Precursors **1–5** are stable to air and moisture, and show good solubility in polar organic solvents such as DMSO, CH₃CN and CH₂Cl₂, and almost insoluble in diethyl ether and petroleum ether. In the ¹H NMR spectra of **1–5**, the benzimidazolium (or imidazolium) proton signals (NCHN) appear at $\delta = 9.64$ –11.44 ppm, which are consistent with the chemical shifts of reported benzimidazolium (or imidazolium) salts.²

Synthetic methods of complexes 6-11 are shown in Scheme 2. The reaction of precursor 2 with HgI₂ in DMSO/CH₃CN gave an anionic complex 6 (Scheme 2 (1)). Treatment of 1 or 5 with HgI_2 in DMSO/CH₃CN in the presence of KOtBu afforded NHCmercury(II) complexes 7 or 11, respectively (Scheme 2 (2) and Scheme 2 (6)). The precursor 2 reacted with CuI in the presence of KOtBu in DMSO/CH₃CN in air for 24 h, then HgI₂ was added to the above suspension. After stirring for 12 h, a mixed dinuclear NHC complex 8 was generated (Scheme 2 (3)). In the reaction, the Cu(I) was oxidated to Cu(II) in the solution by air, then the latter species coordinated with bidentate carbene to form NHC-copper(II) complex, copper-{C,C'-bis[2-(3-"butylimidazolin-2-yliden-1-yl)ethyl]ether} diiodide. After the addition of HgI₂, the Hg(II) coordinated with two iodine atoms in NHCcopper(II) complex to give a mixed dinuclear complex 8. Treatment of 3 with Hg(OAc)₂ in DMSO/CH₃CN in the presence of KOtBu afforded a NHC-mercury(II) complex 9 (Scheme 2 (4)). The NHC-silver(I) complex 10 was prepared by the reaction of 4 with Ag_2O in CH_2Cl_2 (Scheme 2(5)). The complexes 6-11 are stable to air and moisture, and soluble in DMSO, and insoluble in diethyl ether. The NHC-silver(I) complex 10 is light-sensitive in solution, but light-stable as solid. The ¹H NMR spectra of anionic complex 6 is similar to that of precursor 2. In the 1 H NMR spectra of 7-11, the disappearance of the resonances for the benzimidazolium (imidazolium) protons (NCHN) shows the formation of the expected metal carbene complexes, and the chemical shifts of other protons are similar to those of corresponding precursors. In ¹³C NMR spectra of 7–9 and 11, the signals for the carbon appear at 175.8-186.1 ppm, which are comparable to known metal carbene complexes.² The signal of carbene carbon in 10 was not observed. Similar results have been reported for some NHC-silver(I) complexes, which may result from the fluxional behaviour of the NHC complexes.¹⁰



Scheme 2 Preparation of complexes 6–11.

Structures of complexes 6-11

The structures of complexes 6-11 were confirmed by ¹H NMR and ¹³C NMR spectroscopy, and X-ray crystallography. In NHC metal complexes 7-11 (Fig. 2 (a)–Fig. 6 (a)), each complex contains a macrometallocycle (10-membered ring for 7 and 8, 13-membered ring for 9-11) constructed by one metal atom (Hg(II) for 7, 9 and 11, Cu(II) for 8, Ag(I) for 10) and one bidentate chelate biscarbene ligand with a flexible ether or diether chain. In



Fig. 1 (a) Perspective view of **6** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)–I(1) 2.6937(6), Hg (1)–I(3A) 2.9056(5); N(1)–C(7)–N(2) 111.1(6), I(1)–Hg(1)–I(2) 115.293 (19), I(1)–Hg(1)–I(3) 111.901(18), I(3)–Hg(1)–I(3A) 91.685(15), Hg(1)–I (3)–Hg(1A) 88.315(15). (b) 2D supramolecular layer of **6** formed by π – π interactions and C–H···I hydrogen bonds. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity.

complexes **6–11**, both benzimidazole (or imidazole) rings of each complex form the dihedral angles of $24.7-72.6^{\circ}$ ($46.9(1)^{\circ}$ for **6**, $65.6(1)^{\circ}$ for **7**, $72.6(1)^{\circ}$ for **8**, 53.1° for **9**, $24.7(1)^{\circ}$ for **10** and $47.1(1)^{\circ}$ for **11**). In complexes **7–11**, two alkyl chains of each complex point to the opposite directions (ethyl chains for **7** and **10**, butyl chains for **8**, and benzyl groups for **9** and **11**). In contrast, two butyl chains in each cationic unit of complex **6** point to the same direction (Fig. 1 (a)). The internal ring angles (N–C–N) at the carbene center in **7–11** are in the range of $106.2(7)-116(2)^{\circ}$, and these values are consistent with those of known NHC-metal complexes.²

In complex **6**, the anionic unit $[Hg_2I_6]^{2-}$ is formed by two mercury(II) atoms and six iodine atoms (two bridging iodines I(3) and I(3A), and four non-bridging iodines I(1), I(2), I(1A), I(2A)). The co-planar four atoms Hg(1), I(3), Hg(1A) and I(3A) form a quadrangle Hg₂I₂ arrangement (I(3)–Hg(1)–I(3A) = 91.685 (15)° and Hg(1)–I(3)–Hg(1A) = 88.315(15)°). The four nonbridging iodine atoms I(1), I(1A), I(2) and I(2A) lie in both sides of the quadrangle plane (I(1)–Hg(1)–I(2) = 115.293(19)°). The distances between non-bridging iodine and mercury(II) (Hg(1)–I (1) = 2.6937(6) Å and Hg(1)–I(2) = 2.7160(6) Å) are slightly shorter than those between bridging iodine and mercury(II) (Hg (1)–I(3) = 2.9005(6) and Hg(1)–I(3A) = 2.9056(5) Å). The Hg (1)…Hg(1A) separation of 4.0449(3) Å shows no metal-metal interactions (the van der Waals radii of mercury = 1.7 Å).



Fig. 2 (a) Perspective view of **7** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)–C(9) 2.109(15), Hg(1)–C(22) 2.091(13), Hg(1)–I(4) 3.2554(15), Hg(2)–I(4) 2.8315(14); C (9)–Hg(1)–C(22) 158.7(5), N(1)–C(9)–N(2) 107.0(12), I(2)–Hg(2)–I(4) 111.94(5), Hg(1)–I(4)–Hg(2) 102.46(4). (b) 2D supramolecular layer of **7** formed by weak Hg…I bonds and C–H… π contacts. All hydrogen atoms except those participating in the C–H… π contacts were omitted for clarity.

The X-ray crystal structural analysis of 7 show that the Hg(1)is tetracoordinated with two carbene carbons, one oxygen atom and one iodine atom to adopt a distorted tetrahedral geometry. The C(9)–Hg(1)–C(22) angle is $158.7(5)^{\circ}$, and the bond distances of two Hg-C are 2.109(15) Å and 2.091(13) Å, respectively. The Hg...O separation of 2.7073(1) Å is within the range of distances observed in the crown ether and polyethylene glycol complexes of HgX₂ (X = Cl, Br, I).¹¹ In anionic unit $[HgI_4]^{2-}$ of 7, the Hg(2) is also tetracoordinated. It is, however, surrounded by four iodine atoms. The bond angles of six I-Hg(2)-I are in the range of 103.98(5)–121.70(6)°, and the bond lengths of four Hg–I vary from 2.7395(15) Å to 2.8315(14) Å. These values are in the regular range. Additionally, the cationic unit and anionic unit are linked via weak $Hg(1)\cdots I(4)$ bond, and $Hg(1)\cdots I(4)$ distance of 3.2554(15) Å is longer than those of other regular Hg-I bonds (2.7–2.8 Å), but shorter than the sum of the van der Waals radii (3.7 Å). The Hg(1)···Hg(2) distance of 4.7532(10) Å indicates no metal-metal interactions.



Fig. 3 (a) Perspective view of **8** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–C(7A) 2.52(3), Cu (1)–O(1) 2.26(3), Cu(1)–I(1A) 2.970(3), Hg(1)–I(1A) 2.8660(19), Hg(1)–I (2A) 2.7328(18); C(7A)–Cu(1)–C(7B) 162.8(13), O(1)–Cu(1)–C(7A) 81.4 (7), O(1)–Cu(1)–I(1) 128.36(6), Hg(1)–I(1A)–Cu(1) 74.01(7), I(1A)–Cu (1)–I(1B) 103.28(13), I(1A)–Hg(1)–I(1B) 108.70(9), I(2A)–Hg(1)–I(2B) 123.63(10), N(1A)–C(7A)–N(2A) 116(2). (b) 2D supramolecular layer of **8** formed by π – π interactions and C–H··· π contacts. All hydrogen atoms except those participating in the C–H··· π contacts were omitted for clarity.

Interestingly, complex 8 is a mixed copper(II)/mercury(II)dinuclear NHC-metal complex, in which the copper(II) center is pentacoordinated with two carbene carbons, two iodine atoms and one oxygen atom to adopt a slightly distorted trigonal bipyramid geometry. The apical positions of axis are occupied by two carbon atoms with the Cu(1)–C(7A) distance of 2.52 (3) Å and C(7A)–Cu(1)–C(7B) angle of $162.8(13)^\circ$. The equatorial plane is occupied by two bridging iodine atoms and one oxygen atom (the I(1A)–Cu(1)–I(1B) bond angle = $103.28(13)^\circ$, and the Cu-I bond distance = 2.970(3) Å). The Hg(1) is surrounded by four iodine atoms (two bridging iodine atoms I(1A) and I(1B), and two non-bridging iodine atoms (I(2A) and I(2B)) to afford a slightly distorted tetrahedral arrangement, in which the bond angles of six I-Hg(1)-I are in the range of 104.73(5)- $123.63(10)^{\circ}$. The distance between Hg(1) and non-bridging iodine atom (2.7328(18) A) is slightly shorter than that between Hg(1) and bridging iodine atom (2.8660(19) A). These values are comparable to those in the $[Hg_2I_6]^{2-}$ unit of 6. Five atoms Cu(1), Hg(1), I(1A), I(1B) and O(1) are co-planar, and four of them (Cu (1), Hg(1), I(1A) and I(1B)) form a quadrangle geometry. Two non-bridging iodine atoms lie in both sides of the quadrangle



Fig. 4 (a) Perspective view of **9** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)–C(14) 2.074(12), Hg(1)–C(27) 2.104(12), Hg(1)–O(4) 2.566(8), Hg(2)–O(4) 2.483(8), Hg(2)–I(1) 2.6747 (12); C(14)–Hg(1)–C(27) 163.0(4), C(14)–Hg(1)–O(4) 99.5(4), C(27)–Hg (1)–O(4) 97.5(4), O(4)–Hg(2)–I(1) 100.6(2), O(4)–Hg(2)–I(2) 92.0(2), O (4)–Hg(2)–I(3) 104.5(2), I(1)–Hg(2)–I(2) 117.94(4), C(35)–O(4)–Hg(2) 129.4(8), C(35)–O(4)–Hg(1) 96.3(7), Hg(1)–O(4)–Hg(2) 116.7(3), N(1)–C (14)–N(2) 107.1(10), N(3)–C(27)–N(4) 108.1(10). (b) 2D supramolecular layer of **9** formed by two types of π – π interactions. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity.

plane. The quadrangle plane and two benzimidazole rings form the same dihedral angle of $77.2(2)^{\circ}$. The Cu(II) and Hg(II) are connected *via* two bridging iodine atoms (Hg–I–Cu bond angle = $74.01(7)^{\circ}$). The Cu···Hg distance of 3.5134(12) Å shows weak metal-metal interactions, and this distance is similar to that of the Cu–Hg heteronuclear complex reported.¹² The Cu(1)···O(1) separation (2.26(3) Å) is longer than the regular Cu–O bond distance (1.9 Å), however, shorter than the sum of the van der Waals Radii of 3.2 Å.¹³

In complex **9**, both Hg(1) and Hg(2) atoms are tetracoordinated. The former is surrounded by two carbene carbons and two oxygen atoms from acetate group, and the latter is surrounded by three iodine atoms and one oxygen atoms from acetate group. Hg(1) and Hg(2) atoms are connected by one bridging oxygen atom from acetate group. The C(14)–Hg(1)–C(27) angle is 163.0 (4)°, and the distances of Hg–C bonds are 2.074(12) Å and 2.104 (12) Å, respectively. These values are comparable to the corresponding values in complex 7. The O(3)–Hg(1)–O(4) angle is 49.6 (3)°, and the Hg(1)–O(3) and Hg(1)–O(4) separations are 2.6638 (8) Å and 2.566(8) Å, respectively. The distances between Hg(1) and the oxygen atoms from ether chain are 3.183(1) Å and 3.2632 (99) Å, respectively, showing no Hg…O interactions (the sum of





(b)

Fig. 5 (a) Perspective view of **10** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms and PF₆⁻ were omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–C(9) 2.095(6), Ag(1)–C(22) 2.099(6); C(9)–Ag(1)–C(22) 177.5(2), N(1)–C(9)–N(2) 107.2(5). (b) 2D supramolecular layer of **10** formed *via* π – π interactions and C–H··· π contacts. All hydrogen atoms were omitted for clarity.

the van der Waals Radii between mercury atom and oxygen atom = 3.1 Å). The dihedral angle between benzene ring from benzyl group and adjacent benzimidazole ring is $80.4(1)^\circ$. Besides, C–H···O hydrogen bonds in **9** are observed, in which oxygen atom is from acetate group and hydrogen atom is from CH₂ of benzyl group (Table 1).

In the cation of **10**, the C(9)–Ag(1)–C(22) array is nearly linear with a bond angle of 177.5(2)°. The distances of two Ag–C bonds are 2.095(6) Å and 2.099(6) Å, respectively. These values are similar to those of known NHC-silver(1) complexes.^{6a,6b}

In the molecular structure of complex **11**, the Hg(1) atom is tetracoordinated with two carbene carbon atoms and two oxygen atoms from diether chain to form distorted tetrahedral arrangement. The C–Hg–C is almost linear with the bond angle of 170.9(3)°, and two Hg–C bond distances are 2.055(8) and 2.074(8) Å, respectively. The distances of Hg(1)–O(2) and Hg(1)–O(1) are 2.8655(57) Å and 3.0180(52) Å, respectively. The dihedral angle between benzene ring from benzyl group and adjacent imidazole ring is 77.5(1)°.

The conformations of NHC metal complexes bearing ether or diether linkers

As shown in Scheme 3, NHC metal complexes bearing ether or diether linkers adopt two diverse conformations, namely, single nuclear macrocycle complex I with one bidentate chelate carbene ligand (*e.g.*, 7–11) and dinuclear macrocycle complex II with two bidentate carbene ligands (*e.g.*, disilver-bis{C,C'-bis[2-(3-methyl-imidazolin-2-yliden-1-yl)ethyl]ether} di-tetrafluoroborate (12)¹⁴



Fig. 6 (a) Perspective view of **11** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms and $[HgI_4]^{2-}$ anion were omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)–C(10) 2.074(8), Hg(1)–C(19) 2.055(8); C(10)–Hg(1)–C(19) 170.9(3), N (1)–C(10)–N(2) 106.2(7), N(3)–C(19)–N(4) 106.2(7). (b) 1D chains of **11** formed by π – π interactions and C–H···I hydrogen bonds. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity. (c) 2D supramolecular layer of **11** formed by C–H···I hydrogen atoms except those participating in the hydrogen atoms except those participating in the hydrogen atoms except those participating in the hydrogen bonds. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity.

and dimetal-bis{C,C'-bis[2-(3-Rimidazolin-2-yliden-1-yl)ethyl] ether} di-hexafluorophosphate (13)¹⁵ (metal = silver or gold, R =1-naphthylmethylene or 9-anthracenylmethylene). The conformations of complexes may depend mainly on two factors, namely, the length of ether linkers and the types of anions. When linkers are single ether, the conformations of complexes are mostly relative to the types of anions. In the case, if anions

Table 1 H-bonding geometry (A, \circ) for 6, 9 and 11^a

	D–H···A	D–H	Н…А	D····A	D–H···A
6	C(8)–H(8)····I(1) ⁱ	0.97(1)	3.096(1)	3.861(2)	136.8(3)
	C(7)–H(7A)····O(3)	0.97(1)	2.297(8)	3.255(1)	169.2(7)
11	$C(18) - H(18) \cdots I(1)^{i}$	0.93(1)	3.156(5)	3.942(6)	143.4(3)
	$C(9) - H(9) \cdots I(2)^{i}$	0.93(1)	3.197(6)	4.013(7)	147 4(4)
a cu	mmatry and a il y		i = x 0.5		for 11



Scheme 3 The two diverse conformations of NHC metal complexes.

are PF_6^- or BF_4^- , NHC metal complexes adopt conformation II (*e.g.*, **12** and **13**), and if anions are halide anions, NHC metal complexes adopt conformation I (*e.g.*, **7** and **8**). When linkers are diether, NHC metal complexes adopt conformation I (*e.g.*, **9–11**). The other factors, such as different solvents, the size of N-substitutents and benzimidazole (or imidazole) rings, have probably little influence on the formation of diverse conformations.

The crystal packing of complexes 6-11

An interesting feature in the crystal packing of **6** is that 1D supramolecular chain is formed by the π - π stacking interactions from intermolecular benzimidazole rings (the distances of π - π interactions being given in Table 2).¹⁶ In addition, the anionic building units ($[Hg_2I_6]^{2-}$) are packed between the 1D chains to extend 1D chains into 2D supramolecular layers *via* C-H···I hydrogen bonds¹⁷ as shown in Fig. 1 (b) (Table 1).

In the crystal packing of 7 (Fig. 2 (b)), 2D supramolecular layers are formed by cationic macrocycles and anionic unit $[HgI_4]^{2-}$ via weak Hg…I bonds and C–H… π contacts (the data of C–H… π contacts being given in Table 2). In C–H… π contacts, the hydrogen atoms are from ethyl groups.¹⁸

Analysis of the crystal packing of **8** and **10** shows that 2D supramolecular layers are formed by π - π stacking interactions from intermolecular benzimidazole rings and intermolecular C-H \cdots π contacts. In C-H \cdots π contacts, the hydrogen atoms for **8** are from butyl groups, and the hydrogen atoms for **10** are from ethyl groups (Fig. 3 (b) and Fig. 5 (b)).

In the crystal packing of 9, 2D supramolecular layer is formed by two types of the π - π stacking interactions. One is from intermolecular benzimidazole rings, and another is from benzene rings of benzyl group (Fig. 4 (b)).

In the crystal packing of **11**, the double strand 1D supramolecular chain is formed by C–H···I hydrogen bonds and π – π stacking interactions from intermolecular imidazole rings (Fig. 6 (b)). The double strand 1D supramolecular chains are further extended into 2D supramolecular layers through another type of π – π stacking interactions from intermolecular benzene rings of benzyl groups (Fig. 6 (c)).

Fluorescent emission spectra of precursors 1 and 5, and complexes 7 and 11

As shown in Fig. 7, the fluorescent emission spectra of precursors 1 and 5, and complexes 7 and 11 are obtained upon excitation at 232 nm in acetonitrile at room temperature (the fluorescent emission spectra of 2–4 and anionic complex 6 are similar to that of 1, and the fluorescent emission spectra of 8–10 are similar to that of 7). The precursors 1 and 5 show double emission bands in the region of 330–350 nm, which can be attributed to intraligand $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively. Complexes 7 and 11 show also double emission bands at the corresponding positions of their precursors, but the fluorescent emission of 7 and 11 are weaker than those of precursors, which should originate from the metal perturbed intraligand processes. Additionally, 5 and 11 exhibit weak



Fig. 7 Emission spectra of 1 (-·-·), 5 (—), 7 (···) and 11 (—) at room temperature in CH₃CN (5.0×10^{-6} M) solution.

Table 2 Distances (Å) of π - π interactions, and distances (Å) and angles (°) of C-H··· π contacts for 6-11

	π - π			$C-H\cdots\pi$	
Complex	Face-to-face	Center-to-center	$H\cdots\pi$	C–H···π	
6 7 8 9 10 11	3.593(2) (benzimidazole) 	3.736(2) (benzimidazole) 	 2.912(6) 2.821(1) 3.097(3)		

emission bands in the range of 280–300 nm, which is likely to arise from the electronic transitions of the benzene ring.¹⁹

Conclusions

In summary, five N-heterocyclic carbene mercury(II), copper(II) and silver(1) complexes and one anionic complex have been synthesized and characterized. Each of complexes 7-11 possesses a macrometallocycle, respectively, formed by one metal atom and one bidentate chelate carbene ligand. Additionally, we have also known from these complexes in the text and reported complexes that NHC metal complexes bearing ether or diether linkers adopt two diverse conformations in the solid state, namely, single nuclear macrocycle complex with one bidentate chelate carbene ligand and dinuclear macrocycle complex with two bidentate carbene ligands. In the crystal packing of complexes 6-11, 2D supramolecular layers are formed through weak intermolecular interactions including π - π stacking interactions, hydrogen bonds, C–H··· π contacts and weak Hg…I bonds. The macrocyclic structures of these NHC metal complexes suggest that they may have potential applications in the host-guest chemistry. Further studies on new organometallic compounds from the precursors and analogous ligands are under way.

Experimental

General procedures

2,2'-Diiodoethyl ether and 1,2-bis(2-iodoethoxy)ethane were prepared according to the literature methods.²⁰ All manipulations were performed using Schlenk techniques, and solvents were purified by standard procedures. All the reagents for synthesis and analyses were of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus. ¹H and ¹³C{¹H} NMR spectra were recorded on a Varian Mercury Vx 400 spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts, δ , were reported in ppm relative to the internal standard TMS for both ¹H and ¹³C NMR, and *J* values were given in Hz. The elemental analyses of all compounds were obtained from the powder compounds recrystallised, and measured using a Perkin-Elmer 2400C Elemental Analyzer. The luminescent spectra were conducted on a Cary Eclipse fluorescence spectrophotometer.

Preparation of dibenzimidazolium (or diimidazolium) salts

Preparation of bis[2-(3-ethylbenzimidazolium-1-yl)ethyl]ether diiodide (1). A solution of benzimidazole (20.000 g, 0.169 mol) in THF (100 mL) was added to a suspension of oil-free sodium hydride (10.000 g, 50%) in THF (300 mL) and the resulted mixture was stirred for 2 h at 60 °C. Then a solution of ethyl iodide (29.760 g, 0.186 mol) in THF (150 mL) was added dropwise to the above solution. The mixture was continued to stir for 12 h at 60 °C and a brown solution was obtained. The solvent was removed with a rotary evaporator and H₂O (200 mL) was added to the residue. Then the solution was extracted with CH₂Cl₂ (3 × 100 mL), and the extracting solution was dried over anhydrous MgSO₄. After removing CH₂Cl₂, a pale yellow liquid of 1-ethylbenzimidazole was obtained. Yield: 20.000 g (81%). A solution of 1-ethylbenzimidazole (4.930 g, 33.7 mmol) and 2,2'-diiododiethyl ether (5.000 g, 15.3 mmol) in THF (100 mL) was stirred for three days under refluxing, and a pale yellow precipitate was formed. The product was collected by filtration and the filter cake was washed with THF. The pale yellow powder of bis[2-(3-ethylbenzimidazolium-1-yl)ethyl]ether diiodide (1) was obtained. Yield: 6.710 g (71%). Mp: 172–174 °C. Anal. calcd for C₂₂H₂₈I₂N₄O: C 42.74, H 4.56, N 9.06%. Found: C 42.43, H 4.62, N 9.36%. ¹H NMR (400 MHz, DMSO-d₆): δ 1.49 (t, J = 5.6, 6H, CH₃), 3.98 (t, J = 4.2, 4H, CH₂), 4.48 (q, J = 5.6, 4H, CH₂), 4.68 (t, J = 4.2, 4H, CH₂), 7.63 (m, 4H, PhH), 7.94 (d, J = 6.4, 2H, PhH), 8.05 (d, J = 6.4, 2H, PhH), 9.75 (s, 2H, 2-benzimiH) (benzimi = benzimidazole).

The following dibenzimidazolium (or diimidazolium) salts 2, 3 and 5 were prepared in a manner analogous to that for 1.

Preparation of bis[2-(3-"butylbenzimidazolium-1-yl)ethyl]ether diiodide (2). Yield: 4.930 g (79%). Mp: 202–204 °C. Anal. calcd for C₂₆H₃₆I₂N₄O: C 46.30, H 5.38, N 8.31%. Found: C 46.57, H 5.42, N 8.61%. ¹H NMR (400 MHz, DMSO-d₆): δ 0.93 (t, J =5.6, 6H, CH₃), 1.42 (m, 4H, CH₂), 2.08 (m, 4H, CH₂), 3.83 (t, J =4.2, 4H, CH₂), 4.41 (t, J = 5.6, 4H, CH₂), 4.59 (t, J = 4.2, 4H, CH₂), 7.70 (m, 4H, PhH), 7.90 (d, J = 6.4, 2H, PhH), 8.13 (d, J =6.4, 2H, PhH), 9.64 (s, 2H, 2-benzimiH).

Preparation of 1,1'-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]-bis (3-benzylbenzimidazolium-1-yl) diiodide (3). Yield: 2.548 g (80%). Mp: 192–194 °C. Anal. calcd for $C_{34}H_{36}I_2N_4O_2$: C 51.92, H 4.61, N 7.12%. Found: C 51.63, H 4.75, N 7.44%. ¹H NMR (400 MHz, DMSO-d₆): δ 3.49 (t, J = 4.2, 4H, CH₂), 3.80 (t, J = 4.2, 4H, CH₂), 4.67 (t, J = 4.2, 4H, CH₂), 5.81 (s, 4H, CH₂), 7.36–7.65 (m, 14H, PhH), 7.98–8.12 (m, 4H, PhH), 9.94 (s, 2H, 2-benzimiH).

Preparation of 1,1'-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]-bis (3-benzylimidazolium-1-yl) diiodide (5). Yield: 2.320 g (84%). Mp: 107–109 °C. Anal. calcd for $C_{26}H_{32}I_2N_4O_2$: C 45.50, H 4.70, N 8.16%. Found: C 45.86, H 4.95, N 8.53%. ¹H NMR (400 MHz, DMSO-d₆): δ 3.40 (t, J = 4.2, 4H, CH₂), 3.63 (t, J = 4.2, 4H, CH₂), 4.38 (t, J = 4.2, 8H, CH₂), 5.78 (s, 4H, CH₂), 7.30–7.45 (m, 10H, PhH and 4, 5-imiH), 7.73–7.84 (m, 4H, PhH), 9.05 (s, 2H, 2imiH) (imi = imidazole).

Preparation of 1,1'-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]-bis (3-ethylbenzimidazolium-1-yl) di-hexafluorophosphate (4). This compound was prepared via two steps, and the first step is in a manner analogous to that for 1. The second step is an anionic exchange with ammonium hexafluorophosphate: NH_4PF_6 (1.476 g, 9.1 mmol) was added to a methanol solution of 1,1'-[1,2ethanediylbis(oxy-1,2-ethanediyl)]-bis(3-ethylbenzimidazolium-1-yl) diiodide (2.000 g, 3.0 mmol) whilst stirring and a white precipitate was formed immediately. The product was collected by filtration and washed with small portions of cold methanol to give compound 4. Yield: 1.780 g (85%). Mp: 156-158 °C. Anal. calcd for C₂₄H₃₂F₁₂N₄O₂P₂: C 41.27, H 4.62, N 8.02%. Found: C 41.48, H 4.51, N 8.44%. ¹H NMR (400 MHz, DMSO-d₆): δ 1.64 $(t, J = 5.5, 6H, CH_3), 3.40 (t, J = 4.2, 4H, CH_2), 3.73 (t, J = 4.2, 4$ 4H, CH₂), 4.69 (t, J = 4.2, 4H, CH₂), 4.79 (q, J = 5.5, 4H, CH₂), 7.65 (m, 4H, PhH), 7.88 (d, J = 6.3, 2H, PhH), 7.89 (d, J = 6.3, 2H, PhH), 11.44 (s, 2H, 2-benzimiH).

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Preparation of complexes 6-11

Preparation of bis[2-(3-"butylbenzimidazolium-1-yl)ethyllether $di-\mu$ -iodo-bis(diiodomercurate) (6). A suspension of precursor 2 (0.200 g, 0.3 mmol) and mercury(II) iodide (0.140 g, 0.7 mmol) in DMSO (5 mL) and acetonitrile (30 mL) was stirred for 24 h at 80 °C, and a pale yellow solution was formed. The solution was diluted with water (30 mL) and extracted with CH₂Cl₂ (3 \times 20 mL). The extracting solution was dried over anhydrous MgSO₄. After removing CH₂Cl₂, a white powder of 6 was obtained. Yield: 0.292 g (62%). Mp: 180-182 °C. The white powder of 6 was dissolved in DMSO, and slow diffusion of diethyl ether into this solution led to the formation of colourless crystals suitable for X-ray structure analysis at room temperature, within three weeks. Anal. calcd for C₂₆H₃₆Hg₂I₆N₄O: C 19.73, H 2.29, N 3.54%. Found: C 19.88, H 2.47, N 3.34%. ¹H NMR (400 MHz, DMSO-d₆): δ 0.98 (t, $J = 5.6, 6H, CH_3$, 1.47 (m, 4H, CH₂), 2.23 (m, 4H, CH₂), 3.79 $(t, J = 4.2, 4H, CH_2), 4.47 (t, J = 5.6, 4H, CH_2), 4.61 (t, J =$ 4.2, 4H, CH₂), 7.74 (m, 4H, PhH), 7.93 (d, J = 6.4, 2H, PhH), 8.18 (d, J = 6.4, 2H, PhH), 9.88 (s, 2H, 2-benzimiH). ¹³C NMR (100 MHz, DMSO-d₆): δ 138.1 (NCHN), 131.4, 126.9, 126.3, 115.1, 114.1 and 113.3 (PhC), 64.1 (OCH₂), 47.3 (NCH₂), 46.7 (NCH₂), 33.1 (CCH₂C), 18.7 (CCH₂C), 13.6 (CCH₃).

Preparation of mercury-{C,C'-bis[2-(3-ethylimidazolin-2-yliden-1-vl)ethyllether} tetraiodomercurate (7). A suspension of KOtBu (0.090 g, 0.8 mmol), precursor 1 (0.200 g, 0.3 mmol) and mercury(II) iodide (0.310 g, 6.7 mmol) in DMSO (5 mL) and acetonitrile (30 mL) was stirred for 24 h at 80 °C. A brown solution was formed and the solvent was removed with a rotary evaporator. Water (30 mL) was added to the residue. Then the solution was extracted with CH_2Cl_2 (3 \times 20 mL). The extracting solution was dried over anhydrous MgSO₄. After removing MgSO₄ by filtration, the filtrate was concentrated to 10 mL and hexane (5 mL) was added. A pale yellow powder was obtained. Yield: 0.220 g (54%). Mp: 212-214 °C. The pale vellow powder of 7 was dissolved in DMSO, and slow diffusion of diethyl ether into this solution led to the formation of pale yellow crystals suitable for X-ray structure analysis at room temperature. within three weeks. Anal. calcd for C₂₂H₂₆Hg₂I₄N₄O: C 20.79, H 2.06, N 4.41%. Found: C 20.64, H 2.33, N 4.62%. ¹H NMR (400 MHz, DMSO-d₆): δ 1.43 (t, $J = 5.6, 6H, CH_3$, 4.10 (t, $J = 4.2, 4H, CH_2$), 4.52 (q, $J = 5.6, 4H, CH_2$) 4H, CH₂), 4.63 (t, J = 4.2, 4H, CH₂), 7.69 (m, 4H, PhH), 7.90 (d, J = 6.4, 2H, PhH), 8.11 (d, J = 6.4, 2H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 180.2 (C_{carbene}), 132.1, 126.2, 125.6, 114.2, 113.5 and 113.0 (PhC), 70.2 (OCH₂), 48.1 (NCH₂), 47.5 (NCH₂), 13.6 (CCH₃).

Preparation of copper-{C,C'-bis[2-(3-"butylimidazolin-2-yliden-1-yl)ethyl]ether} tetraiodomercurate (8). A suspension of KOtBu (0.090 g, 0.8 mmol), precursor 2 (0.200 g, 0.3 mmol) and anhydrous copper(1) iodide (0.129 g, 0.7 mmol) in DMSO (5 mL) and acetonitrile (20 mL) was stirred for 24 h at 80 °C in air. Then anhydrous mercury(11) iodide (0.320 g, 0.7 mmol) was added to above brown suspension. The resulting mixture was allowed to stir for 12 h at 80 °C. The solvent was removed with a rotary evaporator, and water (30 mL) was added to the

residue. The resulting solution was extracted with CH_2Cl_2 (3 × 20 mL), and the extracting solution was dried over anhydrous $MgSO_4$. After removing $MgSO_4$ by filtration, the filtrate was concentrated to 10 mL. Hexane (5 mL) was added to precipitate a pale yellow powder of 8. Yield: 0.108 g (54%). Mp: 142-144 °C. The pale yellow powder of 8 was dissolved in DMSO, and slow diffusion of diethyl ether into this solution led to the formation of colourless crystals suitable for X-ray structure analysis at room temperature, within three weeks. Anal. calcd for C₂₆H₃₄CuHgI₄N₄O: C 26.23, H 2.88, N 4.71%. Found: C 26.52, H 2.61, N 4.84%. ¹H NMR (400 MHz, DMSO-d₆): $\delta 0.88$ (t, $J = 5.6, 6H, CH_3$), 1.35 (m, 4H, CH₂), 1.93 (m, 4H, CH₂), 3.96 (t, J = 4.2, 4H, CH₂), 4.45 (t, J = 5.6, 4H, CH₂), 4.67 (t, J = 4.2, 4H, CH₂), 7.68 (m, 4H, PhH), 7.93 (d, J = 6.4, 2H, PhH), 8.05 (d, J = 6.4, 2H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 186.1 (C_{carbene}), 133.2, 127.1, 126.0, 114.3, 113.7 and 113.2 (PhC), 69.0 (OCH₂), 48.4 (NCH₂), 47.1 (NCH₂), 32.5 (CCH₂C), 19.9 (CCH₂C), 14.3 (CCH₃).

Preparation of mercury-{C,C'-1,1'-[1,2-ethanediylbis(oxy-1,2ethanediyl)]-bis(3-benzylbenzimidazolin-2-yliden-1-yl)} trijodomercurate acetate (9). This complex was prepared in a manner analogous to that for 7, only instead of mercury(II) iodide with anhydrous mercury(II) acetate. Yield: 0.140 g (40%). Mp: 236-238 °C. The pale yellow powder of 9 was dissolved in DMSO. and slow diffusion of diethyl ether into this solution led to the formation of pale yellow crystals suitable for X-ray structure analysis at room temperature, within three weeks. Anal. calcd for C₃₆H₃₇Hg₂I₃N₄O₄: C 31.52, H 2.72, N 4.09%. Found: C 31.83, H 2.77, N 4.12%. ¹H NMR (400 MHz, DMSO-d₆): δ 1.59 (s, 3H, CH₃), 3.46 (t, J = 4.2, 4H, CH₂), 3.73 (t, J = 4.2, 4H, CH₂), 4.83 (t, J = 4.2, 4H, CH₂), 6.15 (s, 4H, CH₂), 7.35– 7.41 (m, 10H, PhH), 7.56–7.62 (m, 4H, PhH), 7.78 (d, J = 8.2, 2H, PhH), 8.04 (d, J = 8.2, 2H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 184.8 (C_{carbene}), 135.9, 133.2, 129.2, 128.6, 127.7, 126.3, 114.1 and 113.6 (PhC), 70.5 and 68.2 (OCH₂), 52.1 and 49.3 (NCH₂), 32.1 (OCO), 26.7 (CCH₃).

Preparation of silver-{C,C'-1,1'-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]-bis(3-ethylbenzimidazolin-2-yliden-1-yl)} hexafluorophosphate (10). A suspension of 4 (0.200 g, 0.2 mmol) and silver oxide (0.058 g, 0.2 mmol) in dichloromethane (30 mL) was refluxed for 24 h. The resulting mixture was filtered and the filtrate was concentrated to 5 mL. A white powder was precipitated after adding Et₂O (5 mL). Isolation by filtration yielded 10. Yield: 0.102 g (59%). Mp: 176-178 °C. The white powder of 10 was dissolved in DMSO and C₆H₁₂, and slow diffusion of diethyl ether into this solution led to the formation of colourless crystals suitable for X-ray structure analysis at room temperature, within two weeks. Anal. calcd for C₂₄H₃₀AgF₆N₄O₂P: C 43.72, H 4.59, N 8.50%. Found: C 43.53, H 4.68, N 8.34%. ¹H NMR (400 MHz, DMSO-d₆): δ 1.67 (t, $J = 5.4, 6H, CH_3$, 3.40 (t, $J = 4.3, 4H, CH_2$), 3.79 (t, 4H, CH₂), 4.74 (t, J = 4.3, 4H, CH₂), 4.87 (q, J = 5.4, 4H, CH₂), 7.70 (m, 4H, PhH), 7.91 (d, J = 6.4, 2H, PhH), 7.96 (d, J = 6.4, 2H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 133.2, 125.6, 124.3, 113.5, 112.7 and 110.8 (PhC), 71.1 (OCH₂), 47.3 (NCH₂), 46.6 (NCH₂), 12.8 (CCH₃). The carbon was not observed.

Table 3 Summary of crystallographic data for 6-8

	6	7·DMSO	8·2DMSO
Chemical formula	C ₂₆ H ₃₆ Hg ₂ I ₆ N ₄ O	C ₂₂ H ₂₆ Hg ₂ I ₄ N ₄ O·DMSO	C ₂₆ H ₃₄ CuHgI ₄ N ₄ O·2DMSO
FW/g mol ⁻¹	1583.17	1349.38	1346.56
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pccn	$P2_1/c$	C2/c
aĺÅ	13.4814(9)	11.475(3)	20.465(6)
b/Å	15.3581(11)	17.199(5)	11.488(4)
c/Å	19.0334(13)	19.604(4)	19.833(9)
$\alpha /^{\circ}$	90.00	90.00	90.00
βI°	90.00	117.849(12)	115.192(4)
$\gamma /^{\circ}$	90.00	90.00	90.00
V/Å ³	3940.8(5)	3420.9(15)	4219(3)
Ζ	4	4	4
$D_{\rm calcd}/{\rm Mg}~{\rm m}^{-3}$	2.668	2.620	2.120
μ/mm^{-1}	12.506	12.662	7.197
F(000)	2824	2432	2524
Crystal size/mm	0.20 imes 0.18 imes 0.16	$0.24 \times 0.22 \times 0.16$	0.23 imes 0.22 imes 0.20
$\theta_{\min}, \theta_{\max}/^{\circ}$	2.14, 25.00	1.67, 25.03	2.09, 25.01
T/K	296(2)	296(2)	296(2)
No. of data collected	18567	16489	10069
No. of unique data	3479	6044	3695
R _{int}	0.0276	0.1456	0.0528
No. of refined parameters	178	373	208
Goodness-of-fit on F^{2a}	0.981	1.002	1.059
Final R indices ^b $[I > 2\sigma(I)]$			
R_1	0.0283	0.0807	0.0753
wR_2	0.0627	0.1920	0.1843
R indices (all data)			
R_1	0.0382	0.1002	0.1232
\dot{WR}_2	0.0679	0.2077	0.2161
Final R indices" $[I > 2\sigma(I)]$ R_1 wR_2 R indices (all data) R_1 wR_2	0.0283 0.0627 0.0382 0.0679	0.0807 0.1920 0.1002 0.2077	0.0753 0.1843 0.1232 0.2161

^{*a*} GOF = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflection and *p* is the number of parameters refined. ^{*b*} $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 4 Summary of crystallographic data for 9–11

	9 ·0.5H ₂ O	$10 \cdot 0.5 C_6 H_{12}$	11.0.5DMSO
Chemical formula	$C_{36}H_{37}Hg_2I_3N_4O_4 \cdot 0.5H_2O$	$C_{24}H_{30}AgF_6N_4O_2P \cdot 0.5C_6H_{12}$	$C_{26}H_{30}Hg_2I_4N_4O_2 \cdot 0.5DMSO$
FW/g mol ⁻¹	1380.58	701.44	1378.38
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P2_1/c$
aĺÅ	11.510(2)	8.0951(12)	13.5458(8)
b/Å	11.811(2)	12.3444(18)	18.2469(11)
c/Å	15.423(3)	15.870(2)	16.9521(10)
$\alpha /^{\circ}$	84.823(3)	108.903(3)	90.00
βI°	87.271(3)	94.498(3)	111.1540(10)
$\gamma /^{\circ}$	81.578(3)	102.542(2)	90.00
V/Å ³	2064.3(6)	1445.4(4)	3907.7(4)
Ζ	2	2	4
$D_{\rm calcd}/{\rm Mg}~{\rm m}^{-3}$	2.220	1.612	2.343
μ/mm^{-1}	9.713	0.824	11.063
F(000)	1272.0	716	2492
Crystal size/mm	0.38 imes 0.36 imes 0.30	0.24 imes 0.20 imes 0.18	0.28 imes 0.26 imes 0.20
$\theta_{\rm min}, \theta_{\rm max}/^{\circ}$	1.75, 25.03	1.37, 25.03	1.61, 25.03
T/K	296(2)	296(2)	296(2)
No. of data collected	10 580	7347	19 742
No. of unique data	7288	5118	6891
R _{int}	0.0395	0.0272	0.0317
No. of refined parameters	452	372	380
Goodness-of-fit on F^{2a}	1.028	1.045	1.039
Final <i>R</i> indices ^{<i>b</i>} $[I > 2\sigma(I)]$			
R_1	0.0618	0.0560	0.0331
wR ₂	0.1653	0.1384	0.0859
R indices (all data)			
R_1	0.0801	0.0983	0.0497
wR_2	0.1789	0.1667	0.0931

^{*a*} GOF = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflection and *p* is the number of parameters refined. ^{*b*} $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; w $R_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Preparation of mercury-{C,C'-1,1'-[1,2-ethanediylbis(oxy-1,2ethanediyl)]-bis(3-benzylimidazolin-2-yliden-1-yl)} tetraiodomercurate (11). This complex was prepared in a manner analogous to that for 7. Yield: 0.168 g (41%). Mp: 138–140 $^\circ C.$ The pale yellow powder of 6 was dissolved in DMSO, and slow diffusion of diethyl ether into this solution led to the formation of pale yellow crystals suitable for X-ray structure analysis at room temperature, within three weeks. Anal. calcd for C₂₆H₃₀Hg₂I₄N₄O₂: C 23.32, H 2.26, N 4.18%. Found: C 23.76, H 2.13, N 4.38%. ¹H NMR (400 MHz, DMSO-d₆): δ 3.36 (t, J = 4.2, 4H, CH₂), 3.59 (t, J = 4.2, 4H, CH₂), 4.33 (t, J = 4.2, 4H, CH₂), 5.76 (s, 4H, CH₂), 7.32–7.38 (m, 10H, PhH and 4,5-imiH), 7.75-7.80 (m, 4H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 175.8 (Ccarbene), 136.6, 129.5, 128.7 and 124.7 (PhC and imiC), 70.5 and 69.5 (OCH₂), 54.2 and 52.1 (NCH₂).

X-Ray data collection and structure determinations. X-Ray single-crystal diffraction data for complexes 6-11 were collected by using a Bruker Apex II CCD diffractometer at 296(2) K with Mo-K α radiation ($\lambda = 0.71073$ M) by ω scan mode. There was no evidence of crystal decay during data collection in all cases. Semiempirical absorption corrections were applied by using SADABS and the program SAINT was used for integration of the diffraction profiles.²¹ All structures were solved by direct methods by using the SHELXS program of the SHELXTL package and refined with SHELXL²² by the full-matrix leastsquares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . Hydrogen atoms bonded to C atoms were placed geometrically and presumably solvent H atoms were first located in difference Fourier maps and then fixed in the calculated sites. Further details for crystallographic data and structural analysis are listed in Table 3 and Table 4. Figures were generated by using Crystal-Maker.23

In the crystal structure of 7, the solvent molecule DMSO is disordered in two positions with the occupancy factors of 0.70 and 0.30. The C–S and S–O distances were restrained to 1.79 Å and 1.45 Å, respectively. The displacement parameters of disordered atoms were refined with isotropy.

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