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FLUORESCENCE AND CRYSTAL STRUCTURES OF NEW MERCURY(II) MACROCYCLIC N-HETEROCYCLIC CARBENE COMPLEXES WITH ETHER CHAINS

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Polyerther-linked mercury(II) carbene complexes are synthesized by the reaction of carbene precursores with mercury(II) acetate. The binuclear carbene complexes with the chloride ion linkage are easily prepared by the reaction of mononuclear mercury carbene complexes with tetrabutylammoium chloride. The crystal structures reveal that the fluorescence of mercury complexes are related to the coordination mode of the ligands.

Keywords: mercury, N-heterocyclic carbene, fluorescence, X-ray structure.

INTRODUCTION

N-heterocyclic carbene (NHC) complexes have been widely studied in the last decades [1—6]. In recent years, N-heterocyclic carbene (NHC) ligands derived from imidazolium salts have confirmed an increasing use in organometallic chemistry and homogeneous catalysis [7—11]. Recently, Nielsen investigated an ether-functionalized biscarbene complex. Palladium complexes exhibited satisfactory results as precatalysts in a model Heck coupling reaction in the presence of n-Bu_4NBr [12].

A variability of mercury(II) complexes bearing monodentate and chelating N-heterocyclic carbene ligands have been widely explored [13—17]. Notably, Broker and Rogers have investigated a type of polyether-linked mercury carbene complexes [18]. We are interested in mercury N-heterocyclic carbene complexes exhibiting fluorescence. In this report, we describe the preparation, structures, and fluorescent emission spectra of novel mercury carbene complexes with $[HgL_2](PF_6)_2(CH_3CN)$ **2a,b** and $[(HgL_2)_2Cl](PF_6)_3(CH_3OH)(C_4H_6O)$ **3a**,**b** (L = 1,1′-(oxy-1,2-ethanediyl)bis[3-(1-naphthylmethyl)imidazol-2-ylidene], and 1,1′-(oxy-1,2-ethanediyl)bis[3-(9-anthracenylmethyl)imidazol-2-ylidene]).

EXPERIMENTAL

All manipulations were performed using Schlenk techniques, and solvents were thoroughly dried and deoxygenated by the standard methods. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O, hexane, 1,4-dioxane and toluene (Na), CH_2Cl_2, CH_3CN (CaH_2). Ligands **1a,b** were prepared by the reported procedures [19, 20].

Preparation of complex 2a. An acetonitrile solution (50 ml) of 1,1′-(oxy-1,2-ethanediyl)bis[3-(1-naphthylmethyl)-1H-imidazolium-1-yl] hexaluorophosphate salt **1a** (0.730 g, 0.938 mmol) and anhydrous $Hg(OAc)_2$ (0.300 g, 0.938 mmol) was heated at reflux for 2 days. The resulting solution was then left to cool to room temperature. Acetonitrile was removed in vacuo to give a yellow solid which was washed with H_2O to give a white crude product. Recrystallization from acetonitrile and ethyl ether gave white crystals as the product. Yields: 90 %. Found, %: C 39.16, H 3.27, N 5.70. $C_{32}H_{30}N_4OHgP_2F_{12}$. Calculated, %: C 39.33, H 3.09, N 5.73. ^1H NMR (300 MHz, [D_6]DMSO, 25 °C), δ, ppm (*J*, Hz): 7.77—7.90 (m, 6H), 7.536—7.615 (m, 4H), 7.490 (d, $J^3_{\mathrm{H,H}}$ = 7.8, 2H), 7.425 (d, $J^3_{\mathrm{H,H}}$ = 7.8, 2H), 7.384 (d, $J^3_{\mathrm{H,H}}$ = 6.7, 2H), 7.234 (d, $J^3_{\mathrm{H,H}}$ = 6.7, 2H), 5.734 (s, 4H), 4.388 (t, $J^3_{\mathrm{H,H}}$ = 3.6, 4H), 3.902 (t, $J^3_{\mathrm{H,H}}$ = 3.6, 4H). ^{13}C NMR (75MHz, [D$_6$]DMSO, 25 °C), δ, ppm: 177.79, 137.43, 134.10, 133.79, 133.46, 132.64, 130.99, 130.44, 130.35, 129.34, 129.19, 127.17, 126.35, 121.09, 72.038, 56.10, 56.64.

Preparation of complex 2b. Complex **2b** was prepared in a manner analogous to that for **2a**. Starting from **1b** (0.497 g, 0.566 mmol) and Hg(OAc)$_2$ (0.181 g, 0.566 mmol), complex **2b** was obtained as a white powder (0.610 g, 93 %). Found, %: C 44.49, H 3.29, N 5.23. $C_{40}H_{34}F_{12}HgN_4OP_2$. Calculated, %: C 44.60, H 3.18, N 5.20. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C), δ, ppm (*J*, Hz): (s, 2H), 8.36 (d, $J^3_{\mathrm{H,H}}$ = 8.8, 4H), 8.27(d, $J^3_{\mathrm{H,H}}$ = 8.3, 4H), 7.74 (t, 4H), 7.62—7.67 (m, 6H), 6.82 (s, 2H), 6.58 (s, 4H), 4.64 (t, $J^3_{\mathrm{H,H}}$ = 3.7, 4H), 3.96 (t, $J^3_{\mathrm{H,H}}$ = 3.7,4H). ^{13}C NMR (75MHz, [D$_6$]DMSO, 25 °C), δ, ppm: 174.62, 131.11, 130.82, 130.29, 129.58, 127.88, 125.65, 125.19, 123.26, 122.82, 121.62, 68.38, 51.49, 46.42.

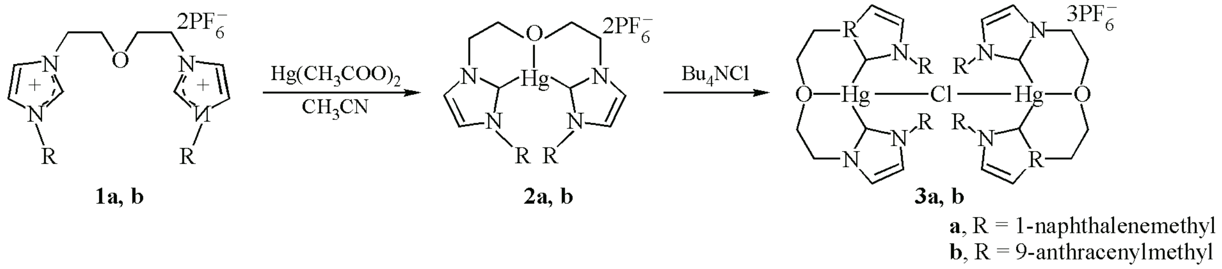
Preparation of complex 3a. An acetone/acetonitrile solution (10 ml) of **2a** and tetrabutylammoium chloride was stirred at room temperature for 2 days. The remaining solution was removed in vacuo to give a white solid which was washed with H$_2$O to give a white crude product. Recrystallization from acetonitrile and ethyl ether gave white crystals as the product. Found, %: C 41.56, H 3.12, N 6.10. $C_{64}H_{60}N_8O_2Hg_2ClP_3F_{18}$. Calculated, %: C 41.67, H 3.28, N 6.07. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C), δ, ppm (*J*, Hz): 7.75—7.88 (m, 12H), 7.53—7.60 (m, 8H), 7.47 (d, $J^3_{\mathrm{H,H}}$ = 7.8, 4H), 7.43 (d, $J^3_{\mathrm{H,H}}$ = 7.8, 4H), 7.39 (d, $J^3_{\mathrm{H,H}}$ = 6.7, 4H), 7.22 (d, $J^3_{\mathrm{H,H}}$ = 6.7, 4H), 5.74 (s, 8H), 4.39 (t, $J^3_{\mathrm{H,H}}$ = 3.7, 8H), 3.90 (t, $J^3_{\mathrm{H,H}}$ = 3.7, 8H). ^{13}C NMR (75MHz, [D$_6$]DMSO, 25 °C), δ, ppm: 177.78, 137.42, 134.11, 133.78, 133.44, 132.63, 130.98, 130.45, 130.36, 129.33, 129.18, 127.17, 126.34, 121.08, 72.04, 56.11, 56.63.

Preparation of complex 3b. Complex **3b** was prepared in a manner analogous to that for **3a**. Found, %: C 46.99, H 3.35, N 5.48. $C_{80}H_{68}ClF_{18}Hg_2N_8O_2P_3$. Calculated, %: C 46.89, H 3.30, N 5.58. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C), δ, ppm (*J*, Hz): 8.91 (s, 4H), 8.38 (d, $J^3_{\mathrm{H,H}}$ = 8.8, 8H), 8.28 (d, $J^3_{\mathrm{H,H}}$ = 8.3, 8H), 7.74 (t, $J^3_{\mathrm{H,H}}$ = 6.9, 8H), 7.66 (d, $J^3_{\mathrm{H,H}}$ = 1.4, 4H), 7.64 (d, $J^3_{\mathrm{H,H}}$ = 6.9, 8H), 6.828 (d, $J^3_{\mathrm{H,H}}$ = 1.4, 4H), 6.59 (s, 8H), 4.65 (t, $J^3_{\mathrm{H,H}}$ = 3.6, 8H), 3.96 (t, $J^3_{\mathrm{H,H}}$ = 3.6, 8H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C), δ, ppm: 174.64, 131.10, 130.82, 130.28, 129.59, 127.89, 125.66, 125.19, 123.25, 122.83, 121.62, 68.35, 51.48, 46.41.

X-ray Crystallography. Crystals of **2a** and **3b** suitable for the X-ray diffraction analysis were grown from layering saturated CH$_3$CN and chlorobenzene solutions with diethyl ether. Suitable crystals of **2a** and **3b** were mounted on a glass fiber in a random orientation. The structures were solved by direct methods and all non-hydrogen atoms were subjected to the anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package. Data collection was performed at room temperature on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using MoK_α radiation (0.71073 Å). An empirical absorption correction was applied using the SADABS program. All hydrogen atoms were generated geometrically (C—H bond lengths fixed at 0.96 Å), assigned the appropriate isotropic thermal parameters, and included in the structure factor calculations

RESULTS AND DISCUSSION

Carbene precursors [RHimy-(CH$_2$OCH$_2$)-imiHR] [I]$_2$ (**1a**,**b**, R = 1-naphthalenemethyl, 9-anthracenylmethyl) were prepared by a reaction of 1-naphthalenemethyl imidazole or 9-anthracenylmethyl imidazole with 1-iodo-2-(2-iodoethoxy)ethane in THF and an ionic exchange reaction with NH$_4$PF$_6$ [19]. The ^{1}H NMR spectra of precursors **1a,b** show that the acidulation C2—H signals appear approximately at 9.0 ppm.



Scheme 1. Synthesis of complexes **2a**,**b** and **3a**,**b**

Under N_2 ligand **1a**,**b** reacted with $Hg(OAc)_2$ in acetonitrile to form complexes **2a**,**b** (Scheme 1). The latter was treated with tetrabutylammoium chloride through an ionic exchange to form chloro-bridged mercury complexes **3a**,**b** (Scheme 1). Complexes **2a**,**b** and **3a**,**b** are soluble in acetonitrile, acetone, dichloromethane and dimethyl sulfoxide and insoluble in ether. They are stable in the air and moisture. The mercury carbene complexes were fully characterized by the ^{1}H NMR and ^{13}C NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction. In the ^{1}H NMR spectrum, the signals of complexes **2a**,**b** and **3a**,**b** are more or less upfield compared to ligands **1a**,**b**, except the disappearance of the imidazolium C2—H signals. The phenomenon shows the formation of the expected mercury carbene complexes. The ^{1}H NMR data (DMSO-d_6, 25 °C) of complexes **2a** supported the coordination of the O atom with mercury; the resonance (CH_2O) is observed at $\delta = 3.902$ ppm. In the ^{13}C NMR spectra, the characteristic coordinated carbon signals were observed at 177.79 ppm, 174.62 ppm, 177.78 ppm, and 174.64 ppm respectively.

The molecular structure of the cation units of complexes **2a** are show in Fig. 1; their crystal data and selected bond distances and angles are given in Table 1. The X-ray structural analysis of **2a** shows that the molecule comprises the $(carbene)_2Hg^{2+}$ cation, the PF_6^- anion, and molecular CH_3CN packed together in the crystal lattice. The Hg(II) cation adopts a T-type tricoordination geometry. Two NHC rings are *trans* to each other; the C(1)—Hg(1)—C(2) angle is 166.3(3)°; the average C—Hg bond distance is 2.063 Å and the Hg—O bond distance is 2.561(5) Å. The dihedral angle between two imidazole rings is 115.5°; two six-membered cycles adopt a *boat-boat* conformation. The C(1)—Hg(1)—O(1) and C(2)—Hg(1)—O(1) angles are 82.9(2)° and 83.6(2)° respectively. The $(carbene)_2Hg^{2+}$ cation

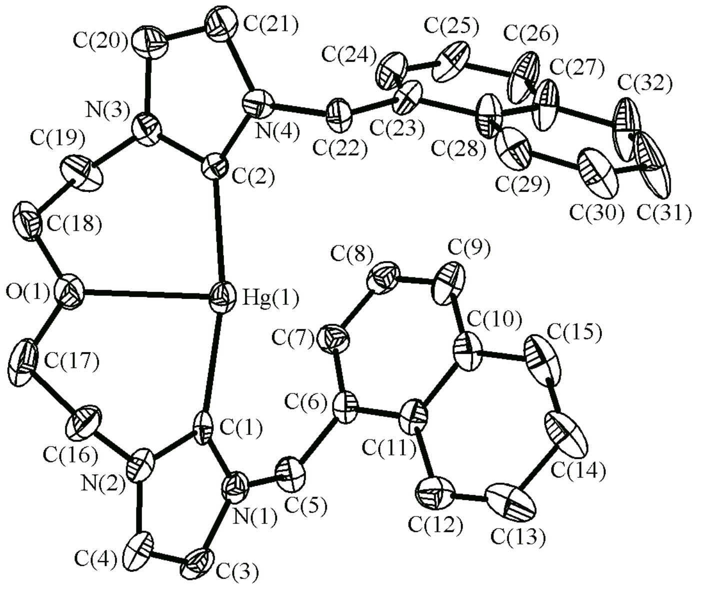


Fig. 1. Crystal structure of **2a**

Table 1

Selected bond lengths (Å) *and bond angles* (deg.) *for* **2a** *and* **3b**

Bond	*d*	Angle	ω	Angle	ω
Hg(1)—C(2)	2.060(6)	C(1)—Hg(1)—O(1)	82.9(2)	C(1)—Hg(1)—O(1)	83.2(4)
Hg(1)—C(1)	2.066(6)	C(2)—Hg(1)—C(1)	166.3(3)	C(1)—Hg(1)—Cl(1)	87.6(4)
Hg(1)—O(1)	2.561(5)	C(2)—Hg(1)—O(1)	83.6(2)	C(23)—Hg(1)—C(1)	163.9(5)
Hg(1)—C(23)	2.095(12)	N(1)—C(1)—Hg(1)	131.0(5)	C(23)—Hg(1)—Cl(1)	102.7(3)
Hg(1)—O(1)	2.590(9)	N(2)—C(1)—Hg(1)	121.6(5)	C(23)—Hg(1)—O(1)	82.3(4)
Hg(1)—C(1)	2.097(13)	N(3)—C(2)—Hg(1)	119.9(5)	O(1)—Hg(1)—Cl(1)	104.2(3)
Hg(1)—Cl(1)	2.933(10)	N(4)—C(2)—Hg(1)	132.4(5)	Hg(1)—Cl(1)—Hg(1A)	152.87(11)

and PF_6^- anions as well as the molecular CH_3CN solvent form a polybasic chain by two non-classic hydrogen bondings C—H---F(N) and the weak Hg---F bonding (Fig. 2). The length of the weak Hg---F bonding is 3.034 Å; the estimates for C…F are 3.15—3.38 Å.

In the cation of **3b**, two Hg atoms are linked by a chloro-bridge and possess a distorted tetrahedral configuration (Fig. 3); the Hg—O distance of 2.590(9) Å is somewhat longer than that of 2.561(5) Å in **2a**. The bridging Hg—Cl distance of 2.9330(10) Å is slightly longer than the bridging Hg—I distance of 2.8942 Å in the known iodo-bridged NHC Hg(II) complex. The C—Hg—C angle of 163.9(5)° is smaller than that in **2a** (166.3(3)°). The Hg—Cl—Hg angle is 152.87(11)°. Furthermore, the packing diagram of **3b** (Fig. 4) shows that they are intra- and intermolecular π—π stacking interactions between the anthracene rings (3.587 Å and 3.455 Å).

The fluorescent emission spectra of ligand **1b**, complexes **2b** and **3b** are shown in Fig. 5. In dichloromethane all compounds exhibit anthracene types of fluorescent emission, but the emissions of

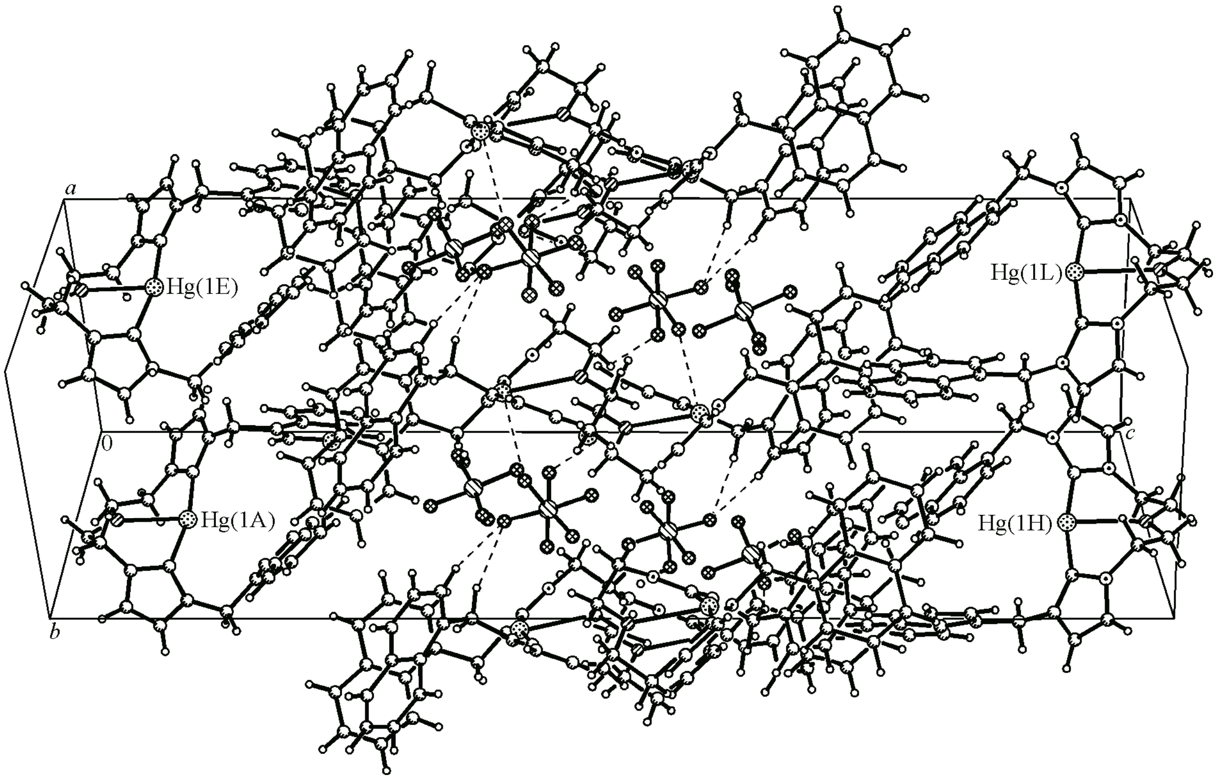


Fig. 2. Hydrogen bonding network of complex **2a**

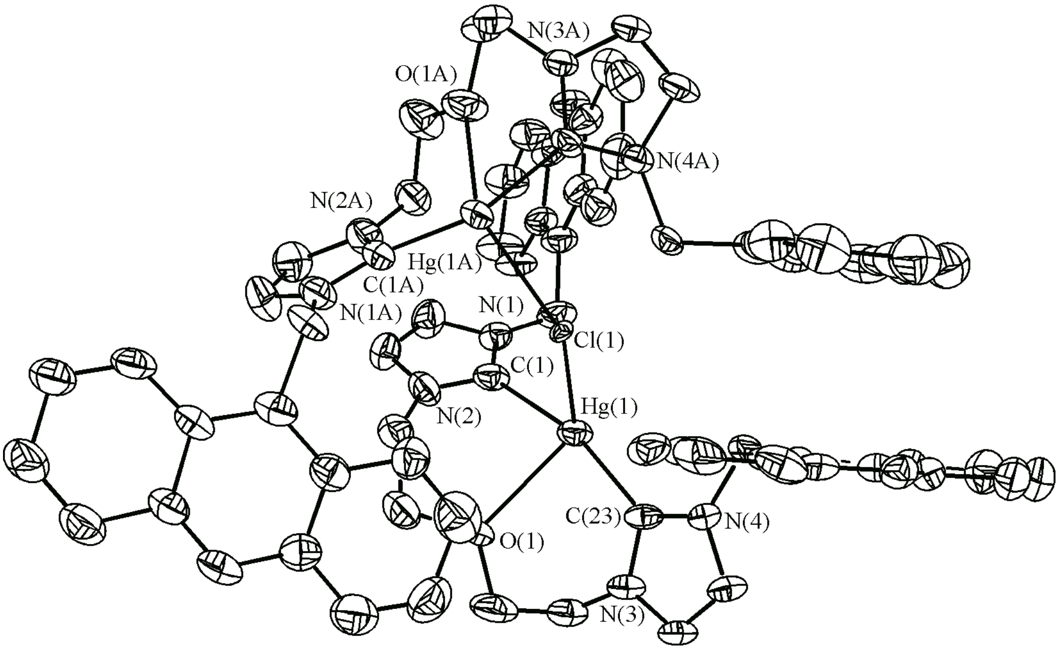


Fig. 3. Crystal structure of **3b**

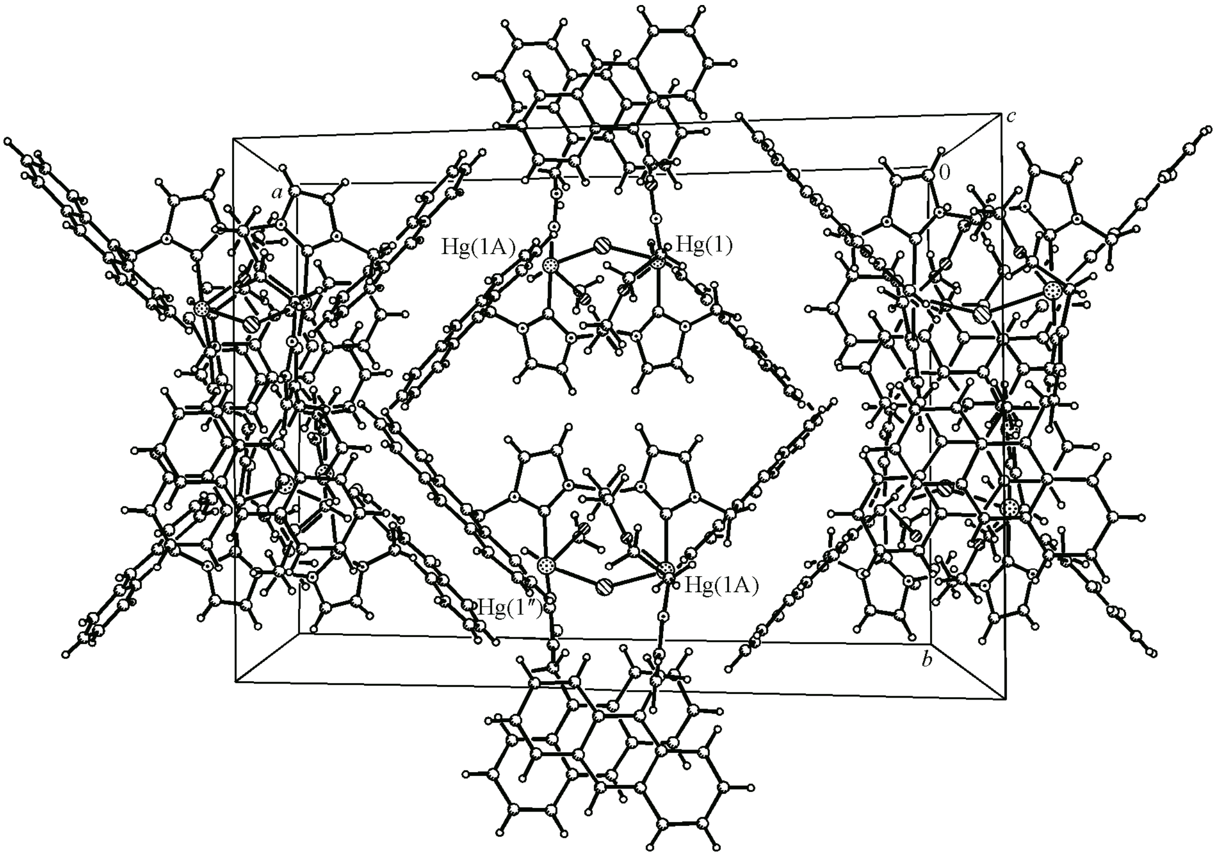


Fig. 4. π—π stacking network of complex **3b**

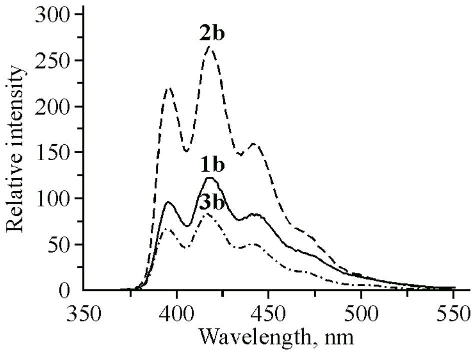


Fig. 5. Emission spectra of ligand **1b** and complexes **2b**, **3b** at room temperature upon 370 nm excitation

2b and **3b** are stronger and weaker than that of **1b** respectively. The former can be attributed to the O atom in the ether chain coordination, which inhibits the photo-induced electron transfer (PET) process of the imidazolium rings towards the anthrancene ring. A reasonable origin of the latter introduces the electron donation of the C1 atom to the Hg atom and the anthrancene ring, which promote the PET process. In addition, the intermolecular π—π stacking interaction in **3b** also shows the decreasing emission.

Supporting information. Crystallographic data (excluding structure factors) for the structure reported in this paper (**2a**, **3b**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC 267787 and 267786. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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