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Synthesis, characterization, and crystal structure determination of two mercury(II) dimer complexes with 4,7-diphenyl-1,10-phenanthroline, 5,5'-dimethyl-2,2'-bipyridine and bromide

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Synthesis, characterization, and crystal structure determination of two mercury(II) dimer complexes with 4,7-diphenyl-1,10-phenanthroline, 5,5'-dimethyl-2,2'-bipyridine and bromide

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Mercury(II) complexes, $\{[\text{Hg}(\text{Ph}_2\text{phen})(\mu\text{-Br})_2\text{Br}_2] \cdot \text{CH}_3\text{CN}$ (**1**) and $\{[\text{Hg}(\text{dmbpy})(\mu\text{-Br})_2\text{Br}_2]$ (**2**) (where Ph_2phen is 4,7-diphenyl-1,10-phenanthroline and dmbpy is 5,5'-dimethyl-2,2'-bipyridine), were synthesized from reaction of HgBr_2 with Ph_2phen and dmbpy in CH_3CN and CH_3OH . Both complexes were thoroughly characterized by elemental analysis, infrared, ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction. Complexes **1** and **2** crystallize in the space group $P2_1/n$ of the monoclinic and $P\bar{1}$ of the triclinic systems and contain four and one molecules per unit cell, respectively. The unit cell dimensions for **1** are: $a = 20.422(4) \text{ \AA}$, $b = 11.384(2) \text{ \AA}$, $c = 20.665(4) \text{ \AA}$, and $\beta = 109.94(3)^\circ$ and for **2** are: $a = 8.7470(17) \text{ \AA}$, $b = 8.8328(18) \text{ \AA}$, $c = 9.4950(19) \text{ \AA}$ and $\alpha = 75.47(3)^\circ$, $\beta = 82.21(3)^\circ$, $\gamma = 85.56(3)^\circ$. According to X-ray structure determination both complexes are five coordinate with three bromides and one bidentate ligand; one bromide is set at a semi-bridging position.

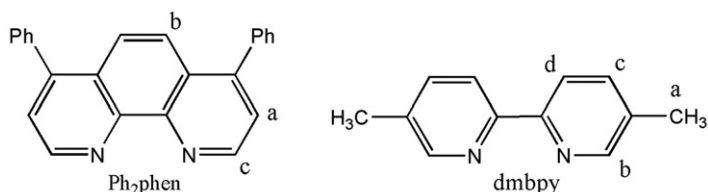
Keywords: Mercury(II); 4,7-diphenyl-1,10-phenanthroline; 5,5'-dimethyl-2,2'-bipyridine; Crystal structure

1. Introduction

The group 12 metal ions are of interest because they possess the properties of both transition and non-transition elements [1], biological activities [2], and have various dimensional supramolecular coordination assemblies [3–7] due to their wide variety of coordination configurations and coordination numbers [7]. However, $\text{Hg}(\text{II})$ complexes remain much less explored [6, 8–13].

1,10-Phenanthroline and 2,2'-bipyridine have been used in modeling complexes to mimic the non-covalent interactions in biological processes [14]. In this study,

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Scheme 1. Ph₂phen and dmbpy.

4,7-diphenyl-1,10-phenanthroline (Ph₂phen; scheme 1) and 5,5'-dimethyl-2,2'-bipyridine (dmbpy; scheme 1) have been selected. Applications of Ph₂phen complexes include stable single-layer light-emitting electrochemical cells [15, 16], electrogenerated chemiluminescence [17, 18], and enhanced interaction of metal complexes with DNA [19–21]. Quite surprisingly, dmbpy has hardly been studied [22] and only a limited number of X-ray crystal structures of these ligands with Hg(II) have been published [23, 24].

2. Experimental

2.1. General methods and materials

All chemicals were purchased from Merck and Aldrich. Infrared (IR) spectra (4000–250 cm⁻¹) of solid samples were taken as 1% dispersion in CsI pellets using a Shimadzu-470 spectrometer. ¹H-NMR spectra were recorded on a Bruker AC-300 spectrometer for protons at 300.13 MHz and for ¹³C at 75.45 MHz in DMSO-d₆ solvent, referred to TMS. Melting points were determined by a Kofler Heizbank Rechart type 7841 melting point apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN–O Rapid analyzer.

2.2. Synthesis of {[Hg(Ph₂phen)(μ-Br)]₂Br₂} · CH₃CN (1)

4,7-Diphenyl-1,10-phenanthroline (0.21 g, 0.63 mmol) in 30 mL acetonitrile was added to a solution of HgBr₂ (0.23 g, 0.63 mmol) in methanol (10 mL) and the resulting colorless solution was stirred for 30 min at 40°C, then left to evaporate slowly at room temperature. After 24 h, colorless prismatic crystals of **1** were isolated (Yield: 0.35 g; 76.9%; m.p.: 265°C). Anal. Calcd (%): C, 42.06; H, 2.45; N, 4.91. Found (%): C, 41.94; H, 2.40; N, 4.85.

¹H NMR (DMSO-d₆, 300 MHz): δ 2.0 (s, CH₃CN, 3H), 7.58 (m, 5H), 7.99 (s, 1H), 8.07 (d, 1H), 9.25 ppm (d, 1H). ¹³C NMR (DMSO-d₆): δ 1.7 (s), 118.6 (s), 125.3 (s), 126.2 (s), 127.1 (s), 129.4 (s), 129.9 (s), 130.1 (s), 136.5 (s), 140.8 (s), 150.2 (s), 151.2 (s) ppm. IR (CsI, cm⁻¹): 3067w, 2889w, 2853w, 2656w, 2555w, 1687s, 1593s, 1550w, 1426s, 1371w, 1308s, 1248w, 1141w, 1126w, 1052w, 1024w, 940w, 865w, 815w, 768m, 689w, 644w, 560w, 446w, 396w, 299w.

2.3. Synthesis of $\{[\text{Hg}(\text{dmbpy})(\mu\text{-Br})_2\text{Br}_2]\} (2)$

5,5'-Dimethyl-2,2'-bipyridine (0.26 g, 1.41 mmol) in 20 mL acetonitrile was added to a solution of HgBr_2 (0.51 g, 1.41 mmol) in methanol (10 mL) and the resulting colorless solution was stirred for 20 min at 40°C. Crystals for X-ray diffraction were obtained by methanol diffusion to a solution of white precipitate in DMSO after 1 week (Yield 0.57 g; 73.9%; m.p. <300°C). Anal. Calcd (%): C, 26.44; H, 2.20; N, 5.14. Found (%): C, 26.31; H, 2.16; N, 5.08. ^1H NMR (DMSO- d_6 , 300 MHz): δ 2.41 (s, 3H), 7.94 (d, 1H), 8.42 (d, 1H), 8.58 (s, 1H) ppm. ^{13}C NMR (DMSO- d_6): δ 18.29 (s), 121.9 (s), 135.8 (s), 140.1 (s), 149.1 (s), 149.8 (s) ppm. IR (CsI, cm^{-1}): 1598w, 1566w, 1478s, 1442m, 1379m, 1311w, 1247m, 1228w, 1160s, 1138w, 1037s, 977w, 916w, 830s, 725m, 682w, 648m, 477w, 411m.

2.4. X-ray structure analysis

Analyses on colorless single crystals of **1** and **2** were carried out on a Bruker SMART CCD area detector diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 120 K for **1** and 298 K for **2**. Absorption correction was done using SADABS [25]. SMART (data collection and cell refinement) [26], SHELXTL (data reduction) [27], ORTEP (molecular graphics) [28], and WinGX (publication material) [29] were also used. As seen from table 1, the chosen crystal for data collection on **1** is slightly large. Although numerical absorption correction was made on this data, the largest peak and the deepest hole are slightly high (3.013 and $-3.143 \text{ e \AA}^{-3}$ from Hg heavy atom) because of choosing a large crystal.

3. Results and discussion

3.1. Synthesis and characterization of **1** and **2**

The reaction between Ph_2phen and HgBr_2 in CH_3CN leads to the formation of prismatic colorless crystals of **1**. Needle crystals of **2** were prepared from reaction of HgBr_2 with dmbpy in methanol and suitable crystals for X-ray diffraction were obtained by methanol diffusion in a solution of white precipitate in DMSO.

Both complexes were characterized by elemental analysis, IR, ^1H , and ^{13}C NMR spectroscopy. The melting points of both complexes were sharp and different from that of the starting materials. Microanalytical data (C, H, N) support the general composition of the complexes and in both cases the structures have been established by single-crystal X-ray diffraction.

A comparison between ^1H and ^{13}C NMR spectra of both complexes and the corresponding ligands clearly indicated coordination of ligands to Hg(II). The ^1H NMR spectrum of **1** exhibited a singlet at 2.1 ppm for acetonitrile, a multiplet at 7.58 ppm for phenyl, a singlet at 7.98 ppm for H_b , a doublet for H_a at 8.07 ppm, and a doublet for H_c at 9.25 for phenanthroline (scheme 1, Ph_2phen). The ^{13}C NMR spectrum of **1** showed 12 resonances in agreement with the suggested structure. The ^1H NMR spectrum of **2** exhibited a singlet for CH_3 at 2.41 ppm, two doublets at 7.94 and 8.42 ppm for H_c and H_d , and one singlet at 8.58 ppm for H_b (scheme 1, dmbpy).

Table 1. Crystallographic and structure refinement data for **1** and **2**.

	1	2
Empirical formula	C ₅₀ H ₃₅ Br ₄ Hg ₂ N ₅	C ₂₄ H ₂₄ Br ₄ Hg ₂ N ₄
Formula weight	1426.61	1089.25
Temperature (K)	120(2)	298(2)
Wavelength λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P2₁/n</i>	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)		
<i>a</i>	20.422(4)	8.7470(17)
<i>b</i>	11.384(2)	8.8328(18)
<i>c</i>	20.665(4)	9.4950(19)
α	90	75.47(3)
β	109.94(3)	82.21(3)
γ	90	85.56(3)
Volume (Å ³), <i>Z</i>	4516.2(16), 4	702.9(3), 1
Calculated density (g cm ⁻³)	2.098	2.573
Absorption coefficient (mm ⁻¹)	10.371	16.613
<i>F</i> (000)	2680	496
Crystal size (mm ³)	0.50 × 0.49 × 0.47	0.28 × 0.05 × 0.04
θ range for data collection (°)	1.73–29.30	2.23–29.25
Index ranges	–28 ≤ <i>h</i> ≤ 28; –14 ≤ <i>k</i> ≤ 15; –28 ≤ <i>l</i> ≤ 28	–9 ≤ <i>h</i> ≤ 12; –12 ≤ <i>k</i> ≤ 12; –13 ≤ <i>l</i> ≤ 12
Data collected	50680	8142
Unique data (<i>R</i> _{int})	12218, 0.0963	3775, 0.0996
Parameters, restraints	552, 0	155, 0
Goodness-of-fit on <i>F</i> ²	1.118	1.323
Final <i>R</i> ₁ , <i>wR</i> ₂ (observed data)	0.0937, 0.1848	0.0836, 0.1867
Final <i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0999, 0.1956	0.0948, 0.1987
Largest difference peak and hole (e Å ⁻³)	3.013, –3.143	1.809, –1.836

The ¹³C NMR spectrum of **2** showed a singlet at 18.29 ppm for CH₃ groups and five singlets at 121.9, 135.8, 140.1, 149.1, 149.8 ppm for the aromatic ring.

The vibrational bands present around 3000 cm⁻¹ in **1** and **2** are assigned as ν (C–H). Bands in the range 1614–1378 cm⁻¹ are assigned to ν (C=N) and ν (C=C) vibrations. Medium to strong vibrations in the region 970–540 cm⁻¹ are assigned to deformation vibrations δ (C=C=N) and δ (C=C=C) in the pyridine and phenyl rings [30, 31]. Far IR spectrum of **1** and **2** (between 500 and 250 cm⁻¹) showed Hg–N stretching for **1** and **2** at 545 and 411 cm⁻¹, respectively [8, 32].

3.2. X-ray crystal structure of **1** and **2**

Compounds **1** and **2** crystallize in the space groups *P2₁/n* and *P* $\bar{1}$. The molecular structure of **1** and **2** with atom numbering scheme are shown in figures 1 and 2, while the crystal packing diagrams are illustrated in figures 3 and 4. The X-ray crystallographic data of both complexes are listed in table 1. Selected bond distances and angles are presented in tables 2 and 3, respectively. Some non-covalent bond parameters, including π – π interaction and hydrogen bond data for both complexes, are presented in tables 4 and 5, respectively.

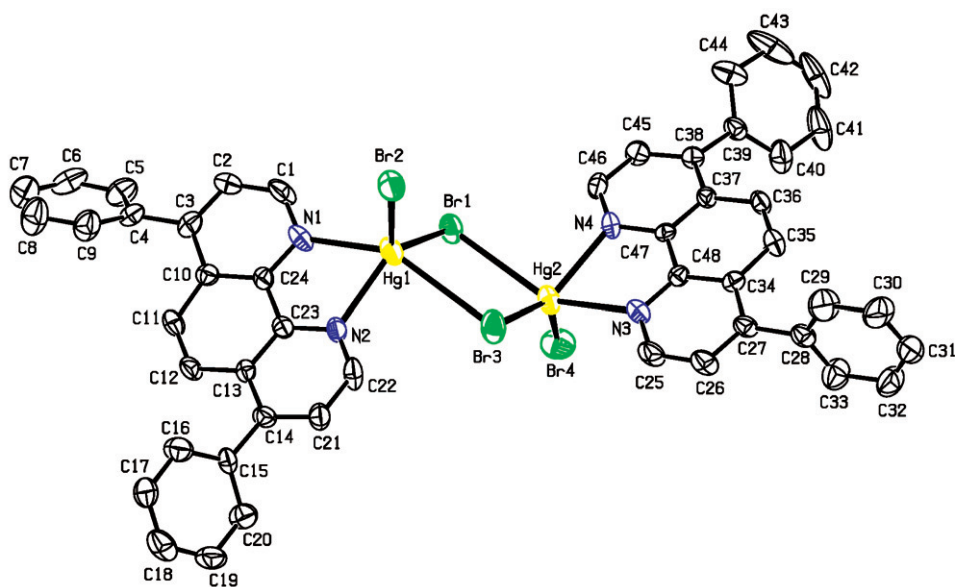


Figure 1. ORTEP view of **1** with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

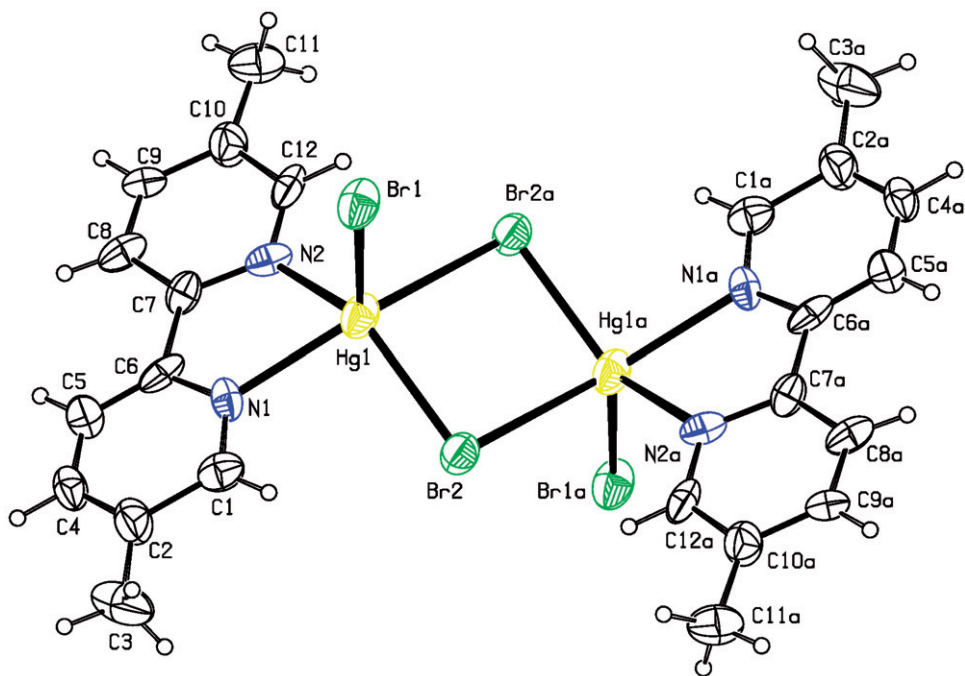


Figure 2. ORTEP view of **2** with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

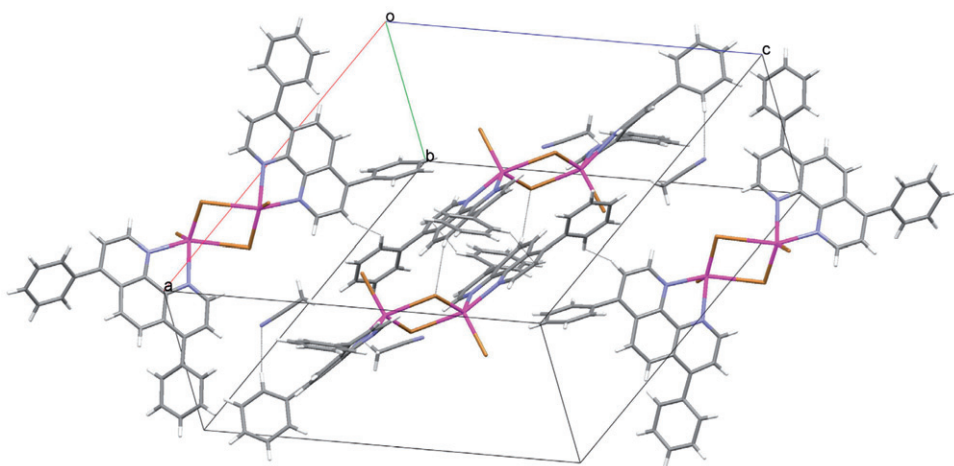


Figure 3. Crystal packing diagram for **1**. Hydrogen bonds are shown as dashed lines.

3.2.1. {[Hg(Ph₂phen)(μ -Br)]₂Br₂} · CH₃CN (1**).** The structure of **1** shows a bromo-bridged dinuclear Hg₂Br₂ unit (figure 1). The geometry around Hg is distorted tetrahedral from two bromides and two nitrogens of 4,7-diphenyl-1,10-phenanthroline ligand. However, mercury is weakly bound to a third bridging bromide with Hg1–Br3 distance of 3.189(2) Å [Hg2–Br1: 3.0583(17) Å]. These bond lengths are longer than normal Hg–Br bond distances. The different Hg–N bond distances (Hg1–N1: 2.388(11) Å and Hg1–N2: 2.352(11) Å) and Hg–Br (Hg1–Br1: 2.5549(16) Å and Hg1–Br2: 2.5280(18) Å) together with small bite angles of 4,7-diphenyl-1,10-phenanthroline (69.3(4)° for N1–Hg1–N2 and 68.0(4)° for N3–Hg2–N4) provide support for the distorted geometry. The complex also consists of one CH₃CN, as solvent of crystallization. The distance between Hg1 and N1–N2–Br3–Br1 plane is 0.795(2) Å and the corresponding distance for Hg2 and N3–N4–Br1–Br3 plane is 0.801(2) Å.

The Hg–N distances are in the range 2.352(11)–2.491(11) Å (average: 2.406(43) Å) (with one bond length (Hg2–N3: 2.491(11) Å) slightly longer than the others). This bonding parameter is similar to most of the previously reported complexes, for instance (1)HgCl₂ (**1**: 2,5-diphenyl-3,4-bis(2-pyridylcyclopenta-2,4-dien-1-one), about 2.41 Å [33], Hg(II) macrocyclic complexes, in the range 2.370(10)–2.445(16) Å, [34] and [Hg(py)₂]₂ (py: pyridazine), 2.42 Å [35], but shorter than Hg–N bond lengths in [HgCl₂(NIT2-thz)₂] (NIT2-thz = 2-(2'-thiazole)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), 2.635(6) Å [36].

The phenanthroline of 4,7-diphenyl-1,10-phenanthroline is planar, whereas the two phenyl groups deviate from the plane.

Average bond distances for terminal Hg–Br bonds (Hg1–Br2: 2.5280(18) Å and Hg2–Br4: 2.5358(19) Å) is 2.5319(18) Å, not significantly different from the corresponding average bond distances for two of bridging bromides (Hg1–Br1: 2.5549(16) Å and Hg2–Br3: 2.5263(17) Å) of 2.5406(16) Å, but do vary significantly from the average value of other Hg–Br distances (Hg1–Br3: 3.189(2) Å and Hg2–Br1: 3.0583(17) Å) (average: 3.1237(2) Å). Therefore, as previously reported [8], there is a semi-bridging interaction between the two bridging bromides, Br1 and Br3 and the Hg centers, Hg2 and Hg1.

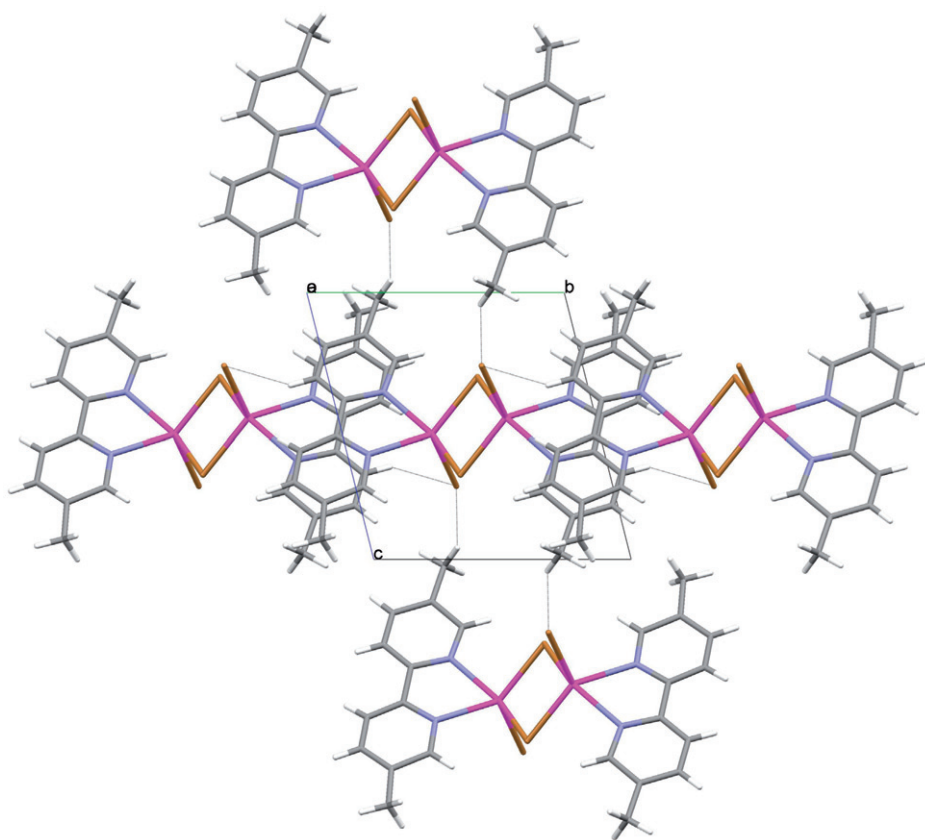


Figure 4. Crystal packing diagram for **2**, in the *a*-direction. Hydrogen bonds are dashed lines.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Hg(1)–Br(1)	2.5549(16)	Hg(2)–Br(3)	2.5263(17)
Hg(1)–Br(2)	2.5280(18)	Hg(2)–Br(4)	2.5358(19)
Hg(1)–Br(3)	3.189(2)	Hg(2)–N(3)	2.491(11)
Hg(1)–N(1)	2.388(11)	Hg(2)–N(4)	2.393(10)
Hg(1)–N(2)	2.352(11)		
Hg(2)–Br(1)	3.0583(17)		
Hg(1)–Br(1)–Hg(2)	95.08(5)	Br(3)–Hg(2)–Br(1)	87.83(5)
N(4)–Hg(2)–N(3)	68.0(4)	Br(4)–Hg(2)–Br(1)	92.38(6)
N(4)–Hg(2)–Br(3)	132.7(3)	N(2)–Hg(1)–N(1)	69.3(4)
N(3)–Hg(2)–Br(3)	92.9(3)	N(2)–Hg(1)–Br(2)	111.8(3)
N(4)–Hg(2)–Br(4)	95.1(3)	N(1)–Hg(1)–Br(2)	101.8(3)
N(3)–Hg(2)–Br(4)	108.1(3)	N(2)–Hg(1)–Br(1)	128.5(3)
Br(3)–Hg(2)–Br(4)	132.15(7)	N(1)–Hg(1)–Br(1)	101.5(3)
N(4)–Hg(2)–Br(1)	90.5(3)	Br(2)–Hg(1)–Br(1)	119.54(6)
N(3)–Hg(2)–Br(1)	151.0(3)		

3.2.2. {[Hg(dmbpy)(μ -Br)₂Br₂] (2). For {[Hg(dmbpy)(μ -Br)₂Br₂] (**2**), like **1**, there is a tendency to form a five coordinate structure as shown in figure 2. Complex **2** contains tetracoordinate mercury(II) with coordination through bipyridine nitrogen and two bromides (Br1 and Br2) bringing the coordination number to four. The asymmetric unit

Table 3. Selected bond distances (Å), angles (°), and torsion angles (°) for **2**.

Hg(1)–N(1)	2.402(18)	Hg(1)–Br(2)	2.597(3)
Hg(1)–N(2)	2.37(2)	Hg(1) ^{#1} –Br(2)	3.069(3)
Hg(1)–Br(1)	2.527(3)	Hg(1)–Br(2) ^{#1}	3.069(3)
Hg(1)–Br(2)–Hg(1) ^{#1}	94.52(9)	Br(1)–Hg(1)–Br(2)	120.13(12)
N(2)–Hg(1)–N(1)	70.0(8)	N(2)–Hg(1)–Br(2) ^{#1}	85.5(6)
N(2)–Hg(1)–Br(1)	106.4(5)	N(1)–Hg(1)–Br(2) ^{#1}	145.7(5)
N(1)–Hg(1)–Br(1)	113.1(5)	Br(1)–Hg(1)–Br(2) ^{#1}	96.33(11)
N(2)–Hg(1)–Br(2)	133.3(5)	Br(2)–Hg(1)–Br(2) ^{#1}	85.48(9)
N(1)–Hg(1)–Br(2)	94.0(5)		
Hg(1) ^{#1} –Br(2)–Hg(1)–N(2)	79.5(9)	Hg(1) ^{#1} –Br(2)–Hg(1)–Br(1)	–94.70(14)
Hg(1) ^{#1} –Br(2)–Hg(1)–N(1)	145.6(5)	Hg(1) ^{#1} –Br(2)–Hg(1)–Br(2) ^{#1}	0.0

Symmetry codes: #1: $-x, -y + 1, -z + 1$.Table 4. $\pi \cdots \pi$ Interactions for **1** and **2**.

Ring(i)–Ring(j)	Cg–Cg distance (Å)	Symmetry code
1^a		
Cg(2)–Cg(9)	3.712(7)	$-x, 2 - y, 2 - z$
Cg(4)–Cg(5)	3.864(8)	$-x, 2 - y, 2 - z$
Cg(5)–Cg(9)	3.893(7)	$-x, 2 - y, 2 - z$
Cg(6)–Cg(7)	3.870(8)	$1 - x, 2 - y, 2 - z$
Cg(7)–Cg(12)	3.859(7)	$1 - x, 2 - y, 2 - z$
Cg(9)–Cg(9)	3.714(8)	$-x, 2 - y, 2 - z$
Cg(9)–Cg(9)	3.714(8)	$-x, 2 - y, 2 - z$
2^b		
Cg(2)–Cg(4)	3.694(16)	$-x, -y, 1 - z$
Cg(4)–Cg(4)	3.794(17)	$-x, -y, 1 - z$

^aCg(1) denotes rings: Cg(2) = Hg(1)–N(1)–C(24)–C(23)–N(2); Cg(4) = N(1)–C(1)–C(2)–C(3)–C(10)–C(24); Cg(5) = N(2)–C(22)–C(21)–C(14)–C(13)–C(23); Cg(6) = N(3)–C(25)–C(26)–C(27)–C(34)–C(48); Cg(7) = N(4)–C(46)–C(45)–C(38)–C(37)–C(47); Cg(9) = C(10)–C(11)–C(12)–C(13)–C(23)–C(24); Cg(12) = C(34)–C(35)–C(36)–C(37)–C(47)–C(48).

^bCg(1) denotes rings: Cg(2) = Hg(1)–N(1)–C(6)–C(7)–N(2); Cg(4) = N(2)–C(7)–C(8)–C(9)–C(10)–C(12).

Table 5. Hydrogen bond geometry of **1** and **2** in crystal packing (Å, °).

C–H \cdots X	C–H	H \cdots X	C \cdots X	C–H \cdots X	Symmetry code
1					
C(2)–H(2) \cdots Br(2)	0.9300	2.8500	3.713(16)	155.00	$1/2 - x, 1/2 + y, 5/2 - z$
C(12)–H(12) \cdots Br(1)	0.9300	2.9300	3.735(14)	146.00	$-x, 2 - y, 2 - z$
C(22)–H(22) \cdots Br(3)	0.9300	2.7900	3.577(16)	143.00	–
C(33)–H(33) \cdots N(5)	0.9300	2.5400	3.47(3)	170.00	$-1/2 + x, 3/2 - y, 1/2 + z$
2					
C(12)–H(12) \cdots Br(2)	0.9300	2.8700	3.56(3)	132.00	$-x, 1 - y, 1 - z$

contains one half-molecule and similar to **1** the geometry at Hg is distorted tetrahedral. Here again mercury is weakly bound to a third bridging Br with Hg1–Br2a distance of 3.069(3) Å.

Table 4 reveals that the average bond distances between Hg and the two nitrogen donors (Hg1–N1: 2.402(18) Å and Hg1–N2: 2.37(2) Å) (average: 2.386(38) Å) are very

similar to **1** and to previously reported complexes for instance the 4,4'-dimethyl-2,2'-bipyridine containing complex, average: 2.3775(6) Å [10], [Hg(Am4DM)Br]₂ (Ham4DM is 2-pyridineformamide *N*(4)-dimethylthiosemicarbazone), average: 2.4025(5) Å [19].

Like **1**, the acute chelate bite angle of 5,5'-dimethyl-2,2'-bipyridine on coordination to Hg(II), N1–Hg1–N2, 70.0(8)° may be the reason for geometrical distortion. The other bond angles around Hg also differ somewhat between the two complexes.

With regard to their Hg-donor bond lengths **1** and **2** are similar to each other. In **2**, just like **1**, there is considerable difference between two of Hg–Br bond distances (Hg1–Br1: 2.527(3) Å and Hg1–Br2: 2.597(3) Å) and the third one (Hg1–Br2a: 3.069(3) Å). In fact, here, similar to **1** there is a semi-bridging interaction and the Hg1–Br2a interaction can be viewed as semi-coordination.

In crystals of **1** and **2**, the Ph₂phen and dmbpy are involved in weak π – π stacking interactions with adjacent units (table 4) [37–42]. Other interactions are also deduced from the crystal structure of **1** and **2**. A more detailed inspection shows that C–H...Br (**1** and **2**) and C–H...N (**1**) hydrogen bonds link the molecules (table 5).

It is evident from packing diagrams (figures 3 and 4) that one bromide is positioned toward Hg from another neighboring molecule, and the distance of Hg1–Br3 and Hg2–Br1 in **1** and Hg1–Br2ⁱ (symmetry code: (i) $-x, 1-y, 1-z$) in **2** are 3.189(2), 3.0583(17), and 3.069(3) Å, respectively. These distances are a little longer than the bond distance observed for bridging Hg–Br–Hg. Therefore, we conclude that there is a semi-bridging interaction between bromide and the neighboring Hg.

4. Conclusion

Two divalent mercury complexes containing substituted phenanthroline and bipyridine ligands have been synthesized and characterized by IR, ¹H, and ¹³C NMR as well as crystal structure determinations. Diffraction studies reveal that both complexes contain a bromo-bridged dinuclear Hg₂Br₂ unit and are coordinated by three bromides and two nitrogens of bidentate ligands. In both complexes there is a semi-bridging interaction between the bridging bromides and neighboring Hg centers. There are weak π – π stacking interactions, between the nitrogen containing rings of neighboring molecules in both complexes, that together with C–H...Br (**1** and **2**) and C–H...N (**1**) hydrogen bonding stabilize the structures.

Supplementary material

CCDC 743322 and 743321 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

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