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Synthesis, characterisation and study of mercury(II) chloride complexes with triphenylphosphine and heterocyclic thiones. The crystal structures of [(benzothiazole-2-thionato)-(benzothiazole-2-thione)(bis-triphenylphosphine) chloro mercury(II)] and [(µ₂-dichloro){(bis-pyrimidine-2-thionato)mercury(II)}{(bis-triphenylphosphine)mercury(II)}] at 100 K

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Abstract

Direct reaction of mercury(II) chloride with triphenylphosphine (PPh₃) and benzothiazole-2-thione (bzthtH) in the molar ratio of 1:1:2 results in the formation of the $[Hg(PPh_3)(bzthztH)(bzthzt)C]]$ (1) (bzthzt = the anion of benzothiazole-2-thione) while the reaction of mercury(II) chloride with triphenylphosphine (PPh₃) and pyrimidine-2-thione (pmtH) in the molar ratio of 1:1:1 gives $[Hg_2Cl_2(PPh_3)_2(pmt)_2]$ (2) (pmt = the anion of pyrimidine-2-thione). The complexes have been characterised by their elemental analyses, melting points and their FTIR, far-IR spectroscopic data. The crystal structure of complex 1 which has been determined by single-crystal X-ray crystallography at r.t. reveals that the molecule is monomeric with tetrahedral geometry around the metal ion. A benzothiazole-2-thione molecule and a benzothiazole-2-thionato anion are coordinated, via sulfur atoms, to the mercury(II) ion [Hg-S(2A) = 2.726(2) and Hg-S(2) = 2.419(2) Å]. A triphenylphosphine molecule is also coordinated through a phosphorus atom to the metal ion [Hg-P = 2.453(2) Å] while the tetrahedral geometry around the mercury is completed by a chlorine atom [Hg-Cl = 2.633(2) Å]. The complex is covalent in the solid state. The crystal structure of complex 2 which has also been established by single-crystal X-ray crystallography at 100(1) K shows that the molecule is binuclear and consists of two different moieties with tetrahedral geometry around each mercury(II) ion. One moiety consists of a mercury(II) ion with two phosphorus atoms from phosphine ligands and two bridging chlorine atoms, while the other consists of a mercury(II) ion and two sulfur atoms of pyrimidine-2-thionato ligands. The entire complex is covalent in the solid state. The two Hg(2)-S(42) bond lengths are 2.3513(11) Å while the two Hg(1)–P(1) bond lengths are 2.4826(9) Å. The two parts of the molecule are linked to each other by two chlorine atoms with Hg(1)-Cl(1) and Hg(2)-Cl(1) bond distances of 2.5310(10) and 3.0472(10) Å, respectively. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The study of the coordination and structural chemistry of mercury(II) halide complexes with ligands con-

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taining a variety of donor atoms has been a matter of interest over several decades [1-5]. The study of mercury complexes with sulfur-containing ligands has attracted considerable interest due to the relevance of this type of molecule as structural and spectroscopic models of biological systems [6–13]. Among the topics of interest in the study of the chemistry of mercury complexes with ligands containing thiolate or thione groups is the potential of these ligands for use in the detoxification of

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mercury from living systems afforded by the binding of mercury ions to the thiolato or thione groups of the ligands rather than to the cystein thiolate groups of proteins [14,15]. In the literature, there are some reports on the interaction of heterocyclic thiones and mercury ions [16–24]. On the other hand, the multiformity of the structural types which have resulted for the mercury(II) complexes with aryl-phosphine ligands provides an area of interest [25–29]. Surprisingly, there are very few reports on the structural characterisation of mixed-ligand mercury(II) complexes with heterocyclic thiones and triaryl-phosphine ligands [30].

Here we report the structural and spectroscopic characterisation of mercury(II) complexes derived from the reaction of mercury(II) chloride with triphenyl-phosphine and benzothiazole-2-thione ($I, C_7H_5NS_2$) or pyrimidine-2-thione ($II, C_4H_4N_2S$) in different molar ratios.



2. Experimental

2.1. Materials and instruments

All solvents used were reagent grade, mercury(II) chloride and triphenylphosphine (Merck) as well as benzothiazole-2-thione and pyrimidine-2-thione (Merck or Aldrich) were used with no other purification prior to use. Elemental analyses for C, H, N, and S were carried out with a Carlo Erba EA model 1108. Melting points were measured with a Stuart Scientific apparatus and are uncorrected. IR spectra in the region of 4000– 370 cm^{-1} were obtained in KBr discs while far-IR spectra in the region of 400–50 cm⁻¹ were obtained in polyethylene discs, with a Perkin–Elmer Spectrum GX FTIR spectrometer.

2.2. Synthesis of $[Hg(PPh_3)(bzthztH)(bzthzt)Cl]$ (1)

A mixture of mercury(II) chloride (0.138 g, 0.5 mmol), triphenylphosphine (0.132 g, 0.5 mmol) and benzothiazole-2-thione (0.167 g, 1.0 mmol) in a 20 ml solution of 1:1 methanol-acetonitrile was stirred for 3 h. The suspension was filtered off and the clear solution was kept in darkness. Slow evaporation of the solvent at room temperature (r.t.) yielded orange crystals suitable for single-crystal analysis by crystallography. M.p. 167°C. *Anal.* Found: C: 46.87; H: 2.99; N: 3.76; S:

15.47. Calc. for $C_{32}H_{24}ClHgN_2PS_4$: C: 46.21; H: 2.91; N: 3.37; S:15.42%. IR (cm⁻¹): 1597m, 1496s, 1451s, 1433vs, 1407vs, 1332s, 1097vs, 1071vs, 1022vs, 1008vs, 985vs, 747vs, 687vs, 601vs, 519vs, 501vs, 486vs. Far-IR (cm⁻¹): 310m, 248s, 192s, 165s, 152s, 141m.

2.3. Synthesis of $[Hg_2Cl_2(PPh_3)_2(pmt)_2]$ (2)

A mixture of mercury(II) chloride (0.138 g, 0.5 mmol), triphenylphosphine (0.132 g, 0.5 mmol) and pyrimidine-2-thione (0.056 g, 0.5 mmol) was suspended in a 20 ml solution of 1:1 methanol-acetonitrile and stirred for 3 h. The suspension was filtered off and the clear solution was kept in darkness. Slow evaporation of the solvent at r.t. yielded pale yellow-white crystals suitable for single-crystal analysis by crystallography. M.p. 220°C. *Anal.* Found: C: 43.29; H: 2.95; N: 4.32; S: 5.85. Calc. for C₄₄H₃₆Cl₂Hg₂N₄P₂S₂: C: 43.36; H: 2.97; N: 4.60; S: 5.26%. IR (cm⁻¹): 1560s, 1537s, 1481m, 1425s, 1370vs, 1201m, 1172s, 1097s, 803s;743vs, 691vs, 519s, 504vs, 489s. Far-IR (cm⁻¹): 248s, 227m, 177m, 172m, 165m, 151s, 134m.

2.4. X-ray data collection and reduction of the intensity data of the complexes

X-ray diffraction data were collected on a Kuma KM4CCD [31] diffractometer equipped with a CCD area detector. The experiment for 1 was carried out at r.t., while for 2 the temperature was set at 100(1) K, using graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. The frames were record using $\Delta \omega = 0.75^{\circ}$ rotation scans. A total of 782 frames in six runs were measured for each structure. Each frame was recorded twice in order to eliminate accidental spots. Reflection indexing, Lorentz and polarisation correction, peak integration and background determinations were performed using the Kuma CRYSALIS RED software package [32]. The unit cell dimensions were initially determined from the 15 appropriately chosen frames and were then refined with all recorded images. Empirical absorption corrections were applied for both data sets; $T_{\min} = 0.40$ for 1 and 0.491 for 2, $T_{\max} = 0.944$ and 0.972 for 1 and 2, respectively. Both structures were solved by direct methods using the program SHELXS-86 [33]. For each structure, full-matrix least-squares refinement with all reflections was carried out with the program SHELXL-93 [34]. Scattering factors incorporated in SHELXL-93 were used. The function $\Sigma w(|F_0|^2 - |F_c|^2)^2$ was minimised with $w^{-1} = [\alpha^2 (F_0)^2 + 0.0504P^2]$ (P = $[\max(F_{0}^{2}, 0) + 2F_{c}^{2}]/3)$). Empirical extinction corrections were also applied to compounds 1 and 2, according to the formula $F'_{c} = kF_{c}[1 + 0.001 \times F_{c}^{2}\lambda^{3}/\sin 2\theta]^{1/4}$. The final values for 1 and 2 are listed in Table 1. The non-hydrogen atoms were refined with anisotropic thermal parameters. The coordinates of the other hydrogen atoms were calculated as 1.2 times U_{eq} for the appropriate carrier carbon atom. Bond lengths and angles for both compounds are listed in Tables 2 and 3. Thermal ellipsoid representations of the molecules together with atomic numbering schemes are shown in Figs. 1 and 2.

2.5. Computational details

Extended Hückel calculations were performed using the program CACAO [35]. The calculations were carried out using crystallographic data of the molecules studied. The EHT parameters for Hg, were those established in the literature.

3. Results and discussion

3.1. General aspects

Crystals of complex 1 were prepared by slow evaporation of the solution remaining after the filtration of

Table 1

Crystal data and the structure refinement details for the complexes ${\bf 1}$ and ${\bf 2}$

$\label{eq:empirical formula C_32H_24ClHgN_2PS_4 C_{44}H_{36}Cl_2Hg_2N_4$	P_2S_2
Formula weight 831.78 1218.90	
Crystal system monoclinic monoclinic	
Space group $P2_1/c$ $C2/c$	
<i>a</i> (Å) 10.412(2) 15.7674(9)	
<i>b</i> (Å) 29.472(6) 13.2146(7)	
c (Å) 11.039(2) 20.6533(10)	
β (°) 111.29(3) 99.140(4)	
$V(Å^3)$ 3156.3(11) 4248.6(2)	
Z 4 2	
$D_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$ 1.75 1.91	
<i>F</i> (000) 1624 2336	
$\mu(mm^{-1})$ 5.30 7.55	
Crystal size (mm) $0.3 \times 0.3 \times 0.2$ $0.2 \times 0.2 \times 0.15$	
θ Range (°) 2–30 2–30	
$hkl \text{ Range} \qquad -11 \le h \le 11, \qquad -21 \le h \le 19,$	
$-30 \le k \le 31, -18 \le k \le 18,$	
$-9 \le l \le 11$ $-28 \le l \le 26$	
Reflections 14771 18062	
measured	
Unique reflections 4045 (0.069) 5511 (0.041)	
$(R_{\rm int})$	
Number of 371 254	
parameters	
Weighting	
scheme:	
1 0.01 0.045	
2 5 0.6	
Extinction 0.00066(14) 0 0.031	
parameter (k)	
<i>R</i> (<i>F</i>) 0.059 0.079	
$wR(F^2)$ 0.089	
Goodness-of-fit 1.78 1.20	
Max/min $\Delta \rho$ 0.9/-1.0 1.9/-2.6	
$(e A^{-3})$	

Table 2

Selected bond lengths (Å) and angles (°) for molecule 1 with e.s.d. values in parentheses

Bond lengths			
Hg(1)-S(2)	2.419(2)	S(1A)-C(2A)	1.747(8)
Hg(1) - P(1)	2.453(2)	S(1A)-C(9A)	1.750(9)
Hg(1)-Cl(1)	2.633(2)	C(2A)-N(3A)	1.320(11)
Hg(1)-S(2A)	2.726(2)	C(2A)-S(2A)	1.690(9)
S(1)–C(9)	1.735(9)	N(3A)-C(4A)	1.392(11)
S(1)–C(2)	1.755(8)	C(4A)-C(9A)	1.386(12)
C(2)–N(3)	1.288(11)	P(1)-C(21)	1.799(8)
C(2)–S(2)	1.726(9)	P(1)-C(11)	1.802(9)
N(3)–C(4)	1.403(11)	P(1)-C(31)	1.812(8)
C(4)–C(9)	1.392(12)		
Bond angles			
S(2) - Hg(1) - P(1)	140.79(7)	N(3A)-C(2A)-S(2A)	128.2(7)
S(2)-Hg(1)-Cl(1)	101.10(8)	N(3A)-C(2A)-S(1A)	110.3(6)
P(1)-Hg(1)-Cl(1)	103.30(8)	S(2A)-C(2A)-S(1A)	121.5(5)
S(2)-Hg(1) S(2A)	108.23(8)	C(2A)-S(2A)-Hg(1)	108.4(3)
P(1)-Hg(1)-S(2A)	97.66(8)	C(2A)-N(3A)-C(4A)	116.5(7)
Cl(1)-Hg(1)-S(2A)	99.10(7)	C(5A)-C(4A)-C(9A)	121.0(9)
C(9)-S(1)-C(2)	89.2(4)	C(5A)-C(4A)-N(3A)	127.2(9)
N(3)-C(2)-S(2)	126.5(7)	C(9A)-C(4A)-N(3A)	111.8(8)
N(3)-C(2)-S(1)	115.1(6)	C(8A)-C(9A)-S(1A)	129.5(7)
S(2)-C(2)-S(1)	118.4(5)	C(4A)-C(9A)-S(1A)	110.1(6)
C(2)-S(2)-Hg(1)	97.5(3)	C(21)–P(1)–C(11)	106.7(4)
C(2)-N(3)-C(4)	111.6(7)	C(21)–P(1)–C(31)	106.6(3)
C(5)-C(4)-N(3)	125.8(8)	C(11)–P(1)–C(31)	107 7(4)
C(9)-C(4)-N(3)	114.3(8)	C(21)-P(1)-Hg(1)	109,3(3)
C(4)-C(9)-S(1)	109.8(6)	C(11)-P(1)-Hg(1)	113.0(3)
C(8)–C(9)–S(1)	129.0(8)	C(31)–P(1)–Hg(1)	113.2(3)
C(2A)-S(1A)-C(9A)	91.3(4)		

the initial product had deposited from the reaction of $HgCl_2$ with triphenylphosphine and benzothiazole-2thione in a molar ratio of 1:1:2 in methanol-acetonitrile solution. Smaller yields of the same product were obtained using a 1:1:1 molar ratio of reactants. Crystals of complex **2** were similarly obtained from the reaction of $HgCl_2$ with triphenylphosphine and pyrimidine-2thione in equimolar ratio. The formulas of the complexes were firstly deduced from their elemental analysis, m.p. and their spectroscopic data. The crystals of the complexes are air stable when they are stored in darkness at r.t.

3.2. IR spectroscopy

The IR spectra of complex 1 shows distinct vibrational bands at 1496 and at 1332 cm⁻¹ which have been assigned as C–N bond vibrations (thioamide bands I and II) and at 1008 and at 747 cm⁻¹ which were attributed to the C–S bond vibrations (thioamide bands III and IV). The corresponding thioamide bands of the free benzothiazole-2-thione ligand are given at 1490, 1320, 1010 and 860 cm⁻¹, respectively [36,37]. The most significant change has been observed in the thioamide band IV, supporting the sulfur donation of the ligand upon its coordination to the metal ion. The 2234

Selected	bond	lengths	(Å)	and	angles	(°)	for	molecule	2	with	e.s.d.
values ir	n parei	ntheses ^a									

Bond lengths			
Hg(1)-P(1)	2.4826(9)	N(41)-C(44)	1.333(6)
Hg(1)-Cl(1)	2.5310(10)	N(41)-C(42)	1.339(5)
Hg(2)–S(42)	2.3513(11)	C(42)–N(43)	1.328(5)
Hg(2)–Cl(1)	3.0472(10)	C(42)–S(42)	1.765(4)
P(1)-C(21)	1.805(4)	N(43)-C(46)	1.340(5)
P(1)-C(11)	1.809(4)	C(44)-C(45)	1.369(7)
P(1)-C(31)	1.814(4)	C(45)-C(46)	1.371(6)
Bond ang les			
$P(1)^{i}-Hg(1)-P(1)$	116.32(4)	C(21)-P(1)-Hg(1)	114.81(12)
P(1)-Hg(1)-Cl(1)	107.10(4)	C(11)-P(1)-Hg(1)	112.85(12)
$P(1)-Hg(1)-Cl(1)^{i}$	113.72(4)	C(31)-P(1)-Hg(1)	108.11(11)
$Cl(1)-Hg(1)-Cl(1)^{i}$	97.39(4)	C(44)-N(41)-C(42)	115.4(4)
$S(42)^{i}-Hg(2)-S(42)$	168.11(5)	N(43)-C(42)-N(41)	126.6(4)
$S(42)-Hg(2)-Cl(1)^{i}$	99.20(4)	N(43)-C(42)-S(42)	119.2(3)
S(42)–Hg(2)–Cl(1)	90.11(4)	N(41)-C(42)-S(42)	114.2(3)
$Cl(1)^{i}-Hg(2)-Cl(1)$	77.21(4)	C(42) S(42)-Hg(2)	99.82(13)
Hg(1)-Cl(1)-Hg(2)	92.70(3)	C(42)-N(43)-C(46)	115.6(3)
C(21)–P(1)–C(11)	107.66(16)	N(41)-C(44)-C(45)	123.3(4)
C(21)–P(1)–C(31)	106.88(17)	C(44)-C(45)-C(46)	116.2(4)
C(11)–P(1)–C(31)	106.02(17)	N(43)-C(46)-C(45)	122.9(4)

^a Symmetry transformations used to generate equivalent atoms: 1-x, y, -z+1/2.

bands at 687, 519, 501 and 486 cm⁻¹ have been attributed to the vibrations of the C–P bond. Further information about the complex formation was obtained from the study of far-IR spectra. The new bands at 137, 192 and 248 cm⁻¹ have been assigned to the vibrations of Hg–P, Hg–S and Hg–Cl bonds, respectively [22,38,39]. The IR spectra of complex **2** shows bands at 1560 1370, 1172 and 803 cm⁻¹ for the thioamide bands I, II, III and IV, respectively, while the bands observed at 690, 508, and 489 cm⁻¹ are characteristic for the vibrations of the P–C bond. The corresponding thioamide bands of the free thione ligand are given at 1510, 1320, 982 and 791 cm⁻¹, respectively [40]. The far-IR spectra of complex **2** contains new bands at 141, 165 and 247 cm⁻¹ which have been attributed to the Hg–P, Hg–S and Hg–Cl bonds, respectively [22,38,39].



Fig. 2. Thermal ellipsoid representations of molecule **2** together with the atomic numbering scheme.

3.3. Structure of the [Hg(PPh₃)(bzthztH)(bzthzt)Cl] (1)

A view of molecule 1 is shown in Fig. 1, while selected bond lengths and angles are given in Table 2. The molecule is a covalent monomer in the solid state with tetrahedral geometry around the metal ion. Two sulfur atoms, one phosphorus atom and one chlorine atom surround the mercury atom to build a distorted tetrahedron. Thus, one of the two benzothiazole-2-thione molecules has been deprotonated upon coordination. The formation of the benzothiazole-2-thionato anion during the reaction of a neutral thione molecule with the [Cu(PPh₃)₃Cl] has also been observed and is described earlier [37]. The Hg(1)-S(2A) bond distance is 2.726(2) Å while the C(2A)-S(2A) and C(2A)-N(3A) bond distances are 1.690(9) and 1.320(11) Å, respectively, indicating that this ligand has been coordinated through its neutral form. The Hg(1)-S(2A) bond length is longer than those found in $[HgBr_2(meimz2SH)]_2$ (Hg-S = 2.407(2) and 2.405(2) Å)



Fig. 1. Thermal ellipsoid representations of molecule 1 together with the atomic numbering scheme.

[20], $[Hg(ditet)_2Cl_2]$ (Hg–S = 2.49(1) and 2.50(1) Å) and in $[Hg(diditet)Cl_2]$ (Hg-S = 2.42(2) Å) [22], where thione ligands have been coordinated to the metal through their neutral form. The second Hg(1)-S(2)bond distance is 2.419(2) Å, while the corresponding C(2)-S(2) and C(2)-N(3) bonds are 1.726(9) and 1.288(11) Å, respectively, indicating a coordination through the anionic form of this ligand. The Hg-S bond length found earlier in $[Hg(PPh_3)_2(SCN_4Ph)_2]$ [30], where the ligand is coordinated to the mercury ion through its anionic form, is 2.566(3) Å. The Hg–P bond length is 2.453(2) Å and is similar to those found in $[Hg(PPh_3)_2(SCN_4Ph)_2]$ [30] (Hg-P = 2.500(3))A). $[Hg(PPh_3)_2(CN)_2]$ [25] (Hg-P = 2.434(5) and 2.589(5) Å,respectively), $[Hg(PPh_3)_2(NO_3)_2]$ [25] (Hg-P = 2.451(1))A) and in $[HgCl_2(PPh_3)_2]$ [28] (Hg-P = 2.462(2)) and 2.478(2) Å). The Hg–Cl bond length is 2.633(2) Å and is longer than those measured in [HgCl₂{Ph₂P(S)CH₂- $CH_2(S)PPh_2$] [3] (Hg-Cl = 2.447(3) and 2.442(3) Å, respectively), $[Hg(ditet)_2Cl_2]$ (Hg-Cl = 2.51(1) and 2.52(1) Å [22], $[{HgCl_2(H_2L)}_2]$ [38] (Hg–Cl = 2.532(6), 2.380(7), 2.585(6) and 2.489(7) Å) and in [HgCl₂- $(PPh_3)_2$ [28] (Hg-Cl = 2.559(2) and 2.545(3) Å). The Cl-Hg-S(2A) angle is 99.10(7)° indicating a N-H…Cl hydrogen bond while the Cl-Hg-S(2) angle is 108.23(8)° and is in accordance to those measured for the complex $[Hg(ditet)_2Cl_2]$ [22] (S(1)-Hg-Cl(1) =108.6(3) and S(2)-Hg-Cl(1) = 104.3(3)). The P-Hg-S-(2A) angle is 97.66(8)° and is in accordance to the corresponding angles found in [Hg(PPh₃)₂(SCN₄Ph)₂] [30] $(P-Hg-S = 100.37(6) \text{ and } 95.7(1)^\circ)$ while the P-Hg-S(2) angle is 140.79(7)°.

3.4. Structure of the $[Hg_2Cl_2(PPh_3)_2(pmt)_2]$ (2)

A view of molecule 2 is shown in Fig. 2, while selected bond lengths and angles are given in Table 3. The molecule is a covalent, binuclear complex which consists of two different moieties with tetrahedral geometry around each mercury(II) ion. One moiety, consists of a mercury(II) ion with two phosphorus atoms from phosphine ligands and two bridging chlorine atoms while the other, consists of a mercury(II) ion and two sulfur atoms of pyrimidine-2-thionato ligands. The whole molecule sits on a two-fold axis of symmetry passing through the two metal atoms. The two Hg-S bond lengths are 2.3513(11) Å and are in accordance with those found in $[HgBr_2(meimz2SH)]_2$ (Hg-S = 2.407(2) and 2.405(2) Å) [20], [Hg(ditet)₂Cl₂] (Hg–S = 2.49(1) and 2.50(1) Å) and in $[Hg(diditet)Cl_2]$ (Hg-S = 2.42(2) Å) [22], while the two Hg-P bond lengths are 2.4826(9) Å and are similar to those found in $[Hg(PPh_3)_2(SCN_4Ph)_2]$ [30] (Hg-P = 2.500(3) Å), $[Hg(PPh_3)_2(CN)_2]$ [25] (Hg-P = 2.434(5) and 2.589(5) Å,respectively), $[Hg(PPh_3)_2(NO_3)_2]$ [25] (Hg-P = 2.451(1))Å) and in $[{\text{HgCl}_2(\text{PPh}_3)_2}_2]$ [29] (Hg-P=2.406(7) Å).

The two parts of the molecule are linked to each other by two chlorine atoms with Hg(1)-Cl(1) and Hg(2)-Cl(1) bond distances 2.5310(10) and 3.0472(10) A, respectively. The corresponding bond distances between mercury(II) and bridging Cl atoms found in the $[{HgCl_2(PPh_3)_2}_2]$ complex [29] are Hg-Cl(2) = 2.623(8) Å and Hg–Cl $(2^i) = 2.658(8)$ Å, respectively. The $Cl(1)-Hg(1)-Cl(1)^{i}$, Hg(1)-Cl(1)-Hg(2)and the $Cl(1)-Hg(2)-Cl(1)^{i}$ angles are 97.39(4), 92.70(3) and 77.21(4)°, respectively. The values of the Cl(2)-Hg-Cl(2ⁱ) and Hg-Cl(2)-Hgⁱ angles measured in the $[{HgCl_2(PPh_3)_2}_2]$ complex [29] are 85.3(3) and 94.6(3)°, respectively. The $P(1)-Hg(1)-P(1)^{i}$ angle is 116.32(4)°, slightly smaller than the value of the corresponding angle measured in [Hg(PPh₃)₂(SCN₄Ph)₂] [30] $(P1-Hg-P2 = 125.6(1)^{\circ})$. The S(42)-Hg(1)-S(42)ⁱ angle is 168.11(5)°.

3.5. Computational study

The rather unusual formation of the complex $[Hg_2Cl_2(PPh_3)_2(pmt)_2]$ (2) prompted us to undertake a computational study in order to verify the factors leading the formation of this type of complex towards the formation of the $[Hg(PPh_3)(bzthztH)(bzthzt)Cl]$ (1) complex. As it has been evidenced, the energy of the LUMO lies 2.979 eV higher than the corresponding HOMO's energy in the case of complex 2 while the energy of the LUMO lies 3.618 eV higher than the corresponding HOMO's energy in the case of complex 1. The differences in the HOMO–LUMO energy values computed could explain the stability of 2. The calculated overlap population in the case of complex 1 is 0.342 and 0.657 e for the Hg(1)-Cl(1) and Hg(1)-P(1)bonds, respectively, and 0.330, 0.572 e for the two Hg(1)-S(2A) and Hg(1)-S(2) bonds. The calculated overlap population in the case of complex 2 is 0.639 e for the two Hg(1)-P bonds and 0.652 e for the two Hg(2)–S bonds, respectively, while the overlap population for the Hg(1)–Cl(1) and Hg(2)–Cl(1) bonds is 0.412 and 0.108 e, respectively. The calculated net charges for the Hg(1) and Hg(2) of complex 2 are -0.179 and 0.266, respectively.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 140 847 for compound 1 and 140 848 for compound 2. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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