

Synthesis, crystal structure and spectral studies of mercury(II) complexes containing the mixed ligands benz-1,3-imidazoline-2-thione, benz-1,3-oxazoline-2-thione, benz-1,3-thiazoline-2-thione, and diphosphine

AHMED S. M. AL-JANABI¹, BAYAZEED H. ABDULLAH² and SUBHI A. AL-JIBORI^{3*}

¹Department of Chemistry, College of Veterinary Medicine, University of Tikrit, Tikrit (Iraq).

²Department of Chemistry, College of Science, University of Sulimanyah, Sulimanyah (Iraq).

³Department of Chemistry, College of Science, University of Tikrit, Tikrit (Iraq).

(Received: February 10, 2009; Accepted: April 15, 2009)

ABSTRACT

Reaction of $[\text{Hg}(\text{OAc})_2]$ with two mole proportion of LH (LH= benz-1,3-imidazoline-2-thione, benz-1,3-oxazoline-2-thione or benz-1,3-thiazoline-2-thione) in the presence Et_3N gave linear complexes of the type $[\text{HgL}_2]$. Treatment of $[\text{HgL}_2]$ with two mole proportion of PPh_3 or one mole proportion of the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ gave tetrahedral complexes of the type $[\text{HgL}_2(\text{PPh}_3)_2]$, $[\text{HgL}_2(\text{m-diphos})_2]$ ($n=1$) or $[\text{HgL}_2(\text{diphos})]$ ($n = 2$ or 3) respectively, While treatment with two mole proportion of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) gave octahedral complexes of the type $[\text{HgL}_2(\text{dppm})_2]$.

The prepared complexes have been characterized by mean of elemental analysis, molar conductance, i.r. spectral data, ^1H , ^{13}C - $\{^1\text{H}\}$, ^{31}P - $\{^1\text{H}\}$ n.m.r. data. Single crystal x-ray analysis of two of the complexes (11 and 13) has revealed the presence of a tetrahedral coordination geometry about mercury.

Key words: Mercury, Phosphine, Thione ligand complexes.

INTRODUCTION

There is considerable interest in the coordination chemistry of mercury(II) with heterocyclic thione^{1,2} because of the importance of such complexes as models in biological system³ as solid-state complexes⁴. Mercury(II) halides and pseudohalides form 1:1 and 1:2 complexes with neutral heterocyclic thione ligands⁵⁻⁷. It was reported previously^{5,8,9} that the reaction of (LH); LH= benz-1,3-imidazoline-2-thione, benz-1,3-oxazoline-2-thione or benz-1,3-thiazoline-2-thione with $[\text{HgX}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or SCN) gave dinuclear halogen or SCN bridged complexes of the type $[\text{HgX}_2(\text{LH})][5]$, while reaction with HgI_2 gave trigonal planar complexes of the type $[\text{HgI}_2(\text{LH})]$. Reaction of HgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or SCN) with two mole equivalents of

LH gave tetrahedral complexes of the type $[\text{HgX}_2(\text{LH})_2][5,8,9]$. However heterocyclic thiones form linear complexes of the type $[\text{ML}_2]$ ($\text{L} =$ deprotonated thione ligands) by deprotonated^{5,10-12}. Mixed ligand complexes of heterocyclic thiones and phosphines have been reported for several metal ions such as silver and rhodium¹³⁻¹⁵. Complexes with mercury seem to be unexplored¹⁶. In the present paper we report the preparation of some mercury(II) complexes containing mixed ligands, tertiary diphosphines and heterocyclic thiones(LH) Fig. 1.

General

The ^1H - and ^{13}C - n.m.r spectra were recorded on Varian Unity 500 and Gemini 2000 spectrometers respectively with CDCl_3 as solvent

and Me₄Si as internal reference. ³¹P - n.m.r spectra were recorded on Gemini 200 spectrometer with CDCl₃ as solvent and H₃PO₄(85%) as external reference. The n.m.r. spectra were determined at the Institute für Anorganische chemie, Martin – Luther-universität Halle- Witten-berg, Germany. I.R. spectra were recorded on a shimadzu FT.IR. 8400 spectrometer in the 200 – 4000 cm⁻¹ range using CsI discs. Elemental analysis were carried out on a CHN analyzer type 1106 (Carlo –Erba). Conductivity measurements were made on a conductivity meter type Philips PW 9526. Melting points were measured on an electro thermal 9300 melting point apparatus.

Starting materials

The compounds [HgX₂] (X= Cl, Br, I, SCN or OAc), PPh₃, dppm, dppe, dppp, benz-1,3-imidazoline -2-thione, benz-1,3-oxazoline -2-thione or benz-1,3-thiazoline-2-thione were commercial products and were used as supplied, [Hg(bzimSH)₂](1), [Hg(bzoxS)₂](2), [Hg(bztzS)₂](3), were prepared according literature methods^{5,10,17}.

X-ray crystallography

Single crystal of 11 and 13 for x-ray diffraction studies were grown at room temperature from CHCl₃ and C₂H₅OH solution. Diffraction data were collected on a STOE-IPDS diffractometer at 200(2)K with Mo- K α radiation ($\lambda=0.71073$ Å, graphite monochromator).

A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in table 4.

The structures were solved by direct methods with SHELXS- 97 and refined using full-matrix least-square routines against F² with SHELXS- 97¹⁸. Non-hydrogen atoms were refined with anisotropic and hydrogen atoms with isotropic displacement parameters. Hydrogen atoms were refined to the "riding model".

Preparation of complexes

[Hg(bztzS)₂(m-dppm)]₂(4)

A solution of dppm (0.22g, 0.56mmol) in EtOH (10cm³) was added to a hot solution of [Hg(bztzS)₂](1) (0.3g, 0.56mmol) in EtOH(10cm³). The mixture was stirred at room temperature for

2h. The pale yellow solid thus formed was filtered off washed with EtOH, CHCl₃, dried under vacuum and recrystallized from Me₂CO (yield 90%). The following complexes were prepared and isolated by a similar method, (9) and (14).

[Hg(bztzS)₂(dppm)]₂ (5)

A solution of dppm (0.29g, 0.76mmol) in EtOH (10cm³) was added to a warm solution of [Hg(bztzS)₂](1) (0.2g , 0.38mmol) in EtOH(10cm³). The mixture was stirred at room temperature for 1.5h. The solid formed was filtered off washed with EtOH, CHCl₃, dried under vacuum and recrystallized from Me₂CO (yield 90%). The following complexes were prepared and isolated by a similar method, (10) and (16).

[Hg(bztzS)₂dppe] (6)

A solution of dppe (0.075g, 0.188mmol) in EtOH (10cm³) was added to a warm solution of [Hg(bztzS)₂](1) (0.1g , 0.188mmol) in EtOH(10cm³). The mixture was stirred at room temperature for 1h. The solid formed was filtered off washed with EtOH, CHCl₃, dried under vacuum and recrystallized from Me₂CO (yield 94%). The following complexes were prepared and isolated by a similar method^{7,11,12,16,17}.

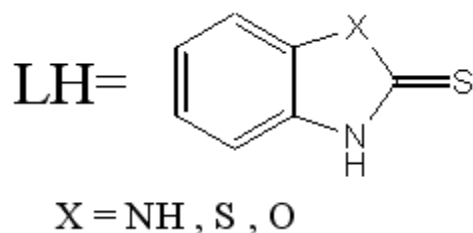
[Hg(bztzS)₂(PPh₃)₂] (8)

A solution of PPh₃ (0.21g, 0.76mmol) in EtOH (10cm³) was added to a warm solution of [Hg(bztzS)₂](1) (0.2g, 0.38mmol) in EtOH(10cm³). The mixture was stirred at room temperature for 2h. The solid thus formed was filtered off washed with EtOH, CHCl₃, dried under vacuum and recrystallized from Me₂CO (yield 90%). Complex¹³ was prepared, isolated and purified by a similar method.

RESULTS AND DISCUSSION

Synthesis of complexes

Treatment of the linear mercury(II) complexes of the type [HgL₂](1), (2), (3)[5,10,17] with one mole proportion of the diphosphines Ph₂P(CH₂)_nPPh₂ (n = 1-3) or two mole proportion of PPh₃ gave tetrahedral complexes of the [HgL₂(m-Ph₂PCH₂PPh₂)₂] (4), (9), (14) or the [HgL₂(Ph₂P(CH₂)_nPPh₂)₂] (n = 2 or 3) (6), (7), (11), (12), (16), (17) or the [HgL₂(PPh₃)₂] (8),(13). The



LH= bzimSH₂, X=NH ; bzoSH X=O ; bztzSH X=S.

Fig 1: The structure of the ligands (LH)

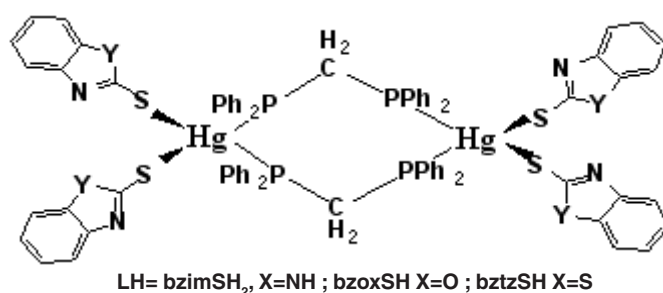


Fig. 2: The structure of the complexes [HgL₂(dppm)]₂

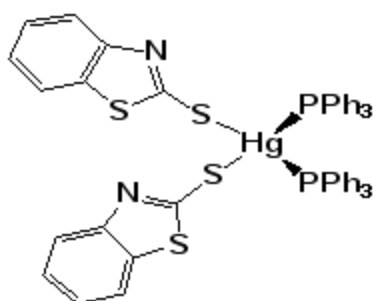


Fig. 3: The structure of the complex [Hg(btzS)₂(PPh₃)₂]

anionic thionato ligands are coordinated as monodentate ligands, via sulfur atoms to mercury(II) ion. The diphosphine Ph₂PCH₂PPh₂ was coordinated as a bidentate bridging ligand, while Ph₂(CH₂)_nPPh₂ (n=2 or 3) were coordinated as bidentate chelates. PPh₃ coordinated as monodentate.

Treatment of the type [HgL₂] with two mole proportion of the diphosphines Ph₂PCH₂PPh₂ gave octahedral complexes of the type [HgL₂(Ph₂PCH₂PPh₂)₂]. The diphosphine Ph₂PCH₂PPh₂ behaves as a bidentate chelate ligands.

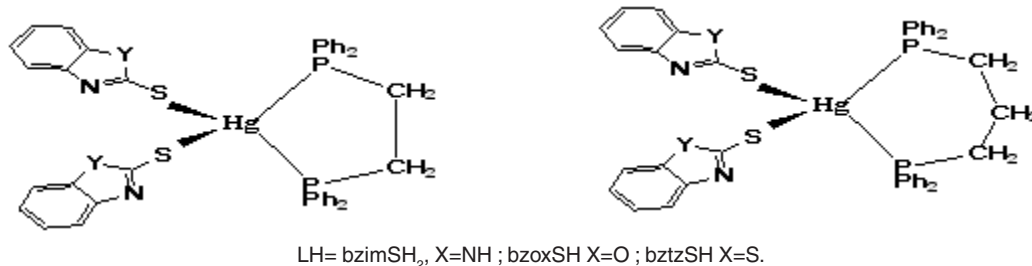


Fig 4: The structure of the complexes [HgL₂(diphos)]₂

Characterization of complexes

The prepared complexes were identified by elemental analysis, i.r. spectra, conductivity measurements and some them by ^{31}P - $\{^1\text{H}\}$, ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. spectra and their data are listed in Tables 1-3. The molar conductivity of the complexes in DMF or DMSO is low enough to suggest that they are non-electrolytes¹⁹.

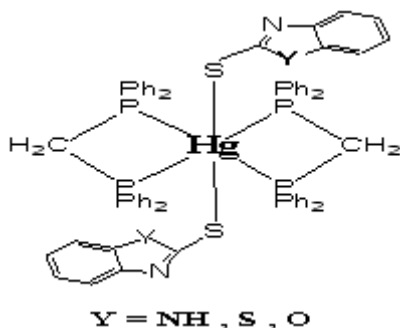


Fig. 5: The structure of the complexes $[\text{HgL}_2(\text{dppm})_2]$

Nuclear magnetic resonance

The ^{31}P - $\{^1\text{H}\}$, ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. data of some the prepared complexes are given in Table 3. The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra of complexes $[\text{HgL}_2(\text{dppm})]$ { $\text{L} = \text{bztzS}(4)$, $\text{bzimSH}(9)$ and $\text{bzoXS}(14)$, showed a singlet for each at $\delta\text{P} = 7.99$, 25.21 and 21.5 p.p.m respectively suggesting a single product. The positive values of the δP indicate that dppm behaves as a bidentate bridging²⁰⁻²². This has been supported by ^1H n.m.r. spectra of complexes (4) and (14) which showed a triplet at $\delta\text{H} = 3.68$ p.p.m with $^2\text{J}(\text{P}-\text{H}) = 6.5\text{Hz}$ and 4.26 p.p.m with $^2\text{J}(\text{P}-\text{H}) = 11.5\text{Hz}$ for the methylene group of the bridging dppm, coupled to two equivalent phosphorus atoms²³.

On the bases of the above n.m.r. data and other identification data given in tables 1 and 2. The structure shown in Fig. 2 has been suggested.

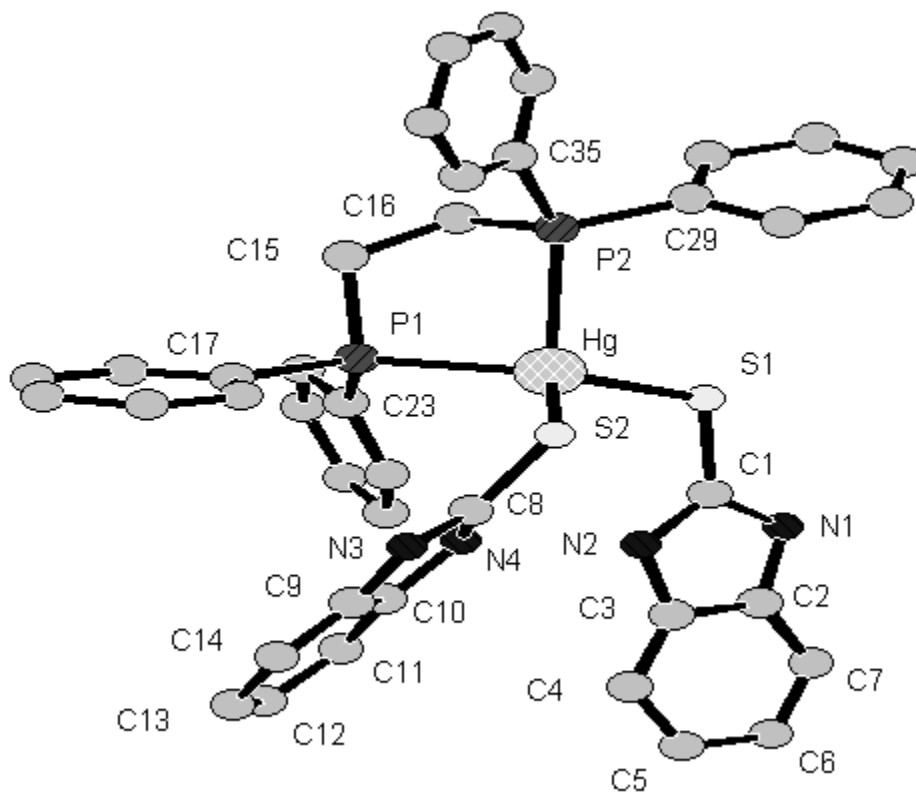


Fig. 6: Molecular structure of complexes (11)

Table 1: Color, Yield, m.p., Elemental analysis and conductivity of complexes (1-17)

Seq.	Complexes	Color	m.p. (°C)	Yield %	Found (calcd.)%			Δ_M	
					C	H	N	DMF	DMSO
1	[Hg(bztzS) ₂]	Yellow	189 - 191	90	-	-	-	21	47
2	[Hg(bzimSH) ₂]	White	281- 183	93	-	-	-	27	27
3	[Hg(bzoxS) ₂]	White	191 - 192	75	-	-	-	9	24
4	[Hg(bztzS) ₂ (dppm)] ₂	Yellow	85 - 88	90	50.5(51.1)	3.2(3.3)	2.9(3.1)	8	5
5	[Hg(bztzS) ₂ (dppm) ₂]	Yellow	155 -156	93	58.6(59.0)	4.1(4.0)	2.0(2.2)	9	3
6	[Hg(bztzS) ₂ (dppe)]	Yellow	203 -205	96	51.8(51.6)	3.6(3.5)	3.3(3.0)	19	13
7	[Hg(bztzS) ₂ (dppp)]	Yellow	174 -175	90	53.0(52.9)	3.5(3.7)	3.2(3.0)	16	9
8	[Hg(bztzS) ₂ (PPh ₃) ₂]	Yellow	165-166	90	44.0(44.3)	3.4(3.6)	2.7(2.7)	11	17
9	[Hg(bzimSH) ₂ (dppm)] ₂	White	276 -278	74	52.8(52.9)	3.6(3.7)	6.5(6.3)	21	22
10	[Hg(bzimSH) ₂ (dppm) ₂]	White	275 -276	75	60.1(60.1)	4.4(4.3)	4.2(4.4)	6	6
11	[Hg(bzimSH) ₂ (dppe)]	White	232 -233	94	53.5(53.4)	3.6(3.7)	6.1(6.2)	7	21
12	[Hg(bzimSH) ₂ (dppp)]	White	238 -240	89	53.5(53.4)	4.3(4.3)	6.3(6.1)	7	23
13	[Hg(bzimSH) ₂ (PPh ₃) ₂]	White	274 -276	72	45.8(45.7)	4.0(3.9)	5.4(5.5)	12	17
14	[Hg(bzoxS) ₂ (dppm)] ₂	White	141 -142	60	53.1(52.9)	3.4(3.4)	3.3(3.1)	10	10
15	[Hg(bzoxS) ₂ (dppm) ₂]	White	113 -114	79	60.4(60.5)	4.0(4.1)	2.4(2.2)	21	10
16	[Hg(bzoxS) ₂ (dppe)]	White	213 -215	73	53.2(53.4)	3.7(3.6)	3.3(3.1)	14	20
17	[Hg(bzoxS) ₂ (dppp)]	White	185 -186	93	54.0(53.9)	3.6(3.8)	3.2(3.1)	12	17

The ³¹P-{¹H} n.m.r. spectrum of [Hg(bztzS)₂(PPh₃)₂](8), showed a singlet at dP=26.21 p.p.m. suggests a single isomer. ¹H and ¹³C-{¹H} n.m.r. data are given in tables 3. On the bases of these results and other identification data given in tables 1 and 2

the structure shown in Fig. 3 has been suggested for complexes (8) and (13).

Although reaction of [HgL₂] with one mole equivalent of dppm gave the binuclear – dppm

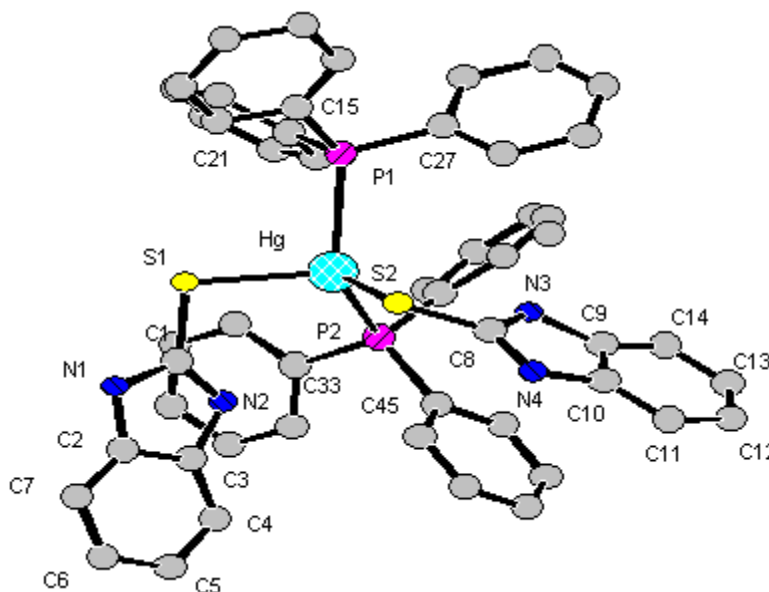
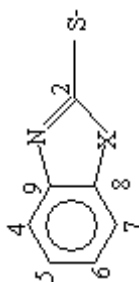
**Fig. 7: Molecular structure of complexes (13)**

Table 2: I.R. spectra data cm^{-1} of the ligands and complexes (1-17)

S.No.	Thioamide bands				v(N-H)	v(C-H)	v(Hg-P)	v(P-C)	v(C-O-C)
	I	II	III	IV					
btzSH	1490 s	1310 m	1024 s	670 s	3118 w	3072w , 3022w			
bzimSH ₂	1505 s	1460 s	1362m	650 s	3152 w	3049w, 2983w			1090m , 820v
bzoXSH	1504 s	1240 m	1010m	740 m	3240 w				
1	1470 m	1260 m	1010s	670m		3051w			
2	1498 s	1436 m	1350s	630 s	3110w	3028w , 2977w			
3	1500 m	1234 s	1000s	740m		3053w,2891w			
4	1480 m	1300 m	979s	670m		3052w			
5	1485m	1310 m	984 s	660w		3056w		500 s	
6	1490 m	1315 m	983 s	665w		3053(w)		478 s	
7	1490 m	1310 m	968 s	600m		3053w		505 s	
8	1493 m	1300 m	990 s	638m		3056w		505 s	
9	1498 m	1426 m	1371	622 m	3139w	3080w		500 m	
10	1490 s	1431 s	1371s	650m	3137w	3055w		505 s	
11	1492 s	1427 s	1371m	650m	3120w	3016w		505 m	
12	1496 s	1431 s	1360s	657w	3140w	3080		505 m	
13	1498 s	1423 s	1365	650m	3130w	3018w		500 s	
14	1475 m	1228 m	1000 m	734m		3056m , 2933 w		500 s	1083v , 820v
15	1475 m	1242 s	1000 s	742s		3053m , 2941 w		505 s	1090m , 810v
16	1475 m	1240 m	1000 s	740s		3053m , 1900 w		505 s	1080m , 820m
17	1475 w	1240 m	1000 m	746s		3051m , 2958 w		505 s	1085m , 820m

S = Strong , W = Weak , M = Medium

Table 3 : The ^{31}P -{ ^1H }, ^1H and ^{13}C -{ ^1H } n.m.r. data (δP p.p.m. and J Hz) of some of the prepared complexes

Complexes	Seq.	δP	δCH_2	$^2\text{J}(\text{P-H})$	δPhenyl	δC_2	δC_4	δC_5	δC_6	δC_7	δC_8	δC_9	δC_{11}
bztzSH						189.9	121.7	127.1	124.2	112.4	129.4	141.3	
BzimSH ₂						168.5	132.5	109.8	122.6	122.6	109.8	132.5	
[MeTi(bzoxS)] ^c						179.0	114.6	122.5	120.5	107.6	150.9		
[Hg(bztzS) ₂ (dppm)] ₂	(4)	7.99	3.68	6.5	7.04-7.50	173.6	120.3	125.0	123.0	119.6	138.0	153.0	26.5 ^d
[Hg(bztzS) ₂ (dppm)] ₂	(5)	-3.55	3.35	3.3	7.05-7.51	175.2	120.2	124.9	122.6	119.2	138.1	153.4	26.3 ^e
[Hg(bztzS) ₂ (dppp)]	(7)	15.87											
[Hg(bztzS) ₂ (PPH ₃) ₂]	(8)	26.21			7.09-7.53	vw ^f	120.2	125.3	123.2	119.4	vw ^f	vw ^f	
[Hg(bzimSH) ₂ (dppm)] ₂	(9)	25.8											
[Hg(bzimSH) ₂ (dppe)]	(11)	33.66											
[Hg(bzimSH) ₂ (dppp)]	(12)	18.1	2.0(2H), 2.9(4H)	6.97-7.50	175.8	120.4	124.7	122.4	119.0	138.3	153.9	19.1,27.8	
[Hg(bzoxS) ₂ (dppm)] ₂	(14)	21.4	4.26	11.5	6.96-7.55	170.2	120.2	123.5	123.0	109.3	142.2	152.2	28.0
[Hg(bzoxS) ₂ (dppm)] ₂	(15)	-2.6	3.45	3.95	6.95-7.37	173.1	116.9	122.8	121.8	108.3	143.2	152.2	26.3
[Hg(bzoxS) ₂ (dppp)]	(17)	19.1			6.98-7.58	172.8	116.3	123.0	122.0	108.9	143.0	152.1	19.3, 28.3, 29.8

a-measured in CDCl₃ unless stated otherwise, b- methylene carbon of the diphosphine

c- From reference 2 for comparison, d- singlet e- triplet f- singlet was very weak

Table 4: Crystal data collection and structure refinement parameters for (11) and (13)

Parameters	(11)	(13)
Empirical formula	C40 H36 Hg N4 P2 S2	C52 H42 Hg N4 O P2 S2
Formula weight	899.38	1065.55
Temperature	220(2) K	220(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, P21/n	monoclinic, P21/c
Unit cell dimensions	a = 11.4598(11) Å b = 19.5471(11) Å c = 16.5921(15) Å	a = 18.2473(18) Å b = 10.7143(7) Å c = 25.929(3) Å
Volume	3691.1(5) Å ³	4994.1(8) Å ³
Z, Calculated density	4, 1.618 Mg/m ³	4, 1.417 Mg/m ³
Absorption coefficient	4.405 mm ⁻¹	3.269 mm ⁻¹
F(000)	1784	2128
Crystal size	0.23 x 0.07 x 0.07 mm	0.15 x 0.22 x 0.48 mm
Theta range for data collection	2.05 to 25.94 deg.	2.06 to 25.00 deg.
Limiting indices	-13<=h<=14, -23<=k<=21, - 20<=l<=20	-21<=h<=20, -12<=k<=11, -30<=l<=30
Reflections	23882 / 7150 [R(int) = 0.0990]	27371 / 8714 [R(int) = 0.1034]
Completeness to theta = 25.00	99.2 %	99.0 %
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7150 / 0 / 437	8714 / 0 / 557
Goodness-of-fit on F ²	0.898	0.969
Final R indices [$>2\sigma(I)$]	R1 = 0.0413, wR2 = 0.0801	R1 = 0.0550, wR2 = 0.1407
R indices (all data)	R1 = 0.0804, wR2 = 0.0912	R1 = 0.0918, wR2 = 0.1561
Largest diff. peak and hole	1.724 and -1.193 e.Å ⁻³	1.854 and -1.935 e.Å ⁻³

Table 5: Selected bond lengths (Å) and angles (°) for complexes (11) & (13)

	(11)	(13)
C(1)-S(1)	1.748(7)	C(1)-S(1) 1.748(7)
C(8)-S(2)	1.747(8)	C(8)-S(2) 1.747(8)
C(15)-C(16)	1.548(9)	C(15)-C(16) 1.548(9)
C(15)-P(1)	1.850(6)	C(15)-P(1) 1.850(6)
C(16)-P(2)	1.843(6)	C(16)-P(2) 1.843(6)
P(1)-Hg	2.5941(16)	P(1)-Hg 2.5941(16)
P(2)-Hg	2.5997(17)	P(2)-Hg 2.5997(17)
S(1)-Hg	2.5453(18)	S(1)-Hg 2.5453(18)
S(2)-Hg	2.4631(17)	S(2)-Hg 2.4631(17)
C(1)-S(1)-Hg	108.6(2)	C(1)-S(1)-Hg 108.6(2)
C(8)-S(2)-Hg	98.2(2)	C(8)-S(2)-Hg 98.2(2)
S(2)-Hg-S(1)	118.93(6)	S(2)-Hg-S(1) 118.93(6)
S(2)-Hg-P(1)	116.62(6)	S(2)-Hg-P(1) 116.62(6)
S(1)-Hg-P(1)	112.89(6)	S(1)-Hg-P(1) 112.89(6)
S(2)-Hg-P(2)	125.02(6)	S(2)-Hg-P(2) 125.02(6)
S(1)-Hg-P(2)	93.93(6)	S(1)-Hg-P(2) 93.93(6)
P(1)-Hg-P(2)	82.82(5)	P(1)-Hg-P(2) 82.82(5)

bridged complexes $[\text{HgL}_4(\text{m-dppm})_2]$, reaction with one mole equivalent of the $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n=2$ or 3 gave the mononuclear chelated – diphosphine complexes $[\text{HgL}_2(\text{diphos})]$ (6), (7), (11), (12), (16) and (17). The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of complexes (7), (11), (12) and (16) showed a singlet each (table 3) indicating the presence of a single chelated isomer for each. These conclusions have been supported by ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. data shown in tables 3. On the basis of these data and other identification data given in tables 1 and 2 the tetrahedral structure shown in Fig. 4 has been suggested for these complexes .

Treatment of the linear complexes $[\text{HgL}_2]$ with two mole properties of dppm gave octahedral complexes of the type $[\text{HgL}_2(\text{dppm})_2]$ (5), (10), (15) as evidence from $^{31}\text{P}\{-^1\text{H}\}$ and ^1H n.m.r. data. Thus $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of complexes (5) and (15) showed a singlet each at $\delta\text{P} = -3.55$ and -2.6 ppm respectively. The negative δP chemical shift values indicate that dppm behaves as a bidentate chelate. The negative δP chemical values reflect the chelate ring strain caused by chelated – δppm ligands²¹. This has been supported by the ^1H n.m.r. data for complexes (5) and (15) which showed a triplet for the methylene group of the δppm ligand at $\delta\text{H} = 3.35$ ppm, $^2\text{J}(\text{P-H}) = 3.3$ Hz and 3.45 p.p.m , $^2\text{J}(\text{P-H}) = 3.94$ Hz respectively. the low dH chemical shift and $^2\text{J}(\text{P-H})$ values indicated a chelated behavior of the dppm ligand²³. $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra have also been recorded and data are given in table 3. On the basis of these data and other identification data given in tables 1 and 2 the octahedral structure shown in Fig. 5 has been suggested for these complexes.

Infrared spectra

The infrared spectra of compounds (4) – (17) recorded in the 250 – 4000 cm^{-1} range showed the usual four thioamide bands required by the presence of the heterocyclic thione ligands. The shifts observed for these bands due to coordination in comparison with the uncoordinated ligands with the lack of the $\nu(\text{SH})$ bands at ca. 2500–2600 cm^{-1} , signify the exclusive S-coordination mode of the thione ligands. The ligand bzoxSH showed $\nu(\text{COC})_{\text{sy}}$ and $\nu(\text{COC})_{\text{asy}}$ at 1090, 820 cm^{-1} respectively. These bands were unaffected on complex formation¹². Moreover the spectra of compounds under investigation contain $\nu(\text{Hg-P})$

stretching vibrations observed in the 312 – 395 cm^{-1} range²⁴ and $\nu(\text{P-C})$ stretching vibrations observed in the 478 – 505 cm^{-1} range²⁵ signify the coordination of phosphines ligands.

X-ray crystallography

The compounds (11) and (13) were structurally determined by x-ray crystallography. The crystallographic and measurement data are shown in Table 4 and representative bond length and bond angles are listed in Table 5. Fig. 6 and 7 present thermal ellipsoid representations of complexes 11 and 13 respectively. Structure 13 contains not exact localized electron density, that was refined as disordered C-and O- atoms (two C and one O, sot ~ 70/30 %) of solvent of crystallization.

In both complexes Hg(II) atom is four coordinated in a tetrahedral geometry by the thiolate and phosphine ligands. The thiolate ligands act as monodentate ligands coordinated through the thiolato sulfur atom. As expected for four coordinate d^{10} metal complexes the structure of (11) adopts a nearly distorted geometry. The derivation from the ideal tetrahedral geometry is apparently due to the steric interaction between the bulky ligands. The steric interaction between dppe and bezimidazole -2- thione unit enlarge the S1-Hg-S2 , S1-Hg-P1, S2-Hg-P1 and S2-Hg-P2 angles to 118.93(6), 112.89(6), 116.62(6) and 125.02(6) $^\circ$, while at the same time depress the P1-Hg-P2 and S1-Hg-P2 angles to 82.82(5) and 93.93(6) $^\circ$ correspondingly. The heterocyclic ligands are not symmetrically placed with respect to the two phosphine. The S1-Hg-P2 angle is smaller than the other S-Hg-P bonds by more than 10 $^\circ$.

The Ag-P bond distance 2.5941(10) and 2.5997(17) \AA are comparable with those observed in similar complexes¹⁶. The Hg-S bond distance 2.5453(18) and 2.461(7) \AA are longer than that observed for other complexes 2.3513 \AA ¹⁶.

In complex (13) the geometry around Hg atom is deviated from a tetrahedral environment. The derivation from the ideal tetrahedral geometry is due to the steric interaction between the two triphenylphosphine, on one hand and between triphenylphosphine and one bezimidazole -2- thione

unit on the other hand enlarge the P1-Hg-P2, P1-Hg-S2, P2-Hg-S1 and P2-Hg-S2 angles to 117.28(7), 110.74(9), 116.07(9) and 112.30(8)°, while at the same time they depress the S1-Hg-S2 and S1-Hg-P1 angles to 98.77(10) and 99.60(8)° respectively.

The heterocyclic ligands are not symmetrically placed with respect to the two phosphine with angle P1-Hg-S1 being ~ 11.7, 15.4° smaller than the P1-Hg-S2, P2-Hg-S1 respectively. The Ag-P bond distance 2.568(2) and 2.557(3)Å are longer than that observed for other complexes¹⁶.

Supplementary data

Supplementary crystallographic data for (11) and (13) can be obtained free of charge from the author (e-mail: subhi_aljibori@yahoo.com).

ACKNOWLEDGEMENTS

We thank the NMR department and x-ray department of the Institute of Chemistry, Martin-Luther-University, Halle Germany for measuring the NMR spectra and x-ray crystallography.

REFERENCES

1. E. S. Raper, *Coord. Chem. Rev.*, **61**: 115 (1985)
2. P. D. Akrivos, *Coord. Chem. Rev.*, **213**: 181 (2001).
3. J. G. Wright, M. J. Natan, F. M. McDonnell, D. M. Ralston and T. V. O, *Halloran Prog. Inorg. Chem.*, **38**, 323, (1990).
4. M. Dochmann, K. J. Webb, *J. Chem. Soc. Dutton Trans.*, 2325 (1991).
5. Z. Popovic, Z. Soldin, D. M. Calogovic, C. G. Povlovic, M. Rajic and G. Giester, *European J. Inorg. Chem.*, 171, (2002).
6. P. A. Dean, *Prog. Inorg. Chem.*, **24**: 109 (1978).
7. D. P. Graddon, *Rev. Inorg. Chem.*, **4**:211 (1982).
8. C. Pert and G. Tosi, *J. Inorg. Nucl. Chem.*, **38**: 1125(1976).
9. N. A. Bell, C. William, C. P. Constable, J. C. Siman, H. W. Ross, B. Michael, E. L. Mark, E. S. Raper, C. S. Sammon, *Inorg. Chim. Acta.* 357: 2091 (2004).
10. C. Pert and G. Tosi, *Can. J. Chem.*, **55**: 1409 (1977).
11. Z. Popovic, D. Matkovic-Galogovic, Z. Soldin, G. Povlovic, N. Davidovic and D. Vikić-Topic, *Inorg. Chim. Acta.*, **294**: 35 (1999).
12. Z. Zugaj, Z. Popovic and D. Mrvos-Sermek, Bell. *Czech and Slovak Crystallogr. Association* **5**: 322 (1998).
13. W. McFarlane, P.D. Akrivos, P. Aslandis, P. Karagiannidis, C. Hatzisymeon, M. Numan and S. Kokkou, *Inorg. Chim. Acta.*, **281**: 121 (1998).
14. R. W. Mitchell, J. D. Rudderick and G. A. Wilkinson, *J. Chem. Soc. A*, 3224 (1971).
15. S. A. Al-Jibori, A. S. S. Al-Zaubi, M. Y. Mahammed and T. A. A. Al-Allaf, *Trans. Met. Chem.*, **27**: 281 (2007).
16. S. K. Hadjikakou and M. Kubicki, *Polyhedron*, **19**: 2231 (2000).
17. T. Kami, T. Fujii and M. Saotome, *Jap. Appl. Chem. Abst.*, **107**: 220333d (1987).
18. G. M. Sheldrick., SHELXS-97, SHELXL-97, Programs for crystal structure determination, Universitität Göttingen, Germany (1997).
19. W. J. Geary, *Coord. Chem. Rev.*, **7**: 81 (1971).
20. C. T. Hunt and A. L. Balch, *Inorg. Chem.*, **20**: 2267 (1981).
21. S. A. Al-Jibori, A. I. Abdullah, and T. A. K. Al-Allaf, *Trans. Met. Chem.*, **32**: 398 (2007).
22. L. J. Al-Hayaly, B. H. Abdullah, A. A. N. Al-Dulaimi and S. A. Al-Jibori, *Orient. J. Chem.*, **24**(2): 38 (2008).
23. P. G. Pringle, *D. Phil Thesis*, Leeds University, U. K. (1983).
24. B. Singh and M. M. P. Rukhayar and R. J. Sinha, *J. Inorg. Nucl. Chem.*, **39**: 29 (1977).
25. J. Chatt and M. Duncanson, *Nature*, **97**: 178 (1956).