

Synthesis and characterization of new metal complexes of thione and phosphines Ligands

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Abstract

The complexes containing mixed of ligands [5-(3-chlorophenyl)-1,3,4-oxadiazole-2-thione(CPoxSH)] and diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ (diphos)($n=1-4$), are prepared by the reaction of $[\text{Hg}(\text{CPoxS})_2]$ or $[\text{M}(\text{H}_2\text{O})_2(\text{CPoxS})_2]$ ($\text{M} = \text{Co}, \text{Ni}$) with one mole proportion of the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ gave tetrahedral complexes of the type $[\text{Hg}(\text{CPoxS})_2(\text{diphos})]$. While gave an octahedral complexes with cobalt(II) and nickel(II) ions of the type $[\text{M}(\text{H}_2\text{O})(\text{CPoxS})_2(\text{diphos})]$ when ($\text{M} = \text{Co}$ and Ni) receptivity.

The prepared complexes were characterized by molar conductivity, elemental analysis, IR, ^1H , ^{13}C - $\{^1\text{H}\}$ and ^{31}P - $\{^1\text{H}\}$ n.m.r.

Keywords: Transition metal, Oxadiazole, Phosphine, Thione

1. Introduction

The chemistry of transition metal complexes containing heterocyclic thione donors continues to be of interest on account of their interesting structural features and also because of their biological importance [1-6]. The combination of the exocyclic thione / thiol group and the heterocyclic molecule, which may contain nitrogen, oxygen, or sulfur or a combination thereof, generates a group of molecules with considerable coordination potential [1-3].

Phosphines and diphosphines are important ligands in transition-metal catalyzed reactions and the electronic and steric effects of the phosphine have a pronounced influence on the organic trans-formation that take place at the transition metal center[7-8].

Mixed ligand complexes of heterocyclic thiones and phosphines have been reported for several metal ions such as Silver(I), Mercury(II), Palladium(II), Platinum(II) and Rhodium(II) [9-11]. Complexes with zinc(II), mercury and transition metal seem to be unexplored [12]. In the presence work, we report as study of the thione ligand [5-(3-chlorophenyl)-1,3,4-oxadiazole-2-thione (CPoxSH)] Figure1. and reaction between metal (II) acetate with thione ligands present Et_3N , and treatment of the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1-4$) with metal (II) complexes of the type $[\text{Hg}(\text{CPoxS})_2]$ or $[\text{M}(\text{H}_2\text{O})_2(\text{CPoxS})_2]$ when ($\text{M} = \text{Co}, \text{Ni}$ and $\text{CPoxS}^- = \text{thionate ligands}$)

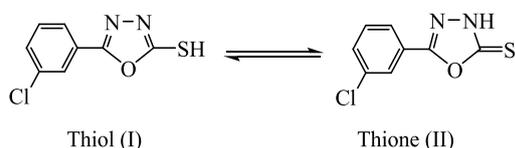


Fig1: The structure of thione ligands (LH)

2. Experimental

2.1 General

The compounds $[\text{MCl}_2 \cdot x\text{H}_2\text{O}]$ ($\text{M} = \text{Ni}$ and Co), $\text{Hg}(\text{OAc})_2$, dppm, dppe, dppp and dppb were commercial products and were used as supplied (These compounds are supply from Sigma-Aldrich and Fluka). IR spectra were recorded on a Shimadzu FT.IR. 8400 spectrometer in the 200 – 4000 cm^{-1}

range using CsI discs. Elemental analysis was carried out on a CHN analyzer type 1106 (Carlo-Erba in AL al-Bayt University). Melting points were measured on an electrothermal 9300 melting point apparatus. The ^1H - and ^{13}C - NMR spectra were recorded on Varian unity 500 and Gemini 2000 spectrometers respectively with DMSO- d_6 as solvent and Me_4Si as internal reference. ^{31}P - $\{^1\text{H}\}$ NMR spectra were recorded on Gemini 200 spectrometer with DMSO- d_6 as solvent and $\text{H}_3\text{PO}_4(85\%)$ as external reference. The NMR spectra and element analysis were determined at the AL al-Bayt University- Jordan and Institute fur Anorganische chemie, Martin – Luther - univassitat Halle- Witten-berg, Germany.

2.2 Synthesis of 5-(3-chlorophenyl)-1,3,4-oxadiazole-2-thiol(CPoxSH)

A mixture of m-chlorobenzoic acid hydrazide[13a] (10mmole, 1.715g) dissolved in $\text{C}_2\text{H}_5\text{OH}$ (50cm^3), KOH (20mmole, 0.112 g) in (60cm^3) $\text{C}_2\text{H}_5\text{OH}$ and CS_2 (20mmole, 1.2cm^3) was refluxed on a water bath for 14h, until the evolution of H_2S gas ceased. The resultant mixture was acidified with acetic acid and the white solid which separated was filtered and recrystallized from $\text{C}_2\text{H}_5\text{OH}$. Yield 76 %, m. p. 170-172 $^\circ\text{C}$ [13b].

2.3 Synthesis of $[\text{Hg}(\text{CPoxS})_2](1)$ complex

A solution of CPoxSH (0.4g, 1.88mmole) in $\text{C}_2\text{H}_5\text{OH}$ (25cm^3) was added to a solution of $\text{Hg}(\text{OAc})_2$ (0.265g, 0.94mmole) in warm $\text{C}_2\text{H}_5\text{OH}$ (30cm^3) and Et_3N (0.3cm^3) was added as a base. The mixture was stirred at room temperature for 3hr. The white solid thus formed was filtered off and washed with $\text{C}_2\text{H}_5\text{OH}$ and recrystallized from $\text{C}_2\text{H}_5\text{OH} / \text{DMSO}$ as white powder (yield 76%), m. p. 276 $^\circ\text{C}$ (decom.) [13b].

2.3 Synthesis of $[\text{Ni}(\text{H}_2\text{O})_2(\text{CPoxS})_2](2)$ complex

A solution of CPoxSH (1.0g, 4.70mmole) in $\text{C}_2\text{H}_5\text{OH}$ (50cm^3) was added to solution of $\text{NiCl}_2 \cdot x\text{H}_2\text{O}$ (0.30g, 2.35mmole) in warm $\text{C}_2\text{H}_5\text{OH}$ (50cm^3) present Et_3N (0.6cm^3) as a base. The mixture was stirred at room temperature for 3hr. The greenish yellow solid thus formed was filtered off and washed with $\text{C}_2\text{H}_5\text{OH}$ and

recrystallized from C₂H₅OH / DMSO as greenish yellow powder (yield 80%), m. p. 250 °C (decom.). The [Co(H₂O)₂(CPoxS)₂](3) complex was prepared by similar method.

2.4 Reaction of [Hg(CPoxS)₂] with (dppm) (1 : 1) ratio

A solution of dppm (0.07g, 0.18mmol) in warm CHCl₃ (20cm³) was added to a warm solution of [Hg(CPoxS)₂](1) (0.112g, 0.18mmol) in CHCl₃ (30cm³). The mixture was stirred at room temperature for 3h. The white solid thus formed was filtered off washed with CHCl₃, dried under vacuum and recrystallized from C₂H₅OH and DMSO (yield 83%).

The following complexes [Hg(CPoxS)₂(dppe)] (5), [Hg(CPoxS)₂(dppp)] (6), [Hg(CPoxS)₂(dppb)] (7), were prepared and isolated by a similar method. The melting points are given in Table3.

2.5 Reaction of [Ni(H₂O)₂(CPoxS)₂] with dppm (1:1) ratio

A solution of dppm (0.1g, 0.26mmol) in CHCl₃(20cm³) was added to a hot solution of [Ni(H₂O)₂(CPoxS)₂](2) (0.134g ,0.26 mmol) in warm CHCl₃(20cm³). The mixture was stirred at room temperature for 2h. The green solid thus formed was filtered off washed with CHCl₃, dried under vacuum and recrystallized from DMSO (yield 78%). The following complexes [M(H₂O)₂(CPoxS)₂dppm], [M(H₂O)₂(CPoxS)₂dppe], [M(H₂O)₂(CPoxS)₂dppp], [M(H₂O)₂(CPoxS)₂dppb] (M= Ni and Co) were prepared and isolated by a similar method. The melting points are given in Table3.

3. Characterization of complexes

The prepared complexes were identified by elemental analysis, IR spectra, conductivity measurements and some of them by ³¹P-¹H, ¹H and ¹³C-¹H NMR

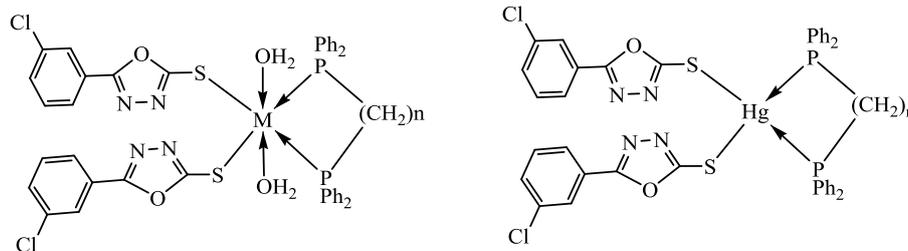


Figure 2 : The structure formula of the [Hg(CPoxS)₂(diphos)] [M(H₂O)₂(CPoxS)₂(diphos)] complexes when M=Co and Ni; n = 1- 4

3.2 Nuclear magnetic resonance spectra

The ³¹P-¹H, ¹H and ¹³C-¹H n.m.r. data of some the prepared complexes are given in Table 3.

The ³¹P-¹H n.m.r. spectra of the complex [Hg(CPoxS)₂(dppm)] (5) (Figure: 3) showed a singlet peak at δP= -11.90 ppm suggesting a single product. The negative values of the δP indicate that dppm behaves as a bidentate chelate [11,17]. This has been supported by the ¹H n.m.r. data for complex (9) which showed a triplet for the methylene group of the dppm ligand at δH= 3.43 ppm, ²J(P-H) = 3.11 Hz, the low δH chemical shift and ²J(P-H) values indicated a

spectra and their data are listed in Tables 1-3. The molar conductivity of the complexes in CHCl₃, DMF or DMSO is low enough to suggest that they are non-electrolytes[14].

3.1 Infrared spectra

The infrared spectra of the ligand and complexes 1-15 recorded in the 4000– 200 cm⁻¹ range with CsI disk (The data of spectra shown in table 2).

(1) The IR spectra of the [Hg(CPoxS)₂(diphos)] complexes shows a strong signal at the range 1639-1653 cm⁻¹ was assigned to (C=N) (15). A positive shift in C=N band indicate that the C=N group is uncoordinated, and a negative shift in C=S and the appearance of a band at the region 315-334 cm⁻¹ range refers to Hg-S[1] indicating that the thionate ligand coordinated through the sulfur atoms. And a bands observed in the 367–402 cm⁻¹ range due to ν(Hg-P) band [11,16,17] and ν(P-C) stretching vibrations observed in the 478 – 505 cm⁻¹ range [17] signify the coordination of phosphines ligands.

(2) [M(H₂O)₂(CPoxS)₂(diphos)] when [M = Co and Ni]. The IR spectra of these complexes show a bands in the region 1610-1651 cm⁻¹ were assigned to (C=N), and a negative shift in this band indicated the thionate ligand coordinated through the nitrogen atom[15]. The appearance of the bands in the region 423-487 cm⁻¹ indicated the thionate ligand coordination behaves as a monodentate ligand through the nitrogen atom[18]. The (M-O) bands are observed in the region 538-567 cm⁻¹ [19]. And bands observed in the 398–458 cm⁻¹ range due to ν(Hg-P) band [16]and ν(P-C) stretching vibrations is observed in the 478 – 530 cm⁻¹ range [17] signify the coordination of phosphines ligands.

chelated behavior of the dppm ligand [17]. ¹³C-¹H n.m.r. spectra have also been recorded and the data are given in table 3. On the bases of the above n.m.r. data and the other identification data given in tables 1 and 2. The tetrahedral structure has been suggested for the complex as shown in figure 2.

Although reaction of [Hg(CPoxS)₂] complexes with one mole proportion of the diphosphine ligand gave a mononuclear chelate – diphosphines complexes of the types [[Hg(CPoxS)₂(dppe)](6) (figure: 4) and [Hg(CPoxS)₂(dppb)](7). The ³¹P-¹H n.m.r. spectra of complexes (6) and (7) given a singlet each (table 3) indicating the presence of single chelated isomer for

each. These conclusions have been supported by CHN analysis, ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. data are shown in tables 3. On the basis of these data and other

identification data given in tables 1 and 2 the tetrahedral structures have been suggested for these complexes as shown in figure 2.

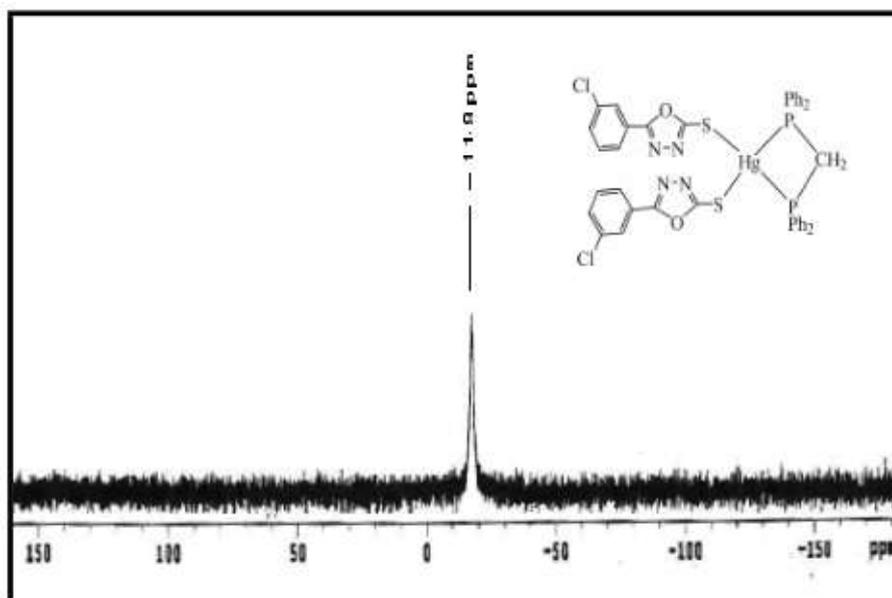


Figure 3: The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum of complex $[\text{Hg}(\text{CPoxS})_2(\text{dppm})](5)$

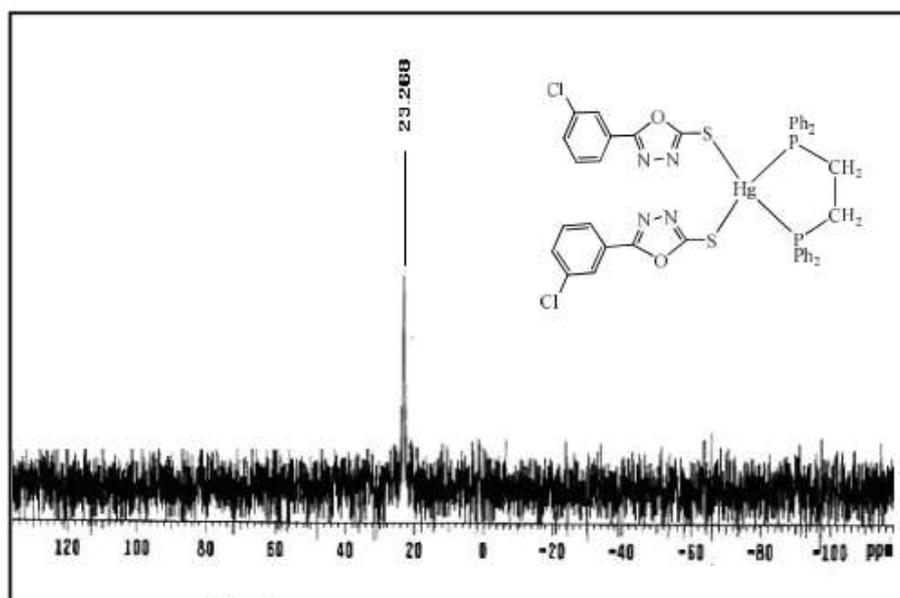


Figure 4 : The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum of complex $[\text{Hg}(\text{CPoxS})_2(\text{dppe})](6)$

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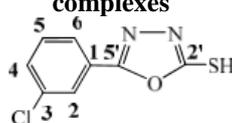
Table 1 . Color, Yield, M.p. and CHN analysis for complexes (1-15)

Seq.	Complexes	Color	Mp °C	Yield	CHN Cacl.(Found)%		
					C	H	N
1	[Hg(CPoxS) ₂]	White	276d	76			
2	[Co(H ₂ O) ₂ (CPoxS) ₂]	Light blue	265-269	67			
3	[Ni(H ₂ O) ₂ (CPoxS) ₂]	Greenish yellow	250d	79			
4	[Hg(CPoxS) ₂ dppm]	White	221-226	83	48.79(47.99)	3.10(3.24)	5.55(5.62)
5	[Hg(CPoxS) ₂ dppe]	White	276-277	76	49.30(49.32)	3.25(3.21)	5.48(5.39)
6	[Hg(CPoxS) ₂ dppp]	White	197-199	78			
7	[Hg(CPoxS) ₂ dppb]	White	250d	59			
8	[Co(H ₂ O) ₂ (CPoxS) ₂ dppm]	Blue	132-135	66	54.49(54.69)	3.90(4.08)	6.20(6.45)
9	[Co(H ₂ O) ₂ (CPoxS) ₂ dppe]	Greenish blue	156-157	91	54.97(55.05)	4.06(4.12)	6.11(6.74)
10	[Co(H ₂ O) ₂ (CPoxS) ₂ dppp]	Blue	219-223	87			
11	[Co(H ₂ O) ₂ (CPoxS) ₂ dppb]	Dark blue	265d	76	54.51(54.55)	3.90(3.98)	6.20(6.11)
12	[Ni(H ₂ O) ₂ (CPoxS) ₂ dppm]	Green	243-244	81			
13	[Ni(H ₂ O) ₂ (CPoxS) ₂ dppe]	Yellowish green	287-289	83			
14	[Ni(H ₂ O) ₂ (CPoxS) ₂ dppp]	Yellowish green	123-127	90			
15	[Ni(H ₂ O) ₂ (CPoxS) ₂ dppb]	green	190-193	73			

Table 2. Selected IR bands (cm⁻¹) of the ligand and complexes (1-15)

	v(O-H)	v(C=N)	v(C=S)	v(N-N)	v(C-Cl)	v(P-C)	v(M-N)	v(M-O)	v(M-S)	v(M-P)
CPoxSH		1636s	1556m	1067s	576s	-	-	-	-	-
1		1642s	1538m	1088m	555m	-	-	-	312w	-
2	3412m	1651s	1531m	1076s	590m	-	415w	543w	315m	-
3	3434m	1938s	1521s	1066s	605s	505s	420w	521m	298w	-
4		1653s	1542s	1078s	553m	505m	-	-	334w	402m
5		1641m	1523s	1077s	590m	521m	-	-	315w	384w
6		1639s	1552m	1066s	576m	505m	-	-	325m	376m
7		1644s	1532s	1076m	565m	520s	-	-	331w	367m
8	3403m	1632m	1550m	1100m	555w	487m				
9	3443b	1640m	1562m	1078s	590w	510m	487m	567m		430w
10	3432b	1623m	1573m	1072m	600m	530m		545w		441m
11	3418m	1636s	1556m	1067s	567m	510s	465m	564w		458m
12	3421m	1642s	1538m	1088m	550m	515s	452w	541w		442w
13	3372m	1651s	1531m	1076s	568s	500m	436w	560w		410w
14	3423b	1938s	1521s	1066s	578m	505m		538w		
15	3372b	1610m	1567s	1091s	576m	500s	423w			398m

s = Strong , w = Weak , m = Medium, b= Broad

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

Complexes	Seq.	δP	δCH ₂	² J(P-H)	δ Phenyl	δC-5'	δC-2'	δC-6	δC-5	δC-3	δC-2,4	δC-1	δ C ₁ ^b
CPoxSH					7.180-7.530	160.71	178.81	125.700	124.500	134.400	128.500	131.800	
[Hg(CPoxS) ₂]	(1)				7.342-7.983	131.800	160.71	178.81	125.700	124.500	134.400	128.500	c
[Hg(CPoxS) ₂ dppm]	(4)	-11.9	3.43	3.110	7.320-7.753	131.933	161.754	170.774	125.765	124.961	134.668	130.092	27.52 ^d
[Hg(CPoxS) ₂ dppe]	(5)	23.268	2.65	2.994	7.125-7.634	131.930	159.922	171.432	125.184	125.096	134.514	131.930	26.23
[Hg(CPoxS) ₂ dppb]	(7)	26.01	1.54(4H) 2.00(4H)		7.130-7.543	131.918	161.167	170.565	125.298	125.054	134.516	126.060	28.625 29.332

a-measured in DMSO-d₆ unless stated otherwise, b- methylene carbon of the diphosphine
c- c- singlet was very weak d-singlet

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تحضير وتشخيص معقدات لليكاندات الثايون والفوسفينات مع ايونات الكوبلت (II)، النيكل (II)

(II) والزئبق

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الملخص

المعقدات الحاوية على نوعين من الليكاندات (5-3-كلوروفينيل)-1،3،4- او كسادايازول-2-ثايون (CPoxSH) مع الفوسفينات $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ حيث (n=1-4)، حضرت من تفاعل بين $[\text{Hg}(\text{CPoxS})_2]$ او $[\text{M}(\text{H}_2\text{O})_2(\text{CPoxS})_2]$ حيث أن (M = Co, Ni) مع مول واحد من الفوسفينات $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ حيث (n=1-4) فأعطت معقدات رباعية السطوح من النوع $[\text{M}(\text{H}_2\text{O})(\text{CPoxS})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)]$ بينما أعطت معقدات ثمانية السطوح من النوع $[\text{Hg}(\text{CPoxS})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)]$. شُخصت المعقدات المحضرة بالتوصيلية المولارية، التحليل الدقيق للعناصر، مطيافية الأشعة تحت الحمراء، ومطيافية الرنين النووي المغناطيسي ل-¹H و ¹³C-¹H و ³¹P-¹H.

الكلمات المفتاحية: العناصر الانتقالية، الاوكسادايازول، الثايون، الفوسفين