

تحضير وتشخيص عدد من معقدات الزئبق(۱۱) مختلطة الليكاند مشتقة من ٥-(٤-بيريدال)-١،٣،١- اوكسادايازول-٢- ثايون مع ليكاندات الفوسفينات الثالثية

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الملخص:

حضرت عدد من معقدات الزنبق(۱۱) لليكاند ٥-(٤-بيريدال)-١،٣،١ وكسادايازول-٢- ثايون مع الفوسفينات الثالثية كليكاندات اضافية، شخصت المركبات المحضرة بواسطة التحليل الدقيق للعناصر، الاشعة تحت الحمراء، الموصلية المولارية، ومطيافية الرنين النووي المغناطيسي. في المعقدات ثنائية النواة (1-4)، اتخذت الليكاندات المتناسقة شكل الرباعي السطوح حول ايون الزنبق المركزي، حيث يرتبط ايون الزئبق بثلاث ذرات هاليد في حيث ترتبط مع ليكاند الثايون من خلال ذرة الكبريت. في المعقد (٦) اظهر ليكاند بشائيونليت تناسق احادي من خلال ذرة الكبريت ايضاً. واظهر ليكاند بس(ثنائي فينيل فوسفينو)ميثان الثايونليت تناسق احادي من خلال ذرة الكبريت ايضاً. واظهر ليكاند بس (ثنائي معقدات ثنائية النواة، في حين اظهرت المعقدات من (7-9) تناسق ثنائي السن المخلبي من خلال ذرتي الفوسفور الفوسفينات الثالثية مع ايون الزئبق في حين يرتبط ليكاند الثايونليت ترتبط بشكل احادي السن معطياً معقدات رباعي السطوح حول الايون المركزي. في حين تسلك الفوسفيات الثالثية في المعقدين (١٠و١) سلوك احادي السن معطياً معقدات الشائية من خلال ذرة الكبريت المناسون المنابع السطوح حول الايون المركزي. في حين تسلك الفوسفيات الثالثية في المعقدين (١٠و١) سلوك احادي السن معطياً معقدات رباعي السطوح ايضاً يرتبط فيها ايون الثايونليت من خلال ذرة الكبريت المنسوري المدي السن معطياً معقدات رباعي السطوح ايضاً يرتبط فيها ايون الثانونليت من خلال ذرة الكبريت المنسوري المدي السن معطياً معقدات رباعي السطوح ايضاً يرتبط فيها ايون الثايونليت من خلال ذرة الكبريت المسلوري المدي السن معطياً معقدات رباعي السطوح ايضاً يرتبط فيها ايون الثانية المينات درات الكبريت المسلوري المركزي المنابع المنابع المهرا المؤلف المؤلفة المؤل

كلمات دالة: الزئبق(١١)، الثايون، الفوسفين، المعقدات.

Synthesis and characterization of mercury(II) mixed ligands complexes derived from 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione with tertiary phosphines ligands

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ABSTRACT

Many new mixed ligand mercury complexes have been synthesized with LH = 5(4-pyridyl)-1,3,4-oxadiazole-2-thione and tertiary phosphines as co-ligands. The compounds have been characterized by elemental analyses, IR, molar conductivity, and NMR spectroscopy. In the binuclear complexes (2-5), both Hg atoms have tetrahedral geometry, the Hg atom bonded to three halide ions and one thione ligand (LH) through the sulfur atom. The complex (6) show that thionlate ligand(L^{Θ}) coordinated monodentate the sulfur is as through atom. The bis(diphenylphosphino)methane (dppm) behave as bidentate bridging ligand to bonded two Hg(II) ions in the complex (7), Whereas in the complexes (7-10), the thionlate ligand bonded as a monodentate fashion via the sulfur atom, while the diphosphines ligands coordinated as bidentate chelating ligands, and the geometry around the Hg center ion is tetrahedral. And in the complexes (11 and 12), the phosphine bonded as monodentate ligand, and the thionlate bonded via the sulfur atom as monodentate to give tetrahedral complexes.

Keywords: Mercury(II), Thione, Phosphine, complex





1. Introduction

The reaction of metal ions with heterocyclic thiones has been the subject of several investigations as these ligands Contain chemically active groups [-N(H)-C(=S)- \leftrightarrow -N=C(-SH)-], and are useful model compounds for sulfur containing analogues of heterocyclic bases[1-5]. Heterocyclic -2-thione bind to a metal in several ways, leading to formation of monomeric or polymeric complexes [1-12]. For example, the 5-phenyl-1,3,4-oxadiazole -2-thione, has several binding mode, such as S-bonding, N-bonding, N, S-bridging[13-19]. The interactions of heavy metals such as Pt(II), Pd(II) and Ag(I) with N,S-donor atoms have been recognized for their anticarcinogenic properties with potential to develop metal-based drugs[1-4]. Recently, some research works involving M(II) ions with thiones and phosphines have been published [20-28].

The aim of the present work, preparation of new mercury(II) complexes with 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione (Hpot) ligand and tertiary diphosphines as co-ligands, and characterization of its.

2. Experimental

2.1. Methods

IR spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer in the 400 – 4000 cm⁻¹ range using KBr discs. Melting points were measured on an electrothermal 9300 melting point apparatus. Elemental analysis was carried out on a CHN analyzer type 1106 Carlo-Erba. The ¹H NMR spectra were recorded on Varian unity 500 spectrometer with DMSO-d6 as solvent and Me₄Si as internal reference. ³¹P NMR spectra were recorded on Gemini 2000 spectrometer with DMSO-d6 as solvent and H₃PO₄(85%) as external reference. The NMR spectra were measured at the Institute fur Anorganische Chemie, Martin-Luther-Universitat, Halle-Wittenberg, Germany. and Al-Bayt University- Jordan. And element analyses were measured at the Al-Bayt University- Jordan.

2.2 Starting materials:

The compound HgCl₂, HgBr₂, HgI₂.xH₂O, Hg(SCN)₂, Hg(Ac)₂.xH₂O, bis(diphenylphosphino) methane (dppm), bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino) propane (dppp), bis(diphenylphosphino)butane (dppb) and Triphenyl phosphine (PPh₃) were commercial products and used as supplied. The Ligand 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione(Hpot), was prepared according to the literature[15].

2.3 Preparation of $[HgCl(\mu-Cl) (Hpot)]_2$ (1)

A solution of $HgCl_2$ (0.300g, 1.103mmole) in EtOH (10ml) was added to a hot solution of 5-(4-Pyridyl)-1,3,4-oxadiazole-2-thione (Hpot) (0.179, 2.206mmol) in EtOH (10ml). The mixture was refluxed for 2hr. The yellow solid formed was filtered off, washed with EtOH, and dried. The yellow solid product was recrystallized from DMSO/EtOH to give pale yellow solid of (1). The following complexes $[HgX(\mu-X) \ (Hpot)]_2 \ (X=Br,\ I\ and\ SCN) \ (2-4)$ were prepared and isolated by a similar method.

2.4 Preparation of $[Hg(pot)_2]$ (5)

A solution of mercury acetate $Hg(oAc)_2$ (0.637g, 1.999mmol) in EtOH (10ml) was added to a hot solution of (Hpot) ligand (0.716, 3.999mmol) in EtOH (10ml) containing a few drops of Et_3N as a base. A yellow ppt. was formed. The mixture was refluxed for 3hr. The resulting yellow precipitate was filtered off, washed with EtOH-water mixture (50-50, v/v), and dried under vacuum. The yellow solid product was recrystallized from DMSO to give pale yellow solid of (5).

2.5 Preparation of [Hg(pot)₂(dppm)] (6)

To a hot suspension of $[Hg(pot)_2]$ (5) (0.145g, 0.260mmol) in CHCl₃ (15ml), a solution of dppm ligand (0.100g, 0.260mmol) in CHCl₃ (15ml) was added. A pale yellow solution was formed. The resulting solution formed was refluxed for 3hr. The resulting pale yellow precipitate was filtered off, washed with chloroform, and dried under vacuum. The pale yellow solid product was recrystallized from DMSO/CHCl₃ to give pale yellow solid of (7).

The following complexes $[Hg(pot)_2(dppe)]$ (7); $[Hg(pot)_2(dppp)]$ (8) and $[Hg(pot)_2(dppb)]$ (9) were prepared and isolated by a similar method.

2.6 Preparation of $[HgL_2(PPh_3)_2]$ (10)

A hot solution of PPh₃ (0.138g, 0.260mmol) in CHCl₃ (15ml) was added to a hot suspension of [Hg(pot)₂] (5) (0.145g, 0.260mmol) in CHCl₃ (15ml). A yellow solution was formed. The resulting solution formed was refluxed for 3hr. The resulting yellow precipitate was filtered off, washed with chloroform, and dried under vacuum. The pale yellow solid product was recrystallized from DMSO/CHCl₃ to give yellow solid of (10). The complex [Hg(pot)₂(S=PPh₃)₂] (11) was prepared and isolated by a similar method.

3. Results and discussion

3.1 Synthesis of Complexes (1-11)

Treatment of ethanolic solution of mercuric halide $HgX_2(X=Cl, Br, I \text{ and }SCN)$ with the ethanolic solution of 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione(Hpot) ligand in (1:2)molar ratio gave complexes of the type $[HgX(\mu-X)(Hpot)]_2$. The ligand (Hpot) behaves as a monodentate neutral ligand coordinated through the sulfur atom for Hpot ligand. While the halogen was coordinated as a monodentate and bidentate bridging to mercury(II) ion (See Fig. 1).

Whereas the treatment of ethanolic solution of $Hg(oAc)_2$ with Hpot ligand present few drops of the Et_3N gave Complex of the type $[Hg(pot)_2]$, and the anionic ligand(pot^{Θ}) behave as monodentate bonded to mercury ion through the sulfur atom.(See Fig. 1)

Fig. 1. Preparation of [HgX(μ-X)(Hpot)]₂ and [Hg(pot)₂] complexes**Treatment of** linear complex of the [Hg(pot)2] with diphosphine (diphos= dppm, dppe, dppp, dppb) in (1:1) molar ratio gave complexes of the [Hg(pot)2(diphos)] or with

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monophosphines (PPh3 and S=PPh3) in (1:2) molar ration gave complexes of the [Hg(pot)2(Phos)2] (Phos: PPh3 and S=PPh3). The thionlate ligand (potΘ) behave as monodentate coordinated to Hg(II) ion through sulfur atom, while the diphos (dppe, dppp, and dppb) behave as bidentate chelating ligand whereas the dppm behave as bidentate chelating ligand to bonded two Hg(II) ion and the Phos behave as monodentate (See Fig. 2).

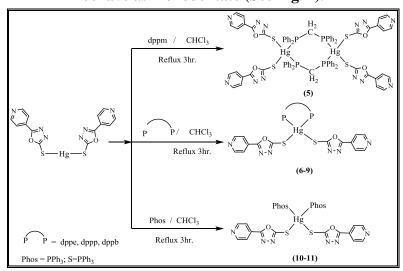


Fig. 2. Preparation of [Hg(pot)₂(diphos)] and [Hg(pot)₂(Phos)₂] complexes 3.2 CHARACTERIZATION OF COMPLEXES

The Complexes were identified by elemental analysis, Conductivity measurements, IR spectra, 1H and 31P-{1H} nmr spectra, and their data are listed in Tables 1-3. The molar conductivity of the prepared complexes in DMSO or DMF is low enough (0.4- 6.8 Ω –1. Mol-1) to suggest that they are non-electrolytes [29].

Table 1: Color, yield %, m.p. and elemental analysis for the prepared complexes

Seq.	Compounds	M.Wt	Color	Yield %	m.p.	$\Lambda_{ m M}(\Omega^{-1}.~{ m Mol}^{-1})$	М%	Elemental analysis. % Calc.(Found)		
					(°C)			С	Н	N
1	Hpot	179.20	Yellow	67	262-264			46.92	2.81	23.45
1	прос	173.20	TEHOW	07	202-204			(47.16)	(2.93)	(23.76)
2	[HgCl(μ-Cl)(Hpot)] ₂	911.38	Yellow	72	256-258	6.8	44.31	18.65	1.12	9.34
-	[rigei(µ-ei)(ripot)]2	311.30	TCHOW	, ,	230 230	0.0		(18.79)	(1.34)	(9.31)
3	[HgBr(µ-Br)(Hpot)] ₂	1079.20	Yellow	90	250-251 ^a	0.9	39.83	15.58	0.93	7.79
•	[11g51(µ 51)(11p0t)]2	1075.20	TCHOW	30	230 231	0.5		(15.91)	(1.15)	(8.01)
4	[HgI(μ-I)(Hpot)] ₂	1267.20	Yellow	88	222-224 ^a	6.4	36.89	13.27	0.80	6.63
•	[β.(μ/μοτ///2	1207.20	10110	00		0.1		(13.46)	(0.95)	(6.51)
5	[Hg(SCN)(μ-SCN)(Hpot)] ₂	991.88	Yellow	74	211-215 ^a	5.8	40.21	21.80	1.02	14.12
•	[116(3611)(# 3611)(11601)]2	331.00	1011011	, ,	211 213	3.0		(22.04)	(1.09)	(14.04)
6	[Hg(pot) ₂]	556.97	Yellow	79	273-275	0.4	35.77	30.19	1.45	15.09
•	[8(Þ-4/2]	550.57		,,,	275 275	0		(30.02)	(1.62)	(14.92)
7	[Hg(pot) ₂ (μ-dppm)] ₂	1882.21	Yellow	83	109-112 a	0.8	21.79	49.76	3.21	8.93
-	[8(p-1/2(p-2-p/)2	1002.21		00	103 111	0.0		(49.71)	(3.44)	(8.72)
8	[Hg(pot)₂(dppe)]	924.42	Yellow	92	184-185	0.9	21.84	50.29	3.39	8.80
	[0(h)7(hh)]							(49.98)	(3.10)	(8.72)
9	[Hg(pot)₂(dppp)]	938.45	Yellow	87	115-116 a	1.2	21.28	50.80	3.54	8.67
	1 00 - 720 11173							(50.78)	(3.62)	(8.61)
10	[Hg(pot) ₂ (dppb)]	952.47	Yellow	74	136-138	1.8	20.67	51.29	3.69	8.55
	C 001 - 720 FF - 72				(51.13)	(3.55)	(8.42)			
11	[Hg(pot) ₂ (PPh ₃) ₂]	1081.55	Yellow	73	89-92°	2.8	18.80	55.53	3.54	7.77
	511 512							(55.34)	(3.61)	(7.64)
12	[Hg(pot) ₂ (S=PPh ₃) ₂]	1145.11	Yellow	84	148-149	3.7	17.94	52.42	3.34	7.34
	1 011:721			<u> </u>	1.0 110	3. ,		(52.67)	(3.22)	(7.29)

a: decomposition temperature

Table 2: Selected IR stretching vibration bands (cm⁻¹) of prepared complexes

Seq.	Compounds	υ NH	υ CH ar	υC=N	υP-Ph	υ N-N	υC-S	υP-C	υM-P
	Hpot	3180w	3083w	1606s		1133s	732m		
1	$[HgCl(\mu-Cl)(Hpot)]_2$	3161w	3074w	1610s		1128s	690m		
2	$[HgBr(\mu-Br)(Hpot)]_2$	3180w	3062w	1604s		1143s	688s		
3	$[HgI(\mu-I)(Hpot)]_2$	3182w	3063w	1598s		1140m	680s		
4	$[Hg(SCN)(\mu-SCN)(Hpot)]_2$	3158w	3058w	1601s		1129m	690m		
5	[Hg(pot) ₂]		3062w	1612m		1128s	681m		
6	$[Hg(pot)_2(\mu-dppm)]_2$		3053m	1598s	1433s	1138s	620m	495s	452m
7	[Hg(pot)₂(dppe)]		3068w	1610s	1436s	1136s	630m	500s	461w
8	[Hg(pot)₂(dppp)]		3052w	1600s	1430s	1128m	635m	500m	458m
9	[Hg(pot) ₂ (dppb)]		3068w	1610m	1434s	1142s	627s	513s	459w
10	$[Hg(pot)_2(PPh_3)_2]$		3049w	1610s	1436s	1137s	628m	500s	476w
11	$[Hg(pot)_2(S=PPh_3)_2]$		3086w	1608s	1433s	1130s	625m	510s	

s: strong; m: medium; w: weak



3.2.1 IR SPECTRA

The IR spectrum of the (Hpot) shown bonds at 3185, 1602, 1133, 1075, 880 cm-1which corresponding to $\upsilon(N\text{-H})$, $\upsilon(C\text{-N})$, $\upsilon(N\text{-N})$, $\upsilon(C\text{-O-C})$ and $\upsilon(C\text{-S})$ respectively, and the stretching vibration of the (NH) group showed in the spectrum because toutomeric conformations exhibiting thiol – thione isomers involving (-N=C-SH) and (-NH-C=S) group in the thiol – thione equilibrium [15].

In the spectra of the prepared complexes (1-4) (Fig. 3), a band due to $\upsilon(NH)$ is visible in the region (3120-3182) cm-1, suggesting the non-involvement of (NH) in coordination, and the negative shift in $\upsilon(C=S)$ shows that the thione sulfur is participating in bonding in complexes 2-5 [15]-[19],[30],[31] (see Scheme 2), A strong band were showed at the region (1604-1598) cm-1, due to the $\upsilon(C=N)$ of pyridyl ring, and $\upsilon(N-N)$ of heterocyclic ring was appeared at the region (1143-1128) cm-1. These are at the same positions for the free ligand which suggested the two (C=N) are not participating in coordination [15]-[19],[30],[31]. The spectrum of the complex 5, shows two strong band at 2093 and 2134cm-1, due to the terminal SCN stretching bridging SCN stretching [30]. Other bands are listed in the Table 2.

The IR spectra of [Hg(pot)2] prepared complex showed a strong band at (1612) cm-1, due to the $\upsilon(C=N)$ of pyridyl ring and at (1128) cm-1 for $\upsilon(N-N)$ group, this indicating the $\upsilon(N-N)$ don't participating in coordination[19],[30].

TREATMENT OF [HGL2] (5) WITH ONE MOLE EQUIVALENT OF DIPHOS GAVE A SINGLE PRODUCT OF THE TYPE [HG(POT)2(DIPHOS)](6-9) OR TWO MOLE EQUIVALENT OF MONOPHOSPHINE (PPH3 OR S=PPH3) GAVE A SINGLET PRODUCT OF THE TYPE [HG(POT)2(PHOS)2] (10-11). IN THE IR SPECTRA OF (5-11) COMPLEXES (FIG. 4AND 5), APPEARANCE OF NEW BANDS AT 452-476 CM-1 DUE TO v(M=P) suggests the formation of the complexes [30]. And a new bands

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WERE OBSERVED, WHICH DIDN'T FOUND IN THE SPECTRUM OF THE [HG(POT)2] COMPLEX, ARE THE $\upsilon(P\text{-Ph})$ and $\upsilon(P\text{-C})$ observed with in the (1430-1436)cm-1 and (495-513)cm-1 range, respectively[32],[33]. It is thought [33] that this vibration arises from the deformation of the planarity of the phenyl ring bonded to a heavy atom (phosphorus).

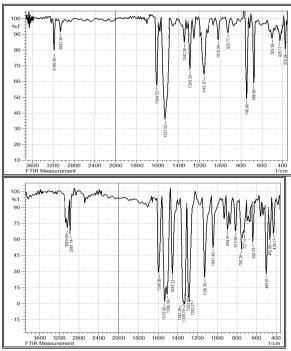


Fig. 3: IR spectrum of $[HgBr(\mu-Br)(Hpot)]_2$

Fig. 4: IR spectrum of [Hg(pot)₂(μ-dppm)]₂

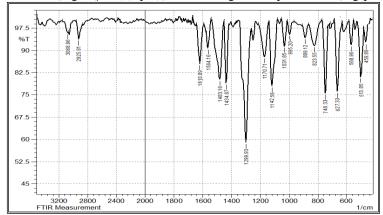


Fig. 5: IR spectrum of [Hg(pot)₂(dppb)]₂

3.2.2 NMR spectra

The ¹H NMR spectrum of Hpot shows a broad signal at 8.37 ppm due to the NH proton. The protons of the pyridine ring between 7.47 - 8.25 ppm ranges. The ¹H nmr



spectrum of the $[Hg(pot)_2]$ (6) showed the pyridyl protons as unresolved multipletes with (7.42-8.38) ppm range. The disappearance of the oxadiazole NH proton at 8.37 ppm this indicated the deprotonated of the thione ligand to give thionlate pot Θ .

The $^{31}\text{P-}\{^{1}\text{H}\}$ NMR spectra of $[\text{Hg(pot)}_{2}(\text{diphos})]$ and $[\text{Hg(pot)}_{2}(\text{Phos})_{2}]$ complexes (7-12). Showed a singlet peak at $\delta p = 6.70$ (Fig. 7), 19.90, 21.35, 23.85 (Fig. 6), 13.67 and 28.69ppm, respectively. The singlet peak indicating the presence of a singlet isomer for each. And the positive chemical shift value of the $[\text{Hg(pot)}_{2}(\mu-\text{dppm})]_{2}$ (7) (Fig.7) indicates that dppm behave as a bidentate bridging ligand [19],[25]. This has been supported by the $^{1}\text{H-}\{^{31}\text{P}\}$ NMR spectrum (Fig. 8), which showed a singlet at $\delta H=2.87$ ppm assigned for the methylene protons of the bridging ligand dppm[8]. Whereas the dppe, dppp, and dppb behave as chelating ligand[19], [25]. These conclusions have been supported by $^{1}\text{H-}\{^{31}\text{P}\}$ NMR data shown in Table 3.

Table 3: ³¹P-{¹H} and ¹H NMR chemical shifts for the prepared complexes in (DMSO-d6 and CDCl₃) solvents

Seq.	Complexes	δP (δ in ppm)	δH (δ in ppm)				
1	Hpot		8.37(b, 1H, NH); 7.47-8.35(m, 8H, pyridyl-H)				
6	[Hg(pot) ₂]		7.42-8.38(m, 8H, pyridyl-H)				
7	[Hg(pot)₂(μ- dppm)]₂	6.70	2.85(s, 2H, CH₂); 7.33-8.25(m, 28H, phenyl + pyridyl-H)				
8	[Hg(pot)₂(dppe)]	19.90	2.31(b, 4H, CH ₂); 7.19-8.34(m, 28H, phenyl + pyridyl-H)				
9	[Hg(pot)₂(dppp)]	21.35	2.01(b, 2H, CH ₂); 2.84(b, 4H, CH ₂); 7.24-8.37(m, 28H, phenyl + pyridyl-H)				
10	[Hg(pot) ₂ (dppb)]	23.85	$1.98(b, 4H, CH_2); 2.68(b, 4H, CH_2); 7.19-8.31(m, 28H, phenyl + pyridyl-H)$				
11	$[Hg(pot)_2(PPh_3)_2]$	13.67	7.22-8.29(m, 38H, phenyl + pyridyl-H)				
12	$[Hg(pot)_2(S=PPh_3)_2]$	28.96	7.16-8.32(m, 38H, phenyl + pyridyl-H)				



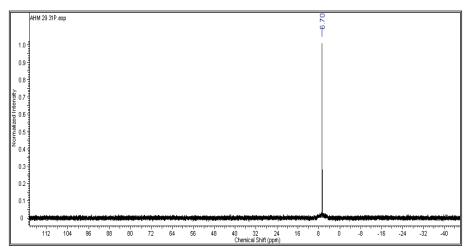


Fig. 6: ³¹P-{¹H}-NMR spectrum of [Hg(pot)₂(μ-dppm)]₂ in CDCl₃ solvent

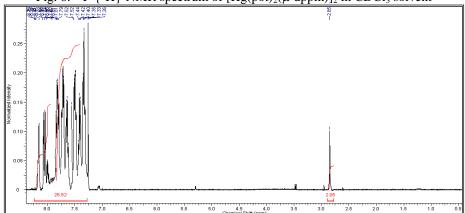


Fig. 7: $^1H\text{-}\{^{31}P\}$ NMR spectrum of $[Hg(pot)_2(\mu\text{-}dppm)]_2$ in CDCl $_3$ solvent

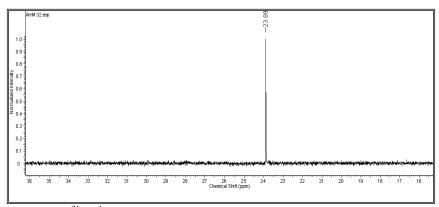


Fig. 8: ³¹P-{ ¹H}-NMR spectrum of [Hg(pot)₂(dppb)] in CDCl₃ solvent

4. Conclusions & Recommendation





Reaction of two moles of Hpot ligand with HgX2 (X = Cl, Br, I, or SCN) afford $[HgX(\mu-X)(Hpot)]$ 2 complex the Hpot ligand behave as monodentate bonded via the sulfur atom to give a tetrahedral arrangement around the Hg(II) ion.

Treatment of [Hg(pot)2] complex with phosphines as co-ligands afford three types of complexes

Binuclear complex with dppm ligand which have [Hg(pot)2(μ-dppm)]2 formula.

Mono nuclear complexes of the type [Hg(pot)2(diphos)] (diphos= dppe, dppp and dppb)

With monophosphines (PPh3 and S=PPh3) afford [Hg(pot)2(phos)2]

Dppm ligand behave as a bidentate bridging ligand bonded with two Hg(II) ion, whereas the (dppe, dppp and dppb) bonded as bidentate chelating ligands. And the pot anion ligand linkage through the sulfur atom to give a tetrahedral geometry around the Hg(II) ion.

Study the thermal behaver of the prepared complexes. And prepared a new complexes of the Hopt ligands with other co-ligands

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References

- E. S. Raper, "Complexes of heterocyclic thione donors", Coord. Chem. Rev., (61), pp.115-184, 1985.
- E. S. Raper, "Copper complexes of heterocyclic thioamides and related ligands", Coord. Chem. Rev., (129), pp.91-159, 1994.
- E. R. Raper, "Complexes of heterocyclic thionates. Part 1. Complexes of monodentate and chelating ligands", Coord. Chem. Rev., (153), pp.119-225, 1996.
- A. A. Isab, M. I.M. Wazeer, W. Ashraf, "Cadmium cyanide complexes with heterocyclic thiones: Solid state and solution NMR studies", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, (72) 1,pp. 218-221, 2009.
- M.K. Bharty, R.K. Dani, S.K. Kushawaha, N.K. Singh, R.N. Kharwar, R.J. Butcher Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Co(II) complexes of 1-phenyl-1H-tetrazole-5-thiol: Synthesis, spectral, structural characterization and thermal studies", Polyhedron, (88),pp.208-211, 2015.
- B., P. Bharati, M.K. Bharty, R.K. Dani, Sanjay Singh, N.K. Singh, "Mononuclear Ag(I), dinuclear and polymeric Hg(II) complexes of 3-mercapto-4-methyl-4H-1,2,4-triazole: Syntheses, spectral, X-ray, photoluminescence and thermal analysis," Polyhedron, (54),pp.131-139, 2013.
- N. A Bell, W. Clegg, S. J Coles, C. P Constable, R. W Harrington, M. B Hursthouse, M. E Light, E. S Raper, C. Sammon, M. R Walker," Complexes of heterocyclic thiones and group 12 metals: Part VI. Preparation and Kirkuk University Journal /Scientific Studies (KUJSS)

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characterisation of complexes of cadmium(II) halides with 1-methylimidazoline-2(3H)-thione, 1,3-thiazolidine-2-thione and 1,3-benzothiazoline-2-thione. Crystal structures of polymeric (1,3-thiazolidine-2-thione)cadmium(II) chloride, bis(1,3-thiazolidine-2-thione) cadmium(II) iodide and monomeric bis(1-methylimidazoline-2(3H)-thione)cadmium(II) bromide," Inorg. Chim. Acta., (357)11,pp. 2091-2099, 2007.

- H. J. Nam, H. Lee, D.Y. Noh," Novel mercury(II) complexes of 1,3-dithiole-2-thiones containing the 2-pyridyl moiety: syntheses, X-ray crystal structures and solution behavior," Polyhedron, (23)1, pp. 115-123m 2004.
- N. A Bell, T. N Branston, W. Clegg, L. Parker, E. S Raper, C. Sammon, C. P Constable," Complexes of heterocyclic thiones and Group 12 metals: Part four. Preparation and characterisation of 1:1 complexes of mercury(II) halides with 1,3-thiazolidine-2-thione and 1,3-benzothiazoline-2-thione. Crystal structure of the discrete trans dimer [(μ-dibromo)bis(trans{(bromo)(1,3-thiazolidine-2-thione)}mercury(II))]", Inorg. Chim, Acta., (319)1,pp. 130-139, 2001.
- Z. Popović, G. Pavlović, D. M. Čalogović, Ž. Soldin, M. Rajić, D. Vikić-Topić, D. Kovaček," Mercury(II) complexes of heterocyclic thiones.: Part 1. Preparation of 1:2 complexes of mercury(II) halides and pseudohalides with 3,4,5,6-tetrahydropyrimidine-2-thione. X-ray, thermal analysis and NMR studies", Inorg. Chim. Acta., (306)2, pp. 142-152, 2000.
- N. A Bell, T. N Branston, W. Clegg, J. R Creighton, L. Cucurull-Sánchez, M. R.J Elsegood, E. S Raper," Complexes of heterocyclic thiones and Group 12 metals: Part 3. Preparation and characterisation of 1:2 complexes of mercury(II) halides with 1-methylimidazoline-2(3H)-thione: the crystal structures of [(HgX2)(1-methylimidazoline-2(3H)-thione)2] (X=Cl, Br, I) at 160 K", Inorg. Chim. Acta., (303)2,pp. 220-227, 2000.
- N. A. Bell, W. Clegg, J. R. Creighton, E.S. Raper," Complexes of heterocyclic thiones and Group 12 metals: Part 2: The chemical and electrochemical synthesis of mercury(II) complexes of 1-methylimidazoline-2(3H)-thionate. The crystal structure of trans-[bis- $\{(\eta 1-S-1-methylimidazoline-2(3H)-thione)(\eta 1-S-1-methylimidazolin$

methylimidazoline-2(3H)-thionate)(μ2-S,N-1-methylimidazoline-2-thionate)mercury(II)}] at 160 K," Inorg. Chim. Acta., (303), pp. 12-16, 2000.

R.K. Dani, M.K. Bharty, S.K. Kushawaha, O. Prakash, V.K. Sharma, R.N. Kharwar, Ranjan K. Singh, N.K. Singh, "Syntheses, spectral and structural characterization of trinuclear and mononuclear Zn(II) complexes of N'-benzoyl hydrazine carboperthioate and 5-phenyl-1,3,4-oxadiazole-2-thione: An approach to DFT calculation, antibacterial and thermal studies", Polyhedron, (81), pp. 261-272, 2014.

R.K. Dani, M.K. Bharty, S. Paswan, Sanjay Singh, N.K. Singh," Mononuclear Ni(II) and dinuclear Cd(II) complexes of 4-phenyl-2H-1,2,4-triazole-3-thione and Mn(II) catalyzed disulphide bond formation in 3,3'-dithiobis (4-phenyl-1,2,4-triazole): Syntheses, structural characterization, thermal analysis and DFT calculation", Inorg. Chim. Acta., (421), pp. 519-530, 2014.

B.M.K. Bharty, S. Kashyap, U.P. Singh, R.J. Butcher, N.K. Singh," Hg(II) complexes of 4-phenyl-5-(3-pyridyl)-1,2,4-triazole-3-thione and 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione and a Ni(II) complex of 5-(thiophen-2-yl)-1,3,4-oxadiazole-2-thione: Synthesis and X-ray structural studies", Polyhedron, (50), pp. 582-591, 2013.

M.K. Bharty, A. Bharti, R.K. Dani, R. Dulare, P. Bharati, N.K. Singh," Synthesis and X-ray structural studies of Cd(II) and Ni(II) complexes of 5-(4-methoxy phenyl), 5-(2-pyridyl) and 5-(2-methoxy phenyl)-1,3,4-oxadiazole-2-thione", J. Molecular Structure, (1011), pp. 34-41, 2012.

N.K. Singh, M.K. Bharty, R. Dulare, R.J. Butcher, "Synthesis and X-ray crystallographic studies of Ni (II) and Cu (II) complexes of [5-(4-pyridyl)-1,3,4] oxadiazole-2-thione/thiol formed by transformation of N-(pyridine-4-carbonyl)-hydrazine carbodithioate in the presence of ethylenediamine", Polyhedron, (28), pp. 2443-2449, 2009.

O. H. Amin, L. J. Al-Hayaly, S. A. Al-Jibori, T. A.K Al-Allaf," Heterobimetallic complexes of palladium(II) and platinum(II) bridged by the ligand 5-phenyl-1,3,4-oxadiazole-2-thione," Polyhedron, (23),pp.2013-2020, 2004.

- S. A. Al-Jibori, T. F. Khaleel, S. A.O. Ahmed, L. J. Al-Hayaly, K. Merzweiler, C. Wagner, G. Hogarth, "Heteroleptic palladium(II) and platinum(II) complexes of 1,1-bis(diphenylphosphino) ferrocene (dppf) and heterocyclic thionates: Crystal structures of $[Pt(Phozt)2(\kappa 2\text{-dppf})]$ (PhoztH = 5-phenyl-1,3,4-oxadiazole-2-thione) and $[Pd(bzoxt)2(\kappa 2\text{-dppf})]$ (bzoxtH = benz-1,3-oxazoline-2-thione)", Polyhedron, (41), pp. 20-24, 2012.
- O. Evangelinou, A.G. Hatzidimitriou, E. Velali, A.A. Pantazaki, N. Voulgarakis, P. Aslanidis, '' Mixed-ligand copper(I) halide complexes bearing 4,5-bis(diphenylphosphano)-9,9-dimethyl-xanthene and N-methylbenzo thiazole-2-thione: Synthesis, structures, luminescence and antibacterial activity mediated by DNA and membrane damage'', Polyhedron, (72), pp. 122-129, 2014.
- S. Nawaz, A. A. Isab, K. Merz, V. Vasylyeva, N. Metzler-Nolte, M. Saleem, S. Ahmad," Synthesis, characterization and antimicrobial studies of mixed ligand silver(I) complexes of triphenylphosphine and heterocyclic thiones: Crystal structure of bis[{ $(\mu 2\text{-diazinane-}2\text{-thione})(\text{diazinane-}2\text{-thione})(\text{triphenylphosphine})\text{silver}(I)$ nitrate}]," Polyhedron, (30),pp.1502-1506, 2011.
- Kaltzoglou, P.J. Cox, P. Aslanidis,"Copper(I) bromide complexes from 1,2-bis(diphenyl phosphano) benzene and some heterocyclic thiones," Inorg. Chim. Acta., (358)11,pp. 3048-3056, 2005.
- M. Kubicki, S.K. Hadjikakou, M.N. Xanthopoulou," Synthesis, characterisation and study of mercury(II) bromide complexes with triphenylphosphine and heterocyclic thiones. The crystal structures of [bis(triphenylphosphine) dibromo mercury(II)] and [dibromo (pyrimidine-2-thionato) (triphenylphosphine) mercury(II)]," Polyhedron, (20)17, pp.2179-2185.
- S.K. Hadjikakou, M. Kubicki." Synthesis, characterization 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-triphenylphosphine) chloro mercury(II)] and [(µ2-dichloro){(bis-triphenylphosphine)



pyrimidine-2-thionato)mercury(II)}{(bis-triphenyl phosphine)mercury(II)}] at 100 K,'' Polyhedron, (19), pp. 2231-2236, 2000.

- T. S Lobana, R. Verma, G. Hundal, A. Castineiras," Metal-heterocyclic thione interactions.: 12. Heterocyclic 2-thiolates of platinum(II) and palladium(II): the crystal structures of first examples of cis-[M(η1-S-pyridine-2-thiolato)2(L-L)] {M=Pt, Pd, L-L=1,2-bis(diphenyl phosphino)ethene} complexes", Polyhedron, (19)8, pp. 899-609, 2000.
- T. S. Lobana, R. Sharma, R. J. Butcher, "Pyridine-2-thione (pySH) derivatives of silver(I): Synthesis and crystal structures of dinuclear [Ag2Cl2(μ -S-pySH)2(PPh3)2] and [Ag2Br2(μ -S-pySH)2(PPh3)2] complexes", Polyhedron, (27)5,pp.1375-1380, 2008.
- A. S. M. AL-Janabi, B. Abdullah and S. A. AL-Jibori, "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", Orient. J. Chem. (25)2, pp. 277-286, 2009.
- A. S. M. AL-Janabi, G.A. AL-Soumadiy and B. A. Khear –Allah," Preparation Ligand 5-(3-chlorophenyl)-1,3,4-oxadiazole-2-thiol by New Method and Complexation with Transition Metals," Orient. J. Chem. (27)4, pp. 1465-1473, 2011.
- W.J. Geary, "The use of conductivity measurements in organic solvents for the characterization of coordination compounds", Coord. Chem. Rev., (7) pp.81-122, 1971.
- K. Nakamoto, Infra-Red and Raman Spectra of Inorganic and Coordination Compounds, 4th ed. John Wiley & Sons, New York, 1986.
- R.M. Silverstein, F.X. Webster, Spectrometric Identification of Organic Compounds, 6th ed., John Wiley & Sons, New York, NY, USA,1997.
- W. Kuchen and H. Buchwald, '' Zur Kenntnis der Organophosphorverbindungen, II. Das Tetraphenyldiphosphin'', Chem. Bar., (91), pp. 2871-2877, 1958.



K. A. Jensen and P. H. Nrelsen, "Infrared Spectra of Some Organic Compounds of Group V B Elements", Acta. Chem. Scand., (17), pp. 1875-1885, 1963.