

Synthesis, characterization and study of mercury(II) complexes with phosphine and heterocyclic thiones

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Abstract

Many new mixed ligand complexes of mercury(II) have been synthesized with LH = 4,5-(diphenyl)-1,2,4-triazole-3-thione (**diptSH**) and tertiary phosphines as co-ligands. The compounds have been characterized by elemental analyses, IR, UV-Vis, 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 thiolate ligand(**diptS⁻**) is coordinated as monodentate through the sulfur atom. The dppm behave as bidentate bridging ligand to bonded two Hg(II) ions in the complex (**7**), Whereas in the complexes (**7-10**), the thionate 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 thionate bonded via the sulfur atom as monodentate to give tetrahedral complexes.

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

1. Introduction

The interest in the coordination chemistry of Hg(I) and Hg(II) has resulted from the inherent toxicity of these ions. Hg(II) and especially $[\text{Hg}(\text{CH}_3)_2]$ is extremely toxic to living organisms and, owing to its bioaccumulation in the food chain, it is dangerous to higher organisms[1,2]. Such toxic behavior derives from the affinity of Hg(II) compounds for cysteinyl sulfur residues in a variety of biosystems[3]. Heterocyclic thiones and thionates are among the ligand systems used to mimic bio-relevant Hg(II)-S interactions [4]. The coordination chemistry of nitrogen-sulfur containing heterocyclic ligands, such as 1,2,4-triazoles, 1,3,4-oxadiazoles, is an emerging and rapidly developing area of research[5-7].

For example, the 5-phenyl-1,3,4-oxadiazole -2-thione, has several ways of binding, such as S-bonding, N-bonding, N, S-bridging[8-14]. 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[1,2]. Recently, some research works involving M(II) ions with thiones and phosphines have been published[15-23]. In the present work, I report the preparation of Hg(II) complexes with 4,5-diphenyl-1,3,4-triazole-3-thione (**diptSH**) ligand and diphosphines as co-ligands.

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. The electronic spectra were performed on an UV-1700 pharماسpec spectrophotometer. 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- d_6 as solvent and Me_4Si as internal reference. ^{31}P NMR spectra were recorded on Gemini 2000 spectrometer with DMSO- d_6 as solvent and $\text{H}_3\text{PO}_4(85\%)$ 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 HgCl_2 , HgBr_2 , $\text{HgI}_2 \cdot x\text{H}_2\text{O}$, $\text{Hg}(\text{SCN})_2$, $\text{Hg}(\text{Ac})_2 \cdot x\text{H}_2\text{O}$, dppm, dppe, dppp, dppb and PPh_3 were commercial products and used as supplied. The Ligand 4,5-(diphenyl) - 1,2,4- triazole -3- thione (**diptSH**) (Fig1) was prepared according to the literature [10].

2.3 Preparation of $[\text{HgCl}(\mu\text{-Cl})(\text{diptSH})_2]$ (**2**)

A solution of HgCl_2 (0.300g, 1.103mmole) in EtOH (10ml) was added to a hot solution of 4,5-(diphenyl)-1,2,4-triazole-3-thione (**diptSH**) (0.179g, 2.206mmol) in EtOH (10ml). The mixture was refluxed for 2hr. The white solid formed was filtered off, washed with EtOH, and dried. The white solid product was recrystallized from DMSO/EtOH to give pale white solid of (**2**).

The following complexes $[\text{HgX}(\mu\text{-X})(\text{DiptSH})_2]$ ($\text{X}=\text{Br}$, I and SCN) (**3-5**) were prepared and isolated by a similar method.

2.4 Preparation of $[\text{Hg}(\text{diptS})_2]$ (**6**)

A hot solution of (**diptSH**) ligand (0.716g, 2.000mmol) in EtOH (10ml) containing a few drops of Et_3N as a base was added to a solution of mercury acetate $\text{Hg}(\text{oAc})_2$ (0.637g, 1.000mmol) in EtOH (10ml), a white ppt. was formed. The mixture was refluxed for 3hr. The resulting white precipitate was filtered off, washed with EtOH-water mixture (50-50, v/v), and dried under vacuum. The white solid product was recrystallized from DMSO/EtOH to give white solid of (**6**).

2.5 Preparation of $[\text{Hg}(\text{diptS})_2(\text{dppm})]$ (**7**)

To a hot suspension of $[\text{Hg}(\text{diptS})_2]$ (**6**) (0.145g, 0.260mmol) in CHCl_3 (15ml), a solution of dppm ligand (0.100g, 0.260mmol) in CHCl_3 (15ml) was added. A pale white solution was formed. The

resulting solution formed was refluxed for 3hr. The resulting pale white precipitate was filtered off, washed with chloroform, and dried under vacuum. The pale white solid product was recrystallized from DMSO/CHCl₃ to give pale white solid of (7).

The following complexes [Hg(diptS)₂(dppe)](8); [Hg(diptS)₂(dppp)](9) and [Hg(diptS)₂(dppb)] (8) were prepared and isolated by a similar method.

2.6 Preparation of [HgL₂(PPh₃)₂] (11)

To a hot suspension of [Hg(diptS)₂] (6) (0.145g, 0.260mmol) in CHCl₃ (15ml), a hot solution of PPh₃ (0.138g, 0.260mmol) in CHCl₃ (15ml) was added. A white solution was formed. The resulting solution formed was refluxed for 3hr. The resulting white precipitate was filtered off, washed with chloroform, and dried under vacuum. The pale white solid

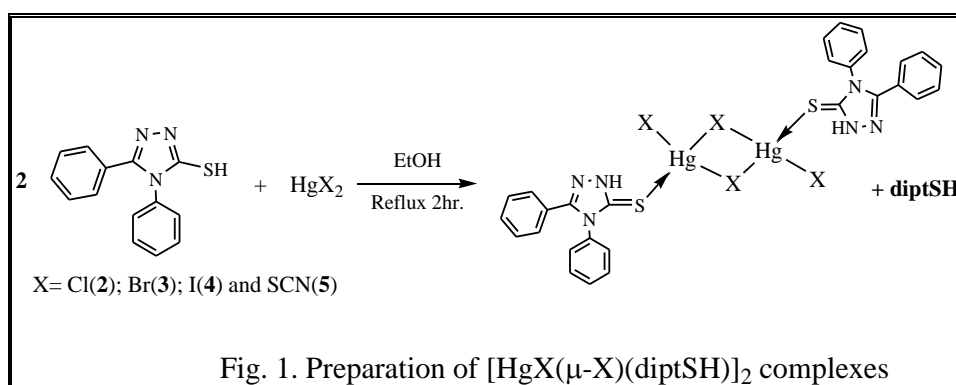
product was recrystallized from DMSO/CHCl₃ to give white solid of (11).

The complex [Hg(diptS)₂(S=PPh₃)₂] (12) was prepared and isolated by a similar method.

3. Results and discussion

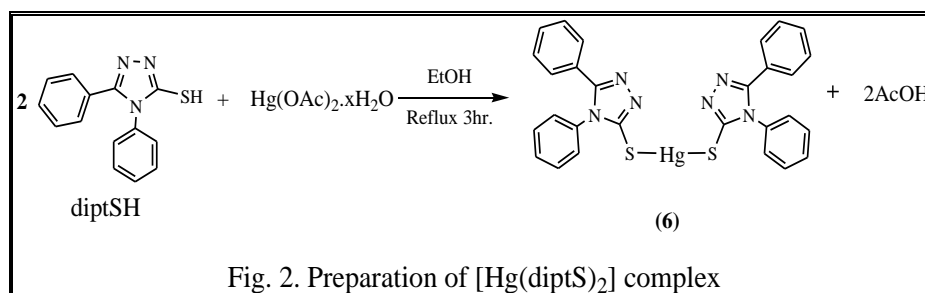
3.1 Synthesis of Complexes (2-10)

Treatment of ethanolic solution of mercuric halide HgX₂(X=Cl, Br, I and SCN) with the ethanolic solution of 4,5-(diphenyl)-1,2,4-triazole-3-thione (diptSH) ligand in (1:1)molar ratio gave complexes of the type [HgX(μ-X)(diptSH)]₂. The ligand (diptSH) behaves as a monodentate neutral ligand coordinated through the sulfur atom for diptSH ligand. While the halogen was coordinated as a monodentate and bidentate bridging to Hg(II) ion (See Fig. 1).



The reaction of one mole of the Hg(oAc)₂ with two mole diptSH ligand in ethanol as a solvent present few drops of the Et₃N gave complex of the type

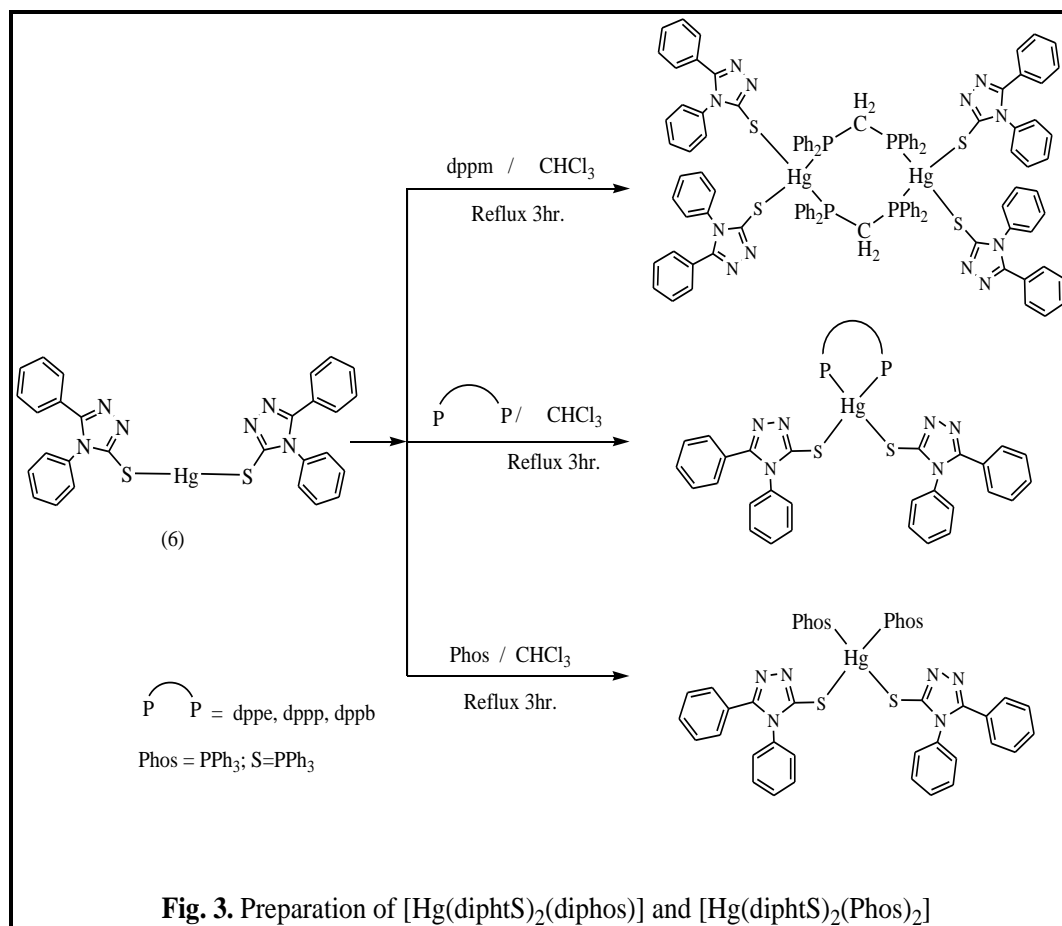
[Hg(diptS)₂], and the anionic ligand(diptS⁻) behave as monodentate bonded through the sulfur atom to Hg(II).(See Fig. 2)



Treatment of linear complex of the [Hg(diptS)₂] with diphosphine (diphos= dppm, dppe, dppp, dppb) in (1:1) molar ratio gave complexes of the [Hg(diptS)₂(diphos)] or with monophosphines (PPh₃ and S=PPh₃) in (1:2) molar ration gave complexes of the [Hg(diptS)₂(Phos)₂] (Phos: PPh₃ and S=PPh₃). The thionlate ligand (diptS⁻) behave as monodentate

coordinated to Hg(II) ion through sulfur atom, while the diptSH behave as monodentate bonded through the sulfur atom to Hg(II). (See Fig. 2)

coordinated to Hg(II) ion through sulfur atom, while the diptSH (dppe, dppp, and dppb) behave as bidentate chelating ligands whereas the dppm behave as bidentate bridging ligand to bonded with two Hg(II) ion, whereas the monophosphine behave as monodentate (See Fig.3).



3.2 Characterization of Complexes

The prepared complexes were identified by elemental analysis, conductivity measurements, electronic spectra, 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 to suggest that they are non-electrolytes [24]. The prepared mercury complexes are diamagnetic and show absorptions in the high energy region due to intra-ligand-charge transfer transitions.

3.2.1 IR spectra

The IR spectrum of the free ligand 4,5-diphenyl-1,2,4-triazole-3-thione (diptSH) in the thione form is expected to give rise to characteristic bands due to $\nu(\text{NH})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$, which occur at 3219, 1613 and 950 cm^{-1} , respectively. The IR spectra of complexes (2-5) show bands at (3189-3251) cm^{-1} due to $\nu(\text{NH})$, indicating the N atoms of the heterocyclic ring is not participating in the bonding. A negative shift of about 40 cm^{-1} in $\nu(\text{C}=\text{S})$ shows that the thione sulfur is participating in bonding with the Hg(II) ion in complexes (2-5)[25,26]. The spectrum of the complex 5, shows two strong band at 2093 and 2134 cm^{-1} , due to the terminal SCN stretching bridging SCN stretching [25]. Other bands are listed in the Table 2.

Whereas in the IR spectrum of complex (6), The disappearance of the triazole NH band indicated the

deprotonated of the ligand and the negative shifted of 110 cm^{-1} $\nu(\text{C}=\text{S})$ shows that the S atom is participating in the bonding.

In the IR spectra of (6-12) Complexes, Appearance of new bands at 432-458 cm^{-1} due to $\nu(\text{M}-\text{P})$ suggests the formation of the complexes[25]. And a new bands were observed, which didn't found in the spectrum of the [Hg(diptS)₂] complex, are the $\nu(\text{P}-\text{Ph})$ and $\nu(\text{P}-\text{C})$ observed with in the (1433-1434) cm^{-1} and (495-521) cm^{-1} range, respectively[27,28]. It is thought [28] that this vibration arises from the deformation of the planarity of the phenyl ring bonded to a heavy atom (phosphorus).

3.2.2 NMR spectra

The ¹H NMR spectrum of diptSH shows a broad signal at 8.21 ppm due to the NH proton. The protons of the phenyl ring between 6.81–7.49 ppm ranges. The ¹H nmr spectrum of the [Hg(diptS)₂] (6) showed the phenyl protons as unresolved multipletes with (7.01-8.03) ppm range. The disappearance of the triazole NH proton at 8.21 ppm this indicated the deprotonated of the thione ligand to give thionlate diptS⁻.

The ³¹P-{¹H} NMR spectra of [Hg(diptS)₂(diphos)] and [Hg(diptS)₂(Phos)₂] complexes (7-12). Showed a singlet peak at $\delta\text{p} = 11.23, 21.98, 24.22, 34.15, 11.27$ and 32.69ppm, respectively. The singlet peak indicating the presence of a single isomer for each. And the positive chemical shift value of the

[Hg(diptS)₂(μ-dppm)]₂ (7) indicates that dppm behave as a bidentate bridging ligand [19],[25]. This has been supported by the ¹H-³¹P NMR spectrum, which showed a singlet at δH=2.65ppm 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 ¹H-³¹P NMR data shown in Table 3.

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

Seq.	Complexes	Color	Yield %	m.p. (°C)	Elemental analysis. % Calc.(Found)		
					C	H	N
1	diptSH	White	72	190-193	66.38 (66.46)	4.38 (3.54)	16.59 (16.81)
2	[HgCl(μ-Cl)(diptS)] ₂	White	84	123-124	32.04 (32.16)	2.11 (2.13)	8.01 (7.98)
3	[HgBr(μ-Br)(diptS)] ₂	White	66	221-223 ^a	27.44 (27.43)	1.81 (1.94)	6.85 (6.81)
4	[HgI(μ-I)(diptS)] ₂	White	79	143-147	23.79 (23.59)	1.57 (1.71)	5.94 (5.62)
5	[Hg(SCN)(μ-SCN)(diptS)] ₂	White	84	170-171	33.71 (33.45)	1.94 (2.04)	12.28 (12.58)
6	[Hg(diptS)] ₂	White	77	243-145 ^a	47.69 (47.52)	2.86 (2.62)	11.92 (12.02)
7	[Hg(diptS) ₂ (μ-dppm)] ₂	White	66	165-167	58.42 (58.71)	3.89 (4.02)	7.71 (7.96)
8	[Hg(diptS) ₂ (dppe)]	White	86	241-245	58.77 (58.45)	4.02 (4.24)	7.61 (7.72)
9	[Hg(diptS) ₂ (dppp)]	White	87	266-267 ^a	59.10 (59.21)	4.15 (4.14)	7.52 (7.61)
10	[Hg(diptS) ₂ (dppb)]	White	76	245-246 ^a	59.43 (57.12)	4.28 (4.23)	7.43 (7.58)
11	[Hg(diptS) ₂ (PPh ₃) ₂]	White	87	152-154	62.51 (56.01)	4.10 (4.23)	6.83 (6.64)
12	[Hg(diptS) ₂ (S=PPh ₃) ₂]	White	83	144-146 ^a	59.41 (59.67)	3.89 (3.56)	6.50 (6.29)

a: decomposition temperature

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

Seq.	Complexes	νNH	νCH _{ar}	νC=N	νP-Ph	νN-N	νC-S	νP-C
1	diptSH	3219w	3054w	1592s		1445m	813m	
2	[HgCl(μ-Cl)(diptSH)] ₂	3189m	3062w	1602s		1460m	732m	
3	[HgBr(μ-Br)(diptSH)] ₂	3251w	3052w	1593m		1465s	735m	
4	[HgI(μ-I)(diptSH)] ₂	3193w	3058w	1585s		1468m	751m	
5	[Hg(SCN)(μ-SCN)(diptSH)] ₂	3212w	3085w	1601s		1449m	732m	
6	[Hg(diptS)] ₂		3084w	1575m		1447m	735m	
7	[Hg(diptS) ₂ (μ-dppm)] ₂		3055w, 2858w	1574m	1435s	1460m	751m	500m
8	[Hg(diptS) ₂ (dppe)]		3072w, 2887w	1609s	1433s	1465s	732m	521s
9	[Hg(diptS) ₂ (dppp)]		3058w, 2860w	1604s	1434s	1449m	735m	513s
10	[Hg(diptS) ₂ (dppb)]		3062w, 2864w	1598m	1434s	1459m	751m	504s
11	[Hg(diptS) ₂ (PPh ₃) ₂]		3052w, 2887w	1589m	1434s	1475m	732m	498s
12	[Hg(diptS) ₂ (S=PPh ₃) ₂]		3058w, 2860w	1590m	1433s	1460m	735m	495s

s: strong; m: medium; w: weak

Table 3: ^{31}P - $\{^1\text{H}\}$ and ^1H NMR chemical shifts for the prepared complexes in (DMSO- d_6 and CDCl_3) solvents

Seq.	Complexes	δP (δ in ppm)	δH (δ in ppm)
1	DiptS		8.37(b, 1H, NH); 7.13-7.45(m, 10H, phenyl-H)
6	$[\text{Hg}(\text{diptS})_2]$		7.01-8.03(m, 8H, phenyl-H)
7	$[\text{Hg}(\text{diptS})_2(\mu\text{-dppm})_2]$	11.23	2.65(s, 2H, CH_2); 6.87-8.10(m, 40H, phenyl-H)
8	$[\text{Hg}(\text{diptS})_2(\text{dpppe})]$	21.98	2.31(b, 4H, CH_2); 7.01-8.04(m, 40H, phenyl-H)
9	$[\text{Hg}(\text{diptS})_2(\text{dppp})]$	24.22	2.11(b, 2H, CH_2); 2.67(b, 4H, CH_2); 6.56-7.88(m, 40H, phenyl-H)
10	$[\text{Hg}(\text{diptS})_2(\text{dppb})]$	34.15	1.76(b, 4H, CH_2); 2.87(b, 4H, CH_2); 6.89-8.01(m, 40H, phenyl-H)
11	$[\text{Hg}(\text{diptS})_2(\text{PPh}_3)_2]$	11.27	6.82-8.02(m, 50H, phenyl-H)
12	$[\text{Hg}(\text{diptS})_2(\text{S}=\text{PPh}_3)_2]$	32.69	6.68-7.93(m, 50H, phenyl-H)

S: singlet; b: broad singlet; m: multipletes

Acknowledgements

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تحضير وتشخيص عدد من معقدات الزئبق (II) مع 4،5-(داي فينل)-1،2،4- تريازول-3- ثايون مع ليكاندات الفوسفين

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الملخص:

تم تحضير عدد من معقدات الزئبق(II) الحاوية على مزيج من الليكاندات، من تفاعل ليكاند 4،5-(داي فينل)-1،2،4- تريازول-3- ثايون مع الفوسفينات الثلاثية كليكاندات اضافية، شخصلت المركبات المحضرة بواسطة التحليل الدقيق للعناصر، مطيافية الاشعة المرئية- فوق البنفسجية ، الاشعة تحت الحمراء، الموصلية المولارية، ومطيافية الرنين النووي المغناطيسي. اتخذت الليكاندات المتناسقة شكل الرباعي السطوح حول ايون الزئبق المركزي في المعقدات ثنائية النواة التي تحمل الصيغة $[HgX(\mu-X)(diptSH)]_2$ حيث ان $(X=Cl, Br, I \text{ and } SCN)$ ، حيث يرتبط ايون الزئبق فيها بثلاث ذرات هاليد وذرة كبريت من ليكاند الثايون. في المعقد (6) اظهر ليكاند الثايونليت تناسق احادي من خلال ذرة الكبريت ايضاً. والمعقد (7) ظهر ارتباط بشكل ثنائي السن الجسري لليكاند الفوسفين dppm ليربط ايويني الزئبق مع بعضهما البعض مكوناً معقدات ثنائية النواة ذات الصيغة $[Hg(diptS)_2(\mu-dppm)]_2$ ، في حين اظهرت المعقدات من (8-10) تناسق ثنائي السن المحلي من خلال ذرتي الفوسفور للفوسفينات الثلاثية (dppb, dppp, dppe) مع ايون الزئبق في حين يرتبط ليكاند الثايونليت بشكل احادي السن معطياً معقدات رباعي السطوح حول الايون المركزي، في حين تسلك الفوسفينات الثلاثية في المعقدين (11 و12) سلوك احادي السن مكوناً معقدات رباعي السطوح حول ايون الزئبق.

الكلمات الدالة: الزئبق(II)، الثايون، الفوسفين، تريازول