New Salicylanilide-Hg(II) complexes with phosphine ligands, Synthesis and spectroscopic investigation
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ABSTRACT
A new complex of the type [Hg(κ²-Saln)₂] (I) was prepared from the reaction of mercury acetate and salicylanilide (HSaln) in (1:2) molar ratio EtOH as a solvent with presence an Et₃N as a base. Treatment of complex (I) with diphosphine (where diphos: dppe, dppp, dpbb dpdf and dppmS₂) in 1:1 (complex: diphos) molar ratio afforded a complexes of the types [Hg(κ²-Saln)₂(diphos)] (2-6), whereas a complexes of the types [Hg(κ²-Saln)₂(phos)] (7,8) when treatment of complex(I) with two moles of monophosphine (PPh₃, or SPPh₃). The prepared complexes were fully characterization by many technical such as elemental analysis, molar conductivity, infrared spectroscopy, and nuclear magnetic resonance (¹H and ³¹P). In complex (I) the (Saln) was bonded as bidentate chelating ligand through the oxygen atoms of the carbonyl and deprotonated hydroxyl group, whereas bonded as monodentate ligand through the oxygen atom of deprotonated hydroxyl group in all other complexes (2-8). The geometry of the complexes (1-8) is a tetrahedral around the mercury (II) ion.

1. Introduction
Salicylanilide (2-Hydroxy-N-phenylbenzamide; or 2-Hydroxybenzanilide, or N-phenylsalicylamide, (HSaln)) is known as a fungicides for topical uses and antimicrobial agents in soaps[1,2]. The salicylanilide compounds have been widely used to treat tinea tonsurans and other fungal infections[3]. In veterinary medicine, the salicylanilides derivatives (such as niclosamide, terenol, oxyclozanide, rafoxanide, and clioxanide) are used to treat tapeworm and fluke infections from domestic animals. HSAln ligand can be showed different coordination fashion to metal ions, being act as monodentate fashion through the oxygen atom of deprotonated hydroxyl group, or through the neutral oxygen of hydroxyl or carbonyl group, and it also has the ability to bonding as a bidentate fashion through oxygen and nitrogen donor atom [9]. Complexes of salicylanilide or its derivatives with metal ions such as Pd(II), Pt(II), Mo(V), Os(VI), and other ions have been recently been synthesized and characterized [10-14]. Herein, we describe the preparation of mixed ligand Hg(II) salicylanilidate (Saln⁻) complexes with phosphine. These prepared complexes were investigated by spectroscopic and physical methods.

2. Experimental
2.1 Materials and Methods:
All chemical compounds (Hg(oAc)₂, xH₂O, salicylanilide, phosphines, EtOH, and CHCl₃) were supplied and used without further purification. IR spectra were recorded on Shimadzu 8400 S FTIR spectrophotometer as KBr disc in (4000-400) cm⁻¹ range. All NMR spectra (¹H and ³¹P-¹H) were recorded on Bruker av 400 NMR spectrometer in DMSO-d₆. The conductivity measurement of the prepared complexes solution (10⁻⁵M) in DMSO-d₆ was measured on Digital conductivity meter CD 2005. Melting points were recorded on SMP40 - Stuart company and were uncorrected.

2.2. Preparation of [Hg(Saln)₂] (1)
An ethanolic solution of HSAln (1.338g; 6.274mmole) in (15ml) was added to a suspension of Hg(oAc)₂, xH₂O (1.000g; 3.137mmole) in EtOH (10ml), with some drops of Et₃N as a base, a clear light brown solution was formed. The mixture was reflexed for 1.5 hr, and filtered off and left aside for evaporation at room temperature. The gum product was recrystallized from an ethanolic solution and dried at 110°C for 10 minutes and put for analytical and spectral measurement.

2.3. Preparation of [Hg(Saln)₂(dppe)] (2)
A yellow green powder was obtained, m.p. 219°C, and cold filtrate added 2 ml of hot water to the filtrate was filtered off and dried at 110°C for 10 minutes and put for analytical and spectral measurement. 

Keywords: Salicylanilide, Hg(II), phosphine, complexes.

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The color of solution was collected and dried under vacuum (Yield: 0.1915 g; 98%; m.p °C: (80-82)).

2.2.2 Preparation of [Hg(Saln)$_2$(dppe)] (2)
A solution of Bis(diphenylphosphine)ethane (dppe) (0.050g; 0.128mmole) in CHCl$_3$ (10ml) was added to a solution of [Hg(Saln)$_2$] (0.080g; 0.128mmole) in CHCl$_3$ (10ml) with stirring. The mixture was stirred for 2hr at room temperature. The creamy solution was filtered and left aside to evaporate the solvent. The gum product was washed with diethyl ether and the white ppt. was collected and dried in oven under vacuum. (Yield: 0.1001g; 76%; m.p °C: (92-93)).

2.2.3 Preparation of [Hg(Saln)$_2$(dppp)] (3)
To solution of complex (1) (0.080g; 0.128mmole) in CHCl$_3$ (10ml), a solution of Bis (diphenylphosphino) propane (dppp) (0.055g; 0.128mmole) in CHCl$_3$ was added with stirring. The color of solution was changed to off white. The solution was stirred at room temperature for 2hr and filtered off and left aside for slow evaporation at room temperature. The gum product was washed with diethyl ether for several times to formed off white ppt. and the was collected and dried in oven under vacuum. (Yield: 0.0676g; 50%; m.p °C: (72-74)).

The [Hg(Saln)$_2$(dppp)] (4); [Hg(Saln)$_2$(dppf)] (5) and [Hg(Saln)$_2$(dppmS$_2$)] (6) complexes was prepared and isolated in a similar method.

2.2.4 Preparation of [Hg(Saln)$_2$(PPh$_3$)$_2$] (7)
A solution of triphenyl phosphine sulfide (0.075g; 0.256mmole) in CHCl$_3$ (10ml) was added to a solution of [Hg(Saln)$_2$] (0.080g; 0.128mmole) in CHCl$_3$ (10ml) with stirring. The color of solution was changed to a light brown. The mixture was stirred for 3hr at room temperature, and filtered off, and left aside for slow evaporation. The gum product was formed and washed with diethyl ether for several times and the light brown ppt. was collected and dried (Yield: 0.041g; 26%; m.p °C: (103-104)). The [Hg(Saln)$_2$(PPh$_3$)$_2$] (8) complex was prepared and isolated in a similar method.

3. Results and Discussion
3.1 Synthesis
The reaction of Salicylanilide (HSaln) with mercury(II) acetate in (2:1) (ligand : metal) molar ratio, in absolute ethanol with some drops of Et$_2$N as a base , gave a light brown complex of the type [Hg(k$^2$-Saln)$_2$] (1) as a sole product (scheme 1). The Saln ligand was coordinated as bidentate chelating ligand through the oxygen atoms of carbonyl group and deprotonated hydroxyl group to afford a tetrahedral geometry around the central atom ion.

All prepared complexes are air stable in solid state, and insoluble in diethyl ether, hexane, methanol and distilled water but soluble in chloroform, dichloromethane, DMSO and DMF. The elemental analysis are listed in Table 1 and they agreed with theoretical analysis. The conductivity of freshly prepared complexes solutions were measured in DMSO at room temperature and that the complexes...
are non-electrolyte [15]. The prepared complexes were characterized by many technical CHN analysis, molar conductivity, IR, NMR spectroscopy (1H and, 31P). The CHN analysis, physical properties, IR and NMR data are listed in Table (1 to 3).

### Table 1. Color, yield, m.p.(°C), and elemental analysis of prepared complexes (1-8)

| Seq. | Complexes       | Color       | m.p.(°C) | Yield % | Λ (Ohm⁻¹.cm² .mol⁻¹) | Elemental analysis Found(cal.) % |
|------|-----------------|-------------|----------|---------|-----------------------|---------------------------------|
|      |                 |             |          |         |                       | C     | H     | N     |
| 1    | [Hg(Saln)₂]     | light brown | 80-82    | 98      | 4.12                  | 50.23 (49.96) 3.62 (3.23) 4.95 (4.48) |
| 2    | [Hg(Saln)₂(dppe)] | White      | 92-93    | 76      | 10.90                 | 61.38 (61.02) 4.59 (4.33) 3.07 (2.74) |
| 3    | [Hg(Saln)₂(dpdp)] | White      | 72-74    | 50      | 10.5                  | 61.52 (6.36) 4.81 (4.47) 2.94 (2.79) |
| 4    | [Hg(Saln)₂(dpp)] | White      | 95-97    | 61      | 11.2                  | 62.01 (61.68) 4.89 (4.60) 3.10 (2.66) |
| 5    | [Hg(Saln)₂(dpdf)] | White      | 119-120  | 47      | 10.34                 | ---- ---- ---- |
| 6    | [Hg(Saln)₂(dpmpS₂)] | Brown      | 128-130  | 49      | 3.90                  | ---- ---- ---- |
| 7    | [Hg(Saln)₂(SPh₃)] | Light brown| 103-104  | 26      | 2.90                  | 61.64 (61.35) 4.38 (4.15) 2.51 (2.13) |
| 8    | [Hg(Saln)₂(PPh₃)] | Light brown| 59-61    | 93      | 11.73                 | 65.01 (64.78) 4.89 (4.38) 2.87 (2.44) |

### 3.2 Spectroscopic studies

#### 3.2.1 Infrared spectra

The IR selected bands of salicylanilide and its complexes are listed in Table 2 and Fig 1 and 2. The IR spectrum of free salicylanilide showed bands at (3302), (3148), (1618) and (1558) cm⁻¹ which due to υ(NH); υ(OH); υ(C=O) and υ(C-N) respectively. In the spectrum of [Hg(Saln)₂], complex showed absence the υ(OH) band, which showed in free ligand at (3302) cm⁻¹ suggested the deprotonated of hydroxyl group and bonded of Hg ion with hydroxate oxygen atom [16-20], and the υ(C=O) was shifted to lower frequency from that of the free ligand, and showed at [1624] cm⁻¹, this shifted indicates that the carbonyl group was coordinated with Hg ion through the oxygen atom [19,20].

The spectra of complexes [2-9], showed the υ(C=O) within (1636-1662) cm⁻¹ range, is higher than from the υ(C=O) of complex (1) (1624) cm⁻¹, which suggest that the carbonyl group are non-involved in coordination to Hg ion [18-20], and suggesting a monodentate of (Saln) ligand through oxygen atom of the deprotonated hydroxyl group [16-20]. The spectra 2-9 displayed new bands at (1435-1450) cm⁻¹ and (498-513) cm⁻¹ range assigned to υ(P-Ph) and υ(P-C) [21-23], indicating the presence of the phosphine ligands in the complexes. This was supported by the appearance of a new medium intensity bands within the (463-489) cm⁻¹ range in the spectra of the complexes which assigned to stretching frequency of υ(Hg-P) bond [24-28]. Other selected bands are shown in Table 2.

### Table 2. Selected IR stretching vibration bands (cm⁻¹) of the prepared complexes (1-8)

| Seq. | compounds | υ(O-H) | υ(NH) | υ(C-H) | υ(C=O) | υ(C-N) | υ(Ph-P) | υ(P-C) | υ(P-Hg) |
|------|-----------|--------|-------|--------|--------|--------|--------|--------|--------|
|      |           |        |       |        | Ar.    | Alph.  |        |        |        |
| 1    | HSaln     | 3148_m | 3302_m | 3059_m | 3059_m | 1618s  | 1558s  |        |        |
| 2    | [Hg(Saln)₂] | 3304_m | 3059_m | 1614s  | 1548s  | 1437s  | 511_m  | 478_m  |        |
| 3    | [Hg(Saln)₂(dppe)] | 3308_m | 3055_m | 2920_s | 1662_s | 1548_s | 1473s  | 511_m  | 478_m  |
| 4    | [Hg(Saln)₂(dpdp)] | 3308_m | 3055_m | 2926_s | 1662_s | 1548_s | 1444_s | 509_m  | 478_m  |
| 5    | [Hg(Saln)₂(dpp)] | 3310_m | 3055_m | 2928_s | 1647_s | 1548_s | 1440s  | 513_m  | 482_m  |
| 6    | [Hg(Saln)₂(dpdf)] | 3309_m | 3055_m | 1643_s | 1543_s | 1448_s | 498_m  | 463_m  |        |
| 7    | [Hg(Saln)₂(dpmpS₂)] | 3309_m | 3053_m | 2924_s | 1636_s | 1541_s | 1450_m | 507_m  | 489_m  |
| 8    | [Hg(Saln)₂(SPh₃)] | 3321_m | 3057_m | 1641_s | 1546_s | 1444_s | 513_m  | 487_m  |        |
| 9    | [Hg(Saln)₂(PPh₃)] | 3304_m | 3053_m | 1568_s | 1541_s | 1435_m | 506_m  | 483_m  |        |

s: strong, m: medium, w : weak
showed at δ7.40, δ7.15 and δ6.98 ppm refer to the protons (H6,7,8), (H4) and (H2,3) respectively.

Table 3: $^1$H and $^{31}$P-$[^1]$H NMR chemical shifts (δ ppm) for the prepared complexes (1-7) measured in DMSO-d$_6$

| Seq. | Complexes       | δP (ppm) | δH (ppm) |
|------|-----------------|----------|----------|
| 1    | [Hg(Saln)$_2$] | 10.61 (s, 2H, NH); 7.99 (d, $^3$J$_{HH}$ = 7.87 Hz, 2H, H1); 7.73 (d, $^3$J$_{HH}$ = 7.87 Hz, 4H, H5, 9); 7.40 (m, 6H, H6, 7, 8); 6.98 (m, 4H, H2, 3). |          |
| 2    | [Hg(Saln)$_2$(dppe)] | 10.35 (s, 2H, NH); 6.55 – 7.88 (m, 38H, H-Ar); 2.42 (s, 4H, CH$_2$-dppe). |          |
| 3    | [Hg(Saln)$_2$(dppp)] | 10.35 (s, 2H, NH); 6.70 – 7.92 (m, 38H, H-Ar), 3.07 (bs, 4H, CH$_2$-dppp), 1.70 (s, 2H, CH$_2$-dppp). |          |
| 4    | [Hg(Saln)$_2$(dppb)] | 10.70 (s, 2H, NH); 6.91 – 8.02 (m, 38H, H-Ar), 2.36 (m, 4H, CH$_2$-dppb), 1.57 (m, 4H, CH$_2$-dppb). |          |
| 5    | [Hg(Saln)$_2$(dppf)] | 10.35 (s, 2H, NH); 6.74 – 7.93 (m, 38H, H-Ar), 4.35 (bs, 4H, dppf), 4.59 (bs, 4H, dppf). |          |
| 6    | [Hg(Saln)$_2$(dppmS$_2$)] | 10.61 (s, 2H, NH); 6.99 – 8.01 (m, 38H, Ar-H), 4.59 (t, $^3$J$_{HH}$ = 9.80 Hz, 2H, CH$_2$-dppmS$_2$). |          |
| 7    | [Hg(Saln)$_2$(SPPH)$_2$] | 10.63 (s, 2H, NH); 6.93-7.99 (m, 48H, H-Ar). |          |
4. Conclusions

In summary, we have synthesized an eight new salicylanilide Hg(II) complexes by the reaction of the (HSaln) ligand with mercury acetate to afford complex of the type \([\text{Hg}(\kappa^2-\text{Saln})_2]\). A complexes of the types \([\text{Hg}(\kappa^2-\text{Saln})(\text{diphos})]_2(2-6)\) or \([\text{Hg}(\kappa^2-\text{Saln})(\text{phos})]_2(7,8)\) were prepared by reaction of complex (1) with diphosphine or monophosphine respectively. The prepared complexes have been characterized by CHN elemental analyses, molar conductivity, IR and NMR (\(^1\)H, and \(^{31}\)P) spectroscopy. In complex (1) the (Saln) was bonded as bidentate chelating ligand through the oxygen atoms of the carbonyl and deprotonated hydroxyl group, whereas bonded as monodentate ligand through the oxygen atom of deprotonated hydroxyl group in all other complexes (2-8). The geometry of the complexes (1-8) is a tetrahedral around the mercury (II) ion.

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معقدات جديدة لليكائد الساليسيلاتيليد - الزئبق (II) مع الفوسفينات، تحضير وتشخيص طيفي

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الملخص

خضّر المعقد الجديد ذي الصيغة [Hg(κ²-Sln)₂] ([1]) من تفاعل خلات الزئبق مع ليكائد الساليسيلاتيليد في الايثانول بنسبة مولية (1:2) لينتج dppf, dppb, dppp, dppe, dppm معقدات ذات صيغة [Hg(κ²-Sln)₂(diphos)] (2-6)، أو مع مولين من ثلاثي فينيل فوسفين سمفايد SPPh₃ أو ثلاثي فينيل فوسفين PPh₃ لينتج معقدات ذات صيغة [Hg(κ²-Sln)₂(phos)₂] (7 و8). شُخصت المعقدات المحضرة بواسطة التحليل الكهرومطيافي، الامطياف الرنين النووي المغناطيسي لمبروتون، الفوسفور ومطيافية الاشعة تحت الحمراء، وقد وجد ان ليكائد الساليسيلاتيليد في المعقد (1) يسلك سلوك ليكائد ثنائي السن عن طريق ذرة الأوكسجين عن مجموعة الكاربونيل واوكسجين مجموعة الهيدروكسيل بعد فقدان البروتون، في حين يسلك ليكائد احادي السد عن طريق ذرة أوكسجين مجموعة الهيدروكسيل الفاقد للبروتون في المعقدات (2-8)، لتنتج شكلًا رباعي السطوح حول أيون الزئبق (II).