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Mixed ligand palladium(II) complexes of *N*-hydroxymethylsaccharin (Sac-CH_2OH): synthesis, characterization and biological studies

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Abstract Reaction of Na_2PdCl_4 with two equivalents of *N*-hydroxymethylsaccharin (Sac-CH_2OH) in the presence of NEt_3 afforded trans-[Pd(κ^2-Sac-$CH_2O)_2$]. Further reaction of [Pd(κ^2-Sac-$CH_2O)_2$] with one equivalent of diphosphine (L_2), $Ph_2P(CH_2)_nPPh_2$, ($n = 1$, dppm; 2, dppe and 3, dppp), $Ph_2P(S)(CH_2)P(S)Ph_2$ (dppmS_2) or $Ph_2P(O)(CH_2)_2P(O)Ph_2$ (dppeO_2) afforded mixed ligand complexes [Pd(κ^1-Sac-$CH_2O)_2(L_2)$], while reaction with two equivalents of Ph_3P, Ph_3PO or Ph_3PS (L) gave *trans*-[Pd(κ^1-Sac-$CH_2O)_2(L)_2$]. The *N*-hydroxymethylsaccharinate anion acts as a monodentate ligand, coordinating to the palladium center through the hydroxymethyl oxygen atom. The complexes were characterized by physicochemical and spectroscopic methods. In addition, the free ligand *N*-hydroxymethylsaccharin and some of the complexes were screened in vitro for antibacterial activity.

Introduction

Saccharin (1,2-benzoisothiazol-3(2*H*)-one-1,1-dioxide or o-benzosulfimide, Hsac) is known as a noncaloric artificial sweetener. Its coordination chemistry has been extensively studied over the years [1–14]. Although for many years it was a suspected carcinogen in rats [15, 16], in the 1990s it was removed from the list of potential human carcinogens [17]. Palladium and platinum saccharinate complexes [7–14] have attracted interest primarily because of their biological properties. Complexes of saccharine derivatives have not been well studied; however, there is a recent report on the synthesis of *N*-substituted saccharine derivatives and their biological activity with respect to selective inhibition of human carbonic anhydrase [18].

In continuation of our recent studies with Pd(II) complexes [7, 19–21], herein we describe the preparation of mixed-ligand saccharinate derivative complexes with phosphines as co-ligands. *N*-hydroxymethylsaccharin (Sac-CH_2OH) was readily prepared (Scheme 1) and its reactions with Na_2PdCl_4 and phosphines gave rise to the complexes [Pd(κ^1-Sac-$CH_2O)_2(L)_n$] ($n = 1$ or 2) in high yields. These complexes were characterized by spectroscopic methods. In addition, the phosphine derivative complexes were screened for activity against several bacterial strains and showed some antibacterial effects compared with the parent compound.

Experimental

Materials and methods

All chemicals and solvents used in this work were commercial products and were used without further purification. *N*-hydroxymethylsaccharin was synthesized according to the literature method [22]. IR spectra were recorded in the 4000–200 cm^{-1} range on a Bruker Tensor 28 spectrometer with a Platinum ATR unit. Melting points were measured on an Electrothermal 9300 melting point

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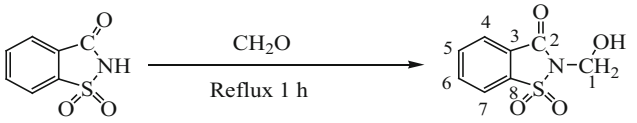


Scheme 1 Preparation of Sac-CH_2OH

apparatus. Elemental analysis was carried out on a CHN analyzer type 1106 Carlo-Erba. The ^{1}H and ^{13}C NMR spectra were recorded on Varian unity 400 and Gemini 200 spectrometers, respectively, with d^6-DMSO as solvent. ^{31}P NMR spectra were recorded on a Gemini 200 spectrometer with d^6-DMSO and $CDCl_3$ as solvents and H_3PO_4 (85 %) as an external reference. The NMR spectra are reported in ppm. The NMR spectra and elemental analysis were carried out at Al-Bayt University-Jordan and Institute fur Anorganische Chemie, Martin-Luther-Universitat, Halle, Germany. *N*-hydroxymethylsaccharin (Sac-CH_2OH) was characterized as follows. White prisms. Anal. Calc. for $C_8H_7NO_4S$; C, 45.1; H, 3.3; N, 6.6, Found: C, 45.1; H, 3.4; N, 6.8 %. IR (KBr): 3290 m υ(O–H); 3093 υ(C–H); 2975 υ(C–H); 1747 υ(C=O); 1595 υ(C=C); 1458 υ(C–N); 1340 $\upsilon_{asy}(SO_2)$; 1184 $\upsilon_{sy}(SO_2)$ cm^{-1}. ^{1}H NMR (d^6-DMSO): δ 8.28 (dd, 1H, H4, ^{3}J(HH) = 7.8 Hz, Ph); 8.12 (dd, 1H, H7, ^{3}J(HH) = 7.8 Hz, Ph); 8.05 (td, 1H, H5, ^{3}J(HH) = 8.8 Hz, ^{4}J(HH) = 1.2 Hz, Ph); 7.99 (td, 1H, ^{3}J(HH) = 8.4 Hz, ^{4}J(HH) = 1.3 Hz, H6); 6.74 (bs, 1H, OH); 5.18 (s, 2H, OCH_2). ^{13}C NMR (d^6-DMSO): δ 161.49 (CO), 140.21 (C3, Ph), 136.09 (C8, Ph), 134.51 (Ph), 129.19 (Ph), 125.09 (Ph), 121.99 (Ph), 68.51 (CH_2). Melting point: 134–136 °C (lit. 135–137) [22]. For antibacterial studies, the test organisms were grown on nutrient agar medium in petri plates [23–26]. Fresh solutions of the compounds were prepared in DMSO and used to soak filter paper disks of 5 mm diameter and 1 mm thickness. The disks were placed on previously seeded plates and then incubated at 37 °C, and the diameter of the inhibition zone around each disk was measured after 24 h (Table 1).

Table 1 A diameter of inhibition zone (mm) of 100 μg/ml of free Sac-CH_2OH and its complexes

Compound	Bacterial species			
	E. coli	*B. subtilis*	*P. aeruginosa*	*S. aureus*
Sac-CH_2OH	23	35	75	>100
1	19	65	20	50
2	07	10	34	35
3	43	27	05	25
6	>100	43	50	20
Ofloxacin	10	05	05	05
Ciprofloxacin	05	05	05	05

Preparation of complex 1

A warm solution of Sac-CH_2OH (0.145 g, 0.68 mmol) in EtOH (10 ml) containing a few drops of Et_3N was added to a solution of Na_2PdCl_4 (0.10 g, 0.34 mmol) in EtOH (15 ml). The mixture was stirred for 15 min at room temperature. The brown-yellow precipitate was filtered off, washed with ethanol and dried under vacuum to afford [Pd(κ^2-Sac-CH_2O)$_2$]·$2H_2O$ (**1**) (Scheme 2). Brown yellow solid. Yield: 0.13 g (68 %). Anal. Calc. for $C_{16}H_{16}N_2O_{10}PdS_2$: C, 33.9; H, 2.8; N, 4.9; Found, C, 34.1; H, 2.9; N, 5.0 %. IR (KBr): 3521 υ(O–H) for H_2O; 3087 υ(=C–H); 2985 υ(C–H); 1673 υ(C=O); 1593 υ(C=C); 1294 $\upsilon_{asy}(SO_2)$: 1174 $\upsilon_{sy}(SO_2)$; 540 υ(Pd–O) cm^{-1}. ^{1}H NMR (d^6-DMSO): δ 7.69 (d, 2H, ^{3}J(HH) = 8.6 Hz, H1); 7.54 (t, 2H, ^{3}J(HH) = 7.9 Hz, H2); 7.30 (d, 2H, ^{3}J(HH) = 8.63 Hz, H4); 6.97 (t, 2H, ^{3}J(HH) = 7.8 Hz, H3); 5.25 (s, 4H, OCH_2). ^{13}C NMR (d^6-DMSO): δ 171.60 (CO), 140.70, 136.11, 133.64, 126.03, 122.89, 61.39 (CH_2). Melting point: 180 °C (decomposes).

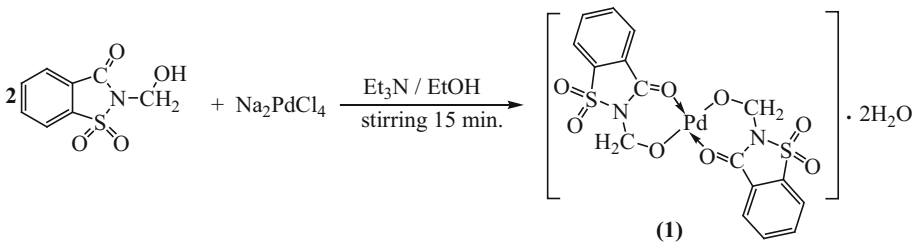
Preparation of complex 2

A solution of dppm (0.131 g, 0.34 mmol) in $CHCl_3$ (10 ml) was added to a suspension of complex **1** (0.145 g, 0.34 mmol) in $CHCl_3$ (15 ml). The resulting yellow solution formed was stirred at 30 °C for 3 h and then left for slow evaporation at room temperature. The yellow precipitate was filtered off, washed with $CHCl_3$ and dried under vacuum (Scheme 3). The related complexes [Pd(Sac-CH_2O)$_2$(dppe)] (**3**), [Pd(Sac-CH_2O)$_2$(dppp)] (**4**), [Pd(Sac-CH_2O)$_2$(dppmS_2)] (**5**) and [Pd(Sac-CH_2O)$_2$(dppeO_2)] (**6**) were prepared and isolated in a similar manner.

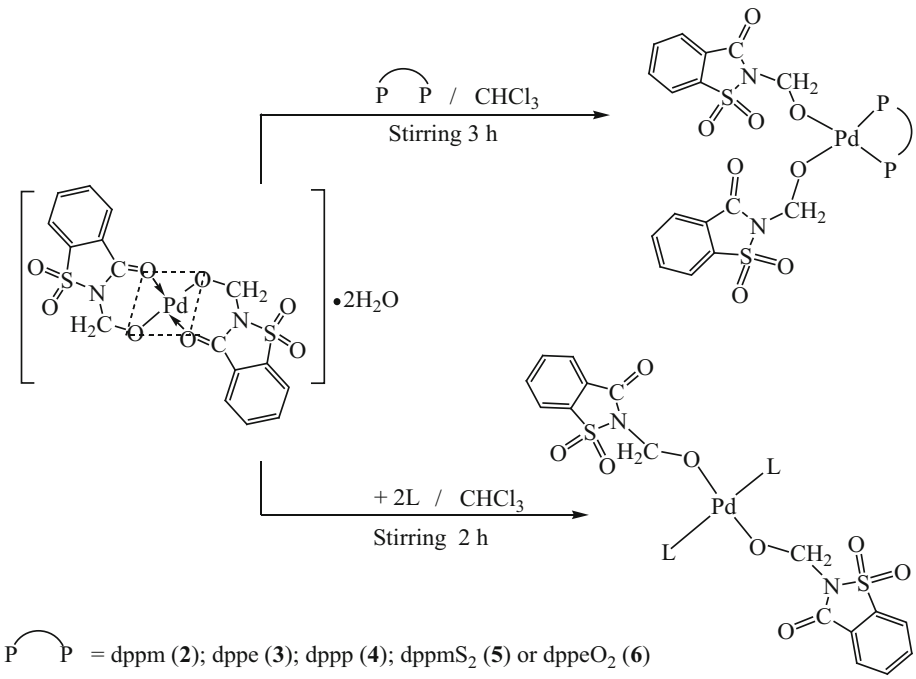
[Pd(Sac-CH_2O)$_2$(dppm)] (**2**): Yellow solid. Yield: 0.236 g (76 %). Anal. Calc. for $C_{41}H_{34}N_2O_8P_2PdS_2$, C, 53.8; H, 3.7; N, 3.1; Found, C, 53.6; H, 3.9; N, 3.0 %. IR (KBr): 3546, 3454 υ(O–H) for H_2O; 3056 υ(=C–H); 2997 υ(C–H); 1695 υ(C=O); 1587 υ(C=C); 1294 $\upsilon_{asy}(SO_2)$; 1164 $\upsilon_{sy}(SO_2)$; 503 υ(P–C); 530 υ(Pd–O) cm^{-1}. ^{1}H NMR (d^6-DMSO): δ 8.46–7.37 (m, 28H, Ar), 5.06 (s, 4H, OCH_2), 2.95 (s, 2H, CH_2). ^{13}C NMR (d^6-DMSO): δ 163.78, 140.70, 136.11, 133.64, 130.58, 126.88, 122.89, 63.76. ^{31}P NMR (d^6-DMSO): δ 29.37. Melting point: 196–199 °C.

[Pd(Sac-CH_2O)$_2$(dppe)] (**3**): Yellow solid. Yield: 84 %. Anal. Calc. for $C_{42}H_{36}N_2O_8P_2PdS_2$, C, 54.3; H, 3.9; N, 3.0; Found, C, 54.4; H, 3.8; N, 3.13 %. IR (KBr): 3064 υ(=C–H); 2929 υ(C–H); 1699 υ(C=O); 1585 υ(C=C); 1292 $\upsilon_{asy}(SO_2)$; 1143 $\upsilon_{sy}(SO_2)$; 507 υ(P–C); 530 υ(Pd–O) cm^{-1}. ^{1}H NMR (d^6-DMSO): δ 7.27–7.66 (m, 28H, Ar), 5.17 (s, 4H, OCH_2), 3.02 (t, 4H, ^{3}J(HH) = 7.9 Hz, CH_2). ^{13}C NMR (d^6-DMSO): δ 161.89, 140.89, 136.11, 132.89,

Scheme 2 Preparation of complex **1**



Scheme 3 Preparation of complexes **2–9**



130.58, 126.93, 122.89, 63.76. ^{31}P NMR (d^6-DMSO): δ 44.46. Melting point: 204–208 °C (decomposes).

[Pd(Sac-CH_2O)$_2$(dppp)] (**4**): Yellow solid. Yield: 80 %. Anal. Calc. for $C_{45}H_{44}N_2O_9P_2PdS_2$, C, 54.6; H, 4.5; N, 2.8; Found, C, 54.3; H, 4.2; N, 3.0 %. IR (KBr): 3083 υ(=C–H); 2987 υ(C–H); 1701 υ(C=O); 1591 υ(C=C); 1302 $\upsilon_{asy}(SO_2)$; 1143 $\upsilon_{sy}(SO_2)$; 480 υ(P–C); 526 υ(Pd–O) cm^{-1}. ^{1}H NMR (d^6-DMSO): δ 8.28–7.96 (m, 28H, Ar); 5.18 (s, 4H, OCH_2); 2.88 (t, 4H, ^3J(HH) = 8.1 Hz, CH_2); 1.90 (b, 2H, CH_2). ^{13}C NMR (d^6-DMSO): δ 164.0, 140.10, 135.36, 132.95, 131.13, 128.40, 122.56, 61.95. ^{31}P NMR (d^6-DMSO): δ 27.67. Melting point: 158–161 °C.

[Pd(Sac-CH_2O)$_2$($dppmS_2$)] (**5**): Yellow solid. Yield: 41 %. Anal. Calc. for $C_{66}H_{56}N_2O_8P_4PdS_6$, C, 55.5; H, 3.9; N, 1.9. Found: C, 55.9; H, 4.2; N, 2.2 %. IR (KBr): 3053 υ(C–H); 2918 υ(C–H); 1703 υ(C=O); 1529 υ(C=C); 1290 $\upsilon_{asy}(SO_2)$; 1126 $\upsilon_{sy}(SO_2)$; 499 υ(P–C); 545 υ(Pd–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.10–8.01 (m, 28H, Ar), 5.20 (bs, 4H, OCH_2), 1.71 (s, 2H, CH_2) ppm. ^{13}C NMR (d^6-DMSO): δ 162.23, 140.47, 136.0, 132.65, 131.07, 126.98, 122.33, 62.13. ^{31}P NMR (d^6-DMSO): δ 24.47. Melting point: 268–272 °C (decomposes).

[Pd(Sac-CH_2O)$_2$($dppeO_2$)] (**6**): Yellow solid. Yield: 81 %. Anal. Calc. for $C_{42}H_{36}N_2O_{10}P_2PdS_2$: C, 52.5; H, 3.8; N, 2.9; Found, C, 52.6; H, 3.6; N, 3.1 %. IR (KBr): 3100 υ(=C–H), 2981 υ(C–H), 1691 υ(C=O), 1587 υ(C=C), 1296 $\upsilon_{asy}(SO_2)$, 1163 $\upsilon_{sy}(SO_2)$, 500 υ(P–C), 526 υ(Pd–O) cm^{-1}. ^{1}H NMR (d^6-DMSO): δ 7.12–7.71 (m, 28H, Ar), 5.04 (s, 4H, OCH_2), 3.08 (t, 4H, ^3J(HH) = 8.0 Hz, CH_2). ^{13}C NMR (d^6-DMSO): δ 162.67, 141.09, 135.89, 132.83, 131.06, 125.87, 123.67, 61.45. ^{31}P NMR (d^6-DMSO): δ 35.48. Melting point: 244–246 °C (decomposes).

Preparation of complex 7

A solution of PPh_3 (0.178 g, 0.68 mmol) in $CHCl_3$ (10 ml) was added to a suspension of complex **1** (0.193 g, 0.34 mmol) in $CHCl_3$ (15 ml) with stirring. The yellow solution so formed was stirred at room temperature for 2 h, then left to evaporate at room temperature. The yellow

precipitate was filtered off, washed with diethyl ether followed by $CHCl_3$ and dried under vacuum (Scheme 3). The complexes $[Pd(Sac\text{-}CH_2O)_2(O{=}PPh_3)_2]$ (**8**) and $[Pd(Sac\text{-}CH_2O)_2(S{=}PPh_3)_2]$ (**9**) were prepared and isolated by similar procedures.

$[Pd(Sac\text{-}CH_2O)_2(PPh_3)_2]$ (**7**): Yellow solid. Yield: 0.32 g (76 %). Anal. Calc. for $C_{52}H_{42}N_2O_8P_2PdS_2$: C, 59.2; H, 4.0; N, 2.6; Found, C, 59.4; H, 4.2; N, 2.4 %. IR (KBr): 3091 υ(=C–H); 2972 υ(C–H); 1692 υ(C=O); 1571 υ(C=C); 1290 $\upsilon_{asy}(SO_2$; 1155 $\upsilon_{sy}(SO_2)$; 522 υ(P–C); 533 υ(Pd–O) cm^{-1}. ^1H NMR (d^6-DMSO): δ 8.28–7.09 (m, 38H, Ar), 5.09 (s, 4H, OCH_2). ^{13}C NMR (d^6-DMSO): δ 163.60, 140.70, 136.11, 132.98, 130.58, 125.76, 122.89, 62.65. ^{31}P NMR (d^6-DMSO): δ 18.05. Melting point: 254–259 °C (decomposes).

$[Pd(Sac\text{-}CH_2O)_2(O{=}PPh_3)_2]$ (**8**): Brown-yellow. Yield: 81 %. Anal. Calc. for $C_{52}H_{42}N_2O_{10}P_2PdS_2$: C, 57.4; H, 3.9; N, 2.6; Found, C, 57.5; H, 3.9; N, 2.7 %. IR (KBr): 3093 υ(C–H); 2933 υ(C–H); 1696 υ(C=O); 1604 υ(C=C); 1288 $\upsilon_{asy}(SO_2)$; 1157 $\upsilon_{sy}(SO_2)$; 522 υ(P–C); 546 υ(Pd–O) cm^{-1}. ^1H NMR (d^6-DMSO): δ 8.06–7.05 (m, 38H, Ar), 5.73 (s, 4H, OCH_2). ^{13}C NMR (d^6-DMSO): δ 163.93, 140.04, 136.49, 132.79, 130.94, 125.64, 121.92, 64.37. ^{31}P NMR (d^6-DMSO): δ 43.23. Melting point: 189–192 °C.

$[Pd(Sac\text{-}CH_2O)_2(S{=}PPh_3)_2]$ (**9**): Dark yellow. Yield: 76 %. Anal. Calc. for $C_{52}H_{42}N_2O_{10}P_2PdS_4$: C, 55.8; H, 3.8; N, 2.5; Found, C, 55.8; H, 3.9; N, 2.7 %. IR (KBr): 3087 υ(C–H); 2873 υ(C–H); 1698 υ(C=O); 1612 υ(C=C); 1292 $\upsilon_{asy}(SO_2)$; 1151 $\upsilon_{sy}(SO_2)$; 503 υ(P–C); 542 υ(Pd–O) cm^{-1}. ^1H NMR (d^6-DMSO): δ 7.97–6.99 (m, 38H, Ar), 5.24 (s, 4H, OCH_2). ^{13}C NMR (d^6-DMSO): δ 163.12, 141.11, 136.52, 132.79, 131.94, 125.68, 121.33, 64.56, 41.17. ^{31}P NMR (d^6-DMSO): δ 17.44. Melting point: 260–262 °C (decomposes).

Results and discussion

In order to prepare the target phosphine derivative complexes, $[Pd(\kappa^1\text{-}Sac\text{-}CH_2O)_2(L)_n]$ ($n = 1, 2$), we first prepared the saccharine derivative complex with palladium(II). Thus, treatment of $Na_2[PdCl_4]$ with two equivalents of *N*-hydroxymethylsaccharin ($Sac\text{-}CH_2OH$) in the presence of NEt_3 afforded *trans*-$[Pd(\kappa^2\text{-}Sac\text{-}CH_2O)_2]$ (**1**) in EtOH (Scheme 2). The parent Pd(II) complex was assigned as the *trans* isomer based primarily on its IR spectrum, which is relatively simple in accordance with the higher symmetry and also with other complexes of the type *trans*-$[Pd(\kappa^1\text{-}Sac\text{-}CH_2O)_2(L)_2]$ (see below). The hydroxymethylsaccharinate anion in complex **1** behaves as a bidentate ligand, coordinating through the carbonyl and CH_2O oxygen atoms. Evidence for this assignment comes from the IR spectrum of complex **1** which displayed υ(C=O) at 1673 cm^{-1}. The reaction of sac derivative complex (**1**) with different diphosphines in an equivalent ratio afforded $[Pd(\kappa^1\text{-}Sac\text{-}CH_2O)_2(L_2)]$ (**2–6**) in 60–85 % yields, as illustrated in Scheme 3. The same reaction with monophosphines gives rise to *trans*-$[Pd(\kappa^1\text{-}Sac\text{-}CH_2O)_2(L)_2]$ (**7–9**) as yellow solids in 70–80 % yields. The $Sac\text{-}CH_2O^-$ in complexes **2–9** behaves as a monodentate ligand coordinated through the oxygen atom of the CH_2O^- group. This was deduced from the high frequency shift of υ(C=O) from 1673 cm^{-1} for complex **1** to 1691–1701 cm^{-1} in the spectra of complexes **2–9**. Complexes **1–9** are stable in DMSO or DMF solutions when kept at room temperature and showed no decomposition over a week as evident from their ^1H NMR spectra. However, they are unstable in hot DMSO or DMF solution, decomposing to black precipitates.

In order to determine the precise coordination sphere, we attempted to grow X-ray quality single crystals of these complexes by dissolving them in DMSO or DMF at room temperature with the addition of a few drops of EtOH or $CHCl_3$. Unfortunately all these attempts were unsuccessful and no crystals suitable for X-ray diffraction studies were obtained.

Spectroscopic and analytical data are in full accordance with the proposed formulations. The ^1H NMR spectra of each complex displayed the expected signals for the saccharinate derivative as well as the phosphine ligands. The single peak observed in their ^{31}P NMR spectra confirmed symmetric coordination around the metal center in these complexes. The *N*-hydroxymethylsaccharinate anion coordinated to the palladium(II) center through hydroxymethyl oxygen in each of these complexes most likely in a square planar geometry.

Antibacterial activities

Antibacterial activities of the free ligand and its complexes were tested in vitro against the bacterial species *Escherichia coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*.

The results of the antibacterial studies are summarized in Table 1. The standard error for the experiment was ± 0.002 μg/ml, and the experiments were repeated three times under similar conditions. DMSO was used as negative control, and ofloxacin and ciprofloxacin were used as positive controls. The results show that the metal chelates are more active than the starting materials and the free ligand, as is frequently the case [26]. The $Sac\text{-}CH_2OH$ ligand shows good activity against the bacterial strain *E. coli* and *B. subtilis*, while all the complexes exhibit excellent in vitro antibacterial activities against both Gram-positive and Gram-negative organisms.

Conclusions

This work has shown that the synthesis of sac derivative complexes of the type $[Pd(Sac\text{-}CH_2O)_2(L)_n]$ containing various phosphine ligands is general and straightforward starting from $Na_2[PdCl_4]$ and readily prepared ligands. Further, the yields of each step are high, reactions can be carried out in air and product isolation is simple. However, crystallization of the synthesized complexes proved to be intractable. The complexes showed some antibacterial activities. Further syntheses of other transition metal complexes with this ligand are in progress.

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