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Synthesis and Spectroscopic Studies of New Palladium(II) Complexes of N-hydroxymethyl Saccharin (Sac-CH_2OH) and Amines or Diaminas Ligands

AHMED S. AL-JANABI[1]*, ADNAN A. AL-DULAIMI[2], HAYFA M. GERGEES[2] and MOHAMMED H. SALEH[2]

[1]Tikrit University/College of Veterinary Medicine–Department of Biochemistry-Tikrit, Iraq.
[2]Department of Chemistry, College of Science, University of Tikrit, Tikrit, Iraq.
* Corresponding author E-mail: dr.ahmed.chem@tu.edu.iq

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ABSTRACT

Treatment of the chelated palladium(II) complex, trans-[Pd(K^2-Sac-$CH_2O)_2$].$2H_2O$ with one mole equivalent of the diammines (L-L), L-L = 2,2'-bipyridine (bipy), ethylene diamine (en), 1,10-phenanthroline (phen), or N,N-dimethyl ethylene diammine (dmen) in EtOH solvent afforded mixed ligand complexes of the type [Pd(K^1-Sac-$CH_2O)_2$(L-L)] in 82-93% yield. While treatment of trans-[Pd(K^2-Sac-$CH_2O)_2$].$2H_2O$ with two mole equivalents of the monoamines (L), L=pyridine (py), 3-methylpyridine (3-mpy) or 3-aminopyridine (3-apy) in EtOH solvent gave trans-[Pd(K^1-Sac-$CH_2O)_2(L)_2$] complexes in 86-89% yield The prepared complexes were characterized by elemental CHN analysis, .conductivity measurements, infrared and ^{1}H nmr spectra.

Keywords: Amine co-ligands, Palladium complexes, Saccharin derivative, Spectroscopic studies.

INTRODUCTION

Saccharin (HSac) is one of the better known and most widely used artificial sweetening agents, its coordination chemistry has attracted considerable interests. The coordination chemistry of saccharinate the deprotonated form of saccharine been extensively studied[1,2]. Sac^- ion can be appeared different coordination modes to metal ions being able to bonded as monodentate mode through the negatively charged N or O atoms of the carbonyl groups. It also has the ability to coordinate as a bidentate or polydentate modes through nitrogen and oxygen donor atoms[1]. The Sac^- complexes with Pd(II) and Pt(II)[3–10], are very important because of their biological properties.

Although coordination chemistry of HSac has been well studied, the chemistry of the HSac derivatives seems to be less explored. Recently, some N-substituted HSac derivatives were synthesized and their biological activity with respect to selective inhibition of human carbonic anhydrase was reported[11]. We expect that complexes of saccharine

derivatives to be interested. We have recently reported the coordination chemistry and biological studies of mixed ligand complexes of Pd(II) Zn(II) and Cd(II) and the coordination chemistry and thermal study of Hg(II) with N-hydroxymethyl saccharinate anion and heterocyclic phosphines or amine as co-ligands[12-15]. As a continuation of our studies on complexes of saccharine derivatives, we reported her, the synthesis and characterization of mixed ligands complexes of Pd(II) with N-hydroxymethyl saccharinate and mono or diammines.

EXPERIMENTAL

Melting points were measured on an electro-thermal 9300 melting point apparatus. CHN element contents were determined using CHN analyzer type 1106 Carlo-Erba. Molar conductivities of freshly prepared $1x10^{-3}$ M of DMSO – complexes solutions were measured at 25°C using Digital conductivity meter. NMR spectra of the compounds were recorded on Gemini 200 spectrometer with DMSO-d_6 as solvent and TMS as an internal reference. IR spectra were recorded on Bruker Tensor 28 spectrometer with a Pt- ATR unit. Na_2PdCl_4, bipyridine (bipy), phenanthroline (phen), ethylenediamine (en), N,N-dimethylethylenediamine (dmen), pyridine (py), 3-methylpyridine (3-mpy) and 3-aminopyridine (3-apy) were supplied and used without purification. N-hydroxymethyl saccharin[16], [Pd(K^2-Sac-CH_2O)$_2$].$2H_2O$ (1)[12] were prepared by literature methods.

Preparation of [Pd(Sac-CH_2O)$_2$(bipy)](2)

To a suspension of [Pd(K^2-Sac-CH_2O)$_2$].$2H_2O$ (1) (0.141 g, 0.250 mmol) in ethanol (15 ml) a hot solution of bipy (0.039 g, 0.250 mmol) in EtOH (15 ml) was added with stirring. The resulting mixture was refluxed for 3 hours. The reddish brown solution was left at room temperature for slow evaporation. The reddish brown solid ppt. was filtered, washed with ethanol and dried. The resulted ppt. recrystallized from DMSO/$CHCl_3$ to afforded reddish brown powder, 0.114g, 84% yield.

The [Pd(K^1-Sac-CH_2O)$_2$(phen)](3); [Pd(K^1-Sac-CH_2O)$_2$(en)](4); and [Pd(K^1-Sac-CH_2O)$_2$(dmen)] (5) complexes were prepared in a similar method in 89, 82 and 93% yield respectively.

Preparation of [Pd(K_1-SacCH_2O)$_2$(py)$_2$] (6)

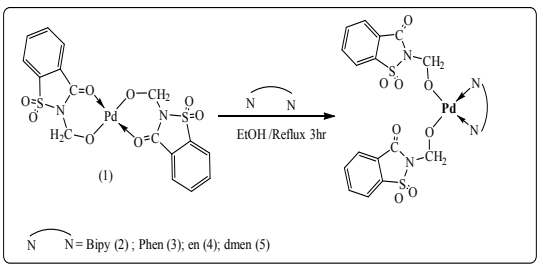
An ethanoic solution of pyridine (py) (0.079 g, 1.000 mmol) (5 ml) was added to a suspension of complex (1) (0.283 g, 0.500 mmol) in EtOH (15 ml). The mixture was stirred for 2 h, then reflux for 3 h, at room temperature. The resulting dark brown solution was filtered and left aside at room temperature for slow evaporate. The brown ppt. produced was filtered, washed with ethanol and dried under vacuum. The resulted ppt. recrystallized from dimethyl sulfoxide with of few drops of ethanol to give brown powder, 0.140g, 86% yield. The [Pd(K^1-Sac-CH_2O)$_2$(3-mpy)$_2$](7) and [Pd(K^1-Sac-CH_2O)$_2$ (3-apy)$_2$](8) complexes were prepared in a similar method, in 89 and 88% yield respectively.

RESULTS AND DISCUSSION.

Synthesis and characterization of [Pd(K^1-Sac-CH_2O)$_2$(L-L)] (2-5) complexes

Treatment of [Pd(K^2-Sac-CH_2O)$_2$].$2H_2O$ (1) with diamine ligands (L-L) {L-L= bipy, phen, en, dmen) in EtOH as a solvent in equivalent molar ratio gave the [Pd(K^1-Sac-CH_2O)$_2$(L-L)] complexes. The resulted complexes are stable at room temperature, and insoluble in common solvents such as ether, ethanol, acetone or chloroform, but soluble in DMSO and DMF. The prepared complexes have been characterization by elemental analysis (Table 1), IR (Table 2) and ^{1}H NMR (Table 3) techniques. The molar conductivity of the complexes in DMSO is low enough to suggest that they are non-electrolytes.

The Sac-CH_2O^- anion ligand behaved as a monodentate towards palladium ion and diamine ligands coordinated as bidentate chelate bonded through the nitrogen atoms to give square planer arrangement around palladium (II) ion. (Scheme 1).



Scheme 1. Preparation of [Pd(K^1-Sac-CH_2O)$_2$(L-L)] (2-5)

IR spectra of the complexes [Pd(*K*^{1}-Sac-$CH_2O)_2$(L-L)](2-5) (Fig.1 for complex 2) showed a band within (1716 - 1726) cm^{-1} range, due to carbonyl group vibration. The frequency of these bands are shifted to higher frequencies from that in [Pd(*K*^{2}-Sac-$CH_2O)_2$].$2H_2O$ which appeared at (1673) cm^{-1} These shifts indicate that (C=O) group is not coordination to palladium (II) ion[12, 17-19].

The stretching vibration of the ν(C=N) .or ν(C-N) of the diamine ligands in the complexes appeared at (1493- 1622) cm^{-1} shifted to lower frequency from that of the non-coordinate ligands. The spectra also showed new bands at (508-528) cm^{-1} and (409-449) attributed to ν(Pd-O) and ν(Pd-N) cm^{-1} respectively [20-22]. Other IR bands for complexes are listed in.Table 2.

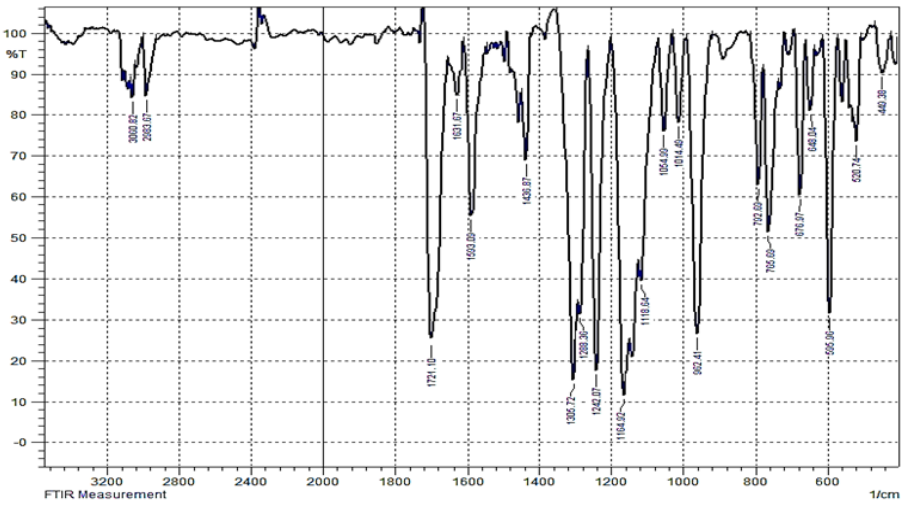


Fig. 1. IR spectrum of [Pd(*K*^{1}-Sac-$CH_2O)_2$(bipy)] (2)

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

Seq.	Compounds	Chemical formula	Color	Yield(%)	m.p.(°C)	ΛM(W^{-1} cm^2 mol^{-1}) 1x10^{-3} M/DMSO	Elemental Analysis Calc.(Found)% C	H	N
1	[Pd(*k*^{2}-Sac-$CH_2O)_2$].$2H_2O$	$C_{16}H_{16}PdN_2O_{10}S_2$	Brown	68	180[a]	9.7	33.9 (34.1)	2.85 (2.9)	4.94 (5.01)
2	[Pd(*k*^{1}-Sac-$CH_2O)_2$(bipy)]	$C_{26}H_{20}PdN_4O_8S_2$	Reddish brown	84	277-280	8	45.46 (45.67)	2.93 (3.16)	8.16 (8.01)
3	[Pd(*k*^{1}-Sac-$CH_2O)_2$(phen)]	$C_{28}H_{20}PdN_4O_8S_2$	Reddish brown	89	289[a]	6.8	47.3 (47.49)	2.84 (2.97)	7.88 (7.98)
4	[Pd(*k*^{1}-Sac-$CH_2O)_2$(en)]	$C_{18}H_{20}PdN_4O_8S_2$	Brown	82	298-303[a]	4.9	36.59 (36.56)	3.41 (3.74)	9.48 (9.81)
5	[Pd(*k*^{1}-Sac-$CH_2O)_2$(dmen)]	$C_{20}H_{24}PdN_4O_8S_2$	Brown	93	249-253	10	38.81 (38.74)	3.91 (4.08)	9.05 (9.18)
6	[Pd(*k*^{1}-Sac-$CH_2O)_2$(py)$_2$]	$C_{26}H_{22}PdN_4O_8S_2$	Brown	86	320[a]	5.7	45.32 (45.67)	3.22 (3.57)	8.13 (8.52)
7	[Pd(*k*^{1}-Sac-$CH_2O)_2$(3-mpy)$_2$]	$C_{28}H_{26}PdN_4O_8S_2$	Brown	89	231-232	3.8	46.9 (45.67)	3.65 (3.9)	7.81 (7.98)
8	[Pd(*k*^{1}-Sac-$CH_2O)_2$(3-apy)$_2$]	$C_{26}H_{24}PdN_6O_8S_2$	Light brown	88	201-205	2.9	43.43 (45.67)	3.36 (3.78)	11.69 (11.88)

a : decomposition temperature

IR spectra of [Pd(*K*^{1}-Sac-$CH_2O)_2$(en)] and [Pd(*K*^{1}-Sac-$CH_2O)_2$(dmen)], display bands at (3178-3287)cm^{-1} assigned to the NH_2 and NH groups of the coordinated ethylenediamine and N,N-dimethyl ethylenediamine shifted to higher frequencies from that of the free ligands[23]. These shifts suggest that both nitrogen atoms of the en or dmen are coordinated[23,24]. The CH_2O protons of

Sac-CH_2O- showed at δH = 5.26-5.36 ppm in the ^{1}H NMR spectra, While the CH_2 protons of the saccharines (Fig. 2) or dmen ligands appeared at δH = 2.65 and 2.91 ppm respectively. The other nmr data are given in Table 3. The other results are in full agreements with the suggested structures.

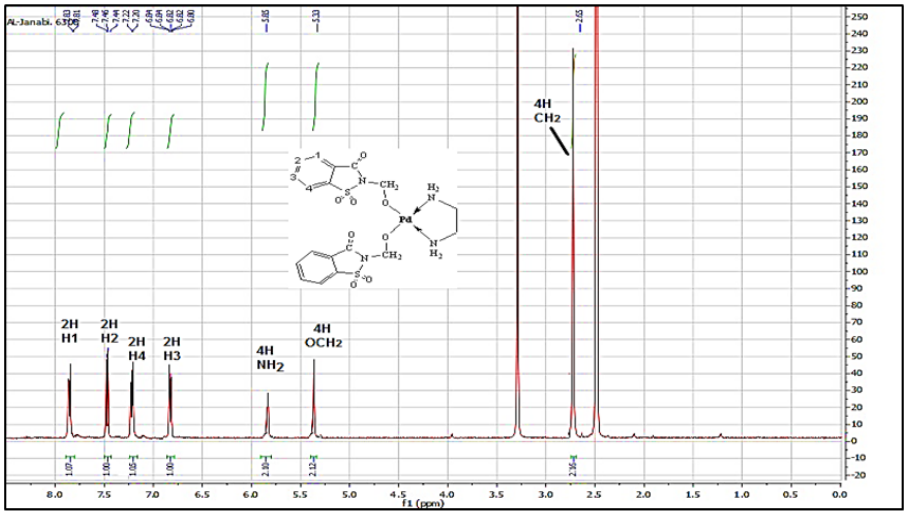


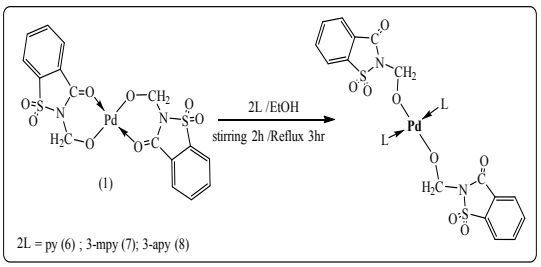
Fig. 2. ^{1}H NMR spectrum of [Pd(K^1-Sac-CH_2O)$_2$(en)] (4) measured in DMSO-d^6

Table 2: Selected IR stretching vibration bands (cm^{-1}) of the prepared complexes (1-8)

Seq.	Complexes	ν(C-H)ar	ν(C-H)aliph	ν(C=O)	ν(C=N) or ν(C-N)	ν(SO_2)asy/sy	ν(Pd-O)	ν(Pd-N)
1	[Pd(κ^2-Sac-CH_2O)$_2$].2H_2O	3087w	2985w	1673s	-	1294s / 1174s	540m	
2	[Pd(κ^1-Sac-CH_2O)$_2$(bipy)]	3060w	2983w	1721s	1593s	1305s / 1164s	520m	449w
3	[Pd(κ^1-Sac-CH_2O)$_2$(phen)]	3084w	2894w	1724s	1622s	1294s / 1160s	512m	436m
4	[Pd(κ^1-Sac-CH_2O)$_2$(en)]	3054w	2988m 2878w	1716s	1512s	1294s / 1174s	528m	409m
5	[Pd(κ^1-Sac-CH_2O)$_2$(dmen)]	3080w	2924w 2999m	1726s	1498s	1294s / 1174s	508m	437m
6	[Pd(κ^1-Sac-CH_2O)$_2$(py)$_2$]	3064w	2927w	1721s	1585s	1292s / 1147s	476m	441m
7	[Pd(κ^1-Sac-CH_2O)$_2$(3-mpy)$_2$]	3058w	2867m 2828w	1730s	1608s	1288s / 1161s	500m	438m
8	[Pd(κ^1-Sac-CH_2O)$_2$(3-apy)$_2$]	3058w	2860w	1728s	1596s	1284s / 1160s	462m	418m

Synthesis and characterization of trans-[Pd(K^1-Sac-CH_2O)$_2$(L)$_2$] (6-8) complexes

These complexes were obtained by refluxing two moles of amine (L: Py, 3-mpy, 3-apy) in EtOH with one mole of [Pd(K^2-Sac-CH_2O)$_2$].2H_2O (1) in EtOH (scheme 2). The synthesized complexes were recrystallized from DMF to give brown powder. All complexes are stable toward air and moisture, and obtained in high yields (over 80%). They are soluble in DMSO and DMF partially soluble in warm $CHCl_3$ or CH_2Cl_2. The complexes have been investigated by CHN analysis, ^{1}H NMR, IR. techniques and molar conductivity measurements. The Amine and Sac-CH_2O^- ligands bonded as bidentate ligands with Pd(II) through the nitrogen of heterocyclic ring in amine ligand and oxygen atom of methoxy group in Sac-CH_2OH ligand respectively, to give square planner complexes.



Scheme 2. Preparation of trans-[Pd(K^1-Sac-CH_2O)$_2$(L)$_2$] (6-8)

In IR spectra of trans-[Pd(K^1-Sac-CH_2O)$_2$(L)$_2$] complexes (6-8) (Fig. 3), the ν(C=N) or ν(C-N) bands of amine ligands (py, 3-mpy, 3-apy) appeared at (1587- 1608) cm^{-1}, this shifted to a lower from

uncoordination ligand. The spectra also showed new bands at (489-532) cm^{-1} and (418-441)cm^{-1} which due to ν(Pd-O) and ν(Pd-N) respectively[12, 17-19], other IR bands of the two complexes are listed in Table2.

IR spectrum of trans-[Pd(K^1-Sac-CH_2O)$_2$ (3-apy)$_2$](8) displayed two bands at 3288 and 3182 cm^{-1} for the asymmetric and symmetric stretching frequencies of NH_2 group. These bands shifted slightly to a higher wave number relative to that in the free ligand. Referring a non-coordinated of the NH_2 group[25,26].

The ^{1}H NMR spectra of complexes(6-8) (Fig. 4 for complex 6) displayed the CH_2O protons of the Sac-CH_2O- at δH = 5.26-5.36 ppm, the other nmr data complexes 6-8 are given in Table 3.

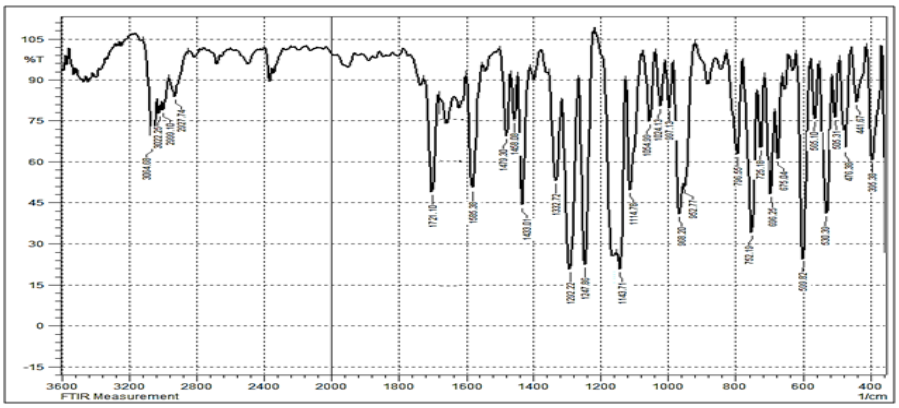
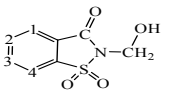


Fig. 3. IR spectrum of trans-[Pd(K^1-Sac-CH_2O)$_2$(Py)$_2$] (6)

Table 3 : ^{1}H NMR data, chemical shifts (δppm) and coupling constants (Hz) for the prepared complexes 1-8 measured in DMSO-d^6



Seq.	Complexes	δH * (ppm)
1	[Pd(k^2-Sac-CH_2O)$_2$].2H_2O	7.69 (d, 2H, $^3J_{HH}$ = 8.60 Hz, H1); 7.54 (t, 2H, $^3J_{HH}$ = 7.90 Hz, H2); 7.30 (d, 2H, ^{3}JHH = 8.63 Hz,H4); 6.97 (t, 2H, $^3J_{HH}$ = 7.80 Hz, H3); 5.25 (s, 4H, OCH_2)
2	[Pd(k^1-Sac-CH_2O)$_2$(Bipy)]	8.78 (d, 2H, $^3J_{HH}$ = 7.98 Hz, H-Bipy); 8.52 (d, 2H, $^3J_{HH}$ = 8.00 Hz, H-Bipy); 8.22-7.80 (m, 4H, H-Bipy); 7.68 (d, 2H, ^{3}JHH = 7.84 Hz, H1); 7.44 (t, 2H, $^3J_{HH}$ = 7.68 Hz, H2); 7.18 (d, 2H, $^3J_{HH}$ = 7.80 Hz,H4); 6.84 (t, 2H, $^3J_{HH}$ = 7.58 Hz, H3); 5.36 (s, 4H, OCH_2)
3	[Pd(k^1-Sac-CH_2O)$_2$(Phen)]	9.12 (d, 2H, $^3J_{HH}$ = 7.88 Hz, H10); 8.56 (dd, 2H, $^3J_{HH}$ = 7.68 Hz, H8); 8.04 (s, 2H, NH); 7.83 (dd, 2H, $^3J_{HH}$ = 7.82 Hz, H9); 7.49 (t, 2H, $^3J_{HH}$ = 7.64 Hz, H11); 7.25 (t, 4H, $^3J_{HH}$ = 6.54 Hz, H5.7); 7.02 (t, 4H, $^3J_{HH}$ = 6.54 Hz, H5.7); 7.28 (d, 2H, $^3J_{HH}$ = 7.84 Hz,H4); 7.04 (t, 2H, $^3J_{HH}$ = 8.01 Hz, H3); 5.32 (s, 4H, OCH_2)
4	[Pd(k^1-Sac-CH_2O)$_2$(en)]	7.82(d, 2H, $^3J_{HH}$ = 7.88 Hz, H1); 7.46 (dd, 2H, $^3J_{HH}$ = 7.48 Hz, H2); 7.21 (d, 2H, $^3J_{HH}$ = 7.62 Hz, H4); 6.84 (dd, 2H, $^3J_{HH}$ = 7.50 Hz, H3); 5.85 (s, 4H, NH_2); 5.33 (s, 4H, OCH_2); 2.65 (s, 4H, CH_2-en)
5	[Pd(k^1-Sac-CH_2O)$_2$(dmen)]	7.76 (d, 2H, $^3J_{HH}$ = 8.02 Hz, H1); 7.50 (t, 2H, $^3J_{HH}$ = 7.56 Hz, H2); 7.38 (d, 2H, 3JHH = 8.00 Hz,H4); 7.10 (t, 2H, $^3J_{HH}$ = 7.9 Hz, H3); 5.36 (s, 4H, OCH_2); 4.94 (s, 2H, dmen-NH); 2.91(s, 4H, CH_2-dmen); 2.60(s, 6H, CH_3-dmen).
6	[Pd(k^1-Sac-CH_2O)$_2$(py)$_2$]	9.08 (dd, 2H, $^3J_{HH}$ = 7.56 Hz, H-Py); 8.54 (dd, 4H, $^3J_{HH}$ = 8.00 Hz, H-Py); 8.21 (d, 4H, $^3J_{HH}$ = 7.90 Hz, H-Py); 7.81 (d, 2H, $^3J_{HH}$ = 8.10 Hz, H1); 7.39 (d, 2H, $^3J_{HH}$ = 7.92 Hz, H2); 7.20 (d, 2H, $^3J_{HH}$ = 7.88 Hz,H4); 6.94 (t, 2H, $^3J_{HH}$ = 8.00 Hz, H3); 5.26 (s, 4H, OCH_2)
7	[Pd(k^1-Sac-CH_2O)$_2$(3-mpy)$_2$]	8.94 (d, 2H, $^3J_{HH}$ = 7.56 Hz, H-mPy); 8.74 (bs, 2H, H-mPy); 8.40 (d, 4H, $^3J_{HH}$ = 7.88 Hz, H-mPy); 8.01 (dd, 4H, $^3J_{HH}$ = 7.90 Hz, H-mPy); 7.78 (d, 2H, $^3J_{HH}$ = 8.00 Hz, H1); 7.42 (d, 2H, 3JHH = 7.89 Hz, H2); 7.28 (d, 2H, $^3J_{HH}$ = 7.90 Hz,H4); 7.02 (t, 2H, $^3J_{HH}$ = 7.90 Hz, H3); 5.36 (s, 4H, OCH_2); 2.75(s, 6H, CH_3-mPy).
8	[Pd(k^1-Sac-CH_2O)$_2$(3-apy)$_2$]	δ 8.82 (t, 2H, H-apy); 8.42-8.10(m, 6H, H-apy); 7.78 (d, 2H, $^3J_{HH}$ = 7.40 Hz, H1); 7.45 (d, 2H, $^3J_{HH}$ = 7.38 Hz, H2); 7.18 (d, 2H, $^3J_{HH}$ = 7.50 Hz, H4); 7.02 (d, 2H, $^3J_{HH}$ = 7.45 Hz, H3); 6.02 (s, 4H, NH_2); 5.26 (s, 4H, OCH_2).

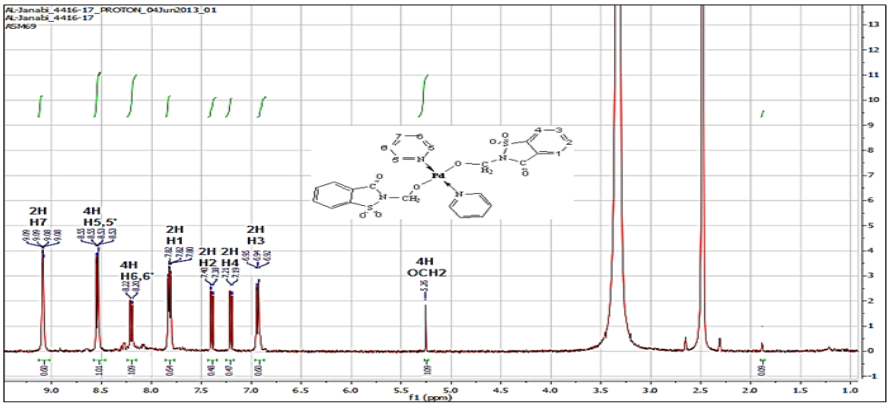


Fig. 4. ^{1}H NMR spectrum of trans-[Pd(K^1-Sac-CH_2O)$_2$(Py)$_2$] (6) measured in DMSO-d^6

CONCLUSION

An eight mononuclear palladium(II) complexes were synthesized and investigated by infrared spectroscopy, elemental analysis, molar conductivity, and proton nuclear magnetic resonance. In trans-[Pd(K_1-Sac-CH_2O)$_2$(L)$_2$], the Pd(II) ion was coordinated with two N-hydroxymethyl saccharinate (Sac-CH_2O^-) ligands through the oxygen atom and two monoamine ligands (L) through the nitrogen atom of heterocyclic ring in the trans configuration. While in [Pd(K^1-Sac-CH_2O)$_2$(L-L)], the (L-L) ligand coordinated with Pd(II) ion as bidentate fashion through the nitrogen atoms, whereas the (Sac-CH_2O^-) ligand coordinate as monodentate fashion through the negatively charged oxygen atom in the cis configuration.

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