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Synthesis and Characterization of Mercury(II) Complexes Containing Mixed Ligands of Mono or Diphosphines and Saccharinate

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ABSTRACT

Tetrahedral mercury(II) complexes of the types [HgCl(sac)$(PPh_3)_2$], [HgCl(sac)(diphos)], [Hg$(sac)_2(PPh_3)_2$] or [Hg$(sac)_2$(diphos)] and octahedral complexes of the type [Hg$(sac)_2(dppe)_2$] or [Hg$(sac)_2(dppp)_2$] {diphos = $Ph_2P(CH_2)nPPh_2$; n=1, dppm; n=2, dppe; n=3, dppp; n=4,dppb} were prepared and characterized by molar conductance, elemental analysis, infrared spectra, ^1H and ^{31}P-{^1H} nmr data.

Key words : Mercury, Saccharinate, Diphosphine.

INTRODUCTION

Saccharin{o-sulfobenzimide; 1,2-benzothiazol-3(2H)-one-1,1-dioxide; Hsac}, most widely used as an artificial sweetening agent Interaction of saccharin. with different biologically relevant cations attracted great interest due to the suspected carcinogenicity of this compound [1-3] which was definitively ruled out in 2001[3-4]. Saccharin ligand has three potential donor sites, it is not expected to use all three towards the same metal because of geometrical constraints. It is therefore likely to acts as a monodentate or a bidentate. metal complexes of this ligand with transition and non transition metals have been studied extensively these have been comprehensively revied[5] and a large number of papers published every year in this field. Saccharinate interacts with some heavy non.-transition metal cations such as Cd(II) and Hg(II) to yield of [Cd$(sac)_2(H_2O)_2$].$2H_2O$.[6] and [Hg$(sac)_2$][7] respectively. Mixed ligands Hg(II) complexes containing saccharinato and nitrogen donor ligands have been reported[8-14]. However mixed ligand complexes of Hg(II) with saccharin and mono or diphosphine seems to be unexplored although such mixed ligand complexes have been reported for some other transition metals[15-17] We expect that mixed ligands complexes of tertiary phosphines and saccharin to be an important class of complexes and exhibit synergic effect attributed to the mixed ligands.

In the present paper we report the synthesis and characterization of some mercury(II) complexes containing mixed ligands, tertiary, mono or diphosphines and saccharin.

EXPERIMENTAL

General

The experimental techniques were the same as those used in our recent paper from this laboratory[18.]

Starting materials

The compounds $HgCl_2$, $Hg(OAc)_2$, dppm, dppe, dppp, dppb, PPh_3 and Nasac were commercial products and were used as supplied. The compounds [HgCl(sac)] and $[Hg(sac)_2]$ were prepared according to literature methods[19,20].

Preparation of complexes (1) – (12).

$[HgCl(Sac)(dppm)]_2$ (1)

A solution of dppm (0.07g, 1.9 mmol.) in warm EtOH (7ml) was added to a suspension of [Hg(sac)Cl] (0.08g, 1.9 mmol.) in hot EtOH (10ml). The mixture was stirred at room temperature for 1h. The pale white solid thus formed was filtered off washed with EtOH, dried under vacuum (yield 67%).The following complexes were prepared and isolated by a similar method; (**2**),(**3**) and (**4**).

$[Hg(sac)_2(dppm)]$ (5)

A solution of dppm (0.05g, 0.1 mmol.) in warm EtOH (7ml) was added to a suspension of $[Hg(sac)_2]$ (0.08g, 0.1 mmol.) in hot EtOH (7ml). The resulting clear solution was filtered off and evaporated. The pale white solid thus formed was filtered off washed with EtOH, dried under vacuum and recrystalized from DMSO, (yield 95%)

$[Hg(sac)_2(dppe)]$ (6)

A solution of dppe (0.07g, 0.18 mmol.) in warm EtOH (7ml) was added to a suspension of $[Hg(sac)_2]$ (0.1g, 0.18 mmol.) in hot EtOH (10ml). The mixture was stirred at room temperature for 1h. The pale white solid thus formed was filtered off washed with EtOH, dried under vacuum (yield 66%). The following complexes were prepared and isolated by a similar method; (7) and (8).

$[Hg(sac)_2(dppe)_2]$ (9)

A solution of dppe (0.079g, 0.17 mmol.) in warm EtOH (10ml) was added to a suspension of $[Hg(sac)_2]$ (0.059g, 0.088 mmol.) in hot EtOH (10ml). The resulting clear solution was filtered off and evaporated to near dryness. n-Hexane (10ml) was added, The pale white solid thus formed was filtered off washed with EtOH, dried under vacuum (yield 89%). The following complexes were prepared and isolated by a similar method; (**10**), (**11**) and (**12**).

RESULTS AND DISCUSSION

Synthesis of complexes

It was reported previously [19] that reaction of $HgCl_2$ with sodium saccharinate in aqueous medium gives [[HgCl(sac)]. Single crystal X-ray diffraction showed that this complex is linear with N-Hg-Cl bond angle 177.6 (3)^{o}. We have previously reported [18] that two coordinate linear mercury(II) complexes may permit for coordination number to be extended to four or may be six. Treatment of the linear mercury(II) complex [HgCl(sac)] with one mole proportion of the diphosphines $Ph_2P(CH)_nPPh_2$ (n=1-4) or two mole proportion of PPh_3 gave tetrahedral complexes of the type $[HgCl(sac)(\mu\text{-}Ph_2PCH_2PPh_2)]_2$(1) or the $[HgCl(sac)\ \{Ph_2P(CH)_nPPh_2\}]$ (n=2,3 or 4) (2), (3), (4), or the $[HgCl(sac)\ \{PPh_3\}_2]$ (11).

Treatment of the linear mercury(II) complex $[Hg(sac)_2]$ [20] with one mole proportion of the diphosphines $Ph_2P(CH)_nPPh_2$ (n=1,2,3 or 4) or two moles proportion of PPh_3 gave tetrahedral complexes of the type $[Hg(sac)_2(diphos)]$ (5), (6), (7), (8), or $[Hg(sac)_2\{PPh_3\}_2]$(12). However treatment with two moles of the diphosphine gave octahedral complexes of the type $[Hg(sac)_2(dppe)_2]$(**9**) or $[Hg(sac)_2(dppp)_2]$(**10**).

Characterization of complexes

The prepared complexes were characterized by elemental analysis, i.r. spectra, conductivity measurements and some of then by $^{31}P\text{-}\{^1H\}$ and ^1H nmr spectra and their data are listed in tables 1-3. The molar conductivity of the complexes in DMF, CH_3OH, $CHCl_3$, DMSO or CH_2Cl_2 is low enough to suggest that they one non-electrolytes[21].

Nuclear magnetic resonance

The $^{31}P\text{-}\{^1H\}$ and ^1H nmr data of some of the prepared complexes are given in Table 3. The $^{31}P\text{-}\{^1H\}$ nmr spectrum of $[HgCl(Sac)(dppm)]_2$(**1**) showed a singlet at dP=23.59ppm with $^2J(^{199}Hg\text{-}^{31}P)$=5166Hz. The positive dP value indicates that dppm behaves as a bidentate bridging[15,22-24]. This

Table 1: Color, Yield, Elemental analyses and conductivity of complexes (1) - (12)

Seq	Complexes	Color	Yield	Found(cal.)%			$(Ohm^{-1}.cm^2$ $.mol^{-1})$ Λ			
			%	N	H	C	$CHCl_3$	CH_3OH	CH_2Cl_2	DMSO
1	$[HgCl(sac)(dppm)]_2$	White	67	2.4 (2.1)	3.7 (3.9)	43.0 (42.7)	-	-	-	5.9
2	[HgCl(sac)(dppe)]	White	60	1.4 (1.5)	5.6 (5.7)	53.8 (53.6)	-	-	2.8	-
3	[HgCl(sac)(dppp)]	White	80	2.8 (2.9)	3.4 (3.4)	48.0 (48.1)	-	-	3.1	-
4	[HgCl(sac)(dppb)]	White	95	3.2 (3.1)	4.5 (4.5)	48.2 (48.5)	-	-	1.9	-
5	$[Hg(sac)_2(dppm)]$	White	95	1.6 (1.6)	4.6 (4.4)	51.1 (50.8)	-	-	-	2.3
6	$[Hg(sac)_2(dppe)]$	White	66	1.7 (1.6)	4.4 (4.3)	51.0 (50.9)	-	-	-	4.3
7	$[Hg(sac)_2(dppp)]$	White	69	2.6 (2.5)	5.3 (5.3)	54.9 (54.6)	-	0.9	-	-
8	$[Hg(sac)_2$ (dppb)]	White	76	2.9 (2.6)	4.6 (4.6)	53.4 (53.1)	2.1	-	-	
9	$[Hg(sac)_2(dppe)_2]$	White	89	2.0 (2.2)	4.8 (4.8)	57.0 (57.1)	-	1.4	-	-
10	$[Hg(sac)_2(dppp)_2]$	White	89	2.2 (1.9)	5.0 (4.8)	60.2 (60.1)	-	2.4	-	-
11	$[Hg(sac)Cl(PPh_3)_2]$	White	95	3.0 (2.7)	4.6 (4.4)	52.7 (52.6)	3.2	-	-	-
12	$[Hg(sac)_2$ $(PPh_3)_2]$	White	89	2.3 (2.3)	4.5 (4.7)	58.1 (58.2)	-	2.1	-	-

has been supported by the ^1H – $\{^{31}P\}$ nmr spectrum which showed a singlet at dH=3.3ppm assigned for the methylene protons of the bridging dppm[25]. The large $^2J(^{199}Hg-^{31}P)$ which is 5166Hz indicated a tetrahedral geometry around mercury[26-29]. The $^{31}P-\{^1H\}$ nmr spectra of the other tetrahedral complexes (**2**), (**6**) and (**7**) each showed a singlet at dP=31.12, 45.00 and 38.56ppm respectively. Complex(**7**) showed $^2J(^{199}Hg-^{31}P)$=5519Hz which suggest four coordinate tetrahedral arrangement around mercury. The $^{31}P-\{^1H\}$ nmr spectra for $[Hg(sac)_2(dppe)_2]$(**9**) and $[Hg(sac)_2(dppp)_2]$**(10**) showed a singlet each at dP=21.96 and 15ppm respectively. The $^2J(^{199}Hg-^{31}P)$ values for these two complexes were low 2195 and 2031Hz respectively which suggest a six coordinate environment around mercury[26-28] .

On the basis of the above nmr data and other identification data given in Tables 1 and 2, the structures shown in Fig. 1 have been suggested

Infrared Spectra

Selected infrared spectroscopic data of the prepared complexes (**1**)–(**12**) are listed in Table 2. All complexes display a sharp strong bands between (1620-1697cm^{-1}) attributed to the u(C=O) of the saccharin ligand coordinated as monodentate though the nitrogen atom[29,30]. Two strong bonds at around (1240-1294) and (1147-

Table 2 : I.R. spectra^a data cm^{-1} of the ligands and complexes (1) – (12)

Seq.	Complexes	υ (C-H)		υ (CO)	υ (CC)	υ (CN)	(CNS)		(SO$_2$)		υ(P-Hg)	υ(P-C)
		Alp.	Ar.				υ$_{as}$	υ$_s$	υ$_{as}$	υ$_s$		
	[Nasac]		3099$_w$ 3072$_w$	1643$_{vs}$	1585$_m$	1450$_m$	966$_s$	1336$_m$	1275$_s$ 1257$_v$	1145$_v$ 1126$_s$		
	[HgCl(sac)]		3078$_w$	1697$_{vs}$ 1635$_{vs}$	1583$_m$	1456$_m$	968$_s$	1338$_m$	1286$_{vs}$ 1251$_{vs}$	1153$_{vs}$		
	[[Hg(sac)$_2$]			1645$_m$	1577$_m$	1413$_m$	960$_s$	1342$_s$	1257$_s$	1153$_m$		
1	[HgCl(sac)(dppm)]$_2$	2924$_w$ 2864$_w$	3051$_w$	1620$_s$	1575$_m$	1430$_s$	945$_m$	1330$_m$	1253s	1147$_{vs}$	335$_{vs}$	513$_m$
2	[HgCl(sac)(dppe)]	2906$_w$	3057$_w$	1634$_s$	1581$_m$	1433$_m$	947$_s$	1340$_m$	1294$_{vs}$ 1247$_m$	1155$_{vs}$	350$_{vs}$	515$_m$
3	[HgCl(sac)(dppp)]	2935$_w$	3055$_w$	1641$_s$	1570$_m$	1430$_s$	951$_s$	1340$_w$	1286$_s$ 1250$_s$	1149$_{vs}$	335$_{vs}$	519$_m$
4	[HgCl(sac)(dppb)]	2935$_w$	3055$_w$	1686$_s$ 1645$_s$	1575$_m$	1438$_m$	957$_s$	1330$_w$	1290v$_s$ 1246$_s$	1151v$_s$	330$_{vs}$	519$_m$
5	[Hg(sac)$_2$(dppm)]	2926$_w$ 2866$_w$	3059$_w$	1645$_{vs}$	1568$_s$	1444$_m$	950$_s$	1334$_m$	1290v$_s$ 1240$_s$	1151$_{vs}$	335$_{vs}$	532$_m$
6	[Hg(sac)$_2$(dppe)]	2964$_w$ 2916$_w$	3059$_w$	1662$_{vs}$	1581$_m$ 1564$_m$	1442$_m$	954$_{vs}$	1330$_m$	1290$_{vs}$ 1244$_s$	1159$_{vs}$	338$_{vs}$	522$_m$
7	[Hg(sac)$_2$(dppp)]	2914$_w$	3059$_w$	1643$_s$	1568$_s$	1442$_m$	951$_s$	1330$_m$	1288$_s$ 1247$_s$	1149$_{vs}$	335$_{vs}$	524$_m$
8	[Hg(sac)$_2$(dppb)]	2926$_w$ 2868$_w$	3059$_w$	1645$_s$	1572$_s$	1425$_m$	953$_s$	1336$_m$	1288$_s$ 1257$_s$	1151$_{vs}$	335$_{vs}$	532$_m$
9	[Hg(sac)$_2$(dppe)$_2$]	2962$_w$ 2906$_w$	3057$_w$	1639$_s$	1577$_m$	1431$_m$	951$_{vs}$	1325$_m$	1286$_{vs}$ 1247$_s$	1147$_{vs}$	338$_{vs}$	522$_m$
10	[Hg(sac)$_2$(dppp)$_2$]	2922$_w$	3057$_w$	1635$_{vs}$	1577$_s$	1433$_m$	949$_s$	1330$_m$	1278$_s$ 1253$_s$	1147$_{vs}$	335$_{vs}$	524$_m$
11	[Hg(sac)Cl(PPh$_3$)$_2$]	-	3056$_W$	1661$_s$	1585$_w$	1433$_s$	951$_s$	1330$_w$	1292$_{vs}$ 1240$_s$	1153v$_s$	332$_{vs}$	511$_s$
12	[Hg(sac)$_2$(PPh$_3$)$_2$]		3056$_W$	1649$_m$	1570$_m$	1431$_m$	953$_s$	1330$_w$	1290$_s$	1151$_{vs}$ 1252$_s$	352$_{vs}$	513$_s$

s= strong, vs = very strong, m= medium , w = weak, a

Table 3: The ^{1}H and ^{31}P-{^{1}H} n.m.r. data^a of the prepared complexes.

Complexes	Seq.	δP	δCH_2	$^2J(^{199}Hg-^{31}P)$	δPh.P.	Solvent
$[HgCl(sac)\ (dppm)]_2$	1	23.59	3.3	5166	7.37-7.88	DMSO
[HgCl(sac) (dppe)]	2	31.12	3.27	-	7.38-7.84	DMSO
$[Hg(sac)_2(dppe)]$	6	45.00	-	-	-	DMSO
$[Hg(sac)_2(dppp)]$	7	38.56	2.13-3.1	5519	7.27-7.38	CD_3OD
$[Hg(sac)_2(dppe)_2]$	9	21.96	3.12	2195	7.16-7.75	CD_3OD
$[Hg(sac)_2(dppp)_2]$	10	15.0	1.378-2.994	2031	7.355-7.67	CD_3OD

^{a}**δ** in ppm, J in Hz

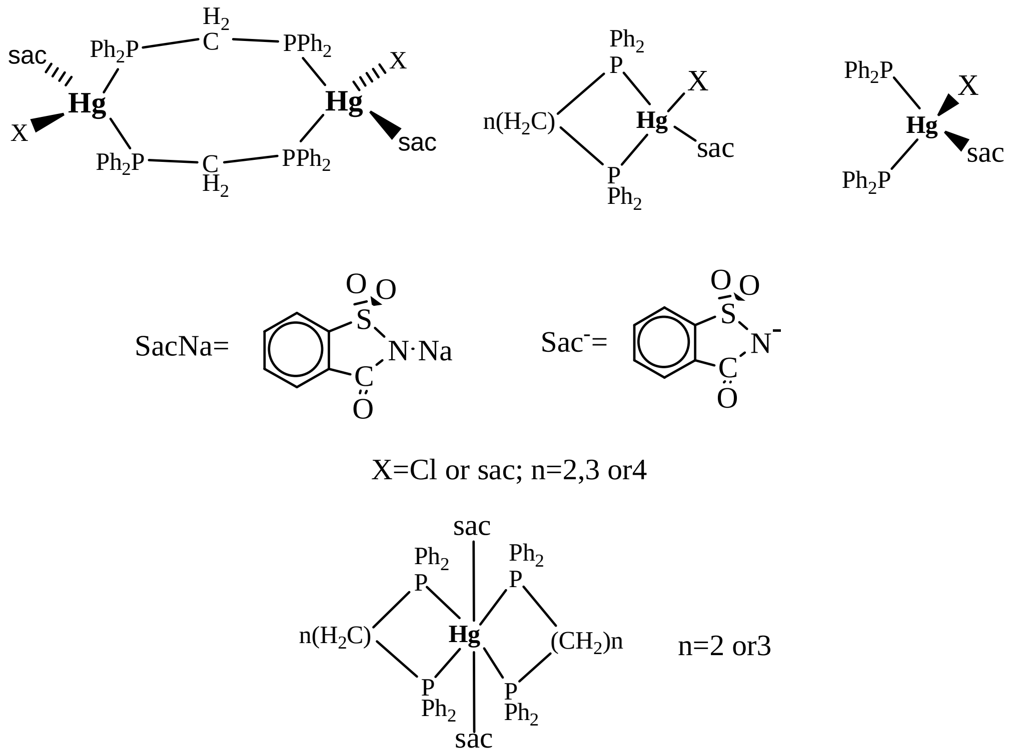

Fig 1. Suggested structures for the prepared mercury(II) complexes Infrared spectra

1153cm^{-1}) are characteristic for the u_{as} SO_2 and u_s SO_2 modes of sac, respectively. Whereas the bands at ca. (1325-1342) and (949-968cm^{-1}) are assigned to the symmetric and asymmetric stretching of the CNS moiety in the sac ion. Additional bands between 332-352cm^{-1} assigned to (P-C).The (C-H) aliphatic appeared at ca. 2906-2935cm^{-1} while the (C-H) aromatic appeared at ca. 3051-3059cm^{-1}.

CONCLUSION

In summery reaction of the linear mercury(II) complex [HgCl(sac)] with mono or diphosphine resulted in the formation of tetrahedral complexes of the type [HgCl(sac)(diphos)]. Reaction of $[Hg(sac)_2]$ with one mole equivalent of diphos. gave tetrahedral complexes of the type

$[Hg(sac)_2(diphos)]$ while reaction with two mole equivalent gave octahedral complexes of the type $[Hg(sac)_2(diphos)_2]$.

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