



Synthesis, characterization and thermal studies of mixed ligand mercury(II) complexes of N-hydroxymethylsaccharin (Sac-CH₂OH) and phosphine or heterocyclic amine co-ligands

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Available online at: www.isca.in, www.isca.me

Received 1st May 2017, revised 5th September 2017, accepted 15th October 2017

Abstract

Reaction of mercury(II) acetate $Hg(Ac)_2$ with two equivalents of N-hydroxymethylsaccharin (Sac-CH₂OH) in the presence of NEt_3 afforded the presumably tetrahedral complex $[Hg(K^2-Sac-CH_2O)_2]$ (1). Reaction of (1) with one equivalent of the bidentate ligands (L-L); $Ph_2P(CH_2)_nPPh_2$, ($n=1$ dppm; 2 dppe; 3 dppp; 4 dppb), $Ph_2P(S)(CH_2)P(S)Ph_2$ (dppmS₂) $Ph_2P(O)CH_2CH_2P(O)Ph_2$ (dppeO₂), bipyridine (bipy) and phenanthroline (phen) afforded tetrahedral complexes of the type $[Hg(K^1-Sac-CH_2O)_2(L-L)]$. The reaction with two equivalents of the monodentate ligands (L); Ph_3P , Ph_3PO , Ph_3PS or pyridine (py) gave $[Hg(K^1-Sac-CH_2O)_2L_2]$. The N-hydroxymethylsaccharinate anion acts as a monodentate ligand to the mercury center through the hydroxymethyl oxygen atom. The complexes were characterized by physico-chemical and spectroscopic methods. The thermal decomposition of six of the prepared complexes were studied using thermogravimetry (TG) and differential thermal analysis (DTA). $[Hg(K^1-Sac-CH_2O)_2(bipy)]$ showed a higher thermal stability.

Keywords: Hg N-hydroxymethylsaccharin, Thermal analysis, Synthesis, NMR, FTIR.

Introduction

There has been a significant interest in the chemistry of metal-bounded saccharinate (sac) ligand over the past two decades since it shows a wide range of metal bonding modes and is potentially useful co-ligand in biological studies.¹ Saccharinate shows a variety of coordination modes to metal centers being able to bind in a monodentate fashion through either the negatively charged nitrogen atom or an oxygen atom of either carbonyl or sulfonyl groups. It also has the ability to bind in a bidentate or even polydentate fashion with the participation of the N- and O-donor atoms.¹

Saccharinate binds readily to the first row divalent metal ions spanning through its deprotonated nitrogen atom²⁻⁸ and can also coordinate with heavy non-transition metal cations such as cadmium and mercury in this manner⁹⁻¹¹. The coordination chemistry of mixed-ligand Hg(II) saccharinate complexes have been extensively studied¹²⁻¹⁹.

Recently, some N-substituted saccharine derivatives were synthesized and their biological activity with respect to selective inhibition of human carbonic anhydrase was reported²⁰. Continuing our recent studies in this area^{21,22}, we herein

describe the preparation of mixed-ligand saccharine derivative complexes of Hg(II) with phosphines or heterocyclic amine co-ligands. Furthermore, the thermal behavior of six of these complexes is reported.

Materials and methods

All chemicals and solvents used in this work were commercial products, and used without further purification. The FT-IR spectra were recorded in the 4000 – 400 cm⁻¹ range on a Bruker Tensor 28 spectrometer with a Platinum ATR unit. 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 400 spectrometer with *d*⁶-DMSO and CDCl₃ as solvent. ³¹P NMR spectra were recorded on a Gemini 200 spectrometer with *d*⁶-DMSO solvent and H₃PO₄(85%) as external reference.

The NMR data are reported in ppm. The NMR spectra and element analysis were carried out at Al-Bayt University-Jordan and Institute für Anorganische Chemie, Martin-Luther-Universität, Halle, Germany. N-Hydroxymethylsaccharin was (Sac-CH₂OH) prepared and characterized according to literature method²³.

The simultaneous TG, DTG- DTA measurements were carried out on a Perkin Elmer SII Diamond TG/DTA thermal analyzer. Samples weighing 5-15 mg of the complexes were placed in the aluminum pans and heated at a rate of $10^{\circ}\text{C min}^{-1}$ between room temperature and 600°C under a nitrogen gas flow rate of 100 ml min^{-1} . The complexes were also visually monitored in a melting point apparatus to observe the changes in the phase as well as the evolution of volatile products.

Synthesis: Preparation of $[\text{Hg}(\text{K}^2\text{-Sac-CH}_2\text{O})_2]$: A warm solution of N-hydroxymethylsaccharin ($\text{Sac-CH}_2\text{OH}$) (0.145 g, 0.680 mmol) in ethanol (10 mL) was added to a solution of mercuric acetate (0.108 g, 0.340 mmol) in ethanol (15 mL). To the mixture, few drops of Et_3N was added with stirring, to give white precipitate. The mixture was stirred for 1 h. The white solid was filtered off, washed with distilled water, ethanol and dried in an oven. The product was recrystallized from DMSO/EtOH to give a white powder. Yield: 0.208 g (97%). Anal. Calc. for $\text{C}_{18}\text{H}_{16}\text{HgN}_4\text{S}$: C, 31.06; H, 2.13; N, 4.76. Found: C, 30.75; H, 1.94; N, 4.48%. IR (KBr): 3093w, 2920w, 1695s (C=O), 1631m, 1294s, 1176s cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 5.14 (s, 4H, OCH_2); 7.44 (dd, $^3J_{\text{HH}} = 7.88\text{ Hz}$, $^4J_{\text{HH}} = 1.43\text{ Hz}$, 2H); 7.54 (dd, $^3J_{\text{HH}} = 7.88\text{ Hz}$, $^4J_{\text{HH}} = 1.43\text{ Hz}$, 2H); 7.76 (d, $^3J_{\text{HH}} = 8.00\text{ Hz}$, 2H); 7.88 (d, $^3J_{\text{HH}} = 7.98\text{ Hz}$, 2H). Melting point: $291\text{-}293^{\circ}\text{C}$.

Preparation of $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{L-L})]$: A solution of bis(diphenylphosphino)methane (dppm) (0.100 g, 0.150 mmol) in CHCl_3 (10 mL) was added with stirring to a suspension of $[\text{Hg}(\text{Sac-CH}_2\text{O})_2]$ (1) (0.059 g, 0.150 mmol) in CHCl_3 (15 mL). The resultant clear solution was stirred at 40°C for 2 h, then filtered off and left to evaporate at room temperature. The produced white solid was filtered, washed with CHCl_3 and dried in an oven. The product was recrystallized from DMF/ CHCl_3 to give a white powder.

The following complexes $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dppe})]$ (3), $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dppp})]$ (4), $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dppb})]$ (5), $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dppmS}_2)]$ (6) and $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dppeO}_2)]$ (7) were prepared and isolated in a similar procedure.

2: White solid. Yield: 0.083 g (52%). Anal. Calc. for $\text{C}_{41}\text{H}_{34}\text{HgN}_2\text{O}_8\text{P}_2\text{S}_2$: C, 48.79; H, 3.40; N, 2.78. Found: C, 49.01; H, 3.48; N, 2.89%. IR (KBr): 3058w, 2927w, 1741s (C=O), 1647m, 1434s, 1290s, 1153s, 487m cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 2.95 (s, 2H, $\text{CH}_2\text{-dppm}$); 5.24 (s, 4H, OCH_2); 7.01-7.88 (m, 28H, H-phenyl). $^{31}\text{P-}\{^1\text{H}\}$ NMR: δ - 2.94. Melting point: $198\text{-}202^{\circ}\text{C}$.

3: White solid. Yield: 85%. Anal. Calc. for $\text{C}_{42}\text{H}_{36}\text{HgN}_2\text{O}_8\text{P}_2\text{S}_2$: C, 49.29; H, 3.55; N, 2.74. Found: C, 49.59; H, 3.53; N, 2.55%. IR (KBr): 3055w, 2904w, 1739s (C=O), 1650m, 1434s, 1271s, 1151s, 511m cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 3.02 (t, 4H, $^3J_{\text{HH}} = 7.88\text{ Hz}$, $2\text{CH}_2\text{-dppe}$); 5.17 (s, 4H, OCH_2); 7.13-7.86 (m, 28H, H-phenyl). $^{31}\text{P-}\{^1\text{H}\}$ NMR: δ 24.46. Melting point: $236\text{-}239^{\circ}\text{C}$.

4: White solid. Yield: 78%. Anal. Calc. for $\text{C}_{43}\text{H}_{38}\text{HgN}_2\text{O}_8\text{P}_2\text{S}_2$: C, 49.78; H, 3.69; N, 2.70. Found: C, 49.71; H, 3.58; N, 2.82%. IR (KBr): 3055w, 2921w, 1739s (C=O), 1689m, 1440s, 1294s, 1153s, 509m cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 1.76 (b, 2H, $\text{CH}_2\text{-dppp}$); 2.75 (b, 4H, $\text{CH}_2\text{-dppp}$); 5.28 (s, 4H, OCH_2); 6.95-7.96 (m, 28H, H-phenyl). $^{31}\text{P-}\{^1\text{H}\}$ NMR: δ 8.45. Melting point: $276\text{-}278^{\circ}\text{C}$.

5: White solid, 78%. Anal. Calc. for $\text{C}_{44}\text{H}_{40}\text{HgN}_2\text{O}_8\text{P}_2\text{S}_2$: C, 50.26; H, 3.83; N, 2.63. Found: C, 50.12; H, 4.05; N, 2.91%. IR (KBr): 3050w, 2908w, 1736s (C=O), 1653m, 1434s, 1290s, 1151s, 505m cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 1.68 (b, 4H, $\text{CH}_2\text{-dppb}$); 2.33 (b, 4H, $\text{CH}_2\text{-dppb}$); 5.16 (s, 4H, OCH_2); 6.88-7.92 (m, 28H, H-phenyl). $^{31}\text{P-}\{^1\text{H}\}$ NMR: δ 57.13. Melting point: $300\text{-}302^{\circ}\text{C}$ (decompose).

6: White solid. Yield: 92%. Anal. Calc. for $\text{C}_{41}\text{H}_{34}\text{HgN}_2\text{O}_8\text{P}_2\text{S}_4$: C, 45.87; H, 3.19; N, 2.61. Found: C, 45.99; H, 3.23; N, 2.77%. IR (KBr): 3058w, 2931w, 1733s (C=O), 1648m, 1434s, 1269s, 1163s, 482m cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 2.91 (s, 2H, $\text{CH}_2\text{-dppmS}_2$); 5.26 (s, 4H, OCH_2); 6.91-8.01 (m, 28H, H-phenyl). $^{31}\text{P-}\{^1\text{H}\}$ NMR: δ - 24.78. Melting point: $158\text{-}161^{\circ}\text{C}$.

7: White solid. Yield: 78%. Anal. Calc. for $\text{C}_{42}\text{H}_{36}\text{HgN}_2\text{O}_{10}\text{P}_2\text{S}_2$: C, 47.80; H, 3.44; N, 2.65. Found: C, 47.59; H, 3.64; N, 2.81%. IR (KBr): 3038w, 2911w, 1740s (C=O), 1661m, 1434s, 1291s, 1153s, 502m cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 2.20 (t, 4H, $^3J_{\text{HH}} = 8.00\text{ Hz}$, $2\text{CH}_2\text{-dppeO}_2$); 4.96 (s, 4H, OCH_2); 7.14-7.83 (m, 28H, H-phenyl). $^{31}\text{P-}\{^1\text{H}\}$ NMR: δ 24.46. Melting point: $239\text{-}243^{\circ}\text{C}$ (decompose).

Preparation of $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{L-L})_2]$ (8): A solution of PPh₃ (0.100 g, 0.38 mmol) in CHCl_3 (10 mL) was added to a suspension of $[\text{Hg}(\text{Sac-CH}_2\text{O})_2]$ (1) (0.126 g, 0.19 mmol) in CHCl_3 (15 mL), with stirring. A clear solution was formed. The mixture was stirred at 40°C for 2 h. The solution was filtered off and left to evaporate at room temperature. The produced white solid was filtered, washed with CHCl_3 / diethyl ether and dried in an oven. The product was recrystallized from DMSO/ CHCl_3 to give white powder. The following complexes were prepared and isolated in a similar method; $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{Ph}_3\text{PS})_2]$ (9) and $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{Ph}_3\text{PO})_2]$ (10).

8: White solid, Yield: 0.211 g (93%). Anal. Calc. for $\text{C}_{52}\text{H}_{42}\text{HgN}_2\text{O}_8\text{P}_2\text{S}_2$: C, 54.33; H, 3.68; N, 2.44. Found: C, 54.51; H, 3.34; N, 2.71%. IR (KBr): 3055w, 2856w, 1733s (C=O), 1654m, 1434s, 1290s, 1163s, 482m, cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 5.16 (s, 4H, OCH_2); 7.08-7.93 (m, 38H, H-phenyl). $^{31}\text{P-}\{^1\text{H}\}$ NMR: δ 14.69. Melting point: $182\text{-}186^{\circ}\text{C}$.

9: White solid. Yield: 86%. Anal. Calc. for $\text{C}_{52}\text{H}_{42}\text{HgN}_2\text{O}_8\text{P}_2\text{S}_4$: C, 51.46; H, 3.49; N, 2.31. Found: C, 51.23; H, 3.30; N, 2.12%. IR (KBr): 3059w, 2913w, 1736s (C=O), 1662m, 1436s, 1289s, 1151s, 505m cm^{-1} . $^1\text{H NMR}$ (d^6 -DMSO): δ 5.27 (s, 4H, OCH_2); 7.14-7.98 (m, 38H, H-phenyl). $^{31}\text{P-}\{^1\text{H}\}$ NMR: δ 29.70. Melting point: 320°C (decompose).

10: White solid. Yield: 67%. Anal. Calc. for $C_{52}H_{42}HgN_2O_{10}P_2S_4$: C, 52.86; H, 3.56; N, 2.37. Found: C, 53.08; H, 3.81; N, 2.46%. IR (KBr): 3069w, 2878w, 1741s (C=O), 1656m, 1434s, 1292s, 1150s, 505m, cm^{-1} . 1H NMR (d^6 -DMSO): δ 5.29 (s, 4H, OCH₂); 7.09-7.83 (m, 38H, H-phenyl). ^{31}P -{ 1H } NMR: δ 40.56. Melting point: 320 °C (decompose).

Preparation of [Hg(Sac-CH₂O)₂(bipy)] (11): A solution of bipy (0.100 g, 0.64 mmol) in CHCl₃(10 ml) was added to a suspension of [Hg(Sac-CH₂O)₂] (1) (0.400 g, 0.64 mmol) in CHCl₃ (10 ml). The resulting clear solution was stirred at room temperature for 3 h, filtered and set aside to evaporate at room temperature. The white solid formed was filtered, washed with CHCl₃ and dried under vacuum. The product was recrystallized from DMF/ EtOH to give white powder.

The [Hg(Sac-CH₂O)₂(phen)] (12) complex was prepared and isolated in a similar method.

11: White solid. Yield: 0.449 g (88%). Anal. Calc. for $C_{26}H_{20}HgN_4O_8S_2$: C, 39.98; H, 2.58; N, 7.17. Found: C, 40.31; H, 2.73; N, 7.39%. IR (KBr): 3066w, 2941w, 1720s (C=O), 1647m(C=N), 1585s, 1294s, 1163m cm^{-1} . 1H NMR (d^6 -DMSO): δ 5.28 (s, 4H, OCH₂); 7.20 (d, 2H, $^3J_{HH} = 5.85$ Hz H-bipy); 7.43-7.57 (m, 8H, H-bipy and Sac-CH₂O); 7.72 (d, 2H, $^3J_{HH} = 5.00$ Hz, H-bipy); 8.19 (d, 2H, $^3J_{HH} = 5.00$ Hz, H-bipy); 8.48 (d, 2H, $^3J_{HH} = 6.43$ Hz, H-bipy). Melting point: 242-245°C.

12: White solid. Yield: 88%. Anal. Calc. for $C_{28}H_{20}HgN_4O_8S_2$: C, 41.77; H, 2.50; N, 6.96. Found: C, 40.31; H, 2.74; N, 7.19%. IR (KBr): 3064w, 2955w, 1730s (C=O), 1687m(C=N), 1583m, 1292s, 1167s, cm^{-1} . 1H NMR (d^6 -DMSO): δ 5.32 (s, 4H, OCH₂); 7.22 (d, 2H, $^3J_{HH} = 7.75$ Hz, H-phen); 7.46 (d, 2H, $^3J_{HH} = 7.75$ Hz; H- Sac-CH₂O), 7.51-7.74 (m, 8H, H-phen and Sac-CH₂O); 8.23 (d, 2H, $^3J_{HH} = 5.00$ Hz H-phen); 8.35(d, 2H, $^3J_{HH} = 6.43$ Hz, H-phen). Melting point: 210-214°C.

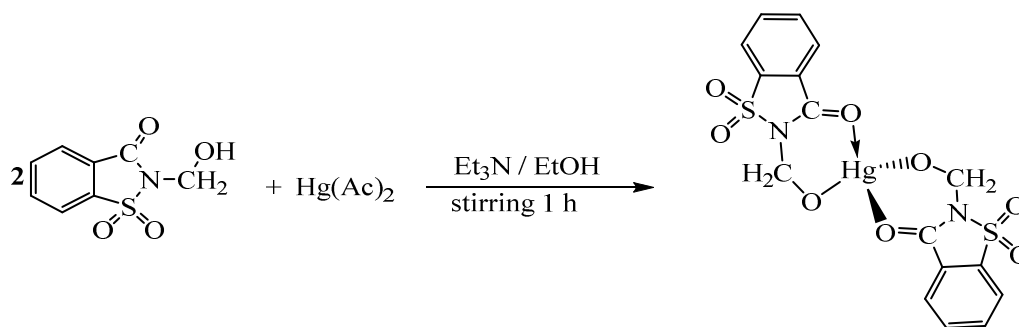
Preparation of [Hg(SacCH₂O)₂(py)₂] (13): A solution of pyridine (0.050 g, 0.63 mmol) in CHCl₃(10 mL) was added to a suspension of [Hg(Sac-CH₂O)₂] (1) (0.210 g, 0.32 mmol) in CHCl₃ (10 mL). The mixture was stirred at room temperature for 3 h, filtered and set aside to evaporate at room temperature for overnight. The white product formed was filtered, washed with EtOH and dried under vacuum. The product was

recrystallized from DMSO/ CHCl₃ in (1:2) ratio to give white powder. Yield 0.215 g (83%). Anal. Calc. for $C_{26}H_{22}HgN_4O_8S_2$: C, 39.87; H, 2.83; N, 7.15. Found: C, 39.71; H, 2.62; N, 7.06%. IR (KBr): 3072w, 2956w, 1726s (C=O), 1685s (C=N), 1585m, 1290s, 1161s cm^{-1} . 1H NMR (d^6 -DMSO): δ 5.246 (s, 4H, OCH₂); 7.42-8.45 (m, 16H, H-py and Sac-CH₂O). Melting point: 270 - 273°C.

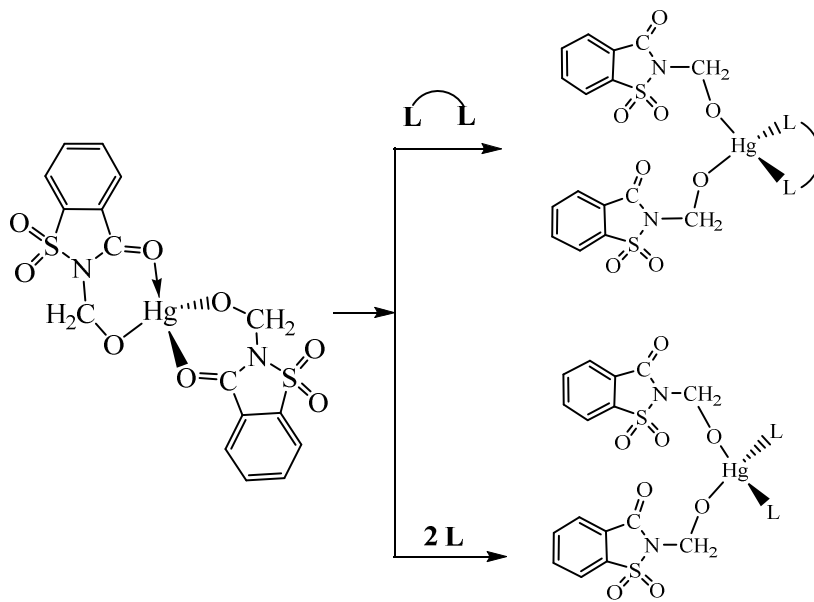
Results and discussion

Synthesis of [Hg(K²-Sac-CH₂O)₂] (1): Treatment of Hg(Ac)₂ with two equivalents of N-hydroxymethylsaccharin (Sac-CH₂OH) in EtOH in the presence of few drops of NEt₃ afforded [Hg(K²-Sac-CH₂O)₂] (1) in 97% yield (Scheme-1). The hydroxymethylsaccharinate anion in complex 1 behaves as a bidentate ligand, coordinating through the carbonyl and CH₂O oxygen atoms presumably afforded a tetrahedral arrangement around Hg(II) center. Evidence for this assignment comes from the IR spectrum of complex 1 which displayed ν (C=O) at 1695 cm^{-1} shifted to a lower frequency from that of the free Sac-CH₂OH, which appeared at 1747 cm^{-1} ²². Characterization proved straightforward and was made on the basis of spectroscopic and analytical techniques (see experimental section).

Synthesis of [Hg(K¹-Sac-CH₂O)₂ (L-L)] (2-7, 11 and 12) and [Hg(K¹-Sac-CH₂O)₂ (L₂)] (8-10 and 13) Reaction of the chelated sac derivative complex 1 with different diphosphines, bipyridine or phenanthroline in an equivalent ratio afforded [Hg(K¹-Sac-CH₂O)₂(L-L)] (2-7,11,12) in 52-92 % yields. The same reaction with monophosphines or pyridine give rise to [Hg(K¹-Sac-CH₂O)₂ (L₂)] (8-10 and 13) as white solids in 83-93 % yields (Scheme 2). The Sac-CH₂O in complexes 2-13 coordinated as a monodentate ligand through the oxygen atom of the CH₂O⁻ group. This was deduce from the high frequency shift of the ν (C=O) from 1695 cm^{-1} for complex 1 to 1721-1741 cm^{-1} in the spectra of complexes 2-13 (Figures-1-3). In complex 2, dppm coordinated to Hg as a bidentate chelate as evidence from the negative chemical shift of phosphine (δ -2.94 ppm)²³ (Figure-4). Complexes 1-13 are stable in the solid state as well as in DMF or DMSO solutions when kept at room temperature. However they are unstable in hot DMSO or DMF solutions decompose to black precipitates.



Scheme-1: Preparation of complex 1.



L = dpmm (2); dppe (3), dppp (4), dppb (5), dpmmS₂ (6), dppeO₂ (7), bipy (11), and phen(12). L = Ph₃P (8), Ph₃PS (9), Ph₃PO (10) and py (13)

Scheme-2: Preparation of the complexes 2-13.

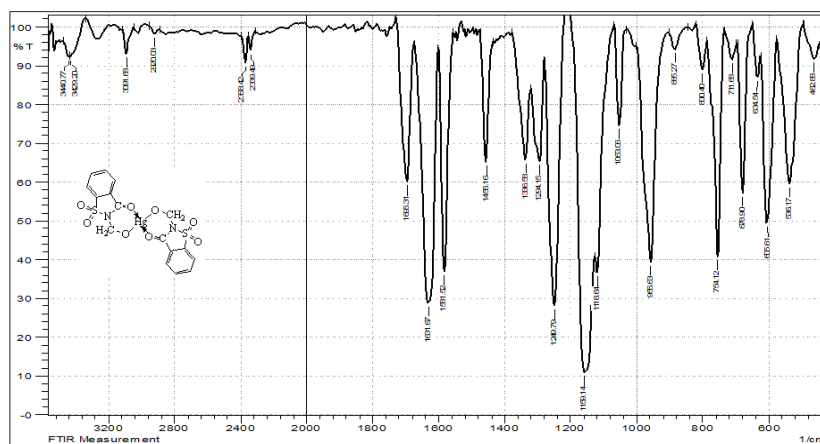


Figure-1: IR spectrum of the complex $[\text{Hg}(\text{K}^2\text{-Sac-CH}_2\text{O})_2]$ (1).

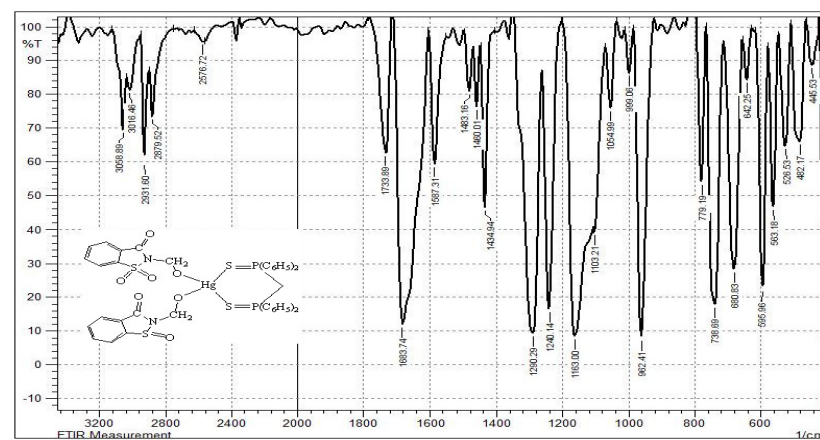


Figure-2: IR spectrum of the complex $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dpmmS}_2)]$ (6).

Thermal study: Thermal decomposition of complexes 6, 8 and 11.

and [Hg(Sac-CH₂O)₂(bipy)] (11), Thebipy complex (11) has the highest thermal stability. Nitrogen donor ligands often improve thermal stability of the complexes²⁴.

Figures-5 and 6 show the TG and DTA curves of the complexes [Hg(Sac-CH₂O)₂(dppmS₂)] (6), [Hg(Sac-CH₂O)₂(PPh₃)₂] (8)

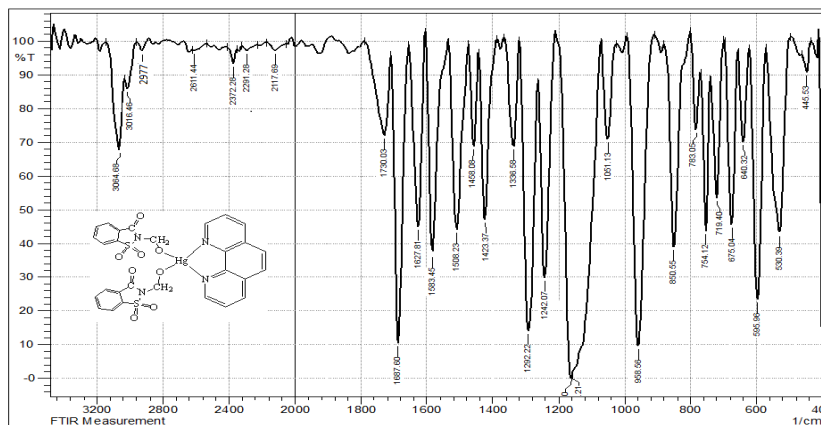


Figure-3: IR spectrum of the complex [Hg(Sac-CH₂O)₂(Phen)] (12).

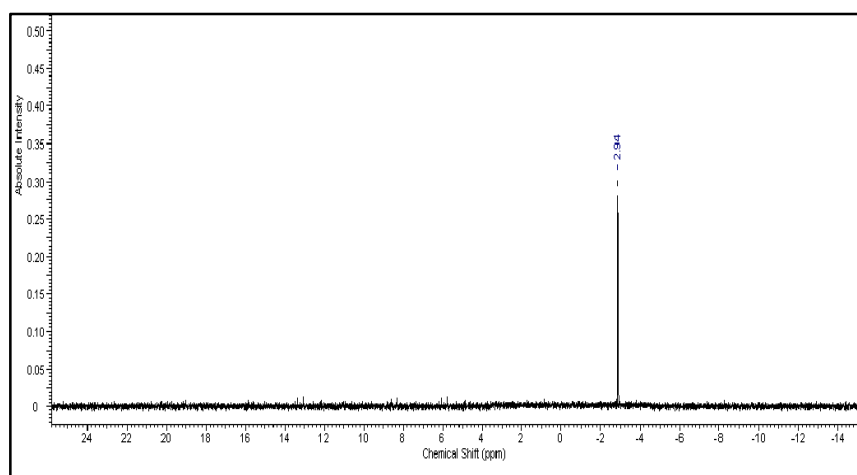


Figure-4: ³¹P-n.m.r spectrum of the complex [Hg(Sac-CH₂O)₂(dppm)] (1).

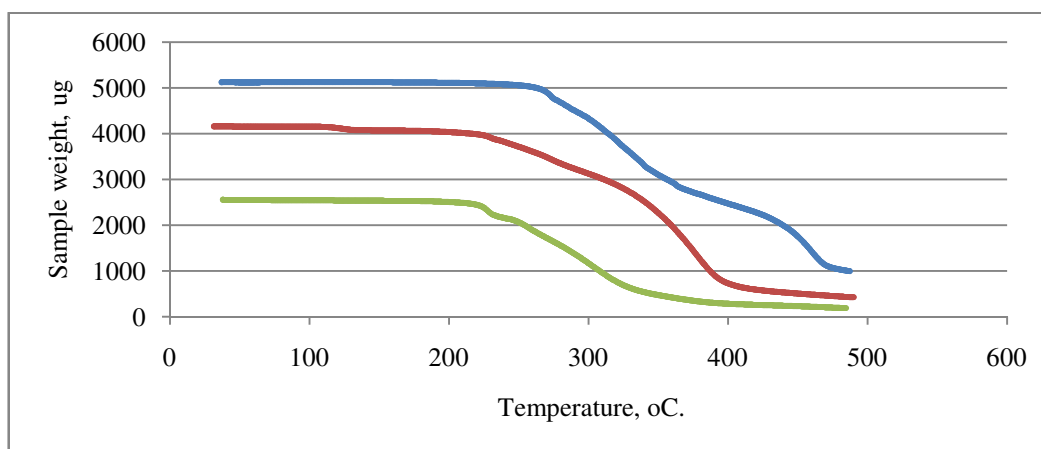


Figure-5: The TG curves of the complexes [Hg(Sac-CH₂O)₂(dppmS₂)] (6), middle curve; [Hg(Sac-CH₂O)₂(PPh₃)₂] (8), Lower curve and [Hg(Sac-CH₂O)₂(bipy)] (11), upper curve.

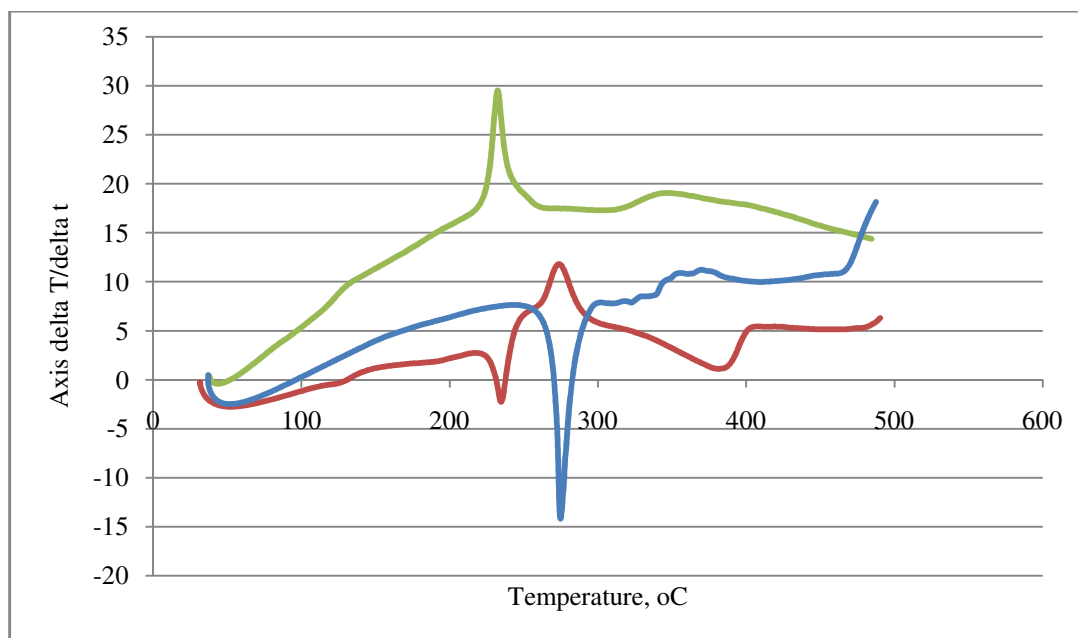


Figure-6: The DTA curves of the complexes $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{dppmS}_2)]$ (6), upper curve; $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{PPh}_3)_2]$ (8), lower curve; and $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{bipy})]$ (11). Middle curve.

The $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{dppmS}_2)]$ (6) (M.W. = 1072.6) undergoes a weight loss of 23.3% (M.W.= 249.8) between 218 – 294°C accompanied by an endothermic peak with a maximum at 233 °C and exothermic peak with a maximum at 273°C. The material behavior was watched with a melting point apparatus and starting from 231°C the material started melting. Thus, the endotherm refers to the melting of the complex.

The exothermic peak refers to the decomposition with the formation of solid product as indicated by the irregular DTA and DTG signals. Gaseous products have to penetrate the solid shell formed by the first decomposition. Between 294 and 438 °C the complex showed the last decomposition step involved the loss of 65% (M.W. = 697.2) of the complex weight. The process is endothermic with peak maximum at 378 °C.

The complex $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{PPh}_3)_2]$ (8) (M.W.=1148.6) showed an exothermic change between 172-242°C with a weight loss of 16.26%. It seems that one of the Sac-CH₂O groups undergoes a disproportionation into CH₂-O and Sac which evaporate under the experimental conditions (ca 15.67% weight loss).

The maximum rate of reaction was at 230 °C and the maximum rate of heat flow at 232°C. The second change occurs between 242 and 360°C with a weight loss of 65.34%. This is a two-step reaction described by two DTG peaks with maxima at 258°C losing 18.2% weight (M.W.=209.0) and ends at 274°C, and maximum rate at 306°C losing 49.65% (M.W.= 70.3) of weight. The overall weight loss was 82.60% referring to the formation of HgO (ca. 82.54%). Mercuric oxide decomposes above 450°C into gaseous mercury and oxygen.

The bipy complex (11) showed relatively a higher thermal stability. It decomposes in a two-steps reaction between 228 and 309°C, losing 19.79% of its weight. The change refers to the loss of the bipyridyl group (Calc. 20.0%). Beyond 314°C, a series of decompositions occur leading to the formation of a stable intermediate at about 420°C which mostly refers to mercuric sulfate. The HgSO₄ sublimes with decomposition at 450°C²⁵.

Thermal decomposition of complexes 7, 12 and 13: Figure-7 shows the TG curves of $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{dppeO}_2)]$ (7) $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{phen})]$ (12) and $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{py})_2]$ (13). The DTA curves of the three complexes are shown in Figure-8. For the $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{phen})]$ (12) complex, the presence of phen attached to the Hg(Sac-CH₂O)₂ moiety improves the thermal stability and the complex melts at 230°C (endothermic peak maximum at 254°C) then starts decomposition.

After complete melting, the decomposition was fast and occurs in three overlapping steps (as indicated by three DTG peak maxima at 347, 370, and 398°C. The overall weight agrees with the loss of most of the organic parts of the complex and leads to the formation of mercuric sulfate. The $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{py})_2]$ (13) complex undergoes a two-steps endothermic decomposition reaction between 110 and 210°C, losing one pyridine molecules in each step (Calc. 20.0%, found 19.6%). Similar behavior was reported by Jasim and Barbooti²⁶ during the thermal decomposition of nitrosodicyan-methanide tetrapyrindinium Mn(II), Cu(II) or Zn(II) complexes, where pyridine molecules are lost in multi-step process. A mono pyridine intermediate could be formed during the decomposition reaction.

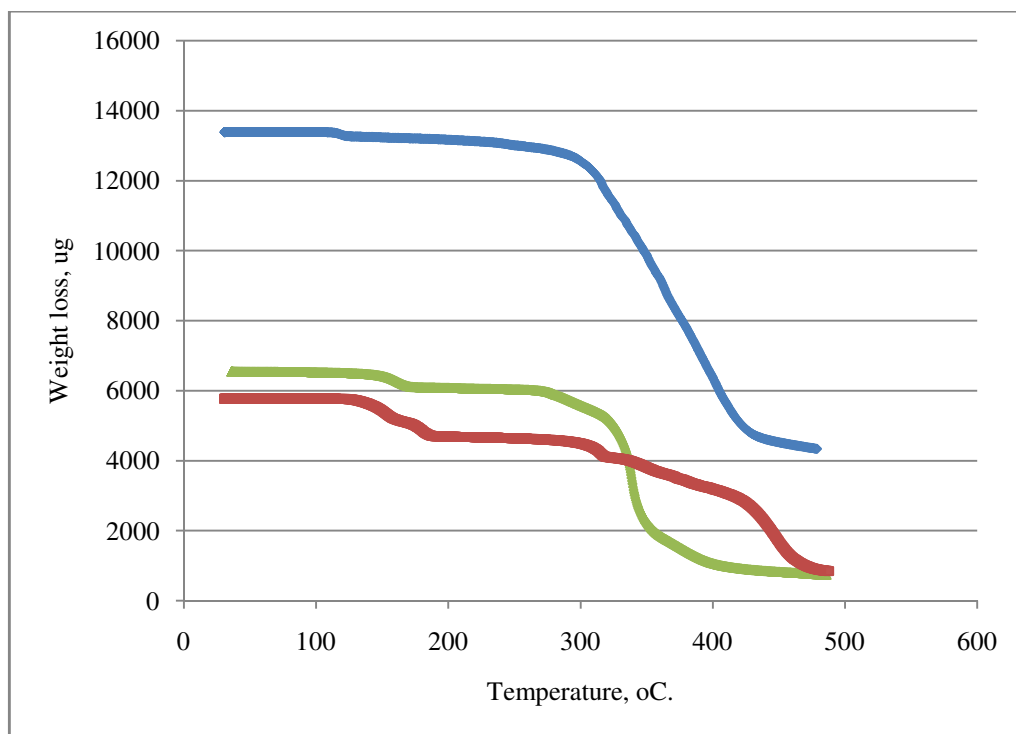


Figure-7: The TG curves of $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dppeO}_2)]$ (7), middle curve; $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{phen})]$ (12), upper; and $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{py})_2]$ (13), Lower curve.

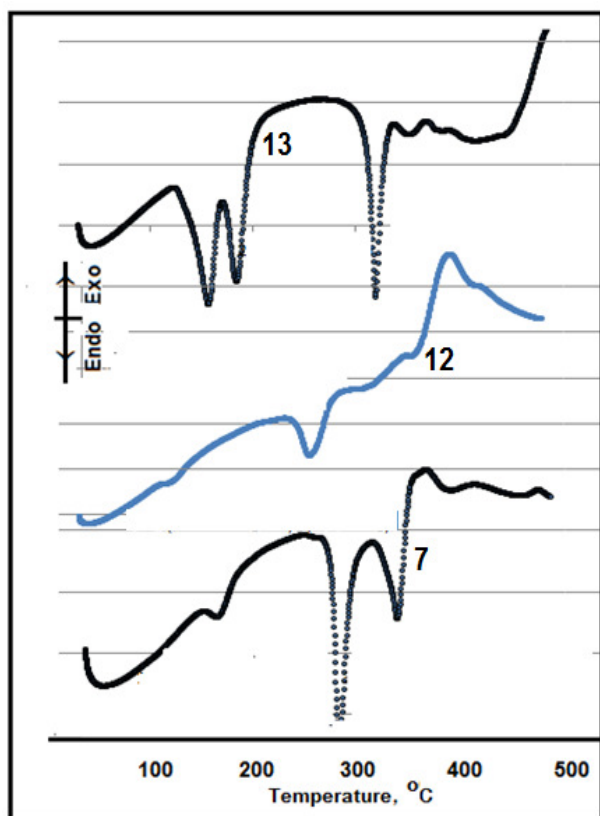


Figure-8: The DTA curves of $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dppeO}_2)]$ (7), $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{phen})]$ (12), $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{py})_2]$ (13).

The remaining $[\text{Hg}(\text{Sac-CH}_2\text{O})_2]$ was stable up to 260°C , where a thermal decomposition reaction was noticed between 260 and 397°C in three steps. The first step is highly endothermic and involved the loss of 10.8% (M.W. 113.9) of weight up till a temperature of 331°C . The second and third steps are less endothermic than the first one, overlap with each other and involved the loss of 14.9% weight loss (M.W. 157.1). Beyond 331°C , the residual material loses 43.1% (M.W. 454.5) in multi-step decomposition reaction that starts endothermic and ended exothermic.

The most likely product was the mercuric sulfide, HgS . Theoretically, HgS decomposition occurs at 585°C . Practical results indicated a maximum rate of decomposition to occur at 350°C at a relatively low heating rate and a nitrogen flow rate of 6.2 L/min^{27} . Mercuric sulfide was identified as the decomposition product of di-*t*-butyl sulfide-mercury (II) chloride²⁸.

The $[\text{Hg}(\text{Sac-CH}_2\text{O})_2(\text{dppeO}_2)]$ (7) (M.W. =1054.6) complex undergoes 6.7% weight loss (M.W. =70.7) between 142 and 184°C with a maximum rate at 163°C . The process is endothermic. The product of this decomposition is stable to around 250°C , where it decomposes in two overlapping steps between 260 and 370°C .

The process was highly endothermic and the DTA peak minima were recorded at 281 and 340°C . The weight loss extents for the two overlapping steps were 9.6% (M.W. = 101.2) and 60.0% (M.W. = 632.76).

Conclusion

A range of new mercury(II) N-hydroxymethyl saccharinate complexes were prepared containing bidentate ligands; diphosphines (dppm, dppe, dppp, dppb), $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2)\text{P}(\text{S})\text{Ph}_2$ (dppmS₂), $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ (dppeO₂), bipyridine (bipy). Phenanthroline (phen) or monodentate ligands; Ph_3P , Ph_3PO , Ph_3PS and pyridine (py) starting from $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2]$. The later has been prepared from the reaction of Mercury(II) acetate and Sac-CH₂OH in the presence of Et₃N, it has presumably a tetrahedral structure with Sac-CH₂O- bonded as a chelate. Consequently it rapidly transforms to complexes of the type $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{L}-\text{L})]$ or $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{L})_2]$ on treatment with bidentate or monodentate ligands respectively. The Sac-CH₂O here coordinated as a monodentate coordinated through the CH₂O oxygen atom. Most of the complexes 6-8, 11-13 decompose on heating immediately after melting. The loss of the two Py groups occurs in two step indicating a different bonding nature with the central metal ion. The $[\text{Hg}(\text{Sac}-\text{CH}_2\text{O})_2(\text{phen})]$ (12) complex showed the highest thermal stability among its group. Mercuric sulfide and mercuric sulfate are possible thermal decomposition products.

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