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SPECTROSCOPIC STUDIES AND THERMAL ANALYSIS OF LEAD(II) AND TIN(II) SOLID COMPLEXES WITH BI-, TRI- AND TETRADENTATE SCHIFF BASES

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ABSTRACT. The Schiff base complexes of Pb(II) and Sn(II) with bidentate (NO), [M(sal-An)$_2$] (sal-An = aniline salicylideneiminato); tridentate (ONO), [M(sal-OAP)H$_2$O)] (sal-OAP = ortho-aminophenol salicylideneiminato); and tetradentate (N$_2$O$_2$), [M(sal-*o*-phdn)] (sal-*o*-phdn = N,N'-*o*-phenylene bis(salicylideneiminato) have been synthesized. The infrared spectra were recorded and full assignments of all observed bands have been made. Differential thermal analysis (DTA) and thermogravimetric (TG) for all complexes were also carried out. The data obtained indicate that the complexes of both bi- and tetradentate ligands are decomposed in one stage, but the complexes of tridentate are decomposed in two steps.

KEY WORDS: Lead, Tin, Schiff base, Infrared spectra, Thermal analysis

INTRODUCTION

Metal-chelated Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition-metal coordination chemistry due to their preparative accessibility, diversity and structural variability [1, 2]. Schiff bases of *o*-phenylenediamine and its complexes have a variety of applications including biological [3, 4], clinical [5] and analytical [6]. Earlier work has shown that some drugs studied increased activity when administered as metal chelates rather than as organic compounds [3, 4] and that the coordination possibility of *o*-phenylenediamine has been improved by condensation with a variety of carbonyl compounds. Tetradentate Schiff bases with a N_2O_2 donor atom set are well known to coordinate with various metal ions, and this has attracted many authors [7-14]. The reactions of tetradentate Schiff bases derived from salicyldehyde and diamine are the subject of many authors [9-14]. To continue our investigation in the field of Schiff base complexes [11-14], we report here the preparation and characterization of some bidentate, [M(sal-An)$_2$] (sal-An = aniline salicylideneiminato); tridentate, [M(sal-OAP)H$_2$O)] (sal-OAP = orthoaminophenol salicylideneiminato) and tetradentate, [M(sal-*o*-phdn)] (sal-*o*-phdn = N,N'-*o*-phenylene bis(salicylidene-iminato)) Schiff base complexes with lead(II) and tin(II). The infrared spectra along with differential thermal analysis (DTA) and thermogravimetric (TG) analysis of the complexes were also carried out. These results enable us to detect the complexes and to make an assessment of the bonding and structure inherent in them. A literature search reveals that little work has been done on the heavy metal (Pb(II) and Sn(II)) complexes of the Schiff base derived from the *o*-phenylenediamine, *o*-aminophenol and aniline with salicylaldehyde.

EXPERIMENTAL

All chemicals used throughout this investigation were of analytical grade. The Schiff bases Sal-AnH (aniline salicylideneimine), Sal-OAPH$_2$ (*o*-aminophenol salicylideneimine) and Sal-*o*-

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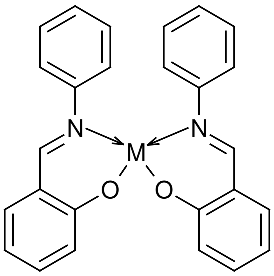
*Corresponding author. E-mail: msrefat@yahoo.com phdnH_2 (N,N'-*o*-phenylenebis(salicylideneimine)) were prepared from the condensation of 0.1 mol of aniline, *o*-aminophenol and *o*-phenylenediamine with 0.1 mol salicylaldehyde for (aniline and *o*-aminophenol) and 0.2 mol for *o*-phenylenediamine in ethanolic solutions according to the known methods [15-17]. The Schiff bases were characterized by their IR and elemental analysis. An ethanolic (20 mL) solution of sal-AnH (0.788 g, 4 mmol) was mixed with metal(II) chloride (M = Pb or Sn), 2 mmol in ethanolic solution (20 mL) and the mixtures refluxed for 2 h on a water bath. The refluxed materials were concentrated and cooled. The solid products obtained were filtered, washed with ethanol and dried in *vacuo* over phosphorus pentoxide. The lead and tin(II) complexes, [M(sal-OAP)(H_2O)], were prepared from the addition of lead or tin chlorides (4 mmol) in acetone to a stoichiometric amounts of the sal-OAPH_2 (0.852 g, 4 mmol) in acetone. The mixtures were stirred at room temperature and the precipitates thus formed were filtered off, washed with acetone and dried in *vacuo* over P_2O_5. The other two complexes [Pb(sal-*o*-phdn)] and [Sn(sal-*o*-phdn)] were prepared in a manner similar to that described above via the reaction of $PbCl_2$ or $SnCl_2$ with sal-ophdnH_2 Schiff base in a molar ratio 1:1 using acetone as solvent at room temperature. The six complexes were characterized by elemental analysis, infrared spectra as well as by their thermal analysis (DTA and TG). Analysis results are reported in Table 1. The percentage of lead and tin metals were determined using atomic absorption method. An atomic absorption spectrometer PYE-UNICAM SP 1900 fitted with a lead and tin lamps was used for this purpose. The infrared spectra of the lead(II) and tin(II) Schiff base complexes were recorded from KBr discs using a Perkin-Elmer 1430 ratio recording Infrared spectrophotometer. Differential thermal analysis (DTA) and thermogravimetric (TG) of the Schiff base complexes [M(sal-An)$_2$], [M(sal-OAP)(H_2O)] and [M(sal-*o*-phdn)] (where M = Pb or Sn(II)) were carried out using a Shimadzu computerized thermal analysis system DT-40. The system includes programs which process data from the thermal analyzer with the Chromotpac C-R3A. The rate of heating of the sample was kept at 5 ^oC min^{-1}. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out under N_2-atmosphere at rate flow 40 mL min^{-1}.

RESULTS AND DISCUSSION

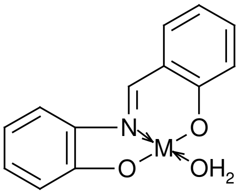
The lead(II) and tin(II) chlorides reacts with the bidentate (NO), tridentate (ONO) and tetradentate (N_2O_2) Schiff bases forming these complexes of monomeric structure where Pb(II) or Sn(II) ion is four coordinated, in the case of bidentate complexes, the metal ions are surrounded by two nitrogens of azomethine groups and two phenolic oxygens of two bidentate Schiff base molecules (Scheme 1), but in the other case of tridentate complexes the metal ions (Pb(II) or Sn(II)) is coordinated through two phenolic oxygen and one nitrogen of azomethine group of tridentate Schiff base and completed the coordination number by one oxygen atom of water molecule (Scheme 2). For tetradentate Schiff base complexes the Pb(II) or Sn(II) is coordinated through two nitrogens of azomethine groups and two phenolic oxygens (Scheme 3).

Table 1. The elemental analysis data.

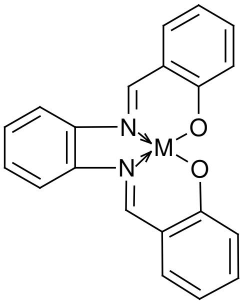
Complexes	% C		% H		% N		% Metal	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
[Pb(sal-An)$_2$]	52.07	51.83	3.33	3.29	4.67	4.59	34.57	34.81
[Sn(sal-An)$_2$]	61.09	59.98	3.91	3.89	5.48	5.42	23.24	23.18
[Pb(sal-OAP)(H_2O)]	35.76	35.12	2.52	2.61	3.20	3.51	47.49	47.82
[Sn(sal-OAP)(H_2O)]	44.86	44.35	3.16	3.26	4.02	4.15	34.13	34.78
[Pb(sal-*o*-phdn)]	46.06	45.92	2.68	2.63	5.37	5.19	39.75	40.11
[Sn(sal-*o*-phdn)]	55.46	55.13	3.23	3.29	6.47	6.11	27.43	27.69



Scheme 1



Scheme 2



Scheme 3

The structure of all above complexes may be found as a slightly irregular tetrahedral. The infrared spectra of the two complexes [Pb(sal-OAP)(H_2O)] and [Sn(sal-OAP)(H_2O)] showed characteristic bands of coordinated water at 3450 and 3550 cm^{-1}, respectively. These two characteristic bands of coordinated H_2O were absent in the spectra of the other four complexes (Table 2).

The ν(C-H) for the phenyl groups in all of these complexes occurred as a number of bands in the range 3180-3000 cm^{-1}, while those of the =CH-groups were shown as expected at 2980-2900 cm^{-1}. The azomethine stretching vibrations, ν(C=N) in all complexes occurred as a strong band around 1605 cm^{-1}. This strong band should be associated with the antisymmetric stretch, ν_{as}(C=N). However, the corresponding ν_{as}(C=N) in the free dibasic Schiff base occurred at 1631 cm^{-1}. The shift of the ν(C=N) stretch to lower energy by 20-30 cm^{-1} indicates that a coordinate bond is formed between nitrogen of the azomethine group of the Schiff bases and the central metal atom [18, 19].

The breathing vibrations of the phenyl groups are assigned to the group of bands occurrred in the 1590-1435 cm^{-1} region. The strong IR band around 1585 cm^{-1} should be associated with the antisymmetric breathing vibration. The descriptions of their assignments follow the expressions developed by Colthup *et al.* [20] and used by others [21]. The -CH deformations of the =CH groups are assigned in the 1400-1330 cm^{-1} range. The various vibrations ν(C-C), ν(C-N) and ν(C-O) in all complexes are assigned to a large number of bands occurred at 1310-1030 cm^{-1} region [21-23]. The CH- in-plane bands were found between 670-550 cm^{-1}, while the CH-out-of-plane motions are assigned to the region 440-360 cm^{-1}.

The metal-oxygen (of the ligand) stretching vibrations ν_{as}(M-O) are assigned around 500 cm^{-1} with different intensities. The corresponding ν_s(M-O) occurred at 485-440 cm^{-1} region for all complexes. ν_{as}(M-N) (N of the Schiff base) was observed around 305 cm^{-1}, while the symmetric stretching vibration, ν_s(M-N) was found around 285 cm^{-1}. These assignments are in agreement with the other Schiff base complexes [24].

Table 2. Infrared frequencies[a] (cm^{-1}) and tentative assignments for [M(sal-An)$_2$], [M(sal-OAP)(H$_2$O)] and [M(sal-*o*-phdn)] (where M = Pb or Sn(II)) complexes.

Frequencies, cm^{-1}						Assignments
[M(sal-An)$_2$]		[M(sal-OAP)(H$_2$O)]		[M(sal-*o*-phdn)]		
M = Pb	M = Sn	M = Pb	M = Sn	M = Pb	M = Sn	
---	---	3450 s, br	3550 m	---	---	ν(O-H); H$_2$O
3045 w	3180 m, br 3080 m, br	3060 ms 3000 ms	3070 m 3030 m	3045 w 3000 vw	3060 w 3040 w	ν (C-H); phenyl
2980 vw 2940 vw	2930 w	2930 w 2900 w	2960 vw 2930 vw	2960 vw 2920 vw	2960 w 2950w 2920 w	ν (C-H); =CH-
1610 s	1600 s	1600 vs	1605 vs	1610 s	1600 s	ν_{as} (C=N); azomethine
1585 s 1560 s 1480 s 1450 ms	1580 s 1485 vs 1450 vs	1580 s 1535 s 1460 vs 1440 ms	1590 vs 1538 s 1465 vs 1440 vs	1580 ms 1560 w 1525 s 1480 s 1455 s 1435 ms	1580 ms 1530 w 1480 vs 1450 s	Phenyl breathing modes
1400 ms 1355 ms	1400 m 1360 m	1410 mw 1380 s 1330 s	1385 s 1345 ms	1400 vw 1385 s 1360 w 1340 ms	1380 m 1358 m	CH-deformation
1270 vs 1230 vw 1185 s 1170 sh 1150 s 1110 w 1070 s 1030 s	1310 m 1250 sh 1225 s 1175 sh 1150 m 1110 m 1075 w 1030 w	1300 vs 1290 w 1270 s 1250 vs 1220 sh 1170 s 1150 vs 1120 s 1110 ms 1045 s	1300 vs 1280 w 1260 vs 1220 s 1175 s 1150 vs 1128 s 1110 ms 1035 s	1310 s 1300 sh 1280 s 1230 s 1190 sh 1180 vs 1150 vs 1120 w 1100 w 1045 ms 1030 s	1305 s 1270 vw 1225 vs 1190 s 1150 m 1100 ms 1075 m 1030 ms	ν (C-C), ν (C-O), ν (C-N)
1000 w 975 vs 940 ms 920 vs 890 vs 840 s 820 vs 750 vs 735 sh 690 vs	1000 vw 960 vw 930 m 890 vw 865 m 750 vs 700 s	980 vw 960 s 910 vs 870 ms 850 ms 845 sh 820 vs 770 sh 750 sh 745 vs 735 vs	1005 vw 965 ms 925 s 880 ms 858 m 835 vs 785 ms 750 s	1000 s 970 s 940 sh 930 ms 910 vs 850 vs 830 s 800 ms 790 ms 760 sh 745 vs	940 m 930 m 915 vw 905 vw 855 m 750 vs	CH-bend; phenyl
610 w 580 w 560 s	600 vw 570 vw 550 vw	660 vs 625 w 600 ms 590 sh 575 vw 550 w	670 vw 630 ms 610 s 557 ms	670 m 640 ms 600 w 585 w	605 m 590 vw 580 vw 570 vw 550 m	CH- in-plane bend; phenyl
530 vs 505 ms	530 vw 510 vw	500 vs	500 ms	540 vs 520 s	510 w	ν_{as} (M-O); O of Schiff base

	490 vw					
460 ms	450 vs	440 vs	450 w	480 s	485 vw	ν_s (M-O); O of Schiff base
430 s 420 vw	425 vw 400 vw 385 vw	394 vw 382 vw	440 w 390 vw 380 vw 360 s	400 vw 385 vw 370 ms	440 vw 420 vw	CH- out- of-plane bend; phenyl
350 w 305 s	340 vw 310 vw	350 s	340 s	330 w	285 vw	ν_{as} (M-N); N of Schiff base
260 vw	295 vw 250 vw	320 s	290 s 250 vw	300 w	285 vw 275 vw	ν_s (M-N); N of Schiff base

s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad.

To make sure about the structure of the complexes under investigation, [Pb(sal-An)$_2$], [Sn(sal-An)$_2$], [Pb(sal-OAP)(H_2O)], [Sn(sal-OAP)(H_2O)], [Pb(sal-*o*-phdn)] and [Sn(sal-*o*-phdn)], differential thermal analysis (DTA) and thermogravimetric (TG) were carried out under a N_2 flow. Figures 1-6 represents the DTA and TG curves. The thermal analysis (TG) data of the six complexes are given in Table 3. The thermal degradation for the two complexes, [Pb(sal-OAP)(H_2O)] and [Sn(sal-OAP)(H_2O)], exhibits approximately two main decomposition steps Figure 3 and 4, respectively. The first stage of decomposition occurs at maximum temperatures 228 and 195 ^{o}C accompanied by a weight loss of 3.95% and 4.97% which is consistent with the loss of one water molecule. The second step of degradation occurs at a maximum temperatures 345 and 439 ^{o}C and is accompanied by a weight loss of 20.23% and 37.34% correspond to the loss of NH_3+2C_2H_2+H_2O and 4.5C_2H_2+0.5N_2 in agreement with our predicted weight loss of 19.95% and 37.68% for Pb(II) and Sn(II) complexes, respectively. The above conclusion was also supported by the fact that the infrared spectra of the final decomposition product show the absence of all bands associated with the sal-OAP and water and instead the characteristic spectra of PbO and SnO_2 are appeared.

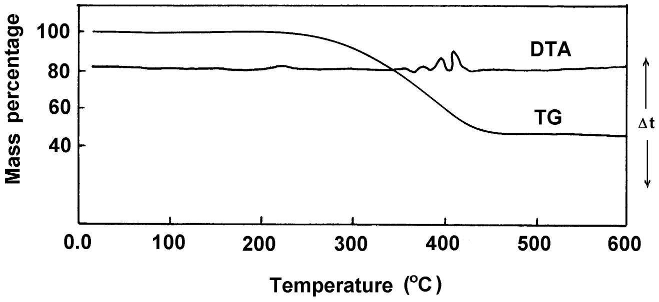


Figure 1. The thermal analysis of [Pb(sal-An)$_2$] complex.

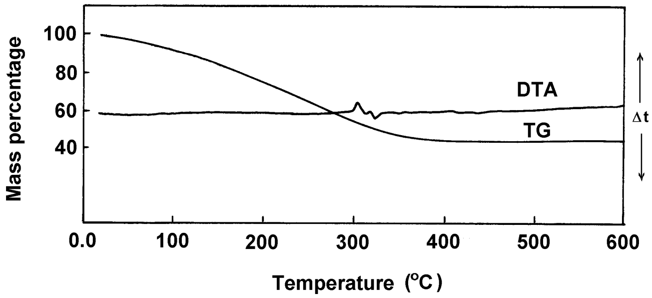


Figure 2. The thermal analysis of [Sn(sal-An)$_2$] complex.

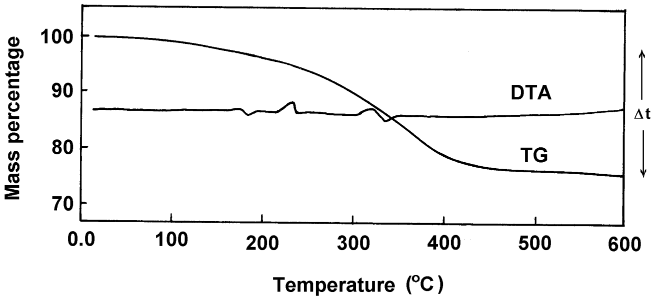


Figure 3. The thermal analysis of [Pb(sal-OAP)(H$_2$O)] complex.

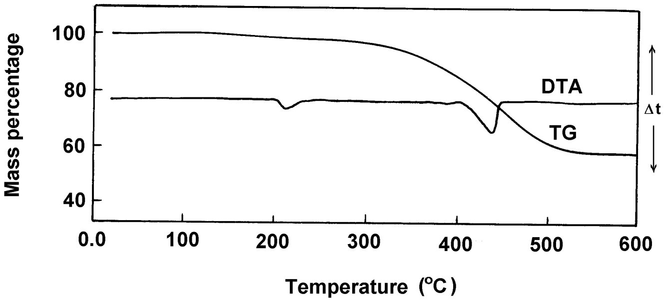


Figure 4. The thermal analysis of [Sn(sal-OAP)(H$_2$O)] complex.

The thermal decomposition of four complexes [Pb(sal-An)$_2$], [Sn(sal-An)$_2$], [Pb(sal-*o*-phdn)] and [Sn(sal-*o*-phdn)] located in one degradation stage at a maximum temperatures 397, 324, 405 and 391 °C, respectively (Figure 1, 2, 5 and 6). The weight loss found at these stages equal to 53.07%, 56.12%, 40.89% and 47.98%, respectively, which may correspond to the loss of $10C_2H_2+N_2+CO$, $10C_2H_2+N_2$, $6C_2H_2+N_2+H_2+CO$ and $7C_2H_2+N_2$, respectively. The calculated weight loss associated with the loss of these species are 52.74%, 56.39%, 41.06% and 48.53%, respectively, in agree quite well with obtained values.

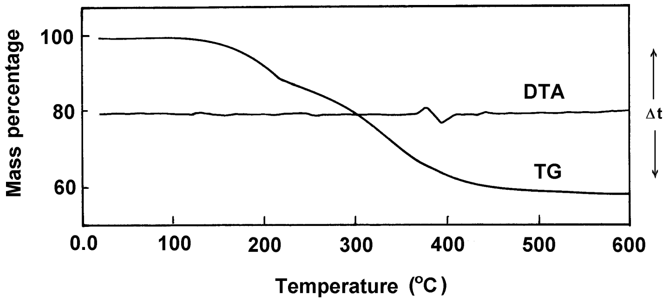


Figure 5. The thermal analysis of [Pb(sal-*o*-phdn)] complex.

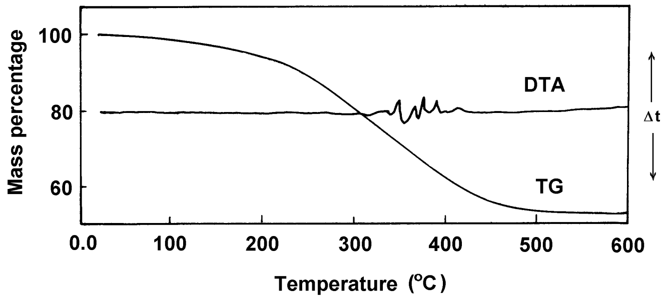


Figure 6. The thermal analysis of [Sn(sal-*o*-phdn)] complex.

Table 3. The maximum temperature, T_{max}/°C, and weight loss values of the decomposition stages for [M(sal-An)$_2$], [M(sal-OAP)(H_2O)] and [M(sal-*o*-phdn)] (where M = Pb or Sn(II)) complexes.

Complex	Decomposition	T_{max}/°C	Lost species	% weight losses	
				Found	Calc.
[Pb(sal-An)$_2$]	First stage	397°C	$10C_2H_2$+N_2+CO	53.07	52.73
[Sn(sal-An)$_2$]	First stage	324°C	$10C_2H_2$+N_2	56.12	56.39
[Pb(sal-AP)(H_2O)]	First stage	228°C	H_2O	3.95	4.13
	Second stage	343°C	NH_3+$2C_2H_2$+H_2O	20.23	19.95
[Sn(sal-OAP)(H_2O)]	First stage	195°C	H_2O	4.97	5.18
	second stage	439°C	$4.5C_2H_2$+0.5 N_2	37.34	37.68
[Pb(sal-*o*-phdn)]	First stage	405°C	$6C_2H_2$+N_2+CO+ H_2	40.89	41.06
[Sn(sal-*o*-phdn)]	First stage	391°C	$7C_2H_2$+N_2	47.98	48.53

Accordingly, the following mechanisms are proposed for the thermal decomposition of the Schiff base complexes:

i) $[Pb(sal\text{-}An)_2] \xrightarrow{397^{o}C} PbO + 5C + 10C_2H_2 + N_2 + CO$

ii) $[Sn(sal\text{-}An)_2] \xrightarrow{324^{o}C} SnO_2 + 6C + 10C_2H_2 + N_2$

iii) $[Pb(sal\text{-}OAP)(H_2O)] \xrightarrow{228^{o}C} [Pb(sal\text{-}OAP)] + H_2O$

$[Pb(sal\text{-}OAP)] \xrightarrow{345^{o}C} PbO + 9C + NH_3 + 2C_2H_2 + H_2O$

iv) $[Sn(sal\text{-}OAP)(H_2O)] \xrightarrow{195^{o}C} [Sn(sal\text{-}OAP)] + H_2O$

$[Pb(sal\text{-}OAP)] \xrightarrow{439^{o}C} SnO_2 + 4C + 4.5C_2H_2 + 0.5N_2$

v) $[Pb(sal\text{-}o\text{-}phdn)] \xrightarrow{405^{o}C} PbO + 7C + 6C_2H_2 + N_2 + CO + H_2$

vi) $[Sn(sal\text{-}o\text{-}phdn)] \xrightarrow{391^{o}C} SnO_2 + 6C + 7C_2H_2 + N_2$

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