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SOLID–SOLID INTERACTIONS IN THE FORMATION OF NEW COORDINATION COMPOUNDS OF TIN DICHLORIDE WITH AROMATIC SCHIFF BASES

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ABSTRACT

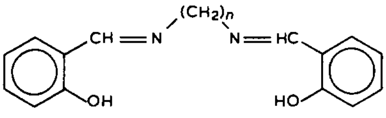
The enthalpic and kinetic parameters associated with the solid–solid interactions between tin dichloride and some aromatic Schiff bases and successive thermal decompositions were evaluated.

The results confirm a hypothesis of ionic-type structure for the adducts formed.

INTRODUCTION

In previous papers [1–3] it has been shown that thermodynamic studies of solid–solid interactions by differential scanning calorimetry (DSC) are possible when the chelating groups are properly chosen. Considering that the Schiff bases derived from salicylaldehyde behave as strong complexing ligands towards some metals, in an attempt to synthesize by solid–solid interactions their tetracoordinate complexes of tin (II), we have obtained the 1 : 1 and 2 : 1 ($SnCl_2$: ligand) addition compounds [4].

The Schiff bases (LH_2) considered are



AH_2 . $n = 2$
BH_2 : $n = 4$
DH_2 . $n = 6$

Elemental analysis, IR and MS studies of the 2 : 1 adducts (prepared previously in methanolic solution) indicated that such compounds have an ionic structure in which only one tin atom is coordinated to the oxygen and nitrogen atoms.

Attempts to prepare the 1 : 2 species were unsuccessful; in fact, in excess of the organic ligand the formation of the 1 : 1 species was favoured.

In this work enthalpic and kinetic parameters, associated with the solid–solid interactions, and successive thermal decompositions were also evaluated.

EXPERIMENTAL

The quadridentate Schiff bases AH_2, BH_2 and DH_2 were synthesized following the procedure described in the literature [5].

DSC measurements. These were performed with a Mettler DSC model 20, using aluminium covered pans and heating rates of 2 and 4°C min^{-1}. The empty pan was used as reference; the ΔH values of the reactions were evaluated using $\Delta H_{\mathrm{melting}}$ of In as the calibration standard (28.38 J g^{-1}).

TG and DTG measurements. These were performed with a Mettler TG model 50 apparatus using alumina crucibles, in a dynamic nitrogen atmosphere (0.2 l h^{-1}), at heating rates of 0.5, 2, 4 and 25°C min^{-1}.

Solid–solid interactions. The reactions were performed by introducing finely powdered stoichiometric mixtures of reactants into the pan or crucible, the total weight of the system being about 4–7 mg.

Evaluation of kinetic parameters. The activation energies, E_a, of the thermal decomposition processes were calculated graphically after introducing the appropriate reaction order, as reported in the literature [6–10].

RESULTS AND DISCUSSION

DSC measurements

The DSC curves of the reactants were investigated before those associated with the solid–solid interactions.

The thermally stable $SnCl_2$ exhibits the melting process at 260°C. The Schiff bases AH_2, BH_2 and DH_2 melt at 120°C ($\Delta H = 34.3$ kJ mole^{-1}), 93°C ($\Delta H = 30.9$ kJ mole^{-1}), and 70°C ($\Delta H = 32.6$ kJ mole^{-1}), respectively.

The DSC curves of all the adducts investigated exhibit an endothermic process in the melting temperature range of the organic ligand. Thermal decomposition processes were observed at 299, 275 and 268°C for the adducts AH_2–$SnCl_2$, BH_2–$SnCl_2$ and DH_2–$SnCl_2$, respectively, at all the investigated stoichiometric ratios. Figure 1 shows the thermal behaviour of the 2 : 1 $SnCl_2$–BH_2 system as an example.

The enthalpic values of the first thermal effect are reported in Table 1. In order to calculate the ΔH_t values, the molecular weights of the mixtures were calculated assuming that all the complexes (1 : 1, 1 : 2 and 2 : 1) were already formed.

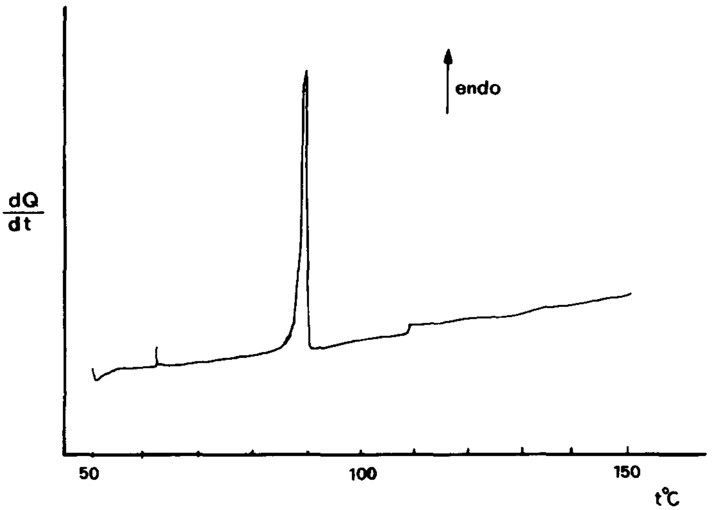


Fig. 1. Thermal behaviour of the system 2 $SnCl_2$–BH_2 (2.058 mg).

From the data reported in Table 1 it is worth noting that, in the range of the possible interactions, even if the thermal behaviour of the systems is qualitatively similar to that observed for the ligands, different ΔH values associated with melting were observed depending on the stoichiometric ratios used.

If we recalculate the ΔH_t values assuming that no reaction occurs and that the thermal effect is due only to the melting of the ligand (considering the weight of the ligand present in the mixture), the new ΔH values obtained do not agree with that due to the melt. This clearly indicates that interaction occurs.

Assuming that ΔH_t is the enthalpic content of the overall process (melting and simultaneous coordination of Schiff base), it is reasonable to evaluate

TABLE 1

System	Range of interaction (°C)	ΔH_t (kJ mole^{-1})	ΔH_r (kJ mole^{-1})
$AH_2(1:1)$	120–127	25.5	−8.8
$AH_2(1:2)$	120–127	58.9	24.2
$AH_2(2:1)$	120–127	23.8	−10.4
$BH_2(1:1)$	93– 96	23.0	−7.9
$BH_2(1:2)$	93– 96	53.1	22.1
$BH_2(2:1)$	93– 96	14.2	−16.7
$DH_2(1:1)$	70– 79	17.5	−15.0
$DH_2(1:2)$	70– 79	51.4	18.8
$DH_2(2:2)$	70– 79	16.7	−15.9

the ΔH_r of the interaction using the expression

$$\Delta H_r = \Delta H_t - \Delta H_m$$

and the results are reported in Table 1.

However, from the data obtained, it is possible to note the endothermicity of the interaction of the 1 : 2 system, and this introduces doubts as to the possibility of obtaining this kind of adduct with respect to the 1 : 1 and 2 : 1 compounds.

Furthermore, considering that in the 1 : 2 system there is an excess of ligand with respect to the $SnCl_2$, we have also considered the possibility that the adduct 1 : 1 was formed in an excess of ligand (as previously found when considering the formation of other coordination compounds) [11]. The theoretical ΔH values due to the contribution of the two simultaneous processes superimpose to give the experimental one reported in Table 1.

For the system $SnCl_2$–2 AH_2, the value of 58.9 is almost the sum of the contributions of the 1 : 1 species (25.5) and the melting of the ligand (34.3). Analogously, the reported ΔH values of 53.1 and 51.4 are the contributions of 23.0 + 30.9 and 17.5 + 32.6 for the B and D ligands, respectively.

Thermal decomposition.

The TG curves of all the reactants were performed showing that they are stable up 295, 180, 200 and 210°C, respectively for $SnCl_2$, AH_2, BH_2 and DH_2.

The thermal decomposition occurs in a single step being due to the vaporization process, as indicated by the reaction order values which are reported together with activation energy values, in Table 2.

System $SnCl_2$–LH_2. The products start to lose stability at temperatures near 200°C, depending on the ligand used. The thermal decomposition occurs in several consecutive steps, as exhibited by the DTG curve. The stoichiometry of the decomposition is in accordance with the scheme

$$\text{(a) } SnCl_2 \cdot LH_2 \xrightarrow{200^\circ C} SnL + 2\,HCl$$

TABLE 2

Reactant [a]	Weight (mg)	Range of vaporization (°C)	E_a (kJ mole^{-1})
$SnCl_2$	11.43	295–470	88
AH_2	3.52	180–260	31
BH_2	3.84	200–320	41
DH_2	4.93	210–300	26

[a] Zero order of reaction was found for all the reactants.

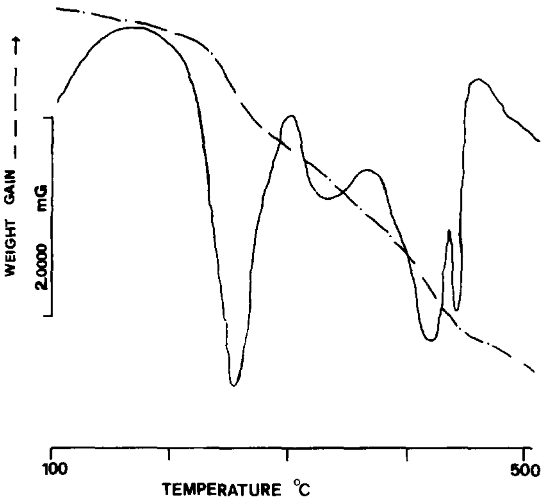


Fig. 2. Thermal decomposition of the adduct $[SnDH_2]Cl_2$ (7.787 mg).

(b) SnL $\xrightarrow{270^\circ\mathrm{C}}$ gaseous products + organic residue

(c) Organic residue $\xrightarrow{450^\circ\mathrm{C}}$ gaseous products

Reaction (c) is confirmed by qualitative analysis of the residue in which the presence of tin was not detected.

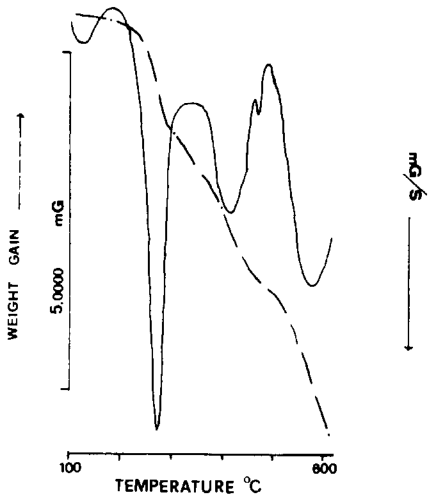
The thermal decomposition of the system $SnCl_2$–DH_2 is reported in Fig. 2.

The kinetic parameters of the thermal processes due to the release of hydrochloric acid are reported in Table 3.

System 2 $SnCl_2$–LH_2. The thermal decomposition of these compounds occurs slowly from 100 to near 250°C and then quickly up to 450°C. At this temperature all the decomposition process is observed.

TABLE 3

Compound	Decomposition temperature (°C)	Reaction order	E_a (kJ mole^{-1})
$SnCl_2$-AH_2	210	1.3	96
$SnCl_2$-BH_2	215	1.3	88
$SnCl_2$-DH_2	225	1.3	135
$(SnCl_2)_2$-AH_2	175	0.5	105
$(SnCl_2)_2$-BH_2	175	0.5	131
$(SnCl_2)_2$-DH_2	180	0.5	119



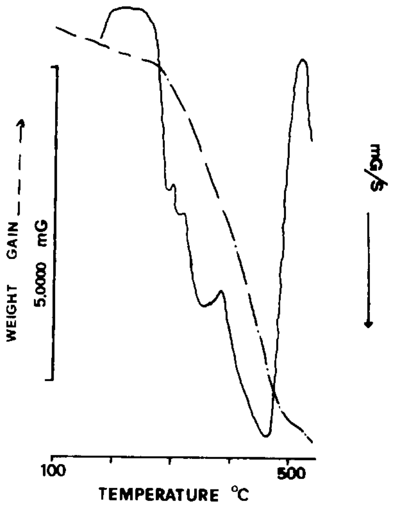


Fig. 3. Thermal decomposition of the adduct $[SnDH_2]SnCl_4$ (9.119 mg).

Fig. 4. Thermal decomposition of the adduct $[SnDH_2]Cl_2DH_2$ (12.023 mg).

The fast thermal decomposition is due to two simultaneous processes, as exhibited by the DTG curves: the first weight corresponds to the release of hydrochloric acid according to the reaction

$$(SnCl_2)_2LH_{2(s)} \rightarrow 2\,HCl_{(g)} - Sn_2LCl_{2(s)}$$

The second thermal decomposition is not stoichiometric, but considering the previously reported MS measurements [4], it is reasonable to assume that such decomposition is simultaneously due to the release of undecomposed $SnCl_2$ and to the formation of gaseous products obtained from the decomposition of the adduct.

Also, for these compounds the thermal decomposition processes observed at near 450°C are due only to a degradation of organic material residue from the previous decomposition. The thermal behaviour of the system 2 $SnCl_2$–DH_2 is reported in Fig. 3.

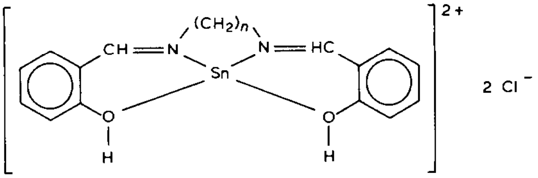
Kinetic parameters relative to the release of HCl are reported in Table 3.

System $SnCl_2$–2 LH_2. Even for these compounds the thermal decomposition starts at temperatures near 200°C, but the curve shows a single decomposition process in the temperature range 200–500°C. Due to the overlapping of the thermal decomposition processes of the $SnCl_2$–LH_2 and of the excess of the ligand, the evaluation of kinetic parameters is not significant.

The thermal behaviour of the system $SnCl_2$–2 DH_2 is reported in Fig. 4.

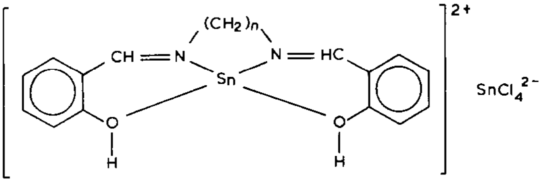
In conclusion, the kinetic data for the release of HCl from the adducts are in accordance with the enthalpic data of the solid–solid interactions.

For the 1 : 1 adducts the following structure can be hypothesized to explain the thermal decomposition mechanism described.



The greater thermal stability of the $[SnDH_2]Cl_2$ adduct with respect to the $[SnAH_2]Cl_2$ and $[SnBH_2]Cl_2$ adducts, as shown by the E_a values, indicates the importance of the length of the aliphatic chain bonded to the nitrogens.

The thermal decomposition mechanism suggests for the 2 : 1 adducts the structure



The reaction order of 0.7 found for both series of adducts indicates that the release of HCl is not simple and that chemical and physical processes take place simultaneously during the decomposition.

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REFERENCES

1 L. Abate and G. Siracusa. Thermochim. Acta, 29 (1979) 157.
2 G. Siracusa and L. Abate, Thermochim. Acta, 35 (1980) 207.
3 G. Siracusa and L. Abate, Thermochim. Acta, 47 (1981) 79.
4 F.A. Bottino, P. Finocchiaro, E. Libertini and A. Recca, J. Coord. Chem., in press.
5 G.E. Batley and D.P. Graddon, Aust. J. Chem., 20 (1967) 877; 20 (1967) 885.
6 C.D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
7 P. Murray and J. White, Trans. Br. Ceram. Soc., 54 (1955) 1951.
8 E.S. Freeman and B. Caroll, J. Phys. Chem., 62 (1958) 394.
9 E.S. Freeman and D.A. Anderson, J. Polym. Sci. 54 (1961) 253.
10 B. Durairaj and K. Venkatarao, Thermochim. Acta, 23 (1978) 109.
11 L. Abate, A. Chisari, R. Maggiore and G. Siracusa, Proc. 22nd ICCC, Budapest, 1982, p. 816.