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THERMAL INVESTIGATION OF SOME HETEROCYCLIC LIGAND COMPLEXES OF TIN(IV) IN THE SOLID STATE

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1,10-phenanthroline (phen), 2,2'-bipyridyl (bipy), pyridine (py) and 4-picoline (4-pic) complexes of dibutyltindichloride (Bu_2SnCl_2) and dimethyltindichloride (Me_2SnCl_2) were synthesized. The complexes were characterized with the help of elemental analyses, IR spectra and thermal analyses. The complexes were found to have the compositions [Bu_2SnCl_2·phen], [Bu_2SnCl_2·bipy], [Me_2SnCl_2·phen], [Me_2SnCl_2·bipy], [Me_2SnCl_2·2py] and [Me_2SnCl_2·2(4-pic)]·H_2O. All these complex compounds appeared to posses octahedral structures. Thermodynamic parameters, such as activation energy E_a^* enthalpy change ΔH and entropy change ΔS, for the dehydration and sublimation of the complexes were evaluated using some standard methods.

Introduction

Although studies on organotin complexes are well known in literature [1–6], works on thermal investigation and stereochemical changes in the solid state are still very less. The main aim of our work is to synthesize some compounds of the type $Me_2SnCl_2 \cdot 2L$ and $R_2SnCl_2 \cdot L'$, where $L =$ pyridine, 4-picoline and $L' =$ 1,10-phenanthroline, 2,2'-bipyridyl and $R =$ butyl, methyl group. All the compounds were characterized by elemental analyses and IR spectral measurements.

Thermal investigation (TG and DTA) has been carried out and some thermodynamic parameters such as activation energy E_a^*, enthalpy change

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ΔH, and entropy change ΔS for the dehydration step and sublimation of the complexes have been evaluated. The stabilities of the compounds have been compared with respect to activation energy.

Experimental

Materials and methods

Dibutyltindichloride and dimethyltindichloride were obtained from Aldrich Chemical Company, Inc. (USA) and were used as received. 1,10-phenanthroline, 2,2'-bipyridyl from LobaChemie Indo Austranal Company, Bombay, India, pyridine and 4-picoline from Fluka AG, Switzerland were used as received. Ethanol and diethyl ether were dried by using standard procedures [7].

Preparation of the complexes

For [Bu_2SnCl_2·phen] the ligand (ca. 6 mmol) in dry ethanol (25 cm^3) was added with constant stirring to a dry ethanolic solution (40 cm^3) containing dibutyltindichloride (ca. 6 mmol). The white lustrous precipitate was collected by filtration, washed carefully with dry diethyl ether, and dried over fused calcium chloride in a desiccator. Yield ca. 85%.

Other complexes [Bu_2SnCl_2·bipy], [Me_2SnCl_2·phen] [Me_2SnCl_2·bipy], [Me_2SnCl_2·2py] and [Me_2SnCl_2·2(4-pic)]·H_2O were prepared similarly.

Elemental analyses, thermal studies and IR spectral data

Carbon, hydrogen and nitrogen were estimated using Carlo Erba 1106 elemental analyser. The results of the elemental analyses are given in Table 1. Thermal investigations (TG and DTA) were carried out using a Shimadzu DT-30 thermal analyser in dynamic nitrogen at a heating rate of 10 deg·min^{-1} using α-alumina as a standard. The activation energy (E_a^*) was computed from the TG curve using the equation of Horowitz and Metzger [8] and from the DTA curves using that of Borchardt and Daniels [9]. The enthalpy change ΔH was evaluated from the DTA curve using the relation [9] $\Delta H = KA$, where K is the heat transfer coefficient (the calibration or cell constant, the cell used was a platinum crucible and its constant K was evaluated from the data obtained using indium metal as a calibrant) and A is the total area under the particular DTA peak measured using a compensating planimeter with an optical tracer of Fuji Corona 027. The entropy change ΔS was calculated using the relation [10] $\Delta S = \frac{\Delta H}{T_m}$ where T_m is the DTA peak temperature in K. IR and far-IR spectra were recorded using Perkin Elmer 781 and 783 models in KBr and polythene discs, respectively.

Table 1 Analytical data (calculated values in parentheses) of 1,10-phenanthroline(phen), 2,2'-bipyridyl (bipy), pyridine (py) and 4-picoline (4-pic) complexes of dibutyltindichloride (Bu_2SnCl_2) and dimethyltindichloride (Me_2SnCl_2)

No.	Complex	Colour	Analysis / %					
			Carbon		Hydrogen		Nitrogen	
1	[Bu_2SnCl_2·phen]	white	48.74	(49.63)	5.63	(5.41)	5.79	(5.79)
2	[Bu_2SnCl_2·bipy]	white	47.04	(47.00)	6.22	(5.70)	6.25	(6.09)
3	[Me_2SnCl_2·phen]	white	41.91	(42.05)	3.45	(3.53)	6.82	(7.01)
4	[Me_2SnCl_2·bipy]	white	38.32	(38.35)	3.77	(3.75)	7.13	(7.45)
5	[Me_2SnCl_2·2py]	white	38.00	(38.14)	4.01	(4.27)	7.71	(7.41)
6	[Me_2SnCl_2·2(4−pic)]·H_2O	white	39.52	(39.66)	4.90	(5.23)	6.29	(6.61)

Results and discussion

[Bu_2SnCl_2·phen] (1) and [Bu_2SnCl_2·bipy] (2)

Compounds (1) and (2) had been reported earlier [6]. We have characterized the compounds by elemental analyses (Table 1) and IR spectra (Table 2). Both compounds show octahedral structures. The IR spectral bands of complexes (1) and (2) at 588 and 633 cm^{-1}, respectively are assigned to an antisymmetric Sn–C stretching mode [2, 3]. The appearance of single Sn–C stretching band in both complexes (1) and (2), have shown that the two butyl groups are in trans positions in both complexes (1) and (2) [6]. Further, the cis-positions of the two chlorine atoms in both (1) and (2), have been confirmed by the appearance of Sn–Cl stretching bands for (1) at 210 and 225 cm^{-1}, and for (2) at 232 and 263 cm^{-1} [2, 3, 6, 11]. In case of (1), the bands at 385 and 413 cm^{-1} and for (2) bands at 417 and 435 cm^{-1} respectively are assigned to ν (Sn–N) frequencies.

Further, the weight loss in the TG curves of (1) and (2) (Fig. 1) in the ranges 180°–278°C and 125°–195°C respectively corresponds to the complete sublimation of the complexes without any stable or unstable intermediate. The DTA curve of (1) shows two endothermic peaks, one sharp peak at

194°C corresponds to the melting and another peak at 264°C for the complete sublimation.

Table 2 IR spectral data[a] (cm^{-1}) for some heterocyclic ligand complexes of Sn(IV)

No.	Complex[b]	ν (Sn–C)	ν_a (Sn–Cl)	ν_s (Sn–Cl)	ν (Sn–N)
1	[Bu_2SnCl_2·phen]	588 (vw)	225 (ms)	210 (ms)	385 (vw) 413 (w)
2	[Bu_2SnCl_2·bipy]	633 (w)	263 (vw)	232 (vw)	417 (vw) 435 (vw)
3	[Me_2SnCl_2·phen]	570 (w)	245 (ms)	240 (s)	408 (vw) 414 (sh)
4	[Me_2SnCl_2·bipy]	560 (w)	242 (ms)	235 (vs)	400 (vw) 416 (vw)
5	[Me_2SnCl_2·2py]	565 (ms)	244 (s)	204 (vs)	472 (vw) 427 (w)
6[c]	[Me_2SnCl_2·2(4–pic)]·H_2O	555 (ms)	248 (s)	238 (s)	484 (vs) 478 (vw)

[a] s, Strong, ms, medium strong, vs, very strong, sh, shoulder, w, weak, vw, very weak

[b] phen, 1,10-phenanthroline, bipy, 2,2'-bipyridyl, py, pyridine, 4-pic, 4-picoline

[c] Bands at 3500 cm^{-1} (br) and 1633 cm^{-1} (vs) indicate the presence of H_2O in the complex (6)

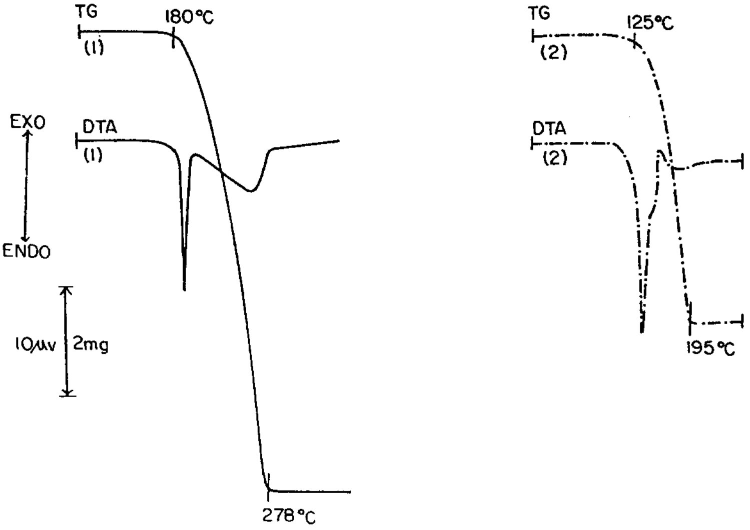

Fig. 1 TG and DTA curves of [Bu_2SnCl_2 · phen] (1) (——), sample mass 8.5 mg and [Bu_2SnCl_2·bipy] (2) (– · –), sample mass 5.2 mg

DTA curve of (2) shows one sharp peak at 175°C along with a shoulder which indicates that sublimation begins before the complete melting and another peak is observed at 214°C which appears for the sublimation of (2). Value of E_a^*, ΔH and ΔS for the complete sublimation of the complexes (1) and (2) are shown in Table 3. With respect to E_a^*, the stability of complex (1) is less than that of the complex (2). This may be due to the less basic character of nitrogen in phenanthroline than the nitrogen in bipyridyl because of the more involvement of the two lone pairs of electrons of the two nitrogen atoms in phenanthroline to maintain the more extended three aromatic sextets as compared to two aromatic sextets of bipyridyl.

[Me_2SnCl_2·phen] (3) and [Me_2SnCl_2·bipy] (4)

Compounds (3) and (4) have been reported earlier [3, 5, 6]. We have characterized the compounds by elemental analyses (Table 1) and IR spectra. The IR spectral bands of (3) and (4) at 570 and 560 cm^{-1} are assigned to an antisymmetric Sn–C stretching mode respectively [2, 3]. The appearance of a single Sn–C stretching band in the complexes (3) and (4) confirms that in both the complexes the two methyl groups are in trans position [4, 6]. The presence of two chlorine atoms in cis position is also confirmed by the appearance of two bands at 240 and 245 cm^{-1} for the complex (3) and at 235 and 242 cm^{-1} for the complex (4) (Table 2) [2, 3, 6, 11]. The ν (Sn–N) bands for the complex (3) appear at 408 and 414 cm^{-1}, and for the complex (4) appear at 400 and 416 cm^{-1} [1]. Further, the weight loss in the TG curves of (3) and (4) in the ranges 196°–308° and 143°–208°C along with the endothermic DTA peaks at 263° and 203°C respectively correspond to the complete sublimation of the complexes without any intermediate (Fig. 2). The values of E_a^*, ΔH and ΔS are given in Table 3.

With respect to E_a^*, complex (3) is less stable than complex (4) because of less basic character of phenanthroline than bipyridyl as explained earlier.

[Me_2SnCl_2·2py] (5) and [Me_2SnCl_2·2(4-pic)]·H_2O (6)

Complexes (5) and (6) have been reported earlier [3, 6]. Both complexes have been characterized by elemental analyses and IR spectra and found to be 1:2 adducts. The presence of lattice water in (6) has been confirmed by the appearance of IR bands at 3500 cm^{-1} (br) [ν(OH)] and 1633 cm^{-1} [δ (HOH)] (Table 3) [11]. Like that of complexes of (1) to (4), complexes (5) and (6) show two absorption bands at 565 and 555 cm^{-1} respectively which are assigned to Sn–C stretching frequencies [2, 3, 5] and indicate that the two methyl groups are in trans position in both the complexes (5) and (6)

Table 3 Thermal parameters of some heterocyclic ligand[a] complexes of Sn^{IV}

No.	Reactions	TG temp. range /	Melting point /	DTA peak temp. / °C	E_a^* / kJ mol^{-1}		Enthalpy change ΔH /	Entropy change ΔS /
		°C	°C	Endo	TG	DTA	kJ mol^{-1}	J K^{-1} mol^{-1}
1	[Bu_2SnCl_2 · phen] → Completely sublimes	180–275	194	264	111	126	41	76
2	[Bu_2SnCl_2 · bipy] → Completely sublimes	125–195	175	214	126	–	–	–
3	[Me_2SnCl_2 · phen] → Completely sublimes	196–308	–	263	133	113	133	247
4	[Me_2SnCl_2 · bipy] → Completely sublimes	143–208	–	203	155	130	91	192
5	[Me_2SnCl_2 · 2py] → Completely sublimes	72–147	–	135	105	112	126	310
6	[Me_2SnCl_2 · 2 (4–pic)] · H_2O → [Me_2SnCl_2 · 2 (4–pic)]	26– 46	–	40	–	–	–	–
	[Me_2SnCl_2 · 2 (4–pic)] → Completely sublimes	80–118	–	148	91	109	107	254

[a] phen, 1,10-phenanthroline; bipy, 2,2'-bipyridyl; py, pyridine; 4-pic, 4-picoline

[4, 6]. This cis positions of the chlorine atoms in (5) and (6) have been confirmed by the appearance of absorption bands at 204 and 244 cm^{-1} for (5) and at 238 and 248 cm^{-1} for (6) [2, 3, 6, 11]. The bands at 427 and 472 cm^{-1} for (5) and at 478 and 484 cm^{-1} for (6) correspond to ν (Sn–N) frequencies [1].

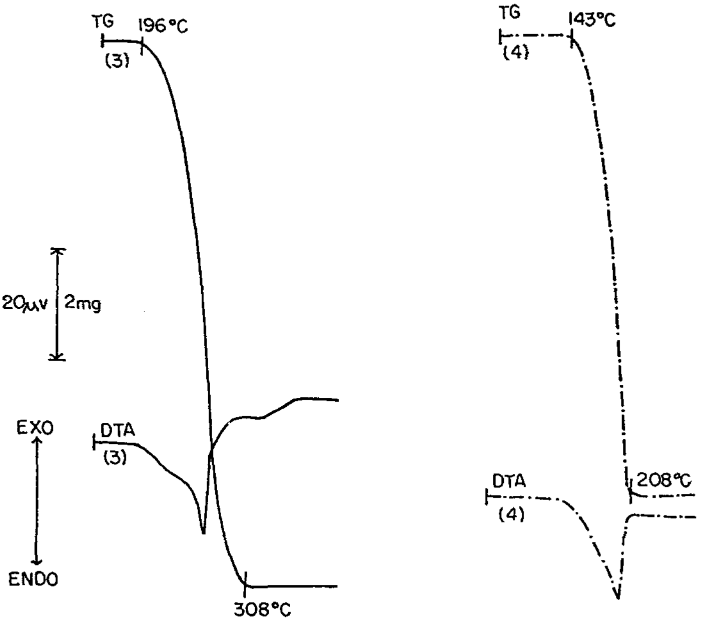

Fig. 2 TG and DTA curves of [Me_2SnCl_2 · phen] (3) (—), sample mass 10.0 mg and [Me_2SnCl_2 · bipy] (4) (— · —), sample mass 8.3 mg

Further, the weight loss in the TG curves of (5) and (6) in the ranges 72°–147°C and 80°–118°C correspond to the complete sublimation of (5) and (6) respectively without any intermediate (Fig. 3). But in case of complex (6), the weight loss in the temperature range 26°–46°C corresponds to one molecule of water. The corresponding DTA peak appears at 40°C and is endothermic in nature. The DTA curves of (5) and (6) show two endothermic peaks at 135° and 148°C respectively. Melting points of (5) and (6) cannot be separately detected in DTA curves as they merge with the peaks of sublimation. The values of E_a^*, ΔH and ΔS are given in Table 3. With respect to E_a^*, [$Me_2SnCl_2 \cdot 2(4\text{-pic})$] is less stable than (5) and this may be attributed to the more steric effect caused by the methyl group of 4-picoline in the complex (6).

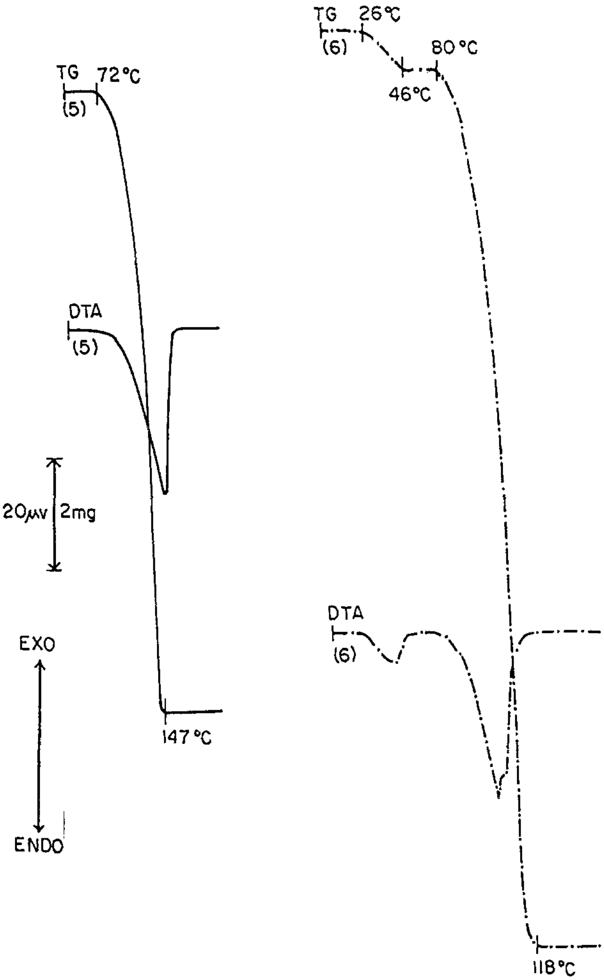

Fig. 3 TG and DTA curves of [$Me_2SnCl_2 \cdot 2py$] (5) (——), sample mass 11,2 mg and [$Me_2SnCl_2 \cdot 2(4-pic)$]$\cdot H_2O$ (6) (– · –), sample mass 16.6 mg

A linear correlation is obtained on plotting E_a^* *vs.* ΔS. This shows that a system with a higher entropy change will require less energy E_a^* for its sublimation [10].

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References

1 V. G. Kumar Das, N. G. Seik Weng and P. J. Smith, Inorg. Chim. Acta, 49 (1981) 149.
2 J. C. Trehan, R. K. Sharma and C. P. Sharma, Polyhedron, 5 (1986) 1227.
3 (Miss) J. P. Clark and C. J. Wilkins, J. Chem. Soc. (A), (1966) 871.
4 R. Vishalakshi, V. K. Jain, S. K. Kulshreshtha and G. S. Rao, Inorg. Chim. Acta, 118 (1986) 119.
5 I. R. Beattie and G. P. McQuillan, J. Chem. Soc. (A), (1963) 1519.
6 Y. Farhangi and D. P. Graddon, J. Organometal. Chem., 87 (1975) 67.
7 A. I. Vogel, A Text Book of Practical Organic Chemistry, 4th edn., ELBS and Longman, London 1980, pp. 269 and 272.
8 H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
9 H. J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
10 S. Mitra and L. K. Singh, J. Chem. Soc., Dalton Trans., (1987) 2089.
11 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn., Wiley Interscience, New York 1978, pp. 227 and 273.

Zusammenfassung — Es wurden 1,10-Phenanthrolin- (Phen), 2,2'-Bipyridyl- (Bipy), Pyridin- (Py) und 4-Picolin- (4-Pic) Komplexe von Dibutylzinndichlorid (Bu_2SnCl_2) und Dimethylzinndichlorid (Me_2SnCl_2) hergestellt. Die Komplexe wurden mittels Elementaranalyse, IR-Spektroskopie und Thermoanalyse charakterisiert. Die ermittelte Zusammensetzung der Komplexe war [$Bu_2SnCl_2 \cdot$Phen], [$Bu_2SnCl_2 \cdot$Bipy], [$Me_2SnCl_2 \cdot$Phen], [$Me_2SnCl_2 \cdot$Bipy], [$Me_2SnCl_2 \cdot 2$Py] und [$Me_2SnCl_2 \cdot 2$(4-Pic)]$\cdot H_2O$. All diese Verbindungen scheinen eine oktaedrische Struktur zu besitzen. Unter Anwendung einiger Standardmethoden wurden für die Dehydratation und die Sublimation der Komplexe einige thermodynamische Parameter, wie z.B. die Aktivierungsenergie E_a, die Enthalpieänderung ΔH und die Entropieänderung ΔS ermittelt.