Synthetic, Spectral and Thermal Studies of Tin(IV) Complexes of 1, 5-Benzodiazepines

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Received 12 October 2007; Accepted 22 December 2007

Abstract: Tin(IV) complexes of 7-substituted 6,7-benzo-1,5-diazepines have been synthesized in absolute alcoholic medium. Elemental analysis indicates that the complexes have 1:2 stoichiometry of the type L_2SnCl_4 . TGA data support this conclusion. Molar conductance values in DMF at 10^{-3} M suggest that, these complexes are non-electrolytes. Infrared spectral data shows the involvement of C=N and NH groups in coordination with the metal ion. X-ray diffraction pattern of few representative complexes indicate that, these are having simple cubic crystal structure. The energy of activation and order of reaction are calculated using TGA data of the complexes. All these information support that Sn(IV) in these complexes exhibits coordination number eight.

Keywords: Thermal studies, Benzodiazepines, Electronic spectra.

Introduction

Tin is a toxic metal¹. The effective antidotes tried to remove toxic metals from human body involves chelating agents^{1,2}. Benzodiazepines are well known for their complexing capabilities³⁻⁷. A few transition metal complexes of 1,4-benzodiazepines have been reported¹⁻⁴ hitherto. We have reported a few transition metal complexes of 1,5-benzodiazepines^{8,9}(DMBDA). There is no report on the synthesis and characterization of tin^{IV} complexes of benzodiazepines. In this paper we report the synthesis, characterization and thermal studies of Tin(IV) complexes with the following benzodiazepines.

(I)

I	a	b	c	d	e	f	g	h
R ₁	H	CH ₃	Cl	NO ₂	H	CH ₃	Cl	NO ₂
R ₂	CH ₃	CH ₃	CH ₃	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅

Experimental

Materials and methods

The chemicals used to prepare the ligands were of reagent grade. Substituted DMBDA were prepared using Thiele and Stimmig method⁹. Tin(IV) chloride from E-Merck was used without further purification.

Preparation of the complexes

To a solution of 0.01 M of the ligand in 25 mL dry ethyl alcohol was added with 0.005 M Tin(IV) chloride with constant stirring. The reaction mixture was stirred for half an hour and the complex separated was filtered, washed with ethyl alcohol and ether and dried over fused calcium chloride. The dried complex was powdered and purified by extracting in Soxhlet thimble using dry ethyl alcohol.

Elemental analysis

Tin(IV) and chloride in the complexes were estimated gravimetrically¹⁰. The nitrogen was determined by Dumas method¹⁰.

Physical measurements

The molar conductance measurements at the complexes were made on Elico CL-24 Conductivity Bridge with cell of cell constant 0.1. The infrared spectra of the ligands and their complexes were recorded on a Hitachi 290 spectrophotometer in the region 4000-250 cm⁻¹. The electronic spectra were taken with a Shimadzu UV-160A spectrophotometer and X-ray diffraction on PW1820 diffractometer with Cu LEF 40KV, 30mA X-ray tube in the 'd' value range of 1.5406 – 14.7184.

Results and Discussion

The elemental analysis (Table 1) conforms to the formation of 1:2 complexes of the type Cl₄Sn(DMBDA)₂. The molar conductance values of the complexes (Table 2) in DMF at 10⁻³ M concentration are too low to account for any dissociation. Hence, these complexes are regarded as non-electrolytes in DMF.

IR spectra

Important infrared frequencies of the ligands, complexes and their assignments are set out in Table 3 & 4. In the IR spectra of ligands, a broad band of medium intensity around 3350 cm⁻¹ has been assigned to ν(NH) vibrations in view of the previous reports¹¹. A high intensity band at 1580 cm⁻¹ and bands in the 1225-960 and 750-650 cm⁻¹ regions have been assigned to ν(C=N), aromatic inplane and outplane vibrations respectively on analogy with previous assignments¹¹⁻¹⁵.

Table 1. Analytical data of complexes

Complex	Empirical formula	% Analysis, Found/ (Calcd.)			
		Nitrogen	Carbon	Chlorine	Tin
(Ia) ₂ SnCl ₄	(C ₁₁ H ₁₂ N ₂) ₂ SnCl ₄	9.29	43.01	24.51	19.50
		(9.30)	(43.00)	(24.80)	(19.30)
(Ib) ₂ SnCl ₄	(C ₁₂ H ₁₃ N ₂) ₂ SnCl ₄	8.86	45.87	22.87	18.67
		(8.90)	(46.00)	(23.00)	(18.90)
(Ic) ₂ SnCl ₄	(C ₁₁ H ₁₁ N ₂ Cl) ₂ SnCl ₄	8.32	39.40	42.71	17.00
		(8.00)	(40.60)	(42.90)	(16.90)
(Id) ₂ SnCl ₄	(C ₁₁ H ₁₁ N ₃ O ₂) ₂ SnCl ₄	12.10	38.04	20.46	17.00
		(12.20)	(38.40)	(20.80)	(16.80)
(Ie) ₂ SnCl ₄	(C ₁₆ H ₁₄ N ₂) ₂ SnCl ₄	7.69	52.55	19.61	16.19
		(7.80)	(52.40)	(19.90)	(16.20)
(If) ₂ SnCl ₄	(C ₁₇ H ₁₆ N ₂) ₂ SnCl ₄	7.41	53.97	18.78	15.61
		(7.40)	(54.00)	(19.00)	(15.40)
(Ig) ₂ SnCl ₄	(C ₁₆ H ₁₃ N ₂ Cl) ₂ SnCl ₄	7.03	48.18	35.63	14.80
		(7.00)	(48.40)	(35.90)	(14.50)
(Ih) ₂ SnCl ₄	(C ₁₆ H ₁₃ N ₃ O ₂) ₂ SnCl ₄	10.27	46.94	17.36	14.42
		(10.30)	(46.80)	(17.50)	(14.40)

Table 2. Molar extinction coefficient data of complexes

Complex	Empirical formula	$\lambda_{\max}$, cm ⁻¹	Molar extinction coefficient(ϵ), L.mol ⁻¹ .cm ⁻¹
(Ia) ₂ SnCl ₄	(C ₁₁ H ₁₂ N ₂) ₂ SnCl ₄	16129	518
		17241	891
		19120	1223
		30675	1583
(Ib) ₂ SnCl ₄	(C ₁₂ H ₁₄ N ₂) ₂ SnCl ₄	15873	418
		19157	1094
		20325	1690
		15385	300
(Ic) ₂ SnCl ₄	(C ₁₁ H ₁₁ N ₂ Cl) ₂ SnCl ₄	16260	450
		19231	780
		28571	2520
		15152	218
(Id) ₂ SnCl ₄	(C ₁₁ H ₁₁ N ₃ O ₂) ₂ SnCl ₄	16393	420
		19380	740
		28011	2458
		16129	600
(Ie) ₂ SnCl ₄	(C ₁₆ H ₁₄ N ₂) ₂ SnCl ₄	19231	1323
		30303	1652
(If) ₂ SnCl ₄	(C ₁₇ H ₁₆ N ₂) ₂ SnCl ₄	19120	188
		31546	244
(Ig) ₂ SnCl ₄	(C ₁₆ H ₁₃ N ₂ Cl) ₂ SnCl ₄	16120	547
		19157	1025
		30120	2500
		16393	523
(Ih) ₂ SnCl ₄	(C ₁₆ H ₁₃ N ₃ O ₂) ₂ SnCl ₄	19608	815
		29412	2580

Table 3. Important infrared frequencies of ligands and their assignments

S. No.	Ligand	$\nu(\text{NH})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$ Aromatic
01	Ia	3500b 3350b	3050s 2980s	1650s	1630m	1570m 1540sh 1520s 1580m
02	Ib	3500b 3400b	3050s 2980s	1660m	1640m	1540sh 1520s 1580m
03	Ic	3500b 3400b	3040s 2980s	1660m	1640m	1520s 1580m
04	Id	3500b 3350b 3450b	3000s 2980s	1660s	1620m	1560sh 1520s 1570s
05	Ie	3500b 3400b 3350b	3050s 2980s	1650s	1630m	1540s 1520s 1580m
06	If	3500b 3400b	3050s 2980s	1660s	1640m	1520s 1540s
07	Ig	3500b 3450b	3040s 2980s	1660s	1640s	1570m 1520s
08	Ih	3500b 3450b	3000s 2980s	1660s	1620m	1580m 1560w 1520s

b = broad, s = sharp, m = medium, sh = shoulder, w = weak

Table 4. Important infrared frequencies of few representative complexes and their assignments.

Complex	$\nu(\text{NH})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$ Aromatic	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$
(Ia) ₂ SnCl ₄	3320s 3250m	1630s	1600s	1570s 1510s	570w 530w 505w 480w 460w 580s 540w	300sh 285sh
(Ib) ₂ SnCl ₄	3270s 3200w	1610s	1600s	1560sh 1540sh	520w 580w 470s 450s 580s 560w	300s 290s
(Ic) ₂ SnCl ₄	3250b 3150bw	1620s	1685sh	1680s 1560w	500w 480s 430s 580s 575w	300s 290s
(Ih) ₂ SnCl ₄	3200bw 3100bw	1520sh	1590s	1580s 1500s	480s 475s 425s	300s 290s

b = broad, s = sharp, m = medium, sh = shoulder, w = weak

In the infrared spectra of complexes the following changes are observed. The band due to $\nu(\text{NH})$ shifts and appears in the region $3320\text{--}3100\text{ cm}^{-1}$ as a medium intensity split band. Coordination of $-\text{NH}$ group to the metal increases the multiplicity associated with nitrogen and thus results in splitting and shifting of the band¹³. In the present context the NH vibration show a low frequency shift compared with the ligands. The $\nu(\text{C}=\text{N})$ band appears in the region $1570\text{--}1600\text{ cm}^{-1}$ as high intensity band indicating that, the $\text{C}=\text{N}$ group is involved in coordination with tin^{IV} through nitrogen. Coordination of these groups to the metal ion leaves the nitrogen atom partially positively charged, resulting in mobilising π electron density associated with $\text{C}=\text{C}$ consequently affecting the bond order. As a result of this $\nu(\text{C}=\text{C})$ appears around 1640 cm^{-1} as a band of varying intensity.

In addition to these changes, we observe medium intensity bands in the region $570\text{--}425\text{ cm}^{-1}$ attributable to $\nu(\text{Sn-N})$ vibrations coupled with $\nu(\text{ligand})$ vibration. The bands appearing in the region $470\text{--}425\text{ cm}^{-1}$ are regarded as due to $\nu(\text{Sn-N})$ vibrations. The medium intensity bands in the region $285\text{--}300\text{ cm}^{-1}$ are assigned to $\nu(\text{Sn-Cl})$ vibrations. The assignments made in these regions are purely tentative and based on the previous reports^{5-7, 15}.

Electronic spectra

The electronic spectra were taken in DMF at 10^{-3} M concentration. The spectra are characterized by two bands in the region $20,000\text{--}33,333\text{ cm}^{-1}$ and are attributed to $\pi\text{--}\pi$ transitions¹⁶. In the spectra of complexes, the ligand bands are replaced by high intensity broad bands. In addition to the usual bands of the ligands, the high intensity band is observed around $29,411\text{ cm}^{-1}$ and attributed to metal-ligand charge transfer band¹⁶. Appearance of this band confirms the formation of complexes.

X-ray (powder) diffraction

The powder diffraction of selected complexes have been indexed for simple cubic systems and the observed $\sin^2\theta$, d-values together with h, k, l and 'a' values are set out in Table 5. The values obtained for unit cell parameters a, b and c remain almost constant indicating viz., $a = b = c$. This is the condition for simple cubic system.

Thermal studies

Thermograms obtained for a few complexes have been recorded and the data are summarized in Table 6. The thermogram for complex Ig shows four breaks. A gradual loss in the weight is observed from $255\text{--}325^\circ\text{C}$ and the loss is about 8.59%. This computes to the loss of two of the four chlorides. The second weight loss is observed from $325\text{--}350^\circ\text{C}$ and the per cent of weight loss is 8.59 which corresponds to the elimination of remaining two chlorides. Further, a steep decrease in the weight of 35.17% in the temperature range of $350\text{--}430^\circ\text{C}$ is attributed to the oxidation of the ligand moiety. After this temperature there is no weight loss, as the formed species is thermally stable. The weight calculations agree well with the formation of SnO_2 .

Table 5. X-ray (powder) diffraction data

Complex	d	$\sin^2\theta$	N	hkl	a	Crystal structure
$(\text{Ig})_2\text{SnCl}_4$	5.71	0.135	2	110	8.075	Simple cubic
	3.95	0.197	4	200	7.900	
	3.40	0.227	5	210	7.600	
	3.15	0.248	6	211	7.710	

Table 6. Thermo gravimetric data of complexes

Complex	Temp. °K	Loss in weight		E ⁰ K. Cal	Order of Reaction	Inference
		Found	Calculated			
(Ia) ₂ SnCl ₄	623	12.07	11.75	34	2.2	Loss due to Cl ₂
	673	12.07	11.75			Loss due to another Cl ₂
	798	27.45	28.48			Loss due to ligand
	998	14.94	15.37			Loss due to sublimation of SnO ₂
(Ig) ₂ SnCl ₄	598	8.59	8.91	23	1.2	Loss due to Cl ₂
	618	8.59	8.91			Loss due to another Cl ₂
	703	33.59	33.69			Loss due to ligand
	996	12.19	11.65			Loss due to sublimation of SnO ₂

The complex Ia lost the weight between 100° and 235°C. The weight loss is gradual. In 235°-350°C range the complex shows the steep decrease in the weight. This is due to the elimination of two chlorides. The other two chlorides are eliminated between 350-400°C and the oxidation of the ligand in 400-560°C with the formation of SnO₂. The percentage loss of weight is in accordance with the suggested empirical formula of the complexes.

The Freeman and Corroll¹⁷ equation has been deployed to evaluate order of reaction and energy of activation from thermograms.

A plot of $\frac{\Delta \log dw/dt}{\Delta \log W_r}$ vs $\frac{\Delta(T^{-1})}{\Delta \log W_r}$ gives a straight line with a slope $\pm E^*/2.303 R$

and intercept is $-x$.

Where, W = weight loss up to time t, W_r = (W_c-W) difference of weight loss between completing of reaction up to time t, E = energy of activation, X = order of reaction and T = absolute temperature.

The dw and W_r for the purpose of plot can be directly determined from thermograms. Intercepts directly gives order of reaction, and using R gas constant, slope can be calculated. The values of order of reaction and energy of activation are shown in Table 5. The high values of energy of activation obtained for these complexes are suggestive of their stability.

On the basis of elemental analysis, spectral and thermal studies the following structure may be assigned to the Cl₄Sn(DMBDA)₂:

Acknowledgement

The authors are thankful to Dr. Yashwanth Bhupal, Principal, Bellary Engineering Collage, Bellary and the President of HKE'S Society and Principal, PDA Collage of Engineering, Gulbarga for the constant encouragement.

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