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

SURESH[#], PADAKI SRINIVAS[‡], T. SURESH[†],
M. REVANASIDDAPPA[*§] and SYED KHASIM[¶]

[#]Department of Applied Science and Biotechnology,
Bellary Engineering College, Bellary – 583 104, Karnataka, India.

[‡]Department of Chemistry, P.D.A. College of Engineering,
Gulbarga – 585 102, Karnataka, India.

[†]Department of Industrial Chemistry, Gulbarga University Post Graduate Centre,
Vinayaka Nagar, Cantonment, Bellary- 583 104, Karnataka, India.

[§]Department of Chemistry, [¶]Department of Physics,
PES School of Engineering,Hosur Road, Bangalore- 560 100 Karnataka, India.
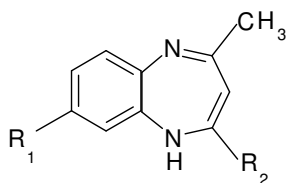
revum@rediffmail.com

Abstract: Tin(IV) complexes of 7-substituted 6,7-benzo-1,5-dizepines 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 metal[1]. The effective antidotes tried to remove toxic metals from human body involves chelating agents[1,2]. Benzodiazepines are well known for their complexing capabilities[3-7]. A few transition metal complexes of 1,4-benzodiazepines have been reported[1-4] 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_6H_5	C_6H_5	C_6H_5	C_6H_5

Experimental

Materials and methods

The chemicals used to prepare the ligands were of reagent grade. Substituted DMBDA were prepared using Thiele and Stimmig method[9]. 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 gravimetrically[10]. The nitrogen was determined by Dumas method[10].

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 o 1.5406 – 14.7184.

Results and Discussion

The elemental analysis (Table 1) conforms to the formation of 1:2 complexes of the type $Cl_4Sn(DMBDA)_2$. 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 $\nu(NH)$ vibrations in view of the previous reports[11]. A high intensity band at 1580 cm^{-1} and bands in the 1225-960 and 750-650 cm^{-1} regions have been assigned to $\nu(C=N)$, aromatic inplane and outplane vibrations respectively on analogy with previous assignments[11-15].

Table 1. Analytical data of complexes

Complex	Empirical formula	% Analysis, Found/ (Calcd.)			
		Nitrogen	Carbon	Chlorine	Tin
$(Ia)_2SnCl_4$	$(C_{11}H_{12}N_2)_2\ SnCl_4$	9.29 (9.30)	43.01 (43.00)	24.51 (24.80)	19.50 (19.30)
$(Ib)_2SnCl_4$	$(C_{12}H_{13}N_2)_2\ SnCl_4$	8.86 (8.90)	45.87 (46.00)	22.87 (23.00)	18.67 (18.90)
$(Ic)_2SnCl_4$	$(C_{11}H_{11}N_2Cl)_2\ SnCl_4$	8.32 (8.00)	39.40 (40.60)	42.71 (42.90)	17.00 (16.90)
$(Id)_2SnCl_4$	$(C_{11}H_{11}N_3O_2)_2\ SnCl_4$	12.10 (12.20)	38.04 (38.40)	20.46 (20.80)	17.00 (16.80)
$(Ie)_2SnCl_4$	$(C_{16}H_{14}N_2)_2\ SnCl_4$	7.69 (7.80)	52.55 (52.40)	19.61 (19.90)	16.19 (16.20)
$(If)_2SnCl_4$	$(C_{17}H_{16}N_2)_2\ SnCl_4$	7.41 (7.40)	53.97 (54.00)	18.78 (19.00)	15.61 (15.40)
$(Ig)_2SnCl_4$	$(C_{16}H_{13}N_2Cl)_2\ SnCl_4$	7.03 (7.00)	48.18 (48.40)	35.63 (35.90)	14.80 (14.50)
$(Ih)_2SnCl_4$	$(C_{16}H_{13}N_3O_2)_2\ SnCl_4$	10.27 (10.30)	46.94 (46.80)	17.36 (17.50)	14.42 (14.40)

Table 2. Molar extinction coefficient data of complexes

Complex	Empirical formula	λ_{max}, cm^{-1}	Molar extinction coefficient(ε), $L.mol^{-1}.cm^{-1}$
$(Ia)_2SnCl_4$	$(C_{11}H_{12}N_2)_2\ SnCl_4$	16129	518
		17241	891
		19120	1223
		30675	1583
$(Ib)_2SnCl_4$	$(C_{12}H_{14}N_2)_2\ SnCl_4$	15873	418
		19157	1094
		20325	1690
$(Ic)_2SnCl_4$	$(C_{11}H_{11}N_2Cl)_2\ SnCl_4$	15385	300
		16260	450
		19231	780
		28571	2520
$(Id)_2SnCl_4$	$(C_{11}H_{11}N_3O_2)_2\ SnCl_4$	15152	218
		16393	420
		19380	740
		28011	2458
$(Ie)_2SnCl_4$	$(C_{16}H_{14}N_2)_2\ SnCl_4$	16129	600
		19231	1323
		30303	1652
$(If)_2SnCl_4$	$(C_{17}H_{16}N_2)_2\ SnCl_4$	19120	188
		31546	244
$(Ig)_2SnCl_4$	$(C_{16}H_{13}N_2Cl)_2\ SnCl_4$	16120	547
		19157	1025
		30120	2500
$(Ih)_2SnCl_4$	$(C_{16}H_{13}N_3O_2)_2SnCl_4$	16393	523
		19608	815
		29412	2580

Table 3. Important infrared frequencies of ligands and their assignments

S. No.	Ligand	v(NH)	v(NH)	v(C=C)	v(C=N)	v(C=C) Aromatic
01	Ia	3500b 3350b	3050s 2980s	1650s	1630m	1570m 1540sh 1520s
02	Ib	3500b 3400b	3050s 2980s	1660m	1640m	1580m 1540sh 1520s
03	Ic	3500b 3400b	3040s 2980s	1660m	1640m	1580m 1520s
04	Id	3500b 3350b 3450b	3000s 2980s	1660s	1620m	1580m 1560sh 1520s
05	Ie	3500b 3400b 3350b	3050s 2980s	1650s	1630m	1570s 1540s 1520s
06	If	3500b 3400b	3050s 2980s	1660s	1640m	1580m 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	v(NH)	v(C=C)	v(C=N)	v(C=C) Aromatic	v(M-N)	v(M-Cl)
(Ia)$_2$SnCl$_4$	3320s 3250m	1630s	1600s	1570s 1510s	570w 530w 505w 480w 460w	300sh 285sh
(Ib)$_2$SnCl$_4$	3270s 3200w	1610s	1600s	1560sh 1540sh	580s 540w 520w 580w 470s 450s	300s 290s
(Ic)$_2$SnCl$_4$	3250b 3150bw	1620s	1685sh	1680s 1560w	580s 560w 500w 480s 430s	300s 290s
(Ih)$_2$SnCl$_4$	3200bw 3100bw	1520sh	1590s	1580s 1500s	580s 575w 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 ν(NH) shifts and appears in the region 3320-3100 cm^{-1} as a medium intensity split band. Coordination of –NH group to the metal increases the multiplicity associated with nitrogen and thus results in splitting and shifting of the band[13]. In the present context the NH vibration show a low frequency shift compared with the ligands. The ν(C=N) band appears in the region 1570-1600 cm^{-1} as high intensity band indicating that, the C=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 mobolising π electron density associated with C=C consequently affecting the bond order. As a result of this ν(C=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 570-425 cm^{-1} attributable to ν(Sn-N) vibrations coupled with ν(ligand) vibration. The bands appearing in the region 470-425 cm^{-1} are regarded as due to ν(Sn-N) vibrations. The medium intensity bands in the region 285-300 cm^{-1} are assigned to ν(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 20,000-33,333 cm^{-1} and are attributed to π-π transitions[16]. 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 cm^{-1} and attributed to metal-ligand charge transfer band[16]. 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 255-325°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 325-350°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 350-430°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
$(Ig)_2SnCl_4$	5.71 3.95 3.40 3.15	0.135 0.197 0.227 0.248	2 4 5 6	110 200 210 211	8.075 7.900 7.600 7.710	Simple cubic

Table 6. Thermo gravimetric data of complexes

Complex	Temp. °K	Loss in weight		E⁰ K. Cal	Order of Reaction	Inference
		Found	Calculated			
(Ia)₂SnCl₄	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)₂SnCl₄	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 SnO_2. The percentage loss of weight is in accordance with the suggested empirical formula of the complexes.

The Freeman and Corroll[17] equation has been deployed to evaluate order of reaction and energy of activation from thermograms.

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

and intercept is –x.

Where, W = weight loss up to time t, Wr = (Wc-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 Wr 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 $Cl_4Sn(DMBDA)_2$:
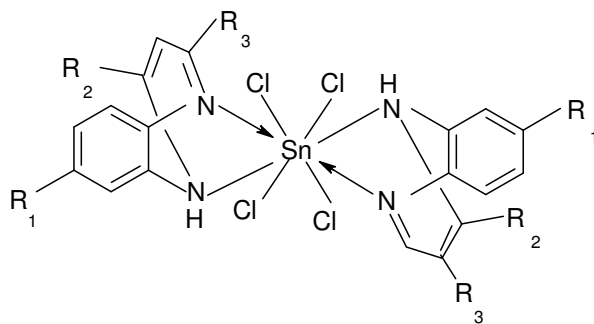
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