COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Series B : Chimie

TOME : 31 ANNÉE : 1985

SYNTHESIS AND CHARACTERIZATION OF SOME TIN (II) COMPLEXES

By

M. A. WASSEF, W. S. HEGAZI and S. A. HUSSEIN

Faculté des Sciences de l'Université d'Ankara
Ankara. Turquie

Communications de la Faculte des Sciences
de l'Université d'Ankara

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SYNTHESIS AND CHARACTERIZATION OF SOME TIN (II) COMPLEXES

By

M. A. WASSEF, W. S. HEGAZI and S. A. HUSSEIN

Department of Chemistry, University College for Women, Ain Shams University, Heliopolis, Cairo, Egypt.

(Received November 23, 1984 and accepted April 2, 1985)

The reactions of Tin (II) chloride with a number of nitrogen and oxygen organic ligands in nonaqueous solvent are reported. Complexes were prepared with dimethyl-o-phenanthroline, tripyridyl dimethyl bipyridyl, pyrazine, hexamine, dimethyl hydrazine, benzotriazole, 3-picoline, methyl pyridine-1-oxide and alizarine-red-S. Adducts obtained from the reactions with diphenylphosphino methane, diphenylphosphino ethane and triphenyl phosphine indicate that the ligands were oxidized, and coordination occured through the oxygen atom. No products were obtained on using xanthone and xanthene as ligands and the compounds were recovered unchanged. Structural aspects of the compounds are discussed.

INTRODUCTION

Stannous chloride dissolves readily in numerous nonaqueous solvents, among these are methanol, ethanol, tetrahydrofuran and ethyl acetate. Compounds of different types can then be isolated from or prepared with the aid of these solutions.

Study on the field of coordination chemistry of Tin (IV)-halides[1-3] and their derivatives [4-6] is well explored; but that of Tin (II) halides has been generally neglected[7]. Few complexes with Tin (II) are reported[8]. Hayakawa and Rheinboldt[10] obtained complexes with diethyl ether and 1,4-dioxane. Stable complexes with bases such as amines are also reported[11].

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*Present address: University of Sokoto, NIGERIA, Faculty of Science Department of Chemistry.

EXPERIMENTAL

Starting materials:

Reagent grade Tin (II) chloride dihydrate (Mn and B), was dehydrated by reaction with acetic anhydride and stored[12]. Solvents were dried by conventional methods[13]. Benzotriazole, m.p. 99°C, (H and W), pyrazine, m.p. 51°C (Merck), methyl pyridine-oxide (Merck), dimethyl hydrazine (K and L), xanthone m.p. 175°C, and xanthane, m.p. 101°C (Aldrich), all are analytical grade reagents and were used without any further purification. The methods. used for purifying the other organic ligands were as mentioned before[14,15].

Analysis:

Microanalysis of carbon and hydrogen were carried out by the Microanalytical Laboratory of the Centre of Research, El Dokky-Cairo, Egypt. Tin was determined as the oxide after careful evapotation with sulphuric acid and then ignited at 850°C[16].

Infrared spectra were measured in the region 4000—400 cm^{-1}, using Nujol or KBr disks, with a Perkin-Elmer spectrophotometer model 398. VIS and UV spectra were recorded, using 1 cm quartz cells, on Perkin-Elmer spectrophotometer model 555.

Molecular weight determinations, conductivities and thermogravimetric analysis were carried out using a Staton thermogravimetric balance.

Synthesis of the complexes:

Tin (II) chloride (10 mmole), dissolved in 25 ml ethyl acetate, was added to a solution of the organic ligand (10 mmole) in the same solvent. The compound precipitated after brief, vigorous stirring, was filtered, washed several times with the same solvent and then dried under vacuum. Recrystallization was performed for those complexes which are soluble in organic solvents without chemical change. Variation of the mole ratio of the reactants from 2:1 to 1:2 had no effect on the products. Yields, m.ps. and analytical data for the products obtained are given in Table (1).

RESULTS AND DISCUSSION

Attempted recrystallization from acetonitrile, in air, of the adducts obtained from the reactions of bis (diphenyl phosphino) methane and

Table 1

Compound	Yield (%)	M.p (°C)	Required (%)			Formula	Found (%)		
			C	H	Sn		C	H*	Sn
1– $SnCl_2$, tripy, $6H_2O$	90	250	33.9	4.3	22.3	$C_{15}H_{23}Cl_2N_3O_6Sn$	34.1	3.5	22.4
2– $SnCl_2$, DM-bipy, $3H_2O$	92	250	33.7	4.3	27.7	$C_{12}H_{18}Cl_2N_2O_3Sn$	34.1	4.8	28.0
3– $SnCl_{28}$, DM-o-phen, $6H_2O$	80	250	33.2	4.8	23.4	$C_{14}H_{24}Cl_2N_2O_6Sn$	33.2	4.7	23.4
4– $SnCl_2$, 1.5 pyrazine, $6H_2O$	89	250	17.2	4.3		$C_6H_{18}Cl_2N_3O_6Sn$	17.6	3.1	
5– $2SnCl_2$, hexamine, $4H_2O$	89	230	12.2	3.4		$C_6H_{20}Cl_4N_4O_4Sn_2$	12.3	4.3	
6– $SnCl_2$, 1.5 DM-hydrazine, $2H_2O$	86	250	11.4	5.1		$C_3H_{16}Cl_2N_3O_2Sn$	11.5	3.2	
7– $SnCl_2$, 3-picoline, $2H_2O$	79	270	22.6	3.5		$C_6H_{11}Cl_2NO_2Sn$	22.5	2.7	
8– $SnCl_2$, Benzotriazole, $2H_2O$	83	270	20.9	2.6		$C_6H_9Cl_2N_3O_2Sn$	22.8	2.6	
9– $SnCl_2$, $\varnothing_3PO$, $4H_2O$	88	250	52.8	4.7		$C_{36}H_{38}Cl_2P_2O_6Sn$	52.1	4.4	
10– $SnCl_2$, Diphos-ethane oxide, $3H_2O$	80	250	46.3	4.4	17.6	$C_{26}H_{30}Cl_2O_5P_2Sn$	46.4	3.5	17.4
11– $SnCl_2$, Diphos-methane oxide, $6H_2O$	70	250	42.0	4.8	16.6	$C_{25}H_{34}Cl_2O_8P_2Sn$	41.7	4.3	16.8
12– $(MePh_3P)_2SnCl_6$	78	250	51.5	4.1	13.4	$C_{38}H_{36}Cl_6P_2Sn$	52.0	4.6	13.5
13– $SnCl_2$, 2-Me-py-1-oxide, $2H_2O$	91	250	21.5	3.3		$C_6H_{11}Cl_2NO_3Sn$	21.5	3.5	
14– $SnCl_2$,Alizarine-Red-S-$3H_2O$	72	250	26.3	3.0		$C_{14}H_{19}Cl_2O_{13}NaSSn$	26.7	2.2	

* The difference observed in the analytical results of hydrogen is due to its low atomic mass compared with the molecular mass of the adducts.

-ethane and triphenyl phosphine gave the oxidized products: $SnCl_2$. Diphos methane dioxide, $6H_20$, $SnCl_2$. Diphos ethane dioxide, $3H_2O$ and $SnCl_2.2Ph_3PO$, $4H_2O$ respectively. These complexes were similar to authentic samples prepared from $SnCl_2$ and the ligands oxides. The reaction between $SnCl_2$ and triphenyl phosphine in an ethanolic solution saturated with HCl gave the product $[Ph_3PH]_2SnCl_6$, which was reported previously, but the method of preparation was different[2].

Infrared spectra:

The ir spectrum of Tin (II) dichloride dihydrate exhibits bands at 3550—3300 cm^{-1} and 1620 cm^{-1} caused by the absorption of water molecules. No other bands are observed in the region 4000—400 cm^{-1}. The Sn-Cl band is reported to appear at low frequency and be affected by coordination[17,18].

The P=O stretching frequency in free Diphos dioxides and in Ph_3PO occurs at 1190 cm^{-1}. When these ligands are involved in coordinate bond formation the frequency decreases because of a decrease in the P=O bond order[19]. This band occurs at 1140, 1170 and 1140 cm^{-1} in the spectra of the adducts of $SnCl_2$ with Diphos methane dioxide, Diphos ethane dioxide and Ph_3PO respectively. The spectra of the dioxide complexes show no bands at 1190 cm^{-1}, hence the phosphine dioxide donate electrons from oxygen atoms. Similar results are reported[20]. The spectrum of bis (triphenyl phosphonium) hexachlorostannate (IV) shows a P-H stretching band at 2430 cm^{-1} [21]. When the compounds was recrystallized from acetonitrile, oxidation occurred, and the P-H stretching band was replaced by a P=O streching band. Similar behaviour was observed with $SnCl_4$ adduct[2].

The frequency of the N-O group in Me-py-N-oxide occurs at 1250 cm^{-1} [22], and shifts to 1190 cm^{-1} in the spectrum of its complex with $SnCl_2$ (Fig. 1). As discussed in detail for py-O-metal complexes[23,24], the lowering of the ν(N-O) stretching frequency is attributed to a decrease of the N-O double bond character as a result of the oxygen-to-metal coordination. The magnitude of the shift is in good agreement with the values reported for the py-O-metal complexes. An absorption band around 565 cm^{-1} identified in the spectrum of the complex and absent in the spectrum of the ligand is assigned to the Sn-O stretching mode which agrees well with the reported value for the absorption around 570 cm^{-1} [25,26].

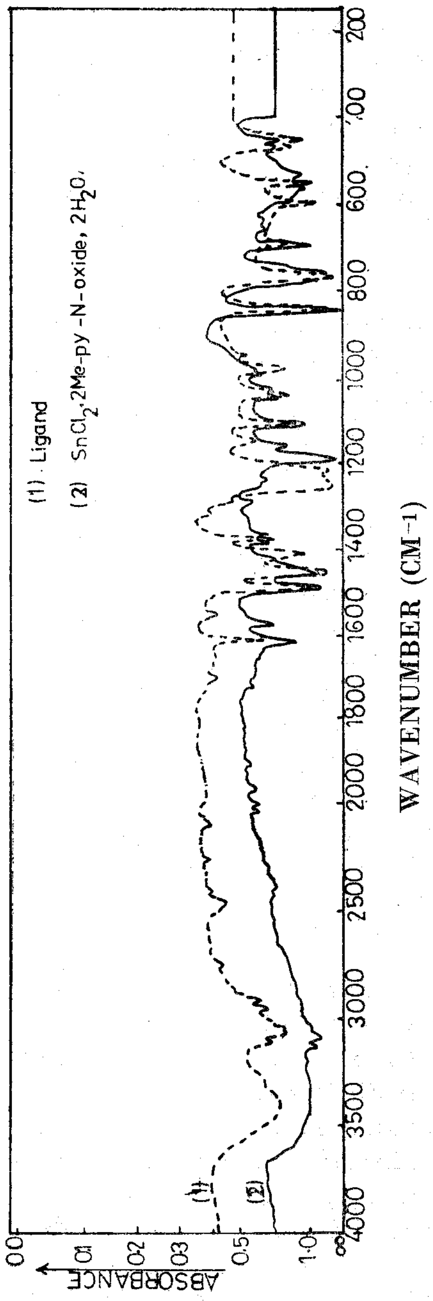

(1) Ligand
(2) SnCl2,2Me-py-N-oxide, 2H2O
(1)
(2)
ABSORBANCE
0.0
0.1
0.2
0.3
0.5
1.0
∞
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (CM-1)

Fig. 1

The ir spectra of the adducts obtained with the nitrogen donors (Table 1) show multiple splitting in the region 860—710 cm^{-1} and 1650 —1400 cm^{-1}, which corresponds to ring vibration.

Thermal analysis:

Thermal decomposition studies for the $SnCl_2$-complexes. xH_2O reported here showed that they decompose on heating in the range 20-850°C as given in Table (2). The molecular weights of the intermediate compounds are calculated from the graphs. Figure (2). is included here for representation. The final products, after heating are either Sn, $SnOCl_2$ or the compounds volatilized.

In the case of the complex formed with alizarin-red-S, $SnCl_2$, Aliz-red-S, $2H_2O$, heating caused loss of water at 100-120°C and then gradual decomposition leading to Sn at 620°C.

Conductivity studies:

Conductivity studies of some of the obtained Sn (II) complexes that dissolved in organic solvents such as MeCN, DMF and DetF show that the solutions of most of the complexes are weak electrolytes. The exceptional compounds are those obtained with Diphos methane and -ethane in DMF and MeCN as slovents respectively. These complexes. have the values corresponding to 1:1 electrolytes as given in Table (3). This is presumably due to the reaction:

$$SnCl_2,L + \text{Solvent} \rightleftarrows [SnCl,L,\text{Solvent}]^+ + Cl^-$$

Interactions of this type are well known[27].

The reaction of Sn (II) chloride with Na-3-alizatin-sulphonate leads to the formation of coloured complex. The reaction is studied spectrophotometrically in the uv and vis regions. The composition of the formed complex in ethanol was determined using the known spectropnotometrical methods: the continous variation[28] and the slope ratio[29] methods. Representative results are shown in Figures (3), (4) and (5). The absorption curve of the reaction mixture in ethanol is characterized by a single maximum at 450 nm compared to $\lambda_{max} = 425$ nm for the ethanolic solution of the ligand[30] (Fig. 3). The results shown in Fig. (4) and (5), obtained on applying the continuous variation methods and the slope ratio method respectively revealed the formation of 1:1 Sn (II) / Aliz. red-S. adduct. This agrees well with the analytical results obtained (Table 1).

Table 2: Thermal Decomposition of Some Tin Dichloride Complexes.

Temp. (°C)	M*obs	Formula	M*cal
1) $SnCl_2$, tripy, $6H_2O$			
20 — 140	513.6	$SnCl_2$, tripy, $5H_2O$	513.0
140 — 210	425.0	$SnCl_2$, tripy	422.9
290 — 700	150.2	SnO_2	150.6
725 — 850	118.3	Sn	118.7
2) $SnCl_2$, SM-bipy, $3H_2O$			
20 — 75	427.8	$SnCl_2$, DM-bipy, $3H_2O$	427.9
75 — 180	410.0	$SnCl_2$,DM-bipy, $2H_2O$	409.9
180 — 200	380.2	$SnCl_2$DM-bipy	373.9
215 — 260	341.0	$SnCl_2$, bipy	343.0
380 — 400	205.0	$SnOCl_2$	205.7
490 — 850	119.0	Sn	118.7
3) $SnCl_2$, DM-o-phen, $6H_2O$			
20 — 60	514.7	$SnCl_2$, DM-o-phen, $6H_2O$	514.8
60 — 125	458.5	$SnCl_2$, DM-o-phen, $3H_2O$	460.8
275 — 310	401.3	$SnCl_2$, DM-o-phen	406.8
410 — 675	152.0	SnO_2	150.6
4) $SnCl_2$, 1.5 pyrazine, $6H_2O$			
20 — 65	417.4	$SnCl_2$,1.5 pyrazine, $6H_2O$	417.7
65 — 130	307.0	SnCl2, 1.5 pyrazine	309.7
170 — 190	260.0	$SnCl_2$, pyrazine	269.0
295 — 375	121.0	Sn	118.7
5) $2SnCl_2$, hexamine, $4H_2O$			
20 — 90	517.4	$2SnCl_2$, hexamine	519.3
130 — 180	258.6	$SnCl_4$	260.5
300 — 359	150.0	SnO_2	150.6
6) $SnCl_2$, 3-picoline, $2H_2O$			
20 — 90	318.5	$SnCl_2$, 3-picoline, $2H_2O$	318.7
90 — 100	300.0	$SnCl_2$,3-picoline, H_2O	300.7
100 — 210	285.0	$SnCl_2$, picoline	282.7
210 — 325	120.0	Sn	118.7
326 — 798		volatile	
7) $SnCl_2$, benzotriazole, $2H_2O$			
20 — 90	334.0	$SnCl_2$, benzotriazole, H_2O	334.5
90 — 120	330.0	$SnCl_2$, benzotriazole	327.6
380 — 490	149.6	SnO_2	150.6
575 — 850	120.0	Sn	118.7
8) $SnCl_2$, $2Ph_3PO$, $4H_2O$			
20 — 125	818	$SnCl_2$, $2Ph_3PO$, $4H_2O$	818.1
125 — 248	782	$SnCl_2$, $2Ph_3PO$, $2H_2O$	287.1
500 — 660	263	$SnCl_4$	260.0
720 — 850	201.2	$SnOCl_2$	205.7
9) $SnCl_2$, Diphos ethane dioxide, $3H_2O$			
20 — 90	674.0	$SnCl_2$, Diphos ethane dioxide, $3H_2O$	674.2
90 — 205	650	$SnCl_2$, Diphos ethane dioxide $2H_2O$	656.0
625 — 850	154	SnO_2	150.6

*Mobs: observed molecular weight and Mcal: calculated molecular weight.

The reaction can be made use of for both qualitative and quantitative determination of Sn (II) ions in solution.

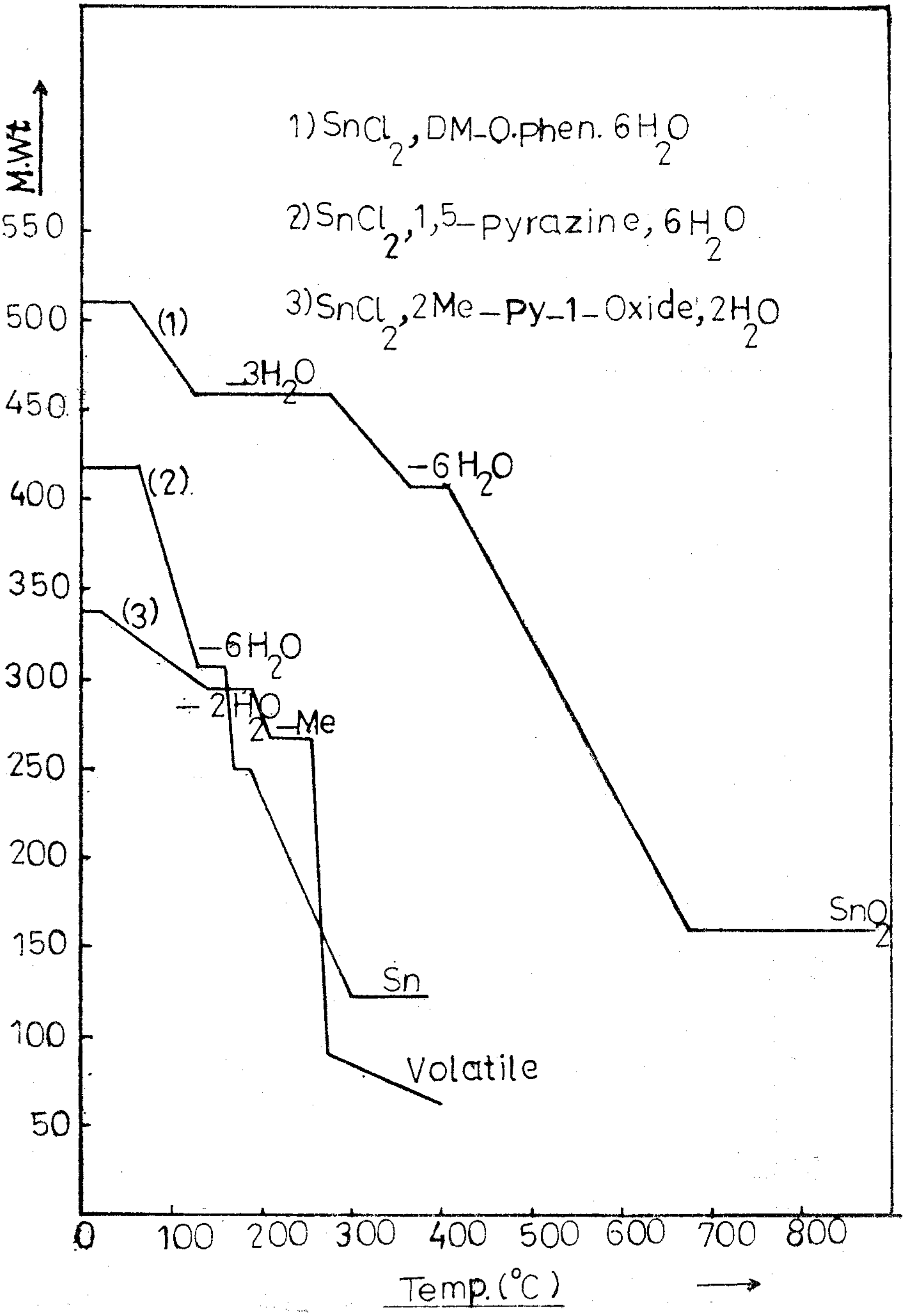
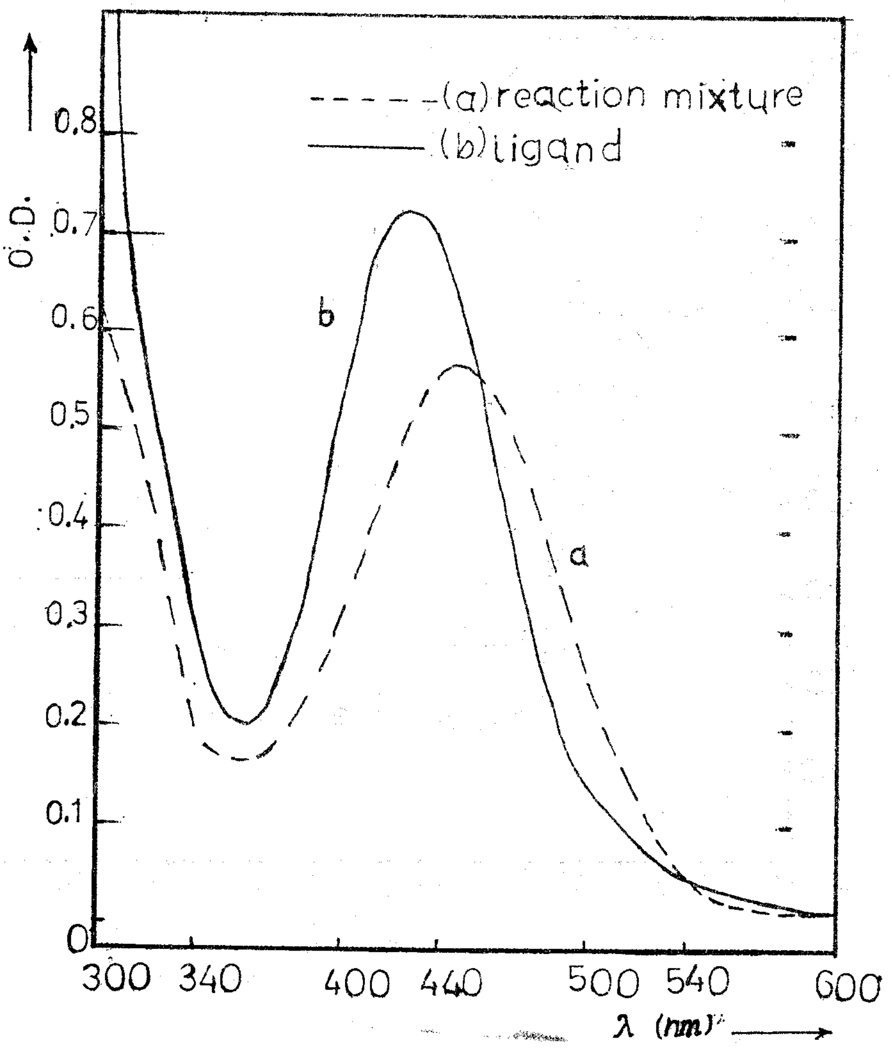
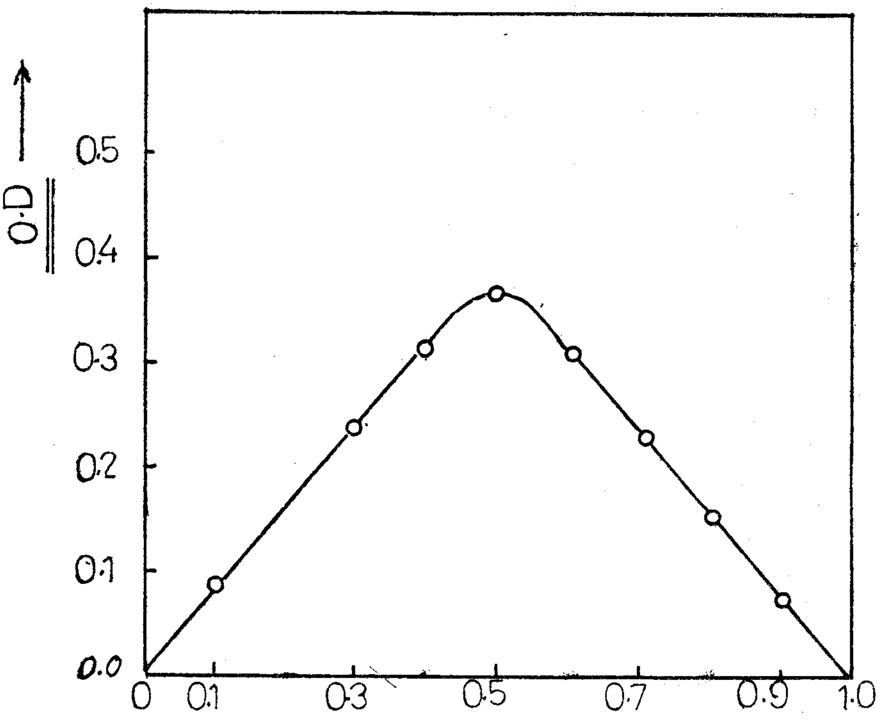

1) $SnCl_2$, DM-O.phen. $6H_2O$
2) $SnCl_2$, 1,5-pyrazine, $6H_2O$
3) $SnCl_2$, 2Me-Py-1-Oxide, $2H_2O$
M.Wt
550
500
450
400
350
300
250
200
150
100
50
0
100
200
300
400
500
600
700
800
Temp. (°C)
(1)
$-3H_2O$
$-6H_2O$
SnO_2
(2)
$-6H_2O$
$-2H_2O$
$-Me$
Sn
(3)
Volatile

Fig. 2

Tablo 3: Conductivities of Some Sn (II) Complexes in Some Organic Solvents (ohm^{-1} cm^2).

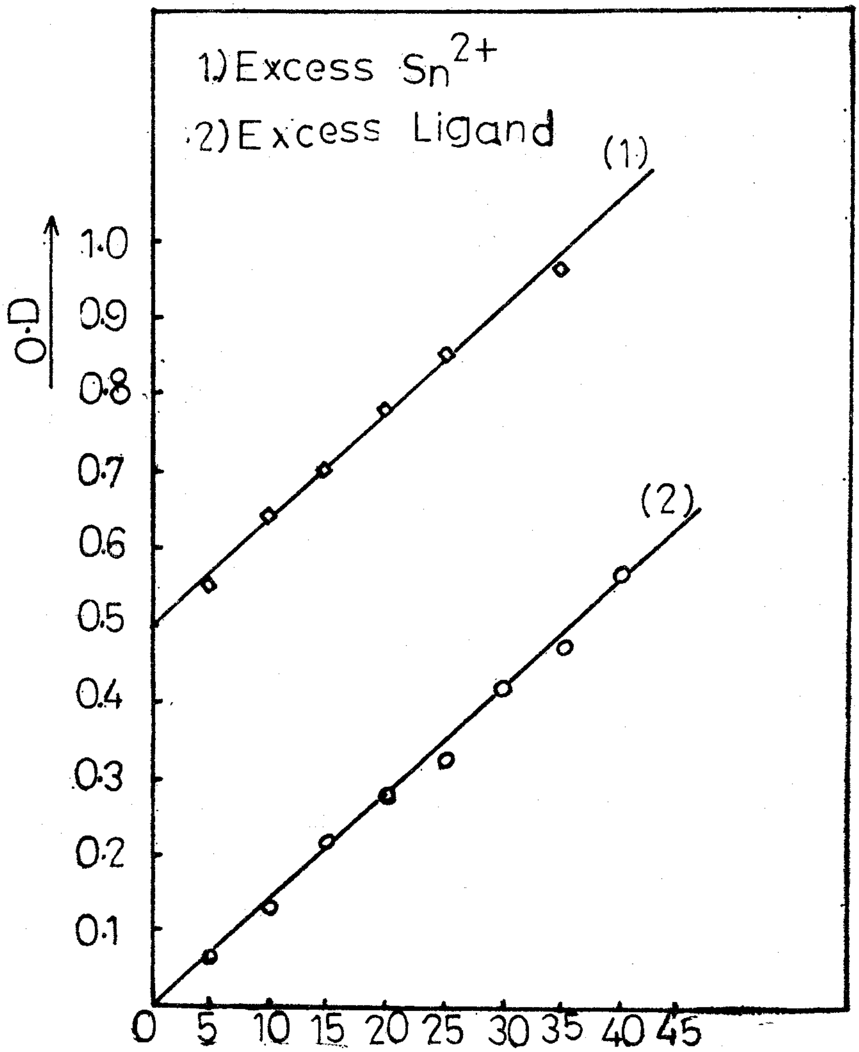
COMPOUND	Solvent		
	MeCN	DMF	DeTF
1– $SnCl_2$, DM-o-phen, $6H_2O$	——	w	——
2– $SnCl_2$, DM-bipy, $3H_2O$	——	w	——
3– $SnCl_2$, 2,2′,2″ tripy, $6H_2O$	——	——	w
4– $SnCl_2$, 1,5-DM-hydrazine, $2H_2O$	——	——	w
5– $SnCl_2$, Bnezotriazole, $2H_2O$	w	——	——
6– $SnCl_2$, 3-picoline, $2H_2O$	w	——	——
7– $SnCl_2$, 1,5-pyrazine, $6H_2O$	——	——	w
8– $SnCl_2$, Diphos-ethane-dioxide, $3H_2O$	107	——	——
9– $SnCl_2$, Diphos-methanedioxide, $6H_2O$	——	115	——
10– $SnCl_2$, Alizarine red-S, $3H_2O$	——	w	——





Sn (II) mole fraction

Fig. 4



[Sn II] or [Ligand] 5×10^{-5} M

Fig. 5

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