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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

Reactions of Tin (IV) Chloride With Some Organic Ligands

by

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

Reactions of Tin (IV) Chloride With Some Organic Ligands

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ABSTRACT

Tin tetrachloride rcacts with organic ligands to give the adducts, $SnCl_4$, L (whcre L = chelating ligandss, 1,2-bis (diphneylphosphino) ethane, methane and their dioxides, 4,4'-dimethyl dipyridyl. With pyridine-N-oxide, being monodentate ligand, tin tetrachloride gives the adduct. $SnCl_4$, 2py-N-oxide.

The reaction with triethyl phosphate is different and the compound $SnCl_2$ $[(EtO)_2PO_2]_2$ was obtained.

Some physical properties of these are discussed.

INTRODUCTION

Tin tetrachloride, being co-ordinationally unsaturated, rtaecs with a nuuber of organic polar solvents that are electron donors to give crystalline addition compounds of the type $SnCl_4$, 2L (L = MeCN, DMF, Me_2SO and Py.) (1). Adducts of 1:1 mole ratio are also known and more rarely 1:4.

Spectroscopic studies of 1:1 adducts with substituted anilines (2) show that the acceptor strength decreases along the series $SnCl_4 > SnBr_4 > SnI_4$.

This work is confined to complexes of tin tetrachloride, which is the strongest of these electron acceptors.

A review by Beattie (3) summarises the properties of Group IVB complex compounds, particularly adducts of the type MX_4, 2L (where M = Si, Ge, Sn and Pb.; X = halogen and L = monodentate ligand).

In a previous paper (4) we reported the preparation and properties of some complex compounds of $SnCl_4$ with organic ligands.

Trialkylphosphines and trialkylarsines are reported to form addition compounds with tin tetrahcloride (5). Other addition compounds containing phosphorus as the donor atom have been reported (6).

Allison and Mann (5) reported the preparation of bridged derivatives of the composition $(R_3P_2)SnCl_4,HgCl_2$ where R = Et and Pr^n.. During this work the attempted preparation of similar bridged compounds was unsuccessful.

EXPERIMENTAL

Microanalyses of carbon, hydrogen and nitrogen were carried out by the Microanalytical Laboratory of El-Nasr Company, Cairo. Analyses of complexes containing phosphorus were carried out by Alfred, Microanalytical laboratory, West Germany. Chloride was determined by Volhard method (7). Tin was determined as stannic oxide, according to the method given by Gilman and Rosenberg (8).

Infrared spectra were measured using a Unicam Sp 200 G. Calibration of frequency reading was made with a polystyene film. Conductivities were measured using a Beckman Electronic switchgear model RA-2A with balance indicator.

Molecular weights were measured using a vapour pressure osmometer model "Knauer". The instrument was calibrated with solutions of benzil in acetonitrile, using the concentration ranges of 0.02–0.1 mole/l.

Thermogravimetric analysis was attempted using a Stanton thermogravimetricbalance.

Materials: Tin tetrachloride (BDH) was used directly without any further purification. Solvents were dried by conventional methods (9). bis (diphenylphosphino) methane, (Diphosmethane), m.p. 120 °C was prepared according to the method described by Hewertson and Watson (10), by the action of diphenylphosphino sodium in liquid ammonia with methylene chloride.

1,2-bis (diphenylphosphino) ethane, (Diphosethane), m.p. 142 °C was obtained by similar reaction using 1,2-dichloroethane. The corresponding dioxides, Diphosmethane dioxide, m.p. 157 °C and Diphosethane dioxide, m.p. 275 °C, were prepared by oxidation of the corresponding Diphos compounds with potassium permanganate in acetone (11).

Bis (diphenyl sulphophosphino) methane, m.p. 234 °C and 1,2-bis (diphenyl sulphophosphino) ethane, m.p. 175 °C, were prepared by the reaction of sulphur with the appropriate phosphine in benzene, and were recrystallised from ethanol (12).

The other organic ligands containing nitrogen were recrystallised from ethyl acetate before use. Triethylphosphate (BDH) was used without any further purification.

Preparations of complex compounds.–An ampoule of anhydrous tin tetrachloride (100 ml) was cooled, opened and added to dry ethyl acetate (500 ml). Stoichiometric quantities of the ligands were dissolved in the same solvent and added to a known volume of the solution of tin tetrachloride. The precipitate formed was filtered, dried and recrystallised whenever possible.

The reactions of tin tetrachloride with bis (diph-enylsulphophosphino) methane and the corresponding ethane were studied under a variety of conditions. No evidence could be found for the formation of simple adducts, probably because of the low donor strength of the sulphur atom with respect to Sn(IV).

Tin tetrachloride reacts with 2,9-dimethylphenan-throline, DM-phen., to given the adduct, $SnCl_4$, 1,5-DM-phen. A complex of Me_2SnCl_2 and tripy. is reported to have the same stoichiometry ratio[13].

The adduct obtained with DM-bipy. and tin tetrachloride, $SnCl_4$, DM-bipy. recrystallises from MeCN to give the complex, $SnCl_4$, DM-bipy-MeCN. It seems that the solvent competes in the coordination sphere of Sn(IV).

Yields, melting points and analytical data are recorded in Table 1.

RESULTS AND DISCUSSION

The reaction of bis (diphenyl phosphino) methane and ethane with tin tetrachloride in dry ethyl acetate, gave the adducts, $SnCl_4$, Diphos methane and $SnCl_4$, Diphos ethane. Attempted recrystallisation from acetonitrile in air gave the corresponding dioxides. The complexes were similar to authentic samples prepared from $SnCl_4$ and Diphos methane dioxides and Diphos ethane dioxide in ethyl acetate.

Table 1.

Coimpound	Yied		Required %					Formuluen	Found %				
	%	M.P°C	C	H	N/P	Cl	Sn		C	H	N/P	Cl	Sn
$SnCl_4$,Diphos methane	95	183	46.5	3.4	9.6	21.9	18.4	$C_{25}H_{22}Cl_4P_2Sn$	46.3	3.6	9.2	21.1	18.5
$SnCl_4$,Diphos methane dioxode	91	195	44.4	3.3	9.1			$C_{25}H_{22}Cl_4O_2P_2Sn$	43.8	3.4	9.6	–	–
$SnCl_4$,Diphos ethane	78	188	47.4	3.7	9.4	21.5	18	$C_{26}H_{24}Cl_4P_2Sn$	47.1	3.7	9.5	21.3	18.1
$SnCl_4$,Diphos ethane dioxide	84	245	45.2	3.5	8.9	20.5	17.2	$C_{26}H_{24}Cl_4O_2P_2Sn$	45.1	3.5	9.0	–	
$SnCl_2$ $[(ETO)_2PO_2]_2$	77	>250	19.4	4.0	12.5	–	23.9	$C_8H_{20}Cl_2O_8P_2Sn$	19.3	4.1	12.4	–	23.8
$SnCl_4$,DM-bipy	86	>250	32.4	2.7	6.3	31.8	26.7	$C_{12}H_{12}Cl_4N_2Sn$	32.1	2.9	6.1	31.6	26.9
$SnCl_2$,DM-bipy-MeCN	79	>250	34.6	3.1	8.6	29.2	24.4	$C_{14}H_{15}Cl_4N_3Sn$	35.0	3.4	8.9	28.7	24.9
$SnCl_2$,1.5DM-phen.	80	266	44.0	3.2	7.3	24.7	20.7	$C_{21}H_{18}Cl_4N_3Sn$	44.4	3.1	6.9	24.7	20.8
$SnCl_4$,2py-N-oxide	81	238	26.6	2.2	6.2	–	26.3	$C_{10}H_{10}Cl_4N_2O_2Sn$	27	2.3	6.5	–	26.7
$SnCl_4$,tripy,$5H_2O$	83	>250	30.8	3.6	7.2	24.3	20.3	$C_{15}H_{21}Cl_4N_3O_5Sn$	29.5	3.3	3.9	24.5	19.7
$SnCl_4$,Pyrazine,$4H_2O$	80	>280	19.5	3.2	11.4	28.8	24.1	$C_3H_{16}Cl_4N_4O_4Sn$	20.0	3.0	1–	–	24.8
$SnCl_4$,Hexamine	90	205	18.0	3.0	14.0	35.4	29.6	$C_6H_{12}Cl_4N_4Sn$	17.9	4.0	9.6	–	

Attempts to prepare addition compounds with the corresponding diphosphinodisulphides were unsuccessful, in conformity with the earlier finding (4, 14).

The compound dichlorobis (diethylphosphate) tin(IV) $SnCl_2[(EtO)_2PO_2]_2$, was separated as white crystals on distilling, under reduced pressure, a hot solution of tin tetrachloride in triethyl phosphate. Ethyl chloride was collected in the cold trap. A complex of the type $Sn[(EtO)_2PO_2]_4$ was not obtained even on heating at 180 °C for several hours. This is presumably because of the low reactivity of chlorine. Dibutyltin dichloride reacts similarly with triethyl phosphate to given the compound $Bu^n_2 Sn[(EtO)_2PO_2]_2$ (15). In both compounds the Sn(IV) presumably exhibits its usual coordination number six.

Infrared studies of the adducts obtained, namely, $SnCl_4$, Diphos methane and ethane show multiple splitting of the bands in the region 800–700 cm^{-1}. The ring vibrations in the region of 1650–1500 cm^{-1} move to lower frequencies with multiple splitting. This is in agreement with previous results (16).

The P = O stretching frequency in free Diphos dioxides occurs at 1190 cm^{-1}, when these ligands are involved in coordination-bond formation the frequency decreases because of a decrease in the P = O bond order (17).

This band occurs at 1125 and 1120 cm^{-1} in the spectra of the adducts, $SnCl_4$, Diphos methane and ethane dioxides, respectivelt. There are no bands at 1190 cm^{-1}. Hence, the phosphine dioxides donate electrons from both oxygen atoms, and the complexes may contain chelate rings.

The P = O stretching band, which occurs at 1270 cm^{-1} in triethyl phosphate (18), appears as a single band in the complex, $SnCl_2[(EtO)_2PO_2]_2$.

The single band indicates that donation is through both oxygen atoms (19). A ring or chelate complex formed between a metal and a bidentate ligand is generally more stable thanthe complex with a monodentate analogue of similar basicity (20).

Infrared measurements at low frequency favour the cis structure (21) A similar complex, $SnCl_2(ac.ac)_2$ was also reported (22).

The infrared spectra of the adducts obtained with the nitrogen donors (Table 1), show multiple splitting in the region 850–700 cm^{-1} and 1650–1400 cm^{-3}, which corresponds to ring vibration.

The spectra of the adducts of $SnCl_4$ with pyrazine and tripyridine indicate a broad band in the region 3000–2500 cm^{-1}, which corresponds to bonded OH. Thermal decomposition of the Sn(IV) complexes shows that they decompose on heating. The molecular weights of the intermediate compounds are calculated from the graphs. The final products, after heating up to 800 °C are usually, SnO_2, $SnOCl_2$ or Sn. Some of these complexes volatilized on heating. Table 2 shows the effect of heat on some of the Sn (IV) complexes.

Table 2. Thermal Decomposition of Some Tin (IV) Chloride Complexes.

Temp. (°C)	Mobs.	Formula	Mcal.
$SnCl_4$, Diphos-ethane			
20 – 200	658.9	$SnCl_4$, Diphos-ethane	658.8
680 – 800	204.3	$SnOCl_2$	205.7
$SnCl_4$, Diphos-ethane dioxode			
20 – 60	690.9	$SnCl_4$, Diphos-ethane Oxide	690.9
120 – 250	658.9	$SnCl_4$, Diphos-ethane	659.0
520 – 800	202	$SnOCl_2$	205.7
$SnCl_4$, Diphos-methane dioxide	676.95	$SnCl_3$, Diphor*jH*ctyânnedi Oxide	(676.95
125 – 160	643.11	$SnCl_3$, Diphos-methane	644.9
580 – 800	203	$SnOCl_2$	205.7
$SnCl_4$, 1.5 DM-o-phen.	572.89	$SnCl_4$, 1.5 (DM-o-phen)	572.89
180 – 240	469.11	$SnCl_4$, DM-o-phen	464.11
510 – 800	114.57	Sn	118.7
$SnCl_4$, tripy) $5H_2O$	583.88	$SnCl_4$, tripy, $5H_3O$	583.87
20–140	583.88	$SnCl_4$, tripy, $5H_2O$	583.87
220 – 310	490.0	$SnCl_4$, tripy.	493. 7
385 – 800	151.8	SnO_2	150.7
$SnCl_4$, 2–2'–bipy.			
20 – 120	410.69	$SnCl_4$, 2–2'–bipy.	416.69
400		Volatile	
$SnCl_4$, DM-bipy, MeCN			
20 – 80	485.79	SnC_{43}, MeCS, DM-bipy	485.79
175 – 300	446.8	SnC_{43}, DM-bipy	444.74
440–500	150.6	SnO_4	150.7
550		Volatile.	

Where M = the molecular weight, Obs = observed and Cal = Calculated).

Conductivity studies.- Conductivity studies of some of the Sn(IV) adducts obtained and dissolved in organic solvents. Their solutions show low molar conductivities. The exceptional compound, $SnCl_4$, DM-bipy. MeCN, having the conductivity characteristic of a 1:1 electrolyte in acetonitrile, 125 ohm^{-1} cm^2, is presumably due to the reaction:

$SnCl_4$, DM-bipy., MeCN $\rightleftarrows$ [$SnCl_3$, DM-bipy., MeCN]$^+$ + Cl^- Interactions of this type are well known[23].

The molar conductivity reported for millimolar solution of 1:1 electrolyte in this solvent is 150 ohm^{-1} cm^2 (24) Table 3, indicated the molecular weights of some of the adducts of Sn(IV) in organic solvents. The dissociation factors, F, show that the complexes of Sn(IV), with

Table 3. Molecular Weight Determinations of Some Sn(IV) Complexes.

Compound	Mobs	Mcalc	F	Solvent
$SnCl_4$, Diphos methane	605.9	644.9	1.06	$MeNo_2$
$SnCl_4$, Diphos methane dioxide	661.2	676.9	1.02	MeCN
$SnCl_4$, Diphos ethane	580	658.9	1.14	$MeNo_2$
$SnCl_4$, DM-bipy, MeCN	288	485.8	1.7	$MeNo_2$
$SnCl_4$, DM-bipy	420	444.7	1.06	MeCN
$SnCl_4$, 1.5 DM-phen	278	572.9	2.1	DMF
$SnCl_4$, 2py-N-Oxide	180	450.7	2.5	$MeNo_2$
$SnCl_4$, tripy, $5H_2O$	408	583.9	1.4	DMF

Where F, is the dissociation factor.

Diphos methane and its dioxide, Diphos ethane, DM-bpiy., tripy. are monomers within the limits of the experimental error. The other complexes undergo dissociation in these solvents.

It is clear that the molecular weight determination imply a more complete dissociation than do the conductometric results for the Sn(IV) complexes. Similar results are reported (25).

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