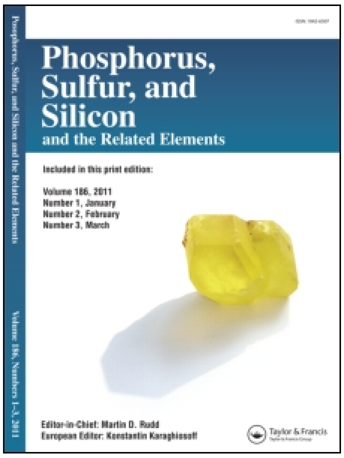

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SOME ASPECTS OF THE COMPLEXES OF SILICON(IV), TITANIUM(IV), ZIRCONIUM(IV), TIN(IV), AND ORGANOTINS WITH 2-METHYLTHIAZOLINE

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Silicon(IV), titanium(IV), zirconium(IV) and tin(IV) chlorides, methyltin trichloride, dibutyltin diacetate and tributyltin chloride complexes of the type $MX_4(MTz)_2$ (where M = Si, Ti or Zr, and X = Cl; or M = Sn and X = Cl, Cl and CH_3, CH_3COO and C_4H_9 or C_4H_9, and Cl, and MTz = 2-methylthiazoline) have been prepared by the reactions of respective metal salt and ligand in acetone medium and extracting the complex from the reaction mixture using petroleum ether. The stability and the composition of the complexes were established on the basis of melting point determinations and elemental analyses, respectively. Molar conductances of the complexes showed them to be covalent in nature. Bonding of ligand, MTz, to metal ion was suggested through nitrogen on the basis of spectral (IR, NMR, UV) studies. An octahedral geometry is proposed for the complexes.

Keywords: Group IV metal halides; 2-methylthiazoline; acetone; IR; NMR; UV

INTRODUCTION

Complexes of Group IV metal halides and organotins with various nitrogen, oxygen and sulfur containing donors have been reported.[1] The complexes of Group IV metal halides and organotin derivatives have been a subject of interest on account of their manifold applications in diverse areas.[2–9] Although thiazolines are potential multidentate ligands, the complexing behavior of thiazoline is not explored thoroughly.[10] There is no report on the complexing behavior of 2-methylthiazoline, C_4H_7NS (Fig. 1), with any metal ion. Thiazolines and sub-

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stituted thiazolines have so far been mainly explored as acetylcholinesterase inhibitor,[11] as antiradiation drug,[12] and as a fungicidal agent.[13,14] Some antibiotics have been synthesized with thiazoline derivatives as their partial skeleton.[15–17] Some drugs have increased activity when administered as metal complexes.[18–20]

In view of the above and as part of our ongoing studies of bonding behavior of multidentate ligands towards Group IV metal halides and organotins,[1] the present paper reports the syntheses and spectro-chemical characterization of the complexes of 2-methyl-thiazoline with silicon(IV), titanium(IV), zirconium(IV), and tin(IV) chlorides, methyltin trichloride, dibutyl-tin dicaetate, and tributyltin chloride.

RESULTS AND DISCUSSION

Silicon(IV), titanium(IV), zirconium(IV), and tin(IV) chlorides, methyltin trichloride, dibutyltin diacetate, and tributyltin chloride complexes of the type $MX_4(MTz)_2$ (where M = Si, Ti or Zr and X = Cl; M = Sn and X = Cl, Cl and CH_3, CH_3COO and C_4H_9, or Cl and C_4H_9; and MTz = 2-methylthiazoline) have been prepared by the reactions of metal salt and ligand in acetone then extracting the complex with petroleum ether. Only one product was formed at both deficient and excess stoichiometric ratios. The general equation for the reaction can be written as

$$MX_4 + 2MTz \rightarrow MX_4(MTz)_2$$

(M = Si, Ti or Zr, and X = Cl; or M = Sn and X = Cl, CH_3 and Cl, C_4H_9 and CH_3COO or C_4H_9 and Cl; and
MTz = 2-methylthiazoline)

Table I lists the analytical data, yields, etc. of the complexes. The complexes

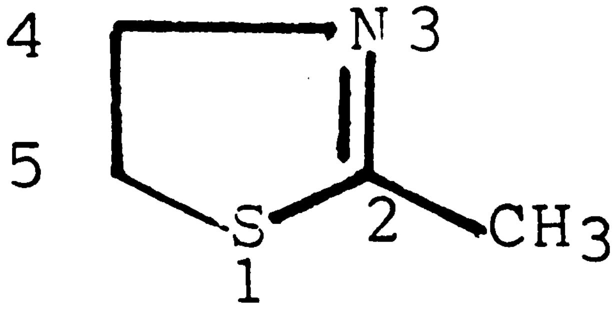

FIGURE 1 2-Methylthiazoline (C_4H_7NS)

TABLE I Analytical data and some physical properties of the complexes

Complex	*m.p. °C*	*% C Found (Calc.)*	*% H Found (Calc.)*	*% N Found (Calc.)*	*% S Found (Calc.)*	*% Cl Found (Calc.)*	*% M Found (Calc.)*	*%*	*Yield Molar Conductivity (Ohm^{-1} cm^{-1} mol^{-1})*
$SiCl_4 \cdot (MTz)_2$	240	25.80	3.70	7.52	17.20	38.10	7.52	70	20
$Si(C_8H_{14}N_2S_2)Cl_4$		(25.82)	(3.76)	(7.53)	(17.23)	(38.11)	(7.55)		
$TiCl_4 \cdot (MTz)_2$	235	24.50	3.52	7.12	16.30	36.00	12.20	75	25
$Ti(C_8H_{14}N_2S_2)Cl_4$		(24.52)	(3.57)	(7.14)	(16.36)	(36.18)	(12.22)		
$ZrCl_4 \cdot (MTz)_2$	245	22.00	3.01	6.40	14.52	32.30	20.85	65	20
$Zr(C_8H_{14}N_2S_2)Cl_4$		(22.08)	(3.22)	(6.43)	(14.73)	(32.58)	(20.96)		
$SnCl_4 \cdot (MTz)_2$	250	20.71	3.00	6.00	13.58	30.12	25.55	70	20
$Sn(C_8H_{14}N_2S_2)Cl_4$		(20.77)	(3.03)	(6.05)	(13.86)	(30.65)	(25.65)		
$CH_3SnCl_3 \cdot (MTz)_2$	252	24.40	3.75	6.25	14.25	24.00	26.74	65	15
$Sn(C_9H_{17}N_2S_2)Cl_3$		(24.44)	(3.84)	(6.33)	(14.50)	(24.05)	(26.84)		
$(C_4H_9)_2Sn(CH_3COO)_2 \cdot (MTz)_2$	248	43.41	6.77	5.00	11.55	—	21.42	60	12
$Sn(C_{20}H_{38}N_2S_2)O_4$		(43.44)	(6.87)	(5.06)	(11.59)		(21.46)		
$(C_4H_9)_3SnCl \cdot (MTz)_2$	242	45.50	7.47	5.28	12.00	6.70	22.01	60	10
$Sn(C_{20}H_{41}N_2S_2)Cl$		(45.54)	(7.77)	(5.31)	(12.16)	(6.72)			

are stable in air. The complexes are insoluble in most of the solvents. However, they are sufficiently soluble in THF to obtain their conductances at 10^{-3} M inTHF. The values of the conductance fall well below those quoted for the uni-univalent electrolytes in THF, showing the covalent nature of the complexes (Table I).[21]

Infrared Spectra

2-Methylthiazoline is a weak base and has potentially two donor atoms; nitrogen and sulfur. The proton attaches to the nitrogen in the reaction of ammonium ions with 2-methylthiazoline in neutral medium and in some reactions the MTz sulfur group is acid labile.[22] Table II presents the characteristic infrared bands for the ligand and complexes in the range 4000-200 cm^{-1}. Tentative assignments have been made. Only those bands of the ligands, which show some variation in the complexes and the new bands, are discussed here. The spectrum of the ligand shows a medium intensity doublet at 1640 cm^{-1} attributable to C=N which is shifted towards lower frequencies and appears as a single band in the complexes. It shows low electron density in the C=N bond which tentatively suggests coordination of the ligand through the nitrogen atom. Two medium intensity bands around 640 cm^{-1} are assigned to C-S-C asymmetric and symmetric stretching vibrations in the ligand. In the complexes, coupling of the C-S-C bands takes place and only a single band appears. Appearance of fewer bands in the ligand on complexation with the metal ion could be related to the change in symmetry where some bands are coupled or superimposed by other bands. The far-IR region is very important because metal-ligand, metal-halogen and tin-carbon vibrations are observed in this region. The metal-halogen vibrations are more intense and are sensitive to the stereochemistry of the complex. Only one Sn-C absorption band is observed in the methyltin trichloride and dibutyltin

TABLE II Some important IR bands of ligands and the complexes (cm^{-1})

Compound/Complex	*ν(C=N)*	*ν(C-S-C)*	*ν(Sn-C)*	*ν(M-Cl)*	*ν(M-N)*
MTz	1640–1650m	630–640m	—	—	—
$SiCl_4 \cdot (MTz)_2$	1610m	635s	—	410s	385m
$TiCl_4 \cdot (MTz)_2$	1612m	630s	—	320m	382w
$ZrCl_4 \cdot (MTz)_2$	1615m	638s	—	365s	390w
$SnCl_4 \cdot (MTz)_2$	1615m	635s	—	332vs	380w
$CH_3SnCl_3 \cdot (MTz)_2$	1618m	635s	510m	332s	370w
$(C_4H_9)_2Sn(CH_3COO)_2 \cdot (MTz)_2$	1618m	632s	520m	—	365m
$(C_4H_9)_3SnCl \cdot (MTz)_2$	1620m	630s	510m, 530m	330s	360w

vs = very strong, s = strong, m = medium and w = weak.

diacetate complexes and two bands in the same region are observed in the tributyltin complex. Only one band was observed in the 410-320 cm^{-1} region, attributed to ν M-Cl, in all the chloro-complexes. Appearance of a single ν M-Cl stretching vibration in the tetrachloro-complexes was assigned to the *trans* positions of the chlorides.[23] A band observed in the range 390-360 cm^{-1} in all the complexes has been assigned to ν M-N. Thus, lending further support to the proposed coordination through nitrogen in the complexes.

NMR Spectra

Table III shows the chemical shifts (in ppm) of various protons in the ligand and complexes. The butyl protons attached to tin appeared at δ in the range 1.38–1.74 ppm as a multiplet due to CH_2 groups and as a clear triplet due to terminal methyl protons within the range of 0.78–1.15 ppm in the dibutyltin and tributyltin complexes. Methyl protons of the methyltin complex appear as a sharp singlet at $\delta = 0.96$ ppm with a double satellite resonance on each side of the main peak, due to coupling of the methyl protons with ^{117}Sn and ^{119}Sn nuclei, with the value of the coupling constant, J (Sn-C-H), at 90 Hz. This value of the coupling constant is higher than the value observed for methyltin trichloride and is in the range of the values observed for six coordinated compounds.[24,25] Thus, the observed value of J (Sn-C-H) is in terms of 6-coordinated tin in a methyltin complex. The downfield shift of methyl and butyl proton resonances in the complexes compared to those in free organotin moieties may be attributed to an increased transfer of electron density from the methyl and butyl groups to 5d orbitals of the tin and eventually to p_π orbitals of the ligand, d_π-p_π bonding, as a consequence of coordination.[26]

TABLE III ^1H NMR chemical shifts of ligand and the complexes

Complex/Compound	*Proton Chemical Shift (ppm)*			
	Sn-Alkyl		*Ligand-Alkyl*	
	CH_3	*CH_2*	*CH_3*	*CH_2*
MTz	—	—	2.10-228t	3.96-4.26q
$SiCl_4.(MTz)_2$	—	—	2.10-2.28t	3.48-3.3.90q
$ZrCl_4.(MTz)_2$	—	—	2.10-2.28t	3.46-3.90q
$SnCl_4$	—	—	2.10-2.28t	3.52-3.93q
CH_3SnCl_3	0.98s	—	—	—
$CH_3SnCl_3.(MTz)_2$	0.96s	—	2.10-2.2.28t	3.65-3.95q
$(C_4H_9)Sn(CH_3COO)_2$	0.86-1.15t	1.46-1.70m	—	—
$(C_4H_9)_2Sn(CH_3COO)_2.(MTz)_2$	0.83-1.10t	1.40-1.74m	2.10-2.28t	3.70-4.01q
$(C_4H_9)_3SnCl$	0.80-1.10t	—	—	—
$(C_4H_9)_3SnCl.(MTz)_2$	0.78-0.98t	1.38-1.66m	2.10-2.28t	3.71-4.10q

The ligand spectrum shows the interesting feature of long range coupling of 2-methyl protons with one set of ring methylenes. A quartet is observed for methylene (C-4) protons and a triplet for the 2-methyl protons. The coupling of this ligand is comparable to that between the methyl protons of angelic acid[27] in which the *trans* type of relationship of the groups and the degree of unsaturation are similar. In angelic acid the coupling is believed to involve hyperconjugation. On coordination the CH_2 signals of the ligand move downfield and CH_3 signals remain unchanged. The downfield movement of CH_2 signals could be due to coordination of nitrogen to metal ion.[28] This also supports the coordination of the ligand to the tin moiety through nitrogen atom of the ligand. The resonances due to CH_3 and CH_2 ligand protons in the complexes (2.1–4.26 ppm) do not get obscured by the alkyl tin proton signals (0.78–1.74 ppm). The number of protons of various groups calculated from the integration curves and those calculated for the expected molecular formula agree well with each other.

Electronic Absorption Spectra

Table IV presents the electronic absorption spectra of the ligand and complexes in the range 100–800 nm. A strong band around 250 nm is observed in the ligand which did not appear to be affected by the nature of the metal ion. This band may be due to $\pi \rightarrow \pi$ transition of the (C═N) chromophore of the ligand.[29,30] Furthermore a weak band is observed in the region 270–315 nm in all the complexes which could be assigned as the charge transfer band. It has been reported[29–31] that a metal/metalloid is capable of forming $d_\pi - p_\pi$ bonds with ligands containing nitrogen as donor atoms. The tin atom has its 5d-orbitals completely vacant and hence L → M bonding can take place by the acceptance of a pair of electrons from the nitrogen donor atom of the ligand. In silicon(IV) and tin(IV) complexes these bands are observed in the higher energy region

TABLE IV Electronic absorption spectra of the ligand and complexes

Compound	*λMax(nm)*	
MTz	250 (2.82)	—
$SiCl_4.(MTz)_2$	252 (2.82)	290 (3.50)
$TiCl_4(MTz)_2$	250 (2.82)	280 (3.62)
$ZrCl_4.(MTz)_2$	251 (2.82)	270 (3.55)
$SnCl_4.(MTz)_2$	250 (2.82)	300 (3.01)
$CH_3SnCl_3.(MTz)_2$	251 (2.82)	310 (3.10)
$(C_4H_9)_2Sn(CH_3COO)_2.(MTz)_2$	250 (2.82)	315 (3.00)
$(C_4H_9)_3SnCl.(MTz)_2$	250 (2.82)	315 (2.98)

compared to one titanium(IV) and zirconium(IV) complexes. The highest intensity is observed in the titanium(IV) complex and the lowest intensity is observed in the tributyltin complex.

The above study suggests that the ligand is coordinated through the nitrogen atom to the metal ions and all the complexes have an octahedral geometry, Fig. 2.

EXPERIMENTAL

All the reactions involving metal halides were carried out under dry atmosphere. Silicon(IV), titanium(IV), zirconium(IV), tin(IV) chlorides, *di*-n-butyltin diacetate; *tri*-n-butyltin chloride (B.D.H. Chemicals), methyltin trichloride and 2-methylthiazoline (Aldrich Chemicals) were used as received. The solvents were dried by standard methods.[32] The M.P. were determined on a Gallenkamp melting point apparatus. Sulfur, chloride and metals of the dry complexes were determined gravimetrically.[33] Elemental analyses for C, H and N were done on a Coleman analyzer. Molar conductances of the complexes were determined at 10^{-3} M concentration in tetrahydrofuran using a Waynekerr universal conductivity bridge type B-221. Infrared spectra were recorded on CsBr discs with a Perkin Elmer RB-31000 infrared spectrometer. Proton magnetic resonance spectra (reference: tetramethylsilane) of the complexes were run on a EM 360L Varian ^{1}H NMR spectrometer at an operating temperature of 38°C. The electronic absorption spectra were recorded in silica cells on a Milton Roy Spectronic 100/plus model in range 100–800 nm.

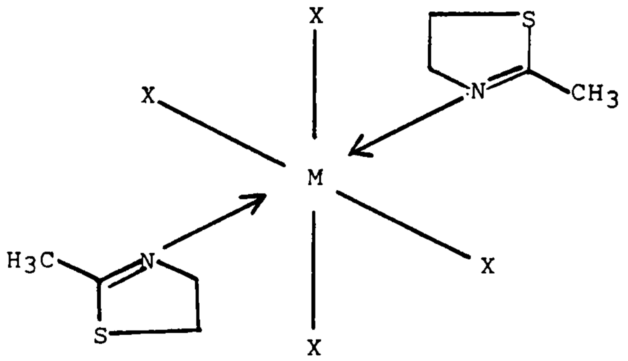

FIGURE 2 Proposed Structures of the Complexes

Preparation of the Complexes

All the complexes were prepared by the following general procedure.

To a 10 mmole of metal salt (1.1 mL of $SiCl_4$(1.69 g), $TiCl_4$(1.89 g), $SnCl_4$(2.61 g), $ZrCl_4$(2.33 g), CH_3SnCl_3 (2.40 g), $(C_4H_9)_2Sn(CH_3COO)_2$ (3.51 g), or $(C_4H_9)_3SnCl$ (3.25 g) in 50 mL acetone was added to 20 mmole (2.02 g) of 2-methylthiazoline. The resulting mixture was left for about three hours with occasional stirring when a viscous mass appeared. The time of appearance of viscous mass varied slightly from one complex to another, ranging from 1–1.5 h in case of titanium and silicon, 2–2.5 h for zirconium and tin, and 2.5–3 h for organotin complexes. Petroleum ether was added to this viscous mass to separate out the complex. The complexes were isolated by filtering on a Buckner funnel and washing twice with acetone and petroleum ether each, and finally with diethyl ether. All the complexes were dried in an oven at 110°C for six hours and then finally in a vacuum desiccator over silica gel.

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