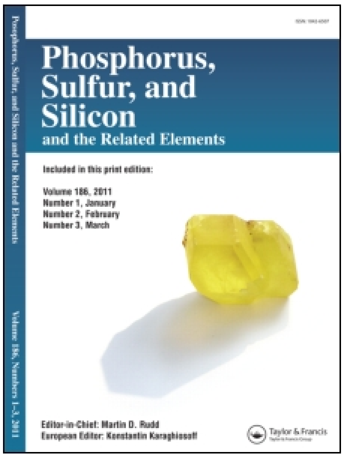

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SCHIFF BASE COMPLEXES OF SOME GROUP IV METAL HALIDES

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SCHIFF BASE COMPLEXES OF SOME GROUP IV METAL HALIDES

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Novel hexa-coordinated complexes of silicon(IV), titanium(IV), zirconium(IV) and tin(IV) chlorides of the general formula ML_2Cl_2 (where L = Schiff base prepared from the coupling reactions of glycine, leucine or cystine with *O*-hydroxyacetophenone), have been synthesized by refluxing the respective metal chloride and Schiff base in situ in an absolute ethanol and acetone mixture. The resulting complexes have been characterized by analytical data, spectroscopic (IR, UV, NMR) studies, melting points and conductance measurements. Chelate structures have been proposed for the complexes.

Key words: Amino acids, acetophenone, IR, UV, NMR, conductivity.

INTRODUCTION

Coordination compounds of Schiff bases have been widely investigated, in view of their novel structural features and potential chelating behavior.[1–3] Chelate extraction presently is one of the most widely used methods for the concentration and determination of trace amounts of metals.[4–6] It is now recognized that synthetic macrocyclic ligands coordinate easily with most metal ions, forming stable chelates.[7–14] The complexes with macrocycles have more symmetric and rigid structures than those containing flexible linear ligands.[15–18] Considerable attention has been given in the past to transition metal complexes of Schiff bases obtained from amino acids.[19–29] There are no reports on the Group IV metal halide complexes of the Schiff bases derived from amino acids. In continuation of our studies[30] on the Group IV metal halide complexes with a variety of ligands and the immense importance of Schiff bases, it was considered worthwhile to explore the coordination behavior of these Schiff bases towards Group IV metal halides.

This study reports the synthesis and spectrochemical properties of the complexes of Si(IV), Ti(IV), Zr(IV) and Sn(IV) chlorides with Schiff bases derived from coupling of glycine, leucine and cystine with *O*-hydroxyacetophenone.

RESULTS AND DISCUSSION

The complexes of the general formula ML_2Cl_2, were synthesized by the substitution reactions of metal chlorides and preformed Schiff base in situ, obtained by the condensation of *O*-hydroxyacetophenone and amino acids, in high yields, according to the following Scheme I.

Products (1) and (2) represent the structures of the Schiff bases and proposed

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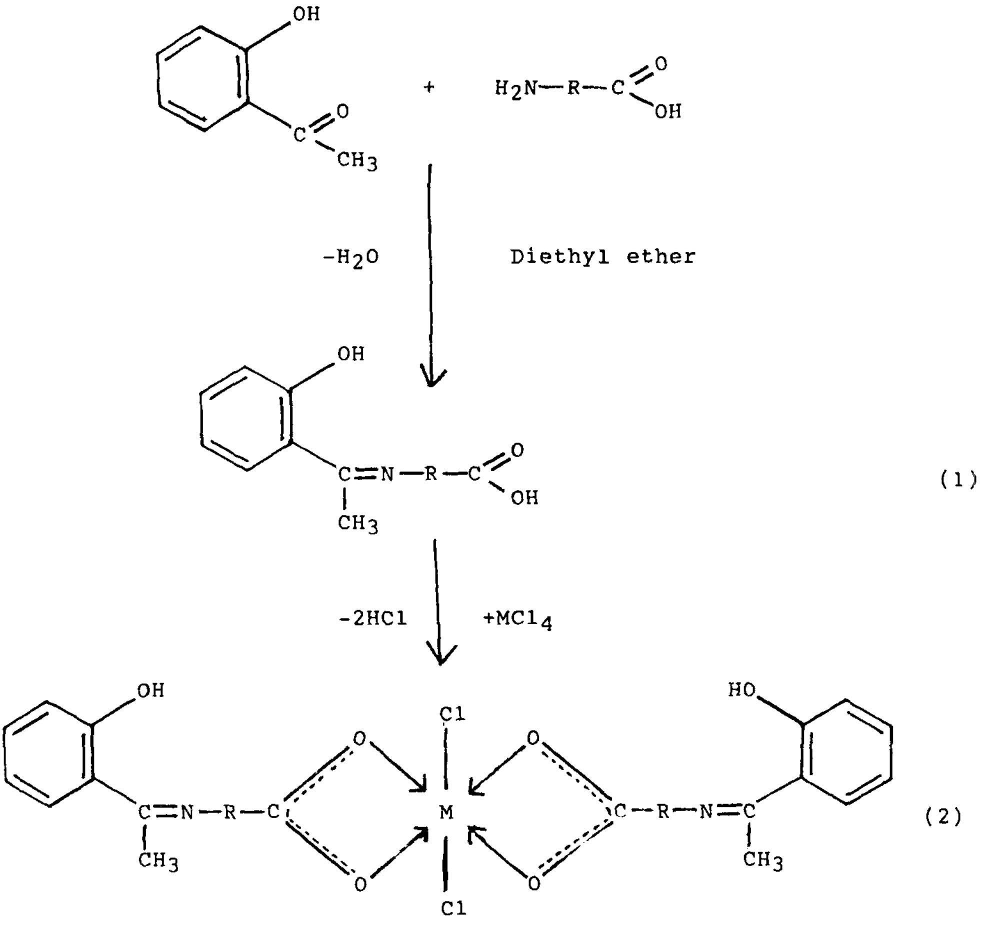

M = Si, Ti, Zr or Sn and R = CH_2-, $(CH_3)_2CHCH_2CH-$ or $HOOC\underset{NH_2}{C}HCH_2S-SCH_2CH-$

SCHEME I

structures of the complexes, respectively. Table I presents the analytical data and some of the physical properties of the complexes. The complexes are not brightly colored and are insoluble in most of the organic solvents. However, they are sufficiently soluble in DMSO to enable their molar conductivities to be measured. The molar conductivity measurements (20–32 Ohm^{-1} cm^2 mol^{-1}) show them to be non-ionic in nature. The adducts are non-hygroscopic, stable to air and decomposition into their constituents.

IR Spectra

Table II presents the important infrared spectral bands and their tentative assignments for the synthesized complexes. The Schiff bases used in the present study are po-

TABLE I

Analytical data and some physical properties of the complexes

Compound/Complex	Colour	M.P. °C	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)	% S Found (Calc.)	% M Found (Calc.)	% Cl Found (Calc.)	% Yield
$SiCl_2.(L\text{-}1)_2$ $Si(C_{20}H_{20}N_2O_6)Cl_2$	Yellowish-brown	>360	49.66 (49.68)	4.11 (4.14)	5.76 (5.80)	-	5.78 (5.82)	14.68 (14.70)	70
$TiCl_2.(L\text{-}1)_2$ $Ti(C_{20}H_{20}N_2O_6)Cl_2$	Off-white	>360	47.71 (47.72)	3.95 (3.98)	5.52 (5.57)	-	9.48 (9.52)	14.10 (14.12)	72
$ZrCl_2.(L\text{-}1)_2$ $Zr(C_{20}H_{20}N_2O_6)Cl_2$	Brown	350	43.91 (43.94)	3.62 (3.66)	5.10 (5.13)	-	16.66 (16.70)	12.98 (13.00)	74
$SnCl_2.(L\text{-}1)_2$ $Sn(C_{20}H_{20}N_2O_6)Cl_2$	Dark-brown	>360	41.81 (41.83)	3.44 (3.49)	4.85 (4.88)	-	20.66 (20.69)	12.34 (12.38)	70
$SiCl_2.(L\text{-}2)_2$ $Si(C_{28}H_{36}N_2O_6)Cl_2$	Off-white	355	56.41 (56.46)	6.03 (6.05)	4.68 (4.70)	-	4.70 (4.72)	11.89 (11.93)	71
$TiCl_2.(L\text{-}2)_2$ $Ti(C_{28}H_{36}N_2O_6)Cl_2$	Brown	>360	54.61 (54.64)	5.82 (5.85)	4.52 (4.55)	-	7.75 (7.79)	11.53 (11.55)	74
$ZrCl_2.(L\text{-}2)_2$ $Zr(C_{28}H_{36}N_2O_6)Cl_2$	Off-white	355	50.02 (50.05)	5.43 (5.47)	4.22 (4.25)	-	13.82 (13.86)	10.76 (10.79)	76
$SnCl_2.(L\text{-}2)_2$ $Sn(C_{28}H_{36}N_2O_6)Cl_2$	Brown	>360	48.97 (49.00)	5.22 (5.25)	4.05 (4.08)	-	17.27 (17.31)	10.30 (10.35)	72
$SiCl_2.(L\text{-}3)_2$ $Si(C_{28}H_{34}N_4O_{10}S_4)Cl_2$	Off-white	350	41.30 (41.32)	4.13 (4.18)	6.85 (6.88)	15.71 (15.74)	3.42 (3.46)	8.70 (8.73)	74
$TiCl_2.(L\text{-}3)_2$ $Ti(C_{28}H_{34}N_4O_{10}S_4)Cl_2$	Yellowish-brown	340	40.31 (40.34)	4.05 (4.08)	6.69 (6.72)	15.35 (15.37)	5.71 (5.75)	8.48 (8.52)	76
$ZrCl_2.(L\text{-}3)_2$ $Zr(C_{28}H_{34}N_4O_{10}S_4)Cl_2$	Brown	350	38.31 (38.35)	3.85 (3.88)	6.35 (6.39)	14.57 (14.61)	10.38 (10.41)	8.07 (8.10)	72
$SnCl_2.(L\text{-}3)_2$ $Sn(C_{28}H_{34}N_4O_{10}S_4)Cl_2$	Brown	>360	37.14 (37.18)	3.73 (3.76)	6.15 (6.20)	14.15 (14.16)	13.10 (13.13)	7.81 (7.86)	70

L-1 = O-Hydroxyacetopheno-glycine, L-2 = O-Hydroxyacetopheno-leucine,

L-3 = O-Hydroxyacetopheno-cystine.

TABLE II

Some important IR frequencies (cm^{-1})[a] of the complexes

Complex	νN-H	ν OCO	ν C-O	ν M-O	ν M-Cl
$SiCl_2.(L\text{-}1)_2$	3400vs	1640s	1280m	520w	360s
$TiCl_2.(L\text{-}1)_2$	3400vs	1643s	1280m	485w	380s
$ZrCl_2.(L\text{-}1)_2$	3400vs	1643s	1280m	495w	350s
$SnCl_2.(L\text{-}1)_2$	3400s	1640s	1280m	500w	350s
$SiCl_2.(L\text{-}2)_2$	3380s	1640m	1285m	510m	365s
$TiCl_2.(L\text{-}2)_2$	3380s	1642m	1285m	490m	375s
$ZrCl_2.(L\text{-}2)_2$	3380s	1643m	1285m	490m	348s
$SnCl_2.(L\text{-}2)_2$	3380s	1641m	1285m	510w	350s
$SiCl_2.(L\text{-}3)_2$	3390s	1642s,br	1290s	520m	360s
$TiCl_2.(L\text{-}3)_2$	3390s	1643s,br	1290s	490m	380s
$ZrCl_2.(L\text{-}3)_2$	3390s	1643m,br	1290s	490w	350s
$SnCl_2.(L\text{-}3)_2$	3390s	1640m,br	1290s	500m	345s

L-1 = O-Hydroxyacetopheno-glycine, L-2 = O-Hydroxyacetopheno-leucine,

L-3 = O-Hydroxyacetopheno-cystine

a = vs, very strong; s, strong; m, medium; or br, broad.

tentially multidentate ligands. There is not much difference in the IR bands of these ligands. A band around 3400 cm^{-1} assignable to the νNH vibration indicates the presence of ketoenamine form of the Schiff bases in the solid state.[31] Some workers have assigned this band due to νOH/NH frequency.[32,33] However, the preferred orientation of the ligand is the imine form which is confirmed by a band assignable to νC—O (phenolic) at 1280 cm^{-1} in the ligands.[26] There is no significant change in the position and intensity of νN—H and νC—O bands in the complexes, compared to Schiff bases. This rules out the possibility of coordination through phenolic oxygen and imino nitrogen. The only possible group for coordination which remains is the carboxylate group. Two bands at 1675 and 1610 cm^{-1} are assigned to OCO asymmetric stretch and coupled imine C═N and C═C stretching vibrations, respectively.[26,34] A band corresponding to ν_{sym} OCO appears at 1350 cm^{-1} in Schiff bases. On complexation these bands disappear and new bands emerge around 1640 cm^{-1} in all the complexes. This is assigned to the bidentate chelating carboxylate group. This suggests that coordination is taking place through carboxylate group. A band around 1500 cm^{-1} may be attributed to the C═C/C═N stretching vibrations of the conjugated imide[26,34] in all the Schiff bases and complexes.

In the lower frequency region, a band around 500 cm^{-1} in the spectra of all the complexes has been assigned to the M—O vibrations, thus lending further support to the coordination through the carboxylate group. In all the complexes a νM—Cl band is observed around 360 cm^{-1}.

UV Spectra

Table III reports the UV absorption spectra of the complexes measured in DMSO-d_6. All the complexes gave bands in the range 220–225 cm^{-1} and in addition to this, titanium and zirconium complexes also showed bands in 320–350 cm^{-1} region. However, the precise assignments of these bands remains to be determined. It is assumed that the intense bands near 220–225 cm^{-1} are due to ligand transitions; $\pi \rightarrow \pi^*$ of the benzenoid/or $n \rightarrow \pi^*$ and weaker band near 320–350 cm^{-1} is either a $n \rightarrow \pi^*$ transition or a charge-transfer (ligand → d orbital) or a $\pi \rightarrow \pi^*$ transition of C=N chromophore.[34–36] From the present data it is clear that the bands in the metal derivatives are stronger than the corresponding Schiff base bands. Also the highest energy bands (220–225 cm^{-1} region) in titanium complexes are at higher energies than the corresponding bands in other complexes, whereas, in the ca. 320–350 cm^{-1} region bands, the zirconium complexes are at higher energy. The latter effect is reasonable for a charge-transfer band because the titanium is more easily reduced [Ti(IV) → Ti(III)] than zirconium. No charge-transfer band is observed for the silicon and tin complexes; perhaps this band may be observed in the far-UV

TABLE III
Electronic absorption spectra of the complexes

Complex	λ max*, nm	
$SiCl_2.(L\text{-}1)_2$	225 (3.41)	350 (3.35)
$TiCl_2.(L\text{-}1)_2$	225 (3.75)	320 (3.50)
$ZrCl_2.(L\text{-}1)_2$	225 (3.80)	330 (3.50)
$SnCl_2.(L\text{-}1)_2$	225 (3.50)	340 (3.20)
$SiCl_2.(L\text{-}2)_2$	220 (3.42)	350 (3.38)
$TiCl_2.(L\text{-}2)_2$	220 (3.80)	325 (3.50)
$ZrCl_2.(L\text{-}2)_2$	220 (3.85)	330 (3.60)
$SnCl_2.(L\text{-}2)_2$	220 (3.50)	340 (3.60)
$SiCl_2.(L\text{-}3)_2$	224 (3.50), 229 (3.30)	350 (3.30)
$TiCl_2.(L\text{-}3)_2$	224 (3.85), 227 (3.80)	325 (3.60)
$ZrCl_2.(L\text{-}3)_2$	224 (3.85), 228 (3.32)	330 (3.65)
$SnCl_2.(L\text{-}3)_2$	224 (3.50), 230 (3.40)	340 (3.25)

* In DMSO Log ε in parentheses.

region. The first absorption band in the cystine Schiff base complexes shows some splitting, while in the other two series of the complexes no splitting of these bands is observed. The splitting of this band cannot be explained unambiguously; most likely, it is due to the lower symmetry of these complexes.

NMR Spectra

^{1}H NMR spectra of the Schiff bases and the complexes have been recorded in DMSO-d_6 (Table IV). The ^{1}H NMR signals due to CH and CH_2 protons α to metal bound carboxylate groups in leucine, cystine and glycine Schiff base complexes, respectively, show downfield shifts (up to 0.8 ppm) compared to their respective free Schiff bases. The downfield shift clearly indicates a decrease in electron density around the carbon α to the carboxylate group due to the coordination of carboxylate oxygens with the metal ion. The other proton signals remain unchanged which may be explained by assuming that the other groups are not interacting with the metal ion and the effect of coordination of carboxylate group diminishes as the distance from the metal ion increases.

On the basis of the above studies, it is clear that the Schiff bases are behaving as

TABLE IV
^{1}H NMR chemical shift[a] of the complexes

Complex	α Proton Chemical Shift (δ ppm)	
	CH_2	CH
$SiCl_2.(L-1)_2$	2.38s	-
$TiCl_2.(L-1)_2$	2.37s	-
$ZrCl_2.(L-1)_2$	2.34s	-
$SnCl_2.(L-1)_2$	2.32s	-
$SiCl_2.(L-2)_2$	-	2.42-2.89m
$TiCl_2.(L-2)_2$	-	2.41-2.89m
$ZrCl_2.(L-2)_2$	-	2.40-2.88m
$SnCl_2.(L-2)_2$	-	2.40-2.88m
$SiCl_2.(L-3)_2$	-	2.44-2.90m
$TiCl_2.(L-3)_2$	-	2.43-2.89m
$ZrCl_2.(L-3)_2$	-	2.43-2.88m
$SnCl_2.(L-3)_2$	-	2.43-2.88m

[a] Downfield chemical shifts (δ values) relative to tetramethylsilane as internal reference.

s = singlet, m = multiplet.

bidentate chelating agents coordinating through the carboxylate oxygens. Chelate structures are proposed for the complexes.

EXPERIMENTAL

All reactions involving metal chlorides were carried out under dry oxygen-free, nitrogen in a dry-box. Silicon(IV), titanium(IV), zirconium(IV), tin(IV) chlorides, *O*-hydroxyacetophenone (B.D.H.) and glycine, leucine and cystine (Sigma Chemicals) were used as received. Solvents were dried using standard methods. Melting points were recorded on a Gallenkamp melting point apparatus. Elemental analysis for carbon, hydrogen and nitrogen were carried out on a Coleman analyzer. Determinations of chlorine, metal and sulphur were done gravimetrically.[37] The molar conductances of the complexes were determined at 10^{-3} M concentration in DMSO using a Waynekerr Universal conductivity bridge type B-221. Infrared spectra were recorded as KBr mulls on a Perkin Elmer 621 spectrophotometer. Proton magnetic resonance spectra (reference: tetramethylsilane) of the complexes were run on a Varian T-60 spectrometer at an operating temperature of 38°C. The electronic absorption spectra were recorded in silica cells on a Unicam SP-800 spectrophotometer in the range of 800–250 nm.

Preparation of the Schiff Bases and the Complexes

The complexes of the general formula ML_2Cl_2 (M = Si, Ti, Zr or Sn and L = *O*-hydroxyacetopheno-amino acid Schiff base) were prepared by reacting the preformed Schiff base with the metal chloride. The Schiff bases were prepared by literature methods with slight modifications.[26,33] In a typical preparation, 20 mmole of the amino acid (1.50 g glycine, 2.62 g leucine or 4.80 g cystine) was dissolved in 25 mL of absolute ethanol and a solution containing 20 mmole (2.4 mL) of *O*-hydroxyacetophenone in 30 mL of absolute ethanol was added. The mixture was refluxed at 50°C for four hours. The Schiff base and water were formed in the reaction mixture. After cooling the reaction mixture to room temperature the Schiff base was isolated by treating the reaction mixture with 50 mL diethyl ether and removing the water by a solvent batch extraction process. Diethyl ether was removed from the Schiff base by heating at 35–40°C for 20 min. To the isolated solution of Schiff base in ethanol, 10 mmole of the metal chloride (1.69 g $SiCl_4$, 1.89 g $TiCl_4$, 2.33 g $ZrCl_4$ or 2.61 g of $SnCl_4$) in 20 mL acetone was added dropwise and the mixture was again refluxed at 50°C for two hours, when a solid appeared. The excess of solvent was removed under reduced pressure. The solid complex was washed with 20 mL of absolute ethanol, 20 mL acetone and 10 mL diethyl ether. The complex was dried in an oven at 110°C for six hours and finally in a vacuum desiccator for four hours.

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