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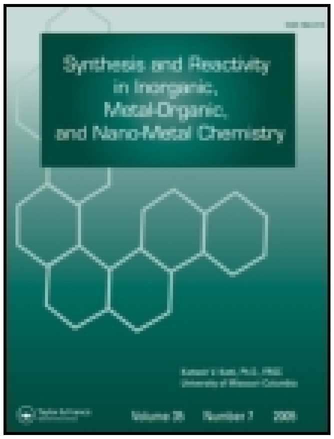

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Synthesis of Some Organometallic Complexes of Ti(IV)/Zr(IV) Involving Sulfur Containing Schiff Base Ligands: Spectral, Electrochemical, Surface Morphology, and Antimicrobial Studies

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Synthesis of Some Organometallic Complexes of Ti(IV)/Zr (IV) Involving Sulfur Containing Schiff Base Ligands: Spectral, Electrochemical, Surface Morphology, and Antimicrobial Studies

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The reactions of bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride with Schiff base derived by condensing thiophene-2-carboxaldehyde (tc), pyridine-2-carboxaldehyde (pc), and 5-methylthiophene-2-caroxaldehyde (mtc) with sulfamethoxazole (sm) have been studied in refluxing tetrahydrofuran under nitrogen atmosphere. The complexes of the type $[Cp_2MCl(L)]Cl$ (L = tc-sm, pc-sm, and mtc-sm; M = Ti/Zr) have been isolated and have been characterized using elemental analyses, molar conductance, mass, ^{1}H NMR, ^{13}C NMR, IR, UV-Vis, CV, TGA, powder XRD, and SEM. The results show that the Schiff base ligands are coordinated to the metal ions in a bidentate manner. Antimicrobial studies were conducted to assess growth inhibition potential of complexes and ligands against various fungal and bacterial strains.

Keywords: Schiff base, IR, NMR, CV, SEM

Introduction

Metal based drugs have been used in medicine for many centuries, but very often only in an empirical fashion. The biological application of organometallic complexes of the fourth group transition metals have been extensively studied.[1–6] The bis(cyclopentadienyl)titanium/zirconium complexes can be viewed as potential anticancer agents owing to their ability to organize organic ligands in three-dimensional space to target receptors, coupled with the redox properties of the tunable metal centre and lability of the metal–carbon bonds.[7–9] Schiff bases are considered as a very important class of organic compounds which have wide applications in the analytical, catalytic, and biological fields. Metal complexes of these ligands are sometimes more effective than the free ligands.[10–14] It has also been observed that a small structural change in the ligand may lead to the enhanced activity of the metal complexes. Among the various classes of biologically active coordination compounds, complexes with sulfonamides constitute an important class of antimicrobial agents.[15,16] A wide range of biological activities of sulfamethoxazole derivatives include pharmacological properties such as antibacterial, anticancer, anti-HIV activity, and agrochemical activities. [17] The literature reveals that investigation on Schiff base metal complexes involving sulfamethoxazole and heterocyclic aldehydes are sparse. The present study describes the synthesis and characterization of three novel Schiff base ligands *viz.* thiophene-2-carboxaldimine-sulfamethoxazole (tc-sm), pyridine-2-carboxaldimine-sulfamethoxazole (pc-sm), and 5-methylethiophene-2-carboxaldemine-sufamethoxazole (mtc-sm) and the complexes containing these three ligands and bis(cyclopentadienyl) titanium(IV)/zirconium(IV) dichloride.

Experimental

Materials and Reagents

All the reactions were carried out strictly under anhydrous condition under N_2 atmosphere. The aldehydes, sulfamethoxazole, bis(cyclopentadienyl)titanium(IV)dichloride and bis (cyclopentadienyl)zirconium(IV)dichloride were obtained from Sigma-Aldrich and used without further purification. Tetrahydrofuran was dried by sodium wire overnight and then refluxed until it gave a blue color with benzophenone. All other reagents and solvents were purchased from commercial sources and were of analytical grade.

Synthesis of Schiff Base Ligands

Sulfamethoxazole (5 mmol) dissolved in dry MeOH (50 mL) in a three-necked 100 mL R.B flask under N_2 atmosphere

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Table 1. Analytical data of the Schiff base ligands and their complexes

			Elemental analysisFound (calcd.) %					
Compound	Empirical formula	Color	C	H	N	M	$\Lambda c(\mathrm{Ohm}^{-1}\mathrm{cm}^{2}\mathrm{mol}^{-1})$	$\lambda_{\max}$(nm)
tc-sm	$C_{15}H_{13}N_3S_2O_3$	Light Yellow	51.08 (51.87)	3.90 (3.75)	12.36 (12.10)	—	—	220, 268, 373
$[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$	$TiC_{25}H_{23}N_3S_2O_3Cl_2$	Brown	48.93 (49.91)	3.98 (3.83)	7.11 (6.99)	8.86 (8.98)	82	222, 265362, 423
$[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$	$ZrC_{25}H_{23}N_3S_2O_3Cl_2$	Brown	45.67 (46.58)	3.62 (3.57)	6.61 (6.52)	15.31 (15.53)	88	225, 265365, 420
pc-sm	$C_{16}H_{14}N_4SO_3$	Yellow	55.12 (56.14)	4.20 (4.09)	16.42 (16.37)	—	—	224, 270 365
$[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$	$TiC_{26}H_{24}N_4SO_3Cl_2$	Deep Brown	53.12 (52.35)	4.83 (4.03)	9.19 (9.39)	8.99 (9.06)	89	226, 269 361, 426
$[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$	$ZrC_{26}H_{24}N_4SO_3Cl_2$	Dark Brown	50.22 (49.13)	4.25 (3.94)	8.12 (8.82)	14.28 (14.41)	83	232, 256 352, 430
mtc-sm	$C_{16}H_{15}N_3S_2O_3$	Yellow	52.85 (53.18)	4.32 (4.15)	11.91 (11.63)	—	—	235, 258 375
$[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$	$TiC_{26}H_{25}N_3S_2O_3Cl_2$	Light Brown	49.65 (50.73)	4.35 (4.06)	6.98 (6.83)	8.69 (8.79)	86	225, 261 361, 421
$[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$	$ZrC_{26}H_{25}N_3S_2O_3Cl_2$	Brown	46.35 (47.71)	3.62 (3.82)	6.85 (6.42)	14.05 (14.25)	86	230, 260 352, 423

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Table 2. ^{1}H and ^{13}C NMR spectral data of Schiff base ligands and their complexes

Ligand/complex	Nucleus	0	—C_5H_5	Aromatic (—CH)	—CH=N	—NH
tc-sm	^{1}H	2.32	—	7.2–7.9	7.17	8.6
	^{13}C	12.38	—	116.2–152.6	157.52	—
$[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$	^{1}H	2.34	6.59	7.25–7.85	7.3	8.58
	^{13}C	12.39	114.5	116.5–152.8	159. 52	—
$[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$	^{1}H	2.36	6.68	7.35–7.92	7.32	8.59
	^{13}C	12.38	114.5	116.3–152.5	160.11	—
pc-sm	^{1}H	2.32	—	7.5–7.75	7.05	8.72
	^{13}C	12.38	—	117.1–153.0	150.41	—
$[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$	^{1}H	2.31	6.54	7.53–7.7	7.26	8.72
	^{13}C	12.39	115.4	117.0–153.2	152.32	—
$[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$	^{1}H	2.33	6.62	7.52–7.89	7.22	8.73
	^{13}C	12.38	115.6	122.3	153.21	—
mtc-sm	^{1}H	2.3	—	7.52–7.68	7.15	8.78
	^{13}C	12.38	—	116.6–152.6	158.13	—
$[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$	^{1}H	2.31	6.57	7.5–7.7	7.32	8.8
	^{13}C	12.39	114.3	116.8–152.6	160.43	—
$[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$	^{1}H	2.35	6.58	7.54–7.77	7.36	8.79
	^{13}C	12.4	114.3	116.5–152.8	161.12	—

was mixed with 5 mmol of thiophene-2-carboxaldehyde (tc-sm)/pyridine-2-carboxaldehyde (pc-sm)/5-methylthiophene-2-carboxaldehyde (mtc-sm) and KOH pellets (5 mmol). The reaction mixture was vigorously stirred at room temperature for15 minutes and then refluxed at 70–80°C for 8 h. The yellow solution was reduced to one-third of its original volume by rotary evaporation. The concentrated filtrate thus obtained was poured into diethylether, when a pale yellow to yellow precipitate was formed. This was collected by vacuum filtration and washed several times with anhydrous ether and then dried in *vacuo* over anhydrous $CaCl_2$. The yields of the isolated ligands were found to be 72–80%.

Synthesis of Ti(IV))/Zr(IV) Schiff Base Complexes

To a refluxing solution of bis(cyclopentadienyl)titanium(IV) dichloride (2 mmol) in 40 mL anhydrous tetrahydrofuran under N_2 atmosphere in a three neck 100 mL R.B flask, 2 mmol of the ligand (tc-sm, pc-sm, and mtc-sm) was added in 1:1 ratio and the reaction mixture was stirred and then refluxed for 36 h. The reddish brown to dark brown colored complex so obtained was filtered, washed with anhydrous tetrahydrofuran and ether and then dried *in vacuo* over anhydrous $CaCl_2$. In the case of Zr(IV) Schiff base complexes reflection was not employed otherwise all the reaction conditions are same. An orange to reddish brown colored product

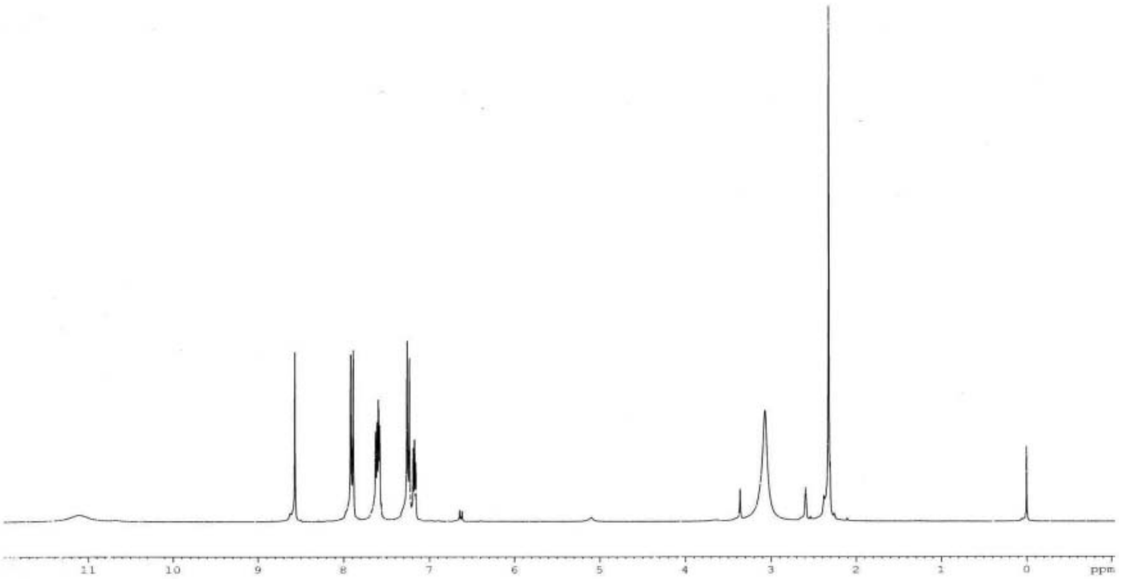

Fig. 1. ^{1}H-NMR spectrum of tc-sm.

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Table 3. IR spectral data of the Schiff base ligands and their complexes (cm^{-1})

Compound	$\nu_{azo.}$(C=N)	$\nu_{ring.}$(C=N)	ν (C—S)	ν (N—H)	$\nu(C_5H_5)$	ν(M—N)	ν(M—S)
tc-sm	1616	1583	628	3454	—	—	—
$[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$	1593	1561	624	3452	3103	—	413
$[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$	1612	1594	622	3453	3100		410
pc-sm	1618	1592	655	3384	—		
$[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$	1598	1590	654	3384	3101	534	
$[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$	1610	1592	648	3385	3103	528	
mtc-sm	1617	1587	665	3361	—		
$[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$	1612	1592	689	3363	3104		417
$[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$	1613	1595	661	3362	3100		412

was formed after 24 h of stirring under nitrogen atmosphere at room temperature.

Physical Measurements

Elemental analyses were done using a Perkin-Elmer elemental analyzer. Molar conductance of the complexes was measured in DMSO (10^{-3}M) solution using a coronation digital conductivity meter. IR spectra were recorded in KBr disc on a JASCO FT/IR-410 spectrometer in the 4000–400 cm^{-1} region. The electronic spectra were recorded on a PerkinElmer Lambda-25 UV-Visible spectrometer. The mass spectra of the ligands and their complexes were recorded on a JEOL-AccuTOF JMS-T100LC mass spectrometer. The ^{1}H-NMR and ^{13}C-NMR spectra of the ligands and their complexes were recorded in JEOL GSX 400 FT–NMR spectrometer. Cyclic voltammetric measurements were carried out in a Bio-Analytical system (BAS) model CV-50 W electrochemical analyzer. The three-electrode cell comprises of a reference Ag/AgCl, auxiliary platinum and working glassy electrodes. Tetrabutylammoniumperchlorate was used as supporting electrolyte. Thermal analysis was carried out on SDT Q 600/V8.3 build 101 thermal analyzer with the conditions; sample mass 6–8 mg, heating rate 20°C/min and nitrogen atmosphere (flow rate 20 mL/min). Powder XRD was recorded on a Rigaku Dmax X-ray diffractometer with Cu-Kα radiation ($\lambda_{K\alpha} = 1.5406$). SEM images were recorded in a Hitachi SEM analyzer.

Results and Discussion

Characterization of Schiff Base Ligands

The Schiff base ligands are soluble in all common organic solvents. The results of elemental analyses (Table 1) of the ligands (tc-sm, pc-sm, and mtc-sm) are in good agreement with those calculated for the suggested formulae. The EI mass spectra of the ligands (tc-sm, pc-sm, and mtc-sm) show a well-defined molecular ion peak at m/z = 348.10 (R. I. = 23%), m/z = 343.11(R. I. = 21%), and m/z = 362.87(R. I. = 18%). These are consistent with the proposed molecular formulae of the ligands. The ^{1}H-NMR spectra of tc-sm, pc-sm, and mtc-sm ligands show peaks at 7.17, 7.05, and 7.15 ppm, respectively (Table 2), characteristic of azomethine[18] proton

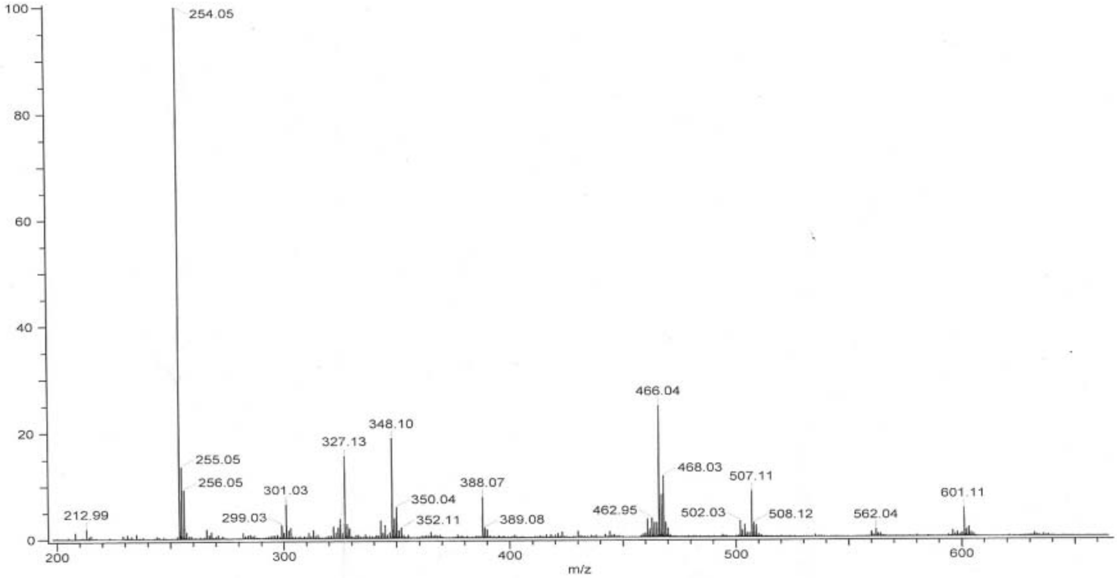

Fig. 2. Mass spectrum of $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$.

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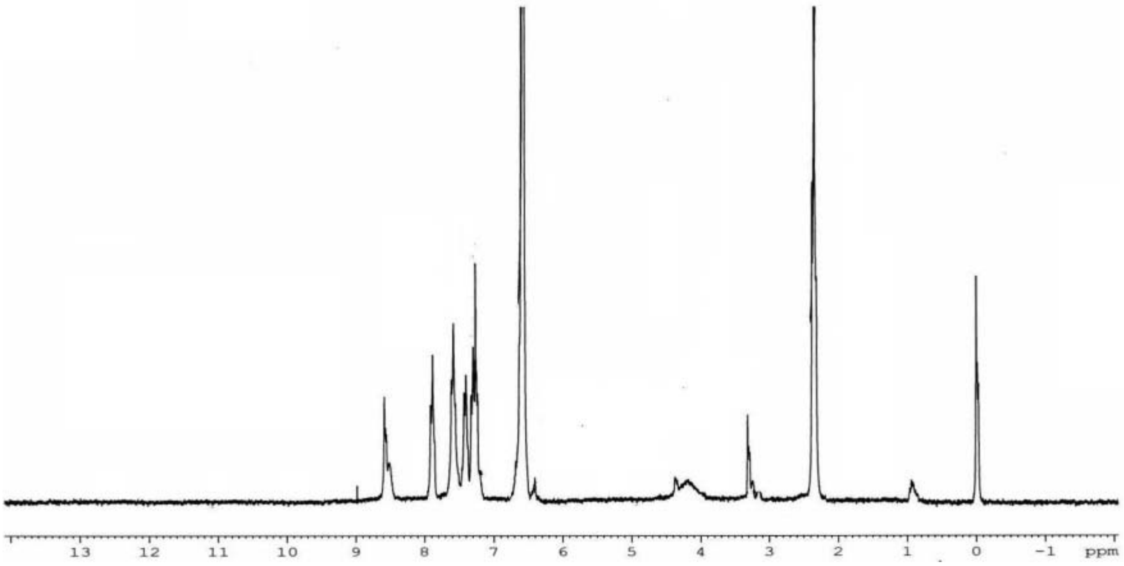

Fig. 3. ^{1}H-NMR spectrum of $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$.

(—CH=N—). The aromatic ring protons are observed in the 7.2–7.9 ppm range.[19] As a representative system, the ^{1}H-NMR spectrum of the Schiff base ligand tc-sm is shown in Figure 1. The ^{13}C-NMR spectra (Table 2) of the ligands (tc-sm, pc-sm, and mtc-sm) show a peak respectively at 157.52, 150.41, and 158.13 ppm. These are assignable to azomethine carbon (—CH=N—).[20] In all the Schiff bases the peak at 12.38 ppm in ^{13}C-NMR spectrum is due to the methyl group present in the ligands.[20] The IR spectral data of the Schiff base ligands are given in Table 3. All the ligands respectively show strong bands at 1616, 1618, and 1617 cm^{-1} due to azomethine stretching frequency. The sharp band present in the region ~3300 and ~1520 cm^{-1} in the IR spectra is due to peptide N-H stretching frequency.[19,20] The UV-Vis spectra of free ligands exhibit a broad band at 365–375 nm, which can be assigned to π-π* and n-π* transition of the azomethine (>C=N) chromophore. The intense absorption band observed at higher energy of 225–270 nm is due to the π -π* transition of the benzene ring of the Schiff base ligands.

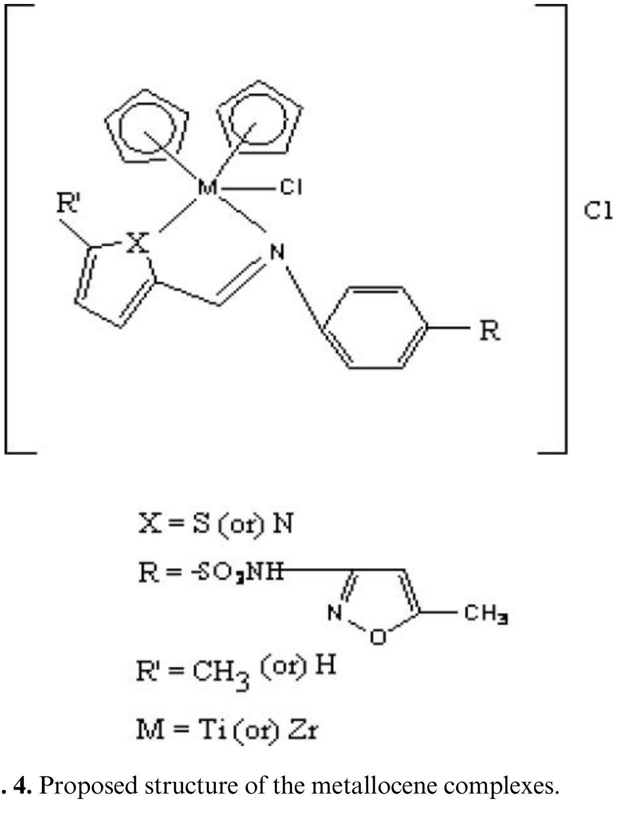

Fig. 4. Proposed structure of the metallocene complexes.

Characterization of Metal Schiff Base Complexes

The analytical data of the metal Schiff base complexes are given in Table 1. The Ti(IV) and Zr(IV) complexes were tend to be soluble in MeOH, EtOH, DMF, DMSO, and insoluble in other common organic solvents. The molar conductance values (Table 1) of metal complexes in DMSO at 10^{-3}M fall in the 83–89 ohm^{-1}cm^{2}mol^{-1} range, which is well within those for the 1:1 electrolites.[21] This demonstrates that the present complexes have 1:1 electrolitic nature. The data show that the $(Cp)_2$metal to Schiff base ligand ratio is 1:1 in all the complex systems. The EI mass spectra of $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$, $[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$, $[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$, $[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$, $[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$, and $[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$ show a peak at m/z = 601.11 (11%), 594.31 (14%), 614.11 (19%), 647.06 (14%), 637.35 (17%) and 656.42 (13%), respectively. This indicates that the complexes are monomeric confirming the $(Cp)_2$metal to Schiff base ligand ratio to be 1:1. The EI mass spectrum of $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$ is shown in Figure 2. The reactions of bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride with Schiff bases can be represented by the following equation:

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Table 4. Electrochemical data of the complexes

Complex	Epc (V)	Epa (V)	ΔEp (mV)	Nature
$[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$	–0.6145	−1.0105	396	Quasireversible
$[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$	−0.6296	−1.0483	419	Quasireversible
$[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$	−0.7820	−1.0075	225	Quasireversible
$[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$	−0.7898	−1.0772	287	Quasireversible
$[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$	−0.7925	−1.0225	230	Quasireversible
$[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$	−0.7990	−1.0520	253	Quasireversible

$$CP_2MCl_2 + L \xrightarrow[N_2/\Delta]{THF} [CP_2MClL]Cl$$

24-36 h

where L = tc-sm, pc-sm or mtc-sm and M = Ti or Zr

NMR Spectra

The ^{1}H-NMR and ^{13}C-NMR spectral data of the Ti(IV)/Zr (IV) complexes are given in Table 2. The ^{1}H-NMR spectrum of $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$ is shown in Figure 3. The peak in the ^{1}H-NMR spectra of free ligands tc-sm, pc-sm and mtc-sm respectively at 7.17, 7.05, and 7.15 ppm, characteristic of azomethine proton(—CH=N—) is slightly shifted to downfield in the spectra of Ti(IV)/Zr(IV) complexes. This difference in (—CH=N—) peak position could arise due to the coordination of its neighboring nitrogen atom, which indicates the metal to coordinate the ligand through azomethine nitrogen atom. The aromatic ring protons observed in the 7.2–7.9 ppm range in the ligands are unchanged in the Ti(IV)/Zr (IV)complexes. The signal in all the Schiff base derivatives at 6.5–6.7 ppm can be assigned to the protons of the cyclopentadienyl ring. The appearance of a single sharp cyclopentadienyl resonance is attributed to the rapid rotation of the cyclopentadienyl ring around the metal ring axis.[22]

The ^{13}C-NMR spectra of Ti(IV)/Zr(IV) complexes (Table 2) show peak at 157.52, 150.41, and 158.13 ppm for the tc-sm, pc-sm, and mtc-sm ligand systems, respectively. These peaks which are assignable to azomethine carbon (—CH=N—) show considerable shift in the complexes indicating the involvement of azomethine nitrogen atoms during coordination.[22] The peak seen at ~12.38 ppm in the complexes is due to the CH_3 group present in the Schiff base ligands.

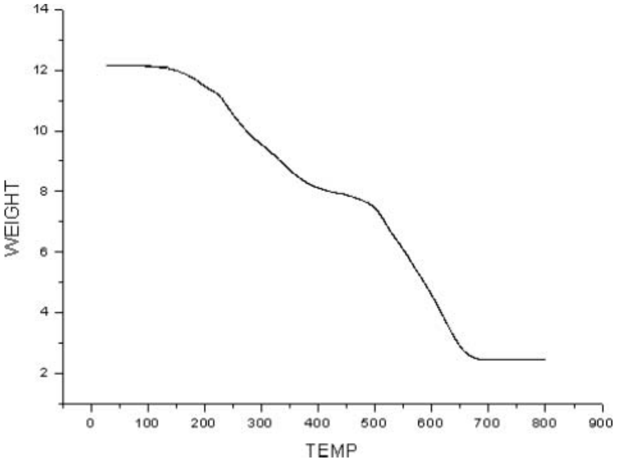

Fig. 5. TGA of $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$.

IR Spectra

The IR spectral data of Ti(IV)/Zr(IV) complexes are given in Table 3. During complexation, IR stretching frequency for the free Schiff base ligands respectively at 1616, 1618, and 1617 cm^{-1} assigned to azomethine bands are shifted to lower frequency indicating the coordination of azomethine nitrogen to the metal ion (Table 3). The sharp band present in the region ~3300 and ~1520 cm^{-1} is due to peptide N-H stretching frequencies which are unchanged in the complexes. This shows the absence of the involvement of N-H group during complex formation.[19,22] The spectra of the metal complexes show new bands in the 410–420 cm^{-1} and 520–540 cm^{-1} regions, which may probably be due to the formation of M-S and M-N bonds, respectively.[22]

Electronic Spectra

The electronic spectra of Ti(IV)/Zr(IV) complexes (Table 1) show two absorption bands respectively at 350–365 and 420–430 nm regions, showing the coordination of azomethine nitrogen to the metal atom and the charge transfer spectrum in accordance with the (n-1)$d^0$$ns^0$ electronic configuration of the metal atoms.[19,22]

The above discussion shows that the ligands act as neutral bidentate chelating agents, and the proposed structure of the Schiff base complexes are shown in Figure 4. These structures are in good agreement with those reported earlier for the well-known pentacoordinate structures for titanium and zirconium complexes.[19,23]

Electrochemistry

The cyclic voltammogram was recorded in MeOH solution at a scan rate of 100 mVs^{-1} in the potential range +2.0 to –2.0V. The cyclic voltammogram of all the complexes (Table 4) shows a well-defined redox process corresponding to the formation of the quasi-reversible M(IV)/M(III)couple.[24–26] The cyclic voltammogram of $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$ and $[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$

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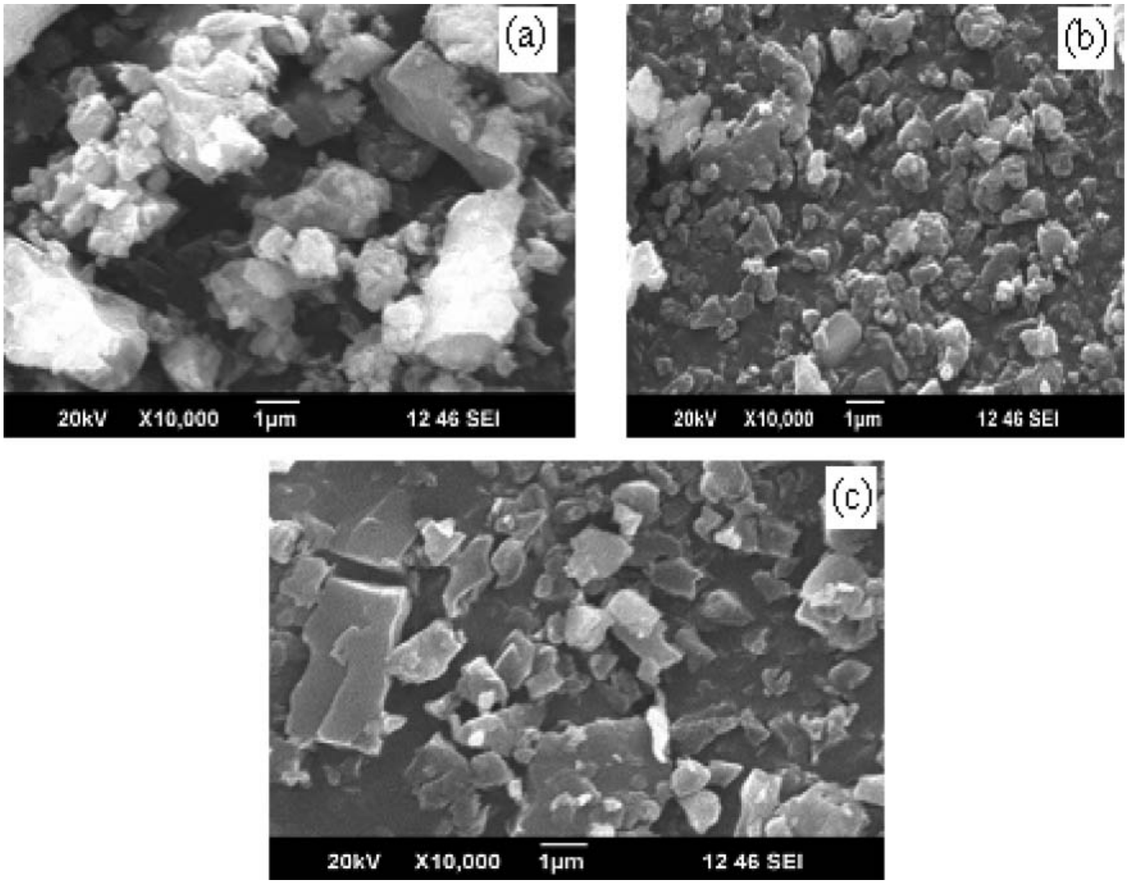

Fig. 6. SEM images of (a) $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$; (b) $[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$, and (c) $[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$.

complexes show a redox processes occurring at negative potential with the cathodic peak potential at –0.6145 and –0.6296 V versus Ag/AgCl and anodic peak potential at –1.0105 and –1.0483 V corresponding to the Ti(IV)/Ti(III) and Zr(IV)/Zr(III) couple, respectively. The peak-to-peak separation (ΔEp = 396 and 419 mV) indicates quasireversible one electron transfer process. The $[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$ and $[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$ complexes displayed reduction couples at –0.7820 V and –0.7898 V versus Ag/AgCl with the corresponding anodic waves at –1.0075 and at –1.0772 V on the reverse scan. The peak separation values (ΔEp = 225 and 287 mV) indicate totally quasireversible character for the one electron transfer reaction. Cyclic voltammogram of the $[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$ and $[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$ complexes show one quasireversible redox processes

Table 5. % Zone of inhibition of the synthesized compounds against the growth of bacteria (mm)

Compound	*E. coli*	*K. pneumonia*	*P. vulgaris*	*P. aeruginosa*	*S. aureus*
tc-sm	9.0	10.5	9.3	7.8	9.5
$[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$	9.5	10.7	9.6	8.0	9.8
$[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$	9.6	10.5	9.5	8.2	9.9
pc-sm	8.6	9.1	9.1	8.1	8.6
$[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$	9.0	9.4	9.2	8.9	8.7
$[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$	8.9	9.6	9.6	9.2	9.1
mtc-sm	9.1	10.3	8.1	10.3	9.2
$[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$	12.6	14.6	11.7	10.8	9.2
$[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$	12.2	13.8	9.8	10.6	10.2
$(C_5H_5)_2TiCl_2$	6.3	6.7	6.1	5.1	5.8
$(C_5H_5)_2ZrCl_2$	5.8	6.2	4.9	4.7	5.2
DMF	2.0	1.8	2.2	2.1	2.3
Ampicillin	17.2	17.7	18.2	17.3	17.5

Table 6. % Zone of inhibition of the synthesized compounds against the growth of fungi (mm)

Compound	*A. niger*	*R. stolonifer*	*A. flavus*	*R. bataicola*	*C. albicans*
tc-sm	9.5	9.2	10.1	9.5	9.2
$[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$	9.8	9.8	10.6	9.8	9.8
$[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$	9.6	9.7	10.4	9.9	9.7
pc-sm	9.5	9.1	9.5	8.3	8.6
$[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$	10.8	9.5	10.0	8.8	9.1
$[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$	10.5	9.6	9.9	9.1	9.1
mtc-sm	10.6	10.2	12.8	9.1	9.5
$[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$	12.3	12.1	13.1	9.6	9.8
$[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$	12.2	11.8	13.1	9.5	9.5
$(C_5H_5)_2TiCl_2$	6.2	5.3	6.6	5.1	6.2
$(C_5H_5)_2ZrCl_2$	5.8	4.8	4.9	6.8	5.2
DMF	2.1	2.6	2.3	1.8	2.1
Ampicillin	18.5	18.1	19.2	19.8	18.2

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occurring at negative potential and with a peak-to-peak separation (ΔEp value) of 230 and 253 mV, respectively. The redox process occurs with the cathodic peak potential at –0.7925 and –0.7990 V and anodic peak potential at –1.0225 and –1.0520 V.

Thermogravimetric Studies

Thermogravimetric studies were made in the temperature range 25–900°C. Thermal decomposition curves of the complexes of Ti(IV) and Zr(IV) show a similar sequence of two decomposition steps. All the materials showed very high stability toward heat. Only a negligible mass loss took place between 25 and 100°C owing to the removal of entrapped solvent molecules. The materials started degrading after 117°C and were completely pyrolyzed at around 678°C. The first step was removal of cyclopentadienyl part and one of the chloride ions at the range of 220–461°C. This follows the removal of the remaining organic ligand moieties leaving metal oxide residue in the second step (476–678°C).

A representative TGA curve of Ti(IV)-tc-sm complex is shown in Figure 5. In this a weight loss 26.97% (calcd. 27.59%) in the temperature range 224–446° C is observed as a first step due to a loss of cyclopentadienyl moiety and one of the chloride ions. The second decomposition step of the complex is observed in the range of 478–672° C. In this step it loses the remaining organic ligand moieties leaving a 19.33% residue. Here the amount of residue obtained is larger than pure metal oxide. It is difficult to decide on the decomposition mechanism since the weight of the residue corresponds to titanium oxide. Because the heating is carried out in nitrogen, the residue cannot be pure titanium oxide but most probably it is carbon or nitrogen containing material.[27,28]

Powder XRD and SEM

Powder XRD pattern of the complexes was recorded over the $2\theta = 0$–80 range. The complexes show sharp crystalline peaks indicating their crystalline nature. The average crystallite sizes of the complexes d_{XRD} were calculated using Scherrer's formula.[29] The $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$, $[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$, $[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$, $[(C_5H_5)_2ZrCl(tc\text{-}sm)]Cl$, $[(C_5H_5)_2ZrCl(pc\text{-}sm)]Cl$, and $[(C_5H_5)_2ZrCl(mtc\text{-}sm)]Cl$ complexes have an average crystallite size of 48–61 nm, suggesting that the complexes are in nanocrystalline phase.

The SEM micrographs of the complexes $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$, $[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$, and $[(C_5H_5)_2TiCl(mtc\text{-}sm)]Cl$ are shown in Figures 6a–c. From the SEM image, it is observed that grains are well resolved and uniformly distributed in the $[(C_5H_5)_2TiCl(tc\text{-}sm)]Cl$ complex. Moreover, the average grain size found from SEM shows that the complex is polycrystalline with nanosized grains. The SEM image of $[(C_5H_5)_2TiCl(pc\text{-}sm)]Cl$ complex shows irregularly shaped agglomerated particles of submicron size and the presence of small grains is in micrometer range.

Antimicrobial Activity

The ligands tc-sm, pc-sm, and mtc-sm and their Ti(IV)/Zr(IV) complexes have been screened for antimicrobial activity against the bacteria (*E. coli, K. pneumonia, P. vulgaris, P. aeruginosa*, and *S. aureus*) and the fungal species (*A. niger, R. stolonifer, A. flavus, R. bataicola*, and *C. albicans*) by paper disc method.[30,31] The concentration for these samples has been maintained as 1000 ppm in DMF. The results obtained are explained on the basis of Overtone's concept and chelation theory.[31,32] The variation in the activity of different complexes against different organisms depends either on the impermeability of the cells of the microbes or difference in ribosomes of microbial cells. The results show that the antibacterial and antifungal activities of ligands may be significantly enhanced on chelation with transition metal ions. Chelation considerably reduces the polarity of the metal ion because of the partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the chelate ring. Such chelation could increase the lipophilic character of the central metal atom, which subsequently favors the permeation through the lipid layer of cell membrane.[33–35] The antibacterial activity of the complexes

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together with parent ligands in DMF has been screened by the paper disk plate method at 1000 ppm concentration. The inhibition zone (mm) around each disk was measured after 24 h and the results of these studies are listed in Table 5. The fungicidal activity of the ligands and the complexes were evaluated in DMF. The discs were placed on the previously seeded plates and incubated at 37°C and the diameter of inhibition zone around each disc was measured after 72 h. The average percentage inhibition was calculated using the expression: inhibition (%) = 100 (C-T)/C, where C and T are the diameters of the fungus colony in control and test plates, respectively and the recorded results are summarized in Table 6. From the antimicrobial studies it is observed that the ligands, tc-sm, mtc-sm, and their complexes have shown good antimicrobial activity towards all the microbes. This may be due to the presence of heterocyclic sulfur atom in these ligands, which enhance the antimicrobial activity.[34,36]

Conclusions

Three new Schiff base ligands tc-sm, pc-sm, mtc-sm, and their cyclopentadienyl Ti(IV)/Zr(IV) complexes were prepared and characterized using various analytical techniques. The NMR, IR, and electronic spectral data show that the Schiff base ligands coordinate with metal ion through azomethine nitrogen and heterocyclic nitrogen or sulfur atoms. Interestingly, Ti(IV) and Zr(IV)complex exhibit nanostructures. It is clear from the antimicrobial data that complexes are slightly more active than the parent ligands.

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