

Spectroscopic characterization of some new coordination compounds of titanium(IV) with Schiff bases of amino acids

Hari Shankar Yadav, Sangeeta Sihag, A. K. Varshney and S. Varshney*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, Rajasthan, India

E-mail : saritavarshney@rediffmail.com

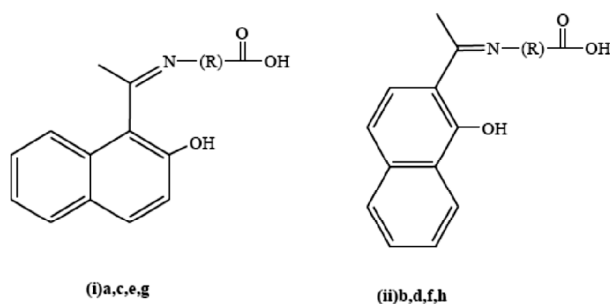
Manuscript received online 03 August 2014, revised 28 December 2014, accepted 08 January 2015

Abstract : Some new coordination compounds of titanium(IV) are synthesized by the reaction of titanium isopropoxide with ligand in 1 : 1 and 1 : 2 molar ratios using dry benzene as reaction medium. Ligands used in these studies are the Schiff bases prepared by the condensation of ketones (1-acetyl-2-naphthol and 2-acetyl-1-naphthol) with amino acids (glycine, leucine, β -alanine and valine) in ethanol. An attempt has been made to probe the structures, bonding pattern and geometries of their coordination compounds by the elemental analysis, molecular weight determination, conductance measurement and IR, NMR (^1H , ^{13}C) spectral evidences. Ligands and their coordination compounds have been screened for their antibacterial and antifungal activities. Their comparative results are quite encouraging.

Keywords : Schiff base, antibacterial activities, antifungal activities, spectral evidences, titanium(IV) complexes.

Introduction

The coordination chemistry of Schiff bases has undergone dramatic growth over last forty years¹⁻⁵. It has been reported that metal complexes of amino acid Schiff bases with transition metals possess great interest due to their pharmacological activities which is frequently higher than the free ligands⁶. The chemistry of amino acid Schiff base ligands and their compounds with metal has also shown high reactivity, specificity and biological significance in many fields such as antifertility, antibacterial and antifungal⁷⁻⁹ studies. The interest in titanium(IV) complexes is due to their different mode of coordination and applicability in different area of science¹⁰⁻¹². Due to the introducing of ($>\text{C}=\text{N}$) azomethine linkage with the titanium ion, the biological activity and efficiency of complexes have affected. In the present paper we report the synthesis of ligands (L^1H_2 - L^8H_2) by the condensation reaction with amino acids (glycine, leucine, β -alanine and valine) and 1-acetyl-2-naphthol and 2-acetyl-1-naphthol with keeping good above expectable facts (antibacterial, insecticide, fungicides) in mind with creative efficiency and their corresponding titanium complexes were also synthesized. The structure of the amino acid Schiff base ligands are shown in Fig. 1.



R = $-(\text{CH}_2)-\{\text{L}^1\text{H}_2\}$ and $\{\text{L}^2\text{H}_2\}$, $-\text{CHCH}_2\text{CHMe}_2-\{\text{L}^3\text{H}_2\}$ and $\{\text{L}^4\text{H}_2\}$, $-(\text{CH}_2)_2-\{\text{L}^5\text{H}_2\}$ and $\{\text{L}^6\text{H}_2\}$, $-\text{CHCHMe}_2-\{\text{L}^7\text{H}_2\}$ and $\{\text{L}^8\text{H}_2\}$

Fig. 1. Structures of the ligands.

Experimental

Materials and analytical methods : The entire chemicals used were of the AR grade and the solvents were dried by standard method¹³ and ethanol was dried over magnesium turnings with the iodine crystals. All the reactions were carried out under strictly anhydrous condition. Infrared spectra were recorded on a FTIR spectrophotometer, using a model A-8400 S, Shimadzu using KBr pellets. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 and $\text{DMSO}-d_6$ solution on a JEOL AL-300 spectrometer. C, H and N were analysed by Vario EL III

Element Analyzer instrument. Titanium was estimated as TiO_2 by direct ignition after treating with ammonium hydroxide. Molecular weights were determined by the Rast's method. Molar conductance measurements were made in anhydrous DMF at 34 ± 1 °C using a Systronics Model 305 conductivity bridge. Melting points were measured by the melting point apparatus.

Synthesis of ligands :

The Schiff base ligands [$\text{L}^1\text{H}_2\text{-L}^8\text{H}_2$] were prepared by the condensation 1-acetyl-2-naphthol and 2-acetyl-1-naphthol with corresponding amino acids (glycine, leucine, β -alanine and valine) in 1 : 1 molar ratio using absolute alcohol as a reaction medium in a round bottom flask. The reaction mixture was refluxed for ~6–7 h and then it was allowed to cool at room temperature. The obtained precipitates were filtered, washed with EtOH and recrystallized from hot EtOH. The crystals finally dried under reduced pressure and yield, m.p.s were recorded.

1-Acetyl-2-naphthol glycine [L^1H_2] (**1(i)a**), creamy solid, m.p. 89 °C; 2-acetyl-1-naphthol glycine [L^2H_2] (**1(ii)b**), shiny yellow solid, m.p. 170 °C; 1-acetyl-2-naphthol leucine [L^3H_2] (**1(i)c**), light brown solid, m.p. 228 °C; 2-acetyl-1-naphthol leucine [L^4H_2] (**1(ii)d**), light yellow solid, m.p. 84 °C; 1-acetyl-2-naphthol β -alanine [L^5H_2] (**1(i)e**), cream solid, m.p. 247 °C; 2-acetyl-1-naphthol β -alanine [L^6H_2] (**1(ii)f**), yellowish powder, m.p. 213 °C; 1-acetyl-2-naphthol valine [L^7H_2] (**1(i)g**), white solid, m.p. 218 °C; 2-acetyl-1-naphthol valine [L^8H_2] (**1(ii)h**), light yellow solid, m.p. 197 °C.

Synthesis of complexes :

The complexes [$\text{Ti}(\text{L})(\text{OPr}^i)_2$] and [$\text{Ti}(\text{L})_2$] have been prepared as solid from the reaction of [$\text{Ti}(\text{OPr}^i)_4$] with azomethine of amino acid LH_2 in 1 : 1 and 1 : 2 molar ratio in dry benzene. The contents were refluxed for ~8–10 h and isopropanol liberated in the reaction was removed azeotropically with benzene. After the completion of the reaction, the excess solvent was removed under reduced pressure. The obtained solid compounds were purified by recrystallization from EtOH 2–3 times and

dried by using a vacuum pump at room temperature. The purity of the compounds was checked by TLC using silica gel-G as an adsorbent.

[$\text{Ti}(\text{C}_{18}\text{H}_{23}\text{NO}_5)$] (**2(i)a**) : Light brown solid; yield 77%; m.p. 219 °C; Calcd. : C, 59.07; N, 3.63; Ti, 11.93 (%), Found : C, 58.98; N, 3.44; Ti, 11.75 (%); Mol. wt. Calcd. : 407.28, Found : 407.12.

[$\text{Ti}(\text{C}_{18}\text{H}_{23}\text{NO}_5)$] (**2(ii)b**) : Yellow brown solid; yield 73%; m.p. 197 °C; Calcd. : C, 59.13; N, 3.55; Ti, 11.87 (%), Found : C, 58.98; N, 3.44; Ti, 11.75 (%); Mol. wt. Calcd. : 407.28, Found : 407.12.

[$\text{Ti}(\text{C}_{24}\text{H}_{33}\text{NO}_5)$] (**2(i)c**) : Cream solid; yield 71%; m.p. 209 °C; Calcd. : C, 62.37; N, 3.13; Ti, 10.49 (%), Found : C, 62.21; N, 3.02; Ti, 10.33 (%); Mol. wt. Calcd. : 463.39, Found : 463.18.

[$\text{Ti}(\text{C}_{24}\text{H}_{33}\text{NO}_5)$] (**2(ii)d**) : Shiny green solid; yield 76%; m.p. 218 °C; Calcd. : C, 62.53; N, 3.07; Ti, 10.67 (%), Found : C, 62.21; N, 3.02; Ti, 10.33 (%); Mol. wt. Calcd. : 463.54, Found : 463.18.

[$\text{Ti}(\text{C}_{21}\text{H}_{27}\text{NO}_5)$] (**2(i)e**) : Brown solid; yield 79%; m.p. 212 °C; Calcd. : C, 60.01; N, 3.47; Ti, 11.55 (%), Found : C, 59.87; N, 3.32; Ti, 11.36 (%); Mol. wt. Calcd. : 421.32, Found : 421.33.

[$\text{Ti}(\text{C}_{21}\text{H}_{27}\text{NO}_5)$] (**2(ii)f**) : Reddish brown solid; yield 81%; m.p. 185 °C; Calcd. : C, 59.99; N, 3.73; Ti, 11.47 (%), Found : C, 59.87; N, 3.32; Ti, 11.36 (%); Mol. wt. Calcd. : 421.77, Found : 421.33.

[$\text{Ti}(\text{C}_{23}\text{H}_{31}\text{NO}_5)$] (**2(i)g**) : Dark brown solid; yield 76%; m.p. 221 °C; Calcd. : C, 61.83; N, 3.27; Ti, 10.92 (%), Found : C, 61.48; N, 3.12; Ti, 10.65 (%); Mol. wt. Calcd. : 449.36, Found : 449.17.

[$\text{Ti}(\text{C}_{23}\text{H}_{31}\text{NO}_5)$] (**2(ii)h**) : Yellow green solid; yield 78%; m.p. 214 °C; Calcd. : C, 61.89; N, 3.29; Ti, 10.87 (%), Found : C, 61.48; N, 3.12; Ti, 10.65 (%); Mol. wt. Calcd. : 449.63, Found : 449.17.

[$\text{Ti}(\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_6)$] (**2(iii)a**) : White solid; yield 81%; m.p. 222 °C; Calcd. : C, 63.87; N, 5.43; Ti, 9.09 (%), Found : C, 63.41; N, 5.28; Ti, 9.03 (%); Mol. wt. Calcd. : 530.87, Found : 530.35.

[Ti(C₂₈H₂₂N₂O₆)] (**2(iv)b**) : Creamy solid; yield 79%; m.p. 210 °C; Calcd. : C, 63.46; N, 5.37; Ti, 9.12 (%), Found : C, 63.41; N, 5.28; Ti, 9.03 (%); Mol. wt. Calcd. : 530.77, Found : 530.35.

[Ti(C₃₆H₃₈N₂O₆)] (**2(iii)c**) : Yellowish orange; yield 71%; m.p. 219 °C; Calcd. : C, 67.37; N, 4.43; Ti, 7.49 (%), Found : C, 67.29; N, 4.36; Ti, 7.45 (%); Mol. wt. Calcd. : 642.66, Found : 642.56.

[Ti(C₃₆H₃₈N₂O₆)] (**2(iv)d**) : White solid; yield 74%; m.p. 228 °C; Calcd. : C, 67.33; N, 4.47; Ti, 7.67 (%), Found : C, 67.29; N, 4.36; Ti, 7.45 (%); Mol. wt. Calcd. : 642.64, Found : 642.56.

[Ti(C₃₀H₂₆N₂O₆)] (**2(iii)e**) : Brown solid; yield 80%; m.p. 212 °C; Calcd. : C, 64.61; N, 5.09; Ti, 8.58 (%), Found : C, 64.53; N, 5.02; Ti, 8.57 (%); Mol. wt. Calcd. : 558.47, Found : 558.40.

[Ti(C₃₀H₂₆N₂O₆)] (**2(iv)f**) : Reddish brown solid; yield 79%; m.p. 195 °C; Calcd. : C, 64.56; N, 5.13; Ti, 8.59 (%), Found : C, 64.53; N, 5.02; Ti, 8.57 (%); Mol. wt. Calcd. : 558.43, Found : 558.40.

[Ti(C₃₄H₃₄N₂O₆)] (**2(iii)g**) : Yellow powder; yield 76%; m.p. 201 °C; Calcd. : C, 66.53; N, 4.61; Ti, 7.82 (%), Found : C, 66.45; N, 4.56; Ti, 7.79 (%); Mol. wt. Calcd. : 614.66, Found : 614.51.

[Ti(C₃₄H₃₄N₂O₆)] (**2(iv)h**) : Dark brown solid; yield 72%; m.p. 216 °C; Calcd. : C, 66.49; N, 4.58; Ti, 7.84 (%), Found : C, 66.45; N, 4.56; Ti, 7.79 (%); Mol. wt. Calcd. : 614.63, Found : 614.51.

Bioassay :

Antibacterial test : *In vitro* antibacterial activity of the ligands [L¹H₂-L⁸H₂] and their corresponding complexes were evaluated against *Escherichia coli* (–) and *Staphylococcus aureus* (+) by using the paper disc plate method^{14–21}. The nutrient agar medium was used as a culture medium for bacterial growth. The compounds under investigation were dissolved in DMSO to get final concentration of 500 and 1000 ppm. The paper disc (Whatman no. 1) having diameter of 5 mm were soaked in these solutions and placed in appropriate medium pre-

viously seeded with tested organism in petridishes. The plate incubated for 24 h at 30 ± 2 °C. The zone of inhibition thus formed around each disc containing the test compound was measured accurately in mm. Streptomycin was used as reference compound for antibacterial activities. The antibacterial activities displayed by ligands and their complexes are shown in Table 1.

Table 1. Antibacterial screening data of the ligands and Ti^{IV} complexes

Compd.	Diameter of inhibition zone (mm)			
	(Conc. in ppm)			
	<i>Escherichia coli</i> (–)		<i>Staphylococcus aureus</i> (+)	
	500 ppm	1000 ppm	500 ppm	1000 ppm
L ¹ H ₂	7	9	11	15
L ² H ₂	8	10	13	16
L ³ H ₂	7	12	13	18
L ⁴ H ₂	9	11	14	17
TiC ₂₀ H ₂₅ NO ₅	10	14	16	19
TiC ₂₀ H ₂₅ NO ₅	12	17	18	18
TiC ₂₀ H ₂₅ NO ₅	11	15	14	19
TiC ₂₀ H ₂₅ NO ₅	16	18	18	18
Streptomycin	18	20	16	19
L ¹ H ₂ and L ² H ₂ = C ₁₄ H ₁₃ NO ₃ , L ³ H ₂ and L ⁴ H ₂ = C ₁₈ H ₂₁ NO ₃ .				

Antifungal test : An antifungal activity of the ligands [L¹H₂-L⁸H₂] and their corresponding complexes was found *in vitro* against *Aspergillus niger* and *Rhizopus phaseoli* by the agar plate technique²². In this method, the medium used is potato dextrose agar medium (composition : potato slices – 200 g, dextrose – 20 g, Agar-Agar – 15 g and distilled water 1000 ml). The solutions of the compounds in different concentration (100 and 200 ppm) in DMF were then mixed with the medium. The linear growth of the fungus was recorded by measuring the diameter of colony and the percent inhibition was calculated. Micostatin was used as reference compound for antifungal activities (Table 2).

Results and discussion

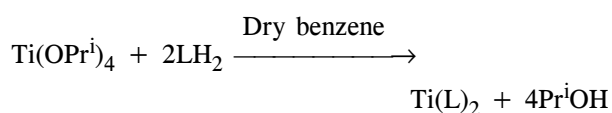
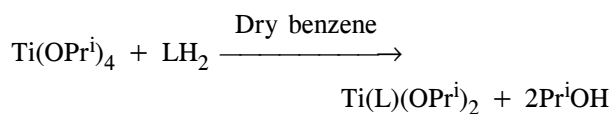
The complexes [Ti(L)(OPrⁱ)₂] and [Ti(L)₂] have been prepared by the reaction of [Ti(OPrⁱ)₄] with amino acid Schiff base ligands (LH₂) in a 1 : 1 and 1 : 2 molar ratio

Table 2. Antifungal activity of the ligands and Ti^{IV} complexes

Micostatin		L ³ H ₂		TiC ₂₄ H ₃₃ NO ₃		L ⁴ H ₂		TiC ₃₆ H ₃₈ N ₂ O ₆	
		100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm
<i>A. niger</i>	IZ	25	24	18	19	24	23	14	18
	(AI)	(1.80)	(1.75)	(1.30)	(1.35)	(1.72)	(1.65)	(1.00)	(1.25)
<i>R. phaseoli</i>	IZ	14	27	21	22	14	26	17	18
	(AI)	(1.93)	(1.57)	(1.50)	(1.54)	(0.98)	(1.86)	(1.18)	(1.27)

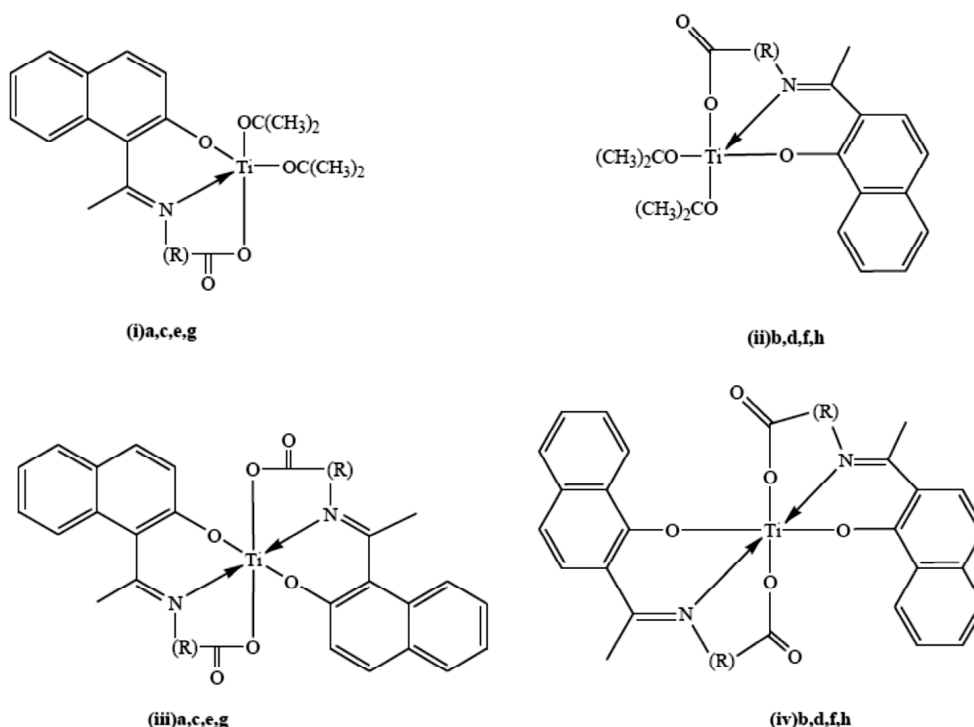
IZ = Inhibition zone (diameter in ppm); AI = Activity index (inhibition zone of tasted compounds), L³H₂ and L⁴H₂ = C₁₈H₂₁NO₃.

in dry benzene as shown below :



The above reaction was feasible with the liberation of isopropanol, which was removed. The reaction was completed in ~8–10 h of refluxing. All the newly synthesized Ti^{IV} complexes with the LH₂ are coloured solid

and good yield. The colour of complexes are associated with the presence of chromophoric azomethine group (–C=N). They are hygroscopic in air atmosphere and soluble in methanol, DMSO, DMF and other organic solvents. The low value of molar conductance (18–22 Ω^{–1} cm² mol^{–1}) of these complexes in anhydrous DMF at the room temperature show them to be non electrolytic in nature. The analytical data of complexes show 1 : 1 (**2(i)**, **(ii)**) and 1 : 2 (**2(iii)**, **(iv)**) metals to ligand ratio and molecular weight measured by the Rast method reveals the monomeric nature of these complexes.



R = –(CH₂)– {L¹H₂} and {L²H₂}, –CHCH₂CHMe₂– {L³H₂} and {L⁴H₂}, –(CH₂)₂– {L⁵H₂} and {L⁶H₂}, –CHCHMe₂– {L⁷H₂} and {L⁸H₂}

Fig. 2. Structures of the complexes.

Spectroscopic characterization :

Infrared spectra :

Absence of $\nu(\text{NH}_2)$ band (3240 cm^{-1}) of amino acid and $\nu(\text{C}=\text{O})$ band (1745 cm^{-1}) of ketone and presence of $\nu(\text{C}=\text{N})$ band occurs^{23,24} at $1620\text{--}1632\text{ cm}^{-1}$ in the spectra of all free ligands ($\text{L}^1\text{H}_2\text{--L}^8\text{H}_2$) indicates the condensation between ketonic group and amino group of amino acids^{25,26}. The broad and strong bands present in the IR spectra of Schiff base ligands in the region $3200\text{--}3400\text{ cm}^{-1}$ and $1280\text{--}1330\text{ cm}^{-1}$ which are assigned to phenolic $\nu(\text{OH})$ and $\nu(\text{C-O})$ vibrations respectively^{27,28}. The $\nu(\text{OH})$ band disappears in the spectra of corresponding complexes $[\text{Ti}(\text{L})(\text{OPr}^i)_2]$ and $[\text{Ti}(\text{L})_2]$ and strong bands of phenolic $\nu(\text{C-O})$ appears in the region $1360\text{--}1390\text{ cm}^{-1}$ in the complexes suggesting the chelation of the oxygen to Ti ion²⁹.

On comparison with the IR spectra of ligands $[\text{L}^1\text{H}_2\text{--}$

$\text{L}^8\text{H}_2]$ all the $[\text{Ti}(\text{L})(\text{OPr}^i)_2]$ and $[\text{Ti}(\text{L})_2]$ exhibit a major downward shift wave number by $12\text{--}20\text{ cm}^{-1}$ in $\nu(\text{C}=\text{N})$ ($1605\text{--}1622\text{ cm}^{-1}$) suggesting the participation of azomethine nitrogen in bonding with the metal ion³⁰. The downward shift can be explained by the donation of electrons of nitrogen ($\text{C}=\text{N}$) to empty d-orbital of Ti^{IV} ion. Two bands at $1670\text{--}1675\text{ cm}^{-1}$ and $1370\text{--}1390\text{ cm}^{-1}$ in the ligands are assigned to asymmetric and symmetric carboxyl groups. These bands are found at $1635\text{--}1640\text{ cm}^{-1}$ and $1415\text{--}1420\text{ cm}^{-1}$ indicating their involvement in bonding to the metal ion. The difference between the positions of asymmetric and symmetric carboxyl groups in the complexes are found as more than 200 cm^{-1} suggesting the covalent nature of the metal-oxygen bond³¹. Bands at ~ 622 and $\sim 550\text{ cm}^{-1}$ in the complexes may be assigned to $\nu(\text{Ti-O})$ and $\nu(\text{Ti-N})$ vibrations respectively^{32,33}. The aforementioned IR spectral data suggest that the ligands bonded via the nitrogen of azomethine

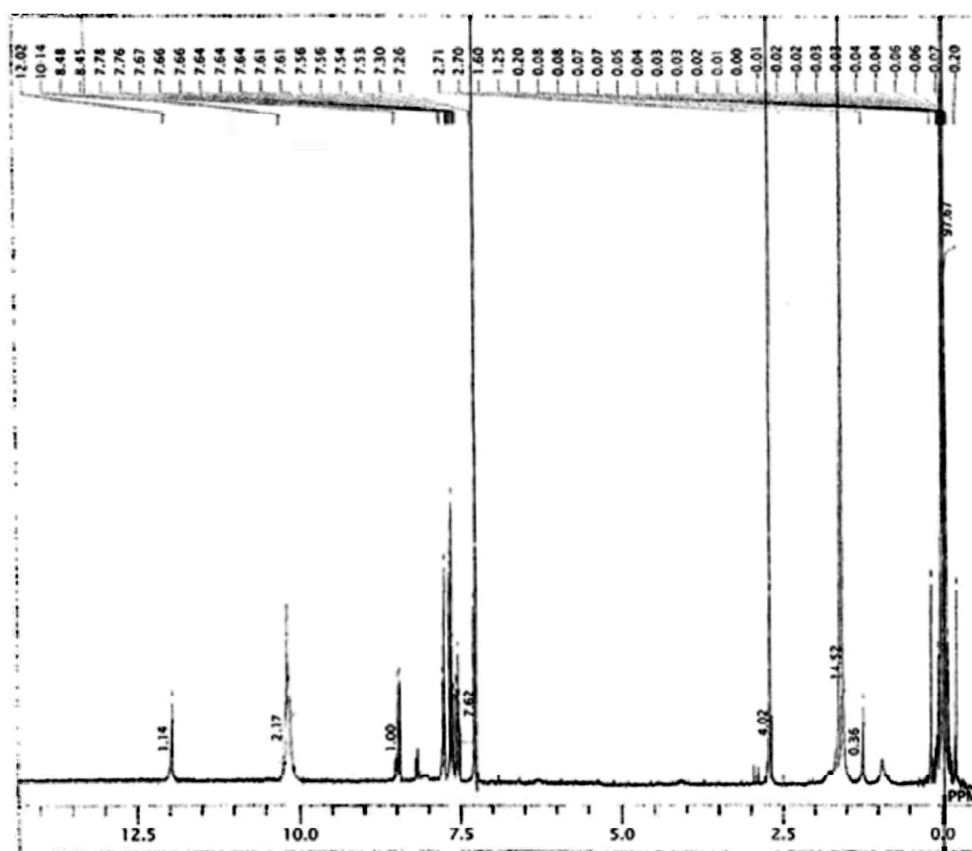


Fig. 3. ^1H NMR spectra of $[\text{L}^1\text{H}_2]$ (1(i)a).

and oxygen of the carboxylate group to the Ti^{IV} ion in the complexes.

^1H NMR spectra :

The proton magnetic resonance (^1H NMR) spectra of amino acid Schiff bases and their corresponding titanium(IV) complexes were recorded in CDCl_3 and TMS was used as an internal reference. The coordination of the ligand via azomethine nitrogen and carboxylate oxygen to the metal is supported by the comparison of the ^1H NMR spectral data of the ligand and its complexes. A sharp signal at δ 1.32–1.47 ppm is observed in the ligand due to $-\text{C}(\text{CH}_3)=\text{N}-$ and it moves downfield (δ 1.49–1.58 ppm) in the complexes³⁴. The singlets present in the ^1H NMR spectra of the ligands in the region $\delta \sim 11.64$ –12.00 ppm (s) may be attributed to $-\text{OH}$ proton were found to be absent in the ^1H NMR spectra of the complexes, which shows deprotonation $-\text{OH}$ proton of carboxylate group and formation of $\text{Ti}-\text{O}$ bond. ^1H NMR

spectra of the ligands at $\sim \delta$ 9.89–10.28 ppm (s) are ascribed to phenolic $-\text{OH}$ and are absent in the spectra of the corresponding titanium(IV) complexes indicates the formation of $\text{Ti}-\text{O}$ bond by the deprotonation of phenolic $-\text{OH}$. The aromatic protons of the Schiff bases derived from glycine, leucine, β -alanine, valine and their corresponding complexes were present as a complex pattern in the region δ 7.28–7.86 ppm (m).

^{13}C NMR spectra :

The ^{13}C NMR spectra for ligands [$\text{L}^1\text{H}_2\text{-L}^8\text{H}_2$] and their corresponding complexes were recorded in CDCl_3 and $\text{DMSO}-d_6$ solution. The signal for $>\text{C}=\text{N}$ was present in the spectra of ligands at δ 163.47–165.87 ppm and appears at δ 166.69–166.87 ppm in the complexes. The downfield shifting of $\delta \sim 2$ –3 ppm clearly defined that the azomethine moiety has been involved during the complexation. The signal for carbon attached to $-\text{OH}$ shows a small shift in comparison and indicates the formation of

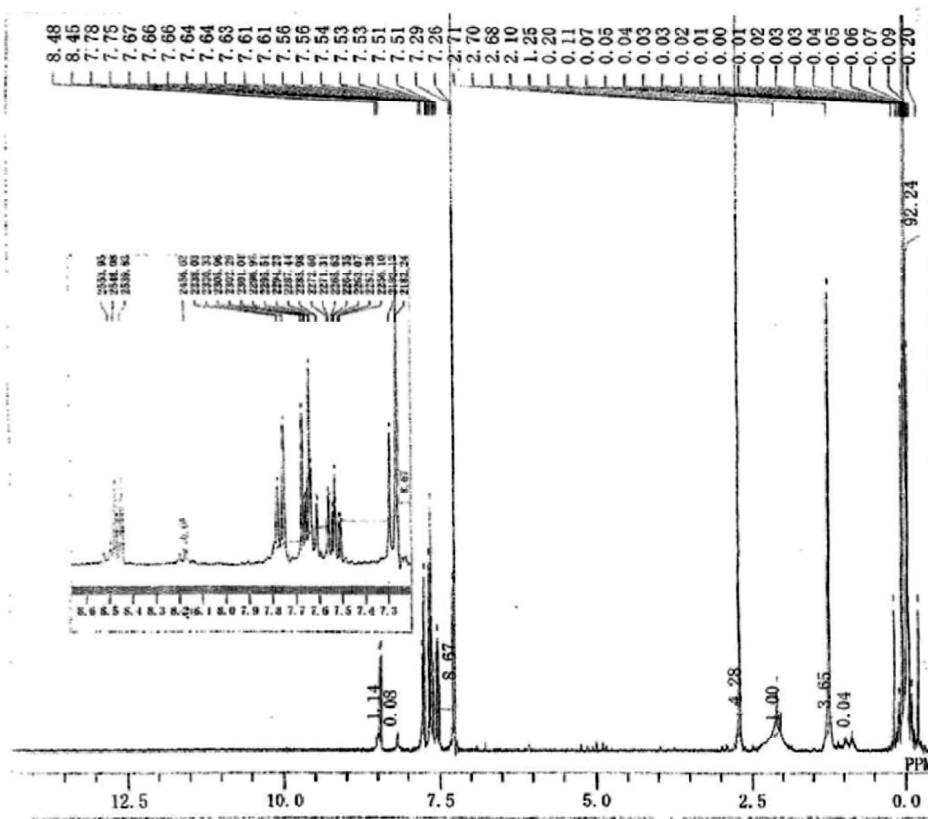


Fig. 4. ^1H NMR spectra of (2(i)a) metal complex of ligand (1(i)a).

Ti-O bond. On the basis of aforementioned discussion and spectral evidences the complexes contain the plausible structure in Fig. 2.

Antimicrobial results :

The results of the antimicrobial screening of the Schiff bases and their complexes against Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria and some selected fungi (*Aspergillus niger* and *Rhizopus phaseoli*) have been found. The inhibition zones were measured in mm and results have been recorded in Tables 1 and 2.

The experimental data clearly indicate that the metal complexes are more potent activity in inhibiting the growth of microorganisms than the ligands. The results further conclude that antimicrobial activity of the complexes increases due to metallation of its ligands³⁵⁻³⁹.

Conclusion

In our present studies we have synthesized biologically active amino acid Schiff bases ligands and their complexes. On the basis of above evidences, trigonal bipyramidal and octahedral geometries may be concluded for resulting complexes. The antibacterial and antifungal activity against (*Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger* and *Rhizopus phaseoli*) tested microorganisms of the studied complexes revealed that the activity increases upon complexation as compared to its ligand. The compounds showed toxicity against all species of fungi and inhibition zone growth of fungi depends on the concentration of the compounds.

Acknowledgement

We are thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur, India for providing laboratory facilities. Hari Shankar Yadav and Sangeeta Sihag are grateful to the Council of Scientific and Industrial Research, New Delhi for awarding a Senior Research Fellowship.

References

1. A. N. Wein, R. Cordeiro, N. Owens, H. Olivier, K. I. Hardcastle and J. F. Eichler, *J. Fluorine Chem.*, 2009, **130**, 197.
2. C. D. Samara, L. Alevizopoulou, L. Iordanidis, E. Samaras and D. Kessissoglou, *J. Inorg. Biochem.*, 2002, **89**, 89.
3. K. S. Abou Melha, *J. Enzym. Inhib. Med. Chem.*, 2008, **23**, 493.
4. L. Tripathi, P. Kumar and A. K. Singhai, *Indian J. Cancer*, 2007, **44**, 62.
5. S. Sharma, M. Bedi, S. Varshney and A. K. Varshney, *J. Indian Chem. Soc.*, 2012, **89**, 41.
6. U. A. Kumar and S. Chandra, *Transition Met. Chem.*, 1993, **18**, 342.
7. S. Rafique, M. Idrees, A. Nasim, H. Akbar and A. Athar, *Biotechnol. Mol. Biol. Rev.*, 2010, **5**, 38.
8. E. Y. Tshuva and J. A. Ashenhurst, *Eur. J. Inorg. Chem.*, 2009, 2203.
9. D. Chen, V. Milacic, M. Frezza and Q. P. Dou, *Curr. Pharm. Des.*, 2009, **15**, 777.
10. Q. Wang, H. Song and G. Zi, *J. Organomet. Chem.*, 2010, **695**, 1583.
11. M. B. Ferrari, S. Capacchi, G. Pelosi, G. Reffo, P. Tarasconi, R. Albertini, S. Pinelli and P. Lunghi, *Inorg. Chim. Acta*, 1999, **134**, 286.
12. H. Groeger, *Chem. Rev.*, 2003, **103**, 2795.
13. W. L. F. Armarego and D. D. Perrin, "Purification of Laboratory Chemicals", 4th ed., Butterworth-Heinemann, 1997.
14. P. Foltinová, V. Sutoris, G. Blöckinger and L. Ebringer, *Folia Microbiol.*, 1978, **23**, 225.
15. R. J. Grayer and J. B. Harbone, *Phytochemistry*, 1994, **37**, 19.
16. A. Saxena, S. K. Sinha and J. P. Tandon, *Antifung. Antibact. Agents*, 1981, **9**, 435.
17. W. L. Drew, A. L. Barry, R. O. Toole and J. C. Sherris, *Appl. Environ. Microbiol.*, 1972, **24**, 240.
18. D. Liu and K. Kwasniewska, *Bull. Environ. Contam. Toxicol.*, 1981, **27**, 289.
19. D. N. Muanza, B. W. Kim, K. L. Euler and L. Williams, *Int. J. Pharmacogn.*, 1994, **32**, 337.
20. O. N. Irob, M. Moo-Young and W. A. Anderson, *Int. J. Pharm.*, 1996, **34**, 87.
21. A. Obeid, A. E. Shekeil, S. A. Aghbari and J. A. Shabi, *J. Coord. Chem.*, 2012, **65**, 2762.
22. D. Thangadurai and K. Natarajan, *Synth. React. Inorg. Metal-Org. Chem.*, 2001, **30**, 569.
23. G. C. Percy and D. A. Thornton, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 599.
24. R. A. Kolinski and B. Korybut-Daszkiewicz, *Inorg. Chim. Acta*, 1975, **14**, 237.
25. L. J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley & Sons, New York, 1971.
26. B. P. Baranwal and A. K. Singh, *Spectrochim. Acta, Part A*, 2010, **77**, 938.

27. H. H. Freedman, *J. Am. Chem. Soc.*, 1961, **83**, 2900.
28. G. B. Pethe, A. R. Yaul, J. B. Devhade and A. S. Aswar, *Der Pharma Chemica*, 2010, **2**, 301.
29. B. Pancholi and M. M. Patel, *J. Polym. Mater.*, 1996, **13**, 261.
30. S. P. McGlynn and J. K. Smith, *J. Mol. Spectros.*, 1961, **6**, 164.
31. N. Sari, P. Gurkan, S. Cete and I. Sakiyan, *Russ. J. Coord. Chem.*, 2006, **32**, 511.
32. K. Issleib and G. Batz, *Z. Anorg. Allg. Chem.*, 1969, **83**, 369.
33. S. A. Parthy, S. Gopinathan and C. Gopinathan, *Synth. Inorg. Metal-Org. Chem.*, 1983, **13**, 385.
34. D. J. Pasto, "Organic Structure Determination", Prentice Hall, London, UK, 1969.
35. M. Godara, M. K. Gupta, S. Varshney and A. K. Varshney, *J. Inst. Chemists*, 2006, **78**, 117.
36. P. K. Mukharjee, K. Saha, S. N. Giri, M. Pal and B. P. Saha, *Indian J. Microbiology*, 1995, **35**, 327.
37. P. G. Cozzi, *Chem. Soc. Rev.*, 2004, **33**, 410.
38. S. B. Ade, D. G. Kolhatkar and M. N. Despande, *Int. J. Pharma. Bio. Sci.*, 2012, **3**, 7.
39. M. Bedi, S. Sharma, S. Varshney and A. K. Varshney, *J. Indian Chem. Soc.*, 2012, **89**, 309.