Some mononuclear titanium(IV) complexes of salicylidene anthranilic acid and
o-vanillinoxime

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Some mononuclear titanium(IV) complexes of salicylidene anthranilic acid (H₁L₁) and o-vanillinoxime (H₂L₂) have been synthesized in a two step, one-pot procedure by the reactions of TiCl₄ and sodium salts of the ligands in different stoichiometric ratios in good yields with an excellent purity.

Titanium tetrachloride¹ is a useful building block in synthesis. Numerous reactions employing titanium tetrachloride and its complexes as reagents have been reported and reviewed²³. During the last decade group IV transition metal chemistry has made a major contribution in providing effective complexes for novel metal-assisted organic transformations⁴−⁶. The sulphur and nitrogen containing complexes of titanium(IV) are becoming more and more important for industrial applications⁷. The use of these derivatives as reagents⁸, leaving groups or protective groups is now becoming common in many of the reactions⁹−¹⁰. It became clear that the transmetallation of classical “carbanions” using titinating agents produces new reagents¹¹ which display a high degree of chemo-, regio- and stereo-selectivity. In spite of the considerable growth of literature on titanium(IV) complexes¹²−¹⁸ containing N, O and S donor ligands, not much work is known about the complexes of Ti(IV) with the title ligands. The basic objective of the present study is to elicit information about the relative coordinating ability of the ligands towards metal atom. In view of this, and in continuation of our earlier studies¹⁴−¹⁶ on Ti(IV) complexes, we now describe some complexes of Ti(IV) with title Schiff bases.

Experimental

All manipulations were carried out under nitrogen atmosphere and with thoroughly dried solvents and glassware. Chemicals and solvents used were dried and purified by standard methods¹⁷. AR grade TiCl₄ from Rideal-de Haen AG Seelze-Hannover, Germany was used as such without further purification. Titanium(IV) was estimated gravimetrically as TiO₂, and chloride and sulphur were estimated gravimetrically as AgCl and BaSO₄, respectively¹⁷. Nitrogen was determined by the Kjeldahl’s method¹⁷. IR spectra were recorded on a Perkin-Elmer model 577 spectrometer in the range 4000-200 cm⁻¹ in KBr discs.¹ H NMR spectra were recorded on a Bruker AC 250 MHz instrument operating at 250MHz in CDCl₃ using TMS as an internal reference. Molecular weights were determined by a Knap vapour pressure osmometer in dilute CHCl₃ solution at 45°C. The ligands N-(salicylidene)anthranilic acid (H₂L₁) and o-vanillinoxime (H₂L₂) were prepared by the literature methods¹⁸−¹⁹. The TLC analysis of the Schiff bases show a single spot, different from that of the starting materials, indicating its purity.

Their elemental analysis correspond to the expected formulae. The progress of the reaction was monitored by TLC on silica gel plate. All the melting points are uncorrected.

Reaction between titanium(IV) chloride and the sodium salt of N-(salicylidene)anthranilic acid in a 1:1 molar ratio (I).

To a clear cold solution of sodium isopropoxide prepared in situ by dissolution of sodium (0.065 g, 2.8 mmol) in isopropanol (25 ml), N-(salicylidene)-anthranilic acid (0.68 g, 2.8 mmol) was added slowly, and the contents were refluxed for 4 h. After cooling, 0.54 g (2.8 mmol) of TiCl₄ in 15 ml of dry benzene was added dropwise, and the mixture was further refluxed for 2 h to ensure completion of the reaction. After filtering off the precipitated NaCl, the desired product (0.99 g, 89%) was isolated by evaporation of the solvent under reduced pressure. The product was further purified by crystallization using dichloromethane-n-hexane mixture. All other titanium(IV) derivatives of N-(salicylidene)anthranilic acid were synthesized analogously. The pertinent data for this and other derivatives are listed in Table 1.
Table 1—Characterization data of titanium (IV) complexes of N-(salicylidene) anthranilic acid and o-vanillinoxime

<table>
<thead>
<tr>
<th>Compd</th>
<th>Mol. wt.</th>
<th>Reactants g. (mmol)</th>
<th>Molar ratio</th>
<th>Reflux time (h)</th>
<th>Yield g (%)</th>
<th>m.p. °C</th>
<th>Found (Calcd), %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ligand</td>
<td>Sodium</td>
<td>TiCl₄</td>
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<tr>
<td>1.</td>
<td></td>
<td>0.68</td>
<td>0.064</td>
<td>0.54</td>
<td>1:1:1</td>
<td>6</td>
<td>0.99 (89)</td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td>0.57</td>
<td>0.055</td>
<td>0.22</td>
<td>2:2:1</td>
<td>5</td>
<td>0.51 (73)</td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>0.94</td>
<td>0.090</td>
<td>0.25</td>
<td>3:3:1</td>
<td>6</td>
<td>0.88 (84)</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>0.96</td>
<td>0.092</td>
<td>0.20</td>
<td>4:4:1</td>
<td>5</td>
<td>0.87 (84)</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>0.29</td>
<td>0.056</td>
<td>0.23</td>
<td>1:2:1</td>
<td>4</td>
<td>0.32 (76)</td>
</tr>
<tr>
<td>6.</td>
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<td>0.28</td>
<td>0.051</td>
<td>0.11</td>
<td>2:4:1</td>
<td>6</td>
<td>0.22 (72)</td>
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<td>0.67</td>
<td>0.092</td>
<td>0.76</td>
<td>1:1:1</td>
<td>5</td>
<td>0.84 (66)</td>
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<tr>
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<td>0.083</td>
<td>0.34</td>
<td>2:2:1</td>
<td>6</td>
<td>0.69 (84)</td>
</tr>
<tr>
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<td>0.55</td>
<td>0.077</td>
<td>0.21</td>
<td>3:3:1</td>
<td>4</td>
<td>0.50 (79)</td>
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<td>0.088</td>
<td>0.18</td>
<td>4:4:1</td>
<td>5</td>
<td>0.46 (66)</td>
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<tr>
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<td>0.31</td>
<td>0.090</td>
<td>0.35</td>
<td>1:2:1</td>
<td>4</td>
<td>0.36 (69)</td>
</tr>
<tr>
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<td>0.23</td>
<td>0.064</td>
<td>0.13</td>
<td>2:4:1</td>
<td>6</td>
<td>0.21 (80)</td>
</tr>
</tbody>
</table>
Reaction between titanium(IV) chloride and the sodium salt of o-vanillinoxime in a 1:1 molar ratio (7)

Compound (7) was prepared by the reaction of o-vanillinoxime (0.67 g, 4.0 mmol) with TiCl₄ (0.76 g, 4.0 mmol) in analogy to the procedure as mentioned earlier for compound 1. All other titanium(IV) derivatives of o-vanillinoxime were synthesized analogously (Table 1).

Results and discussion

Titanium(IV) derivatives of N-(salicylidene)anthranilic acid have been prepared by the reaction of titanium(IV) chloride with the sodium salt of N-(salicylidene)anthranilic acid (prepared in situ) in different stoichiometric ratios in a refluxing dry benzene-isopropanol mixture. These reactions are found to be quite facile and the sodium chloride formed during the course of the reaction is filtered off.

\[ \text{\text{H}_2\text{L}_1} + \text{TiCl}_4 \rightarrow \text{Compd x} \]

where m = 1, n = 2, Compd 5; m = 2, n = 4, Compd 6

Similarly, the disodium salt of the ligand is reacted with TiCl₄ in a 1:1 and 2:1 molar ratios to give titanaacyclic complexes.

\[ \text{\text{H}_2\text{L}_2} + \text{TiCl}_4 \rightarrow \text{Compd y} \]

where m = 1, n = 2, Compd 11; m = 2, n = 4, Compd 12

All the resulting derivatives are coloured solids and soluble in common organic and coordinating solvents. These complexes are further purified by crystallization from dichloromethane-n-hexane mixture and their purity was further checked by TLC on silica gel. Each of the complexes moves as a single spot indicating the presence of only one component and hence their purity. Molecular weight determination in CHCl₃ solution shows monomeric nature of these complexes. The conductivity measurements in nitrobenzene exhibit electrolytic nature of 1:1, 1:2 and 1:3 reaction products, whereas no electrical conductivity is shown by 1:4 reaction product. Elemental analyses are in the good agreement with the calculated values (Table 1).

The \(\nu(C=O)\) mode of the free -CO₂H group (H₂L₁) at 1675 cm⁻¹ is not observed in complexes (1-6) and only \(\nu_m\) and \(\nu_s\) modes of deprotonated -CO₂ group appears at ~ 1575 and 1380 cm⁻¹, respectively, the \(\Delta\nu(\nu_m-\nu_s)\) value (195 cm⁻¹) being consistent with bidentate carboxylate coordination²². The \(\nu(C=N)\) frequency of the free ligand at 1630 cm⁻¹ is shifted to lower frequencies in all the complexes, suggesting coordination through azomethine nitrogen²². In the complexes 5 and 6, the phenolic -OH disappears completely, indicating coordination via oxygen of the -OH group, while in complexes 1-4, appearing at ~ 3460 cm⁻¹ in the free ligand, remains unaffected. These facts support coordination by the ligand as bidentate in the complexes 1-4 and tridentate in the complexes 5 and 6 using the -CH=N, -CO₂ and phenoxide groups²³.

The IR spectra of the complexes 7-12 have been compared with the corresponding ligand (H₂L₂) and from the shifts in frequency and/or from the intensity lowering, the coordination sites have been ascertained. The spectrum of vanillinoxime exhibits bands at 1615 \(\nu(C=N)\) and 3300 cm⁻¹ \(\nu(O-H, N-OH\) and
phenolic-OH). The presence of -OH vibrations in the complexes 7-10 shows that -OH groups are intact and uncoordinated, whereas in complexes 11 and 12, it disappears completely suggesting coordination via phenolic oxygen to titanium metal. There is no significant change in the (C=N) stretching frequency suggesting non-participation of azomethine group in coordination. The band appearing at 1030 cm\(^{-1}\) in the spectrum of the ligand has been assigned to -OCH\(_3\) group vibration. These bands do not show any significant change and remain almost unchanged in the spectra of the complexes. A new band present in the region 544-576 cm\(^{-1}\) may be attributed to Ti-O stretching vibration\(^{24}\) in all the complexes.

The PMR spectrum of the ligand \(H_2L^1\) is characterized by signals at \(\delta\) 11.86, 10.02, 8.65 and 7.92-6.48 ppm, attributable to -COOH proton, phenolic -OH, azomethine proton and phenyl protons, respectively. The PMR spectra of the complexes 1 to 4 are devoid of signal at 11.86, suggesting deprotonation of -COOH group and subsequent involvement in coordination. The band at \(\delta\) 10.12 ppm for complexes 2 and 3, respectively also shows that \(=N\)-OH signal is absent in the spectra of the complexes 7-10, suggesting deprotonation and its subsequent involvement in coordination forming Ti-O bond\(^{24}\). The -OH signal observed at \(\delta\) 13.47 in free ligand also disappeared in compounds 11 and 12, indicating deprotonation and taking part in bonding to titanium atom. The aromatic protons appear over the region \(\delta\) 8.22-6.48 ppm in all the complexes. The pertinent spectral data of the compounds are listed below.

1. IR (KBr): 1600 (C=N), 3465 (O-H), 1575, 1380 (COO), 566 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 8.18-6.54 (m, 8H, ArH), 9.96 (s, 1H, OH), 8.97 (s, 1H, CH=N).
2. IR (KBr): 1612 (C=N), 3455 (O-H), 1570, 1375 (COO), 570 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 8.20-6.48 (m, 16H, ArH), 10.12 (s, 2H, OH), 8.99 (s, 2H, CH=N).
3. IR (KBr): 1615 (C=N), 3460 (O-H), 1580, 1385 (COO), 568 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 8.16-6.52 (m, 24H, ArH), 10.06 (s, 3H, OH), 9.12 (s, 3H, CH=N).
4. IR (KBr): 1610 (C=N), 3450 (O-H), 1585, 1390 (COO), 572 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 8.16-6.56 (m, 32H, ArH), 10.10 (s, 4H, OH), 9.06 (s, 4H, CH=N).
5. IR (KBr): 1614 (C=N), 1574, 1382 (COO), 576 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 8.22-6.46 (m, 8H, ArH), 8.60 (s, 1H, CH=N).
6. IR (KBr): 1610 (C=N), 1575, 1385 (COO), 564 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 8.16-6.54 (m, 16H, ArH), 9.10 (s, 2H, CH=N).
7. IR (KBr): 1615 (C=N), 3225 (O-H), 562 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 7.36-6.76 (m, 3H, ArH), 13.10 (s, 1H, OH), 8.96 (s, 1H, CH=N), 3.86 (s, 3H, OMe).
8. IR (KBr): 1618 (C=N), 3215 (O-H), 560 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 7.42-6.80 (m, 6H, ArH), 12.96 (s, 2H, OH), 8.92 (s, 2H, CH=N), 3.82 (s, 6H, OMe).
9. IR (KBr): 1614 (C=N), 3220 (O-H), 576 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 7.46-6.88 (m, 9H, ArH), 13.16 (s, 3H, OH), 8.96 (s, 3H, CH=N), 3.88 (s, 9H, OMe).
10. IR (KBr): 1620 (C=N), 3210 (O-H), 572 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 7.45-6.78 (m, 12H, ArH), 13.12 (s, 4H, OH), 8.98 (s, 4H, CH=N), 3.78 (s, 12H, OMe).
11. IR (KBr): 1613 (C=N), 556 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 7.38-6.82 (m, 3H, ArH), 8.94 (s, 1H, CH=N), 3.84 (s, 3H, OMe).
12. IR (KBr): 1615 (C=N), 544 (Ti-O)cm\(^{-1}\); \(^1\)H NMR (\(\delta\) ppm): 7.42-6.86 (m, 6H, ArH), 8.92 (s, 2H, CH=N), 3.80 (s, 6H, OMe).

The above studies indicate that the ligands (H\(_2L^1\) and H\(_2L^2\)) act as unidentate to tridentate mode of attachment to the metal atom under different reaction conditions. The central titanium atom appears to acquire coordination numbers four, five, six, seven and eight in different complexes.

References
(b) Fokken S, Spaniol T P & Okuda J, Organometallics, 16 (1997) 4240.