Reaction of titanium(IV) tetraisopropoxide with salicylidene-2-aminopyridine and spectral studies

Raj Kumar Dubey* & Avadhesh Pratap Singh
Synthetic Inorganic and Metallo-organic Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211 002, India
Email: rajalkoxy@yahoo.com

Received 23 February 2014; re-revised and accepted 21 October 2014

Reaction of Ti(OPr)i4 with salicylidene-2-aminopyridine in different molar ratio(s) afforded mononuclear complexes of the type, [(sap)2Ti(OPr)i4, (1-3), (where n = 1-3; sap = salicylidene-2-aminopyridine). The reaction of complex (2) with N-methyl-diethanolamine in equimolar ratio afforded the complex [(sap)2Ti(mdea)] (4). All these complexes have been characterized by elemental (C, H, N and Ti) analyses and spectral (IR, NMR) studies. The molecular structure as well as composition of the complexes has been tentatively assigned on the basis of these spectral and mass fragmentation studies.

Keywords: Coordination chemistry, Alkoxides, Metal alkoxides, Schiff bases, Titanium

Interest in the metal alkoxide chemistry has grown extensively in recent years1 for the synthesis of nanosized TiO2, due to its wide range of applications, such as in highly specific chemical sensors3,4,5, photocaltatysis6,7 and solar cells8,9. Furthermore, there have been interesting developments in the chemistry of titanium(IV) derivatives containing Schiff bases10, reflecting the role of N-arylsalicylaldiminate ligands to reduce the rate of hydrolysis11-13 and catalysis of alkenes14-18. It is interesting to note that tetrakis (N-ethyl-salicylaldiminate) complexes of titanium(IV)19 is six coordinate, whereas the analogous zirconium(IV)20 derivative is eight coordinate. Seven coordinate alkoxides containing organic compound of titanium are elusive in number21. Therefore, the main aim of this investigation was to explore the possibilities for (i) synthesizing titanium(IV) species in seven coordinate state by carrying out the reaction of titanium isopropoxide with the parent Schiff base in 1:3 molar ratio and reaction of the bis derivative (2) with a tridentate ligand such N-methyl-diethanolamine, and, (ii) to examine the involvement of heterocyclic nitrogen for intramolecular Ti—N coordination. Keeping the above facts in view, we report herein the reaction of salicylaldimine-2-aminopyridine (sapH) with Ti(OPr)i4 in different molar ratios. The isolated products were characterized by elemental analysis and various spectroscopic studies (IR, NMR (1H, 13C), mass).

Experimental

Titanium(IV) tetraisopropoxide (Merck, 100 °C/0.3 mmHg) was distilled prior to use. Salicyldehyde and 2-aminopyridine were used without further purification. The solvents used were of reagent grade and purified by standard procedures22. The complexes were analysed23 for titanium content gravimetrically as TiO2. Isopropoxy contents were estimated by the oxidimetric method24 using N-K2Cr2O7 solution in 12.5% H2SO4. Infrared spectra (in the range 4000-400 cm−1) were recorded on a 100 FT-IR/RZX Perkin Elmer FT-IR spectrophotometer. The 1H and 13C NMR spectra of ligands and their complexes were recorded in deuterated chloroform/dimethylsulfoxide on Bruker BrukerAvance II 400 spectrometer. Mass spectra were recorded on Q-ToF Micro Waters LCMS (liquid chromatography-mass spectrometry).

Salicylidene-2-aminopyridine (sapH) was synthesised and characterised by spectral data as reported earlier25. [(PrO)4Ti(sap)] (I) was synthesised as follows: A benzene solution (~70 mL) containing Ti(OPr)i4 (1.072 g, 3.77 mmol) and salicylidene-2-aminopyridine (sapH) (0.748 g, 3.77 mmol) was heated under reflux for ~7 h. The liberated PrOH was fractionated azeotropically and estimated (0.23 g, 3.83 mmol) periodically to check completion of the reaction. Removal of volatile components from the reaction mixture under reduced pressure yielded a yellow solid. Yield: 1.41 g (89%). Recrystallization from a mixture of dichloromethane-n-hexane at room temperature gave analytically pure light yellow solid. Yield: 1.20 g (76%), m. pt.: decomp.; Anal. (%) for C21H30N2O2Ti: C, 59.72; H, 7.16; N, 6.63; Ti, 11.33; Found: C, 59.58; H, 6.97; N, 6.51; Ti, 11.18. IR (v, cm−1): 1607 (CH=N)asymuthene, 1586 (C=N)pyridinic, 1381, 1335, 1188, 1148 (OPr), 1291 (C-O)phenolic, 985 (M-OPr), 580, 565, 547, 525 (Ti-O), 473 (Ti—N); 1H NMR (CDCl3) δ: 9.45 (H, s, CH=N), 6.48-8.52 (6H, m, Ar-H, Py-H), 3.96-4.08 (3H, Sept, OCH(CH3)2), 1.20-1.22 (18H, d, OCH(CH3)2);
A similar procedure was adopted to prepare complexes (2) and (3) by carrying out the reactions of Ti(OPr)₄ and sapH in 1:2 and 1:3 molar ratios, respectively.

[(PrO)₂Ti(sap)] (2): Yellow solid (97%), m. pt.: 283–285 °C; Anal. (%) for C₃₀H₂₆N₄O₂Ti: C, 67.05; H, 4.91; N, 12.03; Ti, 8.54. Found: C, 66.86; H, 4.76; N, 11.91; Ti, 6.76. IR (v, cm⁻¹): 1609 (CH=N)azomethine, 1587 (C=N)pyridinic, 1378, 1357, 1189, 1148 (OPr)₄, 1288 (C-O)phenolic, 986, 1047, 1031 (M-OPr)₄, 580, 564, 546, 524 (Ti-O), 480 (Ti→N); ¹H NMR (CDCl₃) δ: 9.45 (2H, s, CH=N), 6.48-8.51 (12H, m, Ar-H, Py-H), 3.98-4.45 (2H, Sept, OCH(CH₃)₂), 1.20-1.22 (12H, d, OCH(CH₃)₂); ¹³C NMR (CDCl₃) δ: 164.53 (s, CO), 161.53 (s, CN), 117.50-147.80 (Ar-H, Py-H), 64.56 (OCH(CH₃)₂), 2.46. (OCH(CH₃)₂).

[(PrO)Ti(sap)] (3): Orange solid (89%), m. pt.: 283–285 °C; Anal. (%) for C₃₀H₂₆N₄O₂Ti: C, 67.05; H, 4.91; N, 12.03; Ti, 8.54. Found: C, 66.86; H, 4.76; N, 11.91; Ti, 6.76. IR (v, cm⁻¹): 1607 (CH=N)azomethine, 1587 (C=N)pyridinic, 1378, 1357, 1189, 1148 (OPr)₄, 1289 (C-O)phenolic, 987, 1030 (M-OPr)₄, 565, 547 (Ti-O), 477, 455 (Ti→N); ¹H NMR (CDCl₃) δ: 9.44 (3H, s, CH=N), 6.03-8.44 (18H, m, Ar-H, Py-H), 3.89-4.47 (H, Sept, OCH(CH₃)₂), 1.19-1.21 (6H, d, OCH(CH₃)₂); ¹³C NMR (CDCl₃) δ: 163.58 (s, CO), 160.96 (s, CN), 117.3-148.34 (Ar-C/Py-C), 64.63 (OCH(CH₃)₂), 24.78 (OCH(CH₃)₂).

Synthesis of [(mdea)Ti(sap)] (4) was carried out as follows: A benzene solution (~50 mL) containing [(PrO)₂Ti(sap)] (0.98 g, 1.75 mmol) and N-methylidiothalamine (mdeaH₂) (0.208 g, 1.75 mmol) was heated under reflux for ~11 h. The liberated PrOH was fractionated azeotropically and estimated (0.21 g, 3.5 mmol). Removal of volatile components from the reaction mixture under reduced pressure yielded a reddish brown solid. Yield: 0.91 g (93%). Recrystallization from a mixture of dichloromethane-n-hexane at ~20 °C gave analytically pure red solid. Yield: 0.78 g (80%); m. pt.: 127 °C; Anal. (%) for C₂₉H₂₄N₂O₂Ti: C, 62.26; H, 5.22; N, 12.52; Ti, 8.56; Found: C, 62.14; H, 5.05; N, 12.46; Ti, 8.43. IR (v, cm⁻¹): 1608 (CH=N)azomethine, 1588 (C=N)pyridinic, 1314 (C-O)phenolic, 1253 (C-N)mdea, 1095 (C-O)mdea, 568, 534 (Ti-O), 459 (Ti→N); ¹H NMR (CDCl₃) δ: 9.44(2H, s, CH=N), 6.48-8.07 (12H, m, Ar-H, Py-H), 2.58-3.66 (4H, m, OCH₂ mdea), 2.51-2.96 (4H, m, NCH₂ mdea), 2.38(3H, s, NCH₃ mdea).

Results and discussion

The reactions in benzene medium of Ti(OPr)₄ with salicylidene-2-aminopyridine (abbreviated as sapH) in different (1:1, 1:2, 1:3) molar ratios under refluxing conditions afford quantitatively colored solid products of the type [(sap)₂Ti(OPr)₄]ₙ, according to the Scheme 1. However, the product obtained by carrying out reaction in 1:4 molar ratio corresponded in analyses to the compound (3); possibly due to the more crowded nature of the tris-product, which inhibits further reaction.

An interesting mixed-ligand complex of titanium(IV) of the type [(sap₂)Ti(mdea)] was prepared by the interaction of [(sap)₂Ti(OPr)₄] with Me₃N(CH₂CH₂OH) (abbreviated as mdeaH₂) in 1:1 molar ratio in benzene according to the Scheme 1. These yellow or red, solid complexes were also soluble in common organic solvents (e.g. benzene, dichloromethane, chloroform etc.). The compounds (3) and (4) melted sharply.

Infrared spectra of the newly synthesized derivatives exhibit structurally important frequencies in the regions 1381-1148 ν(OPr) and 1047-985 ν(C-O)Ti assigned to terminal isopropoxide group. The salicylidene-2-aminopyridine shows strong and broad absorption band at 3430 cm⁻¹ due to hydrogen bonded OH stretching vibration. This band is absent in the titanium complexes, indicating the involvement of phenolic oxygen in the formation of metal-oxygen bond via metallation in the region 580-524 cm⁻¹, assignable ν(Ti-O) . The non-involvement of pyridine nitrogen in the complex formation is supported by the unaltered position of azomethine nitrogen atom. This fact is further supported by the appearance of new bands in the region 480-455 cm⁻¹, assignable to ν(C=N) mode. (Supplementary data, Fig. S1).
The \(^1\)H NMR spectra of the Schiff base\(^{25}\) shows sharp resonance at 12.86 ppm, which is absent in the complexes, indicating the deprotonation of phenolic proton\(^{26}\). The azomethine hydrogen signal for parent Schiff base\(^{25}\) which appears at 9.23 ppm is shifted to the region 9.45-9.44 ppm for corresponding titanium(IV) complexes. Such lower field shifting of azomethine hydrogen is supportive of the coordination of azomethine nitrogen to titanium atom\(^{31, 32}\). In the \(^1\)H NMR spectra of the isopropoxide-salicylaldiminate complexes the methyl and methine protons of the isopropoxy groups are observed in the region 1.22-1.15 ppm and 4.49-3.98 ppm, respectively\(^{33}\). The signals observed in the region 8.52-6.03 ppm for the parent Schiff bases showed no noticeable shift in case of their complexes. (Supplementary data, Fig. S2).

In the \(^{13}\)C NMR spectrum of the parent Schiff base, the signal for azomethine carbon\(^{25}\) is observed at 158.35 ppm, whereas the corresponding signals in the complexes are observed in the 162.12-160.67 ppm region. Such a downfield shift is characteristic of coordination\(^{27}\) of the azomethine nitrogen to titanium(IV). The signal appearing at 151.14 ppm region in the spectra of free Schiff base due to phenolic carbon\(^{25}\) shifted to 164.53-163.07 ppm.
region in the corresponding titanium(IV) complexes. Such downfield shifts\(^\text{37}\) are consistent with the formation of titanium-oxygen bond resulting from metallation of phenolic OH group. These observations support the bidentate coordination of salicylaldiminate group (Supplementary data, Fig. S3).

The TOF-MS ES\(^+\) spectra of the complexes (1), (2) and (3) were recorded (see Supplementary data, Figs S4-S6) and fragmentation patterns have been suggested (Scheme 2 and Supplementary data, Schemes S1 and S2 respectively). In the spectra of complexes (1), (2) and (3), the molecular peaks observed at \(m/z\) 425.2 [(C\(_{21}\)H\(_{30}\)N\(_{2}\)O\(_{4}\)Ti); calc. mass = 422.3409], 562.2 [(C\(_{30}\)H\(_{32}\)N\(_{4}\)O\(_{4}\)Ti); calc. mass = 560.4664] and 701.6 [(C\(_{39}\)H\(_{34}\)N\(_{6}\)O\(_{4}\)Ti); calc. mass = 698.5920], respectively correspond to the monomeric molecular composition\(^\text{34}\) of the complexes (\(m/z\) 141). Furthermore, in these spectra the base peak\(^\text{35}\) is observed due to the formation of fragment [C\(_{6}\)H\(_{4}\)O\(_{3}\)]\(^+\) at about \(m/z\) 95. Other important peaks are also observed at \(m/z\) 362.1, 253.1, 239.1, 199.05, 164.1, 140.0 in complex (1). The complex (2) shows some prominent peaks at 485.4, 475.4, 446.1, 372.1, 362.1, 293.1, 253.1, 239.1, 142.1, whereas complex (3)
shows some important peaks at 639.5, 587.1, 549.2, 485.4, 475.4, 437.2, 397.1, 386.3, 341.3, 303.2, 288.3, 239.1, 202.2, 145.1 due to the formation of various fragments such as $\text{OPr}^+$, $\text{C}_4\text{H}_2\text{N}^+$, HCN, $'\text{Ti}$.

Supplementary data
Supplementary data associated with this article i.e., Figs S1-S6, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_53A(11) 1397-1401_SupplData.pdf.

Acknowledgement
APS is grateful to Council of Scientific and Industrial Research, New Delhi Govt. of India for the award of SRF. The authors are also grateful to CDRI, Lucknow, for providing the analytical and SAIF, Chandigarh for spectral studies.

References


