

Synthesis, reactions and physicochemical characterization of some new mixed ligand complexes of titanium(IV) containing cyclopentadienyl and Schiff base moieties

Raj K. Dubey*, Nalini Dwivedi and Mrituanjay D. Pandey

Synthetic Inorganic and Metallo-organic Research Laboratory, Department of Chemistry,
University of Allahabad, Allahabad-211 002, Uttar Pradesh, India

E-mail : rajalkoxy@yahoo.com

Manuscript received 26 October 2009, revised 14 December 2010, accepted 12 January 2011

Abstract : The reactions of titanium(IV) chloride with salicylidene-2-aminopyridine (sapII) and alkyl xanthate (KS_2COR) in the 1 : 1 and 1 : 2 molar ratio(s) yield complexes of the type $[(\mu\text{-Cl})_2\text{Ti}_2(\text{Cl})_4(\text{sap})_2]$ (1), $[(\eta^5\text{-C}_5\text{H}_5)_4\text{Ti}_2(\mu\text{-Cl})_2(\eta^2\text{-S}_2\text{COR})_2]$ (2) (where $\text{R} = \text{C}_6\text{H}_{13}$) and $[(\text{Cl})_2\text{Ti}(\text{sap})_2]$ (3) respectively. The complex 2 has been further treated with sodium salts of Schiff base (derived from isatin and aniline) and tetraisopropoxyaluminate in equimolar ratio to produce mixed ligand complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-S}_2\text{COR})(\text{sb})]$ (4) and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-S}_2\text{COR})(\mu\text{-OPr}^i)_2\{\text{Al}(\text{OPr}^i)\}_2]$ (5) respectively. All these complexes have been characterized by elemental analysis (Ti, Cl, C, H, N and S) and spectroscopic data [UV-visible, IR, NMR (^1H and ^{13}C), FAB-MS] and PXRD as well as thermogravimetric analysis.

Keywords : Chloro-titanium(IV), cyclopentadienyl, mixed-ligand complexes, Schiff base, FAB-MS, TGA, XRD.

Introduction

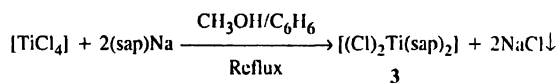
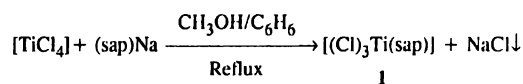
In the recent years coordination compounds have been used in various fields¹. The bidentate xanthate ligand by virtue of its low charge and relative small size is particularly well suited for stabilization of higher co-ordination states of metals². The literature of metal xanthates is quite extensive; there are very few complexes³. Some of the xanthate compounds show microbial activity⁴. Schiff base plays a vital role in the field of coordination chemistry due to their preparative accessibility, diversity and structural variability⁵. The high reactivity, specificity and a number of the applications of Schiff bases in industry, agriculture, medicine and in analytical chemistry and synthesis of macrocyclic ligands have also been employed⁶. Titanium microparticles have been used as filler in the production of a polyether-*block*-amide (Pebax 5533) based composite for medical application⁷. Schiff base complexes of titanium were investigated as precatalysts for ethylene and propene polymerization⁸.

In view of the above fact we are extending our previous efforts for enriching titanium chemistry⁹. We therefore report herein, the synthesis and physicochemical

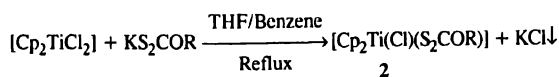
characterization of chloro-(Schiff base) complexes of titanium(IV) and mixed ligand complexes of bis(cyclopentadienyl)titanium(IV) containing alkyl xanthate, Schiff bases and aluminium isopropoxide moieties.

Results and discussion

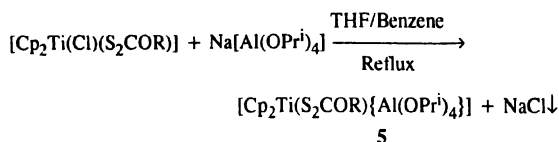
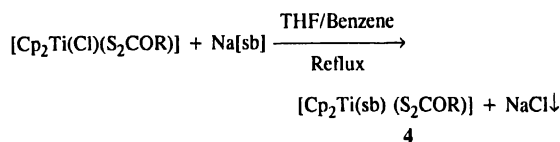
The reactions of titanium(IV) chloride with sodium salt of Schiff base; salicylidene-2-aminopyridine (sapII) in 1 : 1 and 1 : 2 molar ratio(s) produce complexes of the type $[(\text{Cl})_3\text{Ti}(\text{sap})]$ (1) and $[(\text{Cl})_2\text{Ti}(\text{sap})_2]$ (3) respectively, according to the following chemical equations :



Whereas, when bis(cyclopentadienyl)titanium(IV) dichloride was treated with potassium salt of alkyl xanthate in 1 : 1 molar ratio yielded complex $[(\text{C}_5\text{H}_5)_2\text{Ti}(\text{Cl})(\text{S}_2\text{COR})]$ (2) (where $\text{R} = n\text{-C}_6\text{H}_{13}$) which is shown by following chemical equation :



Sodium salts of Schiff bases; isatin-aniline (SIA) and isatin-2-nitroaniline (SIN) (such as NaSIA and NaSIN) and tetraisopropoxyaluminate were added in THF/benzene solution of monochloro-bis(cyclopentadienyl)titanium(IV) hexyl xanthate to afford complexes of the type $[\text{Cp}_2\text{Ti}(\text{sb})\{\text{S}_2\text{COR}\}]$ (4) and $[\text{Cp}_2\text{Ti}(\text{S}_2\text{COR})\{\text{Al}(\text{OPr}^i)_4\}]$ (5) which can be represented by the following chemical equations :



(where sb = SIA or SIN)

All these complexes are coloured solid and are soluble in common organic solvents such as THF, CH_3OH and DMF.

Electronic spectra :

The UV-visible absorption spectra of all these complexes showed broad band at ~ 500 nm, which originate probably due to the charge-transfer transitions. The absence of unpaired electron in the complexes ruled out d-d transition⁹.

Infrared spectra :

The IR bands appeared in the region ~ 3000 cm^{-1} for $\nu_{(\text{C-H})}$, ~ 1450 cm^{-1} for $\nu_{(\text{C-C})}$ and ~ 990 cm^{-1} for $\delta_{(\text{C-H})}$ in the complexes are originated due to cyclopentadienyl ring. The characteristic one band ~ 2980 cm^{-1} showed the pentahapto (η^5) nature of the cyclopentadienyl ring¹⁰.

The xanthate ion can behave as a monodentate or bidentate ligand in these complexes. All the xanthate ligands exhibit four characteristic bands around 1260, 1110, 1055 and 555 cm^{-1} , correspond to $\nu_{(\text{C=S})}$, $\nu_{(\text{C-S})}$, $\nu_{(\text{C-O})}$ and $\nu_{(\text{R-O})}$ stretching vibrations, respectively¹¹. The $\nu_{(\text{C=S})}$ stretching bands were observed in the range 1072–1066 cm^{-1} are lower shifted at ~ 20 cm^{-1} in the

complexes as confirmed coordination through sulphur atom. This was further confirmed by the appearance of new bands around 335–319 cm^{-1} assignable to $\nu_{(\text{Ti-S})}$ ⁹. The bands appeared in the range 1628–1624 cm^{-1} in the ligands due to $\nu_{(\text{C=N})}$ ¹² which get shifted to lower frequency 1618–1600 cm^{-1} in the complexes suggesting the coordination of the azomethine nitrogen to titanium metal. The most significant broad band at 3465 cm^{-1} assignable to ν_{OH} group disappears in the metal complexes showing the deprotonation of phenolic proton on complexation and subsequent formation of M–O bond. Bands appeared in the range 1270–1269 cm^{-1} may be ascribed to the $\nu_{(\text{C-O})}$ stretching frequency, which was shifted to higher frequency region suggesting the coordination through oxygen atom to the metal ion¹³. In titanium(IV) chloro complexes, terminal titanium chloride $\nu_{(\text{Ti-Cl})}$ stretching frequencies observed¹⁴ in the range 390–375 cm^{-1} consistent with six-coordination at titanium. Whereas $\nu_{(\text{Ti-Cl})\text{br}}$ stretching frequency was observed at ~ 230 cm^{-1} and ~ 245 cm^{-1} , attributable¹⁵ to two bridging modes through ($\mu\text{-Cl}$) between two metal atom indicated by lowering in frequency. The appearance of new bands in the range 430–500 cm^{-1} and 415–397 cm^{-1} assigned to $\nu_{(\text{Ti-O})}$ ¹⁶ and $\nu_{(\text{Ti-N})}$ ¹⁰ respectively. The spectra of alkoxo-bridged (bimetallic) complex exhibited typical frequencies for metal-alkoxy group $\nu_{(\text{C-O})\text{Ti}}$ at 1162–1128 cm^{-1} for terminal isopropoxy group and at 991–952 cm^{-1} for bridging isopropoxy groups. The band observed at 622–590 cm^{-1} has been showed for $\nu_{(\text{Al-O})}$ ¹⁷.

¹H NMR spectra :

A strong signal appeared in the proton NMR spectra of Schiff base ligands at δ 12.65 ppm due to phenolic proton¹⁸, whereas this signal was disappeared in its corresponding titanium(IV) complexes which is the indication for coordination through phenolic oxygen to titanium metal after deprotonation of phenolic proton. Another signal was observed at δ 8.64 ppm due to azomethine proton which gets shifted downfield (δ 10.23–8.9 ppm) in the spectra of complexes. This suggested that coordination takes place through azomethine nitrogen to the metal ion¹⁹. The signal was appeared at δ 11.2 ppm in the spectra of the ligands due to NH of isatin ring whereas this signal was disappeared in their metal complexes⁹. In addition, there appeared sharp singlet near δ 6.52–6.65

ppm²⁰ showing the rapid rotation of the ring about the metal ring axis. The chemical shifts appeared at δ 7.8–8.4 ppm in spectra of ligands due to aromatic ring protons which shifted slightly downfield in the complexes²¹.

In complex **5**, the methine protons of the terminal and the bridging isopropoxy groups were observed at δ 3.90–3.99 ppm and δ 4.06–4.25 ppm, respectively, while the corresponding methyl protons were observed in the region δ 1.15–1.19 ppm and δ 1.19–1.22 ppm as a doublet, indicating that these are magnetically nonequivalent.

¹³C NMR spectra :

The spectra of organotitanium(IV) complexes showed a considerable shift of the signals towards the lower field as compared to the ligands. The complexes showed one

It is observed in the complex **5** that methyl carbon signals of the terminal and the bridging isopropoxy groups were observed at 24.11–25.25 ppm and 25.21–26.12 ppm respectively, while methine carbons of the terminal and the bridging isopropoxy groups were observed at 59.88–60.50 ppm and 61.26–63.92 ppm respectively.

FAB-MS spectra :

FAB-MS spectrum of complex $[\text{Cl}_3\text{Ti}(\text{sap})]_2$ (**1**) (Fig. 1) showed an important peak at m/z 699, which corresponds to the dimeric molecular association; the dimerization takes place through bridging chlorine atom between two titanium(IV) centers. Several peaks were observed in mass spectrum at m/z 699, 625, 598, 519, 485,

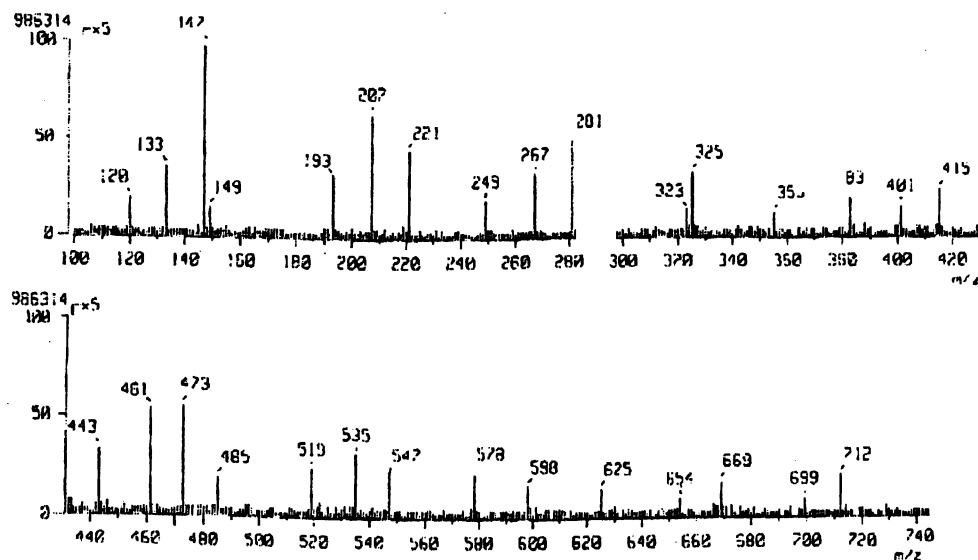
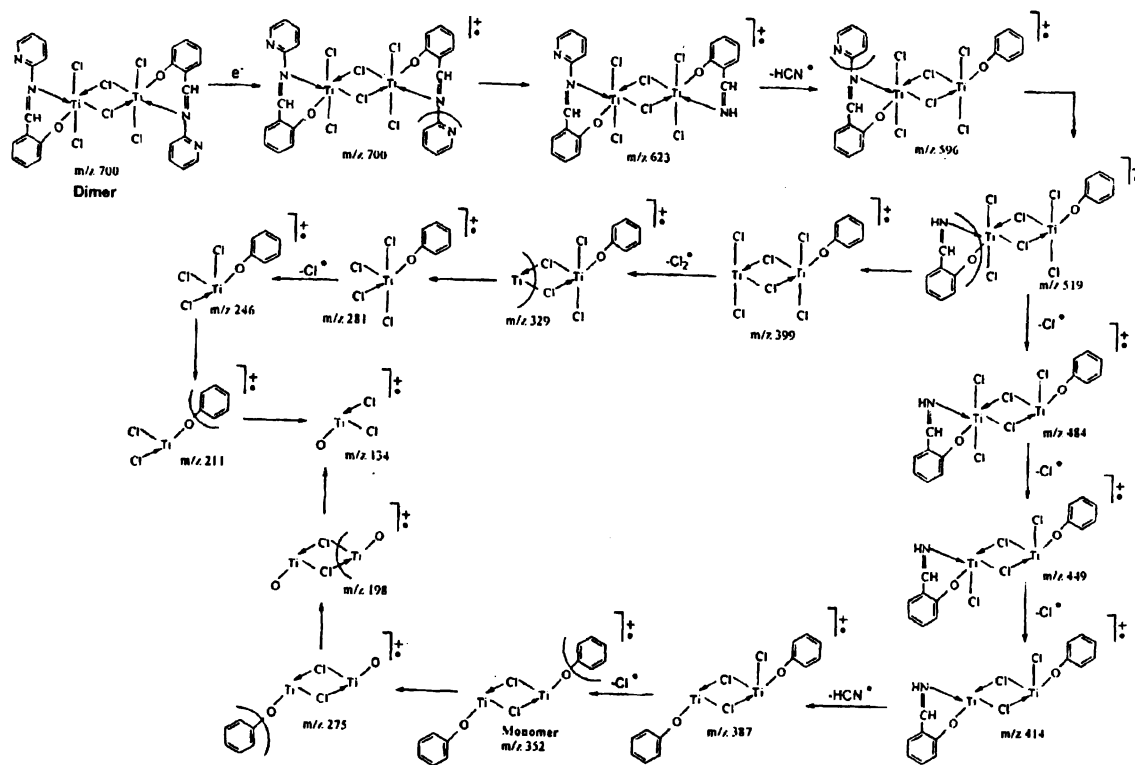


Fig. 1. FAB-MS spectrum of complex $[(\mu\text{-Cl})_2\text{Ti}_2(\text{sap})_2(\text{Cl}_4)]$ (**1**).

resonance at δ 117 ppm due to cyclopentadienyl ring. The appearance of carbon signal of the -CS_2 group at δ 135.0 in the ligands, which get shifted down field in the complexes confirming the bidentate nature of the CS_2 ligand group. The spectra of complexes showed signals in the range δ 160.97–154.30 ppm due to azomethine carbon indicated the coordination of azomethine nitrogen to the titanium metal. Signals were observed at δ 163.63–158.80 ppm in titanium(IV) complexes due to phenolic carbon which assigned coordination of phenolic oxygen to the metal via metal oxygen bond formation.

443, 401, 383, 355, 325, 281, 249, 207, 193, 133 due to fragmentation of complex. The fragmentation pattern is shown in Scheme 1.

The FAB-MS spectrum of $[\text{Cp}_2\text{TiCl}(\text{S}_2\text{COR})]_2$ (**2**) (Fig. 2) showed a molecular ion peak at m/z 780 which corresponds to the molecular weight of the complex in the dimeric nature. The fragmentation pattern of the complex **2** is given in Scheme 2. The spectrum of the complex $[\text{Cp}_2\text{Ti}(\text{S}_2\text{COR})(\text{SIA})]$ (**4**) showed a peak at m/z 576, corresponds to molecular weight of the complex in its monomeric form (Fig. 3). It also showed several peak indicat-



Scheme 1. FAB-MS fragmentation pattern of complex $[(\mu\text{-Cl})_2\text{Ti}_2(\text{sap})_2(\text{Cl})_4]$ (1).

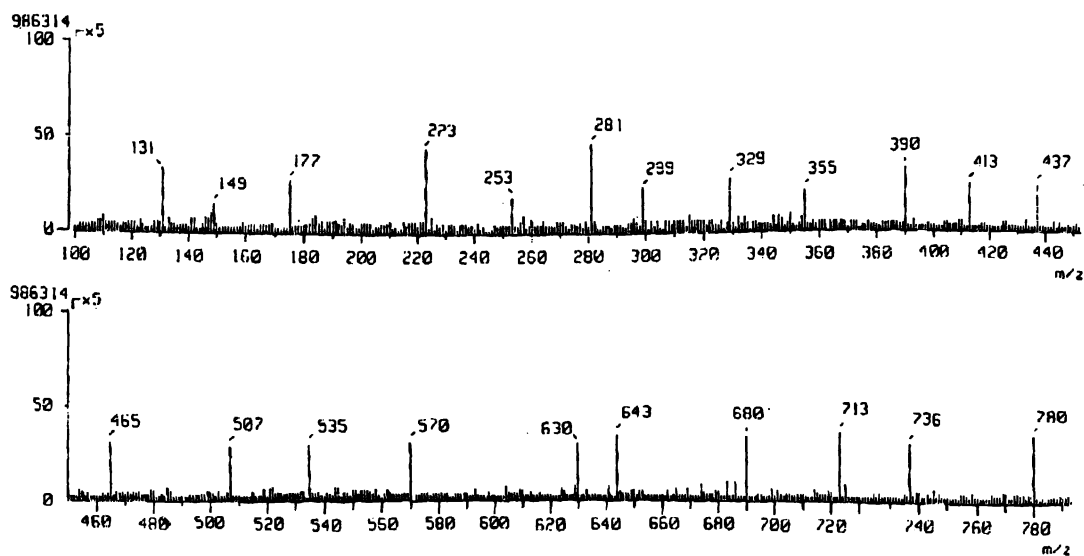
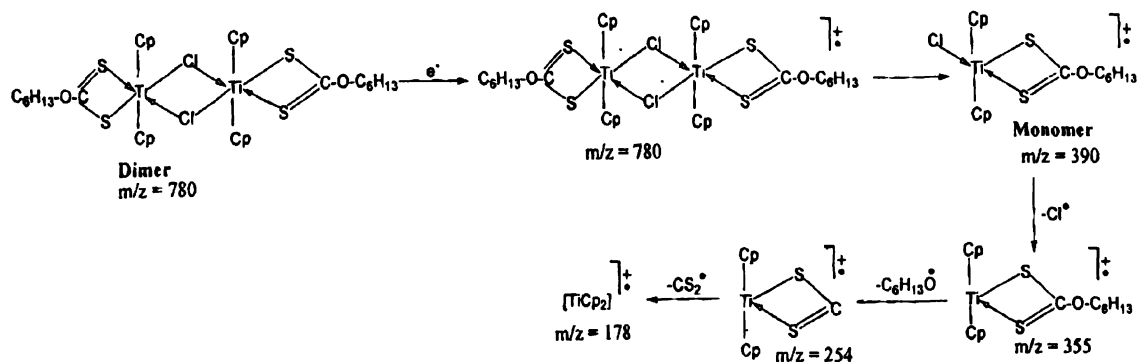


Fig. 2. FAB-MS spectrum of complex $[(\eta^5\text{-C}_5\text{H}_5)_4\text{Ti}_2(\eta^2\text{-S}_2\text{COR})_2(\mu\text{-Cl})_2]$ (2).



Scheme 2. FAB-MS fragmentation pattern of complex $[(\eta^5\text{-C}_5\text{H}_5)_4\text{Ti}_2(\eta^2\text{-S}_2\text{COR})_2(\mu\text{-Cl})_2]$ (2)

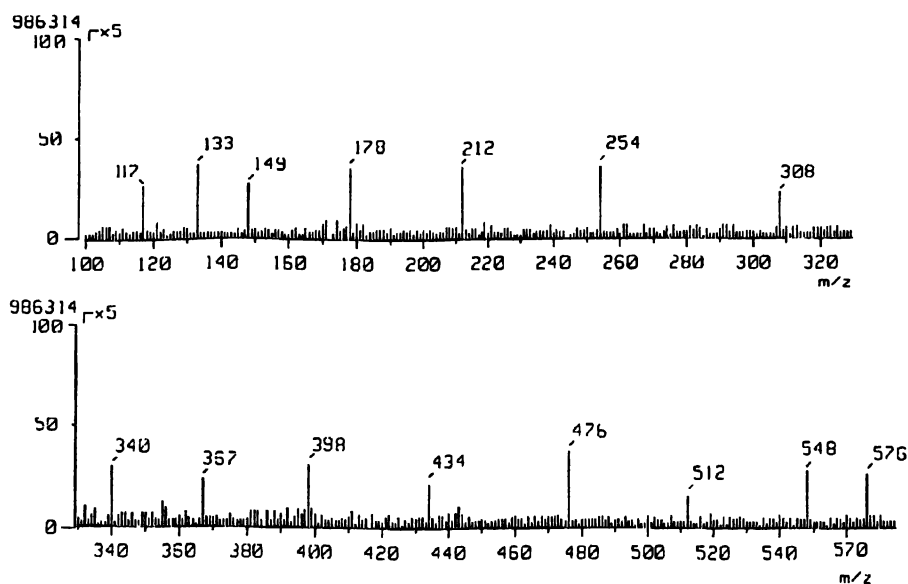


Fig. 3. FAB-MS spectrum of complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-S}_2\text{COR})_2(\text{SIA})]$ (4).

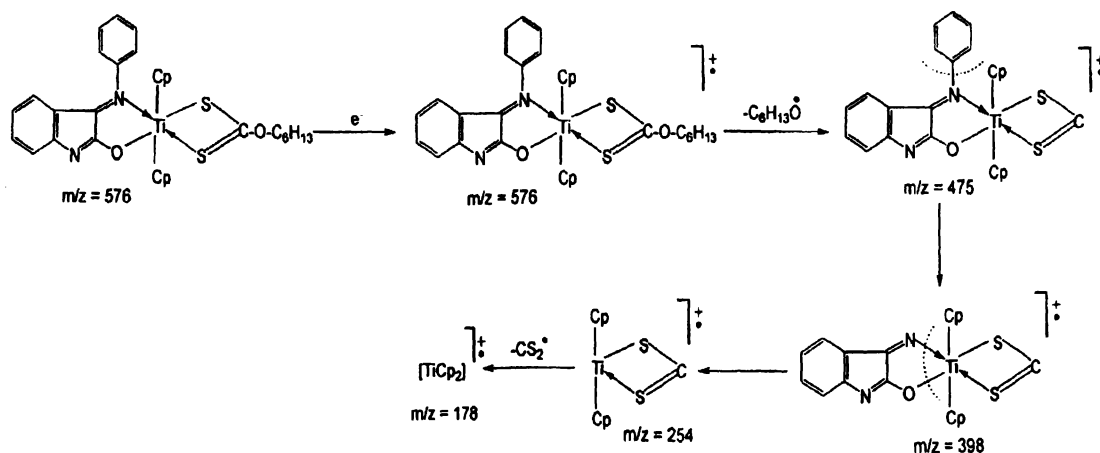
ing the fragmentation of ligand from complex by the formation of radical cation. The fragmentation pattern of this complex is shown in Scheme 3.

Thus these spectral data suggest that the Schiff base ligands [salicylidene-2-aminopyridine (sapH), isatin-aniline (SIA) and isatin-2-nitroaniline (SIN)] and xanthate ligand act as monobasic, bidentate chelating agents. On the basis of above studies, the chloro-bridged structures may be tentatively proposed.

Thermogravimetric analysis :

Thermogravimetric analysis is one of the important techniques for the studies of the thermal reaction sequence of simple and complex compound²². Thermogravimetric

analysis of complex $[\text{Cl}_3\text{Ti}(\text{sap})]_2$ (1) was carried out up to 700 °C (Fig. 4). The % weight loss was measured from ambient temperature up to 700 °C at heating rate of 10 °C per min. Thermogram shows a gradual mass loss indicating moisture loss due to hygroscopic nature. The molecular mass of the complex is 700. Initial weight was taken 2.8605 mg and final weight found to be 1.752 mg and the total weight loss was 1.1085 mg. The % weight loss of the complex is 39.1004% which is equal to the 273.7028 weight of the complex. It is clear that the elimination of chlorine and organic constituents of the coordinated ligand from the complex molecule. Thus it tends to



Scheme 3. FAB-MS fragmentation pattern of complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-S}_2\text{COR})_2(\text{SIA})]$ (4).

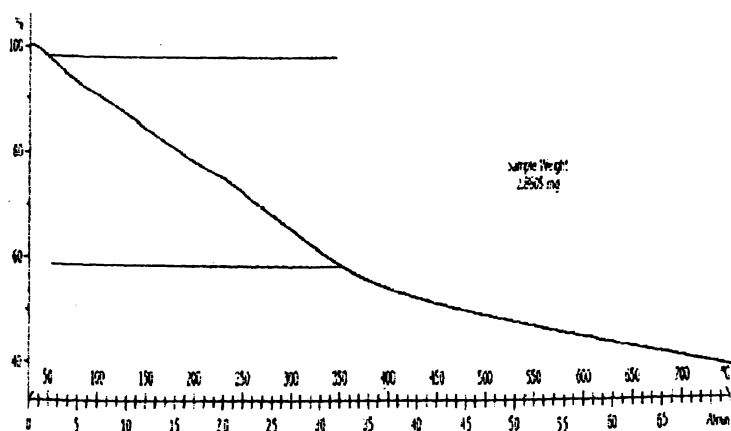


Fig. 4. TGA curve of the complex $[(\mu\text{-Cl})_2\text{Ti}_2(\text{sap})_2(\text{Cl}_4)]$ (1).

go in the formation of monomeric form. Thereafter weight of the residue is 426.2972. The decomposition continues up to ~ 650 °C and reaches to a stable product as stable metal oxide.

X-ray powder diffraction study :

XRD study of the complex $[\text{Cl}_3\text{Ti}(\text{sap})]_2$ (1) was made with the help of X-ray diffraction by powder pattern method using $\text{CuK}\alpha$ radiation with $\lambda = 1.5406$ Å. The powder-XRD pattern was recorded in the 2θ range between 15.239 and 81.554 with a step size of 0.0167. The X-ray powder diffractogram of titanium(IV) complex exhibits amorphous in nature. The PXRD of this complex is given in Fig. 5.

The parameters of the prepared material are calculated for the titanium(IV) complex 1 which is summarized in Table 1.

Experimental

All the solvents and reagents were purified by standard literature procedure²³. The alkylxanthate², Schiff bases [salicylidene-2-aminopyridine (sapH)²⁴, isatin-aniline (SIA) and isatin-2-nitroaniline (SIN)²⁵] and sodium tetraalkoxyaluminate²⁶ were prepared by the reported method. Titanium tetrachloride and bis(cyclopentadienyl)titanium(IV) dichloride were purchased from Merck, Germany. Chloride, titanium and sulphur were estimated as reported method²⁷. Elemental analyses were

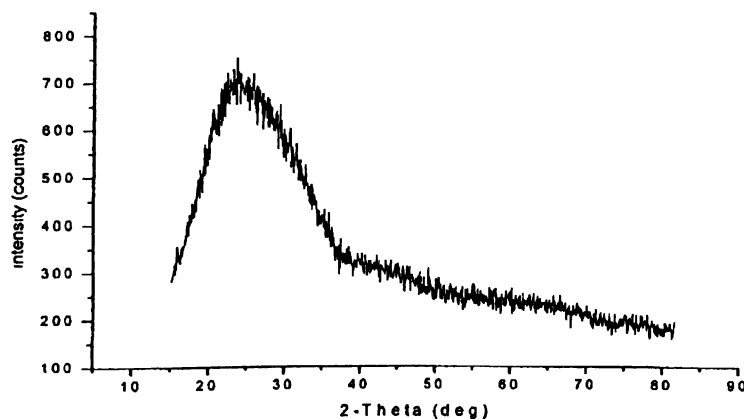
Fig. 5. PXRD of the complex $[(\mu\text{-Cl})_2\text{Ti}_2(\text{sap})_2(\text{Cl})_4]$ (1).

Table 1. Parameter of titanium(IV) complex

Parameters	$[(\mu\text{-Cl})_2\text{Ti}_2(\text{sap})_2(\text{Cl})_4]$ (1)
Empirical formula	$\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_2\text{Cl}_6\text{Ti}_2$
Formula weight	700
Wave length (Å)	1.5406
Step size	0.01671
Powder used	1.6 Kw

carried out on a Perkin-Elmer series II model 2400. The electronic spectra of the compound were recorded in DMF using 10 mm quartz cell on a Perkin-Elmer Lambda 15 UV-Vis spectrophotometer. The infrared spectra of the ligands and the complexes in the range $4000\text{--}200\text{ cm}^{-1}$ were recorded in KBr pellets on Perkin-Elmer 1000 FTIR spectrophotometer. The NMR spectra of ligands and complexes are recorded in $\text{DMSO-}d_6$ on Bruker DRX-300 spectrometer at the sweep width of 300 MHz and a sweep time of 300 s. The FAB-mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 kV, 10 mA) as the FAB gas. The thermogravimetric (TG) analysis of the solid complex was recorded on Mettler Toledo from ambient to $750\text{ }^\circ\text{C}$ with heating rate of $10\text{ }^\circ\text{C min}^{-1}$ using nitrogen atmosphere. The X-ray powder diffraction was carried out at ambient temperature using Rigaku D/max-2200 PC diffractometer with $\text{Cu-K}\alpha_1$ radiation.

Synthesis of $[(\mu\text{-Cl})_2\text{Ti}_2(\text{sap})_2(\text{Cl})_4]$ (1) :

A freshly prepared sodium salt of salicylidene-2-aminopyridine (1.816 g, 9.16 mmol) in methanol (20 cm^3) was added in methanolic solution of anhydrous titanium(IV) chloride (1.738 g, 9.16 mmol) in 1 : 1 molar ratio with constant stirring. The reaction mixture was allowed to

reflux for $\sim 4\text{ h}$, during which time the colour of the solution become orange. The precipitated NaCl (0.534 g, 9.16 mmol) was removed by filtration, followed by drying under reduced pressure to afford brown coloured solid which was purified by recrystallisation from methanol. Yield : (2.53 g, 79%) (Found : C, 40.00; H, 2.34; N, 7.5; Cl, 29.15; Ti, 13.48. Calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_2\text{Cl}_6\text{Ti}_2$: C, 41.14; H, 2.57; N, 8.00; Cl, 30.00; Ti, 13.71 %).

Synthesis of $[(\text{Cl})_2\text{Ti}(\text{sap})_2]$ (3) :

Similar procedure was adopted for the synthesis of complex 3 by interaction of titanium(IV) chloride and sodium salt of Schiff base in 1 : 2 molar ratio(s). Yield : (2.06 g, 77%) (Found : C, 56.02; H, 3.13; N, 9.75; Cl, 12.89; Ti, 8.93. Calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_2\text{Cl}_2\text{Ti}$: C, 56.25; H, 3.52; N, 10.94; Cl, 13.67; Ti, 9.38 %).

$[(\eta^5\text{-C}_5\text{H}_5)_4\text{Ti}_2(\eta^2\text{-S}_2\text{COR})_2(\mu\text{-Cl})_2]$ (2) :

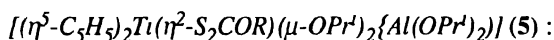
A freshly prepared solution of bis(cyclopentadienyl)-titanium(IV) dichloride (0.567 g, 2.3 mmol) in tetrahydrofuran (30 ml) was added to THF/benzene solution of potassium hexyl xanthate (0.50 g, 2.3 mmol) with constant stirring and refluxed for $\sim 6\text{ h}$. The filtrate was concentrated to $\sim 30\text{ ml}$. To this petroleum ether ($\sim 30\text{ ml}$) was added and the solution was allowed to stand overnight to obtain light yellow coloured compound $[(\text{C}_5\text{H}_5)_2\text{Ti}(\text{S}_2\text{COR})(\text{Cl})]$ which was dried under reduced pressure and recrystallised from methanol/chloroform. Yield : (0.583 g, 65%) (Found : C, 52.25; H, 5.42; Cl, 8.53; S, 16.33; Ti, 12.04. Calcd. for $\text{C}_{34}\text{H}_{46}\text{Cl}_2\text{O}_2\text{S}_4\text{Ti}_2$: C, 52.31; H, 5.90; Cl, 8.97; S, 16.41; Ti, 12.31 %).

$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-S}_2\text{COR})(\text{sb})]$ (4) :

Chlorobis(cyclopentadienyl)titanium hexyl xanthate complex (0.89 g, 2.30 mmol) in THF/benzene mixture

was added to a stirred solution of sodium salt of isatin-aniline (SIA) (0.56 g, 2.30 mmol) and refluxed at room temperature for ~6 h. The filtrate was dried under reduced pressure. The product was found to be $[(C_5H_5)_2Ti(S_2COR)(SIA)]$ (4). Yield : (0.82 g, 62%) (Found : C, 64.55, H, 5.24; N, 4.82; S, 10.96, Ti, 8.28. Calcd for $C_{31}H_{32}N_2O_2S_2Ti$: C, 64.58, H, 5.56; N, 4.86; S, 11.11; Ti, 8.33%).

The same synthetic procedure was adopted for reaction of titanium hexyl xanthate with other Schiff base isatine-2-nitroaniline (SIN)



Chlorobis(cyclopentadienyl)titanium hexyl xanthate complex (0.42 g, 1.08 mmol) in THF (~30 ml) was added to the THF/benzene (~30 ml) solution of sodium tetraisopropoxyaluminate (0.303 g, 1.08 mmol). The reaction mixture was stirred with refluxing for ~6 h. The light yellow coloured precipitate was filtered and dried under reduced pressure. The complex was further crystallized by THF-benzene mixture. Yield : (0.47 g, 70%) (Found : C, 55.55; H, 8.03; Al, 4.24; S, 10.13; Ti, 7.35. Calcd. for $C_{29}H_{51}AlO_5S_2Ti$: C, 56.31, H, 8.25; Al, 4.37; S, 10.30; Ti, 7.77%)

Acknowledgement

Authors are thankful to Director, CDRI, Lucknow for providing spectral and analytical data and IIT, Kanpur for thermal analysis. Nanophosphor Application Center, University of Allahabad, Allahabad is also acknowledged for XRD study. MDP is thankful to CSIR, New Delhi, India for providing financial assistance.

References

- 1 J A McCleverty and T J Meyer, "Comprehensive Coordination Chemistry II From Biology to Nanotechnology", Vol 9, 'Applications of Coordination Chemistry', Elsevier, Amsterdam, 2003
- 2 S R Rao, "Xanthates and Related Compounds", Marcel Dekker, New York, 1971
- 3 W Friebohn, G Schilling, M Zoller and E Amtmann, *J Med Chem*, 2004, **47**, 2256. D Nath and A N Bhat, *Indian J Chem, Sect A*, 1976, **14**, 281. O P Pandey, S K Sengupta and S C Tripathi, *Polyhedron*, 1984, **3**, 695
- 4 Y Xu, J P Lay and F Korte, *Bulletin of Environ Contam Toxicology*, 1988, **41**, 683
- 5 Yu E Alexeev, B I Kharisov, T C Hernandez Garcia and A D Garnovskii, *Coord Chem Rev*, 2010, **254**, 794
- 6 E Jungreis and S Thabet, In H A Flaschka and A J Barnard, (eds.), "Chelates in Analytical Chemistry", Marcel Dekker, New York, 1969, **2**, 149
- 7 J G Lyons, J E Kennedy, S Lordan, L M Geever and C L Higginbotham, *J Mater Sci*, 2010, **45**, 3204
- 8 M Strianese, M Lamberti, M Mazzeo, C Tedesco and C Pellicchia, *J Mole Catalysis A Chemical*, 2006, **258**, 284
- 9 R K Dubey and M D Pandey, *J Indian Chem Soc*, 2009, **86**, 1262. R K Dubey, M D Pandey, N Dwivedi and A P Singh, *Vijnana Parishad Anusandhan Patrika*, 2009, **52**, 265
- 10 A K Srivastava, O P Pandey and S K Sengupta, *J Indian Chem Soc*, 2007, **84**, 427
- 11 A Bhatt, A K Srivastava, O P Pandey and S K Sengupta, *J Indian Chem Soc*, 2007, **84**, 431
- 12 K Singh, M S Barwa and P Tyagi, *Polyhedron*, 2006, **25**, 3095
- 13 N S Biradar, B R Patil and V H Kulkarni, *J Inorg Nucl Chem*, 1975, **37**, 1901
- 14 George Socrates, "Infrared and Raman Characteristic Group Frequencies Tables and Charts", 3rd ed, 2001, 304
- 15 J R Dalziel, R D Klett, P A Yeats and F Aubke, *Can J Chem*, 1974, **52**, 321
- 16 R K Sharma, R V Singh and J P Tandon, *Synth React Inorg Metal-Org Chem*, 1979, **9**, 519
- 17 C J Carmalt, C W Dinnage, I P Parkin, A J P White and D J Williams, *J Chem Soc Dalton Trans*, 2001, **18**, 2554
- 18 K Poonia, M Swami, A Chaudhary and R V Singh, *Indian J Chem, Sect A*, 2008, **47**, 996
- 19 L K W Henri, J Tagenine and B M Gupta, *Indian J Chem, Sect A*, 2001, **40**, 999
- 20 P C Wailes, R S P Coutts and H Weigold, "Organometallic Chemistry of Titanium, Zirconium and Hafnium", Academic Press, New York, 1974
- 21 R M Silverstein, C C Bassler and T C Morrill, "Spectroscopic Identification of Organic Compounds" 4th ed, John Wiley and Sons, 1981
- 22 R K Dubey and P Baranwal, *Main Group Metal Chemistry*, 2009, **32**, 321
- 23 W L F Argarego and D D Perrin, "Purification of Laboratory Chemicals", 4th ed, Butterworth, Henemann, Oxford, 1997
- 24 R Thomas, K J Thomas and G Parmeswaran, *J Indian Chem Soc*, 1996, **73**, 529
- 25 A M A Hassaan, *Trans Met Chem*, 1990, **15**, 283
- 26 M I Karpovskaya, N Y Turova and A V Novoselova, *Russ J Inorg Chem*, 1978, **23**, 1392
- 27 A I Vogel, "A Text Book of Quantitative Inorganic Analyses", 4th ed, Longmans Green Co Ltd London, 1972. A I Vogel, "A Text Book of Practical Organic Chemistry", 4th ed, Longman Green Co Ltd London, 1978