

Glycol modified *cis*-diisopropoxy-bis(*N*-phenylsalicylideneiminato) titanium(IV). Syntheses, characterization, X-ray structures of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$, $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\}\text{O}]_3$ and their low temperature transformation to pure grains of nanosized titania

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Abstract

$\text{Ti}(\text{OPr}^i)_4$ reacts with *N*-phenylsalicylideneimine in anhydrous benzene in 1:2 molar ratio to afford precursor $[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2]$ (**A**). Further reactions of **A** with various glycols yield heteroleptic complexes of the type $[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{O}-\text{G}-\text{O}\}]$ [where $-\text{G}- = (\text{CH}_2)_2$ (**1**), $(\text{CH}_2\text{CHCH}_3)$ (**2**), $(\text{CH}_3\text{CHCH}_2\text{CH}_3)$ (**3**), $(\text{CH}_2\text{CHC}_2\text{H}_5)$ (**4**), $\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2$ (**5**), $(\text{CH}_2)_3$ (**6**), $(\text{CH}_2\text{CH}_2\text{CHCH}_3)$ (**7**), $(\text{CH}_3)_2\text{CCH}_2\text{CHCH}_3$ (**8**), $(\text{CH}_2)_5$ (**9**) and $(\text{CH}_2)_6$ (**10**)]. FAB mass spectroscopic studies of some of the derivatives suggest their monomeric nature. Single crystal X-ray diffraction study of **A** reveals *cis*-orientation of the isopropoxy groups $[\text{O}(3)-\text{Ti}(1)-\text{O}(4) = 102.23(11)^\circ]$ and distorted octahedral geometry around the titanium atom. Crystal structure of a trinuclear titanoxane $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\}\text{O}]_3$, obtained from the partial hydrolysis of **A**, exhibit the formation of a six-membered Ti_3O_3 ring. Complete hydrolysis and low temperature (300–500 °C) transformation of precursor **A**, as well as of **1** and **7** to pure TiO_2 have also been achieved using sol–gel technique. The XRD patterns indicate formation of anatase phase of TiO_2 . The XRD and SEM observations on all the three samples indicate the formation of pure grains of nanosized titania. TGA curves of **A** and **7** suggest occurrence of multiple large thermal events.

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1. Introduction

The use of $\text{Ti}(\text{OR})_4$ in sol–gel [1] and CVD [2] processes for materials is very well known. TiO_2 (the anatase TiO_2 is the most active phase in comparison to rutile and brookite phases) an n-type semiconductor, finds a variety of applications in microelectronic devices [3] as well as in catalytic [4] and photo-catalytic processes [5].

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The synthesis of metallo-organic compounds of titanium has experienced strong advances not only due to their applications in materials [6] and catalysis [7] but also due to the interesting exhibition of structural variations [8]. The essential condition of the sol–gel technology for material synthesis is good control over the rate of hydrolysis of the precursor alkoxide to give suitable size, shape and porous structures of TiO_2 . This could be achieved by partial substitution of some of the alkoxy groups in $\text{Ti}(\text{OR})_4$ by suitable modifiers [8h,8i] such as β -diketone, *N*-phenylsalicylideneimine, etc.

Our previous studies on *N*-phenylsalicylideneimine substituted aluminium(III)isopropoxide complexes indicated that the modified ligand is capable of stabilizing aluminium(III) atoms in hexa- and tetra-coordination states in the dinuclear complexes [9].

In order to modify $\text{Ti}(\text{OPr}^i)_4$, amenable for sol-gel applications, we carried out the reactions of $\text{Ti}(\text{OPr}^i)_4$ with *N*-phenylsalicylideneimine to give a precursor material, $[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OPr}^i\}_2]$ (**A**). Further modification of **A** with a variety of glycols yields heteroleptic derivatives. Herein, we report the syntheses, characterization, X-ray structures of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$, $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\text{O}\}_3]$ and their low temperature transformation to pure grains of nanosized titania by the sol-gel technique.

2. Experimental

All manipulations for the synthesis of **A** and **1–10** were carried out in strictly anhydrous conditions. Solvents and reagents used were dried by conventional methods and distilled prior to use. *Due precautions were taken to handle health hazard chemicals, like benzene.* $\text{Ti}(\text{OPr}^i)_4$ [10] and *N*-phenylsalicylideneimine [11] were prepared as reported in the literature. Titanium was estimated as TiO_2 [12] and the liberated isopropanol by oxidimetric method [13].

IR spectra were recorded on SHIMADZU, FTIR 8400 Spectrometer in dry KBr powder. NMR [^1H and $^{13}\text{C}\{^1\text{H}\}$] data were collected on JEOL FX 300 FT NMR spectrometer in CDCl_3 solutions at 300.4 and 75.45 MHz frequencies for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, respectively. FAB mass spectra of some of the complexes were obtained on a JEOL SX 102/DA-6000 mass spectrometer using *m*-nitrobenzyl alcohol matrix. Microanalyses were carried out on a Heraeus Carlo Erba 1108 analyzer. XRD patterns were obtained on a Philips-1840 diffractometer using Fe source at λ 1.937 Å. SEM images have been taken on a Philips XL30 Scanning Electron Microscope with the powders spread thin on a conducting carbon tape. Thermogravimetric analysis was performed on Mettler Toledo Star SW 701 with the heating rate of 25–900/10 °C.

2.1. Synthesis

2.1.1. Preparation of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (**A**)

A benzene solution of $\text{Ti}(\text{OPr}^i)_4$ (1.71 g, 6.02 mmol) was added to a benzene solution of *N*-phenylsalicylideneimine (2.38 g, 12.07 mmol). The mixture was heated up to reflux. Completion of the reaction was monitored by estimating the liberated isopropanol oxidimetrically in the azeotrope. The resulting mixture was concentrated *in vacuo* to give a yellow solid [3.33 g, m.p. 110 °C]. This was recrystallized from isopropanol to give single crystals suitable for X-ray diffraction analysis.

2.1.2. Preparation of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2[\text{OCH}_2\text{CH}_2\text{O}]$ (**1**)

To the benzene solution of **A** (1.68 g, 3.01 mmol), 0.19 g (3.06 mmol) of ethylene glycol was added. The reaction mixture was refluxed and the progress of the reaction was monitored by estimating liberated isopropanol. Remaining solution was dried *in vacuo* to give a yellow solid [1.50 g, m.p. 70 °C].

All other derivatives have been prepared by a similar route and their synthetic and analytical details are summarized in Table 1.

2.2. Hydrolytic studies

2.2.1. Partial hydrolysis of **A**

When partial hydrolysis of **A** (~0.8 g) was carried out in dichloromethane (~4 ml) with a few droplets of water hanging on the inner surface of the stopper of the flask some good quality crystals of $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\text{O}\}_3]$ appeared in the following day. These were characterized by single crystal X-ray diffraction analysis and NMR spectroscopy. [^1H NMR (in δ ppm): 7.03 (m, N-Ph); 6.72–7.45 (m, C_6H_4); 8.02 (s, CH=N), $^{13}\text{C}\{^1\text{H}\}$ NMR (in δ ppm): 117.2–133.1 (all aromatic carbons); 161.1 (CH=N)].

2.2.2. Complete hydrolysis of **A**

Compound **A** (~3 g) was dissolved in isopropanol (~31 ml). To this, a drop of water was added and stirred for 24 h. Gelation occurred immediately. Some more quantity of water (one drop) was added and the mixture was stirred for 3 days. The whole mixture was dried in an oven (at 100 °C) overnight. A yellow coloured powder was obtained. This was washed several times with *n*-hexane and with isopropanol and sintered at 300 °C for 2 h to give a white powder, which was characterized as pure TiO_2 [C, 0.25%; H, 1.11%; N, Nil].

2.2.3. Complete hydrolysis of **1** and **7**

Two more compounds $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2[\text{OCH}_2\text{CH}_2\text{O}]$ (**1**) and $[\text{Ti}(\text{OC}_6\text{H}_4\text{CH}=\text{NPh})_2(\text{OCH}_2\text{CH}_2\text{CHOCH}_2)]$ (**7**) were hydrolyzed using a similar path as adopted for the complete hydrolysis of **A**, with the only difference being drying it in an oven at 100 °C. The yellow powder was washed three times with acetone-*n*-hexane mixture to remove the free ligand present in the system and sintered at 500 °C for 2 h. The organic content was almost nil [C, 0.26% and 0.60%; H, 0.77% and 1.08% in **1** and **7**, respectively].

2.3. Crystal structure analyses of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (**A**) and its hydrolysis product $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\text{O}\}_3]$

X-ray data were collected at 200 K with a Nonius KapkaCCD diffractometer equipped with a rotating anode and graded multilayer X-ray optics to obtain monochrome

Table 1
Physical and analytical data for $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^f)_2$ (**A**) and glycolatobis(*N*-phenylsalicylideneiminato) titanium(IV) complexes

Reactants (g)		Complexes	Colour (yield, g)	Elemental analyses (%) found (calc.)					M.p. (°C)
$\text{Ti}(\text{OPr}^f)_4$	$\text{HO}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}$			Liberated Pr^fOH	C	H	N	Ti	
1.71	2.38	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^f)_2$ (A)	Yellow (3.33)	0.70 (0.72)	68.7 (68.8)	6.0 (6.1)	5.0 (5.0)	8.5 (8.6)	110
A	HO–G–OH	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2\text{--CH}_2\text{--O}\}$ (1)	Yellow (1.49)	0.34 (0.36)	67.0 (67.2)	4.9 (4.8)	5.7 (5.6)	9.5 (9.6)	70
1.67	0.19								
1.65	0.22	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2\text{--CH}(\text{O})\text{--CH}_3\}$ (2)	Yellow (1.51)	0.32 (0.35)	67.5 (67.7)	5.4 (5.1)	5.7 (5.4)	9.3 (9.3)	80
1.94	0.31	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{CH}_3\text{--CH}(\text{O})\text{--CH}(\text{O})\text{--CH}_3\}$ (3)	Dark Yellow (1.82)	0.38 (0.42)	67.9 (68.2)	5.1 (5.3)	5.2 (5.3)	9.1 (9.1)	75
1.91	0.31	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2\text{--CH}(\text{O})\text{--CH}_2\text{--CH}_3\}$ (4)	Dark Yellow (1.80)	0.39 (0.42)	68.1 (68.2)	5.7 (5.3)	5.1 (5.3)	9.0 (9.1)	74
2.25	0.48	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OC}(\text{CH}_3)_2\text{--C}(\text{CH}_3)_2\text{O}\}$ (5)	Yellow (2.22)	0.38 (0.48)	68.9 (69.1)	5.7 (5.8)	4.9 (5.0)	8.6 (8.6)	100
2.15	0.29	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2\text{--CH}_2\text{--CH}_2\text{O}\}$ (6)	Yellow (1.97)	0.41 (0.46)	67.3 (67.7)	5.4 (5.1)	5.3 (5.4)	9.3 (9.3)	138
2.03	0.33	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2\text{--CH}_2\text{--CH}(\text{O})\text{--CH}_3\}$ (7)	Yellow (1.91)	0.44 (0.43)	68.1 (68.2)	5.4 (5.3)	5.5 (5.3)	9.0 (9.1)	69
2.09	0.44	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{(\text{CH}_3)_2\text{C}(\text{O})\text{--CH}_2\text{--CH}(\text{O})\text{--CH}_3\}$ (8)	Yellow (2.07)	0.40 (0.45)	69.0 (69.1)	5.7 (5.8)	5.0 (5.0)	8.6 (8.6)	^a
1.15	0.21	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2\text{--}(\text{CH}_2)_3\text{--CH}_2\text{O}\}$ (9)	Yellow (1.13)	0.24 (0.25)	68.5 (68.6)	5.6 (5.6)	5.1 (5.2)	8.9 (8.8)	^a
1.73	0.36	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2\text{--}(\text{CH}_2)_4\text{--CH}_2\text{O}\}$ (10)	Yellow (1.72)	0.32 (0.37)	69.0 (69.1)	5.8 (5.8)	4.9 (5.0)	8.6 (8.6)	98

^a Hydrolyzed during measurements.

Table 2

Crystallographic data of compounds $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (A) and $[\{\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\text{O}\}_3 \cdot 2\text{CH}_2\text{Cl}_2$

	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$	$[\{\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\text{O}\}_3 \cdot 2\text{CH}_2\text{Cl}_2$
Empirical formula	$\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}_4\text{Ti}$	$\text{C}_{80}\text{H}_{64}\text{Cl}_4\text{N}_6\text{O}_9\text{Ti}_3$
Formula weight (g mol^{-1})	558.490	1538.81
Crystal size (mm)	$0.21 \times 0.15 \times 0.09$	$0.17 \times 0.14 \times 0.1$
Crystal colour, habit	200(2)	yellow platelet
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
a (Å)	11.4790(2)	23.153(5)
b (Å)	13.3095(3)	14.121(3)
c (Å)	21.3403(4)	23.025
α (°)	106.1305(12)	90
β (°)	92.5176(14)	92.86(3)
γ (°)	107.7134(8)	90
Volume (Å ³)	2953.98(10)	7519(3)
Z	4	4
D_{calc} (g cm^{-3})	1.25581(4)	1.3594(5)
Absorption coefficient (mm^{-1})	0.327	0.514
$F(000)$	1176	3168
Index ranges	$-14 \leq h \leq 14$, $-16 \leq k \leq 16$, $-26 \leq l \leq 26$	$-26 \leq h \leq 26$, $-16 \leq k \leq 15$, $-26 \leq l \leq 26$
θ Range (°)	3.20–26.00	3.16–24.12
Reflections collected	21 759	43 233
Independent reflections	11 535	11 926
Observed reflections	6999	8850
Parameter/restrains	701/2	904/0
R_1/wR_2 (all data)	0.1091/0.1607	0.0530/0.1277
R_1/wR_2 (final)	0.0567/0.1432	0.0755/0.1389
Goodness of fit	1.016	1.035
Minimum/maximum ρ_e (e Å^{-3})	–0.591/0.547	–1.014/1.107
Temperature (K)	200(2)	200(2)
Diffractometer used	Nonius Kappa CCD	Nonius Kappa CCD
Scan type	area detection	area detection
Solution	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97

MoK α radiation ($\lambda = 0.71073$ Å). Data collection and cell refinement gave cell constants corresponding to triclinic cells for (A) and monoclinic cells for $[\{\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\text{O}\}_3]$ whose dimensions and other experimental parameters are given in Table 2. The structures were solved with

direct methods with SIR-97 and refined with SHELXL-97 by full-matrix least-squares on F^2 . All but the disordered non-hydrogen atoms were refined anisotropically, the hydrogen atoms were calculated in geometrically optimized positions.

Table 3

Fragmented molecular ions/ m/e values of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (A) and $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{CH}_3\text{--CH(O)--CH(O)--CH}_3\}$ (3)

Complex	Fragmented ions	m/e Value
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (A)	$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2]$	558
	$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)\{\text{OCH}_3\}]^+$	530
	$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{O}\}]^+$	456
	$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2]^+$	440
	$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}\}]^+$	349
	$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}\{\text{O}\}]^+$	260
	$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}]^+$	244
	$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{CH}_3\text{--CH(O)--CH(O)--CH}_3\}$ (3)	$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{CH}_3\text{--CH(O)--CH(O)--CH}_3\}]^+$
$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{CH}_3\text{--CH(O)--OH}\}]^+$		501
$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{CH(O)--OH}\}]^+$		486
$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}\}\{\text{CH(O)--OH}\}]^+$		395
$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}\{\text{C}_6\text{H}_4\text{CH}\}\{\text{CH(O)--OH}\}]^+$		379
$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}\{\text{C}_6\text{H}_4\text{CH}\}\{\text{H}_2\text{O}\}]^+$		351
$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}\{\text{C}_6\text{H}_4\}]^+$		320
$[\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}]^+$		244

Table 4

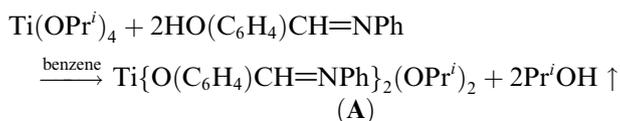
Some important IR absorption of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OPr}^i\}_2$ (**A**) and glycolatobis(*N*-phenylsalicylideneiminato) titanium(IV) complexes

	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{Ti}-\text{O})_{(\text{glycol})}$	$\nu(\text{Ti}-\text{N})$
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OPr}^i\}_2$ (A)	1545	985	609	478
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}_2-\text{O}\}$ (1)	1558	1030	610	475
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}(\text{O})-\text{CH}_3\}$ (2)	1557	1025	610	478
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{CH}_3-\text{CH}(\text{O})-\text{CH}(\text{O})-\text{CH}_3\}$ (3)	1553	1015	625	472
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{CH}_3\}$ (4)	1560	1000	615	480
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OC}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2\text{O}\}$ (5)	1558	1000	627	488
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}_2-\text{CH}_2\text{O}\}$ (6)	1555	1032	615	470
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_3\}$ (7)	1550	1022	625	472
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{(\text{CH}_3)_2\text{C}(\text{O})-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_3\}$ (8)	1555	1032	622	478
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-(\text{CH}_2)_3-\text{CH}_2\text{O}\}$ (9)	1557	1030	620	480
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-(\text{CH}_2)_4-\text{CH}_2\text{O}\}$ (10)	1554	1080	615	480

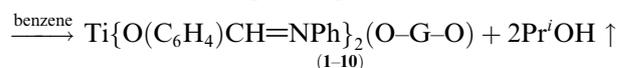
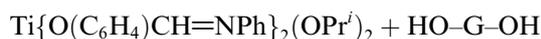
^a All these absorptions are of strong intensity.

3. Results and discussion

Reactions of *N*-phenylsalicylideneimine with $\text{Ti}(\text{OPr}^i)_4$ in 1:2 molar ratio in anhydrous benzene yield $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OPr}^i\}_2$ (**A**):



Further reaction of **A** with glycols in 1:1 molar ratio afforded heteroleptic complexes of the type $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{O}-\text{G}-\text{O}\}$ (**1–10**)



[where $-\text{G}- = (\text{CH}_2)_2$ (**1**), $(\text{CH}_2\text{CHCH}_3)$ (**2**), $(\text{CH}_3\text{CHCH}-\text{CH}_3)$ (**3**), $(\text{CH}_2\text{CHC}_2\text{H}_5)$ (**4**), $\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2$ (**5**), $(\text{CH}_2)_3$ (**6**), $(\text{CH}_2\text{CH}_2\text{CHCH}_3)$ (**7**), $(\text{CH}_3)_2\text{CCH}_2\text{CHCH}_3-$ (**8**), $(\text{CH}_2)_5$ (**9**), $(\text{CH}_2)_6$ (**10**).]

The progress of the above reactions was monitored by estimating liberated isopropanol in the benzene-isopropanol azeotrope by oxidimetric method. All these reactions were found to be quite facile and quantitative yielding yellow coloured sharp melting solids. These complexes are soluble in common organic solvents. The FAB

Table 5

¹H and ¹³C{¹H} NMR spectral data for $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OPr}^i\}_2$ (**A**) and glycolatobis(*N*-phenylsalicylideneiminato) titanium(IV) complexes

Complex	¹ H NMR data (δ ppm)	¹³ C{ ¹ H} NMR data (δ ppm)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OPr}^i\}_2$ (A)	1.22 (d, 12H, $J = 6.08$ Hz, CH ₃); 4.94 (m, 2H, CH); 7.00 (m, 10H, N-Ph); 6.54–7.46 (m, 8H, C ₆ H ₄); 7.93 (s, 2H, CH=N)	39.7 (CH ₃); 76.6 (CH); 116.4–148.0 (all aromatic carbons); 160.7 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}_2-\text{O}\}$ (1)	4.43 (b, 4H, OCH ₂); 7.01 (m, 10H, N-Ph); 7.21–7.47 (m, 8H, C ₆ H ₄); 7.89 (s, 2H, CH=N)	76.4 (OCH ₂); 117.0–148.5 (all aromatic carbons); 160.9 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}(\text{O})-\text{CH}_3\}$ (2)	1.21 (d, 3H, 6.04 Hz, CH ₃); 4.50 (br, 2H, OCH ₂); 4.83 (br, 1H, OCH); 6.97 (m, 10H, N-Ph); 7.19–7.48 (m, 8H, C ₆ H ₄); 8.30 (s, 2H, CH=N)	25.0 (CH ₃); 56.0 (OCH ₂); 79.5 (OCH); 117.2–148.4 (all aromatic carbons); 161.1 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{CH}_3-\text{CH}(\text{O})-\text{CH}(\text{O})-\text{CH}_3\}$ (3)	1.27 (m, 6H, CH ₃); 5.50 (br, 2H, OCH); 7.09 (m, 10H, N-Ph); 7.21–7.36 (m, 8H, C ₆ H ₄); CH=N (not observed)	24.8 (CH ₃); 76.4 (OCH); 117.0–148.2 (all aromatic carbons); 162.5 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{CH}_3\}$ (4)	1.10 (m, 3H, CH ₃); 1.40 (m, 2H, CH ₂); 4.57 (br, 2H, OCH ₂); 4.87 (m, 1H, OCH); 7.06 (m, 10H, N-Ph); 7.23–7.45 (m, 8H, C ₆ H ₄); 7.91 (s, 2H, CH=N)	25.2 (CH ₃); 27.7 (CH ₂); 63.9 (OCH ₂); 80.0 (OCH); 117.2–148.4 (all aromatic carbons); 161.0 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OC}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2\text{O}\}$ (5)	1.28 (s, 12H, CH ₃); 7.04 (m, 10H, N-Ph); 7.13–7.44 (m, 8H, C ₆ H ₄); 8.10 (s, 2H, CH=N)	24.7 (CH ₃); 101.4 (CO); 117.2–148.4 (all aromatic carbons); 161.0 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}_2-\text{CH}_2\text{O}\}$ (6)	2.19 (m, 2H, CH ₂); 4.72, 4.83 (br, 4H, each OCH ₂); 6.95 (m, 10H, N-Ph); 7.24–7.40 (m, 8H, C ₆ H ₄); 8.02 (s, 2H, CH=N)	32.1 (CH ₂); 73.9 (OCH ₂); 117.1–148.3 (all aromatic carbons); 161.0 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_3\}$ (7)	1.21 (d, 3H, 5.86 Hz, CH ₃); 2.49 (m, 2H, CH ₂); 4.70 (m, 2H, OCH ₂); 5.00 (m, 1H, OCH); 6.92 (m, 10H, N-Ph); 7.15–7.45 (m, 8H, C ₆ H ₄); 7.96 (s, 2H, CH=N)	23.3 (CH ₃); 32.0 (CH ₂); 53.0 (OCH ₂); 79.6 (OCH); 117.2–149.0 (all aromatic carbons); 162.6 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{(\text{CH}_3)_2\text{C}(\text{O})-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_3\}$ (8)	1.38 (br, 9H, all CH ₃); 2.01 (br, 2H, CH ₂); 5.12 (br, 1H, OCH); 6.95 (m, 10H, N-Ph); 7.25–7.45 (m, 8H, C ₆ H ₄); 8.00 (s, 2H, CH=N)	23.6, 26.3, 27.4 (each CH ₃); 31.5 (CH ₂); 51.5 (OCH); 83.7 (CO); 117.2–150.1 (all aromatic carbons); 162.6 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-(\text{CH}_2)_3-\text{CH}_2\text{O}\}$ (9)	1.36 {br, 2H, CH ₂ (3)}; 1.49 {br, 4H, CH ₂ (2,4)}; 3.55 {br, 4H, OCH ₂ (1,5)}; 6.84 (m, 10H, N-Ph); 7.16–7.34 (m, 8H, C ₆ H ₄); 7.51 (s, 2H, CH=N)	21.9 {CH ₂ (3)}; 33.3 {CH ₂ (2,4)}; 62.6 {OCH ₂ (1,5)}; 117.2–148.4 (all aromatic carbons); 161.0 (CH=N)
$\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2\{\text{OCH}_2-(\text{CH}_2)_4-\text{CH}_2\text{O}\}$ (10)	1.72 {br, 4H, CH ₂ (3)}; 2.00 {br, 4H, CH ₂ (2)}; 5.84 {br, 4H, CH ₂ (1)}; 7.06 (m, 10H, N-Ph); 7.26–7.44 (m, 8H, C ₆ H ₄); 7.97 (s, 2H, CH=N)	25.0 {CH ₂ (3)}; 31.0 {CH ₂ (2)}; 73.1 (OCH ₂); 117.1–148.3 (all aromatic carbons); 161.0 (CH=N)

mass spectral studies of two of the representative compounds $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (**A**) and $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{CH}_3\text{CH}(\text{O})\text{CH}(\text{O})\text{CH}_3)$ (**3**) (Table 3) indicate their monomeric nature. Appearance of some molecular ion peaks at higher m/e than the molecular ion in the FAB mass spectra may be due to reassociation of the fragments.

IR spectra of all these derivatives have been recorded in KBr and some relevant data are summarized in Table 4. Absence of hydroxyl group absorption of *N*-phenylsalicylideneimine as well as of glycols in the IR spectra of all these derivatives indicates deprotonation and concomitant bond formation of the ligand moieties with the titanium atom. Strong intensity absorption at around 575 cm^{-1} in all the derivatives may be assigned to $\nu(\text{Ti}-\text{O})(\text{salen})$. Absorption in the region $610\text{--}627\text{ cm}^{-1}$ in the spectrum of all the glycolato derivatives (**1–10**) is due to $\nu(\text{Ti}-\text{O})(\text{glycol})$ mode [14]. A downfield shift of $\nu(\text{C}=\text{N})$ was observed in all the complexes as compared to the free ligand indicating the chelating mode of attachment of the ligand moiety. This fact was further supported by the appearance of a new absorption band in the region $470\text{--}488\text{ cm}^{-1}$, due to $\nu(\text{Ti}-\text{N})$ mode in all these complexes [15].

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of all these derivatives have been recorded in CDCl_3 and the data are given in Table 5. Consistent with the IR spectral observations, the hydroxyl proton resonances of the free *N*-phenylsalicylideneimine (at δ 13.31 ppm) and of the glycols (around δ 2.0–3.5 ppm) were absent in the ^1H NMR spectra of all these derivatives. A significant downfield shift in the $\text{CH}=\text{N}$ proton resonance (0.31–1.10 ppm) of *N*-phenylsalicylideneimine moiety on complexation suggests bidentate mode of attachment of this ligand *via* O and N in all these complexes which gets further support from X-ray diffraction study of **A**. Appearance of only one doublet for isopropyl-Me groups in the ^1H NMR of **A**, indicates its fluxional behaviour in solution. These methyl groups appear to be diastereotopic from the crystal structure analysis.

However, no significant shift in the $\text{CH}=\text{N}$ carbon resonance in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of all these derivatives was observed.

Other proton and carbon resonances for *N*-phenylsalicylideneimine [9] and glycolate [14] moieties appeared at the expected positions and with desirable multiplicities in all these derivatives.

Selected bond lengths and angles for $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (**A**) and its hydrolysis product $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\text{O}\}_3]$ are summarized in Tables 6 and 7 and their ORTEP plots are displayed in Figs. 1 and 2, respectively.

The molecular structure of **A** reveals two formula units in the asymmetric cell. They show a distorted octahedrally configured Ti centre with *cis*-orientation of both isopropoxy and both *N*-phenylsalicylideneimine ligands. Each nitrogen atom of the five-membered *N,O*-chelate lies in *trans*-position to the oxygen atom of the OPr^i ligand, the

Table 6

Selected bond lengths (Å) and angles (°) of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_3(\text{OPr}^i)_2$ (**A**)

Ti1–O1	1.920(2)	C1–C2	1.403(4)	O1–Ti1–O2	162.55(10)
Ti1–O2	1.903(2)	C2–C3	1.364(4)	O1–Ti1–O3	95.62(9)
Ti1–O3	1.805(2)	C3–C4	1.389(5)	O1–Ti1–O4	96.57(9)
Ti1–O4	1.790(2)	C4–C5	1.362(4)	O1–Ti1–N1	81.11(9)
Ti1–N1	2.286(3)	C5–C6	1.408(4)	O1–Ti1–N2	86.41(8)
Ti1–N2	2.320(3)	C6–C7	1.431(4)	O2–Ti1–O3	95.47(10)
O1–C1	1.321(3)	C8–C9	1.384(4)	O2–Ti1–O4	94.19(10)
O2–C14	1.311(4)	C8–C13	1.374(5)	O2–Ti1–N1	85.07(9)
O3–C27	1.403(6)	C9–C10	1.393(6)	O2–Ti1–N2	80.86(9)
O4–C30	1.383(5)	C10–C11	1.365(6)	O3–Ti1–O4	102.23(11)
N1–C7	1.296(4)	C11–C12	1.376(6)	O3–Ti1–N1	166.93(9)
N1–C8	1.441(4)	C12–C13	1.375(6)	O3–Ti1–N2	86.57(10)
N2–C21	1.442(4)			O4–Ti1–N1	90.74(10)
N2–C20	1.283(4)			O4–Ti1–N2	170.34(10)
C1–C6	1.408(5)			N1–Ti1–N2	80.61(9)

corresponding oxygen atoms of both chelates are also *trans*-positioned. The bond lengths of Ti–O within the chelate ring (Ti1–O1 1.920(2), Ti1–O2 1.903(2) Å) are about 0.10 Å longer than those towards the OPr^i -ligands (Ti1–O3/O4 \approx 1.80 Å). The distances Ti–N differ only slightly around 2.30 Å, whereby the shorter one (Ti1–N1 2.286(3) Å) corresponds with the longer O–C bonds (O3–C27 1.403(6) Å) and vice versa Ti1–N2 2.320(3), O4–C30 1.383(5) Å. The distortion from regular octahedron arises from the smaller angles than 180° (O1–Ti1–O2 162.55(10), O3–Ti1–N1 166.93(9), O4–Ti1–N2 170.34(10)°), O3–Ti1–N1 166.93(9), as well as from the different angles (O3–Ti1–O4 102.23(11), N1–Ti1–N2 80.61(9)°). The six-membered titanacyclic system is exactly planar, the *N*-

Table 7

Selected bond lengths (Å) and angles (°) of $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\text{O}\}_3]$

Ti1–O8	1.812(3)	O8–Ti1–O9	96.53(12)	O5–Ti2–O8	97.55(12)
Ti1–O9	1.823(3)	O8–Ti2–O10	96.67(12)	O5–Ti2–O10	98.61(12)
Ti2–O8	1.852(3)	O9–Ti3–O10	97.32(12)	N5–Ti2–O8	86.76(12)
Ti2–O10	1.826(3)	Ti1–O8–Ti2	138.86(16)	N5–Ti2–O10	176.59(12)
Ti3–O9	1.808(3)	Ti1–O9–Ti3	142.25(16)	N5–Ti2–N1	83.77(12)
Ti3–O10	1.835(3)	Ti2–O10–Ti3	136.87(15)	N1–Ti2–O10	92.85(12)
Ti1–O2	1.916(3)	O1–Ti2–O5	156.79(12)	N1–Ti2–O8	170.46(12)
Ti1–O3	1.902(3)	O1–Ti2–N1	80.28(12)	Ti2–N1–C7	124.6(3)
Ti1–N2	2.326(3)	O1–Ti2–N5	82.64(12)	Ti2–N1–C1	119.8(2)
Ti1–N3	2.351(3)	O1–Ti2–O8	97.46(12)	N1–C7–C8	126.7(4)
Ti2–O1	1.907(3)	O1–Ti2–O10	97.14(12)	C7–N1–C1	115.3(4)
Ti2–O5	1.886(3)	O5–Ti2–N1	82.02(12)	C7–C8–C9	122.8(4)
Ti2–N1	2.317(3)	O5–Ti2–N5	80.61(12)	C8–C9–O1	120.9(4)
Ti2–N5	2.318(4)			C9–O1–Ti2	140.2(3)
Ti3–O4	1.913(3)				
Ti3–O6	1.896(3)				
Ti3–N4	2.322(3)				
Ti3–N6	2.295(4)				
N1–C1	1.447(5)				
N1–C7	1.290(5)				
C7–C8	1.439(6)				
C8–C9	1.408(6)				
O1–C9	1.331(5)				

bonded phenyl substituent is turned off the chelate plane of about 62° .

The trinuclear titanoxane obtained by partial hydrolysis of **A** crystallizes together with two molecules of CH_2Cl_2 . Its molecular structure reveals a non-planar six-membered ring system of alternating three titanium and three oxygen atoms. It is interesting to note here that in a similar titanoxane, $\text{Ti}(\text{acac})_2\text{O}$ (with O,O'-chelating ligand) a dimer with planar Ti_2O_2 ring was obtained [8h]. Each Ti centre exhibits a distorted octahedral configuration with two O

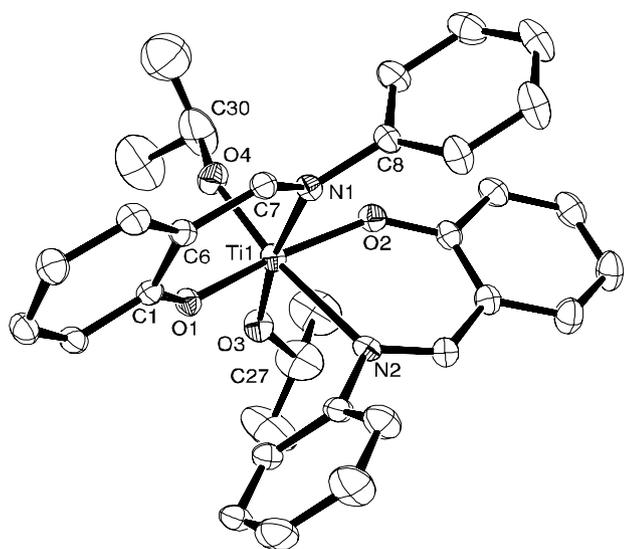


Fig. 1. Ortep plot of $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}')_2$ (**A**) (25% probability, H atoms are omitted).

atoms of the ring and the N and O atoms of two chelating *N*-phenylsalicylideneimino ligands in *cis*-position. The bonds Ti–O within the titanoxane ring lie between 1.80 and 1.85 Å (Ti3–O10 1.808(3), Ti2–O8 1.852(3) Å) and are a little bit shorter than those towards the chelate system with 1.88–1.91 Å (Ti2–O5 1.886(3), Ti1–O2 1.916(3) Å). Within the bent ring system the three Ti-centred angles are about 97° (O8–Ti–O9 $96.53(12)^\circ$, O9–Ti3–O10 $97.32(12)^\circ$), whereas the angles Ti–O–Ti differ more, namely between $136.87(15)^\circ$ for Ti2–O10–Ti3 and $142.25(16)^\circ$ for Ti1–O9–Ti3. In the following lines, only the bond lengths and angles around Ti2 centre are discussed according to the labels as shown in Fig. 2. The values for Ti2 are representative also for Ti1 and Ti3. The very long Ti–N distances vary similarly as Ti–O do with values between 2.29 and 2.35 Å (Ti3–N6 2.295(4), Ti1–N3 2.351(3) Å). The distortion of ideal octahedral geometry mainly derives from the three *trans*-angles O1–Ti2–O5 $156.79(12)^\circ$, N1–Ti2–O8 $170.46(12)^\circ$ and N5–Ti2–O10 $176.59(12)^\circ$ as well as from all *cis*oid angles. Whereas the four O–Ti–O angles are enlarged to 97 – 98° , all O–Ti–N angles within the titanacycle are reduced to 80 – 82° . Those, however, between imine N atoms and titanoxane O atoms lie about 90° (N5–Ti2–O8 $86.76(12)^\circ$, N1–Ti2–O10 $92.85(12)^\circ$). The bond lengths and angles of the chelate ring are very similar to those found for **A**. The imine distance N1–C7 1.290(5) pm is shorter than the phenolic one O1–C9 1.331(5) as well as the aromatic bond C8–C9 1.408(6) Å is shorter than C7–C8 1.439(6) Å. Within the six-membered titanacycle, the largest angle is $140.2(3)^\circ$ for C9–O1–Ti2, whereas the smallest is $89.28(12)^\circ$ for O1–Ti2–N1.

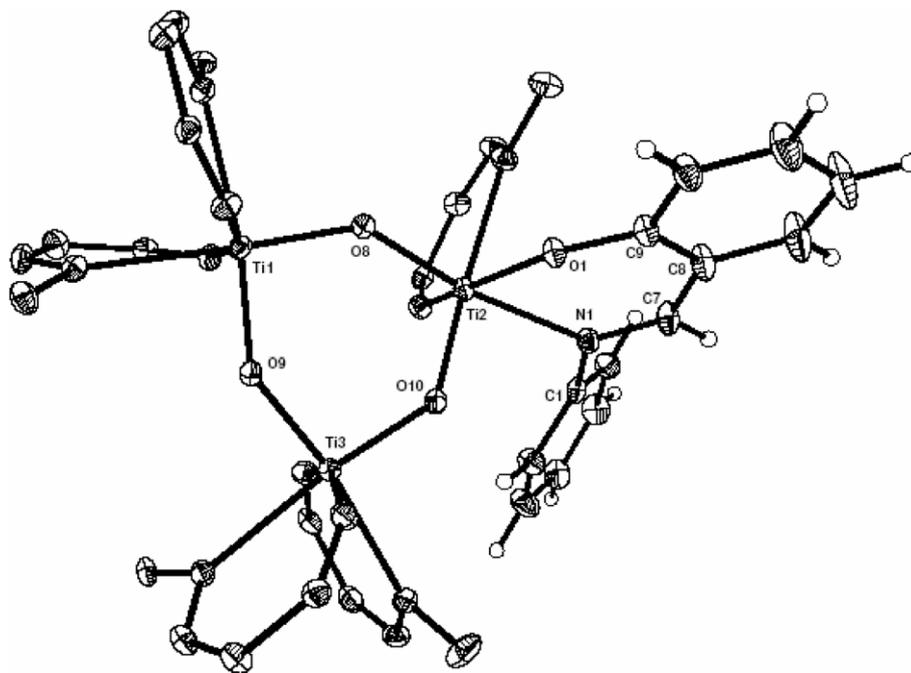


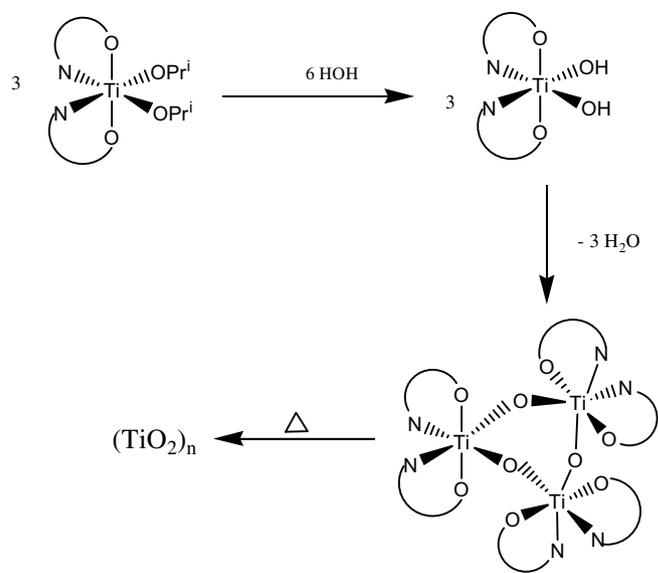
Fig. 2. Ortep plot of $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\}\text{O}]_3$ (25% probability) with only one complete chelate ligand on Ti2, the phenyl groups of the other five are omitted.

The interplanar angle between the chelating plane O1–Ti2–N1 and that of the planar chelate ligand is about 11° . The *N*-phenyl substituent is turned off the major plane of the chelate by about 46° .

Modification of $\text{Ti}(\text{OPr}^i)_4$ with *N*-phenylsalicylideneimine provides some stability to the product, **A**, towards hydrolysis. An intermediate hydrolysis product, $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\text{O}\}_3]$, was obtained when controlled hydrolysis of **A** was carried out. It is interesting to mention here that the formation of the same product is reproducible. This suggests that it is a kinetically stable species during hydrolysis pathway of **A** (Scheme 1). Complete hydrolysis of **A** and sintering at 300°C yields pure TiO_2 (as confirmed from its XRD—Fig. 3a). Similarly, complete hydrolysis of further glycol modified **1** and **7** afforded pure TiO_2 at a sintering temperature of 500°C (Fig. 3b and c).

It is worthwhile to mention here that a comparison of the XRD patterns of the three samples of pure TiO_2 obtained during the course of the present investigation reveals formation of pure anatase phase at low temperatures (at 300°C for **A**, at 500°C for **1** and **7** as compared to $>600^\circ\text{C}$ reported in the literature) [6a].

Calculations of the average particle size of TiO_2 grains obtained from **A**, **1** and **7** using *Debye Scherrer equation* [16] for the longest peak in the XRD-spectra reveals average particle size 12.3 nm for **A**, 9.7 nm for **1** and 8.9 nm



for **7**. Both Secondary electron and backscattered electron images of TiO_2 obtained from **A** were recorded at magnifications of $1000\times$, $4000\times$ and $10000\times$ to compare the grain sizes (Fig. 4a–d).

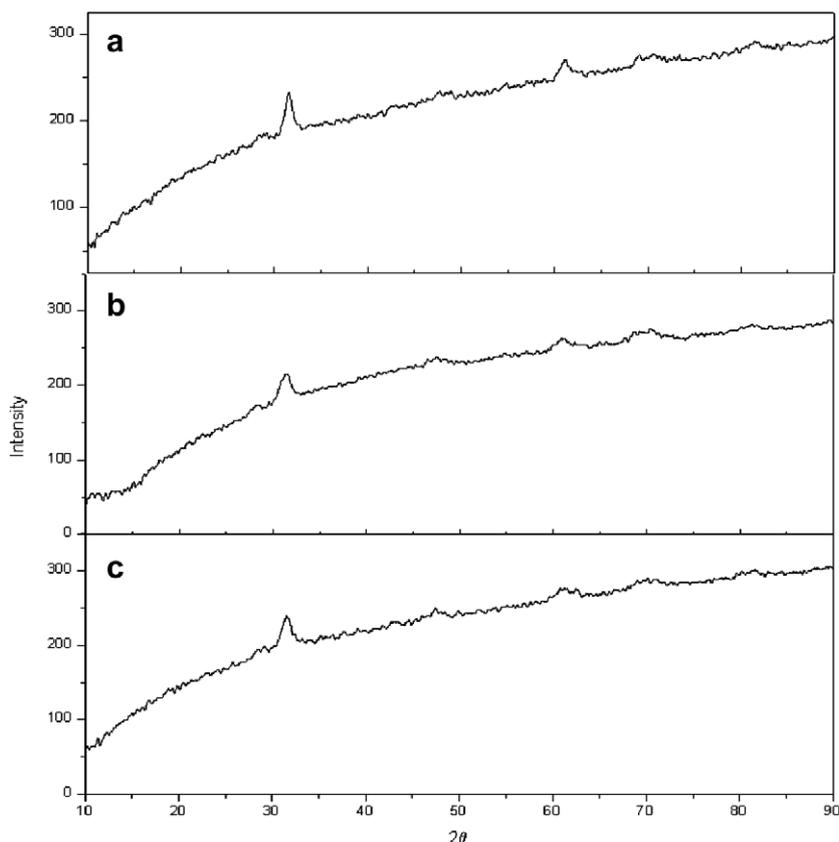


Fig. 3. XRD patterns for pure TiO_2 obtained from (a) **A**, (b) **1** and (c) **7**.

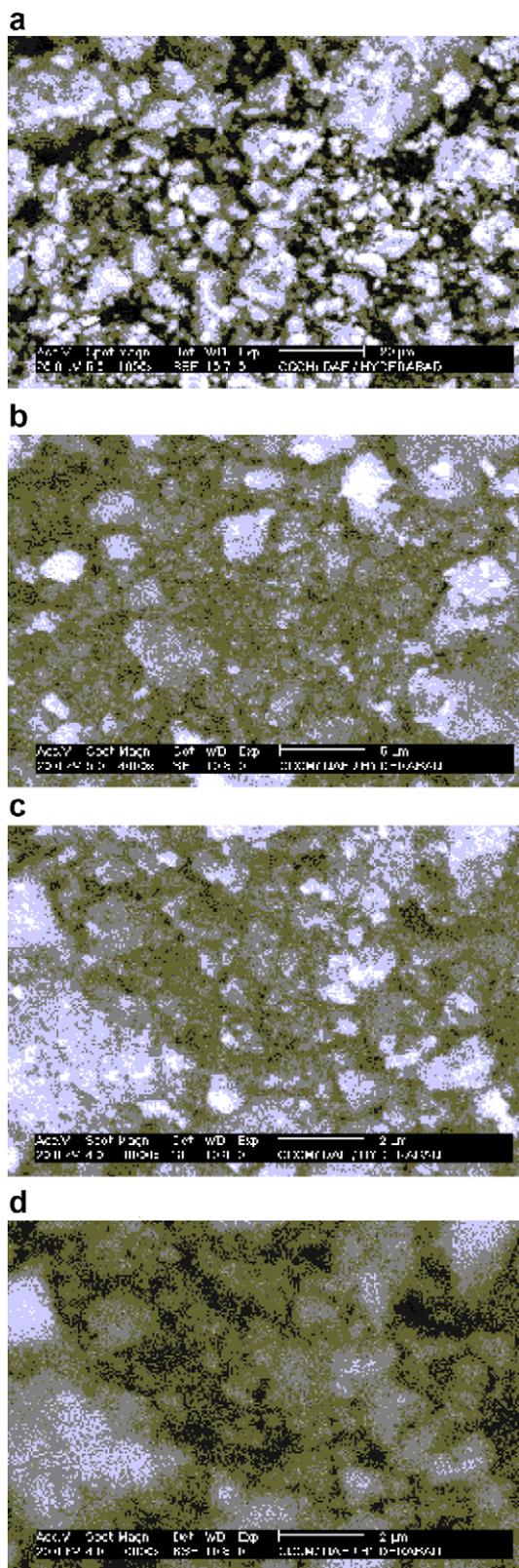


Fig. 4. SEM images of pure TiO_2 obtained from **A** sintered at $300\text{ }^\circ\text{C}$: (a) $1000\times$ SE image, (b) $4000\times$ SE image, (c) $10000\times$ SE image and (d) $10000\times$ BSE image.

Further, scanning electron micrograph of the products obtained from **A** ($300\text{ }^\circ\text{C}$), **1** ($500\text{ }^\circ\text{C}$) and **7** ($500\text{ }^\circ\text{C}$) (Fig. 5a–c) showed agglomerated particles made up of nano-

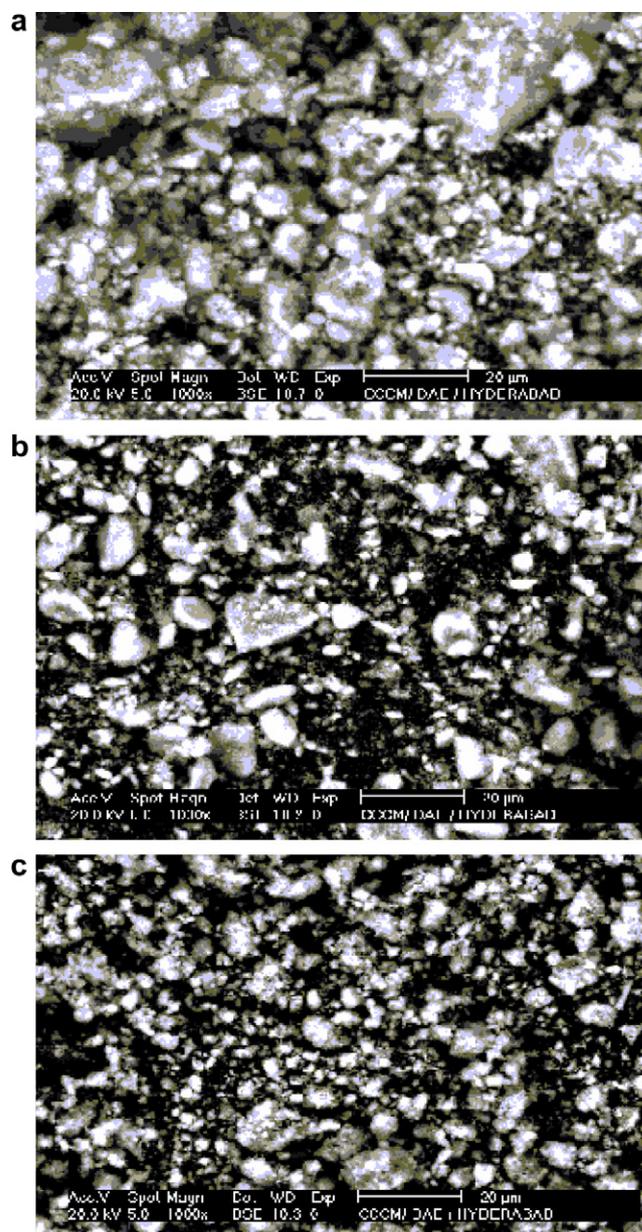


Fig. 5. SEM images of pure TiO_2 obtained from (a) **A**, (b) **1** and (c) **7**.

sized grains. Only slight variation of the grains at two different temperatures was observed. The minimum particle sizes of TiO_2 grains appeared to be obtained from **7**.

Thermal gravimetric analysis (TGA) was undertaken on two of the derivatives, **A** and **7** (Fig. 6a and b). Appearance of multiple weight loss steps in the TGA curves of both **A** and **7** indicate multiple thermal events due to organic pyrolysis. It is of interest to note that compound **7** is thermally less stable as compared to **A**.

4. Conclusion

The single crystal X-ray diffraction studies of two of the derivatives $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (**A**) and $[\{\text{Ti}(\text{O}(\text{C}_4\text{H}_4)\text{CH}=\text{NPh})_2\text{O}\}_3]$ revealed *cis*-orientation of the N, O

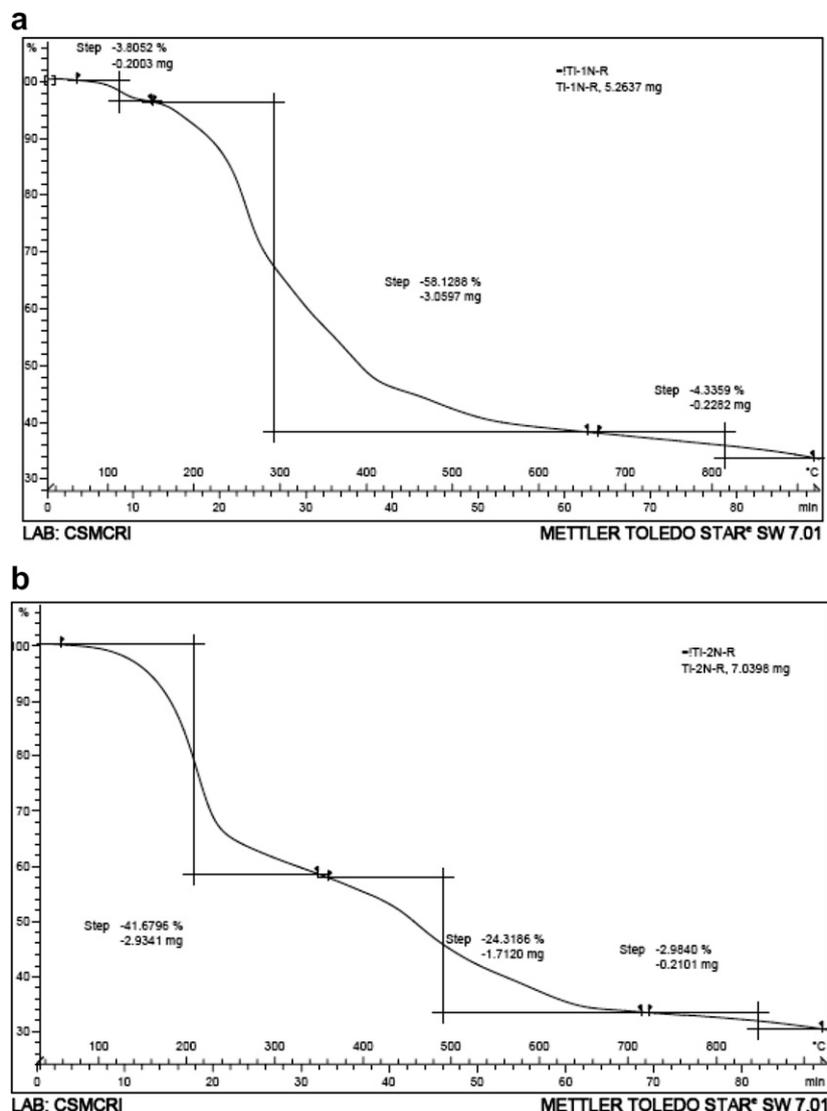


Fig. 6. TGA curves (weight % vs. temperature °C) of (a) A and (b) 7.

atoms of salicylideneimine moiety. Complete hydrolysis of some of the derivatives in isopropanol, afforded pure nanocrystalline anatase TiO_2 as reflected by XRD and SEM studies. It may be inferred from the above results that the modified glycolatobis(*N*-phenylsalicylideneiminato) titanium(IV) complexes are potential precursors for material synthesis by sol–gel technology.

5. Supplementary material

CCDC 623848 and 628329 contain the supplementary crystallographic data for $\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh}\}_2(\text{OPr}^i)_2$ (A) and $[\{\text{Ti}(\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NPh})_2\text{O}\}_3]$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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