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# Reactivity of *cis*-bis(acetylacetonato)dichlorotitanium(IV) towards hydroxy-containing ligands: isolation and characterisation of products †

**P. Venkateshwara Rao,[a] Chebrolu Pulla Rao,*[a] Elina K. Wegelius,[b] Erkki Kolehmainen[b] and Kari Rissanen[b]**

[a] *Bioinorganic laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai - 400 076, India. E-mail: cprao@ether.chem.iitb.ernet.in*
[b] *Department of Chemistry, University of Jyvaskyla, Jyvaskyla, Fin 40351, Finland*

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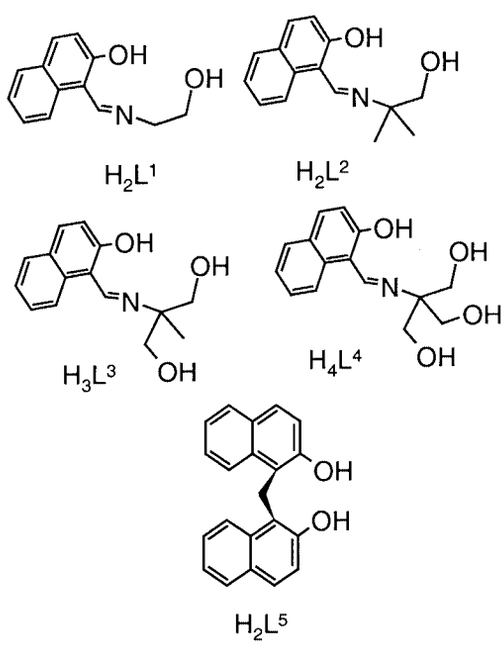
The reactivity of *cis*-[Ti(acac)$_2$Cl$_2$] with a number of OH containing ligands has been explored. Corresponding products have been synthesized, isolated and characterised. Three dimensional structures of some of the products were established by single crystal X-ray diffraction. The reactivity of these ligands towards non-oxo titanium centres has been found to be different from that of oxometal centres of $V^V$, $Mo^{VI}$ and $U^{VI}$. All the products of $Ti^{IV}$ isolated were mononuclear complexes possessing one or two ligands. Both the molecular and crystal structures of the titanium products are found to be different from those of the oxometal ones.

## Introduction

The chemistry of hydroxy (OH) rich ligands with oxometal centres, such as $VO^{2+}$, $VO^{3+}$, *cis*-$VO_2^+$, *cis*-$MoO_2^{2+}$ and *trans*-$UO_2^{2+}$, is well understood.[1–5] However their co-ordination behaviour towards non-oxo metal species has not received much attention in spite of some interesting aspects of the complexation chemistry of these ligands particularly in differentiating *cis* from *trans* dioxometal centres. It is rather interesting to understand the co-ordination role of hydroxy rich ligands with non-oxo metal centres possessing oxophilicity. The synthesis, configuration and reactivity aspects of some titanium(IV) bis(acetylacetonate)[6] and bis(β-diketonate)[7] complexes have been reported. Some phenoxo-bound Schiff base complexes[8] have been used in synthesis as precursors or as catalysts. In all these reactions the nuclearity of titanium is preserved in its products. However, when reactions were carried out using $TiCl_4$ the nuclearity of the products was found to be increased by bridging the titanium centres through an oxo group.[9] Therefore, we have chosen *cis*-bis(acetylacetonato)dichlorotitanium(IV), *cis*-[Ti(acac)$_2$Cl$_2$], as a non-oxo metal precursor possessing oxophilic character for studying its reactivity towards ligands containing varying numbers of OH groups $H_2L^1$–$H_2L^5$. The corresponding products were isolated and characterised primarily by NMR studies and in a few cases also by single crystal X-ray diffraction methods.




## Experimental

All operations were carried out under a nitrogen/argon atmosphere using standard Schlenk apparatus unless otherwise mentioned. All the solvents were dried and distilled under nitrogen from either sodium diphenylketyl or calcium hydride immediately before use. The ligands, $H_2L^1$ to $H_4L^4$ were prepared and confirmed as reported by us earlier.[10] The complex *cis*-[Ti(acac)$_2$Cl$_2$] **1** was prepared by treating $TiCl_4$ with two equivalents of acetylacetone and isolated and purified by recrystallisation before use.[11] Synthetic details of $H_2L^5$ and also of the products obtained (**2a**, **2b**, **3a**, **3b**, **3c** and **4a**) from the reactions of **1** with different ligands are given in this paper.

### Preparations

**1,1′-Methylenebis(2-naphthol) (MBN), $H_2L^5$.** To a solution of 3.44 g (20 mmol) 2-hydroxy-1-naphthaldehyde in 25 ml MeOH was added 2-amino-2-methylpropan-1-ol (1.9 ml, 20 mmol) and the reaction mixture stirred under reflux for 3 h. It was then cooled to room temperature and subsequently to 0 °C and equilibrated. At 0 °C, solid $NaBH_4$ (0.760 g, 20 mmol) was added pinch by pinch over a period of about 0.5 h. After

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4469/

Also available: stereoviews. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/4469/, otherwise available from BLDSC (No. SUP 57674, 2 pp.) or the RSC library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

This paper is dedicated to Professor Stephen J. Lippard on his 60th birthday.

completing the addition, the temperature was slowly raised to ambient and stirring continued for 3 h. Solvent was evaporated to dryness in order to obtain an off-white residue. To this a solution of sodium acetate (4.00 g) in 30 ml of water was added and the product extracted into dichloromethane. The dichloromethane fraction was dried over anhydrous $MgSO_4$, filtered and concentrated to give a white fluffy product, $H_2L^5$, in 70% yield. NMR ($CDCl_3$): $^1H$, $\delta$ 4.82 (s, 2 H, $CH_2$); 7.05, 7.66, 8.21 (d, 2 H each, aromatic); 7.33, 7.45 (t, 2 H, aromatic); $^{13}C$, $\delta$ 21.8 ($CH_2$), 117.1, 118.1, 119.6, 123.1, 123.3, 126.9, 128.9, 129.8, 133.5 and 151.6 (aromatic).

**[Ti($L^1$)(acac)Cl] 2a.** To 15 ml of $CH_3CN$, $H_2L^1$ (0.215 g, 1 mmol) and sodium acetate (0.082 g, 1 mmol) were added and the mixture was stirred at room temperature. A solution of complex **1** (0.316 g, 1 mmol) dissolved in 15 ml of $CH_3CN$ was added dropwise. The initial yellow solution turned into a reddish suspension, and was stirred at room temperature for 6 h. The solution was then filtered and the filtrate concentrated. Hexane was added upon which small red crystals of the product were formed. The product was separated through filtration, washed with hexane and dried under vacuum. Yield 55%. Calc. (%) C, 54.64; H, 4.59; N, 3.54. Obs. (%) C, 54.98; H, 4.27; N, 3.77. FTIR (KBr, $cm^{-1}$) 1608 ($\nu$C=N). $^1H$ NMR ($CDCl_3$): $\delta$ 9.42 (s, 1 H, CH=N); 8.16 (d, 1 H), 7.86 (d, 1 H), 7.74 (d, 1 H), 7.56 (t, 1 H), 7.37 (t, 1 H) and 6.91 (d, 1 H, naphthalene H); 4.94 (m, 1 H, $CH_2CH_2O$); 4.62 (m, 3 H, $CH_2CH_2O$); 2.04 (s, 6 H, $2CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 67.6, 74.2, 105.3, 112.9, 119.7, 124.0, 128.2, 128.6, 129.1, 133.1, 136.6, 165.39, 191.3, 157.9 (C=NH).

**[Ti($L^2$)(acac)Cl] 2b.** A mixture of $H_2L^2$ (0.121 g, 0.5 mmol) and sodium acetate (0.041 g, 0.5 mmol) in 15 ml of acetonitrile was stirred at room temperature. Complex **1** (0.158 g, 0.5 mmol) in 15 ml of acetonitrile was added dropwise, the initial yellow suspension turning to reddish orange, which was then refluxed for 3 h. The reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was evaporated to dryness and recrystallised from $CH_3CN$ by adding hexane. Red single crystals were obtained in 75% yield. Calc. (%) C, 59.69; H, 5.23; N, 3.30. Obs. (%) C, 59.48; H, 5.44; N, 3.24. FTIR (KBr, $cm^{-1}$) 1608 ($\nu$C=N). $^1H$ NMR ($CDCl_3$): $\delta$ 9.41 (s, 1 H, HC=N); 8.20 (d, 1 H), 7.88 (d, 1 H), 7.78 (dd, 1 H), 7.60 (dt, 1 H), 7.39 (dt, 1 H) and 6.93 (d, 1 H, napthalene H); 5.97 (s, 1 H, CH, acac); 4.89, 4.32 (d, 1 H each, bound $CH_2O$); 2.28, 2.00 (s, 3 H each, $CH_3$); 1.71, 1.60 (s, 3 H each, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 25.0, 28.5 ($CH_3$, $L^2$); 25.6, 26.4 ($CH_3$, acac); 74.4 (*tert*-carbon); 85.8 ($CH_2O^-$, $L^2$); 105.3 (CH=, acac); 113.2, 119.4, 119.6, 123.9, 128.2, 128.7, 129.3, 133.4, 136.6, 164.4 (aromatic); 155.2 (CH=N, $L^2$); 189.8, 192.2 (CO, acac).

**[Ti($L^1$)$_2$] 3a.** To 15 ml of $CH_3CN$, $H_2L^1$ (0.215 g, 1 mmol) and sodium acetate (0.082, 1 mmol) were added and the mixture was stirred at room temperature. Complex **1** (0.158 g, 0.5 mmol) in 15 ml of $CH_3CN$ was added dropwise. The initial yellow solution turned to a yellow suspension and was stirred for 6 h at room temperature. It was then filtered and the yellow solid obtained extracted into $CHCl_3$, filtered and concentrated to dryness under vacuum. The product was washed with hexane and dried under vacuum. Yield 58%. Calc. (%) C, 65.83; H, 4.67; N, 5.90. Obs. (%) C, 65.74; H, 4.54; N, 5.30. FTIR (KBr, $cm^{-1}$) ($\nu$C=N). $^1H$ NMR ($CDCl_3$): $\delta$ 9.55 (s, 2 H, HC=N); 8.18 (d, 2 H), 7.79 (d, 2 H), 7.72 (d, 2 H), 7.56 (d, 2 H), 7.34 (t, 2 H) and 6.88 (d, 2 H, napthalene H); 4.63, 4.49 (m, 4 H, $CH_2CH_2O^-$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 67.5 ($CH_2CH_2O^-$); 71.0 ($CH_2O^-$); 111.7, 119.4, 121.5, 123.2, 127.8, 129.1, 133.5, 136.1, 166.0 (aromatic); 159.1 (CH=N).

**[Ti($L^2$)$_2$] 3b.** A solution of complex **1** (0.158 g, 0.5 mmol) in 15 ml of $CH_3CN$ was added dropwise to a solution of $H_2L^2$ (0.243 g, 1 mmol) and sodium acetate (0.082 g, 1 mmol) in 15 ml $CH_3CN$. The resulting orange suspension was refluxed for 4 h then cooled to room temperature and filtered through Celite. The filtrate was evaporated to dryness and the residue recrystallised from $CH_3CN$ by adding hexane. Yellow single crystals were obtained, washed with hexane and dried under vacuum. Yield 66%. Calc. (%) C, 67.93; H, 5.70; N, 5.28. Obs. (%) C, 67.61; H, 5.74; N, 5.48. FTIR (KBr, $cm^{-1}$) 1611 ($\nu$C=N). $^1H$ NMR ($CDCl_3$): $\delta$ 9.49 (s, 2 H, HC=N); 8.20 (d, 2 H), 7.81 (d, 2 H), 7.74 (d, 2 H), 7.56 (dt, 2 H), 7.34 (dt, 2 H) and 6.94 (d, 2 H, naphthalene H); 4.45, 4.15 (d, 2 H each, bound $CH_2O$); 1.67, 1.57 (s, 6 H each, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 24.14, 27.68 ($CH_3$); 72.60 (*tert*-carbon); 82.25 ($CH_2O^-$); 112.16, 119.4, 121.3, 123.1, 127.7, 127.9, 129.2, 133.9, 135.9, 165.1 (aromatic); 155.6 (CH=N).

**[Ti($L^1$)($L^2$)] 3d.** A mixture of $H_2L^1$ (0.054 g, 0.25 mmol) and sodium acetate (0.021 g, 0.25 mmol) was added to 20 ml of $CH_3CN$ and stirred at room temperature. Complex **2b** (0.106 g, 0.25 mmol) in 15 ml of $CH_3CN$ was added dropwise. The initial yellow suspension turned orange-yellow and was refluxed for 4.5 h, then cooled to room temperature and filtered through Celite. The filtrate was concentrated to give a yellow, microcrystalline solid. Yield 49%. Calc. (%) C, 66.94; H, 5.22; N, 5.57. Obs. (%) C, 66.50; H, 5.00; N, 5.26. FTIR (KBr, $cm^{-1}$) 1612 ($\nu$C=N). $^1H$ NMR ($CDCl_3$): $\delta$ 9.55 (s, 1 H, HC=N of $L^1$); 9.47 (s, 1 H, HC=N of $L^2$); 8.19 (t, 2 H), 7.80 (d, 2 H), 7.73 (d, 2 H), 7.56 (m, 2 H), 7.34 (t, 2 H) and 6.91 (dd, 2 H, naphthalene H); 4.60, (m, 1 H), 4.48 (m, 3 H, $CH_2CH_2O^-$, $L^1$); 4.46, 4.21 (d, 1 H each, bound $CH_2O^-$, $J$ = 9.27 Hz); 1.67, 1.57 (2s, 3 H each, $CH_3$, $L^2$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 27.5, 24.5 ($CH_3$, $L^2$); 72.7 (*tert*-carbon, $L^2$); 67.5 ($CH_2$, $L^1$); 70.9 ($CH_2O^-$, $L^1$); 82.5 ($CH_2O^-$, $L^2$); 111.8, 112.0, 119.4, 119.4, 121.3, 121.5, 123.1, 123.1, 127.8, 127.7, 127.9, 129.1, 129.2, 133.5, 133.9, 135.9, 136.0, 165.1, 166.0 (aromatic); 155.6 (CH=N, $L^2$); 159.0 (CH=N, $L^1$).

**[Ti($L^5$)(acac)$_2$] 4a.** To 15 ml of $CH_3CN$, $H_2L^5$ (0.30 g, 1 mmol) was added and stirred at room temperature. Complex **1** (0.316 g, 1 mmol) in 15 ml of $CH_3CN$ was added dropwise to give a deep red solution which was refluxed for 6 h. The reaction mixture was then cooled to room temperature and the solvent evaporated to dryness to remove volatile products. The residue was redissolved in $CH_3CN$. Small, red single crystals were obtained. Yield 62%. Calc. (%) C, 68.39; H, 5.18. Obs. (%) C, 67.93; H, 5.64. $^1H$ NMR ($CDCl_3$): $\delta$ 8.36 (br, 2 H), 7.72 (d, 3 H), 7.53 (d, 2 H), 7.38 (br, 2 H) and 6.94 (br, 3 H, naphthalene H); 5.97 (s, 2 H, acac H); 5.15, 4.74 (br, 1 H each, $CH_2$); 2.06 (m, 6 H, $2CH_3$).

### Spectral studies

Fourier transform infrared spectra were recorded on an Impact 400 Nicolet FTIR machine in KBr matrix, $^1H$ and $^{13}C$ NMR spectra using a JEOL JNM GSX-270 FT or Varian XL-300 spectrometer in $CDCl_3$ or $(CD_3)_2SO$ (complexes) or $CDCl_3$ (ligands).[10]

### X-Ray crystallography

Standard procedures were used for mounting the crystals. The diffraction data were collected on an Enraf Nonius CAD-4 diffractometer in the $\omega$–$2\theta$ scan mode using Mo-K$\alpha$ radiation (0.71073 Å). The structures were solved using SHELXS 86[12] and refined using SHELXL 93[13] program packages. The diagrams were generated using ORTEP III and PLUTON 98 programs.[14] The hydrogen atoms were fixed through the SHELXL program. Empirical absorption corrections were carried out for all the data. Full matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms was used. The hydrogen atoms were treated as riding atoms with fixed thermal parameters. Other details of data collection and structure refinement are provided in Table 1.

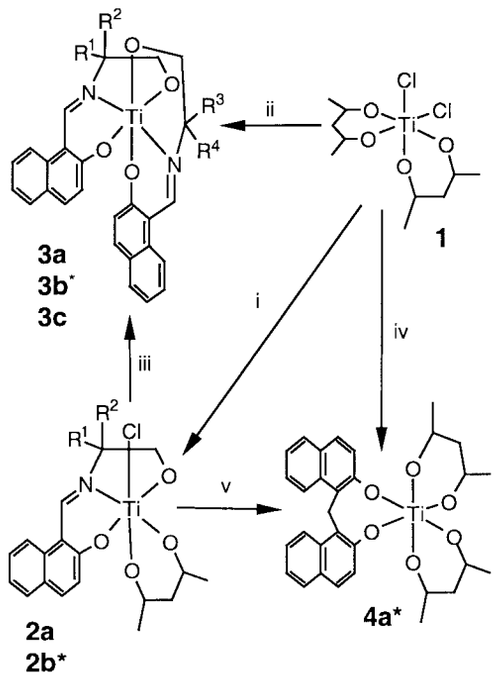
CCDC reference number 186/1706.

See http://www.rsc.org/suppdata/dt/1999/4469/ for crystallographic files in .cif format.

## Results and discussion

### Reactivity

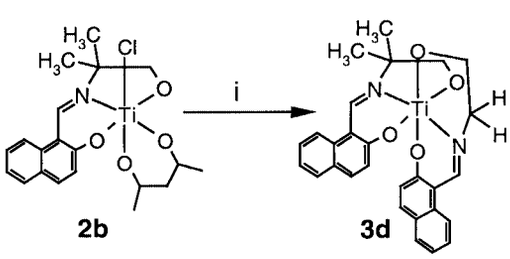
Scheme 1 represents the reaction scheme. When *cis*-[$TiCl_2$-




**Scheme 1** Reaction scheme: (i) for **2a** $H_2L^1$, $NaO_2CMe$, $CH_3CN$, rt, 6 h; for **2b** $H_2L^2$, $NaO_2CMe$, $CH_3CN$, reflux, 3 h; (ii) for **3a** $2H_2L^1$, $2NaO_2CMe$, $CH_3CN$, rt, 6 h; for **3b** $2H_2L^2$, $2NaO_2CMe$, $CH_3CN$, reflux, 4 h; (iii) for **3a** $H_2L^1$, $NaO_2CMe$, $CH_3CN$, rt, 6 h; for **3b** $H_2L^2$, $NaO_2CMe$, $CH_3CN$, reflux, 4 h; for **3c** $H_4L^4$, $NaO_2CMe$, $CH_3CN$, rt, 6 h; (iv) for **4a** $H_2L^5$, $NaO_2CMe$, $CH_3CN$, reflux, 6 h; (v) $H_2L^5$, $NaO_2CMe$, $CH_3CN$, reflux, 4 h; '*' indicates single crystal structure determination.

$(acac)_2$], **1** was treated with $H_2L^2$ in 1 : 1 mol ratio in $CH_3CN$ the reaction yielded a heteroleptic complex **2b**. However, when the same reaction was carried out in 1 : 2 mol ratio it resulted in the formation of a homoleptic complex, **3b**. Similar reactions of **1** with $H_2L^1$ yielded corresponding complexes, **2a** and **3a** respectively. Further, the conversion of **2a** into **3a** and **2b** into **3b** may be achieved by treating **2a** and **3a** with one equivalent of $H_2L^1$ and $H_2L^2$ respectively. However, reactions of **1** with $H_3L^3$ or $H_4L^4$ in both 1 : 1 and 1 : 2 ratios yielded products that are generally insoluble in common organic solvents. Such a difference in the reactivity of $H_3L^3$ and $H_4L^4$ over that of $H_2L^1$ and $H_2L^2$ with **1** is interpretable based on the presence of additional $CH_2OH$ groups in $H_3L^3$ and $H_4L^4$ (one in the case of $H_3L^3$ and two in the case of $H_4L^4$).

Reaction of complex **2b** with one equivalent of $H_2L^1$ in acetonitrile yielded **3d** as shown in Scheme 2. However, the




**Scheme 2** The conversion of complex **2b** into **3d**: (i) $H_2L^1$, $NaO_2CMe$, $CH_3CN$, rt, 6 h.

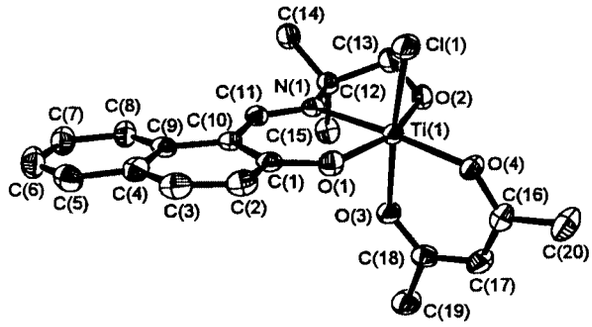



**Fig. 1** Molecular structure of complex **2b** showing 50% probability level thermal ellipsoids and using ORTEP for all non-hydrogen atoms (as in all structures).

reaction with one equivalent of $H_3L^3$ with a view to obtaining a mixed ligand complex of titanium led to a mixture of non-characterisable products. In contrast, the reaction of **2b** with $H_4L^4$ led to homoleptic complex **3c**.

Reaction of complex **1** with $H_2L^5$ ligand in 1 : 1 ratio yielded a mixed ligand complex **4a**. Even the reactions of **1** with $H_2L^5$ ligand in 1 : 2 or 1 : 3 ratio yielded **4a** rather than the expected products possessing more than one $L^5$ in the co-ordination sphere of Ti. Reactions of **2b** carried out with $H_2L^5$ both in the absence and in the presence of bases, such as sodium acetate or aniline, yielded only complex **4a** by replacing $L^2$ and chloro-groups, but not the expected mixed ligand complex, [$Ti(L^5)$-$(L^2)$(solvent)]. Thus **2b** has shown good reactivity towards different ligands containing OH groups of alkoxo and phenoxo types.

Reaction of complex **4a** with one equivalent of $H_2L^2$ did not yield the expected product, [$Ti(L^5)(L^2)$(solvent)], instead uninterpretable NMR spectra indicating the presence of a mixture of products. Similarly one or two equivalents of $H_2L^5$ both in the absence and in the presence of base did not give the expected products.

### Structures of compounds 2b, 3b and 4a

Though all the three compounds crystallised in centrosymmetric space groups (Table 1), there exists no centre of symmetry in any of the molecules. The six bond lengths and the fifteen bond angles covering the primary co-ordination sphere are given in Table 2.

The molecular structure of complex **2b** is shown in Fig. 1 using ORTEP. The titanium(IV) centre is octahedral possessing $L^2$, a bidentate acac group and a chloro-group. The tridentate ligand, $L^2$ occupies the equatorial positions by co-ordinating through its alkoxo and phenoxo oxygens and an imine nitrogen. The metric parameters around the metal centre (Table 2) are clearly indicative of the distortion in the octahedral geometry around titanium. The *trans* angles range from 157.8 to 170.9° indicating a large distortion in the primary co-ordination sphere. Five-membered chelate bite angles in **2b** range from 77.1 to 82.5°.

The structure of complex **3b** possesses two tridentate ligands $L^2$ as shown in Fig. 2. Each ligand is bound through oxygen atoms of alkoxo and phenoxo groups and also through an imine nitrogen. The ligands are bound in a meridional fashion as seen from the stereoview of **3b**. The metric parameters around the titanium centre are clearly indicative of the distortion in the octahedral geometry. The *trans* angles range from 156.7 to 174.3° exhibiting a large deviation of ≈23°. The 5-membered chelate bite angles range from 77.3 to 80.2°.

The molecular structure of complex **4a** possesses one ligand $L^5$ and two acac groups as shown in Fig. 3. The stereoview demonstrates that $L^5$ adopts a partially open book type structure. All the three ligands act as bidentate. Based on the metric parameters around the titanium centre, the complex is

**Table 1** Summary of crystallographic data for complexes **2b**, **3b** and **4a**

| | **2b** | **3b** | **4a** |
|---|---|---|---|
| Molecular formula | $C_{20}H_{22}ClNO_4Ti$ | $C_{30}H_{30}N_2O_4Ti$ | $C_{31}H_{28}O_6Ti$ |
| *M* | 423.74 | 530.46 | 544.43 |
| *T*/K | 293(2) | 293(2) | 293(2) |
| Crystal System | Orthorhombic | Monoclinic | Monoclinic |
| Space group | *Pbca* | $P2_1/n$ | $P2_1/n$ |
| Cell constants | | | |
| *a*/Å | 8.757(1) | 13.769(2) | 8.254(1) |
| *b*/Å | 16.150(8) | 10.985(2) | 22.121(4) |
| *c*/Å | 27.766(3) | 17.055(2) | 14.582(2) |
| *β*/° | — | 102.38(1) | 102.34(1) |
| *V*/Å$^3$ | 3927(2) | 2519.8(6) | 2601.1(7) |
| *Z* | 4 | 2 | 2 |
| $D_c$/g cm$^{-3}$ | 1.433 | 1.398 | 1.390 |
| Total reflections | 3607 | 4613 | 4896 |
| Unique reflections | 3455 | 4419 | 4562 |
| Parameters | 244 | 344 | 353 |
| Final *R* | 0.0394 | 0.0370 | 0.0376 |
| *R′* | 0.1043 | 0.0848 | 0.0876 |

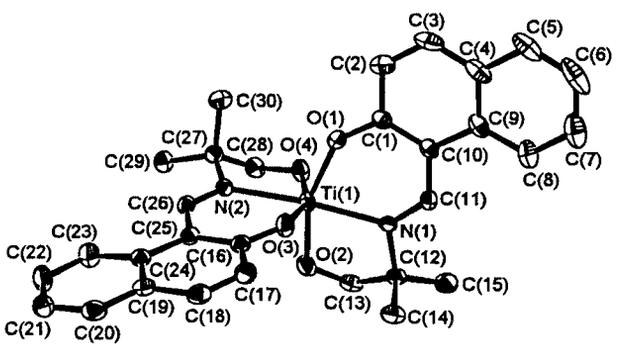



**Fig. 2** Molecular structure of complex **3b**.

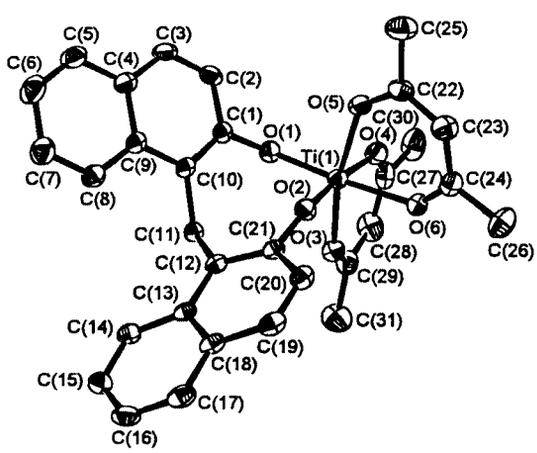



**Fig. 3** Molecular structure of complex **4a**.

identified as distorted octahedral. The *trans* angles are in the range 166.8–175.7°. The bite angle of $L^5$ is about 10° wider owing to its chelate ring size when compared to the other complexes. The structure of **4a** has close resemblance to that of $[Ti(acac)_2(OC_6H_3Pr^i_2\text{-}2,6)_2]$[15] where the phenoxo-ligands are monodentate, while **4a** has bidentate ligand $L^5$.

Comparison of metric parameters around the metal centre reveals a trend in the distortion of octahedral geometry, **2b** > **3b** > **4a**. The Ti–O bond lengths are in the order, Ti–$O_{alk}$ < Ti–$O_{phe}$ < Ti–$O_{acac}$ in all the complexes reported in this paper and further are in agreement with those in the literature.[8] Weak intermolecular hydrogen bond interactions occur between C3–H3 and O3 and C8–H8 and O4 in the lattice of **2b**. The lattice structure indicating these bonds in **2b** is shown in Fig. 4. The hydrogen bond parameters are as follows (H · · · O, C · · · O and C–H · · · O): 2.566, 3.477 Å, 158.7°, 2.570, 3.301 Å, 133.1°. However, no such interactions are observed in the crystal lattice of **3b** or **4a**.

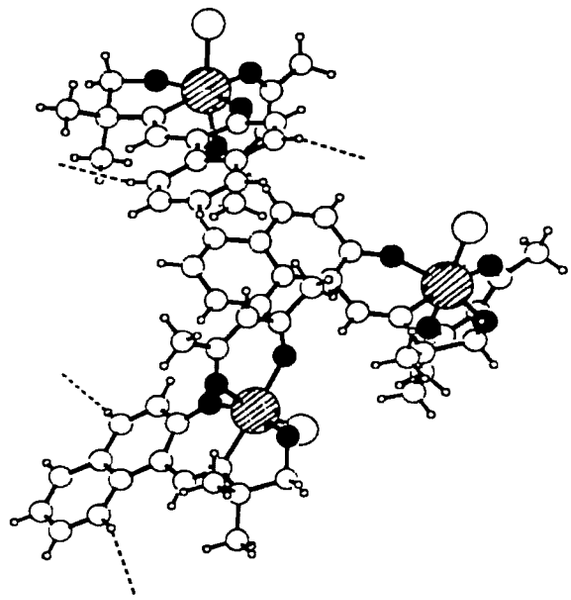


**Fig. 4** Lattice structure of complex **2b** showing intermolecular hydrogen bond interaction (---). Filled circles refer to oxygen, hatched circles to the metal.

## Spectral studies

Proton NMR spectra of complexes **2a**, **2b**, **3a**, **3b** and **3d** showed disappearance of the phenolic proton and one of the alkoxo-OH protons. The spectra also exhibited a downfield shift of the imine proton by 0.79, 0.48, 0.92, and 0.56 ppm upon co-ordination in **2a**, **2b**, **3a**, and **3b** respectively when compared with the corresponding unbound ligands. In case of **3d** two singlet peaks were observed for the imine protons of $L^1$ and $L^2$ at $\delta$ 9.55 and 9.47 respectively and were shifted downfield by 0.92 and 0.54 ppm.

For complex **2a** the bound $CH_2CH_2O^-$ appeared as multiplets centred at $\delta$ 4.94 (1 H) and 4.62 (3 H). Similarly, in the case of **3a**, these were observed at $\delta$ 4.63 (1 H) and 4.49 (3 H). For **2b** the protons of the bound $CH_2O^-$ group appeared as an 'AB' quartet, where the doublets are centred around $\delta$ 4.32 and 4.89, exhibiting a downfield shift of 0.89 and 1.42 ppm respectively in comparison with those for the corresponding "free" ligand. Similarly, in the case of **3b**, the doublets are centred around $\delta$ 4.45 and 4.15 indicating downfield shifts of 0.98 and 0.68 ppm respectively. For **3d** the $CH_2O^-$ protons of $L^1$ appeared as two sets of multiplets centred around $\delta$ 4.60 and 4.49 respectively. The protons of the bound $CH_2O^-$ group of $L^2$ in **3d** appear as an 'AB' type quartet, where the individual doublets are centred around $\delta$ 4.46 and 4.21.

The methyl protons of $L^2$ appeared as two singlets for complex **2b**, and these are shifted downfield by 0.17 and 0.33 ppm with respect to those of free $L^2$. Similarly the methyl protons from the acac group also appeared as two singlets. For **3b** the methyl protons of $L^2$ appeared as two singlets shifted downfield by 0.28 and 0.18 ppm respectively. For **3d** the methyl protons of $L^2$ appeared at $\delta$ 1.67 and 1.57.

The proton NMR spectrum of complex **4a** showed methyl protons of acac as a singlet at $\delta$ 2.06 and the methine proton of acac also as a singlet at $\delta$ 5.79. The protons of the methylene group that bridges the two naphthyl rings of $L^5$ appeared as two broad peaks centred at $\delta$ 5.15 and 4.74.

FTIR spectra of all the products **2a**, **2b**, **3a**, **3b**, **3c**, **3d**, and **4a** were compared with the spectra of the corresponding ligands and precursors. Products **2a**, **2b**, **3a**, **3b** and **4a** did not exhibit

**Table 2** Selected bond lengths (Å) and angles (°) in complexes **2b**, **3b** and **4a**

| **2b** | | **3b** | | **4a** | |
|---|---|---|---|---|---|
| Ti(1)–O(1) | 1.892(2) | Ti(1)–O(1) | 1.918(2) | Ti(1)–O(1) | 1.861(2) |
| Ti(1)–O(2) | 1.803(2) | Ti(1)–O(2) | 1.857(2) | Ti(1)–O(2) | 1.806(2) |
| Ti(1)–O(3) | 2.028(2) | Ti(1)–O(3) | 1.936(2) | Ti(1)–O(3) | 2.009(2) |
| Ti(1)–O(4) | 1.968(2) | Ti(1)–O(4) | 1.856(2) | Ti(1)–O(4) | 2.034(2) |
| Ti(1)–N(1) | 2.167(2) | Ti(1)–N(1) | 2.158(2) | Ti(1)–O(5) | 1.988(2) |
| Ti(1)–Cl(1) | 2.347(1) | Ti(1)–N(1) | 2.178(2) | Ti(1)–O(6) | 2.045(2) |
| O(1)–Ti(1)–O(2) | 157.79(9) | O(1)–Ti(1)–O(2) | 157.42(7) | O(1)–Ti(1)–O(2) | 93.99(7) |
| O(1)–Ti(1)–O(3) | 88.08(9) | O(1)–Ti(1)–O(3) | 90.64(7) | O(1)–Ti(1)–O(3) | 96.39(7) |
| O(1)–Ti(1)–O(4) | 103.19(8) | O(1)–Ti(1)–O(4) | 90.06(7) | O(1)–Ti(1)–O(4) | 90.55(7) |
| O(1)–Ti(1)–N(1) | 80.73(8) | O(1)–Ti(1)–N(1) | 80.20(6) | O(1)–Ti(1)–O(5) | 92.33(7) |
| O(1)–Ti(1)–Cl(1) | 87.98(7) | O(1)–Ti(1)–N(2) | 104.80(7) | O(1)–Ti(1)–O(6) | 175.66(7) |
| O(2)–Ti(1)–O(3) | 93.40(9) | O(2)–Ti(1)–O(3) | 93.47(7) | O(2)–Ti(1)–O(3) | 93.10(7) |
| O(2)–Ti(1)–O(4) | 98.98(9) | O(2)–Ti(1)–O(4) | 94.77(8) | O(2)–Ti(1)–O(4) | 174.55(7) |
| O(2)–Ti(1)–N(1) | 77.13(8) | O(2)–Ti(1)–N(1) | 77.26(7) | O(2)–Ti(1)–O(5) | 96.18(7) |
| O(2)–Ti(1)–Cl(1) | 93.76(7) | O(2)–Ti(1)–N(2) | 97.78(7) | O(2)–Ti(1)–O(6) | 88.50(7) |
| O(3)–Ti(1)–O(4) | 82.48(8) | O(3)–Ti(1)–O(4) | 156.68(7) | O(3)–Ti(1)–O(4) | 83.38(7) |
| O(3)–Ti(1)–N(1) | 89.45(8) | O(3)–Ti(1)–N(1) | 97.39(7) | O(3)–Ti(1)–O(5) | 166.79(7) |
| O(3)–Ti(1)–Cl(1) | 169.91(7) | O(3)–Ti(1)–N(2) | 79.89(7) | O(3)–Ti(1)–O(6) | 87.01(7) |
| O(4)–Ti(1)–N(1) | 170.86(8) | O(4)–Ti(1)–N(1) | 105.69(7) | O(4)–Ti(1)–O(5) | 86.64(7) |
| O(4)–Ti(1)–Cl(1) | 89.38(7) | O(4)–Ti(1)–N(2) | 77.41(7) | O(4)–Ti(1)–O(6) | 87.16(7) |
| N(1)–Ti(1)–Cl(1) | 99.07(7) | N(1)–Ti(1)–N(2) | 174.25(7) | O(5)–Ti(1)–O(6) | 83.01(7) |

any peaks in the $\nu_{OH}$ region. The binding of the imine function through nitrogen has been revealed by the low frequency shift of 15 to 18 $cm^{-1}$ observed with the $\nu_{CN}$ peaks.

In $^{13}C$ NMR spectra the imine carbon in complexes **2a**, **2b**, **3b** and **3d**($L^2$) showed downfield shifts of 1.5, 0.9, 1.24 and 1.33 ppm respectively. However, **3a** and **3d**($L^1$) showed marginal upfield shifts for the imine carbon by 0.37 and 0.44 ppm respectively.

Considerable downfield shifts were also observed with the bound $CH_2O^-$ carbon in complexes **2a**, **2b**, **3a** and **3d**($L^1$) by 12.5, 27.3, 9.2 and 9.1 ppm respectively. The bound methylene carbon of $L^2$ shifted downfield by 23.7 ppm for **3b** and 24.0 ppm for **3d**. In effect, the downfield shift observed in the carbon chemical shift of the bound $CH_2O^-$ in the 1:1 complex is higher than that in the 1:2 complex due to a decrease in the effective positive charge of the metal centre per ligand in the 1:2 case. Thus the downfield shifts observed for **2a** and **2b** are higher than those for **3a** and **3b** respectively. Such shifts observed in mixed ligand complexes parallel the behaviour of the 1:2 cases as expected.

The methine carbon of the acac group was shifted upfield by about 3.5 ppm for both complexes **2a** and **2b**. The carbonyl carbon of the acac group appeared as two peaks each for **2a** and **2b**. For **2a** the carbonyl carbons were shifted downfield by 0.44 and 1.66 ppm. In the case of **2b** one peak was shifted upfield by 1.84 and the other downfield by 0.57 ppm when compared with those of **1**.

## Conclusions

The ligands $L^1$ to $L^4$ differ in the nature of the substituents (H, $CH_3$ or $CH_2OH$), which in turn reflects the number of $CH_2OH$ functions present in the molecules. On the other hand, $L^5$ possesses only two phenyl OH groups and no $CH_2OH$ group. Reactivity studies carried out at titanium, as reported in this paper, clearly indicated the influential roles played by these ligands. While $L^1$ and $L^2$ can coexist on the same titanium centre to give a mixed ligand product from the reactions, $L^4$ does not give mixed ligand ones in combination with $L^1$ or $L^2$, rather it replaces these ligands and provides only a homoleptic complex. However, all the reactions involving $L^3$ have given intractable products. Even the ligand $L^5$ displaces the $L^1$ or $L^2$ from the complexes and gives product **4a** containing only one $L^5$ ligand.

Reactions of $V^VO$ ($V{=}O^{3+}$, *cis*-$O{=}V{=}O^+$), $Mo^{VI}O$ (*cis*-$O{=}Mo{=}O^{2+}$) and $U^{VI}O$ (*trans*-$O{=}U{=}O^{2+}$) with $L^1$ to $L^4$ have resulted in the formation of corresponding complexes [5,10] where the metal to ligand ratio is 1:1. However, the reactions of these ligands with non-oxo $Ti^{IV}$ resulted not only in 1:1 but also 1:2 complexes (**3a**, **3b**, **3c** and **3d**) due to the absence of any Ti=O moiety. All the complexes of $Ti^{IV}$ reported in this paper are mononuclear, in spite of the fact that in some cases there exists additional unbound $CH_2OH$ groups. Thus this property of titanium complexes is in agreement with that observed in the case of oxometal complexes using the same ligands. The coordination numbers exhibited in $V^VO$, $Mo^{VI}O$, $U^{VI}O$ and non-oxo titanium(IV) complexes are 5, 6, 7 and 6 respectively. Only the lattice structure of **2b** has shown some weak intermolecular interactions. In this context the nature of the titanium complex is somewhat intermediate to that observed between $Mo^{VI}O$ and $U^{VI}O$ lattice structures. In effect, the reactivity of these OH containing ligands has been found to be somewhat different in the case of the non-oxo titanium when compared to that of the oxometal centres of $V^V$, $Mo^{VI}$ and $U^{VI}$.

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