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Self-assembly of double stranded dinuclear titanium(IV)–Schiff base complexes and formation of intramolecular μ-oxo bridges

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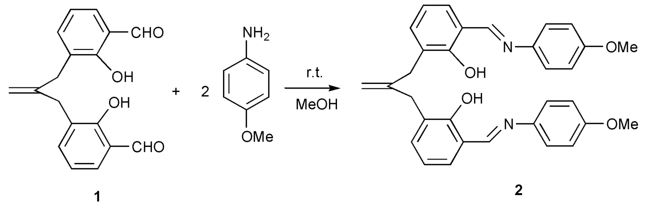
The reaction of titanium isopropoxide with a Schiff base ligand containing an isobutenyl linker leads to double stranded dinuclear titanium(IV)–Schiff base complexes through self-assembly with concomitant formation of intramolecular μ-oxo bridges upon hydrolysis.

Self-assembly processes in metallo-supramolecular chemistry involves the selective binding between metal ions and appropriate ligands.[1,2] This leads to the formation of a plethora of organized structures useful for nanotechnology.[2] Schiff bases are an important class of ligands in molecular design devoted to energy storage[3] (molecular batteries) and also in transition metal catalysis.[4] Recently, we have reported highly selective formation of a new series of polyamine macrocycles using tandem Claisen rearranged bis-hydroxybenzaldehyde **1** and diamines.[5] Having realized the potential use of bis-hydroxybenzaldehyde **1** as a useful building block for the preparation of new macrocycles, we are further interested in the self-assembly studies of corresponding Schiff base ligand **2** with metal complexes. Our strategy, in the preparation of polydentate Schiff base ligands from bishydroxybenzaldehyde **1** derivatives containing an isobutenyl linker has the unique advantage for modifications in either the aldehyde or amine components of the Schiff base. Recent interest in self-assembly studies using titanium(IV) alkoxides[2] is due to their widespread applications as precursors both in catalysis[4] and in high-tech applications.[6] Herein, we report our new findings on the self assembly studies of double stranded titanium(IV)–Schiff base complexes accompanied by intra-molecular mono- and bis-μ-oxo bridge formation upon hydrolysis.

Schiff base ligand **2** was prepared from **1** and *p*-methoxyaniline in methanol (Scheme 1).† Ligand **2** was further used in studies with Ti(O^{i}Pr)$_4$. Reaction of ligand **2** was carried out with 0.5 equiv. of Ti(O^{i}Pr)$_4$ in dry tetrahydrofuran at room temperature for 6 h and led to a yellow solid **3**.‡ The positive ESI-MS in acetonitrile showed a peak at *m*/*z* 1262 for **3**. This *m*/*z* value obtained for **3** indicates the presence of at least two molecules of ligand **2** and two titanium(IV) ions in the molecular structure of **3**. Single crystal X-ray analysis has been conducted§for pale yellow crystals of **3** obtained from dichloromethane/hexane (3:2). This revealed the formation of a double stranded dinuclear titanium(IV) complex with intramolecular Ti–O–Ti bridge formation between two titanium(IV) atoms (Fig. 1(a)). This is in accordance with the positive ESI-MS peak at *m*/*z* 1262 for M + Na. The ^{1}H NMR spectra of **3** showed an upfield shift for the imine (CH=N) proton by 0.6 ppm after complexation.‡ The reaction of ligand **2** with 1 equiv. of Ti(O^{i}Pr)$_4$ in dry tetrahydrofuran at room temperature for 12 h gave a pale yellow solid.‡ FAB-MS analysis of the compound showed peak at *m*/*z* 1136 indicating the formation of dinuclear titanium complex **4** with the absence of isopropoxy groups on the titanium atoms in contrast to structure **3**. Positive ESI-MS studies also showed a peak at *m*/*z* 1159 which corresponds to M + Na. Single crystal X-ray analysis for **4** revealed the formation of a double stranded dinuclear titanium complex **4** with Ti_2O_2 bridge formation in the core (Fig. 1(b)) with an inversion centre between the two titanium atoms.§



Scheme 1 Synthesis of ligand **2**.

Formation of complexes **3** and **4** is interesting from the fact that overall two titanium(IV) atoms are flanked between two ligands through bonding, in addition two titanium atoms are also linked through either mono- or bis-μ-oxo bridge formation between themselves. The attachment of the two termini of Schiff bases to two different titaniums is mainly due to the influence of isobutenyl linker, forcing the two ends to react with different titaniums. In fact, it was also observed that the two hydroxy groups in the free ligand **2** are found to be in a transoid confirmation in solid state.[7] Overall, the influence of isobutenyl linker forces the ligand self-assembly to form double stranded dinuclear titanium(IV) complexes. The difference in the ligand orientation between complexes **3** and **4** is of note (Scheme 2). The helical twist of the ligand in **3** is due to the steric constraints exerted by the isobutenyl linker. It has also been observed earlier that the isobutenyl linker in crownophanes forces the two aryl groups not to be in the same plane.[8] Ligand **2** adopts a twisted orientation in complex **3** while in complex **4** the ligand adopts a parallel orientation due to the formation of a bis-μ-oxo bridge. Hence, the formation of mono- and bis-μ-oxo bridges between in **3** and **4**, respectively, has further fine tuned the orientation of the ligand: twisting in **3** *cf.* a parallel orientation in **4**.

To confirm whether the formation of mono- or bis-μ-oxo complexes in **3** and **4** is due to the difference in the amounts of Ti(O^{i}Pr)$_4$ used or simply due to the moisture content in the

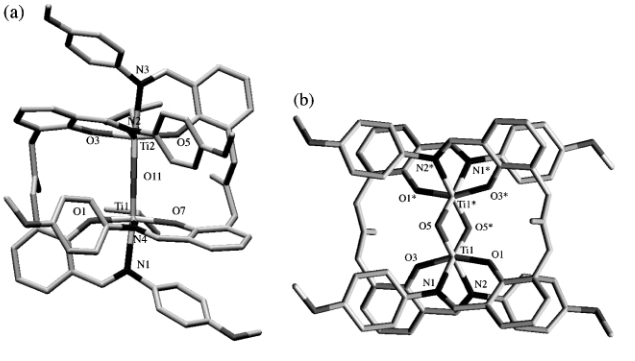


Fig. 1 Molecular structures for complexes **3** (a) and **4** (b) measured by X-ray analysis; Selected bond lengths (Å) and angles (°): (a) Ti1–O1 1.909(3), Ti1–O7 1.918(3), Ti1–O11 1.806(3), Ti1–N1 2.313(4), Ti1–N4 2.326(4), Ti2–O3 1.935(3), Ti2–O5 1.927(3), Ti2–O11 1.811(3), Ti2–N2 2.274(4), Ti2–N3 2.324(4); Ti1–O11–Ti2 166.0(2); (b) Ti1–O1 1.910(2), Ti1–O3 1.903(2), Ti1–O5 1.837(3), Ti1–O5* 1.852(2), Ti1–N1 2.295(4), Ti1–N2 2.285(3); Ti1–O–Ti1 95.4, Ti1–Ti1* 2.727.

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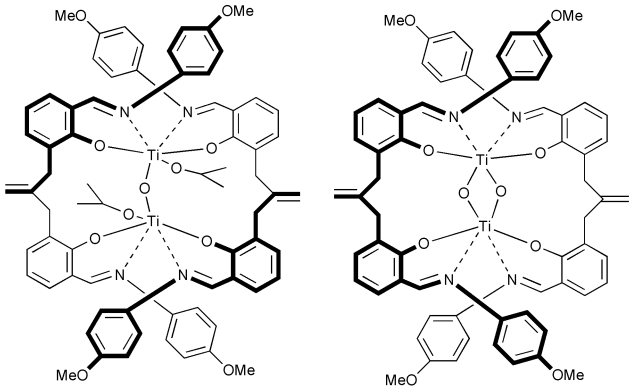

3
twisted

4
parallel

Scheme 2 Schematic representation of ligand **2** in complexes **3** and **4**, repectively. Bold lines are at the front, thin lines are at the back.

reaction medium, we have carried out a reaction with one equivalent of **2** and Ti(O^{i}Pr)$_4$ and the reaction was followed by ESI-MS. The reaction mixture checked after 6 and 12 h revealed that formation of either **3** or **4** is highly dependent on the moisture content in the reaction medium. The positive ESI-MS spectra measured for the sample prepared in dry acetonitrile showed a major peak for **3** and minor peaks for **4** and unreacted ligand **2**. In contrast, a sample prepared in normal acetonitrile (not dehydrated) showed a peak for **4** and unreacted ligand **2** and no peak for **3** was observed. This clearly shows the highly sensitive nature of complexes **3**, **4** and also the complex precursor to **3**. We could not observe any peak for a complex precursor to **3** in ESI-MS. We have also observed that complex **3** is very sensitive to moisture when in solution, although it is somewhat more stable in the solid state.

For titanium(IV) based titanoxanes, hydrolytic self-assembly is generally an uncontrolled pathway.[9] Here, the isobutenyl linker in ligand **2** contributed to the formation of mono- and bis-μ-oxo bridges in a controllable fashion. Further, addition of a calculated amount of water to **3** led to the formation of **4** by hydrolysis of a second set of isopropoxy groups in **3**. Positive ESI-MS clearly showed an *m/z* peak at 1137 (M + H$^+$) together with a small peak at 1159 for M+Na. This demonstrates that the formation of the μ-oxo bridges in **3** and **4** is through controlled hydrolysis.

From the Cambridge crystal structure data base, it is interesting to note that in the majority of studied titanium complexes, the oxygen atoms in Ti–O–Ti linkages are bound or coordinated additionally to other atoms or groups. Comparison of the O–Ti–O and Ti–O–Ti bond angles and Ti–O bond distances in complexes **3** and **4** are broadly in agreement with the reported values for similar structures where the oxygens in Ti–O–Ti are divalent.[10] Facile formation of intramolecular oxo-bridges may be due to the proximity of isoproproxy groups in the dinuclear complex precursor to **3**. In literature cases usually the oxo-bridge is formed intermolecularly between two salen–titanium complexes.

In summary, a novel self-assembly of double stranded dinuclear titanium(IV)–Schiff base complexes with mono- and bis-μ-oxo bridges has been described here. These complexes may find application in catalysis[11] and in materials chemistry. Further studies will be focussed on the modifications in the Schiff base ligand **2** to obtain highly organized molecular structures with other metal combinations.

Notes and references

† Ligand **2**: δ_H (500 MHz, CDCl$_3$): 3.52 (s, 4H, CH$_2$), 3.84 (s, 6H, OMe), 4.84 (s, =CH$_2$), 6.92–6.94 (m, 6H, Ar), 7.25–7.27 (m, 8H, Ar), 8.61 (s, 2H, CH=N), 13.70 (s, 2H, OH).

‡ *Preparation* of **3**: ligand **2** (0.126 g, 0.25 mmol) was stirrred with Ti(O^{i}Pr)$_4$ (0.035 g, 0.125 mmol) in dry THF for 6 h at r.t. The solvent was removed under vacuum and dried. The pure crystalline compound was obtained from CH$_2$Cl$_2$/hexane (3:2). Yield: 60%; ESI-MS: *m/z* 1262 (M + Na). δ_H (500 MHz, CDCl$_3$): 1.20 (d, 6H, *J* 6.2, CH$_3$), 2.43 (d, 2H, *J* 13.1, CH$_2$), 3.66 (s, 6H, OMe), 3.81 (d, 2H, *J* 13.1, CH$_2$), 4.02 (m, 1H, OCH), 4.87 (s, 2H, =CH$_2$), 6.4–7.2 (m, 14H, Ar), 8.03 (s, 2H, CH=N). *Analysis* for **3**: $C_{70}H_{70}N_4O_{11}Ti_2$. Calc.: C, 67.85; H, 5.69; N, 4.52. Found: C, 67.91; H, 5.30; N, 4.22%. *Preparation* of **4**: as for **3**; the pure crystalline compound obtained from CH$_2$Cl$_2$/THF (1:1) with slow evaporation under vacuum. Compound **4** was not soluble once crystallized so that NMR spectra could not be measured. Yield: 70%; FAB-MS: *m/z* 1136; ESI-MS: *m/z* 1159 (M + Na).

§ *Crystal data* for **3**: $C_{72}H_{74}N_4O_{11}Ti_2Cl_4$, M_w = 1409.01, monoclinic, space group = $P2_1/n$ (no. 14), Z = 4, a = 13.5241(5), b = 21.6644(7), c = 23.3745(7) Å, β= 97.455(1)°, V = 6790.6(4) Å^3, D_c = 1.378 g cm^{-3}. The data were collected at −80 °C on a Rigaku RAXIS-RAPID Imaging Plate diffractometer, λ(Mo-Kα) = 0.7107 Å, μ = 4.56 cm^{-1}, 62324 measured and 15489 unique reflections ($2\theta_{max}$ = 55.00°, R_{int} = 0.069). R = 0.069, R_w = 0.137. Two molecules of dichloromethane were present in crystal lattice. The molecular formula of **3** is $C_{70}H_{70}N_4O_{11}Ti_2$ with M_w = 1239.06.

Crystal data for **4**: $C_{72}H_{72}N_4O_{12}Ti_2$, M_w = 1281.18, triclinic, space group = $P\bar{1}$ (no. 2), Z = 1, a = 12.115(2), b = 14.049(3), c = 9.924(1) Å, α = 98.118(9), β = 93.263(4), γ = 71.151(6)°, V = 1582.2(5) Å^3, D_c = 1.344 g cm^{-3}. The data were collected at –80 °C on a Rigaku RAXIS-RAPID Imaging Plate diffractometer, λ(Mo-Kα) = 0.7107 Å, μ= 3.20 cm^{-1}, 12844 measured and 6810 unique reflections ($2\theta_{max}$ = 55.00°, R_{int} = 0.075). R = 0.080, R_w = 0.183. Two disordered tetrahydrofuran solvent molecules were found for one molecule of complex **4** in the crystal lattice. The molecular formula of **4** is $C_{64}H_{56}N_4O_{10}Ti_2$ with M_w = 1136.88.

CCDC reference numbers 170678 and 170679. See http://www.rsc.org/suppdata/cc/b1/b106447a/ for crystallographic data in CIF or other electronic format.

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7 X-Ray structural analysis of several ligands with an isobutenyl linker including ligand **2** have been studied and it was found that the two hydroxy groups are in transoid conformation due to influence of the isobutenyl linker. These results will be published elsewhere in due course.

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