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# Titanium(IV) Complexes of Hydrazones and Azines

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The coordination modes of various azines (C=N–N=C) and hydrazones (C=N–$NR_2$) with titanium(IV) are investigated. Five ligands were studied, two hydrazones **1H–2H** and three azines **$3H_2$–$5H_2$**, and it was found that hydrazones form monomers and azines form dimers in the solid state. The hydrogen-bonded arrays observed for the hydrazones were significantly different for the two ligands, with one forming a ribbon like structure and the other a chain. For the azines the supramolecular structures are also discussed. A pronounced twist is observed in the azine ligand upon complexation to the metal centre, which is rationalised in terms of the favourable interactions observed in the solid-state.


## Introduction

There is continuing interest in the synthesis of new titanium(IV) complexes for use in catalysis and supramolecular chemistry.[1–7] As a consequence it is pertinent to design new ligands that may impart different steric effects at the metal centre. Thus, we have investigated the coordination of $Ti^{IV}$ with a variety of hydrazone (C=N–$NR_2$) and azine (C=N–N=C) ligands. To the best of our knowledge, there are only two reported titanium–azine crystal structures and no titanium–hydrazone complexes, where R = H, have been structurally characterised.[8,9] Azine complexes of transition metals, for example ruthenium, iron, copper and zinc are known to form dimers in the solid state, with either a *cis* or *trans* configuration, Figure 1.[10–14]

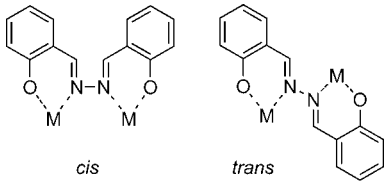


Figure 1. Two possible isomers for azine complexes.

In contrast, hydrazone complexes of transition metals (e.g. vanadium and copper) tend to form monomeric structures.[15–17] Hydrazones (where R = H) can form supramolecular arrays in the solid state due to the presence of the protic $NH_2$ group available for hydrogen bonding, a feature which is being exploited in the crystal engineering field.[18–23] The ligands chosen for this study are shown in Figure 2, with the expectation of conveying different steric demands on the titanium(IV) centre and facilitating the formation of different arrays in the solid state.

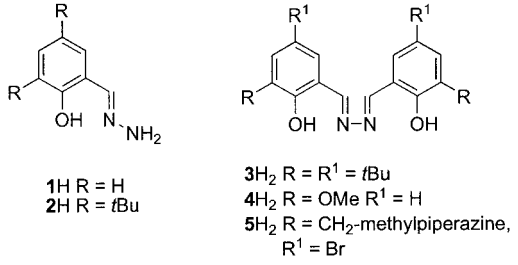


Figure 2. Hydrazones **1**H and **2**H, azines $\mathbf{3}H_2$, $\mathbf{4}H_2$ and $\mathbf{5}H_2$.

## Results and Discussion

Two equivalents of each hydrazone **1**H and **2**H react readily with $Ti(OiPr)_4$ to form the desired complexes $Ti(\mathbf{1})_2(OiPr)_2$ and $Ti(\mathbf{2})_2(OiPr)_2$. Each of the ligands is deprotonated at the phenolic moiety and chelates to the metal centre through the resulting phenoxide and the imine nitrogen of the hydrazone group. The amine group does not coordinate to the metal centre. The coordination sphere of the titanium is completed by two terminal isopropoxide ligands, Figure 3.

Each titanium centre has a distorted octahedral geometry with the two aryl oxide ligands adopting a *trans* configuration and the imine donors assuming a *cis* configuration, see Table 1 for selected bond lengths and angles. The bond lengths and angles are in agreement with literature pre-

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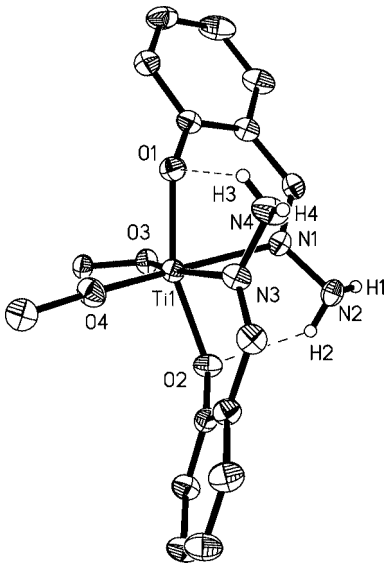


Figure 3. Crystal structure of complex Ti(**1**)$_2$(O*i*Pr)$_2$. Ellipsoids are shown at the 50% probability level, the hydrogen atoms not involved in hydrogen bonding and the isopropoxide methyl groups have been omitted for clarity. The same labelling scheme was used for complex Ti(**2**)$_2$(O*i*Pr)$_2$. The dashed lines represent the *intramolecular* hydrogen bonding, between H(2)–O(2) and H(3)–O(1). The hydrogen atoms were located in the penultimate difference Fourier map and refined freely.

cedent.[24–30] The $^1$H and $^{13}$C NMR spectra of the complexes suggest that the gross solid-state structures are maintained in solution with well-defined resonances for the isopropoxide region.

Table 1. Selected bond lengths [Å] and angles [°] for complexes Ti(**1**)$_2$(O*i*Pr)$_2$ and Ti(**2**)$_2$(O*i*Pr)$_2$.

| | Ti(**1**)$_2$(O*i*Pr)$_2$ | Ti(**2**)$_2$(O*i*Pr)$_2$ |
|---|---|---|
| Ti(1)–O(1) | 1.950(1) | 1.912(2) |
| Ti(1)–O(2) | 1.940(1) | 1.913(2) |
| Ti(1)–O(3) | 1.846(1) | 1.778(2) |
| Ti(1)–O(4) | 1.761(1) | 1.852(2) |
| Ti(1)–N(1) | 2.268(1) | 2.282(2) |
| Ti(1)–N(3) | 2.264(1) | 2.271(2) |
| O(1)–Ti(1)–O(2) | 158.89(5) | 160.80(7) |
| O(3)–Ti(1)–O(4) | 102.79(5) | 101.75(8) |
| O(1)–Ti(1)–O(4) | 97.78(5) | 94.33(7) |
| N(1)–Ti(1)–N(3) | 79.90(5) | 81.86(7) |

Both *intra*- and *intermolecular* hydrogen bonds are observed. The intramolecular hydrogen bonds are shown in Figure 3, where one hydrogen atom of each $NH_2$ group interacts with a phenoxide oxygen centre, see Table 2 for the hydrogen bonding parameters, which are similar for both complexes. The main structural distinction between Ti(**1**)$_2$(O*i*Pr)$_2$ and Ti(**2**)$_2$(O*i*Pr)$_2$ arises due to their patterns of intermolecular hydrogen bonding. For Ti(**1**)$_2$(O*i*Pr)$_2$ both H(1) and H(4) are invoked in hydrogen bonding (Figure 4) forming a ribbon-like structure in the solid state. H(1) bonds to an isopropoxide oxygen {O(3)} of a neighbouring molecule and H(4) binds to a hydrazone $NH_2$ group {N(2)} of a third molecule. For Ti(**2**)$_2$(O*i*Pr)$_2$ only *one* intermolecular hydrogen bond is seen in the solid state, between H(1) and an isopropoxide O(4), and this forms a chain-like structure. The absence of a hydrogen bond from H(4) to N(2) of an adjacent molecule is presumably related to the increase in steric bulk of the ligand.

One equivalent of each azine was treated with two equivalents of Ti(O*i*Pr)$_4$ to form complexes Ti$_2$(**3**)(O*i*Pr)$_6$, Ti$_2$(**4**)(O*i*Pr)$_6$ and Ti$_2$(**5**)(O*i*Pr)$_6$. The structure of Ti$_2$(**4**)(O*i*Pr)$_6$ is shown in Figure 5. In all cases the azine bridges between two titanium centres in a *cis* fashion. The coordination sphere around each titanium atom being completed by coordination of two terminal and two bridging isopropoxide moieties. The titanium centre is pseudooctahedral with the bond lengths and angles in the expected range, Table 3.[24–30] The core of each complex consists of three rings, one Ti$_2$O$_2$ ring made up of the two titanium centres and the two bridging alkoxides, and two five-membered rings made up of the two titanium centres, a bridging alkoxide and the azine N–N bond. The $^1$H and $^{13}$C NMR spectra suggests that the solid-state structure is maintained in solution, with distinct resonances observed for the isopropoxide moieties; for example for the azine complexes three distinct O*i*Pr methine resonances are observed in both the $^1$H and $^{13}$C NMR spectra.

The ligand shows a distortion away from planarity, which manifests itself by analysis of the torsion angle {C(8)–N(1)–N(1A)–C(8A)} of 55.7(4)° for complex Ti$_2$(**4**)(O*i*Pr)$_6$. The ligand distortion suggests that there is little conjugation between the two salicylaldimine units of the azine and that the N–N bond has little π-bonding character. For complex Ti$_2$(**3**)(O*i*Pr)$_6$ this torsion angle is very similar at 53.2(5)° to Ti$_2$(**4**)(O*i*Pr)$_6$. However, there is a significant increase in this torsion angle for complex Ti$_2$(**5**)(O*i*Pr)$_6$ at 66.6(4)°. A possible explanation is that the ligand distorts to form favourable Br···N interactions with a neighbouring molecule, Figure 6. The interaction results in an ordering of the piperazine amine nitrogen atom such that its lone pair is directed towards the bromine atom of a neighbouring molecule, with

Table 2. Summary of the hydrogen bonding parameters for complexes Ti(**1**)$_2$(O*i*Pr)$_2$ and Ti(**2**)$_2$(O*i*Pr)$_2$, the hydrogen atoms were freely refined in all cases. [1]: $-x+1, -y+1, -z+1$; [2]: $x, y, z$; [3]: $-x, -y+1, -z+1$; [4]: $-x+1, y+1/2, -z+1/2$.

| | Ti(**1**)$_2$(O*i*Pr)$_2$ | | | | Ti(**2**)$_2$(O*i*Pr)$_2$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | <(DHA) | D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | <(DHA) |
| N(2)–H(1)···O(3)[1] | 0.88(2) | 2.19(3) | 3.055(2) | 175(2) | N(2)–H(1)···O(4)[4] | 0.87(3) | 2.18(3) | 3.013(3) | 159(3) |
| N(2)–H(2)···O(2)[2] | 0.90(2) | 2.17(2) | 2.845(2) | 131(2) | N(2)–H(2)···O(2)[2] | 0.85(3) | 2.23(3) | 2.875(3) | 133(3) |
| N(4)–H(3)···O(1)[2] | 0.86(2) | 2.27(2) | 2.821(2) | 122(2) | N(4)–H(3)···O(1)[2] | 0.80(3) | 2.29(3) | 2.876(3) | 130(3) |
| N(4)–H(4)···N(2)[3] | 0.86(2) | 2.42(2) | 3.252(2) | 162(2) | | | | | |

  

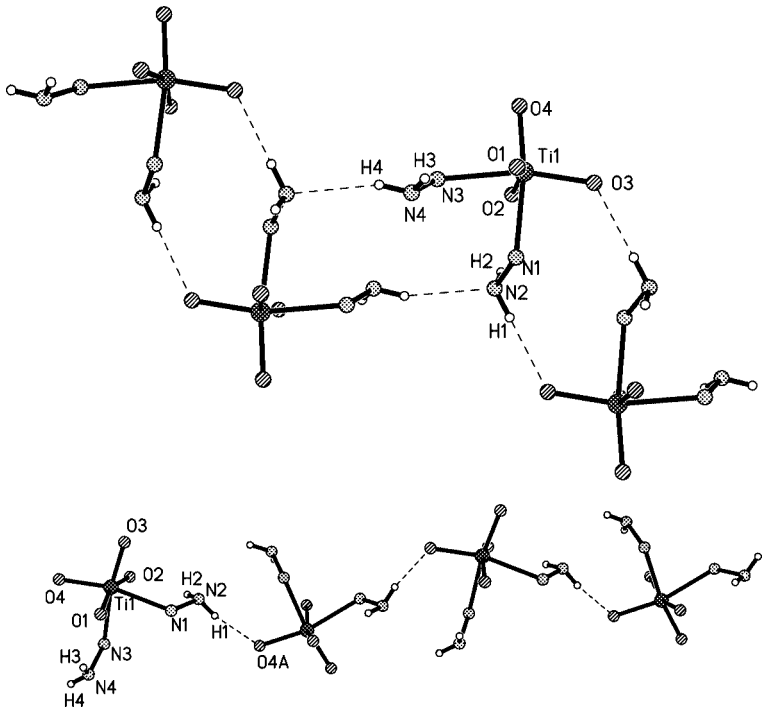


Figure 4. Hydrogen-bonded supramolecular arrays formed in the case of Ti(**1**)$_2$(O*i*Pr)$_2$ (top) containing $R_2^2(10)$ and $R_2^2(12)$ ring motifs[31,32] and Ti(**2**)$_2$(O*i*Pr)$_2$ (bottom). The dashed lines represent the intermolecular hydrogen bonds.

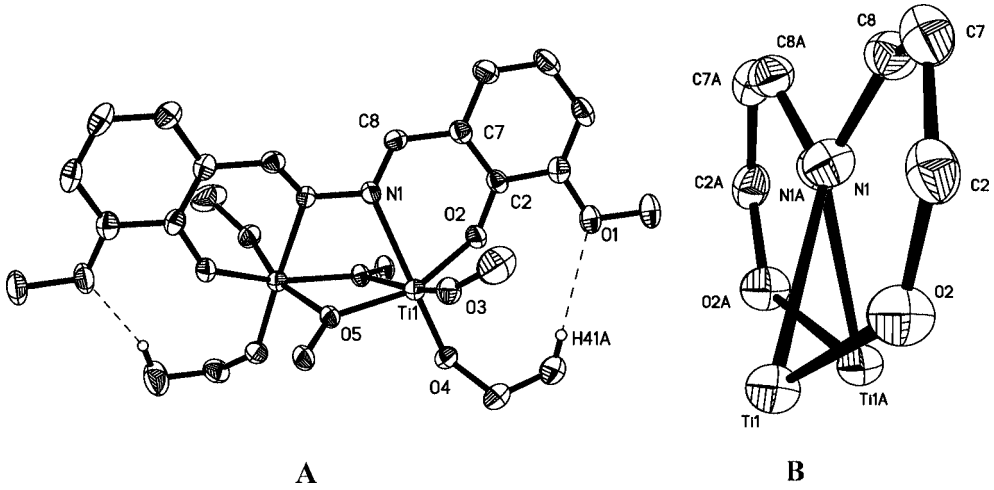


Figure 5. **A** The crystal structure of complex Ti$_2$(**4**)(O*i*Pr)$_6$. The ellipsoids are shown at the 50% probability level and the hydrogen atoms not involved in the weak intramolecular interaction have been removed for clarity. In the case of Ti$_2$(**4**)(O*i*Pr)$_6$ a weak interaction is observed between H(41A) and O(1), D–H 0.86(4) Å, H···A 2.67(4) Å, D···A 3.474(4) Å, <(DHA) 155(4)°, and is shown as a dashed line, H(41A) was identifiable in the penultimate difference Fourier map and refined freely. **B** View down the N(1)–N(1A) bond highlighting the {C(8)–N(1)–N(1A)–C(8A)} torsion angle.

Table 3. Selected bond lengths [Å] and angles [°] for complexes Ti$_2$(**3**)(O*i*Pr)$_6$, Ti$_2$(**4**)(O*i*Pr)$_6$ and Ti$_2$(**5**)(O*i*Pr)$_6$.

| Ti$_2$(**3**)(O*i*Pr)$_6$ | | Ti$_2$(**4**)(O*i*Pr)$_6$ | | Ti$_2$(**5**)(O*i*Pr)$_6$ | |
|---|---|---|---|---|---|
| Ti(1)–O(1) | 1.921(3) | Ti(1)–O(2) | 1.930(2) | Ti(1)–O(1) | 1.934(2) |
| Ti(1)–O(4) | 1.786(3) | Ti(1)–O(3) | 1.797(2) | Ti(1)–O(2) | 1.796(2) |
| Ti(1)–O(5) | 1.799(3) | Ti(1)–O(4) | 1.798(2) | Ti(1)–O(3) | 2.003(2) |
| Ti(1)–O(6) | 2.007(3) | Ti(1)–O(5) | 1.990(2) | Ti(1)–O(4) | 1.795(2) |
| Ti(1)–O(7) | 2.060(3) | Ti(1)–N(1) | 2.320(2) | Ti(1)–N(1) | 2.315(2) |
| Ti(1)–N(1) | 2.317(3) | N(1)–Ti(1)–O(4) | 165.34(7) | N(1)–Ti(1)–O(4) | 169.52(7) |
| N(1)–Ti(1)–O(5) | 166.86(1) | O(2)–Ti(1)–O(5) | 157.79(7) | O(2)–Ti(1)–O(3) | 92.95(7) |
| O(6)–Ti(1)–O(7) | 73.04(9) | O(2)–Ti(1)–O(3) | 93.53(8) | O(4)–Ti(1)–O(3) | 99.15(7) |

  

a Br–N interaction of 3.034 Å, which falls within the typical range,[33–35] to render the formation of a supramolecular ladder.

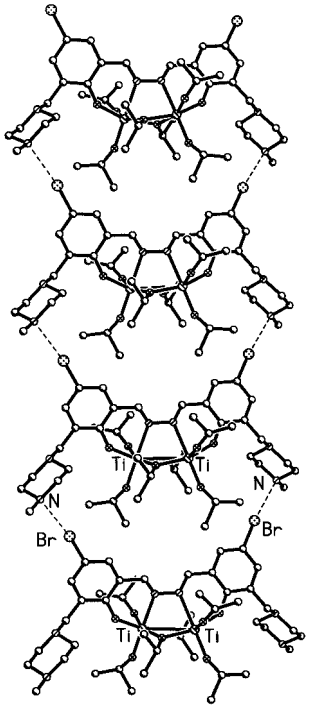


Figure 6. Bromine–nitrogen interactions in complex $Ti_2$(**5**)(O*i*Pr)$_6$.

## Conclusions

In conclusion X-ray structures of five novel titanium(IV) azine and hydrazone complexes are reported. The hydrazone complexes form monomers which have interesting supramolecular structures, with Ti(**1**)$_2$(O*i*Pr)$_2$ forming a ribbon-like array and Ti(**2**)$_2$(O*i*Pr)$_2$ forming a chain-like structure. By increasing the steric bulk the hydrogen bonding motifs are significantly altered. The azine complexes form dimers in the solid state. At the molecular level the substituents on the salicylaldimine aryl oxide groups had little effect on the structures. However, on the supramolecular level introduction of Lewis basic groups in the *ortho* position allowed formation of a weak intramolecular C–H···O interaction and intermolecular N–Br interactions, which induced the formation of a supramolecular ladder.

## Experimental Section

For the preparation and characterisation of complexes, all reactions and manipulations were performed under argon using standard Schlenk or glove-box techniques and all solvents were freshly distilled from suitable drying agents and degassed prior to use. Ligand **1**H was purchased from Aldrich, **2**H and **3**H$_2$–**5**H$_2$ were synthesised using literature procedures[36] and recrystallised from petroleum ether prior to use. Ti(O*i*Pr)$_4$ was purchased from Aldrich and purified by vacuum distillation prior to use. $^1$H/$^{13}$C NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer and referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analysis was performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath. Due to the propensity of the complexes to hydrolyse reliable elemental analysis could not be obtained in some cases. Crystallographic data were collected on a Nonius KappaCCD area detector diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) at a temperature of 150(2) K, and all structures were solved by direct methods and refined on all $F^2$ data using the SHELXL-97 suite of programs.[37] Hydrogen atoms not involved in hydrogen bonding were included in idealised positions and refined using the riding model. Absorption corrections were applied on merit. See Table 4 for full crystallographic parameters.

CCDC-607937 to -607941 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Ti(1)$_2$(O*i*Pr)$_2$:** A solution of salicylaldehyde hydrazone (0.82 g, 6 mmol), was prepared in dry toluene (10 mL) under an inert atmosphere. To this Ti(O*i*Pr)$_4$ (0.9 mL, 3 mmol) was added to give a bright yellow solution. This solution was vigorously stirred for 1 h. The solvent was removed in vacuo to give a pale yellow solid product. This product was suspended in hexane and toluene added until dissolution occurred on warming. Standing at room temperature yielded a crop of yellow blocks. Yield 1.12 g (85%). M.p. 140–143 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 1.04 [d, $J$ = 6 Hz, 12 H, CH(C$H_3$)$_2$], 4.63 [sept, $J$ = 6 Hz, 2 H,C$H$(CH$_3$)$_2$], 5.57 (s, 4 H, NH$_2$), 6.69 (dd, $J$ = 5 and 1 Hz, 2 H, Ar-H), 6.78 (d, $J$ = 8 Hz, 2 H, Ar-H), 7.00 (d, $J$ = 8 Hz, 2 H, Ar-H), 7.18 (m, 2 H, Ar-H), 7.62 (s, 2 H, imine CH) ppm. $^{13}$C{$^1$H} ($CDCl_3$): $\delta$ = 25.6 [CH(*C*H$_3$)$_2$], 79.2 [*C*H(CH$_3$)$_2$], 118.5, 118.9, 122.0, 131.3, 132.3 (Ar), 146.9 (NCH), 162.4 (Ar-O) ppm. $C_{20}H_{28}N_4O_4Ti$ (436.3): calcd. C 55.1, H 6.47, N 12.84; found C 54.8, H 6.40, N 12.70.

**Ti(2)$_2$(O*i*Pr)$_2$:** An analogous procedure to that for Ti(**1**)$_2$(O*i*Pr)$_2$ was followed. Yield 0.39 g (59%), m.p. 220–224 °C (dec.) $^1$H NMR ($CDCl_3$): $\delta$ = 0.90 [two overlaying doublets, $J$ = 6 Hz, 12 H, CH(C$H_3$)$_2$], 1.22 [s, 18 H, C(CH$_3$)$_3$], 1.46 [s, 18 H, C(CH$_3$)$_3$], 4.55 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 5.48 (s, 4 H, NH$_2$), 6.87 (s, 2 H, Ar-H), 7.29 (s, 2 H, Ar-H), 7.70 (s, 2 H, NCH) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 26.0 [CH(*C*H$_3$)$_2$], 30.2 [C(*C*H$_3$)$_3$], 31.9 [C(*C*H$_3$)$_3$], 34.5 [*C*(CH$_3$)$_3$], 35.6 [*C*(CH$_3$)$_3$], 78.6 [*C*H(CH$_3$)$_2$], 121.2, 125.9, 127.1, 137.6, 139.6 (Ar), 148.7 (NCH), 159.7 (Ar-O) ppm. $C_{36}H_{60}N_4O_4Ti$ (660.8): calcd. C 65.4, H 9.15, N 8.48; found C 66.2, H 9.35, N 7.90.

**Ti$_2$(3)(O*i*Pr)$_6$:** A solution of 2,4-di(*tert*-butyl)salicylaldehyde azine (0.36 g, 1 mmol), was prepared in dry toluene (10 mL) under an inert atmosphere. To this Ti(O*i*Pr)$_4$ (0.6 mL, 2 mmol) was added to give a yellow solution. This solution was vigorously stirred for 1 h. Reduction in volume of the toluene and standing at room temperature yielded a crop of yellow blocks. Yield 0.46 g (57%), m.p. 243–246 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 0.77 [br., 12 H, CH(C$H_3$)$_2$], 1.02 [d, $J$ = 6 Hz, 6 H, CH(C$H_3$)$_2$], 1.20 [d, $J$ = 6 Hz, 6 H, CH(C$H_3$)$_2$], 1.21–1.29 [m, 30 H, 2× CH(C$H_3$)$_2$ and 2× C(CH$_3$)$_3$)], 1.46 [s, 18 H, C(CH$_3$)$_3$], 4.37 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 4.77 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 4.88 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 7.12 (s, 2 H, Ar-H), 7.37 (s, 2 H, Ar-H), 7.89 (s, 2 H, NCH) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 22.0 [CH(*C*H$_3$)$_2$], 22.1 [CH(*C*H$_3$)$_2$], 23.7 [CH(*C*H$_3$)$_2$], 23.7 [CH(*C*H$_3$)$_2$], 23.8 [CH(*C*H$_3$)$_2$], 23.9 [CH(*C*H$_3$)$_2$], 27.9 [C(*C*H$_3$)$_3$], 29.5 [C(*C*H$_3$)$_3$], 32.1 [*C*(CH$_3$)$_3$], 33.3 [*C*(CH$_3$)$_3$], 72.3 [*C*H(CH$_3$)$_2$], 75.1 [*C*H(CH$_3$)$_2$], 75.9 [*C*H(CH$_3$)$_2$], 117.8, 126.2, 127.0, 135.8, 136.4 (Ar), 149.6 (NCH), 159.8 (Ar-O) ppm. $C_{48}H_{84}N_2O_8Ti_2$ (912.9): calcd. C 63.2, H 9.27, N 3.07; found C 63.0, H 9.14, N 3.39.

  

Table 4. Crystal data of the complexes Ti(**1**)$_2$(O*i*Pr)$_2$, Ti(**2**)$_2$(O*i*Pr)$_2$, Ti$_2$(**3**)(O*i*Pr)$_6$, Ti$_2$(**4**)(O*i*Pr)$_6$ and Ti$_2$(**5**)(O*i*Pr)$_6$.

| Complex | Ti(**1**)$_2$(O*i*Pr)$_2$ | Ti(**2**)$_2$(O*i*Pr)$_2$ | Ti$_2$(**3**)(O*i*Pr)$_6$ | Ti$_2$(**4**)(O*i*Pr)$_6$ | Ti$_2$(**5**)(O*i*Pr)$_6$ |
|---|---|---|---|---|---|
| Empirical formula | $C_{20}H_{28}N_4O_4Ti$ | $C_{39}H_{67}N_4O_4Ti$ | $C_{55}H_{92}N_2O_8Ti_2$ | $C_{34}H_{56}N_2O_{10}Ti_2$ | $C_{44}H_{74}Br_2N_6O_8Ti_2$ |
| Formula mass | 436.36 | 703.87 | 1005.11 | 748.61 | 1070.71 |
| Crystal system | triclinic | monoclinic | triclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P\bar{1}$ | $C2/c$ | $C2/c$ |
| $a$ [Å] | 9.644(2) | 17.118(3) | 13.433(3) | 11.172(1) | 30.193(4) |
| $b$ [Å] | 10.188(3) | 13.160(2) | 14.276(3) | 15.376(2) | 9.862(1) |
| $c$ [Å] | 11.142(3) | 18.425(3) | 17.623(4) | 22.973(4) | 17.667(3) |
| $\alpha$ [°] | 97.437(1) | 90 | 77.595(1) | 90 | 90 |
| $\beta$ [°] | 92.913(1) | 98.237(1) | 72.174(1) | 95.451(1) | 95.214(1) |
| $\gamma$ [°] | 94.571(1) | 90 | 64.645(1) | 90 | 90 |
| $V$ [Å$^3$] | 1080.0(5) | 4107.8(1) | 2893.6(1) | 3928.5(9) | 5238.8(1) |
| $Z$ | 2 | 4 | 2 | 4 | 4 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.342 | 1.138 | 1.154 | 1.266 | 1.358 |
| Reflections collected | 12218 | 52194 | 37102 | 18362 | 33197 |
| $\theta$ range [°] | 3.28–27.50 | 3.61–27.49 | 3.65–25.68 | 3.56–26.37 | 3.82–27.51 |
| Independent reflections [$R_{int}$] | 4922 [0.0350] | 9332 [0.0793] | 10966 [0.1136] | 3934 [0.1257] | 5985 [0.044] |
| Goodness-of-fit | 1.002 | 1.045 | 1.025 | 1.029 | 1.057 |
| $R_1$,$wR_2$ [$I > 2\sigma(I)$][a] | 0.0374, 0.0975 | 0.0566, 0.1449 | 0.0683, 0.1630 | 0.0494, 0.1138 | 0.0340, 0.0810 |
| $R_1$, $wR_2$ [all data][a] | 0.0486, 0.1043 | 0.0890, 0.1648 | 0.1245, 0.1935 | 0.0787, 0.1289 | 0.0407, 0.0865 |

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

**Ti$_2$(4)(O*i*Pr)$_6$:** An analogous procedure to that for Ti$_2$(**3**)(O*i*Pr)$_6$ was followed. Yield 0.86 g (57%), m.p. 147–148 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 0.80 [2 overlaying doublets, $J$ = 6 Hz, 12 H, CH(C$H_3$)$_2$], 1.12 [2 overlaying doublets $J$ = 6 Hz, 12 H, CH(C$H_3$)$_2$], 1.23 [d, $J$ = 6 Hz, 6 H, CH(C$H_3$)$_2$], 1.32 [d, $J$ = 6 Hz, 6 H, CH(C$H_3$)$_2$], 3.84 (s, 6 H, OCH$_3$), 4.39 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 4.71 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 4.95 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 6.59 (m, 2 H, Ar-H), 6.85 (s, 2 H, Ar-H), 6.92 (s, 2 H, Ar-H), 7.87 (s, 2 H, NCH) ppm. $^{13}$C{$^1$H}($CDCl_3$): $\delta$ = 25.2 [CH(*C*H$_3$)$_2$], 26.1 [CH(*C*H$_3$)$_2$], 27.0 [CH(*C*H$_3$)$_2$], 27.2 [CH(*C*H$_3$)$_2$], 27.5 [CH(*C*H$_3$)$_2$], 27.5 [CH(*C*H$_3$)$_2$], 59.4 (OCH$_3$), 76.3 [*C*H(CH$_3$)$_2$], 79.6 [*C*H(CH$_3$)$_2$], 80.7 [*C*H(CH$_3$)$_2$], 118.1, 120.6, 122.2, 126.1, 151.5 (Ar), 152.8 (NCH), 158.8 (Ar-O). $C_{34}H_{56}N_2O_{10}Ti_2$ (748.6): calcd. C 54.6, H 7.54, N 3.74; found C 54.5, H 7.49, N 3.69.

**Ti$_2$(5)(O*i*Pr)$_6$:** An analogous procedure to that for Ti$_2$(**3**)(O*i*Pr)$_6$ was followed. Yield 0.89 g (83%), m.p. 175–179 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 0.80 [2 overlaying doublets, $J$ = 6 Hz, 12 H, CH(C$H_3$)$_2$], 0.99 [d, $J$ = 6 Hz, 6 H, CH(C$H_3$)$_2$], 1.12 [d, $J$ = 6 Hz, 6 H, CH(C$H_3$)$_2$], 1.24 [2 overlaying doublets, $J$ = 6 Hz, 12 H, CH(C$H_3$)$_2$], 2.24 [s, 6 H, NCH$_3$], 2.41 [br. m, 16 H, piperazine CH$_2$], 3.47–3.68 [m, 4 H, NCH$_2$Ph], 4.34 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 4.64 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 4.89 [sept, $J$ = 6 Hz, 2 H, C$H$(CH$_3$)$_2$], 7.20 [s, 2 H, Ar-H], 7.53 (s, 2 H, Ar-H), 7.74 (s, 2 H, NCH) ppm. $^{13}$C{$^1$H} ($CDCl_3$): $\delta$ = 22.8 [CH(*C*H$_3$)$_2$], 23.1 [CH(*C*H$_3$)$_2$], 24.6 [CH(*C*H$_3$)$_2$], 24.8 [CH(*C*H$_3$)$_2$], 24.9 [CH(*C*H$_3$)$_2$], 24.9 [CH(*C*H$_3$)$_2$], 45.2 [NCH$_3$], 52.3, 54.3 (piperazine CH$_2$), 55.0 (N*C*H$_2$Ar), 73.8 [*C*H(CH$_3$)$_2$], 77.0 [*C*H(CH$_3$)$_2$], 78.0 [*C*H(CH$_3$)$_2$], 106.9, 119.9, 129.5, 131.3, 135.7 (Ar), 149.0 (NCH), 161.5 (Ar-O) ppm. $C_{44}H_{74}N_6O_8Ti_2Br_2$ (1070.6): calcd. C 49.4, H 6.97, N 7.85; found C 48.1, H 6.61, N 7.52.

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