Peripheral Electrophilic Properties of Dichloro[*NN'*-ethylenebis(salicylideneiminato)]titanium(IV): A Route leading to a Stable Ti–H–B Unit †

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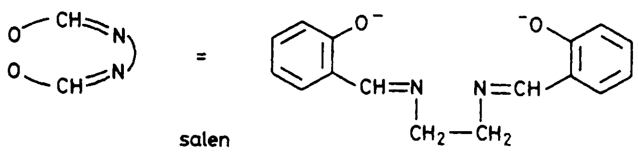
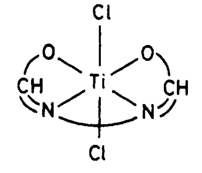
The title complex [Ti(salen)Cl$_2$] (1) [salen = *NN'*-ethylenebis(salicylideneiminate)] reacts with a thf solution of LiBH$_4$ to give [{Ti(salen)(BH$_4$)$_2$}$_2$]·2thf (2) as an orange crystalline solid. Complex (2) is formed by the substitution of Cl$^-$ by BH$_4^-$ followed by addition of BH$_4^-$ to the imino-groups of the salen ligand. The i.r. spectrum shows the disappearance of bands due to –C=N– and the presence of strong bands due to Ti–H and B–H vibrations, which are shifted to lower values in the deuteriated derivative [{Ti(salen)(BD$_4$)$_2$}$_2$]·thf (3). Crystals of (2) are formed in dimeric units having crystallographic $C_i(\bar{1})$ symmetry. Each metal atom surrounded by the sexidentate ligand (salen)(BH$_4$)$_2$ having a H$_2$N$_2$O$_2$ set of donor atoms achieves seven-co-ordination by sharing one of the salen oxygens with the other titanium of the dimeric unit. Other relevant structural features of complex (2) are the presence of BNH$_2$ groups bonded to titanium through a bridging hydrogen, and the consequent existence of two electron-deficient four-membered rings, B–H–Ti–N. The Ti(salen)(BH$_4$)$_2$ unit is supposed to form from a titanium-promoted activation of the >C=N– bond in [Ti(salen)Cl$_2$]. [{Ti(salen)(BH$_4$)$_2$}$_2$]·2thf (2) crystallises in the space group $P2_1/c$ with a = 11.802(9), b = 20.039(15), c = 9.272(6) Å, β = 90.00(5)°, and Z = 2. The final R factor was 0.068 for 1 028 observed reflections.

It is well known that polydentate, unsaturated ligands like the *NN'*-ethylenebis(salicylideneiminate) dianion (salen) provide rigid co-ordination spheres for the metal as well as the unusual stabilization of a wide range of oxidation states.[1] This depends on the possible multiple metal–ligand interaction involving both the donor atoms and the π orbitals of the delocalised ligand. The electronic flexibility of the ligand leads to the peculiar properties of some cobalt and iron complexes. They undergo easy redox processes including those related to the reversible co-ordination of small molecules such as O$_2$,[2] CO$_2$,[3] S$_2$,[4] and the stabilization of metal–carbon σ bonds.[5] Redox reactions carried out on transition metal chelate complexes lead either to the change in the oxidation state of the metal or to the generation of electrophilic and nucleophilic sites on the ligand.[6] Since titanium in a low oxidation state is able to promote the co-ordination and the activation of small molecules like N$_2$, CO, and H$_2$,[7] our attention was focused on some precursors of low-valent titanium complexes, containing ligands, such as salen, which stabilize various oxidation states of the metal.[8] For this purpose, [Ti(salen)Cl$_2$] (1)[9] can be regarded as an interesting starting parent compound for low-valent titanium complexes and for organometallic derivatives of titanium(IV). Reduction of [Ti(salen)Cl$_2$] to the corresponding titanium(III) complex, [Ti(salen)Cl], was achieved by zinc metal.[10]

The present paper reports the reaction of complex (1) with LiBH$_4$ leading to the addition of BH$_4^-$ to the salen ligand rather than to the expected reduction of the metal. A novel sexidentate ligand co-ordinates titanium with a H$_2$N$_2$O$_2$ set of donor atoms. Some of these results have been briefly communicated.[11]





[Ti(salen)Cl$_2$] (1)

Experimental

Unless otherwise stated, all the reactions described were carried out under an atmosphere of purified nitrogen; solvents were purified by standard methods. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Magnetic susceptibility measurements were carried out with a Faraday balance. Dichloro[*NN'*-ethylenebis(salicylideneiminato)]-titanium(IV)[9] was prepared by an improved method given below. Lithium tetrahydroborate was recrystallized from Et$_2$O.

Dichloro[NN'-*ethylenebis*(*salicylideneiminato*)]*titanium*(IV).—*NN'*-Ethylenebis(salicylideneimine), H$_2$salen (14.90 g, 55.60 mmol), suspended in tetrahydrofuran (thf) (100 cm^3) was reacted with a toluene (25 cm^3) solution of TiCl$_4$ (6.0 cm^3, 54.50 mmol). The final red-orange suspension was refluxed for 30 min, the solvent completely evaporated, and the red solid dried *in vacuo*. The solid residue recovered using a water–acetone mixture (1 : 1) was rapidly filtered in air, washed with acetone, and dried *in vacuo* (19.3 g) (Found: C, 49.85; H,

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† *Supplementary data available* (No. SUP 23393, 13 pp.): observed and calculated structure factors, thermal parameters for non-H atoms, atomic co-ordinates and thermal parameters for H atoms and thf, bond distances and angles for salen, thf. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Final fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Ti	0.934 9(4)	−0.066 5(2)	0.429 2(6)
O(1)	0.918 4(15)	0.007 4(7)	0.571 2(17)
O(2)	1.028 3(14)	−0.134 5(8)	0.481 7(21)
N(1)	0.810 0(18)	−0.015 2(10)	0.306 2(24)
N(2)	0.829 0(19)	−0.147 7(10)	0.357 8(24)
C(1)	0.814 7(27)	0.029 9(13)	0.616 7(34)
C(2)	0.787 3(28)	0.030 7(12)	0.760 1(40)
C(3)	0.682 5(37)	0.054 3(19)	0.802 3(40)
C(4)	0.607 3(27)	0.077 7(19)	0.696 8(58)
C(5)	0.634 4(30)	0.075 8(17)	0.555 3(45)
C(6)	0.739 0(29)	0.052 9(14)	0.514 5(38)
C(7)	0.774 3(25)	0.051 8(12)	0.362 9(39)
C(8)	0.709 2(22)	−0.055 0(13)	0.274 4(31)
C(9)	0.744 7(24)	−0.127 9(13)	0.246 8(32)
C(10)	0.884 2(26)	−0.211 2(12)	0.306 9(29)
C(11)	0.969 9(24)	−0.241 2(14)	0.399 5(30)
C(12)	0.988 6(31)	−0.311 3(14)	0.403 6(32)
C(13)	1.072 6(33)	−0.338 0(16)	0.483 6(44)
C(14)	1.138 9(30)	−0.299 4(15)	0.570 1(41)
C(15)	1.126 9(24)	−0.229 3(13)	0.571 5(32)
C(16)	1.040 1(27)	−0.202 8(13)	0.482 9(35)
B(1)	0.899 2(31)	−0.019 3(16)	0.188 9(38)
B(2)	0.784 2(26)	−0.147 2(16)	0.515 8(37)

3.55; N, Cl, 18.65; 7.30. $C_{16}H_{14}Cl_2N_2O_2Ti$ requires C, 49.85; H, 3.65; Cl, 18.45; N, 7.25%.)

Reaction of [Ti(salen)Cl_2] (1) *with* $LiBH_4$.—Solid [Ti(salen)Cl_2] (6.75 g, 17.53 mmol) was added to a thf (100 cm^3) solution of $LiBH_4$ (1.04 g, 47.82 mmol). The red solid dissolved giving (20 min) an orange solution, from which an orange crystalline solid separated (5.10 g) on standing as [{Ti(salen)$(BH_4)_2$}$_2$]·*x*thf (2) containing variable amounts of thf depending on the crystallization rate. An *X*-ray analysis was carried out on [{Ti(salen)$(BH_4)_2$}$_2$]·2thf (Found: C, 57.55; H, 7.10; N, 6.85. $C_{40}H_{60}B_4N_4O_6Ti_2$ requires C, 57.75; H, 7.20; N, 6.75%). Complex (2) is diamagnetic, insoluble in hydrocarbons, and decomposes by the action of co-ordinating solvents. The i.r. spectrum [Nujol and poly(chlorotrifluoroethylene) mulls] shows strong B–H and Ti–H bands at 2 460s, 2 410s, 2 325m, 1 995ms, and 1 820 cm^{-1} and the absence of any C–N bands at around 1 600 cm^{-1}. The deuteriated form of the final complex, [{Ti(salen)$(BD_4)_2$}$_2$]·thf (3), was prepared by the same procedure using a thf solution of $LiBD_4$. The i.r. spectrum shows B–D and Ti–D bands at 1 885, 1 780, 1 735, and 1 295 cm^{-1}.

X-*Ray Structural Analysis*.—The crystals of complex (2) are red-orange plates up to 0.3 mm in length. Weissenberg and precession photographs showed 2/*m* diffraction symmetry and systematic extinctions indicated the space group $P2_1/c$. The diffraction pattern was characterized by sharp spots superimposed to streaking along the a^* axis direction. A crystal of (2) (0.1 × 0.15 × 0.2 mm) was chosen for intensity data collection and sealed in a Lindemann capillary.

Crystal data. $C_{32}H_{44}B_4N_4O_4Ti_2{\cdot}2C_4H_8O$, $M = 831.99$, Monoclinic, $a = 11.802(9)$, $b = 20.039(15)$, $c = 9.272(6)$ Å, $\beta = 90.00(5)°$, $U = 2\,192.8$ Å^3, $Z = 2$, $D_c = 1.26$ g cm^{-3}, and $F(000) = 880$.

Structure determination and refinement. X-Ray data were collected on a Philips PW 1100 single-crystal automatic diffractometer, using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å, $\mu = 4.05$ cm^{-1}) employing the θ—2θ scan technique in the range 5.3—40° with a maximum scan time of 40 s. A reflection was monitored after every 100 data collected and no apparent decay in intensity was detected. 1 093 Independent reflections were collected of which 1 028 [$F_o > 3\sigma(F_o)$] contributed to the last cycles of refinement.

Integrated intensities were corrected for Lorentz and polarization effects but not for absorption in view of the small dimensions of the crystal and low absorption coefficient. The structure was solved by standard Patterson and Fourier methods and all non-hydrogen atoms of the Ti(salen)$(BH_4)_2$ moiety were located. After some block-matrix least-squares cycles, which reduced the *R* factor to 0.11, a difference-Fourier map showed five peaks attributed to the thf heavy atoms and those of boron hydrogens bonded to titanium. The other hydrogen atoms were introduced in calculated positions according to the usual sp^2 or sp^3 geometry. The final full-matrix least-squares cycles, with anisotropic thermal parameters for heavy atoms and isotropic fixed parameters for hydrogens employing the weighting scheme $w = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$, gave a final *R* of 0.068. In the last cycle 228 parameters were refined using unit weights. Neutral-atom scattering values were taken from ref. 12 for non-hydrogen atoms and from ref. 13 for hydrogen atoms. Calculations were performed using programs contained in the *X*-RAY system,[14] at the CNUCE of Pisa on an IBM 370/158 computer. Final atomic co-ordinates of complex (2) are listed in Table 1, selected bond distances and angles are given in Table 2.

Results and Discussion

The complex [Ti(salen)Cl_2] (1) reacts with a thf solution of $LiBH_4$ according to equation (i). Complex (1) dissolved producing an orange-yellow solution, from which (2) crystallized out as orange crystals containing variable amounts of solvents.

$$\underset{(1)}{[\mathrm{Ti(salen)Cl_2}]} + 2\,\mathrm{LiBH_4} \xrightarrow{\mathrm{thf}} \tfrac{1}{2}\,\underset{(2)}{[\{\mathrm{Ti(salen)(BH_4)_2}\}_2]{\cdot}x\mathrm{thf}} + 2\,\mathrm{LiCl} \qquad \text{(i)}$$

Reaction (i) must be carried out with an excess of $LiBH_4$, since a $LiBH_4$–Ti mol ratio lower than 2 : 1 produces deep green solutions containing titanium(III) species (see below). Complex (2) is diamagnetic as expected for a titanium(IV) derivative. Its i.r. spectrum [Nujol and poly(chlorotrifluoroethylene) mulls] shows the absence of any C=N band in the 1 600 cm^{-1} region, with strong bands appearing between 2 500 and 1 800 cm^{-1}. The nature of (2) and the occurrence of reaction (i) can be explained on the basis of an *X*-ray analysis carried out on [{Ti(salen)$(BH_4)_2$}$_2$]·2thf.

The crystals are composed of dimeric units (Figure 1) having $C_i(1)$ symmetry, packed with thf molecules. The packing of this structure shown in Figure 2 deserves some comments. The crystal packing consists of layers of [{Ti(salen)$(BH_4)_2$}$_2$] molecules lying on *bc* planes at *a* = 0, 1, 2, *etc.*; Figure 2 shows this arrangement viewed along the *c* axis. Tetrahydrofuran molecules fill the holes resulting at $a = \frac{1}{2}, \frac{3}{2}$, *etc.* in a wafer-like arrangement, without any bond interaction involving the titanium complex, the shortest distances being greater than 2.4 Å. Boron hydrogen atoms (Figure 2), pointed towards the thf molecule, are in fact shifted $\frac{1}{2}$ along the *c* direction. This probably agrees with the absence of any preferred orientation for thf molecules, allowing some extent of disorder in the packing of thf units.

To emphasize the various structural peculiarities of the structure shown in Figure 1, a simplified sketch of the dimeric complex (2) is shown below.The donor atoms bonding titanium are provided by the new sexidentate ligand formed from the addition of two BH_4^- groups to the imino-units of the

Table 2. Selected bond distances (Å) and angles (°) for complex (2)

Ti–O(1)	1.99(2)	N(1)–B(1)	1.52(4)	H(1B1)–Ti–O(1)	125.0(1.0)	C(1)–O(1)–Ti	122.0(2.0)
Ti–O(1′)	2.10(2)	N(1)–C(8)	1.46(3)	H(1B1)–Ti–O(1′)	74.0(8.0)	C(1)–O(1)–Ti′	123.0(1.0)
Ti–O(2)	1.82(2)	C(8)–C(9)	1.54(4)	H(1B1)–Ti–O(2)	101.0(1.0)	Ti–O(1)–Ti′	109.8(8)
Ti–N(1)	2.13(2)	C(9)–N(2)	1.49(4)	H(1B1)–Ti–N(1)	67.0(2.0)	C(16)–O(2)–Ti	144.0(2.0)
Ti–N(2)	2.16(2)	N(2)–B(2)	1.56(4)	H(1B1)–Ti–N(2)	86.0(2.0)	C(7)–N(1)–B(1)	120.0(2.0)
Ti–H(1B1)	1.84(10)	N(2)–C(10)	1.52(3)	H(1B1)–Ti–H(1B2)	151.0(8.0)	C(8)–N(1)–B(1)	113.0(2.0)
Ti–H(1B2)	1.85(10)	C(10)–C(11)	1.45(4)	O(1)–Ti–O(1′)	70.2(7)	Ti–N(1)–B(1)	83.0(2.0)
O(1)–C(1)	1.37(4)	C(11)–C(12)	1.42(4)	O(1)–Ti–N(1)	85.9(8)	C(7)–N(1)–C(8)	109.0(2.0)
C(1)–C(2)	1.37(5)	C(11)–C(16)	1.37(4)	O(1)–Ti–N(2)	135.1(8)	Ti–N(1)–C(7)	116.0(2.0)
C(1)–C(6)	1.38(5)	C(12)–C(13)	1.35(5)	O(1)–Ti–O(2)	116.1(8)	Ti–N(1)–C(8)	114.0(2.0)
C(2)–C(3)	1.38(5)	C(13)–C(14)	1.36(5)	O(1)–Ti–H(1B2)	69.0(2.0)	C(9)–N(2)–Ti	114.0(2.0)
C(3)–C(4)	1.40(6)	C(14)–C(15)	1.41(4)	N(1)–Ti–N(2)	78.4(8)	C(9)–N(2)–C(10)	107.0(2.0)
C(4)–C(5)	1.35(7)	C(15)–C(16)	1.42(4)	N(1)–Ti–O(2)	157.7(9)	Ti–N(2)–C(10)	119.0(2.0)
C(5)–C(6)	1.37(5)	C(16)–O(2)	1.38(3)	N(1)–Ti–O(1′)	107.3(7)	C(9)–N(2)–B(2)	115.0(2.0)
C(6)–C(7)	1.47(5)	B(1)–H(1B1)	1.23(12)	N(2)–Ti–H(1B2)	92.0(2.0)	C(10)–N(2)–B(2)	116.0(2.0)
C(7)–N(1)	1.50(3)	B(2)–H(1B2)	1.42(12)	N(2)–Ti–O(2)	82.4(8)	Ti–N(2)–B(2)	84.0(1.0)
B(1)–H(2B1)	0.99(14)	B(2)–H(2B2)	1.33(13)	N(2)–Ti–O(1′)	154.7(8)	N(1)–C(7)–C(6)	115.0(2.0)
B(1)–H(3B1)	0.84(13)	B(2)–H(3B2)	1.11(13)	N(2)–Ti–H(1B2)	70.0(2.0)	N(2)–C(10)–C(11)	117.0(2.0)
				O(2)–Ti–O(1′)	85.6(7)	N(1)–B(1)–H(1B1)	105.0(4.0)
				O(2)–Ti–H(1B2)	92.0(2.0)	N(2)–B(2)–H(1B2)	103.0(4.0)
				O(1′)–Ti–H(1B2)	132.0(2.0)	B(1)–H(1B1)–Ti	104.0(4.0)
						B(2)–H(1B2)–Ti	101.0(4.0)

Primed atoms denote the transformation 2 − *x*, −*y*, 1 − *z*.

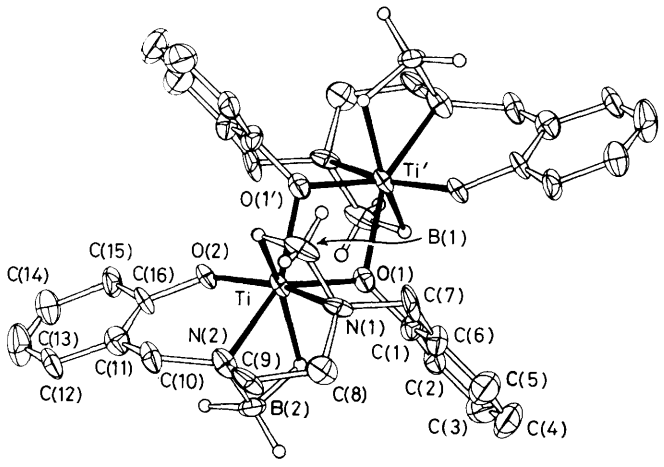
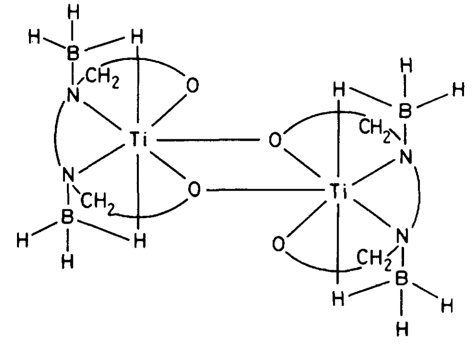


Figure 1. ORTEP drawing of $[\{Ti(salen)(BH_4)_2\}_2]$. The thermal ellipsoids probability is 30%

salen ligand. The seventh co-ordination site around each titanium is filled by an oxygen atom from an adjacent (salen)$(BH_4)_2$ unit. The salen unit is no longer planar, and the C–N bond distances correspond to a single bond [C(7)–N(1) 1.50(3) and C(10)–N(2) 1.52(3) Å]. These values along with the tetrahedral geometry around C(7), N(1), N(2), and C(10) confirm the reduction of the salen ligand. The $H_2N_2O_3$ set of donor atoms describes a distorted capped octahedron as shown in Figure 3, while dihedral angles between the co-ordination polyhedron faces are given in Table 3.

The Ti–O and Ti–N bond distances (Table 2) within each monomeric unit fall in the usual range and they compare well with those found for $[Ti(salen)Cl_2]$ [15] and [Ti(salen)Cl(py)] (py = pyridine).[10] The bridging oxygen atom is bonded at a significantly longer distance [Ti–O(1′) 2.10(2) Å]. The NBH_2 groups bond titanium at a rather short distance with a single hydrogen atom [Ti–H(1B1) 1.84(10) and Ti–H(1B2) 1.85(10) Å].[16] Although rather approximate, because of the high standard deviations, these values indicate a strong titanium–hydrogen interaction. This makes the corresponding B–H bonds weaker [B(1)–H(1B1) 1.23(12) and B(2)–H(1B2) 1.42(12) Å] compared with B–H bond distances for the terminal hydrogens not involved in binding titanium [B(1)–H(2B1) 0.99(14), B(1)–H(3B1) 0.84(13), B(2)–H(2B2), 1.33(13), B(2)–H(3B2) 1.11(13) Å] (Table 2). The bonding mode of the NBH_2 groups generates two four-membered rings containing six valence electrons for four two-centre bonds.



The electronic picture for such electron-deficient units is very close to that usually employed for the BH_2B unit in borane chemistry.

The most significant spectroscopic information on complex (2) comes from the i.r. spectrum, whose analysis, however, is made difficult because of strong absorptions in the region 1 600—800 cm^{-1} due to the organic ligand. In the region free from the complex absorption of the organic ligand, strong bands occur at 2 460s, 2 410s, 2 325m (sh), 1 995ms, and 1 820ms cm^{-1} which are shifted in the corresponding deuteriated analogue $[\{Ti(salen)(BD_4)_2\}_2]$·thf (3), down to 1 885, 1 780, 1 735, and 1 295 cm^{-1}. The ν_H/ν_D isotopic shifts range between 1.33 and 1.35 [17] for the first three bands to 1.41 for the fifth, while we were unable to identify the shifted absorption due to the vibration observed at 1 995 cm^{-1} in complex (2). On the basis of the isotopic shifts we can attribute the first three bands to B–H stretching modes, the higher two being due to the terminal hydrogens (t), while the

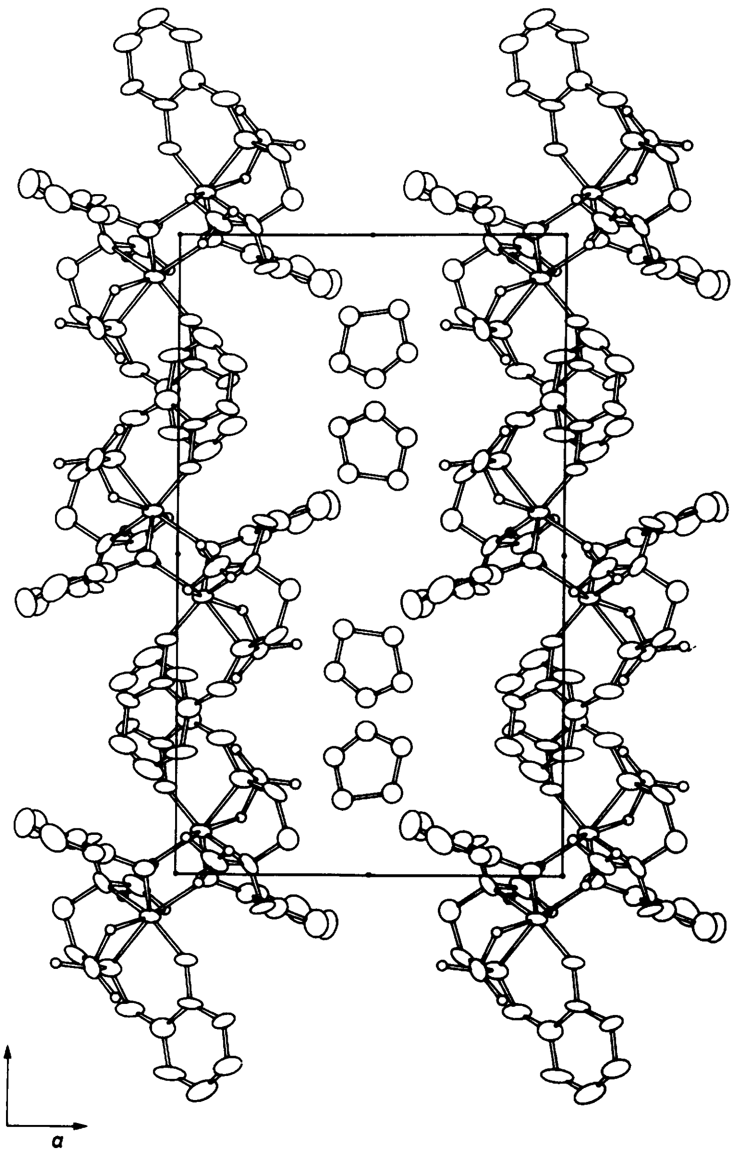


Figure 2. The crystal packing projected along the *c* axis. The thermal ellipsoids probability is 50%

Table 3. Dihedral angles (°) between the co-ordination polyhedron faces

		(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
H(1B1)-N(2)-N(1)	(A)								
N(1)-H(1B2)-N(2)	(B)	109.3							
N(2)-H(1B2)-O(2)	(C)		104.3						
N(2)-H(1B1)-O(2)	(D)	122.7		103.5					
O(2)-H(1B2)-O(1)	(E)			124.5					
O(2)-O(1)-O(1′)	(F)					159.7			
O(1′)-O(1)-N(1)	(G)						82.7		
O(1′)-N(1)-H(1B1)	(H)	106.9						155.1	
N(1)-H(1B2)-O(1)	(I)		144.1			91.8		110.7	
H(1B1)-O(2)-O(1′)	(L)				142.3		96.1		98.5

Primed atoms denote the transformation $2 - x, -y, 1 - z$

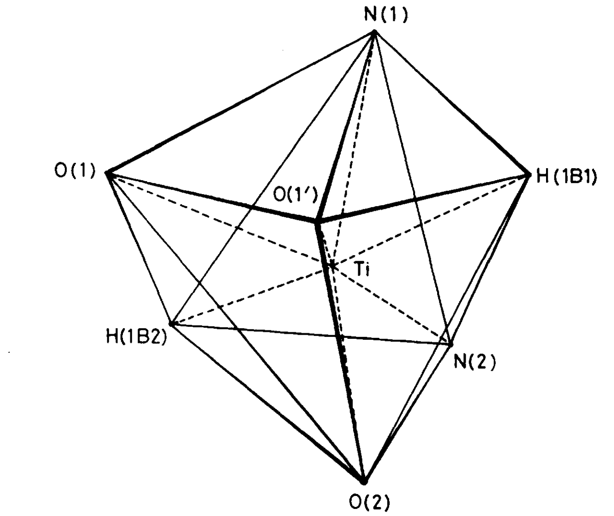
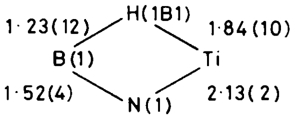
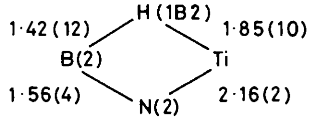
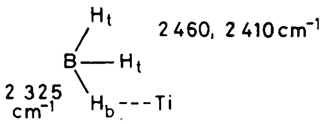
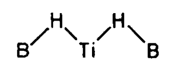


Figure 3. Co-ordination polyhedron around titanium atom. The triangular face O(1)–H(1B1)–O(2) of the original octahedron is modified by the presence of the capping atom O(1′)

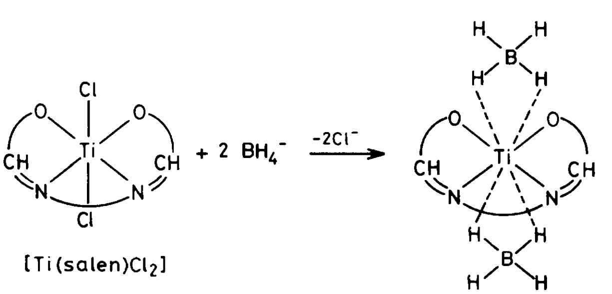








1 995, 1 820 cm^{-1}



(ii)

[Ti(salen)Cl$_2$]

(4)

third belongs to the bridging (b). The stretching bands at 1 995 and 1 820 cm^{-1} must be considered as the asymmetric and symmetric vibrations due to the TiH$_2$ unit sketched above. Since (2) is not soluble in hydrocarbons and it is decomposed by co-ordinating solvents, any dynamic inspection of it by n.m.r. spectroscopy is prevented.

The structural characteristics of (2) however, allow consideration of the Ti–HBH$_2$ unit as a potential source for the so far unreported titanium-hydrido species.[7]

Complex (2) can be assumed to be a potential reducing agent.[18] The reducing properties of (2) have been observed when reaction (i) is carried out with a LiBH$_4$–Ti mol ratio of lower than 2:1. In these conditions, evolution of H$_2$ is observed, along with the appearance of a green colour diagnostic for the presence of titanium(III) or titanium(II) species. The same results have been observed reacting (1) with (2) in thf.

Such a reaction produces a mixture of titanium complexes whose isolation and identification was, however, unsuccessful. Formation of complex (2) can be viewed as a metal-assisted reduction of the metal-bonded salen. This is relevant to all reductions carried out using BH$_4^-$ species requiring a transition-metal catalyst.[18]

Therefore reaction (i) can be described as involving two well separated steps: (*a*) the substitution of Cl$^-$ by BH$_4^-$ to form (4), reaction (ii), and (*b*) where (2) is formed from the addition of BH$_4^-$ to the –CH=N– units of the salen ligand. The electrophilic nature of the C=N bond is enhanced by an acidic titanium(IV) making this transfer easier.[19]

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