Synthesis and *X*-Ray Crystal Structure of the Dimeric Compound $[C_{16}H_{16}N_2O_2Ti(BH_3)_2]_2$, a Dimer of *NN'*-Ethylenebis(salicylidenaminato)titanium Containing Seven-co-ordinate Titanium(IV) and Amino-borane as Donor Groups

By Giuseppe Fachinetti, Carlo Floriani,* Marcello Mellini, and Stefano Merlino

(*Istituto di Chimica Generale ed Istituto di Mineralogia, Università di Pisa,* 56100 *Pisa, Italy*)

Summary The reaction of dichloro-*NN'*-ethylenebis(salicylidenaminato)titanium(IV), [Ti(salen)Cl_2], with lithium tetrahydroborate gave, *via* addition of BH_4^- to the imino-functions of the ligand, a dimeric seven-co-ordinate titanium(IV) compound containing amine-boranes as donor groups; its crystal and molecular structure together with spectroscopic data are reported.

Some organometallic derivatives of titanium in low oxidation states are powerful species for the activation of normally unreactive molecules, *e.g.*, N_2, CO, and H_2[1] or those containing covalent bonds.[2] These reports do not include any study of the chemical behaviour when titanium is co-ordinated with a polydentate or macrocyclic ligand. It is well known that Schiff's base complexes of various transition metals interact with small molecules, such as O_2,[3] CO_2,[4] and CO.[5]

Dichloro-*NN'*-ethylenebis(salicylidenaminato)titanium(IV), [Ti(salen)Cl_2], $C_{16}H_{14}Cl_2N_2O_2Ti$, (I),[6] may be considered a suitable 'model' both for investigating the reactivity of titanium carrying an unusual ligand's environment, and for obtaining reduced titanium species. We report the reaction of (I) with one of the most common inorganic reducing agent, BH_4^-, which gave unexpected results.

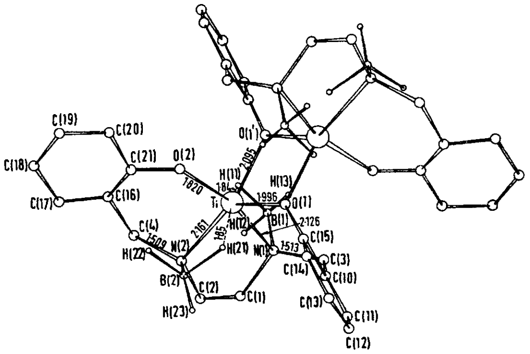


Figure 1. The structure of (II).

The reaction of (I) with an excess of lithium tetrahydroborate in tetrahydrofuran (THF) gave an orange solution from which orange crystals of an air-stable, diamagnetic compound, having molecular formula $[C_{16}H_{16}N_2O_2Ti(BH_3)_2]_2$†

---

† By slow crystallisation from THF, (II) was obtained as a THF adduct.

(II), were obtained in 60% yield. The i.r. spectra of (II) do not show the C=N band around 1610—1630 cm^{-1} which suggests that the reaction results in the reduction of the imino-groups. No change in the oxidation state of the metal occurs. The insolubility of (II) in hydrocarbons and its decomposition in basic solvents prevented n.m.r. spectroscopic measurements.

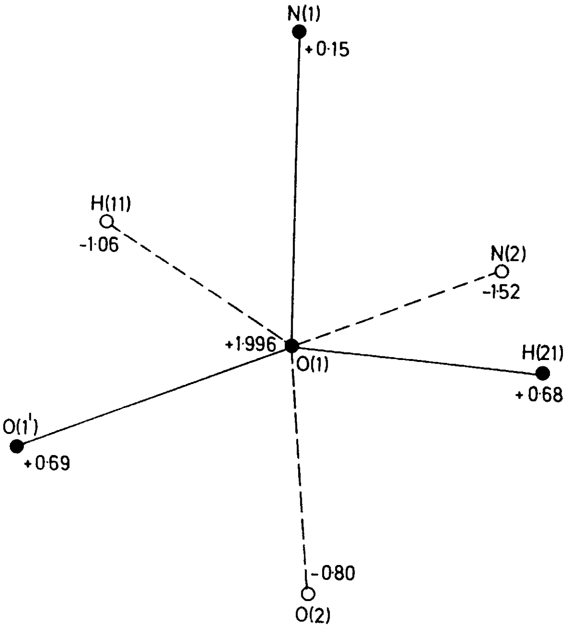
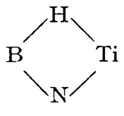


Figure 2. The capped octahedral geometry around Ti viewed along the Ti–O(1) bond in (II).

Crystal data: (II)·2THF, $C_{40}H_{60}B_4N_4O_6Ti_2{\cdot}C_8H_{16}O_2$, monoclinic, space group $P2_1/c$; $a = 11{\cdot}802(3)$, $b = 20{\cdot}039(7)$, $c = 9{\cdot}272(3)$ Å; $\beta = 90{\cdot}0°\ 3'$, $D_c = 1{\cdot}25$ g cm^{-3}, $Z = 2$. The intensity measurements were collected on a Philips diffractometer (PW 1100) up to $2\theta = 30°$ (Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å). The structure was solved by Patterson and Fourier methods. A Fourier difference synthesis revealed all the hydrogen atoms except those of the THF molecule affected by some kind of disorder. The final reliability index R was 0·05. The crystals are composed of discrete dimeric molecules with $C_i(\bar{1})$ symmetry packed with THF molecules.

The structure of (II) is shown in Figure 1 which also shows some relevant bond lengths (standard deviations: Ti–O, 0·008 and Ti–N, 0·012 Å). The geometrical arrangement around titanium of the $H_2N_2O_3$ set of donor atoms can be described in terms of idealised structure of a capped octahedron. Figure 2 shows the inner co-ordination geometry of titanium viewed along the Ti–O(1) bond. The B–H, B–N, Ti–N, and Ti–O bond distances are in the usual range. The geometry around N and B is tetrahedral. The C(3)–N(1) and C(4)–N(2) distances as well as the tetrahedral geometry around C(3) and C(4) confirmed the reduction of the Schiff's base. Strong Ti–H interaction results from the short observed bond length, although this conclusion must be considered tentative in view of the high standard deviation (Ti–H, 0·15 Å) as compared with the Ti–H bond distances [1·75(8) Å] in $[(\eta^5\text{-}C_5H_5)_2TiH_2BH_2]$.[7] It seems relevant to note the existence of the electron-deficient four-membered rings (A) containing six electrons for bond formation. The i.r. spectrum [Nujol and poly(chlorotrifluoroethylene) mulls] showed, in the region free from the complex absorption by the organic ligand, bands [2460s, 2410s, 2325m, sh, 1995m, s, and 1820m, s cm^{-1}] due to H_2BHTi units, as confirmed by the shifted bands in the deuteriated complex, $[C_{16}H_{14}D_2N_2O_2Ti(BD_3)_2]_2$ (III), [1855, 1780, 1735, and 1295 cm^{-1}]. The absorption assignable (1820 cm^{-1}) to the Ti–H stretching mode showed a larger shift ($\nu_H/\nu_D = 1{\cdot}41$) compared to those due to B–H stretching vibrations (1·33—1·35).[8]



(A)

The stable transition metal tetrahydroborate complexes may be considered as a model for understanding the detailed manner in which BH_4^- acts as a reducing agent for the metal. Complexes like (II) can be considered as the intermediate 'models' for explaining the metal-catalysed reduction of some organic species by BH^-_4.[9] The metal-promoted reduction or hydrolysis of co-ordinated Schiff's base may be examples of the general metal–ion catalysis of nucleophilic organic reactions.[10]

Support from the C.N.R. (Rome) is acknowledged.

(*Received, 26th January* 1976; *Com.* 076.)

---

[1] E. E. van Tamelen, *Accounts Chem. Res.*, 1970, **3**, 361; J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1972, **94**, 1219; J. E. Bercaw, *ibid.*, 1974, **96**, 5087.

[2] G. Fachinetti and C. Florinani, *J.C.S. Chem. Comm.*, 1972, 790; *ibid.*, 1974, 66; *J.C.S. Dalton*, 1974, 2433.

[3] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946; A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55.

[4] C. Floriani and G. Fachinetti, *J.C.S. Chem. Comm.*, 1974, 615.

[5] V. L. Goedken and S. M. Peng, *J.C.S. Chem. Comm.*, 1974, 914, and references therein.

[6] G. Gilli, D. W. J. Cruickshank, R. L. Beddoes, and O. S. Mills, *Acta Cryst.*, 1972, **B28**, 1889; N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3847

[7] K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.*, 1973, **12**, 232.

[8] N. Davies, B. D. James, and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1969, 2601; S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, 1968, **7**, 1051.

[9] I. I. Creaser and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1975, 974.

[10] M. L. Bender, *Adv. Chem. Series*, 1963, **37**, 19.