A coordination network based on d^0 transition-metal centers: synthesis and structure of the [2,4]-connected layered compound $[(TiCl_4)_2Si(C_6H_4CN\text{-}p)_4]\cdot1.5C_7H_8$

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The tetrafunctional silane $Si(C_6H_4CN\text{-}p)_4$ forms a coordination network with $TiCl_4$ consisting of 4,2-connected layers containing large (56 atom) rings.

There has been considerable recent interest in the construction and study of coordination networks based on coordinate bonds between polyfunctional ligands and various metal centers.[1–8] These materials often possess well defined (crystalline) structures which are related to those for more condensed mineral phases such as diamond,[1] $SrSi_2$,[9] α-$ThSi_2$,[10] rutile[11] and PtS.[12] Since coordination networks may possess large pores or channels,[12,13] which in principle might contain strategically located transition metal centers, there is interest in developing such systems as selective, heterogeneous catalysts.[14] A few reports have appeared on the use of tetrahedral ligands, in combination with Cu and Ag, as building blocks for construction of coordination networks.[1,2] Our work in this area is based on the tetrafunctional silane $Si(C_6H_4CN\text{-}p)_4$ **1**, which has been used to prepare Ag-containing networks.[15]

To our knowledge, there have been no reports on three-dimensional coordination networks based on early transition metal d^0 centers. Such materials might be expected to function as catalysts for a variety of reactions, including alkene polymerization.[16] Here we report initial efforts in this area, involving the synthesis and characterization of the titanium-containing network solid $[(TiCl_4)_2Si(C_6H_4CN\text{-}p)_4]\cdot1.5C_7H_8$, which has a layered structure related to that of α-HgI_2.

Layering a solution of $TiCl_4$ (2 equiv.) in benzene over a solution of **1** in dichloromethane resulted in the slow precipitation of a yellow solid, which was isolated by filtration after 5 d and dried under vacuum for 4 h. By combustion and ¹H NMR analysis, this material is formulated as $(TiCl_4)_2Si(C_6H_4CN\text{-}p)_4\cdot0.6C_6H_6$ **2a**.† Light-yellow crystals of **2b** were obtained in 55% yield by heating a sealed tube containing **2a** and toluene to 140 °C for 10 h, followed by slow cooling over 6 h to room temp.‡ The IR spectrum of **2b** exhibits bands for the nitrile groups which are blue shifted to 2231 and 2271 cm^{-1} with respect to the band for the tetrahedral ligand **1** (ν_{CN} 2229 cm^{-1}).[17]

The structure of **2b** consists of [4,2]-connected infinite layers formed by the linking of molecules of **1** by $TiCl_4$ units (Fig. 1).§ Each molecule of **1** is coordinated to four Ti centers, each of which links two units of **1** via cis-coordination of nitrile groups in the roughly octahedral titanium coordination sphere. There are two independent Ti centers in the unit cell, which possess slightly different bond distances and angles. The octahedral coordination geometries for the independent titanium centers are significantly distorted such that the 'trans' chloride ligands form Cl–Ti–Cl angles of 162.31(3) and 160.67(7)°. These chloride ligands are associated with Ti–Cl distances [2.253(2)–2.310(2) Å] which are longer than those for chloride ligands trans to the nitrile groups [2.209(2)–2.241(2) Å]. The silicon centers are in distorted tetrahedral environments, such that the C–Si–C bond angles range from 103.2(2)–113.7(2)°. The N–Ti–N angles for the two pseudo-octahedra are 78.0(2)
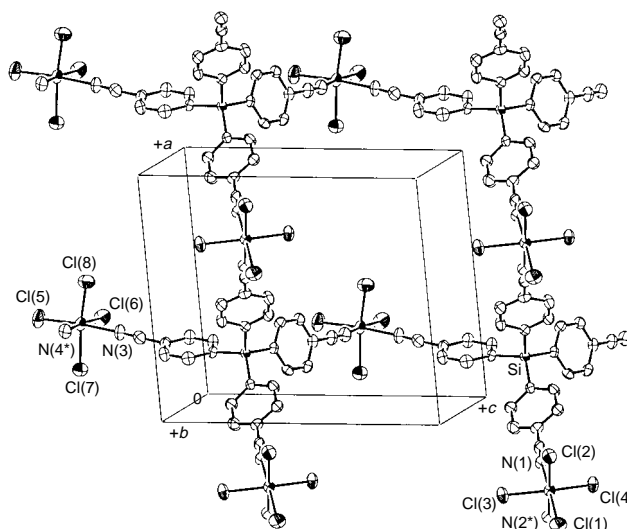

Fig. 1 ORTEP diagram illustrating part of a net in the structure of **2b**

and 81.4(2)°. For comparison, Zaworotko has previously reported two-dimensional frameworks based on tetrahedral building blocks.[6]

The layers in the structure lie in the *ac* plane, and there are two such layers in each repeat along the *b*-axis, which are overlapping and related by centers of inversion in the structure. The tetrahedral ligands **1** form a square network in each net, with $TiCl_4$ groups protruding above and below the planes. A simplified drawing of two overlapping nets, illustrating their 'buckled' character, is given in Fig. 2. All of the 'upward' $TiCl_4$ groups pack in a rough column along the *b*-axis, as do all the 'downward' $TiCl_4$ groups. Disordered toluene molecules are packed between the layers, to fill voids in the structure. The two-dimensional framework of **2b** may therefore be described as a [4,2]-connected net, with tetraconnected silicon centers and biconnected titanium centers in a 1:2 ratio.[18] Thus, this
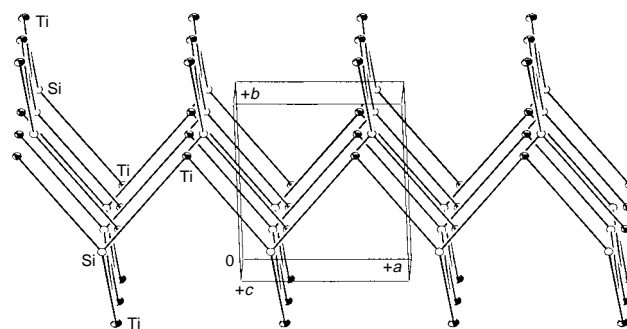

Fig. 2 A view of two overlapping nets in the structure of **2b**. The $-NCC_6H_4-$ linkages are depicted as long 'bonds', the titanium centers are shown as shaded ellipsoids, and the silicon atoms appear as unshaded ellipsoids.

structure is related to those adopted by some binary compounds with the AX_2 formula. Since the titanium centers link the tetrahedral building blocks **1** *via cis*-bonding of nitrile groups, the structure of **2b** is similar to that of α-HgI_2 in which the tetrahedral Hg centers lie in a plane.[19]

Thermogravimetry (TG) of **2a** and **2b** indicate that these networks are somewhat thermally unstable. Thus, the TG traces for these materials exhibit significant mass losses (*ca.* 32 and 35%, respectively) over the temperature range 25–280 °C, but **2a** loses mass much faster than **2b** during this step, which corresponds to loss of solvent as well as some decomposition of the framework. Both **2a** and **2b** exhibited the same decomposition step over the temperature range 340–500 °C.

A preliminary test of **2b** as a catalyst for the polymerization of propylene in the presence of triethylaluminium as cocatalyst (heptane solvent, 1 atm propylene) produced only 0.400 g of polypropylene from 0.190 g of **2b**.[20,21] The heptane-soluble fraction (atactic, M_n = 24 400; PDI = 3.3, by gel permeation chromatography using polystyrene standards) represented 75% of the sample by mass and the remaining (presumably isotactic) heptane-insoluble fraction (M_n = 93 000; PDI = 2.1) was slightly soluble in THF.

Footnotes and References

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† The ¹H NMR spectrum of **2a** in [²H₆]acetone revealed a 5 : 3 ratio of **1**[15] to benzene. Anal. Found: C, 44.87; H, 2.57; N, 6.37. Calc. for $C_{31.60}H_{19.60}Cl_8N_4SiTi_2$: C, 43.99; H, 2.29; N, 6.49%).

‡ The ¹H NMR spectrum of **2b** in [²H₆]acetone revealed a 2 : 3 ratio of **1**[15] to toluene. Anal. Found: C, 47.87; H, 2.56; N, 5.82. Calc. for $C_{38.50}H_{28}Cl_8N_4SiTi_2$: C, 48.46; H, 2.96; N, 5.87%.

§ *Crystal data*: $C_{38.5}H_{28}Cl_8N_4SiTi_2$, M = 954.18, triclinic, space group $P\bar{1}$ (no. 2), a = 12.4273(5), b = 13.4378(5), c = 14.1035(5) Å, α = 110.423(1), β = 96.468(1), γ = 90.752(1)°, U = 2189.6(1) Å³, Z = 2, D_c = 1.447 g cm⁻³, μ(Mo-Kα) = 9.12 cm⁻¹, $F(000)$ = 962. The data collection was performed at −86 °C with Mo-Kα radiation (λ = 0.710 69 Å) using a Siemens SMART diffractometer with a CCD area detector, by the ω–2θ scan method within the limits 3.00 < 2θ < 45.00°. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92) and refined by full-matrix least-squares analysis based on 4580 observed reflections [I > 3.00$\sigma(I)$] and 437 variable parameters and converged with unweighted and weighted agreement factors of R = 0.049, R_w = 0.062. All non-hydrogen atoms except those in the disordered solvent regions were refined anisotropically. CCDC 182/669.

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