Formation and Structural Characterisation of an Unusual Cyclic Hexameric Oxotitanium Complex

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$Ti_6O_6(MDEA)_6 \cdot 2CH_2Cl_2$ (MDEA = *N*-methyldiethoxoamine) was obtained by the controlled hydrolysis of the $Ti(MDEA)_2$ complex and analysed by X-ray diffraction. The compound consists of a ring of six $[TiO_5N]$ octahedra, edge bridged by μ_2-oxide and a μ_2-alkoxide arm of the aminoalkoxide ligand.

Introduction

Modification of metal alkoxides is a common technique in the formation of sol-gel materials, and is used to control the hydrolysis rate and condensation pathways of the oxo-alkoxide fragments. The modification involves the introduction of bi- or multidentate anionic ligands, such that the reactivity of the resulting compound is lower than the parent alkoxide thus allowing size control of the primarily formed oxo-particles. Examples of titanium oxo-complexes include oxo-alkoxides,[1−5] β-diketonates,[6−8] carboxylates,[9−15] and related complexes.[16−22] These exhibit a rich variation in structural types characterised by different coordination modes of the ligands, variations in linkages of the coordination polyhedra, degree of hydrolysis, and coordination number of the central atom. The titanium oxo-alkoxides exhibit degrees of condensation {defined as z/x for $[Ti_xO_z](OR)_{4x-2z}$} from 0.33 to 1.33,[3] while the degree of condensation accessible to the titanium carboxylates and other derivatives is more limited due to the increased coordination requirement of the modifying ligands. Mixed-metal complexes have been reported which further extend the range of structural features available.[23,24]

The coordination number for titanium is commonly 6, although ligand constraints have resulted in complexes with coordination numbers of 5[8,25−27] and 7.[25,26,28,29] Di- and polynuclear titanium complexes are generally characterised by vertex- and edge-sharing polyhedra, although a diolatoalkoxide containing a rare face-sharing linkage was recently reported.[25]

Amino alcohols have been applied as modifiers, and have been demonstrated to exhibit favourable properties for application in titanium sol-gel chemistry[30,31] and MOCVD.[32] Several derivatives of triethanolamine have been reported,[26,27,29,33−35] two of which contain oxo- linkages,[26,34] but crystalline derivatives of other amino alcohols are rare[28,36] and none of these are oxo-complexes.

Results and Discussion

We have isolated a crystalline derivative of *N*-methyldiethanolamine (MDEA), of composition $Ti_6O_6(MDEA)_6 \cdot 2CH_2Cl_2$. This compound was obtained by the hydrolysis and condensation of $Ti(MDEA)_2$ **(2)** prepared from the reaction of $Ti(OPr)_4$ with two equivalents of $MDEAH_2$. It is difficult to be definitive about the sequence of substitution and hydrolysis reactions occurring, but it seems necessary to first form the bis MDEA complex from $Ti(OPr)_4$, which can then be carefully hydrolysed to form **1**. Although **1** contains a single equivalent of MDEA per titanium, we have been unsuccessful in our attempts to prepare and isolate this product using this reactant ratio. The hexameric oxo complex **1** is much more hydrolytically stable than the parent bis complex which is highly hydrophilic. Crystals of **1** retained their integrity for several hours in the open air, degrading only due to the loss of dichloromethane molecules of crystallisation. This also occurred if the crystals were stored in sealed containers in the absence of dichloromethane vapour. In contrast, crystals of **2** became soft and waxy almost immediately on exposure to atmospheric moisture. The preparation and isolation of **2** will be reported later in a full paper, together with data on other related complexes.

Compound **1** consists of a ring of six $[TiO_5N]$ edge-linked octahedra (Figure 1). This contrasts with titanium oxo-carboxylates which include a high proportion of corner-shared octahedra. Each titanium is coordinated to a single MDEA ligand incorporating one terminal alkoxide, one μ_2-bridging alkoxide, and one terminal amine (Figure 2). The six μ_2-oxide bridges are located on the inside edge of the ring, alternating above and below the plane of the ring. The methylamine groups similarly appear on alternating faces of the ring, but are located on the outside edge of the ring. Each of these methyl groups is involved in a C−H···O interaction with the terminal alkoxide oxygen of an adjacent diethoxomethylamino group {C(25)−H(25A)···O(14), H···O = 233 pm}. Two molecules of dichloromethane are co-crystallised with each macrocycle, and are located one on each face of the ring, with their

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hydrogen atoms pointing towards the plane of the ring and their chlorine atoms pointing away from the ring. Significant hydrogen bonding occurs between these dichloromethane protons and the closest μ_2-oxide bridges {C(120)−H(12C)···O(10), H···O = 229 pm, C···H···O = 154°}. The total assembly is pseudo-centrosymmetric.

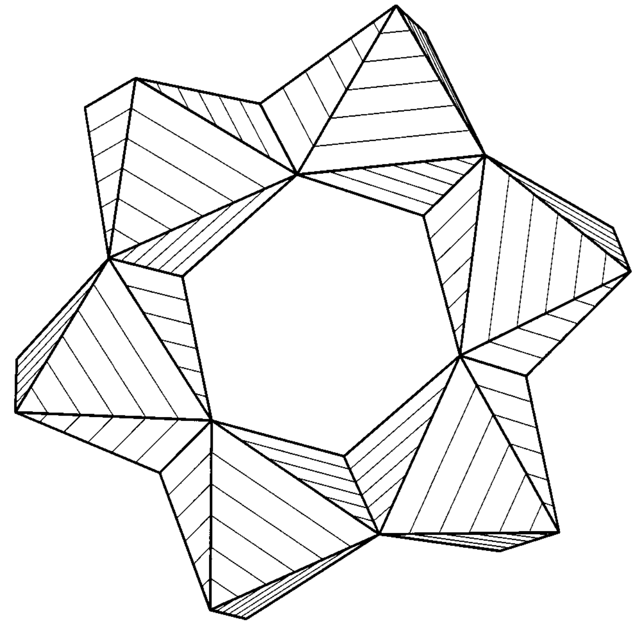

Figure 1. Molecular geometry of the coordination polyhedra in $[Ti_6(\mu_2\text{-}O_6)(\mu_2\text{-}OCH_2CH_2NCH_3{\cdot}CH_2CH_2O)_6{\cdot}2CH_2Cl_2$

The narrow bite angles (74, 76 and 79°) made by the coordinated MDEA, and the long Ti−N bond (av. = 235 pm), result in a coordination geometry around titanium that is extremely distorted from an ideal octahedron. The Ti−O bond lengths of the oxo bridges alternate long and short around the ring, with the shorter distances (av. = 175.7 pm) being *trans* to the long Ti−N bonds, and the longer distances (av. = 196.3 pm) being *trans* to the shorter terminal alkoxy arm of the MDEA.

The MDEA ligand coordinated to Ti(6) exhibits conformational disorder. Conformational rigidity may be preserved in the other MDEA ligands by the proximity of the dichloromethane to the ligands coordinated to Ti(1), Ti(2), Ti(4) and Ti(5). The MDEA coordinated to Ti(3) {which is pseudosymmetrically related to Ti(6)} is also held in one conformation by hydrogen bonding with a molecule of dichloromethane {C(31)−H(31A)···Cl(2), H···Cl = 270 pm} and weak intermolecular hydrogen bonding with a bridging oxygen from an adjacent macrocycle {C(32)−H(32B)···O(24), H···O = 258 pm}.

The macrocycle hole size, measured between opposite oxygens (less 140 pm for oxygen van der Waals radii), is 451, 447 and 480 pm for O(10)···O(40), O(30)···O(60) and O(20)···O(50) respectively. Related six- and eight-membered "coronate" complexes of Fe have been prepared with MDEA and triethanolamine ligands.[37] Bridging in these complexes is solely via the μ_2-alkoxo groups of the amino alcohols as the complexes do not include oxo ligands.

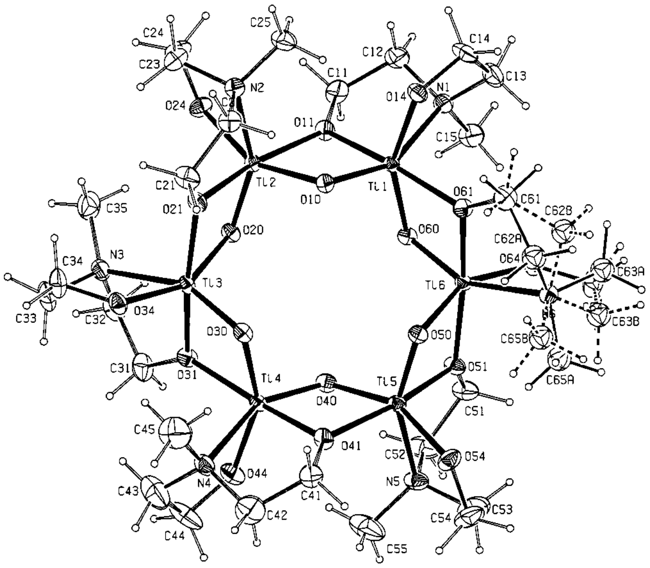

Figure 2. X-ray crystal structure of the hexameric assembly **1** (ORTEP drawing) showing the conformational disorder in the ligand attached to Ti(6)

Experimental Section

Hexakis[titanium(μ_2-oxo)(*N*-methyldiethoxoamine)] (1): A sample of $Ti(MDEA)_2$ (0.1 g) was dissolved in dry dichloromethane (5.0 mL). A layer of moist diethyl ether (10 cm^3) was carefully added and left to diffuse slowly into the the dichloromethane solution over 4 days. The crystalline product precipitated from solution, and X-ray quality crystals were removed from the side of the flask. Yield 0.06 g.

X-ray Crystallographic Study:[38] $C_{32}H_{70}{\cdot}Cl_4N_6O_{18}Ti_6$, Fw = 1256.14. Monoclinic, space group $P\ 2_1/c$, a = 1101.63(2), b = 2238.60(5), c = 2108.43(5) pm, β = 100.203(1)°, $V = 5117.4(2){\cdot}10^6$ pm^3, $d_{calc} = 1.63\ Mg{\cdot}m^{-3}$ for $Z = 4$, $\mu = 1.171\ mm^{-1}$, $\lambda(\text{Mo-}K_\alpha)$ = 71.073 pm, T = 158 K. A tabular crystal 0.80 × 0.50 × 0.40 mm was cut from a larger block immersed in mounting oil and rapidly mounted under a nitrogen stream on a Siemens P4 SMART diffractometer with a Siemens CCD area detector. The data collection nominally covered a hemisphere of reciprocal space, by a combination of two sets of exposures (14322 reflections). Each exposure took 15 s, the first at 0.3° intervals over a total of 52.8° in ω; the second covered 360° in ϕ (the mounting axis). Crystal decay was monitored by repeating the initial 10 frames at the end of the data collection and analyzing the duplicate reflections. The data (θ = 2.62 to 26.08°) were corrected for Lorentz and polarization factors and crystal decay (SAINT) and an empirical absorption correction (SADABS) was applied giving 7184 unique data.

The structure was solved by direct methods (SHELXS-97)[38] and successive difference-Fourier syntheses. Refinement was by full matrix least-squares based on wF_o^2 using $w = 1/[\sigma^2(F_o^2) + (0.0635{*}P)^2 + 0.34{*}P]$ where $P = (F_o^2 + 2F_c^2)/3$ and F_o and F_c are the observed and calculated structure factor amplitudes from SHELXL-97.[39] The disorder found for the ligand bound to Ti(6) was modelled using two conformations which refined to occupancies of 0.680(4) and 0.320(4) (see Figure 2). All hydrogen atoms were refined as riding atoms with isotropic thermal parameters set at 1.2 times the atom to which they were bound. All other atoms were refined with anisotropic thermal parameters. Refinement converged at R_1 = 0.0454, [for 5723 reflections with $I > 2\sigma(I)$], 588 parameters, wR_2 = 0.1320; final GOF = 1.008. The final difference map showed no peak larger than 1.047 eA^{-3} and no hole larger than -0.604 eA^{-3}, and these were < 120 pm from Ti and C atoms.[40]

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[40] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127303. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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