Inorganica Chimica Acta, 99 (1985) L25–L27

Preparation and Crystal Structure of Tetrameric $[Ti_4(C_6H_{15}N_3)_4(\mu\text{-}O)_6]Br_4\cdot 4H_2O$ Containing an Adamantane Ti_4O_6 Core

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Received November 7, 1984

The instability of the titanyl group, $Ti^{IV} = O$, relative to the $V^{IV} = O$ bond [1] has in the past led to the isolation and characterization of a variety of dimeric, trimeric and tetrameric complexes of titanium(IV), all of which contain the Ti–O–Ti structural moiety. The tetrameric complexes [2–5] appear to have an eight-membered $[Ti(\mu\text{-}O)]_4$ ring which is not strictly planar in all cases reported to date. The titanium(IV) centers are always in a pseudooctahedral environment: in many instances three of these coordination sites are occupied by cyclopentadienylat anions [3, 5] ($\eta^5\text{-}C_5H_5^-$, $\eta^5\text{-}CH_3C_5H_4^-$) but tetrameric species with O, N donor ligands such as oxalate [2] or nitrilotriacetate [4] are also known. Complexes of titanium(IV) with macrocyclic N-donor ligands have only recently been prepared and their chemistry has not been explored extensively [6, 7].

We report here the preparation and crystal structure of a tetrameric Ti(IV) complex containing the facially coordinating cyclic triamine 1,4,7-triazacyclononane and the novel adamantane like $[Ti_4(\mu\text{-}O)_6]^{4+}$. The small macrocyclic N_3-donor (6e$^-$ donor) resembles the $\eta^5\text{-}C_5H_5^-$ ligand in its electronic and steric properties.

A solution of titanyl-bis(acetonylacetonate), $TiO(acac)_2$ (0.26 g), and 1,4,7-triazacyclononane [8], $[9]aneN_3$ (0.15 g) in dry acetone (50 ml) was stirred at 50 °C for 30 min and treated with an aqueous solution (40 ml) of sodium bromide (0.20 g) and refluxed for 10 min. After allowing this solution to stand at 8 °C for 2 d colorless crystals of X-ray quality of $[Ti_4(C_6H_{15}N_3)_4(\mu\text{-}O)_6]Br_4\cdot 4H_2O$ were filtered off (yield: 0.5 g). Aqueous solutions of this complex are stable for at least 2 d at 25 °C.

The complex crystallizes in the orthorhombic system, space group *Pnma* with cell dimensions $a = 13.886(3)$, $b = 17.613(3)$, $c = 18.702(2)$ Å and $Z = 4$. Intensity data were collected on an Enraf–Nonius CAD 4 diffractometer using Mo-K_α radiation with ω–2θ scan technique ($2\theta < 60°$). The structure was solved by Patterson and Fourier Syntheses.

3149 independent reflections ($I \geqslant 2\sigma(I)$) were refined by least squares procedures to final discrepancy factors $R = 0.062$ and $R_w = 0.07$ with anisotropic thermal parameters for all non-hydrogen atoms. A total of 260 parameters were refined. The hydrogen atoms were calculated but not refined. An absorption correction was carried out ($\mu(MoK_\alpha = 41.85$ cm^{-1}). Final atomic coordinates are given in Table I; bond distances and bond angles are summarized in Table II.

The structure of the tetrameric cation is shown in Fig. 1; it possesses crystallographically imposed C_s symmetry (Ti(1), Ti(2), O(1), O(3), N(1) and N(3) are located on a mirror plane). This leads to an usual disorder phenomenon. The cyclic triamines coordinated to Ti(3) and Ti(3*) form each three membered rings, Ti–N–C–C–N with a λλλ- or δδδ-conformation. In contrast, due to the crystallographic mirror plane, these rings at Ti(1) and Ti(2) apparently have no such conformation at all. Close inspection of the anisotropic thermal parameters in Table I reveals that the carbon atoms C(1), C(2), C(3), C(4), C(5) and C(6) exhibit quite large values as compared to those of all nitrogens and atoms C(7)–C(12). The former set of C-atoms shows λλλ or δδδ conformation, whereas the latter do not. This indicates a statistical disorder of λλλ- and δδδ-conformated rings attached to Ti(1) and Ti(2) in the cell. In addition, Br(3) is also statistically disordered and two locations with occupancy factors of 90% for Br(3) and 10% for Br(3a) were found.

The $Ti_4(\mu\text{-}O)_6$ core has an adamantane-like skeleton. This structural type has only recently been found in $[F_{12}Ta_4O_6]^{4-}$ [9] and $[(C_6H_{15}N_3)_4Mn_4O_6]^{4+}$ [10]. The four Ti-atoms occupy the corners of a nearly regular tetrahedron and the μ_2-oxo bridges are located above the centre of the six edges of this tetrahedron. The average Ti–O distance is 1.834 Å, which compares well with those found in tetrameric complexes containing an eight-membered ring $Ti_4(\mu_2\text{-}O)_4$ (Ti–O = 1.80 Å [5], 1.90 Å [4]), and indicates considerable double bond character.

The average Ti–O–Ti bond angle of 125.6° is much smaller than that observed in the eight-membered rings (~ 160°). The Ti–N bonds are rather long (av. 2.230 Å) [7] and weak, due to a *trans* influence of the strong Ti–O bonds.

Each Ti center is in a distorted octahedral environment of three facially coordinated nitrogens of the cyclic amine and three *cis*-μ-oxo groups. The average

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0020-1693/85/$3.30

TABLE I. Atomic Coordinates

ATOM	x	y	z	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
Ti1	0.4006(1)	0.2500	0.5122(1)	0.011	0.018	0.014	0.000	0.000	0.000
Ti2	0.1967(1)	0.2500	0.4266(1)	0.016	0.019	0.013	0.000	−0.003	0.000
Ti3	0.2168(1)	0.1573(1)	0.5773(1)	0.018	0.009	0.017	0.000	0.002	0.001
Br1	0.4092(1)	0.2500	0.7577(1)	0.047	0.042	0.035	0.000	−0.002	0.000
Br2	0.3383(1)	0.2500	0.0395(1)	0.037	0.145	0.090	0.000	−0.026	0.000
Br3	0.4295(1)	0.4420(1)	0.3293(1)	0.067	0.059	0.064	0.017	0.008	0.035
Br3A	0.4030(8)	0.4563(7)	0.3622(6)	0.066					
O1	0.3281(4)	0.2500	0.4312(3)	0.010	0.022	0.013	0.000	0.000	0.000
O2	0.3452(3)	0.1691(2)	0.5593(2)	0.018	0.012	0.018	0.001	0.002	0.006
O3	0.1871(4)	0.2500	0.6169(3)	0.020	0.009	0.016	0.000	0.007	0.000
O4	0.1678(3)	0.1704(2)	0.4869(2)	0.020	0.013	0.016	−0.005	−0.004	0.001
Ow1	0.1519(6)	0.6437(4)	0.3953(4)	0.114	0.064	0.103	0.001	−0.036	0.023
Ow2	0.2358(6)	0.5014(4)	0.4097(3)	0.145	0.057	0.062	−0.007	0.036	0.018
N1	0.5236(6)	0.2500	0.5886(4)	0.019	0.067	0.008	0.000	0.002	0.000
N2	0.5091(4)	0.1726(3)	0.4638(3)	0.022	0.026	0.027	0.005	0.006	−0.002
N3	0.0515(6)	0.2500	0.3773(4)	0.014	0.062	0.022	0.000	0.002	0.000
N4	0.2078(4)	0.3271(4)	0.3318(3)	0.047	0.046	0.022	−0.021	−0.011	0.013
N5	0.2302(4)	0.0314(3)	0.5640(3)	0.041	0.014	0.029	−0.002	0.000	−0.001
N6	0.2535(4)	0.1133(3)	0.6857(2)	0.036	0.017	0.018	−0.002	0.001	0.003
N7	0.0789(4)	0.1102(3)	0.6198(3)	0.030	0.016	0.031	−0.005	0.003	0.002
C1	0.5809(8)	0.1811(7)	0.5828(4)	0.131	0.120	0.029	0.109	−0.034	−0.009
C2	0.5753(8)	0.1420(7)	0.5198(6)	0.095	0.093	0.101	0.076	−0.075	−0.048
C3	0.5657(7)	0.2108(5)	0.4092(5)	0.105	0.066	0.069	−0.048	0.079	−0.039
C4	0.0359(7)	0.3243(8)	0.3381(7)	0.029	0.155	0.148	0.035	0.010	0.122
C5	0.1123(8)	0.3592(6)	0.3137(7)	0.079	0.044	0.140	−0.016	−0.073	0.042
C6	0.255(1)	0.2896(6)	0.2722(4)	0.153	0.121	0.033	−0.060	0.047	−0.017
C7	0.3063(6)	0.0051(4)	0.6117(4)	0.045	0.018	0.054	0.017	0.004	0.001
C8	0.2907(6)	0.0336(4)	0.6867(4)	0.055	0.026	0.036	0.007	−0.007	0.008
C9	0.1678(6)	0.1246(4)	0.7314(3)	0.057	0.026	0.021	−0.004	0.019	0.004
C10	0.0786(6)	0.0922(5)	0.6962(4)	0.048	0.035	0.041	0.001	0.018	0.009
C11	0.0542(6)	0.0439(5)	0.5749(5)	0.036	0.038	0.070	−0.025	0.002	0.010
C12	0.1370(6)	−0.0100(4)	0.5730(4)	0.050	0.024	0.050	−0.016	0.004	−0.009

TABLE II. Bond Distances (Å) and Angles (°).

Ti1–O1	1.820(6)	Ti2–N4	2.238(6)
Ti1–O2	1.844(4)	Ti3–O2	1.826(5)
Ti1–N1	2.226(8)	Ti3–O3	1.841(1)
Ti1–N2	2.225(6)	Ti3–O4	1.838(4)
Ti2–O1	1.827(6)	Ti3–N5	2.240(6)
Ti2–O4	1.844(4)	Ti3–N6	2.230(6)
Ti2–N3	2.217(9)	Ti3–N7	2.233(6)
O1–Ti1–O2	99.6(1)	N4–Ti2–N4*	74.7(2)
O1–Ti1–N1	163.5(3)	O1–Ti2–O4	100.9(1)
O1–Ti1–N2	92.1(1)	O1–Ti2–N3	158.2(3)
O2–Ti1–N2	90.8(1)	O1–Ti2–N4	88.2(2)
O2–Ti1–O2*	101.2(2)	O4–Ti2–O4*	99.0(2)
O2–Ti1–N2	90.2(2)	O4–Ti2–N3	93.2(1)
O2–Ti1–N2*	162.0(2)	O4–Ti2–N4	163.9(2)
N1–Ti1–N2	75.0(2)	O4–Ti2–N4*	92.2(2)
N2–Ti1–N2*	75.6(2)	N3–Ti2–N4	74.5(2)
O2–Ti3–O3	101.0(2)	Ti1–O1–Ti2	126.3(3)
O2–Ti3–O4	100.3(2)	Ti1–O2–Ti3	125.8(3)
O2–Ti3–N5	90.7(2)	Ti3–O3–Ti3*	125.1(3)

TABLE II. *(continued)*

O2–Ti3–N7	161.0(2)	Ti2–O4–Ti3	125.3(3)
O2–Ti3–N6	89.1(2)		
O3–Ti3–O4	100.1(2)		
O3–Ti3–N5	160.4(2)		
O3–Ti3–N6	89.6(2)		
O3–Ti3–N7	89.6(2)		
O4–Ti3–N5	93.1(2)		
O4–Ti3–N6	164.9(2)		
O4–Ti3–N7	93.2(2)		
N5–Ti3–N6	74.8(2)		
N5–Ti3–N7	75.1(2)		
N6–Ti3–N7	75.1(2)		

O–Ti–O bond angle is 100°, whereas the corresponding N–Ti–N angles are ~ 75°.

In the infrared the Ti_4O_6 core exhibits a strong band at 730 cm^{-1}. The same band has been observed for the Mn_4O_6 cluster [10] and similar bands have

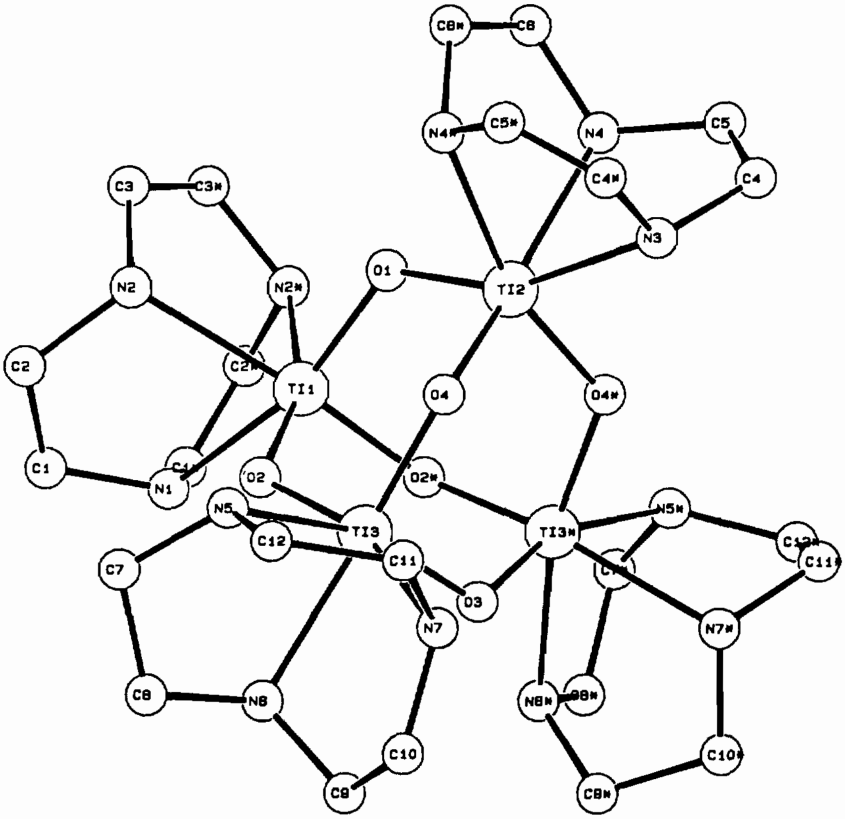

Fig. 1. Structure of [Ti$_4$(C$_6$H$_{15}$N$_3$)$_4$(μ-O)$_6$]$^{4+}$. Atoms N(1), Ti(1), O(1), Ti(2), N(3) and O(3) lie on a mirror plane.

been reported for Cp$_6$Ti$_6$O$_8$ [11], Cp$_5$V$_5$O$_6$ [12] and Cp$_4$Cr$_4$O$_4$ [12].

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