Synthesis and Characterization of Mononuclear Octahedral Titanium(IV) Complexes Containing Ti═O, $Ti(O_2)$, and $Ti(OCH_3)_x$ (x = 1–3) Structural Units

Peter Jeske,[†] Gabriele Haselhorst,[†] Thomas Weyhermüller,[†] Karl Wieghardt,[*,†] and Bernhard Nuber[‡]

Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-44780 Bochum, Germany, and
Anorganisch-Chemisches Institut der Universität, D-69120 Heidelberg, Germany

Received September 22, 1993[®]

The oxidation of $[(Me_3tacn)Ti^{III}Br_3]$ (where Me_3tacn is 1,4,7-trimethyl-1,4,7-triazacyclononane) in water with $Na_2[S_2O_8]$ yields upon addition of $NaClO_4$ yellow-orange $[(Me_3tacn)Ti^{IV}Br_3]ClO_4$ (**1**). The series $[(Me_3tacn)Ti^{IV}Br_x(OCH_3)_{(3-x)}]^+$ (x = 2 (**2**); x = 1 (**3**); x = 0 (**4**)) has been synthesized by oxidation reactions of $[(Me_3tacn)TiBr_3]$ with air in acetonitrile/methanol mixtures and methanol as solvents. Complexes **1**, $[(Me_3tacn)TiBr(OCH_3)_2](ClO_4)$ (**3**), and $[(Me_3tacn)Ti(OCH_3)_3]BPh_4$ (**4**) have been structurally characterized by X-ray crystallography. Crystal data: for **1**, monoclinic $P2_1/n$, a = 11.146(6) Å, b = 12.640(5) Å, c = 12.871(5) Å, β = 91.19(4)°, V = 1812.9(14) Å^3, Z = 4; for 3, monoclinic $P2_1/c$; a = 11.837(3) Å, b = 12.635(3) Å, c = 13.044(2) Å, β = 92.34(2)°, V = 1949.2(9) Å^3, Z = 4; for **4**, monoclinic $P2_1/n$, a = 10.394(2) Å, b = 21.483(4) Å, c = 15.741(3) Å, β = 90.30(3)°, V = 3514.8(12) Å^3, Z = 4. Two orange-red peroxotitanium(IV) complexes $[(Me_3tacn)Ti(O_2)(NCO)_2]$ (**5**) and $[(Me_3tacn)Ti(O_2)Cl_2]$ (**6**) have been isolated from acetonitrile solutions of $[(Me_3tacn)_2Ti_2^{III}(NCO)_4(\mu\text{-}O)]$ and $[(Me_3tacn)TiCl_3]$ which had been exposed to air and H_2O_2, respectively. Crystal data for **5**: monoclinic $P2_1/n$, a = 8.602(3) Å, b = 12.478(5), c = 14.671(4) Å, β = 91.18(3)°, V = 1574.4(12) Å^3, Z = 4. Complexes **5** and **6** contain an $\eta^2\text{-}O_2^{2-}$ ligand. Three new octahedral titanyl complexes, $[(Me_3tacn)Ti(O)Cl_2]$ (**7**), $[(tiptacn)Ti(O)(NCS)_2]$ (**8**), and $[(tiptacn)Ti(O)(NCO)_2]$ (**9**), were obtained from acetonitrile solutions of $[(Me_3tacn)TiCl_3]$, $[(tiptacn)Ti(NCS)_3]$, and $[(tiptacn)Ti(NCO)_2(OCH_3)]$ by interaction with oxygen where tiptacn represents 1,4,7-isopropyl-1,4,7-triazacyclononane. Crystal data for **7**: monoclinic $P2_1/a$, a = 12.815(3) Å, b = 7.829(2) Å, c = 15.146(6) Å, β = 114.67(3)°, V = 1380.9(10) Å^3, Z = 4. The Ti═O distance was found to be 1.637(3) Å. All new compounds have been studied by infrared and Raman spectroscopy in solution and in the solid state.

Introduction

In a recent paper[1] we have described some synthetic and structural aspects of classical Werner-type coordination chemistry of octahedral titanium(III) and (IV) complexes containing the tridentate macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn). We reported at that time that mononuclear $[(Me_3tacn)Ti^{III}Cl_3]$ can be obtained in a pure *blue* and a compositionally disordered *green* form via two different synthetic routes. From infrared spectral data it was inferred that the green form contains the putative titanyl complex $[(Me_3tacn)Ti^{IV}(O)Cl_2]$ as impurity because a Ti═O stretching mode at 938 cm^{-1} had been detected which is absent in the pure blue form. The green color was found to be due to a strong absorption in the visible at 390 nm which again is absent in the blue form. Both forms display a weaker asymmetric absorption maximum at 690 nm which is assigned to a d–d transition of the Ti^{III} ion ($^2T_2 \rightarrow {}^2E$ in O_h symmetry). It was implied that $[(Me_3tacn)Ti(O)Cl_2]$ should be yellow with a charge transfer band at 390 nm. Since we had not been able to synthesize a pure sample of this putative impurity, these conclusions remain speculative.

In this paper we show that the situation is even more complex. We have now synthesized and fully characterized monomeric *colorless* $[(Me_3tacn)Ti^{IV}(O)Cl_2]$ **7**, which displays a (Ti═O) stretching mode at 933 cm^{-1} in the infrared, and orange $[(Me_3tacn)Ti^{IV}(O_2)Cl_2]$ (**6**), which exhibits a charge transfer (CT) band at 427 nm in the electronic absorption spectrum. The difference of 37 nm between the CT band of green $[(Me_3tacn)TiCl_3]$ and **6** arises because in the green form the CT bands of pure blue $Me_3tacnTiCl_3$ and **6** are superimposed. We propose that the green form of $[(Me_3tacn)TiCl_3]$ actually is a *ternary* mixture of $[(Me_3tacn)TiCl_3]$, **6**, and **7**. We also report the synthesis of similar colorless titanyl complexes containing the bulky macrocycle 1,4,7-triisopropyl-1,4,7-triazacyclononane[2] (tiptacn) and a second orange-red η^2-peroxotitanium(IV) species $[(Me_3tacn)Ti(O_2)(NCO)_2]$ (**5**).

In the second section we investigate the oxophilicity of octahedral titanium(IV) in a systematic fashion. We have found that oxidation of $[(Me_3tacn)Ti^{III}Br_3]$[1] in a variety of methanol/methoxide containing solvent mixtures allows the isolation of salts of the complete series of $[(Me_3tacn)Ti^{III}Br_x(OCH_3)_{(3-x)}]^+$ complexes where x varies from 0 to 3. These four complexes have been structurally characterized by X-ray crystallography. Their infrared and Raman spectra recorded both in the solid state and in solution allow an assessment of the effect of accumulating π-donor ligands on the Ti–N, Ti–Br, and Ti–O bond strength.

Experimental Section

The macrocyclic ligands 1,4,7-trimethyl-1,4,7-triazacyclononane[3] (Me_3tacn) and 1,4,7-triisopropyl-1,4,7-triazacyclononane[2] (tiptacn) and the complexes $[(Me_3tacn)Ti^{III}Br_3]$,[1] $[(Me_3tacn)Ti^{III}Cl_3]$,[1] $[(Me_3tacn)Ti^{III}(NCS)_3]$,[1] and $[\{Me_3tacn)Ti(NCO)_2\}_2(\mu\text{-}O)]$[4] have been prepared according to published procedures.

Caution! In this work we have used perchlorate as counteranion. Although we have not encountered any problems, it should be noticed that perchlorates are potentially explosive. Only small quantities of complexes should be prepared and handled with appropriate care.

[†] Ruhr-Universität Bochum.

[‡] Universität Heidelberg.

[®] Abstract published in *Advance ACS Abstracts*, April 15, 1994.

(1) Bodner, A.; Jeske, P.; Weyhermüller, T.; Wieghardt, K.; Dubler, E.; Schmalle, E.; Nuber, B. *Inorg. Chem.* **1992**, *31*, 3737.

(2) Haselhorst, G.; Stötzel, S.; Strassburger, A.; Walz, W.; Wieghardt, K.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1993**, 83.

(3) Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086.

(4) Jeske, P.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1994**, *33*, 47.

0020-1669/94/1333-2462$04.50/0

Table 1. Crystallographic Data for Complexes **1**, **3**, **4**, **5**, and **7**

	1	**3**	**4**	**5**	**7**
chem formula	$C_9H_{21}N_3Br_3ClO_4Ti$	$C_{11}H_{27}N_3BrClO_6Ti$	$C_{36}H_{50}BN_3O_3Ti$	$C_{11}H_{21}N_5O_4Ti$	$C_9H_{21}N_3Cl_2OTi$
fw	558.4	460.2	631.5	335.2	306.9
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/a$
a, Å	11.146(6)	11.837(3)	10.394(2)	8.602(3)	12.815(3)
b, Å	12.640(5)	12.635(3)	21.483(4)	12.478(5)	7.829(2)
c, Å	12.871(5)	13.044(2)	15.741(3)	14.671(4)	15.146(6)
β, deg	91.19(4)	92.34(2)	90.30(3)	91.18(3)	114.67(3)
V, Å^3	1812.9(14)	1949.2(9)	3514.8(12)	1574.4(12)	1380.9(10)
Z	4	4	4	4	4
T, K	298	298	298	298	298
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	2.05	1.57	1.19	1.41	1.47
μ, mm^{-1}	7.18	2.63	0.275	0.56	0.99
R^a (obs data)	0.040	0.062	0.053	0.059	0.053
R$_w$^{a} (obs data)	0.037	0.052	0.047	0.054	0.052

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum w(F_o - F_c)^2/\sum w|F_o|^2\}^{1/2}$. $w = 1/\sigma^2(F) + 0.0001F^2$.

[(Me$_3$tacn)Ti^{IV}Br$_3$](ClO$_4$) (1). A reaction mixture of green [(Me$_3$tacn)Ti^{III}Br$_3$] (0.46 g, 1.0 mmol) and Na$_2$[S$_2$O$_8$] (0.5 g, 2.1 mmol) in water (20 mL) was stirred at ambient temperature for 2 h after which time a clear yellow solution was obtained. Addition of NaClO$_4$·H$_2$O (0.50 g) initiated the precipitation of yellow-orange microcrystals which were collected by filtration and recrystallized from a saturated acetonitrile solution. X-ray quality crystals (0.35 g) were obtained in 62% yield. Anal. Calcd for $C_9H_{21}N_3Br_3O_4ClTi$: C, 19.4; H, 3.8; N, 7.5; ClO$_4$, 17.8. Found: C, 19.2; H, 3.9; N, 7.5; ClO$_4$, 17.6. 80-MHz ^{1}H NMR (CH$_3$CN-*d*$_3$, δ): 3.30 (s, 9H, –C*H*$_3$), 3.3–3.9 (m, 12H, –C*H*$_2$–).

[(Me$_3$tacn)Ti^{IV}Br$_2$(OCH$_3$)](ClO$_4$) (2). The synthesis of this complex has been described in a previous paper.[1]

[(Me$_3$tacn)Ti^{IV}Br(OCH$_3$)$_2$](ClO$_4$) (3). A mixture of [(Me$_3$tacn)Ti^{III}Br$_3$] (0.46 g; 1.0 mmol) in methanol (50 mL) was heated to reflux in the presence of air for 6 h until a clear, faint yellow solution was obtained. Cooling to room temperature and addition of NaClO$_4$·H$_2$O (1.0 g) and storage at –18 °C for 18 h yielded colorless microcrystals which were slowly recrystallized from an acetonitrile solution. Yield: 0.30 g (65%). Anal. Calcd for $C_{11}H_{27}N_3BrClO_6Ti$: C, 28.7; H, 5.9; N, 9.1; ClO$_4$, 21.6. Found: C, 28.6; H, 6.1; N, 9.3; ClO$_4$, 22.0. 80-MHz ^{1}H NMR (CH$_3$CN-*d*$_3$, δ): 2.75 (s, 3H, –C*H*$_3$, 2.95 (s, 6H, –C*H*$_3$, 2.9–3.3 (m, 12H, –C*H*$_2$–), 4.40 (s, 6H, –OC*H*$_3$).

[(Me$_3$tacn)Ti^{IV}(OCH$_3$)$_3$][BPh$_4$] (4). To a suspension of [(Me$_3$tacn)Ti^{III}(NCS)$_3$] (0.39 g, 1.0 mmol) in methanol (30 mL) was added Na[OCH$_3$] (0.18 g, 3.3 mmol) and stirred at ambient temperature in the presence of air for 12 h. To the clear, yellowish solution was added Na[BPh$_4$] (0.50 g). When this solution was allowed to stand in a closed vessel for 5–7 d, colorless crystals precipitated which were collected by filtration, washed with small amounts of methanol and diethyl ether, and air-dried. Yield: 0.18 g (29%). Anal. Calcd for $C_{36}H_{50}N_3BO_3Ti$: C, 68.5; H, 7.9; N, 6.7. Found: C, 69.0; H, 8.0; N, 6.7. 80-MHz ^{1}H NMR (CH$_3$CN-*d*$_3$, δ): 2.65 (s, 9H, –C*H*$_3$), 2.7–3.1 (m, 12H, –C*H*$_2$–), 4.2 (s, 9H, –OCH$_3$), 6.7–7.5 (m, 20H, BPh$_4^-$). **[(Me$_3$tacn)Ti^{IV}(O$_2$)(NCO)$_2$] (5).** A suspension of [{Me$_3$tacn)Ti^{III}(NCO)$_2$}$_2$(μ-O)] (0.31 g, 0.5 mmol) in acetonitrile (30 mL) was stirred at ambient temperature in the presence of air until an orange solution was obtained. From this solution precipitated within 4–5 d orange-red crystals which were collected by filtration, washed with diethyl ether, and air-dried. Yield: 0.12 g (36%). Anal. Calcd for $C_{11}H_{21}N_5O_4Ti$: C, 39.4; H, 6.3; N, 20.9. Found: C, 39.5; H, 6.6; N, 20.9.

[(Me$_3$tacn)Ti^{IV}(O$_2$)Cl$_2$] (6). To a suspension of [(Me$_3$tacn)TiCl$_3$] (0.32 g, 1.0 mmol) in acetonitrile (30 mL) was added 35% hydrogen peroxide (2.5 mL). Stirring at room temperature produced an orange-red solution from which orange-red crystals precipitated within 4–5 d. These were collected by filtration, washed with diethyl ether, and air-dried. Yield: 0.14 g (43%). As described in the text this material always contains substantial amounts of [(Me$_3$tacn)Ti(O)Cl$_2$]. Anal. Calcd for $C_9H_{21}N_3O_2Cl_2Ti$: C, 33.5; H, 6.5; N, 13.0; Cl, 22.0. Found: C, 33.9; H, 6.8; N, 12.9; Cl, 20.4.

[(Me$_3$tacn)Ti(O)Cl$_2$] (7). Blue crystals of [(Me$_3$tacn)Ti^{III}Cl$_3$] (1.0 g, 3.0 mmol) in acetonitrile (100 mL) were stirred at ambient temperature in the presence of air until the blue color had faded and a clear, colorless solution was obtained (2–3 h). From this solution precipitated within 4–5 d colorless, translucent crystals suitable for X-ray crystallography. Yield: 0.57 g (62%). Anal. Calcd for $C_9H_{21}N_3Cl_2OTi$: C, 35.3; H, 6.9; N, 13.7; Cl, 23.2. Found: C, 35.2; H, 7.1; N, 13.6; Cl, 22.6.

[(tiptacn)Ti(O)(NCS)$_2$] (8). A solution of TiCl$_3$ (2.8 g, 18 mmol) in deoxygenated acetonitrile (60 mL) was heated to reflux until a clear blue solution was obtained. After the solution was cooled to room temperature deoxygenated 1,4,7-triisopropyl-1,4,7-triazacyclononane (6.0 g, 24 mmol) was added. The reaction mixture was gently heated to 40 °C whereupon a greenish-brown solution was obtained from which green microcrystals of [(tiptacn)TiCl$_3$] precipitated. These were collected by filtration, washed with water, acetonitrile, and diethyl ether, and air-dried. Yield: 5.4 g (73%). This material was used to prepare [(tiptacn)Ti(NCS)$_3$] and [(tiptacn)Ti(NCO)$_2$(OCH$_3$)] in the following fashion: (a) [(tiptacn)TiCl$_3$] (0.41 g, 1.0 mmol) reacted in a deoxygenated tetrahydrofuran/water mixture (1:1) (20 mL) with NaSCN (0.81 g; 10 mmol) at room temperature within 3 h to produce a blue suspension. The green precipitate of [(tiptacn)Ti(NCS)$_3$] was collected under an argon atmosphere by filtration. Yield: 0.28 g (58%). (b) [(tiptacn)TiCl$_3$] (0.41 g, 1.0 mmol) and NaOCN (0.50 g, 7.7 mmol) in a deoxygenated mixture of water (15 mL), tetrahydrofuran (10 mL), and methanol (3 mL) were heated to 50 °C under an argon atmosphere. After 2–3 h the color of the solution had changed from green to purple and a purple precipitate of [(tiptacn)Ti(NCO)$_2$(OCH$_3$)] had formed which was collected by filtration. Yield: 0.27 g (65%). (c) Green [(tiptacn)Ti(NCS)$_3$] (0.48 g, 1.0 mmol) in acetonitrile (50 mL) was stirred in the presence of air until a clear yellowish solution was obtained (1–2 h). Within 1 h faint yellow crystals of **8** precipitated which were recrystallized from an acetonitrile/water mixture (1:1). Yield: 0.37 g (84%). Anal. Calcd for $C_{17}H_{33}N_5S_2OTi$: C, 46.9; H, 7.6; N, 16.1; S, 14.7. Found: C, 46.3; H, 7.5; N, 15.8; S, 14.6.

[(tiptacn)Ti(O)(NCO)$_2$] (9). Purple [(tiptacn)Ti^{III}(NCO)$_2$(OCH$_3$)] (0.42 g, 1.0 mmol) in acetonitrile (50 mL) was stirred at ambient temperature in the presence of air until a clear colorless solution was obtained. Within 1 h colorless crystals precipitated which were recrystallized from acetonitrile. Yield: 0.35 g (87%). Anal. Calcd for $C_{17}H_{33}N_5O_3Ti$: C, 50.6; H, 8.2; N, 17.4. Found: C, 50.7; H, 8.4; N, 17.4.

X-ray Crystallography. Crystal data, data collection, and refinement are summarized in Table 1 (and corresponding tables in the supplementary material). Graphite-monochromated Mo Kα X-radiation was used throughout. Unit cell parameters were determined in all cases by the automatic indexing of 25–30 centered reflections. Intensity data were corrected in the usual fashion for Lorentz, polarization, and absorption effects (empirical ψ-scans of seven reflections in the range $6 \le 2\vartheta \le 50°$). The structures were solved by conventional Patterson and difference Fourier (**3**, **5**) and direct methods (**1**, **4**, **7**) by using the SHELXTL-PLUS program package.[5] The function minimized during full-matrix least-squares refinement was $\sum w(|F_o|-|F_c|)^2$ where $w^{-1} = \sigma^2(F) + 0.0001F^2$ or $w^{-1} = \sigma^2(F)$. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 6. The positions of the hydrogen atoms were placed at calculated positions with group isotropic thermal parameters (methylene H atoms) while the methyl groups were treated as rigid bodies. All non-hydrogen atoms were refined with anisotropic thermal parameters.

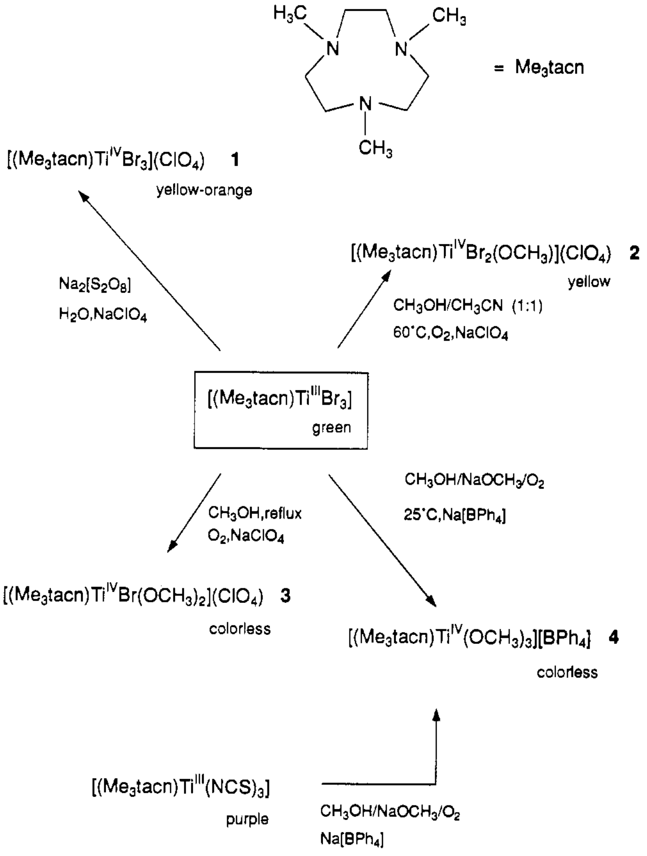
Physical Measurements. Infrared spectra of solid samples were recorded in the range 400–4000 cm^{-1} on a Perkin-Elmer 1720 X FT IR spectrometer as KBr disks and in the range 100–500 cm^{-1} on a Perkin-Elmer 1700 X FT IR spectrometer as CsI disks. Acetonitrile solution infrared spectra were recorded as thin films between KBr disks against

---

(5) Sheldrick, G. M. Full-matrix least-squares structure refinement program package SHELXTL-PLUS, Universität Göttingen.

(6) *International Tables of Crystallography*; Kynoch: Birmingham, England, 1974, Vol. IV, pp 99, 149.

Scheme 1. Synthesis of $Ti^{IV}Br_3$ and $Ti^{IV}(OHC_3)_x$ Complexes



the pure solvent (thickness of the films was ~60 μm). Raman spectra of solid samples and acetonitrile solutions were recorded in the range 100–3600 cm^{-1} on a Perkin-Elmer 1760 X FT near-IR spectrometer connected to 180° backscattering FT Raman equipment. A Nd-YAG laser (λ = 1064 nm) was used. ^{1}H NMR spectra were recorded on a Bruker WP 80 NMR spectrometer. The apparatus used for cyclic voltammetry has been described previously.[1] Acetonitrile solutions of complexes (~10^{-3} M) that contained 0.10 M tetra-*n*-butylammonium hexafluorophosphate ($[TBA]PF_6$) were used. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode (LiCl, C_2H_5OH) at ambient temperature and are uncorrected for the junction potential. UV–vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer in the range 210–1100 nm.

Results

Syntheses of Complexes. Synthetic routes are summarized in Scheme 1 and 2. Oxidation of green $[(Me_3tacn)Ti^{III}Br_3]$ in water with peroxodisulfate gives in a colorless solution from which upon addition of $NaClO_4{\cdot}H_2O$ yellow-orange crystals of $[(Me_3tacn)TiBr_3](ClO_4)$ (**1**) precipitated. When the oxidation of the above starting material is carried out by air in an acetonitrile/methanol mixture (1:1) yellow crystals of $[(Me_3tacn)TiBr_2(OCH_3)](ClO_4)$ (**2**) were obtained in ~40% yield. The synthesis and crystal structure of **2** have been described previously.[1] The dimethoxo analogue of **2** was obtained when the air oxidation of $[(Me_3tacn)TiBr_3]$ was carried out in pure methanol as solvent: Colorless crystals of $[(Me_3tacn)TiBr(OCH_3)_2](ClO_4)$ (**3**) were obtained. Finally, colorless crystals of $[(Me_3tacn)Ti(OCH_3)_3][BPh_4]$ (**4**) were isolated when the comparatively more readily oxidizable complexes $[(Me_3tacn)Ti^{III}(NCS)_3]$ or $[(Me_3tacn)TiBr_3]$ were oxidized by air in methanol containing $Na[OCH_3]$ and $Na[BPh_4]$. Thus the synthetic routes outlined in Schemes 1 and 2 give access to a complete series of compounds where the three bromo ligands in **1** are formally successively substituted by methoxo ligands but the $(Me_3tacn)Ti^{IV}$ fragment is retained.

When the dinuclear species $[\{(Me_3tacn)Ti^{III}(NCO)_2\}_2(\mu\text{-}O)]$[4] dissolved in acetonitrile was oxidized by air, a clear red-orange solution was obtained from which orange-red crystals of the peroxotitanium(IV) species $[(Me_3tacn)Ti(O_2)(NCO)_2]$ (**5**) precipitated in 36% yield. Although the X-ray crystal determination (see below) clearly shows the presence of this complex, infrared and Raman spectroscopy as well as cyclic voltammetry show that this material contains appreciable amounts of the titanyl complex $[(Me_3tacn)Ti(O)(NCO)_2]$. We have not been able to fully separate these two species, but note that the titanyl complex $[(tiptacn)Ti(O)(NCO)_2]$ (**9**) has been obtained (see below) in analytically pure form, where tiptacn represents 1,4,7-triisopropyl-1,4,7-triazacyclononane. The synthesis and crystal structure of $[(Me_3tacn)Ti(O)(NCS)_2]$ has been reported previously.[1]

Scheme 2. Synthesis of Ti=O and $Ti(O_2)$ Complexes

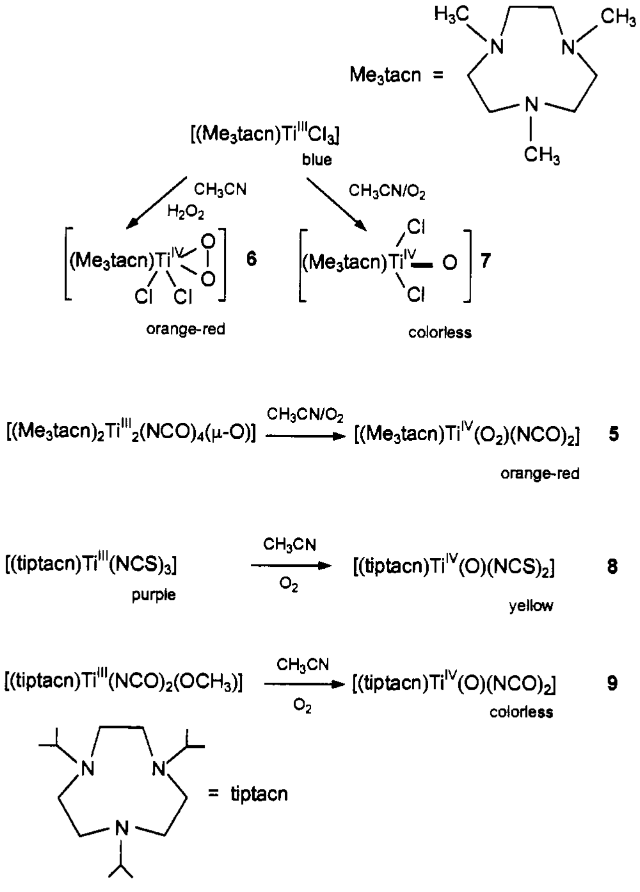


Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1**

atom	*x*	*y*	*z*	*U*(eq)[a]
Ti	2521(1)	1556(1)	4285(1)	43(1)
Br(1)	4180(1)	993(1)	3262(1)	70(1)
Br(2)	947(1)	1132(1)	3044(1)	74(1)
Br(3)	2365(1)	14(1)	5324(1)	81(1)
N(1)	1244(6)	2451(5)	5280(5)	46(3)
N(2)	2633(6)	3206(5)	3650(5)	44(3)
N(3)	3771(6)	2346(6)	5437(5)	48(3)
C(1)	1038(8)	3545(8)	4883(7)	64(4)
C(2)	1450(8)	3695(7)	3817(7)	62(4)
C(3)	3611(8)	3833(7)	4214(8)	69(4)
C(4)	4424(8)	3180(8)	4863(7)	63(4)
C(5)	3079(9)	2855(8)	6302(7)	66(4)
C(6)	1791(8)	2498(9)	6336(7)	68(4)
C(7)	60(9)	1946(9)	5390(8)	81(5)
C(8)	2857(10)	3259(8)	2530(7)	74(5)
C(9)	4671(9)	1618(8)	5918(8)	76(4)
Cl(1)	2469(2)	-3701(2)	6028(2)	62(1)
O(11)	2736(6)	1151(6)	54(5)	93(3)
O(12)	2296(7)	2369(6)	-1232(6)	108(4)
O(13)	1551(6)	689(6)	-1363(6)	95(3)
O(14)	3549(6)	972(8)	-1553(6)	122(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **3**

atom	*x*	*y*	*z*	*U*(eq)[a]
Br(1)	1025(1)	1743(1)	4069(1)	90(1)
Ti(1)	2423(1)	516(1)	3309(1)	56(1)
N(1)	2305(6)	1439(5)	1816(5)	71(3)
N(2)	3391(5)	−478(5)	2273(5)	66(3)
N(3)	1033(5)	−316(5)	2368(4)	65(3)
C(1)	3075(9)	977(8)	1078(7)	116(5)
C(2)	3895(7)	241(8)	1529(7)	100(5)
C(3)	2670(8)	−1283(7)	1722(6)	92(4)
C(4)	1542(8)	−1375(7)	2138(7)	96(4)
C(5)	697(7)	231(8)	1418(6)	90(4)
C(6)	1098(9)	1337(7)	1427(6)	101(5)
C(7)	2583(7)	2577(6)	1971(6)	105(5)
C(8)	4316(7)	−998(7)	2888(6)	110(5)
C(9)	−1(7)	−510(7)	2954(6)	104(4)
O(1)	3636(5)	1239(4)	3690(4)	86(2)
C(11)	4468(8)	1644(8)	4257(6)	130(5)
O(2)	2337(5)	−449(4)	4239(3)	82(2)
C(12)	2257(8)	−1022(7)	5095(6)	129(5)
Cl(1)	7070(2)	915(2)	1474(2)	87(1)
O(11)	6920(8)	1158(6)	2459(5)	199(5)
O(12)	8078(6)	1260(7)	1175(7)	202(5)
O(13)	6959(8)	−170(6)	1333(6)	177(5)
O(14)	6248(6)	1424(6)	848(5)	142(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

A second orange-red peroxotitanium(IV) complex [(Me$_3$tacn)Ti(O$_2$)Cl$_2$] (**6**) has been isolated in crystalline form from an acetonitrile solution of [(Me$_3$tacn)Ti^{III}Cl$_3$] to which a solution of 35% H_2O_2 was added. Analysis of the infrared and Raman spectra and an X-ray structure determination (see below) revealed that crystals of **6** are also always cocrystallized with the corresponding colorless titanyl species [(Me$_3$tacn)Ti(O)Cl$_2$] (**7**). In our previous paper[1] we had failed to isolate and characterize this complex. Only the μ-oxo bridged complex [(Me$_3$tacn)$_2$Ti$_2$^{IV}Cl$_4$(μ-O)]Cl$_2$·2.5H$_2$O had been identified at that time. We have now discovered that **7** forms in 62% yield when [(Me$_3$tacn)TiCl$_3$] is oxidized by air in water-free acetonitrile. Similarly, oxidation of [(tiptacn)Ti^{III}(NCS)$_3$] and [(tiptacn)Ti(NCO)$_2$(OCH$_3$)] dissolved in dry acetonitrile by air yielded yellow crystals of [(tiptacn)Ti^{IV}(O)(NCS)$_2$] (**8**) and colorless [(tiptacn)Ti^{IV}(O)(NCO)$_2$] (**9**). Both **8** and **9** are genuine octahedral titanyl complexes with a Ti═O group.

Crystal Structure Determinations. The crystal structures of **1**, **3**, **4**, **5**, and **7** have been determined by single-crystal X-ray crystallography; the structure of **2** has been reported previously.[1] Tables 2–6 give the respective atom coordinates. Table 7 summarizes selected bond distances and angles of complexes, and Figures 1–5 display the structures.

A common structural feature of the structures reported here is the (Me$_3$tacn)Ti^{IV} fragment which contains a facially coordinated tridentate cyclic amine. The three five-membered chelate rings $\overline{\mathrm{Ti{-}N{-}C{-}C{-}N}}$ of the bound macrocycle adopt either ($\lambda\lambda\lambda$) or ($\delta\delta\delta$) conformation and, consequently, octahedral complexes containing the (Me$_3$tacn)Ti fragment exist in two enantiomeric forms. Since all investigated complexes crystallize in the monoclinic centric space group $C_{2h}{}^5$, both forms are present in the unit cell. The C–C and C–N distances are all in the usual range observed for single bonds of this type and will not be discussed further in the following.

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **4**

atom	*x*	*y*	*z*	*U*(eq)[a]
Ti(1)	2520(1)	747(1)	1351(1)	52(1)
N(1)	2736(6)	659(3)	2795(3)	52(3)
N(2)	691(7)	1191(4)	1866(4)	67(3)
N(3)	3147(7)	1711(3)	1768(4)	61(3)
O(1)	2052(5)	1010(2)	325(3)	76(2)
O(2)	4150(5)	551(3)	1198(3)	88(3)
O(3)	1774(6)	−6(3)	1380(3)	88(3)
C(1)	1407(8)	566(4)	3120(5)	70(4)
C(2)	542(7)	1070(4)	2803(5)	81(4)
C(3)	818(9)	1874(4)	1691(5)	77(4)
C(4)	2058(10)	2106(4)	1993(6)	92(5)
C(5)	3986(8)	1608(4)	2521(6)	84(4)
C(6)	3358(8)	1202(4)	3170(5)	71(4)
C(7)	3480(9)	92(4)	2996(6)	79(4)
C(8)	−432(9)	959(5)	1412(6)	112(6)
C(9)	3930(10)	2007(4)	1089(6)	96(5)
C(10)	2227(9)	1047(5)	−531(5)	87(4)
C(11)	5286(12)	338(9)	944(8)	317(14)
C(12)	1490(14)	−477(5)	863(7)	177(8)
B	7325(10)	−1424(5)	3568(7)	77(5)
C(13)	6706(7)	−1751(4)	2668(4)	41(3)
C(14)	7217(7)	−2296(4)	2338(5)	52(3)
C(15)	6646(10)	−2584(4)	1647(6)	71(4)
C(16)	5555(11)	−2355(5)	1282(6)	79(5)
C(17)	5027(8)	−1823(5)	1612(6)	71(4)
C(18)	5605(8)	−1529(4)	2294(5)	55(3)
C(19)	6992(6)	−653(3)	3623(5)	44(3)
C(20)	7207(7)	−270(5)	2942(5)	59(4)
C(21)	7086(8)	363(5)	3001(6)	66(4)
C(22)	6732(7)	624(4)	3764(7)	63(4)
C(23)	6507(8)	252(5)	4440(6)	64(4)
C(24)	6646(7)	−378(4)	4376(5)	48(3)
C(25)	8946(7)	−1436(3)	3613(6)	48(3)
C(26)	9545(9)	−1325(3)	4387(5)	62(4)
C(27)	10846(10)	−1247(4)	4445(7)	77(4)
C(28)	11600(9)	−1273(4)	3734(8)	79(5)
C(29)	11018(9)	−1375(4)	2963(6)	71(4)
C(30)	9712(8)	−1450(3)	2912(5)	52(3)
C(31)	6634(8)	−1858(4)	4358(4)	45(3)
C(32)	5357(8)	−1760(4)	4539(5)	52(3)
C(33)	4741(9)	−2127(5)	5136(6)	71(4)
C(34)	5400(12)	−2589(5)	5547(6)	81(5)
C(35)	6657(12)	−2693(4)	5362(6)	81(5)
C(36)	7269(9)	−2330(4)	4774(6)	66(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^{-3}) for **5**

atom	*x*	*y*	*z*	*U*(eq)[a]
Ti(1)	179(1)	1894(1)	2497(1)	39(1)
N(1)	2126(4)	2644(3)	1672(2)	43(1)
N(2)	1345(3)	2979(3)	3508(2)	43(1)
N(3)	−731(3)	3626(3)	2087(2)	42(1)
C(1)	3420(4)	2787(3)	2345(3)	54(2)
C(2)	2882(4)	3391(3)	3178(3)	53(2)
C(3)	259(5)	3884(3)	3671(3)	52(2)
C(4)	−214(5)	4432(3)	2784(3)	50(1)
C(5)	−35(5)	3841(3)	1197(3)	51(2)
C(6)	1707(5)	3700(3)	1245(3)	49(1)
C(7)	2625(5)	1899(3)	942(3)	65(2)
C(8)	1599(5)	2375(3)	4369(3)	64(2)
C(9)	−2445(5)	3684(4)	1965(3)	63(2)
O(1)	1712(4)	897(2)	2637(2)	74(1)
O(2)	448(5)	649(3)	3122(3)	98(2)
N(4)	−1793(4)	1901(3)	3281(3)	68(2)
C(10)	−2986(5)	1763(3)	3609(3)	48(2)
O(4)	−4199(4)	1638(3)	3948(2)	76(1)
N(5)	−898(4)	1393(3)	1344(3)	63(1)
C(11)	−1379(6)	683(4)	936(3)	64(2)
O(5)	−1925(5)	−10(3)	489(3)	128(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Crystals of **1** consist of well-separated monocations [(Me$_3$tacn)TiBr$_3$]$^+$ (Figure 1) and perchlorate anions. The titanium(IV) ions are in a pseudooctahedral ligand environment composed of a facially coordinated triamine and three bromide ions. Although the three Ti–N bonds are within experimental error identical (average 2.244 Å), the Ti–Br bonds are not. Ti–Br(3) at 2.372(2) Å is significantly shorter than the other two Ti–Br bonds at an average of 2.404 Å. Since no obvious electronic reason can account for this observation (Ti(IV) has a d^0 electronic configuration), we ascribe this to packing effects in the solid state. The Br–Ti–Br bond angles are larger by ~7.5° than the

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **7**

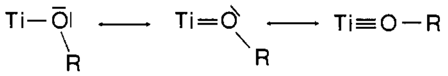
atom	*x*	*y*	*z*	*U*(eq)[a]
Ti(1)	4774(1)	–20(1)	7507(1)	25(1)
Cl(1)	3906(1)	1701(2)	6112(1)	44(1)
Cl(2)	5234(1)	2238(1)	8650(1)	39(1)
O(1)	3665(2)	–907(4)	7596(2)	39(1)
N(1)	6598(3)	395(4)	7399(2)	32(1)
N(2)	4949(3)	–2297(4)	6645(2)	32(1)
N(3)	6080(3)	–1715(4)	8673(2)	32(1)
C(1)	6389(4)	–393(5)	6448(3)	40(2)
C(2)	5928(3)	–2196(6)	6361(3)	43(2)
C(3)	5104(4)	–3746(5)	7316(3)	43(2)
C(4)	6120(4)	–3463(5)	8288(3)	43(2)
C(5)	7227(3)	–874(6)	9034(3)	40(1)
C(6)	7554(3)	–474(5)	8216(3)	39(1)
C(7)	6896(4)	2228(5)	7377(4)	46(2)
C(8)	3857(4)	–2560(6)	5772(3)	49(2)
C(9)	5743(4)	–1878(6)	9505(3)	47(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ideal octahedral angle of 90° whereas the N–Ti–N angles at 77.7° are smaller due to the steric constraints of the macrocyclic ligand.

The crystal structure of [(Me$_3$tacn)TiBr$_2$(OCH$_3$)](ClO$_4$) (**2**) has been reported previously.[1] For comparison with the other structures we briefly summarize pertinent structural data here: Ti–Br = 2.451(3) Å, Ti–O = 1.723(12) Å, Ti–N = 2.287(17) (in trans position to the OCH$_3$ group) and 2.203(12) Å (trans to the Br$^-$ ligands), O–C = 1.42(2) Å, Ti–O–C = 171.4(12)°, Br–Ti–Br = 95.6(1)°, and O–Ti–Br = 97.7(3)°.

Crystals of **3** consist of the monocation [(Me$_3$tacn)TiBr(OCH$_3$)$_2$]$^+$ (Figure 2) and perchlorate anions. The Ti(IV) center is again in a pseudo-octahedral environment composed of the macrocyclic ligand, a bromide ion and two methoxo groups on *cis* position relative to each other. Interestingly, the Ti–Br distance increases to 2.502(2) Å and the average Ti–O distance increases also to 1.741 Å in comparison to those in **2**. It should be noted that the two coordinated methoxo ligands in **3** are not quite equivalent; the Ti–O(1) distance is longer by 0.032 than the Ti–O(2) bond length, which is just outside the experimental error. The two Ti–O–C bond angles corroborate this notion: this angle is 161.7(5)° for the more weakly bound methoxo group but 167.9(5)° for the more tightly bound methoxo group in accord with the following resonance structures. As we will show later this is largely a solid-state effect; in solution the two methoxo groups are equivalent.



Crystals of **4** consist of the monocation [(Me$_3$tacn)Ti(OCH$_3$)$_3$]$^+$ (Figure 3) and [BPh$_4$]$^-$ anions. The cation contains three facially coordinated methoxo ligands which are not equivalent in the solid state. Three different Ti–O distances ranging from 1.764(6) to 1.795(6) Å and concomitantly three different Ti–N distances in the range 2.266(7)–2.291(5) Å are observed. The Ti–O–C bond angles vary from 139.8(6)° for the most weakly bound to 168.1(7)° for the most tightly bound methoxo group in accord with the resonance structures depicted above. The three sums of one Ti–N and one Ti–O bond in trans position relative to this bond are 4.067, 4.043, and 4.061 Å, respectively, i.e. nearly constant. The O–Ti–O bond angles at an average of 101.7° are distinctly larger than the regular octahedral angle of 90°. This is a clear indication of considerable Ti=OR double bond character (π-bonding). In (Me$_3$tacn)M(O)$_3$ and related complexes (M = Mo,

Table 7. Selected Bond Distances (Å) and Angles (deg)

Complex **1**			
Ti–Br(1)	2.400(2)	Ti–N(1)	2.241(7)
Ti–Br(2)	2.408(2)	Ti–N(2)	2.244(7)
Ti–Br(3)	2.372(2)	Ti–N(3)	2.248(7)
Br(1)–Ti–Br(2)	97.4(1)	Br(1)–Ti–Br(3)	97.6(1)
Br(2)–Ti–Br(3)	97.5(1)	Br(1)–Ti–N(1)	165.7(2)
Br(2)–Ti–N(1)	91.6(2)	Br(3)–Ti–N(1)	92.1(2)
Br(1)–Ti–N(2)	91.5(2)	Br(2)–Ti–N(2)	90.6(2)
Br(3)–Ti–N(2)	166.9(2)	N(1)–Ti–N(2)	77.3(3)
Br(1)–Ti–N(3)	91.2(2)	Br(2)–Ti–N(3)	165.8(2)
Br(3)–Ti–N(3)	92.5(2)	N(1)–Ti–N(3)	77.9(2)
N(2)–Ti–N(3)	77.8(2)		
Complex **3**			
Ti–Br(1)	2.502(2)	Ti–O(1)	1.757(5)
Ti–N(1)	2.269(6)	Ti–O(2)	1.725(5)
Ti–N(2)	2.201(6)	O(1)–C(11)	1.311(10)
Ti–N(3)	2.270(6)	O(2)–C(12)	1.338(9)
Br(1)–Ti–N(1)	90.2(2)	N(3)–Ti–O(1)	163.7(2)
Br(2)–Ti–N(2)	165.1(2)	Br(1)–Ti–O(2)	95.8(2)
N(1)–Ti–N(2)	77.4(2)	N(1)–Ti–O(2)	164.4(2)
Br(1)–Ti–N(3)	91.4(2)	N(2)–Ti–O(2)	94.4(2)
N(1)–Ti–N(3)	75.9(2)	N(3)–Ti–O(2)	89.5(2)
N(2)–Ti–N(3)	77.8(2)	O(1)–Ti–O(2)	103.9(3)
Br(1)–Ti–O(1)	96.4(2)	Ti–O(1)–C(11)	161.7(5)
N(1)–Ti–O(1)	89.8(3)	Ti–O(2)–C(12)	167.9(5)
N(2)–Ti–O(1)	91.7(2)		
Complex **4**			
Ti–N(1)	2.291(5)	Ti–N(2)	2.279(7)
Ti–N(3)	2.266(7)	Ti–O(1)	1.776(5)
Ti–O(2)	1.764(6)	Ti–O(3)	1.795(6)
O(1)–C(10)	1.363(9)	O(2)–C(11)	1.330(15)
O(3)–C(12)	1.330(13)		
N(1)–Ti–N(2)	76.1(2)	N(1)–Ti–N(3)	76.2(2)
N(2)–Ti–N(3)	75.8(3)	N(1)–Ti–O(1)	162.5(2)
N(2)–Ti–O(1)	88.1(2)	N(3)–Ti–O(1)	92.9(2)
N(1)–Ti–O(2)	91.5(2)	N(2)–Ti–O(2)	162.2(3)
N(3)–Ti–O(2)	89.0(3)	O(1)–Ti–O(2)	102.1(3)
N(1)–Ti–O(3)	86.6(2)	N(2)–Ti–O(3)	90.4(3)
N(3)–Ti–O(3)	160.0(3)	O(1)–Ti–O(3)	101.2(2)
O(2)–Ti–O(3)	101.7(3)	Ti–O(2)–C(11)	168.1(7)
Ti–O(3)–C(12)	139.8(6)	Ti–O(1)–C(10)	151.7(6)
Complex **5**			
Ti–N(1)	2.286(3)	Ti–O(1)	1.821(5)
Ti–N(2)	2.231(3)	Ti–O(2)	1.815(4)
Ti–N(3)	2.372(3)	Ti–N(4)	2.069(4)
Ti–N(5)	2.012(4)	N(4)–C(10)	1.156(6)
O(5)–C(11)	1.178(6)	N(5)–C(11)	1.141(6)
O(4)–C(10)	1.176(5)	O(1)–O(2)	1.348(5)
N(1)–Ti–N(2)	77.3(1)	O(1)–Ti–N(4)	122.7(2)
N(1)–Ti–N(3)	74.6(1)	O(2)–Ti–N(4)	79.6(2)
N(2)–Ti–N(3)	75.9(1)	N(1)–Ti–N(5)	90.7(1)
N(1)–Ti–O(1)	78.6(1)	N(2)–Ti–N(5)	160.2(1)
N(2)–Ti–O(1)	91.5(1)	N(3)–Ti–N(5)	85.8(1)
N(3)–Ti–O(1)	152.3(1)	O(1)–Ti–N(5)	101.7(2)
N(1)–Ti–O(2)	122.0(2)	O(2)–Ti–N(5)	102.1(2)
N(2)–Ti–O(2)	97.6(1)	N(4)–Ti–N(5)	95.7(2)
N(3)–Ti–O(2)	161.0(2)	Ti–N(5)–C(11)	146.9(4)
O(1)–Ti–O(2)	43.5(2)	Ti–N(4)–C(10)	167.5(4)
N(1)–Ti–N(4)	155.6(1)	N(4)–C(10)–O(4)	179.0(5)
N(2)–Ti–N(4)	89.5(1)	N(5)–C(11)–O(5)	176.3(5)
N(3)–Ti–N(4)	82.4(1)	Ti–O(1)–O(2)	68.0(2)
		Ti–O(2)–O(1)	68.5(2)
Complex **7**			
Ti–Cl(1)	2.357(2)	Ti–Cl(2)	2.371(2)
Ti–O(1)	1.637(3)	Ti–N(1)	2.432(4)
Ti–N(2)	2.275(4)	Ti–N(3)	2.283(3)
Cl(1)–Ti–Cl(2)	96.2(1)	Cl(1)–Ti–O(1)	102.4(1)
Cl(2)–Ti–O(1)	102.5(1)	Cl(1)–Ti–N(1)	88.3(1)
Cl(2)–Ti–N(1)	89.8(1)	O(1)–Ti–N(1)	162.6(1)
Cl(1)–Ti–N(2)	93.2(1)	Cl(2)–Ti–N(2)	161.7(1)
O(1)–Ti–N(2)	90.6(1)	N(1)–Ti–N(2)	74.9(1)
Cl(1)–Ti–N(3)	160.9(1)	Cl(2)–Ti–N(3)	89.4(1)
O(1)–Ti–N(3)	94.1(1)	N(1)–Ti–N(3)	73.5(1)
N(2)–Ti–N(3)	76.9(1)		

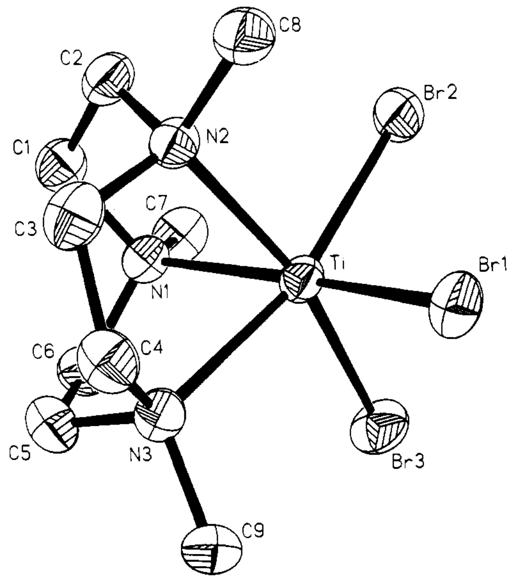


Figure 1. Structure of the monocation in crystals of **1** (ellipsoids are drawn at the 40 % probability level).

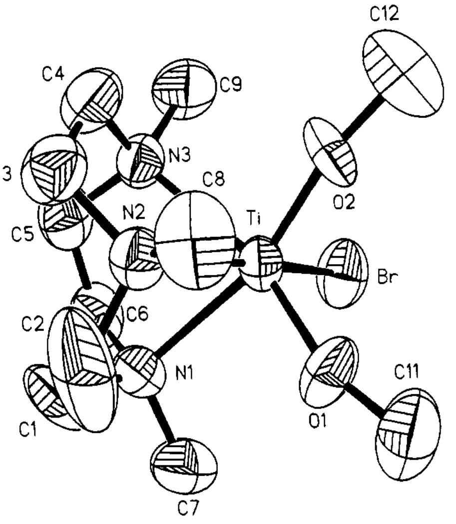


Figure 2. Structure of the monocation in crystals of **3**.

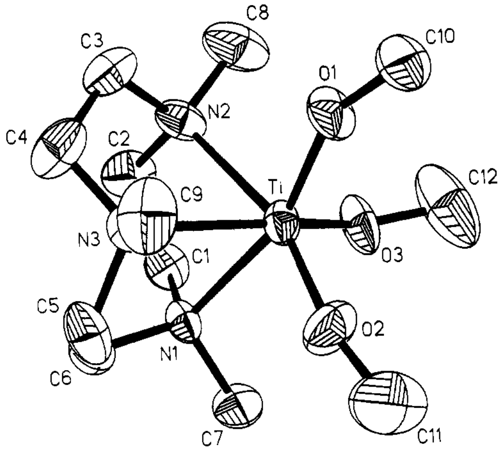


Figure 3. Structure of the monocation in crystals of **4**.

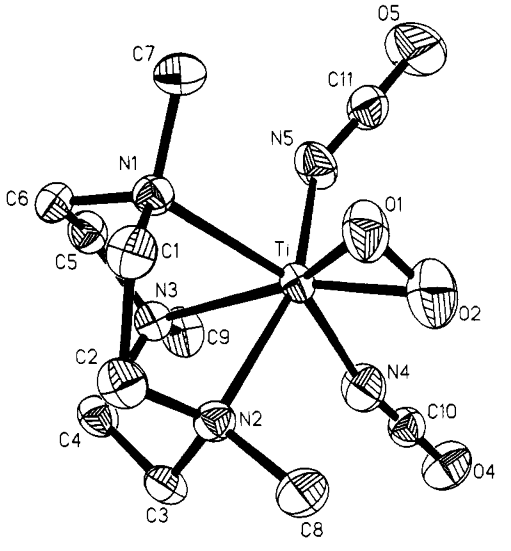


Figure 4. Structure of the peroxotitanium(IV) species in compositionally disordered crystals of **5**.

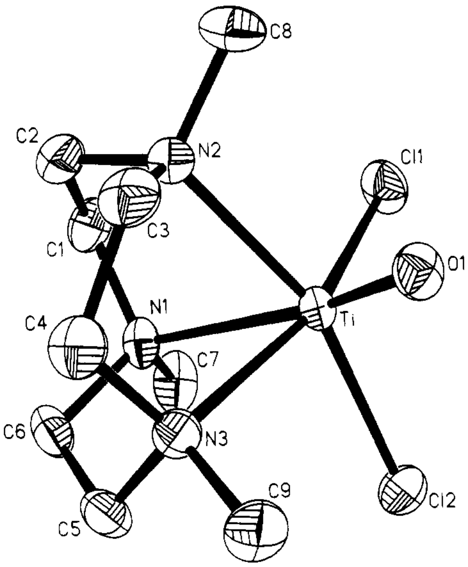


Figure 5. Structure of the monocation in crystals of **7**.

W) which contain three terminal oxo groups similar O–M–O angles have been observed at ~103°.[2,7]

Figure 4 shows the structure of the neutral molecules in a orange-red crystal of **5**. Although vibrational spectroscopy and the electrochemistry unambiguously establishes that these crystals also contain molecules of [(Me$_3$tacn)Ti(O)(NCO)$_2$], this has not been detected by X-ray crystallography. Only the unreasonably short observed O–O distance of 1.348(5) Å is an indication that a compositional disorder prevails. In all other crystallographically characterized peroxotitanium(IV) complexes this bond distance is in the range 1.42–1.48 Å.[8] Parkin has recently summarized the effects of compositional disorder of crystals on X-ray structure determinations.[20] We refrain from a discussion of the metrical details of the present structure which does, however, establish the atom connectivity in [(Me$_3$tacn)Ti(O$_2$)(NCO)$_2$] unambiguously.

We have also carried out a complete single-crystal X-ray structure determination of an orange-red crystal of [(Me$_3$tacn)-Ti(O$_2$)Cl$_2$] (**6**) which also contains an appreciable amount of [(Me$_3$tacn)Ti(O)Cl$_2$)] (**7**). The crystal data are as follows: orthorhombic space group $Pbn2_1$, a = 7.86(1) Å, b = 12.873(2) Å, c = 13.839(3) Å, V = 1401.5(10) Å^3, Z = 4. On the basis of 2884 observed unique reflections ($I \geq 2.5\sigma(I)$) and 156 least-squares parameters, the structure refined smoothly to final discrepancy factors of R = 0.055 and R_w = 0.053. Five distinct

---

[7] (a) Wolowiec, S.; Kochi, J. K. *Inorg. Chem.* **1991**, *30*, 1215. (b) Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Anorg. Allg. Chem.* **1990**, *587*, 174.

[8] (a) Schwarzenbach, D. *Inorg. Chem.* **1970**, *9*, 2391. (b) Schwarzenbach, D.; Girgis, K. *Helv. Chim. Acta* **1975**, *58*, 2391. (c) Schmidt, R.; Pausewang, G. *Z. Anorg. Allg. Chem.* **1988**, *559*, 135. (d) Mimoun, H.; Postel, M.; Casabianca, F.; Fischer, J.; Mitschler, A. *Inorg. Chem.* **1982**, *21*, 1303.

positions for oxygen atoms with variable occupancy factors were found and refined: two disordered Ti(O_2) groups accounting for ~50% of **6** and one Ti=O group of **7** (~50%) were detected. In this instance X-ray crystallography clearly showed the compositional disorder.

Colorless crystals of **7** consist of neutral molecules of [(Me$_3$tacn)Ti(O)Cl$_2$] (Figure 5). Complex **7** is the second structurally characterized octahedral titanyl complex.[9] The Ti=O bond length of 1.637(3) Å is short and indicates considerable double-bond character; in [(Me$_3$tacn)Ti(O)(NCS)$_2$] this bond is at 1.638(3) Å.[1] In five-coordinate titanyl porphyrin complexes the Ti=O bond length is 1.62 Å whereas in the seven-coordinate species [TiO(CO$_3$)$_3$]$^{4-}$ the Ti=O bond is longer at 1.680(2) Å, which is a consequence of two relatively strong hydrogen bonding contacts to the Ti=O group.[9f] The Ti–N$_{amine}$ distances in **7** are not equivalent; two relatively short Ti–N bonds in cis position with respect to the oxo ligand and a long Ti–N distance in trans position are observed. The difference Δ[(Ti–N$_{trans}$) – (average Ti–N$_{cis}$)] of 0.153 Å clearly demonstrates a sizable structural *trans*-influence of the oxo group; for [(Me$_3$tacn)Ti(O)(NCS)$_2$] this difference is 0.18 Å. The average Ti^{IV}–Cl distance in **7** of 2.364(2) Å is slightly larger than the corresponding average Ti^{III}–Cl bond length of 2.352(1) Å in [(Me$_3$tacn)TiCl$_3$], which is somewhat counterintuitive since the ionic radius of octahedral Ti(III) is slightly larger (0.67 Å) than the one of Ti(IV) (0.61 Å). It is interesting to note that in the μ-oxo bridged analogue [(Me$_3$tacn)$_2$Ti^{III}Ti^{IV}Cl$_4$(μ-O)]Cl·2H$_2$O the average Ti–Cl bond length is 2.320(2) Å.[1] This may be taken as an indication that strong π-donation of the terminal Ti=O group in **7** exerts also a small structural *cis*-influence of the order of ~0.03 Å.

Vibrational Spectroscopy. Infrared (CsI disks) and Raman spectra of samples of complexes **1**–**4** have been recorded in the range 100–800 cm^{-1}. In addition, infrared spectra of acetonitrile solutions of these species have been measured. The results are summarized in Table 8; Figure 6 displays the spectra in the range 100–800 cm^{-1} for complexes **1**–**4**.

All investigated complexes contain the (Me$_3$tacn)Ti^{IV} fragment, and consequently, bands due to (Ti–N) stretch and deformation modes are observed in the ranges 410–460 and 320–330 cm^{-1}, respectively. For this fragment two (Ti–N) stretching (ν_s and ν_{as}, $\nu_1(A_1)$ and $\nu_3(E)$) and two Ti–N deformation bands (δ_s and δ_{as}; $\nu_2(A_1)$ and $\nu_4(E)$) are expected. We observe in all cases three (Ti–N) stretching and one deformation band regardless of the symmetry of the respective N$_3$TiXYZ core (idealized C_{3v} for **1** and **4** and C_s for **2** and **3**). It is interesting to note that these frequencies shift slightly to lower energies in the order **1** > **2** > **3** > **4**. This is taken as an indication for an increasing weakening of the Ti–N bonds with an increasing number of π-donating methoxo ligands. This effect is—barely significantly—also reflected in the average Ti–N bond lengths of complexes **1**–**4** which increase from 2.244 Å in **1** to 2.279 Å in **4**.

The Ti–Br stretching modes ν_s and ν_{as} are clearly detected in the vibrational spectra of **1** and **2** in the range 335–365 cm^{-1}; for **3** only one Ti–Br stretching mode at 358 cm^{-1} in the infrared and at 357 cm^{-1} in the Raman spectrum is observed. Two aspects are of importance here. First, in the spectra of **1** the crystallographically determined inequivalency of the Ti–Br distances (C_s symmetry of the N$_3$TiBr$_3$ core) is not detectable. This may be due to an accidental degeneracy of two modes. Second, the energy of the symmetric ν(Ti–Br) stretching frequency decreases in the order **1** > **2** > **3** which is in agreement with the crystallographically determined decrease of the average Ti–Br bond distance with an increasing number of π-donating methoxo groups (zero in **1** and two in **3**).

Table 8. Infrared and Raman Spectroscopic Data of Complexes **1**–**4** in the Range 100–620 cm^{-1}

complex	IR, cm^{-1} ^{a}	Raman, cm^{-1} ^{a}	IR, cm^{-1} ^{b}	assignt
1	140 (w)^c			
	178 (w)			
	201 (w)	199 (vs)		
		248 (w)		
	321 (vw)			δ(TiN$_3$)
	337 (w)	335 (w)		ν(Ti–Br)
	365 (m)	363 (w)		
	422 (w)	422 (m)	418 (vw)	ν(Ti–N)
	440 (vw)	442 (m)	438 (vw)	
	458 (m)	458 (s)	456 (w)	
2	155 (w)			
	192 (w)	194 (vw)		
		223 (s)		
	235 (vw)	234 (sh)		
	252 (w)	252 (s)		
	324 (vw)			δ(TiN$_3$)
	346 (sh)	345 (s)		ν(Ti–Br)
	363 (s)	361 (s)		
	420 (w)	419 (m)	418 (m)	ν(Ti–N)
	432 (w)		431 (w)	
	457 (m)	458 (s)	456 (m)	
	620 (sh)	619 (m)	620 (sh)	ν(Ti–O)
3	154 (w)			
	192 (w)	187 (s)		
	215 (vw)	215 (s)		
		240 (sh)		
	252 (vw)	254 (s)		
	330 (vw)			δ(TiN$_3$)
	358 (s)	357 (m)		ν(Ti–Br)
	416 (w)	417 (w)	416 (w)	ν(Ti–N)
	425 (w)		427 (w)	
	453 (m)	454 (s)	451 (m)	
	578 (m)	580 (s)	592 (w)	ν(Ti–O)
	590 (m)	591 (s)	612 (m)	
4	172 (vw)			
	210 (vw)	212 (m)		
		240 (m)		
	250 (w)	252 (s)		
	265 (w)	265 (s)		
	330 (vw)			δ(TiN$_3$)
	411 (w)	412 (w)	410 (w)	ν(Ti–N)
	426 (w)	425 (vw)	425 (w)	
	449 (m)	449 (s)	447 (m)	
	565 (sh)	566 (m)		
	568 (s)	570 (m)	571 (m)	ν(Ti–O)
	587 (s)	588 (w)	589 (s)	

[a] Measured as polycrystalline solid samples; IR (CsI disks). [b] Measured in acetonitrile solution. [c] Abbreviations: m = medium; w = weak; vw = very weak; s = strong; sh = shoulder.

The ν(Ti–O) stretching modes of **2**–**4** are observed in the range 565–620 cm^{-1}. The tris(methoxo) species **4** displays three such frequencies in the solid-state infrared and Raman spectrum which agrees with the crystallographically determined inequivalency of all three coordinated CH$_3$O$^-$ groups. In contrast, the solution infrared spectrum of **4** exhibits only two ν(Ti–O) stretching frequencies at 571 cm^{-1} (ν_{as}) and 589 cm^{-1} (ν_s) (Figure 7) which may be taken as indication that in solution the three methoxo ligands in **4** are equivalent.

The ν_s(Ti–O) mode is shifted to lower energy with increasing number of methoxo ligands: **2** at 620, **3** at 590, and **4** at 587 cm^{-1}. Thus accumulation of π-donor leads to a weakening of the individual double or triple Ti–O bond character. In the infrared spectra of **2** and **3** the ν(C–O) stretching mode of the methoxo ligands is hidden by the intense ν(ClO$_4$) frequency at 1089 cm^{-1} but for the tetraphenylborate salt **4** this mode is clearly detected by two intense bands at 1083 and 1158 cm^{-1}, indicating also the presence of at least two inequivalent methoxo ligands in agreement with the crystal structure.

The infrared and Raman spectra of the (η^2-peroxo)titanium(IV) complexes **5** and **6** display the expected bands due to presence

---

(9) (a) Guilard, R.; Latour, J. M.; Lecomte, C.; Marchon, J.-C.; Protas, J.; Ripoll, D. *Inorg. Chem.* **1978**, *17*, 1228. (b) Dwyer, P. N.; Puppe, L.; Buchler, J. W.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 1782. (c) Hiller, W.; Strähle, J.; Kobel, W.; Hanack, M. *Z. Kristallogr.* **1982**, *159*, 173. (d) Feltz, A. *Z. Chem.* **1967**, *7*, 158. (e) Dehnicke, K.; Pausewang, G.; Rüdorff, W. Z. *Z. Anorg. Allg. Chem.* **1969**, *366*, 64. (f) Peng-Ju, L.; Sheng-Hua, H.; Kun-Yao, H.; Ru-Ji, W.; Mak, C. W. *Inorg. Chim. Acta* **1990**, *175*, 105.

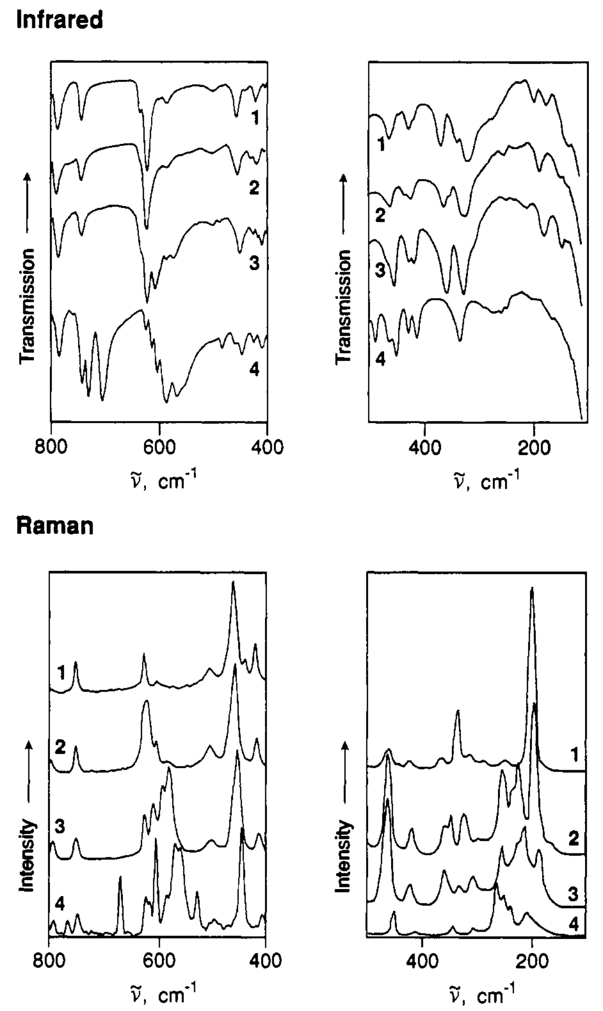


Figure 6. Infrared (top) and Raman (bottom) spectra of solid samples of complexes **1**–**4**.

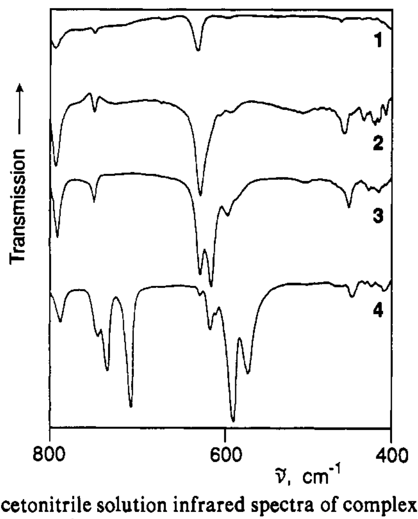


Figure 7. Acetonitrile solution infrared spectra of complexes **1**–**4** in the range 400–800 cm^{-1}.

Table 9. Selected Vibrational Data of Solid Samples of Complexes **5**–**8**[a]

complex	IR, cm^{-1}	Raman, cm^{-1}	assignt
5	938 (s)[b]	935 (s)	ν(Ti=O)
	907 (s)	906 (m)	ν(O–O)
	621 (s)	522 (m)	$\nu_s(TiO_2)$
	565 (m).		$\nu_{as}(TiO_2)$
	2218 (s)	2212	ν(NCO)
	2186 (s)	2187	
6	933 (s)	932 (s)	ν(Ti=O)
	907 (s)	906 (m)	ν(O–O)
	614 (s)	615 (m)	$\nu_s(TiO_2)$
	564 (m)		$\nu_{as}(TiO_2)$
7	933 (s)	932 (vs)	ν(Ti=O)
8	955 (s)	950 (vs)	ν(Ti=O)
	2066 (vs)	2060 (s)	ν(NCS)
	2033 (vs)	2032 (s)	
9	948 (vs)	949 (vs)	ν(Ti=O)
	2222 (vs)	2220 (s)	ν(NCO)
	2189 (vs)	2186 (m)	

[a] Infrared spectra were recorded as KBr disks. [b] Abbreviations: vs = very strong; s = strong; m = medium.

Table 10. UV–Vis Spectral Data for Complexes in the Range 210–1100 nm in Acetonitrile Solution

complex	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})
1	252 (1.2 × 10^4), 312 (4.7 × 10^3), 394 (7.7 × 10^3)
2	284 (5.8 × 10^3), 381 (2.0 × 10^3)
3	270 (sh)
4	*a*
5	215 (1.0 × 10^4), 239 (9.5 × 10^3), 410 (325)[b]
6	240 (5.4 × 10^3), 275 (sh), 427 (290)[b]
7	242 (6.6 × 10^3), 270 (3.5 × 10^3)
8	233 (5.7 × 10^3), 290 (2.3 × 10^4), 316 (2.8 × 10^4)
9	217 (1.5 × 10^4), 252 (1.2 × 10^4)

[a] Two absorption maxima due to the tetraphenylborate anion ($\pi \rightarrow \pi^*$ transitions) at 265 and 275 nm are observed. [b] Molar absorption coefficients were calculated on the assumption that the samples are 100% pure, which they are not. The values are therefore only approximate values—they could be twice as high (see text).

of side-on coordinated peroxide: a ν(O–O) stretching frequency at 907 cm^{-1} for **5** and **6**, a $\nu_s(Ti(O)_2)$) at 621 for **5** and 614 cm^{-1} for **6**, as well as a $\nu_{as}(Ti(O_2))$ at 565 and 564 cm^{-1}, respectively, in the infrared (Table 9). Similar bands have been reported for $K_2[Ti(O_2)F_4]\cdot H_2O$[8c] and $[Ti(O_2)(PhNO_2)_2]OPN_3C_6H_{18}$.[8d]

In addition, a strong band at 938 cm^{-1} for **5** and at 933 cm^{-1} for **6** has been observed. This mode is assigned to a ν(Ti=O) stretching mode of the corresponding titanyl impurity [(Me$_3$tacn)Ti(O)(NCO)$_2$] or **7** which display this band at 942 and 933 cm^{-1}, respectively, in the infrared and Raman spectrum. Thus from these data it is clear that crystals of **5** and **6** are compositionally disordered; they contain substantial amounts of titanyl species.

Electronic Spectra. Electronic spectra of acetonitrile solutions of complexes were recorded in the range 210–1100 nm, the results are summarized in Table 10. Complexes **1**–**4** containing a titanium(IV) central ion with d^0 electronic configuration display ligand-to-metal charge transfer bands in the UV region only. The yellow tribromo species **1** displays an absorption maximum at 394 nm which moves to shorter wavelengths upon successive substitution of bromo by methoxo ligands. It has not been possible to unambiguously identify these charge transfer bands for **4** due to the overlapping $\pi \rightarrow \pi^*$ transitions of the tetraphenylborate anion. This agrees well with the notion that three methoxo ligands affect a stronger splitting than three bromo ligands of the low-lying, filled molecular orbitals having mostly ligand character and higher-energy, empty MO's having mostly metal character.

It is also worth noticing that the octahedral titanyl complexes **7**–**9** of the present series are essentially colorless. No oxo-to-metal charge transfer bands have been identified. This observation rules out the suggestion that **7** is the sole impurity in the *green* form of [(Me$_3$tacn)Ti^{III}Cl$_3$],[1] for which a strong absorption maximum at 390 nm has been observed contrasting in this respect the pure blue form. Only the η^2-peroxotitanium(IV) species **5** and **6** display charge transfer maxima in the visible (410 and 427 nm, respectively).

Electrochemistry. Cyclic voltammograms (CV) of complexes dissolved in acetonitrile containing 0.10 M [TBA]PF$_6$ supporting electrolyte were recorded at a Pt-button working electrode in the potential range −2.0 to +2.0 V vs Ag/AgCl (saturated LiCl in ethanol). Table 11 summarizes the results.

Table 11. Summary of Electrochemical Data for Complexes[a]

complex	potential, *V* vs Ag/AgCl[b]	complex	potential, *V* vs Ag/AgCl[b]
1	+0.53 (r)	**6**	+1.67 (qr), −1.42 (irr), −1.76 (irr)
2	−0.06 (r)	**7**	−1.76 (irr)
3	−0.92 (r)	**8**	−1.32 (irr)
4	−1.58 (irr)	**9**	−1.32 (irr)
5	+1.61 (qr), −1.52 (irr), −1.77 (qr)		

[a] Measured in dry acetonitrile at 20 °C. Conditions: 0.10 M tetra-*N*-butylammonium hexafluorophosphate; [complex] ~ 10^{-3} M; Pt-button working electrode, Pt-wire auxiliary electrode; Ag/AgCl (saturated LiCl/C_2H_5OH) reference electrode; scan rates 50–200 mV/s. [b] $E_{1/2}$(V) values $(E_{p,a} + E_{p,c})/2$ for reversible (r) and quasi-reversible (qr) processes and peak potentials for irreversible (irr) processes at 50 mV s^{-1} scan rate are listed.

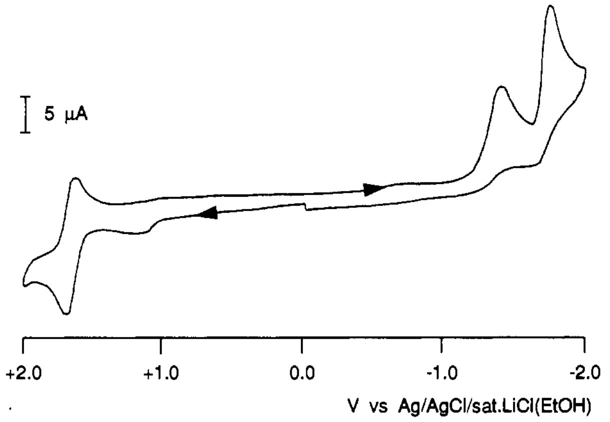


Figure 8. Cyclic voltammogram of an acetonitrile solution of contaminated crystals of **6** (0.10 M [TBA](PF_6) supporting electrolyte: Pt-button working electrode, scan rate 50 mV/s^{-1}).

Complexes **1**–**3** display a reversible one-electron transfer wave according to eq 1 as has been deduced from the diagnostic criteria and coulometry.

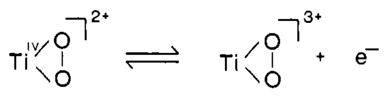
$$[(Me_3tacn)Ti^{IV}Br_x(OCH_3)_{3-x}]^+ \underset{-e^-}{\overset{+e^-}{\rightleftarrows}} [(Me_3tacn)Ti^{III}Br_x(OCH_3)_{3-x}]^0 \quad (1)$$

$$x = 1, 2, 3$$

Interestingly, substitution of one bromo by a methoxo ligand stabilizes the tetravalent oxidation state of the respective titanium(IV) ion by ~ 700 mV. The trismethoxo species **4** is only irreversibly reduced at a very negative potential of −1.58 V vs Ag/AgCl.

Stabilization of Ti(IV) is also quite dramatically achieved by one terminal oxo ligand. Thus complexes **7**–**9** are also only irreversibly reduced at potentials more negative than −1.32 V vs Ag/AgCl.

Figure 8 shows the cyclic voltammogram of the peroxo species **6**, which is known to be cocrystallized with the titanyl complex **7**. The CV of **5** is very similar. Both **5** and **6** display a quasi-reversible oxidation wave at +1.61 and +1.67 V vs Ag/AgCl which may be assigned to the formation of η^2-superoxotitanium(IV) species, eq 2.



(2)

On the other hand, two irreversible reduction peaks are observed at very negative potentials in the CVs of **5** and **6**. For **6** the irreversible reduction at −1.76 V is clearly identical with the reduction of **7** which is known to be present in crystals of **6** (infrared spectrum). The same holds for the irreversible wave at −1.77 V vs Ag/AgCl in the CV of **5**, which corresponds to the reduction of pure $[(Me_3tacn)Ti(O)(NCO)_2]$.[1] The irreversible reductions at −1.52 for **5** and −1.42 V vs Ag/AgCl for **6** belong to the corresponding peroxotitanium(IV) species.

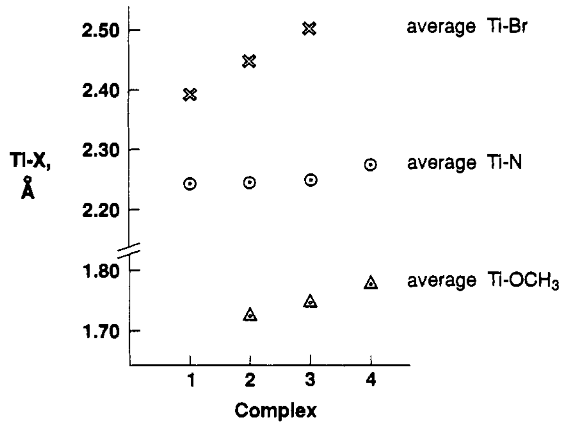


Figure 9. Comparison of averaged Ti–X bond distances in complexes **1**–**4**.

Discussion

Mono- and polynuclear alkoxotitanium(IV) complexes constitute a well characterized, important class of coordination compounds.[10,11] The π-donating capability of the oxygen donor atom of the alkoxy or phenoxy ligands has been invoked to explain the observed relatively short Ti–OR distances. The propensity of the strongly Lewis acidic titanium(IV) centers for attaining a noble gas electron configuration via formation of $p_\pi \rightarrow d_\pi$ double or triple oxygen-to-titanium bonds is a further important factor.[11] The present series of mononuclear octahedral, mono-, di-, and trimethoxo-coordinated complexes **2**–**4** in conjunction with the tribromo analogue **1** allows a detailed assessment of these factors.

Figure 9 compares average Ti–Br, Ti–N, and Ti–O bond lengths in complexes **1**–**4**. Clearly, a monotonic increase of the average Ti–Br distance is observed with an increasing number of methoxo ligands on going from complex **1** to complex **3**. The same, although somewhat less pronounced, is true for the Ti–O bonds which also increase with an increasing number of coordinated methoxo groups in complexes **2**–**4**. On the other hand, the average Ti–N bond distances in **1**–**3** are constant; only for **4** is a slight increase observed. To our knowledge the tetranuclear complex $[Ti(OCH_3)_4]_4$ is the only other structurally characterized octahedral alkoxotitanium(IV) species containing three terminal facially bound methoxo ligands. Here also the three methoxo ligands are not equivalent in the solid state.[12]

The following trends nicely show that π-donation of an individual alkoxo ligand decreases with the presence of an increasing number of these ligands. (a) The Ti–O distance increases and, concomitantly, the average Ti–O–C bond angle decreases in the series **2**–**4**. The expected increase of the O–C distance with increasing titanium-to-oxygen multiple bond character is small and within the experimental error limits of our structure determinations. (b) Deviations of the O–Ti–O angles in **3** and **4** from the ideal octahedral angle—they are obtuse—are very similar to those observed in high-valent early transition metal complexes containing a *cis*-trioxo group.[7]

Electrostatic considerations imply that a titanium(IV) ion in an octahedral ligand environment will only accept a certain maximal electron density from σ- and π-donation of the ligands

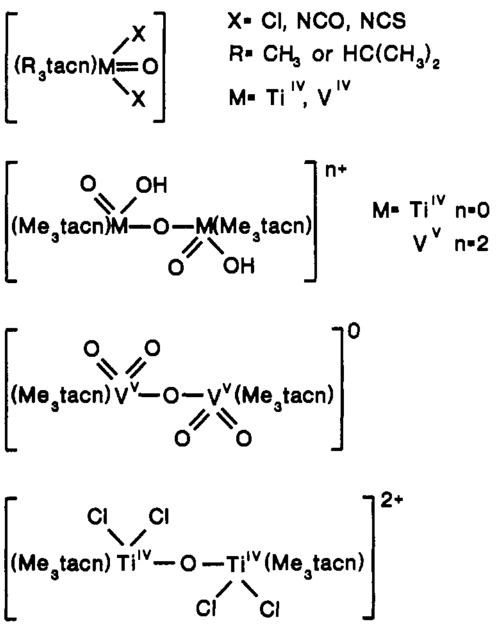
---

(10) McAuliffe, C. A.; Barratt, D. S. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987, Vol. 3, p 323.

(11) (a) Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259. (b) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269.

(12) Wright, D. A.; Williams, D. A. *Acta Crystallogr. Sect. B* **1968**, *B24*, 1107.

Scheme 3



(charge neutralization). Alkoxo ligands are good σ- and π-donors and accumulation of more than one such ligand will lead to weaker individual interactions. With two or three alkoxo ligands as in **3** and **4** this charge neutralization can occur in a symmetrical fashion leading to two (or three) equivalently bound alkoxo ligands or in an asymmetric fashion as is observed in the solid state structures. We propose that complexes **1–4** are ideal test cases for the improvement, development and testing of universal force fields[13] for molecular mechanics calculation of transition metal complexes.

The second important aspect of this work is the discovery that octahedral titanyl complexes **7–9** with a Ti=O group are synthetically readily available from titanium(III) precursor complexes by oxidation with dioxygen in an aprotic solvent. In the presence of water alcohols the same reaction yields dinuclear oxo-bridged species.[1] It is of significance that analogous vanadyl species of complexes **7–9** namely [(Me$_3$tacn)VOCl$_2$],[14] [(Me$_3$tacn)VO(NCO)$_2$],[15] and [(tiptacn)VO(NCS)$_2$][2] have been reported. Scheme 3 summarizes some mononuclear and dinuclear species which have now been characterized in vanadium(IV,V) and titanium(IV) chemistry. Therefore, titanyl complexes no longer constitute a laboratory curiosity; Classical Werner-type species as well as organometallic complexes of the type (Me$_5$C$_5$)$_2$Ti(O)L[16] have been synthesized and structurally characterized. The Ti=O bond distance is in the range 1.61–1.68 Å and depends on the coordination number and involvement of the oxo group in intermolecular hydrogen bonding;[9] the corresponding V=O distance in monooxo vanadium(IV) and -(V) complexes is shorter (1.55–1.59 Å).[17] As Comba and Merbach[18] have pointed out, the Ti^{IV}=O group is more basic and more susceptible to electrophilic attack by protons leading to Ti–O–Ti species than the same vanadyl complexes with a V^{IV}=O unit. An organometallic example for this notion has recently been reported by Andersen et al.[16] who have shown that the mononuclear complexes (Me$_5$C$_5$)$_2$MO (M = V, Ti) decompose with formation of tetranuclear oxo bridged species ([Me$_5$C$_5$)$_4$M$_4$(μ-O)$_6$]. It is noted that the analogous Werner-type tetranuclear species with an adamantane-like core structure, [([9]aneN$_3$)$_4$Ti$_4$(μ-O)$_6$]Br$_4$, has also been described.[19,20]

Finally, we would like to further comment on the crystal structure determination of the η^2-peroxotitanium(IV) complex **5**. The single-crystal X-ray analysis does not immediately reveal that actually a compositionally disordered crystal has been studied. Inspection of the thermal parameters (U_{eq} in Table 5 and anisotropic thermal parameters in the supplementary material) shows that the oxygens O(1) and O(2) of the side-on coordinated peroxo group have only marginally larger thermal parameters than those of other lighter atoms like nitrogen and carbon. It is only the unusually short O–O distance which alerts one's suspicion. Without the clear infrared spectroscopic and electrochemical evidence for the presence of colorless [(Me$_3$tacn)Ti(O)(NCO)$_2$] in these crystals of **5**, it would have been impossible to establish the compositional disorder by using X-ray crystallography alone. This is reminiscent of the problems encountered in the structure determination of [Ir(dppe)$_2$(η^2-O$_2$)PF^6.[21] For a detailed discussion of the effects of compositional disorder on the accuracy of structure determinations by X-ray crystallography see ref 20.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support of this work.

Supplementary Material Available: For complexes **1**, **3**, **4**, **5**, and **7** listings of crystallographic data, bond lengths and angles, anisotropic thermal parameters, and calculated positions of hydrogen atoms (28 pages). Ordering information is given on any current masthead page.

---

(13) Rappe', A. K.; Colwell, K. S.; Casewit, C. J. *Inorg. Chem.* **1993**, *32*, 3438.

(14) Köppen, M.; Fresen, G.; Wieghardt, K.; Llusar, R. M.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1988**, *27*, 721.

(15) Knopp, P.; Wieghardt, K.; Nuber, B.; Weiss, J.; Sheldrick, W. S. *Inorg. Chem.* **1990**, *29*, 363.

(16) Smith III, M. R.; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7049.

(17) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(18) Comba, P.; Merbach, A. *Inorg. Chem.* **1987**, *26*, 1315.

(19) Wieghardt, K.; Ventur, D.; Tsay, Y. H.; Krüger, C. *Inorg. Chim. Acta* **1985**, *99*, L25.

(20) Parkin, G. *Chem. Rev.* **1993**, *93*, 887.

(21) (a) McGinnety, J. A.; Payne, N. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 6301. (b) Nolte, M. J.; Singleton, E.; Laing, M. *J. Am. Chem. Soc.* **1975**, *97*, 6396.