Kinetics and Mechanism of Some Reactions of Chelated Complexes of Titanium(IV) with Hydrogen Peroxide. Synthesis and Crystal Structure of Cesium Tetra-μ-oxo-tetrakis[(nitrilotriacetato)titanate(IV)] Hexahydrate

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The preparation and characterization of three complexes of titanium(IV) are reported: [TiO(dipic)(OH$_2$)]·3H$_2$O, [TiO-(IDA)(OH$_2$)]·2H$_2$O, and Cs$_4$[[TiO(NTA)]$_4$]·6H$_2$O (dipic = dipicolinate, IDA = iminodiacetate, NTA = nitrilotriacetate). The crystal data for the title compound, Cs$_4$[Ti$_4$O$_4$(C$_6$H$_6$NO$_6$)$_4$]·6H$_2$O, are as follows: monoclinic space group $P2_1/a$ [C$_{2h}^5$, No. 14] with a = 20.355 (7) Å, b = 10.918 (2) Å, c = 22.756 (5) Å, β = 94.74 (2)°, V = 5032 Å^3, and ρ(calcd) = 2.16 g cm^{-3} for Z = 4. Diffraction data were collected on a Syntex R3 automated four-circle diffractometer by using θ–2θ scan and Mo Kα radiation, and the structure was solved by standard methods, resulting in a conventional final R factor of 6.7% for 3376 independent data. Distinct cyclic tetrameric units of {[TiO(NTA)]$_4$}$^{4-}$ have been identified with four asymmetric μ-oxo bridges. The titanium(IV) ions are six-coordinated (distorted octahedra). The formation of 1:1 peroxo–titanium(IV) complexes in acidic perchloric media from the reaction of the above complexes with H$_2$O$_2$ has been studied: rate = k[H$_2$O$_2$][Ti(IV)]. It is shown that with [H$^+$] = 0.05–1.0 M monomeric species are reactive—presumably [Ti(dipic)(OH$_2$)$_3$]$^{2+}$, [Ti(IDA)(OH$_2$)$_3$]$^{2+}$, and [Ti(NTA)(OH$_2$)$_2$]$^+$, respectively (k = 164, 176, 170 M^{-1} s^{-1} at 25 °C; I = 1.0 M (LiClO$_4$)). An I$_d$ mechanism is proposed. With [H$^+$] < 0.01 M a tetrameric species appears to be the kinetically relevant species of the reaction of {[TiO(NTA)]$_4$}$^{4-}$ with H$_2$O$_2$.

Introduction

During the past years a renewed interest in the chemistry of peroxo complexes of the early transition metals has led to a series of papers concerning the structural chemistry of this type of complexes.[2-10] This has prompted us and others to study some kinetic and mechanistic aspects of reactions of transition-metal complexes with hydrogen peroxide.[10-16]

The formation of orange 1:1 peroxo–titanium(IV) complexes from acidic perchlorate solutions of Ti(IV) and H$_2$O$_2$ has been studied by Orhanović and Wilkins.[10] A rather complex rate law has been reported which did not allow the assignment of reaction paths. The main obstacle appears to be uncertainty regarding the structure of the titanium(IV) species in solution at a given pH and of the respective peroxo–titanium(IV) complexes.

Schwarzenbach and Schwarzenbach have synthesized[2] and characterized by X-ray crystallography[3-5] a number of monomeric and dimeric peroxo–titanium(IV) complexes containing chelating ligands such as pyridine-2,6-dicarboxylate (dipicolinate (dipic)) and nitrilotriacetate (NTA).

We report here the preparation and characterization of complexes of titanium(IV) with tridentate dipicolinate and iminodiacetate and the tetradentate ligand nitrilotriacetate. These complexes are considered to be precursor complexes of Schwarzenbach's peroxo complexes. The kinetics of the reactions of these species in perchloric acid with H$_2$O$_2$ have been measured.

Experimental Section

Material and Apparatus. Raman spectra were recorded on a Coderg LRT 800 laser Raman spectrophotometer using the 514.5-nm exciting

line of an Ar laser (Spectra Physics 164). UV–visible spectra were recorded on a UNICAM SP 8-100 spectrophotometer. Fast kinetic runs were followed on a Durrum stopped-flow spectrophotometer; slower runs were measured by conventional spectrophotometric methods.

Triply distilled water was used to make up stock solutions for kinetic experiments. Lithium perchlorate was obtained by neutralization of Li$_2$CO$_3$ with perchloric acid. Commercially available ligands (dipicolinic acid, iminodiacetic acid, and nitrilotriacetic acid) were used as received. Stock solutions of hydrogen peroxide were titrated with 0.1 M solutions of Ce(IV) in sulfuric acid (1.5 M) with use of a ferroin indicator.

Kinetic Measurements. The formation of yellow monoperoxo–titanium(IV) species was studied by measuring the increase of absorbance at λ 400 nm as a function of time. Solutions containing the desired concentrations of perchloric acid, lithium perchlorate as supporting electrolyte, and the respective titanium(IV) complex were generally mixed with solutions containing H$_2$O$_2$ only. In the case of the readily soluble complex Cs$_4$[[TiO(NTA)]$_4$]·6H$_2$O, an aqueous solution of this complex was mixed with solutions containing HClO$_4$, LiClO$_4$, and H$_2$O$_2$. Values of pseudo-first-order rate constants were obtained from the slopes of ln ($A_t - A_\infty$) vs. time plots, where A_t is the absorbance at time t and A_∞ that after the reaction is complete. Such plots were linear for 5 half-lives.

Preparation of Complexes. Abbreviations used are dipic = pyridine-2,6-dicarboxylate, IDA = iminodiacetate, and NTA = nitrilotriacetate. A solution of commercially available (Merck) TiCl$_3$ (~1 M) dissolved in hydrochloric acid (~3 M) was used for the preparation of the following complexes.

[TiO(dipic)(OH$_2$)]·3H$_2$O. To 9.2 g of the above solution of TiCl$_3$ was added dropwise concentrated nitric acid until the solution was colorless. Small amounts of this solution were then added to a solution of dipicolinic acid (1.7 g) in 100 mL of water. Colorless microcrystals precipitated immediately which were filtered off and washed with ethanol and ether. Anal. Calcd: C, 27.93; H, 3.68; N, 4.65; Ti, 15.91. Found: C, 28.1; H, 3.8; N, 4.8; Ti, 15.9. In vacuo over P$_2$O$_5$ three molecules of water of crystallization per formula unit were readily lost.

[TiO(IDA)(OH$_2$)]·2H$_2$O. A colorless solution of Ti(IV) in hydrochloric acid was prepared as described above and added dropwise to a solution of disodium iminodiacetate (5 g) in 90 mL of water. Within a few minutes a colorless microcrystalline precipitate formed which was filtered off and washed with ethanol and ether. Anal. Calcd: C, 19.29; H, 4.45; N, 5.62; Ti, 19.23. Found: C, 18.9; H, 4.1; N, 5.4; Ti, 19.3. In vacuo over P$_2$O$_5$ two molecules of H$_2$O of crystallization per formula unit were lost.

Cs$_4$[[TiO(NTA)]$_4$]·6H$_2$O. To 18 g of the solution containing TiCl$_3$ in HCl was added a solution of 7.2 g of nitrilotriacetic acid in 100 mL of H$_2$O at 25 °C. Solid Cs$_2$CO$_3$ was added until the pH of the solution was ~4.5. The violet solution was discolored upon addition

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Table I. Summary of Crystal Data and Intensity Data Collection for Cs₄{[TiO(NTA)]₄}·6H₂O

A. Crystal Parameters at 23 °C

$a = 20.355\ (7)$ Å $Z = 4$
$b = 10.918\ (2)$ Å   cryst system: monoclinic
$c = 22.756\ (5)$ Å   space group: $P2_1/a$ (C_{2h}^5, No. 14)
$\beta = 94.74\ (2)°$ mol wt 1647.5
$V = 5032$ Å³   Cs₄[Ti₄C₂₄H₂₄N₄O₂₈]·6H₂O
$d_{\text{calcd}} = 2.10$ g cm⁻³

B. Measurement of Intensity Data

diffractometer: Syntex R3
radiatn: graphite-monochromated Mo Kα (λ 0.710 69 Å)
data collecn: θ–2θ mode (2θ range: 3–56°)
reflcn measd: +h, +k, ±l
scan rate: 2.0–29.3°/min
scan width: $[2\theta(K\alpha_1) - 0.8]° - [2\theta(K\alpha_2) + 0.8]°$
bkgd estimatn: stationary crystal, stationary counter at the extremities of each 2θ scan; each for half the time taken for the 2θ scan
std rflcns: 3 every 100 rflcns; no decay observed
rflcns collected: 3376 ($I \geqslant 1.5\sigma(I)$)
abs coeff: $\mu = 35.7$ cm⁻¹

of small amounts of hydroxylammonium chloride. During this procedure the pH of the solution dropped to ~1.0. A colorless precipitate formed immediately which was filtered off. From a minimum amount of water at 50 °C the cesium salt was very slowly recrystallized. Colorless crystals were collected and washed with ethanol and ether. Anal. Calcd: C, 17.48; H, 2.20; N, 3.40; Ti, 11.63; Cs, 32.27. Found: C, 17.4; H, 2.2; N, 3.5; Ti, 11.8; Cs, 33.2.

[TiO(HNTA)]. A 0.5-g sample of Cs₄{[TiO(NTA)]₄}·6H₂O was dissolved in 50 mL of 0.2 M HCl. Upon heating of the solution, to 70 °C, a colorless precipitate formed which was filtered off and washed with ethanol and ether. Anal. Calcd: C, 28.48; H, 2.79; N, 5.54. Found: C, 29.0; H, 2.6; N, 5.4.

Description of the X-ray Diffraction Study and Solution of the Structure. The crystal of Cs₄{[TiO(NTA)]₄}·6H₂O finally selected for the structural analysis was of approximate dimensions 0.09 × 0.14 × 0.20 mm. The unit cell parameters were obtained at 23 °C by a least-squares refinement of the high angular settings of 25 reflections (Table I).

Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was also applied.[20] Careful comparison of observed and calculated structure factor amplitudes indicated that the intensities of three strong reflections at small θ (200, 002, -202) were seriously reduced—probably by secondary extinction. These reflections were omitted in the final refinement.

The structure was solved via a three-dimensional Patterson synthesis which readily yielded the positions of the cesium and titanium atoms. A difference Fourier synthesis revealed unambiguously the positions of all remaining nonhydrogen atoms. Several cycles of refinement—using the SHELX program[20]—converged at $R = \sum \|F_o| - |F_c\|/\sum|F_o| = 0.067$. During the last cycles the temperature factors of all nonhydrogen atoms were treated in the anisotropic form. In the final stage of refinement, no parameter shifted more than 0.4σ, where σ is the standard deviation. The data to parameter ratio is admittedly small (5.4:1). Four attempts using different crystals from different batches did not improve this ratio. The quality of the crystals did not allow the collection of intensity data with 2θ > 56°.

The atomic scattering factors for neutral Cs, Ti, C, N, and O were taken from ref 21. Anomalous dispersion corrections were applied to the Cs and Ti atoms. The final positional parameters are given in Table II. A list of observed and calculated structure factors and a list of anisotropic temperature factors are available as supplementary material.

Results

Preparation and Characterization of Complexes. Dipicolinic acid and iminodiacetic acid react with solutions containing Ti(IV) in aqueous hydrochloric acid to form colorless precipitates of analytical composition [TiO(dipic)(OH₂)]·3H₂O and [TiO(IDA)(OH₂)]·2H₂O, respectively. Three or two molecules of water per formula unit are easily removed in vacuo over P₂O₅, respectively. This implies the presence of one coordinated molecule of H₂O per Ti(IV) center. From the infrared spectra of the solids it is concluded that dipicolinate and iminodiacetate anions are bonded as tridentate

Table II. Final Positional Parameters for Cs₄{[TiO(NTA)]₄}·6H₂O

atom	x	y	z	atom	x	y	z
Cs(1)	0.93323 (8)	0.2023 (2)	0.95585 (7)	C(22)	0.9059 (9)	0.261 (2)	0.1315 (9)
Cs(2)	0.65161 (8)	0.0290 (1)	0.37000 (7)	C(23)	0.560 (1)	0.069 (2)	0.8071 (9)
Cs(3)	0.13594 (9)	0.1810 (2)	0.54277 (8)	C(24)	-0.001 (1)	0.357 (2)	0.8303 (9)
Cs(4)	0.12165 (9)	0.0867 (2)	0.83733 (9)	C(25)	0.493 (1)	0.111 (2)	0.2396 (9)
O(5)	0.027 (1)	0.033 (2)	0.105 (1)	C(26)	0.561 (1)	0.159 (2)	0.2228 (8)
O(6)	0.745 (1)	0.148 (2)	0.548 (1)	Ti(3)	0.9155 (2)	0.1669 (3)	0.4829 (2)
O(7)	0.728 (1)	0.255 (3)	0.234 (1)	N(3)	0.3991 (7)	0.183 (1)	0.4117 (6)
O(8)	0.379 (1)	0.862 (3)	0.342 (1)	O(3)	0.9678 (6)	0.078 (1)	0.4338 (5)
O(9)	0.172 (2)	0.600 (4)	0.233 (1)	O(31)	0.2830 (8)	0.062 (1)	0.5096 (6)
O(10)	0.236 (1)	-0.005 (3)	0.204 (1)	O(32)	0.3532 (7)	0.216 (1)	0.5182 (6)
Ti(1)	0.6155 (2)	0.0821 (3)	0.9852 (2)	O(33)	0.5599 (7)	0.087 (1)	0.4715 (6)
N(1)	0.6972 (7)	0.187 (1)	0.0381 (6)	O(34)	0.4886 (7)	0.220 (1)	0.5028 (6)
O(1)	0.0639 (6)	0.394 (1)	0.0502 (6)	O(35)	0.7954 (8)	0.084 (2)	0.3391 (8)
O(11)	0.2687 (9)	0.098 (1)	0.8900 (8)	O(36)	0.8382 (7)	0.110 (1)	0.4324 (7)
O(12)	0.3350 (7)	0.048 (1)	0.9693 (6)	C(31)	0.854 (1)	0.411 (2)	0.433 (1)
O(13)	0.7905 (7)	0.109 (1)	0.9132 (6)	C(32)	0.8266 (9)	0.376 (2)	0.4886 (9)
O(14)	0.1866 (7)	0.420 (1)	0.9290 (6)	C(33)	0.4665 (9)	0.134 (2)	0.4047 (8)
O(15)	0.114 (1)	0.047 (1)	0.9802 (8)	C(34)	0.5091 (9)	0.147 (2)	0.4627 (9)
O(16)	0.5984 (7)	0.252 (1)	0.9616 (6)	C(35)	0.870 (1)	0.252 (2)	0.3587 (9)
C(11)	0.710 (1)	0.115 (2)	0.0937 (9)	C(36)	0.831 (1)	0.142 (2)	0.376 (1)
C(12)	0.2968 (9)	0.020 (2)	0.9216 (9)	Ti(4)	0.0303 (2)	0.0132 (3)	0.3934 (2)
C(13)	0.759 (1)	0.186 (2)	0.0033 (9)	N(4)	0.8969 (8)	0.049 (1)	0.6711 (7)
C(14)	0.245 (1)	0.378 (2)	0.9456 (9)	O(4)	0.4185 (7)	0.431 (1)	0.5447 (6)
C(15)	0.173 (1)	0.187 (2)	0.0477 (9)	O(41)	0.9867 (8)	0.090 (1)	0.2190 (6)
C(16)	0.122 (1)	0.155 (2)	-0.008 (1)	O(42)	0.4924 (6)	0.418 (1)	0.3169 (6)
Ti(2)	0.5115 (2)	0.0796 (3)	0.1054 (1)	O(43)	0.1990 (7)	0.205 (1)	0.3911 (7)
N(2)	0.4505 (8)	0.060 (1)	0.1862 (6)	O(44)	0.0969 (7)	0.144 (1)	0.3972 (6)
O(2)	0.4395 (6)	-0.001 (1)	0.0622 (6)	O(45)	0.4798 (8)	0.160 (1)	0.6629 (7)
O(21)	0.8656 (7)	0.177 (1)	0.1222 (8)	O(46)	0.5034 (7)	0.352 (1)	0.6357 (7)
O(22)	0.4580 (6)	0.230 (1)	0.1019 (5)	C(41)	0.922 (1)	0.014 (2)	0.7321 (10)
O(23)	0.4941 (9)	0.252 (1)	0.8176 (7)	C(42)	0.015 (1)	0.058 (2)	0.2671 (8)
O(24)	0.4613 (6)	0.080 (1)	0.8607 (6)	C(43)	0.167 (1)	0.010 (2)	0.3489 (9)
O(25)	0.5998 (7)	0.193 (1)	0.2639 (6)	C(44)	0.157 (1)	0.129 (2)	0.3813 (9)
O(26)	0.5728 (6)	0.156 (1)	0.1692 (5)	C(45)	0.893 (1)	0.184 (2)	0.6644 (10)
C(21)	0.3894 (11)	0.135 (2)	0.173 (1)	C(46)	0.962 (1)	0.229 (2)	0.6560 (9)

Table III. Bond Lengths (Å) with Standard Deviations

A	B	dist, Å	A	B	dist, Å	A	B	dist, Å	A	B	dist, Å
Ti(1)	O(16)	1.96 (1)	Ti(2)	O(26)	2.02 (1)	Ti(3)	O(36)	1.97 (1)	Ti(4)	O(46)	1.98 (1)
Ti(1)	N(1)	2.28 (2)	Ti(2)	N(2)	2.31 (2)	Ti(3)	N(3)	2.31 (1)	Ti(4)	N(4)	2.28 (2)
Ti(1)	O(1)	1.90 (1)	Ti(2)	O(2)	1.91 (1)	Ti(3)	O(3)	1.88 (1)	Ti(4)	O(4)	1.91 (1)
Ti(1)	O(12)	1.98 (1)	Ti(2)	O(22)	1.96 (1)	Ti(3)	O(32)	2.01 (2)	Ti(4)	O(42)	1.99 (1)
Ti(1)	O(14)	2.01 (1)	Ti(2)	O(24)	1.97 (1)	Ti(3)	O(34)	1.96 (1)	Ti(4)	O(44)	1.97 (1)
Ti(1)	O(2)	1.74 (1)	Ti(2)	O(1)	1.74 (1)	Ti(3)	O(4)	1.76 (1)	Ti(4)	O(3)	1.78 (1)
N(1)	C(11)	1.50 (3)	N(2)	C(21)	1.50 (3)	N(3)	C(31)	1.48 (3)	N(4)	C(41)	1.48 (3)
N(1)	C(13)	1.54 (3)	N(2)	C(23)	1.44 (3)	N(3)	C(33)	1.50 (3)	N(4)	C(43)	1.49 (3)
N(1)	C(15)	1.48 (3)	N(2)	C(25)	1.54 (3)	N(3)	C(35)	1.48 (3)	N(4)	C(45)	1.49 (3)
C(11)	C(12)	1.22 (3)	O(21)	C(22)	1.24 (3)	O(31)	C(32)	1.24 (3)	O(41)	C(42)	1.24 (2)
O(13)	C(14)	1.24 (3)	O(23)	C(24)	1.23 (3)	O(33)	C(34)	1.23 (2)	O(43)	C(44)	1.20 (3)
O(15)	C(16)	1.21 (3)	O(25)	C(26)	1.23 (2)	O(35)	C(36)	1.24 (3)	O(45)	C(46)	1.28 (3)
O(14)	C(14)	1.30 (3)	O(24)	C(24)	1.29 (3)	O(34)	C(34)	1.31 (3)	O(44)	C(44)	1.32 (3)
O(12)	C(12)	1.32 (2)	O(22)	C(22)	1.31 (3)	O(32)	C(32)	1.31 (3)	O(42)	C(42)	1.28 (2)
O(16)	C(16)	1.30 (3)	O(26)	C(26)	1.26 (2)	O(36)	C(36)	1.33 (3)	O(46)	C(46)	1.33 (3)
C(11)	C(12)	1.51 (3)	C(21)	C(22)	1.53 (3)	C(31)	C(32)	1.47 (3)	C(41)	C(42)	1.51 (3)
C(13)	C(14)	1.49 (3)	C(23)	C(24)	1.60 (3)	C(33)	C(34)	1.53 (3)	C(43)	C(44)	1.53 (3)
C(15)	C(16)	1.60 (3)	C(25)	C(26)	1.55 (3)	C(35)	C(36)	1.52 (3)	C(45)	C(46)	1.52 (3)

ligands via two oxygen atoms of the carboxylic groups and the nitrogen atom, respectively. The lack of ν(Ti=O) stretching frequencies in the region 900–1050 cm^{-1} indicates that—at least in the solid state—the complexes are not monomeric species with a Ti=O structural unit. On the assumption that the titanium(IV) centers are six-coordinate, dimeric,[17] trimeric, or tetrameric[18] neutral complexes are conceivable with two μ-oxo bridges (Ti–O–Ti) per Ti(IV) ion.

Both complexes are insoluble in water. The solubility increases considerably in acidic solution (HCl, HClO$_4$). From kinetic experiments it is shown (vide infra) that in solutions with [H$^+$] > 0.1 M monomeric species are predominantly present. It has not been possible to establish their precise structure. Cationic complexes containing aquo ligands or neutral complexes with a titanyl group, Ti=O, are possible: [Ti(dipic)(OH$_2$)$_3$]$^{2+}$ or [TiO(dipic)(OH$_2$)$_2$] and [Ti(IDA)-(OH$_2$)$_3$]$^{2+}$ or [TiO(IDA)(OH$_2$)$_2$]. The good solubility in concentrated acids and the fact that no ν(Ti=O) stretching frequencies in the Raman spectra of such solutions have been observed favor a cationic structure.

An anionic complex of Ti(IV) with coordinated nitrilotriacetato ligands has been prepared from acidic solutions of TiCl$_3$ and nitrilotriacetic acid by addition of hydroxylammonium chloride (oxidation of Ti(III)). Colorless crystals of analytical composition Cs[TiO(NTA)]·1.5H$_2$O were obtained when solid Cs$_2$CO$_3$ was added. Approximately one molecule of water per formula unit is easily removed in vacuo over P$_2$O$_5$. The infrared spectrum again exhibits no absorption due to a ν(Ti=O) stretching frequency. The Raman spectrum of the solid shows bands of moderate intensities at 659, 526, and 439 cm^{-1} which are tentatively assigned to vibrations of Ti–O–Ti moieties. The X-ray structure analysis of the cesium salt (vide infra) reveals the presence of tetrameric anions of {[TiO(NTA)]$_4$}$^{4-}$.

In acidic solution ([H$^+$] > 0.05 M) monomeric species are present as is demonstrated from kinetic experiments. [Ti(NTA)(OH$_2$)$_2$]$^+$ is thought to be the most probable structure. Interestingly, a neutral Ti(IV) complex is generated when acidic solutions of the above cesium salt are heated to ca. 70 °C. A colorless precipitate is afforded: [TiO(HNTA)]. The infrared spectrum shows coordinated carboxylato groups and an uncomplexed COOH group; no evidence for a titanyl group has been detected, indicating a polymeric structure with μ-oxo bridges.

Syntheses and characterization of yellow 1:1 peroxo–titanium(IV) complexes with chelating ligands (dipicolinate, nitrilotriacetate) have been described by Schwarzenbach and co-workers.[2] From strongly acidic solutions monomeric species[4] have been isolated whereas from less acidic solutions (pH >3) dinuclear species[3] with μ-oxo bridges have been obtained. The reaction of [TiO(dipic)(OH$_2$)]·3H$_2$O with H$_2$O$_2$ in acidic solution affords [Ti(O$_2$)(dipic)(OH$_2$)$_2$], the crystal structure of which is known;[4] at higher pH (4.5) a dinuclear complex can be isolated: K$_2$[Ti$_2$(O$_2$)$_2$(O)(dipic)$_2$(OH$_2$)$_2$]·2H$_2$O.[2,3]

[TiO(IDA)(OH$_2$)]·2H$_2$O reacts in perchloric acid media ([H$^+$] > 0.05 M) with H$_2$O$_2$ to yield a 1:1 peroxo–titanium-(IV) complex which has not been isolated. In the pH range 0–1 this species has a maximum of absorption at λ 401 nm (ϵ 679 L cm^{-1} mol^{-1}) which is shifted at higher pH values (>2) to 360 nm (ϵ 910), indicating the formation of a dinuclear species.

Cs$_4${[TiO(NTA)]$_4$}·6H$_2$O reacts in acidic solutions (pH <0.1) with H$_2$O$_2$ affording a yellow presumably monomeric 1:1 peroxo–titanium(IV) complex, [Ti(O$_2$)(NTA)(OH$_2$)]$^-$ (λ_{max} 410 nm, ϵ 1.3 × 10^3). It has not been possible to isolate a crystalline material. At pH 0.1 a dinuclear species is formed (λ 375 nm, ϵ 1.1 × 10^3) which has previously been isolated as the potassium[2] or sodium salt,[5] Na$_4$[Ti$_2$(O$_2$)$_2$(O)(NTA)$_2$]·11H$_2$O.

Crystal Structure of Cs$_4${[TiO(NTA)]$_4$}·6H$_2$O. Bond distances and bond angles of the complex anion are listed in Tables III and IV. The molecular geometry and the atomic labeling scheme for {[TiO(NTA)]$_4$}$^{4-}$ are shown in Figure 1. The structure consists of four distinct tetrameric {[TiO(NTA)]$_4$}$^{4-}$ anions, 16 cesium cations, and 24 molecules of water of crystallization per unit cell. Each tetrameric unit consists of two crystallographically independent halves; the second halves are generated by a center of symmetry. The titanium(IV) centers are six-coordinated with two cis μ-oxo bridging atoms, respectively, forming a puckered eight-membered ring. The μ-oxo bridges are not symmetric. A short Ti–O bond (average bond distance ~1.74 Å) and a longer bond (~1.90 Å) alternate. The Ti–O–Ti bond angles are in the range of 150–170°. The short Ti–O bonds of the bridging oxygen atoms indicate considerable double-bond character (Ti=O). The nitrilotriacetato ligand is bonded in the conventional fashion to the titanium(IV) center as a tetradentate ligand.

The tetrameric structure found here is very similar to that reported for (NH$_4$)$_2$[TiO(C$_2$O$_4$)$_2$]·H$_2$O.[18] The present structure analysis gives further evidence that complexes of Ti(IV) with a discrete titanyl moiety are the exception.[17]

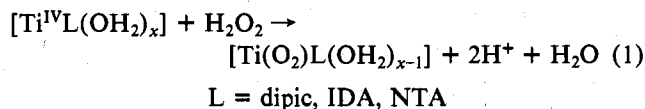(17) Clark, R. J. H. "The Chemistry of Titanium and Vanadium"; Elsevier: Amsterdam, 1968.

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Table IV. Bond Angles (Deg) of Ti(IV) Octahedra[a]

A	B	C	angles	angles[b]
O(2)	Ti(1)	O(16)	103.1	103.9
O(2)	Ti(1)	N(1)	172.5	169.6
O(2)	Ti(1)	O(1)	100.7	100.1
O(2)	Ti(1)	O(12)	103.2	92.8
O(2)	Ti(1)	O(14)	93.5	102.9
O(14)	Ti(1)	O(16)	87.4	153.0
O(14)	Ti(1)	N(1)	78.9	77.2
O(14)	Ti(1)	O(1)	165.8	90.4
O(14)	Ti(1)	O(12)	87.8	89.9
O(12)	Ti(1)	O(16)	153.5	86.3
O(12)	Ti(1)	N(1)	76.7	76.8
O(12)	Ti(1)	O(1)	89.1	166.7
O(1)	Ti(1)	O(16)	89.2	87.4
O(1)	Ti(1)	N(1)	86.8	90.3
N(1)	Ti(1)	O(16)	76.8	76.0
O(24)	Ti(2)	N(2)	76.1	76.2
O(24)	Ti(2)	O(2)	88.6	88.7
O(24)	Ti(2)	O(22)	153.2	88.9
O(24)	Ti(2)	O(26)	86.8	151.4
O(24)	Ti(2)	O(1)	105.2	102.0
O(1)	Ti(2)	N(2)	172.6	170.2
O(1)	Ti(2)	O(2)	101.3	100.1
O(1)	Ti(2)	O(22)	101.6	93.5
O(1)	Ti(2)	O(26)	94.1	106.5
O(26)	Ti(2)	N(2)	78.7	75.2
O(26)	Ti(2)	O(2)	164.6	89.0
O(26)	Ti(2)	O(22)	89.6	86.8
O(22)	Ti(2)	N(2)	77.1	76.9
O(22)	Ti(2)	O(2)	87.9	166.4
O(2)	Ti(2)	N(2)	86.0	89.5
Ti(1)	O(1)	Ti(2)	161.8	168.5
Ti(1)	O(2)	Ti(2)	169.8	148.8

[a] All other bond angles are omitted for the sake of brevity. The standard deviation for all angles is 0.6°. [b] Bond angles for the second independent tetrameric anion (Ti(3), Ti(4), Ti(3)', Ti(4)'). The atomic numbering scheme for these angles is deduced by addition of 2 to the first digit of each atom (A, B, C), e.g., O(14)-Ti(1)-N(1) → O(34)-Ti(3)-N(3).

Kinetics of the Reactions of Ti(IV) Complexes with H_2O_2 in Acidic Perchlorate Media, $[H^+] = 1.0-0.05$ M.

The kinetics of the formation of yellow monoperoxo–titanium(IV) species from monomeric cations $[Ti(dipic)(OH_3)_3]^{2+}$, $[Ti(IDA)(OH_2)_3]^{2+}$, and $[Ti(NTA)(OH_2)_2]^+$, respectively, and H_2O_2 (eq 1) in perchloric acid media, $[H^+] = 1.0-0.05$ M, have been

$$[Ti^{IV}L(OH_2)_x] + H_2O_2 \rightarrow$$
$$[Ti(O_2)L(OH_2)_{x-1}] + 2H^+ + H_2O \quad (1)$$

$$L = dipic, IDA, NTA$$

studied at λ 400 nm, various temperatures, and an ionic strength of 1.0 M (adjusted with $LiClO_4$). Stopped-flow traces were obtained by using pseudo-first-order conditions with $[H_2O_2]$ in at least 10-fold excess over $[Ti(IV)]_t$. A single step was observed in all cases (increase in absorbance). Pseudo-first-order rate constants, k_{obsd}, s^{-1}, are listed in Table V. A first-order dependence on $[H_2O_2]$ has been established for all reactions; the respective rates were found to be independent of $[H^+] = 0.05-1.0$ M (eq 2). In a different set of experi-

$$rate = k[H_2O_2][Ti(IV)]_t \quad (2)$$

ments the first-order dependence of the rate of reaction on the concentration of $[Ti(IDA)(OH_2)_3]^{2+}$ and $[Ti(NTA)(OH_2)_2]^+$, respectively, was established by using pseudo-first-order conditions with the total titanium(IV) concentration, $[Ti(IV)]_t$, in large excess over $[H_2O_2]$. Second-order rate constants, k, $M^{-1} s^{-1}$, were within experimental error identical for both sets of experiments. This is considered to be excellent evidence that in the pH range investigated monomeric complexes of titanium(IV) are reactive. In the case of $[Ti(dipic)(OH_2)_2]^{2+}$ no kinetic experiments with excess $[Ti(IV)]_t$ could be per-
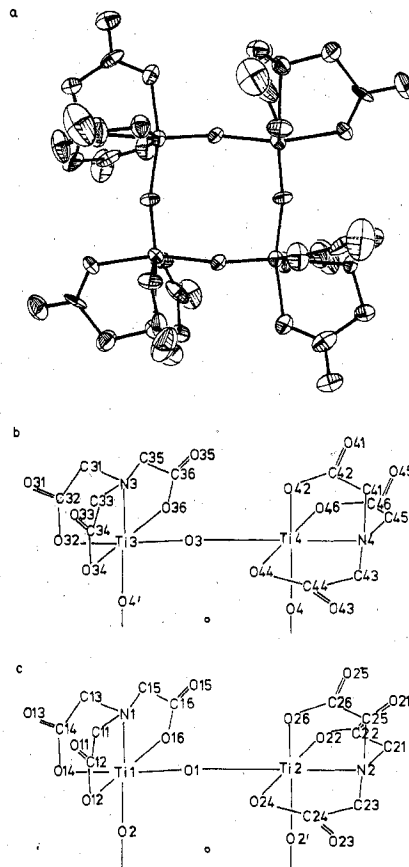
Figure 1. (a) Perspective view of the complex $\{[TiO(NTA)]_4\}^{4-}$ anion (50% probability ellipsoids); (b) and (c) atomic numbering schemes for the two crystallographically independent halves of the tetrameric anions. The open circles represent centers of symmetry.
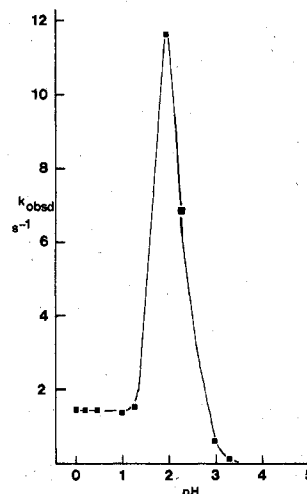
Figure 2. Dependence of k_{obsd} of the "$Cs_4\{[TiO(NTA)]_4\}$"–H_2O_2 reaction on pH ($[Ti(IV)]_t = 10^{-4}$ M and $[H_2O_2] = 0.01$ M at 25 °C; $I = 1.0$ M ($LiClO_4$)).

formed due to the low solubility of the complex.

The temperature dependence of the rates has also been studied; activation parameters were calculated by using a least-squares program (Table VI).

Kinetics of the Reaction of $Cs_4\{[TiO(NTA)]_4\}\cdot6H_2O$ with H_2O_2 in Acidic Perchlorate Media, $[H^+] = (0.05-5) \times 10^{-4}$ M.

Due to the good solubility of $Cs_4\{[TiO(NTA)]_4\}\cdot6H_2O$ it has been possible to study the effect of pH over a wider range on the observed rate constant. This is demonstrated in Figure 2 which shows the effect of pH on the pseudo-first-order rate

Table V. Pseudo-First-Order Rate Constants, k_{obsd}, for the Reactions of $[Ti(IDA)(OH_2)_3]^{2+}$, $[Ti(dipic)(OH_2)_3]^{2+}$, and $[Ti(NTA)(OH_2)_2]^+$ with H_2O_2, Respectively[a]

T, °C	[H⁺], M	10² × [H₂O₂], M	10⁴ × [Ti]ₜ, M	k_{obsd}, s⁻¹
		[Ti(dipic)(OH₂)₃]²⁺		
15	1.0	0.05	0.8	0.058
		0.10		0.097
		1.00		0.89
		5.00		4.36
		10.0		8.9
25		0.22		0.58
		1.08		2.03
		2.17		3.4
		4.34		6.8
	0.4	4.4		6.8
	0.2	4.4		6.7
35		0.05		0.25
		0.10		0.42
		1.0		3.3
		5.0		15.1
		10.0		33.1
		15.5		52.0
		[Ti(IDA)(OH₂)₃]²⁺		
15	1.0	0.05	1.0	0.059
		0.10		0.12
		1.0		1.04
		5.0		4.94
		10.0		9.71
		15.5		14.8
	0.01	1.0		0.92
	0.10	15.5		13.5
	0.30	15.5		13.1
25	1.0	0.05		0.092
		0.10		0.14
		1.0		1.66
		10.0		17.6
	0.75	1.0		1.77
	0.50			1.81
	0.30			1.23
	0.10			1.43
	0.05			1.55
	0.01			2.05
	0.005			3.08
	1.0	0.005	92.0	3.26
			33.0	1.12
			16.4	0.51
			9.7	0.31
			3.6	0.14
35	1.0	0.05	1.0	0.18
		0.10		0.31
		1.0		3.22
		5.0		15.8
		10.0		32.6
		15.5		47.6

T, °C	[H⁺], M	10² × [H₂O₂], M	10⁴ × [Ti]ₜ, M	k_{obsd}, s⁻¹
		[Ti(NTA)(OH₂)₂]⁺		
15	0.75	0.05	1.0	0.043
		0.10		0.075
		0.40		0.36
		1.0		0.91
		3.88		3.28
	0.10	1.0		0.68
	0.05			0.64
	0.01			8.98
	0.005	0.05		0.20
		0.10		0.44
		0.40		1.96
		1.00		5.13
		4.0		19.4
	0.001	1.0		0.21
	0.0005			0.028
25	1.0	1.0	1.0	1.54
	0.75	0.05		0.082
		0.10		0.15
		0.40		0.67
		1.0		1.67
		3.9		6.77
	0.30	1.0		1.45
	0.10	1.0		1.39
	0.05	0.05		0.08
		0.10		0.15
		0.40		0.26
		1.00		1.51
	0.01			11.7
	0.005	0.05		0.23
		0.10		0.80
		0.40		2.95
		1.00		6.76
		3.95		23.9
	0.75	0.005	4.7	0.073
			14.4	0.25
			30.0	0.505
	0.005		4.6	0.11
			10.3	0.19
			14.4	0.27
			30.2	0.41
			92.2	1.22
35	0.75	0.05	1.0	0.17
		0.10		0.31
		0.40		1.10
		1.0		2.9
		3.9		13.4
	0.10	1.0		3.6
	0.05			3.3
	0.01			13.7
	0.005	0.05		0.48
		0.10		0.95
		0.40		4.00
		1.0		9.8
		4.0		35.0

[a] $\mu = 1.0$ M ($LiClO_4$).

constant ($[H_2O_2] = 0.01$ M and $[Ti(IV)]_t = 1 \times 10^{-4}$ M at 25 °C; $I = 1.0$ M ($LiClO_4$)). A maximum value is obtained at ca. pH 2; at pH >2 a marked decrease is observed. The use of buffer solutions for the reaction at even higher pH values (>4) has not been pursued because the observed first-order rate constants were found to be dependent on the nature of the respective buffer used (acetate or phthalate buffers at pH 5.5).

At constant $[H^+] = 0.005$ M a first-order dependence of the rate on $[H_2O_2]$ was established by using pseudo-first-order conditions with $[H_2O_2]$ in excess over $[Ti(IV)]_t$. In a second set of experiments $[Ti(IV)]_t$ was in excess over $[H_2O_2]$, revealing a first-order dependence on $[Ti(IV)]_t$. But contrary to the results obtained at $[H^+] = 0.75$ M (Table V) the values

for the second-order rate constants (evaluated from slopes of plots of k_{obsd} vs. [excess component], respectively) differ by a factor of 4. $k' = 640$ M⁻¹ s⁻¹ when $[H_2O_2]$ is the excess concentration; but, $[Ti(IV)]_t$ being in excess over H_2O_2, $k' = 160$ M⁻¹ s⁻¹. This indicates that at pH >2 a tetrameric titanium(IV) complex is the reactive species. If the complex concentration is one-fourth of the $[Ti(IV)]_t$, the observed rate law at a constant pH is as in eq 3. The pH dependence of

$$\text{rate} = k [H_2O_2][\{Ti_4O_4(NTA)_4\}^{4-}] \qquad (3)$$

k_{obsd} may be analyzed as follows. In the range of $[H^+] = 0.05$–0.01 M dimeric and finally a tetrameric Ti(IV) species are formed as a function of pH. The precise structure of these species is not known but coordinated water molecules should

Table VI. Summary of Kinetic Data of the Reactions of Monomeric Ti(IV) Complexes with $H_2O_2{}^a$

complex	k, M^{-1} s^{-1}	T, °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
Ti(dipic)	86	15	11.0 ± 0.3	−11.5 ± 1.1
	164	25		
	320	35		
Ti(IDA)	99	15	9.9 ± 0.4	−15 ± 1.2
	176	25		
	326	35		
Ti(NTA)	87	15	10.4 ± 0.3	−13.5 ± 1.0
	170	25		
	302	35		
TiO^{2+} + NCS^- ^{b}	2.2 × 10^3	25	11.7	−4.0
TiO^{2+} + HF^b	1.86 × 10^3	25	10.6	−8.0

^{a} $[H^+]$ = 0.05–1.0 M; I = 1.0 M $(LiClO_4)$. ^{b} Reference 19 (I = 0.50 M).

be present which undergo substitution reactions with H_2O_2. At pH >2 the cyclic tetrameric anion $\{[TiO(NTA)]_4\}^{4-}$ becomes the predominant species in solution which does not have labile coordinated aqua ligands. Therefore, this anion does not react with H_2O_2 (or only very slowly). Only a protonated and/or open-chained tetrameric species reacts rapidly with H_2O_2 ($[H^+]$ = 0.01–0.001 M). The breakdown of the tetrameric structure at $[H^+]$ > 0.01 M results in a decrease of rate. Because of the complexity of the equilibria involved, the uncertainty regarding the precise structures of reacting species, and the poor quality of the kinetic runs at pH >1.5, we refrained from studying this pH effect in a more quantitative fashion.

Discussion

It is now well established that titanium(IV) complexes containing a true titanyl moiety, Ti=O, are rarely found[17] in solution or in the solid state. Polymeric species with μ-oxo bridges, Ti–O–Ti, apparently prevail. The absence of strong absorbances in the infrared spectra (800–1050 cm^{-1}, ν(Ti=O) stretching frequency) of our complexes and the X-ray investigation of $Cs_4\{[TiO(NTA)]_4\}\cdot6H_2O$ revealing a tetrameric anion keep in line with this observation. On the other hand,

convincing evidence has been presented that the titanium(IV) aquo ion in aqueous perchloric acid is TiO^{2+}.[19,22] An I_d mechanism for 1:1 formation reactions of TiO^{2+} with NCS^-, HF, and pyrophosphate has been proposed.

From our kinetic experiments we conclude that in perchloric acid media, $[H^+]$ = 0.05–1.0 M, monomeric species of $[Ti(dipic)(OH_2)_3]^{2+}$, $[Ti(IDA)(OH_2)_3]^{2+}$, and $[Ti(NTA)(OH_2)_2]^+$, respectively, are present. The good solubility and the Raman spectra indicate the absence of neutral complexes with a Ti=O group. The reactions of these species with H_2O_2 are not dependent on the hydrogen ion concentration. Values of the respective second-order rate constants (Table VI) fall within a narrow range, and the activation parameters are very similar. They agree well with values obtained for the 1:1 complexing of the TiO^{2+} aquo ion with NCS^- and HF.[19] In addition, the rate constant k_0 = 120 M^{-1} s^{-1} (25 °C, I = 3.0 M) of the $[H^+]$-independent term of the reaction of TiO^{2+} with H_2O_2[10] is also in excellent agreement with the values in Table VI. Therefore, we feel that the present data lend further support to an I_d assignment for the substitution of an aquo ligand coordinated to titanium(IV).

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Structural, Spectroscopic, and Theoretical Studies of an Exchange-Coupled Manganese(II)–Copper(II) Dimer

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Crystals of the dimeric complex dichloroaquo(pyridine *N*-oxide)copper(II) which have been doped with manganese(II) contain characterizable quantities of an exchange-coupled Mn(II)–Cu(II) dimer. The EPR spectrum exhibits the fine structure characteristic of a spin quintet (S = 2). The fact that the ground state of the mixed dimer is a quintet indicates that the exchange interactions are antiferromagnetic. The crystal structure of the pure host material has been determined. The complex crystallizes in a triclinic lattice with one centrosymmetric dimer per unit cell. The orientations of the magnetic tensors for the Mn(II)–Cu(II) dimer have been determined and related to the molecular structure. Most of the important features of the spectrum of the mixed dimer can be explained by a set of spin wave functions which are eigenfunctions of the simple isotropic exchange operator ($\mathcal{H}$ = JS·S′).

Introduction

Since the early work of Bleaney and Bowers on copper(II) acetate monohydrate, there has been a continuous interest in

the spectroscopic and magnetic properties of magnetically coupled dimers. An enormous number of dimeric complexes are now known which contain two interacting paramagnetic centers. Many structural, spectroscopic, and magnetic investigations have been carried out in an effort to elucidate the nature and origin of the magnetic coupling in these complexes.

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