

## The Structure and Reactivity towards Oxygen Transfer of Pyrazinedicarboxylato Peroxo Titanium Derivatives. Molecular and Crystal Structure of Peroxo(pyrazine 2-carboxylato 3-carboxyl)(acetylacetonato)(hexamethylphosphortriamide) Titanium(IV)

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### Abstract

The synthesis and properties, with respect to oxygen transfer to olefins, of four peroxo Ti(IV) complexes of pyrazine- and pyridinedicarboxylic acids, are reported. The X-ray structure of Ti-[pz(COO)(COOH)](acac)(HMPA), **1**, was performed; it essentially revealed that the pyrazine ligands are non-bridging: the carboxylate group at the 2 position is deprotonated while the other carboxylate forms intramolecular hydrogen bonds. Strong stabilization of the peroxo moiety precluded oxygen transfer from **1** to organic substrates. On the other hand, pyrazine- and pyridine-2,5-dicarboxylic acids yielded polymeric compounds **2–4** where both carboxylate groups of the ligands are deprotonated. Complexes **2–4** epoxidize tetramethylethylene; the reactivity thus revealed is attributed to the breaking of the pyrazine or pyridine bridges in solution, which liberates a vacant site on the metal. Crystal data for **1**:  $C_{23}H_{46}N_8O_{10}P_2Ti_2$ , triclinic,  $a = 16.295(6)$ ,  $b = 15.247(6)$ ,  $c = 15.398(6)$  Å,  $\alpha = 90.36(2)^\circ$ ,  $\beta = 115.50(2)^\circ$ ,  $\gamma = 89.21(2)^\circ$ ; space group  $P1$ ,  $Z = 4$ .

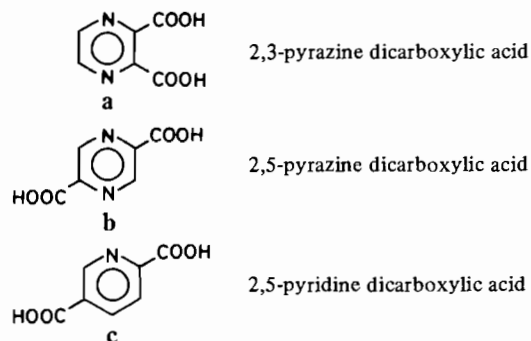
### Introduction

The synthesis of well-defined transition metal peroxides and their oxidizing properties towards organic substrates provide a heuristic approach to the understanding of catalytic oxidation reactions. The ability of titanium to transfer oxygen is elegantly exemplified in the asymmetric transformation of allylic alcohols into epoxyalcohols [1] or of sulfides into chiral sulfoxides [2], by  $t$ -BuOOH in the presence of the already popular titanium tetra isopropoxidetartaric acid complexes as catalyst.

We have already reported unusually stable titanium peroxo complexes in which strong stabilization of the peroxotitanium moiety by picolinato, hydroxy-quinolino or hydroximato ligands was achieved and oxygen transfer precluded from the resulting peroxo complexes [3]. These results were interpreted in terms of saturation of the metal.

This, together with the dimeric structures of the  $Ti(OPr^i)_4$  tartramide catalysts [4], led us to question the influence of pyridine or pyrazine dicarboxylato ligands, which are known to be excellent bridging ligands when coordinated to transition metals, on the structure and reactivity of titanium peroxo complexes.

We report here our results which demonstrate that either monomeric complexes of remarkable stability, or polymeric complexes in which some reactivity towards oxygen transfer is disclosed, can be obtained, depending on the nature of the carboxylato ligands a–c.



### Experimental

All chemicals and reagents were of reagent grade. 2,5-pyrazinedicarboxylic acid was prepared from 2,5-dimethyl pyrazine according to the method of Stroehr [5]. The analytical and IR data are gathered

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in Table IV\*. The IR spectra were recorded on a Perkin-Elmer 577 spectrometer, and the NMR spectra on a Bruker WH-90 spectrometer.

*Preparation of  $Ti(O_2)[2,3pz(COO)(COOH)](acac)(HMPA)$  (1)*

2,3-pyrazine dicarboxylic acid (3.85 g, 22.9 mmol) and HMPA (8 g, 45.7 mmol) were added to a suspension of  $TiO(acac)_2$  (6 g, 22.5 mmol) in 150 ml of dichloromethane. Dropwise addition of 5 ml of  $H_2O_2$  (30% solution) to this suspension at room temperature resulted in a deep orange–red solution. The organic phase was then separated, dried over  $Na_2SO_4$ , and concentrated to 10% to precipitate complex 1. Recrystallization from hexane yielded 6.5 g of orange crystals of 1 (41%). 1 is soluble in most common solvents.

*Preparation of  $Ti(O_2)[2,5pz-COO]_2(HMPA)$  (2)*

The same procedure applied to 1.24 g (4.6 mmol) of  $TiO(acac)_2$ , 0.80 g (4.7 mmol) of 2,5-pyrazine dicarboxylic acid, and 0.85 g (4.8 mmol) of HMPA gave, after recrystallization from a mixture of dichloromethane and diethyl ether (1:10), 0.75 g of 2 (46%). 2 is poorly soluble in  $CH_2Cl_2$  and  $CH_3NO_2$ , and insoluble in most other common solvents.

*Preparation of  $Ti(O_2)[2,5py(COO)_2](HMPA)(H_2O)$  (3) and  $Ti(O_2)[2,5py(COO)_2](HMPA)_2$  (4)*

The analogous complex 3 was prepared similarly from 1.5 g (5.7 mmol) of  $TiO(acac)_2$ , 1.1 g (5.8 mmol) of pyridine 2,5-dicarboxylic acid and 2.0 g (11.2 mmol) of HMPA (75%). The solubility of 3 is very poor in all common solvents. Recrystallization was possible, however, in the presence of a tenfold excess of HMPA in dichloromethane at 4 °C and afforded brownish-orange crystals of 4 (70%) for which solubility is fairly good in the common solvents.

*Reactions of 1–4 with Tetramethylethylene*

In a typical procedure, the peroxidic complex (0.2–0.5 mmol) was dissolved in dichloromethane containing an internal standard, under argon atmosphere. The olefin was introduced at the initial stage of the reaction, and the evolution of the oxidation was followed by GLC analysis of aliquot samples. The oxygenated products were identified by GLC–MS coupling.

*X-ray Measurements*

Suitable single crystals of 1 were obtained by slow evaporation of hexane solutions at room temperature. A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of 1 belong to the triclinic system. The unit-cell dimensions and their standard deviations were

obtained and refined at room temperature with Cu  $K\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) by using 25 carefully selected reflections and the standard Philips software. Final results:  $C_{23}H_{46}N_8O_{10}P_2Ti_2$ ,  $M_r = 704.5$ ,  $a = 16.295(6)$ ,  $b = 15.247(6)$ ,  $c = 15.398(6) \text{ \AA}$ ,  $\alpha = 90.36(2)$ ,  $\beta = 115.50(2)$ ,  $\gamma = 89.21(2)^\circ$ ,  $V = 3452 \text{ \AA}^3$ ,  $Z = 4$ ,  $d_c = 1.355 \text{ g cm}^{-3}$ ,  $d_o = 1.33 \pm 0.02 \text{ g cm}^{-3}$ ,  $\mu = 35.07 \text{ cm}^{-1}$ ,  $F_{000} = 1488$ , space group  $P1$ .

A parallelepipedic crystal of  $0.22 \times 0.20 \times 0.22 \text{ mm}$  was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four-circle diffractometer, controlled by a P852 computer, using graphite monochromated radiation and standard software at room temperature. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the  $2\sigma$  level. The total scan width in the  $\theta/2\theta$  flying step-scan used was  $\Delta\theta = 0.80 + 0.143 \tan(\theta)^\circ$  with a step width of  $0.05^\circ$  and a scan speed of  $0.024^\circ \text{ s}^{-1}$ . All measurements were performed in the bisecting geometry. 9592 reflections were recorded ( $5^\circ < \theta < 57^\circ \pm h$ ,  $\pm k$ ,  $l$ , no equivalents). The resulting data-set was transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used [6], with the exception of a local data-reduction program.

Three standard reflections measured every hour during the entire data-collection period had a mean loss of 7% in intensity, which was corrected using a time-dependent linear interpolation function.

The raw step-scan data were converted to intensities using the Lehmann–Larson method [7] and then corrected for Lorentz, polarization and absorption factors, the latter being computed by the numerical integration method of Busing and Levy [8] (transmission factors between 0.39 and 0.61). A unique data set of 5667 reflections having  $I > 3\sigma(I)$  was used for determining and refining the structure.

Space group  $P1$  was assumed on the basis of a  $N(z)$  cumulative test on  $[F_o]$  and the statistics on the normalized structure factors. The structure was solved by direct methods using MULTAN [9]. After refinement of the heavy atoms, a difference-Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates ( $C-H = 0.95 \text{ \AA}$ ) and isotropic temperature factors of  $10 \text{ \AA}^2$ , but not refined. Full least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$  converged to  $R = 0.072$  and  $R_w = 0.105$  ( $w = 1/(\sigma_{\text{count}}^2 + (pI)^2)$ ). The unit-weight observation was 1.90 for  $p = 0.08$ . No corrections for extinction were applied. A final difference map revealed no significant maxima. The scattering factors coefficients and anomalous dispersion coefficients are from refs. 10 and 11, respectively.

\*Supplementary material.

TABLE I. Table of Positional Parameters and their Estimated Standard Deviations<sup>a</sup>

Atom	x	y	z	B(A <sup>2</sup> )
T11	0.20360(8)	0.71466(8)	0.95106(8)	3.90(3)
P1	0.1940(1)	0.9300(1)	0.8735(1)	4.13(4)
P2	-0.4055(1)	0.7046(1)	0.9073(1)	4.86(5)
N1	0.0542(3)	0.7269(3)	0.8294(3)	3.4(1)
C2	-0.0061(4)	0.7495(4)	0.8640(4)	3.5(1)
C3	-0.0966(4)	0.7598(4)	0.8052(4)	3.6(1)
N4	-0.1287(3)	0.7509(4)	0.7099(4)	4.6(1)
C5	-0.0697(4)	0.7303(5)	0.6752(4)	4.4(2)
C6	0.0210(4)	0.7184(4)	0.7343(4)	3.7(1)
C7	0.0386(4)	0.7663(5)	0.9728(4)	4.4(2)
O8	-0.0112(3)	0.7929(4)	1.0101(3)	6.6(1)
O9	0.1233(3)	0.7551(3)	1.0142(3)	4.3(1)
C10	-0.1687(4)	0.7835(5)	0.8391(4)	4.1(2)
O11	-0.2011(3)	0.8558(3)	0.8293(3)	5.7(1)
O12	-0.1945(3)	0.7151(3)	0.8723(3)	6.0(1)
O13	0.2040(3)	0.8355(3)	0.9012(3)	4.3(1)
N14	0.2904(5)	0.9760(5)	0.9335(5)	7.4(2)
C15	0.3630(8)	0.9385(9)	1.015(1)	13.1(5)
C16	0.3082(8)	1.0654(8)	0.911(1)	12.5(5)
N17	0.1190(4)	0.9854(4)	0.8961(4)	5.8(2)
C18	0.1404(8)	1.0174(8)	0.9901(6)	11.1(3)
C19	0.0217(5)	0.9740(6)	0.8417(7)	7.8(3)
N20	0.1575(4)	0.9374(4)	0.7576(4)	5.3(2)
C21	0.1848(5)	0.8747(6)	0.7062(5)	6.9(2)
C22	0.1219(7)	1.0207(6)	0.7039(6)	8.4(3)
O23	0.2864(3)	0.7197(3)	1.0790(3)	11.6(3)
O24	0.3279(3)	0.6962(3)	1.0164(3)	11.5(3)
O25	0.2249(3)	0.6695(3)	0.8382(3)	5.3(1)
C26	0.2266(4)	0.5916(5)	0.8090(5)	5.0(2)
C27	0.2569(6)	0.5812(7)	0.7307(6)	7.9(3)
C28	0.2045(5)	0.5189(5)	0.8475(5)	5.5(2)
C29	0.1699(5)	0.5208(5)	0.9147(5)	4.7(2)
C30	0.1407(6)	0.4387(5)	0.9450(6)	7.1(3)
O31	0.1591(3)	0.5926(3)	0.9536(3)	4.9(1)
O32	-0.3116(3)	0.7344(4)	0.9338(3)	6.3(1)
N33	-0.4383(6)	0.6191(5)	0.8392(5)	8.3(2)
C34	-0.4847(9)	0.6290(9)	0.7353(7)	12.3(5)
C35	-0.386(1)	0.5373(9)	0.868(1)	16.0(6)
N36	-0.4178(4)	0.6801(5)	1.0032(4)	6.2(2)
C37	-0.3592(6)	0.7085(7)	1.0956(6)	7.8(3)
C38	-0.4887(8)	0.624(1)	1.0069(9)	15.1(5)
N39	-0.4781(5)	0.7840(6)	0.8509(6)	8.7(3)
C40	-0.4585(8)	0.8506(8)	0.7990(8)	10.9(4)
C41	-0.5712(8)	0.791(1)	0.842(1)	20.1(7)
T12	0.78873(8)	0.22260(8)	0.54438(8)	4.06(3)
P3	0.8057(1)	0.4363(1)	0.6308(1)	4.15(4)
P4	-0.3967(1)	0.7973(1)	0.4096(1)	5.08(5)
N42	0.9390(3)	0.2299(3)	0.6667(3)	3.5(1)
C43	0.9981(4)	0.2499(4)	0.6311(4)	3.5(1)
C44	1.0903(4)	0.2577(4)	0.6909(4)	3.7(1)
N45	1.1234(4)	0.2472(4)	0.7858(4)	4.6(1)
C46	1.0628(4)	0.2284(5)	0.8190(4)	4.4(2)
C47	0.9717(4)	0.2179(4)	0.7618(4)	3.9(1)
C48	0.9552(4)	0.2708(4)	0.5240(4)	4.0(2)
O49	1.0030(3)	0.2963(4)	0.4869(3)	6.2(1)
O50	0.8694(3)	0.2616(3)	0.4821(3)	4.6(1)
C51	1.1614(4)	0.2805(5)	0.6544(4)	4.1(2)
O52	1.1851(3)	0.2114(3)	0.6198(3)	6.0(1)

(Continued)

TABLE I. (Continued)

Atom	x	y	z	B(A <sup>2</sup> )
O53	1.1944(3)	0.3506(3)	0.6667(3)	5.6(1)
O54	0.7921(3)	0.3432(3)	0.6012(3)	4.7(1)
N55	0.8796(4)	0.4917(4)	0.6089(4)	5.3(2)
C56	0.8555(7)	0.5254(7)	0.5123(6)	9.8(3)
C57	0.9775(5)	0.4748(6)	0.6616(6)	7.3(3)
N58	0.8475(4)	0.4403(4)	0.7484(4)	5.6(2)
C59	0.8850(6)	0.5206(6)	0.8042(6)	7.2(3)
C60	0.8157(6)	0.3772(6)	0.7975(6)	8.6(3)
N61	0.7115(4)	0.4873(5)	0.5767(5)	6.7(2)
C62	0.6298(8)	0.4494(9)	0.509(1)	17.0(7)
C63	0.7010(7)	0.5812(7)	0.5929(9)	10.9(4)
O64	0.7059(3)	0.2309(3)	0.4166(3)	16.7(3)
O65	0.6643(3)	0.2080(3)	0.4787(3)	16.5(3)
O66	0.7654(3)	0.1770(3)	0.6537(3)	5.4(1)
C67	0.7687(4)	0.0984(5)	0.6856(5)	5.0(2)
C68	0.7379(6)	0.0906(7)	0.7646(6)	8.8(3)
C69	0.7955(5)	0.0271(5)	0.6515(5)	5.7(2)
C70	0.8292(5)	0.0299(5)	0.5821(5)	5.0(2)
C71	0.8608(7)	-0.0523(6)	0.5510(6)	8.1(3)
O72	0.8360(3)	0.0978(3)	0.5410(3)	5.1(1)
O73	-0.3002(3)	0.7704(4)	0.4460(3)	5.7(1)
N74	-0.4578(6)	0.7272(8)	0.3362(7)	14.2(4)
C75	-0.4334(9)	0.6484(8)	0.3087(8)	12.2(4)
C76	-0.541(2)	0.737(2)	0.274(2)	56(2)
N77	-0.4233(6)	0.8889(6)	0.3550(6)	11.7(3)
C78	-0.445(2)	0.887(1)	0.258(1)	67.9(9)
C79	-0.410(2)	0.966(1)	0.386(1)	30(1)
N80	-0.4232(4)	0.8069(6)	0.4981(4)	7.1(2)
C81	-0.3645(6)	0.8068(7)	0.5938(6)	7.2(2)
C82	-0.5173(8)	0.805(2)	0.476(1)	28(1)

<sup>a</sup>Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

Final atomic parameters for non-hydrogen atoms with their estimated standard deviations are listed in Table I.

## Results

### Synthesis, Characterization and X-ray Crystal Structure of the Monomeric $Ti(O_2)[2,3pz(COO)(COOH)](acac)(HMPA)$ Complex (**1**)

Addition of  $H_2O_2$  to a  $CH_2Cl_2$  suspension of titanyl acetylacetonate in the presence of 1 equivalent of 2,3-pyrazine dicarboxylic acid and 2 equivalents of HMPA resulted in a progressive dissolution, producing a deep orange  $CH_2Cl_2$  solution. Workup of the organic phase afforded the orange crystalline compound **1** which analyzes as  $Ti(O_2)(pzH)(acac)(HMPT)_2$ .

The IR spectrum of **1** exhibited three absorption bands at 902, 625 and 595  $cm^{-1}$ , attributable to the characteristic  $\nu(O-O)$ ,  $\nu_s(M-O)$  and  $\nu_{as}(M-O)$  peroxidic stretching vibrations. Coordination of HMPA to titanium was shown by a lowered  $\nu(P=O)$

vibration at 1185  $cm^{-1}$ , while the presence of free HMPA was evidenced by the 1220  $cm^{-1}$  vibration [3]. Compound **1** showed two  $\nu(COO)$  asymmetric bands, one at 1716  $cm^{-1}$  and another at 1672  $cm^{-1}$ , assigned to a carboxylic acid function and a Ti-bound carboxylate, respectively, through comparison with 1700  $cm^{-1}$  for the diacid and 1621 for its potassium salt [12]. The broad weak bands occurring around 2400 and 1900  $cm^{-1}$  for **1** are characteristic of intramolecular hydrogen bonding [13]. The IR absorptions at 1525 and 1590  $cm^{-1}$  were assigned to the acetylacetonato group. The  $^1H$  NMR data ( $CDCl_3$  solution) are consistent with the proposed formula. The signal attributable to the methyl protons of the coordinated HMPA molecule ( $\delta = 2.2$  ppm;  $J_{PH} = 10$  Hz) is shifted upfield from the resonance of the free ligand ( $\delta = 2.51$  ppm), as they are in the cone of anisotropy of the aromatic ring of the pyrazine dicarboxylato ligand ( $Ti-O-P = 167^\circ$ ). The acidic proton appears at 7.4 ppm; three lines are measured at  $\delta 1.7$ , 2.0 ( $CH_3$ ) and 5.6 ppm ( $CH$ ) for the acetylacetonato group.

In the crystalline state **1** is monomeric; a second HMPA moiety is non-bonded to the metal and acts as a solvent molecule. There are two such couples in the asymmetric unit which are not very different; an attempt to superpose them shows that the 22 non-hydrogen atoms of the surrounding of Ti2 superposes with the corresponding atoms of the coordination polyhedron of Ti1 within 0.6 Å.

Figure 1 shows one molecule of **1** together with the labeling scheme used. The labels for the first HMPA solvent molecule are P2, O32 to C41. The surrounding of Ti2 is labeled P3 from NH2 to O72, and the second HMPA solvent molecule P4 from O73 to C82. Table II gives significant bond lengths and angles.

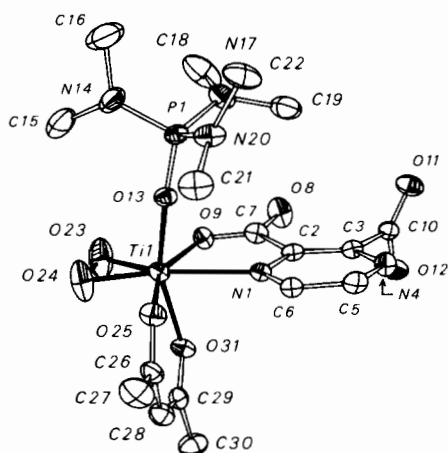


Fig. 1. ORTEP plot of one molecule of **1**. Ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted for clarity.

The coordination polyhedra around the Ti atoms are deformed pentagonal bipyramids, the equatorial positions being occupied by the oxygen atoms of the peroxy group, a nitrogen and an oxygen atom of the pyrazine dicarboxylic (PDC) ligand and one oxygen atom of the acac ligand. The apical positions are occupied by the second oxygen atom of the acac ligand and the oxygen atom of the HMPA moiety. For each Ti atom, there is a second HMPA which is not bonded to the metal. Thus, the direct surroundings of the metal atoms are very similar to those already found in other peroxy-complexes of titanium, such as peroxy-bis(picolinato)(hexamethylphosphoric triamide) titanium IV<sup>4</sup>, (**5**), or the two titanium IV dipicolinato peroxy complexes characterized by Schwarzenbach [14, 15]. The main difference is that in **1** the peroxy group and the pyrazine dicarboxylato ligand are in the equatorial plane, whereas in **5**, for example, the Ti-peroxy plane is perpendicular to those containing the picolinato rings and the titanium atoms. The peroxy groups are  $\pi$ -bonded to the metal, and the Ti–O–O triangles have geometries like those found in **5**, **6** or **7**, with equivalent metal–oxygen

TABLE II. Selected Bond Distances (Å) and Angles (deg) with e.s.d.s for **1**

Lengths	
Ti1–O23	1.849(4)
Ti1–O24	1.852(4)
Ti2–O64	1.849(4)
Ti2–O65	1.851(4)
Ti1–N1	2.352(4)
Ti2–N42	2.364(4)
Ti1–O9	2.026(5)
Ti2–O50	2.029(5)
Ti1–O25	2.027(5)
Ti1–O31	2.013(5)
Ti2–O66	2.008(5)
Ti2–O72	2.051(5)
Ti1–O13	2.002(4)
Ti2–O54	2.023(5)
O23–O24	1.437(8)
O64–O65	1.437(8)
PDC: mean bond lengths	
N–C	1.333(2)
C–C	1.375(4) intracyclic
C–C	1.526(4) extracyclic
C–O	1.246(3) coordinated
C–O	1.311(4) non bonded
C=O	1.188(4) non bonded
HMPT: bond lengths	
P=O	1.482(2)
P–N	1.567–1.646
N–C	1.246–1.488
Acac: bond lengths	
C–O	1.248–1.290
C–C	1.352–1.396 (intracyclic)
C–C	1.492–1.507 (extracyclic)
Angles	
O23–Ti1–O24	45.7(2)
Ti1–O23–O24	67.2(2)
Ti1–O24–O23	67.0(2)
O64–Ti2–O65	45.7(2)
Ti2–O64–O65	67.2(2)
Ti2–O65–O64	67.1(2)
Ni1–Ti1–O9	72.6(1)
N42–Ti2–O50	72.5(2)
O25–Ti1–O31	84.5(2)
O66–Ti2–O72	84.4(2)
O13–Ti1–O23	104.2(2)
O13–Ti1–O24	98.9(2)
O54–Ti2–O64	105.8(2)
O54–Ti2–O65	100.1(2)
O13–Ti1–N1	78.6(2)
O54–Ti2–N42	77.2(1)
O13–Ti1–O9	91.3(2)
O54–Ti2–O50	91.4(2)
O13–Ti1–O25	86.9(2)
O54–Ti2–O66	86.4(2)
O13–Ti1–O31	157.8(1)
O54–Ti2–O72	155.0(1)
Ti1–O13–P1	169.5(3)
Ti2–O54–P3	167.6(4)

bonds of 1.825(3) Å average, and normal O–O distances (average 1.438(5) Å), as well as normal Ti–O–O and O–Ti–O angles (see Table II).

The most surprising feature is that the PDC ligand is bonded to titanium using only two of the possible bonding sites; thus PDC has the same coordination mode as the monopicolinate ligand in **5**. The PDC ligands are nearly planar. In Table II are given the mean bond lengths; the Ti and Ti–O bonds are slightly greater than those found in **5**, perhaps due to some *trans*-effect.

The HMPA is weakly bonded to titanium with Ti–O bond lengths of 2.002(3) and 2.023(3) Å. As usual with this ligand [16], the Ti–O–P moiety is non-linear. The acac ligand has a normal geometry, as seen from the values given in Table II, with Ti–O bond lengths in the range of those found in the Ti–PCD moiety. There are no unusual intermolecular contacts.

*Polymeric Peroxo Complexes: Ti(O<sub>2</sub>)[2,5-pz(COO)<sub>2</sub>]/(HMPA)<sub>n</sub> (2) and Ti(O<sub>2</sub>)[2,5-py(COO)<sub>2</sub>]/LL' (3–4)*

The same synthetic procedure which yielded **1** when applied to ligands **b** and **c** afforded compounds **2b**, **3** and **4c** listed in Table III. The complexes are microcrystalline, stable in air and insoluble in most of the common organic solvent. This insolubility is indicative of their non-electrolytic, polymeric nature. The peroxydic nature of compounds **2–4** was ascertained by peroxidic oxygen cerimetric titration and by their IR spectra, which exhibit the absorptions attributable to the characteristic C<sub>2v</sub> peroxy vibrations (Table IV\*).

The IR spectrum measured for **2** shows a single ν(COO)(asym) band at 1670 cm<sup>-1</sup> and no evidence of H bonding, consistent with a polymeric formulation with bridging pyrazine 2,5-dicarboxylato groups. Compounds **3** and **4** also show bands attributable to similar polymeric structures: the non-symmetric pyridine 2,5-dicarboxylato ligand shows as two close ν(COO)(asym) bands in the region assigned to a bound carboxylate [17].

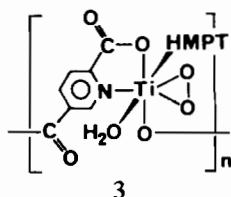
Coordination of water to titanium in complex **3** is evidenced by absorptions at 3300 cm<sup>-1</sup> (broad) and 1730 cm<sup>-1</sup>; this water molecule in **3** is easily replaced by basic ligands such as HMPA to produce complex **4**, which is slightly more soluble. The <sup>1</sup>H NMR spectrum measured for CD<sub>2</sub>Cl<sub>2</sub> solutions of **4** show the three pyridine protons as a AB system and a singlet in the 8 ppm region; HMPA appears as a doublet at δ 2.40 (36H; J<sub>PH</sub> = 10 Hz), corresponding to an upfield shift of 0.11 ppm with respect to the free ligand, as observed in compound **1** we therefore assign this shift to the protons of coordinated HMPA being in the cone of anisotropy of the pyridine ring.

\*Supplementary material.

TABLE III. Elemental Analysis and IR Data on Titanium Peroxo Compounds 1–4

Ligand	Complex	Analysis				Infra-red (cm <sup>-1</sup> ; KBr pellet)					
		%C found (calc.)	%H found (calc.)	%N found (calc.)	%P found (calc.)	%Ti found (calc.)	νOO	ν <sub>s</sub> MO	ν <sub>as</sub> MO	νC=O	νP=O
<b>a</b>	Ti(O <sub>2</sub> )[2,3-pz(COO)(COOH)](HMPA)·HMPA <b>1</b>	39.05 (39.22)	6.49 (6.57)	15.73 (15.90)	9.20 (8.79)	6.68 (6.80)	902	625	595	1672 1716	1185
<b>b</b>	Ti(O <sub>2</sub> )[2,5-pz(COO) <sub>2</sub> ](HMPA)·2H <sub>2</sub> O <b>2</b>	31.25 (31.15)	5.24 (5.35)	15.18 (14.53)	6.71 (7.06)	10.38 (9.92)	885	610	540	1670	1190
<b>c</b>	Ti(O <sub>2</sub> )[2,5-py(COO) <sub>2</sub> ](HMPA)(H <sub>2</sub> O) <b>3</b>	35.52 (35.42)	5.16 (5.22)	12.61 (12.66)	6.95 (6.99)		905	605	530	1660 1680(sh)	1185
	Ti(O <sub>2</sub> )[2,5-py(COO) <sub>2</sub> ](HMPA) <sub>2</sub> ·H <sub>2</sub> O <b>4</b>	36.47 (36.72)	6.68 (6.64)	15.45 (15.77)	9.58 (9.98)	7.76 (7.71)	925	590	540	1665 1680(sh)	1195

All these results are in agreement with the polynuclear bridged structure illustrated in Scheme 1 for compound 3.



Scheme 1.

## Reactivity

The monomeric peroxo-titanium derivative **1** was found to be very stable and to behave very much like the analogous peroxo picolinato titanium complex **5** [3]. It can be kept in the light at room temperature in open vessels without any visible evolution for months, and it does not decompose under heating at 80 °C. Its reduction by iodine is very slow and requires heating at *ca.* 60 °C to be initiated.

Compound **1** was found to be most reluctant to react with olefins, allylic alcohols or cyclic ketones. As is the case with compound **5**, no reaction was observed between **1** and such a highly nucleophilic olefin as tetramethylethylene (in a 20/1: olefin/Ti ratio) after 48 h at 50 °C under anaerobic conditions; the unaltered peroxo complex was quantitatively recovered.

On the other hand, the polymeric peroxo derivatives **2–4** were found to decompose slowly but to be immediately reduced by iodine at room temperature. More significant, compounds **2–4** epoxidize tetramethylethylene (10-fold excess); the yields in epoxide were found to be *ca.* 15% with compound **3**, with respect to the metal after 48 h, while compounds **2** and **4** yielded 5% conversion under the same conditions.

## Discussion

Pyrazine dicarboxylates are known to be excellent bridging ligands when coordinated to transition metals and are frequently used to study the interactions of metals over extended distances [18]. The bridging ability of these ligands is such that, to the best of our knowledge, there is only one compound reported so far in which pyrazine 2,3-dicarboxylic acid acts as a chelating non-bridging ligand:  $Co[2,3-pz(COO)(COOH)]_2(H_2O)_2$  [19], to which compound **1** is now to be added.

The 2,5-pyrazine dicarboxylate dianion ideally possesses  $C_{2h}$  symmetry; its planarity and aromaticity have prompted investigations of its transition metal complexes and polymers as potential semiconductors

[20]. Both terminal and bridging behavior have, however, been reported for ligand **b**; when reacted with  $Ru(bipy)_2Cl_2$ , 2,5-pyrazine dicarboxylic acid yielded simultaneously the monomeric  $Ru(bipy)_2[2,5-pz(COO)(COOH)]PF_6$  and dimeric  $(bipy)_2Ru[2,5-pz(COO)_2]Ru(bipy)_2(PF_6)_2$  derivatives [13]. On the contrary, pyridine dicarboxylic acids having one carboxylic group in an *ortho* position with respect to the nitrogen atom generally give monomeric complexes with five-membered chelate rings, leaving the second carboxylic group uncoordinated [12].

Our results are in marked contrast with the above data; the only compound which formed in our hands when  $TiO(acac)_2$  was reacted with pyrazine 2,3-dicarboxylic acid, in various stoichiometries, in the presence of  $H_2O_2$  and HMPA, is the monomeric complex **1**,  $Ti(O_2)[pz(COO)(COOH)](acac)(HMPA)$ . Compound **1** thus appears to be the second example in which pyrazine 2,3-dicarboxylic acid does not behave as a bis-chelating bridging ligand.

On the other hand, when we conducted the same reaction with pyrazine 2,5-dicarboxylic acid, which was expected to behave very much like its 2,3 analogue, the polymeric complex **2** was obtained through bridging pyrazine dicarboxylato groups. Even more surprising is the formation of the similar polymeric compounds **3** and **4** in the case of pyridine 2,5-dicarboxylic acid which, having a single aza atom, is expected to be less prone to bridging than pyrazine dicarboxylates. The reason why pyrazine, in compound **1**, is not bridging remains a mystery to us.

Only a few peroxo transition-metal complexes are inactive as oxygen-transfer agents [3, 21]. It has been proposed that the epoxidation of olefins can occur only if a vacant site is available on the metal centre. This hypothesis clearly finds support in our results; it explains simply the rather puzzling inertness of complex **1**, but also accounts for the epoxidation of tetramethylene by complexes **2–4**. Thus the breaking of some of the pyrazine 2,5-dicarboxylato or pyridine 2,5-dicarboxylato bridges when compounds **2–4** are put in solution creates a vacant site on the metal at the point of the breakage. The olefin can then coordinate to the metal and subsequently be oxidized. The lower activity of **2** and **4** as compared with **3** is tentatively assigned to the presence of more basic ligands on the metal.

## Supplementary Material

Table IV: Selected mean planes (1 page); Tables V and VI: bond lengths and angles in the organic parts; Table VII: thermal parameters for non-hydrogen atoms; Table VIII: positional and thermal parameters for hydrogen atoms; Table IX: listing of structure factor amplitudes ( $F_o$  and  $F_c \times 10$ ) for all observed reflections (25 pages).

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