119. Crystal Structure of the Orthorhombic Modification of a Mononuclear Peroxotitanium(IV) Dipicolinate

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Summary. The deep red diaquoperoxotitanium dipicolinate $[TiO_2(C_7H_3O_4N)(H_2O)_2]2H_2O$ crystallises in a pleochroic triclinic and a nonpleochroic orthorhombic modification. The structure of the former has been reported earlier. The structure of the latter, described in this paper, has been determined from X-ray diffractometer data and refined to $R = 0.034$. In both forms the complex occurs as the free acid, but the modes of packing are completely different. Bond lengths and angles agree closely. As in the other peroxotitanium(IV) chelate structures so far determined, titanium has an approximately pentagonal bipyramidal coordination with the peroxo group and the chelate ligand occupying equatorial sites and the waters forming the apices. The relationship proposed earlier between the basicity of the ligands and the bond lengths and colours of the related compounds is substantiated. The final difference *Fourier* maps obtained with normal and modified refinement procedures clearly reveal bonding electron densities. They indicate a pentagonal bipyramidal sp^3d^3 hybridisation of titanium with bent $Ti-O_{peroxo}$ bonds, again in agreement with the triclinic form and other peroxotitanium chelates.

1. Introduction. – The synthesis and chemistry of a series of peroxo complexes of titanium(IV) with chelating agents such as dipicolinic acid (2,6-pyridinedicarboxylic acid), nitrilotriacetic acid and EDTA have recently been discussed by *Schwarzenbach et al.* [1]. The crystal structures of four of these complexes have also been elucidated by X-ray diffraction techniques [2–4]. The diaquo complex dipicolinate, which is a strong acid ($pK = 1.85$ in aqueous solution) has been found to crystallize in two polymorphic forms – as deep red triclinic crystals which exhibit pleochroism and also as orthorhombic crystals of the same colour, but which are not pleochroic. The latter modification appears to be more stable. The molecules in the structure of the triclinic form [3] are all parallel and are linked by hydrogen bonds, the shortest and most symmetric ones being formed by the acidic protons. This seemed to indicate that the complex is near a transitional state towards a hydroxonium salt. The lack of pleochroism in the orthorhombic form is obviously due to a different packing arrangement of the molecules. It was therefore of interest to examine whether it is in fact a true hydroxonium salt, in contrast to a free acid, and also whether the stereochemistry of the complex is in any way different from that observed in the earlier structure. Moreover, a useful check on the accuracy of bond lengths and bonding electron densities could be expected.

2. Crystal Data and Structure Determination. – Table 1 gives the crystal data and salient features of the structure analysis. Intensity data were collected on an automatic *Picker* FACS-1 diffractometer by the 2θ scan technique and corrected for absorption. The atomic form factors

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for Ti^{4+}, C, N and O were taken from *Cromer & Waber* [5] and for H from *Stewart* et al. [6]. There is thus a lack of four electrons per formula unit in the calculated structure factors. Cell parameters were refined on the diffractometer.

Table 1. *Crystal Data and Structure Determination*

Formula	$C_7H_{11}NO_{10}Ti$
Formula weight	317.1
Symmetry and space group	Orthorhombic, Pbcn
Cell parameters	$a = 8.909(3)$ Å, $b = 12.197(5)$ Å, $c = 10.769(4)$ Å
Number of formula weights per unit cell	4
Density	$D_{obs} = 1.76$ g/cm³; $D_{calc} = 1.80$ g/cm³
Absorption coefficient (μ_{MoK_α})	8.16 cm^{-1}
Colour and morphology	Deep red. Tabular, elongated along [001]. {110} faces prominent
Dimensions of crystal used for data collection	$0.36 \times 0.32 \times 0.12$ mm³
Radiation	MoK_α, Graphite monochromator
($\sin\theta/\lambda_{max}$)	0.705 Å^{-1}
Reflections measured	1720, 1321 with intensity $> 3\sigma$
Structure determination	*Patterson* and *Fourier* methods
Refinement	Anisotropic temperature factors 7 H atoms: Positional parameters & isotropic B's 4 H atoms: positional parameters only
No. of variable parameters	110
R-value	0.034
Goodness of fit	3.92
Standard deviations of interatomic distances	Ti—N: 0.002 Å Ti—O: 0.001 Å C—C(N): 0.002 Å O—O: 0.002 Å C—H: 0.02 Å O(4)—H: 0.02 Å O(5)—H: 0.03 Å

The six hydrogen atoms in the asymmetric unit were obtained from a difference map computed after the refinement of the structure to an R-value of 0.047. While the hydrogen atoms associated with the pyridine ring and the coordinated water molecule could be clearly seen at heights of 0.52–0.68 el/Å³, the other two hydrogen atoms belonging to the crystal water were found in lower maxima of 0.28 and 0.32 el/Å³, the electron density being rather smeared out in this region. These two hydrogen atoms showed during refinement abnormally high B-values, which had to be kept fixed in order to achieve convergence. Secondary extinction was refined and was found to be negligible. The final positional and thermal parameters are given in Table 2. A list of observed and calculated structure factors is available on request from one of the authors (*D.S.*).

Computations were made on the *CDC*-6400/6500 ETHOS system of ETH-Zürich. The programmes of the X-RAY System [7] as adapted to the ETHOS system by *Schwarzenbach* were used, supplemented by data reduction and absorption factor programmes developed in our laboratory. ORTEP [8] was used for illustrations.

3. Discussion of the Structure. – The point symmetry of the complex in this structure is 2. Fig. 1 shows a stereogram of the chelate molecule including interatomic distances. Bond angles are shown in Fig. 2. These values and the stereochemistry

Table 2. *Atomic coordinates and temperature parameters*

Standard deviations are given in parenthesis. The expression for temperature factor is of the form $\exp[-2\pi^2 \Sigma h_i h_j a_i^* a_j^* U_{ij}]$

Atom	10^4x	10^4y	10^4z	$10^4U_{11}^{+}$	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Ti[a]	0	2373(.3)	2500	297(2)	216(1)	289(2)	0	2(2)	0
N[a]	0	4148(1)	2500	289(8)	250(8)	266(8)	0	–1(9)	0
O(1)	2581(2)	4220(1)	4924(1)	614(8)	430(7)	500(7)	–75(6)	–293(7)	17(6)
O(2)	1538(1)	2878(1)	3826(1)	456(7)	294(5)	403(6)	25(5)	–127(6)	20(5)
O(3)	513(1)	995(1)	3027(1)	458(7)	308(5)	678(9)	19(5)	–57(6)	82(6)
O(4)[b]	1631(1)	2532(1)	1212(1)	433(7)	404(7)	458(8)	–57(6)	129(6)	–77(6)
O(5)[c]	3888(2)	3912(1)	1214(2)	822(11)	487(9)	945(14)	–234(9)	–117(11)	138(9)
C(1)	1751(2)	3892(1)	4089(1)	332(8)	350(8)	330(9)	–16(7)	–39(8)	15(7)
C(2)	883(2)	4681(1)	3296(1)	291(8)	272(7)	280(8)	–15(6)	–10(7)	–14(6)
C(3)	917(2)	5813(1)	3329(2)	377(9)	285(8)	399(9)	–52(7)	1(8)	–46(7)
C(4)[a]	0	6381(2)	2500	421(12)	249(10)	490(14)	0	39(14)	0
H(41)	1799(27)	1941(21)	704(23)	1257(105)					
H(42)	2441(25)	2944(17)	1274(19)	833(79)					
H(51)	3551(33)	4445(23)	690(26)	1393					
H(52)	3707(43)	4229(27)	1671(31)	1393					
H(C3)	1633(18)	6203(12)	3942(14)	424(48)					
H(C4)[a]	0	7231(17)	2500	420(63)					

[a] site symmetry 2, [b] coordinated water oxygen, [c] crystal water oxygen, [d] Isotropic U for hydrogen atoms.

agree well with the results for the triclinic modification, as well as for the difluoro [3] and the nitrilotriacetate (NTA) complexes [4]. Thus titanium has an approximately pentagonal bipyramidal seven-fold coordination with two carboxylic oxygens, one nitrogen and two oxygens of the peroxo group forming a distorted pentagon and two water oxygens at the apices. The peroxo group is attached laterally to the Ti ion. The pentagon is virtually planar, the distance of Ti from the least squares plane being less than standard deviation.

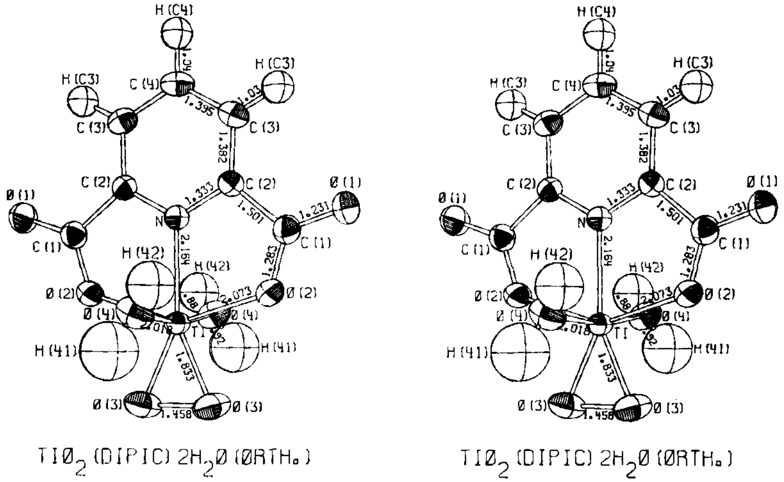

Fig. 1. *Stereogram of the orthorhombic diaquocomplex including bond lengths in* Å. Standard deviations are given in Table 1

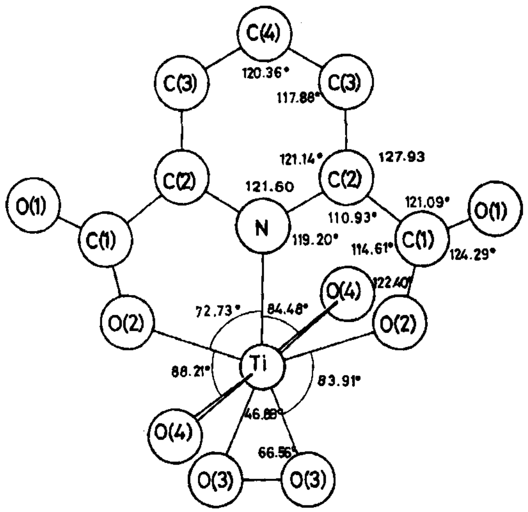

Fig. 2. *Bond angles in the orthorhombic diaquocomplex.* The standard deviations, in degrees, are O—Ti—O: 0.05–0.06; O—Ti—N: 0.03–0.04; Ti—N—C: 0.08; C—N—C: 0.14; Ti—O—C: 0.10; Ti—O—O: 0.06; and angles in the dipicolinic acid: 0.12–0.17

The O–O distance in the peroxide is 1.458 Å. This agrees well with the values 1.464, 1.463 and 1.469 Å in the triclinic diaquo, difluoro and NTA complexes respectively. The Ti–O_{peroxo} distance of 1.833 Å may be compared with the values 1.834 and 1.856 Å, 1.846 and 1.861 Å and 1.889 and 1.892 Å respectively and the Ti–O_{water} apical distance of 2.018 Å with the Ti–O (F) values of 2.022 and 2.055 Å in the triclinic diaquo, 1.853 and 1.887 Å in the difluoro and 1.819 and 2.065 Å in the NTA complexes. It is therefore clear that while the O–O bond distance of the peroxo group is practically the same in all the structures, there is a small but significant variation in the Ti–O_{peroxo} and apical distances. These differences have been interpreted [3] in the following way. As one proceeds from the deep red diaquo through the orange difluoro to the pale yellow dinuclear NTA complex, the apical ligands (successively H_2O, F^- and μ-oxygen) become more basic. The colours of the complexes are ascribed to a charge transfer between the peroxo group and the metal atom: the more basic the apical ligands and stronger their binding to the titanium, the more difficult becomes the electron transfer and therefore higher is the frequency of the absorption band. There is thus a progressive increase in the Ti–O_{peroxo} bond lengths down the series and a corresponding decrease in the apical bond lengths. These ideas are also substantiated by the difference electron density maps discussed in Section 5.

The atoms Ti, C(4), N, O(1), O(2), O(3), C(1), C(2), C(3) and the corresponding atoms related by the 2-fold axis lie virtually in a plane, the maximum deviation being 0.06 Å for O(2). Further, the plane of Ti and the peroxo group forms an angle of 3.7° with the plane of the pyridine ring and of 5° with the plane defined by Ti and the three coordinating atoms of the dipicolinic acid ligand, viz. N and O(2). The line joining Ti and the two water oxygens O(4) is nearly perpendicular to the above planes, making angles of 4.8°, 1.2° and 0.2° with the respective normals. The carboxyl groups consisting of the atoms C(1), C(2), O(1) and O(2) are turned out of the plane defined by Ti and the three coordinating atoms, N and O(2), by 4.0° and the plane of the pyridine ring by 3.0°.

4. Crystal Packing. – A stereoscopic view of the structure down the *c* axis is shown in Fig. 3. The molecules lie in rows parallel to the *b* axis. The main planes of the molecules of neighbouring rows along *a* lie approximately parallel to (101) and $(10\bar{1})$ respectively, enclosing an angle of 79.2°. This explains the absence of pleochroism, since the pleochroism of the triclinic modification is due to the fact that all the molecules there are lined up parallel to each other. Absorption of visible light with polarisation perpendicular to the main plane of the molecule is small and the deep red colour is due to absorption of light with polarisation parallel to the main plane [3]. Adjacent molecules along a row in the present structure are well separated by the *b* translation, the distance between the centre of the peroxo group of one molecule to H(C4) of the neighbouring pyridine ring being 4.59 Å. There exist channels along *c* surrounded by the hydrophylic oxygen atoms with larger distances to the hydrophobic parts (pyridine groups) of the molecules.

Three protons belonging to the two water molecules in the asymmetric unit take part in hydrogen bond formation. The coordinated water oxygen O(4) utilises its protons to form two hydrogen bonds — with a crystal water oxygen atom O(5) and a carboxylic oxygen atom O(1) of a neighbouring complex. O(1) also accepts another

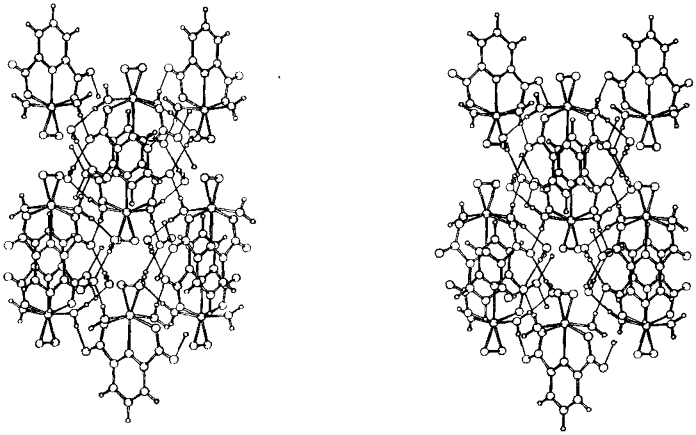

Fig. 3. *Stereoscopic view of the structure as seen down the* c *axis.* The horizontal axis is *a* and the vertical axis *b*. The small circles indicate hydrogens and the single lines denote hydrogen bonds

bond through a proton from the crystal water, the second proton of which does not appear to be utilised in H-bond formation. Each of the oxygen atoms O(1), O(4) and O(5) is thus involved in two bonds, which form a set of zig-zag chains running along the *b* axis and linking the complex molecules with the crystal waters into a three-dimensional network. The corresponding distances and angles are shown in Table 3. The complex clearly occurs as the free acid and not as a hydroxonium salt. In fact, it seems to be farther away from such a state than the triclinic modification. The molecule could, of course, not retain its point symmetry were it allowed to lose one proton.

Table 3. *Hydrogen bonding scheme in orthorhombic diaquo peroxo Ti dipic complex.* Distances in Å and angles in degrees. Standard deviations are enclosed in brackets

O(4)–H(41)	0.92(2)	H(41)–O(4)–H(42)	111(2)
O(4)–H(42)	0.88(2)	O(4)–H(41)–O(1)	169(2)
H(41)–O(1)	1.74(2)	O(4)–H(42)–O(5)	170(2)
H(42)–O(5)	1.75(2)		
O(4)–O(1)	2.644(2)		
O(4)–O(5)	2.622(2)		
O(5)–H(51)	0.91(3)	H(51)–O(5)–H(52)	88(4)
O(5)–H(52)	0.65(3)	O(5)–H(51)–O(1)	166(3)
H(51)–O(1)	2.02(3)		
O(5)–O(1)	2.911(2)		

5. Electron Density from *Fourier* Maps. – On the completion of the refinement, a difference *Fourier* map was computed using the final positional and thermal parameters. This is in very good agreement with the corresponding map of the triclinic form. Most of the atoms, however, were observed to be in negative regions of about 0.2 el/Å^3, O(3) and C(1) in particular being close to holes of about 0.35 el/Å^3. This may be due to the fact that the scattering factors used were for Ti^{4+}, which results in a deficiency of 4 electrons per formula unit in the calculated model. The

F_{obs} scale factor is therefore expected to be too low. A small peak of 0.30 el/Å^3 was found in the vicinity of the crystal water oxygen atom O(5). Fig. 4 shows the difference electron density maps in the main plane of the molecule (Ti, Dipic and peroxo groups) as well as in the plane of Ti and the apical bonds O(4). Despite the uncertainty in the scale factor and the fact that the positional parameters determined by X-rays do not correspond exactly to atom centres, these maps can be interpreted at least qualitatively on the basis of bonding electron density. The figure shows that there

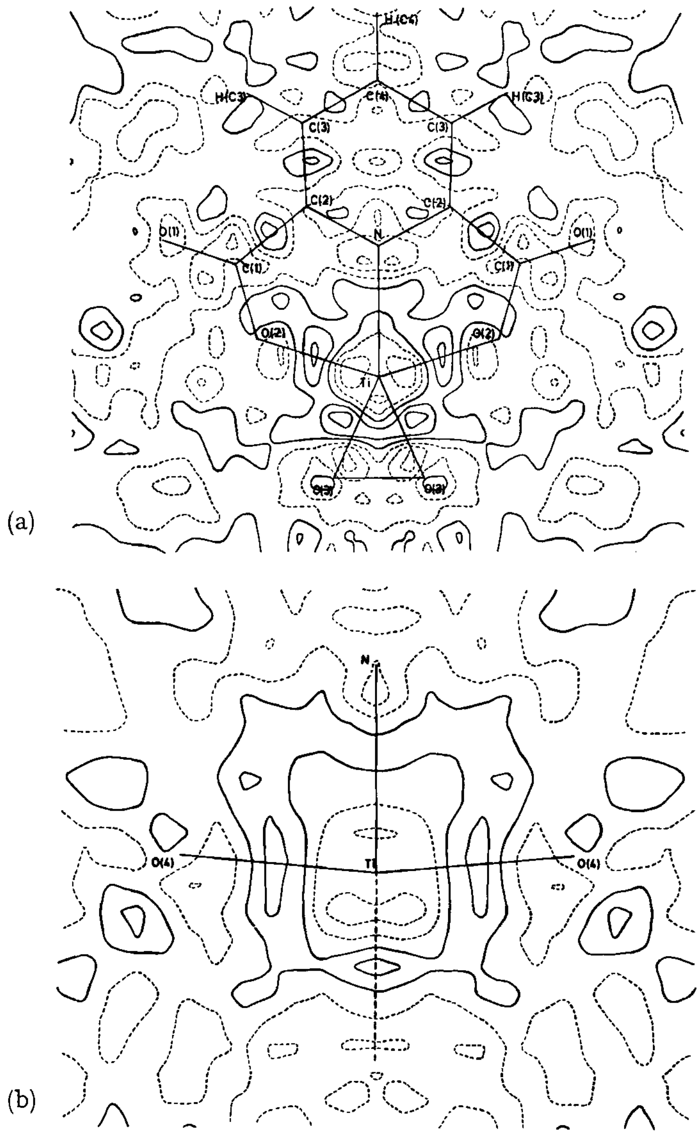

Fig. 4. *Difference electron density maps in the* (a) *equatorial and* (b) *apical planes.* Normal refinement with Ti^{4+} form factor. Contour intervals at 0.1 el/Å^3. Broken lines indicate negative contours

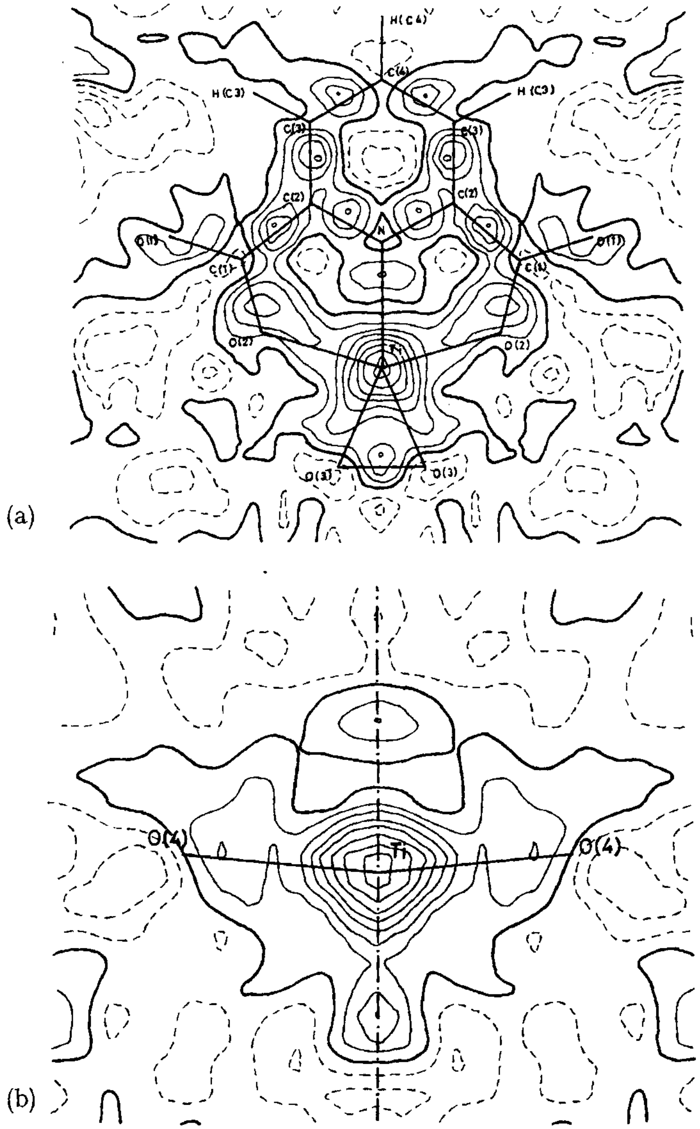

Fig. 5. *Difference electron density maps in the* (a) *equatorial and* (b) *apical planes.* Refinement with modified weights, Ti^{4+} form factor

are maxima on every bond in the molecule, the highest being 0.31 el/Å^3 near the Ti–O(3) bond, the next ones being 0.21 el/Å^3 on Ti–O(2), 0.14 el/Å^3 on Ti–O(4) and 0.09 el/Å^3 on Ti–N. On the C–C bonds there are maxima varying between 0.04 and 0.18 el/Å^3, and 0.15 el/Å^3 near the C–O bond. There is also a small characteristic bridge of electron density across the Ti-peroxide bonds as found in the triclinic form and the NTA complex. Its maxima form an angle of about 70° with Ti and indicate

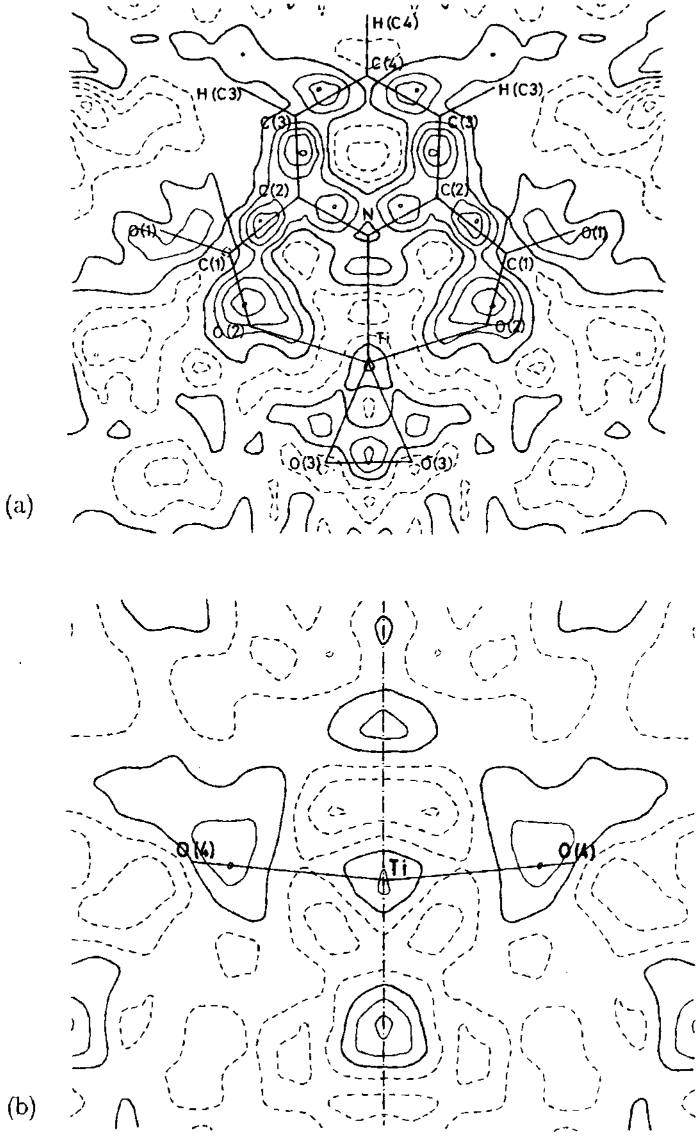

Fig. 6. *Difference electron density maps in the* (a) *equatorial and* (b) *apical planes.* Refinement with modified weights and the form factor for neutral Ti

bent bonds, as may be expected for a pentagonal bipyramidal sp^3d^3 hybridisation of Ti. It is gratifying to note that the higher value of residual electron density on the Ti–O_{peroxo} bonds as compared to that on the apical bonds corresponds well with the shorter bond length of 1.833 as compared to 2.018 Å. These results fit well into the earlier discussion relating the Ti–O_{peroxo} and apical bond distances in the series of peroxotitanium chelates with their colours [3] [9].

It has been pointed out recently [10] that structure parameters closer to the nucleus can be obtained with a least squares refinement using weights favouring high order data. Other advantages mentioned are faster convergence, and considerable saving in computer time through the use of block diagonal refinement due to reduced correlations. The modified weights suggested are

$$w'(h) = w(h) \exp\left[\frac{r \sin^2\theta}{\lambda^2}\right] \text{ with } r = \frac{8\pi^2 q}{p(p+q)},$$

w(h) being the experimental weights. p is an adjustable constant in the approximation of treating atomic peaks as *Gaussian* in shape and has values 3 to 4 $Å^{-2}$ for second row atoms [11]. The value of q is chosen to give the desired degree of sharpening. A typical value suggested for r is 20 $Å^2$,with $p \simeq 3$ $Å^{-2}$ and $q \simeq 9$ $Å^{-2}$.

A refinement of the structure with $r = 20$ $Å^2$ and form factors corresponding to Ti^{4+} led to slightly lower temperature factors and a higher scale on F_{obs}. It was also interesting to find that the $Ti–O_{peroxo}$ and apical bond distances increased by 0.005 to 0.012 Å. The corresponding difference electron density maps (Fig. 5) show larger maxima than before on all the bonds. There is also a high peak of 0.5 el/$Å^3$ at the Ti position. The four additional electrons appear to be centred on titanium and smeared out along the bonds in accordance with the *Pauling* electronegativity rule [12]. Similar results (Fig. 6) with virtually identical structure parameters were obtained when the refinement was repeated using the scattering factor for neutral Ti, which is practically the same as for Ti^{4+} at $\sin\theta/\lambda > 0.5$. The peak at the Ti position, of course, vanished. These maps give a surprisingly clear, though qualitative picture of bonding electron density and are in very good agreement with the corresponding maps obtained for the triclinic diaquodipicolinate and the dinuclear NTA complex.

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