

CRYSTAL STRUCTURE OF AMMONIUM TITANYL OXALATE; TETRAMERIC UNITS OF
CYCLO-TETRA-DI- μ -OXO-CIS-DIOXALATO TITANATE (IV)

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Previous investigations of the structures of $(\text{TiO})^{2+}$ complexes such as $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ have given sufficient evidence that discrete $(-\text{Ti}=\text{O})$ species are rarely found (1). I.R.-spectroscopic and X-ray investigations have shown or suggested the existence of $-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$ links in most of the so called titanyl compounds.

In the case of $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$, however, i.r. indications of such links were not definite, due to carbon-oxygen frequencies in a broad absorption band in the region $700-900 \text{ cm}^{-1}$. The possibility of hydroxyl or water groups as ligands could not be excluded. Thermogravimetric analysis demonstrated that water in the compound left in two steps (2), so there might be a possibility for crystal and coordinated water, as found in the recently published structure investigation of $(\text{NH}_4)_2\text{VO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ (3).

EXPERIMENTAL

Crystals of $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ could easily be prepared by a newly developed method of synthesis which is faster and less

complicated than the usual way of dissolving the gel-like titanyl-hydroxide in acidified oxalate solution (4,5,6). In a cold, hydrolysed but clear solution of TiCl_4 in water (about 0.5 M) two equivalents of solid oxalic acid were dissolved, after which 4-5 equivalents of ammonia were carefully added. This addition was performed such that the solution stayed clear without turbidity of hydroxylated titanium species. The pH should then be about 1-2. About half the volume of ethanol was then added slowly without stirring to get two slightly mixed layers. After standing overnight colourless crystals of the compound could be isolated in a good yield (80%). The same method has also been applied to the K^+ and $\text{C}_5\text{H}_5\text{NH}^+$ salt using KOH or pyridine instead of ammonia, but pyridine should be used in a large excess.

Intensities were measured by means of an automatic single-crystal diffractometer using Mo-K_α radiation (graphite monochromator). The positions of the atoms were determined by means of conventional Patterson and Fourier methods. The crystal structure reported here is based on 2500 reflections, with $\sin \theta/\lambda$ up to 0.59.

RESULTS

The crystals of the ammonium salt are monoclinic with $a = 13.47$, $b = 11.33$ and $c = 17.64 \text{ \AA}$, $\beta = 126.66^\circ$, $Z = 8$ molecules per unit cell, density $D_m = 1.80$, $D_c = 1.803 \text{ g cm}^{-3}$, space group $P2_1/c$.

Distinct cyclic tetrameric units $\{\text{TiO}(\text{C}_2\text{O}_4)_2\}^{2-}_4$ have been found in the unit cell. Positions and isotropic temperature factors of the 34 independent non-hydrogen atoms have been refined yielding an R-value of 0.070. An overall view of the structure of the tetramer is given in fig.1.

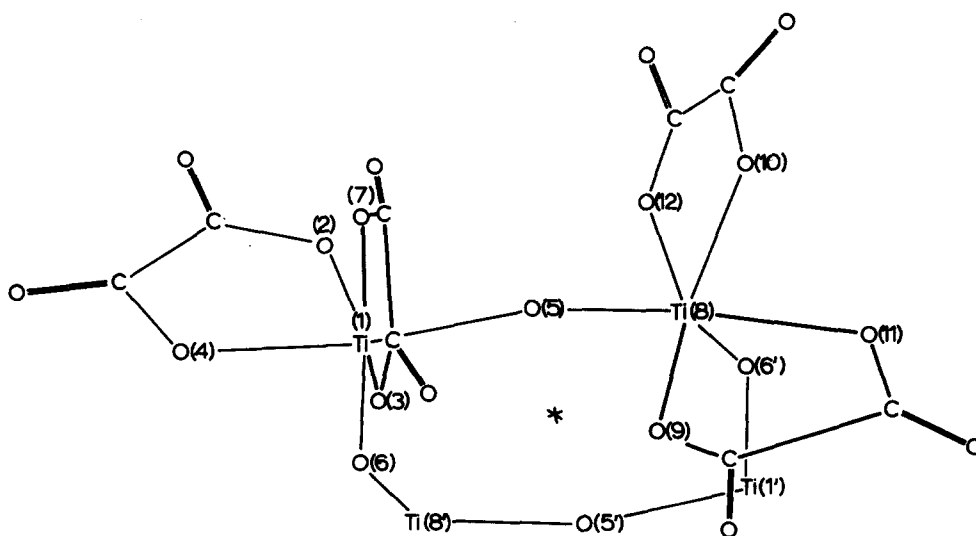


FIG. 1

Two octahedrons of the tetramer; the other two are related to the ones shown by a centre of symmetry in point *.

The titanium atoms are six-coordinated, with two bridging oxygen atoms *cis* to one another and two bidentate oxalate groups together forming a distorted octahedron. Four of such octahedrons are connected in a cyclic tetramer of which two are symmetry independent. The four titanium atoms nearly form a square with sides of 3.50 and 3.39 Å and angles of 86° and 94°. The four bridging oxygen atoms form a diamond with a side of 2.71 Å and angles of 107° and 73° and are oriented such that one diagonal of the diamond is shorter and one longer than the sides of the square formed by the titanium atoms. The angles Ti(1)-O(5)-Ti(8) and Ti(1)-O(6)-Ti(8') are 152° and 139° respectively. The eight atoms together form an eight-ring system with short Ti-O distances of 1.84 and 1.78 Å alternately, probably due to $d\pi-p\pi$ 3-center 2-electron bonds in Ti-O-Ti sets. The Ti-O distances *trans* to the bridging oxygen atoms are much longer, 2.06 and 2.10 Å respectively, as is to be expected from the charge displacement due to the $d\pi-p\pi$ bonding.

The other two Ti-O distances do not differ much from 1.98 Å. As for the angles O-Ti-O in each octahedron, most differ from 90°, the most significant deviations being between 8 to 12 degrees. From asymmetry in these deviations it could be concluded that the distortion is not simply digonal.

Most of the NH_4^+ and H_2O groups (not shown in the figure) are hydrogen bonded to the oxalate-oxygen atoms of both tetramers in the unit cell. The two kinds of crystal water have to be ascribed to different environmental influences.

The tetrameric structure found here is different from other known tetrameric titanium compounds such as $[\text{Ti}(\text{OC}_2\text{H}_5)_4]_4$ (7), $[(\pi\text{-C}_5\text{H}_5)\text{TiClO}]_4$ (8). In the former the octahedrons share edges in stead of corners leading to both two- and three-coordinated oxygen atoms. In the latter the titanium atoms are surrounded tetrahedrally, the tetrahedrons sharing corners.

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