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Ammonium di-μ-oxalatotitanate(III) dihydrate: an eight-coordinate, polymeric titanium(III) complex

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Abstract

The preparation, magnetic and spectral properties and crystal structure of ammonium di-μ-oxalatotitanate(III) dihydrate are described. $NH_4[Ti(C_2O_4)_2]\cdot 2H_2O$, $M_r = 278.01$, hexagonal, $P6_222$, $a = 8.935(3)$ $c = 10.878(4)$ Å, $V = 752.1(7)$ Å^3, $Z = 3$; $R = 0.045$ for 426 absorption-corrected independent reflections and 48 parameters. The crystals are isomorphous with those of ammonium di-μ-oxalatoindate(III) dihydrate. The titanium atoms are coordinated by eight oxalate oxygen atoms in a square-antiprismatic arrangement, and bridging oxalate groups link the coordination polyhedra to form a right-handed spiral structure about 6_2 crystal axes.

Introduction

In 1977 spectroscopic and preliminary X-ray crystallographic data supporting the assignment of eight-coordinate polymeric structures to the compounds $M[Ti(ox)_2]\cdot 2H_20$ ($ox = C_2O_4$; $M = NH_4$, K or Na) were reported [1]. A different crystalline modification of the ammonium compound, $NH_4[Ti(ox)_2]\cdot 2H_2O$, from that previously reported, which was observed to form when the reaction mixture was kept for some days, has now been prepared in a form suitable for X-ray diffraction structural analysis.The results show the titanium(III) ion to be in an eight-coordinate environment which is approximately square-antiprismatic, with bridging oxalato ligands. The compound was found to be unusually stable and resistant to air oxidation.

Experimental

Preparation of $NH_4[Ti(ox)_2]\cdot 2H_2O$

The preparation was carried out under dinitrogen using aqueous solutions which had been deoxygenated by purging with dinitrogen. 0.26 g of $TiCl_3\cdot 6H_20$ (1.0×10^{-3} mol) was added to a hot solution of 0.25 g (2.0×10^{-3} mol) of oxalic acid dihydrate in 10 ml of water. 0.14 g of ammonium oxalate (1.0×10^{-3} mol) in 10 ml of hot water was added dropwise while stirring. On cooling the resulting solution, fine gold-coloured crystals (**I**) separated, but when the mixture was left for 3 days at room temperature recrystallisation took place, giving larger dark red crystals (**II**) which were separated from the solution by filtration and stored under dinitrogen.

Elemental analysis

Found: C, 16.6; H, 2.9; N, 4.9. Calc. for $C_4H_8NO_{10}Ti$: C, 17.3; H; 2.9; N 5.0%.

Magnetic susceptibility

Magnetic susceptibility was determined at room temperature (24 °C) using a Faraday balance; $\mu_{eff} = 1.62$ BM.

X-ray powder diffractometry

Some of the larger crystals (**II**) and some of the initial form (**I**) were compared with $K[Ti(ox)_2]\cdot 2H_2O$ by X-ray powder diffractometry using the Debye-Scherrer method.

Infrared spectra

IR spectra were recorded by the KBr disc technique using Perkin-Elmer IR 180 and Beckman IR 4260 spectrophotometers. Apart from absorption bands due to the ammonium ion and lattice water the spectra recorded were typical of oxalato complexes [2]. The spectra for the two crystalline forms of $NH_4[Ti(ox)_2]\cdot 2H_2O$ were very similar.

Diffuse reflectance spectra

The diffuse reflectance spectra of the two crystalline forms of $NH_4[Ti(ox)_2]\cdot 2H_2O$ and, for comparison, of

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$K[Ti(ox)_2]\cdot 2H_2O$ and $Na[Ti(ox)_2]\cdot 2H_2O$ were recorded using a Beckman 5240 spectrophotometer, in the range 5000–17 000 cm^{-1} and are shown in Fig. 1. The spectra of $Na[Ti(ox)_2]\cdot 2H_2O$, $K[Ti(ox)_2]\cdot 2H_2O$ and $NH_4[Ti(ox)_2]\cdot 2H_2O$ (**I**) are clearly similar, showing a broad, low-intensity band at about 12 600 cm^{-1} and another at about 7000 cm^{-1}. The spectrum of $NH_4[Ti(ox)_2]\cdot 2H_2O$ (**II**) shows a relatively more intense band at about 13 500 cm^{-1} and one at about 5950 cm^{-1}.

Single crystal X-ray diffractometry

Experimental details are given in Table 1.

A few single crystals were selected and photographed (Cu Kα radiation, $\lambda = 1.5418$ Å), using precession methods, which gave approximate cell dimensions and established the space group as one of $P6_2$, $P6_4$, $P6_222$ or $P6_422$. The expectation that the Ti was eight coordinate suggested that the correct group was $P6_222$ or its enantiomer $P6_422$, with the Ti atom located at a special position with point symmetry 222. One of the crystals was then irradiated on an Enraf-Nonius CAD4 diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Accurate cell parameters were determined by a least-squares analysis of the setting angles of 24 reflections ($16 \leqslant \Theta \leqslant 17°$). During the data collection the intensities of three reference reflections were monitored every hour and orientation was checked periodically. The data were Lp-processed and empirical absorption correction applied, since crystal absorption varied by 38% for a set of chosen equivalent reflections.

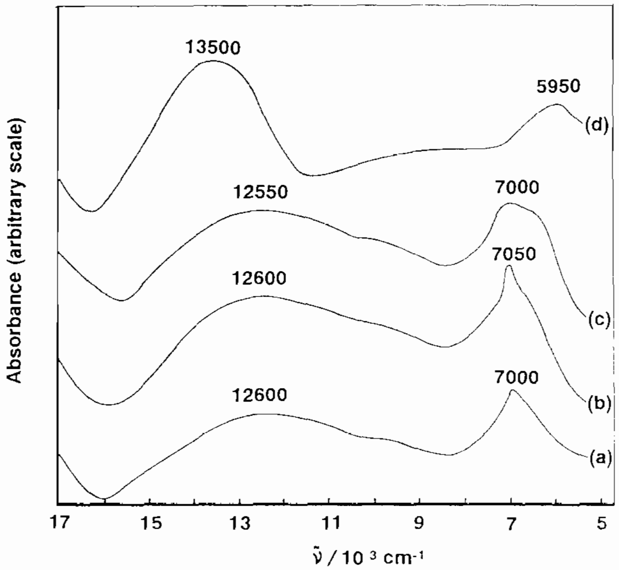

Fig. 1. Diffuse reflectance spectra of $K[Ti(ox)_2]\cdot 2H_2O$ (a), $Na[Ti(ox)_2]\cdot 2H_2O$ (b), $NH_4[Ti(ox)_2]\cdot 2H_2O$ (**I**) (c) and $NH_4[Ti(ox)_2]\cdot 2H_2O$ (**II**) (d).

TABLE 1. Experimental details of crystal, data collection, structure solution and refinement of $NH_4[Ti(C_2O_4)_2]\cdot 2H_2O$ (**II**)

Molecular formula	$C_4H_8O_{10}NTi$
M_r (g mol $^{-1}$)	278.01
Space group	$P6_222$
a (Å)	8.935(3)
b (Å)	8.935(3)
c (Å)	10.878(4)
V (Å^3)	752.1(7)
Z	3
ρ_c	1.84
$F(000)$ (e)	423
μ(Mo Kα) (cm^{-1})	8.4
Dimensions of crystal (mm)	$0.2 \times 0.2 \times 0.3$
Scan mode	ω-2θ
Scan width in ω (°)	$(0.85 + 0.35 \tan \theta)$
Aperture width (mm)	$(1.12 + 1.05 \tan \theta)$
Scan speed	variable, 40 s max. time
Crystal decay	none
No. reflections collected	570
No. reflections with $I_{rel} > \sigma I_{rel}$, N	426
No. parameters, NP	48
$R = \Sigma \lVert F_o\rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.045
$R_w = \Sigma w^{1/2} \lVert F_o\rvert - \lvert F_c \rVert / \Sigma w^{1/2} \lvert F_o \rvert$	0.043
w	$0.1512/[\sigma^2F + 0.0042F]^2)$
Max./min. residual e density (Å^3)	± 0.6

Solution and refinement of the structure

The structure was refined and analysed using SHELX-76 [3]. Ti was placed at Wyckoff position 3(c), where three two-fold axes intersect, and a difference Fourier map revealed the rest of the atomic positions. The carbon atoms lie on two-fold axes, positions 6(j), and the N atom and water O atoms occupy sites 3(a) and 6(h), respectively. H atoms and oxalate O atoms occupy general positions. Full-matrix least-squares refinement based on F_c resulted in $R = 0.0448$ and $R_w = 0.0427$, with non-hydrogen atoms refined anisotropically: relevant constraints were applied to the anisotropic temperature factor tensors [4]. Refinement of the enantiomeric structure ($P6_422$, found structure reflected in $z = 0$) gave a significantly [5] poorer agreement. Maximum shift/error ratio and electron density in the final refinement cycle and difference map were respectively < 0.02 and 0.6 e Å^{-3}. Scattering factors were from International Tables for X-ray Crystallography [6].

Results and discussion

X-ray powder diffraction

The X-ray powder diffraction photographs showed that the crystal structure of the initial form **I**, and of $NH_4[Ti(ox)_2]\cdot 2H_2O$ and $K[Ti(ox)_2]\cdot 2H_2O$ were isomorphous as previously reported [1], but the second form **II** was shown to have a different structure.

Crystal structure

Final fractional atomic coordinates are reported in Table 2 and selected bond lengths and angles are given in Table 3. The crystal structure is depicted in Fig. 2. The features of this unusual and beautiful structure which have been emphasised in the Figure are (i) the coordination polyhedron around Ti, which has been drawn bounded by single lines; (ii) the spiral arrangement of μ-oxalato-titanate polyhedra around the *c* axis; this spiral motif is hexagonal in projection (down *c*) and two such intertwined spirals, separated by a 180° rotation about *c*, make up the repeating unit of the structure; and (iii) enclose a hydrogen-bonded alternating chain of NH_4^+ ions and H_2O molecules also lying along the *c* axis. For the sake of clarity, Fig. 2 shows only one strand of the spiral. Neighbouring spirals are connected by the bridging oxalato groups. All of the H atoms of the ammonium ions are involved in hydrogen bonds, with H to O(H_2O) distances of 1.886 Å and the hydrogens of the water molecules take part in weaker interactions with oxalate oxygens, with O to H distances of 2.05 Å. The isomorphism with ammonium di-μ-oxalatoindate(III) dihydrate [7] is striking; variable fractional coordinates of corresponding non-hydrogen atoms differ by a maximum of no more than 10σ and the majority agree within 4σ. Replacing the titanium atom with the larger indium atom results in a linear size increase of the coordination polyhedron of around 3.7%. (In–O distances are 2.197 and 2.351 Å); this is reflected in an increase of *a* of 1% to 9.025 Å and a 4.3% increase in *c* to 11.343 Å, while the increase in cell volume is 6.4%.

TABLE 2. Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å^2, $\times 10^3$) for $NH_4[Ti(C_2O_4)_2]\cdot 2H_2O$ (**II**)

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}
Ti(1)	5000	5000	3333	9(1)
O(1)	5511(3)	3140(3)	4430(3)	19(1)
O(2)	2727(3)	3495(3)	4372(2)	15(1)
O(3)	2504(6)	0	5000	52(1)
C(1)	6920(3)	13840(6)	5000	13(1)
C(2)	2104(3)	4209(7)	5000	10(1)
N(1)	0	0	0	46(2)

TABLE 3. Bond lengths (Å) and angles (°) for non-hydrogen atoms

Ti–O(1)	2.270(3)	C(1)–O(1)–Ti	114.4(2)
Ti–O(2)	2.116(3)	C(2)–O(2)–Ti	120.1(3)
C(1)–O(1)	1.254(3)	O(2)–C(2)–O(2)′	127.1(5)
C(2)–O(2)	1.240(3)	O(1)–C(1)–O(1)′	128.8(4)
C(1)–C(2)	1.509(3)	O(1)–Ti–O(1)′	116.6(1)
		O(2)–Ti–O(2)′	115.4(1)
		O(1)–Ti–O(2)	74.6(1)
		O(1)–Ti–O(2)′	72.8(1)

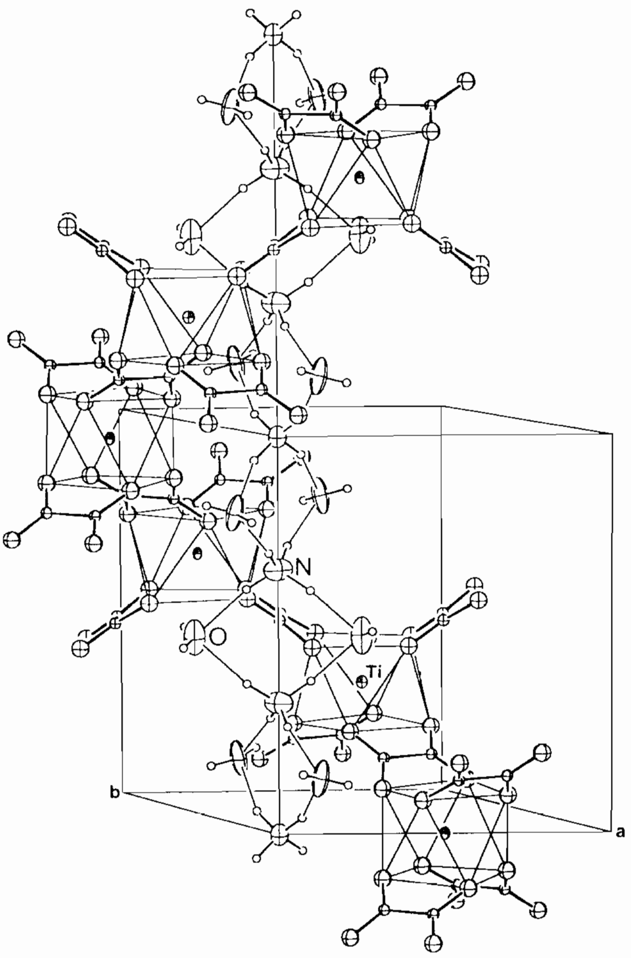

Fig. 2. The crystal structure of $NH_4[Ti(ox)_2]\cdot 2H_2O$ (**II**). Coordination polyhedra around Ti are shown bounded by single lines and the spiral arrangement of μ-oxalato-titanate polyhedra around the *c* axis is indicated by one of the two such intertwined spirals which make up the repeating unit. A hydrogen-bonded alternating chain of NH_4^+ ions and H_2O molecules is shown along the *c* axis.

Anion structure and electronic spectrum

Figure 3 shows the anion with atomic numbering. As shown the complex anion consists of eight oxygen atoms of four oxalate ions arranged in an approximately square-antiprismatic configuration around the central titanium atom. The squares of four oxygen atoms above and below the titanium are twisted through an angle of 38° relative to one another about the vertical axis, that is 7° less than the 45° required for a true square antiprism. The point group symmetry of the TiO_8 unit is therefore D_4 rather than D_{4d}. The angle, Θ, between the Ti–O bonds and the vertical axis, is approximately 58° (58.3° for Ti–O(1) and 57.7° for Ti–O(2)). The bridging oxalate ions are very nearly planar and the bond lengths and angles are similar to those found for other oxalatotitanium(III) complexes [8, 9] and particularly close to those reported for the bridging oxalate

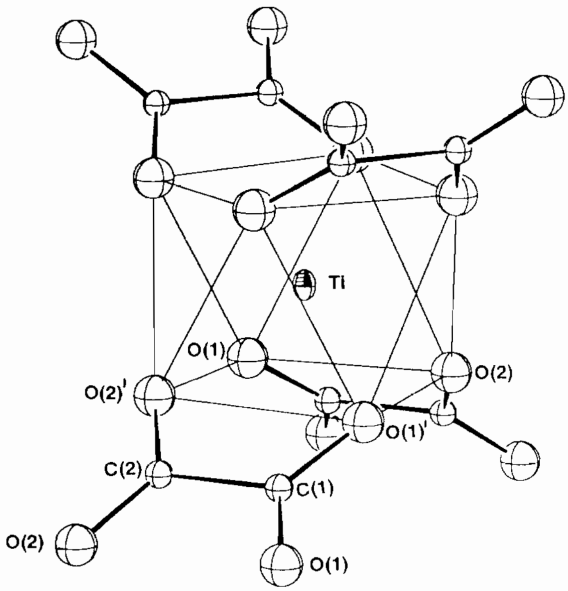

Fig. 3. The structure of the μ-oxalato-titanium(III) anion showing the square-antiprismatic arrangement of the oxygen atoms of the oxalate groups around the titanium. The atoms are labelled and numbered (other atoms are symmetry generated).

group in $[Ti_2(ox)_3(H_2O)_6]$ [10]. In the structure suggested for $NH_4[Ti(ox)_2]\cdot 2H_2O$ (I) (and $K[Ti(ox)_2]\cdot 2H_2O$, $Na[Ti(ox)_2]\cdot 2H_2O$) [1], which also involves a square-antiprismatic configuration, the oxalate ion bridges between the lower and upper oxygen squares, in contrast to the O(1) to O(2) of the structure **II** now reported, and θ was estimated at 55.2°. The ratio of the absorption band frequencies in the diffuse reflectance spectra of the former compounds of 1.80 is consistent with the value estimated from the crystal-field energy diagrams of Parish and Perkins [11] (estimated ratio 1.84) and Kepert [12] (1.77) for $\theta = 55.2°$ in a square-antiprismatic complex.

The energy level diagrams in both publications show an intersection of the $E_2(d_{x^2-y^2}, d_{xy})$ and $E_3(d_{xz}, d_{yz})$ levels for θ between 57 and 58°, which implies that the energies of the corresponding d orbitals in $NH_4[Ti(ox)_2]\cdot 2H_2O$ (**II**) should be similar at this θ value. The 7° deviation from true square-antiprismatic geometry found in $NH_4[Ti(ox)_2]\cdot 2H_2O$ (**II**) would imply a small separation of $d_{x^2-y^2}$ and d_{xy} orbital energies but we would expect the absorptions due to electronic transitions between d_{z^2} and the four other d orbitals to be largely unresolved leading to a single band of relatively higher intensity than for other configurations. The frequency of the observed band at 13 500 cm^{-1} is close to what would be predicted for a D_{4d} configuration, with $\theta = 58°$, and assuming the same Dq value for all the eight-coordinate oxalatotitanium(III) complexes compared. There does not then appear to be a ready assignment for the band at 5950 cm^{-1} and we must assume that it does not arise from a simple d–d transition.

Supplementary material

A copy of the table of structure factors and other details of X-ray crystallographic measurements are available from the authors on request.

Acknowledgements

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