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Neutron structural refinement of $Te(OH)_6 \cdot 2Na_3P_3O_9 \cdot 6H_2O$, study of the hydrogen bonds

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Abstract. A neutron-diffraction refinement of the crystal structure of sodium trimetaphosphate-tellurate has been made by using 406 independent reflections to a final R value of 0.054. This neutron analysis has been carried out in order to locate the hydrogen atoms and thereby complete the previous X-ray study. Acid molecules $Te(OH)_6$ and water molecules as well as their environments are described.

Introduction

Sodium trimetaphosphate-tellurate is an addition compound of telluric acid; its crystal structure has been described previously: $a = 11.67(1)$, $c = 12.12(1)$ Å, $P6_3/m$, $Z = 2$, $M = 949.5$ g, $D_x = 2.225$ g cm^{-3} (Boudjada et al., 1981). Telluric acid has the property of forming with mineral or organic anions, compounds characterized by the independent coexistence of acid molecules and chosen anions. As in most previously described compounds of this type (Andersen et al., 1983; Averbuch-Pouchot, 1983), it has not been possible to locate hydrogen atoms using X-rays. It is

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necessary to know the hydrogen positions in these compounds, in order to be able to understand the role of hydrogen bonding with respect to the aptitude of telluric acid to form addition compounds. In this refinement, the aim is to locate hydrogen in the acid group and water molecule.

Experimental

The sample was mounted on a glass fiber and placed on the computer-controlled 4 circle diffractometer P32 at the SILOE reactor of the C.E.N. Grenoble. The working wavelength (λ = 1.18 Å) was obtained by means of the (200) reflection of a bent copper monochromator. The largest single crystal available was very small for neutron diffraction. The greatest dimension (along the *c* axis) was 1.28 mm, the basis was roughly hexagonal with an average side length of 0.6 mm, the total volume was near 0.72 mm^3.

However due to the rather large flux and to the good experimental conditions of this apparatus, the measurements were made in a reasonable time (less than 2 weeks). Nearly 900 reflections were measured up to $\sin \theta/\lambda = 0.6$ Å^{-1} ($2\theta = 90°$). Intensities were collected at room temperature using an ω step-scan method. Equivalent reflections were also measured. The (500) and (0$\bar{5}$0) reflections were used as standard reflections and measured every 50 data: no significant variation was observed. Evaluation of the value of the integrated intensity and of its standard deviations, together with the correction of the Lorentz factor, were performed by the COLL5 program (Lehmann, 1984).

The average value of the equivalent reflections was obtained with the ARRNGE program (Brown et al., 1981) based on the CCSL system (Cambridge crystallographic subroutine Library) in $P6_3/n$ group. Due to the very small dimensions of the crystal ($\mu R \simeq 0.1$) no absorption correction was applied.

Structure refinement

The crystal structure was refined by a least-squars method with SHELX76 program (Sheldrick, 1976). 406 independent reflections were used with $F > 3\,\sigma(F)$. The Fermi lengths are: $b_{\mathrm{Te}} = 0.58 \times 10^{-12}$ cm (Boucherle et al., 1982, Lindqvist et al., 1973), $b_{\mathrm{p}} = 0.51 \times 10^{-12}$ cm, $B_{\mathrm{Na}} = 0.36 \times 10^{-12}$ cm, $b_{\mathrm{O}} = 0.58 \times 10^{-12}$ cm, $b_{\mathrm{H}} = -0.374 \times 10^{-12}$ cm.

Except for hydrogen atoms, the positions determined by X-rays (Boudjada et al., 1981) were used at the beginning of the calculations. The hydrogen atoms were located from a Fourier synthesis.

Table 1. Coordinates, anisotropic thermal vibration parameters[a] and equivalent isotropic temperature factors[b] in $Te(OH)_6 \cdot 2Na_3P_3O_9 \cdot 6H_2O$ ($\times 10^4$)

Atoms	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	0	0	0	351(38)	300(37)	300(37)	621(109)	150(18)	0	0
P	4980(5)	7477(5)	4930(4)	169(14)	180(22)	218(23)	119(31)	95(20)	2(22)	28(23)
Na(1)	1310(10)	5709(10)	$\frac{1}{4}$	220(29)	230(50)	148(45)	323(75)	75(41)	0	0
Na(2)	1532(10)	8709(10)	$\frac{1}{4}$	286(30)	168(47)	276(52)	429(73)	81(43)	0	0
O(E1)	2382(5)	4808(4)	1280(4)	250(14)	260(23)	230(24)	221(31)	96(20)	16(21)	29(21)
O(L)	4033(4)	5947(4)	5263(4)	172(13)	161(20)	196(21)	191(24)	82(16)	−18(18)	25(18)
O(E2)	6122(4)	8045(4)	5696(4)	230(14)	151(21)	274(21)	231(26)	68(17)	−48(24)	−33(25)
O(Te)	1367(7)	17(9)	932(6)	408(17)	470(36)	801(57)	305(40)	504(39)	−128(36)	−128(38)
O(W1)	3833(7)	378(8)	$\frac{1}{4}$	256(20)	349(42)	161(34)	309(59)	96(33)	0	0
O(W2)	3509(8)	3264(8)	$\frac{1}{4}$	260(19)	312(37)	358(44)	298(50)	217(34)	0	0
H(1)	3992(10)	939(10)	1874(9)	460(27)	623(59)	480(59)	316(61)	287(49)	58(51)	94(52)
H(2)	3716(9)	2881(9)	3135(10)	409(24)	532(49)	359(45)	474(65)	267(41)	−9(52)	93(47)
H(3)	2105(14)	641(11)	732(11)	513(29)	704(75)	473(60)	362(63)	377(56)	−58(66)	−13(55)

[a] The anisotropic temperature factor is: $\exp[2\,\pi^2\,(h^2\,a^{*2}\,{}^2U_{11} + k^2\,b^{*}2\,U_{22} + l^2\,c^{*2}\,U_{33} + hka^{*}\,b^{*}\,U_{12} + hla^{*}\,c^{*}\,U_{13} + klb^{*}\,c^{*}\,U_{23})]$

[b] $U_{\mathrm{eq}} = \frac{1}{3}\sum_i\sum_j U_{ij}\,a_i^{*}\,a_j^{*}\,a_i\,a_j$

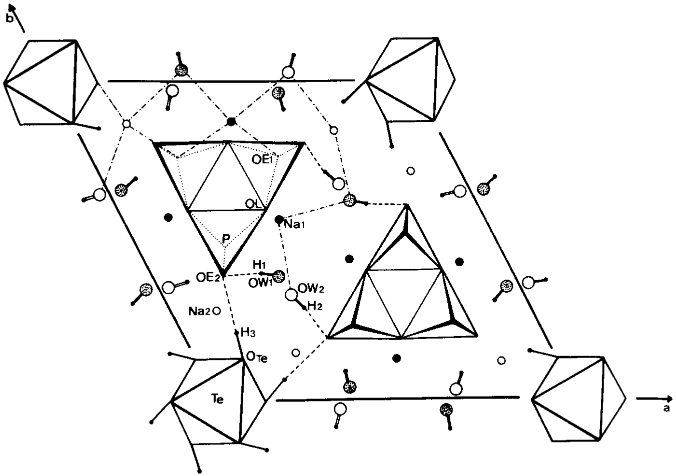

Fig. 1. Projection of $Te(OH)_6 \cdot 2Na_3P_3O_9 \cdot 6H_2O$ along *c*

All the positions and anisotropic thermal parameters were refined (Table 1). After the final least-squares cycle, the shift/error ratio was zero for all parameters and $R = 0.054$, $Rw = 0.061$ ($R = \Sigma|F_{obs}-F_{cal}|/\Sigma|F_{obs}|$, $Rw = \Sigma\sqrt{w}|F_{obs}-F_{cal}|/\Sigma\sqrt{w}|F_{obs}|$, $w = 1/[\sigma^2(F) + 0.01\ F^2]$).

After refinement the positions obtained for sodium and oxygen atoms are only slightly different from those determined by X-rays, except for one oxygen atom O(Te): the position is $x,y,\bar{z}$ instead of x,y,z located by X-rays; using the X-rays position, the R factor did not go below 0.20. The neutron positions have been introduced in the X-rays data refinement: the R factor was only 0.09 instead of 0.04. These results seem to show the existence of two different phases; although the same crystal preparation procedure (Boudjada et al., 1981) was used, the X-ray and neutron analyses were made using crystals grown from two different solutions[1].

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[1] Additional material to this paper can be ordered referring to the no. CSD 51415, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Table 2. Interatomic distances (Å) and angles (°) from neutron and X-ray diffraction data for $Te(OH)_6$ · groups

	Neutron	X-ray
(6 ×) Te–O(Te)	1.947(10)	1.923(3)
(6 ×) O(Te)–H(3)	0.839(20)	
(6 ×) H(3)...O(E2)	1.861(19)	
(6 ×) Te–H(3)	2.355(17)	
(6 ×) O(Te)–O(E2)	2.675(12)	2.723(5)
(6 ×) O(Te)–O(Te)	2.760(12)	2.755(5)
(6 ×) O(Te)–O(Te)	2.745(10)	2.684(5)
(6 ×) Te–O(Te)–H(3)	108.8(1.2)	
O(Te)–H(3)...O(E2)	163.4(5.8)	
O(Te)–Te–O(Te)	90.3(3)	91.5(1)
	89.7(2)	88.5(1)

Structure description

Figure 1 is a projection of the atomic arrangement along *c*. The unique change arising in the atom positions and resulting from the new position of the $Te(OH)_6$ oxygen atom, is an octahedron rotation of 60°. One can note the layered nature of the molecular arrangement: the planes containing both $Te(OH)_6$ octahedra and P_3O_9 groups stack, parallel to (a, b) at $z \simeq 0$ and $z \simeq 0.5$. Rows of the $Te(OH)_6$ and P_3O_9 groups alternate in these planes, parallel to the $\vec{a}-\vec{b}$ vector according to the scheme $Te(OH)_6-P_3O_9-P_3O_9-Te(OH)_6$... Acid molecules and trimetaphosphate groups are joined by a plane network of hydrogen bonds, parallel to (a,b); the coordination polyhedra of sodium atoms make a second connection between these groups.

Discussion

$Te(OH)_6$ groups

As in all previously described addition compounds of telluric acid, $Te(OH)_6$ groups are almost regular octahedra. They are centrosymmetric. Their main characteristics including the hydrogen bonds are shown in Table 2; the bond distances and angles obtained from X-ray diffraction data are included. Lengths Te–O(Te) of 1.946 Å, are consistent with the distances derived from X-ray [keeping the modification of O(Te) coordinates in mind]; they are in good agreement with those found in telluric acid (Mullica et al., 1980, Lindqvist et al., 1973) from neutron diffraction [α-form: 1.98(1) and 1.81(1) Å; β-form: six values spread between 1.907(1) and 1.914(1) Å].

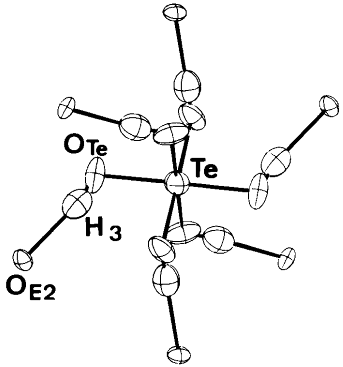

Fig. 2. Perspective representation of an acid molecule in $Te(OH)_6 \cdot 2Na_3P_3O_9 \cdot 6H_2O$

$Te(OH)_6$ octahedra share all their oxygen atoms with sodium polyhedra [Na(2)]; in addition the six identical hydrogen bonds are scattered in planes parallel to (a,b) together with the six P_3O_9 groups; according to the convention of Hamilton and Ibers (1968), the description of their hydrogen bond is (6,6) (see below N.B.).

The O(Te)....O(E2) length, 2.675(12), indicates an ordinary hydrogen bond but since this value is less than 2.7 Å it can be assumed to be a strong bond (Sokolov, 1965). When compared to telluric acid, the distances O(Te)–H are shorter [wide range, α-form: 0.90(2)–0.96(2) Å, β-form: 0.977(3)–0.990(3) Å] whereas H...O lengths are longer than those measured in the β-form [α: 1.65(2)–2.10(2) Å, β: 1.698(3)–1.750(3) Å]. The short O(Te)–H(3) distance can be related to the rather large Te–O(Te) distance (compared to β form of telluric acid for example); the latter distance is probably due to the electrostatic repulsion between the Te and H(3) cations. Therefore the O(Te)–Te bond is weak and thermal vibration of the O(Te) atom is anisotropic and large, normally to the O(Te)–Te bond direction. Figure 2 shows a $Te(OH)_6$ octahedron with the acceptor oxygen atoms O(E2).

N.B. – Hamilton and Ibers give a description for the hydrogen bondings with two numbers: N and M.

N = number of the hydrogen bonds originating from a given molecule X.

M = number of molecules hydrogen-bonded to X.

Table 3. Bond distances (Å) and angles (°) in the water molecules

H_2O(W1)	Neutron	X-ray
(2 ×) O(W1)–H(1)	0.957(15)	
(2 ×) H(1)...O(E2)	1.903(13)	
(2 ×) O(W1)–O(E2)	2.841(8)	2.804(3)
O(W1)–Na(1)	2.370(18)	2.398(5)
O(W1)–Na(2)	2.403(12)	2.377(5)
O(E2)–O(W1)–O(E2)	100.6(0.3)	
H(1)–O(W1)–H(1)	104.8(1.3)	
Na(1)–O(W1)–Na(2)	89.4(0.4)	
(2 ×)H(1)–O(W1)–Na(1)	121.9(1.3)	
(2 ×)H(1)–O(W1)–Na(2)	108.1(0.8)	
O(W1)–H(1)...O(E2)	166.0(3.7)	
H_2O(W2)	Neutron	X-ray
(2 ×) O(W2)–H(2)	0.979(14)	
(2 ×) H(2)–O(E2)	1.848(13)	
(2 ×) O(W2)–O(E2)	2.821(9)	2.838(4)
O(W2)–Na(1)	2.405(14)	2.367(5)
O(W2)–Na(2)	2.373(16)	2.424(5)
O(E2)–O(W2)–O(E2)	101.6(4)	
H(2)–O(W2)–H(2)	103.7(4)	
Na(1)–O(W2)–Na(2)	90.0(0.6)	
(2 ×) H(2)–O(W2)–Na(1)	118.5(0.9)	
(2 ×) H(2)–O(W2)–Na(2)	113.1(0.9)	
O(W2)–H(2)...O(E2)	172.1(5.3)	
H(1)–H(1)	1.517(15)	
H(2)–H(2)	1.539(17)	

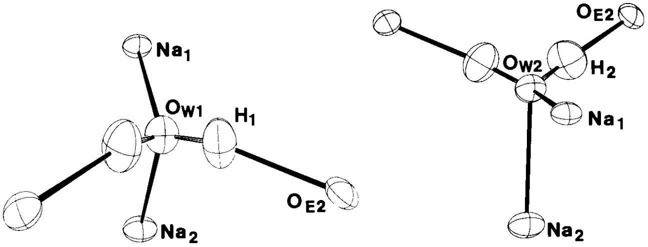

Fig. 3. View on the two water molecules. Acceptor oxygens and coordinated cations Na^+ are depicted. Angles between the water plane and O(W)–Na(1) and O(W)–Na(2) are respectively 30 and 60° for O(W1) and 40 and 50° for O(W2)

Water molecules

As observed in Figure 1, water planes are perpendicular to (a,b); according to the space group symmetry, they undergo a rotation of $\pi/3$ around the c axis, from one plane to another. Their main geometrical features obtained using neutrons and X-rays are shown in Table 3. They are comparable to those observed in water molecules, in crystalline hydrates (Chiari et al., 1982); the O(W1)–O(E2) and O(W2)–O(E2) distances indicate weaker hydrogen bonding.

The coordination of each atom O(W) is an irregular tetrahedron; as observed in Table 3, angles do not deviate much from the ideal value of 109.5° but they are closer to the values found in gas phases (in crystal hydrates, angles vary around 109°) (Chiari et al., 1982, Ferraris et al., 1972). Coordinated cations are approximatively along the two lone pair directions. In the classification of the hydrate water molecules based on the coordination of the lone-pair orbitals proposed by Chidambaram et al., (1964) and revised by Ferraris et al., (1972), these two molecules belong to the 2A class. Angles εi between the O(W)–Na$^+$ and the water plane [30 and 60° for O(W1) for Na(1) and Na(2) respectively and 40 and 50° for O(W2)] as well as the values of ε = Na(1)–O(W)–Na(2) (almost 90°) are consistent with the characteristics of class 2A (Ferraris et al., 1972) (on average $\varepsilon i \approx 50°$ and $\varepsilon \approx 90°$).

Conclusion

The water molecules of this hydrate salt have the same features as those met in other crystalline hydrates (though the standard deviations on angles are large). Otherwise, in spite of a few small differences due to the different number of bonds, the $Te(OH)_6$ group in this compound presents the same characteristics as those measured in telluric acid; this could explain the numerous addition compounds obtained with this acid (Boudjada et al., 1983, Tran Qui et al., 1984).

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