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The Crystal Structure of Dipotassium Tellurate(IV) Trihydrate, $K_2TeO_3.3H_2O$

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$K_2TeO_3.3H_2O$ crystallizes in space group *Pnma* with $a = 8{\cdot}895$ (6), $b = 6{\cdot}964$ (3), $c = 12{\cdot}385$ (7) Å, $Z = 4$. Refinement based on 1336 independent reflections gave a final R of 0·036. The TeO_3^{2-} anion has a pyramidal configuration with Te—O bond distances in the range 1·848–1·852 Å and O—Te—O angles close to 100°. Both potassium ions exhibit sixfold oxygen coordination (K—O: 2·684–2·983 Å).

Introduction

A number of tellurate(IV) structures have been studied in recent years and the literature has been reviewed by Johansson (1978). No structural information on tellurous acid, H_2TeO_3, is available. It is possible to precipitate tellurous acid, but the precipitate is unstable and loses water (Dutton & Cooper, 1966). Structures containing free TeO_3^{2-} ions also seem to be rather unstable. The reason for this is that the Te^{IV} free $5s^2$ electron pair is probably very easily polarized. Distortion of the free electron pair leads to rearrangements in the electron density of the pyramidal Te—O bonds in the TeO_3^{2-} ions. The free TeO_3^{2-} ion thus tends to form condensed tellurate(IV) groups, chains, layers or three-dimensional nets (Lindqvist & Johansson, 1976).

The Te^{IV}—O coordination polyhedra are usually also irregular in the condensed structures and often have one or two extra weak Te—O interactions in addition to three or four strong Te—O bonds (Zemann, 1971).

A detailed understanding of tellurate(IV) chemistry requires knowledge of accurate dimensions for the unpolarized TeO_3^{2-} ion, and we have therefore started structural investigations of ammonium and alkali-metal tellurates(IV).

Experimental

The crystals were prepared by melting equimolecular amounts of TeO_2 and K_2CO_3 in a platinum crucible under $CO_2(g)$. The mixture, which is very hygroscopic, was cooled in air, and after about 1 h it was possible to separate single crystals of $K_2TeO_3.3H_2O$ suitable for X-ray structure determination. The crystals are also hygroscopic, and dissolve rapidly if the relative humidity exceeds 40%. If $K_2TeO_3.3H_2O$ is allowed to dissolve in humid air, crystals of a new, more stable potassium tellurate(IV) are formed.

It was, however, possible by working in dry air to mount a crystal of $K_2TeO_3.3H_2O$ in a glass capillary. Cell dimensions and intensity data were obtained from measurements on a Syntex $P2_1$ diffractometer. Crystallographic and experimental data are listed in Table 1.

The reflections were measured in 96 steps and the intensities were evaluated from a profile analysis according to the Lehmann & Larsen (1974) method using the program *LELA* (Lindqvist & Ljungström, 1978). The intensities were corrected for Lorentz and polarization effects with a local program (*SYN*) and the absorption correction was carried out with the program *DATAPH* (Coppens, Leiserowitz & Rabinovich, 1965, as modified by W. C. Hamilton).

Table 1. *Experimental data*

(*a*) Physical and crystallographic data

Formula:	$K_2TeO_3.3H_2O$	a	= 8·895 (6) Å
M_r:	307·86	b	= 6·964 (3)
Space group:	*Pnma*	c	= 12·385 (7)
Absorption coefficient	$25{\cdot}12\ cm^{-1}$	V	= 767·2 (4) $Å^3$
(Mo $K\alpha$):		Z	= 4
D_c:	$2{\cdot}515\ g\ cm^{-3}$	$F(000)$	= 196
Crystals:	Hygroscopic, colourless parallelepipeds		

(*b*) Data collection

Crystal dimensions:	0·10 × 0·10 × 0·30 mm
Radiation:	λ(Mo $K\alpha$) = 0·71069 Å
Monochromator:	Graphite crystal
Scan mode:	$\omega/2\theta$
Maximum 2θ angle:	60·0°
Scan interval ($\Delta\omega$):	1·0–1·2°
Scan speed (in ω):	$1{\cdot}0$–$6{\cdot}0°\ min^{-1}$
Standard reflection:	(011) in intervals of 25 reflections, 10 500 ± 200 counts, stable
Recorded reflections:	2290
Independent reflections:	1336
Significant reflections	832 $[I/\sigma(I) > 3{\cdot}0]$
Cell refinement:	15 reflections with $5{\cdot}6 < 2\theta < 26{\cdot}3°$

Determination of the structure

The intensity data had systematic extinctions for $0kl$: $k + l = 2n + 1$ and $hk0$: $h = 2n + 1$, indicating the space group to be either $Pn2_1a$ or $Pnma$. Patterson and electron-density calculations showed that the structure belonged to $Pnma$ with all Te and K atoms and $\frac{1}{3}$ of the O atoms occupying special positions on the mirror planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$ (Table 2).

Initially refinement was carried out with the program *BLOCK* (Lindgren, 1977), and an R of 0·056 was obtained for a structural model with isotropic temperature factors. The final cycles of refinement were performed with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970), including anisotropic temperature factors and an isotropic extinction parameter. The final R was 0·036 and the corresponding parameters are listed in Table 2.* The scattering factors for Te (Cromer & Waber, 1965), K and O (Doyle & Turner, 1968) were corrected for the real part of the anomalous scattering (Cromer, 1965). The observations were weighted according to the formula: $w = (20·0 + F_o + 0·004F_o^2)^{-1}$ (Cruickshank, 1970), and the corresponding weight analysis is shown in Table 3.

Table 2. *Final atomic coordinates in* $K_2TeO_3.3H_2O$

Estimated standard deviations are in parentheses. W denotes the oxygen atom in a water molecule.

	x	y	z
Te	−0·00566 (7)	$\frac{1}{4}$	0·21899 (5)
K(1)	0·4893 (2)	$\frac{1}{4}$	−0·0974 (2)
K(2)	0·0519 (2)	$\frac{1}{4}$	−0·0728 (2)
O(1)	0·3564 (9)	$\frac{1}{4}$	0·3926 (7)
O(2)	0·1081 (6)	0·0427 (8)	0·1731 (5)
$W(1)$	0·3033 (6)	0·0067 (9)	0·0046 (4)
$W(2)$	0·2702 (9)	$\frac{3}{4}$	0·2501 (7)

Table 3. *Weight analysis after the last cycle of refinement*

N is the number of reflections in the F_o-interval and $w\Delta^2$ are normalized sums.

F_o-interval	N	$w\Delta^2$	F_o-interval	N	$w\Delta^2$
0·0–15·4	92	2·78	35·8–44·4	83	0·40
15·4–19·7	88	1·90	44·4–54·2	85	0·39
19·7–24·9	82	1·02	54·2–66·1	79	0·33
24·9–29·6	82	1·06	66·1–88·3	77	0·43
29·6–35·8	83	0·39	88·3–297·4	81	1·00

Discussion

$K_2TeO_3.3H_2O$ is a purely ionic compound built up from K^+ and TeO_3^{2-} ions and H_2O molecules. The potassium–oxygen interactions are shown in Table 4, and both K(1) and K(2) are seen to have distorted octahedral coordination. The dimensions of the TeO_3^{2-} ion are compared with those of SO_3^{2-} and SeO_3^{2-} in Table 5.

K(1) only coordinates water oxygen atoms, while K(2) interacts both with water molecules and with two TeO_3^{2-} ions (see Fig. 1). The mean K–O coordination distances are 2·806 and 2·837 Å for K(1) and K(2)

Table 4. *Distances* (Å) *and angles* (°) *within the potassium coordination polyhedra and oxygen–oxygen contacts*

(W denotes the oxygen atom in a water molecule.)

K(1)–W(1) ×2	2·684 (6)	K(2)–W(2)	2·705 (8)
K(1)–W(1) ×2	2·814 (6)	K(2)–O(2) ×2	2·779 (6)
K(1)–W(2)	2·856 (8)	K(2)–O(1)	2·830 (9)
K(1)–W(2)	2·983 (8)	K(2)–W(1) ×2	2·965 (6)
W(1)–K(1)–W(1)	127·8 (1) ×2	O(1)–K(2)–O(2)	92·2 (2) ×2
W(1)–K(1)–W(1)	79·1 (2) ×2	O(1)–K(1)–W(1)	102·0 (2) ×2
W(1)–K(1)–W(1)	78·3 (3)	O(1)–K(2)–W(2)	177·9 (3)
W(1)–K(1)–W(2)	140·7 (1) ×2	O(2)–K(2)–O(2)	94·4 (3)
W(1)–K(1)–W(2)	79·7 (2) ×2	O(2)–K(2)–W(1)	161·8 (2) ×2
W(1)–K(1)–W(1)	78·9 (2)	O(2)–K(2)–W(1)	96·4 (2) ×2
W(1)–K(1)–W(2)	77·2 (2) ×2	O(2)–K(2)–W(2)	86·4 (2) ×2
W(1)–K(1)–W(2)	140·0 (1) ×2	W(1)–K(2)–W(1)	69·7 (2)
W(2)–K(1)–W(2)	99·2 (1)	W(1)–K(2)–W(2)	79·7 (2) ×2

Table 5. *Distances* (Å) *and angles* (°) *for* Te–O *in* $BaTeO_3.H_2O$, $Cu(NH_3)TeO_3.H_2O$ *and* $K_2TeO_3.3H_2O$, *and for* S–O *and* Se–O *in* Na_2SO_3 *and* $CuSeO_3.2H_2O$

$Cu(NH_3)TeO_3.H_2O$[a]		$BaTeO_3.H_2O$[b]	
Te–O(2)	1·870 (7)	Te–O(1)	1·858 (6)
Te–O(3)	1·877 (7)	Te–O(2)	1·847 (7)
Te–O(1)	1·885 (8)	Te–O(3)	1·859 (6)
Te–O(3′)	2·950 (7)	Te–O(4)	3·035 (7)
Te–O(3″)	3·082 (7)	Te–O(5)	3·332 (9)
Te–O(1′)	3·236 (9)		
O(1)–Te–O(2)	96·1 (4)	O(1)–Te–O(2)	98·8 (3)
O(1)–Te–O(3)	94·7 (3)	O(1)–Te–O(3)	96·5 (3)
O(2)–Te–O(3)	97·6 (3)	O(2)–Te–O(3)	102·7 (3)
$K_2TeO_3.3H_2O$		Na_2SO_3[c]	
Te–O(1)	1·848 (8)	S–O	1·504 (3) ×3
Te–O(2)	1·852 (6) ×2	O–S–O	105·69 (17)
Te–O(1)	3·872 (8)		
Te–O(2)	3·959 (6) ×2	$CuSeO_3.2H_2O$[d]	
O(1)–Te–O(2)	97·7 (3)	Se–O(1)	1·77 (5)
O(1)–Te–O(2)	97·7 (3)	Se–O(2)	1·78 (5)
O(2)–Te–O(2)	102·4 (4)	Se–O(3)	1·72 (5)
		O(1)–Se–O(2)	98·5
		O(1)–Se–O(3)	103·5
		O(2)–Se–O(3)	96·0

(*a*) Johansson & Lindqvist (1977).
(*b*) Nielsen, Hazell & Rasmussen (1971).
(*c*) Larsson & Kierkegaard (1969).
(*d*) Gattow (1958).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33617 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

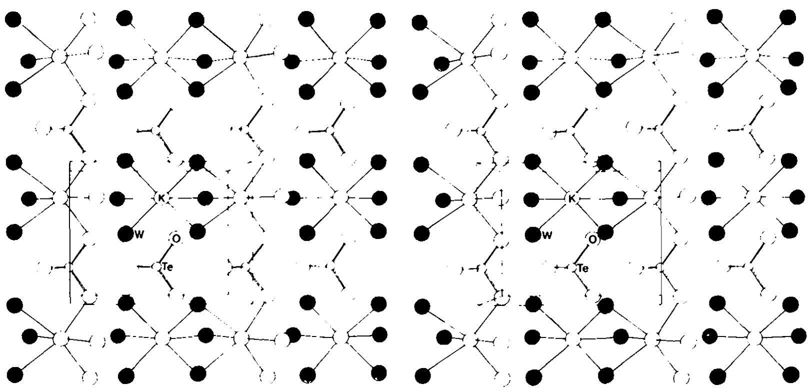

Fig. 1. A stereoscopic picture of the structure projected along the *c* axis (*ORTEP*; Johnson, 1965). *W* denotes the oxygen atom in a water molecule.

Table 6. *Hydrogen bonding in* $K_2TeO_3.3H_2O$

O(1)–*W*(1)	2·671 (8) Å ×2	O(2)–*W*(2)	2·673 (8) Å
O(2)–*W*(1)	2·726 (8)	O(2)–*W*(1)–O(2)	99·4 (4)°
O(1)–*W*(1)–O(2)	96·9 (3)°		

respectively, which are in good agreement with the values 2·72–2·91 (8) Å given in *International Tables for X-ray Crystallography* (1962) for sixfold coordination.

In addition to electrostatic forces, the structure is held together by rather strong hydrogen bonds (see Fig. 1 and Table 6).

The TeO_3^{2-} ion in $K_2TeO_3.3H_2O$ is pyramidal. Previously, isolated TeO_3^{2-} ions have only been found in $BaTeO_3.H_2O$ (Nielsen, Hazell & Rasmussen, 1971) and in $Cu(NH_3)TeO_3.H_2O$ (Johansson & Lindqvist, 1977), and the dimensions are compared in Table 5.

The mean values found in $K_2TeO_3.3H_2O$ for the Te—O bond and the O—Te—O angles, 1·851 (4) Å and 99·3 (2)° respectively, are to be considered representative for an unpolarized TeO_3^{2-} ion. This statement is supported by the fact that there is no 'backbonding', *i.e.* interactions between oxygen atoms and the Te^{IV} free electron pair, in $K_2TeO_3.3H_2O$. The free space on the 'rear-side' of Te^{IV} is astonishingly large with no contact shorter than 3·87 Å. In the case of both $BaTeO_3.H_2O$ and $Cu(NH_3)TeO_3.H_2O$ weak 'backbonding' with Te—O distances of about 3 Å may be considered to occur. The unsymmetrical octahedral oxygen coordination in $Cu(NH_3)TeO_3.H_2O$, with three strong interactions on one side and three very weak on the other side of the Te^{IV} atom, has also been compared with similar geometries in Te^{IV} halogen compounds (Johansson & Lindqvist, 1976). The Te^{IV}—O distances of about 3 Å correspond undoubtedly to weak interatomic interactions (Lindqvist & Moret, 1973; Brown, 1974).

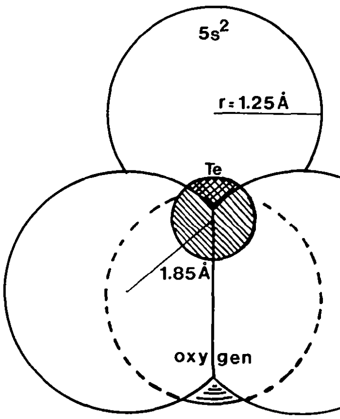

Fig. 2. The TeO_3^{2-} ion indicating the estimated radius of the $5s^2$ free electron pair.

The present results for $K_2TeO_3.3H_2O$ provide new information concerning the action range of the Te^{IV} $5s^2$ free electron pair. Galy, Meunier, Andersson & Åström (1975) have demonstrated that in condensed tellurates(IV) the Te^{IV} free electron pair has, on average, a volume corresponding to that of an oxygen atom. However, condensed tellurates(IV) always exhibit interactions between the Te^{IV} free electron pair and neighbouring oxygen atoms; and the spatial distribution of the free electron-pair density is probably not spherical. In $K_2TeO_3.3H_2O$, on the other hand, there is enough space for a spherical distribution corresponding to a radius of ~1·25 Å (assuming a van der Waals radius for O of 1·4 Å; Pauling, 1952). This radius for the free $5s^2$ electron pair (Fig. 2) may be used in an approximation of the unpolarized TeO_3^{2-} ion.

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Quantifying the Concept of Coordination Number

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Mathematical requirements necessary for the quantification of coordination numbers of irregular coordination polyhedra are listed. A general mathematical formula is given and applied to the case of the CsCl structure using the concept of the polyhedral atomic volume. As a function of the atomic radii difference, the coordination number in this structure varies smoothly from 8 to 14 to 6. The partial coordination numbers of 8 and 6, corresponding to first and second nearest neighbors, are also functionally related to the generalized coordination number.

The determination of the coordination number (CN) of an atom in a structure or molecule is clearly recognized as an important first step in the characterization of that atom's contribution to the bulk material properties. The host of interdependent chemical and physical properties that are known to be CN dependent for various elements include size or radius, atomic valence, bond characteristics (including type, hybridization, ionicity, strength and energy), radical or species stability and reactivity, phonon and electronic spectra, as well as electrical and magnetic properties (Pauling, 1960; Goodenough, 1963). In particular, we note that Templeton (1953, 1955) has developed a simple formula for obtaining a good estimate of the Madelung constant given only the coordination numbers and the stoichiometry. In light of the above, it is not surprising that the set of coordination numbers for a substance constitute some of the principal data sought and reported in structure determinations, whether the material of interest be gaseous (Herzberg, 1960–1966), liquid (Smith, 1964), crystalline (Frank & Kasper, 1958), or amorphous [insulating (Konnert & Karle, 1973), semi-conducting (Renninger & Averbach, 1973), or metallic (Gilman, 1975)].

While the coordination number or ligancy of a central atom is often readily obtained by enumerating the number of neighbors bonded to the central atom, there are numerous cases where the criteria for the enumeration process are indistinct. Consider, for example, the first, second, and third 'shells' of ligands and solvent molecules enclosing transition-metal ions in

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