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The Crystal Structure of Sodium Metatellurate

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Single crystals of Na_2TeO_4 were prepared from the $NaNO_3$ melt. The symmetry corresponds to *Pbcn* with $a = 5{\cdot}798$ (6), $b = 12{\cdot}24$ (1), $c = 5{\cdot}214$ (5) Å, $Z = 4$. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. The final R of 0·071 is based on 230 independent intensities. The structure consists of TeO_6 octahedra sharing edges and forming infinite chains, similar to those in $KTeO_3(OH)$. The chains are held together by the Na^+ ions. The Te–O distances range from 1·85 (2) to 2·04 (2) Å and O–O from 2·50 (3) to 2·89 (3) Å. Both Na^+ ions are surrounded by O atoms in an approximately octahedral arrangement, with Na–O from 2·21 (2) to 2·70 (2) Å.

Introduction

The $HTeO_4^-$ and TeO_4^{2-} ions are formed by gradual dissociation of metatelluric acid, H_2TeO_4. The structure of H_2TeO_4 (Moret, Phillipot, Maurin & Lindqvist, 1974) involves infinite sheets of TeO_6 octahedra connected through four corners. The sheets are held together by hydrogen bonds. Structural information on the second phase of H_2TeO_4 (Glemser, Mya-Tha & Schwarzmann, 1966) is lacking.

A representative of compounds with the $HTeO_4^-$ anion is $KTeO_3(OH)$. The determination (Lammers, 1964) and redetermination (Lindqvist, 1972) of its structure have shown that the compound contains infinite chains built up by edge-sharing TeO_6 octahedra. The chains are held together by K^+ ions and by strong hydrogen bonds.

Structural data on compounds of the M_2TeO_4 (M = alkali metal) type are incomplete. There are some indications of tetrahedral Te coordination in K_2TeO_4 (Patry, 1936) and in Rb_2TeO_4 and Cs_2TeO_4 (Tarte & Leyder, 1971) from powder patterns and infrared spectra. A structure of the inverse spinel type with Te atoms in octahedral holes was suggested for Li_2TeO_4 (Tarte & Preudhomme, 1971). The lattice parameters of Li_2TeO_4 were refined from powder data (Norbert, Cachau-Herreillat, Moret & Maurin, 1973). Tetrahedral TeO_4 was assumed to exist in Na_2TeO_4 (Jung & Triftshäuser, 1968), but X-ray powder patterns and infrared spectra exclude this, and suggest a linear polymeric anion, similar to that in $KTeO_3(OH)$ (Erickson & Maddock, 1970).

Experimental

Single crystals of Na_2TeO_4 were prepared by dehydrating $Na_2H_4TeO_6$, mixing the product with $NaNO_3$ (in a weight ratio of 1:20) and heating to 330°C, followed by slow cooling to room temperature (over approximately two days). The colourless needles of Na_2TeO_4, elongated along [001], were separated by dissolving the $NaNO_3$ in water. The Na_2TeO_4 crystals are rehydrated to $Na_3H_5Te_2O_{10}$ in air within one month and in water in a few days (Kratochvíl, 1972). Preliminary cell dimensions and space group were determined from Weissenberg photographs. These cell dimensions were refined by least squares from calibrated powder diffractometer data with *MPEX* (Weiss, 1974). The density was measured pycnometrically. The linear absorption coefficient was calculated from the values given in *International Tables for X-ray Crystallography* (1962). The crystal data are summarized in Table 1.

Table 1. *Crystal data of* Na_2TeO_4

$a = 5{\cdot}798$ (6) Å
$b = 12{\cdot}24$ (1)
$c = 5{\cdot}214$ (5)
$V = 370{\cdot}0$ Å^3
$Z = 4$

$D_m = 4{\cdot}28$ g cm^{-3}
$D_x = 4{\cdot}26$
Space group *Pbcn*
μ(Cu $K\alpha$) = 682·9 cm^{-1}

Single crystals with dimensions from 0·1 to 0·3 mm were used for collecting the intensities. To prevent rehydration, the crystals were coated with a thin layer of plexiglass. The intensities were recorded on films from the $0kl$–$3kl$, $h0l$–$h4l$ and $hk0$–$hk4$ layers by the Weissenberg method with Cu $K\alpha$ radiation. Corrections were made for Lorentz and polarization effects, absorption and the split α_2–α_2 doublet with *KOREKCE* (Podlahová, Kratochvil & Loub, 1975).

Structure determination and refinement

The coordinates of the Te and Na atoms were deduced from Patterson maps. After two Fourier syntheses, the positions of both O atoms were determined.

The scale factors were refined by full-matrix least squares leading to $R = 0{\cdot}218$. The coordinates and isotropic temperature factors were then refined with the constant scale factors. The determination of the structure was completed by refining anisotropic temperature factors. Values of $R = \Sigma|F_o - |F_c||/\Sigma F_o = 0{\cdot}071$ and $R_w = (\Sigma w|F_o - |F_c||^2/\Sigma wF_o)^{1/2} = 0{\cdot}098$ were obtained for 230 independent non-zero reflexions.* The parameters were refined by minimizing $\Sigma w(F_o - |F_c|)^2$ with a Cruickshank weight $w = \sqrt{[1/(a + F_o + cF_o^2)]}$, with $a = 50$ and $c = 1000$. The scattering factors were those of Cromer & Waber (1965) for Te, Na^+ and O. The final positional parameters are given in Table 2.

The Patterson and Fourier summations were performed with *TSLPATT* and *TLSFOUR* (Sklenář, 1974). A local version of the Busing, Martin & Levy (1962) *ORFLS* was employed for all refinements. Interatomic distances and angles were computed with *VZDAL* and *UHEL* (Podlahová, Kratochvíl & Loub, 1975) and are listed in Table 3. All computations were carried out on Tesla 200 and Hewlett-Packard 9830A computers.

Table 2. *Fractional coordinates*

The e.s.d.'s are given in parentheses.

	x	y	z
Te	$\frac{1}{2}$	0·4284 (1)	$\frac{3}{4}$
Na(1)	$\frac{1}{2}$	0·7297 (14)	$\frac{3}{4}$
Na(2)	$\frac{1}{2}$	0·1374 (12)	$\frac{3}{4}$
O(1)	0·3246 (32)	0·5509 (17)	0·5707 (43)
O(2)	0·2977 (39)	0·3268 (15)	0·6144 (47)

Table 3. *Interatomic distances and angles*

The values were not corrected for thermal motion. The notation is in accordance with Fig. 1.

Te–Te^{i}	3·142 (2) Å	O(1^{i})–Te–O(1^{ii}) O(1)–Te–O(1^{iii})	92·9 (9)°
Te–O(1) Te–O(1^{ii})	2·04 (2)	O(1)–Te–O(1^{i}) O(1^{ii})–Te–O(1^{iii})	76·9 (7)
Te–O(1^{i}) Te–O(1^{iii})	1·97 (2)	O(1^{i})–Te–O(2^{i}) O(1^{iii})–Te–O(2)	94·9 (9)
Te–O(2) Te–O(2^{i})	1·85 (2)	O(1^{i})–Te–O(2) O(1^{iii})–Te–O(2^{i})	95·0 (9)
O(1)–O(1^{i}) O(1^{ii})–O(1^{iii})	2·50 (3)	O(1)–Te–O(2) O(1^{ii})–Te–O(2^{i})	90·2 (8)
O(1)–O(1^{iii}) O(1^{ii})–O(1^{i})	2·89 (3)	O(1)–Te–O(1^{ii})	85·1 (7)
O(1)–O(2) O(1^{ii})–O(2^{i})	2·75 (3)	O(2)–Te–O(2^{i})	95·6 (9)
O(1^{i})–O(2^{i}) O(1^{iii})–O(2)	2·81 (3)	O(1^{ii})–Te–O(2) O(1)–Te–O(2^{i})	170 (1)
O(1^{iii})–O(2^{i}) O(1^{i})–O(2)	2·82 (3)	O(1^{i})–Te–O(1^{iii})	165 (1)
O(1)–O(1^{ii})	2·76 (3)		
O(2)–O(2^{i})	2·74 (3)		

Discussion

The structure provides clear evidence for the octahedral coordination of Te by O atoms. The compound contains infinite chains of $[TeO_4]_n^{2n-}$ built up by sharing the edges of neighbouring Te–O octahedra, thus resembling $KTeO_3(OH)$. The chains are held together by Na^+ ions. The structure is illustrated in Fig. 1. This Te–O arrangement represents a manner of condensation of octahedral oxo-anions so far unknown.

The Te–O lengths range from 1·85 (2) to 2·04 (2) Å. The terminal Te–O bonds are shorter than the bridge bonds, in agreement with other tellurates (Lindqvist, 1974). Both Na^+ ions have six O neighbours with Na–O ranging from 2·21 (2) to 2·70 (2) Å. The distances were not corrected for thermal motion in view of the high stability. There is

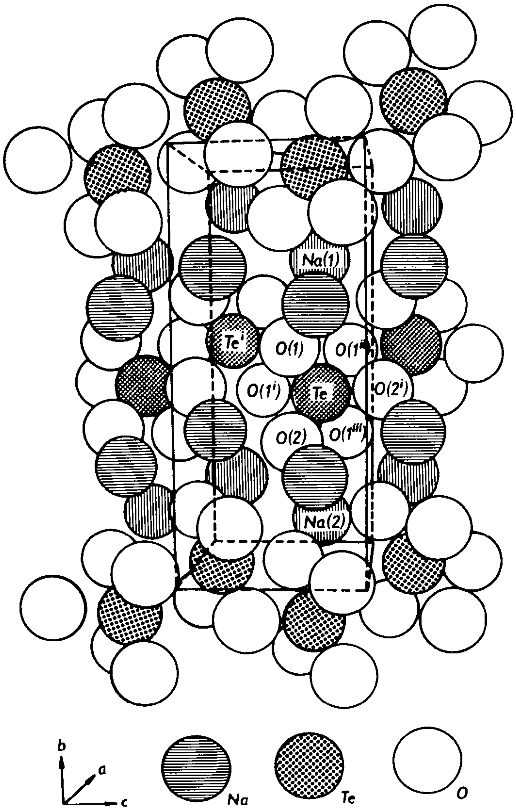

Fig. 1. A schematic picture of the structure of Na_2TeO_4.

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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 32529 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

almost no difference in the bond distances and angles in the Te—O octahedra in Na_2TeO_4 compared with those reported for $KTeO_3(OH)$, in spite of the different charge and the presence of strong hydrogen bonds in the latter.

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The Crystal Structures of Free Radical Salts and Complexes.
XI. The Crystal Structure and Electrical Properties of [1,2-Di(*N*-methyl-4-pyridinium)ethane]$^{2+}$(7,7,8,8-Tetracyanoquinodimethane)$_4^{2-}$

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The structure and electrical conductivity are reported for [1,2-di(*N*-methyl-4-pyridinium)ethane]$^{2+}$(7,7,8,8-tetracyanoquinodimethane)$_4^{2-}$, (DMPA)$^{2+}$(TCNQ)$_4^{2-}$. The complex is triclinic, space group $P\bar{1}$ with a = 7·6728, b = 13·4610, c = 12·9636 Å, α = 101·059, β = 91·159, γ = 90·402°, Z = 1. The structure was solved by the Patterson method and refined to R = 0·074 for 1245 reflexions. The TCNQ's are stacked plane-to-plane in isolated groups of four, each group consisting of a pair of dimers with mean interplanar spacings of 3·20 Å within each dimer and 3·39 Å between dimers.

Introduction

The radical anion salts of TCNQ are of considerable interest as electronic materials; several exhibit metallic behaviour. However, in these one-dimensional systems the metallic state is unstable and lattice distortions result in the occurrence of insulating behaviour at low temperatures. In two complexes, HMTSF(TCNQ) (Bloch, Cowan, Bechgaard, Pyle, Banks & Poehler, 1975) and (DEPE)$^{2+}$(TCNQ)$_4^{2-}$ I (Ashwell, Eley & Willis, 1976), the insulating state is suppressed and metallic conductivities have been observed for $T < 1$ K. (DEPE)$^{2+}$(TCNQ)$_4^{2-}$ I also exhibits Pauli paramagnetism (Ashwell, Eley, Willis & Woodward, 1977; Craik, 1976) and a temperature-independent thermoelectric power of -35 μV K^{-1} (Ashwell, Eley & Willis, 1976), characteristic of an organic metal. (DEPE)$^{2+}$-

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