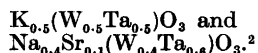


Bronze-Type Structure of KNb₂O₅F and KTa₂O₅F

ARNE MAGNÉLI and STINA NORD

*Institute of Inorganic and Physical Chemistry,
University of Stockholm, Stockholm, Sweden*

The structural type of tetragonal potassium wolfram bronze¹ has been found to be present in several oxide compounds of transition metals of the general formula A_xTrO_3 (A is a mono- or divalent metal, Tr is a transition metal, $x \leq 0.6$). The structure is characterized by a framework of TrO_6 octahedra joined by corners in such a way as to enclose linear arrangements of voids. The latter, which are the sites of the A atoms, are of two kinds *viz.* either with a cage-like environment analogous to that of the A atoms in a perovskite structure, or in fivesided tunnels composed of oxygen atoms. The tetragonal framework which has a constant composition of TrO_3 is often deformed to adopt a lower symmetry or a superstructure. It is otherwise quite resistant towards chemical changes, as is evident from the ready substitution of A as well as of Tr atoms leading to phases such as

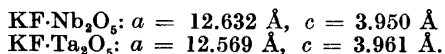


The present investigation was undertaken in order to find out if the non-metal part of the framework can be correspondingly changed by substitution, *viz.* by partially replacing oxygen by fluorine. In order to maintain electroneutrality pentavalent niobium or tantalum could then be substituted for hexavalent wolfram.

The starting materials for the syntheses were potassium fluoride, niobium pentoxide and tantalum pentoxide, all of reagent grade. Stoichiometric amounts of fluoride and oxide in 1:1 proportion were intimately mixed and pressed into pellets which were sealed in thin evacuated platinum tubes and heated for 24 h at 900°C. The products thus obtained formed white crystalline powders.

X-Ray powder photographs were taken in a Guinier camera with $CuK\alpha_1$ radiation and with potassium chloride added to the specimens as an internal standard. The patterns thus obtained were those required by phases of the tetragonal potassium

wolfram bronze type with the unit-cell dimensions:



The densities determined from the loss of weight in benzene are in concordance with a cell content of five formula units of $KF \cdot Nb_2O_5$ ($d_{obs} = 4.25$, $d_{calc} = 4.28 \text{ g/cm}^3$) and $KF \cdot Ta_2O_5$ ($d_{obs} = 6.6$, $d_{calc} = 6.66 \text{ g/cm}^3$).

The powder patterns gave no evidence of deviations from the tetragonal symmetry or of a superstructure. Previous experience, however, has shown that such superstructure reflections may be very weak and are preferentially looked for in single-crystal photographs.³

Further studies on bronze-type structures are in progress.

This investigation was carried out within a research program supported by the *Swedish Natural Science Research Council*.

1. Magnéli, A. *Arkiv Kemi* 1 (1949) 213.
2. Galasso, F., Katz, L. and Ward, R. *J. Am. Chem. Soc.* 81 (1959) 5898.
3. Magnéli, A. *Arkiv Kemi* 1 (1949) 269.

Received July 16, 1965.

On the Crystal Structure of a Potassium Tellurate

OLIVER LINDQVIST and
FREDRIK WENGELIN

*Department of Inorganic Chemistry, Chalmers
University of Technology and the University
of Gothenburg, Gibraltargatan 5 A,
Göteborg S, Sweden*

As the first member in a newly begun series of crystal structure determinations of tellurates, the structure of $K_4H_4Te_2O_{10}(H_2O)_x$, where x is probably 6, has been investigated, and a preliminary report is given in this note.

Weissenberg photographs corresponding to the reflections $h0l-h4l$ and $hk0-hk1l$ have been recorded, using $CuK\alpha$ radiation. From the reflections obtained, the space group was presumed to be either $C2/c$

(No. 15) or *Cc* (No. 9).¹ The cell dimensions, calculated from the Weissenberg photographs, were $a = 15.3 \text{ \AA}$, $b = 6.9 \text{ \AA}$, $c = 18.2 \text{ \AA}$ and $\beta = 116^\circ$. The volume of the unit cell is thus $1.7_3 \times 10^3 \text{ \AA}^3$ corresponding to a cell content of four formula units and a calculated density of 2.6_3 g/cm^3 .

Hitherto the $hk0$ and $h0l-h4l$ data have been used in the structure determination. The coordinates of the tellurium atoms were deduced from Patterson projections calculated with the Fourier program written by Larsson.² It was found that the tellurium atoms occupy one eight-fold position $8(f)$ in *C2/c* with $x = 0.090$, $y = 0.079$ and $z = 0.079$.

Successive Fourier summations were then performed using the above mentioned Fourier program.² The potassium atoms were found to occupy two positions $8(f)$ in *C2/c*, and eight different positions $8(f)$ were found for the oxygen atoms. A four-fold oxygen position $4(c)$ with $x = 0.000$, $y = 0.267$ and $z = 0.250$ was also indicated in some of the Fourier summations, but in order to ascertain if this is a true position or a peak due to anomalous diffraction effects more extensive data will have to be considered.

A least-squares refinement based on $h0l-h4l$ data was performed using the program of Åsbrink and Brändén.³ After four cycles of refinement the R value dropped from 0.218 to 0.142. The parameters obtained after the fourth cycle are given in Table 1.

Table 1. Preliminary atomic parameters in the structure of $K_4H_4Te_2O_{10}(H_2O)_x$ ($x \approx 6$). (All atoms occupy positions $8(f)$ in *C2/c*).

	x	y	z	B (in \AA^2)
Te	0.086	0.080	0.078	1.34
K ₁	0.155	0.155	0.407	2.27
K ₂	0.495	0.123	0.349	2.10
O ₁	0.109	0.052	0.187	2.80
O ₂	0.193	0.231	0.092	2.07
O ₃	0.465	0.423	0.044	1.45
O ₄	0.007	0.313	0.066	1.90
O ₅	0.348	0.335	0.426	2.08
O ₆	0.296	0.061	0.310	3.57
O ₇	0.382	0.310	0.195	2.49
O ₈	0.311	0.033	0.032	1.94

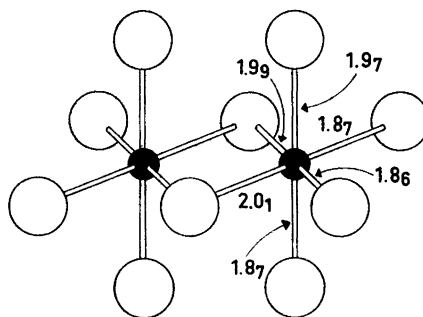


Fig. 1. The Te—O bonds in the anion $[\text{Te}_2\text{O}_6(\text{OH})_4]^{4-}$.

The tellurium atoms are octahedrally coordinated by oxygen, two such octahedra sharing a common edge to form a dimeric tellurate ion (Fig. 1). The Te—Te distance in these anions was found to be 3.1_0 \AA . The average Te—O distance is 1.9_3 \AA , which is in good agreement with the Te—O distances found by Raman in his determination of the structure of $\text{KTeO}(\text{OH})_5\text{H}_2\text{O}$.⁴

A complete three-dimensional refinement is under progress, and a detailed presentation of the structure of $\text{K}_4\text{H}_4\text{Te}_2\text{O}_{10}(\text{H}_2\text{O})_x$ will soon be published in *Acta Chem. Scand.*

The authors wish to thank the National Swedish Office for Administrative Rationalisation and Economy (earlier Swedish National Board for Computing Machinery) for making it possible for them to use the FACIT EDB computer in Stockholm and the SAAB D21 computer at the Crystallographic Group at the Department of Medical Biochemistry, the University of Gothenburg. Thanks are also due to the Swedish Natural Science Research Council for financial aid.

1. *International Tables for X-ray Crystallography*, 2nd. Ed., The Kynoch Press, Birmingham, England 1952.
2. Larson, K. *Arkiv Kemi* **23** (1964) 17.
3. *IUCr World List of Crystallographic Computer Program*, 1st Ed., program 6023 (1962).
4. Raman, S. *Inorg. Chem.* **3** (1964) 634.

Received July 16, 1965.