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Extended Mo–Nb Bonds in $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$—A Molybdenum Bronze with the Tetragonal (I) Tungsten Bronze Structure

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$K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ crystallizes in the tetragonal system, space group *P*4/*mbm*. The unit cell dimensions are $a = 12.5591(9)$ Å, $c = 3.976(1)$ Å, $V = 627.2(2)$ Å^3, and $Z = 1$. The structure was refined to $R = 0.021$, $R_w = 0.032$, with 321 observed reflections ($I > 3\,\sigma(I)$) and 51 variable parameters. The structure of $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ is of the tetragonal (I) tungsten bronze type with Nb partially occupying the trigonal interstitial sites forming infinite zigzag chains of Nb–Mo bonds along the crystallographic *c*-axis.

Introduction

For over a century, the term "bronze" has been used to describe the intense color, metallic luster, and metallic or semiconducting properties of a variety of transition metal oxides. These oxides are usually ternary compounds of the type $A_xM_yO_z$, where *M* is Ti, V, Mn, Nb, Ta, Mo, W, or Re and *A* is H, NH_4+, alkali, alkaline earth, rare earth, group 11, group 12, or other metal ions. The alkali metal tungsten bronzes, A_xWO_3, were studied most extensively and have been reviewed in the past (*1–4*). Extensive reviews of ternary bronzes were also presented by Banks and Wold (*1*) and Hagenmuller (*2*) nearly 20 years ago. Interest in all types of transition metal oxide bronzes has continued in recent years. However, in the past decade most of the interest has been focused on the study of molybdenum bronzes, especially on the "blue bronzes" $A_{0.3}MoO_3$ (A = K, Rb, Tl), due to their unique structural and physical properties. A brief review of the molybdenum bronzes (results up to ca. 1980) was given in a chapter of lower valence molybdenum oxides (*5*). A recent review of molybdenum bronzes with quasi-low-dimensional properties updates some of these results (*6*). A comprehensive review of molybdenum bronzes and oxides with quasi-low-dimensional properties was recently given in a book edited by Schlenker (*7*).

Molybdenum bronzes may be classified on the basis of their color, stoichiometry, and structure as the blue bronzes, $A_{0.3}MoO_3$ with A = K, Rb, and Tl; the red bronzes, $A_{0.33}MoO_3$ with A = Li, Na, K, Rb, Cs, and Tl; and the purple bronzes, $A_{0.9}Mo_6O_{17}$ with A = Li, Na, K, and Tl. The recently prepared rare-earth molybdenum bronzes, $A_{0.08}MoO_3$ (A = La, Ce, Eu, Gd, or Lu), are another class in this system (*8*). The blue bronze of $Cs_{0.25}MoO_3$ is unique both in stoichiometry and in structure (*9*). A purple bronze of $La_2Mo_2O_7$ was discovered by McCarroll *et al.* in a fused-salt electrolysis (*10*).

A relatively new class of compounds are the hydrogen molybdenum bronzes, H_xMoO_3 ($0 < x \leq 2.0$), in which the hydrogen atoms are topotactically inserted

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into the MoO_3 matrix to yield four unique phases: $H_{0.23-0.40}MoO_3$, blue, orthorhombic; $H_{0.85-1.04}MoO_3$, blue, monoclinic; $H_{1.55-1.72}MoO_3$, red, monoclinic; and H_2MoO_3, green, monoclinic (*11,12*). $K_{0.89-0.93}MoO_3$, $K_{0.5}MoO_3$, and $Rb_{0.27}MoO_3$ synthesized at high pressure have not been well characterized yet, but are known to be isostructural with their W bronze analogues (*13*). We report here the synthesis and crystal structure of a new molybdenum bronze, $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$, which contains extended Mo–Nb bonding.

Experimental

Prior to use, K_2CO_3 (Aldrich, 99+ %) was dried at 300°C for 1 hr, Nb_2O_5 (Alfa Product, 99.5%) at 1100°C for 9 hr, and B_2O_3 (Alfa Product, 99.99%) at 200°C for 6 hr in air. $KNbO_3$ was prepared by the reaction of K_2CO_3 with a stoichiometric amount of Nb_2O_5 in an alumina crucible at 900°C in air for 15 hr. $K_2O \cdot B_2O_3$ was prepared by heating a pressed pellet containing stoichiometric amounts of K_2CO_3 and B_2O_3 in an alumina crucible at 900°C overnight. NbO_2 (Alfa Products, 99+ %) and Nb (Johnson Matthey, 99.8%) were used as obtained without any further purification.

The discovery of $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ was quite unintentional. In an attempt to prepare $K_5Nb_8O_{18}$ with $K_2O \cdot B_2O_3$ as a flux in a molar ratio of 1.0 : 1.3, a mixture containing stoichiometry amounts of $KNbO_3$, NbO_2, Nb, and $K_2O \cdot B_2O_3$ was thoroughly mixed and pelletized. This pellet was then put in a molybdenum boat in a sealed quartz tube, which, in turn, was sealed in another quartz tube. The reaction was held at 1150°C for 3 days and slowly cooled (−10°C/hr) to 850°C before being quenched in air. Black hexagonal column-like crystals grown on the wall of the molybdenum boat were found along with light blue transparent needle crystals in the bulk product. Attempts to synthesize a polycrystalline single phase $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ were not successful.

A black hexagonal column-like crystal having approximate dimensions of $0.15 \times 0.15 \times 0.33\ mm^3$ was selected for both elemental analysis and single crystal X-ray crystallographic study. The qualitative elemental analysis with a scanning electron microscope indicated the presence of K, Mo, and Nb, and the composition was established as a result of X-ray single crystal structural refinement. Because the scattering factors of Nb and Mo are quite similar, the criterion used to distinguish the Nb from Mo was based on the metal–oxygen bond distances. The intensity data were collected with an Enraf–Nonius CAD4 diffractometer at room temperature. Graphite-monochromated Mo$K\alpha$ radiation was employed to collect data with $4° \leq 2\theta \leq 50°$. A scan mode of ω–2θ was used. Lattice parameters obtained from a least-squares refinement of 25 accurately centered reflections with $11.7° \leq 2\theta \leq 23.3°$ corresponded to a tetragonal system with unit cell dimensions $a = 12.5591(2)$ Å, $c = 3.976(1)$ Å, and $V = 627.2(2)$ Å^3. No apparent decay of the intensities of three standard reflections was observed in the course of data collection. Intensity data were corrected for Lorentz polarization effects. The linear absorption coefficient for Mo$K\alpha$ is 56.68 cm^{-1}. The empirical correction based on ψ scan was thus applied. Data collected in the quadrant $(h, k, \pm l)$ were averaged to give a total of 367 unique reflections of which 321 reflections with $I > 3\sigma(I)$ were considered as observed and used in the subsequent structure solution and refinement.

The space group *P4/mbm* was chosen based on the systematic absences of $0kl$: $k \neq 2n$, $0k0$: $k \neq 2n$, and $h00$: $h \neq 2n$, and the statistical test of intensities. The structure was solved by direct methods (SHELXS-86) (*14*) and refined by full-matrix least-squares techniques in the MolEN program package (*15*) to $R = 0.021$ and $R_w = 0.032$, with a secondary extinction coefficient of 1.076×10^{-6}. The final electron density difference map was flat with a maximum of 0.7523 e^-/Å^3 near Mo(2) and a minimum of −0.763 e^-/Å^3 near the symmetry related Mo(2).

TABLE I

X-RAY CRYSTALLOGRAPHIC DATA FOR $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$

Empirical formula	$K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$
Formula weight	1644.21
Crystal system	Tetragonal
Space group	*P*4/*mbm* (#127)
a, Å	12.5591(9)
c, Å	3.976(1)
V, Å^3	627.2(2)
Z	1
Calcd density, g/cm^3	4.352
Crystal size, mm	0.15 × 0.15 × 0.33
μ (Mo$K\alpha$), cm^{-1}	56.68
Diffractometer	Enraf–Nonius CAD4
α, Å, graphite-monochromated	0.71069
2θ range, °	4–50
Scan mode	ω-2θ
No. reflections collected	367
No. observations ($I > 3\,\sigma(I)$)	321
No. variables	51
Goodness of fit indicator[a]	1.68
Largest peak in final diff. map, e^-/Å^3	0.758
Transmission coefficient	0.73–0.96
R^b, Rw^c	0.021, 0.032

[a] Quality of fit = $[\Sigma\omega(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.
[b] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[c] $R_w = [\Sigma\omega(|F_o-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$; $\omega = 1/(\sigma^2|F_o|)$.

Details of the data collection and refinement of $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ are presented in Table I. Final positional parameters and selected bond distances are given in Tables II and III, respectively. The interatomic bond angles (2 pages) and the anisotropic thermal parameters of atoms (1 page), as well as the observed and calculated structure factors (3 pages) are available as supplementary materials.

Structural Description and Discussion

The tetragonal (I) tungsten bronze (TTB) structure, first reported by Magneli (*16*), consist of an assemblage of corner-shared MO_6 octahedra (M is commonly Ti, Nb, Ta, or W) arranged in a manner that results in the presence of three types of interstitial sites (namely, pentagenal, tetragonal, and trigonal) in which a variety of cations can be accommodated. The composition and resulting properties of a number of these compounds have been summarized by Jamieson *et al.* and the occupancy of the various sites discussed (*17*).

In contrast to the known Mo bronzes (except the high pressure prepared forms), which have layer-type structure with edge and corner-sharing MoO_6 octahedra forming infinite two-dimensional (2D) sheets, $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ adopts the TTB-type structure with MoO_6 octahedra corner-shared in three dimensions (3D). It is worthwhile to mention that $K_{0.5}MoO_3$ prepared at 65 kbar pressure is the only other molybdenum bronze known to have a TTB-type structure (*13*). The unit cell structure of $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ is illustrated in Fig. 1.

TABLE II

ATOMIC COORDINATES AND B_{eq}[a] for $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$

Atom	Position[b]	Multiplier	x	y	z	B_{eq}, Å^2
Mo(1)	8j	0.46	0.79218(3)	0.07636(3)	0.500	1.376(9)
Mo(2)	2c	0.116	0.500	0.000	0.500	1.56(1)
Nb	4g	0.048	0.1192(2)	0.381	0.000	0.71(3)
K(1)	4g	0.235	0.32775(9)	0.172	0.000	1.96(2)
K(2)	2a	0.099	0.500	0.500	0.000	0.72(3)
O(1)	2d	0.125	0.500	0.000	0.000	2.5(1)
O(2)	8j	0.50	0.6542(3)	0.0006(3)	0.500	3.11(8)
O(3)	4h	0.25	0.2121(3)	0.288	0.500	1.87(8)
O(4)	8i	0.5	0.7885(3)	0.0761(4)	0.000	2.52(9)
O(5)	8j	0.5	0.9299(2)	0.1421(2)	0.500	1.28(6)

[a] $B_{eq} = 8\,\pi^2/3\;\Sigma U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$, where the temperature factors are defined as $\exp(-2\,\pi^2\,\Sigma h_ih_ja_i^*a_j^*U_{ij})$.
[b] Space group *P*4/*mbm* (#127).

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) FOR $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$

Mo(1)	O(2)	1.978(4)	K(1)	O(1)	3.061(1)
	O(3)	1.980(4)		O(2)	2.955(4) [4]^a
	O(4)	1.9909(1) [2]^a		O(3)	2.860(2) [2]
	O(5)	1.917(3)		O(4)	3.200(5) [2]
	O(5)′	2.017(3)			
				O(5)	3.324(3)^b [4]
				O(4)′	3.445(3)^b [2]
Mo(2)	O(1)	1.990(0) [2]			
	O(2)	1.937(4) [4]	K(2)	O(4)	2.824(4) [4]
				O(5)	2.815(4) [8]
Nb	O(1)	2.119(2)			
	O(4)	2.194(4) [2]			
	Mo(1)	2.995(2) [4]			
	Mo(2)	2.907(1) [2]			
	O(2)	2.525(2)^b [4]			
	O(3)	2.586(2)^b [2]			

[a] [ ] indicates the number of contacts of this distance and type.

[b] Nonbonding distances.

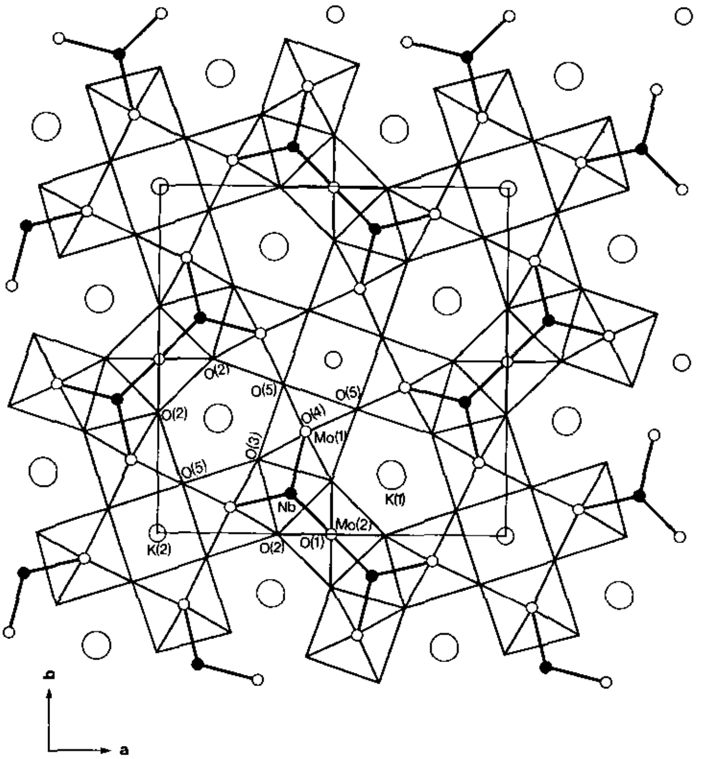

FIG. 1. Polyhedral representation of the unit cell structure of $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ viewed down the c-axis. The Mo and Nb atoms are represented by the small open and solid circles, respectively. Two vertices along the c-axis of the Mo(1) (O(4) × 2) and Mo(2) (O(1) × 2) octahedra are not shown. The interstitial sites referred to in the text as A, B, and C are the tetragonal, pentagonal and trigonal sites, respectively.

Four Mo(1)O_6 octahedra corner-share to give a tetragonal interstitial site (A). The pentagonal interstitial site (B) is formed by four Mo(1)O_6 and one Mo(2)O_6 octahedra, which are interconnected by corner-sharing. The trigonal interstitial site (C) is surrounded by three corner-sharing octahedra, two of which are Mo(1)O_6 and the other is Mo(2)O_6. As in $K_{0.40-0.57}WO_3$ (*16, 18*), the K atoms in $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ occupy the A (K(2)) and B (K(1)) sites. Interestingly, the octahedral sites in $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ are not fully occupied by Mo atoms, and yet the Nb atoms partially occupy the trigonal interstitial sites, forming extended metallic bonds with the neighboring Mo atoms. Such partial occupancy of the C sites has previously been observed only in $K_6Ta_{10.8}O_{30}$ (*19*) and $K_{5.75}Nb_{10.85}O_{30}$ (*20*), where the octahedral sites are fully occupied and the A and B sites are either fully or nearly fully occupied; thus the excess Ta or Nb atoms are forced to occupy the C sites. In these latter compounds excess Ta or Nb is necessary for achieving electrical neutrality, whereas $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ is a reduced compound. The criterion used to locate the Nb atom was based on the metal–oxygen distances of the C site, which were significantly longer than the octahedral Mo–O bond distances (Table II).

The Nb are nine-coordinated (Fig. 2) with six Nb–Mo bond distances of 2.995(2) (4 ×) and 2.907(1) (2 ×) Å and three Nb–O bond lengths of 2.119(2) and 2.194(4) (2 ×) Å. These Nb–Mo bond distances (ave. 2.966 Å) are comparable to the Nb–Nb distance (2.977 Å) found in NbO (*21, 22*), but do not agree well with the average Mo–Mo distance (2.81 Å) found in MoO_2(*23*). The Nb–O bond distances (ave. 2.169 Å) are comparable to the Nb–O distances (1.950–2.192 Å) reported in the literatures (*24*). The Nb · · · O(2) distance of 2.525(2) Å and Nb · · · O(3) of 2.586(2) Å given in Table III are therefore too long to be considered as bonding. The Nb–Mo bonds in $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ are extended along the *c*-axis leading to infinite zigzag chains, which are observed for the first time in transition metal oxide bronzes. In the case of $K_6Ta_{10.8}O_{30}$ (*19*), although the corresponding Ta · · · Ta distances (ave. 2.967 Å) are within the Ta–Ta metallic bond distance, they are not considered as bonding because the Ta^{5+} (d^0) ions do not provide electrons for the Ta–Ta bonds. The average Mo(1)–O bond distance (1.979 Å) and the Mo(1)–Nb distance (2.995(2) Å) are significantly longer

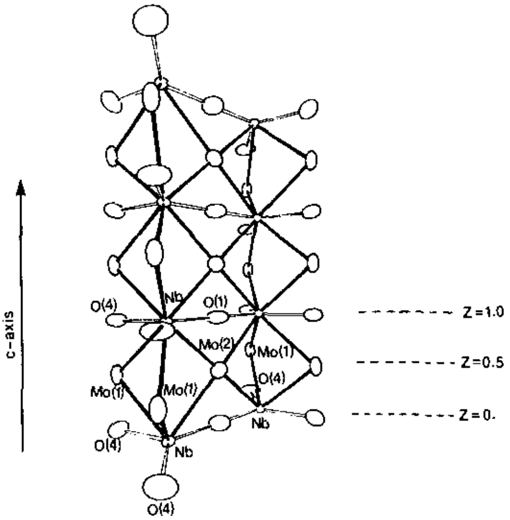

FIG. 2. ORTEP drawing (50% thermal ellipsoids) of a perspective view of the $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ structure showing the infinite zigzag chains of Nb–Mo bonds along the *c*-axis.

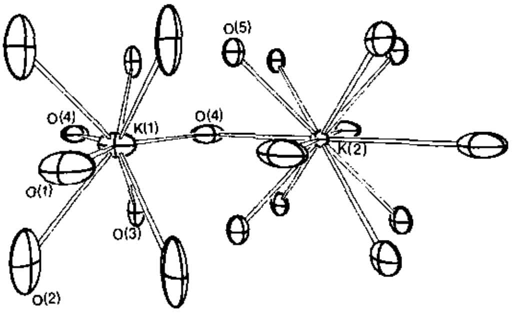

FIG. 3. ORTEP drawing (50% thermal ellipsoids) of the coordination environments about the K atoms in $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$. The additional longer contacts to K(1) are not shown for clarity.

than the corresponding bond distance of Mo(2)–O (ave. 1.955 Å) and Mo(2)–Nb (2.907(1) Å), even though the coordination number of Mo(1) (6 O, 2Nb) is smaller than that of Mo(2) (6 O, 4Nb). As observed in other TTB-type structures, one of the two crystallographically independent MoO_6 octahedra (in this case, Mo(1)) is more distorted, with Mo(1)–O distances varying from 1.917(3) to 2.017(3) Å, compared to 1.937(4) to 1.990(0) Å for Mo(2)–O.

The coordination environments of K(1) and K(2) are presented in Fig. 3. K(1) is nine-coordinated and its coordination geometry may be described as a tricapped trigonal prism with additional longer contacts. The bonded K(1)–O distances range from 2.860(2) to 3.200(5) Å (ave. 3.02 Å) and the additional nonbonded contacts are 3.324 (3) Å to O (5) and 3.445 (3) Å to O (4). K (2) has 12 nearest oxygen atoms in cubooctahedral coordination with K(2)–O(4) bond distances of 2.824(4) Å and K(2)–O(5) of 2.815(4) Å. The tricapped trigonal prismatic geometry of K(1) is interconnected with the cubooctahedral geometry of K(2) through a bridging O(4).

In conclusion, a new molybdenum bronze of $K_{5.3}Mo_{9.2}Nb_{0.8}O_{30}$ with the TTB-type structure has been discovered and structurally characterized. The composition of the compound was estimated from the X-ray single crystal structural refinement. The number of metal-centered electrons (MCE) per $Mo_{9.2}Nb_{0.8}O_{30}^{5.3-}$ cluster unit derived from the formula is 4.5 e^-, which facilitate the formation of infinite zigzag chains of Nb–Mo bonds along the *c*-axis.

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