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Structural Effects of Vanadium Substitution in $Mo_{17}O_{47}$

NOROBU YAMAZOE,* THOMMY EKSTRÖM and LARS KIHLBORG

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden

A crystal of the composition $(Mo_{1-x}V_x)_{17}O_{47}$, $x \approx 0.07$, prepared by thermal decomposition of $(Mo,V)_5O_{14}$, has been studied by X-ray diffraction. The structure, obtained by least squares refinement, has been compared with that of unsubstituted $Mo_{17}O_{47}$. The main change is an increased off-center displacement of the metal atoms within the polyhedra in the direction of the short *c* axis. About 2/3 of the vanadium is substituting in two particular sites, while the rest seems more or less statistically distributed over the remaining seven positions. A short metal-metal distance, likely to indicate a metal-metal bond, has increased only very slightly, and this leads to the conclusion that only a part of the formally available valence electrons are engaged in this bond.

$Mo_{17}O_{47}$ and Mo_5O_{14} are two molybdenum oxides which form only at rather low temperatures.[1] It has been shown that their formation temperature can be markedly increased by a partial substitution of titanium, tungsten, or vanadiumgroup metals for molybdenum.[2-5] For example, while pure $Mo_{17}O_{47}$ forms only below 560 °C and has been observed to decompose at 630 °C, a corresponding vanadium containing phase is obtained at temperatures as high as 760 °C as a product of the thermal decomposition of $(Mo,V)_5O_{14}$.[2] Even more striking stabilization effects have been reported for Mo_5O_{14}.

The crystal structures of $Mo_{17}O_{47}$[6] and Mo_5O_{14}[7] have MoO_6 octahedra and MoO_7 pentagonal bipyramids as building units, forming networks which are rather complicated in two dimensions. The MoO_7 pentagonal bipyramids share their equatorial edges with five octahedra and by connection to the corners of identical polyhedra above and below form characteristic units which have been called "pentagonal columns".[8,9] In $Mo_{17}O_{47}$ these pentagonal columns are pairwise connected by component octahedra sharing edges, with a very short metal-metal distance across the shared edge (Fig. 1).

In view of these features it was considered very interesting to learn how the substituting metal atoms are distributed and how the ternary structures have changed compared to those of the unsubstituted phases. This paper is concerned with $Mo_{17}O_{47}$ in which Mo was partly substituted by V. A similar study of $(Mo,Ta)_5O_{14}$ will be presented elsewhere.

EXPERIMENTAL

The crystal used in this study could be assumed to have a composition close to $(Mo_{0.93}V_{0.07})_{17}O_{47}$, which will be abbreviated $(Mo,V)_{17}O_{47}$ in the following. It had been prepared by thermal decomposition of a monophasic sample of $(Mo_{0.93}V_{0.07})_5O_{14}$ by heating at 780 °C for a short time and subsequently annealed for three weeks at 760 °C. The thermal treatment was done in a sealed, evacuated silica tube. The parent phase had been prepared from appropriate amounts of MoO_3, MoO_2, and V_2O_5 and its composition could be assumed the same as that of the reaction mixture since it formed as a single phase in a closed system.[2] The vanadium content was supposed to remain essentially unchanged during the decomposition since only trace amounts of a second phase, *viz.* Mo_8O_{23}, were observed in the product. A precise knowledge of the vanadium content was not essential for the present study, however.

X-Ray powder patterns were recorded by means of a Guinier-Hägg focusing camera using $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å) and KCl ($a = 6.2930$ Å) as internal standard. The lattice constants of $(Mo,V)_{17}O_{47}$ were found to be significantly different from those of the binary $Mo_{17}O_{47}$ (Table 1). The relative differences given in Table 1 are nearly the same as those observed

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* On leave from Department of Applied Chemistry, Kyushu University, Fukuoka City, Japan.

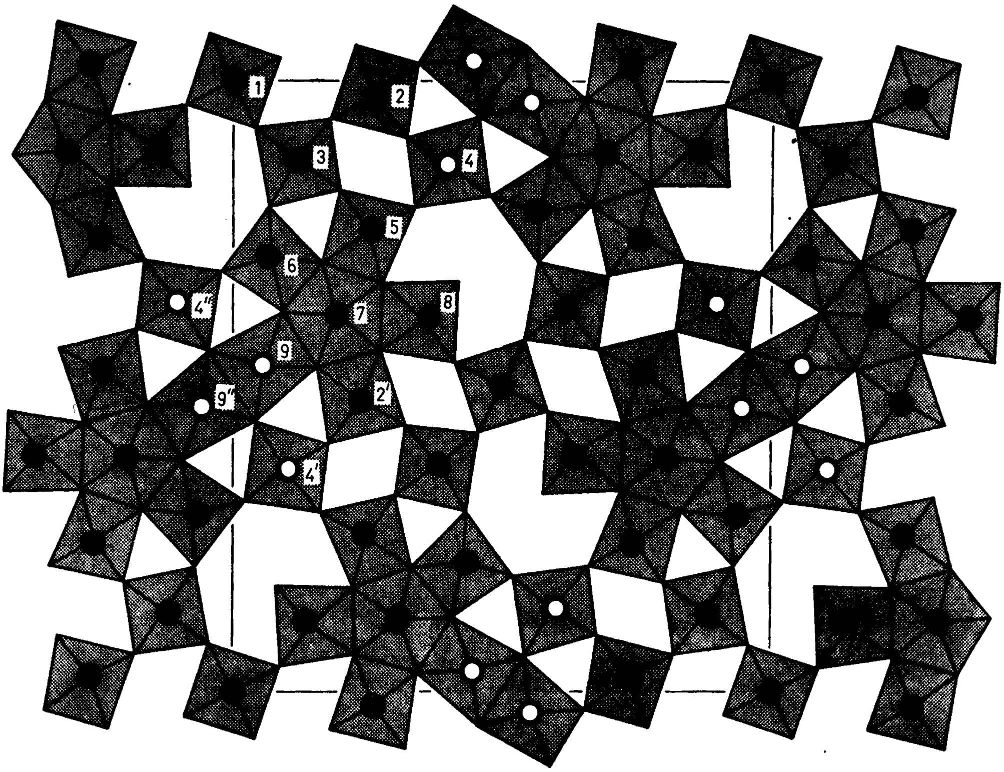

Fig. 1. The structure of $(Mo,V)_{17}O_{47}$ in projection along [001]. The unit cell is outlined; the *a* axis is vertical, *b* horizontal. MO_6 octahedra and MO_7 pentagonal bipyramids are shown with (filled and open) circles indicating the metal atom positions. The open circles indicate the positions where most of the vanadium substituates.

for $(V_{0.05}Mo_{0.95})_5O_{14}$ with respect to pure Mo_5O_{14}.

A needle-like crystal with the size 10 μm × 10 μm × 250 μm (elongated along the *c* axis) was selected for the single crystal X-ray study. The Weissenberg photographs were very similar to those of $Mo_{17}O_{47}$ and the space group was therefore assumed to be the same, *Pba2* (No. 32). X-Ray diffraction data were collected with a Siemens AED diffractometer using Mo*K*α radiation. The lattice parameters of the crystal were in good agreement with those of the powder. Out of about 2000 reflections with $\theta < 26.6°$, measured within one octant, 985 reflections had $\sigma(I)/I < 0.35$ and were used for the structure refinement. Corrections for Lorentz-polarization and absorption effects were applied. All calculations were carried out on an IBM 360/75 computer, using programs which have been described elsewhere.[10,11] The full matrix program FALFA[11] was used for the least squares refinement. The atomic scattering

Table 1. Lattice parameters of $(Mo_{0.93}V_{0.07})_{17}O_{47}$ and $Mo_{17}O_{47}$.

	$(Mo_{0.93}V_{0.07})_{17}O_{47}$	$Mo_{17}O_{47}$	Difference %
a (Å)	21.531 ± 0.004	21.615	−0.389
b (Å)	19.534 ± 0.004	19.632	−0.499
c (Å)	4.001 ± 0.001	3.9515	+1.253
Cell volume (Å^3)	1682.8	1676.8	+0.358

Table 2. Analysis of the weighting scheme used. w = weighting factor, $\Delta = |F_{\text{obs}} - F_{\text{calc}}|$.

Interval F_{obs}	Number of reflections	$\overline{w\Delta^2}$ (normalized)	Interval $\sin\theta$	Number of reflections	$\overline{w\Delta^2}$ (normalized)
0−82	155	1.42	0.0−0.214	166	0.96
82−88	71	1.48	0.214−0.269	138	0.85
88−96	96	1.08	0.269−0.308	129	0.78
96−106	99	0.81	0.308−0.339	110	0.75
106−118	94	0.82	0.339−0.365	88	0.92
118−134	123	0.78	0.365−0.388	95	0.93
134−153	98	0.78	0.388−0.408	101	1.18
153−180	85	0.83	0.408−0.427	72	1.88
180−229	80	0.77	0.427−0.494	62	1.38
>229	84	1.11	0.444−0.460	24	1.01

Table 3. The refined parameters for $(\text{Mo}_{0.93}\text{V}_{0.07})_{17}\text{O}_{47}$. Space group: *Pba*2 (No. 32). Equivalent positions: x,y,z; $\bar{x},\bar{y},z$; $\frac{1}{2}-x,\frac{1}{2}+y,z$; $\frac{1}{2}+x,\frac{1}{2}-y,z$ (Mo1 and O1 in 2-fold positions). Parameters without standard deviations (within parentheses) were kept fixed.

	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B(\sigma)$	Occupancy factor (σ)
Mo1	0	0	0.579	0.22(15)	2×0.453(18)
Mo2	0.02427(16)	0.26120(23)	0.5789(32)	0.12(10)	0.921(30)
Mo3	0.12948(19)	0.11753(21)	0.4006(29)	0.26(11)	0.903(29)
Mo4	0.13558(20)	0.40039(27)	0.4117(32)	0.36(12)	0.823(28)
Mo5	0.24223(18)	0.25749(23)	0.5626(36)	0.43(11)	0.946(30)
Mo6	0.28823(18)	0.06502(23)	0.5773(34)	0.30(10)	0.929(30)
Mo7	0.38259(20)	0.19341(21)	0.4062(30)	0.09(10)	0.917(29)
Mo8	0.38568(25)	0.36643(26)	0.4096(29)	1.31(13)	0.946(32)
Mo9	0.46517(20)	0.05591(25)	0.5619(33)	0.39(12)	0.846(28)
O1	0	0	0.020(19)	1.9(11)	
O2	0.0227(16)	0.2640(21)	0.026(14)	2.0(8)	
O3	0.1286(18)	0.1219(19)	0.994(12)	1.9(8)	
O4	0.1331(14)	0.4025(18)	0.998(8)	0.7(6)	
O5	0.2459(16)	0.2571(18)	−0.010(10)	1.2(7)	
O6	0.2867(14)	0.0685(17)	−0.002(9)	0.8(6)	
O7	0.3829(17)	0.1957(19)	0.993(10)	1.4(7)	
O8	0.3879(13)	0.3584(15)	0.992(9)	0.2(6)	
O9	0.4635(14)	0.0565(18)	0.992(10)	0.8(7)	
O10	0.0746(15)	0.0447(16)	0.491(10)	0.6(6)	
O11	0.0588(14)	0.1782(15)	0.503(9)	0.4(6)	
O12	0.0875(13)	0.3215(16)	0.543(13)	0.8(6)	
O13	0.0575(18)	0.4577(21)	0.494(13)	2.2(9)	
O14	0.2037(16)	0.0672(19)	0.496(11)	1.5(7)	
O15	0.1773(16)	0.1986(19)	0.486(11)	1.5(8)	
O16	0.2062(14)	0.3396(16)	0.479(9)	0.5(6)	
O17	0.1869(19)	0.4758(22)	0.550(20)	2.9(9)	
O18	0.2950(12)	0.1692(15)	0.501(8)	0.0(5)	
O19	0.3322(13)	0.2808(17)	0.481	0.4(6)	
O20	0.3291(19)	0.4241(23)	0.465(14)	2.7(10)	
O21	0.3798(17)	0.0940(19)	0.518(11)	1.5(7)	
O22	0.4683(14)	0.1558(17)	0.499(11)	0.9(7)	
O23	0.4381(15)	0.2719(18)	0.480(11)	1.2(7)	
O24	0.4577(19)	0.4116(23)	0.496(13)	2.6(10)	

factors for neutral atoms given by Cromer and Waber[12] were used with the anomalous dispersion corrections published by Cromer.[13]

Starting from the positional parameters reported for $Mo_{17}O_{47}$[6] the least squares refinement was carried out in several steps with successively increasing number of variables. A compound scattering curve formed from 93 % Mo and 7 % V were used for all metal positions and occupancy factors were introduced as additional variables to simulate any uneven vanadium distribution. An isotropic secondary extinction parameter was introduced and refined in the last few least squares cycles. The refinement was terminated when the shifts of the variables became less than 5 % of the corresponding standard deviations. The discrepancy index $R = \sum||F_{obs}| - |F_{calc}||/\sum|F_{obs}|$ was then 0.064. Hughes' weighting scheme was found appropriate for the refinement and a weight analysis obtained in the last cycle is given in Table 2. A list of observed and calculated structure factors may be obtained from this laboratory on request.

RESULTS

The final positional parameters and isotropic temperature factors for all atoms are listed in Table 3 together with the occupancy factors for the metal positions. The atomic coordinates are very close to the corresponding ones in $Mo_{17}O_{47}$.

The occupancy factors should reveal any deviation of the V/Mo distribution from the average composition at the particular site. The mean value of the occupancy factors is expected to come out as unity if there are no vacancies on the metal sites and if a correct value for the gross composition was used in the formation of the compound scattering factor curve. In the present case the mean value is only 0.904. Metal vacancies are not very likely for structural reasons, and it was not believed that the gross V/Mo ratio, assumed to be 0.07/0.93, was so much in error as this figure would indicate (V/Mo = 0.28/0.72). The occupancy factors are, however, strongly correlated with the scale factor (correlation coefficients ranging from −0.67 to −0.80) and are dependent on the particular scattering factor curves used for the three kinds of atoms. This latter was demonstrated by a test calculation in which the scattering curves of the ionized atoms Mo^{5+}, V^{5+} and O^{-} were used instead of those for neutral atoms. This refinement gave an average occupancy of 0.957, with only insignificant changes in the positional parameters. The deficiency of the average occupancy is thus thought to be essentially a computational artifact and for the evaluation of the vanadium distribution it seemed justified to normalize the occupancy factors on the condition that their sum (taking the site multiplicity into account) should be equal to the number of metal atoms in the unit cell. The normalized occupancy factors are listed in Table 4.

The normalized occupancy factor A for a position is related to the actual statistical vanadium content, x, at that position by the

$$A = (f_{Mo}/f_M)(1-x) + (f_V/f_M)x$$

equation where f_{MO} and f_V are the atomic scattering factors of Mo and V, respectively, and f_M is that used in the refinement and equal to $0.93\ f_{Mo} + 0.07\ f_V$. Since f_{Mo}/f_M vary only

Table 4. Some quantities calculated to metal atoms.

Metal atom	Normalized occupancy factor	Calc. content of V (%)	Asymmetry of O − M − O bonds along [001] $d_1 - d_2$ (Å)	
			$(Mo,V)_{17}O_{47}$	$Mo_{17}O_{47}$
Mo 1	0.502	6 ± 7	0.48 ± .15	0.36
Mo 2	1.02	3 ± 6	0.43 ± .12	0.47
Mo 3	1.00	7 ± 6	0.77 ± .10	0.24
Mo 4	0.91	24 ± 6	0.61 ± .08	0.50
Mo 5	1.05	−2 ± 6	0.57 ± .08	0.57
Mo 6	1.03	2 ± 6	0.65 ± .08	0.64
Mo 7	1.01	4 ± 6	0.69 ± .08	0.46
Mo 8	1.05	−2 ± 6	0.69 ± .09	0.26
Mo 9	0.94	20 ± 5	0.57 ± .08	0.44
Average		6.9	0.607	0.436

slightly with sin θ/λ approximate values of x can be calculated by this equation, choosing an adequate value for sin θ/λ. This was done for sin $\theta/\lambda = 0.30$ and the resulting x values are listed in the third column of Table 4.

Although the accuracy is rather poor, the conclusion can be drawn that the larger amount of vanadium, accounting for about 2/3 of the total, is located at the two sites $M(4)$ and $M(9)$. As seen in Fig. 1 these positions are in the octahedra which lie in the middle of a pair of pentagonal columns, including the octahedra which form the bridge with the short metal-metal separation.

As mentioned above, the effects of the substitution on the crystal structure are rather small. The main changes are in the z parameters. The metal atoms form puckered layers by displacements from the centers of the polyhedra, giving rise to considerable divergence in the Mo – O bond lengths in the c direction. This puckering is more pronounced in $(Mo,V)_{17}O_{47}$ than in $Mo_{17}O_{47}$, which is reflected in the increase in the length of the c axis (Table 1). The average asymmetry $|d_n - d_{n'}|$, where d_n and $d_{n'}$ are the bond lengths $M_n - O_n$ and $M_n - O_{n'}$ approximately parallel to c, is 0.61 Å in $(Mo,V)_{17}O_{47}$ compared to 0.44 Å in $Mo_{17}O_{47}$. The values for the individual metal atoms are given in Table 4. It is seen that these values are not significantly different and, for instance, no enhanced asymmetry can be observed for the two sites with high vanadium content.

The changes in the rest of the $M - O$ bond lengths, those approximately parallel to the ab plane, are very small; the average difference compared to $Mo_{17}O_{47}$ is 0.036 Å, which is the same value as the average standard deviation. The differences seem to be of random nature and no particular pattern can be recognized.

It has been proposed [5,9] that non-bonding valence electrons destabilize structures containing pentagonal columns. Such structures will then be more stable if the extra electrons are engaged in localized bonding, indicated by short metal-metal distances, or if the number of electrons is reduced by substitution.

The formal number of extra electrons per slice, one polyhedron thick, of a pentagonal column is 4 in $Mo_{17}O_{47}$ and this number is reduced to 3.4 by the vanadium substitution. As mentioned above, the structure contains short metal-metal separations Mo(9) – Mo(9″). If the extra valence electrons are forming metal-metal bonds, one should expect that this interaction should be weaker in the vanadium substituted phase, resulting in a lengthening of the metal-metal distance. The Mo(9) – Mo(9″) distance is in fact longer, but only slightly: 2.649 ± 0.010 Å in $(Mo,V)_{17}O_{47}$ compared to 2.626 ± 0.007 Å in $Mo_{17}O_{47}$.

From the smallness of this effect it can be concluded that only part of the available valence electrons are engaged in the metal-metal interaction, and it is mainly the number of electrons not involved in this which is reduced by the substitution. In MoO_2, which has similar metal-metal pairs and where the formal number of electrons per pair is 4, the separation is only 2.5106 ± 0.0005 Å.[14] The present values, however, are closer to the corresponding distance in VO_2, 2.6191 ± 0.0004 Å,[15] with half as many electrons per pair.

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