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The mixed oxide $MoVAlO_7$

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A single crystal of $MoVAlO_7$, vanadium aluminium molybdate, has been grown. The present structure determination is more precise than a previous powder-pattern investigation [Knorr, Jacubus, Dabrowska & Kurzawa (1998). *Eur. J. Solid State Inorg. Chem.* **35**, 519–530]. A three-dimensional $[MoAlO_6]_n^{3n-}$ network surrounds infinite strings of $[VO]^{3+}$ groups [V—O = 1.586 (4) Å] lying in the mirror planes.

Comment

A detailed study of the $Mo_{1+x}V_{2-x}O_8$ and $V_{2-x}Mo_xO_5$ phases of the MoO_3–V_2O_5–V_2O_4 system has been undertaken in order to determine their homogeneity range domains, the existence of super- or modulated structures and also their magnetic and electric behaviours (Galy *et al.*, 2002). For the former phase, *i.e.* $Mo_{1+x}V_{2-x}O_8$, synthesized at 903 K, the x limit values have been established as $0.12 < x < 0.18$; in the meantime, magnetic properties have indicated the presence of V^{4+} cations, leading to the formulation $Mo^{6+}_{1+x}V^{5+}_{2-2x}V^{4+}_xO_8$, this latter phase being a semiconductor (E_a = 0.22 eV). During an attempt to test the electrical response, a pellet was placed in an alumina crucible and heated to 973 K; surprisingly, an extremely strong reaction occurred between the $Mo_{1+x}V_{2-x}O_8$ pellet and the crucible. In the complex mixture obtained, one small crystal, nicely prismatic and with a green colour, was detected. This crystal was quite different from the crystals of the phases of our system and was studied by X-ray single-crystal techniques in order to determine its structure and therefore its chemical composition (see details of the structure determination below).

The crystal structure shows three different types of coordination for the Mo, V and Al atoms. A perspective view, oriented along [010], is shown in Fig. 1. The Mo atom is surrounded by four O atoms, making a regular MoO_4 tetrahedron (see Table 1); the V atoms are located inside an oxygenated VO_5 square pyramid, while the Al atom is at the centre of a regular octahedron. The VO_5 square pyramids share opposite basal edges, alternately pointing up and down, making an infinite string elongated along the helicoidal twofold axis parallel to [010]. These strings are surrounded by a kind of ring alternately built up of four MoO_4 tetrahedra and four AlO_6 octahedra through shared corners, ...Al—O2—Mo—O3—Al... (Fig. 2). Along [010], the two other O atoms of the MoO_4 tetrahedron (atom O1 repeated by the mirror plane perpendicular to the y axis) connect two successive AlO_6 octahedra which share edges with the VO_5 square pyramids *via* O4 atoms. $MoVAlO_7$ exhibits a three-dimensional network. We note the short V—O5 distance typical of the classical multiple bond between V^{5+} and oxygen in the apical position of the VO_5 square pyramid, pulling V above the basal square plane of O atoms (Table 1). The unexpected composition of such a crystal drove us to confirm immediately by solid-state synthesis the formation of this phase (see *Experimental*). A green powder was obtained and all the reflections of the X-ray powder pattern were indexed with the single-crystal data. The measured density of $MoVAlO_7$ is in good agreement with the calculated density. The $MoVAlO_7$ formula was then established. Following this work and knowing the molecular formula, a search was undertaken in the literature. A structure determination by X-ray powder diffraction of the same compound was published by Knorr *et al.* (1998), but these authors were unable to grow single crystals because the phase melted incongruently at 963 K. A comparison of both structural determinations shows a reasonable agreement of the general atomic architecture. The cell parameters are similar [a = 12.7312 (6), b = 5.3763 (3), c = 8.1644 (3) Å and V = 558.8 Å^3 (Knorr *et al.*, 1998)], but, of

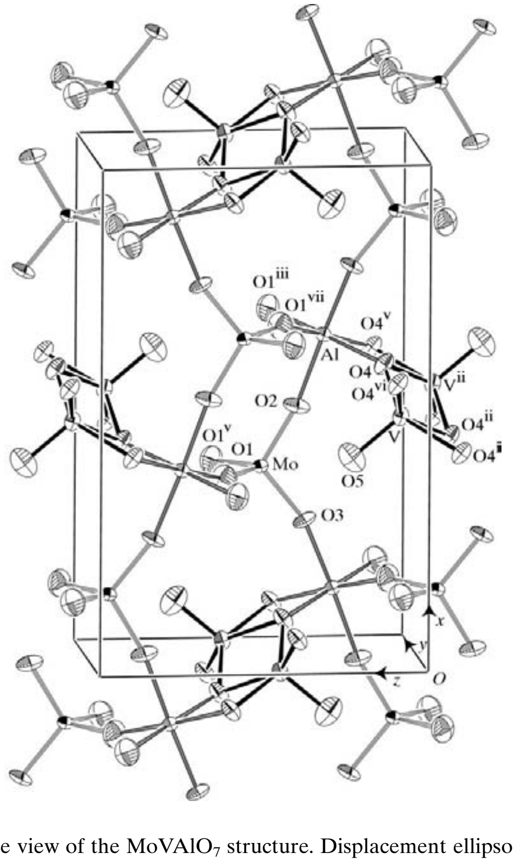

Figure 1
Perspective view of the $MoVAlO_7$ structure. Displacement ellipsoids are plotted at the 90% probability level.

course, the single-crystal study allows us to obtain very accurate bond-length and angle data. It is then readily seen that all metal–oxygen distances are in excellent agreement with the known distances in well established structures. The short V—O distance of 1.586 (4) Å compares especially well with the corresponding distance in V_2O_5, *i.e.* 1.577 (3) Å (Enjalbert & Galy, 1986); the V—O distance of 1.48 Å found by Knorr *et al.* (1998) is really too short. On this basis, calculation of bond-valence sums according to Brown & Altermatt (1985) gives a good agreement for the oxidation states of Mo, V and Al. These calculations also strengthen the fact that Knorr *et al.* (1998) had underestimated the uncertainties of their measurements by some 4σ. In both the MoO_4 and AlO_6 polyhedra, the rather regular O$\cdots$O distances fluctuate between O3$\cdots$O2 = 2.882 (3) Å, when MoO_4 connects the apices of two AlO_6 octahedra, and O4$\cdots$O4$^{\rm v}$ = 2.464 (3) Å, for the edge shared between the VO_5 square pyramid and AlO_6 [symmetry code: (v) $x, \frac{3}{2} - y, z$]. This last value is associated with the smallest bond angles [O4—Al—O4$^{\rm v}$ = 80.02 (14)° and O4—V$^{\rm ii}$—O4$^{\rm v}$ = 77.02 (13)°; symmetry code: (ii) $1 - x, 1 - y, -z$], such angles being reasonably attributed to a strong repulsion between the V^{5+} and Al^{3+} cations. The same phenomenon appears also for the edge-sharing VO_5 square pyramids, the O4$\cdots$O4$^{\rm ii}$ distance diminishing to 2.425 (3) Å, with an O4—V—O4$^{\rm ii}$ angle of 79.20 (10)°. The VO_5 square pyramids are really extremely distorted; note that the O4$\cdots$O4$^{\rm vi}$ interatomic distance is 2.915 (3) Å [symmetry code: (vi) $x, \frac{1}{2} - y, z$], and that the V—O bonds to the basal 'square' plane are rather different, with V—O4 = 1.822 (2) Å and V—O4$^{\rm i}$ = 1.980 (2) Å [symmetry code: (i) $1 - x, y - \frac{1}{2}, -z$]. Such distortions explain why some authors, substituting bigger cations like Fe^{3+} and Cr^{3+} for Al^{3+}, have found a triclinic distortion of the network (Le Bail *et al.*, 1995).

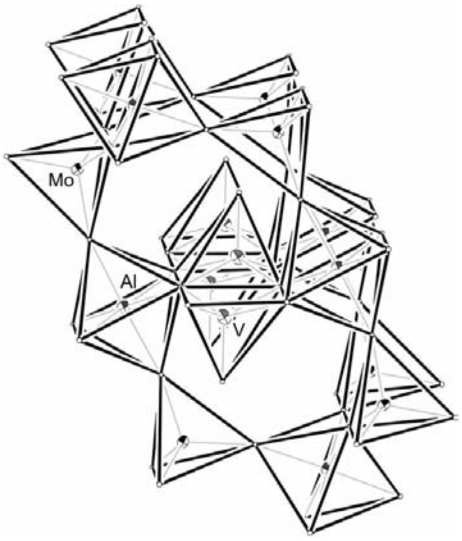

Figure 2
The three-dimensional network of MoO_4 and AlO_6 polyhedra around the $[V_2O_6]_n^{2n-}$ infinite chains of edge-shared VO_5 square pyramids.

Experimental

$AlVMoO_7$ was prepared by direct interaction of a 2:1:1 stoichiometric mixture of MoO_3, V_2O_5 and Al_2O_3 (99.5% Aldrich Chemical Company). The carefully ground mixture was introduced into an open quartz tube and heated for 24 h at 963 K. The density was determined using an Accupyc 1330 Micromeritics pycnometer.

Crystal data

$MoVAlO_7$
$M_r = 285.86$
Orthorhombic, *Pnma*
$a = 12.7360$ (2) Å
$b = 5.3790$ (4) Å
$c = 8.1660$ (6) Å
$V = 559.43$ (6) Å^3
$Z = 4$
$D_x = 3.394$ Mg m^{-3}
$D_m = 3.38$ (2) Mg m^{-3}
D_m measured by helium pycnometry
Mo $K\alpha$ radiation
Cell parameters from 3861 reflections
$\theta = 2$–32°
$\mu = 4.04$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, green
0.08 × 0.05 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
ψ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\rm min} = 0.842$, $T_{\rm max} = 0.930$
3861 measured reflections
1054 independent reflections
878 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\rm max} = 32.0°$
$h = -18 \rightarrow 18$
$k = -7 \rightarrow 7$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.083$
$S = 1.05$
1054 reflections
56 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 1.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -2.76$ e Å^{-3}
Extinction correction: *SHELXL*96
Extinction coefficient: 0.0061 (12)

Table 1
Selected geometric parameters (Å, °).

Mo—O1	1.744 (3)	V—V$^{\rm ii}$	2.9315 (6)
Mo—O2	1.752 (3)	V—Al$^{\rm ii}$	3.0138 (15)
Mo—O3	1.757 (3)	Al—O1$^{\rm iii}$	1.843 (3)
V—O5	1.586 (4)	Al—O3$^{\rm iv}$	1.855 (3)
V—O4	1.822 (2)	Al—O2	1.893 (3)
V—O4$^{\rm i}$	1.980 (2)	Al—O4	1.918 (2)
O1—Mo—O1$^{\rm v}$	105.29 (19)	O1$^{\rm iii}$—Al—O1$^{\rm vii}$	90.00 (18)
O1—Mo—O2	109.67 (10)	O1$^{\rm iii}$—Al—O3$^{\rm iv}$	91.27 (12)
O1—Mo—O3	110.85 (10)	O1$^{\rm iii}$—Al—O2	90.18 (12)
O2—Mo—O3	110.39 (16)	O3$^{\rm iv}$—Al—O2	177.96 (16)
O5—V—O4	105.85 (11)	O1$^{\rm iii}$—Al—O4$^{\rm v}$	94.98 (11)
O4$^{\rm vi}$—V—O4	106.13 (14)	O1$^{\rm vii}$—Al—O4$^{\rm v}$	174.91 (12)
O5—V—O4$^{\rm i}$	106.78 (13)	O3$^{\rm iv}$—Al—O4$^{\rm v}$	89.70 (11)
O5—V—O4$^{\rm ii}$	106.78 (13)	O2—Al—O4$^{\rm v}$	88.74 (12)
O4—V—O4$^{\rm ii}$	79.20 (10)	O1$^{\rm iii}$—Al—O4	174.90 (11)
O4$^{\rm i}$—V—O4$^{\rm ii}$	77.02 (13)	O4$^{\rm v}$—Al—O4	80.02 (14)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, -z$; (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, \frac{1}{2} + y, 1 - z$; (iv) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (v) $x, \frac{3}{2} - y, z$; (vi) $x, \frac{1}{2} - y, z$; (vii) $1 - x, 1 - y, 1 - z$.

The cell parameters and space group (*Pnma*) were clearly established. Since the cell volume was close to that of the $Mo_{1+x}V_{2-x}O_8$ phase, a rough formula of $[Mo_3O_8]$ was tried. In the Fourier and subsequent refinements of the three main electron-density peaks, it appeared, following the values of the displacement parameters, that one peak was surely Mo, the second V, and that the remaining peak

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was less populated in electrons. This last crystallographic site we ascribed to aluminium. The difference Fourier map gave five independent O-atom positions. Refinement of the positional and anisotropic displacement parameters gave a very good R factor. The resulting formula was MoVAlO_7, with $Z = 4$ units per cell.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*96.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1347). Services for accessing these data are described at the back of the journal.

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