The title compounds were prepared by reactions of binary and tertiary oxides in evacuated silica tubes at temperatures between 400 and 550°C. Their crystal structures were determined and refined from single-crystal X-ray diffractometer data. For Hg$_2$AsO$_3$: PI, $a = 913.9(1)$ pm, $b = 551.3(1)$ pm, $c = 1429.1(2)$ pm, $\beta = 110.65(1)^\circ$, $Z = 2$, $R = 0.043$ (1129 structure factors, 66 variable parameters). Hg$_2$AsO$_3$: P2$_1$/c, $a = 359.2(1)$ pm, $b = 475.2(1)$ pm, $c = 858.8(1)$ pm, $\alpha = 93.32(1)^\circ$, $\beta = 79.60(1)^\circ$, $\gamma = 89.30(1)^\circ$, $Z = 2$, $R = 0.034$ (1763 F2, 32 v). Hg$_2$AsO$_3$: P2$_1$/a, $a = 367.3(1)$ pm, $b = 1650.3(1)$ pm, $c = 1425.5(1)$ pm, $\beta = 89.99(1)^\circ$, $Z = 8$, $R = 0.028$ (1666 F91 v). Hg$_2$AsO$_3$: R3c, $a = 1083.5(1)$ pm, $c = 8.3950(8)$ Å, $Z = 8$. The structure was refined to $R = 0.037$ (1661 F62v).

HgMoO$_4$:Hg$_2$O$_6$, and Hg$_2$O$_6$ are Hg(III) compounds with Hg$_2$O$_6$ as a mixed valent Hg(II) compound with Hg$_2$O$_6$ and isolated Hg atoms. In Hg$_2$AsO$_3$, the mercury atoms form almost equilateral Hg$_3$ groups with the oxidation number +1. The molybdenum atoms have distorted octahedral coordination. These Mo$_6$ octahedra share corners and edges, thus forming two-dimensionally infinite sheets. The vanadium atoms are irregularly surrounded by five oxygen atoms. These coordination polyhedra share edges, thus forming infinite (V$_2$O$_3$)$_n$ chains, which are aligned parallel to each other. The tetrahedral AsO$_4$ groups are linked only via Hg triangles. Thus, the central atoms of the anions are in their highest oxidation state and the compounds may be represented by the formula (Hg$_2$)$_n$(Mo$_6$O$_{18}$)$_2$(AsO$_4$)$_n$. Furthermore, the composition point of view. At a first sight, neglecting the bond orientation in phases II and III, they exhibit a 12-fold orientational disorder of phase I with one of the N-O bonds oriented parallel to an edge of Ti-cube. Refinements rule out the earlier models proposed in literature for phases II and III in which the nitrate ions are oriented normal to the diagonal of Ti-cube.

PS08.01.26 CRYSTAL STRUCTURE OF MIXED-VALENCE α-CoO$_2$V$_2$O$_5$ WITH UNUSUAL METAL DISTRIBUTION. Yoshihiko Okai, Tatsushi Yaoz, and Naochi Yamamoto, Faculty of Integrated Human Studies, Faculty of Engineering, Kyoto University, Kyoto 606 Japan

In the CoO$_2$V$_2$O$_5$ system studied at 600°C only CoO$_2$V$_2$O$_5$ is found as a (VIV) mixed-valence compound. It was originally formulated as Co$_{1+y}$V$_{2+y}$O$_{5+y+1}$ with two polymorphs $\alpha$ and $\beta$ phases. $\alpha$ phase transforms reversibly into $\beta$ phase at 650 $\pm$8°C. It was reported that a phase crystallizes in the body-centered orthorhombic system but the structure has remained unknown. In the present study single crystals of $\alpha$-Co$_2$V$_2$O$_5$ were grown in the hydrothermal Co$_2$-V$_2$O$_5$ system. It crystallizes in the orthorhombic system Ibm with $a=14.2928$ Å, $b=9.8906$ Å, $c=8.3950$ Å, and $Z=8$. The structure was refined to $R_{wp}=0.034/0.030$ for 1558 reflections with $l=301$. There are three kinds of metal sites, namely octahedral M (16k) for M=Co, V (1), tetrahedral V (2) (8j) and trigonal-bipyrindal V (3) (8j) where M site is occupied by Co and V atoms evenly. The framework structure is constructed as zigzag chains of edge-shared MO$_6$ octahedra running along the c-axis are linked by sharing O(5) atoms along the b-axis forming slabs of MO$_6$ octahedra parallel to the bc-plane and the slabs are joined by V=O tetrahedra and V=O trigonal bipyramids. The valence states of metal sites were estimated as Co$^{2+}$ and V$^{4+}$ for M and V$^{5+}$ for V(2) and V(3). It is noteworthy that the metal distribution over M site is not random but restricted to Co-O(5)-V in neighboring MO$_6$ through O(5) vertex, which accounts for the even occupancies of Co and V atoms in M site and further ensures the stoichiometric composition Co$_2$V$_2$O$_5$.

The magnetic susceptibility curve exhibits a sharp peak at 8K suggesting the onset of antiferromagnetic order and the value of effective moment is well corresponding to the formula (Co$^{2+}$O$_5$V$^{4+}$O$_{5/2}$V$^{5+}$O$_{6}$).