Novel Polyanionic Topologies in Ag_2VAsO_6 and $Ag_6V_2As_2O_{13}$

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Dedicated to Professor Heinrich Nöth on the occasion of his 85 birthday

Two new silver vanadate arsenates, Ag_2VAsO_6 and $Ag_6V_2As_2O_{13}$, have been prepared applying high oxygen pressure syntheses in stainless-steel autoclaves. Ag_2VAsO_6 crystallizes in space group $P\bar{1}$ with unit cell parameters $a = 639.1(1)$, $b = 646.1(1)$, $c = 706.6(1)$ pm, $\alpha = 116.105(3)$, $\beta = 91.759(4)$, $\gamma = 90.067(4)°$, and $Z = 2$ ($R_1 = 0.058$, 3935 independent reflections). The structure consists of AsO_4 tetrahedra and VO_6 octahedra which are linked to form two-dimensional $^2_\infty[VAsO_6]^{2-}$ polyanions, separated by silver cations. $Ag_6V_2As_2O_{13}$ ($C2/c$, $a = 1895.9(2)$, $b = 536.40(6)$, $c = 1308.5(2)$ pm, $\beta = 113.578(2)°$, $Z = 4$; $R_1 = 0.030$, 2571 independent reflections) displays as primary building units AsO_4 tetrahedra and VO_5 trigonal bipyramids which are condensed by sharing edges to one-dimensional $^1_\infty[V_2As_2O_{13}]^{6-}$ ladder-like strands, set apart by the silver cations. These heteropolyanions are without precedent.

Key words: Silver, Vanadates, Arsenates, Crystal Structure, High Pressure Synthesis

Introduction

In their highest oxidation states realized, both, arsenic and vanadium, feature closed-shell electronic configurations of spherical electron density distribution. Since moreover the ionic radii for As^{5+} and V^{5+} differ just slightly, one might expect pentavalent vanadium and arsenic to express comparable crystal-chemical properties. In fact, the opposite is true. Even the binary pentoxides display distinctly different, and in both cases singular crystal structures hosting vanadium in a distorted octahedral $5 + 1$ [1] and arsenic to equal shares in a tetrahedral and octahedral [2, 3] coordination by oxygen. Singular disparities can be found throughout the oxide chemistry of this pair of elements. Ag_3VO_4 [4, 5] and Ag_3AsO_4 [6], for instance, although containing complex anions of comparable shape and size, form completely different crystal structures. Moreover, Ag_3AsO_4 is thus far known to exist only in one modification, while Ag_3VO_4 has been shown to undergo two temperature-driven, reversible structural phase transitions [4]. In order to elaborate on these strikingly different crystal chemistries of arsenic and vanadium in oxides, we have started to investigate the quaternary system $Ag_2O/V_2O_5/As_2O_5$, thus creating a structurally competitive situation for As^{5+} and V^{5+}. In order to make sure that both of them achieve the pentavalent state, we applied high oxygen pressures during the solid-state syntheses. Again one would assume that extended homogeneity ranges, like, *e. g.*, $Ag_3V_{1-x}As_xO_4$, exist. Contrary to this expectation, stoichiometric, fully ordered quaternary oxides Ag_2VAsO_6 and $Ag_6V_2As_2O_{13}$ have been encountered, representing a novel family of heteropolyoxometalates.

Ternary silver arsenates(V) so far have been of interest exclusively in the context of basic research. In addition to Ag_3AsO_4 [6], recently $AgAsO_3$ has been reported, which displays a novel type of polyanion with As^{5+} in tetrahedral and octahedral coordination [7].

Silver vanadates(V) have attracted considerably more interest because of their potential for application in catalysis [4, 8], including photocatalysis [5, 9], as *p*-type transparent conductors [10], or as materials for medical primary batteries [11]. Correspondingly, besides Ag_3VO_4 and its polymorphs, several silver vanadates(V), $Ag_4V_2O_7$ [12], $Ag_2V_4O_{11}$ [13], AgV_6O_{15} [14], and $AgVO_3$ [15] have been reported.

Table 1. Crystal structure data for Ag_2VAsO_6 and $Ag_6V_2As_2O_{13}$ at 298 K.

Compound	Ag_2VAsO_6	$Ag_6V_2As_2O_{13}$
Formula weight	437.60	1106.94
Crystal size, mm^3	$0.05 \times 0.05 \times 0.05$	$0.15 \times 0.11 \times 0.07$
Crystal system	triclinic	monoclinic
Space group (no.); Z	$P\bar{1}$ (2); 2	$C2/c$ (15); 4
Lattice parameters		
a, pm	639.1(1)	1895.9(2)
b, pm	646.1(1)	536.40(6)
c, pm	706.6(1)	1308.5(2)
α, deg	116.105(3)	90
β, deg	91.759(4)	113.578(2)
γ, deg	90.067(4)	90
V, Å^3	261.86(7)	1219.6(2)
ρ_{xray}, g cm^{-3}	5.55	6.03
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	153.8	163.4
Diffractometer	SMART APEX-I	SMART APEX-II
Radiation; λ, pm	MoK_α; 71.073	MoK_α; 71.073
Absorption correction	Multi-scan, TWINABS [19]	Multi-scan, SADABS [18]
2θ range, deg	$6.38 \le 2\,\theta \le 70.24$	$4.68 \le 2\,\theta \le 69.94$
Index range hkl	$-9 \le h \le 9$ $-10 \le k \le 8$ $0 \le l \le 11$	$-29 \le h \le 30$ $-8 \le k \le 8$ $-21 \le l \le 21$
Refl. collected / unique / R_{int}	6099 / 3935 / 0.064	9233 / 2571 / 0.029
No. of ref. parameters	93	106
Transmission: t_{max} / t_{min}	0.497 / 0.337	0.394 / 0.193
Twin volume fractions	0.700(1) / 0.300	– / –
R_1 [$F^2 > 2\,\sigma\,(F^2)$]	0.058	0.030
wR (F^2) (all data)	0.190	0.075
Extinction coefficient	0.009(2)	0.00142(8)
Largest diff. peak/hole, e Å^{-3}	2.73 / −3.17	1.52 / −1.94
Deposition no.	CSD-425757	CSD-425758

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for Ag_2VAsO_6 and $Ag_6V_2As_2O_{13}$ U_{eq} (pm^2) at 298 K.

Atom	Site	x	y	z	U_{eq}
Ag_2VAsO_6 ($P\bar{1}$)					
Ag1	2i	0.3858(1)	0.1157(2)	0.2464(1)	398(2)
Ag2	2i	0.3778(1)	0.6209(1)	0.2835(1)	371(2)
As	2i	0.1498(1)	0.6569(1)	0.8052(1)	92(2)
V	2i	0.0822(2)	0.1216(2)	0.7308(1)	99(2)
O1	2i	0.3768(7)	0.6073(9)	0.6819(7)	156(8)
O2	2i	0.1888(7)	0.7733(9)	0.0713(6)	137(7)
O3	2i	0.0095(8)	0.4089(8)	0.7198(7)	150(8)
O4	2i	0.0015(7)	0.8361(8)	0.7446(7)	137(8)
O5	2i	0.7929(7)	0.0016(9)	0.4981(6)	137(7)
O6	2i	0.2717(7)	0.2149(9)	0.9086(7)	179(9)
$Ag_6V_2As_2O_{13}$ ($C2/c$)					
Ag1	8f	0.29473(2)	0.51895(5)	0.29434(2)	233.6(8)
Ag2	8f	0.30235(2)	0.50068(5)	0.54205(3)	264.5(8)
Ag3	8f	0.49522(2)	0.47712(5)	0.61078(3)	292.1(9)
As	8f	0.12160(2)	0.49865(5)	0.04443(2)	122.2(8)
V	8f	0.09147(3)	0.47457(8)	−0.22522(4)	124.5(9)
O1	4e	0	0.3622(5)	¼	141(5)
O2	8f	0.0723(1)	0.4012(4)	0.1202(2)	177(4)
O3	8f	0.2136(1)	0.3965(4)	0.1106(2)	190(4)
O4	8f	0.0850(1)	0.3497(4)	−0.0805(2)	173(4)
O5	8f	0.1014(1)	0.1775(4)	−0.2542(2)	200(4)
O6	8f	0.1182(1)	0.8110(4)	0.0303(2)	188(4)
O7	8f	0.1761(1)	0.6108(5)	−0.1623(2)	228(4)

Experimental Section

Synthesis

The title compounds were prepared by reacting Ag_2O, V_2O_5, and As_2O_3 in stainless-steel autoclaves at elevated oxygen pressures [16]. The oxides were intimately mixed and placed into gold tubes which were sealed on one side and mechanically closed (not gas-tight) on the other. Orange, translucent $Ag_6V_2As_2O_{13}$ was obtained from stoichiometric amounts ($Ag_2O : V_2O_5 : As_2O_3 = 3 : 1 : 1$) under an oxygen pressure of 55 MPa, at a temperature of 750 K and within a reaction time of 36 h. Yellow, translucent Ag_2VAsO_6 was prepared ($Ag_2O : V_2O_5 : As_2O_3 = 2 : 1 : 1$) applying an oxygen pressure of 40 MPa, at 750 K and within a reaction time of 72 h.

1 mL of H_2O was added to the starting mixtures as a mineralizer for each synthesis. The crystalline products were filtered off, washed with deionized water and dried in air. The compounds are stable towards air and water.

X-Ray structure determination

Room-temperature single-crystal diffraction data were collected on three-circle diffractometers (Bruker AXS, Karlsruhe, Germany) equipped with a SMART-CCD (APEX-I and APEX-II) at 298 K, using MoK_α radiation ($\lambda = 71.073$ pm). The collection and reduction of data were carried out with the BRUKER SUITE software package [17]. The intensities were corrected for absorption effects applying a multi-scan method with SADABS [18] in the case of $Ag_6V_2As_2O_{13}$. Crystals of Ag_2VAsO_6 turned out to be systematically twinned (dovetail twin). The data of the two different twin domains were corrected for absorption, which has allowed determining the volume fraction with TWINABS [19]. Both structures were solved by Direct Methods and refined by full matrix least-squares fitting with the SHELXTL software package [20]. Experimental details of data collection and crystallographic data are given in Table 1, atomic coordinates and displacement parameters in Table 2.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers given in Table 1.

Results and Discussion

Orange $Ag_6V_2As_2O_{13}$ and yellow Ag_2VAsO_6 were prepared from stoichiometric amounts of the respective binary oxides, Ag_2O, V_2O_5, and As_2O_3 by high oxygen pressure syntheses in stainless-steel autoclaves. After washing the raw products with deionized water, single-phase products were obtained.

Ag_2VAsO_6 and $Ag_6V_2As_2O_{13}$ feature polyoxoanions with unprecedented topologies, and without any similarities to respective binary systems. While the arsenic atoms are in a tetrahedral coordination in either case, the coordination number of the slightly bigger vanadium atoms is expanded to 5 and 6, corresponding to a trigonal bipyramid and a distorted octahedron, see Table 3.

Ag_2VAsO_6 (space group $P\bar{1}$, Pearson code $aP20$, Wyckoff sequence $i10$) contains pairs of distorted VO_6 octahedra sharing one common edge. The same building unit has been found before in $BaVAsO_6$ [21]. The V_2O_{10} units are condensed with six AsO_4 tetrahedra by vertex sharing, whereby each AsO_4 tetrahedron interconnects three dinuclear units, see Fig. 1. One oxygen atom of each polyhedron (tetrahedron or octahedron) is in a terminal position, and bonded to the central atom (V or As) exclusively. The resulting two-dimensional polyanions ${}^2_\infty[VAsO_6]^{2-}$ are oriented perpendicular to the a axis, and neighboring layers are separated be Ag^+ cations. The As–O (167.3 – 170.0 pm) and V–O (162.7 – 232.6 pm) bond lengths agree well with those reported in the literature [21], where the shortest ones always belong to the terminal oxygen atoms.

Table 3. Selected bond lengths (pm) for Ag_2VAsO_6 and $Ag_6V_2As_2O_{13}$ at 298 K with estimated standard deviations in parentheses.

Ag_2VAsO_6		**$Ag_6V_2As_2O_{13}$**	
Ag1–O1	221.6(5)	Ag1–O3	237.1(2)
Ag1–O2	234.5(5)	Ag1–O3	241.5(2)
Ag1–O4	249.5(5)	Ag1–O5	246.8(2)
Ag1–O5	254.3(5)	Ag1–O6	249.1(2)
Ag2–O1	223.5(5)	Ag2–O3	226.9(2)
Ag2–O2	242.2(5)	Ag2–O6	231.1(2)
Ag2–O3	248.1(5)	Ag2–O7	255.0(2)
Ag2–O5	251.4(5)	Ag3–O1	255.1(2)
As–O1	167.4(4)	Ag3–O2	247.4(2)
As–O2	170.0(4)	Ag3–O4	244.6(2)
As–O3	168.7(5)	Ag3–O5	234.2(2)
As–O4	168.4(5)	Ag3–O6	237.7(2)
V–O2	217.6(4)	As–O2	169.5(2)
V–O3	194.8(5)	As–O3	169.8(2)
V–O4	195.9(5)	As–O4	169.8(2)
V–O5	168.3(4)	As–O6	168.4(2)
V–O5	232.6(5)	V–O1	185.2(2)
V–O6	162.7(5)	V–O2	201.9(2)
V–V	308.0(2)	V–O4	205.8(2)
		V–O5	166.6(2)
		V–O7	168.4(2)

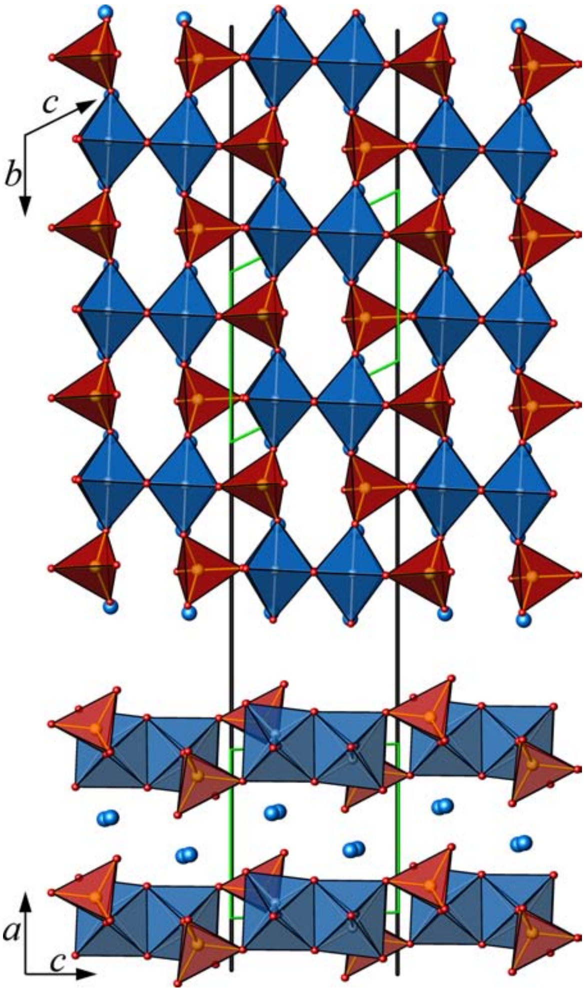

Fig. 1 (color online). Crystal structure of Ag_2VAsO_6. Top: view along [1 0 0], bottom: view along [0 1 0], with margins of the unit cell (green). Color code: AsO_4 tetrahedra (red), VO_6 octahedra (blue), blue spheres (Ag), red spheres (O). Black vertical lines direct attention to the structural relation between both compounds (see text).

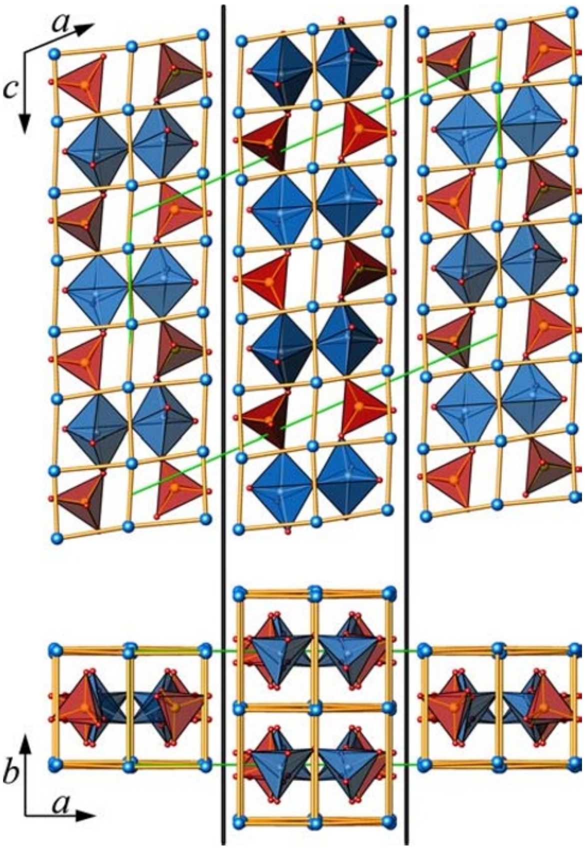

Fig. 2 (color online). Crystal structure of $Ag_6V_2As_2O_{13}$. Top: view along [0 1 0], bottom: view along [0 0 1]. Color code (*c.f.* Fig. 1): AsO_4 tetrahedra (red), VO_5 trigonal bipyramids (blue). Orange sticks emphasize the cuboidal arrangement of silver atoms, centered by the respective AsO_4 and VO_5 polyhedra.

$Ag_6V_2As_2O_{13}$ crystallizes monoclinically with space group $C2/c$ (Pearson code $mC92$, Wyckoff sequence $f11e$) in a unique structure type. Two distorted trigonal bipyramids VO_5, are condensed by one common corner to form V_2O_9 dinuclear units. These units are interlinked with AsO_4 tetrahedra by common vertices in order to build up one-dimensional ${}^{1}_{\infty}[V_2As_2O_{13}]^{6-}$ ladder-like, isolated rods (see Fig. 2), oriented along the c axis. Each polyhedron (bipyramid and tetrahedron) is surrounded by eight silver atoms in a cuboidal arrangement, which results in two-dimensional double layers of face-sharing cubes alternately occupied with VO_5 and AsO_4, see Fig. 2. The ${}^{1}_{\infty}[V_2As_2O_{13}]^{6-}$ rods in $Ag_6V_2As_2O_{13}$ can be derived from the ${}^{2}_{\infty}[VAsO_6]^{2-}$ layers in Ag_2VAsO_6 by cutting them along a virtual line passing through the AsO_4 tetrahedra (black, bold line in Figs. 1 and 2), and additional replacement of the O–O edge in the V_2O_{10} unit by one oxygen atom.

Conclusions

Applying high oxygen pressures, first examples of silver vanadato(V) arsenates(V) have been prepares by solid state reaction of respective mixtures of binary oxides. The resulting quaternary oxides display novel heteropolyoxo anions, where V^{5+} and As^{5+} show distinctly different crystal chemical properties. Since the pentavalent cations differ only slightly in size, another factor appears to be relevant. Obviously, the underlying electron configurations differ in as much as V^{5+} has empty low energy 3*d* states available for back bonding effects from oxygen, while for As^{5+} the 3*d* orbitals are fully occupied.

The building principles of the polyoxo anions offer plenty of freedom for generating further connectivity patterns, thus the energy landscape [22] of vanadatoarsenates is expected to be particularly rich in candidates, with new structures.

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