

Refinement of the Crystal Structure of Low Temperature Li_3VO_4 and Analysis of Mean Bond Lengths in Phosphates, Arsenates, and Vanadates

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Low-temperature (β_{II}) Li_3VO_4 is orthorhombic with $a = 6.3259 \pm 12$, $b = 5.4460 \pm 8$, and $c = 4.9469 \pm 9$ Å and space group, $Pmn2_1$. The structure, refined by least squares to a final $\omega R = .092$, is isotypic with that β_{II} Li_3PO_4 . It can be described as an ordered wurtzite structure with rows of Li(1) atoms alternating with rows of Li(2)-V-Li(2) atoms along [100]. All cations are tetrahedrally coordinated with mean distances $\langle \text{Li}(1)-\text{O} \rangle = 1.969$ Å, $\langle \text{Li}(2)-\text{O} \rangle = 1.995$ Å, and $\langle \text{V}-\text{O} \rangle = 1.717$ Å.

An analysis of mean tetrahedral distances in 62 phosphates, 21 arsenates, and 22 vanadates resulted in values of 1.537 ± 0.009 Å, 1.683 ± 0.010 Å and 1.721 ± 0.012 Å, respectively. A regression analysis of mean bond distance with average cation electronegativity shows a low correlation. However, if the mean distances are corrected for mean oxygen coordination, a high correlation exists between corrected bond distances (effective ionic radii) and mean electronegativity. This correlation suggests that the bond strength of nontetrahedral cations affects to some degree the mean and, therefore, the individual tetrahedral bond distances in phosphates, arsenates, and vanadates.

Introduction

In a recent publication (1) interatomic distances in germanates were analyzed as a function of oxygen coordination and the electronegativity of the cations. It was suggested that interatomic distances in tetrahedral oxyanions depend on both the number and nature of the cations surrounding the oxygen ions. Because the effect appeared to be more pronounced for vanadates than for germanates, several vanadates containing cations of widely differing electronegativity were chosen for careful structure refinement. The compounds chosen for this study were Li_3VO_4 , LiVO_3 , $\text{Cu}_5\text{V}_2\text{O}_{10}$, $\text{Cu}_3\text{V}_2\text{O}_8$ and $\text{Pb}_2\text{V}_2\text{O}_7$. The results of crystal structure refinements have been shown to vary depending upon how the data are taken and treated (2). In order to obtain a set of results consistent in this regard we have carried out a number of structure refinements of vanadates to be used for analysis of bond distances. In this paper we report the refinement of the crystal structure of low temperature Li_3VO_4 , and an analysis of mean tetrahedral distances in phosphates, arsenates, and vanadates.

Kohlmuller and Martin (3), Reisman and Mineo (4) and Wickham (5) in studies of the $\text{Li}_2\text{O}-\text{V}_2\text{O}_5$ System showed that Li_3VO_4 melts congruently at 1152°C and on cooling undergoes three reversible phase transitions. Recently West and Glasser (6) studied these transitions in detail and found at least five different forms of Li_3VO_4 . Low temperature Li_3VO_4 is one of these polymorphs and has been named the β_{II} phase by West and Glasser. Kohlmuller and Martin (3) published a powder diffraction pattern of β_{II} Li_3VO_4 but were unable to determine the structure type from these data. Blasse (7) prepared Li_3VO_4 and indexed the powder diffraction pattern on the basis of the high-temperature form of Li_3PO_4 ; however, because of the ease of reversibility of the high-low transition, it is probable that he had the low temperature form. In 1967 Tarte (8) identified the structure of β_{II} Li_3VO_4 as isotypic with that of β_{II} Li_3PO_4 by comparison of the X-ray powder patterns and ir spectra.

Experiments

Reagent grade Li_2CO_3 (B and A) and spectrographic grade V_2O_5 (Johnson-Matthey) were

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mixed in stoichiometric quantities, heated in a Pt crucible to 1200°C for 4 hr, cooled to 900°C at 5°C/hr, and allowed to cool from 900°C to room temperature with the furnace. The product was composed of translucent orange fragments.

X-ray diffraction patterns were obtained at 25°C using a H \ddot{a} gg-Guinier camera with monochromatic $\text{CuK}\alpha$ radiation. The "d" values were calculated using $\lambda(\text{CuK}\alpha) = 1.54051 \text{ \AA}$ with KCl internal standard ($a = 6.2931 \text{ \AA}$). The pattern was indexed on the basis of the orthorhombic cell reported for Li_3PO_4 consistent with the space group extinctions for $Pmn2_1:h0l$, $h + l = 2n$. The cell dimensions thus obtained were: $a = 6.3259 \pm 12$, $b = 5.4460 \pm 8$, $c = 4.9469 \pm 9 \text{ \AA}$ and $V = 170.42 \text{ \AA}^3$.

Differential thermal analysis carried out on a DuPont series 900 unit showed endothermic peaks on heating at 717°, 780°, and 1150°C. These transitions correspond reasonably well with those found by Reisman and Mineo at 724°, 773° and 1152°C. The endotherms at 540° and 1058°C reported by West and Glasser (6) were not observed.

A single crystal was selected and ground into a sphere of radius 0.021 cm ($\mu r = 0.81$). Precession patterns confirmed the space group extinctions assumed earlier from powder data. Space group $Pmn2_1$ was assumed by analogy with Li_3PO_4 (9). Other crystal data are formula weight = 135.76, $D_x = 2.644 \text{ g/cm}^3$ and $\mu(\text{MoK}\alpha) = 37.7 \text{ cm}^{-1}$.

Intensities were collected on a Syntex automatic diffractometer using $\text{MoK}\alpha$ radiation, 4° takeoff angle, a graphite monochromator ($2\theta = 12^\circ$) and a scintillation detector. Reflections were scanned in the 2θ - θ mode at 2.0–24.0°/min depending on the peak count through an angle of

2° plus the α_1 - α_2 separation. Background counts were made at the extreme of each scan for times equal to the peak count. A total of 960 symmetry-independent reflections were measured out to $2\theta = 100.4^\circ$; 890 were considered to be observed. A number of reflections saturated the counter and were not included in the data: these are 002, 10 $\bar{1}$, 101, 200, 400, 01 $\bar{1}$, 110, 210, 020, and 230. Intensities with less than three times the standard deviation of the background were considered unobserved. The intensities were corrected for absorption and Lorentz and polarization factors using the X-ray 67 Program System for X-ray Crystallography written by J. M. Stewart, Univ. of Maryland and adapted to the CDC 6400 computer by H. D. Grundy.

Starting with the atomic positional parameters for Li_3PO_4 (9) the structure was refined using the full-matrix least-squares program CUDLS (10). The scattering factors for Li^+ , V^+ , and O^- were taken from the International Tables for Crystallography, Vol. III (11). Real and imaginary anomalous dispersion corrections for V were taken from Cromer (12). Refinement of the atom parameters and isotropic temperature factor reduced ωR to 3.8% using unit weights. Several more cycles of refinement using isotropic temperature factors and a weighting scheme, $\omega = (0.0264 - 0.0067|\text{Fo}| + 0.0012|\text{Fo}|^2)^{-1}$ reduced ωR to 0.0291 and R to 0.0229 where

$$\omega R = \{\sum \omega ||\text{Fo}| - |\text{Fc}|^2 / \sum \omega |\text{Fo}|^2\}^{1/2}.$$

At this point the parameter shifts were less than 10% of the standard deviation of the shift. The standard deviation of an observation of unit weight was 0.98.

The final values of parameters for Li_3VO_4 are

TABLE I
ATOM PARAMETERS FOR Li_3VO_4^a

Atom	x	y	z	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li(1)	0.2470(5)	0.3315(4)	0.9872(22)	0.0126(8)	0.0147(10)	0.0178(10)	-0.0006(6)	-0.0029(24)	0.0005(13)
Li(2)	1/2	0.8326(6)	0.9848(30)	0.0128(11)	0.0150(15)	0.0179(15)	—	—	0.0003(19)
V	0	0.82961(4)	0	0.0057(1)	0.0076(1)	0.0075(1)	—	—	0.0002(1)
O(1)	0.2239(2)	0.6804(2)	0.8931(2)	0.0081(2)	0.0109(4)	0.0119(3)	0.0013(2)	0.0010(3)	-0.0006(3)
O(2)	0	0.1296(3)	0.8952(3)	0.0090(3)	0.0076(5)	0.0129(4)	—	—	0.0012(4)
O(3)	1/2	0.1736(3)	0.8478(3)	0.0086(4)	0.0122(7)	0.0093(4)	—	—	-0.0002(3)

^a Estimated standard deviations are in parentheses.

^b Calculated from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where $T = \exp[-(\beta_{11}h^2 + 2\beta_{12}hk + \dots)]$ is the temperature factor appearing in the structure factor equation and b_i 's are reciprocal lattice vectors.

TABLE III
BOND DISTANCES AND ANGLES IN Li_3VO_4^a

Bond	Distance, Å	Angle	(°)	Angle	(°)
Li(1)–O(1)	1.974(4)	O(1b)–Li(1)–O(2)	108.0(3)	O(2)–Li(1)–O(3)	107.8(3)
–O(1b)	1.968(11)	–O(3)	106.5(3)	–O(1)	114.3(3)
–O(2)	1.976(4)	–O(1)	107.3(4)	O(3)–	–O(1)
–O(3)	1.961(5)				112.6(3)
$\langle \text{Li}(1)\text{--O} \rangle = 1.969$					
Li(2)–O(1)	1.997(4)	O(1)–Li(2)–O(2b)	107.1(5)	O(2b)–Li(2)–O(3)	105.5(4)
–O(1a)	1.997(4)	–O(3)	107.2(4)	–O(1a)	107.1(5)
–O(2b)	1.992(15)	–O(1a)	121.9(5)	O(3)–	–O(1a)
–O(3)	1.994(6)				107.1(4)
$\langle \text{Li}(2)\text{--O} \rangle = 1.995$					
V–O(1)	1.717(1)	O(1)–V–O(1a)	111.22(5)	O(1a)–V–O(2)	110.98(5)
–O(1a)	1.717(1)	–O(2)	110.98(5)	–O(3b)	107.64(5)
–O(2)	1.714(1)				
–O(3b)	1.720(1)	–O(3b)	107.64(5)	O(2)–V–O(3b)	108.20(7)
$\langle \text{V--O} \rangle = 1.717$					

^a Symmetry transformations $a = -x, y, z$; $b = 1/2 - x, -y, 1/2 + z$; $c = x + 1/2, -y, z + 1/2$

oxygens located at $z = 0.893, 0.895, \text{ and } 0.848$. The magnitude of these peaks indicates probably less than 1/2 % of the twin image.

Notice should be taken of the anomalously high estimated standard deviations for the z coordinates of both Li ions in the present structure and in Li_3PO_4 . Although the correlation coefficient between the z coordinates and the U_{13} values for the same ion are as high as 0.36, refining these parameters separately had no effect. It is thus likely that this effect results from small terms in the matrix arising from the nearly special positions occupied by these ions.

The absolute configuration of the crystal was determined by refining the parameters in both the (+ z) and (– z) configuration. The ωR value for the + z configuration was 0.0291 and for the – z configuration, 0.0298. The hypothesis that the crystal has the + z configuration may be tested using Hamilton's (13) significance test by comparing the ratio of $\omega R(xy\bar{z})/\omega R(xyz) = 1.034$. The value of $R_{1,916,0.005}$ is 1.004. We can thus reject at the 0.005 confidence level the choice of the – z configuration.

Discussion

Description of Structure

The structure can be described as an ordered wurtzite structure. Figure 1 shows that the

oxygens are hexagonal close-packed with Li(1) atoms running along the [100] directions at $y \cong 1/3, z \cong 0$ and $y \cong 2/3, z \cong 1/2$. In alternate rows along [100] are rows of Li(2)–V–Li(2) at $y \cong 1/6, z \cong 1/2$, and $y \cong 5/6, z \cong 0$. The relationship of the orthorhombic Li_3VO_4 cell to the hexagonal wurtzite cell is: $a_{\text{ortho}} = 2a_{\text{hex}} + 2b_{\text{hex}}$, $b_{\text{ortho}} = a_{\text{hex}} - b_{\text{hex}}$ and $c_{\text{ortho}} = c_{\text{hex}}$. A comparison

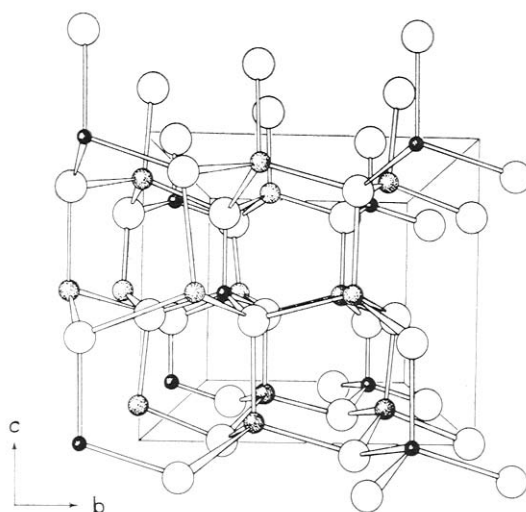


FIG. 1. Perspective of $\beta_{11}\text{Li}_3\text{VO}_4$. Large open spheres are oxygen atoms, shaded spheres are lithium atoms, and small solid spheres are vanadium atoms.

of the pseudo-orthorhombic ZnO cell (14) with the Li_3VO_4 cell is consistent with ionic radii of IVZn^{2+} (0.60) and $\frac{1}{4}(3\text{IVLi}^+ + \text{IVV}^{5+})$ (.54):

	<i>a</i>	<i>b</i>	<i>c</i>
ZnO	6.500 Å	5.630	5.207
Li_3VO_4	6.326 Å	5.446	4.947

As described by Keffer *et al.* (9) all atoms are tetrahedrally coordinated with corner-shared lithium and vanadium tetrahedra. The average $\text{Li}(1)\text{-O}$ and $\text{Li}(2)\text{-O}$ distances in $\beta_{11}\text{Li}_3\text{VO}_4$ are 1.969(6) and 1.995(7) Å as compared with 1.957(16) and 2.004(17) Å in $\beta_{11}\text{Li}_3\text{PO}_4$ (9). The distance predicted from the effective ionic radii of Shannon and Prewitt (15) for four coordinated Li^+ and O^{2-} is 1.970 Å. The mean V-O distance is 1.717(1) and may be compared with that predicted from the radii, 1.735 Å. The individual Li-O and V-O distances are not significantly different from the mean values of their tetrahedra.

The VO_4 tetrahedral angles are close to the ideal value of 109.5° ranging from 107.6° to 111.2° whereas the LiO_4 groups deviate significantly from ideality with angles ranging from 105.5° to 121.9° . The oxygen atoms, being tightly bonded to the V atoms, would be expected to form a regular tetrahedron; however, the weaker bonds to the Li atoms result in large deviations from regularity. This deviation is more clearly seen by looking at the environment of the three

oxygen atoms in Table IV. The V-O-Li angles range from 110.8 to 116.9° while the Li-O-Li angles range from 101.3 to 109.4° . This behavior can probably be explained by the greater repulsion between $\text{Li}^+\text{-V}^{5+}$ than $\text{Li}^+\text{-Li}^+$.

Mean Interatomic Distances in Phosphates, Arsenates, and Vanadates

It has frequently been assumed that mean interatomic distances in tetrahedral oxyanions are relatively constant from one structure to another. The relative constancy of the mean tetrahedral lengths have been demonstrated for sulfates by Baur (16), Jönsson and Hamilton (17), Larson (18), and Taesler and Olavsson (19), for phosphates by Baur and Khan (20), by Whitaker and Jeffrey (21), and by Mootz and Wunderlich (22), and for arsenates by Baur and Khan (20). The numerous tables of ionic radii [Goldschmidt *et al.* (23), Pauling (24), Zachariasen (25), Ahrens (26) and Shannon and Prewitt (15)] are based on the assumption that average interatomic distances are relatively constant for any specific set of polyhedral M-O distances and Baur's (27) scheme for predicting distances from bond strength variation around oxygen atoms is predicated on the relative constancy of average interatomic distances. However, Baur and Khan (20) indicate that some averages of individual phosphate groups are significantly different from the overall average of a number of accurately determined structures containing phosphate groups. Cruickshank and Robinson (28) note that mean S-O lengths increase in going from SO_4^{2-} to neutral molecules. Furthermore, several authors have proposed that average interatomic distances depend on average oxygen coordination number and that individual interatomic distances depend on the electronegativity of other cations in the structure [Noll (29), Lazarev (30), Brown and Gibbs (31), and Shannon (1)]. It was therefore felt worthwhile to look in detail at the average interatomic distances in phosphates, arsenates, and vanadates.

In Table V the mean bond distances in a number of accurately determined tetrahedrally coordinated phosphate, arsenate, and vanadate crystal structures are listed along with mean electronegativities of the cations as was recently done for germanate structures. The mean electronegativity values were calculated as described in reference (1). The standard deviations, $\bar{\sigma}$, listed in column 3 of Table V were estimated from the e.s.d.'s of individual distances. Following the list

TABLE IV
ANGLES ABOUT OXYGEN ATOMS

Bonds	Angle ($^\circ$)
$\text{V-O}(1)\text{-Li}(1)$	115.9
$\text{-Li}(1b)$	113.5
$\text{-Li}(2)$	116.6
$\text{Li}(1)\text{-Li}(1b)$	102.8
$\text{-Li}(2)$	105.6
$\text{Li}(2)\text{-Li}(1b)$	100.5
$\text{V-O}(2)\text{-Li}(1)$	117.0
$\text{-Li}(1a)$	117.0
$\text{-Li}(2)$	113.5
$\text{Li}(1)\text{-Li}(1a)$	104.5
$\text{-Li}(2)$	101.3
$\text{Li}(2)\text{-Li}(1a)$	101.3
$\text{V-O}(3)\text{-Li}(1)$	112.4
$\text{-Li}(1a)$	112.4
$\text{-Li}(2)$	110.8
$\text{Li}(1)\text{-Li}(2a)$	109.4
$\text{-Li}(2)$	105.7
$\text{Li}(2)\text{-Li}(1a)$	105.7

TABLE V
Mean Electronegativities and Mean Tetrahedral
Distances in Phosphates, Arsenates, and Vanadates

(A) Phosphates

\bar{X}	\bar{R}	$\bar{\sigma}$	Compound	Reference*
2.200	1.542	.003	H3 P 04	70 ACBCA 26 1826
2.190	1.540	.020	P2 05	64 ACCRA 17 679
2.170	1.522	.003	MO O P 04	70 ACSAA 24 427
2.160	1.543	.005	FE AL2(P 04)2(OH)2(OH2)6*2 H2 O	69 NJMMA 430
2.150	1.532	.010	MN FE2(P 04)2(OH)2*8 H2 O	69 AMMIA 54 1312
2.140	1.534	.020	MN FE2(OH)2(P04)2(H2 O)6*2 H2 O	65 AMMIA 50 1884
2.130	1.535	.020	(AL P 04 OH OH2)2*(FE(OH2)6)	67 NATWA 54 561
2.120	1.530	.020	FE AL2(P04)2(OH)2(OH2)4*2 H2 O	68 AMMIA 53 1025
2.110	1.539	.005	H3 P 04*1/2 H2 O	70 ACBCA 26 1826
2.110	1.542	.002	FE3 P2 08*4 H2 O	66 JCPSA 44 2223
2.100	1.544	.003	MG H P 04*3 H2 O	67 ACCRA 23 418
2.100	1.535	.010	FE FE5 (OH)5 (P 04)4*6 H2 O	67 ACCRA 22 173
2.090	1.526	.011	SI P2 07	70 ACBCA 26 233
2.080	1.525	.004	AL3 P2 08(OH)3*5 H2 O	68 ZEKGA 127 21
2.070	1.544	.002	NA2 H2 P2 07*6 H2 O	71 ACBCA 27 291
2.070	1.535	.002	CA (H2 P 04)2*H2 O	71 ACBCA 27 2247
2.060	1.551	.004	NA2 H P 04*7 H2 O	70 ACBCA 26 1584
2.050	1.549	.020	FE1.8 MN.8 CA1.4 P2 08	68 AMMIA 53 742
2.030	1.534	.007	A-CO2 P2 07	UNPU1 REF 32
2.030	1.538	.007	A-CU2 P2 07	67 ACCRA 22 665
2.040	1.516	.015	B-CU2 P2 07	68 CJCHA 46 605
2.020	1.530	.004	K H5 (P 04)2	71 ACSAA 25 512
2.010	1.540	.006	CA H P 04*2 H2 O	71 JCSIA 3725
2.000	1.538	.005	NA4 P2 07*10 H2 O	67 ACCRA 22 43
2.000	1.519	.003	AL2 (P 04) (OH)3	68 AMMIA 53 1096
1.970	1.529	.015	SR AL3 (P 04)2 (OH)5*H2 O	71 NJMMA 69 241
1.940	1.542	.015	CD2 P2 07	69 CJCHA 47 3409
1.920	1.533	.009	A-ZN2 P2 07	70 JSSCB 1 120
1.910	1.558	.015	B-ZN2 P2 07	65 CJCHA 43 1147
1.900	1.528	.009	NB O P 04	66 ACSAA 20 72
1.900	1.515	.002	AL P 04	66 ZEKGA 161 123
1.870	1.540	.012	CD ZN2 P2 08	68 CJCHA 46 903
1.870	1.537	.005	A-ZN3 P2 08	UNPU1 REF 33
1.860	1.530	.008	B-ZN3 P2 08	67 CJCHA 45 2303
1.870	1.548	.010	G-ZN3 P2 08	UNPU1 REF 33
1.850	1.538	.005	K H2 P 04	53 PRLAA 220 397
1.840	1.548	.016	NA4 P4 012*4 H2 O	61 ACCRA 14 555
1.830	1.546	.007	CA2 MN (P 04)2*2 H2 O	70 ACBCA 26 640
1.810	1.537	.020	B-MN3 P2 08	69 CJCHA 47 2215
1.810	1.541	.002	CA H P 04	71 JCSIA 3725
1.790	1.536	.006	(MN,FE)2 F P 04	69 ZEKGA 130 1
1.770	1.522	.009	K ZR2 (P 04)3	69 ZEKGA 130 148
1.760	1.542	.004	MN2 P 04 CL	UNPU1 REF 34
1.740	1.535	.010	A-MG2 P2 07	67 ACCRA 23 289
1.750	1.543	.009	B-MG2 P2 07	65 CJCHA 43 1139
1.730	1.534	.010	LI AL P 04 (OH,F)	59 ACCRA 12 988
1.710	1.531	.013	NA ZR2 (P 04)3	68 ACSAA 22 1822
1.700	1.547	.013	LI K2 P3 09*H2 O	62 ACCRA 15 1280
1.670	1.544	.003	LI FE P 04	69 CIWYA 68 290
1.660	1.526	.008	MG3 P2 08	68 ACSAA 22 1466
1.590	1.534	.009	A-CA2 P2 07	68 INOCA 7 1345
1.600	1.542	.020	B-CA2 P2 07	66 ACCRA 21 942
1.570	1.540	.010	LI MN P 04	60 ACCRA 13 325
1.560	1.549	.005	NA3 P3 09	65 ACCRA 18 226
1.560	1.523	.014	A-SR2 P2 07	68 ACSAA 22 1419
1.530	1.540	.008	CA10 (P 04)6 (OH)2	64 NATUA 204 1050
1.410	1.540	.002	CA2 P 04 CL	70 INOCA 9 2259
1.350	1.542	.002	NA4 P2 07	UNPU1 REF 35
1.290	1.555	.020	LI3 P J4	60 ACCRA 13 863
1.280	1.546	.007	LI3 P 04	67 INOCA 6 119
1.260	1.526	.004	NA3 P 04*12 H2 O	71 ACBCA 27 2124

WEIGHTED AVERAGE = 1.537, STANDARD DEVIATION = .009

TABLE V—continued

(B) Arsenates

\bar{X}	\bar{R}	$\bar{\sigma}$	Compound	Reference*
2.190	1.693	.010	AS2 O5.5/3 H2 O	66 ACCRA 21 808
2.140	1.683	.012	CU2 AS O4 OH*3H2 O	66 ACCRA 21 437
2.080	1.704	.026	CU3 AS O4 (OH)3	65 ACCRA 18 777
2.070	1.667	.010	ZR(H AS O4)2*H2 O	69 ACBCA 25 2658
2.060	1.678	.004	NA2 H AS O4*7 H2 O	70 ACBCA 26 1584
2.060	1.688	.004	NA2 H AS O4*7 H2 O	70 ACBCA 26 1574
2.020	1.686	.009	CA H AS O4*2 H2 O	69 ACBCA 25 1544
2.010	1.683	.014	ZN4 AS2 O8 (OH)2*2 H2 O	71 AMMIA 56 1147
2.000	1.687	.020	CU3 AS2 O8	68 CJCHA 48 917
1.990	1.690	.007	CO3 AS2 O8	70 CJCHA 48 881
1.960	1.682	.010	CO8 AS3 O16	70 CJCHA 48 3124
1.920	1.679	.030	MN7 (OH)8 (AS O4)2	68 AMMIA 53 733
1.910	1.678	.014	ZN2 CU AS2 O8	69 ZEKGA 130 231
1.890	1.697	.012	CD3 AS2 O8	70 ZEKGA 132 332
1.790	1.686	.008	CA H AS O4	70 ACBCA 26 403
1.740	1.661	.006	MG2 AS2 O7	70 CJCHA 48 890
1.720	1.694	.010	LI MO O2 AS O4	70 ACSAA 24 3711
1.540	1.683	.003	MG8.5 AS3 O16	UNPU1 REF 36
1.400	1.687	.005	NA4 AS2 O7	UNPU1 REF 37
1.390	1.684	.001	CA2 AS O4 CL	70 INOCA 9 2259
1.260	1.669	.006	NA3 AS O4*12 H2 O	71 ACBCA 27 2124

WEIGHTED AVERAGE = 1.683, STANDARD DEVIATION = .010

(C) Vanadates

1.820	1.724	.005	CU5 V2 O10	UNPU1 REF 38
1.800	1.734	.004	NI3 V2 O8	UNPU1 REF 33
1.790	1.725	.005	CU3 V2 O8	UNPU1 REF 38
1.780	1.732	.005	CO3 V2 O8	UNPU1 REF 39
1.750	1.730	.002	CO2 V2 O7	UNPU1 REF 39
1.730	1.723	.012	P82 V2 O7	UNPU1 REF 38
1.730	1.722	.007	FE V O4	72 JSSCB 4 29
1.660	1.717	.020	CD2 V2 O7	67 CJCHA 45 2297
1.640	1.720	.008	ZN3 V2 O8	71 CJCHA 49 3056
1.630	1.715	.005	ZN2 V2 O7	UNPU1 REF 40
1.590	1.707	.020	MN2 V2 O7	67 ACSAA 21 590
1.440	1.728	.001	MG3 V2 O8	71 CJCHA 49 1629
1.430	1.720	.020	ER V O4	68 CPLT1 2 47
1.420	1.706	.008	Y V O4	68 ACBCA 24 292
1.380	1.721	.005	ND V O4	71 JSSCB 3 458
1.310	1.727	.002	LI V O3	UNPU1 REF 38
1.290	1.695	.010	CA3 V2 O8	UNPU1 REF 40
1.220	1.731	.010	K V O3	60 ZEKGA 114 257
1.210	1.707	.002	CA2 V O4 CL	70 INOCA 9 2259
1.180	1.707	.030	BA3 V2 O8	70 ZEKGA 131 161
1.150	1.717	.002	LI3 V O4	THIS PAPER
1.140	1.691	.007	NA3 V O4*12 H2 O	71 ACBCA 27 2124

WEIGHTED AVERAGE = 1.721, STANDARD DEVIATION = .012

* CODENS FOR PERIODICAL TITLES, Vol II, ASTM Data Series DS 23A, Phila., 1966.

of compounds in Table V are the grand mean $M^{5+}-O$ distances (weighted by $1/\bar{\sigma}$) and their standard deviations. The grand mean $P^{5+}-O$ distance for 62 phosphates is 1.537 ± 0.009 and agrees well with that found by Whitaker and

Jeffrey (21), 1.537 ± 0.001 Å, using a mixture of eight hydrous and anhydrous phosphates, by Baur (27), 1.537 Å, using 174 P-O distances, by Baur and Khan (20), 1.539 Å, using nine H-containing phosphates, and by Mootz and

Wunderlich (22), 1.539 Å, using nine H-containing phosphates. The grand weighted mean $\text{As}^{5+}\text{-O}$ distance of 1.683 ± 0.010 Å listed in Table V for 21 arsenates is in agreement with that of 1.680 Å tabulated for three arsenates by Baur

and Khan (20). The grand mean $\text{V}^{5+}\text{-O}$ distance calculated from 22 vanadates is 1.721 ± 0.012 Å.

In Figs. 2a-c we have plotted the mean tetrahedral distances (R) in phosphates, arsenates, and vanadates vs the mean cation electronegativity

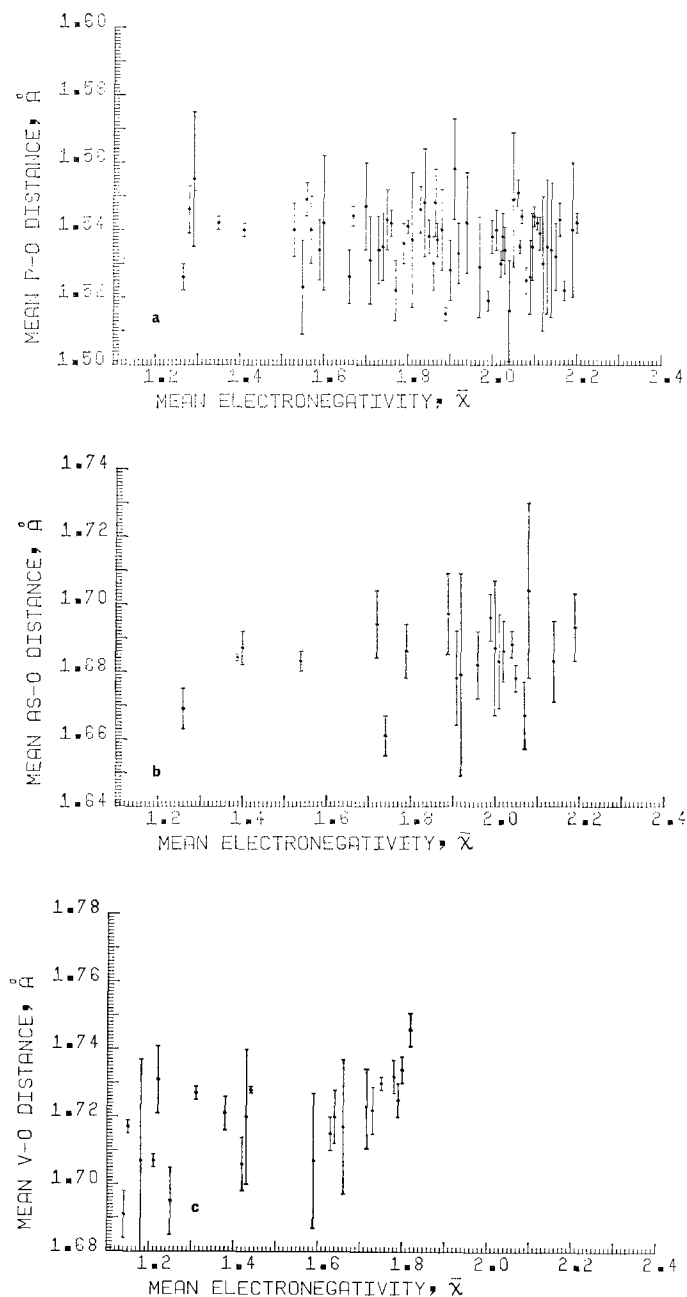


FIG. 2. (a) Mean P-O distance vs mean cation electronegativity. Vertical bars represent average e.s.d. quoted by authors. (b) Mean As-O distance vs mean cation electronegativity. (c) Mean V-O distance vs mean cation electronegativity.

TABLE VI
CORRELATIONS OF ELECTRONEGATIVITY WITH MEAN TETRAHEDRAL $\text{P}^{5+}\text{-O}$, $\text{As}^{5+}\text{-O}$,
AND $\text{V}^{5+}\text{-O}$ DISTANCES UNCORRECTED AND CORRECTED FOR COORDINATION OF
OXYGEN

Ion	N	Slope*, m	Intercept, C_1	Correlation coefficient, r_{cc}	Goodness of fit $\left\{\frac{\sum(\Delta r)^2}{N-2}\right\}^{1/2}$	Probability that $r > r_{cc}$
(a) Uncorrected ^a						
P^{5+}	62	-0.004	1.545	0.12	0.009	$\gg 0.10$
As^{5+}	21	0.004	1.676	0.15	0.010	$\gg 0.10$
V^{5+}	22	0.024	1.686	0.55	0.010	< 0.01
(b) Corrected ^b						
P^{5+}	62	0.029	0.120	0.68	0.009	< 0.001
As^{5+}	20	0.036	0.255	0.85	0.010	$\ll 0.001$
V^{5+}	22	0.051	0.279	0.80	0.010	< 0.001

$$^a R = m\bar{\chi} + C_1$$

$$^b r = m\bar{\chi} + C_1$$

values, $\bar{\chi}$. In addition a least-squares regression analysis of R on $\bar{\chi}$ was calculated for the three sets of data with R weighted by $1/\bar{\sigma}$. The results are tabulated in Table VIa. It is apparent that there is little or no dependence of the mean P-O and As-O distances on $\bar{\chi}$ and only a slight dependence of V-O distances on $\bar{\chi}$. This is in agreement with Baur (41) who found no correlation of individual Si-O distances with the electronegativity of the M ion for a series of isostructural pyroxenes with the formula $\text{MM}'\text{Si}_2\text{O}_6$. However, the scatter of the individual mean bond distances from the grand mean value suggests that other factors affect the mean distance. Among these factors one would suspect first those factors which determine an individual tetrahedral $\text{M}^{5+}\text{-O}$ bond distance: (1) the number, (2) the valence, (3) the distance, and (4) the electronegativity of cations other than M^{5+} bonded to oxygen. Using just factors (1), (2), and to some extent (3), Baur (27) was able to predict within 0.01 Å the individual bond distances in many tetrahedral oxyanions. In addition to these factors, mean distances in $\text{V}^{5+}\text{-O}$ polyhedra can be shown to depend on the degree of distortion from regularity (42). Since this effect has not been carefully analyzed in tetrahedra and because it is believed to be smaller than factors 1-4, it will be ignored in the following discussion. All of these factors are closely inter-related and it is difficult to distinguish individual effects.

If one accepts the analyses of bond distances carried out for a variety of oxides by Shannon and Prewitt (15) and for silicates by Brown and Gibbs (43), mean bond distances also depend on oxygen coordination. If this dependence is removed by correcting the mean bond distances for oxygen coordination and thus deriving effective ionic radii of P^{5+} , As^{5+} , and V^{5+} as a function of $\bar{\chi}$, plots of $r(\text{M}^{5+})$ vs $\bar{\chi}$ (Fig. 3a-c) show a marked slope. Linear regression analysis of these data result in correlation coefficients of 0.68, 0.85 and 0.80 respectively for P^{5+} , As^{5+} and V^{5+} . In view of the fact that electronegativities have been shown to depend on hybridization and therefore the coordination (44), this strong correlation between r and $\bar{\chi}$ is surprisingly good. However, the goodness of fit parameters are only slightly better than the standard deviations obtained for the mean \bar{R} values.

It is informative to look at the $\text{V}^{5+}\text{-O}$ plot in more detail. Although $\bar{\chi}$ does not differ greatly for Li_3VO_4 and LiVO_3 (1.15 and 1.31, respectively), the radii are appreciably different ($r = 0.337$ and 0.360 Å). The mean electronegativity values do not take into consideration that all oxygen atoms in Li_3VO_4 are coordinated to only one V atom whereas in LiVO_3 two of the oxygen atoms share two V atoms. The result is two very long bonds at 1.795 and 1.821 Å and two short bonds at 1.662 and 1.628 Å. These two long bonds evidently increase the average bond distance.

Another discrepancy occurs when the average

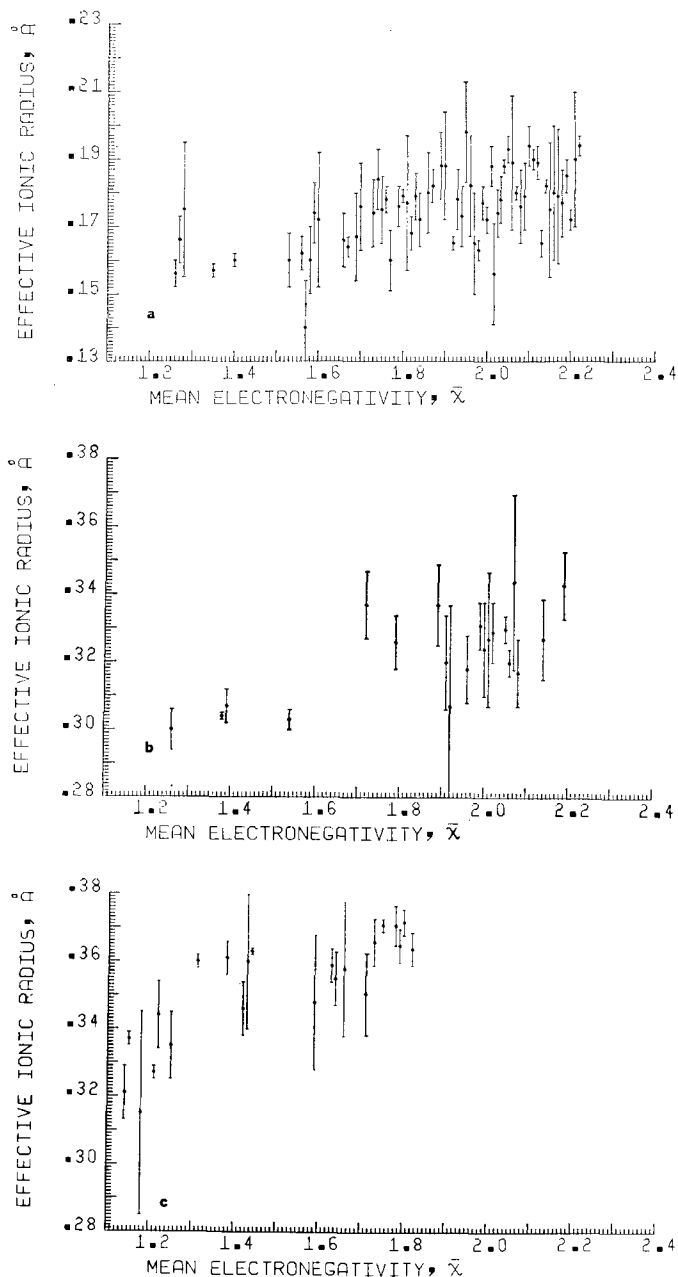


FIG. 3. (a) Effective ionic radius of P^{5+} vs mean cation electronegativity. (b) Effective ionic radius of As^{5+} vs mean cation electronegativity. (c) Effective ionic radius of V^{5+} vs mean cation electronegativity.

cation electronegativity of $Na_3VO_4 \cdot 12H_2O$ is calculated. Since the composition is dominated by H atoms, $\bar{\chi} = 2.1$. Indeed if this value of $\bar{\chi}$ were used in the r vs $\bar{\chi}$ plot, it would deviate significantly from the trend indicated in Fig. 3c. It is apparent that this number is not a good indication of the electronegativity of the nontetrahedral

atoms bonded to the oxygen atoms of the VO_4 tetrahedra. Each H atom is weakly bonded to these oxygen atoms. The bond strength assigned by Tillmans and Baur (45) is 0.17 per H atom and thus is approximately equivalent to a six-coordinated Na atom in bond strength. Thus in Table V we have treated these H atoms like Na

atoms and obtain a value of $\bar{\chi} = 1.14$. Similar values were obtained for $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$.

Evidently the mean electronegativity parameter, although it provides a good correlation between r and $\bar{\chi}$ (omitting $\text{Na}_3\text{XO}_4 \cdot 12\text{H}_2\text{O}$ where $X = \text{P, As and V}$) and it has the advantage of simplicity when comparing a large number of distances, is not entirely appropriate for determining the effects of next nearest neighbours on mean bond distances. Unfortunately it does not take into account (1) structural differences such as exist between orthovanadates and metavanadates, and (2) differences between strongly and weakly bonded H atoms. An approach which analyzes the explicit effects of cations around each individual oxygen atom in terms of valence, coordination number, electronegativity, and distance will likely be more successful. Gopal (46) has shown that an analysis similar to Baur's (27) made on tetrahedral V-O distances can predict individual V-O distances to within 0.01 Å. Because this approach considers only valence and CN of the cations surrounding each oxygen atom, it suggests that consideration of electrostatic bond strength alone or in combination with electronegativity might be more effective than $\bar{\chi}$ as a parameter.

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