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Crystal Chemical Aspects of Vanadium: Polyhedral Geometries, Characteristic Bond Valences, and Polymerization of (VO_n) Polyhedra

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The distribution of bond lengths in $(V^{3+}O_6)$ polyhedra shows a maximum between 1.98 and 2.04 Å, and limits of 1.88 and 2.16 Å, respectively. The bond lengths in $(V^{4+}O_n)$ and $(V^{5+}O_n)$ ($n = 5, 6$) polyhedra show distinct populations which allow us to define the following types of bonds: (1a) vanadyl bonds in $(V^{4+}O_n)$ polyhedra, shorter than 1.74 Å; (1b) vanadyl bonds in $(V^{5+}O_5)$ polyhedra, shorter than 1.76 Å; (1c) vanadyl bonds in $(V^{5+}O_6)$ polyhedra, shorter than 1.74 Å; (2a) equatorial bonds in $(V^{4+}O_n)$ polyhedra, in the range 1.90 to 2.12 Å; (2b) equatorial bonds in $(V^{5+}O_5)$ polyhedra, longer than 1.76 Å; (2c) equatorial bonds in $(V^{5+}O_6)$ polyhedra with one vanadyl bond, in the range 1.74 to 2.10 Å; (2d) equatorial bonds in $(V^{5+}O_6)$ polyhedra with two vanadyl bonds, in the range 1.80 to 2.00 Å; (3a) *trans* bonds in $(V^{4+}O_6)$ polyhedra, longer than 2.10 Å; (3b) *trans* bonds in $(V^{5+}O_6)$ polyhedra with one vanadyl bond, longer than 2.15 Å; (3c) *trans* bonds in $(V^{5+}O_6)$ polyhedra with two vanadyl bonds, longer than 2.025 Å. The average equatorial bond length in $(V^{4+}O_n)$ and $(V^{5+}O_n)$ polyhedra can be used to calculate the mean valence state of V in mixed-valent structures. We define characteristic bond valences for vanadyl, equatorial, and *trans* bonds in different coordinations and examine which binary linkages are possible and which linkages occur in minerals and synthetic compounds. Here, $V^{5+}-O-V^{5+}$, $V^{5+}-O-V^{4+}$, and $V^{4+}-O-V^{4+}$ linkages between vanadyl−*trans* and equatorial−equatorial bonds occur often in synthetic compounds, whereas the corresponding $V^{4+}-O-V^{4+}$ linkages are rare in minerals.

Introduction

In the past few years, new synthetic strategies have been developed to find suitable catalysts for higher selectivity in chemical reactions. At first, these new synthetic pathways included aluminosilicate and aluminophosphate zeolites, which show high selectivity for molecular shape through their well-defined pores and cages. Subsequent work has attempted to combine the well-known catalytic properties of transition elements with the shape-selective capacity of zeolites (e.g., vanadium−KVS-5[1]). Synthesis of compounds containing vanadium increased dramatically after the work of Centi et al.[2] which described the catalytic conversion of C_4 hydrocarbons to maleic anhydride over divanadyldiphosphate, $(VO)_2P_2O_7$; the product of catalytic conversion, maleic anhydride, is used for the production of unsaturated polyesters. In $(VO)_2P_2O_7$, $(V^{4+}O_5)$ pyramids link with diphosphate groups to form a dense layer structure. Subsequent synthesis of a large number of vanadium compounds has yielded exotic new structure types; examples include a vanadium phosphate double helix[3] and microporous vanadium phosphates[4−6] with V_5O_9 groups in the shape of a spiked helmet.

Evans[7] surveyed the crystal chemistry of vanadium compounds, mainly with reference to mineral structures, and Evans and White[8] developed a classification scheme for 119 vanadium minerals. Recently, Zavalij and Whittingham[9] discussed the crystal chemistry of vanadium oxides with open frameworks, addressing vanadate compounds constructed from $(^{[5]}VO_5)$ and $(^{[6]}VO_6)$ polyhedra and without other oxyanion groups such as (SiO_4), (PO_4), (SO_4), and (AsO_4). Crystal-chemical data for vanadium-bearing structures, including synthesis and magnetic, optical, and catalytic properties, are summarized in Clark[10] and Boas and Pessoa.[11]

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Electron Configuration and Coordination Number of Vanadium in an Oxide Environment

Vanadium has three oxidation states in minerals: 3+, 4+, and 5+. Trivalent V has the electron configuration $3s^23p^63d^2$ and occurs mainly in octahedral coordination. In an octahedral ligand field, the two unpaired d electrons occupy the t_{2g} orbitals and are responsible for the paramagnetic and optical properties of V^{3+}-compounds. Many minerals containing V^{3+} as the only transition element are green (e.g., V-bearing tourmaline or garnet).

Tetravalent V has the electron configuration $3s^23p^63d^1$ and occurs in [5]- or [6]-coordination. In both coordinations, the degenerate t_{2g} and e_g orbitals are further split[12] and the d electron occupies one of the nonbonding orbitals ($3d_{xy}$); it is responsible for the paramagnetic and optical properties of V^{4+}. The color of minerals containing V^{4+} are in the green/blue range, but minor contents of V^{5+} or interaction with other transition metals or OMCT bands (oxygen−metal charge transfer) can produce different colors. Thus, sincosite, $Ca(VO)_2(PO_4)_2(H_2O)_5$, and simplotite, $Ca(VO)_2(VO_4)_2(H_2O)_5$, are green, minasragrite, $VOSO_4\ (H_2O)_5$, and pentagonite, $Ca(VO)(Si_4O_{10})(H_2O)_4$, are blue, and many mixed-valent V^{4+}/V^{5+} minerals are black or dark colored [e.g., corvusite, $(Ca,Fe)V_8O_{20}(H_2O)_8$, and melanovanadinite, $Ca_2V_8O_{20}(H_2O)_{10}$].

Pentavalent V has the electron configuration $3s^23p^63d^0$ and forms different kinds of coordination polyhedra: tetrahedral coordination, which occurs also in structures with other transition elements of d^0 configuration (e.g., Ti^{4+}, Cr^{6+}, Mo^{6+}, W^{6+}), and [5]- and [6]-coordination. Minerals containing V^{5+} are almost always colored even though they have no d electrons. Interactions with other transition metals, minor amounts of V^{4+}, and OMCT bands cause a broad range of colors from red through brown [descloizite, $ZnPb(VO_4)(OH)$] and orange [schoderite, $Al_2(PO_4)(VO_4)(H_2O)_8$] to yellow [carnotite, $K_2(UO_2)_2(V_2O_8)(H_2O)_3$] and green [fernandinite, $Ca_{0.6}(V_8O_{20})(H_2O)_{10}$].

Bonding in VO_n Polyhedra: Vanadyl, Equatorial, and *Trans* Bonds

Clark[10] defined a *vanadyl* bond as one which has a short bond length in the range 1.57−1.68 Å; it is a multiple bond with a π-component arising from electron flow from $O(p\pi)$ to $V(d\pi)$ orbitals. When there are two vanadyl bonds present in a polyhedron, they are in a *cis* arrangement.[13] This *cis* arrangement for metals with d electrons is preferred over the *trans* arrangement because the strongly π-donating O ligands then share exclusively one $d\pi$ orbital each (d_{xz}, d_{yz}) and share a third (d_{xy}), whereas in the *trans* configuration, they would have to share two $d\pi$ orbitals and leave one unused.[14] In an infared spectrum,[15] the vanadyl bond gives rise to a very strong sharp V=O stretching band at 985 ± 50 cm^{-1}.

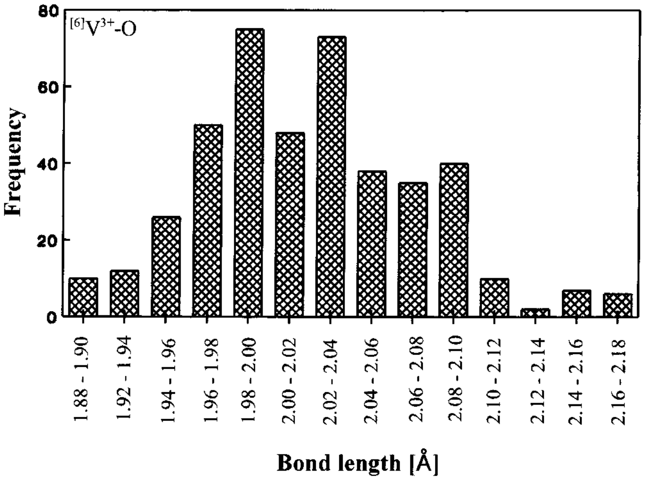

Figure 1. The distribution of individual $^{[6]}V^{3+}-O$ bond lengths in minerals and inorganic structures: values between 1.98 and 2.08 Å are most common.

In [5]- and [6]-coordinated ($V^{4+}O_n$) and ($V^{5+}O_n$) polyhedra, *equatorial* bonds occur in a *cis* arrangement to the vanadyl bonds, and they are longer than the vanadyl bonds. Optical spectra of compounds with vanadyl bonds[12] show that σ-bonds involve the $sp\sigma$-hybrids of the equatorial O atoms and the V $4s - 3d_{z^2}$, $4p_x$, $4p_y$, and $3d_{x^2-y^2}$ orbitals, and Selbin[15] showed the presence of π-bonding from the equatorial ligands. In ($V^{4+}O_6$) and ($V^{5+}O_6$) polyhedra, the sixth ligand is *trans* to a vanadyl bond. This *trans* bond is usually longer than the equatorial bonds; it forms a σ-bond with the $4p_z$ V orbital.[12]

The number of vanadyl, equatorial, and *trans* bonds in a polyhedron may be indicated by using a multiple coordination number in which the numbers of bonds are listed in the order vanadyl + equatorial (+ *trans*). Thus, [1 + 4]-coordination indicates [5]-coordination with one vanadyl bond and four equatorial bonds, and [2 + 2 + 2] coordination indicates [6]-coordination with two vanadyl bonds, two equatorial bonds, and two *trans* bonds.

Polyhedral Geometry and Bond Length Distribution

Most of the data considered here are taken from recently published vanadium phosphate structures with *R* indices < 10% for which the X-ray data were collected from single crystals under normal conditions (no high-pressure or high-temperature data). In some cases, structural data from well-refined vanadates, including minerals, were added. Bond lengths and corresponding references are deposited as supplementary data.

Vanadium(III). The data for vanadium(III) includes bond lengths from 72 octahedra from 47 structures. The distribution of individual $V^{3+}-O$ bond lengths (Figure 1) shows a maximum between 1.98 and 2.04 Å, and minimal and maximal bond length limits of 1.88 and 2.18 Å, respectively. In minerals, V^{3+} often replaces Fe^{3+} in octahedral coordination as the radii (0.64 for V^{3+}, 0.645 for Fe^{3+} [16]) and average bond lengths [2.01(5) Å

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Table 1. Comparison of Actual and Predicted Mixed Valences for V

compound	SV[a]	R[b]	Z[c]	V^{5+}[d]	V^{4+}[e]	ref
$K_{0.5}{}^{[6]}V^{4.5+}OPO_4(H_2O)_{1.5}$	4.50	1.956	4.55	4.69	4.45	24
$Tl_3{}^{[5]}V^{4.5+}{}_2O_3(V^{4+}OPO_4)_2(HPO_4)$	4.50	1.939	4.45	4.69	4.45	25
$K_3{}^{[5]}V^{4.5+}{}_2O_3(V^{4+}O)(PO_4)_2(HPO_4)$	4.50	1.935	4.49	4.58	4.35	26
$Cu_{0.5}(OH)_{0.5}[{}^{[6]}V^{4.5+}OPO_4](H_2O)_2$	4.50	1.966	4.43	4.64	4.41	27
$Na_{0.5}{}^{[6]}V^{4.5+}OPO_4(H_2O)_2$	4.50	1.960	4.51	4.67	4.44	24

[a] SV: stoichiometric valence. [b] R: average equatorial bond in [Å]. [c] Z: mean valence calculated from the equations given in the text. [d] V^{5+}: bond-valence sum calculated from the $V^{5+}-O$ curve of Brown and Altermatt.[20] [e] V^{4+}: bond-valence sum calculated from the $V^{4+}-O$ curve of Brown and Altermatt.[20]

Table 2. Bond Lengths in $V-O_n$ Polyhedra

no. and kind of polyhedra	bond[a]	$\langle V-O\rangle$[b]
72 octahedra [6], overall mean:	$V^{3+}-O_{all}$	2.01(5)
84 square pyramids [1+4]:	$V^{4+}-O_V$	1.59(2)
	$V^{4+}-O_E$	1.98(4)
overall mean	$V^{4+}-O_{all}$	1.90(15)
93 octahedra [1+4+1]:	$V^{4+}-O_V$	1.60(4)
	$V^{4+}-O_E$	2.00(5)
	$V^{4+}-O_T$	2.27(12)
overall mean	$V^{4+}-O_{all}$	1.98(21)
34 square pyramids [1+4]:	$V^{5+}-O_V$	1.59(3)
	$V^{5+}-O_E$	1.89(6)
overall mean	$V^{5+}-O_{all}$	1.83(13)
125 octahedra [1+4+1]:	$V^{5+}-O_V$	1.61(3)
	$V^{5+}-O_E$	1.92(9)
	$V^{5+}-O_T$	2.31(8)
overall mean	$V^{5+}-O_{all}$	1.93(22)
49 polyhedra [2+3]:	$V^{5+}-O_V$	1.66(4)
	$V^{5+}-O_E$	1.95(8)
overall mean	$V^{5+}-O_{all}$	1.83(16)
66 octahedra [2+2+2]:	$V^{5+}-O_V$	1.67(4)
	$V^{5+}-O_E$	1.93(6)
	$V^{5+}-O_T$	2.20(14)
overall mean	$V^{5+}-O_{all}$	1.93(23)

[a] Vanadyl bond, $V-O_V$; equatorial bond,$V-O_E$; *trans* bond, $V-O_T$. [b] σ of $\langle V-O\rangle$ (=x) is $((x_i - \langle x\rangle)^2/n - 1)^{1/2}$.

for $^{[6]}V^{3+}-O$, Table 2; 2.01(1) Å for $Fe^{3+}-O$,[17]] are very similar [when necessary, coordination numbers are given in square brackets as left superscripts to the element symbol]. Schindler and Hawthorne[18] argued that, unlike Fe^{3+}, the degenerate t_{2g} orbitals in $^{[6]}V^{3+}$ can decrease their energy by spontaneous structural distortion, giving rise to more distorted ($V^{3+}O_6$) octahedra. Therefore, V^{3+} occurs in the kieserite-type structure of $[V^{3+}(PO_4)(H_2O)]$,[19] whereas Fe^{3+} does not.

Vanadium(IV). The coordination polyhedra for V^{4+} are square pyramidal or square dipyramidal. In [5]-coordination, V^{4+} is displaced from the plane of the equatorial anions in the direction of the vanadyl O atom, and the angles between the vanadyl bond and the four equatorial bonds are in the range 100 to 110°. In [6]-coordination, there is an additional anion *trans* to the vanadyl anion (Figure 2a). We denote this [5]-coordination as [1 + 4] and this [6]-coordination as [1 + 4 + 1].

The data for the [1 + 4 + 1]- and [1 + 4]-coordinated vanadium(IV) bond length distributions include bond lengths from 92 dipyramids and 83 pyramids from 54 and 62 structures, respectively. Variations in individual bond lengths are shown in Figure 3a for [1 + 4]-coordination. Vanadyl bonds extend over the range 1.48−1.66 Å with a maximum at 1.59 Å; equatorial bonds are in the range 1.80−2.12 Å with a maximum at 1.97 Å.

Figure 3b shows the distribution of individual bond lengths for [1 + 4 + 1]-polyhedra. Vanadyl bonds extend over the range 1.48−1.74 Å with a maximum at 1.60 Å; equatorial bonds are in the range 1.86−2.16 Å with a maximum at 2.00 Å. Figure 3, parts a and b, shows gaps between the vanadyl and equatorial bonds; all vanadyl bonds are shorter than 1.74 Å. The average equatorial $V^{4+}-O$ bond length is 1.98(1) Å for [1 + 4]-coordination and 2.00(1) Å for [1 + 4 + 1]-coordination.

The variation in *trans* bond lengths in [1 + 4 + 1]-coordination is shown in Figure 4. We have not included anions with bond valences less than 0.1 vu (corresponding to distances longer than 2.6 Å). *Trans* bond lengths extend over the range 2.00 to 2.60 Å with a maximum at 2.20−2.32 Å.

Definition of Bond Types for $V^{4+}O_n$ Polyhedra. Inspection of Figures 3 and 4 shows that there are distinct populations of V−O bond lengths separated by ranges in which no bond lengths occur. This feature allows us to define following different types of $V^{4+}-O$ bonds: (1) a vanadyl bond is shorter than 1.74 Å; (2) an equatorial bond is *cis* to the vanadyl bond and is between 1.80 and 2.12 Å; (3) a *trans* bonds is *trans* to the vanadyl bond, and is longer than 2.0 Å.

Vanadium(V). In tetrahedral coordination, $V^{5+}-O$ bond lengths range from 1.6 to 2.0 Å. Shannon and Calvo[20] discussed the bond length variation of tetrahedrally coordinated V^{5+} and found a grand mean $V^{5+}-O$ bond length of 1.72(1) Å. Data for the [1 + 4], [2 + 3], [1 + 4 + 1], and [2 + 2 + 2]-coordinated vanadium(V) bond length distributions include 34, 49, 125, and 66 polyhedra, taken from 28, 39, 34, and 50 structures, respectively.

[5]- and [6]-coordinated V^{5+} are characterized by the occurrence of one and two strong vanadyl bonds, respectively. Their presence in mineral and synthetic structures causes a larger variation of vanadyl, equatorial and *trans* bond lengths in ($V^{5+}O_n$) polyhedra than in ($V^{4+}O_n$) polyhedra. Figures 5 and 6 show the variation of vanadyl, equatorial, and *trans* bond lengths in different ($V^{5+}O_n$) polyhedral geometries. There are distinct populations of V−O bond lengths, separated by ranges in which no, or only a few, bond lengths occur. This feature allows us to define different types of $V^{5+}-O$ bonds and different ($V^{5+}O_n$) coordinations.

Vanadyl Bonds. In [5]-coordination ([1 + 4] and [2 + 3]), there is a minimum at 1.74−1.76 Å; in [6]-coordination ([1 + 4 + 1] and [2 + 2 + 2]), there is a minimum at 1.74−1.75 Å. Thus, we can define a vanadyl bond in [5]- and [6]-coordinations as a bond shorter than 1.74 Å.

Equatorial Bonds in [5]-Coordination. In [5]-coordination, the equatorial bond can be defined as a bond longer than 1.74 Å. Figure 5 shows the variation in length for [1 + 4]- and [2 + 3]-coordinations. The varia-

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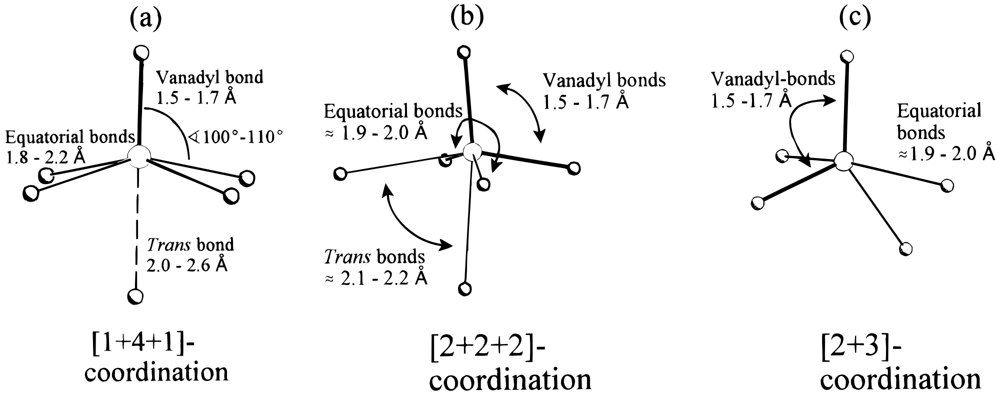

Figure 2. Coordination geometries in (V–O$_n$) polyhedra: (a) [1 + 4 + 1]-coordination; (b) [2 + 2 + 2]-coordination with two *cis* vanadyl bonds and two *trans* bonds in a *trans* arrangement to each vanadyl bond; (c) [2 + 3]-coordination with two vanadyl bonds in the *cis* position.

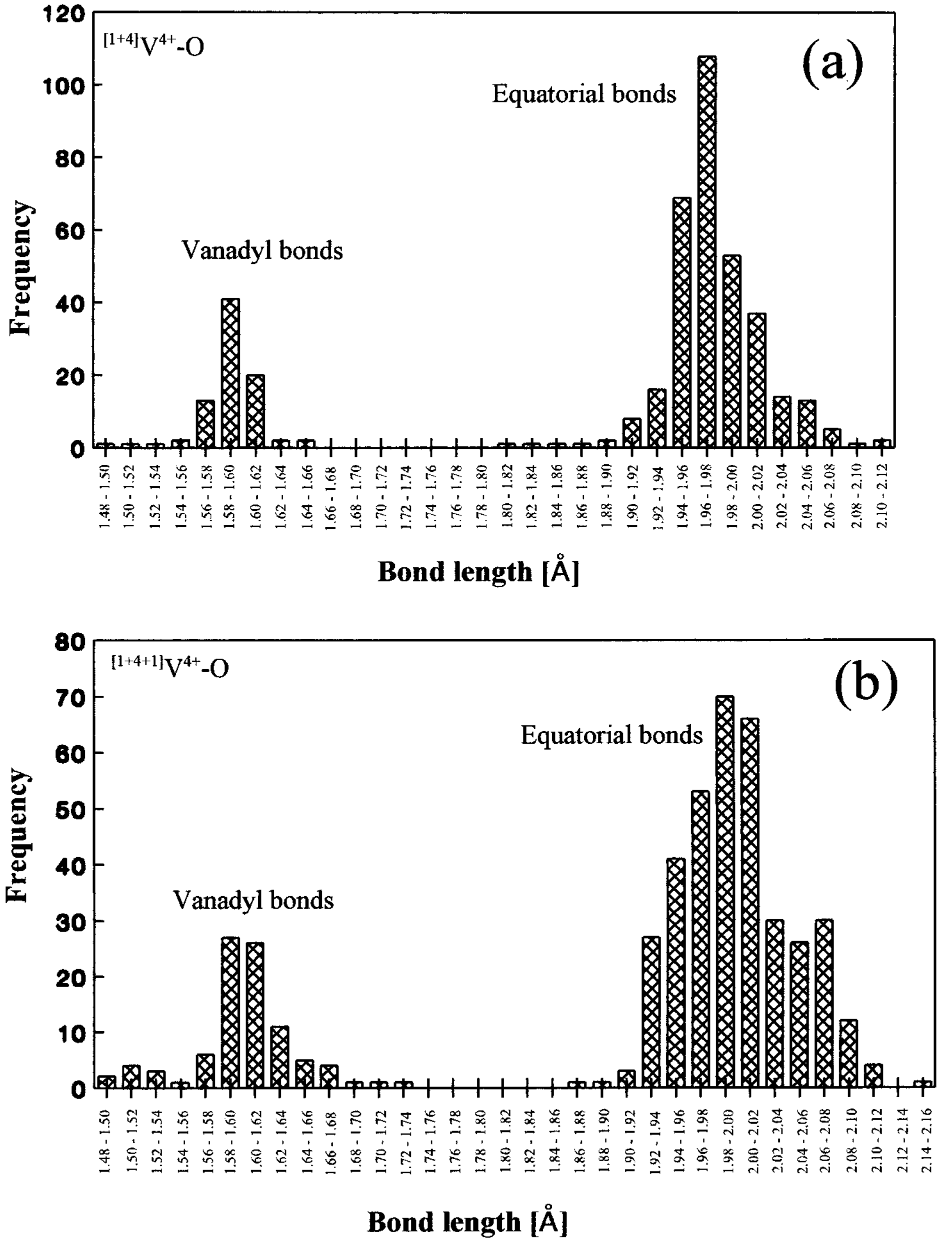

Figure 3. The distribution of individual bond lengths in ($V^{4+}O_5$) polyhedra in mineral and inorganic crystal structures: (a) [1 + 4]-coordination and (b) [1 + 4 + 1]-coordination.

tion in equatorial bond length for [1 + 4]-coordination is generally between 1.74 and 2.04 Å, with a maximal frequency at 1.88 Å (Figure 5a). For [2 + 3]-coordination, the equatorial bond lengths are in the range 1.74

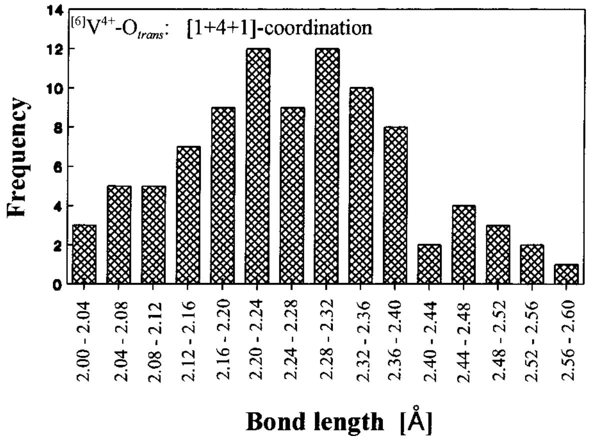

Figure 4. The distribution of individual *trans* bond lengths in ($V^{4+}{-}O_6$) polyhedra in mineral and inorganic crystal structures where V^{4+} is in [1 + 4 + 1]-coordination.

to >2.06 Å and the maximal frequencies occur at 1.87 and 1.97 Å.

Equatorial and *Trans* Bonds in [6]-Coordination. Figure 6a shows the equatorial and *trans* bond length distributions for [6]-coordination. There is a minimum at 2.10−2.15 Å between the equatorial and *trans* bond length distributions in polyhedra with one vanadyl bond. Thus, in [6]-coordination with one vanadyl bond, we can define the equatorial bond as *cis* to the vanadyl bond and with a bond length in the range 1.74−2.125 Å. A *trans* bond is defined as *trans* to the vanadyl bond and longer than 2.125 Å. The equatorial bond length distribution has maxima at 1.825 and 2.00 Å, and shows a variation similar to that of the equatorial bonds in [1 + 4]-coordination; thus, this coordination is designated as a [1 + 4 + 1]-coordination.

In the distribution of bond lengths in polyhedra with two vanadyl bonds, there are three equal and distinct

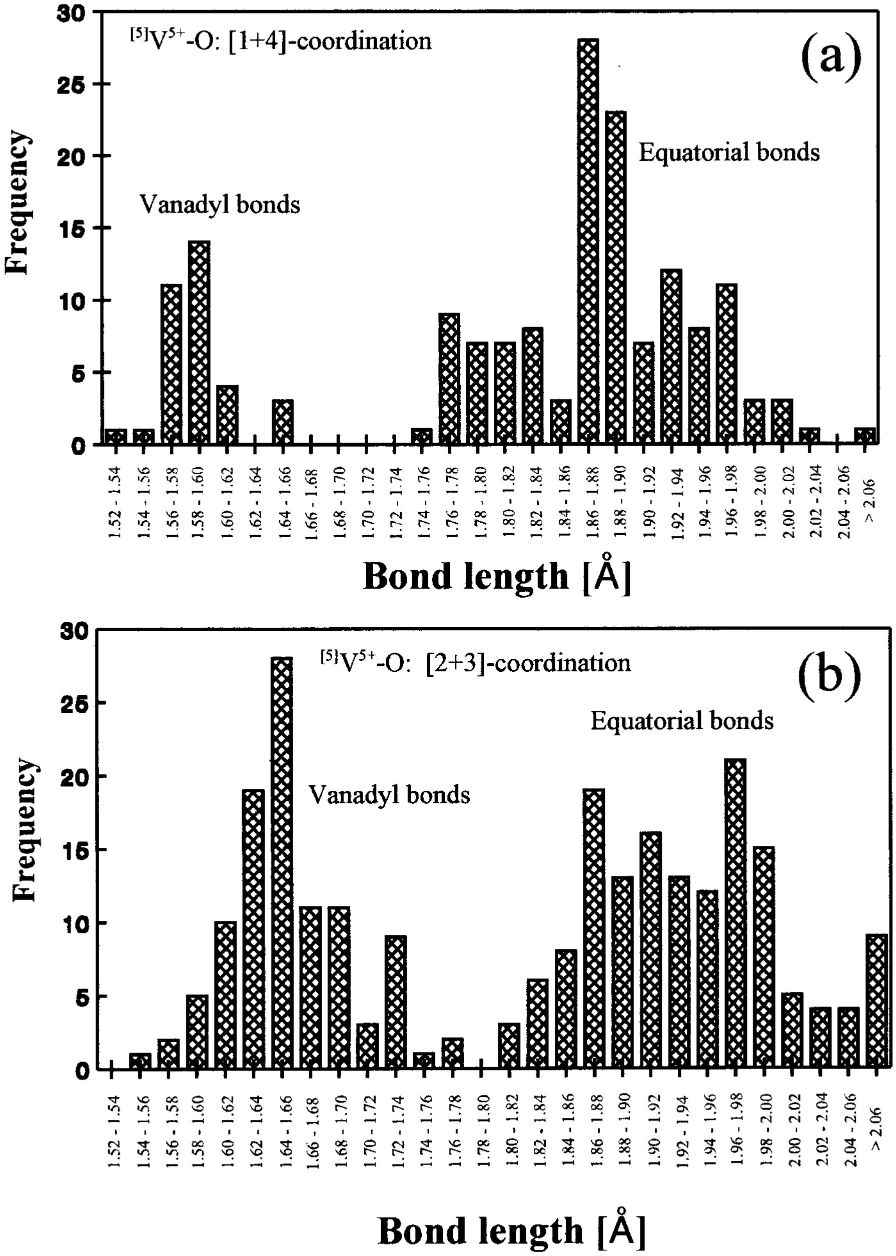

Figure 5. The distribution of individual bond lengths in ($V^{5+}O_5$) polyhedra in mineral and inorganic crystal structures: (a) [1 + 4]-coordination and (b) [2 + 3]-coordination.

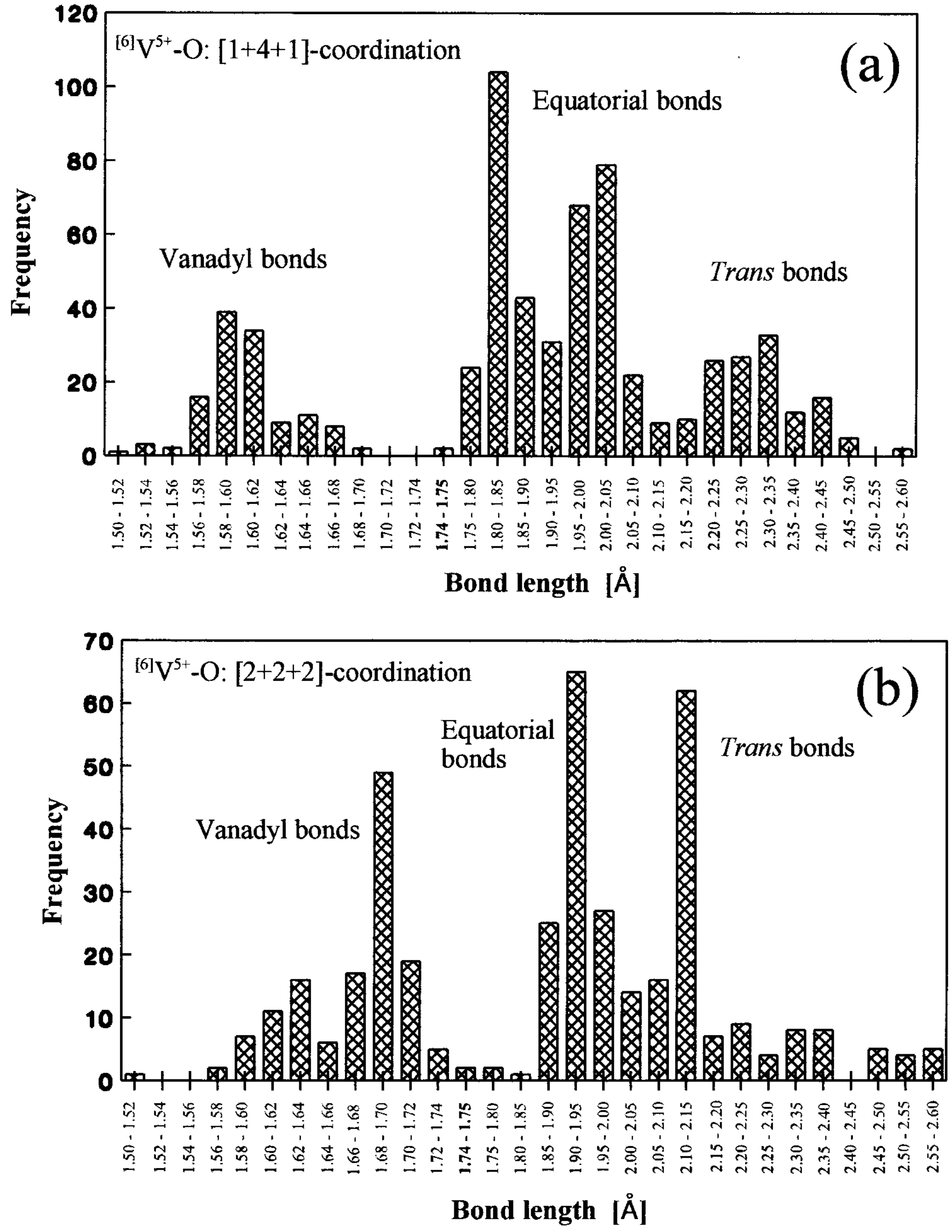

Figure 6. The distribution of individual vanadyl, equatorial, and *trans* bonds in ($^{[6]}V^{5+}O_6$) polyhedra in mineral and inorganic crystal structures: (a) [1 + 4 + 1]-coordination and (b) [2 + 2 + 2]-coordination.

populations, indicating [2 + 2 + 2]-coordination with two vanadyl, two equatorial, and two *trans* bonds (Figure 6b). The equatorial and *trans* bonds can be distinguished in Figure 6b by their lengths: equatorial bonds range from 1.75 to 2.025 Å with a maximum frequency at 1.925 Å and *trans* bonds are longer than 2.025 Å with a maximum frequency at 2.125 Å.

Closer inspection of individual bond length distributions in [1 + 4]-, [2 + 3]-, and [1 + 4 + 1]-coordinations and the occurrence of more than one maximum in the equatorial bond length distributions show the existence of [1 + 1 + 2 + 1]-, [1 + 2 + 2]-, [2 + 1 + 2]-, [2 + 2 + 1]-, and [1 + 2 + 2 + 1]-coordinations. This variability of equatorial bond lengths is characteristic for ($V^{5+}O_n$) coordination polyhedra and display different interactions between O(pπ) and V(dπ) orbitals. Here, we distinguish the ($V^{5+}O_n$) coordinations only according to the number of vanadyl bonds and treat all equatorial bonds as equivalent.

General Geometrical Features of V $^{5+}O_n$ Polyhedra. the general geometrical features of ($V^{5+}O_n$) polyhedra can be summarized as follows:

(1) There is more than one maximum in the distribution of V−O equatorial bond lengths in [1 + 4]-, [2 + 3]-, and [1 + 4 + 1]-coordinations.

(2) The average equatorial bond lengths are 1.89(6) Å for [1 + 4]-coordination and 1.92(10) Å for [1 + 4 + 1]-coordination (Table 2).

(3) [1 + 4]- and [1 + 4 + 1]-coordinations with four similar equilateral bonds occur as square−pyramidal and square−dipyramidal coordination polyhedra (Figure 2a).

(4) Geometrical distortion of square−pyramidal or square−dipyramidal coordination polyhedra occurs, e.g., in [2 + 2 + 2]- and [2 + 3]-coordinations (Figure 2, parts b and c).

Zavalij and Whittingham[9] classified $^{[5]}V^{5+}$ polyhedra into three major groups: trigonal−bipyramids with one vanadyl bond, square−pyramids with one vanadyl bond, and distorted trigonal−bipyramids with two vanadyl bonds. In this context, Addison et al.[21] introduced an angular structural parameter to distinguish between either square−pyramidal, distorted square−pyramidal, distorted trigonal−bipyramidal, or trigonal−bipyramidal. In this work, we use only the term square−pyramid for [1 + 4] coordination with four similar equatorial bonds. In all other cases, we use the terms [1 + 4]- or [2 + 3]-coordination without considering if the geometry of the polyhedron is closer to square−pyramidal or trigonal−dipyramidal.

Identification of V^{4+} and V^{5+}. To identify the valence of V in [5]- or [6]-coordination, the bond-valence sum [using the curves of Brown and Altermatt[22] or Brese and O'Keeffe[23]] can be calculated. However, the V−O bond length distributions are also characteristic of the valence state of V: (1) two vanadyl bonds occur only in ($V^{5+}O_n$) polyhedra; (2) the average equatorial bond lengths in polyhedra with one vanadyl bond are characteristic of both coordination and valence state:

$$\langle {}^{[5]}V^{4+} - O_E \rangle = 1.98\ \text{Å}$$

$$\langle {}^{[6]}V^{4+} - O_E \rangle = 2.00\ \text{Å}$$

$$\langle {}^{[5]}V^{5+} - O_E \rangle = 1.89\ \text{Å}$$

$$\langle {}^{[6]}V^{5+} - O_E \rangle = 1.92\ \text{Å}$$

In mixed-valence vanadium compounds, the bond-valence sum can be calculated from the bond-valence curves for V^{4+} or V^{5+}, leading to an ambiguity in the average valence state. However, an unambiguous determination of the average valence of V can be derived by comparison of the average equatorial bond length in a specific (VO_n) polyhedron with the above average equatorial bond lengths for V^{4+} and V^{5+} in their different coordinations.

The equatorial bond lengths for V^{4+} are about 0.1 Å longer than for V^{5+} polyhedra. The corresponding linear equations are as follows:

$$\text{[5]-coordination:} \quad \langle Z \rangle = (25.99 - 11.11)R \qquad (1)$$

$$\text{[6]-coordination:} \quad \langle Z \rangle = (29.00 - 12.50)R \qquad (2)$$

where R is the average equatorial bond distance and $\langle Z \rangle$ is the average valence.

Table 1 lists five well-refined crystal structures of V phosphates[24−27] where the mixed valence of V is unequivocally determined by fixed stoichiometry and the valence states of the other cation and anions. The mean valence of V predicted from the bond-valence curves for V^{4+}−O and V^{5+}−O [20] and from the above predictive equations are also listed in Table 1. The root-mean-square deviations for the three methods are 0.04, 0.16, and 0.06, respectively, indicating that the predictive equations developed above are the most effective method for calculating the mean value of V in mixed-valent structures. The equatorial bond lengths of V^{4+} and V^{5+} reflect the difference in oxidation state well, while the vanadyl and *trans* bonds do not do it in any significant way (Table 2). The four equatorial bonds correspond here to the grand mean of all six bonds in a comparison such as between Fe^{2+} and Fe^{3+} in octahedral coordination where the difference in mean bond lengths is also about 0.1 Å.

In a method applied by Skowron and Brown (1990),[28] the calculated bond-valence sums of V^{4+} and V^{5+} are multiplied by the corresponding occupation factors of V^{4+} and V^{5+}, yielding an average valence state. This method is based on a knowledge of the V^{4+}/V^{5+} ratio, whereas determinations of the valence via the above-mentioned method do not need any assumptions about the V^{4+}/V^{5+} ratio. Thus, their and our results cannot be compared with each other.

The mean values of the vanadyl ($V-O_V$), equatorial ($V-O_E$), and *trans* bonds ($V-O_T$), together with the overall means, are given for all coordinations discussed above in Table 2.

Characteristic Bond-Valence, Lewis Acid, and Lewis Base Strengths and the Valence-Matching Principle

Brown[29] introduced the idea of a characteristic bond-valence by examining the range of bond valences around a specific cation in a wide range of crystal structures. The mean bond-valence of a cation correlates with its electronegativity. Electronegativity is a measure of the electrophilic strength of the cation, and the correlation with characteristic bond-valence indicates that the latter is a measure of the Lewis acid strength of the cation (see also O'Keeffe and Brese[30]). Thus, Brown[29] defined the Lewis acid strength of a cation as its characteristic bond valence and the Lewis base strength of an anion as its characteristic bond valence. From this emerges the valence-matching principle: stable structures will form when the Lewis acid strength of the cation closely matches the Lewis base strength of the anion.

Characteristic Bond Valences in (VO_n) Polyhedra

We have defined characteristic coordination geometries for ($V^{4+}O_n$) and ($V^{5+}O_n$) polyhedra and have calculated the corresponding average equatorial bond lengths. Now, we define the characteristic bond valences for vanadyl, equatorial, and *trans* bonds in different coordinations. For (VO_n) coordinations where vanadyl and equatorial bond lengths show a broad distribution, the maximal, average, and minimal bond valences are given in Table 3.

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Table 3. Average and Range of Lewis Acid Strengths[a] for Different Bonds in Polyhedra with [5]- and [6]-Coordinated Vanadium

coordination	vanadyl bond [vu]	equatorial bond [vu]	*trans* bond [vu]
V^{4+}: [1+4]	2.00 > 1.69 > 1.40	0.96 > 0.59 > 0.40	
V^{4+}: [1+4+1]	2.00 > 1.63 > 1.13	0.81 > 0.56 > 0.40	0.56 > 0.27 > 0.10
V^{5+}: [1+4]	2.00 > 1.78 > 1.47	1.19 > 0.79 > 0.53	
V^{5+}: [1+4+1]	2.00 > 1.68 > 1.32	1.19 > 0.73 > 0.42	0.42 > 0.25 > 0.10
V^{5+}: [2+3]	2.00 > 1.47 > 1.19	1.19 > 0.67 > 0.50	
V^{5+}: [2+2+2]	1.93 > 1.43 > 1.25	1.19 > 0.71 > 0.55	0.55 > 0.34 > 0.10

[a] Bond-valence parameters from Brown and Altermatt.[22]

The data of Table 3 allow us to systematize some aspects of vanadium crystal chemistry: Using the valence-sum rule,[29] we can examine which linkages [vanadyl−vanadyl, vanadyl−equatorial, vanadyl−*trans*, equatorial−equatorial, equatorial−*trans* and *trans*−*trans* of the (VO_n) polyhedra] are possible, and which actually occur in minerals and synthetic compounds.

Occurrences of Binary V−V Linkages between ($^{[1+4]}V^{4+}$), ($^{[1+4+1]}V^{4+}$), ($^{[1+4]}V^{5+}$), ($^{[2+3]}V^{5+}$), ($^{[1+4+1]}V^{5+}$), and ($^{[2+2+2]}V^{5+}$) Polyhedra in Structures of Minerals and Synthetic Compounds

Nomenclature. Linkage between (VO_n) polyhedra in mineral and synthetic structures can be denoted as $^{[n]}V^{Z}{-}_{b}O_{b}{-}^{[n]}V^{Z}$, where [*n*] denotes the coordination, (e.g. [1 + 4 + 1] or [2 + 3]), b is the type of bond between V and O (v = vanadyl, eq = equatorial, t = *trans*) and Z is the valence state of V (4+ or 5+). For example, the notation $^{[2+3]}V^{5+}{-}_{v}O_{eq}{-}^{[1+4+1]}V^{5+}$ denotes linkage through a common O atom between a vanadyl bond from V^{5+} in [2 + 3]-coordination and an equatorial bond from V^{5+} in [1 + 4 + 1]-coordination.

Vanadyl−Vanadyl Linkages. For all vanadyl−vanadyl bonds, the bond-valence incident at the linking anion significantly exceeds the maximum possible value of 2.00 vu. For example in the binary linkage $^{[2+2+2]}V^{5+}{-}_{v}O_{v}{-}^{[2+2+2]}V^{5+}$, the range (and average value) for the incident bond-valence sum at the linking anion is (1.93 > 1.43 > 1.25) + (1.93 > 1.43 > 1.25) = 3.86 > 2.86 > 2.50 vu, and, therefore, polyhedra cannot link through vanadyl−vanadyl bonds. Thus, there are no vanadyl−vanadyl linkages in mineral or synthetic structures (Table 3).

Vanadyl−Equatorial Linkages. Combining vanadyl and equatorial bonds of the six different kind of coordinations gives 42 possible binary vanadyl−equatorial linkages; in all of these linkages, the average bond-valence sums exceed and the minimum bond valences do not exceed the maximum possible value of 2.00 vu. Thus, these binary linkages are only possible if the bond valence of the vanadyl or equatorial bond is smaller than its average bond valence (Table 3). Four of these binary linkages occur in mineral and synthetic structures; they are listed in Table 4 with their incident bond-valence sums at the linking anion, their general occurrence (if mineral, synthetic compound or both) and one example.[25,31−50]

As an example, the binary linkage $^{[1+4+1]}V^{4+}{}_{v}O_{eq}{-}^{[2+2+2]}V^{5+}$ has an incident bond-valence sum at the linking anion of (2.00 > 1.63 > 1.13) vu + (1.19 > 0.71 > +0.55) vu = (3.19 > 2.34 > 1.68) vu This binary linkage does not occur in mineral and synthetic structures, but could exist according to the valence-sum rule.[29]

Vanadyl−*Trans* Linkages. There are 21 possible vanadyl−*trans* linkages and their incident bond-valence sums are in the range 1.29−2.56 vu, with an average value of ~2.00 vu. Hence, all these linkages are possible. In some cases (e.g., $^{[2+3]}V^{5+}{-}_{v}O_{t}{-}^{[1+4+1]}V^{5+}$), the incident bond-valence is sufficiently low that another *trans* bond could be involved in linkage at the anion. There are six different binary vanadyl−*trans* linkages in mineral and synthetic structures, but only two ($^{[1+4+1]}V^{4+}{-}_{v}O_{t}{-}^{[1+4+1]}V^{4+}$ and $^{[2+2+2]}V^{5+}{-}_{v}O_{t}{-}^{[2+2+2]}V^{5+}$) occur in minerals (Table 4).

Equatorial−Equatorial Linkages. There are 21 possible binary equatorial−equatorial linkages, and in all of them, the average bond-valence sum does not exceed 2 vu at the linking anion. In some cases, the incident bond-valence is close to 2 vu, whereas in others, the incident bond-valence is close to 1 vu. In the latter case, the linking anion could be monovalent (OH, F, Cl), or other linkages (either to V and/or other high-valence cations) are required. Thus, three equatorial bonds meeting at a common vertex are possible for all polyhedra, whereas four equatorial bonds at a common vertex seem likely only for about one-third of the possible configurations. At an equatorial−equatorial vertex, up to four incident *trans* bonds are also formally possible if allowed by packing restrictions, e.g. for the minimum bond-valence sum of $^{[1+4+1]}V^{5+}{-}_{eq}O_{eq}{-}^{[1+4+1]}V^{5+}$:(1.19 > 0.73 > 0.42) + (1.19 > 0.73 > 0.42) = (2.38 > 1.46 > 0.84) vu.

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Table 4. Occurrence of Binary V−V Linkages between Polyhedra with ${}^{[1+4]}V^{4+}$, ${}^{[1+4+1]}V^{4+}$, ${}^{[1+4]}V^{5+}$, ${}^{[2+3]}V^{5+}$, ${}^{[1+4+1]}V^{5+}$, and ${}^{[2+2+2]}V^{5+}$ and Their Incident Bond-Valence Sums[a]

type	range of incident bond-valence sums [vu]	occurrence	example
Vanadyl−Equatorial Linkages			
${}^{[2+3]}V^{5+}{-}_{v}O_{eq}{-}{}^{[2+3]}V^{5+}$	3.19 > 2.14 > 1.69	synth.	$Tl(VO_2)(HPO_4)$[25]
${}^{[1+4+1]}V^{4+}{-}_{eq}O_{v}{-}{}^{[2+2+2]}V^{5+}$	2.74 > 1.99 > 1.65	min.+ synth.	$Ca_{4.5}(AlV_{12}V_2O_{40})(H_2O)_{28}$, sherwoodite[31]
${}^{[1+4+1]}V^{5+}{-}_{eq}O_{v}{-}{}^{[2+3]}V^{5+}$	3.19 > 2.20 > 1.61	min.+ synth.	α-ZnV_3O_8[32]
${}^{[1+4+1]}V^{5+}{-}_{eq}O_{v}{-}{}^{[2+2+2]}V^{5+}$	3.12 > 2.16 > 1.67	min.+ synth.	$Li_{1.2}V_3O_8$[33]
Vanadyl−*Trans* Linkages			
${}^{[1+4]}V^{4+}{-}_{v}O_{t}{-}{}^{[1+4+1]}V^{4+}$	2.56 > 1.96 > 1.50	synth.	$Ba(VO_2)(PO_4)_2$[34]
${}^{[1+4+1]}V^{4+}{-}_{v}O_{t}{-}{}^{[1+4+1]}V^{4+}$	2.56 > 1.90 > 1.23	min.+ synth.	$KVOPO_4$[35]
${}^{[1+4+1]}V^{4+}{-}_{v}O_{t}{-}{}^{[2+2+2]}V^{5+}$	2.55 > 1.97 > 1.23	synth.	$Cs_2[(V_2O_3)(HPO_4)_2(H_2O)$[36]
${}^{[2+2+2]}V^{5+}{-}_{v}O_{t}{-}{}^{[1+4+1]}V^{5+}$	2.35 > 1.68 > 1.35	synth.	$Cs_2[(V_2O_3)(HPO_4)_2(H_2O)$[36]
${}^{[1+4+1]}V^{5+}{-}_{v}O_{t}{-}{}^{[1+4+1]}V^{5+}$	2.42 > 1.93 > 1.42	synth.	β-$VOPO_4$[37]
${}^{[2+2+2]}V^{5+}{-}_{v}O_{t}{-}{}^{[2+2+2]}V^{5+}$	2.48 > 1.77 > 1.35	min.+ synth.	$Ca_{1.44}(V_{7.6}Fe_{0.4}O_{20})(H_2O)_4$, fernandinite[38]
Equatorial−Equatorial Linkages			
${}^{[1+4]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[1+4]}V^{4+}$	1.92 > 1.18 > 0.80	min.+ synth.	$Ca(V_4O_{10})(H_2O)_5$,[39] melanovanadinite
${}^{[1+4]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[1+4+1]}V^{4+}$	1.77 > 1.15 > 0.80	synth.	MIL-7 (HT)[40]
${}^{[1+4]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[1+4]}V^{5+}$	2.15 > 1.38 > 0.93	synth.	Na−FVP-1[5]
${}^{[1+4]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[1+4+1]}V^{5+}$	2.15 > 1.32 > 0.82	min.+ synth.	$Na_{0.76}V_6O_{15}$,[41] bannermanite
${}^{[1+4]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[2+3]}V^{5+}$	2.15 > 1.26 > 0.90	synth.	$K_5H_2(V_{15}O_{36}(CO_3))(H_2O)_{14.5}$[42]
${}^{[1+4+1]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[1+4+1]}V^{4+}$	1.62 > 1.12 > 0.80	min.+ synth.	phosphovanvdylite[43]
${}^{[1+4+1]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[1+4+1]}V^{5+}$	2.00 > 1.29 > 0.82	min.+ synth.	$(CN_3H_6)_3[V^{4+}V^{5+}{}_5O_{13}(COCH_2)_3\ (CH_2OH)_2](H_2O)_{4.5}$[44]
${}^{[1+4+1]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[2+3]}V^{5+}$	2.00 > 1.23 > 0.90	min.+ synth.	MIL-7 (LT)40
${}^{[1+4]}V^{5+}{-}_{eq}O_{eq}{-}{}^{[1+4]}V^{5+}$	2.38 > 1.58 > 1.06	min.+ synth.	$K_2(UO_2)_2(V_2O_8)(H_2O)_3$,[45] carnotite
${}^{[1+4]}V^{5+}{-}_{eq}O_{eq}{-}{}^{[1+4+1]}V^{5+}$	2.38 > 1.52 > 0.95	min.+ synth.	$Na_{0.76}V_6O_{15}$,[41] bannermanite
${}^{[1+4]}V^{5+}{-}_{eq}O_{eq}{-}{}^{[2+3]}V^{5+}$	2.38 > 1.46 > 1.03	min.+ synth.	$Ca(VO_3)(H_2O)_4$, rossite[46]
${}^{[1+4+1]}V^{5+}{-}_{eq}O_{eq}{-}{}^{[1+4+1]}V^{5+}$	2.38 > 1.46 > 0.84	min.+ synth.	$Li_{1.2}V_3O_8$[33]
${}^{[1+4+1]}V^{5+}{-}_{eq}O_{eq}{-}{}^{[2+2+2]}V^{5+}$	2.38 > 1.44 > 0.97	min.+ synth.	$(Na_{0.7}Ca_{0.3})(V_{7.6}Fe_{0.4})O_{20}(H_2O)_4$,[38] corvusite
${}^{[2+3]}V^{5+}{-}_{eq}O_{eq}{-}{}^{[2+3]}V^{5+}$	2.38 > 1.34 > 1.00	min.+ synth.	$K(VO_3)(H_2O)$[47]
${}^{[2+2+2]}V^{5+}{-}_{eq}O_{eq}{-}{}^{[2+2+2]}V^{5+}$	2.38 > 1.42 > 1.10	min.+ synth.	$Ca_{1.44}(V_{7.6}Fe_{0.4}O_{20})(H_2O)_4$, fernandinite[38]
Equatorial−*Trans* Linkages			
${}^{[1+4+1]}V^{4+}{-}_{eq}O_{t}{-}{}^{[1+4+1]}V^{4+}$	1.37 > 0.83 > 0.50	min.+ synth.	phosphovanadylite[43]
${}^{[1+4+1]}V^{4+}{-}_{eq}O_{t}{-}{}^{[2+2+2]}V^{5+}$	1.36 > 0.90 > 0.65	min.+ synth.	$(Na_{0.7}Ca_{0.3})(V_{7.6}Fe_{0.4})O_{20}(H_2O)_4$,[38] corvusite
${}^{[1+4+1]}V^{4+}{-}_{t}O_{eq}{-}{}^{[2+2+2]}V^{5+}$	1.75 > 0.98 > 0.65	min.+ synth.	$Li_{1.2}V_3O_8$[33]
${}^{[1+4+1]}V^{5+}{-}_{eq}O_{t}{-}{}^{[2+2+2]}V^{5+}$	1.74 > 1.07 > 0.52	min.+ synth.	$(Na_{0.7}Ca_{0.3})(V_{7.6}Fe_{0.4})O_{20}(H_2O)_4$,[38] corvusite
${}^{[1+4+1]}V^{5+}{-}_{t}O_{eq}{-}{}^{[2+2+2]}V^{5+}$	1.61 > 0.96 > 0.65	min.+ synth.	$Li_{1.2}V_3O_8$[33]
Trans−*Trans* Linkages			
${}^{[1+4+1]}V^{4+}{-}_{t}O_{t}{-}{}^{[1+4+1]}V^{4+}$	1.12 > 0.54 > 0.20	synth.	$VOHPO_4(H_2O)_{0.5}$[48]
${}^{[1+4+1]}V^{4+}{-}_{t}O_{t}{-}{}^{[1+4+1]}V^{5+}$	0.98 > 0.52 > 0.20	synth.	$(CN_3H_6)_3[V^{4+}V^{5+}{}_5O_{13}(COCH_2)_3\ (CH_2OH)_2](H_2O)_{4.5}$[44]
${}^{[1+4+1]}V^{4+}{-}_{t}O_{t}{-}{}^{[2+2+2]}V^{5+}$	1.11 > 0.61 > 0.20	min.+synth.	$K_7(AsV_{14}O_{40})(H_2O)_{12}$[49]
${}^{[1+4+1]}V^{5+}{-}_{t}O_{t}{-}{}^{[1+4+1]}V^{5+}$	0.84 > 0.50 > 0.20	min.+ synth.	$Ca_3(V_{10}O_{28})(H_2O)_{16}$, pascoite[50]
${}^{[1+4+1]}V^{5+}{-}_{t}O_{t}{-}{}^{[2+2+2]}V^{5+}$	0.97 > 0.59 > 0.20	min.+ synth.	$Ca_3(V_{10}O_{28})(H_2O)_{16}$, pascoite[50]
${}^{[2+2+2]}V^{5+}{-}_{t}O_{t}{-}{}^{[2+2+2]}V^{5+}$	1.10 > 0.68 > 0.20	min.+ synth.	$Ca_3(V_{10}O_{28})(H_2O)_{16}$, pascoite[50]

[a] MIL-7(HT): $(VO_2)(OH)(H_2O)[O_3P(CH_2)_3PO_3)](H_2O)(NH_4)$. MIL-7(LT): $(V_2O_3)(H_2O)[O_3P(CH_2)_3PO_3)](H_2O)(NH_4)$. FVP-1: $Na_v[((V^{4+}{}_{4-w}$-$V^{5+}{}_{1+w})O_9(PO_4)_2](PO_4)_x(OH)_y(H_2O)_z$. ($v = 2.8-4.0$, $w = -0.1-1.1$, $x = 0-0.2$, $y = 0-2.1$,$z = 7-10$). Phospovanadylite: $(Ba_{0.38}Ca_{0.2}K_{0.06}Na_{0.02})$-$[(V_{3.44}Al_{0.46})(OH)_{5.66}O_{2.34})(PO_4)_2](H_2O)_{12}$.

Fifteen of the 21 possible binary linkages occur in crystal structures of minerals or synthetic compounds. Three of them occur only in synthetic structures: ${}^{[1+4]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[1+4+1]}V^{4+}$, ${}^{[1+4]}V^{4+}{-}_{eq}O_{eq}{-}[1+4]V^{5+}$, and ${}^{[1+4]}V^{4+}{-}_{eq}O_{eq}{-}{}^{[1+4]}V^{5+}$.

Equatorial−*Trans* Linkages. Combining equatorial with *trans* bonds for all (VO_n) coordinations gives 21 possible equatorial−*trans* linkages. For those linkages, the average incident bond-valence sums are all approximately ∼1 vu; the linking anion may be monovalent (OH, F, Cl) or divalent with other strong incident bonds or numerous weak incident bonds (e.g., one equatorial bond and four or five *trans* bonds). Five out of the 21 possible linkages occur in both mineral and synthetic structures (Table 4).

***Trans*−*Trans* Linkages.** All six possible binary *trans*−*trans* linkages occur in mineral or synthetic structures (Table 4), four of them in minerals. Their incident bond-valence sums are in the range 0.2−1.2 vu and numerous other weak bonds can connect with the same vertex. This occurs in the decavanadate polyanion $[V_{10}O_{28}]^{6-}$, where six ${}^{[n]}V^{Z}{-}_{b}O$ bonds are incident at one central O atom: ${}^{[1+4+1]}V^{5+}{}_{t}O$, ${}^{[1+4+1]}V^{5+}{}_{t}O$, ${}^{[1+4+1]}V^{5+}{}_{t}O$, ${}^{[1+4+1]}V^{5+}{}_{t}O$, ${}^{[2+2+2]}V^{5+}{}_{t}$ O, ${}^{[2+2+2]}V^{5+}{}_{t}O$. The corresponding incident bond-valence sum at the linking O atom is $(0.42 > 0.25 > 0.10) \times 4 + (0.55 > 0.34 > 0.10) \times 2 = (2.78 > 1.68 > 0.60)$ vu.

General Occurrence of Binary Linkages

Minerals. There are 132 possible combinations of binary ${}^{[n]}V^{Z}{-}_{b}O_{b}{-}{}^{[n]}V^{Z}$ linkages; in 111 cases, the minimum (and in 83 cases) the average incident bond-valence sums do not exceed 2 vu. Only 26 of these linkages occur in minerals (Table 4). One reason might be that many V^{4+}/V^{5+} minerals occur as secondary phases in the oxidation zone of rocks containing V^{3+} minerals. Under these conditions, 5+ is the most stable oxidation state for vanadium, accounting for its dominant role in the crystal chemistry of V minerals.

Linkages between $({}^{[n]}V^{5+}O_n)$ polyhedra occur in the vanadium bronzes, in minerals with the carnotite

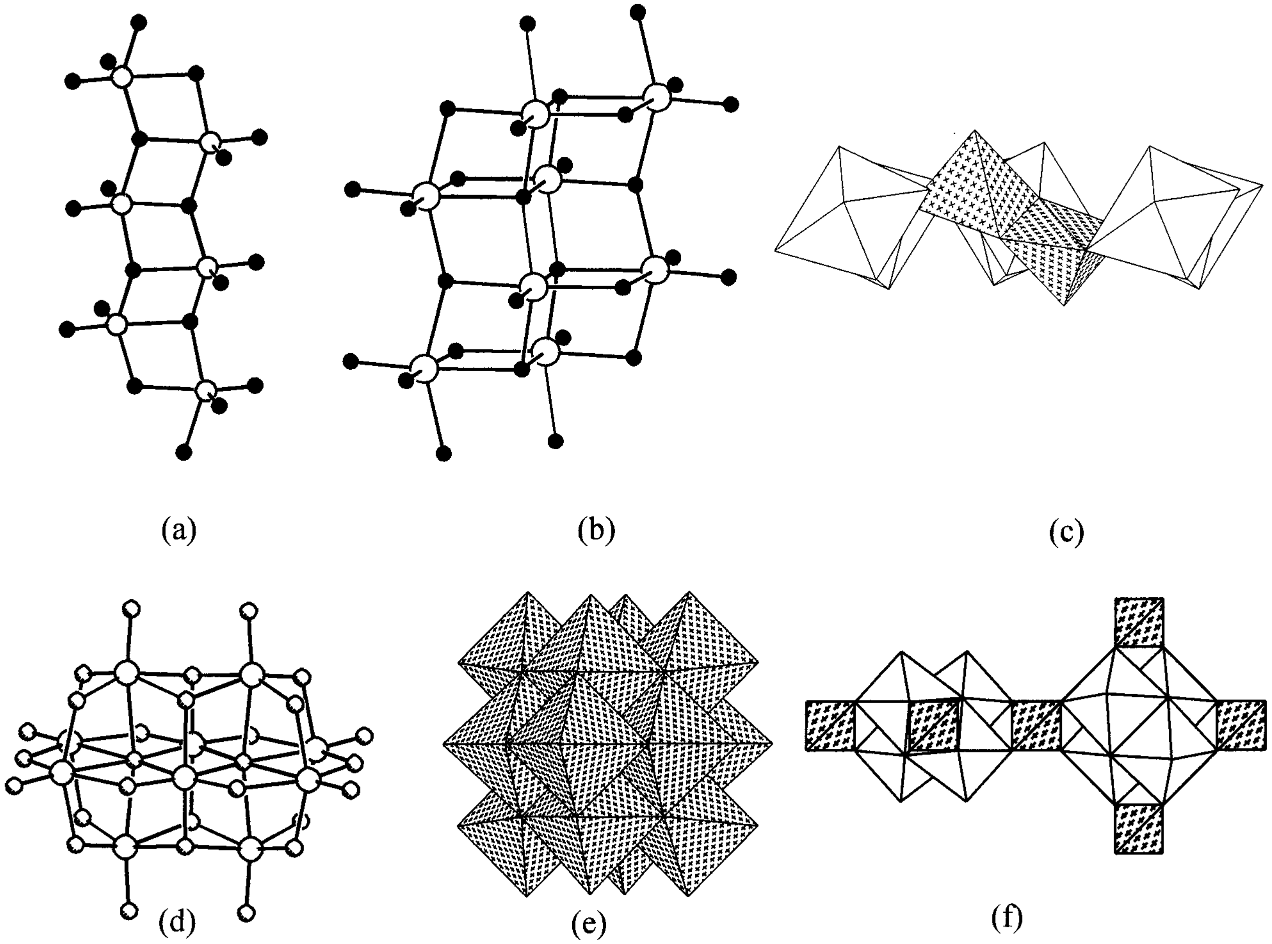

Figure 7. Structural units in selected vanadium minerals: (a) the divanadate chains in rossite with edge-shared [5]-coordinated polyhedra; (b) the tetravanadate chain in which V is in [6]-coordination; (c) two $^{[1+4]}V^{5+}$ polyhedra share common edges in the carnotite structure (marked with dots); (d) the $[V_{10}O_{28}]^{6-}$ group in pascoite, with 10 condensed (VO_6) polyhedra; (e) the $[V_2{}^{4+}V^{5+}{}_{12}O_{40}]$ group in the structures of sherwoodite and $K_7(AsV_{14}O_{40}(H_2O)_{12}$; (f) the $[V_3AlO_2(OH)_6)(PO_4)_{4/2}]^{1-}$ units in phosphovanadylite (the phosphate tetrahedra are dotted); in parts a, b, and d, V atoms are indicated with larger white circles.

structure, and as heteropolyhedral anions or infinite $[VO_3]$ chains. $[VO_3]$ chains occur in the structure of rossite, $Ca(VO_3)_2(H_2O)_4$,[46] where $^{[1+4]}V^{5+}{-}_{eq}O_{eq}{-}^{[1+4]}V^{5+}$ and $^{[1+4]}V^{5+}{-}_{eq}O_{eq}{-}^{[2+3]}V^{5+}$ linkages occur (Figure 7a). Pascoite, $Ca_3V_{10}O_{28}(H_2O)_{16}$,[45] contains isolated heteropolyhedral $[V_{10}O_{28}]^{6-}$ decavanadate polyanions in which $(^{[1+4+1]}V^{5+}O_6)$ and $(^{[2+2+2]}V^{5+}O_6)$ polyhedra link by equatorial–equatorial, vanadyl–equatorial and *trans*–*trans* bonds (Figure 7d). Another hetropolyhedral $[AlV^{5+}{}_{12}V^{4+}{}_2O_{40}]^{9-}$ polyanion occurs in the structure of sherwoodite, $Ca_{4.5}[AlV_{14}O_{40}](H_2O)_{28}$ [31] (Figure 7e). In the center of the polyanion, an (AlO_6) octahedron is surrounded by two $^{[1+4+1]}V^{4+}$ bipyramids and 12 $^{[2+2+2]}V^{5+}$ polyhedra. Here, the polyhdera are linked by the rare binary linkages $^{[1+4+1]}V^{4+}{-}_{eq}O_v{-}^{[2+2+2]}V^{5+}$ and $^{[1+4+1]}V^{4+}{-}_tO_t{-}\ ^{[2+2+2]}V^{5+}$. The layer structure of carnotite, $K_2(UO_2)_2(V_2O_8)(H_2O)_3$,[45] is built from edge-sharing $(^{[1+4]}V^{5+}O_n)$ pyramids $^{[1+4]}V^{5+}{-}_{eq}O_{eq}{-}^{[1+4]}V^{5+}$ connected by (UO_7) polyhedra (Figure 7c).

The natural vanadium bronzes may be classified[51] according to whether the layers contain connected tetravanadate chains, divanadate chains or combinations of the two (Figure 7, parts a and b). Examples are hewettite, $Ca(V_6O_{16})(H_2O)_6$ (tetravanadate + divanadate chains[52]), corvusite, $(Ca,Fe)(V_8O_{20})(H_2O)_3$ (tetravanadate chains[38]), and shcherbinaite, V_2O_5 (divanadate chains[53]). Thus, the hewetite structure-type[33] contains the following binary linkages: $^{[2+3]}V^{5+}{-}_{eq}O_{eq}{-}^{[2+3]}V^{5+}$, $^{[2+2+2]}V^{5+}{-}_{eq}O_{eq}{-}^{[2+2+2]}V^{5+}$, $^{[2+2+2]}V^{5+}{-}_tO_{eq}{-}^{[2+2+2]}V^{5+}$, $^{[2+2+2]}V^{5+}{-}_{eq}O_t{-}^{[1+4+1]}V^{5+}$, $^{[2+2+2]}V^{5+}{-}_tO_t{-}^{[1+4+1]}V^{5+}$, $^{[2+3]}V^{5+}{-}_vO_{eq}{-}^{[1+4+1]}V^{5+}$, $^{[2+2+2]}V^{5+}{-}_vO_{eq}{-}^{[1+4+1]}V^{5+}$, $^{[1+4+1]}V^{5+}{-}_{eq}O_{eq}{-}^{[1+4+1]}V^{5+}$, and $^{[2+2+2]}V^{5+}{-}_{eq}O_{eq}{-}^{[1+4+1]}V^{5+}$.

The $V^{4+}{-}O{-}V^{4+}$ binary linkage is rare in minerals (Table 4), but occurs in melanovanadinite, $Ca(V_4O_{10})(H_2O)_5$,[39] phosphovanadylite, $(Ba_{0.38}Ca_{0.2}K_{0.06}Na_{0.02})[(V_{3.44}Al_{0.46})(OH)_{5.66}O_{2.34})\ (PO_4)_2](H_2O)_{12}$,[43] and duttonite, $V_2O_4(H_2O)_2$.[54] Melanovanadinite contains layers of edge-sharing $[^{[1+4]}V^{4+}{}_2O_8]$ dimers connected by $(^{[4]}V^{5+}O_4)$ groups. The structure of phosphovanadylite consists of four edge-sharing $(^{[1+4+1]}V^{4+}O_6)$ dipyramids, $^{[1+4+1]}V^{4+}{-}_{eq}O_{eq}{-}^{[1+4+1]}V^{4+}$, which are connected by phosphate tetrahedra to adjoining identical groups (Figure 7e.). In duttonite, $(V_2O_4)(H_2O)_2$,[54] $^{[1+4+1]}V^{4+}$ dipyramids share common edges over equatorial linkages and common corners over vanadyl–*trans* linkages.

Synthetic Compounds. In their review of the structural chemistry of vanadium oxides, Zavalij and Whit-

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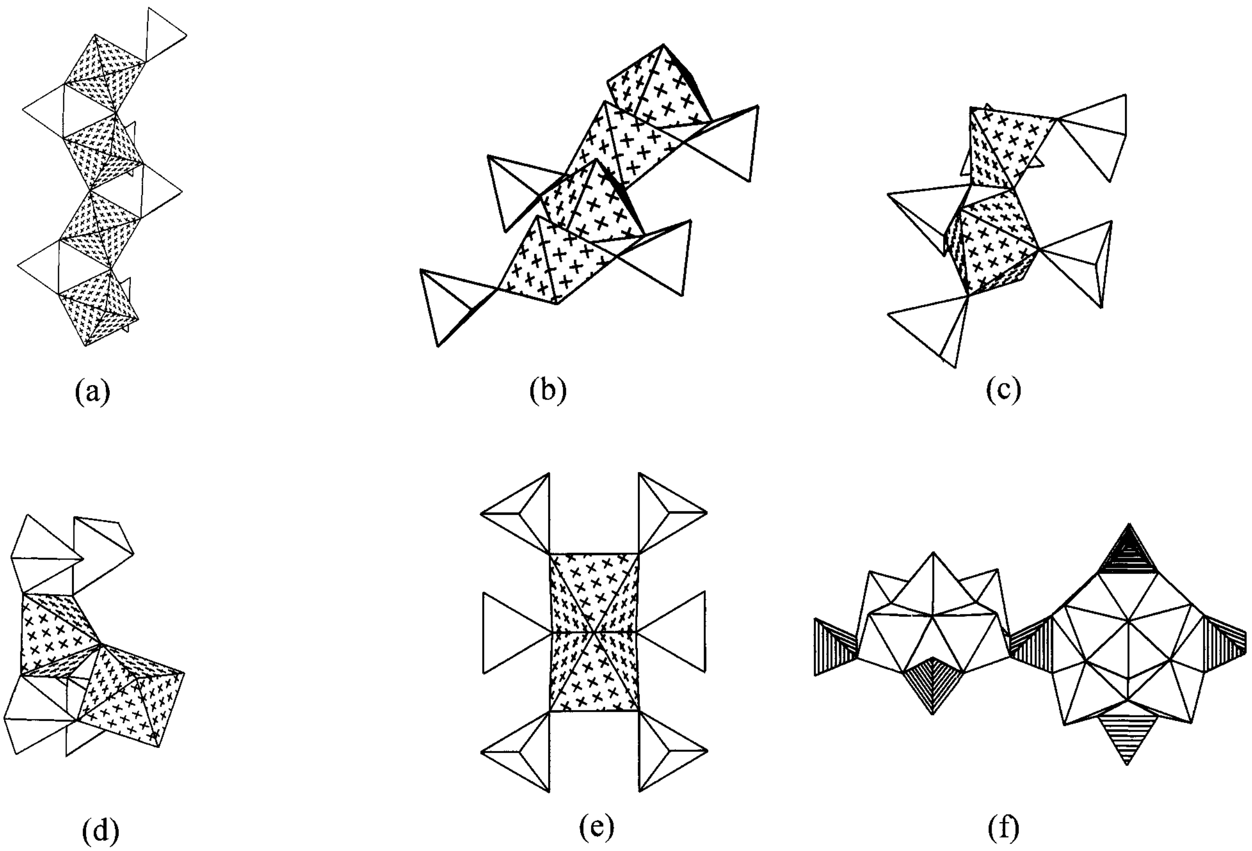

Figure 8. Structural units in selected vanadium compounds with rare binary $^{[n]}V^{Z}-{}_{b}O_{b}-{}^{[n]}V^{Z}$ linkages: (a) infinte chain of (VO_6) polyhedra; (b) infinite chains of $^{[2+3]}V^{5+}$ polyhedra in $Tl(VO_2)(HPO_4)$; (c) the isolated polyhedral group in the structure of MIL-7 (see text); (d) one $^{[1+4]}V^{4+}$ pyramid is connected with one $^{[1+4+1]}V^{4+}$ dipyramid in $Ba(VO)_2(PO_4)_2$; (e) two $^{[1+4+1]}V^{4+}$ dipyramids share faces in $VOHPO_4(H_2O)_{0.5}$; (f) two $[V_5O_9]$ groups in FVP-1 are connected via one phosphate tetrahedron (the phosphate tetrahedra are marked with stripes); in parts a−e are the (VO_n) polyhedra indicated with dots.

tingham[9] discussed various topologies of vanadium oxide frameworks. In many of these compounds, there are similar binary $^{[n]}V^{Z}-{}_{b}O_{b}-{}^{[n]}V^{Z}$ linkages as in V minerals. Prominent structural features are several (VO_n) chains in which mostly equatorial−equatorial and equatorial−*trans* linkages (see hewettite) occur. In many of these structures, V^{5+} can be also in tetrahedral coordination where the $^{[4]}V^{5+}$ atoms are linked to O atoms of equatorial bonds. The average $^{[4]}V-O$ bond valence is 1.25 vu, and according to Table 2, all $^{[4]}V^{5+}-O_{eq}-{}^{[n]}V^{Z}$ are possible for $n = [1 + 4 + 1]$, $[2 + 2 + 2]$, $[1 + 4]$, and $[2 + 3]$ and $z = V^{4+}$ and V^{5+}. Many of these compounds were synthesized at high-temperature. Thus, their crystal chemistry is dominated by $^{[n]}V^{5+}-O-{}^{[n]}V^{5+}$ linkages, where V^{4+} can replace V^{5+} in $[1 + 4]$- and $[1 + 4 + 1]$-coordinations. This explains the occurrence of similar binary linkages as in V minerals.

Rare binary linkages do occur in such compounds as vanadium phosphates and polyvanadates (Table 4) which can be synthesized under moderate temperature and (sometimes) slightly reducing conditions. These compounds can be snthesized under hydrothermal conditions or in aqueous solution, and the reducing agents can be organic solvents, elementary vanadium or reducing acids such as $H_3P^{3+}O_3$ or $H_3As^{3+}O_3$. In these compounds, the highest degree of polymerization of (VO_n) polyhedra involves chains of polyhedra (Figure 8a,b). Similar to phosphovanadylite, these chains are connected by phosphate tetrahedra to adjoining chains. This is in contrast to the natural V bronzes and many other vanadates listed by Zavalij and Whittingham,[9] where chains of (VO_n) polyhedra are polymerized to form layers and frameworks.

Chains of (VO_6) polyhedra occur in $KVOPO_4$,[35] $Cs_2[(V_2O_3)(HPO_4)_2](H_2O)$,[36] and β-$VOPO_4$[37] (Figure 8a). In $KVOPO_4$, $^{[1+4+1]}V^{4+}$ polyhedra connect through vanadyl−*trans* bonds, whereas in $Cs_2[(V_2O_3)(HPO_4)_2](H_2O$ and β-$VOPO_4$, there are vanadyl−*trans* linkages between $^{[1+4+1]}V^{4+}$ and $^{[1+4+1]}V^{5+}$ and $^{[1+4+1]}V^{5+}$ and $^{[1+4+1]}V^{5+}$ polyhedra, respectively. A chain of $^{[2+3]}V^{5+}$ polyhedra occurs in $Tl(VO_2)(HPO_4)$,[25] where the polyhedra are connected by vanadyl−equatorial bonds (Figure 8b). Other rare binary linkages occur in isolated polyhedral groups, e.g. $(VO_2)(OH)(H_2O)[O_3P(CH_2)_3PO_3](H_2O)_2(NH_4)$ (also known as MIL-7(HT)),[40] $(V_2O_3)(H_2O)[O_3P(CH_2)_3PO_3)](H_2O)_2(NH_4)$ (also known as MIL-7(LT)),[40] $Ba(VO_2)(PO_4)_2$,[34] $(VOHPO_4(H_2O)_{0.5}$,[48] and $Na_v[((V^{4+}{}_{4-w}V^{5+}{}_{1+w})O_9(PO_4)_2](PO_4)_x(OH)_y(H_2O)_z$ ($v = 2.8-4.0$, $w = -0.1-1.1$, $x = 0-0.2$, $y = 0-2.1$, $z = 7-10$) (also known as FVP-1).[5] In MIL-7,[40] there is a high- (HT) and a low-temperature form (LT). In the HT form, $^{[1+4]}V^{4+}$ and $^{[1+4+1]}V^{4+}$, and in the LT form $^{[1+4+1]}V^{4+}$ and $^{[1+4]}V^{5+}$, polyhedra link through equatorial−equatorial bonds (Figure 8c). In $Ba(VO)_2(PO_4)_2$,[34] $^{[1+4]}V^{4+}$ pyramids and $^{[1+4+1]}V^{4+}$ dipyramids link via vanadyl−*trans* linkages with $^{[1+4+1]}V^{4+}$ dipyramids (Figure 8d). In $(VOHPO_4(H_2O)_{0.5}$,[48] two $^{[1+4+1]}V^{4+}$ polyhedra share faces involving equatorial−equatorial and *trans*−*trans* linkages (Figure 8e). In FVP-1[5] and other synthetic compounds, there are isolated $[V_5O_9]$ groups, where four $^{[1+4]}V^{4+}$ and one

$^{[1+4]}V^{5+}$ pyramids link through equatorial−equatorial linkages (Figure 8f). The [V_5O_9] group in FVP-1 is connected to the next identical group by phosphate tetrahedra, similar to the linkage of [V_4O_8] groups in phosphovanadylite.[55]

Summary

The bond length distributions in ($V^{4+}O_n$) and ($V^{5+}O_n$) ($n = 5, 6$) polyhedra show distinct populations which can be used to define *vanadyl*, *equatorial*, and *trans* V−O bonds. These definitions can be used to define different coordinations of V in the form of the notation [$a + b + c$], where the sequence of numbers gives the amount of vanadyl (a), equatorial (b), and *trans* (c) bonds, respectively. The mean equatorial bond length in ($V^{4+}O_n$) and ($V^{5+}O_n$) polyhedra were used to develop an effective scheme for calculating the average valence state of V in mixed-valent structures. The definition of characteristic bond valences for vanadyl, equatorial, and *trans* bonds allow us to specify which kinds of binary linkages are possible in vanadate structure, and to examine their occurrence in minerals and synthetic compounds. Vanadium bronze minerals and many synthetic vanadate structures are characterized by polymerization of (VO_n) chains to form layers and frameworks. In the chainlike character of these structures, equatorial−equatorial and equatorial−*trans* linkages dominate. Rare binary $^{[n]}V^{Z}{-}_{b}O_{b}{-}^{[n]}V^{Z}$ linkages occur in compounds synthesized under hydrothermal conditions or in aqueous solution and under slightly reducing conditions. The structure of these compounds are characterized by infinite (VO_n) chains or isolated finite polyhedral groups.

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Supporting Information Available: Bond lengths and corresponding references. This material is available free of charge via the Internet at http://pubs.acs.org.

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