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$Cu(VO)(SeO_3)_2$ (A) and (B) Forms: Synthesis and Crystal Structures of New Copper(II)–Vanadyl(IV) Diselenites

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Two forms of copper(II) vanadyl(IV) diselenite $CuVO(SeO_3)_2$ have been synthesized by solid state reaction. The form (A) belongs to the monoclinic system space group $P2_1/c$ with $a = 7.983(1)$ Å, $b = 8.877(2)$ Å, $c = 8.437(2)$ Å, and $\beta = 100.62(2)°$. It is a layered structure built up of CuO_6 and VO_6 octahedra associated, respectively, by pairs via edge sharing which are making $[Cu_2O_{10}]$ and $[V_2O_{10}]$ dimers. These dimers are building a layer $[CuVO_7]_n$ upon which are fixed the selenium (IV) cations. The lone pairs of the selenium (IV) are packed in a double layer perpendicular to the [001] direction. Form (B) crystallizes in the orthorhombic system, space group *Pnma* with $a = 7.071(2)$ Å, $b = 8.223(2)$ Å, and $c = 9.500(2)$ Å. The structure also exhibits dimers associated via edge and corner sharing along the [100] and [010] directions, which build up layers parallel to the (001) plane; they are held together by Se–O bonds. The connection via V–O–Cu induces a local order that does not respect the three-dimensional order of the network. © 1999 Academic Press

INTRODUCTION

The study of the crystal chemistry of low-dimensional compounds is the object of intense research worldwide, owing to their specific and sometimes exotic magnetic properties. Copper (II) containing compounds were extensively studied because of the interest raised by the discovery of high T_c superconductors (1–4). Recently the advantage of studying vanadium (IV) compounds has been highlighted by the discovery of a spin gap in CaV_2O_5 and CaV_4O_9 (5, 6), compounds belonging to the family CaV_nO_{2n+1} ($n = 2, 3, 4$), discovered and characterized by Bouloux and Galy (7). Owing to the coordination versatility of vanadium, it is possible to isolate the spin sites; i.e., V^{4+}, by varying the oxidation state of vanadium: vanadium (V) does not carry a spin. A good example of this strategy is given by $Na_{1.286}V_2O_5$ (8).

Another way of obtaining low dimensional compounds is to use the so-called lone pair cations, such as Te IV, which are assumed to act as "structural scissors" (the lone pair is denoted by E) (9). Such cations are, for example, As III, Se IV, Sn II, Sb III, Te IV, I V, Tl I, Pb II, Bi III for which the stereochemical role of the lone pair E has been particularly emphasized (10–13). As an example this has proved to be successful with Se IV, two original compounds having been characterized with V IV in the system VO_2–SeO_2: $VOSe_2O_5$ and $VOSeO_3$. In the former three isolated parallel strings $[VO_5]_n$ of VO_6 octahedra connected by $[Se_2O_5E_2]$ groups have been evidenced whereas double chains $[V_2O_8]_n$ linked by $[SeO_3E]$ groups are present in $VOSeO_3$ (14, 15). The copper (II)–selenium (IV)–oxygen system has also been investigated and a few phases characterized: –$CuSe_2O_5$ (16); –$CuSeO_3$ and Cu_2OSeO_3 (17); –$Cu_4O(SeO_3)_3$ (18), the three latter phases crystallizing in various modifications, but the ternary diagram CuO–VO_2–SeO_2 has not received attention.

The purpose of this work is to present the synthesis and the crystal structure of the first member of this system, $Cu(VO)(SeO_3)_2$, in its both (A) and (B) allotropic forms.

EXPERIMENTAL

Single crystals of composition $Cu(VO)(SeO_3)_2$ were grown by solid state reaction starting from the stoichiometric mixture of CuO (Aldrich, 99.99%), VO_2, and SeO_2. VO_2 was prepared by heating under vacuum an equimolar mixture of V_2O_5 and V_2O_3 at 850°C for 24 hr. V_2O_3 itself was obtained by reducing V_2O_5 (Aldrich 99.6%) under hydrogen at 800°C. Owing to the tendency of SeO_2 to adsorb water, the powder was recrystallized at 350°C prior to use. The mixture was sealed under vacuum in a Pyrex tube and heated at 480°C for 8 days followed by a slow cooling at a rate of 10°C/hr down to 300°C and then furnace cooled. Two types of crystals were present in the batch: brown platelet-like crystals (form (A)) and small black translucent parallelepipeds (called form (B) in the following). Energy

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TABLE 1
Crystallographic Parameters of $CuVO(SeO_3)_2$ (A) and (B) Forms

	Form (A)	Form (B)
	Crystal Data	
Formula	$CuVO(SeO_3)_2$	$CuVO(SeO_3)_2$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pnma*
a [Å]	7.983(1)	7.071(2)
b [Å]	8.877(2)	8.223(2)
c [Å]	8.437(2)	9.500(2)
β (°)	100.62(2)	
V [Å]^3	587.6(2)	552.4(2)
Z	4	4
Formula weight (g)	384.40	384.40
ρ calc [g/cm^3]	4.34	4.62
μ [Mo$K\alpha$ cm^{-1}]	175.8	187.0
Morphology	Platelet	Parallelepiped
Dimension (mm)	$0.12 \times 0.06 \times 0.006$	$0.11 \times 0.08 \times 0.06$
	Data collection	
Temperature [°C]	23	23
Wavelength [Mo$K\alpha$] [Å]	0.71069	0.71069
Monochromator	Graphite	Graphite
Scan mode; Scan width [°]	ω–2θ; $1.1 + 0.35 \tan\theta$	ω–2θ; $0.8 + 0.35 \tan\theta$
Take off angle [°]	4.5	4.5
Max Bragg angle [°]; Tmax [s]	35; 80	35; 80
hkl range	$0 \rightarrow 12/0 \rightarrow 14/-13 \rightarrow 13$	$0 \rightarrow 11/0 \rightarrow 13/-15 \rightarrow 15$
	Structure refinement	
Reflections for cell refinement	25 with $5.96° \leq \theta \leq 27.87°$	25 with $6.15° \leq \theta \leq 21.08°$
Reflections collected	2873	2722
Reflections unique used	1707	1078
Parameters refined	100	71
Largest difference peak/hole (eÅ^3)	1.39/1.37	1.87/1.70
$R = \sum\|\|Fo\| - \|Fc\|\|/\sum\|Fo\|$	0.0347	0.0340
$R_w = [\sum_w(\|Fo\|^2 - \|Fc\|^2)^2/\sum_w(Fo^2)^2]^{1/2}$	0.0808	0.0785

X-ray dispersive analysis (EDX) gave the same molar ratio, Cu:V:Se = 1:1:2, for both cases, corresponding to the starting composition $CuVSe_2O_7$.

Single-crystal X-ray diffraction analyses were performed using an Enraf-Nonius CAD4 diffractometer with Mo$K\alpha$ radiation selected by a graphite monochromator. The orientation matrix and accurate cell values were derived from least squares refinement of the setting angles of 25 reflections. Crystal data for both (A) and (B) forms are reported in Table 1. Correction of Lorentz-polarization and empirical absorption (psi-scan (19)) were applied to the *hkl* data. Sir92 (20) was used to determine both structures by direct methods and their refinement was performed with Shelxl-96 (21), are consistent with the space group $P2_1/c$. The final atomic coordinates, thermal parameters, and selected interatomic distances and angles are listed in Tables 2 and 4. Copper (II) and vanadium (IV) both exhibit very distorted CuO_6 and VO_6 octahedra (see Figs. 1a and 1b). In the case of Cu II, which sits in the plane formed by O1O2O2^{i}O3, four short bonds are established ranging from 1.927(4) to 1.997(4) Å; two longer bonds, Cu–O4 = 2.468(5) Å and Cu–O5 = 2.495(4) Å, are directed to the apices of the CuO_6 octahedron, a distortion induced by the Jahn–Teller effect. Vanadium presents a characteristic coordination with a short vanadyl bond, V–O7 = 1.598(4) Å, toward one apex of the VO_6 octahedron, four bonds between 1.983(4) and 2.098(4) Å with the oxygen atoms of the equatorial plane and a longer bond to the remaining apex, V–O6 = 2.197(4) Å. These CuO_6 and VO_6 octahedra are associated in pairs (dimers), $[Cu_2O_{10}]$ and $[V_2O_{10}]$, via edge sharing, O2–O2^{i} and O6–O6^{iii}, respectively (Fig. 2a). These dimers alternate in the Oy and Oz directions building

STRUCTURAL DETERMINATIONS

Form (A)

The (A) form of $Cu(VO)(SeO_3)_2$ crystallizes in the monoclinic system. The extinction conditions for *hkl* reflections

TABLE 2
Fractional Atomic Coordinates and Thermal Parameters for $Cu(VO)(SeO_3)_2$ (A) Form

Atom	Wyckoff site	x	y	z	U_{eq} (Å^2)	Site occupancy
Se1	4*e*	0.12616(7)	0.23108(6)	0.25556(6)	0.0075(1)	1
Se2	4*e*	0.67396(7)	0.32848(6)	0.28339(6)	0.0064(1)	1
Cu	4*e*	0.37204(9)	0.37731(8)	0.51904(8)	0.0103(1)	1
V	4*e*	0.3036(1)	0.5073(1)	0.0567(1)	0.0068(2)	1
O1	4*e*	0.2727(5)	0.1832(4)	0.4257(4)	0.0101(7)	1
O2	4*e*	0.5800(5)	0.4086(4)	0.4300(5)	0.0102(7)	1
O3	4*e*	0.1755(5)	0.3914(4)	0.6210(5)	0.0112(7)	1
O4	4*e*	0.2283(5)	0.3953(4)	0.2345(4)	0.0108(7)	1
O5	4*e*	0.5845(5)	0.3443(4)	0.7734(4)	0.0092(7)	1
O6	4*e*	0.5582(5)	0.4047(4)	0.1109(4)	0.0088(7)	1
O7	4*e*	0.1397(5)	0.6062(5)	−0.0148(5)	0.0136(8)	1

Anisotropic temperature factors (A) form

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se1	0.0069(2)	0.0082(2)	0.0079(2)	−0.0007(2)	0.0025(2)	−0.0003(2)
Se2	0.0068(2)	0.0066(2)	0.0059(2)	0.0006(2)	0.0016(2)	0.0004(2)
Cu	0.0125(3)	0.0088(3)	0.0109(3)	−0.0029(2)	0.0056(2)	−0.0032(2)
V	0.0080(4)	0.0064(3)	0.0062(3)	0.0000(3)	0.0015(3)	0.0000(3)
O1	0.016(2)	0.007(2)	0.006(1)	0.001(1)	0.002(1)	−0.001(2)
O2	0.016(2)	0.007(2)	0.011(2)	−0.002(1)	0.009(1)	−0.002(1)
O3	0.011(2)	0.012(2)	0.012(2)	0.005(1)	0.003(1)	0.001(1)
O4	0.016(2)	0.010(2)	0.005(2)	0.004(1)	0.001(1)	−0.004(2)
O5	0.014(2)	0.005(2)	0.008(1)	−0.002(1)	−0.001(1)	0.002(1)
O6	0.008(2)	0.010(2)	0.009(2)	0.003(1)	0.003(1)	0.001(1)
O7	0.012(2)	0.015(2)	0.014(2)	0.004(2)	0.002(2)	0.004(2)

an infinite $[CuVO_7]_n$ sheet parallel to (100) (Fig. 2b) The dimers are tilted with respect to one another and share apices in the Oy direction, whereas in the Oz direction two octahedra of the same $[Cu_2O_{10}]$ dimer are linked via two apices to the same edge of a VO_6 octahedron of the following dimer. This gives, in the projection onto the (100) plane, the peculiar serrated shape illustrated in Fig. 3. The (A) form appears then as a layered structure with the selenium atoms located above and below each layer. Owing to the stereochemical activity of the $4s^2$ lone pair, Se1 and Se2 are coordinated to three oxygen atoms and their coordination polyhedron becomes a tetrahedron if one takes into account the lone pair E. These tetrahedra are not connected in the same way to the dimers. The $Se1O_3E$ tetrahedron shares one edge (O4–O1) with one copper (II) containing octahedron and is linked via $O3^{ii}$ to a free apex of the following copper (II) containing dimers (Fig. 2a). The $Se2O_3E$ tetrahedron is connected via O2 and O6 to the middle of two dimers occupied respectively by Cu II and V IV and via $O5^{ii}$ to two successive dimers.

Form (B)

The reflection conditions, $0kl$ $k+l=2n$ and $hk0$ $h=2n$, were consistent with the space groups $Pnma$ and $Pn2_1a$. We

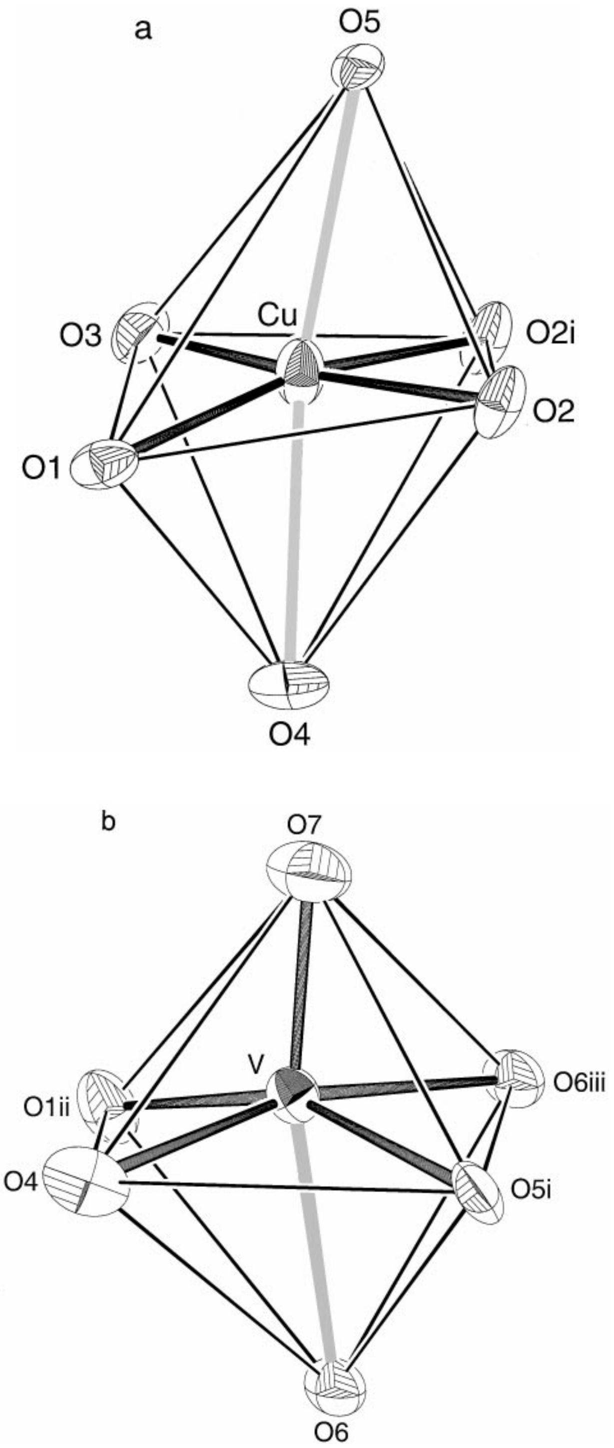

FIG. 1. Coordination polyhedra of copper (a) and vanadium (b) in (A) $Cu(VO)(SeO_3)_2$ (displacement ellipsoids are shown at 85% probability level).

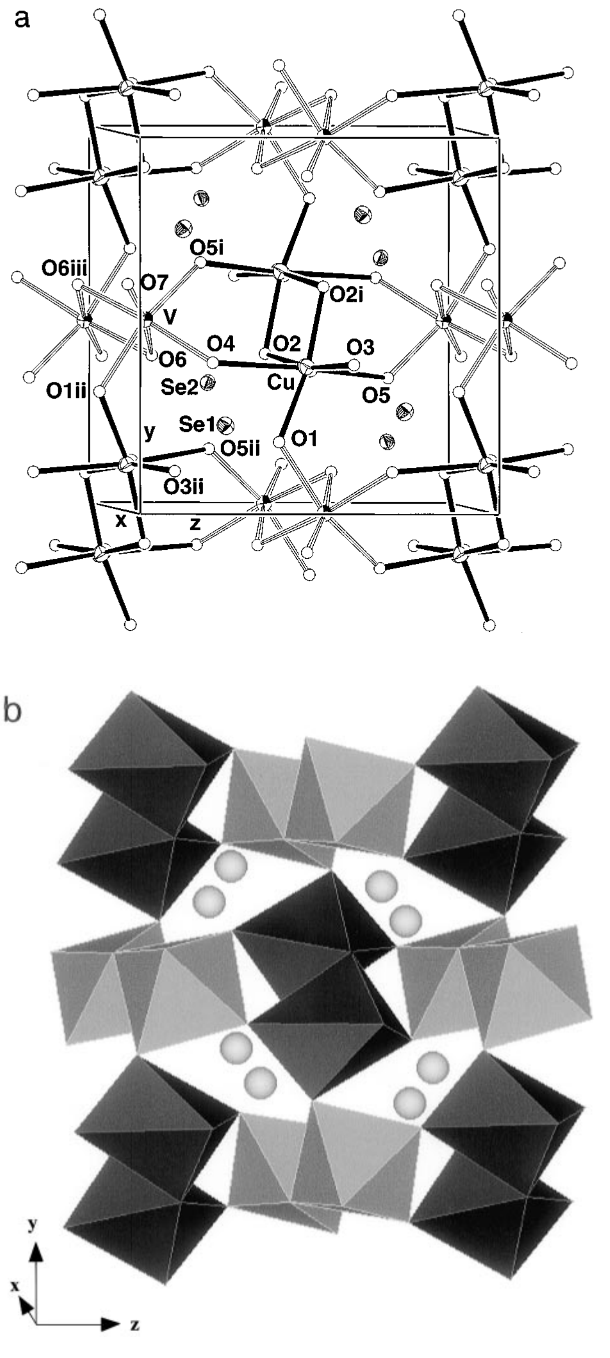

FIG. 2. (a) Ortep representation of (A) Cu(VO)$(SeO_3)_2$ with atom labels; (b) Projection of (A) Cu(VO)$(SeO_3)_2$ onto the plane (100) slightly tilted for clarity. The polyhedra occupied by vanadium and copper atoms are in gray and black, respectively.

performed the refinements for the two groups. The best reliability factors were obtained in the centrosymmetric space group *Pnma*, $R = 0.0340\%$ and $Rw = 0.0785\%$; for $Pn2_1a$ we found $R = 0.0354\%$ and $R_w = 0.0806\%$ while the number of adjustable parameters was almost doubled. Furthermore it was possible to refine all the atoms with anisotropic thermal parameters in *Pnma*, whereas the thermal parameters of the oxygen atoms were nonpositive definite in $Pn2_1a$. It is worth mentioning that the refinement in the noncentrosymmetric space group $Pn2_1a$ leads to two independent sites for copper and vanadium (i.e., ordering) both surrounded by six oxygen atoms making an octahedron. Electron microscopy analysis not presented here does not show any indication of a surstructure. The space group $Pn2_1a$ would permit an easier description of the structure; however, the parameters of the refinement (*R* factors, number of parameters, thermal parameters) and bond length consideration (a vanadyl double bound V=O equal to 1.717(3) Å in $Pn2_1a$ versus 1.64(1) in *Pnma*) drive us to the choice of *Pnma*. The final atomic coordinates, thermal parameters, and selected interatomic distances and angles for the space group *Pnma* are listed in Tables 3 and 4.

The description in the centrosymmetric space group *Pnma* leads to copper (II) and vanadium (IV) located statistically in the same octahedron, i.e., $O1O2O3O4O3^iO5$. If Cu II and V IV admit the same coordination polyhedron they are of course alternatively present and owing to their different bonding scheme, two sites are clearly evidenced inside the octahedron. These sites, one for Cu and one for V, are occupied at 50% and are separated by 0.24 Å. As a result of this unexpected situation the oxygen O5 does not sit exactly on the symmetry center $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; it has been located and well refined with half site occupancy and a reasonable thermal parameter in a general nearby position *xyz*. For the sake of clarity, Figs. 4a and 4b depict the environment of Cu and V independently. Cu is close to the center of the octahedron in a quasi-planar coordination but it is driven slightly out of

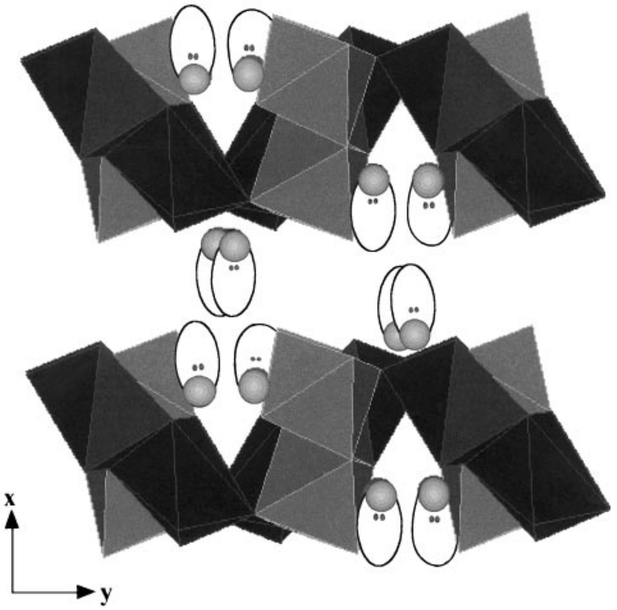

FIG. 3. Projection of (A) Cu(VO)$(SeO_3)_2$ onto the plane (001).

TABLE 3
Fractional Atomic Coordinates and Thermal Parameters for Cu(VO)(SeO$_3$)$_2$ (B) Form

Atom	Wyckoff site	x	y	z	U_{eq} (Å^2)	Site occupancy
Se1	4c	0.25923(9)	1/4	0.14062(6)	0.0098(2)	1
Se2	4c	0.16566(9)	1/4	0.76167(6)	0.0087(2)	1
Cu	8d	0.2071(9)	0.440(1)	0.452(1)	0.0105(8)	0.5
V	8d	0.240(1)	0.434(2)	0.453(2)	0.0103(9)	0.5
O1	4c	0.2914(8)	1/4	0.3215(5)	0.0119(8)	1
O2	4c	0.2057(7)	1/4	0.5807(5)	0.0111(8)	1
O3	8d	0.1028(5)	0.5917(4)	0.5919(3)	0.0139(6)	1
O4	8d	0.1922(5)	0.5920(4)	0.3018(3)	0.0151(6)	1
O5	8d	0.456(1)	0.489(1)	0.492(9)	0.018(1)	0.5

Anisotropic temperature factors (B) form

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se1	0.0131(3)	0.0089(2)	0.0076(2)	0	−0.0005(2)	0
Se2	0.0104(3)	0.0090(2)	0.0069(2)	0	−0.0011(2)	0
Cu	0.021(2)	0.004(1)	0.0067(7)	0.0014(6)	0.004(2)	0.006(2)
V	0.019(3)	0.005(1)	0.007(1)	0.0006(7)	0.003(2)	0.008(2)
O1	0.023(2)	0.006(2)	0.007(1)	0	0.002(2)	0
O2	0.023(2)	0.005(2)	0.006(2)	0	−0.001(2)	0
O3	0.025(2)	0.006(1)	0.011(1)	−0.001(1)	0.000(1)	0.000(1)
O4	0.021(2)	0.012(1)	0.012(1)	0.004(1)	0.003(1)	−0.002(1)
O5	0.020(4)	0.017(3)	0.017(3)	0.002(3)	0.001(3)	−0.004(3)

the oxygen equatorial plane by an interaction with the oxygen O5^{ii} (distance Cu–plane [O1, O2, O3, O4] = 0.09 Å). The four Cu–O distances in the equatorial plane range from 1.901(12) to 2.084(11) Å, the two remaining distances toward the octahedron apices being Cu–O3^{i} = 2.246(9) Å and Cu–O5^{ii} = 2.511(9) Å. The vanadium coordination polyhedron is characteristic of the valence state of this element; i.e., IV, with a short vanadyl double bond V=O5 = 1.635(14) Å and four longer ones in between 1.955(17) and 2.093(14) Å. The vanadium distance to the basal plane in this square pyramid is 0.30 Å; to complete the octahedron it is necessary to take into account the oxygen atom O3^{i} located at a distance of 2.471(14) Å.

It is noted that both Cu and V sites are displaced toward O5. If one assumes that one octahedron is occupied by vanadium with the short V–O5 vanadyl bond, there is no choice for the opposite metallic site. It is automatically occupied by Cu, with a Cu^{ii}–O5 distance of 2.511(9) Å (Fig. 4c). This results from the fact that copper cannot be bound to the O5 site closer to its equatorial oxygen plane because Cu–O5 would become too short, Cu–O5 = 1.84 Å. Therefore, CuO$_6$ and VO$_6$ octahedra are corner shared via O5.

A description of the general network is given by the projection of the structure onto the (100) plane (Fig. 5) and the projection of the [CuVO$_7$]$_n$ layer along the direction [001] presented in Fig. 6 together with Se atoms and their lone pairs, which pack in the large voids left in this layer. The structure can then be described as constituted of an elementary building block: two octahedra CuO$_6$ and VO$_6$ sharing an O5 corner being associated by edge-sharing O1–O2 and O3–O3^{i} in the [010] and [100] directions (Fig. 5). Nothing prevents having locally the sequences Cu–Cu, V–V, or Cu–V between two building blocks along these directions without disrupting the network three-dimensional order. The cohesion of the network in the [001] direction is ensured by the selenium atoms Se1 and Se2 which present the characteristic coordination of Se IV. They are alternatively linked via two oxygens atoms, O3–O3^{i} and O4^{v}–O4^{vi} to one layer and via a third oxygen atom, O1 or O2 for Se1 or Se2, respectively, to the following. In Fig. 5 we deliberately represented the tetrahedra occupied by the selenium atoms if one takes into account the lone-pair sphere of influence E of Se IV. These lone pairs E point along the [100] direction, i.e., toward the space available between [CuVO$_7$]$_n$ layers.

TABLE 4
Selected Interatomic Distances (Å) and Angles (°) for Cu(VO)(SeO$_3$)$_2$ (A) and (B) Forms

Form (A)

Cu–O1	1.997(4)	V–O1^{ii}	2.011(4)	O5^{ii}–Se2–O6	99.2(2)
Cu–O2	1.964(4)	V–O4	1.983(4)	O5^{ii}–Se2–O2	100.1(2)
Cu–O2^{i}	1.970(4)	V–O5^{i}	2.028(4)	O6–Se2–O2	102.1(2)
Cu–O3	1.927(4)	V–O6^{iii}	2.098(4)	O5–Cu–O4	164.7(2)
Cu–O4	2.4680(5)	V–O6	2.197(4)	O1–Cu–O2	105.8(2)
Cu–O5	2.4950(4)	V–O7	1.598(4)	O2–Cu–O2^{i}	78.6(2)
Se1–O1	1.730(4)	Se2–O2	1.715(3)	O2^{i}–Cu–O3	88.9(2)
Se1–O3^{ii}	1.671(4)	Se2–O5^{ii}	1.688(4)	O3–Cu–O1	86.3(2)
Se1–O4	1.695(4)	Se2–O6	1.713(4)	O7–V–O6	165.4(2)
Cu–Cu^{i}	3.044(4)	O3^{ii}–Se1–O4	108.1(2)	O5^{i}–V–O6^{iii}	91.0(2)
Cu–V^{iv}	3.482(7)	O3^{ii}–Se1–O1	101.3(2)	O6^{iii}–V–O1^{ii}	88.2(2)
V–V^{iii}	3.445(4)	O4–Se1–O1	91.9(2)	O1^{ii}–V–O4	88.3(2)
				O4–V–O5^{i}	86.9(2)

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

Form (B)

Cu–O1	2.084(11)	V–O1	1.992(15)	O4^{v}–Se2–O4^{vi}	100.8(2)
Cu–O2	1.983(12)	V–O2	1.955(17)	O4^{v}–Se2–O2	97.2(2)
Cu–O3	1.963(10)	V–O3	2.093(14)	O4^{vi}–Se2–O2	97.2(2)
Cu–O3^{i}	2.246(9)	V–O4	1.966(16)	O5–Cu–O3^{i}	173.9(2)
Cu–O4	1.901(12)	V–O5	1.635(14)	O1–Cu–O4	93.4(2)
Cu–O5^{ii}	2.511(9)	V–O3^{i}	2.471(14)	O4–Cu–O3	94.0(2)
Se1–O1	1.733(5)	Se2–O2	1.742(4)	O3–Cu–O2	94.7(2)
Se1–O3^{iii}	1.691(3)	Se2–O4^{v}	1.686(4)	O2–Cu–O1	77.1(2)
Se1–O3^{iv}	1.691(3)	Se2–O4^{vi}	1.686(4)	O5+–V–O3^{i}	168.0(2)
Cu–V	0.239(1)	Cu–Cu^{i}	3.219(7)	O1–V–O4	94.4(7)
Cu^{vii}–V	3.083(7)	V–V^{vii}	3.021(7)	O4–V–O3	88.3(5)
Cu–V^{i}	3.448(8)	O3^{iii}–Se1–O3^{iv}	100.7(2)	O3–V–O2	91.6(6)
V–V^{i}	3.678(9)	O3^{iii}–Se1–O1	101.3(2)	O2–V–O1	80.0(6)
Cu–Cu^{viii}	3.127(7)	O3^{iv}–Se1–O1	101.3(2)		

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

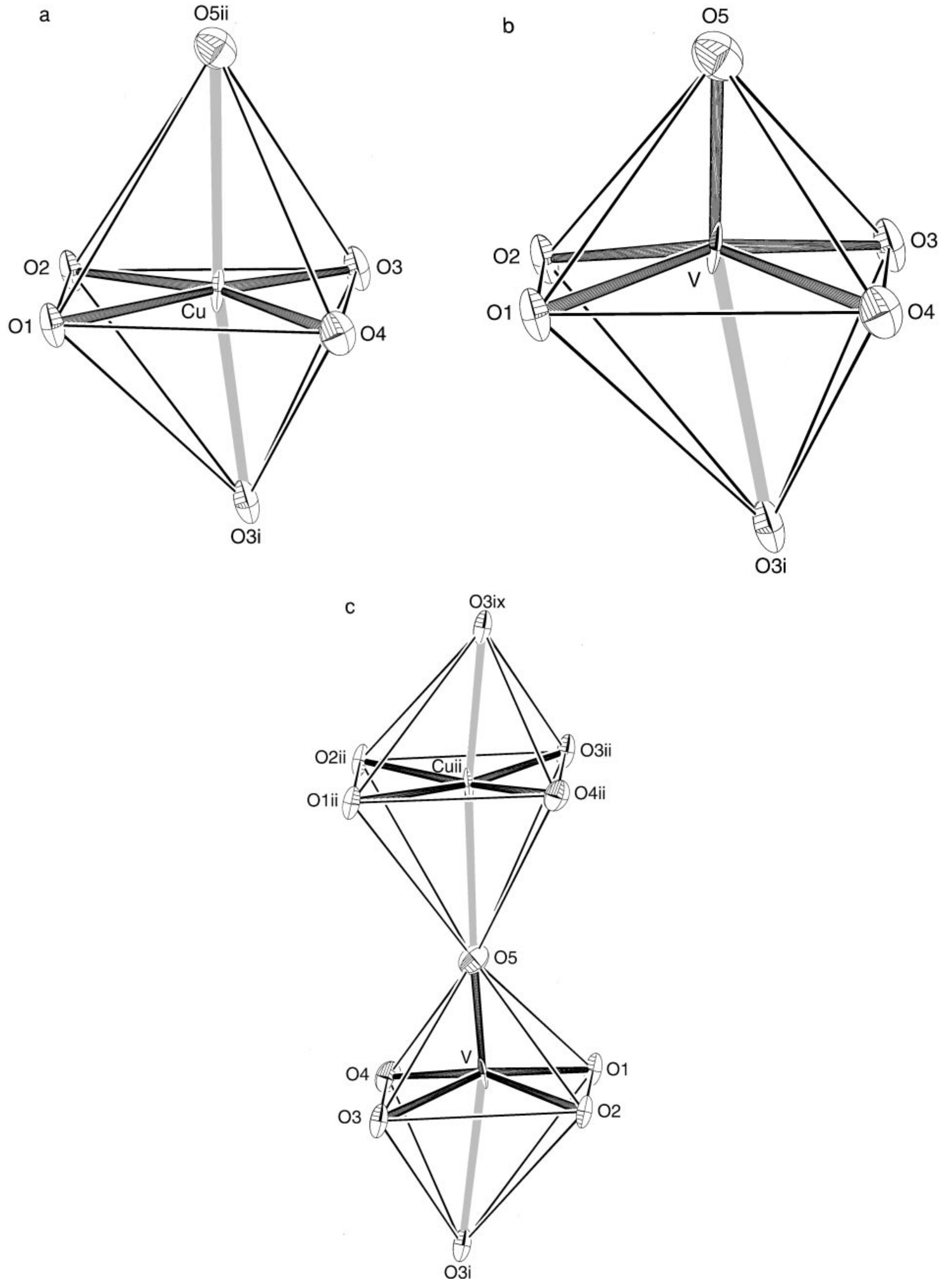

FIG. 4. Coordination polyhedra of copper (a) and vanadium (b) in (B) Cu(VO)(SeO$_3$)$_2$; (c) Connection between Cu and V polyhedra.

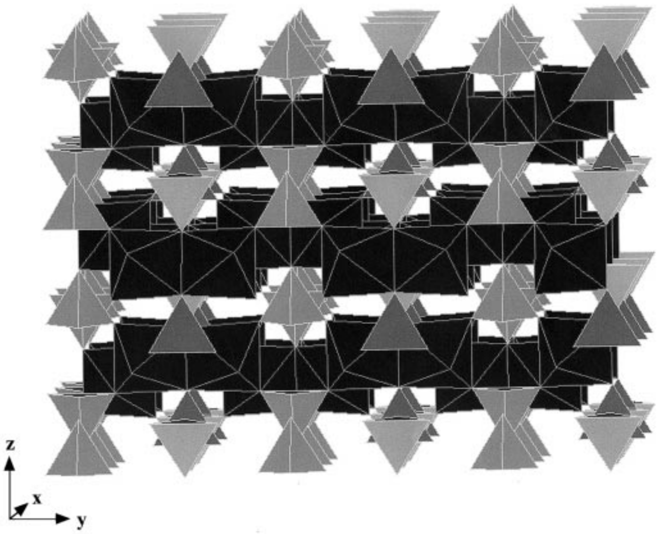

FIG. 5. Perspective view of (B) $Cu(VO)(SeO_3)_2$ along the [100] direction slightly tilted for the sake of clarity. For this drawing O5 occupies the site $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and the same site is appointed for Cu and V.

DISCUSSION AND CONCLUSION

Once the structure of these two forms (A) and (B) of $Cu(VO)(SeO_3)_2$ is known, it is straightforward to link it to the crystal morphology. The platelet shape of the form (A) is a consequence of the presence of transition-metal oxygen layers isolated from each other by the selenium atoms, of which $4s^2$ lone pairs point toward the space left between the layers. Such a geometry is quite common with ns^2 cation-containing compounds, such as the red PbO form (22), Aurivillius phases (23), and the high-T_c superconductor phase $Bi_2Sr_2CaCu_2O_8$ (24). These double layers of lone pairs, separating the $[CuVO(SeO_3)_2]_n$ layers, explain the fact that the cell volume of the (A) form is around 10% higher than that of the (B) form. In the form (B), the selenium atoms do not play the same role. They are bonded to two successive transition-metal oxygen layers giving rise to this three-dimensional structure. The analysis of numerous structures of various oxides has shown that the lone pairs E have roughly an oxygen size, complete a hcp oxygen packing, or sit in similar site of cations having quasi-identical volume, like K or Ba (10) (example: Ba and O form a hexagonally close packing in $BaNiO_3$ and the general packing architecture in (B) form reminds us of the $BaNb_2O_6$ one (25); the Ba atoms occupying a similar site to the lone pair E of Se IV).

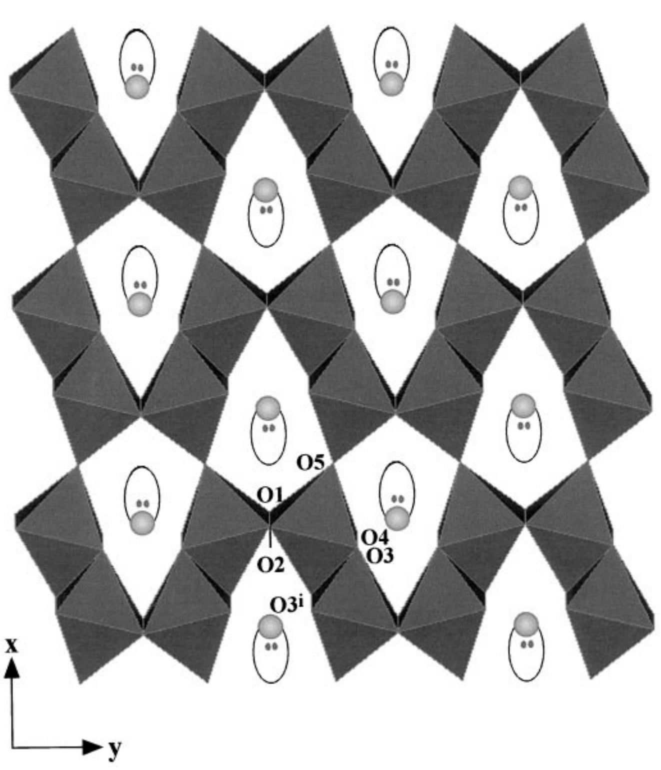

FIG. 6. Projection of the copper–vanadium–oxygen layer of (B) $Cu(VO)(SeO_3)_2$ and location of Se IV atoms together with their lone pair E along the [001] direction (same criteria as in Fig. 5).

Interestingly, it is possible to describe both structures using the same building units: dimers and tetrahedra. However it is difficult to find a structural mechanism that could describe a transition from (A) to (B). Thermal analysis has to be performed in order to check whether (A) or (B) is the high-temperature form. As a first experiment we have tried to prepare powder corresponding to these two phases but, surprisingly, it was only possible to synthesize the (B) form, which appears to be the most stable. Nevertheless it is not common to obtain crystals with the same composition but with different structure in the same batch.

In view of the particular structural arrangement of the transition metals polyhedra and therefore the spin $\frac{1}{2}$ sites found in these two $CuVO(SeO_3)_2$ forms, interesting magnetic properties are expected, the study of which is currently under investigation.

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