

# Hydrothermal Synthesis and Crystal Structure of $\text{Ba}_6[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}$ with an Unusual Arrangement of $\text{V}^{\text{IV}}\text{--O}$ Polyhedra

Yasushi Kanke,<sup>\*,1</sup> Yoshio Oka,<sup>†</sup> and Takeshi Yao<sup>‡</sup>

<sup>\*</sup>National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan; <sup>†</sup>Department of Natural Environment Sciences, Faculty of Integrated Human Studies, Kyoto University, Kyoto 606-8501, Japan; and <sup>‡</sup>Department of Fundamental Energy Science, Graduate School of Energy Sciences, Kyoto University, Kyoto 606-8501, Japan

Received October 28, 1999; in revised form January 10, 2000; accepted January 20, 2000

A new  $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$  mixed-valence polyoxovanadate compound  $\text{Ba}_6[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}$  has been hydrothermally synthesized in an  $\text{NaVO}_3\text{--BaI}_2\text{--}(\text{CH}_3)_4\text{NI}$  aqueous solution system. The compound crystallizes cubic,  $Im\bar{3}$ ,  $a = 16.8323(2)$  Å, and  $Z = 6$ . The structural analysis gave  $wR2 = 0.0597$  for all of the unique 2641 reflections and 83 parameters and  $R1 = 0.0229$  for 2217 reflections with  $F_o > 4\sigma(F_o)$ . The phase contains discrete  $[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})]^{12-}$  polyoxovanadate ion and three types of  $\text{Ba}^{2+}$  cations, two of which connect the polyoxovanadate ion three-dimensionally. The remaining  $\text{Ba}^{2+}$  cation is attached to the discrete ion and is hydrated. The polyoxovanadate ion contains four  $\text{V}_2\text{O}_7$  units of corner-sharing tetrahedral  $\text{VO}_4$  pairs and one  $\text{V}_2^{\text{IV}}\text{O}_{10}(\text{H}_2\text{O})$  unit. The two types of units are linked by corner-sharing. The  $\text{V}_2^{\text{IV}}\text{O}_{10}(\text{H}_2\text{O})$  unit shows two types of unusual  $\text{V--O}$  polyhedral arrangements. One is a couple of  $\text{VO}_5(\text{H}_2\text{O})$  octahedra sharing the water molecule, and the other consists of a  $\text{VO}_6$  octahedron and a  $\text{VO}_5$  square pyramid sharing a corner oxygen and includes a distant water molecule.  $\text{Ba}_6[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}$  exhibits Curie–Weiss-like paramagnetic behavior without any magnetic transition down to 5 K, probably reflecting the discrete location of the polyoxovanadate ion.

© 2000 Academic Press

**Key Words:** polyoxovanadate; hydrothermal synthesis; crystal structure; paramagnetism.

## INTRODUCTION

A great number of polyoxovanadates are known for oxidation states of vanadium with mixed valences of  $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$  as well as a single valence of  $\text{V}^{\text{V}}$  or  $\text{V}^{\text{IV}}$  (1). In the mixed-valence states, vanadium ions of different valences may adopt different oxygen coordination: for example,  $\text{VO}_4$  tetrahedron and  $\text{VO}_5$  trigonal bipyramid for  $\text{V}^{\text{V}}$  and  $\text{VO}_5$  square pyramid and  $\text{VO}_6$  octahedron for  $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ . This leads to a wide

variety of polyhedral structures of structural interest as well as magnetic properties that arise from the  $d^1$  state of  $\text{V}^{\text{IV}}$ .

Polyoxovanadates are prepared by solution processes usually at moderate temperatures below  $100^\circ\text{C}$ . Recently hydrothermal methods using reaction temperatures above  $100^\circ\text{C}$  have been applied in the synthesis of polyoxovanadates aiming at new compounds. Actually Zubieta and his co-workers reported several isopoly- or heteropolyvanadates synthesized by hydrothermal methods (2). Hydrothermal methods have also been applied to develop new vanadium oxide bronzes with mixed valences of  $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$  (3). In the present study, we were successful in synthesizing hydrothermally a mixed-valence barium decavanadate and carried out a single-crystal X-ray diffraction study. Unusual arrangements of  $\text{V--O}$  polyhedra were found for  $\text{V}^{\text{IV}}\text{O}_6$  octahedra and  $\text{V}^{\text{IV}}\text{O}_5$  square pyramids.

## EXPERIMENTAL

The title compound was synthesized in the hydrothermal system of  $\text{NaVO}_3\text{--BaI}_2\text{--}(\text{CH}_3)_4\text{NI}$ . A 50 ml mixed solution of 0.15 M  $\text{NaVO}_3$ , 0.15 M  $\text{BaI}_2$ , and 0.003 M  $(\text{CH}_3)_4\text{NI}$  was sealed in a Pyrex ampoule followed by hydrothermal treatment at  $280^\circ\text{C}$  for 40 h in an autoclave. The treatment gave a yellow clear supernatant solution with pH 4.3 and precipitates consisting of dark purple cubic crystals and dark brown powders. The cubic crystals were easily isolated by repeated supersonic separations with distilled water. A crystalline phase of the brown powder was identified by powder X-ray diffractometry to be  $\text{BaV}_3\text{O}_8$  (4) and that of the cubic crystal was unidentified.

Quantitative X-ray microanalysis of the cubic crystals was performed using  $\text{BaAl}_2\text{O}_4$  and  $\text{LaVO}_4$  as reference materials, which gave a Ba/V ratio of  $(6.07 \pm 0.04)/10$ . The average oxidation number of vanadium of the cubic crystals was determined by visible spectroscopy to be 4.77(2) from the concentrations of  $[\text{V}^{\text{IV}}\text{O}(\text{H}_2\text{O})_5]^{2+}$  and

<sup>1</sup>To whom correspondence should be addressed. Fax: +81-298-58-5650. E-mail: kanke@nirim.go.jp.

[V<sup>V</sup>O<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> in a dilute HCl solution of the crystals. A weight loss of 2.5% was detected by thermogravimetry. A density of 3.91(1) g cm<sup>-3</sup> was obtained by pycnometry using distilled water at 22°C. An infrared spectrum obtained by a Nujol method gave a 1625 cm<sup>-1</sup> band as well as a broad band around 3400 cm<sup>-1</sup>, indicating the existence of water molecules. The spectrum showed no evidence of (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>. The analytical results indicate the composition of the cubic crystal to be Ba<sub>6</sub>V<sub>10</sub>O<sub>30</sub> · 3.5H<sub>2</sub>O. Magnetic susceptibility of the phase was obtained with a SQUID magnetometer by using 114.6 mg of crystal specimen under an external magnetic field of 1000 Oe.

Preliminary four-circle diffraction study at Kyoto revealed that the dark purple crystal is body-centered cubic with  $a = 16.8 \text{ \AA}$  and Laue group of  $m\bar{3}$ . An  $N(z)$  test (5) on the intensities preferred centrosymmetric  $Im\bar{3}$  among three possible space groups  $I23$ ,  $I2_13$ , and  $Im\bar{3}$ . The specimen for structural analysis was selected by means of oscillation and Weissenberg photographs. The size of the specimen was 0.20 mm, 0.18 mm, 0.22 mm, 0.18 mm, 0.18 mm, and 0.20 mm along  $[110]$ ,  $[101]$ ,  $[011]$ ,  $[1\bar{1}0]$ ,  $[10\bar{1}]$ , and  $[01\bar{1}]$ , respectively. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using  $\omega$ - $\theta$  scan with  $\Delta\omega = (1.0 + 0.35 \tan \theta)^\circ$ . The lattice parameter  $a$  was refined to be 16.8323(2)  $\text{\AA}$  from Bragg angles of 22 reflections in the region  $60^\circ < 2\theta < 65^\circ$ . The analytical composition of Ba<sub>6</sub>V<sub>10</sub>O<sub>30</sub> · 3.5H<sub>2</sub>O, the cell volume of 4769.03(10)  $\text{\AA}^3$ , and the observed density of 3.91(1) g cm<sup>-3</sup> gave the number of the formula unit  $Z = 6$  with the reasonable calculated density of 3.920 g cm<sup>-3</sup>. Measured reflections satisfied the conditions  $h \geq 0$ ,  $k \geq 0$ ,  $l \geq 0$ ,  $h \leq k$ ,  $h \leq l$ ,  $h + k + l \neq \text{odd}$ , and  $2\theta \leq 80^\circ$ . Of the resulting 2802 reflections, 394 were unobserved. Three standard reflections 800, 080, and 008 were measured every 4 h. Deviation of intensity was within 0.7% during the total exposure time of 199.8 h. No decay correction was applied. Absorption correction was applied with  $\mu = 10.11 \text{ mm}^{-1}$  by ABST in PLATON (6). The obtained transmission range was 0.2042–0.2599. Among the 2802 reflections, 2641 were unique for  $Im\bar{3}$  ( $R_{\text{int}} = 0.0179$ ). All of the 2802 reflections were used for structural analysis by SHELXL (7). Atomic scattering factors for neutral atoms and their dispersions are taken from Ref. (8). The refinements were carried out on the basis of  $I = F^2$ .

## RESULTS

The space group  $Im\bar{3}$  and the lattice parameter  $a = 16.8323(2) \text{ \AA}$  of the present phase reminded us of Ba<sub>5.33</sub>(H<sub>3</sub>O)<sub>0.33</sub>[V<sub>10</sub>O<sub>30</sub>] with the space group  $Im\bar{3}$  and  $a = 16.9439(2) \text{ \AA}$ , reported by Zubieta and his co-workers (2). The Ba(1) and Ba(2) atoms were easily located on the basis of their structural data. Remaining atoms were found by subsequent Fourier synthesis.

The V(1) and V(2) atoms were found in the first stage. However, a differential Fourier synthesis showed a large negative peak at the V(2) position and a positive peak close to the V(2) position. The positive peak was assigned to the V(3) atom. The second refinement was carried out by varying the occupancies of the V(2) and V(3) sites, designated by  $g(V(2))$  and  $g(V(3))$ , respectively. The resulting  $g(V(2)) + g(V(3))$  was essentially one, reflecting that the V(2) and V(3) sites are too close to be occupied simultaneously. The V(1), V(2), and V(3) atoms correspond to the V(1), V(2), and V(2A) atoms in Ref. (2), respectively. A subsequent differential Fourier synthesis gave a positive peak which was too large to be assigned to an O atom. The peak was assigned to the partially occupied Ba(3) atom, which is missing in Ref. (2). The O(1)–O(5) atoms were found in the next stage, and anisotropic thermal parameters were applied to the Ba(1)–Ba(3), V(1)–V(3), and O(1)–O(5) atoms. Subsequently the partially occupied O(6) and O(7) atoms were located only 0.99  $\text{\AA}$  apart. Indeed, the sum of their occupancies  $g(O(6)) + g(O(7))$  was close to 1 but less than 1, and  $g(O(6))$  and  $g(O(7))$  were close to  $g(V(2))$  and  $g(V(3))$ , respectively. The O(1)–O(7) atoms correspond to the O(1), O(2), O(4), O(3), O(5), O(6A), and O(6) atoms in Ref. (2), respectively. The obtained composition was Ba<sub>5.99</sub>V<sub>9.87</sub>O<sub>30.79</sub>. The occupancy  $g(\text{Ba}(3))$  was fixed at  $\frac{1}{6}$ , and a constraint

TABLE 1

Atomic Coordinates and Equivalent Thermal Parameters in Ba<sub>6</sub>[V<sub>10</sub>O<sub>30</sub>(H<sub>2</sub>O)] · 2.5H<sub>2</sub>O (Cubic,  $Im\bar{3}$ ,  $a = 16.8323(2) \text{ \AA}$ ,  $Z = 6$ ,  $wR2 = 0.0597$ ,<sup>a</sup>  $R1 = 0.0383$ ,<sup>b</sup>  $S = 1.200$ ,<sup>c</sup>  $\Delta/\sigma < 0.001$ , and  $-1.74 < \Delta\rho < 2.50 \text{ e \AA}^{-3}$  for all of the unique 2641 reflections and 83 parameters;  $R1 = 0.0229$ <sup>b</sup> for 2217 reflections with  $F_o > 4\sigma(F_o)$ )

Atom	Position	Occupancy	x	y	z	100 $U_{\text{eq}}$ ( $\text{\AA}^2$ )
Ba(1)	24g	1	0	0.33216(1)	0.27784(1)	1.312(4)
Ba(2)	8c	1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1.198(5)
Ba(3)	24g	$\frac{1}{6}$	0	0.15438(12)	0.06097(17)	4.42(5)
V(1)	48h	1	0.09737(2)	0.12256(2)	0.32820(2)	0.969(6)
V(2)	12e	0.6394(33)	0	$\frac{1}{2}$	0.13763(6)	0.86(2)
V(3)	12e	1 - $g(V(2))$	0	$\frac{1}{2}$	0.09125(10)	0.70(4)
O(1)	48h	1	0.10656(11)	0.22076(10)	0.34165(10)	1.58(3)
O(2)	48h	1	0.09592(11)	0.26170(11)	0.16492(10)	1.79(3)
O(3)	48h	1	0.08025(11)	0.41911(11)	0.11950(13)	2.16(4)
O(4)	24g	1	0	0.09807(19)	0.29186(17)	2.16(5)
O(5) <sup>d</sup>	6b	1	0	$\frac{1}{2}$	0	3.29(14)
O(6)	12e	$g(V(2))$	0	$\frac{1}{2}$	0.2339(3)	1.80(10)
O(7) <sup>e</sup>	12e	1 - $g(V(2))$	0	$\frac{1}{2}$	0.2927(10)	3.6(3)
O(8) <sup>e</sup>	48h	$\frac{5}{16}$	0.0337(7)	0.1244(8)	0.1036(8)	6.5(3)

<sup>a</sup> $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$  and  $w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 28.0205P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . <sup>b</sup> $R1 = \sum\|F_o\| - |F_c|/\sum\|F_o\|$ . <sup>c</sup> $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$  where  $n$  ( $= 2641$ ) is the number of reflections and  $p$  ( $= 83$ ) is the total number of parameters refined. <sup>d</sup> $2g(V(2)) - 1$  corresponds to H<sub>2</sub>O. <sup>e</sup>H<sub>2</sub>O.

$g(V(2)) + g(V(3)) = 1$  was added in the next stage, according to the analytical result,  $Ba_6V_{10}O_{30} \cdot 3.5H_2O$ . The resulting composition was  $Ba_6V_{10}O_{30.78}$ .

A comparison between the analytical composition and the structural composition indicates that at least one of the O(1)–O(7) atoms corresponds to  $H_2O$  and that an additional O atom of  $H_2O$  should exist. As will be discussed later,  $g(O(6))$  and  $g(O(7))$  were constrained to  $g(V(2))$  and  $1 - g(V(2))$ , respectively, and the O(7) atom and a  $2g(V(2)) - 1$  portion of the O(5) atom were assigned to  $H_2O$ . The resulting composition was  $Ba_6V_{10}O_{30} \cdot H_2O$ . A subsequent differential Fourier synthesis found the remaining  $2.5H_2O$  as the largest positive peak, which was assigned to the O(8) atom. The occupancy  $g(O(8))$  was fixed at  $\frac{5}{16}$  to meet the composition  $Ba_6V_{10}O_{30} \cdot 3.5H_2O$ . Anisotropic thermal parameters were not applicable to the O(8) atom. Atomic fractional coordinates and equivalent isotropic thermal parameters are shown in Table 1 (9). Interatomic distances and bond valences (10) are listed in Tables 2 and 3, respectively.

**TABLE 2**  
Interatomic Distances (Å)

V(1)–O(2) <sup>i</sup>	1.6572(17)	Ba(1)–O(2) <sup>ii, iii</sup>	2.7616(18)
O(1)	1.6755(17)	O(1) <sup>ii, iii</sup>	2.8083(17)
O(3) <sup>i</sup>	1.7285(17)	O(7)	2.8361(15) <sup>b</sup>
O(4)	1.7973(12)	O(1) <sup>vi, vii</sup>	2.8580(17)
		O(3) <sup>viii, ix</sup>	2.867(2)
V(2)–O(6)	1.621(6)	O(6)	2.9202(14) <sup>b</sup>
O(3) <sup>ii, iii, iv, v</sup>	1.9422(17)	O(3) <sup>ii, iii</sup>	3.327(2)
O(5)	2.3166(11)		
		Ba(2)–O(1) <sup>i, ii, vii, ix, x, xi</sup>	2.9072(18)
V(3)–O(5)	1.5359(18)	O(2) <sup>j, ii, vii, ix, x, xi</sup>	2.969(2)
O(3) <sup>ii, iii, iv, v</sup>	1.9761(18)		
O(7)	3.391(17) <sup>a</sup>	Ba(3)–O(8) <sup>xii, xiii</sup>	2.766(13) <sup>c</sup>
		O(8) <sup>xiv, xv</sup>	2.872(15) <sup>c</sup>
		O(8) <sup>i, xvi</sup>	2.881(13)
		O(2) <sup>ii, iii</sup>	2.989(3)
		O(4) <sup>x, xvii</sup>	3.022(3)
V(2)–V(3)	0.781(2) <sup>d</sup>	Ba(3)–Ba(3) <sup>xiv</sup>	2.052(6) <sup>d</sup>
V(2)–O(7)	2.610(17) <sup>e</sup>	Ba(3)–O(8) <sup>ii, iii</sup>	1.045(13) <sup>d</sup>
V(3)–O(6)	2.402(6) <sup>e</sup>	Ba(3)–O(8) <sup>x, xvii</sup>	2.307(14) <sup>d</sup>
		O(6)–O(7)	0.989(17) <sup>d</sup>
		O(8)–O(8) <sup>iii</sup>	1.13(2) <sup>d</sup>
		O(8)–O(8) <sup>i</sup>	1.96(2) <sup>d</sup>
		O(8)–O(8) <sup>x</sup>	1.96(2) <sup>d</sup>

Note. Symmetry code: (i)  $x, y, z$ , (ii)  $x, y, z$ , (iii)  $-x, y, z$ , (iv)  $x, 1 - y, z$ , (v)  $-x, 1 - y, z$ , (vi)  $-1/2 + z, 1/2 - x, 1/2 - y$ , (vii)  $1/2 - z, 1/2 - x, 1/2 - y$ , (viii)  $-1/2 + y, 1/2 - z, 1/2 - x$ , (ix)  $1/2 - y, 1/2 - z, 1/2 - x$ , (x)  $y, z, x$ , (xi)  $1/2 - x, 1/2 - y, 1/2 - z$ , (xii)  $y, z, -x$ , (xiii)  $-y, z, -x$ , (xiv)  $x, y, -z$ , (xv)  $-x, y, -z$ , (xvi)  $-z, x, y$ , (xvii)  $-y, z, x$ .

<sup>a</sup>Too long to be considered as a bond.

<sup>b</sup>One of the O(6) and O(7) positions is occupied and the other vacant (see text).

<sup>c</sup>The O(8)<sup>xii</sup> and O(8)<sup>xiv</sup> positions (1.96(2) Å), the O(8)<sup>xiv</sup> and O(8)<sup>xv</sup> ones (1.13(2) Å), and the O(8)<sup>xv</sup> and O(8)<sup>xiii</sup> ones (1.96(2) Å) cannot be occupied simultaneously.

<sup>d</sup>Forbidden (too short).

<sup>e</sup>Forbidden (see text).

**TABLE 3**  
Bond Valences

Bond	Bond valence		Bond	Bond valence	
	V <sup>IV</sup>	V <sup>V</sup>		V <sup>IV</sup>	V <sup>V</sup>
V(1)–O(2) <sup>i</sup>	1.341	1.411	O(5)–V(2) <sup>ii, xiv</sup>	0.237	0.250
O(1)	1.162	1.223	V(3) <sup>ii, xiv</sup>	1.955	2.058
O(3) <sup>i</sup>	0.965	1.016	$\sum O(5) - 2V(2)$	0.474	0.500
O(4)	1.554	1.635	$\sum O(5) - V(2)V(3)$	2.192	2.308
$\sum V(1) - O$	5.022	5.285	$\sum O(5) - 2V(3)$	3.910	4.116
V(2)–O(6)	1.554	1.635	O(6)–V(2)	1.554	1.635
O(3) <sup>ii, iii, iv, v</sup>	0.652	0.686	Ba(1) <sup>ii, v</sup>		0.182
O(5)	0.237	0.250	$\sum O(6) - V(2)Ba$	1.918	1.999
$\sum V(2) - O$	4.399	4.629			
			O(7)–Ba(1) <sup>ii, v</sup>		0.229
V(3)–O(5)	1.955	2.058	V(3)	0.013	0.014
O(3) <sup>ii, iii, iv, v</sup>	0.595	0.626	$\sum O(7) - V(3)Ba$	0.471	0.472
O(7)	0.013	0.014			
$\sum V(3) - O(5)O(3)$	4.335	4.562	O(8)–Ba(3) <sup>xvi</sup>		0.276
$\sum V(3) - O(5)O(3)O(7)$	4.348	4.576	Ba(3) <sup>xiv</sup>		0.207
			Ba(3) <sup>x</sup>		0.202
			$\sum O(8) - Ba$		0.685
Ba(1)–O(2) <sup>ii, iii</sup>		0.280			
O(1) <sup>ii, iii</sup>		0.246			
O(7)		0.229	Ba(3)–O(8) <sup>xii, xiii</sup>		0.276
O(1) <sup>vi, vii</sup>		0.215	O(8) <sup>xiv, xv</sup>		0.207
O(3) <sup>viii, ix</sup>		0.210	O(8) <sup>i, xvi</sup>		0.202
O(6)		0.182	O(2) <sup>ii, iii</sup>		0.151
O(3) <sup>ii, iii</sup>		0.061	O(4) <sup>x, xvii</sup>		0.138
$\sum Ba(1) - OO(7)$		2.253	$\sum Ba(3) - O$		1.465 <sup>a</sup>
$\sum Ba(1) - OO(6)$		2.206			
Ba(2)–O(1) <sup>i, ii, vii, ix, x, xi</sup>		0.189			
O(2) <sup>i, ii, vii, ix, x, xi</sup>		0.160			
$\sum Ba(2) - O$		2.094			

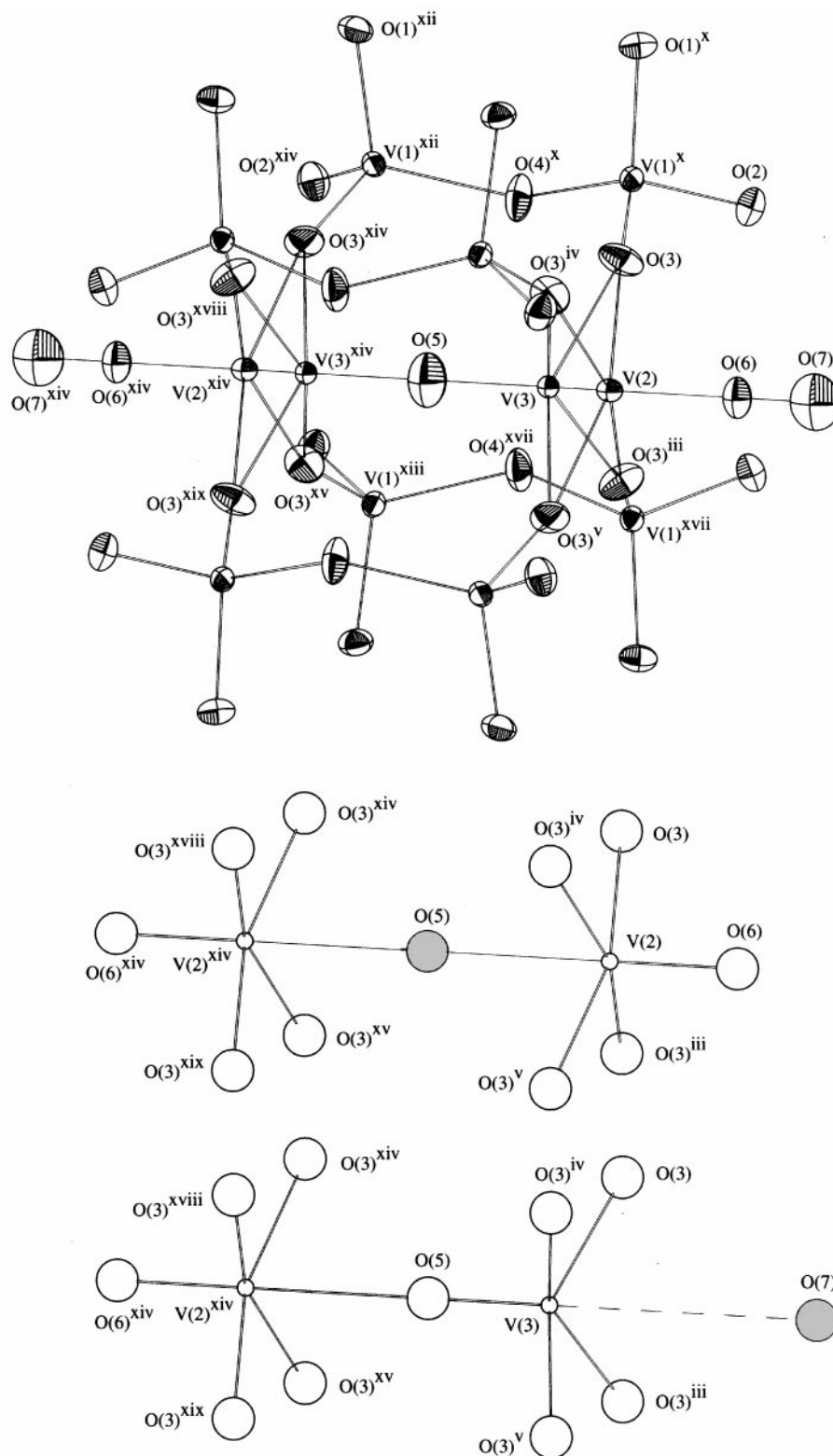
<sup>a</sup>See footnote *c* of Table 2. One of the O(8)<sup>xii</sup> and O(8)<sup>xiv</sup> positions and one of the O(8)<sup>xiii</sup> and O(8)<sup>xv</sup> positions are vacant.

## DISCUSSION

### Coordination Spheres of V Atoms and Arrangement of V–O Polyhedra

Possible coordination spheres of the V atoms are shown in Fig. 1. The V(1) atom forms a V(1)O<sub>4</sub> tetrahedron with the O(1)–O(4) atoms. Two V(1)O<sub>4</sub> tetrahedra make a V<sub>2</sub>O<sub>7</sub> unit by sharing the O(4) vertex. Four V<sub>2</sub>O<sub>7</sub> units surround the V(2) and V(3) atoms with two O(3)<sub>4</sub> rectangles, forming a polyoxovanadate ion. Since  $g(V(2)) + g(V(3)) = 1$  was obtained, one of the adjacent V(2) and V(3) sites is occupied and the other vacant. As will be rationalized in the following, the V(2) atom forms a VO<sub>6</sub> octahedron (V(2)O(6)O(3)<sub>4</sub>O(5)) while the V(3) atom forms a VO<sub>5</sub> square pyramid (V(3)O(5)O(3)<sub>4</sub>), respectively (Table 2), where V(2)–O(6) (1.621(6) Å) and V(3)–O(5) (1.5359(18) Å) correspond to double bonds.

Let us consider possible arrangements of the V(2) and V(3) atoms. The V(3)–O(5)–V(3) arrangement is forbidden,



**FIG. 1.** Structure of the polyoxovanadate ion with all possible arrangements (top). Anisotropic thermal vibrations are shown using 50% probability. Structures of the  $O(6)=V(2)-O(5)_{\text{water}}-V(2)=O(6)$  arrangement (middle) and the  $O(6)=V(2)-O(5)=V(3)\cdots O(7)_{\text{water}}$  arrangement (bottom). Shaded circles represent  $H_2O$  molecules. Symmetry codes: (xviii)  $x, 1-y, -z$ ; (xix)  $-x, 1-y, -z$ .

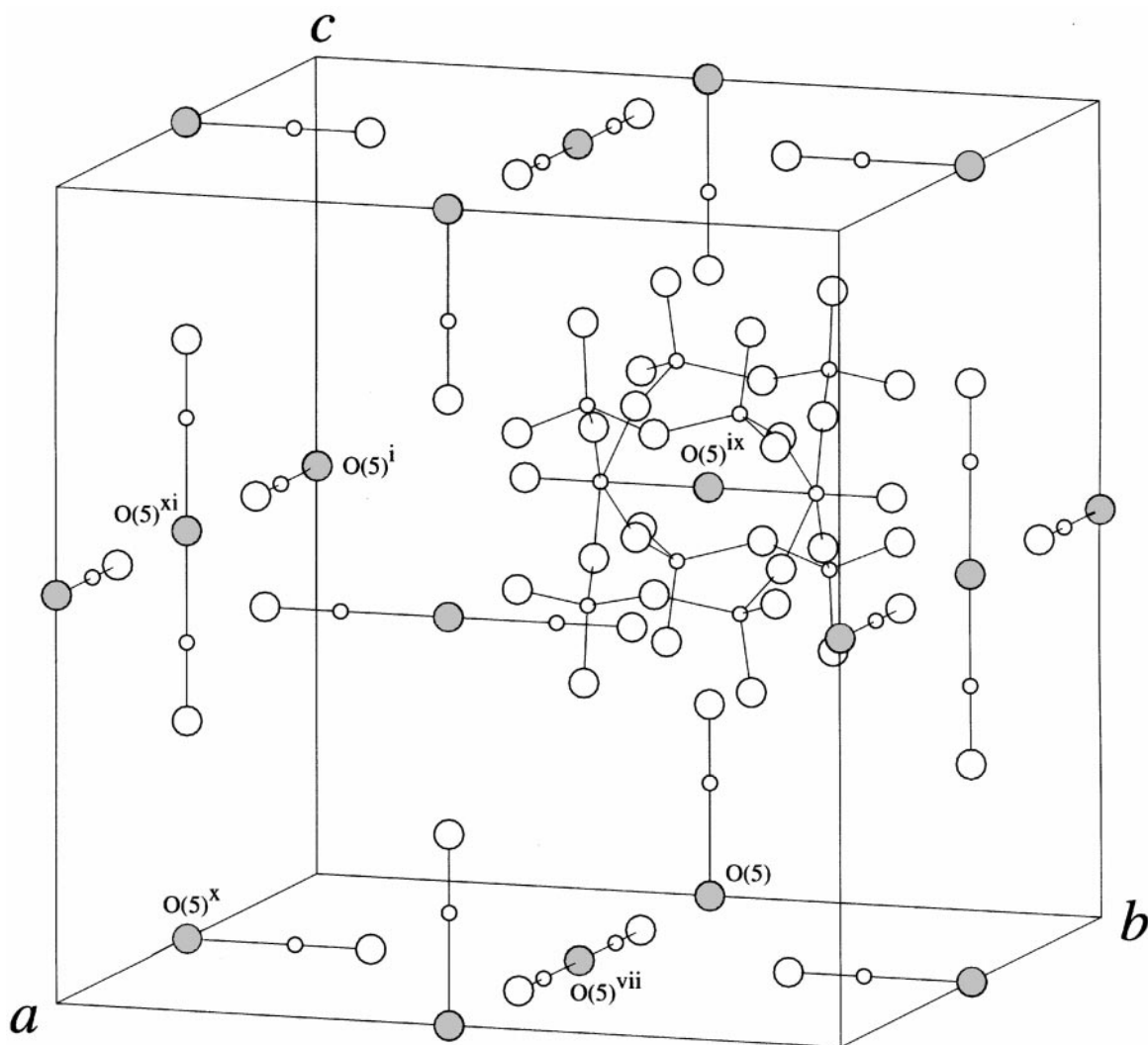


FIG. 2. Location of the  $[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})]^{12-}$  polyoxovanadate ion in a unit cell. For conciseness, all of the ions are drawn with the  $\text{V}(2)\text{-H}_2\text{O-V}(2)$  arrangement and only one polyoxovanadate ion is shown completely.

because the O(5) atom shows a too high bond valence sum (hereafter BVS) of ca. 4 (Table 3). Acceptable arrangements are therefore  $\text{V}(2)\text{-O}(5)\text{-V}(2)$  and  $\text{V}(2)\text{-O}(5)\text{-V}(3)$ , or more precisely  $\text{O}(6)=\text{V}(2)\text{-O}(5)\text{-V}(2)=\text{O}(6)$  and  $\text{O}(6)=\text{V}(2)\text{-O}(5)=\text{V}(3)\text{---O}(7)$  as depicted in Fig. 1, which agrees with  $g(\text{V}(2)) > g(\text{V}(3))$ ,  $g(\text{V}(2)) = g(\text{O}(6))$ , and  $g(\text{V}(3)) = g(\text{O}(7))$  (Table 1). Possible occupations are therefore  $\text{V}(2)\text{-O}(6)$  pair and  $\text{V}(3)\text{-O}(7)$  pair. However, the  $\text{V}(3)\text{-O}(7)$  distance (3.391(17) Å) is too long to be considered as a V-O bond (Table 2). Thus the coordination sphere obtained for  $\text{V}(2)\text{O}_6$  octahedron is  $\text{V}(2)\text{O}(6)\text{O}(3)_4\text{O}(5)$  and that for  $\text{V}(3)\text{O}_5$  square pyramid is  $\text{V}(3)\text{O}(5)\text{O}(3)_4$ . It is noticeable that the  $\text{V}(2)\text{O}_6\text{-V}(2)\text{O}_6$  and  $\text{V}(2)\text{O}_6\text{-V}(3)\text{O}_5$  arrangements are distributed randomly.

The O(7) atom shows a too low BVS even if the  $\text{V}(3)\text{-O}(7)$  "bond" is counted (Table 3), indicating that the O(7) atom

corresponds to  $\text{H}_2\text{O}$ . The obtained model includes non-water O(1)–O(6) atoms and a water O(7) atom. The O(5) atom in the  $\text{V}(2)\text{-O}(5)\text{-V}(3)$  arrangement and all of the O(6) atom are nonwater O atoms, because they form V–O double bonds. However, the O(5) atom in the  $\text{V}(2)\text{-O}(5)\text{-V}(2)$  arrangement shows a BVS of 0.47 which is too low for an oxide O atom and therefore the O(5) atom in the  $\text{V}(2)\text{-O}(5)\text{-V}(2)$  arrangement is a water O atom. Thus obtained  $\text{O}(6)=\text{V}(2)\text{-O}(5)_{\text{water}}\text{-V}(2)=\text{O}(6)$  and  $\text{O}(6)=\text{V}(2)\text{-O}(5)=\text{V}(3)\text{---O}(7)_{\text{water}}$  arrangements (Fig. 1) are consistent with the BVS of the O(5) atom (Table 3). Taking into account that one side of the O(5) position is always occupied by the V(2) atom, namely  $\frac{1}{2} \leq g(\text{V}(2)) \leq 1$ , the probability of the former arrangement is  $2g(\text{V}(2)) - 1$  and the probability of the latter arrangement is  $2 - 2g(\text{V}(2))$ . The composition of the polyoxovanadate ion is fixed at  $[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})]^{12-}$

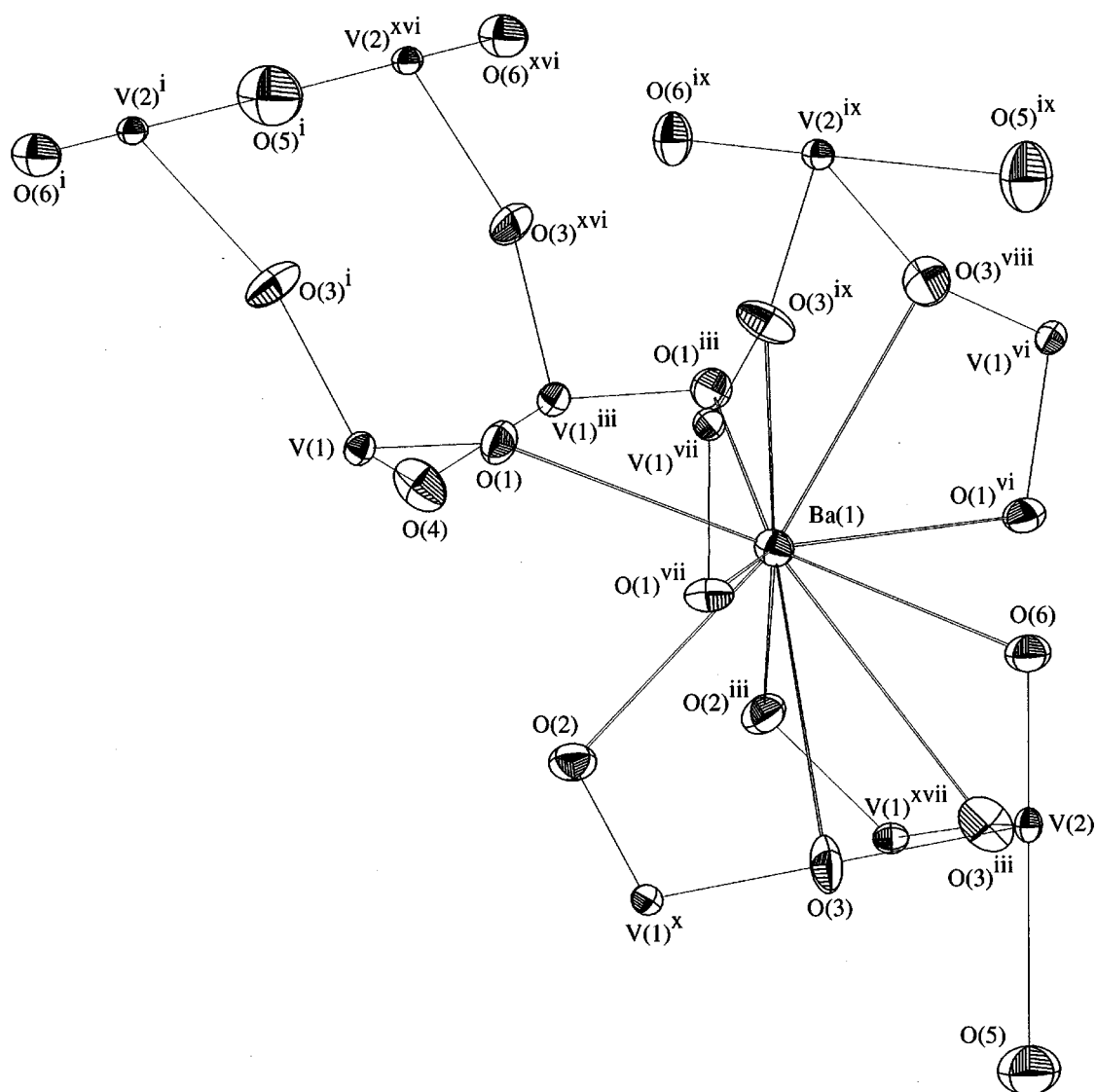


FIG. 3. Linkage among the Ba(1) atom and adjacent three polyoxovanadate ions. The V(2)–O–V(3) arrangement is neglected for conciseness. Anisotropic thermal vibrations are shown using 50% probability.

independent of  $g(\text{V}(2))$ . The total composition becomes  $\text{Ba}_6[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}$ , including the O(8) atom. The BVS and the composition indicate that the V(1) cation is pentavalent and the V(2) and V(3) cations are tetravalent.

#### Linkage of the Polyoxovanadate Ions through the Ba Atoms

The Ba(1) and Ba(2) atoms play a role in connecting the discrete polyoxovanadate ions (Figs. 2–4). Hereafter, each polyoxovanadate ion is expressed by its constituent O(5) atom, for example the O(5)<sup>ix</sup> polyanion. The Ba(1) atom is coordinated by 11 O atoms and binds three polyoxovanadate ions (Table 2, Figs. 2 and 3). The Ba(1) atom shares two O(2)–O(3) edges and a corner O(6) (or O(7)) atom with the

O(5) polyanion, two O(1)–O(3) edges with the O(5)<sup>ix</sup> polyanion, and two corner O(1) atoms with the O(5)<sup>i</sup> polyanions (Figs. 1 and 3). Thus, all 11 of the O atoms are used for binding the three polyanions. The Ba(2) atom is coordinated by 12 O atoms and binds six polyanions (Table 2, Figs. 2 and 4). The Ba(2) atom and each polyanion share an O(1)–O(2) edge (Figs. 1 and 4).

The Ba(3) sites form a 12-membered cluster at the (0, 0, 0) and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  positions, namely, in the void surrounded by the polyanions. Considering the occupancy, however, each cluster accommodates only two Ba(3) atoms. The Ba(3) atom is coordinated by two O(2) and two O(4) atoms, and by three or four O(8) water molecules (Table 2, Fig. 5). The Ba(3) atom and O(5) polyanion share a pair of O(2)–O(4)

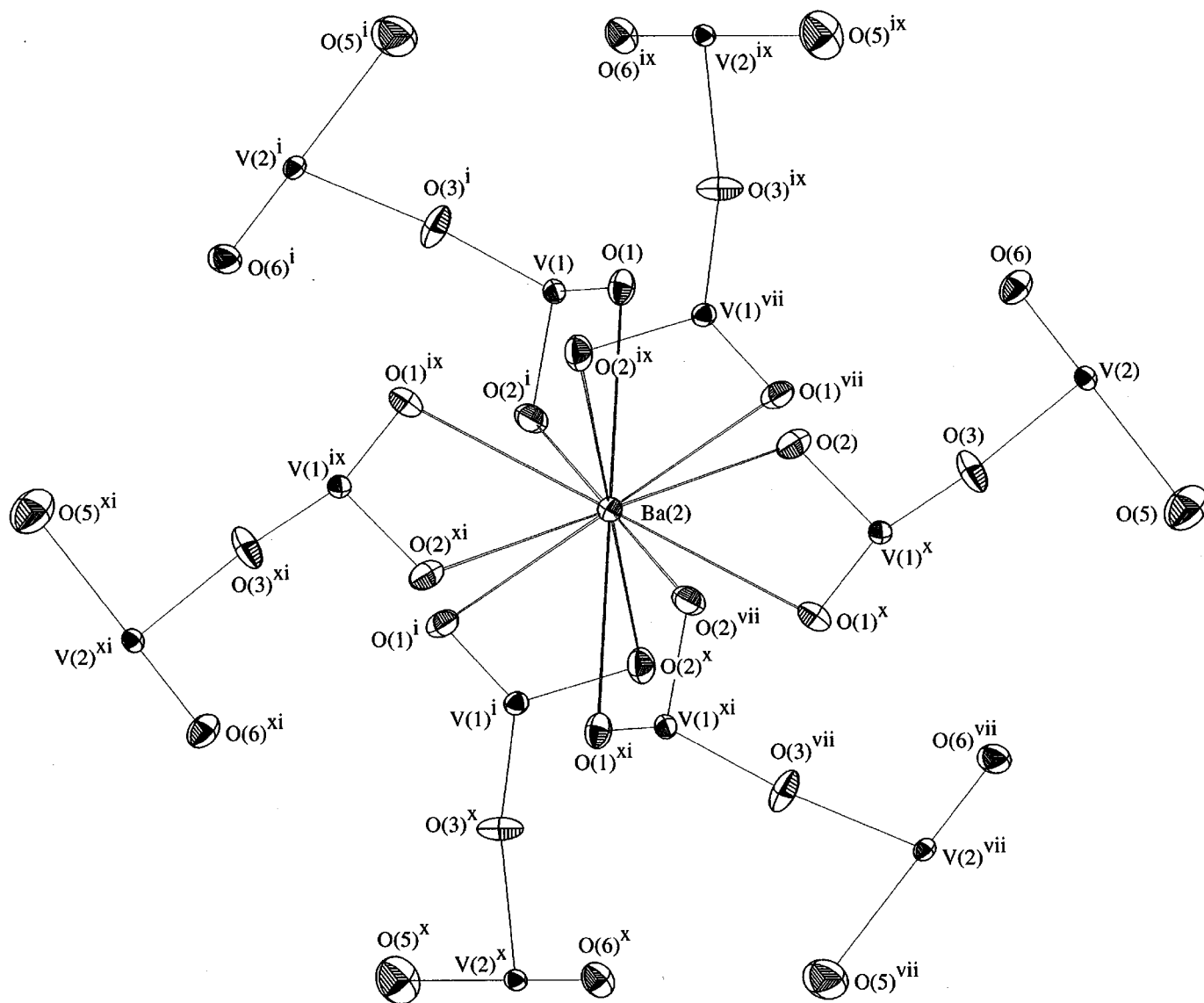


FIG. 4. Linkage among the Ba(2) atom and adjacent six polyoxovanadate ions. The V(2)–O–V(3) arrangement is neglected for conciseness. Anisotropic thermal vibrations are shown using 50% probability.

edges. In Fig. 5, the four O(8) sites indicated by dashed-line circles are occupied partially. Considering the occupancy (Table 1), a quarter of the Ba(3) atom is coordinated by three O(8) water molecules and the other by four O(8) water molecules.

#### Magnetic Property of $Ba_6[V_{10}O_{30}(H_2O)] \cdot 2.5H_2O$

The present phase is paramagnetic and free from any magnetic transition down to 5 K (Fig. 6), probably reflecting the discrete location of the polyoxovanadate ion. The magnetic susceptibility can be analyzed as a sum of the Curie–Weiss term and the temperature-independent term. The obtained Curie constant, Weiss temperature, and

temperature-independent susceptibility are  $0.6802(7)$  emu  $K \text{ mol}^{-1}$ ,  $0.48(7)$  K, and  $-8.0(2) \times 10^{-5}$  emu  $\text{mol}^{-1}$ , respectively, where “mol” corresponds to the composition  $Ba_6[V_{10}O_{30}(H_2O)] \cdot 2.5H_2O$ . The Curie constant gives the  $V^{IV}/V^V$  ratio of 1.81/8.19, which is consistent with 2/8 obtained from the analytical composition.

#### Comparison with the Related Phase $Ba_{5.33}(H_3O)_{0.33}[V_{10}O_{30}]$

The present  $Ba_6[V_{10}O_{30}(H_2O)] \cdot 2.5H_2O$  ( $a = 16.8323(2)$  Å) appears to be related with  $Ba_{5.33}(H_3O)_{0.33}[V_{10}O_{30}]$  ( $a = 16.9439(2)$  Å) reported by Zubieta and his co-workers (2). Both phases were synthesized hydrothermally, but the starting materials and reaction temperatures were totally

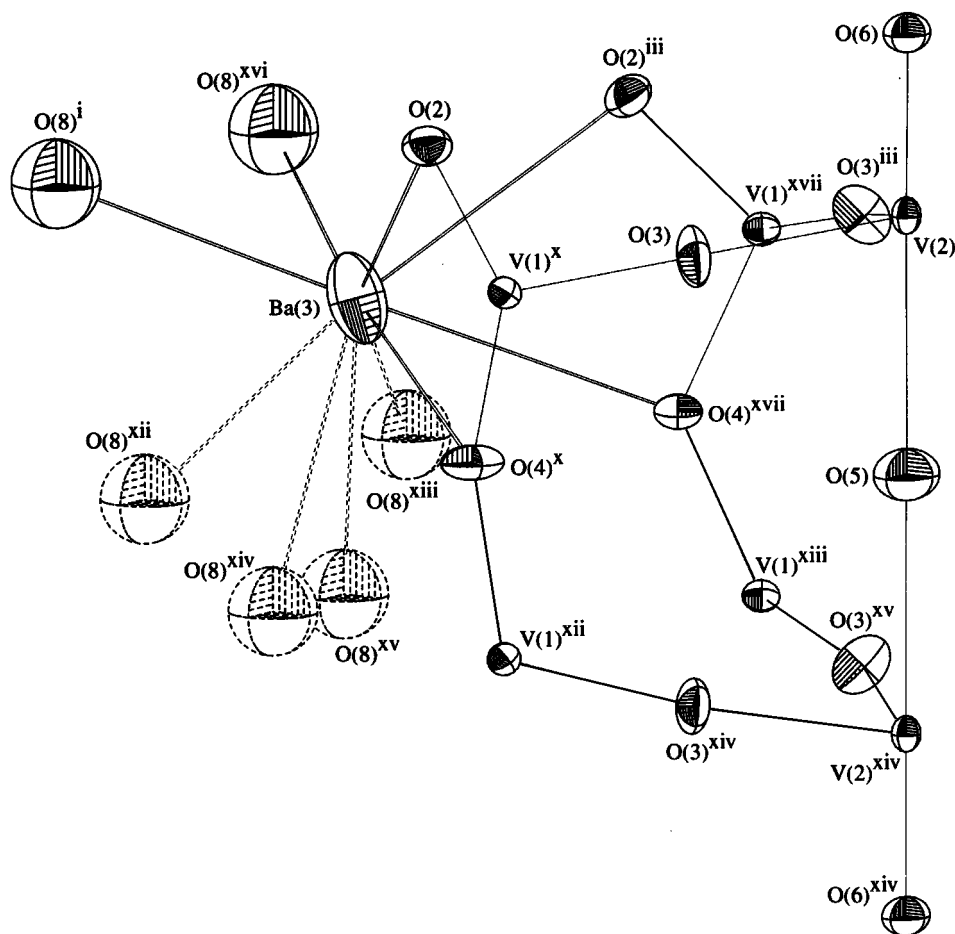


FIG. 5. Coordination sphere of the Ba(3) atom with its adjacent one polyoxovanadate ion and Ba atoms. The V(2)–O–V(3) arrangement is neglected for conciseness. Anisotropic thermal vibrations are shown using 50% probability. The thermal parameter of O(8) is isotropic.

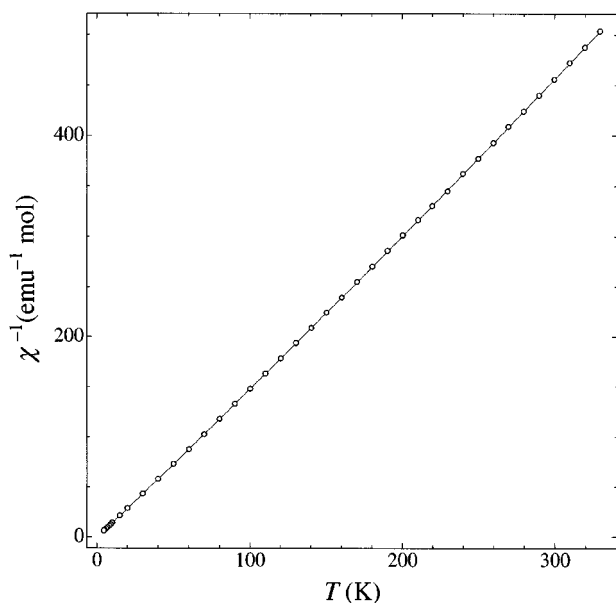


FIG. 6. Inverse magnetic susceptibility of  $\text{Ba}_6[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}$  versus temperature.

different in the two studies. Moreover, the lattice parameters and the total compositions of the two are significantly different.  $\text{Ba}_{5.33}(\text{H}_3\text{O})_{0.33}[\text{V}_{10}\text{O}_{30}]$  lacks the Ba(3) atom and the charge neutrality is achieved by introducing questionable  $\text{H}_3\text{O}^+$ . In addition, Zubietta *et al.* did not clarify the significant difference in the coordination spheres of the V(2) and V(3) atoms. Consequently, the present  $\text{Ba}_6[\text{V}_{10}\text{O}_{30}(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}$  is distinguishable from  $\text{Ba}_{5.33}(\text{H}_3\text{O})_{0.33}[\text{V}_{10}\text{O}_{30}]$ .

#### ACKNOWLEDGMENTS

The authors are grateful to Dr. K. Kato for valuable advice on structural analysis, Prof. J. Umemura for infrared spectroscopy, Dr. M. Ishii for valuable comments on analyzing the infrared spectroscopy data, Prof. Z. Hiroi for magnetic susceptibility, Mr. A. Sato for help in diffraction experiment, and Mr. K. Kosuda for X-ray microanalysis.

#### REFERENCES

1. M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.* **30**, 34 (1991).
2. Y. Zhang, R. C. Haushalter, and J. Zubietta, *Inorg. Chim. Acta* **277**, 263 (1998) and references therein.



3. T. Chirayil, P. Y. Zavalij, and M. S. Whittingham, *Chem. Mater.* **10**, 2629 (1998) and references therein.
4. Y. Oka, T. Yao, and N. Yamamoto, *J. Solid State Chem.* **117**, 407 (1995).
5. E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.* **3**, 210 (1950).
6. A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1999.
7. G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
8. "International Tables for Crystallography," Vol. C, Kluwer Academic Publishers, Dordrecht, 1992.
9. Additional material from this paper can be ordered by referring to No. CSD-410989, the name of the author, and the citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.
10. N. E. Brese and M. O'Keeffe, *Acta Crystallogr. B* **47**, 192 (1991).