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The first three-dimensional vanadium hypophosphite

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The title synthesized hypophosphite has the formula $V(H_2PO_2)_3$. Its structure is based on VO_6 octahedra and $(H_2PO_2)^-$ pseudo-tetrahedra. The asymmetric unit contains two crystallographically distinct V atoms and six independent $(H_2PO_2)^-$ groups. The connection of the polyhedra generates $[VPO_6H_2]^{6-}$ chains extended along *a*, *b* and *c*, leading to the first three-dimensional network of an anhydrous transition metal hypophosphite.

Comment

During the past few decades, several metal hypophosphite compounds have been reported in the literature, incorporating alkali, alkaline earth (Galigné & Dumas, 1973; Kuratieva *et al.*, 2005), transition (Marcos *et al.*, 1993, 1994; Kuratieva *et al.*, 2002), lanthanide and group 14 metals. Several lines of interest have led us to investigate this class of compounds. Among them are: (i) the study of low-dimensional structures suitable for catalytic or ion-exchange properties supported by the low degree of connectivity of the $(H_2PO_2)^-$ oxoanion; (ii) the characterization of lanthanide ions involving the use of the $(H_2PO_2)^-$ ligand (Seddon *et al.*, 1999; Tanner *et al.*, 1999, 2000); (iii) the application of anhydrous metal hypophosphites as mild reducing agents, reagents in catalytic syntheses of organophosphorous compounds and antioxidants (Naumova *et al.*, 2004*a*,*b*). Another area of interest was the magnetic properties of some hypophosphite complexes of transition metals (Marcos *et al.*, 1992; Yoshida *et al.*, 2009).

Although a number of crystal structures of hypophosphites are known, there is a lack of structural data for anhydrous transition metal hypophosphites. In fact, only two such compounds have been characterized by X-ray diffraction, namely $Fe(H_2PO_2)_3$ (Kuratieva & Naumov, 2006), exhibiting a layered structure built up from iron hypophosphite chains, and $Zn(H_2PO_2)_2$ (Tanner *et al.*, 1997), comprising a two-dimensional structure.

At the same time and to the best of our knowledge, only one vanadium hypophosphite has been isolated. It is hydrated and exhibits a one-dimensional structure (Le Bail *et al.*, 1994)

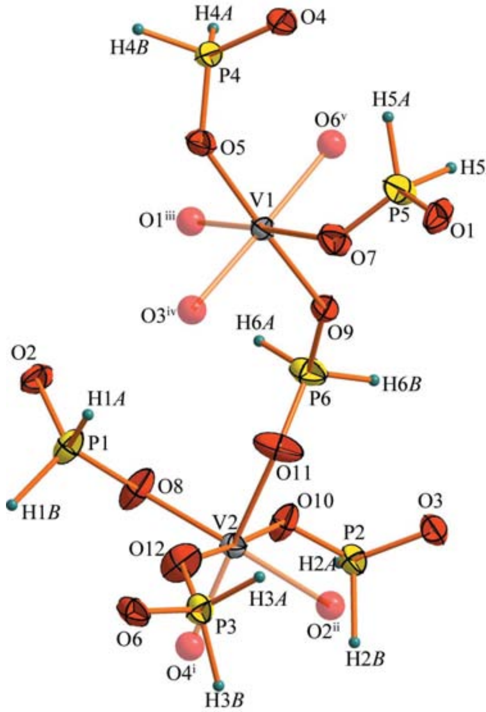

Figure 1
The asymmetric unit of $[V_2P_6O_{12}H_{12}]^{12-}$; the displacement ellipsoids of the independent atoms are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. [Symmetry codes: (i) $x, y, z-1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.]

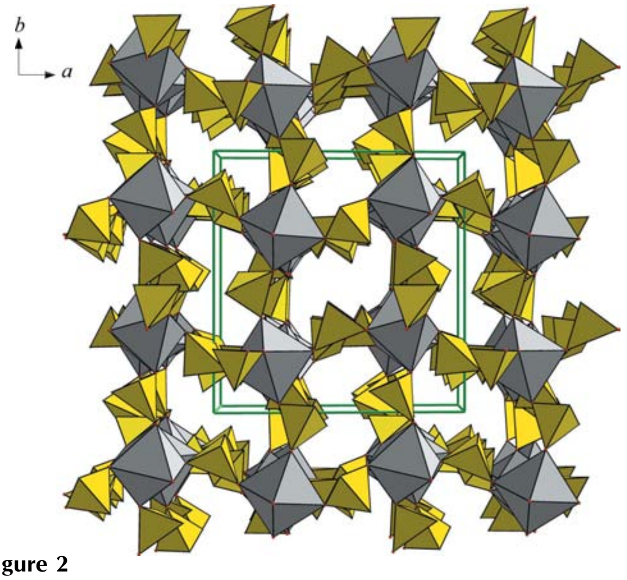

Figure 2
A perspective view of $V(H_2PO_2)_3$ along the [001] direction.

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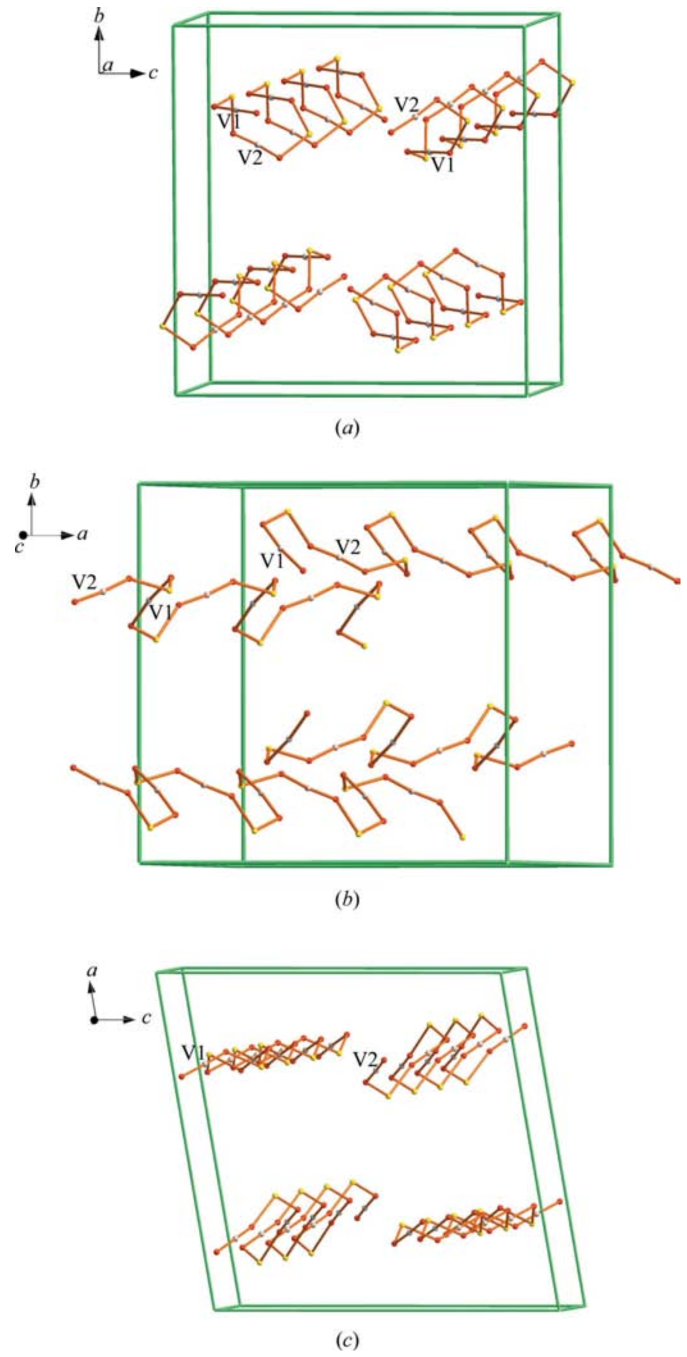

Figure 3
A representation of the V—O—P—O—V chains along (*a*) the [100] direction, (*b*) the [001] direction and (*c*) the [010] direction. Generic labels V1 and V2 are used to depict these atoms in any asymmetric unit.

where the metallic cation is involved in an oxovanadium group. The aim of our study is to enlarge the hypophosphite family of compounds, especially for metals like vanadium, which adopt different coordination geometries.

Our study reports the first anhydrous vanadium phosphinate. The asymmetric unit (Fig. 1) contains two independent V atoms and six phosphinate ions, all situated on general positions. Atoms V1 and V2 both exhibit a slightly distorted octahedral geometry, where the mean values of the V—O bond lengths are 1.998 (3) and 1.997 (3) Å, respectively. The hypophosphite groups have pseudo-tetrahedral geometry. The bond distances and angles (Table 1) in the $(H_2PO_2)^-$ pseudo-tetrahedra are similar to those observed in other hypophosphite compounds. The $V^{III}O_6$ octahedra share all their vertices with six distinct pseudotetrahedra, and each $(H_2PO_2)^-$ anion has both of its O atoms linked to two adjacent metallic centers, acting as a bidentate bridging ligand. This type of connection involves the formation of V—O—P—O—V chains through the three directions of space, leading therefore to a three-dimensional network (Fig. 2). The junction of the V1, V2, O and P atoms along the *a* axis describes helicoidal chains, while along the *c*-axis direction it forms a sawtooth curve (Figs. 3*a* and 3*b*). Along the *b* axis, the V2—O—P—O—V2 chains follow a helicoidal pattern with an elliptical cross section and the V1—O—P—O—V1 chains might be assimilated to a sinusoid (Fig. 3*c*). While in oxovanadium(IV) hypophosphite (Le Bail *et al.*, 1994), the one-dimensional aspect of the structure is related to the anisotropic environment of the vanadium, in the title compound the three-dimensionality is favored by the isotropic bonding scheme of the cation owing to its +3 oxidation state.

Experimental

Vanadium(III) hypophosphite was synthesized by a hydrothermal method. A mixture of deionzed water, vanadium(V) oxide, 50% hypophosphoric acid and lithium carbonate in a 10.437:0.1:2:0.428 molar ratio was placed in a Teflon acid digestion bomb (23 ml, Parr Instruments), heated at 423 K for 48 h and cooled to room temperature over a period of 24 h. The green product was filtered off, washed with deionized water and dried at room temperature in a desiccator. The comparison of the X-ray powder diffraction pattern of the synthesized product with the simulated one from this structure revealed that the title compound is present as a minor phase. The major phase remains unknown. While lithium ions are not present in this structure, the presence of lithium carbonate seems to be necessary to obtain the title compound, as synthesis attempts performed without the lithium source were unsuccessful. We assume that the hypophosphoric acid is responsible for the reduction of the vanadium ions observed during the synthesis (V^{5+} to V^{3+}), as no other reducing agent is present.

Crystal data

$V(H_2PO_2)_3$
$M_r = 491.8$
Monoclinic, $P2_1/n$
$a = 11.4985$ (3) Å
$b = 11.7771$ (5) Å
$c = 11.5999$ (4) Å
$\beta = 99.807$ (2)°
$V = 1547.89$ (9) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.88$ mm^{-1}
$T = 293$ K
0.15 × 0.05 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
20258 measured reflections
3550 independent reflections
2426 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.117$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.091$
$S = 1.04$
3550 reflections
219 parameters
Only H-atom coordinates refined
$\Delta\rho_{\rm max} = 0.50$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.54$ e Å^{-3}

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The H atoms were located in a Fourier difference map and their positional parameters were refined freely, while their $U_{\rm iso}$(H) values were fixed at 0.049 Å^2. The refinement of the structure was carried out on a merohedrally twinned crystal. The transformation matrix used was ($00\bar{1}, 0\bar{1}0, \bar{1}00$). The refined volume fractions were 0.0544 (7) and 0.9456 (7).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX*/*LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3018). Services for accessing these data are described at the back of the journal.

Table 1
Selected geometric parameters (Å, °).

V1—O7	1.984 (3)	P1—H1*B*	1.43 (5)
V1—O5	2.007 (3)	P2—O10	1.508 (3)
V2—O4$^{\rm i}$	1.976 (3)	P4—O4	1.484 (4)
V2—O2$^{\rm ii}$	2.023 (3)	P5—H5*A*	1.25 (6)
O7—V1—O1$^{\rm iii}$	177.79 (15)	O12—P3—O6	114.1 (2)
O9—V1—O3$^{\rm iv}$	93.05 (14)	H3*A*—P3—H3*B*	108 (3)
O9—V1—O5	175.46 (15)	O4—P4—H4*A*	103 (2)
O6$^{\rm v}$—V1—O5	87.22 (13)	O4—P4—H4*B*	121 (2)
O3—P2—O10	117.3 (2)	H5*A*—P5—H5*B*	81 (3)

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

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