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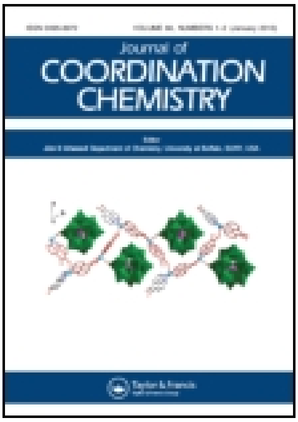

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$K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$: a synthetic leucophosphite

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$K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]·2H_2O$: a synthetic leucophosphite

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A new iron(III)/vanadium(III) phosphate, $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]·2H_2O$ (**1**), has been obtained by hydrothermal synthesis and characterized by single crystal X-ray diffraction, Scanning electron microscopy–energy dispersive X-ray spectroscopy, Inductively coupled plasma atomic emission spectroscopy (ICP), thermogravimetric analysis, and FTIR spectroscopy. Single crystal X-ray diffraction reveals a 3D open framework (monoclinic, space group $P2_1/n$, $a = 9.6391(7)$ Å, $b = 9.8063(7)$ Å, $c = 9.7268(7)$ Å, $\beta = 100.71(1)°$, and $V = 903.38(11)$ Å^3). This structure presents Fe^{III} and V^{III} in a 4.4 : 1 M ratio with the metal ions in two different crystallographic sites. Both metallic centers have distorted octahedral environments, linked by PO_4 tetrahedra, forming channels along the *a*-axis. The asymmetric unit of $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]·2H_2O$ presents a $\{M_4(OH)O(PO_4)_4(H_2O)_2\}^{3-}$ anionic entity, charge balanced by three K^+, which are located within the channels. It is also possible to distinguish M_4O_2 units whose M^{III} polyhedra are linked by vertex and edges.

Keywords: Hydrothermal synthesis; Fe(III)/V(III) phosphate; Leucophosphite analog; Butterfly units

1. Introduction

The structural diversity shown by iron phosphates in natural minerals [1] has inspired preparation of synthetic materials by hydrothermal synthesis [2]. As an example of a naturally occurring iron phosphate, leucophosphite, $K_2[Fe_4(OH)_2(H_2O)_2(PO_4)4]·2H_2O$, structure was described by Moore [3] in 1972 and further elucidated by Rietveld refinement from neutron diffraction data [4]. $K[(FeV)(PO_4)_2(OH)(H_2O)]·H_2O$ [5], $\{C_2N_2H_{10}\}[Fe(HPO_4)_2(OH)]$ [6], and $[Fe_2(NH_4)(OH)(PO_4)_2]·2H_2O$ [7] are the examples of synthetic analogs of leucophosphite.

Metal phosphates present interesting catalytic and electrocatalytic [8–12], sorptive [13, 14] and magnetic properties [15–17]. These materials have different dimensionalities such

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*Corresponding author. Email: diego.venegas@usach.cl as chains [18], lamellar [19] or 3D structures [20]. Metal phosphates consist of corner or edge connected MO_6 (M = transition metal) octahedra, sharing corners with tetrahedral PO_4 units. These octahedral units can form different types of structures, depending on the form of interconnection.

In this article we report a new mixed Fe^{III}/V^{III} phosphate framework $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$, in which the μ_3-oxygen bridges present a partial occupancy of a hydrogen.

2. Experimental

Reaction mixture of 1,2-phenylendiamine (0.0918 g, 0.85 mmole), K_3PO_4 (0.9021 g, 4.25 mmole), $NaVO_3$ (0.1036 g, 0.85 mM), and $FeCl_3\cdot 6H_2O$ (0.4595 g, 1.7 mM) in 5 mL H_2O, in a molar ratio 1 : 5 : 1 : 2 : 327, respectively, were added to a 23 mL Teflon-lined stainless steel Parr reactor. The initial and final pH values of the reaction mixture were 6.03 and 7.81, respectively. The hydrothermal reaction to obtain $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ was carried out at 130 °C for 72 h, and then heated at 200 °C for 40 h under autogenous pressure. After cooling to room temperature, the obtained dark brown crystals were filtered off and dried in a desiccator, suitable for single X-ray diffraction characterization, and not recrystallized.

The iron and vanadium analyses for **1** were done with an ICP–OES Perkin–Elmer, Optima 3300 DV analyzer. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS) analyses were obtained using SEM–EDX JSM 5410 equipment. Infrared spectra of the powder samples were recorded from 4000 to 400 cm^{-1} at room temperature on a Perkin Elmer FTIR spectrophotometer, model BX II, using KBr pellets. The thermogravimetric analysis was done using Netzsch TG 209 F1 Iris equipment. The thermogram was recorded between 25 °C and 1000 °C in a N_2 atmosphere, with a heating rate of 10 °C min^{-1}, and a flux of inert gas of 20 mL min^{-1}.

An X-ray diffraction quality crystal of **1** was taken directly from the reaction mixture. Preliminary scans on a Bruker Smart Apex Area Detector Diffractometer showed acceptable crystal quality. Data collection was made at 150 K using separations of 0.3° between frames and 10 s by frame. Data integration was made using SAINT-NT [21]. The structure was solved by direct methods using XS in SHELXTL-NT [22], and completed (nonH atoms) by Fourier difference synthesis. Refinement until convergence was obtained using XL SHELXTL and SHELXL97 [23]. One possible hydrogen position was located in the difference Fourier map and refined with the constraint of the O–H distance to be 0.85 Å. $U_{iso}(H)$ values were not refined. The nature of the metal content from SEM–EDXS and the content of the metals from ICP data were used as input for the final refinement of the structure. All metal positions were supposed to contain Fe and V with occupancies of 0.81 and 0.19, which were held constant. Molecular diagrams were prepared using ORTEP-3 for Windows and Diamond-3.2e, supplied by Crystal Impact [24]. Crystal data are provided in table 1.

3. Results and discussion

$K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ (**1**) was prepared by hydrothermal synthesis in the presence of 1,2-phenylenediamine, this reagent was necessary to obtain the crystalline phase [5, 25]. Since a source of V^V was used in the synthesis, 1,2-phenylenediamine must

Table 1. Crystal data and structure refinement parameters for $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ (**1**).

Empirical formula	$K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$
Formula weight	821.64
Crystal shape/color	Rhombohedral/dark brown
Temperature (*K*)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.6391(7)
b (Å)	9.8063(7)
c (Å)	9.7268(7)
β (°)	100.71(1)
Volume (Å^3)	903.38(11)
Z	2
Density (calcd)	3.032
Abs. coeff.	4.310
F(0 0 0)	403
T_{min}, T_{max}	0.637, 0.782
Reflections/parameters	3267
Goodness-of-fit on F^2	1.168
Final *R* indexes ($I > 2\sigma(I)$)	$R_1 = 0.0241$, $wR_2 = 0.0686$
Indexes (all data)	$R_1 = 0.0248$, $wR_2 = 0.0689$

be the reducing agent that permits obtaining the Fe^{III}/V^{III} framework. Hydrothermal synthesis has been reported to produce metal species in which reduction is observed, when the reaction is done in the presence of a nitrogen-containing base [5, 26]. For example, when 2,2′-bipyridine (bipy) is used in a hydrothermal reaction the V^V source is reduced to V^{IV} [27]. The SEM–EDXS infers the presence of vanadium, together with iron (figure 1S). The ratio of vanadium to iron was also quantified by ICP measurements, and a Fe/V molar ratio of 4.4:1 was determined. This ratio is the same as the one obtained by SEM–EDXS analysis.

The FTIR spectrum shows the typical broad-band at 3350 cm^{-1}, which can be assigned to OH and H_2O (figure 2S). Three bands at 1060, 1010, and 960 cm^{-1} were assigned to stretching modes of PO_4^{3-} [5]. The TGA data show weight loss of 7.4% at 160 °C, consistent with the release of four H_2O, being the calculated value 8.7% on the basis of $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ (figure 3S).

The asymmetric unit of $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ (**1**) presents a $\{M_4(OH)O(PO_4)_4(H_2O)_2\}^{3-}$ anionic unit (figure 1), charge balanced by three K^+. $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ is proposed on the basis of charge balance and thermogravimetric analysis, and is compared with some features of related structures [5, 28].

The asymmetric unit of $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$, which is one half of the reported formula, presents ten different oxygen atoms, eight corresponding to phosphate, O2, O3, O5, O6, O7, O8, O9, and O10, while O4 is in an apical position, and corresponds to water as reported by Shi *et al.* [5]. Considering the charge balance, O1, which is a μ_3-bridge, should be a hydroxo with the hydrogen having half occupancy. Within this unit, there are two different slightly non regular octahedral M^{III} centers. The environment around M1 is defined by four oxygen atoms from four phosphates (M1–O3^i, 1.961(2); M1–O5, 1.967(2); M1–O2, 1.983(2); M1–O6, 2.014(2) Å) and one μ_3-oxygen (M1–O1, 2.185(2) Å), while the sixth coordination position is occupied by one oxygen from water with a M1–O4 distance of 1.953(2) Å. The environment around M2 is defined by two

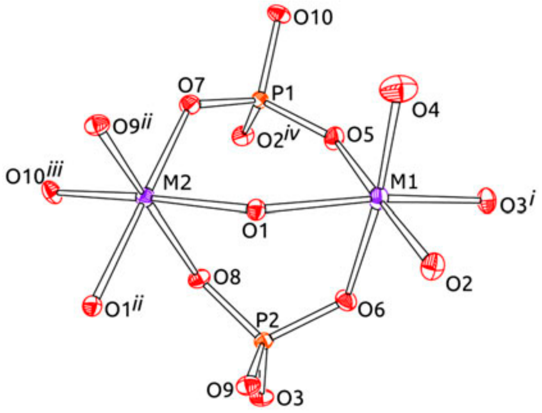

Figure 1. The asymmetric unit of $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$, showing some equivalent atoms. Symmetry codes: ^{i}: ½−*x*, −½+*y*, 3/2−*z*; ^{ii}: −*x*, 2−*y*, 2−*z*; ^{iii}: ½−*x*, ½+*y*, 5/2−*z*; ^{iv}: ½+*x*, 3/2−*y*, ½+*z*.

oxygen atoms of two μ_3-bridges (M2–O1, 2.118(2); M2–O1^{ii}, 2.148(2) Å) and two oxygen atoms from two phosphates (M2–O7, 1.943(2) Å; M2–O10^{iii}, 1.945(2) Å) in the equatorial positions. In the apical positions two oxygen atoms correspond to different phosphates (M2–O8, 1.969(2) Å; M2–O9^{ii}, 1.999(2) Å), thus generating a distorted octahedral coordination sphere. M_4O_2 units are formed by a central pair of edge sharing MO_6 octahedra, to which two additional MO_6 octahedra are bonded by corner sharing, as shown in figure 2.

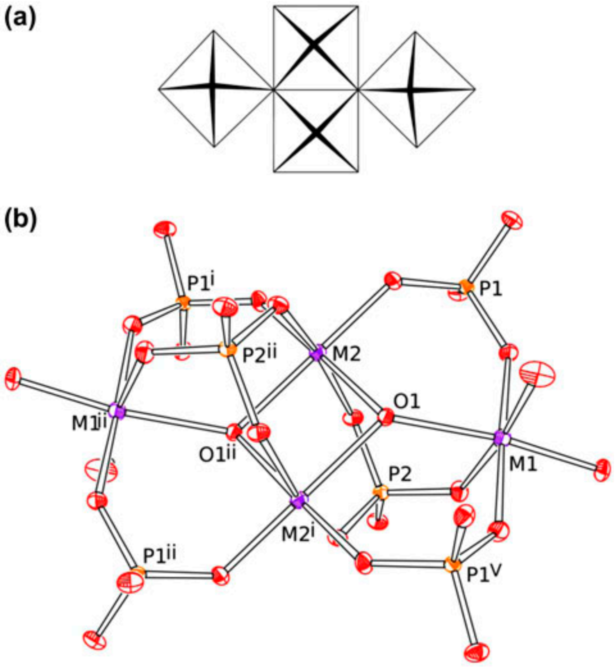

Figure 2. (a) Polyhedral scheme of the tetranuclear M_4O_2 unit. (b) Butterfly cluster M_4O_2. Symmetry codes: ^{i}: ½−*x*, ½+*y*, 5/2−*z*; ^{ii}: −*x*, 2−*y*, 2−*z*; ^{V}: −½+*x*, 3/2−*y*, −½+*z*.

These four metals are located on the same plane, while μ_3-oxygen atoms are localized at 0.53 Å above and below this plane, with a deviation angle of *ca*. 32.1°. Selected bond distances and angles are given in table 2.

The 3D structure is generated by connecting the butterfly-type tetrameric units by PO_4 groups, as shown in figure 3. Channels running along the *a*-axis hosting K^+ and water are shown in figure 4S.

It is important to state that $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ crystallizes in the monoclinic, space group $P2_1/n$, $a = 9.6391(7)$ Å, $b = 9.8063(7)$ Å, $c = 9.7268(7)$ Å, and $\beta = 100.71(1)°$, while the reported structure $K[(FeV)(PO_4)_2(OH)(H_2O)]\cdot H_2O$ [5] also crystallizes as a monoclinic crystal system. However, the space group is $P2_1/c$ and the cell parameters are $a = 9.7210(19)$ Å, $b = 9.6500(19)$ Å, $c = 12.198(4)$ Å, and $\beta = 128.569(18)°$. Therefore, the different Fe/V ratio and the difference in the oxygen protonation cause alteration of the cell parameters.

For the related structure of leucophosphite, $K[Fe_2(PO_4)_2(OH)(H_2O)]\cdot H_2O$, the presence of hydroxo and water was confirmed by neutron powder diffraction measurements, and Rietveld refinement. Leucophosphite has the same butterfly cluster corresponding to the Fe_4O_2 unit as **1**; this unit also forms part of a 3D arrangement together with the phosphate. For leucophosphite, neutron diffraction measurements establish that within this Fe_4O_2 cluster, each oxygen connecting three Fe^{III} centers is a hydroxo. For leucophosphite the average metal-oxygen distances Fe^{III}-O are *ca*. 2.03 Å, while the distance between the metal center and the μ_3-bridge is 2.159 Å [3, 4]. For structure **1**, an oxo and a hydroxo can be proposed from charge balance. The metal to oxygen distances involved in the μ_3-bridge of **1** (M1–O1, 2.185 Å; M2–O1, 2.118 Å; M2–O1^{ii}, and 2.148 Å) are significantly longer than the average of the other metal to oxygen distances present in the structure, which are shorter than 2 Å.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

M1–O4	1.953(2)	M1–O5	1.968(2)
M2–O1	2.116(2)	M1–O2	1.983(2)
M1–O3^{i}	1.961(2)	M1–O6	2.015(2)
M2–O1^{iii}	2.146(2)	M1–O1	2.184(2)
M1···M2	3.784(2)		
M2···M2^{i}	3.071(2)		
M1···M2^{i}	3.863(2)		
M1^{ii}···M1	7.004(2)		
O4–M1–O3^{i}	93.63(11)	O8–M2–O1	82.82(8)
O4–M1–O5	87.46(10)	O9^{ii}–M2–O1	85.13(8)
O3^{i}–M1–O5	92.56(9)	O7–M2-O1^{ii}	177.68(9)
O4–M1–O2	92.49(10)	O10^{iii}–M2–O1^{ii}	90.80(9)
O3^{i}–M1–O2	85.62(9)	O8–M2–O1^{ii}	84.05(8)
O5–M1–O2	178.18(9)	O9^{ii}–M2–O1^{ii}	86.09(8)
O4–M1–O6	173.42(11)	O1–M2–O1^{ii}	87.89(8)
O3^{i}–M1–O6	92.14(9)	O7–M2–O10^{iii}	90.68(9)
O5–M1–O6	89.13(9)	O7–M2–O8	97.60(9)
O2–M1–O6	91.10(9)	O10^{iii}–M2–O8	94.63(9)
O4–M1–O1	88.99(10)	O7–M2–O9^{ii}	91.96(9)
O3^{i}–M1–O1	172.67(9)	O10^{iii}–M2–O9^{ii}	97.20(9)
O5–M1–O1	94.39(8)	O8–M2–O9^{ii}	164.68(9)
O2–M1–O1	87.43(8)	O7–M2–O1	90.70(9)
O6–M1–O1	85.66(8)	O10^{iii}–M2–O1	177.24(9)
M2–O1–M2^{i}	92.11(8)	M2–O1–M1	123.11(9)
M2^{i}–O1–M1	126.18(10)		

Symmetry codes: ^{i}: $0.5-x$, $-0.5+y$, $1.5-z$; ^{ii}: $-x$, $2-y$, $2-z$; ^{iii}: $0.5-x$, $0.5+y$, $2.5-z$; ^{iv}: $0.5+x$, $1.5-y$, $0.5+z$.

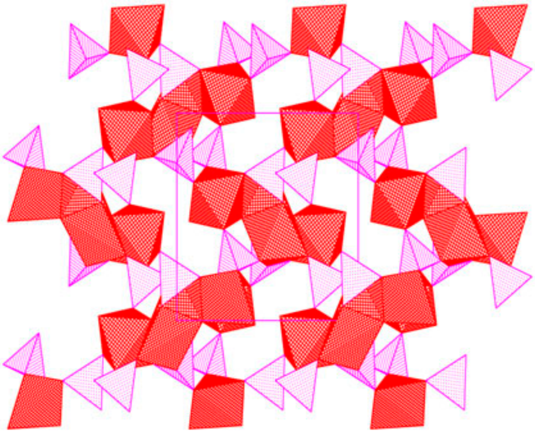

Figure 3. Polyhedral packing view of the structure of $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ along [100], showing the phosphates (purple) connecting the tetranuclear units. (see http://dx.doi.org/10.1080/00206814.2013.791685 for color version)

4. Conclusions

The presence of 1,2-phenylenediamine in the reaction mixture is crucial to reduce V^V used in the synthesis to V^{III}, and to obtain the Fe^{III}/V^{III} framework $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ (**1**). Thus, 1,2-phenylenediamine is a stronger reducing agent in hydrothermal conditions than 2,2′-bipyridine and 1,10-phenanthroline. The obtained molar ratio of Fe/V is 4.4:1 and can be compared with the reported heterometallic $K_2[(FeV)_2(PO_4)_4(OH)_2(H_2O)_2]\cdot 2H_2O$, in which the ratio of Fe/V is 1 : 1. In the latter structure a centrosymmetric $[M_4(\mu_3\text{–}OH)_2(PO_4)_4(H_2O)_2]^{2-}$ tetranuclear unit is present. Therefore, a new structure has been obtained, with vanadium not being in an equimolar ratio, but only replacing statistically some of the irons in the framework, and with a tetranuclear unit $[M_4(\mu_3\text{–}(OH)O(PO_4)_4(H_2O)_2]^{3-}$ that can also be described as centrosymmetric in average. Finally, the different Fe/V ratio and the difference in the oxygen protonation between the studied structure $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2]\cdot 2H_2O$ and the previously reported one, $K[(FeV)(PO_4)_2(OH)(H_2O)]\cdot H_2O$, alters the cell parameters.

Supplementary data

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247–808-666; E-mail: crysdata@fiz-karlsruhe.de, or http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD number (CSD 424859). TGA, SEM-EDXS and FT-IR spectrum of **1**.

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