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A New Zinc Pyrovanadate, Zn$_3$(OH)$_2$V$_2$O$_7$.2H$_2$O, from X-ray Powder Data

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Abstract

Hydrothermally prepared zinc dihydroxide divanadate dihydrate crystallizes in the trigonal system (space group P$\bar{3}$m1). Its structure was solved *ab initio* from conventional X-ray powder data. Zn atoms occupy three of four octahedral sites in a close-packed layer of O atoms. These layers are connected by pyrovanadate groups and form a porous framework. Relatively large cavities are filled by water molecules.

Comment

Recently, mild hydrothermal reactions driven by template cations such as tetramethylammonium (Whittingham *et al.*, 1995) and/or hydrated transition metals were successfully used to obtain metastable vanadium oxide phases. These compounds, with relatively open frameworks, are of particular interest as cathode materials in lithium batteries and electrochromic devices. We have also shown that the tetramethylammonium ion is capable of providing a range of new vanadium oxides, Li$_x$V$_{2-y}$O$_{4-y}$.H$_2$O (Chirayil, Zavalij & Whittingham, 1996a) and Li$_x$V$_{2-y}$O$_{4-y}$ (Chirayil, Zavalij & Whittingham, 1996b), and their intercalates [N(CH$_3$)$_4$]V$_4$O$_{10}$ (Zavalij, Whittingham, Boylan, Pecharskii & Jacobson, 1996), [N(CH$_3$)$_4$]V$_3$O$_7$ (Zavalij, Chirayil & Whittingham, 1997). This work presents the crystal structure of a new zinc hydroxide pyrovanadate, which was found during systematic investigations of the hydrothermal interactions in the system ZnCl$_2$–V$_2$O$_5$–[N(CH$_3$)$_4$]OH.

The title structure is built up of zinc oxide layers which are kept apart by pyrovanadate columns (Fig. 1). This brucite type of layer is formed by close-packed terminal O atoms of pyrovanadate and hydroxide groups. The Zn atoms occupy three of four octahedral sites. The

remaining site is surrounded by pyrovanadate tetrahedra. The OH group forms a hydrogen bond (Table 1) to the water molecules that fill cavities in the porous framework. The size of these cavities is much greater than is required. Therefore, the water molecules are disordered around the site $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2}$ and are able to make strong hydrogen bonds. The two distances Ow· · ·O2 of length 2.84 (2) Å indicate the presence of two hydrogen bonds formed by H atoms of the water molecules.
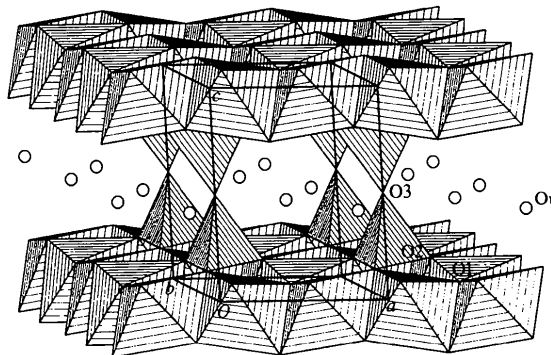

Fig. 1. Polyhedral representation of Zn$_3$(OH)$_2$V$_2$O$_7$.2H$_2$O.

The structure of the zinc hydroxide pyrovanadate is very similar to that of thallium pyrovanadate, Tl$_4$V$_2$O$_7$ (Jouanneaux, Joubert, Evain & Ganne, 1992), where the V$_2$O$_7$ group is at the same position as in the zinc compound and two Tl atoms occupy the positions of the water molecule (Ow) and the hydroxide group (O1). The Zn site is unoccupied. The copper pyrovanadate compound Cu$_3$(OH)$_2$V$_2$O$_7$.2H$_2$O, with the same stoichiometry as the title compound (Basso, Palenzona & Zefiro, 1988; Lafontaine, Le-Bail & Ferey, 1990), is almost identical to the zinc compound. The lattice of the copper compound (space group C2/m) is derived from the hexagonal lattice of the zinc compound by a
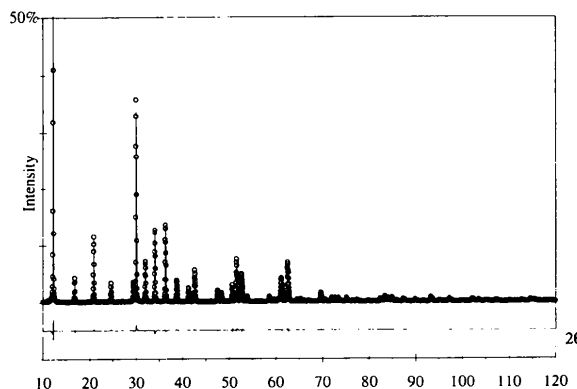

Fig. 2. Comparison of observed (circles) and calculated (solid line) intensities for Zn$_3$(OH)$_2$V$_2$O$_7$.2H$_2$O. The difference pattern appears below.

monoclinic deformation: $a_{mon} = a_{hex}3^{1/2}$, $b_{mon} = a_{hex}$ and $c_{mon} = c_{hex}$. It is interesting that even in the monoclinically deformed lattice, the water molecules remain disordered; moreover, the bridging O atom of the pyrovanadate group is disordered as well. In the case of the title compound, this O atom (O3) also has a significantly higher U_{iso} value: 0.03 *versus* 0.01 Å^2 for the other O atoms.

Experimental

The title compound was prepared by hydrothermal treatment of $ZnCl_2$, V_2O_5 and tetramethylammonium hydroxide, [$N(CH_3)_4$]OH, in a 1:1:3 molar ratio at pH 5.6. The reaction mixture was heated in a Teflon-lined Parr reactor for 2.5 d at 438 K. White crystalline powder resulted.

Crystal data

$Zn_3(OH)_2V_2O_7.2H_2O$	Cu $K\alpha_1$, $K\alpha_2$ radiation
$M_r = 480.05$	$\lambda = 1.54056, 1.54439$ Å
Trigonal	$\mu = 27.4$ mm^{-1}
$P\bar{3}m1$	$T = 295$ K
$a = 6.05098\,(5)$ Å	$25 \times 25 \times 1$ mm
$c = 7.19498\,(9)$ Å	White
$V = 228.145\,(7)$ Å^3	
$Z = 1$	
$D_x = 3.4937\,(1)$ Mg m^{-3}	
D_m not measured	

Data collection

Scintag XDS2000 diffractometer	$h = 0 \rightarrow 3$
ω/θ scans	$k = 0 \rightarrow 5$
Specimen mounting: packed powder pellet	$l = -7 \rightarrow 8$
	$2\theta_{min} = 10$, $2\theta_{max} = 120°$
	Increment in $2\theta = 0.03°$
Specimen mounted in reflection mode	

Refinement

Refinement on I_{net}	$w = 1/[Y_i + \sigma(Y_i)]$
$R_p = 0.052$	$(\Delta/\sigma)_{max} = 0.01$
$R_{wp} = 0.085$	$\Delta\rho_{max} = 0.54$ e Å^{-3}
$R_{exp} = 0.020$	$\Delta\rho_{min} = -0.6$ e Å^{-3}
9 profile parameters	Extinction correction: none
Profile function: pseudo-Voigt	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
152 reflections	
18 parameters	
H-atom parameters not refined	

Table 1. *Selected geometric parameters (Å, °)*

Zn—O1^i	1.941 (2)	Zn—O2^{vi}	2.226 (2)
Zn—O1^{ii}	1.941 (2)	V—O2^{vii}	1.695 (2)
Zn—O2^{iii}	2.226 (2)	V—O2^v	1.695 (2)
Zn—O2^{iv}	2.226 (2)	V—O2^{viii}	1.695 (2)
Zn—O2^v	2.226 (2)	V—O3	1.781 (1)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$Ow	0.95	1.90	2.84 (2)	169

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - y, x - y, z - 1$; (iv) $-x + y, -x, z - 1$; (v) $y, -x + y, 1 - z$; (vi) $1 + x - y, x, 1 - z$; (vii) $-x, -y, 1 - z$; (viii) $x - y, x, 1 - z$.

The powder diffraction pattern was indexed in a hexagonal system using the *TREOR* program (Werner, Eriksson & Westdahl, 1985) with merit $M(20) = 124$. The space group $P\bar{3}m1$ was chosen from general considerations and confirmed by the subsequent structure refinement. The structure was solved by direct methods using the integrated intensities. Zn and V atoms were found on the E map and four O atoms, including one of the water molecules, were localized from the subsequent difference Fourier map among the first five peaks. After $R_{int} = 10\%$ was reached, the Rietveld refinement was applied. The difference Fourier map showed that the water molecule is not exactly located at $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ but is disordered around a threefold axis. This correction significantly improved the R factors and atomic displacement parameters. The final refinement (Fig. 2) was performed using the *CSD* crystallographic package (Pecharskii, Akselrud & Zavalij, 1987) in the isotropic (metal atoms in anisotropic) approximation of the atomic displacement parameters. The *CSD* preferred-orientation correction $I_{corr} = I_{obs}/[1 + (\tau^2 - 1)\sin^2\varphi]^{1/2}$ was applied with axis 001; $\tau = 0.702$ (5).

Data collection: *DMS Software* (Scintag Inc., 1994). Cell refinement: *CSD* (Akselrud *et al.*, 1993). Data reduction: *CSD*. Program(s) used to solve structure: *CSD*. Program(s) used to refine structure: *CSD*. Molecular graphics: *STRUVIR* [VRML version of *STRUPLO* (Fisher, 1985) created by A. Le-Bail]. Software used to prepare material for publication: *CSD*.

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