Title: Hydrothermal Synthesis and Crystal Structure of a Novel Phosphate: CdMn₄(HPO₄)₂(PO₄)₂.4H₂O

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Abstract

The new cadmium and manganese-based phosphate CdMn₄(HPO₄)₂(PO₄)₂.4H₂O was synthesized by a hydrothermal method and its structure investigated by single crystal X-ray diffraction. The accuracy of the resulting structural model was verified using the Bond-Valence-Sum (BVS) and Charge-Distribution (CD) methods. This phase is a new member of the Hureaulite family and crystallizes within the monoclinic system (space group C2/c, a = 17.6932(5) Å, b = 9.1862(3) Å, c = 9.5417(3) Å, β = 96.562(1)°, and Z = 4). In this crystal structure the metal cations are statically distributed over three independent sites. The first two are located at the general position 8f and are entirely filled by Cd(1)²⁺/Mn(1)²⁺ and Cd(3)²⁺/Mn(3)²⁺ while the remaining site is situated at the special position 4e(2) and fully occupied by Cd(2)²⁺/Mn(2)²⁺. The main structural groups of the asymmetric unit consist of three distorted [(Cd(1)/Mn(1))O₅(OH)₂], [(Cd(2)/Mn(2))O₆], and [(Cd(3)/Mn(3))O₄(OH)₂₂] octahedra with two regular PO₄ and HPO₄ groups. The 3D-structure is made up of five sequential octahedral (Cd/Mn)O₁₆(OH)₆ units of edge-sharing running along the [001] direction. The connecting PO₄ and HPO₄ groups bind the interconnected units to one another by corners-sharing to create a 3D-framework defining a sizable void along the [001] direction hosting some H₂O molecules.

Keywords

Crystal structure, X-ray diffraction, Hureaulite, Hydrothermal synthesis

Introduction

Over the past decade, much research has been devoted to the conception and design of novel transition metal phosphates [1]. The increased interest in such phases is mostly attributable to their interesting prospective uses, structural variety, and topological diversity [2]. These features are mainly related to the particular chemical behavior of the open mixed frameworks based on metal polyhedra, PO₄³⁻ and HPO₄²⁻ groups. Indeed, the arrangement of such units confers to the crystal structures a high level of thermal, chemical [3] and mechanical stability, creating ideal void spaces that can accommodate cations of different oxidation degrees and sizes [4]. This ability confers attractive physico-chemical properties to phosphate-based materials such electronic, magnetic, optical [5], and electrochemical features [6]. Additionally, hydrated materials belonging to the Hureaulite family are microporous materials and may be used as supplements to create highly corrosion-resistant surfaces and boost steel’s wear resistance [7]. In lithiferous pegmatites, Hureaulite is a frequent mineral occurring as a result of the hydrothermal deterioration of triphylite-lithiophilite or another (Fe/Mn) primary phosphate. Hydrothermal processing of Mn-rich phosphate solutions can also yield hureaulite. Hydrothermal synthesis and the treatment under vari-
ous physical and chemical conditions have both been used to
create simple and mixed hureaulite crystals. In other works,
hureaulite crystals were obtained at ambient temperature and
pressure by a reflux procedure [8]. In connection with our
systematic hydrothermal studies of metal orthophosphates,
we have previously synthesized and characterized a number
of compounds with various 3D-networks viz. $\text{M}_6\text{Mn}_2(\text{HPO}_4)_3(\text{PO}_4)_2$ ($\text{M} = \text{Pb, Sr}$) (Monoclinic system, space group $P2_1/c$ and $Z = 2$) [9, 10], $\gamma$-AgZnPO$_4$, belonging to ABW ze-
olite family (Monoclinic system, space group $P2_1/n$ and $Z = 4$) [11], $\text{AgCo}_2(\text{HPO}_4)(\text{PO}_4)_2$ (Orthorhombic system, space

group $\text{Ima}2$ and $Z = 4$) [12] that crystallize in $\alpha$-CrPO$_4$, struc-
ture-type, $\text{AgMg}_2(\text{HPO}_4)(\text{PO}_4)_2$ member of the well-known
alluaudite group (Monoclinic system, space group $C2/c$ and $Z = 2$) [13]. Other phosphates that are the first representatives
of their series like $\text{AgSr}_2\text{Cu}_3(\text{PO}_4)_2$ (Triclinic system, space
group $P-1$ and $Z = 2$) [14], and $\text{SrFe}(\text{HPO}_4)(\text{PO}_4)_2$ (Triclinic
system, space group $P-1$ and $Z = 2$) [15] were likewise isolated.
Moreover, a special focus was devoted to the systematic study
of $\text{CdO-MnO-P}_2\text{O}_5$-$\text{H}_2\text{O}$ resulting in the elaboration of the new
phosphate $\text{CdMn}_4(\text{HPO}_4)_3(\text{PO}_4)_2$ $\cdot$ $\text{H}_2\text{O}$ with a Hureau-
lite-like structure. The crystal structure of this phosphate was
determined through single crystal X-ray diffraction and its
structural model’s correctness was verified using the BVS [16]
approach and CD evaluation [17].

**Experimentation**

**Synthesis**

Single crystals of the novel compound $\text{CdMn}_4(\text{HPO}_4)_3(\text{PO}_4)_2$ $\cdot$ $\text{H}_2\text{O}$ were grown hydrothermally with the
appropriate reaction mixture of Mn, CdCl$_2$, and H$_3$PO$_4$ (85%
by weight) according to the molar ratio Mn:Cd:P = 3:2:4. The
process was carried out under autogenous pressure at 468 K
for 3 days in an appropriate autoclave reactor with PTFE lined vessel (23 ml) filled with 12 ml of deionized water. The
resulting product was filtered, rinsed with deionized water,
and dried at room temperature. The structure is determined at
nanoscopic scale.

**Results and Discussion**

**Structure determination**

Adequate single crystal was fixed by a small diameter glass
fibre to a Bruker X8 APEX2 diffractometer for the collection
of X-ray diffraction data. The gathering of intensities was per-
formed by means of the X-ray MoKα radiation ($\lambda_{\text{Mo}} = 0.71073$
Å) via the $\varphi$ and $\omega$ scanning modes. Acquired intensities were
afterwards corrected for Lorentz and polarization effects by
means of SAINT program [18]. Additionally, further absorption
corrections were carried out using SADABS program
[19] and resulted in a total of 20791 intensities of which 5338
are independent and 4587 with $I > 2\sigma(I)$ requirement. Based
on these crystal data, the structural determination of this new
phosphate was performed via WinGX package [20]. The crys-
tal structure was solved by Direct Methods with SHELXT
2014/7 program [21] and refined by full-matrix least-squares
using SHELXL2018/3 [22] program. As a result of structural
resolution Cd, Mn, and P atoms were located initially. After

**Table 1: Crystallographic data, X-ray collection details and structure re-
finement results for CdMn$_4$(HPO$_4$)$_3$(PO$_4$)$_2$·4H$_2$O.**

<table>
<thead>
<tr>
<th>Crystallographic details</th>
<th>Chemical formula</th>
<th>$M_r$</th>
<th>786.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>System, space group</td>
<td>Monoclinic, C2/c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>296</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$, $b$, $c$ (Å)</td>
<td>17.6932 (5), 9.1862 (3), 9.5417 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>96.562 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1540.68 (8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Mo Kt}$</td>
<td>$\lambda = 0.71073$ Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>5.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Data gathering**

- $\theta_{\text{min}}, \theta_{\text{max}}$ (°) 3.2, 42.3
- Miller indices -33 ≤ $h$ ≤ 29, -17 ≤ $k$ ≤ 17, -16 ≤ $l$ ≤ 17
- Measured reflections 20791
- Independent reflections 5338
- Reflections with $I > 2\sigma(I)$ 4587
- $R_{\text{int}}$ 0.029
- $(\sin \theta / \lambda)_{\text{max}}$ (Å$^{-1}$) 0.947

**Refinement**

$R(F) > 2\sigma(F)$, $wR(F)$, $S$ 0.022, 0.050, 1.03
Number of parameters 139
$\Delta \rho_{\text{max}}$ (e Å$^{-3}$) -0.66, -0.64

several successive refinement and Fourier-difference analysis,
the remaining oxygen and hydrogen atoms were positioned
with $d_{\text{N-H}}$ = 0.82Å to fulfill the asymmetric unit. In this crys-
tal structure, the position of the hydrogen atoms has been re-
efined isotropically by adopting a riding model with $U_{\text{iso}}(H) = 1.5$
$U_{\text{eq}}(O)$. During the last refinement cycle, the lowest
and highest residual electron densities are $\Delta \rho_{\text{max}}$ = -0.64 e Å$^{-3}$
at 0.43 Å from P1 and $\Delta \rho_{\text{min}} = 0.66$ e Å$^{-3}$ locating at 0.64Å from
Mn1. Crystallographic features, data gathering details and
structure refinement results are listed in table 1.

Elemental coordinates and their respective displacement
parameters are reported in table 2. Selection of inter-atomic
bond lengths and angles are given in table 3 and geometrical
features of hydrogen bond are listed in table 4. All representa-
tions were done by means of Vesta-3 [23].

**Structural description**

The principal building groups of the asymmetric unit in the
spiritual structure of $\text{CdMn}_4(\text{HPO}_4)_3(\text{PO}_4)_2$ $\cdot$ $\text{H}_2\text{O}$ are three
distorted $[(\text{Cd}(1)/\text{Mn}(1))\text{O}_2(\text{OH})_2]$ $\cdot$ $[(\text{Cd}(2)/\text{Mn}(2))$
$\text{O}_2]$, and $[(\text{Cd}(3)/\text{Mn}(3))\text{O}_2(\text{OH})_2]$ octahedra with two
regular PO$_4^{3-}$/HPO$_4^{2-}$ tetrahedra. The 3D-framework results
from (Cd/Mn)$_2$O$_2$(OH)$_2$ octahedral pentameretic entities of
dge-sharpening running along the [100] direction (Figure 1).
Neighboring entities are interconnected by corner-sharing
$[(\text{Cd}(1)/\text{Mn}(1))\text{O}_2(\text{OH})_2] - [(\text{Cd}(3)/\text{Mn}(3))\text{O}_2(\text{OH})_2]$ and bridged by apical PO$_4^{3-}$
and HPO$_4^{2-}$ units. Such polyhedral arrangement generates a large cavities extending parallel to the
[001] direction that accommodates terminal H$_2$O molecules of
$[(\text{Cd}(3)/\text{Mn}(3))\text{O}_2(\text{OH})_2]$ groups (Figure 2). Additional
interstitial Hydrogen interaction O—H···O contributes to the cohesion of the crystal structure. The geometrical
characteristics of those O-H-O are entirely in line with those described in the literature, particularly $\text{M}_2\text{Mn}_3(\text{HPO}_4)_2(\text{PO}_4)_2$ ($\text{M} = \text{Pb}, \text{Sr}$) [9, 10].

**Structural investigation**

The accuracy and stability of the given structural model was assessed herein by means of the BVS and CD analytical approaches. The electrical charge distribution calculations were performed with the CHARDI2015 program [24], while the BVS values were obtained with the EXPO2014 program [25] (Table 5).

Considering the present structural model all constituent elements of the asymmetric unit are in general positions (Wyckooff position 8f) except (Cd2/Mn2) that are positioned on 4e position. Distribution of the positively charged elements on the first ten independent crystallographic sites reveals that the cations (Cd$^{2+}/\text{Mn}^{2+}$), P$^{5+}$, and H$^+$ occupy fully their respective positions. The calculated charge values Q(j) corresponding to the various cations are in complete accordance with their respective C(j).SO(j) values. This result is also supported by the charge ratios C(j)/Q(j) $\approx$ 1 in all cases and the smaller divergence of Q(i) from C(j) which is corroborated by the absolute mean (MAPD = 7.8%). A close comparison between the computed cationic V(j), compared to their formal valences, reveals that the BVS calculations lead to the expected results with an interesting global instability index (GII) of 0.092 v.u.

In the structure of this Cd/Mn-Hureaulite half of the crystallographic sites are occupied by cations. The first three are mutually filled by Cd1/Mn1, Cd2/Mn2, and Cd3/Mn3 with occupancy rates of 0.395(2)/0.606(2), 0.095(2)/0.905(2), and 0.942(2)/0.056(2), respectively. These mixed sites are closely bounded to six adjacent O atoms resulting in more or less deformed octahedra with significant traction stress (Under bonding effect). In this asymmetric unit both P atoms are ar-

Table 2: Atomic positions and isotropic or equivalent thermal parameters (Å$^2$) in CdMn$_4$(HPO$_4$)$_2$(PO$_4$)$_2$.4H$_2$O.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U $^<em>$/U$^</em>$</th>
<th>Occ. (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd1</td>
<td>8f</td>
<td>0.17489 (2)</td>
<td>1.02882 (2)</td>
<td>0.86620 (2)</td>
<td>0.00913 (3)</td>
<td>0.395 (2)</td>
</tr>
<tr>
<td>Mn1</td>
<td>8f</td>
<td>0.17489 (2)</td>
<td>1.02882 (2)</td>
<td>0.86620 (2)</td>
<td>0.00913 (3)</td>
<td>0.606 (2)</td>
</tr>
<tr>
<td>Cd2</td>
<td>4e</td>
<td>0.000000</td>
<td>1.10366 (2)</td>
<td>1.250000</td>
<td>0.00881 (5)</td>
<td>0.095 (2)</td>
</tr>
<tr>
<td>Mn2</td>
<td>4e</td>
<td>0.000000</td>
<td>1.10366 (2)</td>
<td>1.250000</td>
<td>0.00881 (5)</td>
<td>0.905 (2)</td>
</tr>
<tr>
<td>Mn3</td>
<td>8f</td>
<td>0.31910 (2)</td>
<td>0.91115 (2)</td>
<td>0.68516 (2)</td>
<td>0.00964 (4)</td>
<td>0.942 (2)</td>
</tr>
<tr>
<td>Cd3</td>
<td>8f</td>
<td>0.31910 (2)</td>
<td>0.91115 (2)</td>
<td>0.68516 (2)</td>
<td>0.00964 (4)</td>
<td>0.056 (2)</td>
</tr>
<tr>
<td>P1</td>
<td>8f</td>
<td>0.16055 (2)</td>
<td>0.73824 (3)</td>
<td>0.62771 (3)</td>
<td>0.00652 (5)</td>
<td>0.104 (2)</td>
</tr>
<tr>
<td>P2</td>
<td>8f</td>
<td>0.00232 (2)</td>
<td>0.82066 (3)</td>
<td>1.08928 (3)</td>
<td>0.00721 (5)</td>
<td>0.019 (2)</td>
</tr>
<tr>
<td>O1</td>
<td>8f</td>
<td>0.07628 (4)</td>
<td>0.73412 (8)</td>
<td>0.65777 (8)</td>
<td>0.0104 (2)</td>
<td>0.0114 (2)</td>
</tr>
<tr>
<td>O2</td>
<td>8f</td>
<td>0.16333 (4)</td>
<td>0.76055 (9)</td>
<td>0.46742 (8)</td>
<td>0.0109 (2)</td>
<td>0.0115 (2)</td>
</tr>
<tr>
<td>O3</td>
<td>8f</td>
<td>0.20089 (4)</td>
<td>0.59525 (8)</td>
<td>0.67326 (8)</td>
<td>0.0127 (2)</td>
<td>0.0115 (2)</td>
</tr>
<tr>
<td>O4</td>
<td>8f</td>
<td>0.20237 (4)</td>
<td>0.86518 (9)</td>
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<td>0.0127 (2)</td>
<td>0.0115 (2)</td>
</tr>
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<td>O5</td>
<td>8f</td>
<td>0.00362 (4)</td>
<td>0.88993 (9)</td>
<td>0.94442 (8)</td>
<td>0.0127 (2)</td>
<td>0.0115 (2)</td>
</tr>
<tr>
<td>O6</td>
<td>8f</td>
<td>0.01195 (2)</td>
<td>0.7156 (2)</td>
<td>1.08075 (9)</td>
<td>0.0157 (2)</td>
<td>0.0115 (2)</td>
</tr>
<tr>
<td>H6</td>
<td>8f</td>
<td>-0.0170 (9)</td>
<td>0.726 (2)</td>
<td>1.008 (2)</td>
<td>0.036 (6)*</td>
<td>0.0115 (2)</td>
</tr>
<tr>
<td>O7</td>
<td>8f</td>
<td>0.15367 (4)</td>
<td>0.72971 (9)</td>
<td>1.13261 (8)</td>
<td>0.0125 (2)</td>
<td>0.0127 (2)</td>
</tr>
<tr>
<td>O8</td>
<td>8f</td>
<td>0.07625 (4)</td>
<td>0.93321 (9)</td>
<td>1.20408 (8)</td>
<td>0.0129 (2)</td>
<td>0.0127 (2)</td>
</tr>
<tr>
<td>O9</td>
<td>8f</td>
<td>0.26100 (5)</td>
<td>1.08249 (9)</td>
<td>0.53182 (8)</td>
<td>0.0127 (2)</td>
<td>0.0127 (2)</td>
</tr>
<tr>
<td>H9A</td>
<td>8f</td>
<td>0.241933</td>
<td>1.147159</td>
<td>0.575491</td>
<td>0.019*</td>
<td>0.019*</td>
</tr>
<tr>
<td>H9B</td>
<td>8f</td>
<td>0.287807</td>
<td>1.133976</td>
<td>0.487601</td>
<td>0.019*</td>
<td>0.019*</td>
</tr>
<tr>
<td>O10</td>
<td>8f</td>
<td>0.42335 (5)</td>
<td>1.0122 (2)</td>
<td>0.6521 (2)</td>
<td>0.0208 (2)</td>
<td>0.0208 (2)</td>
</tr>
<tr>
<td>H10A</td>
<td>8f</td>
<td>0.435067</td>
<td>1.078223</td>
<td>0.708092</td>
<td>0.031*</td>
<td>0.031*</td>
</tr>
<tr>
<td>H10B</td>
<td>8f</td>
<td>0.462555</td>
<td>0.970597</td>
<td>0.636459</td>
<td>0.031*</td>
<td>0.031*</td>
</tr>
</tbody>
</table>

Figure 1: Edge-sharing [[Cd(1)/Mn(1)]O$_5$(OH$_2$)], [[Cd(2)/Mn(2)]O$_6$], and [[Cd(3)/Mn(3)]O$_4$(OH$_2$)$_2$] octahedra building a pentameric entity parallel to the [100] direction.

Figure 2: Perspective view of CdMn$_4$(HPO$_4$)$_2$(PO$_4$)$_2$.4H$_2$O crystal structure along the c-axis revealing hydrogen bonding (dashed lines).
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Table 3: Main bond lengths and angles in CdMn₄(HPO₄)₂(PO₄)₂.4H₂O.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
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<tr>
<td>Cd1/Mn1—O2</td>
<td>2.1826 (8)</td>
<td>Cd1/Mn1—O3</td>
<td>3.2542 (8)</td>
</tr>
<tr>
<td>Cd1/Mn1—O4</td>
<td>2.2197 (8)</td>
<td>Cd3/Mn3—O10</td>
<td>2.1346 (8)</td>
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<td>Cd1/Mn1—O8</td>
<td>2.2234 (8)</td>
<td>Cd3/Mn3—O7</td>
<td>2.1768 (8)</td>
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<td>Cd1/Mn1—O5</td>
<td>2.2500 (8)</td>
<td>Cd3/Mn3—O2</td>
<td>2.1926 (8)</td>
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<td>Cd2/Mn2—O1</td>
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<tr>
<td>Cd2/Mn2—O1</td>
<td>2.2557 (8)</td>
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</table>

Table 4: Hydrogen-bond geometry (Å, °) in CdMn₄(HPO₄)₂(PO₄)₂.4H₂O structure.

<table>
<thead>
<tr>
<th>D—H···A</th>
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<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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<td>O6—H6···O1</td>
<td>0.82  (1)</td>
<td>1.80 (1)</td>
<td>2.6137 (11)</td>
<td>175 (2)</td>
</tr>
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<td>O6—H6···O2</td>
<td>0.82  (1)</td>
<td>2.65 (2)</td>
<td>3.1097 (12)</td>
<td>117 (2)</td>
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<tr>
<td>O9—H9A···O7</td>
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<td>2.05</td>
<td>2.8150 (12)</td>
<td>155</td>
</tr>
<tr>
<td>O9—H9B···O7</td>
<td>0.82  (1)</td>
<td>1.85</td>
<td>2.6668 (11)</td>
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<tr>
<td>O10—H10B···O6</td>
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<td>2.02</td>
<td>2.7455 (13)</td>
<td>147</td>
</tr>
<tr>
<td>O10—H10A···O1</td>
<td>0.82  (1)</td>
<td>1.95</td>
<td>2.7294 (13)</td>
<td>160</td>
</tr>
</tbody>
</table>

ranged in a conventional tetrahedral environment, with the coordination ratios ECoN(P1)/CN(P1) = 4/4 and ECoN(P2)/CN(P2) = 3.98/4. The monovalent cations H₆⁺, H₉⁻A, H₉⁻B, H₁₀⁻A, and H₁₀⁻B which are implied in weak hydrogen bonding exhibit suitable results of ECoN(H₆⁺) = 1.33, ECoN(H₉⁻A) = 1.16, ECoN(H₉⁻B) = 1.29, ECoN(H₁₀⁻A) = 1.17, and ECoN(H₁₀⁻B) = 1.22 [26].

Conclusion

Single crystals of the novel phase CdMn₄(HPO₄)₂(PO₄)₂.4H₂O have been elaborated under mild hydrothermal conditions and characterized by single-crystal X-ray diffraction. The correctness of the resulting structural model was confirmed by means of BVS and CD methods. According to the current structural model, all atoms of the asymmetric unit are in general positions (Wyckoff position 8f), with the exception of Cd2/Mn2, which is in 4e position. The cationic charge distribution on the first
ten independent crystallographic sites reveals that (Cd\(^{2+}/\)Mn\(^{2+}\)), P\(^{5-}\), and H\(^+\) fully occupy their sites. In addition, the calculated charge values Q(j) assigned to the various cations are in perfect agreement with the weighted values C(j)SO(j). This finding is confirmed by charge ratios C(j)/Q(j) = 1 in all cases, as well as the lowest divergence of Q(j) from C(j), which is supported by the absolute mean (MAPD = 7.8%). A comprehensive examination of the computed cationic valences V(j) and their formal charges indicates that the BVS calculations provide the expected results, with an interesting GII of 0.092 v.u. The 3D-net framework results from (Cd/Mn)\(_{10}\)O\(_6\)(OH)\(_2\) octahedral pentameric entities of edge-sharing extending along the [100] direction. Adjacent entities are linked to each other by corner-sharing [[Cd(1)/Mn(1)]O\(_6\)(OH)\(_2\)], [[Cd(3)/Mn(3)]O\(_6\)(OH)\(_2\)], PO\(_4\)\(^3-\), and HPO\(_4\)\(^2-\). This polyhedral disposition creates sizable cavities parallel to the [001] direction which contain the terminal H\(_2\)O molecules of the [[Cd(3)/Mn(3)]O\(_6\)(OH)\(_2\)] polyhedra. The cohesiveness of the crystal structure is enhanced by additional O—H...O interstitial H-interactions.

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**Conflict of Interest**

None.

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**References**


