Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1224). Services for accessing these data are described at the back of the journal.

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Monoclinic $InPO_4{\cdot}2H_2O$

Kazumasa Sugiyama,[a] Jihong Yu,[b] Kenji Hiraga[a] and Osamu Terasaki[c]

[a]Institute for Materials Research (IMR), Tohoku University, Sendai 980-8577, Japan, [b]CREST, Japan Science and Technology Corporation (JST), and Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan, and [c]Department of Physics, Graduate School of Science, and Center for Interdisciplinary Research, Tohoku University, Sendai 980-8578, Japan. E-mail: kazumasa@imrtuns.imr.tohoku.ac.jp

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Abstract

A new monoclinic phase of indium phosphate dihydrate, $InPO_4{\cdot}2H_2O$, was prepared from a hydrothermal synthesis of H_3PO_4, $In(OH)_3$ and H_2O in the presence of HF and $C_7H_{13}N$ (quinuclidine). The structure is isostructural with $AlPO_4{\cdot}2H_2O$ (metavariscite). The geometry of the H atoms in the title compound is consistent with that of metavariscite.

Comment

The previously known structure of indium phosphate dihydrate, $InPO_4{\cdot}2H_2O$, is orthorhombic (*Pbca*, a = 10.187, b = 8.842 and c = 10.327 Å; Mooney-Slater, 1961; Xu *et al.*, 1995). We report here the structure of monoclinic $InPO_4{\cdot}2H_2O$. The title compound is isostructural with $AlPO_4{\cdot}2H_2O$ (metavariscite; $P2_1/n$, a = 5.178, b = 9.514, c = 8.454 Å and β = 90.35°; Borensztajn, 1966; Kniep & Mootz, 1973).

The a-axis projection of the crystal structure, formed by the linkage of PO_4 tetrahedra and $InO_4(H_2O)_2$ octahedra, is shown in Fig. 1. One-dimensional eight-membered-ring channels are formed along the a axis, which are intersected by six-membered-ring channels along the b and c axes.

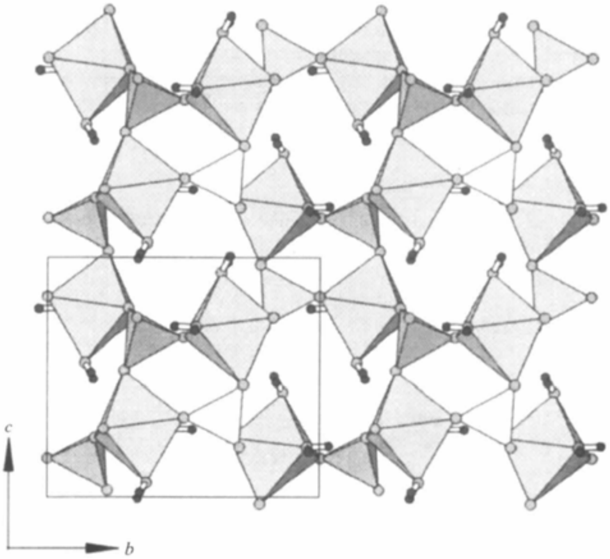

Fig. 1. The a-axis projection of the structure of monoclinic $InPO_4{\cdot}2H_2O$. Translation along the a axis produces a three-dimensional framework of eight-membered rings. Small circles indicate the H atoms.

The two distinct In—O*W*1 [2.128 (3) Å] and In—O*W*2 [2.174 (3) Å] distances are attributed to endothermic dehydration reactions at about 528 and 645 K, observed by common differential thermal analysis. In—O*W*2 is the longest among six In—O distances, whereas In—O*W*1 shows no appreciable difference from the In—O1, In—O3 and In—O4 distances. This feature of the indium coordination contrasts with the situation in orthorhombic $InPO_4{\cdot}2H_2O$ (Mooney-Slater, 1961; Xu *et al.*, 1995), where two In—O*W* distances are the first and second longest among six In—O distances. The large value of U^{33} for O*W*1 may suggest a possible disordered distribution of water molecules in the channels. Such features of the O*W*1 site are also seen in the structure of monoclinic $AlPO_4{\cdot}2H_2O$, including a relatively short Al—O*W*1 distance compared with Al—O1, Al—O3 and Al—O4 (Kniep & Mootz, 1973).

The hydrogen bonds involving atoms H1*A*, H1*B* and H2*A* can be described as single hydrogen bonds (Table 3). On the other hand, that involving H2*B* is indicated to be a bifurcated hydrogen bond, as also seen in metavariscite (Kniep & Mootz, 1973). The total weight loss of 14.3% on heating from 523 to 973 K (thermogravimetric analysis) is in good agreement with the calculated value of 14.6%.

Experimental

A mixture of H_3PO_4, $In(OH)_3$, HF, H_2O and organic $C_7H_{13}N$ (quinuclidine) with a molar ratio of 2:1:2:80:2 was sealed in a Teflon-lined autoclave. The autoclave was heated to 443 K and kept at this temperature for 10 d, and then quenched with water. The crystals obtained were filtered off, washed with distilled water and dried at 323 K. The starting chemical composition appears to be important for the synthesis of the title compound, for example, the formation of the orthorhombic phase was favored in the products synthesized from a mixture with a ratio of 1.2:1:2:80:2.

Crystal data

$InPO_4{\cdot}2H_2O$
$M_r = 245.82$
Monoclinic
$P2_1/n$
$a = 5.4508\,(12)$ Å
$b = 10.2229\,(12)$ Å
$c = 8.8830\,(17)$ Å
$\beta = 91.50\,(2)^\circ$
$V = 494.82\,(16)$ Å^3
$Z = 4$
$D_x = 3.300$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.25\text{–}19.26^\circ$
$\mu = 5.042$ mm^{-1}
$T = 298\,(2)$ K
Plate
$0.12 \times 0.07 \times 0.06$ mm
White

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.677$, $T_{\max} = 0.767$
2267 measured reflections
2163 independent reflections

1857 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 34.98^\circ$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 14$
3 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.068$
$S = 1.071$
2163 reflections
74 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.7323P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.980$ e Å^{-3}
$\Delta\rho_{\min} = -0.815$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
In	0.40951 (3)	0.33006 (2)	0.30193 (2)	0.00935 (6)
P	−0.08927 (12)	0.14992 (7)	0.18222 (8)	0.00841 (12)
O1	0.1699 (4)	0.1722 (2)	0.2501 (3)	0.0162 (4)
O2	−0.1192 (5)	0.2192 (2)	0.0299 (2)	0.0174 (4)
O3	−0.2793 (4)	0.2051 (2)	0.2899 (2)	0.0139 (4)
O4	0.1270 (4)	0.0014 (2)	0.1649 (2)	0.0131 (4)
O*W*1	0.0975 (5)	0.4551 (3)	0.2896 (6)	0.0470 (11)
O*W*2	0.4439 (5)	0.3646 (3)	0.0619 (3)	0.0258 (5)

Table 2. *Selected bond distances (Å)*

In—O2$^{\rm i}$	2.097 (2)	In—O*W*2	2.174 (3)
In—O1	2.119 (2)	P—O2	1.532 (2)
In—O*W*1	2.128 (3)	P—O3	1.536 (2)
In—O3$^{\rm ii}$	2.128 (2)	P—O1	1.538 (2)
In—O4$^{\rm iii}$	2.131 (2)	P—O4	1.539 (2)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O*W*1—H1*A*$\cdots$O1$^{\rm i}$	0.811 (3)	1.846 (2)	2.585 (4)	151.0 (2)
O*W*1—H1*B*$\cdots$O4$^{\rm ii}$	0.892 (3)	1.768 (2)	2.650 (3)	169.4 (2)
O*W*2—H2*A*$\cdots$O3$^{\rm iii}$	0.868 (3)	1.954 (2)	2.769 (3)	155.9 (2)
O*W*2—H2*B*$\cdots$O2$^{\rm iv}$	0.824 (3)	2.101 (3)	2.827 (4)	146.9 (2)
O*W*2—H2*B*$\cdots$O1$^{\rm iii}$	0.824 (3)	2.477 (3)	3.083 (4)	131.3 (2)

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

All the non-H atoms were refined anisotropically. The positions of the H atoms were obtained from difference Fourier syntheses. Nevertheless, the accuracy of the present analysis allows no further refinement. Only an isotropic displacement parameter was refined for the four independent H-atom positions. It should be added that the introduction of split atoms for O*W*1 did not improve the reliability of the structural model, although the average In—O*W*1 distance was increased by 0.013 to 2.141 (5) Å. The largest residual peak in the difference Fourier maps was located at (0.082,0.901,0.200), 0.73 Å from the In atom, and the largest hole at (0.142,0.834,0.307), 1.00 Å from In.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ATOMS* (Dowty, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1113). Services for accessing these data are described at the back of the journal.

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Nitrate d'argent et de césium: $AgCs(NO_3)_2$

FATMA BEN AMOR,[a]* DALILA HELLALI[b] ET HMIDA ZAMALI[a]

[a]*Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisie, et* [b]*Département de Chimie, Faculté des Sciences de Monastir, Route de Kairouan, 5000 Monastir, Tunisie. E-mail: tahar.jouini@fst.rnu.tn*

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Abstract

The structure of silver caesium dinitrate, $AgCs(NO_3)_2$, consists of NO_3^- layers perpendicular to the [100] direction. The Ag^+ and Cs^+ cations are located between the layers, forming AgO_5 and CsO_{12} polyhedra. The NO_3^- groups are planar.

Commentaire

Si les structures de $AgNO_3$ (Meyer *et al.*, 1978) et $CsNO_3$ (Dean *et al.*, 1985) ont été bien établies, celle du sel double $AgCs(NO_3)_2$ n'a fait l'objet d'aucune détermination structurale. Seule son existence a été signalée dans les systèmes $AgNO_3$·$CsNO_3$ (Flor & Sinistri, 1968; Gioia Lobbia & Cingolani, 1975; Hellali *et al.*, 1999) et $AgNO_3$·$CsNO_3$·H_2O (Khutsistova, 1988). Dans ce travail, la synthèse et l'étude structurale de $AgCs(NO_3)_2$ sont présentées. La structure de $AgCs(NO_3)_2$ est constituée de couches $N1O_3^-$ et $N2O_3^-$ alternées perpendiculaires à la direction [100], entre lesquelles se placent les cations Ag^+ et Cs^+ (Fig. 1). Les couches $N1O_3$ sont de plans moyens situés à $x = 0$ et $x = 0{,}5$ et celles de type $N2O_3$ à $x = 0{,}25$ et $x = 0{,}75$. Dans la couche $N2O_3$, deux atomes d'azote sont distants de 3,380 (9) Å. Cette distance est supérieure à celle séparant deux atomes d'azote dans la couche $N1O_3$ (3,083 Å), mais inférieure à celle séparant N1 de N2 [4,837 (11) Å]. Ces distances encadrent la valeur 3,265 Å trouvée dans $AgNO_3$ (Meyer *et al.*, 1978). Les groupements $N1O_3$ et $N2O_3$ sont plans et s'orientent perpendiculairement l'un par rapport à l'autre [90,0 (4)°]. Chaque cation Ag^+ est situé au centre d'une pyramide à base carrée d'atomes d'oxygène dont trois proviennent de deux groupements $N2O_3$ [2,317 (8)–2,590 (11) Å] et les deux autres d'un groupement $N1O_3$ [2,474 (7) Å]. Chaque cation Cs^+ est environné par douze atomes d'oxygène appartenant respectivement à huit groupements $N1O_3$ [3,123 (4)–3,716 (7) Å] et à quatre groupements $N2O_3$ [3,100 (7)–3,578 (9) Å]. Les distances Ag—O [2,317 (8)–2,590 (11) Å] et Cs—O [3,100 (7)–3,716 (7) Å] sont proches de celles rencontrées respectivement dans les composés $AgNO_3$ (Meyer & Capponi, 1982) et $CsNO_3$ (Pohl & Gross, 1993).

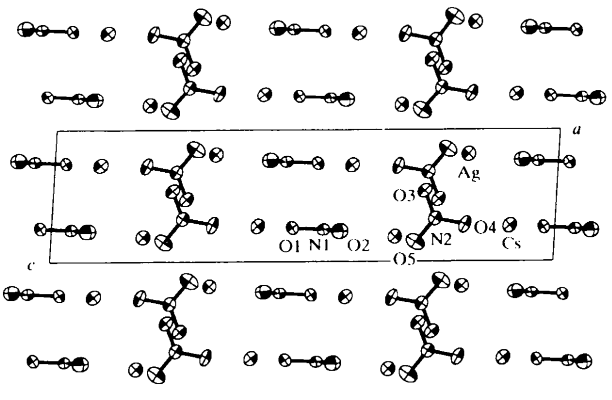

Fig. 1. Projection de la structure de $AgCs(NO_3)_2$ selon [010]. Les ellipsoïdes d'agitation isotropique ont une probabilité de 50%.

Partie expérimentale

Les réactifs utilisés sont $AgNO_3$ et $CsNO_3$ purs (Aldrich: 99,99%) préalablement séchés à 380 K pendant plus de 24 h. Un mélange de $AgNO_3$ et $CsNO_3$ pris dans le rapport molaire 1:1 et placé dans un creuset en platine a été porté à 620 K. Après fusion, il a été refroidi à 298 K. Il a été ensuite dissous dans l'eau et abandonné à température ambiante pendant plusieurs jours pour laisser apparaître des cristaux de $AgCs(NO_3)_2$.

Données cristallines

$AgCs(NO_3)_2$
$M_r = 364{,}80$
Monoclinique
$C2/m$
$a = 20{,}430$ (4) Å
$b = 5{,}591$ (4) Å
$c = 5{,}2880$ (6) Å
$\beta = 93{,}260$ (10)°
$V = 603{,}0$ (5) Å^3
$Z = 4$
$D_x = 4{,}018$ Mg m^{-3}
D_m pas mesurée

Mo $K\alpha$ radiation
$\lambda = 0{,}71069$ Å
Paramètres de la maille à l'aide de 25 réflexions
$\theta = 10{,}40$–$13{,}89$°
$\mu = 9{,}269$ mm^{-1}
$T = 293$ (2) K
Parallélépipède
0,36 × 0,14 × 0,14 mm
Incolore