Crystal structure of sodium cadmium diaqua *catena*-[monoboro-diphosphate]-hydrate, $NaCd(H_2O)_2[BP_2O_8] \cdot 0.8H_2O$

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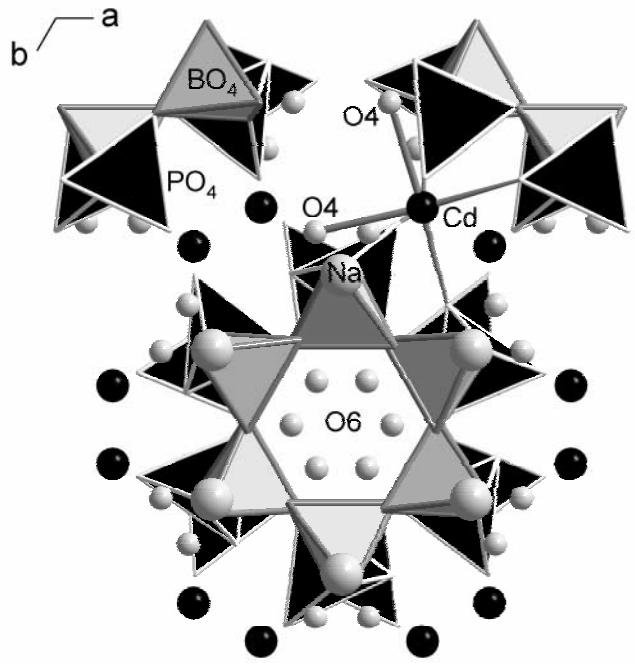

Abstract

$BCdH_6NaO_{10.8}P_2$, hexagonal, $P6_122$ (No. 178), $a = 9.713(1)$ Å, $c = 16.136(3)$ Å, $V = 1318.4$ Å^3, $Z = 6$, $R_{gt}(F) = 0.047$, $wR_{ref}(F^2) = 0.105$, $T = 273$ K.

Source of material

$NaCd(H_2O)_2[BP_2O_8] \cdot 0.8H_2O$ was prepared under mild hydrothermal conditions. A mixture of 0.459 g $CdCl_2 \cdot 2.5H_2O$, 1.900 g $Na_2B_4O_7 \cdot 10H_2O$, 6.436 g $NaBO_2 \cdot 4H_2O$, and 5 ml (85%) H_3PO_4 was heated at 363 K in deionized water (10 ml) under stirring until the components were completely dissolved. The clear solution (pH = 2.0) was transferred to a teflon autoclave (internal volume 27 ml) with filling degree 70% and heated at 443 K for four days. All the starting materials were of analytical grade without further purification. The chemical composition of the title compound was confirmed by ICP-AES analysis.

Discussion

A considerable number of borophosphates has been characterized in the past few years; however no cadmium based compounds have been reported so far. Here we report the first Cd-based borophosphate, $NaCd(H_2O)_2[BP_2O_8] \cdot 0.8H_2O$. Its crystal structure belongs to the family of borophosphate-hydrates with the general formula $M_x^I M_y^{II}(H_2O)_2[BP_2O_8] \cdot zH_2O$ (M^I = Li, Na, K, Rb, Cs; M^{II} = Mg, Mn, Fe, Co, Ni, Zn, Cu; $x = 0.35 - 1$, $y = 1 - 1.3$, $z = 0.2 - 1$) [1,2].

The crystal structure of the title compound contains infinite one-dimensional anionic tetrahedral ribbons $^1_\infty\{[BP_2O_8]^{3-}\}$, which form helical arrangements around the 6_1 screw axis. The spiral ribbons are built up from four-membered rings in which BO_4 and PO_4 groups alternate. Each BO_4 belongs to two adjacent four-membered rings of tetrahedra along the ribbon in such a way that all vertices of the BO_4 tetrahedra participate in bridging functions with PO_4 tetrahedra. The free loops of the borophosphate helices are occupied by Na^+ cations, which are surrounded by six oxygen atoms from adjacent phosphate groups (O2) and water molecules ($O4_{H_2O}$, $O6_{H_2O}$) in an irregular environment. The double helix $^1_\infty\{Na[BP_2O_8]^{2-}\}$ is completed by forming a central channel running along the 6_1 screw axis. The channel is filled with disordered water molecules ($O6_{H_2O}$), resulting in the formula $\{Na[BP_2O_8]^{2-} \cdot 0.8H_2O\}$. The Cd^{2+} ions are coordinated to four oxygen atoms of PO_4 groups (O2, O5) and two water molecules ($O4_{H_2O}$), resulting in an octahedral coordination $Cd(O_P)_4(O_{H_2O})_2$ connecting neighboring ribbons. Bond lengths and angles within the anionic partial structure are consistent with related borophosphates [3-6].

Table 1. Data collection and handling.

Crystal:	colorless hexagonal bipyramid, size 0.08 × 0.08 × 0.09 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	29.48 cm^{-1}
Diffractometer, scan mode:	Brucker SMART CCD, ω/φ
$2\theta_{max}$:	56.46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8039, 1072
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1072
$N(param)_{refined}$:	77
Programs:	SHELXL-97 [7], DIAMOND [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
O(6)	6*a*	0.80	0.889(6)	0	0	0.23(3)
B	6*b*		0.1525(7)	2x	1/4	0.015(2)
H(1)	12*c*		0.94(2)	–0.15(1)	0.231(9)	0.05
H(2)	12*c*		0.61(2)	0.17(1)	0.048(8)	0.05
H(3)	12*c*		0.8094	0.2446	0.0332	0.05

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	6*b*	0.45073(4)	2*x*	1/4	0.0140(3)	0.0116(4)	0.0136(3)	$U_{22}/2$	–0.0039(2)	0
P	12*c*	0.8376(2)	0.2224(2)	0.2509(1)	0.0109(8)	0.0108(8)	0.0080(8)	0.0035(6)	0.0021(7)	0.0032(8)
Na	6*b*	0.8116(6)	2*x*	1/4	0.078(4)	0.111(7)	0.027(3)	$U_{22}/2$	–0.003(3)	0
O(1)	12*c*	0.8151(6)	0.2284(6)	0.3462(3)	0.012(2)	0.016(3)	0.008(2)	0.008(2)	0.001(2)	0.002(2)
O(2)	12*c*	0.8691(7)	0.3791(6)	0.2171(3)	0.017(3)	0.014(2)	0.018(2)	0.010(2)	–0.003(2)	0.002(2)
O(3)	12*c*	0.9821(6)	0.1968(6)	0.2368(3)	0.014(2)	0.016(3)	0.011(2)	0.007(2)	–0.001(2)	–0.005(2)
O(4)	12*c*	0.6978(7)	0.1854(8)	0.0546(4)	0.014(3)	0.026(3)	0.033(3)	0.005(3)	–0.003(2)	0.010(3)
O(5)	12*c*	0.6981(7)	0.0793(7)	0.2116(3)	0.010(3)	0.023(3)	0.020(3)	0.005(2)	–0.003(2)	0.000(2)

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