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ORIGINAL PAPER

Synthesis and Crystal Structure of Sodium Arsenate Oxyhydroxide: $Na_4(AsO_4)OH$

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Abstract Single crystals of $Na_4(AsO_4)OH$ were grown using the hydroflux method and characterized by single crystal X-ray diffraction. $Na_4(AsO_4)OH$ crystallizes in the orthorhombic space group *Pnma* with $a = 8.9467(11)$ Å, $b = 7.3854(9)$ Å, and $c = 8.2395(10)$ Å. The moisture sensitive material exhibits a three-dimensional crystal structure consisting of isolated $AsO_4{}^{3-}$ tetrahedra with the charge balance maintained by Na^+ and OH^-. The asymmetric unit consists of one arsenic atom, three sodium atoms, four oxygen atoms, and one hydroxyl hydrogen atom. Arsenic, sodium, and oxygen atoms, as well as the hydroxyl hydrogen, are located on mirror planes; sodium is located on an inversion center.

Keywords Crystal growth · Crystal structure · Hydroflux · $Na_4(AsO_4)OH$

Introduction

New methods for growing single crystals of arsenic oxyhydroxides are of interest due to the difficulty inherent to growing arsenic oxyhydroxide crystals using many of the traditional methods. The recently developed hydroflux method [1–3] combines the hydrothermal and hydroxide flux methods to create conditions in which a flux [4] can be melted at relatively low temperatures due to the presence of notable quantities of water. The low temperature both makes conducting experiments more convenient and allows certain crystals to form that would not do so under high temperature crystal growth conditions. We were able to obtain $Na_4(AsO_4)OH$ single crystals out of a sodium hydroxide hydroflux.

$Na_4(AsO_4)OH$ is isotypic with $Na_4(VO_4)OH$, which was recently crystallized from a Na_2O melt by Kerp et al. [5], and with $Na_4[P_{0.5}Mn_{0.5}O_4][O]$, which was prepared from a NaOH flux and might be a hydroxide as well [6]. Related arsenates include $Na_5[AsO_4][O]$, reported by Haas et al. [7] and arsenates belonging to the Adelite mineral family reported by Qurashi et al. [8] The Adelite mineral has a composition of $CaMg(AsO_4)(OH)$, where the $AsO_4{}^{3-}$ tetrahedra are isolated by $CaO_7(OH)$ and $MgO_4(OH)_2$ polyhedra. In the title compound, the $AsO_4{}^{3-}$ polyhedra are preserved, but the Ca^{2+} and Mg^{2+} cations are replaced by four Na^+ cations to maintain the charge balance, resulting in $Na_4(AsO_4)(OH)$, an Adelite related structure type. In this study, we report on the synthesis and crystal structure of $Na_4(AsO_4)OH$.

Experimental

Materials and Methods

Single crystals of $Na_4(AsO_4)OH$ were grown out of a hydroflux of sodium hydroxide containing approximately 34 % water by weight. The reaction was carried out in a 25 mL polytetrafluoroethylene (PTFE) lined stainless steel autoclave. A mixture of 4/3 mmol (0.1320 g) of As_2O_3 (Alfa Aesar, 99.95 %), 0.1 mol (6.194 g) of Na_2O (Alfa Aesar, reagent grade), and ~6 g (6.0027 g) of deionized H_2O were added to the autoclave, and the autoclave was sealed. Na_2O was used to exclude the $CO_3{}^{2-}$ contained in commercial NaOH. The autoclave was heated to 230° at

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Table 1 Crystal data and structure refinement for $Na_4(AsO_4)OH$

Empirical formula	$Na_4(AsO_4)OH$	
Formula weight	247.89	
Temperature	100(2) K	
Crystal system	Orthorhombic	
Space group	*Pnma*	
Unit cell dimensions	a = 8.9467(11) Å	α = 90°
	b = 7.3854(9) Å	β = 90°
	c = 8.2395(10) Å	γ = 90°
Volume	544.42(12) Å3	
Z	4	
Density (calculated)	3.024 Mg/m3	
Absorption coefficient	6.500 mm−1	
Crystal size	0.240 × 0.200 × 0.180 mm3	
Theta range for data collection	3.361–32.600°	
Reflections collected	6,813	
Independent reflections	1,060 [R(int) = 0.0249]	
Data/restraints/parameters	1,060/0/58	
Goodness-of-fit on F2	1.140	
Final R indices [I > 2 sigma(I)]	R1 = 0.0182, wR2 = 0.0488	
R indices (all data)	R1 = 0.0197, wR2 = 0.0492	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.793 and −0.838 e Å−3	

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $Na_4(AsO_4)OH$

	X	Y	Z	U(eq)
As(1)	1,368(1)	2,500	6,492(1)	5(1)
Na(1)	1,297(1)	142(1)	3,470(1)	9(1)
Na(2)	3,726(1)	2,500	2,378(1)	8(1)
Na(3)	0	0	0	12(1)
O(1)	1,290(1)	630(1)	7,651(1)	8(1)
O(2)	2,901(1)	2,500	5,298(2)	10(1)
O(3)	−155(1)	2,500	5,249(2)	9(1)
O(4)	1,166(1)	2,500	1,532(2)	7(1)
H(4)	1,460(30)	2,500	580(40)	34(10)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

5 °C/min, held for 24 h, and then cooled slowly to 33 °C at a rate of 0.3 °C/min, at which point the oven was shut off. After cooling, the liquid in the autoclave was poured out, and the crystals inside were scraped off the sides and rinsed out of the autoclave with methanol. The yield was approximately 45 % based on As_2O_3.

Table 3 Selected bond lengths [Å] and angles [°] for $Na_4(AsO_4)OH$

As(1)–O(1)	1.6807(9)
As(1–O(1)#1	1.6808(9)
As(1)–O(2)	1.6875(12)
As(1)–O(3)	1.7046(12)
Na(1)–O(1)#6	2.3328(9)
Na(1–O(4)	2.3661(11)
Na(1)–O(3)#2	2.4420(10)
Na(1)–O(1)#2	2.5558(9)
Na(1)–O(3)	2.6211(11)
Na(1)–O(2)	2.7136(11)
Na(2)–O(1)#8	2.3221(10)
Na(2)–O(1)#6	2.3221(10)
Na(2)–O(4)#9	2.3601(14)
Na(2)–O(3)#10	2.3855(15)
Na(2)–O(4)	2.3947(14)
Na(2)–O(2)	2.5166(14)
Na(3)–O(1)#2	2.3010(9)
Na(3)–O(1)#11	2.3010(9)
Na(3)–O(4)	2.4676(9)
Na(3)–O(4)#12	2.4676(9)
Na(3)–O(2)#7	2.6448(9)
Na(3)–O(2)#6	2.6448(9)
O(1)–As(1)–O(1)#1	110.56(7)
O(1)–As(1)–O(2)	111.41(3)
O(1)#1–As(1)–O(2)	111.41(3)
O(1)–As(1)–O(3)	107.92(4)
O(1)#1–As(1)–O(3)	107.92(4)
O(2)–As(1)–O(3)	107.44(7)
O(1)#6–Na(1)–O(4)	91.74(4)
O(1)#6–Na(1)–O(3)#2	108.50(4)
O(4)–Na(1)–O(3)#2	149.20(5)
O(1)#6–Na(1)–O(1)#2	132.77(4)
O(4)–Na(1)–O(1)#2	82.83(4)
O(3)#2–Na(1)–O(1)#2	66.38(4)
O(1)#6–Na(1)–O(3)	141.51(4)
O(4)–Na(1)–O(3)	82.17(4)
O(3)#2–Na(1)–O(3)	94.695(19)
O(1)#2–Na(1)–O(3)	84.34(3)
O(1)#6–Na(1)–O(2)	80.08(3)
O(4)–Na(1)–O(2)	85.90(4)
O(3)#2–Na(1)–O(2)	119.62(4)
O(1)#2–Na(1)–O(2)	145.34(4)
O(3)–Na(1)–O(2)	61.64(4)
O(1)#8–Na(2)–O(1)#6	168.89(6)
O(1)#8–Na(2)–O(4)#9	88.22(2)
O(1)#6–Na(2)–O(4)#9	88.22(2)
O(1)#8–Na(2)–O(3)#10	95.18(3)
O(1)#6–Na(2)–O(3)#10	95.18(3)
O(4)#9–Na(2)–O(3)#10	87.55(5)
O(1)#8–Na(2)–O(4)	91.28(2)

Table 3 continued

O(1)#6–Na(2)–O(4)	91.28(2)
O(4)#9–Na(2)–O(4)	174.58(4)
O(3)#10–Na(2)–O(4)	97.88(5)
O(1)#8–Na(2)–O(2)	84.60(3)
O(1)#6–Na(2)–O(2)	84.60(3)
O(4)#9–Na(2)–O(2)	84.69(5)
O(3)#10–Na(2)–O(2)	172.24(5)
O(4)–Na(2)–O(2)	89.89(5)
O(1)#2–Na(3)–O(1)#11	180.0
O(1)#2–Na(3)–O(4)	86.15(4)
O(1)#11–Na(3)–O(4)	93.85(4)
O(1)#2–Na(3)–O(4)#12	93.85(4)
O(1)#11–Na(3)–O(4)#12	86.15(4)
O(4)–Na(3)–O(4)#12	180.0
O(1)#2–Na(3)–O(2)#7	82.14(3)
O(1)#11–Na(3)–O(2)#7	97.86(3)
O(4)–Na(3)–O(2)#7	79.93(3)
O(4)#12–Na(3)–O(2)#7	100.06(3)
O(1)#2–Na(3)–O(2)#6	97.86(3)
O(1)#11–Na(3)–O(2)#6	82.14(3)
O(4)–Na(3)–O(2)#6	100.07(3)
O(4)#12–Na(3)–O(2)#6	79.94(3)
O(2)#7–Na(3)–O(2)#6	180.0

Symmetry transformations used to generate equivalent atoms

#1 $x, -y+1/2, z$; #2 $-x, -y, -z+1$; #3 $-x, y+1/2, -z+1$

#4 $-x+1/2, y+1/2, z+1/2$; #5 $-x+1/2, -y, z+1/2$; #6 $-x+1/2, -y, z-1/2$

#7 $x-1/2, y, -z+1/2$; #8 $-x+1/2, y+1/2, z-1/2$; #9 $x+1/2, y, -z+1/2$

#10 $x+1/2, -y+1/2, -z+1/2$; #11 $x, y, z-1$; #12 $-x, -y, -z$

#13 $x, y, z+1$; #14 $-x, y+1/2, -z$

Table 4 Anisotropic displacement parameters (Å^2 × 10^3) for $Na_4(AsO_4)OH$

	U11	U22	U33	U23	U13	U12
As(1)	5(1)	5(1)	4(1)	0	0(1)	0
Na(1)	8(1)	9(1)	10(1)	1(1)	1(1)	0(1)
Na(2)	7(1)	7(1)	10(1)	0	0(1)	0
Na(3)	16(1)	15(1)	7(1)	−2(1)	3(1)	−6(1)
O(1)	10(1)	6(1)	8(1)	2(1)	0(1)	0(1)
O(2)	9(1)	12(1)	10(1)	0	5(1)	0
O(3)	9(1)	10(1)	8(1)	0	−3(1)	0
O(4)	8(1)	8(1)	6(1)	0	1(1)	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2hka^*b^*U^{12}]$

Table 5 Hydrogen bonds for $Na_4(AsO_4)OH$ [Å and °]

D–H···A	D(D-H)	D(H···A)	D(D···A)	<(DHA)
O(4)–H(4)···O(1)#15	0.83(4)	2.78(3)	3.4851(16)	143.5(13)
O(4)–H(4)···O(1)#11	0.83(4)	2.78(3)	3.4851(16)	143.5(13)
O(4)–H(4)···O(3)#10	0.83(4)	3.10(3)	3.6042(18)	121(2)

Symmetry transformations used to generate equivalent atoms

#1 $x, -y+1/2, z$; #2 $-x, -y, -z+1$; #3 $-x, y+1/2, -z+1$

#4 $-x+1/2, y+1/2, z+1/2$; #5 $-x+1/2, -y, z+1/2$; #6 $-x+1/2, -y, z-1/2$

#7 $x-1/2, y, -z+1/2$; #8 $-x+1/2, y+1/2, z-1/2$; #9 $x+1/2, y, -z+1/2$

#10 $x+1/2, -y+1/2, -z+1/2$; #11 $x, y, z-1$; #12 $-x, -y, -z$

#13 $x, y, z+1$; #14 $-x, y+1/2, -z$; #15 $x, -y+1/2, z-1$

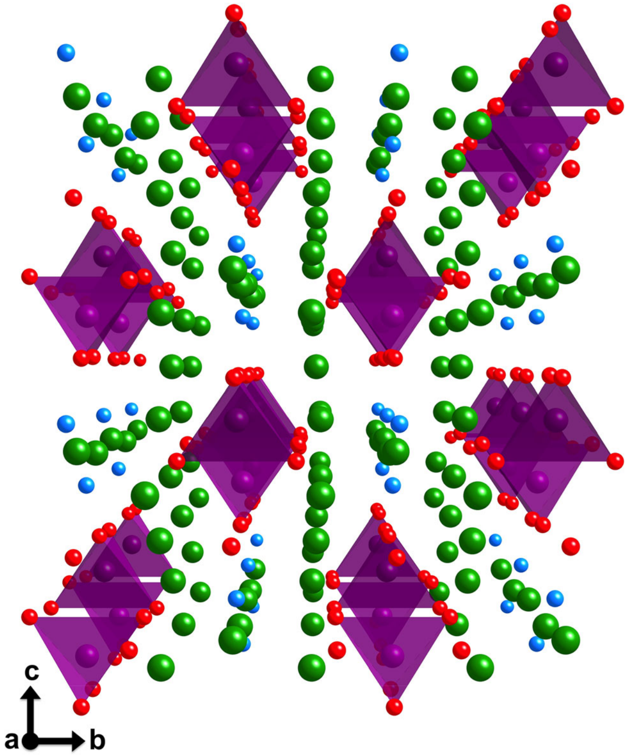

Fig. 1 Extended view of the crystal structure of $Na_4(AsO_4)OH$ along the *a*-axis, with oxygen atoms in *red*, AsO_4 tetrahedra in *purple*, sodium atoms in *green*, and hydroxide atoms in *blue* (Color figure online)

Energy-Dispersive Spectroscopy (EDS)

Elemental analysis was performed on the flux-grown crystals using an FEI Quanta 200 scanning electron microscope (SEM) with EDS capabilities. The crystals were mounted on carbon tape and analyzed using a 30 kV accelerating voltage and an accumulation time of 20 s. As

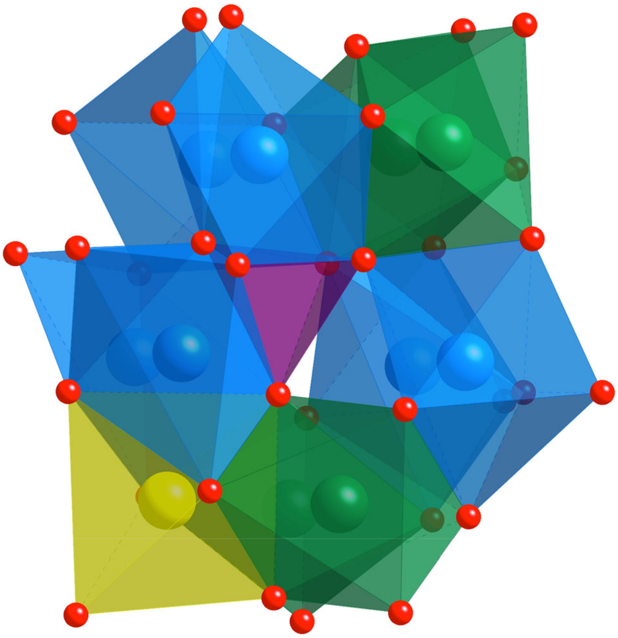

Fig. 2 The arsenic AsO_4 tetrahedra share edges with the $Na(1)O_6$ polyhedra and corners with the $Na(2)O_6$ and $Na(3)O_6$ octahedra. The AsO_4 tetrahedron is shown in *purple*, Na(1), Na(2), and Na(3) polyhedra are shown in *blue*, *yellow*, and *green*, respectively (Color figure online)

a qualitative measure, EDS confirmed the presence of each reported element in the title compound.

Crystallographic Study

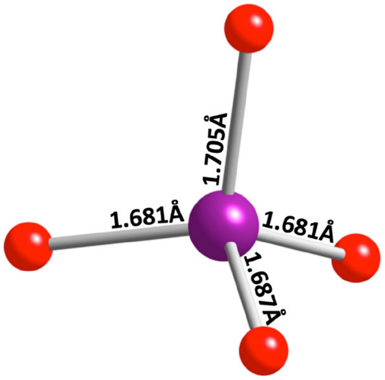

Fig. 4 View of a single AsO_4 tetrahedra, with bond lengths labeled

X-ray intensity data from a colorless block-like crystal were collected at 100(2) K using a Bruker SMART APEX diffractometer (Mo Ka radiation, $\lambda = 0.71073$ Å) [9]. The data collection covered 99.6 % of reciprocal space to $2\theta_{\max} = 65.2°$, with an average reflection redundancy of 6.1, and $R_{\text{int}} = 0.029$ after absorption correction. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT + and SADABS programs [9]. Final unit cell parameters were determined by least-squares refinement of 3,858 reflections from the data set. An initial structural model was obtained by direct methods using SHELXS [10]. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2013/4 [10] using the ShelXle interface [11].

The compound crystallizes in the orthorhombic system. The pattern of systematic absences in the intensity data was consistent with the space groups *Pnma* and *Pna*2_1, the former of which was confirmed by structure solution. The

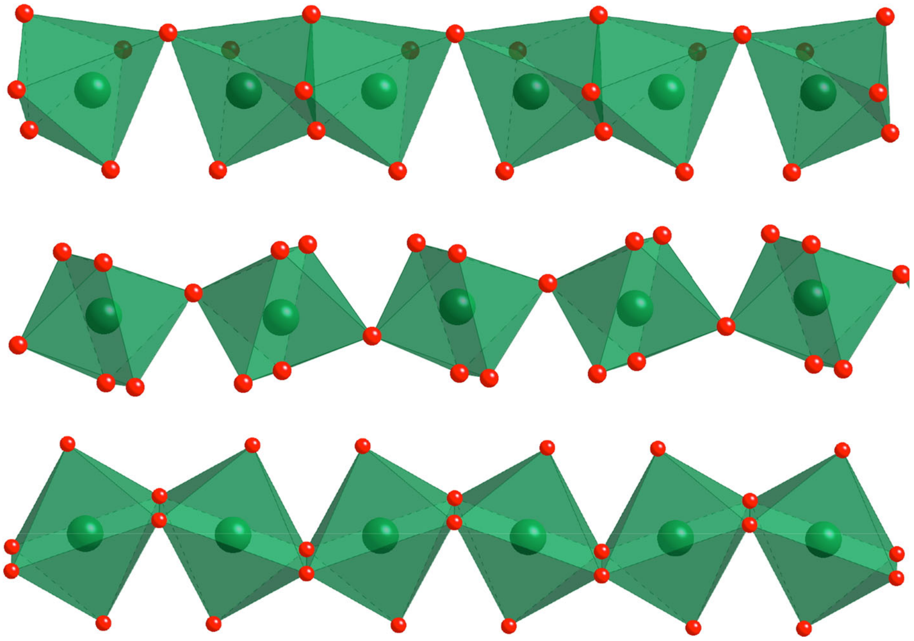

Fig. 3 Depiction of the Na1 (*top*), Na2 (*middle*), and Na3 (*bottom*) chains in $Na_4(AsO_4)OH$

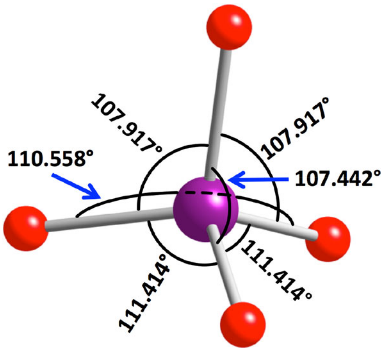

Fig. 5 View of a single AsO_4 tetrahedra, with bond angles labeled

asymmetric unit consists of one arsenic atom, three sodium atoms, four oxygen atoms, and one hydroxyl hydrogen atom. Arsenic As(1), sodium Na(2), oxygen atoms O(2), O(3), and O(4), and the hydroxyl hydrogen H(4) are located on mirror planes (site 4*c*). Na(1) and O(1) are located on general positions. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydroxyl hydrogen atom was located in a Fourier difference map and refined freely. The largest residual electron density peak and hole in the final difference map are +0.79 and −0.84 $e^-/Å^3$, located 1.64 and 0.70 Å from As(1), respectively. Final atomic coordinates were standardized using Structure Tidy [12–14].

Results and Discussion

Plentiful clear, colorless crystals were obtained from the hydroflux reaction. To avoid sample decomposition, the crystal structure of the moisture sensitive crystals was determined by minimizing exposure to air prior to data collection. The crystals were quickly mounted and transferred into a nitrogen stream. $Na_4(AsO_4)OH$ crystallizes in the orthorhombic space group *Pnma* with $a = 8.9467(11)$ Å, $b = 7.3854(9)$ Å, and $c = 8.2395(10)$ Å. Crystallographic information is summarized in Table 1, the atomic coordinates can be found in Table 2, selected interatomic distances are listed in Table 3, anisotropic displacement parameters are tabulated in Table 4, and the hydrogen bonds in $Na_4(AsO_4)OH$ are listed in Table 5.

The material exhibits a three-dimensional crystal structure consisting of isolated AsO_4^{3-} tetrahedra (Figs. 1, 2, 3), chains of alternating face and corner shared $Na(1)O_6$ polyhedra running down the y-direction, chains of corner sharing $Na(2)O_6$ octahedra running down the x axis ($Na(2)O_6$ polyhedra are not connected to each other along the y-direction), and chains of edge shared $Na(3)O_6$ octahedra running down the y-axis. These sodium-containing chains are in turn connected via corner and edge sharing to create a complex 3-D network in which the AsO_4 tetrahedra occupy available cavities. The AsO_4 tetrahedra are distorted with bond lengths ranging from 1.681 to 1.705 Å (Fig. 4), and bond angles ranging from 107.44° to 111.414° (Fig. 5). The arsenic AsO_4 tetrahedra share corners with $Na(3)O_6$ and $Na(2)O_6$ octahedra and edges with the $Na(1)O_6$ polyhedra (Figs. 1, 2, 3).

As mentioned earlier, the title compound is related to the previously reported compounds, $Na_4(VO_4)OH$ (isostructural with $Na_4(AsO_4)OH$ in this work) and $Na_5(VO_4)O$, with space groups of *Pnma* and *Pbcm*, respectively. Although overall structural features in these two structures, including the isolated MO_4 tetrahedra ($M = V$, As) are similar, the major difference is found in the coordination environment of the O(4) atom that is not bonded to any M atoms. In $Na_5(VO_4)O$, the O(4) atom is observed in a distorted ONa_6 polyhedra, while in $Na_4(MO_4)OH$ ($M = V$, As) the O(4) atom is placed in a severely distorted ONa_6 polyhedra due to the presence of the H atom attached to the O(4) atom forming –OH group.

Conclusion

Single crystals of $Na_4(AsO_4)OH$ were grown from a hydroflux. The title compound exhibits a new composition and is isostructural to a recently reported vanadate, $Na_4(VO_4)OH$. The arsenic is located in isolated, distorted AsO_4 tetrahedra.

Despite the lack of stability in the title compound, analogs of this compound, such as $Na_4(AsO_4)F$, may be stable enough to examine the properties of the structure; thus, this compound has future research potential.

Supporting Information

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +497247808666; e-mail: crystdata@fiz-karlsruhe.de) on quoting the depository number CSD-428481.

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