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New Layered Polyborates $Cs_2M_2B_{10}O_{17}$ (M = Na, K)

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The polyborates $Cs_2M_2B_{10}O_{17}$ (M = Na, K) have been prepared and their structures determined by single-crystal X-ray diffraction methods. They crystallize in the monoclinic space group $C2/c$ ($Z = 8$) with unit-cell parameters $a = 21.643(3)$ Å, $b = 6.558(2)$ Å, $c = 11.072(2)$ Å, $\beta = 105.43(1)°$, $V = 1514.8(6)$ Å^3 for the Na compound and $a = 22.547(9)$ Å, $b = 6.614(2)$ Å, $c = 11.288(4)$ Å, $\beta = 103.25°$, $V = 1638.3(8)$ Å^3 for the K analogue. The new structural type contains a 2-dimensional borate matrix that is built from a complete condensation of the ring system B_5O_{11}. The Cs atoms reside within the borate matrix, and the Na (K) atoms are placed between the thick Cs borate sheets.

Introduction

Polyborates have long been important for the production of a variety of glasses. During the past few years, greater interest has developed in crystalline examples because of the high UV transparency, exceptional optical damage threshold, and high second-harmonic conversion efficiency of the nonlinear optical (NLO) crystal LiB_3O_5 (LBO).[1] We also recently synthesized and identified the polyborate $CsLiB_6O_{10}$ (CLBO) as a promising new NLO material.[2] This finding has prompted considerable interest in the generation of related compounds. As part of our effort to identify similar materials and to expand and codify the structural chemistry of mixed alkali-metal borates, we report here two new compounds, $Cs_2Na_2B_{10}O_{17}$ and $Cs_2K_2B_{10}O_{17}$, that have resulted from studies of the systems $Cs_2O-M_2O-B_2O_3$ (M = Na, K). Although centrosymmetric, negating optical second-harmonic generation, these new materials do adopt unique layered structural arrangements, and such general features have long been important for ion-exchange reactions and more recently for the preparation of nanocomposites. In this contribution, we highlight some of the important structural characteristics of these new compounds. While the orthoborate $CsNa_2BO_3$ was recently described by Schläger and Hoppe,[3] no other phases have been reported for the K_2O system.

Experimental Section

Synthesis. Powder samples of $Cs_2Na_2B_{10}O_{17}$ and $Cs_2K_2B_{10}O_{17}$ were prepared by heating in air stoichiometric mixtures of the reagents Cs_2CO_3 (Aldrich, 99.995%), $NaNO_3$ (JTB, ACS grade), KNO_3 (JTB, ACS grade), and B_2O_3 (Alfa, 99.98%). The mixtures were heated in Pt crucibles at 893 K for 1 h, cooled, ground, and again heated at 973 K for 8 h. Powder diffraction patterns of these materials, obtained with a Philips diffractometer, matched those generated from the results of the single-crystal studies and the computer program LAZY-PULVERIX.[4] Crystals of $Cs_2Na_2B_{10}O_{17}$ were grown in a Pt crucible from a melt of molar composition 1 Cs_2O:1.05 Na_2O:2.75 B_2O_3, while crystals of $Cs_2K_2B_{10}O_{17}$ were grown directly from a stoichiometric melt. Each sample was melted by ramping to the maximum temperature at approximately 200 K/h followed by a soak time of 30 min. The melt containing Na was cooled at a rate of 6 K/h from 1003 to 800 K, and the melt containing K, from 983 to 780 K; below the stated minimum temperatures each was rapidly cooled to room temperature at 100 K/h. Transparent, colorless crystals of approximate dimensions 0.10 × 0.08 × 0.06 mm for the Na compound and 0.08 × 0.05 × 0.04 mm for the K compound were physically separated from the respective matrices for single-crystal measurements, though only a few small crystals were found in the solidified K melt.

Crystallographic Study. The crystals were mounted on glass fibers and analyzed on a Rigaku AFC6R X-ray diffractometer. The unit-cell parameters were derived from least-squares refinements with the setting angles of 20 automatically-centered reflections in the range $30 < 2\theta < 36°$. Intensity data were collected at room temperature by using the ω-scan technique with a rate of $8°(\omega)$/min and peak widths of $(1.60 + 0.30 \tan\theta)°$ for $Cs_2Na_2B_{10}O_{17}$ and $(1.30 + 0.30 \tan\theta)°$ for $Cs_2K_2B_{10}O_{17}$. The cell constants and Laue symmetry *2/m* correspond to the monoclinic system. The intensity data were collected over the range of indices $0 \leq h \leq 30$, $0 \leq k \leq 9$, $-15 \leq l \leq 15$ for the Na compound and $0 \leq h \leq 36$, $0 \leq k \leq 10$, $-18 \leq l \leq 18$ for the K compound. From 2456 measured reflections for the Na crystal, a total of 1598 were observed $[F_o^2 > 3\sigma(F^2)]$; for the K crystal, 1815 measured reflections resulted in 768 observations. The intensities of three representative reflections measured after every block of 200 data varied by an average of 0.5% for the Na crystal and 2.3% for the K crystal. The lower observed rate and generally weaker intensities associated with the K crystal are reflective of its poorer crystal quality.

The atomic parameters were determined by using programs of the TEXSAN crystallographic software package[5] on a μ-VAX II computer. The crystals exhibited systematic absences hkl, $h + k = 2n + 1$, and h0l, $l = 2n + 1$, which were consistent with the space group $C2/c$. The Cs atoms were located by using the direct methods program SHELXS,[6] and the remaining atoms were positioned from successive analyses of difference electron density maps. After full-matrix, least-squares refinements of the models with isotropic displacement coefficients on each atom, absorption corrections were applied by using the program DIFABS.[7] The data were averaged with $R_{\text{int}} = 0.042$ for the Na compound and 0.117 for the K compound. The models were then refined with anisotropic displacement coefficients on each atom in the Na compound. For the K compound, only atoms Cs, K, O2, O7, O9, B1, and B3 were refined with anisotropic coefficients. Final refinement resulted in the residuals $R = 0.039$ and $R_w = 0.045$ for $Cs_2Na_2B_{10}O_{17}$ and $R = 0.079$ and $R_w = 0.085$ for $Cs_2K_2B_{10}O_{17}$. Neutral-

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Table 1. Crystallographic Data for $Cs_2M_2B_{10}O_{17}$ (M = Na, K)

	$Cs_2Na_2B_{10}O_{17}$	$Cs_2K_2B_{10}O_{17}$
fw	707.88	724.10
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a, Å	21.643(3)	22.547(9)
b, Å	6.558(2)	6.614(2)
c, Å	11.072(2)	11.288(4)
β, deg	105.43(1)	103.25(4)
V, $Å^3$	1514.80	1638.3(8) Å
Z	8	8
ρ_{calc}, g cm^{-3}	3.104	2.935
μ(Mo Kα), cm^{-1}	49.33	50.13
T, K	298	298
$R(F_o)^a$	0.039	0.079
$R_w(F_o)^b$	0.045	0.085

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

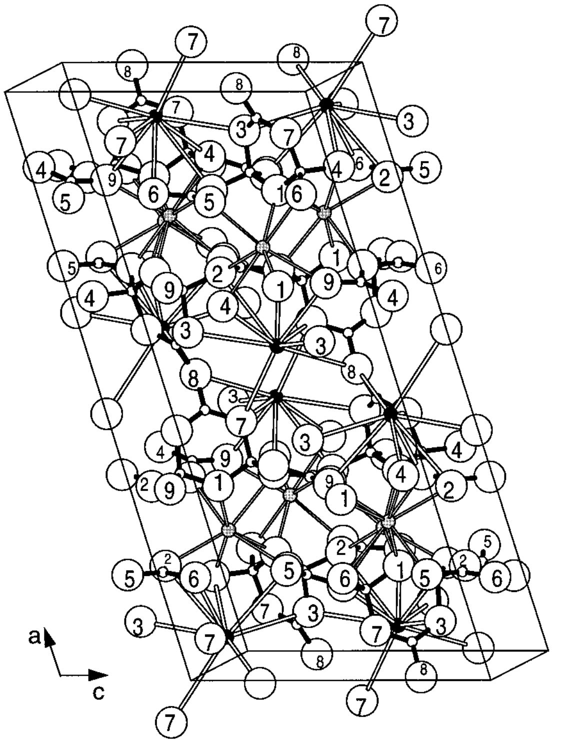

Figure 1. Labeled drawing of the structure of $Cs_2Na_2B_{10}O_{17}$ as viewed along the *b* axis. Large open circles represent O atoms, small open circles represent B atoms, small filled circles represent Cs atoms, and small shaded circles represent Na atoms in all figures.

atom scattering factors were taken from the common source.[8] The largest peaks in the final difference electron density maps corresponded to 0.62% and 1.44% of a Cs atom for the Na and K compounds, respectively. Crystallographic data are summarized in Table 1, and atomic positional parameters and displacement coefficients are listed in Table 2.

Both the Na and K compounds dissolve in H_2O (pH = 5.5). Amorphous solids are recovered following evaporation of the water at 408 K. Conversion to polycrystalline forms of $Cs_2Na_2B_{10}O_{17}$ and $Cs_2K_2B_{10}O_{17}$ is achieved by firing the samples at 973 K.

Results and Discussion

A labeled drawing of the structure of $Cs_2Na_2B_{10}O_{17}$ is shown in Figure 1. Except for small atomic displacements, the K analogue is isostructural (Table 2). The nature of the structure is best appreciated by considering the polyhedral representation of Figure 2. Here, a thick, 2-dimensional polyborate framework composed of BO_4 and BO_3 groups is seen to propagate in the *bc* plane. The Cs atoms are sequestered within the polyborate matrix, while the Na (K) atoms bridge adjacent layers. In its gross features, with the presence of both complex, negatively charged layers and associated charge-compensating cations, this structure is reminiscent of those adopted by clay-type materials.

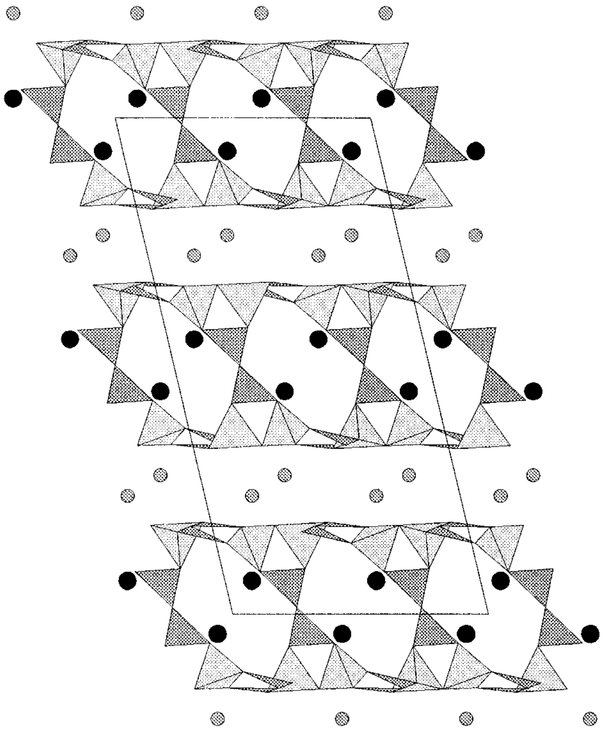

Figure 2. Polyhedral drawing of $Cs_2K_2B_{10}O_{17}$ as viewed along the *b* axis.

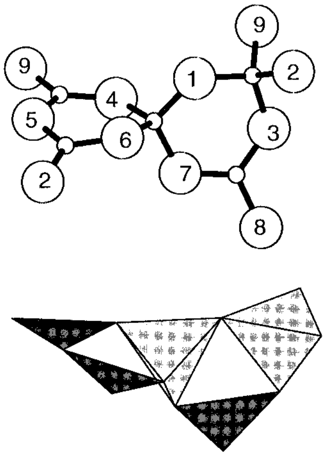

Figure 3. Drawings of the double-ring B_5O_{11} group.

The B−O framework may be considered to result from the complete condensation of the simple B_5O_{11} unit. As seen in Figure 3, this group contains condensed B_3O_7 ($2\Delta + 1T$) [Δ = triangular coordination, T = tetrahedral coordination of B] and B_3O_8 ($1\Delta + 2T$) rings; these two rings share a tetrahedrally coordinated B atom. Such a group exists as an isolated entity in the compound $Bi_3B_5O_{12}$.[9] In this form, the group contains six bridging O atoms, each bound by two B atoms, so five different formulations are possible for condensation of B_5O_{11} groups through the five terminal O atoms. The title compounds result from full condensation and are represented by the formula $2 \times (B_5O_6O_{5/2}) = B_{10}O_{17}$. From an enumeration of borate formulas that result from condensation of common borate

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Table 2. Atomic Parameters for $Cs_2M_2B_{10}O_{17}$ (M = Na, K)

	M = Na				M = K			
atom	*x*	*y*	*z*	B_{eq},[a] Å^2	*x*	*y*	*z*	B_{eq},[a] Å^2
Cs	0.44159(2)	0.19304(6)	0.40364(4)	2.06(1)	0.4456(1)	0.1910(3)	0.4064(2)	3.17(7)
M	0.2670(1)	0.0473(4)	0.3162(2)	1.71(9)	0.2712(3)	0.0819(8)	0.3255(4)	1.8(2)
B1	0.4447(3)	−0.305(1)	0.2636(6)	1.2(2)	0.448(2)	−0.323(4)	0.264(2)	3(1)
B2	0.3194(3)	0.428(1)	0.4956(5)	1.0(2)	0.334(1)	0.443(3)	0.515(2)	1.1(4)
B3	0.3343(3)	−0.222(1)	0.5631(5)	1.1(2)	0.351(1)	−0.213(3)	0.574(2)	2(1)
B4	0.3548(3)	−0.323(1)	0.3597(5)	1.1(2)	0.364(1)	−0.314(4)	0.371(2)	1.1(4)
B5	0.3445(3)	−0.137(1)	0.1499(6)	1.0(2)	0.354(1)	−0.152(3)	0.162(2)	1.0(4)
O1	0.1812(2)	0.2667(6)	0.2563(3)	0.8(1)	0.1679(6)	0.264(2)	0.238(1)	0.7(2)
O2	0.3189(2)	0.2267(6)	0.5239(3)	1.2(1)	0.3261(7)	0.247(2)	0.545(1)	1.3(6)
O3	0.4163(2)	0.1613(6)	0.6797(4)	1.4(1)	0.4212(7)	0.189(2)	0.682(1)	1.8(3)
O4	0.3561(2)	−0.1769(6)	0.4626(3)	1.4(1)	0.3688(7)	−0.168(2)	0.471(1)	1.4(3)
O5	0.1833(2)	−0.0782(6)	0.4174(3)	1.4(1)	0.1663(7)	−0.093(2)	0.401(1)	1.1(3)
O6	0.3262(2)	0.4817(6)	0.3811(3)	1.1(1)	0.3353(7)	0.488(2)	0.399(1)	1.2(3)
O7	0.4221(2)	−0.3654(6)	0.3603(4)	1.3(1)	0.4269(8)	−0.371(2)	0.367(1)	2.1(6)
O8	0	0.100(1)	$^1/_4$	1.9(2)	0	0.168(4)	$^1/_4$	2.8(5)
O9	0.3293(2)	0.0821(6)	0.1501(3)	1.2(1)	0.3454(8)	0.070(2)	0.160(1)	1.4(6)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

rings,[10] we have found the formula $B_{10}O_{17}$ to be unique. In essence, the structural nature of the borate matrix is fixed by the stoichiometry. This relationship between structure and composition, uncommon in solid-state borate chemistry, holds under the assumption that all O atoms are coordinated by no more than two B atoms. The only other condensation of B_5O_{11} groups that has been reported for anhydrous systems is represented by the sharing of four of the terminal O atoms—$B_5O_6OO_{4/2}$ = B_5O_9—in the compounds $CaNaB_5O_9$[11] and $SrKB_5O_9$.[12]

Interatomic distances and angles are listed in Table 3. Atoms B1, B2, and B3 occupy distorted triangular planar sites, while atoms B4 and B5 reside in distorted tetrahedral sites. The interatomic distances and angles within these triangles and tetrahedra are normal. B−O bonds in the triangles vary from 1.340(7) to 1.393(7) Å in the Na compound and from 1.32(3) to 1.42(3) Å in the K compound. The distances in the distorted tetrahedra range from 1.446(7) to 1.508(7) Å in $Cs_2Na_2B_{10}O_{17}$ and from 1.45(3) to 1.49(3) Å in $Cs_2K_2B_{10}O_{17}$.

In $Cs_2Na_2B_{10}O_{17}$, the Cs atom is bound by nine O atoms in a site having no symmetry other than the identity element. Among these connections, seven Cs−O distances cover the range 2.947(4)−3.335(4) Å, while the remaining two are longer than 3.5 Å. On the basis of bond-valence calculations,[13] we find that each of these two long bonds contributes only 6% to the Cs valence. The mean distance of these nine interactions is 3.281 ± 0.200 Å, which compares to a distance of 3.12 Å calculated from crystal radii.[14] The Na atom is surrounded by seven O atoms with Na−O distances falling in the range 2.304(4)−2.561(4) Å. The mean distance 2.505 ± 0.112 Å is comparable to the average distance 2.490 ± 0.244 Å observed in $NaLiB_4O_7$[15] and the value 2.46 Å computed from crystal radii for a 7-coordinate Na atom. The Cs- and Na-centered polyhedra share three O atoms—O2, O4, and O9.

In $Cs_2K_2B_{10}O_{17}$, the environment of the Cs atom is similar to that found in the Na analogue. The nine Cs−O bond distances vary from 2.94(1) to 3.59(2) Å, averaging 3.30 ± 0.21 Å. The K atom is also surrounded by nine O atoms. K−O distances range from 2.61(1) to 3.13(2) Å with a mean distance of 2.89 ± 0.19 Å. Because of the large size of the K atom in comparison with that of the Na atom and small attendant displacements of the atoms, in particular atom O6, the K- and

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $Cs_2M_2B_{10}O_{17}$ (M = Na, K)

	M = Na	M = K		M=Na	M=K
Cs−O2	3.280(4)	3.43(3)	O2−Cs−O3	42.7(1)	41.2(4)
Cs−O3	3.252(4)	3.28(1)	O2−Cs−O4	52.9(1)	55.9(3)
Cs−O3	3.335(4)	3.52(1)	O2−Cs−O6	42.89(9)	41.3(3)
Cs−O4	3.221(4)	3.12(1)	O2−Cs−O8	124.81(9)	124.5(3)
Cs−O6	3.091(4)	3.15(1)	O3−Cs−O4	60.8(1)	67.9(3)
Cs−O7	3.565(4)	3.59(2)	O3−Cs−O6	77.3(1)	74.1(4)
Cs−O7	2.947(4)	2.94(1)	O3−Cs−O8	131.7(1)	130.3(3)
Cs−O8	3.570(5)	3.44(2)	O4−Cs−O6	89.0(1)	90.2(4)
Cs−O9	3.268(4)	3.25(1)	O4−Cs−O7	135.1(1)	135.7(4)
			O4−Cs−O8	162.60(7)	162.5(3)
			O4−Cs−O9	70.8(1)	72.5(3)
			O6−Cs−O8	83.39(9)	84.7(3)
			O6−Cs−O9	70.8(1)	75.0(4)
			O7−Cs−O8	40.7(1)	42.6(4)
			O8−Cs−O9	91.93(7)	90.0(3)
M−O1	2.304(4)	2.61(1)	O1−M−O2	95.7(2)	109.8(4)
M−O1	2.401(4)	2.70(1)	O1−M−O4	159.1(2)	164.2(4)
M−O2	2.561(4)	2.73(1)	O1−M−O9	106.0(2)	112.5(4)
M−O4	2.61(5)	2.94(1)	O1−M−O5	110.8(2)	105.3(4)
M−O5	2.510(5)	2.93(2)	O2−M−O4	68.1(1)	65.8(4)
M−O6	2.585(5)	3.07(1)	O2−M−O5	86.9(1)	97.1(4)
M−O9	2.563(5)	2.78(2)	O2−M−O9	114.5(2)	113.8(5)
M−O2		3.11(1)	O4−M−O5	92.3(1)	99.6(4)
M−O6		3.13(2)	O4−M−O9	93.0(1)	82.6(4)
			O5−M−O9	158.4(2)	146.5(4)
B1−O3	1.351(7)	1.32(3)	O3−B1−O7	123.7(5)	123.5(27)
B1−O7	1.350(7)	1.39(3)	O3−B1−O8	119.1(5)	121.2(23)
B1−O8	1.393(7)	1.42(3)	O7−B1−O8	117.2(5)	114.1(16)
B2−O2	1.356(7)	1.36(2)	O2−B2−O5	121.7(5)	119.0(19)
B2−O5	1.391(7)	1.38(3)	O2−B2−O6	118.6(5)	119.0(18)
B2−O6	1.361(6)	1.35(3)	O1−B1−O2	119.6(5)	121.3(18)
B3−O4	1.353(7)	1.34(3)	O4−B3−O5	120.0(5)	122.7(20)
B3−O5	1.340(7)	1.39(3)	O4−B3−O9	123.4(5)	123.2(20)
B3−O9	1.354(7)	1.39(3)	O5−B3−O9	116.6(5)	114.0(20)
B4−O1	1.440(7)	1.37(2)	O1−B4−O4	108.4(5)	112.0(18)
B4−O4	1.484(7)	1.47(3)	O1−B4−O6	110.4(5)	110.4(18)
B4−O6	1.470(7)	1.53(3)	O1−B4−O7	112.3(4)	112.0(19)
B4−O7	1.480(7)	1.48(3)	O4−B4−O6	111.2(4)	111.5(17)
			O4−B4−O7	107.4(5)	106.7(18)
			O6−B4−O7	107.1(5)	103.9(17)
B5−O1	1.446(7)	1.45(3)	O1-B5-O2	112.7(5)	112.2(17)
B5−O2	1.478(7)	1.46(2)	O1−B5−O3	111.5(5)	109.8(16)
B5−O3	1.508(7)	1.49(3)	O1−B5−O9	107.2(5)	108.4(16)
B5−O9	1.475(7)	1.48(2)	O2−B5−O3	105.7(5)	106.4(17)
			O2−B5−O9	111.2(4)	112.6(16)
			O3−B5−O9	108.6(4)	107.3(17)

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Cs-centered polyhedra are now interconnected through four O atoms—O2, O4, O6, and O9.

With the exception of atom O5, which is 3-coordinate, the O atoms of the Na analogue bind four metal atoms—two of these being B atoms. Atoms O2, O4, O6, and O9 also bind one Cs and one Na atom; atoms O3, O7, and O8 bind two Cs atoms; and atom O1 binds two Na atoms. The environments of all O atoms in the K derivative resemble those in $Cs_2Na_2B_{10}O_{17}$, except that two atoms, O2 and O6, are 5-coordinate and both bind one Cs and two K atoms.

The compound $Cs_2Na_2B_{10}O_{17}$ may be viewed as resulting from the reaction $2CsB_3O_5 + Na_2B_4O_7$. As such, the Cs−Na compound exists along the phase line defined by the end members CsB_3O_5 and $Na_2B_4O_7$. The existence of additional phases along this line can readily be deduced by performing and analyzing two additional reactions: $CsB_3O_5 + Cs_2Na_2B_{10}O_{17}$ and $Cs_2Na_2B_{10}O_{17} + Na_2B_4O_7$. These reactions have been executed according to the procedures outlined in the Experimental Section, and we observe no unidentifiable peaks in the powder X-ray diffraction traces. Therefore, no additional, new phases exist along said phase line.

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Supporting Information Available: Tables listing complete crystallographic and data collection information and anisotropic displacement coefficients (4 pages). Ordering information is given on any current masthead page.

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