

The twinned crystal structure of tripotassium benzene-1,3,5-tris- (trifluoroborate)

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Received 15 April 2010
Accepted 28 April 2010
Online 8 May 2010

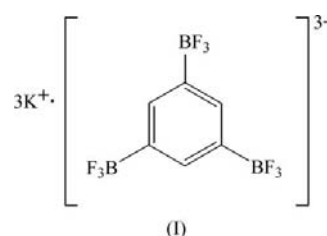
The title compound, $3\text{K}^+\cdot\text{C}_6\text{H}_3\text{B}_3\text{F}_9^{3-}$, crystallizes as discrete anions and cations which are connected by $\text{K}\cdots\text{F}$ and $\text{K}\cdots\pi$ interactions. Two of the $-\text{BF}_3$ residues attached to the aromatic ring adopt a conformation with all F atoms out of the plane of the aromatic ring, whereas the third residue has an almost synperiplanar conformation for one of the $\text{F}-\text{B}-\text{C}-\text{C}$ torsion angles. It is remarkable that only one of the K^+ cations interacts with the arene ring and that only one side of the aromatic ring coordinates to a K^+ cation. As a result, a sandwich structure does not occur. All K^+ ions show a coordination mode that cannot be conveniently described with a polyhedron. The anions are located in the (102) planes with the K^+ cations located between these planes. The investigated crystal was a nonmerohedral twin with the fractional contribution of the minor twin component being 0.405 (4). The title compound is the first example of a structure containing a benzene ring substituted with three $-\text{BF}_3$ groups. Only eight other structures have been reported in which a benzene ring carries at least one $-\text{BF}_3$ group. Just five of these contain a K^+ ion, but in none of these is the K^+ ion coordinated to the aromatic ring.

Comment

For oligoanionic arene rings we expect minimization of Coulombic repulsion to be realized by the location of a cation between the centres of two arene rings. We suppose that arenes bearing multiple borate moieties are compounds with a high tendency to form a multi-decker sandwich structure motif in the solid state. Multi-decker sandwich complexes are promising candidates for nanoscale applications as one-dimensional wires and spin-chains.

Our research focuses on the synthesis of aromatic borates (Haghiri Ilkhechi *et al.*, 2005). Potassium organotrifluoroborates attracted our attention because they were reported to be highly stable towards air and moisture (Molander & Ellis,

2007). In their pioneering work, Vedejs *et al.* (1995) described the synthesis of potassium organotrifluoroborates by treating organoboronic acids with excess potassium hydrogen fluoride (KHF_2) in an aqueous medium. Corresponding organodifluoroboranes were obtained by subsequent fluoride abstraction. This work was followed by the report of Genêt & Darses (1997), who employed organotrifluoroborates in transition-metal-catalysed C–C-bond-forming reactions with arene-diazonium tetrafluoroborates. The scope of applications in organic synthesis was expanded by Molander *et al.*, who implemented organotrifluoroborates in Suzuki–Miyaura-type cross-coupling reactions with a variety of carbon electrophiles, notably aryl triflates (Molander & Bernardi, 2002) and aryl halides (Molander & Biolatto, 2003).



The key aspect of organotrifluoroborate chemistry is the tetracoordination of the B atom. In contrast to most trivalent organoboranes, the trifluoroborates do not suffer from protodeboronation or oxidative cleavage of the C–B bond. This stability provides access to a variety of chemical reactions that have been conducted in the presence of the trifluoroborate moiety, like, for example, halogen–metal exchange (Molander & Ellis, 2006), Wittig reactions (Molander *et al.*, 2007) and ozonolysis of unsaturated C–C bonds (Molander & Cooper, 2007).

Our motivation to synthesize $3\text{K}^+\cdot[1,3,5-(\text{F}_3\text{B})_3\text{C}_6\text{H}_3]^{3-}$, (I), lies in its potential application as an oligotopic aryl nucleo-

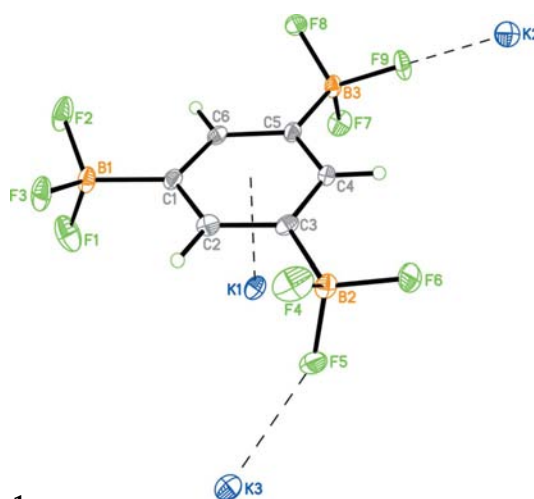
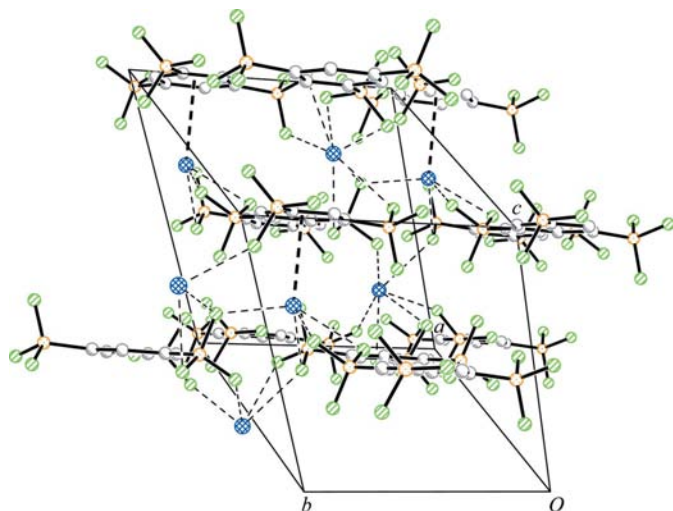
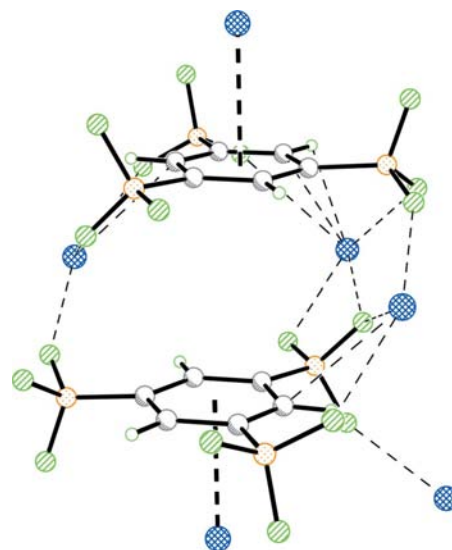


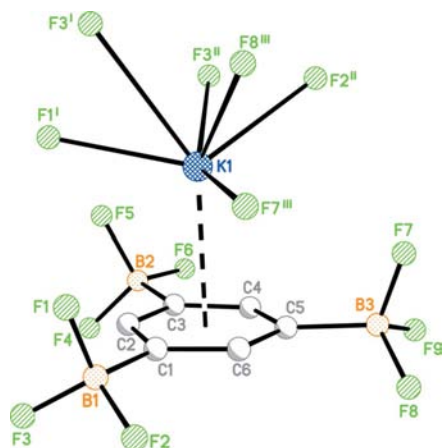
Figure 1
Perspective view of the asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

**Figure 2**

Packing diagram of the title compound. Short $K \cdots F$ contacts are drawn as dashed lines, the $K \cdots \pi$ contacts are drawn as solid lines. Colour codes in the electronic version of the paper: C (grey), B (light brown), F (green) and K (blue).

**Figure 4**

Shielding of the aromatic ring. The second asymmetric unit was generated by the symmetry operation $(-x + 1, -y + 1, -z + 2)$.

**Figure 3**

The environment of the K1 cation. H atoms have been omitted. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z + 1$.]

phile for Suzuki–Miyaura-type cross-coupling reactions and in the development of borate salts with novel structural motifs.

The asymmetric unit of the structure of the title compound (Fig. 1) is composed of one benzene-1,3,5-tris(trifluoroborate) trianion and three K^+ cations. All three C–B bond lengths are essentially equal [C1–B1 = 1.603 (5) Å, C3–B2 = 1.604 (5) Å and C5–B3 = 1.604 (5) Å]. The B–F bond lengths range from 1.413 (5) Å for B2–F4 to 1.434 (5) Å for B1–F3 and B2–F5. The C–C bond lengths show typical values for aromatic compounds. Two BF_3 groups adopt a conformation with all three F atoms out of the plane of the aromatic ring [torsion angles C2–C1–B1–F3 = 33.8 (6)° and C6–C5–B3–F8 = 37.5 (5)°], whereas the third has one F atom almost in the ring plane [torsion angle C4–C3–B2–F6 = 5.8 (6)°].

The anions are located in the (102) planes, with the K^+ cations situated between these planes (Fig. 2). Anions and

cations are connected by $K \cdots F$ and $K \cdots \pi$ interactions. Cation K1 is located 2.917 Å from the centre of the aromatic ring (Fig. 3). The $K \cdots C$ distances range from 3.179 (4) Å for K1 \cdots C2 to 3.314 (4) Å for K1 \cdots C4. In addition, there are five short contacts less than 3.0 Å between K1 and F atoms [a sixth contact amounts to 3.022 (3) Å] (Table 1). It is remarkable to note that only one side of the aromatic ring shows a close $K \cdots \pi$ contact, whereas the centre of the other side has no close contact less than 4.0 Å to any symmetry-equivalent K^+ cation. This side of the aromatic ring is shielded by another anion which is oriented in a parallel fashion with an interplanar distance of 4.07 Å. However, the two rings are not exactly stacked over one another and their centres show a displacement of 2.96 Å (Fig. 4). Nevertheless, there is no possibility for a K^+ cation to approach this side of the ring. Cation K2 has six short contacts to F atoms of less than 3.0 Å and two slightly longer ones (Table 1 and Fig. 5). For cation K3, four short contacts to F atoms (less than 2.8 Å), three of approximately 3.0 Å and two slightly longer ones can be found (Table 1 and Fig. 6). The coordination geometry around all three K^+ cations is rather irregular and cannot be described conveniently by any polyhedron. This is a typical feature of K^+ cations.

The solid-state structural motif of the title compound shows realization of a η^6 -coordination of one K^+ cation. Currently there is no example in the literature with a main group metal cation coordinated to an arene ring with multiple borate residues in a η^6 fashion. A recent search in the Cambridge Structural Database (CSD, Version 5.31 of November 2009, plus two updates; Allen, 2002) showed that a benzene ring substituted with at least one BF_3 group is a very rare structural element, because only eight structures containing this fragment were found. The first two of these do not contain a metal ion and, as a result of that, no structural motif similar to the title compound is possible.

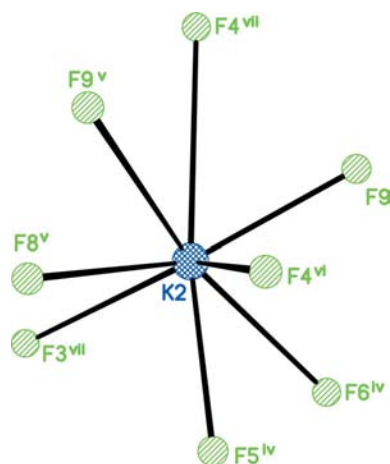


Figure 5
The environment of the K2 cation. [Symmetry codes: (iv) $-x, -y + 1, -z + 2$; (v) $-x + 1, -y, -z + 2$; (vi) $x, y - 1, z$; (vii) $-x + 1, -y + 1, -z + 2$.]

In 1-diisopropylaminomethyl-2-(trifluoroboryl)benzene (CSD refcode DECSAG; Coghlan *et al.*, 2005), there is a diisopropylaminomethyl residue *ortho* to the BF₃ substituent of the benzene ring. However, this molecule is neutral and there is no cation at all available for possible coordination.

Tetra-*n*-butylammonium phenyltrifluoroborate (CSD refcode NELRIF; Quach *et al.*, 2001) crystallizes as discrete tetra-*n*-butylammonium ions and phenyltrifluoroborate ions without any close contacts between anions and cations. The positively charged N atom is surrounded by the bulky *n*-butyl groups and cannot form any close contact to other atoms.

(1-3,5,6- η -Cyclooctadienyl)ruthenium phenyltrifluoroborate (CSD refcode OCRUBF; Ashworth *et al.*, 1977) is the first example of these eight structures containing a metal ion. In this case, an Ru atom is bonded in a η^6 fashion to the aromatic ring and to the double bonds of a cyclooctadienyl ring. Although there are F atoms available for potential coordination, no short Ru \cdots F interactions are observed. For this structure, it can be concluded that Ru prefers the coordination to π -electrons instead of to F atoms.

In (dibenzo-18-crown-6)(trifluoro[2-[(trifluoroacetyl)amino]phenyl]borate)potassium chloroform solvate (CSD refcode XONFIQ; Hudnall *et al.*, 2006), a K⁺ cation is coordinated by two F atoms of the BF₃ group, with K \cdots F distances of 2.774 and 2.940 Å, and by the six O atoms of a crown ether fragment. The K⁺ cation is not coordinated by the aromatic ring. The K \cdots O interactions are by far stronger than any potential K \cdots π interaction.

In aqua({5-*tert*-butyl-4-hydroxy-3-[(2,6-diisopropylphenyl)iminomethyl]phenyl}trifluoroborate-*F*)(18-crown-6)potassium perdeuterobenzene solvate (CSD refcode FIMLIX) and $\{\mu_2$ -2-*tert*-butyl-6-[(2,6-diisopropylphenyl)iminomethyl]-4-(trifluoroborate)phenolato-*F,F',N,O*\}(18-crown-6)methyl(trimethylphosphine)palladium(II)potassium acetonitrile solvate (CSD refcode FIMMAQ; Groux *et al.*, 2005), there is an aromatic ring substituted with one BF₃ group and three other residues. However, the K⁺ ion in these two structures is only coordinated by F atoms and O atoms, with K \cdots F distances ranging

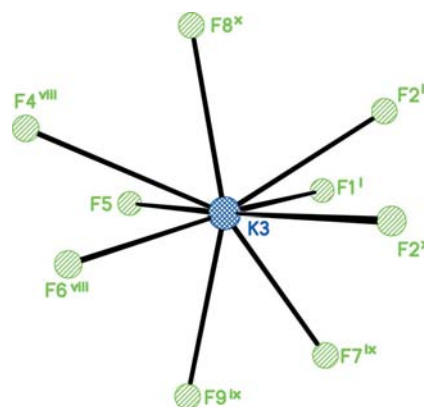


Figure 6
The environment of the K3 cation. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (viii) $-x, -y + 2, -z + 2$; (ix) $x, y + 1, z$; (x) $x - 1, y + 1, z$.]

from 2.657 to 3.153 Å in the first and from 2.654 to 3.125 Å in the second structure, respectively. Thus, these two structures are two further examples demonstrating that a K \cdots O or K \cdots F interaction is stronger than a K \cdots π contact and the former contacts are preferred to the latter.

The crystal structure of *catena*- $\{[\mu_4$ -1,2-bis(trifluoroboryl)-tetrafluorobenzene]dipotassium\} (CSD refcode ECUFUE; Chase *et al.*, 2006) is, in principle, comparable with that of the title compound because it lacks strong donor groups, *e.g.* O atoms. It features an aromatic ring with two BF₃ groups in an *ortho* relationship and four fluoro ligands on the remaining aromatic C atoms. The electron-withdrawing character of these fluoro substituents removes negative charge from the π -system of the ring and prevents the K⁺ cation coordinating to the aromatic ring. Both K⁺ cations only show contacts to F atoms displaying an irregular coordination mode. This example shows that a certain π -electron density is required for the coordination of an aromatic ring to a K⁺ ion. Incidentally, there is no example in the CSD where a benzene ring substituted with at least one F atom coordinates to a K⁺ ion.

Of the eight structures revealed by the CSD search, potassium trifluorophenylborate (CSD refcode YUHJUG; Conole *et al.*, 1995) is the structure which is the most similar to that of the title compound. The aromatic ring is substituted with only one BF₃ group and, as a result, there is just one K⁺ counter-ion. However, no K \cdots π interaction occurs. The K⁺ ion has seven short contacts to F atoms, ranging from 2.640 (5) to 2.951 (5) Å and one slightly longer one of 3.422 (6) Å. The benzene ring, on the other hand, acts as an acceptor of two C–H hydrogen bonds each from either side of the ring C–H = 1.18 Å, H \cdots Cgⁱ = 2.80 Å and C–H \cdots Cgⁱ = 153°; C–H = 1.11 Å, H \cdots Cgⁱⁱ = 2.97 Å and C–H \cdots Cgⁱⁱ = 144°; Cg is the centre of gravity of the benzene ring; symmetry codes: (i) $-\frac{1}{2} - x, y, -\frac{1}{2} + z$; (ii) $\frac{1}{2} - x, y, \frac{1}{2} + z$. In the title compound, on the other hand, C–H \cdots π contacts are impossible because the H atoms are shielded by the BF₃ substituents in the *ortho* position to them. The C–H \cdots π interactions may be the reason for the absence of K \cdots π contacts in potassium trifluorophenylborate, but from just one example, it cannot be

deduced without a doubt that the C—H $\cdots\pi$ interactions are the decisive reason that the K⁺ ions do not coordinate to the aromatic ring.

Summarizing, it can be said that the molecular geometry of the anion has no unusual features. The coordination to the K⁺ cations, on the other hand, shows K $\cdots\pi$ contacts, a feature which has not been observed previously for aromatic rings bearing a BF₃ group. Since only one of two possible K \cdots arene contacts is observed in the title structure, it can be concluded that this interaction is rather weak. The structures retrieved from the CSD show that other interactions (*e.g.* K \cdots O) are stronger than K $\cdots\pi$ interactions and therefore the former are more often observed than the latter.

Experimental

The synthesis of aryltrifluoroborates from arylboronic acid pinacol esters has been reported previously (Yuen & Hutton, 2005). To ensure complete conversion to the trianion, we applied a larger excess of the fluoride source per boron functionality than described in the literature.

In a glass tube (1.5 cm diameter, 16 cm length), a solution of potassium hydrogen fluoride (0.78 g, 10.0 mmol) in water (3.0 ml) was carefully layered with water (3.0 ml). 1,3,5-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (0.22 g, 0.5 mmol), synthesized according to a literature procedure (Morgan *et al.*, 2000), was dissolved in a mixture of hexane (8.0 ml) and diethyl ether (5.0 ml) and this solution was placed on top of the water layer. After 5 d, a colourless solid deposited on the inner surface of the glass vessel within the aqueous phase. One week later, crystals were discovered floating in the lower phase close to the interface between the two layers.

To our knowledge, there are no other synthetic routes described in the literature which lead to aromatic compounds with more than one trifluoroborate substituent attached to the central ring when starting out from the corresponding arylboronic acid pinacol esters. Our method has not yet been tested on a large preparative scale. Attempts to obtain the title compound *via* typical procedures that have been reported for various mono-trifluoroborate-substituted aromatic compounds failed. We assume that the tendency of aromatic trifluoroborate compounds to undergo hydrolysis increases with the number of BF₃ residues connected to the central aromatic ring. Consequently, this will complicate the isolation of pure material from aqueous media.

Crystal data

3K ⁺ ·C ₆ H ₃ B ₃ F ₉ ³⁻	$\gamma = 71.14 (3)^\circ$
$M_r = 395.81$	$V = 640.7 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.4025 (15) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.9349 (18) \text{ \AA}$	$\mu = 1.16 \text{ mm}^{-1}$
$c = 11.160 (2) \text{ \AA}$	$T = 173 \text{ K}$
$\alpha = 68.66 (3)^\circ$	$0.35 \times 0.30 \times 0.28 \text{ mm}$
$\beta = 74.28 (3)^\circ$	

Data collection

Stoe IPDS II two-circle diffractometer	6291 measured reflections
Absorption correction: multi-scan (MULABS; Spek, 2009; Blessing, 1995)	2378 independent reflections
$T_{\min} = 0.688$, $T_{\max} = 0.738$	2185 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.093$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$	192 parameters
$wR(F^2) = 0.180$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
2378 reflections	$\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

K1—F1 ⁱ	2.677 (3)	K2—F9 ^v	3.042 (3)
K1—F2 ⁱⁱ	2.758 (3)	K2—F4 ^{vii}	3.380 (3)
K1—F8 ⁱⁱⁱ	2.761 (2)	K3—F5	2.610 (3)
K1—F7 ⁱⁱⁱ	2.785 (3)	K3—F6 ^{viii}	2.713 (3)
K1—F3 ⁱⁱ	2.805 (3)	K3—F7 ^{ix}	2.753 (3)
K1—F3 ⁱ	3.022 (3)	K3—F1 ⁱ	2.785 (3)
K2—F9	2.620 (2)	K3—F9 ^{ix}	2.993 (3)
K2—F5 ^{iv}	2.655 (3)	K3—F8 ^x	3.000 (3)
K2—F8 ^v	2.723 (3)	K3—F2 ⁱ	3.029 (3)
K2—F4 ^{vi}	2.727 (3)	K3—F4 ^{viii}	3.302 (3)
K2—F6 ^{iv}	2.787 (3)	K3—F2 ^x	3.314 (3)
K2—F3 ^{vii}	2.893 (3)		

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x, -y + 1, -z + 2$; (v) $-x + 1, -y, -z + 2$; (vi) $x, y - 1, z$; (vii) $-x + 1, -y + 1, -z + 2$; (viii) $-x, -y + 2, -z + 2$; (ix) $x, y + 1, z$; (x) $x - 1, y + 1, z$.

Having encountered problems during the determination of the unit-cell parameters of several crystals of (I), all of which looked to be of good quality, the unit cell was eventually determined using approximately two thirds of the initial reflections. The same unit cell in a different orientation was obtained for the remaining third of the reflections, indicating that the crystals were twinned. The structure could be solved, but anisotropic refinement converged with $wR2 = 0.442$ and $R1 = 0.134$ using all data. At this point, the anisotropic displacement parameters appeared strange and high residual peaks showed up in difference electron-density maps (highest peak = 2.06 e \AA^{-3} and deepest hole = -0.96 e \AA^{-3}). The twin law $(-1 \ 0 \ 0 / -0.587, 1, -0.477/0 \ 0 -1)$, corresponding to a rotation of 2.17° about $[010]$, was obtained using the program *TWINLAW* (Bolte, 2004). The file containing the reflection data was then modified using the program *HKL F5* (Bolte, 2004), using a distance of 0.017 \AA^{-1} as the maximum distance for overlap of two reflections of the different domains. With this treatment, $R1$ dropped below 0.1 and all H atoms could now be located in a difference Fourier map. They were refined using a riding model with isotropic displacement parameters $U_{\text{iso}}(\text{H})$ set at $1.2U_{\text{eq}}(\text{C})$ and with C—H = 0.95 \AA . The fractional contribution of the minor twin component refined to 0.405 (4).

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3143). Services for accessing these data are described at the back of the journal.

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