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A novel supramolecular organic–inorganic adduct containing α-Keggin-type $[PW_{12}O_{40}]^{3-}$ anions and benzo-15-crown-5 molecules

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Key indicators

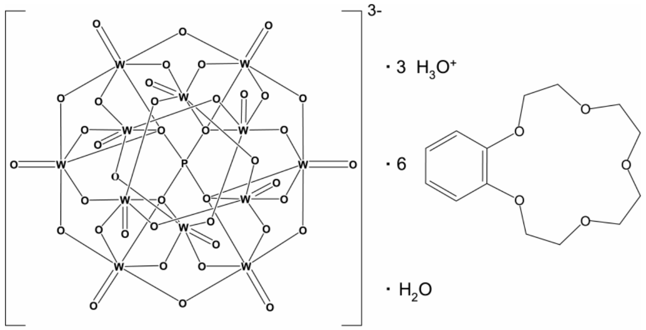
Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.018 Å
H-atom completeness 92%
Disorder in solvent or counterion
R factor = 0.039
wR factor = 0.083
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound, tris(hydroxonium) μ_{12}-phosphato-tetracosa-μ_2-oxo-dodecaoxododecatungsten hexakis(benzo-15-crown-5)–methanol–water (1/1/1), $(H_3O)_3[PW_{12}O_{40}]\cdot 6C_{14}H_{20}O_5\cdot CH_3OH\cdot H_2O$ (where $C_{14}H_{20}O_5$ is benzo-15-crown-5), has been determined at 180 K. $[PW_{12}O_{40}]^{3-}$ anions are typical of α-Keggin structures, and the $[H_3O\cdot(C_{14}H_{20}O_5)_2]^+$ sandwich-type moieties contain a large number of short O···O close contacts, suggesting strong hydrogen bonding within them.

Comment

Although the first polyoxometalates were reported almost 200 years ago, only recent advances in X-ray crystallography and analytical techniques have allowed a full structural characterization of such metal–oxygen clusters. The increasing interest behind these complexes relates to the multitude of possible different structures, and to their applications in medicine, catalysis, electrical conductivity, sorption, non-linear optical and magnetic materials, liquid crystals and photosensitive materials (Pope & Müller, 1994, 2001; Müller *et al.*, 1998, and references therein; Pope, 1983). Crown ether molecules have been widely used in supramolecular chemistry, either acting as hosts in molecular recognition events by selectively choosing the guest species, or conferring interesting catalytic or chemical transportation properties on the final compounds (Lu *et al.*, 1997; Neier *et al.*, 1995; Lehn, 1988).In particular, it is well known that crown ethers can stabilize water molecules or oxonium ions through hydrogen bonding, significantly increasing the quality and stability of the crystals (You *et al.*, 2002; You, Wang, Zhang *et al.*, 2000; You, Wang, He *et al.*, 2000; Nagano, 1979).



(I)

Following our recent research on the synthesis and structural characterization of novel hybrid compounds containing α-Keggin-type polyoxometalates and lanthanide coordination

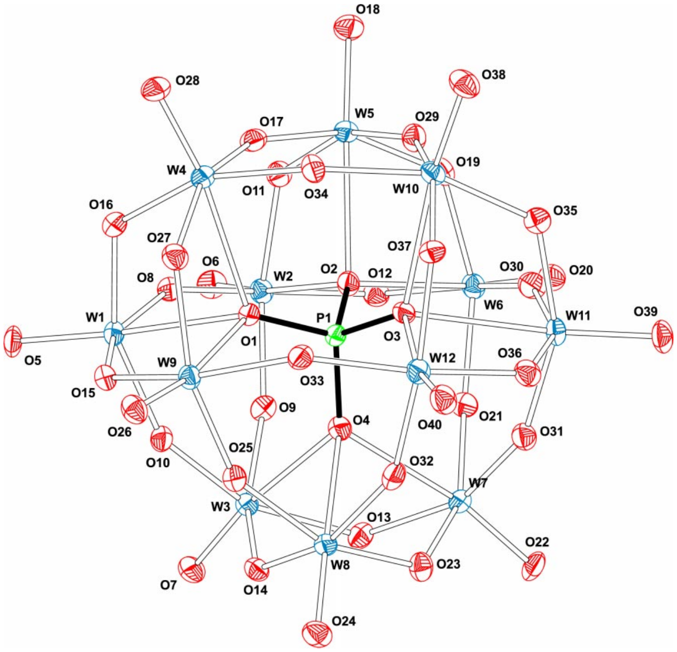


Figure 1
A view of the structure of the $[PW_{12}O_{40}]^{3-}$ anion in the title compound, showing the labelling scheme for all atoms. Displacement ellipsoids are drawn at the 30% probability level in this and the other figures.

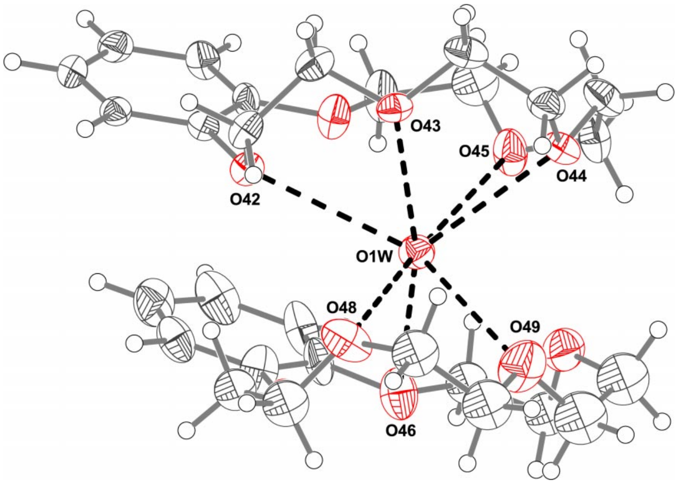


Figure 2
A view of the intermolecular O···O contacts (dashed lines) between the O1*W* hydroxonium ion and the two adjacent benzo-15-crown-5 molecules. For O···O distances, see Table 2.

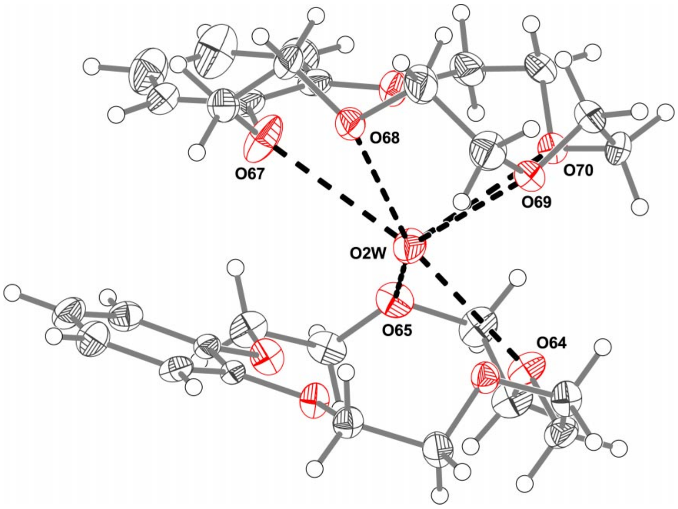


Figure 3
A view of the intermolecular O···O contacts (dashed lines) between the O2*W* hydroxonium ion and the two adjacent benzo-15-crown-5 molecules.

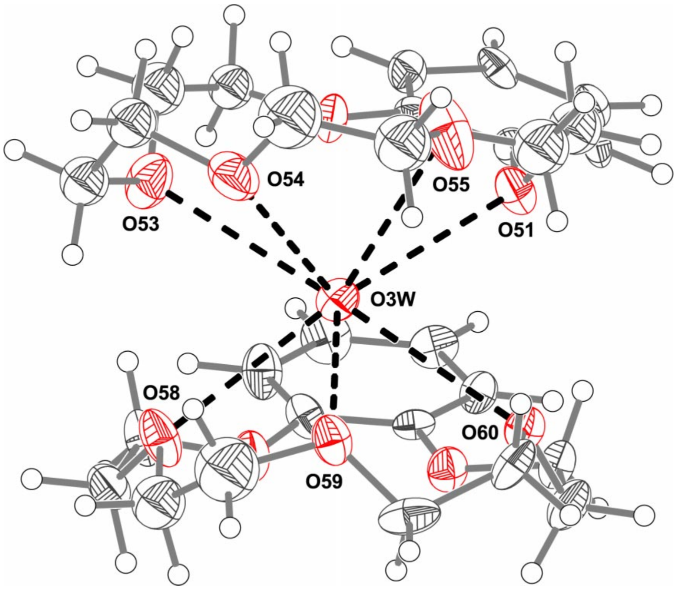


Figure 4
A view of the intermolecular O···O contacts (dashed lines) between the O3*W* hydroxonium ion and the two adjacent benzo-15-crown-5 molecules.

compounds (Soares-Santos, Nogueira, Félix *et al.*, 2003; Soares-Santos, Nogueria, Paz *et al.*, 2003; Cavaleiro *et al.*, 1999; Gamelas *et al.*, 1999), we came across the title compound, (I). Interestingly, as revealed by a search in the Cambridge Structural Database (Allen, 2002), only one other adduct of $[PW_{12}O_{40}]^{3-}$ anions and benzo-15-crown-5 molecules, *viz.* $(H_3O)_3[PW_{12}O_{40}]\cdot 6C_{14}H_{20}O_5\cdot 13H_2O$, has been reported (You, Wang, Zhang *et al.*, 2000).

The title compound, (I), contains one crystallographically unique $[PW_{12}O_{40}]^{3-}$ anion, which does not show any significant crystallographic disorder (Fig. 1), in constrast to what was observed by You, Wang, Zhang *et al.* (2000) and is usually found in other related compounds containing α-Keggin-type anions (see, for example, Lu *et al.*, 1997; Neier *et al.*, 1995). W centres exhibit a distorted $\{WO_6\}$ coordination environment, with all the W—O bond distances, *cis*-O—W—O and *trans*-O—W—O angles within the ranges 1.686 (6)–2.447 (6) Å, 71.2 (2)–104.1 (3)° and 154.4 (3)–171.5 (3)°, respectively (Table 1). The W—O bonds can be further divided into several groups according to the different type of O atoms, all within the usual range of values found in related compounds (Table 1): O_a, bridging the W and P centres [2.421 (6)–2.447 (6) Å]; O_b and O_c, connecting adjacent W centres whose octahedra are corner- and edge-shared, respectively [1.886 (6)–1.939 (6) Å]; O_d, the terminal O atoms [1.686 (6)–1.704 (6) Å]. The central P atom is surrounded by four O atoms, in a coordination geometry closely resembling a regular tetrahedron (Fig. 1 and Table 1). Benzo-15-crown-5 molecules appear in pairs, each pair intercalated by one water molecule, in which only the O atom was successfully located from difference Fourier maps. The large number of close O···O contacts between these water molecules (O1*W*, O2*W* and O3*W*) and the neighbouring benzo-15-crown-5 molecules suggests the presence of very strong hydrogen bonding within the three sandwich-type moieties (Figs 2, 3 and 4; Table 2). Furthermore, in order to balance the anion charge, we believe it is reasonable to consider these water molecules as probable protonation sites, leading to the formation of hydroxonium species H_3O^+. The hydrogen-bonding network is further extended by one O—H···O interaction between the methanol molecule and the $[PW_{12}O_{40}]^{3-}$ anion (Table 3). The crystal packing is rather complex (Fig. 5), with the $[PW_{12}O_{40}]^{3-}$ anions and the $[H_3O\cdot(C_{14}H_{20}O_5)_2]^+$ sandwich-type cationic moieties close-packed.

Experimental

All chemicals were purchased from Aldrich and used without further purification. A solution of benzo-15-crown-5 (0.13 g, 0.50 mmol) in acetonitrile (*ca* 10 ml) was added dropwise to a solution of methanol (*ca* 40 ml) containing $H_3PW_{12}O_{40}$ (1.40 g, 0.50 mmol) and $TbCl_3.6H_2O$ (0.19 g, 0.50 mmol). The resulting solution was stirred thoroughly at ambient temperature for 24 h and then filtered. The filtrate was allowed to stand at ambient temperature; good-quality orange crystals suitable for X-ray diffraction were obtained after two days. Selected FT—IR data (cm^{-1}): ν_{as}(P—O$_a$) 1078 (*s*); ν_{as}(W—O$_d$, terminal W—O stretch) 987 (*s*) and 978 (*s*); ν_{as}(W—O$_b$—W, corner-shared W—O—W stretching mode) 895 (*s*); ν_{as}(W—O$_c$—W, edge-shared W—O—W stretching mode) 815 (*s*); ν(Ar—O—C) 1256 (*m*) and 1214 (*w*); ν(C—O—C) 1126 (*m*). Selected Raman data (cm^{-1}): ν_s(W—O$_d$, terminal W—O stretch) 1005; ν_{as}(W—O$_d$, terminal W—O stretch) 991; ν_{as}(W—O$_b$—W, corner-shared W—O—W stretching mode) 896; ν_{as}(W—O$_a$) 215; ν(Ar—O—C) 1256; ν(C—O—C) 1128.

Crystal data

$(H_3O)_3[PW_{12}O_{40}]\cdot 6C_{14}H_{20}O_5\cdot$-
$CH_4O\cdot H_2O$
$M_r = 4594.10$
Monoclinic, $P2_1/n$
$a = 16.890$ (3) Å
$b = 42.101$ (8) Å
$c = 17.393$ (4) Å
$\beta = 101.66$ (3)°
$V = 12112$ (4) Å^3
$Z = 4$

$D_x = 2.519$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 118671 reflections
$\theta = 1.0$–25.0°
$\mu = 11.46$ mm^{-1}
$T = 180$ (2) K
Block, orange
0.12 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.269$, $T_{max} = 0.559$
71608 measured reflections
20465 independent reflections

16507 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 25.0$°
$h = -20 \rightarrow 20$
$k = -49 \rightarrow 50$
$l = -20 \rightarrow 20$

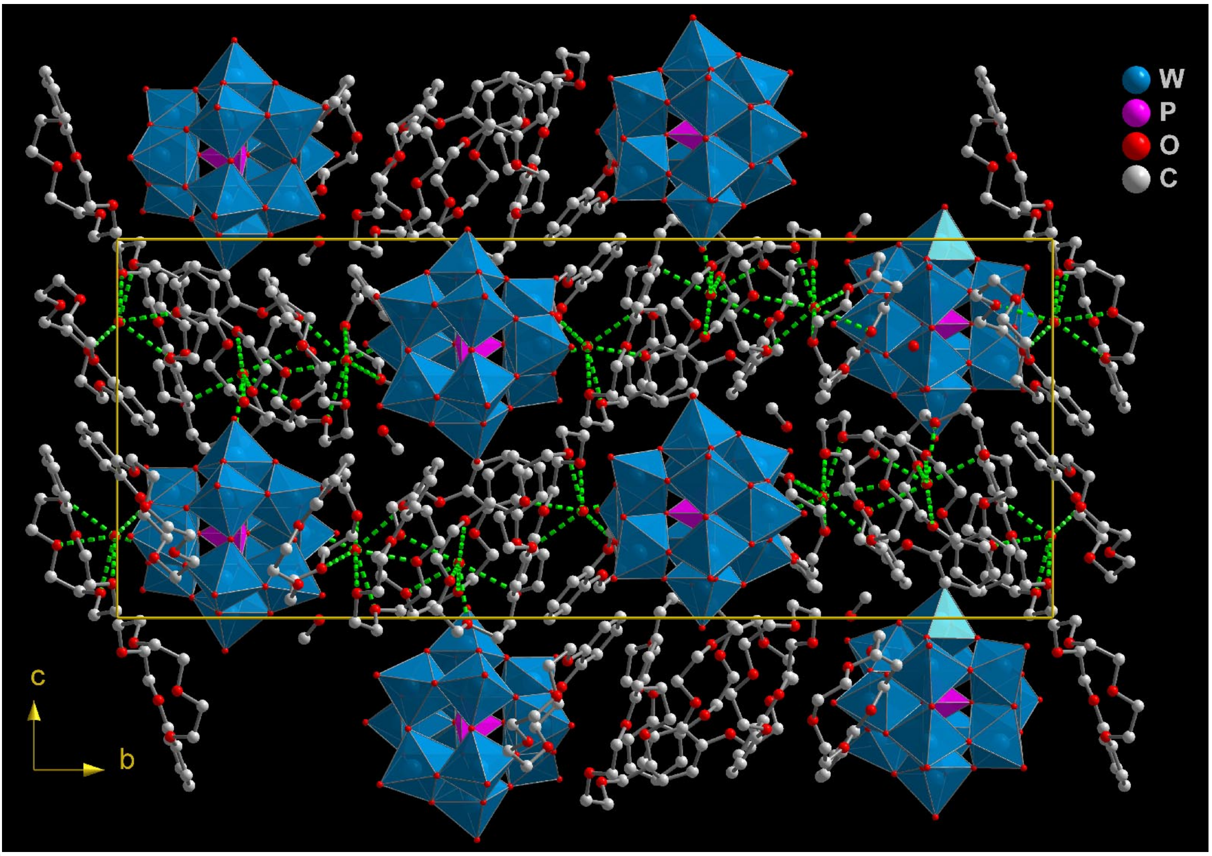


Figure 5
Perspective view of (I) along the *a* axis, with the $[PW_{12}O_{40}]^{3-}$ anions represented as polyhedra. O···O contacts between the hydroxonium H_3O^+ ions and the benzo-15-crown-5 molecules (Table 2) are represented as green dashed lines. H atoms have been omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.083$
$S = 1.04$
20465 reflections
1449 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 121.8552P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.82$ e Å^{-3}
$\Delta\rho_{min} = -1.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

W1—O5	1.699 (6)	W7—O13	1.911 (6)
W1—O8	1.886 (6)	W7—O31	1.912 (6)
W1—O10	1.908 (6)	W7—O23	1.915 (6)
W1—O16	1.915 (6)	W7—O4	2.447 (6)
W1—O15	1.939 (6)	W8—O24	1.687 (6)
W1—O1	2.443 (6)	W8—O32	1.892 (6)
W2—O6	1.686 (6)	W8—O25	1.910 (6)
W2—O9	1.896 (6)	W8—O23	1.911 (6)
W2—O12	1.905 (6)	W8—O14	1.928 (6)
W2—O8	1.935 (6)	W8—O4	2.458 (6)
W2—O11	1.936 (6)	W9—O26	1.696 (6)
W2—O2	2.444 (6)	W9—O15	1.898 (6)
W3—O7	1.688 (6)	W9—O25	1.898 (6)
W3—O14	1.900 (6)	W9—O33	1.926 (6)
W3—O10	1.904 (6)	W9—O27	1.929 (6)
W3—O9	1.908 (6)	W9—O1	2.444 (6)
W3—O13	1.920 (6)	W10—O38	1.697 (6)
W3—O4	2.444 (6)	W10—O29	1.896 (6)
W4—O28	1.698 (6)	W10—O35	1.901 (6)
W4—O34	1.899 (6)	W10—O37	1.906 (6)
W4—O27	1.900 (6)	W10—O34	1.917 (6)
W4—O17	1.922 (6)	W10—O3	2.447 (6)
W4—O16	1.928 (6)	W11—O39	1.693 (6)
W4—O1	2.432 (6)	W11—O36	1.900 (6)
W5—O18	1.695 (6)	W11—O31	1.904 (6)
W5—O17	1.889 (6)	W11—O30	1.915 (6)
W5—O11	1.904 (6)	W11—O35	1.928 (6)
W5—O29	1.915 (6)	W11—O3	2.458 (6)
W5—O19	1.922 (6)	W12—O40	1.687 (6)
W5—O2	2.421 (6)	W12—O33	1.889 (6)
W6—O20	1.686 (6)	W12—O37	1.922 (6)
W6—O30	1.893 (6)	W12—O32	1.922 (7)
W6—O19	1.909 (6)	W12—O36	1.930 (6)
W6—O21	1.916 (6)	W12—O3	2.441 (6)
W6—O12	1.931 (6)	P1—O4	1.517 (6)
W6—O2	2.435 (6)	P1—O3	1.525 (6)
W7—O22	1.704 (6)	P1—O2	1.542 (6)
W7—O21	1.904 (6)	P1—O1	1.543 (6)

Table 2
Contact distances (Å).

O1*W*···O42	2.965 (10)	O2*W*···O69	2.780 (10)
O1*W*···O43	2.962 (11)	O2*W*···O70	2.929 (11)
O1*W*···O44	2.885 (10)	O3*W*···O51	2.873 (11)
O1*W*···O45	2.913 (11)	O3*W*···O53	2.915 (12)
O1*W*···O46	2.989 (13)	O3*W*···O54	2.914 (12)
O1*W*···O48	2.928 (12)	O3*W*···O55	2.976 (12)
O1*W*···O49	2.884 (13)	O3*W*···O58	2.881 (11)
O2*W*···O64^{i}	2.801 (10)	O3*W*···O59	2.887 (11)
O2*W*···O65^{i}	2.786 (10)	O3*W*···O60	2.974 (11)
O2*W*···O67	2.884 (11)	O4*W*···O46^{ii}	3.07 (3)
O2*W*···O68	2.951 (10)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O71—H71···O16^{i}	0.84	2.35	3.17 (2)	164

Symmetry code: (i) $x, y, 1+z$.

All H atoms attached to carbon were included at their idealized positions, and allowed to ride on their parent atoms, with C—H = 0.95–0.99 Å and U_{iso} = 1.2 (for the benzo-15-crown-5 molecules) or 1.5 (for the methanol molecule) times U_{eq}(C). Four water molecules were directly found in difference Fourier maps. O1*W*, O2*W* and O3*W*, the water molecules located in the insterstitial spaces between benzo-15-crown-5 molecules (Figs 2–4), have been successfully refined with anisotropic displacement parameters; O4*W* was found to be affected by disorder and was refined with an isotropic displacement parameter. No attempt was made to find or to place geometrically the H atoms on these water molecules.

In order to balance the charge, three H atoms besides those in the four water molecules and in the benzo-15-crown-5 molecules must be included in the formula. The most probable protonation sites are the three strongly hydrogen-bonded O1*W*, O2*W* and O3*W* molecules, forming hydroxonium H_3O^+ species (Figs 2–4 and Table 2). The C and O atoms of the methanol molecule were refined with independent isotropic displacement parameters. The H atom of the OH group was placed geometrically to give the best hydrogen-bonding interactions (Table 3), with O—H = 0.84 Å.

Several C atoms of the benzo-15-crown-5 molecules were found to be affected by disorder, with anisotropic treatment leading to extended ellipsoids. These atoms (C13, C21–C28, C35, C36, C38, C40, C41, C43, C51 and C52) were refined using independent isotropic displacement parameters. The highest peak in the final difference synthesis is 0.87 Å from W6, and the deepest hole is 0.85 Å from W12.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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