

An open-framework three-dimensional indium oxalate: [In(OH)(C₂O₄)(H₂O)]₃ · H₂O

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Abstract

By hydrothermal reaction of In₂O₃ with H₂C₂O₄ · 2H₂O in the presence of H₃BO₃ at 155 °C, an open-framework three-dimensional indium oxalate of formula [In(OH)(C₂O₄)(H₂O)]₃ · H₂O (**1**) has been obtained. The compound crystallizes in the trigonal system, space group *R*3*c* with *a* = 18.668(3) Å, *c* = 7.953(2) Å, *V* = 2400.3(7) Å³, *Z* = 6, *R*₁ = 0.0352 at 298 K. The small pores in **1** are filled with water molecules. It loses its filled water at about 180 °C without the change of structure, then the bounded water at 260 °C, and completely decomposes at 324 °C. The residue is confirmed to be In₂O₃.

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1. Introduction

The synthesis of new compounds with open-framework structures has received considerable attention because of their potential applications in separation processes, ion exchange and catalysis. Aluminosilicate represents the predominant class of open-framework materials [1]. After Wilson et al. [2], the interest has focused primarily on aluminum phosphates and substituted variants [3–6]. The synthesis of other chemistry composition open-framework materials such as borates, germanates, chalcogenides, halides, nitrides, oxides, phosphonates, and carboxylates has also been accomplished [7,8]. In the past few years, there has been considerable effort in designing open-framework structures formed by metal organic carboxylates because of its interesting structural features and the quality for apt design [9,10]. The oxalate ion acts as a rigid bidentate ligand that can facilitate the formation of extended structures by bridging metal centers. Many metal oxalate structures are reported. Some of these structures are monomers, dimers, chains, and some are layered oxalates with honeycomb networks [11,12]. Three-dimen-

sional (3-D) structures are formed if oxalate units link the layers [13]. Recently, rare earth or yttrium (III) oxalate open frameworks were reported, which showed more interesting structural features because of its high coordination [14]. Similar to rare earth metal, the heavy group 13 element, indium has a high coordinated number and can construct novel open frameworks. Although several indium oxalates have been reported [15–19], only a few of them are of open frameworks [19]. In this paper, we report the hydrothermal synthesis of one open-framework 3-D indium oxalate, [In(OH)(C₂O₄)(H₂O)]₃ · H₂O.

2. Experimental section

2.1. Materials and analyses

All reagents were of analytical grade and were used as obtained from commercial sources without further purification. IR spectra were recorded in the 400–4000 cm⁻¹ range using a Magna-IR 750 FTIR spectrometer. Elemental analyses were carried out on Elementar Vario EL III microanalyzer. Thermogravimetric (TG)–Differential Scanning Calorimetric (DSC)–Mass Spectrometric (MS)

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(TG–DSC–MS) analysis was performed with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ using a NETZSCH STA449C instrument.

2.2. Preparation of $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$ (**1**)

A mixture of In_2O_3 (2.00 g, 7.20 mmol), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (1.83 g, 14.42 mmol), H_3BO_3 (10.0 g, 161.7 mmol), and deionized H_2O (12 ml, 0.67 mol) with a mole ratio of 1.0:1.0: 11.2: 46.5 was placed in a 50-mL teflon-lined stainless-steel autoclave, and the autoclave was sealed, heated to $155\text{ }^\circ\text{C}$ under autogenous pressure for 120 h, and then cooled to room temperature at a rate of $5\text{ }^\circ\text{C/h}$. The pH values of the system before and after synthesis are about 1 and 2, respectively. Colorless crystalline product was filtered, washed with hot distilled water, and dried at ambient temperature to give about 3.4 g of complex **1** (yield 95% based on In_2O_3). Complex **1** is stable and insoluble in water and most organic solvents. Anal. Calcd. for $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$: C, 9.84; H, 1.51%. Found: C, 9.94; H, 1.72%.

2.3. Crystallographic studies

Intensity data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated MoK_α ($\lambda = 0.71073\text{ \AA}$) radiation by using the $\omega - 2\theta$ scan method at room temperature. The structure was solved with direct methods and refined on F^2 with full-matrix least-squares methods using SHELXS-97 and SHELXL-97 programs, respectively [20]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were added in the riding model and refined isotropically with $\text{O-H} = 0.82\text{ \AA}$. The crystallographic data are summarized in Table 1, and the selected bond lengths are listed in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 276310. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1
Crystallographic and structure refinement parameters for $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$

Formula	$[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$	Z	6
f_w	731.62	d_{calcd} (g cm^{-3})	3.037
Cryst syst	Trigonal	T (K)	298
Space group	$R\bar{3}c$	λ (MoK_α) (\AA)	0.71073
(a) \AA	18.668(3)	(μ) (mm^{-1})	4.395
(c) \AA	7.9530(16)	$R_1(I > 2\sigma(I))^a$	0.0352
		$wR_2(\text{all data})^a$	0.1496

$$^a R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}, \quad wR_2 = \left[\frac{\sum(F_o^2 - F_c^2)^2}{\sum(F_o^2)} \right]^{1/2}, \\ w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 11.5P], \quad \text{where } P = (F_o^2 + 2F_c^2)/3.$$

Table 2
Selected bond distances (\AA) for $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}^a$

In(1)–O(1)	2.068(10)	In(1)–O(8)	2.289(8)
In(1)–O(1a)	2.117(11)	O(2)–C(6)	1.270(12)
In(1)–O(2)	2.223(7)	O(4)–C(6b)	1.243(12)
In(1)–O(3)	2.308(13)	O(3)–C(7)	1.239(13)
In(1)–O(4)	2.245(8)	O(5)–C(7b)	1.235(12)
In(1)–O(5)	2.241(7)	C(6)–C(7)	1.540(13)

^aSymmetry code: (a) $-y, -x, z + \frac{1}{2}$; (b) $x + \frac{1}{3}, x - y + \frac{2}{3}, z + \frac{7}{6}$.

3. Results and discussion

3.1. Synthesis

The formation of **1** was found to be sensitive to the existence of H_3BO_3 . Without H_3BO_3 , $[\text{In}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ [15] was found when $\text{C}_2\text{O}_4^{2-}:\text{In}^{3+} > 1.5:1$, or a mixture of $[\text{In}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ and compound **1** was found when $1:1 < \text{C}_2\text{O}_4^{2-}:\text{In}^{3+} < 1.5:1$. With H_3BO_3 , compound **1** was the main phase $\text{C}_2\text{O}_4^{2-}:\text{In}^{3+} > 1:1$. To ensure the high yield of compound **1**, much H_3BO_3 was needed.

3.2. Structural description

There are one indium (III) atom, one oxalate ligand, one water molecule and one μ -OH group in an asymmetric unit of the open framework of **1**. The indium (III) atom binds to four oxygen atoms from two oxalate ligands, one oxygen atom from water molecule and two oxygen atoms from μ -OH groups to form a slightly distorted pentagonal bipyramid (Fig. 1). The equatorial pentagonal plane is formed by four oxalate oxygen atoms, O2, O3, O4, O5, and one water oxygen atom, in which the five oxygen atoms and In are almost coplanar with a mean deviation 0.11 \AA , while two axial positions are occupied by O1 and O1ⁱ from two μ -OH groups with the O1–In–O1ⁱ bond angle of $175.9(3)^\circ$ (Fig. 1). The bond valences [21] of O1 and O8 are 1.197 and 0.351, respectively, indicating O1 and O8 are actually hydroxyl group and water molecule, respectively. The high coordination number conformation of indium ions in complex **1** is also observed in some In^{III} -oxalate [17–19] and In^{III} -terephthalate [22] complexes where each of the indium ions is coordinated by seven or eight oxygen atoms.

There are two ways to link the indium (III) atoms together as shown in Fig. 2. Firstly, the indium (III) atoms are linked by μ -OH groups to form $[\text{In}(\mu\text{-OH})]_n$ chains along [001] (see Fig. 2a). They are also linked by oxalate ligands to form $[\text{In}(\text{C}_2\text{O}_4)]_n$ chains (see Fig. 2b). These chains connect to each other to form net-layer framework shown in Fig. 2c, and these layers link together by oxalate ligands to form a 3-D framework (Fig. 3) possessing a 1-D tunnel along the [001] direction. Fig. 4 shows a cross-section layer of the framework, where zigzag rings, which are extended to the whole layer, each consist of

12 indium atoms, 12 oxalate ligands, and 6 μ -OH groups. Two indium atoms link together by one μ -OH group to form a pillar, the pillars connect to each other by the oxalate ligands to form zigzag rings. The rings are parallel each other and further link along c -axis into 1-D tunnels. There are water molecules in the tunnels.

The IR spectrum of complex **1** is shown in Fig. 5. The broad peaks centered at 3470 cm^{-1} are mainly attributed to be due to the symmetric and asymmetric stretching modes of water molecules. The bending mode of water expected

around 1600 cm^{-1} is overlapped with the intense oxalate band. The antisymmetric stretching mode of oxalate ion is obtained at 1647 cm^{-1} . The peaks 1364 and 1321 cm^{-1} are corresponding to the symmetric stretching mode of oxalate ion. The peak around 1097 cm^{-1} is due to the bending mode of μ -OH. The strong band observed around 813 cm^{-1} corresponds to the in-plane deformation mode of oxalate ion.

TG–DSC–MS analysis of complex **1** was carried out in a flow of argon atmosphere as shown in Fig. 6. The water

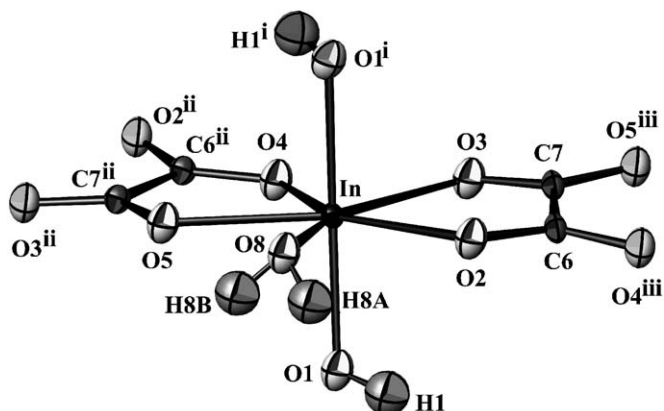


Fig. 1. ORTEP drawing (at 30% probability) of the coordination environment of indium atoms in $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$. Symmetry codes: (i) $1-y, 1-x, z+1/2$; (ii), $x+1/3, x-y+2/3, z+1/6$; (iii), $x-1/3, x-y+1/3, z-1/6$.

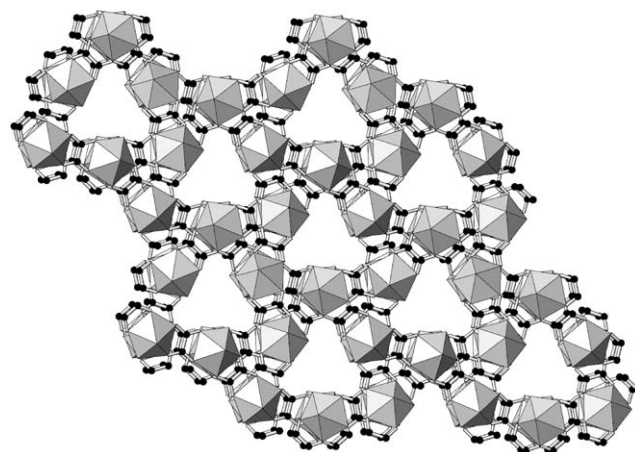


Fig. 3. Packed structure of complex $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$, showing 1-D tunnels parallel to the $[001]$ direction.

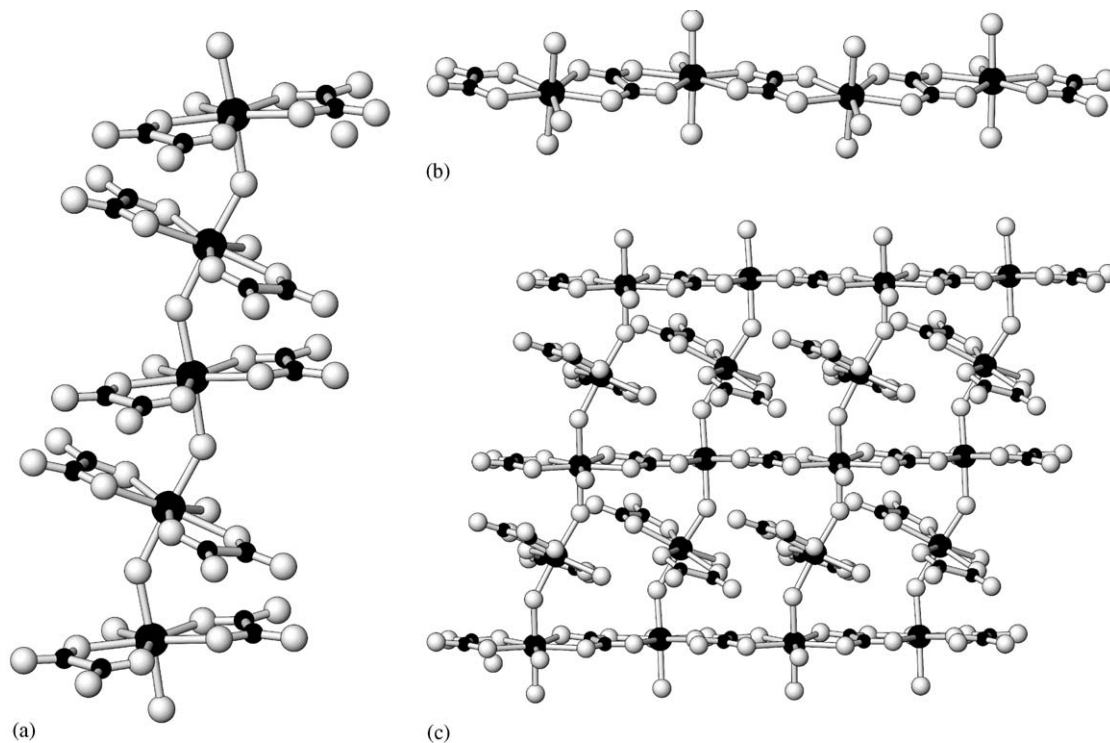
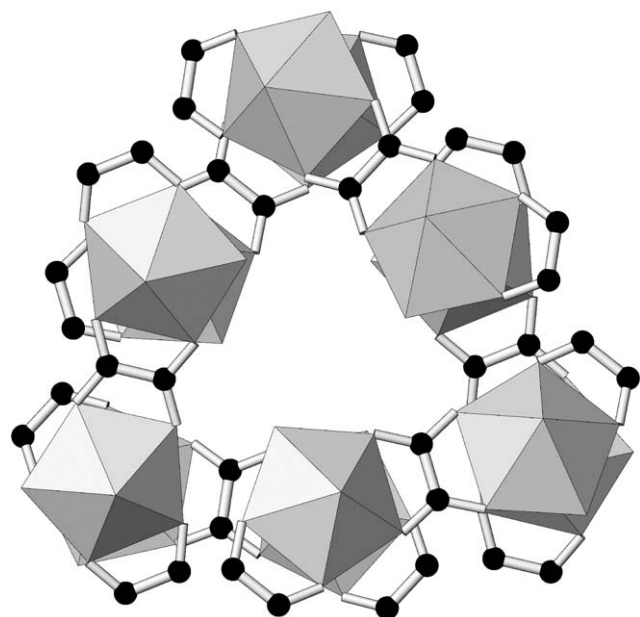
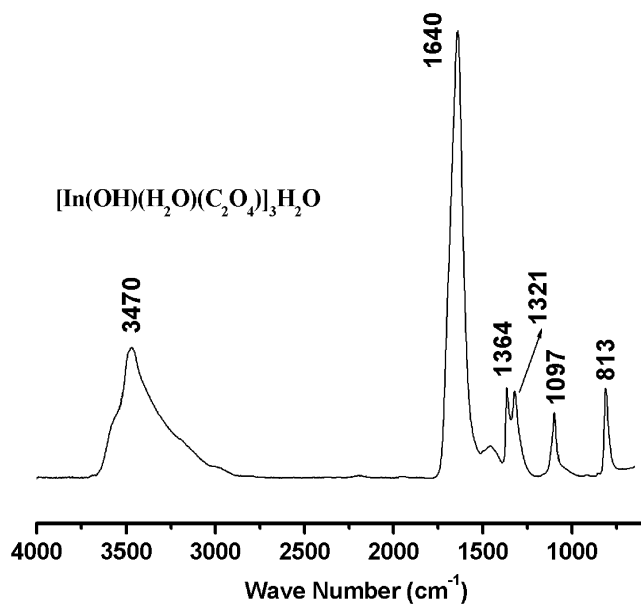


Fig. 2. View of the different linkages of In of $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$. (a) linked by μ -OH groups; (b) linked by oxalate ligands; (c) combined linkage with μ -OH groups and oxalate ligands. In, large black circles; C, small black circles; O, white circles.

Fig. 4. Zigzag ring of $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$.Fig. 5. IR spectrum of $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$.

molecular in the tunnels is left between 100 and 180 °C without changing the structure. In Fig. 7, the X-ray diffraction patterns of Complex 1 treated under different conditions are shown. When heating at the temperature between 100 and 180 °C, the X-ray diffraction patterns just shift to high angles with the change of intensity of some diffraction peaks. After exposed the heated sample to saturated moisture for 2 h, the diffraction patterns change back to that of Complex 1. When the exposed time is too short, mixture patterns (shown as pattern e) from both heated sample and complex 1 (converted from the heated sample after absorbing the moisture) are obtained. This

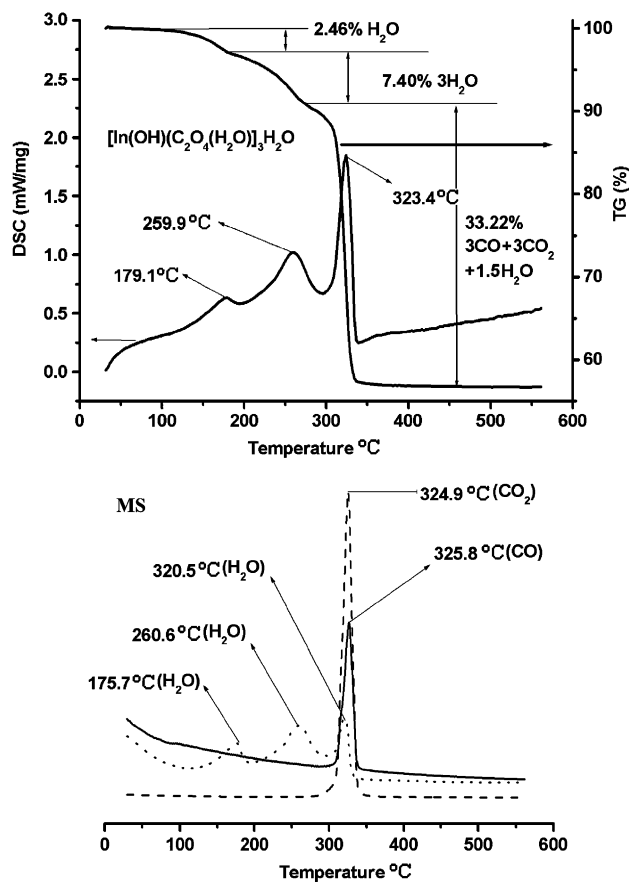
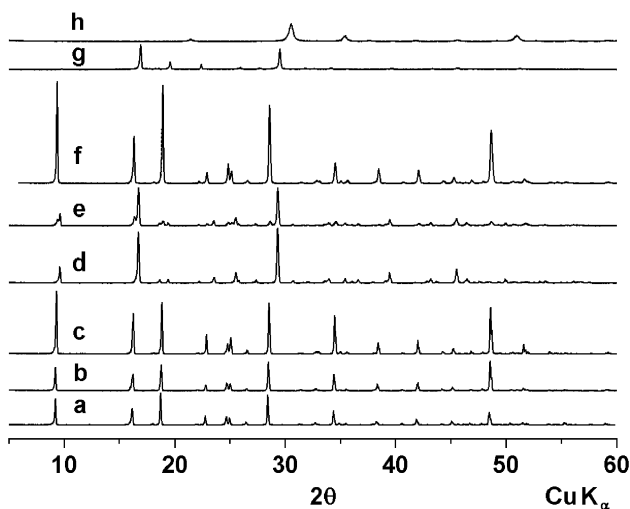
Fig. 6. TG–DSC–MS curves for $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$.

Fig. 7. X-ray diffraction patterns of $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$ after different treatments. (a) $[\text{In}(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_3 \cdot \text{H}_2\text{O}$ as obtained (referred as Sample A); (b) heating Sample A at 120 °C for 12 h (Sample B); (c) treating Sample B with saturated moisture for 2 h (Sample C); (d) heating Sample C at 180 °C for 12 h (Sample D); (e) leaving Sample D in air for 20 min (Sample E); (f) treating Sample D with saturated moisture for 2 h (Sample F); (g) heating Sample F at 240 °C for 12 h (Sample G); (h) heating Sample G at 330 °C for 12 h.

means that the absorption and desorption of the water molecular in the tunnels are reversible. Heating from 180 to 270 °C results in the depart of water molecular linked to In atoms with the degradation of the structure as shown in Fig. 7. During these steps, only H₂O is detected by MS without CO and CO₂. Further heating from 270 to 350 °C results in complete collapse of the material of **1** with the simultaneous removal of oxalate ligands and μ -OH, H₂O, CO, and CO₂ are found by MS. The residual weight 56.92% (calcd.: 56.94%) corresponds to In₂O₃, which is confirmed by X-ray diffraction patterns shown in Fig. 7.

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