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Structure and Thermal Decomposition of Potassium Bis-μ-peroxo Hexacarbonatodicerate(IV) Dodecahydrate*

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Abstract

The crystal structure reveals the novel anion $(CO_3)_3Ce(O_2)_2Ce(CO_3)_3^{8-}$ in which the peroxy groups are edge-on, bridging and doubly-bidentate. Ce–O = 2.331–2.373 Å. Each CO_3^{2-} group is symmetrically bidentate. Ce–O = 2.39–2.46 Å.

On heating, water is lost in two stages between 40 and 200 °C followed by decomposition into CeO_2 and K_2CO_3 by 450 °C. $K_4Ce(CO_3)_3O_2 \cdot 6H_2O$, triclinic $P\bar{1}$, $a = 8.8871(10)$, $b = 10.3923(13)$, $c = 10.9582(11)$ Å, $\alpha = 66.85(1)$, $\beta = 68.42(1)$, $\gamma = 74.37(1)°$. $R = 0.031$ for 277 parameters and 2817 reflexions.

Introduction

The dark red colour of conc. solutions containing peroxide and Ce(IV) and of the materials isolated from these solutions has been known since 1885. The early work was reviewed by Meloche [1], who established the analyses of the crystalline carbonates as $Ce_2O_4(CO_3)_2 \cdot 4K_2CO_3 \cdot 12H_2O$ and $Ce_2O_4(CO_3)_2 \cdot 4Na_2CO_3 \cdot 30H_2O$. The crystal structure and properties of the potassium compound are reported in this paper; a low temperature structure determination of the sodium compound is in progress along with attempts to isolate the less stable peroxo-carboxylatocerates in crystalline form.

Experimental

Identical dark red needles of the title compound, I, were prepared by the methods described by Meloche [1] and Job [2] starting from ammonium cerium(III) nitrate or from ammonium cerium(IV) nitrate. The crystals dehydrate in the atmosphere at room temperature but are stable at 20 °C in a stoppered vial.

Diffuse reflectance spectra at 20 °C were recorded on a Unicam SP700 spectrometer as described previously [3]. Thermogravimetric analyses and differential thermal analyses were carried out in air, heating at 8° $\min^{-1}$. Triclinic, $P\bar{1}$, $a = 8.8871(10)$, $b = 10.3923(13)$, $c = 10.9582(11)$ Å, $\alpha = 66.85(1)$, $\beta = 68.42(1)$, $\gamma = 74.37(1)$, $U = 855.53$ Å^3, $F(000) = 584$, $Z = 2$, $D_x = 2.39$, MoKα radiation, $\lambda = 0.71069$ Å, $\mu = 34.9$ cm.

Structure Determination

Oscillation and Weissenberg photographs showed I to be triclinic. Since the compound is known to lose water readily in air, a crystal 0.3 × 0.4 × 0.2 mm was mounted in a Lindemann glass capillary before data collection on an Enraf–Nonius CAD4-F diffractometer (SERC Service at Edinburgh University). Intensities were collected for one hemisphere of reciprocal space to a θ limit of 25°. Intensities of 2 standard reflexions were checked every hour and crystal orientation verified every 200 reflexions. Intensities were corrected for a drift of 7.4% during data collection and for absorption using a ψ scan technique on the diffractometer.

Lorentz and polarisation corrections were applied. The 3214 observed reflexions gave 3002 unique reflexions (internal consistency 0.016) of which 2817 had $F > 2\sigma(F_o)$. Only the last were used in the refinement of the structure.

All calculations were performed on the Dundee University DEC10 computer using the SHELX76 [4], XANADU [5] and PLUTO [6] program packages. Atomic scattering parameters were from International Tables for X-ray Crystallography [7].

The direct methods routines in SHELX76 did not yield an immediately recognisable fragment containing the cerium atom and four potassium atoms. However, an unambiguous position for the cerium atom was derived from the Patterson map. A structure factor calculation based on the cerium atom alone was followed by a Fourier map which showed all the potassium, carbonate and peroxide ions. Least-squares refinement to R 0.12 revealed

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all the water oxygen atoms in a difference synthesis. Using anisotropic thermal parameters for all non-hydrogen atoms refinement converged at R 0.0308 with all the hydrogen atoms at positions suggested by a difference Fourier map. Since several of the H–O–H angles were unacceptable the parameters in the Tables Ia, Ib and II refer to a final refinement to R 0.0312 using the DFIX facility in SHELX76 to constrain O–H and H•••H to be 1.00 Å and 1.60 Å respectively.

Tables Ia, Ib and II of observed and calculated structure factors and hydrogen atom coordinates are available from the authors.

Final refinement (Minimising $\Sigma w\|F_o - F_c\|^2$), 277 refined parameters, $wR = 0.044$, $w = 1.3130/(\sigma^2(F) + 0.000898\ (F)^2)$, mean shift/e.s.d. 0.012 (excluding H atoms), max shift/e.s.d. 0.044 (excluding H atoms), max difference peak 1.5 e/Å^3 (close to Ce).

Results and Discussion

Atomic coordinates and equivalent isotropic thermal parameters are given in Table Ia, and anisotropic thermal paramaters in Table Ib. Table II contains selected bond lengths and angles. The structure contains the novel anion $[(CO_3)_3Ce(O_2)_2Ce(CO_3)_3]^{8-}$. This anion has a centre of symmetry at 1/2, 0, 0 with Ce•••Ce 3.523(1) Å and the cerium

TABLE Ia. Coordinates × 10^{-4} for Non-hydrogen Atoms with e.s.d.s in Parentheses. $U_{eq}/U \times 10^{-3}$.[a]

Atom	x/a	y/b	z/c	U_{eq}/Å^2
Ce1	3448(1)	1394(1)	333(1)	15(1)
K1	6506(1)	3997(1)	7731(1)	34(1)
K2	2181(1)	5628(1)	9329(1)	29(1)
K3	7070(1)	229(1)	2890(1)	36(1)
K4	7874(2)	1321(1)	5649(1)	40(1)
O1	3688(4)	9077(3)	408(3)	24(1)
O2	4264(4)	9000(3)	1534(3)	23(1)
C3	7592(5)	7146(5)	2100(4)	21(1)
O4	7917(4)	8417(3)	1283(3)	26(1)
O5	6821(4)	6551(3)	1726(3)	24(1)
O6	7998(5)	6577(4)	3208(4)	36(1)
C7	5504(5)	7260(4)	−1636(4)	19(1)
O8	5617(4)	6631(3)	−399(3)	23(1)
O9	5007(4)	6713(3)	−2231(3)	29(1)
O10	5901(4)	8523(3)	−2242(3)	25(1)
C11	9818(5)	8128(5)	−2067(5)	22(1)
O12	9014(4)	7092(3)	−1155(3)	26(1)
O13	−995(4)	−614(3)	−2065(3)	26(1)
O14	1212(4)	7924(3)	7156(3)	29(1)
O15	1408(5)	8137(4)	−56(4)	42(1)
O16	1695(6)	1211(5)	4724(4)	53(1)
O17	4824(5)	2130(5)	4993(4)	51(1)
O18	9430(5)	2260(5)	6887(5)	52(1)
O19	6672(6)	4227(4)	5100(5)	52(1)
O20	8995(5)	5316(5)	7485(6)	58(1)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

TABLE Ib. Anisotropic Temperature Factors × 10^{-3} with e.s.d.s in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce1	14(1)	14(1)	17(1)	−7(1)	−4(1)	−1(1)
K1	31(1)	32(1)	34(1)	−14(1)	−1(1)	−6(1)
K2	27(1)	23(1)	37(1)	−12(1)	−10(1)	1(1)
K3	38(1)	33(1)	40(1)	−11(1)	−16(1)	−5(1)
K4	49(1)	42(1)	31(1)	−17(1)	−11(1)	−4(1)
O1	18(2)	26(2)	29(2)	−13(1)	−4(1)	−6(1)
O2	21(2)	24(2)	18(2)	−5(1)	−4(1)	0(1)
C3	17(2)	24(2)	21(2)	−10(2)	−5(2)	3(2)
O4	26(2)	24(2)	30(2)	−9(1)	−11(1)	−5(1)
O5	30(2)	21(1)	24(2)	−9(1)	−8(1)	−6(1)
O6	42(2)	41(2)	28(2)	−5(2)	−19(2)	−8(2)
C7	13(2)	21(2)	23(2)	−11(2)	−3(2)	1(2)
O8	29(2)	19(1)	23(2)	−8(1)	−10(1)	−2(1)
O9	33(2)	35(2)	29(2)	−15(1)	−13(1)	−9(1)
O10	31(2)	23(2)	22(2)	−8(1)	−9(1)	−4(1)
C11	20(2)	27(2)	22(2)	−10(2)	−8(2)	−2(2)
O12	22(2)	22(2)	30(2)	−10(1)	−3(1)	−2(1)
O13	21(2)	21(2)	30(2)	−8(1)	−2(1)	−3(1)
O14	19(2)	35(2)	26(2)	−12(1)	0(1)	1(1)
O15	33(2)	52(2)	51(2)	−29(2)	−7(2)	−14(2)
O16	69(3)	54(2)	29(2)	−16(2)	0(2)	−15(2)
O17	48(2)	67(3)	36(2)	−17(2)	−17(2)	2(2)
O18	50(3)	49(2)	64(3)	−23(2)	−22(2)	−6(2)
O19	60(3)	45(2)	51(3)	−7(2)	−23(2)	−13(2)
O20	39(2)	58(3)	91(4)	−47(3)	−10(2)	−8(2)

TABLE II. Bond Lengths (Å) and Bond Angles (°) in the $[Ce(O_2)(CO_3)_2]^{8-}$ Anion.

(a) To cerium

Ce(1)•••Ce(1)	3.523(1)	O(1)–Ce(1)–O(2)	36.4(1)
Ce(1)–O(1)	2.331(4)	O(1)–Ce(1)–O(2)	36.2(1)
Ce(1)–O(1)	2.345(4)	O(4)–Ce(1)–O(5)	53.9(1)
Ce(1)–O(2)	2.367(3)	O(8)–Ce(1)–O(10)	53.6(1)
Ce(1)–O(2)	2.373(3)	O(12)–Ce(1)–O(13)	56.3(1)
Ce(1)–O(4)	2.412(4)	O(1)–Ce(1)–O(4)	75.3(1)
Ce(1)–O(5)	2.458(4)	O(2)–Ce(1)–O(10)	75.5(1)
Ce(1)–O(8)	2.447(3)	O(1)–Ce(1)–O(5)	122.5(1)
Ce(1)–O(10)	2.402(3)	O(2)–Ce(1)–O(8)	123.0(1)
Ce(1)–O(12)	2.426(3)		
Ce(1)–O(13)	2.390(4)		

(b) Within ligands

O(1)–O(2)	1.468(6)	O(4)–C(3)–O(5)	116.6(4)
C(3)–O(4)	1.310(5)	O(5)–C(3)–O(6)	123.2(4)
C(3)–O(5)	1.285(7)	O(6)–C(3)–O(4)	120.1(5)
C(3)–O(6)	1.263(6)	O(8)–C(7)–O(9)	122.8(4)
C(7)–O(8)	1.281(6)	O(9)–C(7)–O(10)	121.2(4)
C(7)–O(9)	1.257(8)	O(10)–C(7)–O(8)	115.9(5)
C(7)–O(10)	1.297(5)	O(12)–C(11)–O(13)	113.5(3)
C(11)–O(12)	1.308(5)	O(13)–C(11)–O(14)	124.0(4)
C(11)–O(13)	1.313(5)	O(14)–C(11)–O(12)	122.6(4)
C(11)–O(14)	1.236(5)		

atoms symmetrically bridged by the edge-on doubly bidentate peroxide groups. Each cerium atom is 10-coordinate with all four peroxide oxygen atoms at 2.331–2.373 Å and three bidentate carbonate groups with Ce–O in the range 2.390–2.458 Å. Figs. 1 and 2 show that this anion has pseudo-mirror symmetry, with the mirror plane passing through Ce, C(11), O(12), O(13), O(14) and normal to the plane containing the two peroxide groups. The coordination geometry is approximately [1 + 5 + 4] (Fig. 2) giving a sixteen-sided polygon which is a more regular version of that found in salts of the monomeric anion $Ce(CO_3)_5^{6-}$ [8, 9] as shown in Fig. 3. Similar dimer formation across a rectangular face has been found recently in the caesium salt of tetrahydrofurantetracarboxylic acid [10] which has dimeric [1 + 3 + 4] coordination.

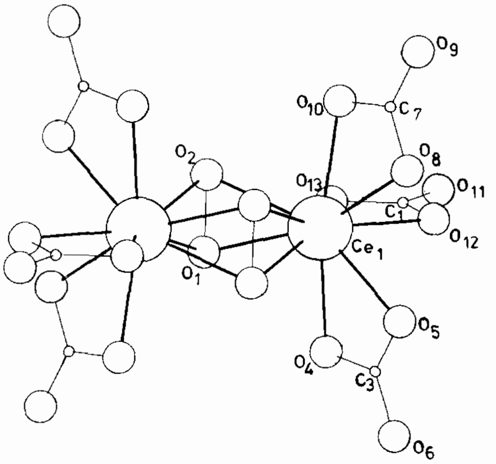

Fig. 1. Perspective view of the anion $[(CO_3)_3Ce(O_2)_2Ce(CO_3)_3]^{8-}$.

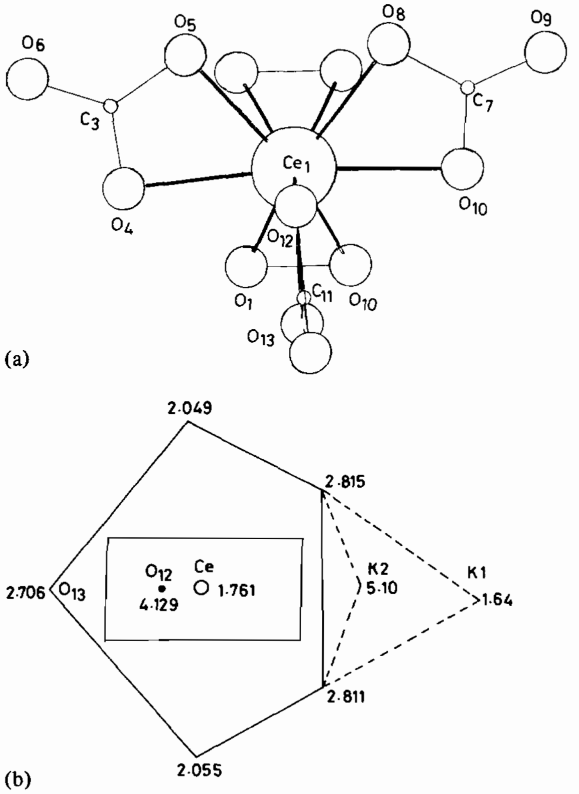

Fig. 2. Views of half the dimeric anion projected onto the plane O(1), O(2), O(1)′, O(2)′. (a) Showing the ligands, (b) showing the [1 + 5 + 4] coordination geometry and the positions of K(1) and K(2). In (b) the height of the coordinated atoms above the plane O(1), O(2), O(1)′, O(2)′ is given in Å. The angles between the normal to this plane and the normals to the planes Ce(1)O(4)O(5), Ce(1)O(8)O(10) and Ce(1)O(12)O(13) are 152.7(4), 152.6(4) and 90.1(5)° respectively.

The average Ce–peroxide distance, 2.354 Å, is 0.068 Å (17σ) less than the average Ce–carbonate distance, 2.422 Å. Using Shannon and Prewitt ionic radii [11] this suggests a radius for O_2^{2-} of 1.19 ± 0.02 Å. This is consistent with that obtained from the shorter Ba–O distance in BaO_2 (1.18 Å) [12] and with those from $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2 \cdot 4H_2O$ (1.21 Å) [13] and from $Mo(O_2)_4^{2-}$ (1.19 Å) [14]. These values suggest that metal–peroxide distances do not offer an easy guide to the covalent or ionic nature of the bonding.

The carbonate groups are all planar. They are distorted from 3-fold symmetry so that the C–O bonds which are not coordinated to Ce are shorter (1.252(4) Å) than those which are coordinated

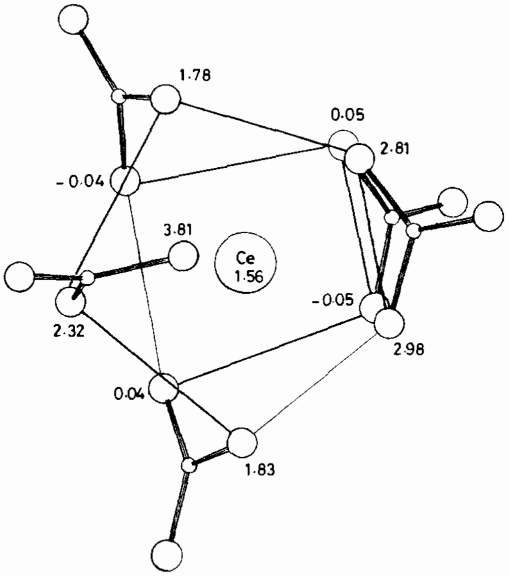

Fig. 3. View of the anion in $Na_6Ce(CO_3)_5 \cdot H_2O$ (from ref. 8) for comparison with Fig. 2. The sixteen sided polygonal coordination sphere is very similar although the carbonate groups are differently arranged.

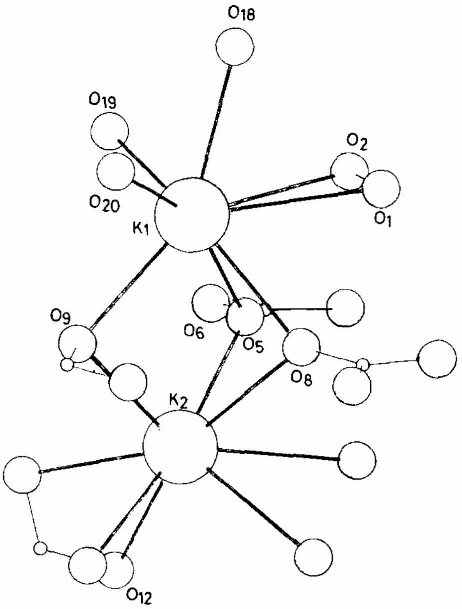

Fig. 4. Coordination of K(1) and K(2) showing the dimer.

(1.299(4) Å) and the angles at carbon in the Ce–O–C–O rings are smaller (115.3(4)°) than the other O–C–O angles (122.3(4)°). This shows clearly that the interaction of carbonate with cerium(IV) is much stronger than the interaction with the potassium ions. The angle at carbon in M–O–C–O rings in carbonate complexes ranges from 120°, with C–O 1.28 Å, in fully ionic situations to 108°, with C–O 1.33 Å, in Co(III) complexes with strong interactions [15].

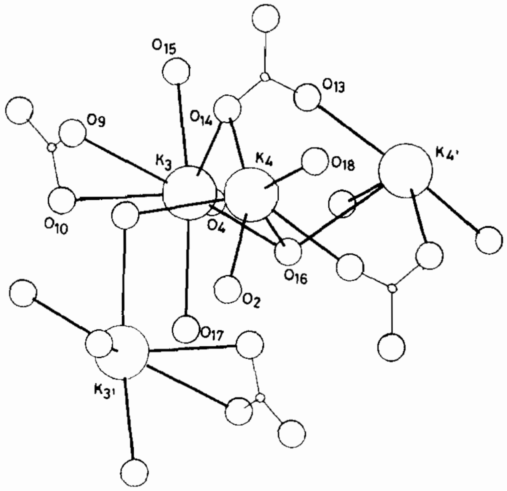

Fig. 5. Coordination of K(3) and K(4).

Comparison with the guanidinium [8] and sodium [9] salts of $Ce(CO_3)_5^{6-}$ (see above) suggests that the presence of the peroxide leads to stronger cerium–carbonate bonds in the present structure.

Among the 4 potassium ions there are 29 contacts to oxygen of carbonate, water or peroxide below 3.10 Å. Of these 18 lie between 2.70 and 2.85 Å, assigning 5-coordination to K(1), K(2) and K(4) and 3-coordination to K(3). There are no contacts to peroxide in this range. K(1) is 3.051(6), 3.097(6) Å from O(1) and O(2) respectively, K(4)–O(2) = 2.908(4) Å. Including all contacts under 3.100 Å K(1) and K(2) are 8-coordinate, K(3) 6-coordinate and K(4) 7-coordinate, all with very irregular geometry. There are seven K···K distances in the range 3.28–4.17 Å. K(1) and K(2) form a dimeric unit (Fig. 4) bridged by O(5), O(8) and O(9), with K(1) and K(2) 0.21 and 0.05 Å respectively from the plane Ce(1), O(12), O(13). Figure 2(b) shows the relationship of K(1) and K(2) to the cerium coordination sphere. Neighbouring K(1), K(2) units are linked by the water molecule O(20). K(3) and K(4) also form dimeric units but these are part of a more complex chain structure (Fig. 5). The range of K–O distances is consistent with those found in other complexes containing potassium and carbonate ions, for example 2.65–3.00 Å in $KAgCO_3$ [16] and 2.78(6) Å in $K_2Mg(CO_3)_2 \cdot 4H_2O$ [17]. Extrapolation from the Ba–O distances in BaO_2 (2.68, 2.79 Å) [12] suggests ionic contacts between K^+ and O_2^{2-} in the range 2.83 to 2.94 Å so that all three K–peroxide interactions in the present compound must be regarded as weak ionic forces.

Thermal Decomposition

Figure 6 shows that the tg and d.t.a. traces for **I** are in broad agreement with some displacement of

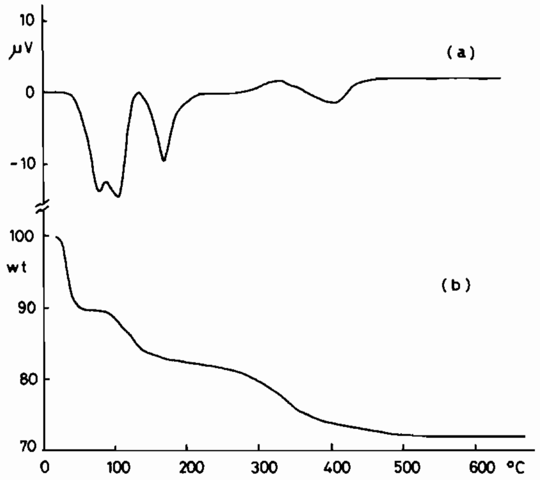

Fig. 6. Thermal decomposition of $K_4Ce(O_2)(CO_3)_2 \cdot 6H_2O$: (a) differential thermal analysis, (b) thermogravimetry.

the temperature scale arising from the very different geometry of the instruments. Dehydration occurs in two stages of $3H_2O$ each over the temperature ranges 40–115 °C and 125–220 °C for the d.t.a. experiment. The lower temperature endotherm shows two overlapping reactions. Meloche [1] reported that a trace of water remained after heating **I** at 140 °C for 2 h, in good agreement with the present results. Under d.t.a. conditions the anhydrous material appears to be stable from 220–265 °C above which decomposition occurs by:

$$K_4Ce(O_2)(CO_3)_3 \longrightarrow 2K_2CO_3 + CeO_2 + CO_2 + (O_2)_{0.5}$$

This reaction is not a single step. A small exotherm in the region 265–340 °C is overlapped by an endotherm complete by 435 °C. The overall weight loss from room temperature is 27.7(±0.5)% compared with the theoretical value of 27.3% for the formation of K_2CO_3 and CeO_2 from **I**. The products were confirmed by X-ray powder diffraction.

Other Properties

The red colour of **I** is caused by a broad absorption band of moderate intensity observed at 24 000 cm^{-1} in the diffuse reflectance spectrum which forms a continuous envelope with the band at 30–32 000 cm^{-1} which usually appears in oxo-salts of Ce(IV). The 24 000 cm^{-1} band can be assigned as an electron-transfer transition from peroxide to Ce(IV). The relatively high energy of this transition is in agreement with the observations of Meloche [1], confirmed in the present work, that Ce(IV) does not oxidize peroxide readily in basic solution. Solutions of **I** in aqueous K_2CO_3 give the same spectrum as the solid and are stable at 20 °C in daylight for long periods.

Acknowledgements

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