# [Cr$_8$(PhCO$_2$)$_{16}$O$_4$]·4CH$_3$CN·2H$_2$O: structural origin of magnetic anisotropy in a molecular spin cluster

## John Fielden,[a] Arkady Ellern[b] and Paul Kögerler[a]*

[a]Ames Laboratory, Iowa State University, Ames, IA 50011, USA, and [b]Department of Chemistry, Iowa State University, Ames, IA 50011, USA
Correspondence e-mail: kogerler@ameslab.gov

The Cr$_4$O$_4$ hetero-cubane-centered octachromium(III) cluster [Cr$_8$(PhCO$_2$)$_{16}$O$_4$] crystallizes from fluorobenzene–acetonitrile as dodeca-$\mu_2$-benzoato-tetrabenzoatotetra-$\mu_4$-oxido-octachromium(III) acetonitrile tetrasolvate dihydrate, [Cr$_8$-(C$_7$H$_5$O$_2$)$_{16}$O$_4$]·4C$_2$H$_3$N·2H$_2$O, (I). Crystals produced by this method are significantly more stable than the originally published dichloromethane pentasolvate, [Cr$_8$(PhCO$_2$)$_{16}$O$_4$]·-5CH$_2$Cl$_2$ [Atkinson *et al.* (1999). *Chem. Commun.* pp. 285–286], leading to a significantly higher quality structure and allowing the production of large quantities of high-quality nondeuterated and deuterated material suitable for inelastic neutron scattering (INS) measurements. Compound (I) reveals a higher symmetry structure in which the cluster sits on a twofold rotation axis, and is based on an asymmetric unit containing four crystallographically independent Cr positions, two oxide ligands, eight benzoate ligands, two acetonitrile solvent molecules and one disordered water molecule. All the Cr atoms are six-coordinate, with an octahedral geometry for the inner cubane and a more highly distorted coordination environment in the outer positions. Despite the higher symmetry, the coordination geometries observed in (I) are largely similar to the dichloromethane pentasolvate structure, indicating that crystal-packing effects have little influence on the molecular structure of [Cr$_8$(PhCO$_2$)$_{16}$O$_4$]. Close structural analysis reveals that the high magnetic anisotropy observed in the INS measurements is a consequence of the distorted coordination geometry of the four outer Cr atoms.

## Comment

The chemistry of metal carboxylates is exceptionally structurally rich, giving rise to a wide range of clusters (*e.g.* Affronte *et al.*, 2007; Engelhardt *et al.*, 2008; Sessoli *et al.*, 1993; Tasiopoulos *et al.*, 2004) and network structures (*e.g.* Cornia *et al.*, 1999; Fielden *et al.*, 2009; Moushi *et al.*, 2006; Wang *et al.*, 2004) as a consequence of the range of coodination modes offered by the CO$_2^-$ group. As carboxylate brid-

ging modes frequently give rise to strong magnetic interactions between metal centers, discrete and infinite three-dimensional metal carboxylates are intensively investigated for their magnetic properties. One such cluster is the {Cr$_8$} heterocubane [Cr$_8$(PhCO$_2$)$_{16}$O$_4$], which has recently been the subject of detailed inelastic neutron scattering (INS) measurements (Vaknin *et al.*, 2010).

The {Cr$_8$} cubane-type cluster was originally published in 1999 (Atkinson *et al.*, 1999) and was synthesized by heating the triangular [Cr$_3$(PhCO$_2$)$_6$O(OH)(H$_2$O)$_2$] precursor at 648–673 K under inert gas. Crystallization was originally achieved as [Cr$_8$(PhCO$_2$)$_{16}$O$_4$]·5CH$_2$Cl$_2$ [Cambridge Structural Database (CSD; Allen, 2002) refcode HIPGIW (Atkinson *et al.*, 1999)] from CH$_2$Cl$_2$–$^n$PrOH. While we could produce single crystals on a small scale using this technique, we were unable to produce polycrystalline material on the >5 g scale needed for INS. Furthermore, the included dichloromethane solvent is easily lost under ambient conditions, producing degraded crystals in which the cluster is apparently vulnerable to hydrolysis by atmospheric water. These issues mandated a search for an alternative crystallization method, and we identified the fluorobenzene–acetonitrile solvent system as a more readily scalable method that produces higher quality crystals which exhibit no hydrolysis under ambient conditions. These allowed room-temperature determination of a crystal structure of the acetonitrile–water solvate {Cr$_8$} cubane, [Cr$_8$(PhCO$_2$)$_{16}$O$_4$]·4CH$_3$CN·2H$_2$O, (I), with the adventitious water molecules thought to result from the acetonitrile (Fisher, *ca* 0.3% H$_2$O). This structure is significantly higher in quality than the published structure of [Cr$_8$(PhCO$_2$)$_{16}$O$_4$]·-5CH$_2$Cl$_2$ obtained at 150 K ($R1 = 0.0496$ versus 0.1025, $R_{\text{int}} = 0.052$ versus 0.0832, and $\theta_{\text{max}} = 26.38°$ versus 25.11°).



(I)
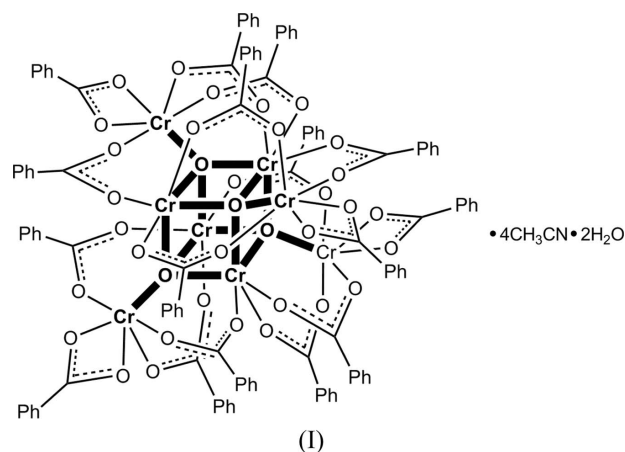
Compound (I) crystallizes in the space group $C2/c$, and as such the cluster adopts a higher symmetry than seen in [Cr$_8$(PhCO$_2$)$_{16}$O$_4$]·5CH$_2$Cl$_2$ ($P2_1/c$). The asymmetric unit (Fig. 1$a$) contains only a half rather than a complete {Cr$_8$} cubane cluster, *i.e.* four six-coordinate Cr atoms, two terminal and six bridging benzoate ligands, two oxide ligands and half of the solvent molecules (omitted from the figure for clarity). None of these atoms is located on a special position. The complete $\mu_4$-oxide-bridged {Cr$_8$O$_4$} core (Figs. 1$b$ and 1$c$), with terminal and bridging benzoate ligands, is generated from the

# metal-organic compounds
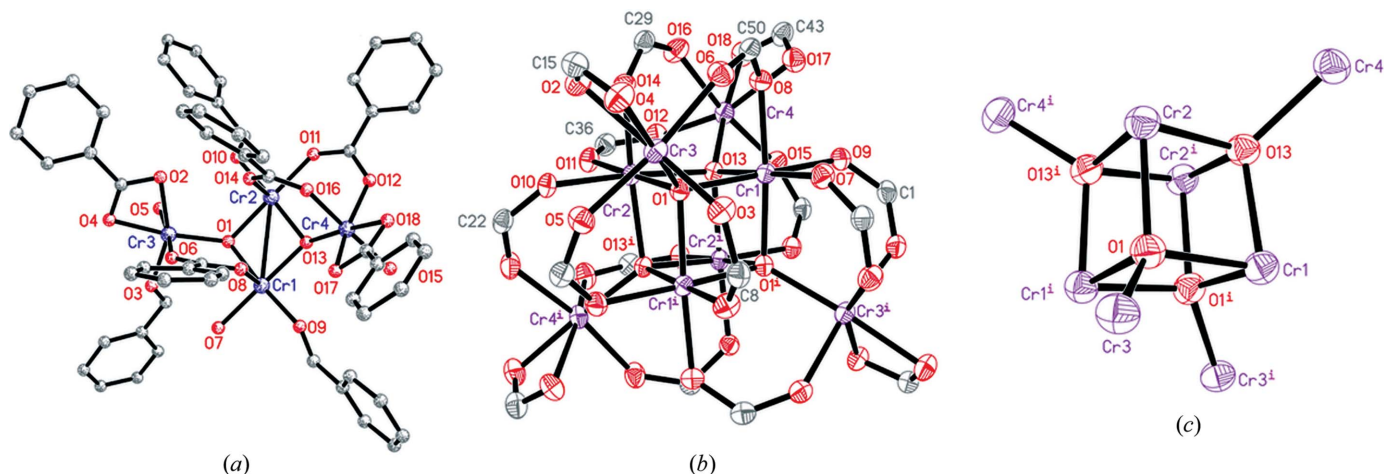


**Figure 1**
(*a*) The asymmetric unit of (I), showing the numbering scheme for Cr and O atoms. For clarity, a ball-and-stick representation is used, and H atoms, solvent molecules, and labels for C atoms have been omitted. (*b*) The complete structure of (I), with displacement ellipsoids drawn at the 30% probability level, omitting solvent molecules, H atoms, and phenyl groups. (*c*) The {$Cr_8O_4$} core in (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x + 2, y, -z + \frac{1}{2}$.]

asymmetric unit by a twofold rotation axis passing through the centre of the cubane and the faces described by atoms Cr1/Cr1$^i$/O1/O1$^i$ and Cr2/Cr2$^i$/O13/O13$^i$ [symmetry code: (i) $-x + 2$, $y, -z + \frac{1}{2}$]. In the crystal structure of (I), the {$Cr_8$} cubane packs in rows running parallel to the crystallographic *b* axis. As in [$Cr_8(PhCO_2)_{16}O_4$]·5$CH_2Cl_2$ (HIPGIW), there is no evidence for strong intermolecular interactions (*e.g.* hydrogen bonds) or other important intermolecular contacts.

Coordination bond lengths and angles for (I) are listed in Table 1, with the higher quality data obtained resulting in consistently lower standard uncertainties than seen in HIPGIW. The absence of potentially distorting intermolecular interactions in either structure means that the differences between their coordination bond lengths and angles are small, although the lower-symmetry structure has a wider range of Cr—O bond distances and O—Cr—O angles than seen in compound (I) (Table 2). As the crystals of (I) seem to be stable, these slight crystal-packing-induced differences may account for the small differences in magnetic susceptibility between (I) and [$Cr_8(PhCO_2)_{16}O_4$]·5$CH_2Cl_2$ (Luban *et al.*, 2003; Vaknin *et al.*, 2010).

More significantly, INS measurements on compound (I) have indicated that this material must have a high zero-field splitting (ZFS), as the magnetic energy spectrum cannot be accurately described by an isotropic model (Vaknin *et al.*, 2010). This was not apparent from the previously obtained 2–290 K magnetic susceptibility data, and prompted us to re-examine the structures of both (I) and [$Cr_8(PhCO_2)_{16}O_4$]·5$CH_2Cl_2$ to elucidate if slight geometric differences in the $CrO_6$ environments could possibly account for significant differences in ZFS. In compound (I), the coordination environments of the central four Cr atoms (Cr1/Cr2 and their symmetry-generated positions Cr1$^i$/Cr2$^i$) show only relatively small deviations from octahedral, with Cr—O bond distances varying only ±2% from the average value of 1.979 (2) Å and with *cis*-O—Cr—O angles deviating less than ±10% from the ideal value of 90° (see Tables 1 and 2). In HIPGIW, these inner

Cr (Cr1–Cr4) environments show a slightly higher variation of ±3% from an average Cr—O distance of 1.984 (8) Å, and a very slightly larger deviation of the angles from 90°. However, the outer Cr atoms of both structures [Cr3/Cr4/Cr3$^i$/Cr4$^i$ in (I) and Cr5–Cr8 in HIPGIW] show significant distortion in their angles due to restrictions imposed by the $\kappa^2$-chelating coordination mode of the terminal benzoate ligands (see Fig. 2). These two environments both have one very small O—Cr—O angle ($\varphi$ in Fig. 2, *ca* 65°) and one that is rather wide ($\theta$, *ca* 108°). For both structures, the average outer Cr—O bond distances are little different from those of the inner Cr atoms, although the variation [±3% in (I) and ±4% in HIPGIW] is slightly larger. Therefore, it seems likely that the magnetic anisotropy apparent in the INS measurements is a consequence of the highly distorted coordination bond angles of the outer Cr atoms, which are apparent in both structures.

In order to probe the effects of this distortion on the resulting ZFS, we have carried out point-charge electrostatic model (PCEM) calculations of the individual outer $CrO_6$
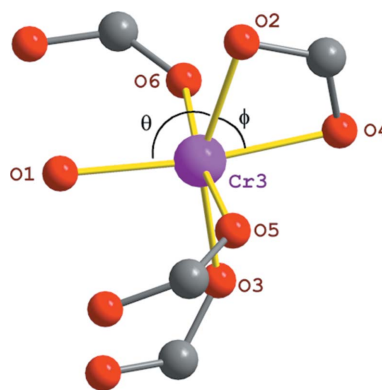


**Figure 2**
Ball-and-stick representation of the distorted coordination environment of one of the outer Cr positions (Cr3) of (I), showing the large and small O—Cr—O angles $\theta$ and $\varphi$.

polyhedra of both structures using the computational framework *CONDON* (Schilder & Lueken, 2004) and the standard ligand field and spin orbit-coupling parameter sets. The resulting eigenvalues for the corresponding individual Cr atoms do indeed show a clear splitting compared with a regular $O_h$-symmetric $CrO_6$ octahedron. Importantly, the differences in the eigenvalues of the resulting 28 Kramers doublets (stemming from the $^4F$ ground term of $Cr^{3+}$) for the outer $CrO_6$ octahedra in (I) and for those in HIPGIW are very small and amount to 0.01–2.4%. For example, the splitting between the lowest $|\pm 3/2\rangle$ doublet and the first excited $|\pm 1/2\rangle$ doublet results in values of 14.02 cm$^{-1}$ for Cr3 in (I) and 13.81 cm$^{-1}$ for Cr5 in HIPGIW. This confirms that compound (I), within the resolution of INS measurements, represents a magnetochemically virtually identical equivalent to HIPGIW, despite small geometric differences.

## Experimental

Benzoic acid (21.74 g, 0.178 mol) and KOH (10.99 g, 0.196 mol) were dissolved in water (500 ml) with heating to 353 K, resulting in a solution with a pH value of ~5.3. The pH was adjusted to ~8.0 by addition of aqueous KOH, before a solution of $Cr(NO_3)_3·9H_2O$ (20.01 g, 0.05 mol) in water (30 ml) was added, resulting in instantaneous production of a pale-blue precipitate. After heating and stirring for a further 30 min, the precipitate was recovered by filtration, washed with water (4 × 50 ml), and methanol (3 × 50 ml), and air-dried to yield the pale-blue intermediate $[Cr_3(PhCO_2)_6O$-$(OH)(H_2O)_2]$ (yield 15.87 g, 0.0167 mol, 100%). The amorphous precipitate was heated under a constant stream of argon at 648 K for 1 h, producing dark-green crude $[Cr_8(PhCO_2)_{16}O_4]$ (yield 12.96 g). The crude material was dissolved in fluorobenzene (125 ml), filtered, and crystallized in a PFTE flask by the addition of acetonitrile (1500 ml), yielding compound (I) as a mixture of dark-green single crystals and microcrystalline powder (yield 5.76 g, 0.0022 mol, 35%). FT–IR (KBr disc, $v$, cm$^{-1}$): 3424 (*m*), 3066 (*m*), 3030 (*w*), 2933 (*vw*), 1965 (*vw*), 1921 (*vw*), 1821 (*vw*), 1611 (*vs*), 1572 (*vs*), 1543 (*m*), 1498 (*s*), 1423 (*vs*), 1311 (*w*), 1180 (*m*), 1159 (*w*), 1070 (*w*), 937 (*vw*), 876 (*m*), 830 (*vw*), 811 (*vw*), 716 (*s*), 685 (*s*), 634 (*m*), 559 (*s*), 516 (*m*).

### Crystal data

| | |
|---|---|
| $[Cr_8(C_7H_5O_2)_{16}O_4]·4C_2H_3N·2H_2O$ | $V = 12210\ (4)$ Å$^3$ |
| $M_r = 2618.01$ | $Z = 4$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a = 23.406\ (5)$ Å | $\mu = 0.77$ mm$^{-1}$ |
| $b = 18.970\ (4)$ Å | $T = 293$ K |
| $c = 27.592\ (6)$ Å | $0.20 \times 0.20 \times 0.10$ mm |
| $\beta = 94.730\ (4)°$ | |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 50439 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2001) | 12440 independent reflections |
| $T_{min} = 0.86$, $T_{max} = 1.00$ | 8093 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.052$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.050$ | 778 parameters |
| $wR(F^2) = 0.147$ | H-atom parameters constrained |
| $S = 1.06$ | $\Delta\rho_{max} = 0.52$ e Å$^{-3}$ |
| 12440 reflections | $\Delta\rho_{min} = -0.37$ e Å$^{-3}$ |

**Table 1**
Selected geometric parameters (Å, °).

| Cr1—O7 | 1.952 (2) | Cr3—O5 | 1.965 (2) |
|---|---|---|---|
| Cr1—O8 | 1.959 (2) | Cr3—O6 | 1.968 (2) |
| Cr1—O9 | 1.959 (2) | Cr3—O3 | 1.977 (3) |
| Cr1—O1$^i$ | 1.970 (2) | Cr3—O1 | 1.990 (2) |
| Cr1—O13 | 2.002 (2) | Cr3—O4 | 2.014 (2) |
| Cr1—O1 | 2.013 (2) | Cr3—O2 | 2.032 (2) |
| Cr2—O10 | 1.946 (2) | Cr4—O12 | 1.940 (3) |
| Cr2—O14 | 1.952 (2) | Cr4—O16 | 1.959 (3) |
| Cr2—O11 | 1.976 (2) | Cr4—O15 | 1.969 (3) |
| Cr2—O13 | 1.977 (2) | Cr4—O13 | 1.974 (2) |
| Cr2—O1 | 2.018 (2) | Cr4—O18 | 2.018 (2) |
| Cr2—O13$^i$ | 2.021 (2) | Cr4—O17 | 2.024 (3) |
| | | | |
| O7—Cr1—O8 | 85.61 (10) | O5—Cr3—O3 | 88.02 (11) |
| O7—Cr1—O9 | 88.06 (10) | O6—Cr3—O3 | 95.40 (11) |
| O8—Cr1—O9 | 88.77 (10) | O5—Cr3—O1 | 94.50 (9) |
| O7—Cr1—O1$^i$ | 95.89 (9) | O6—Cr3—O1 | 92.52 (10) |
| O9—Cr1—O1$^i$ | 95.51 (9) | O3—Cr3—O1 | 96.85 (10) |
| O8—Cr1—O13 | 94.78 (9) | O5—Cr3—O4 | 86.10 (11) |
| O9—Cr1—O13 | 91.58 (9) | O6—Cr3—O4 | 86.36 (11) |
| O1$^i$—Cr1—O13 | 83.76 (9) | O3—Cr3—O4 | 91.12 (10) |
| O7—Cr1—O1 | 96.94 (10) | O5—Cr3—O2 | 86.34 (11) |
| O8—Cr1—O1 | 92.28 (9) | O6—Cr3—O2 | 87.49 (10) |
| O1$^i$—Cr1—O1 | 83.35 (9) | O1—Cr3—O2 | 107.15 (9) |
| O13—Cr1—O1 | 83.41 (9) | O4—Cr3—O2 | 64.91 (10) |
| O10—Cr2—O14 | 88.39 (10) | O12—Cr4—O16 | 87.99 (12) |
| O10—Cr2—O11 | 87.24 (10) | O12—Cr4—O15 | 94.87 (12) |
| O14—Cr2—O11 | 87.64 (10) | O12—Cr4—O13 | 94.39 (10) |
| O14—Cr2—O13 | 95.79 (9) | O16—Cr4—O13 | 94.15 (9) |
| O11—Cr2—O13 | 95.24 (9) | O15—Cr4—O13 | 93.72 (10) |
| O10—Cr2—O1 | 93.68 (9) | O12—Cr4—O18 | 92.38 (11) |
| O14—Cr2—O1 | 91.55 (9) | O16—Cr4—O18 | 85.32 (11) |
| O13—Cr2—O1 | 83.91 (8) | O15—Cr4—O18 | 86.45 (11) |
| O10—Cr2—O13$^i$ | 92.49 (9) | O16—Cr4—O17 | 84.67 (12) |
| O11—Cr2—O13$^i$ | 98.75 (9) | O15—Cr4—O17 | 89.56 (11) |
| O13—Cr2—O13$^i$ | 83.10 (9) | O13—Cr4—O17 | 108.25 (10) |
| O1—Cr2—O13$^i$ | 82.05 (8) | O18—Cr4—O17 | 64.93 (11) |

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

**Table 2**
Comparison of mean coordinate bond lengths (Å) and ranges for coordinate bond lengths and angles (°) in (I) and $[Cr_8(PhCO_2)_{16}O_4]·$5CH$_2$Cl$_2$ (CSD refcode HIPGIW; Atkinson *et al.*, 1999).

Only *cis*-O—Cr—O angles (ideally 90°) are reported.

| | | Cubane Cr positions | | Outer Cr positions |
|---|---|---|---|---|
| (I) | Cr1 | Mean = 1.976 (2)<br>1.952 (2)–2.013 (2)<br>83.35 (9)–96.9 (1) | Cr3 | Mean = 1.991 (2)<br>1.965 (2)–2.032 (2)<br>64.9 (1)–107.15 (9) |
| | Cr2 | Mean = 1.982 (2)<br>1.946 (2)–2.021 (2)<br>82.05 (8)–98.75 (9) | Cr4 | Mean = 1.981 (2)<br>1.940 (3)–2.024 (3)<br>64.9 (1)–108.3 (1) |
| HIPGIW | Cr1 | Mean = 1.989 (8)<br>1.968 (8)–2.022 (7)<br>82.8 (3)–96.9 (3) | Cr5 | Mean = 1.987 (8)<br>1.956 (8)–2.023 (8)<br>65.1 (3)–106.4 (3) |
| | Cr2 | Mean = 1.983 (8)<br>1.960 (7)–2.017 (8)<br>82.9 (3)–97.4 (3) | Cr6 | Mean = 1.992 (9)<br>1.959 (9)–2.055 (9)<br>64.9 (3)–109.0 (3) |
| | Cr3 | Mean = 1.986 (8)<br>1.952 (8)–2.039 (8)<br>81.7 (3)–99.1 (3) | Cr7 | Mean = 1.988 (8)<br>1.953 (7)–2.045 (9)<br>64.8 (3)–105.3 (3) |
| | Cr4 | Mean = 1.979 (8)<br>1.928 (7)–2.038 (8)<br>82.5 (3)–97.8 (3) | Cr8 | Mean = 1.980 (9)<br>1.939 (8)–2.044 (9)<br>64.8 (4)–109.4 (3) |

Solvent water molecule O19*A*/O19*B* is disordered over two positions; refinement indicates that their occupancies are equal. A rela-

tively high $U_{eq}(max)/U_{eq}(min)$ ratio is observed for the C atoms of the chromium benzoate cluster; this is a consequence of slight disorder and has not been restrained. All carbon-bound H atoms were placed in geometrically idealized positions, with C—H = 0.93 (aromatic) or 0.96 Å (methyl), and constrained to ride or ride and rotate on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms and $1.5U_{eq}(C)$ for idealized methyl H atoms. The H atoms on solvent water molecule O19A/O19B could not be located and are not included in the structural model.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3055). Services for accessing these data are described at the back of the journal.

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