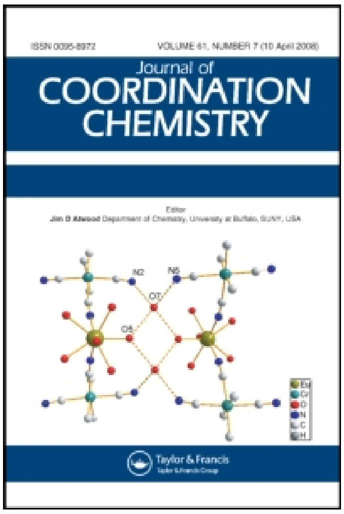

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Synthesis, characterization and crystal structure of a new linear trinuclear manganese(II) complex, $[Mn_3(PhCH=CHCO_2)_6(BPY)_2] \cdot H_2O$ (BPY=2,2-bipyridine)

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Synthesis, characterization and crystal structure of a new linear trinuclear manganese(II) complex, $[Mn_3(PhCH{=}CHCO_2)_6(BPY)_2] \cdot H_2O$ (BPY = 2,2-bipyridine)

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A new trinuclear manganese(II) complex, $[Mn_3(PhCH{=}CHCO_2)_6(bpy)_2] \cdot H_2O$ (**1**) (bpy = 2,2-bipyridine), was synthesized by the reaction of $Mn(OH)_2$ with cinnamate in H_2O/methanolic solution and its solid state structure was determined by single crystal X-ray diffraction. Structural analyses suggest that **1** consists of a linear arrangement of three Mn(II) centers, bridged by six cinnamate carboxylate groups. Four of these carboxylates are syn–syn bidentate, and two are monodentate bridging plus bidentate chelating. Mn(2) on a crystallographic inversion center has a slightly disorted octahedral geometry; the terminal six-coordinate Mn(1) atoms are significantly distorted octahedra. Weak intermolecular interactions such as C–H···O hydrogen-bonding and π–π stacking are responsible for supramolecular assembly of the molecules. Compound **1** was characterized by infrared spectrum, thermogravimetric and X-ray powder diffraction analyses.

Keywords: Manganese(II) complex; Linear trinuclear cluster; Cinnamate; Crystal structure

1. Introduction

Polynuclear manganese complexes attract considerable attention in bioinorganic chemistry and solid-state physics [1]. Dinuclear manganese sites have been found in catalases, alginases, and ribonucleotide reductases [2], and a tetranuclear manganese cluster has been found as the active site for photosynthetic water oxidation in the oxygen-evolving complex (OEC) of photosystem II [3–5]. As a result, many model complexes have been prepared with different oxygen donor ligands such as hydroxyl, oxo, and carboxylato and nitrogen donor ligands such as 2,2-bipyridine (bpy), 1,10-phenanthroline (phen) or other bidentate amines, to mimic amino acid sites. Some polynuclear manganese complexes function as single-molecule magnets (SMMs) below a critical temperature [6], displaying magnetization hysteresis, quantum tunneling

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of magnetization [7] and quantum phase interference [8], promising new materials for data storage. Interest in Mn(II)-carboxylate coordination chemistry has been stimulated by the fascinating structures of Mn(II)-carboxylate clusters and the structural details of the active site(s) that may influence the mechanisms of catalysis [9]. Consequently, a large number of polynuclear Mn(II)/carboxylate/nitrogen-donor (bpy or phen) complexes have been prepared, and structural data are available from the Cambridge Structure Database (CSD); however, only five manganese(II) complexes with bridging carboxylate groups display a linear trinuclear system: $[Mn_3(CH_3CO_2)_6(bpy)_2]$ [10], $[Mn_3(ClCH_2CO_2)_6(bpy)_2]$ [11], $[Mn_3(PhCO_2)_6(bpy)_2]$ [12], $[Mn_3((CH_3)_2CHCO_2)_6(bpy)_2]$ [13], and $[Mn_3((CH_3)_2CHCO_2)_6(Phen)_2]$ [13]. We are endeavoring to prepare polynuclear transition metal complexes using diverse carboxylic acids in the presence of bpy or phen ligands, and here a new linear trinuclear manganese(II) complex, $[Mn_3(O_2CCH{=}CHPh)_6(bpy)_2] \cdot H_2O$ (**1**).

2. Experimental

2.1. *Physical measurements*

All chemicals, reagent grade, were commercially available and used without further purification. Elemental analysis was performed using a Perkin–Elmer 2400 CHNS/O analyzer. The infrared spectrum in KBr pellets in the range 4000–400 cm^{-1} was recorded using a Shimadzu FTIR–8900 spectrophotometer. Combined measurements on thermogravimetric and differential thermal analysis (TG/DTA) were carried out in the range 25–600°C on powdered samples under nitrogen using Seiko Exstar 6000 TG/DTA6300 equipment with a heating rate of 10°C min^{-1}. X-ray powder diffraction was performed using a Rigaku D_max/3b diffractomerter.

2.2. *Synthesis*

Freshly prepared $Mn(OH)_2$ (0.089 g, 1.0 mmol), obtained from 2.0 mL (1.0 M) NaOH and a stirred aqueous solution of $MnCl_2 \cdot 4H_2O$ (0.194 g, 1.0 mmol) in 5 mL H_2O, was added to a stirred aqueous solution of 2,2-bipyridine (0.167 g, 1.0 mmol) and cinnamatic acid (0.144 g, 2.0 mmol) in 20 mL H_2O/methanol (v/v 1 : 1). The mixture was further stirred for ca 60 min at room temperature, and the pH of the mixture was controlled in the range of 7–8 with 1.0 M NaOH solution. The mixture was further stirred for another 2 h, filtered and the resultant filtrate was allowed to slowly evaporate at room temperature. Yellow prismatic crystals suitable for single crystal X-ray diffraction were obtained 7 days later in a yield of 85% based on the initial $Mn(OH)_2$ input. Anal. Calcd for $C_{74}H_{60}Mn_3N_4O_{13}$ (%): C, 64.58; H, 4.17, N, 4.14; Found: C, 64.53; H, 4.22, N, 4.07. IR (cm^{-1}): 3400m, 3020w, 1960w, 1640s, 1580vs, 1565s, 1554m, 1400vs, 1250m, 1020m, 980s, 879m, 771s, 714s, 683s, 590m, 490w.

2.3. *X-Ray crystallography*

A suitable single crystal of $[Mn_3(PhCH{=}CHCOO)_6(bpy)_2]$ (**1**, prism, yellow, dimensions $0.32 \times 0.26 \times 0.20\ mm^3$) was used for the structure determination. X-ray data were collected using a Bruker SMART Apex II CCD area detector single-crystal diffractometer, with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å), using the $\Psi/2\vartheta$ scan method. The integration process yielded a total of 8933 reflections for **1**, of which 5915 [$R(\mathrm{int}) = 0.0362$] were independent. Absorption corrections were applied using the SADABS program [14] (maximum and minimum transmission coefficients, 0.885 and 0.822). The structures were solved using the SHELXL–97 program [15, 16] by weight atoms methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in the riding mode. Hydrogen atoms for water molecules were not generated because of disorder of oxygen. Convergence was reached at a final $R_1 = 0.0585$ [for $I > 2\sigma(I)$], $wR_2 = 0.1745$ [for all data], 427 parameters, with allowance for the thermal anisotropy for all non-hydrogen atoms. The weighting scheme employed was $w = 1/[\sigma^2\ (F_o^2) + (0.1073\mathrm{P})^2 + 0.6181\mathrm{P}]$, where $P = (F_o^2 + 2F_c^2)/3$; and the goodness of fit on F^2 was 1.049 for all observed reflections. Finally, all non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares and hydrogen atoms with isotropic displacement parameters. Detailed information about the crystal data and structure determination is summarized in table 1. Selected interatomic distances and bond angles are given in table 2.

Table 1. Summary of crystal data, data collection, structure solution and refinement details for $C_{74}H_{60}Mn_3N_4O_{13}$.

Empirical formula	$C_{37}H_{30}Mn_{1.5}N_2O_{6.5}$
Formula weight	690.03
Description	Yellow
Crystal size (mm^3)	0.32 × 0.26 × 0.20
Temperature (K)	298(2)
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions (Å, °)	
a	11.3568(11)
b	11.5791(11)
c	14.0100(13)
α	74.757(2)
β	70.418(2)
γ	78.221(2)
Volume (Å^3)	1661.0(3)
Z, D_{Calcd} (g cm^{-3})	2, 1.380
$F(000)$	713
μ (mm^{-1})	0.629
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
θ Range (°)	1.58–25.20
Reflections collected	8933
Unique reflections (R_{int})	5915 (0.0176)
Data, restraints, parameters	5915, 0, 427
Goodness of fit on F^2	1.049
R_1, wR_2 [$I \geq 2\sigma$ (I)]^a	0.0585, 0.1637
R_1, wR_2 (all data)^a	0.0713, 0.1745
A, B values in w^b	0.1073, 0.6181
$\delta\rho_{\max}$, $\delta\rho_{\min}$ (e Å^{-3})	0.887, −0.264

[a] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.
[b] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected interatomic distances (Å) and bond angles (°) for **1**.

Mn1–O1	2.088(3)	Mn2–O2	2.151(2)
Mn1–O3	2.088(3)	Mn2–O2$^{\#1}$	2.151(2)
Mn1–O5	2.389(3)	Mn2–O4	2.154(3)
Mn1–O6	2.218(2)	Mn2–O4$^{\#1}$	2.154(3)
Mn1–N1	2.240(3)	Mn2–O6	2.221(2)
Mn1–N2	2.283(3)	Mn2–O6$^{\#1}$	2.221(2)
O1–Mn1–O3	96.22(12)	O2–Mn2–O2$^{\#1}$	180.00(13)
O1–Mn1–O6	100.18(10)	O2–Mn2–O4	91.47(11)
O1–Mn1–N1	111.75(11)	O2–Mn2–O4$^{\#1}$	88.53(11)
O1–Mn1–O5	156.67(11)	O2–Mn2–O6	89.17(10)
O1–Mn1–N2	91.79(11)	O2–Mn2–O6$^{\#1}$	90.83(10)
O3–Mn1–O6	105.57(11)	O2$^{\#1}$–Mn2–O4$^{\#1}$	91.47(11)
O3–Mn1–N1	89.89(10)	O2$^{\#1}$–Mn2–O4	8.53(11)
O3–Mn1–N2	161.78(11)	O2$^{\#1}$–Mn2–O6$^{\#1}$	89.17(10)
O3–Mn1–O5	93.05(12)	O2$^{\#1}$–Mn2–O6	90.83(10)
O6–Mn1–N1	142.80(10)	O4–Mn2–O4$^{\#1}$	180.000(1)
O6–Mn1–N2	89.00(10)	O4–Mn2–O6	92.19(10)
O6–Mn1–O5	56.62(10)	O4–Mn2–O6$^{\#1}$	87.81(10)
N1–Mn1–O5	89.58(10)	O4$^{\#1}$–Mn2–O6	87.81(10)
N1–Mn1–N2	71.93(10)	O4$^{\#1}$–Mn2–O6$^{\#1}$	92.19(10)
N2–Mn1–O5	85.82(10)	O6–Mn2–O6$^{\#1}$	180.000(1)

Symmetry codes: #1 = $-x + 1$, $-y + 2$, $-z + 1$.

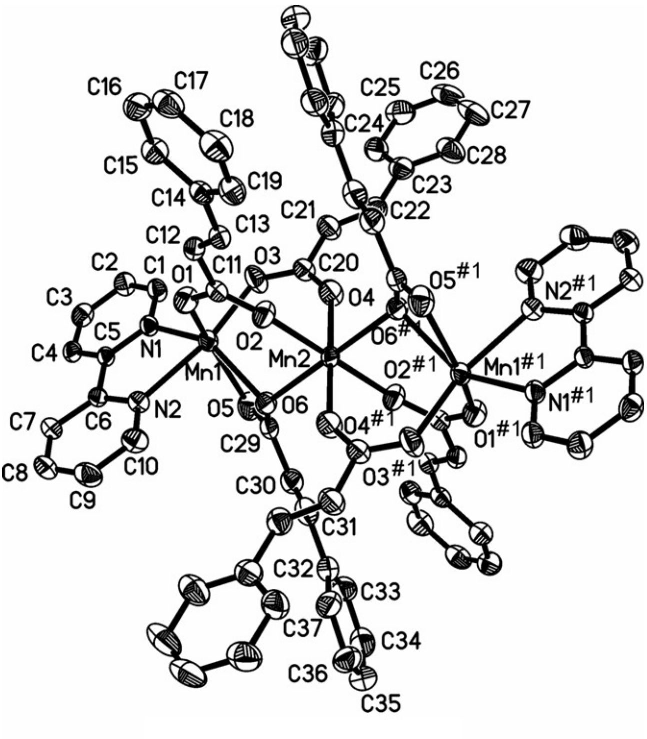
3. Results and discussion

3.1. *Crystal structure of [$Mn_3(PhCH{=}CHCOO)_6(bpy)_2$] • H_2O (1)*

The title compound consists of [$Mn_3(PhCH{=}CHCOO)_6(bpy)_2$] and lattice water molecules. As shown in figure 1, [$Mn_3(PhCH{=}CHCOO)_6(bpy)_2$] consists of a linear array of three manganese(II) centers with Mn $\cdots$ Mn separations of 3.527 Å with the 2,2-bipyridine ligands on the exterior manganese atoms, comparable to other linear trinuclear Mn(II) complexes with bridging carboxylate groups [10–13]. Four carboxylates are bidentate syn–syn, linking the peripheral Mn(1) atoms, and the other two cinnamatic carboxylate groups are monodentate bridging plus bidentate chelating with the carboxylate oxygen atoms (O5, O6) chelating the terminal Mn1 atoms and one oxygen (O6) bridging two Mn centers.

The central Mn(2) on a crystallographic inversion center, is octahedrally coordinated by six cinnamatic carboxylate oxygen atoms. All three *trans* angles of Mn2 are 180.00°, and the Mn2–O distances range from 2.151(2) to 2.221(2) Å, indicating a slightly distorted octahedron.

The Mn1 atoms are octahedrally coordinated by two nitrogen atoms of 2,2-bipyridine and four oxygen atoms of three cinnamato ligands with the axial apical positions occupied by two oxygen atoms (O1, O5) from two crystallagraphic different cinnamate ligands; the equatorial plane is defined by two aromatic pyridyl nitrogen atoms (N1, N2) and two oxygen atom (O3, O6) with O6 shifted by 1.1710 Å from the basal plane (figure 1). The Mn1–N1 bond distance (2.240(3) Å) is shorter than Mn1–N2 bond (2.283(3) Å), and similar to those in [$Mn_3(O_2CCH(CH_3)_2)_6(bpy)_2$] [13], where the Mn1–N1 and Mn1–N2 distances are 2.2495(17) and 2.2858(16) Å, respectively. The Mn1–O5 bond length (2.389(3) Å) is longer than the other Mn1–O



$\#1 = -x+1, -y+2, -z+1$

Figure 1. ORTEP view of **1** with atomic labelling (the lattice water molecule and hydrogen atoms are omitted for clarity, and the displacement ellipsoids are drawn at 30% probability).

distances (d(Mn1–O) = 2.088(3)–2.218(2) Å), but the Mn1–O5 bond length is shorter than that observed in related complexes [10–13]. The *cis* bond angles at the central Mn1 atom from the apical O1 and O5 range from 56.62(10)–111.75(11)°; the trans bond angle ∠O1–Mn1–O5 is 156.67(11)°, suggesting a significant deviation from the value for a perfect octahedral geometry.

Along the $[1\bar{1}0]$ direction, $[Mn_3(PhCH{=}CHCOO)_6(bpy)_2]$ is interlinked *via* C–H ··· O^i weak hydrogen–bonding interactions (d(C4–H4A ··· O5) = 3.219(8) Å, ∠C4–H4A–O5 = 145.67°; symmetry code *i*: $-x$, $1-y$, $1-z$) to form 1D chains [17], which are stabilized by π–π stacking interactions between the neighboring 2,2-bipyridine groups; the distance between the centroids of the aromatic ring at (x, y, z) and the aromatic ring at the symmetry position ($2^\circ - x$, $1-y$, $1-z$) is 3.637 Å (figure 2). The resulting chains are further assembled by π–π stacking interactions between the neighboring 2,2-bipyridine groups and phenyl groups of cinnamate into 3D supermolecular structure (figure 3); the distance between the centroids of the aromatic ring at (x, y, z) and the phenyl ring (C23–C28) at the symmetry position ($1+x$, y, z) is 3.461 Å.

3.2. *Synthesis and solution properties*

Reaction of freshly prepared $Mn(OH)_2$, 2,2-bipyridine and cinnamatic acid in aqueous methanolic solution with the pH of the solution controlled in the range of 7–8 with

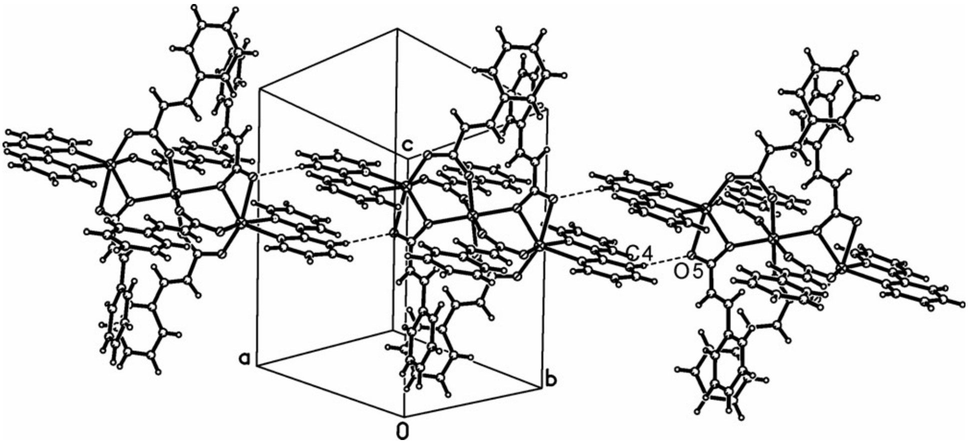


Figure 2. Supramolecular assembly of the complex molecules into 1D chain along [1$\bar{1}$0] direction by C–H ··· O hydrogen-bonding interactions and π–π stacking interactions.

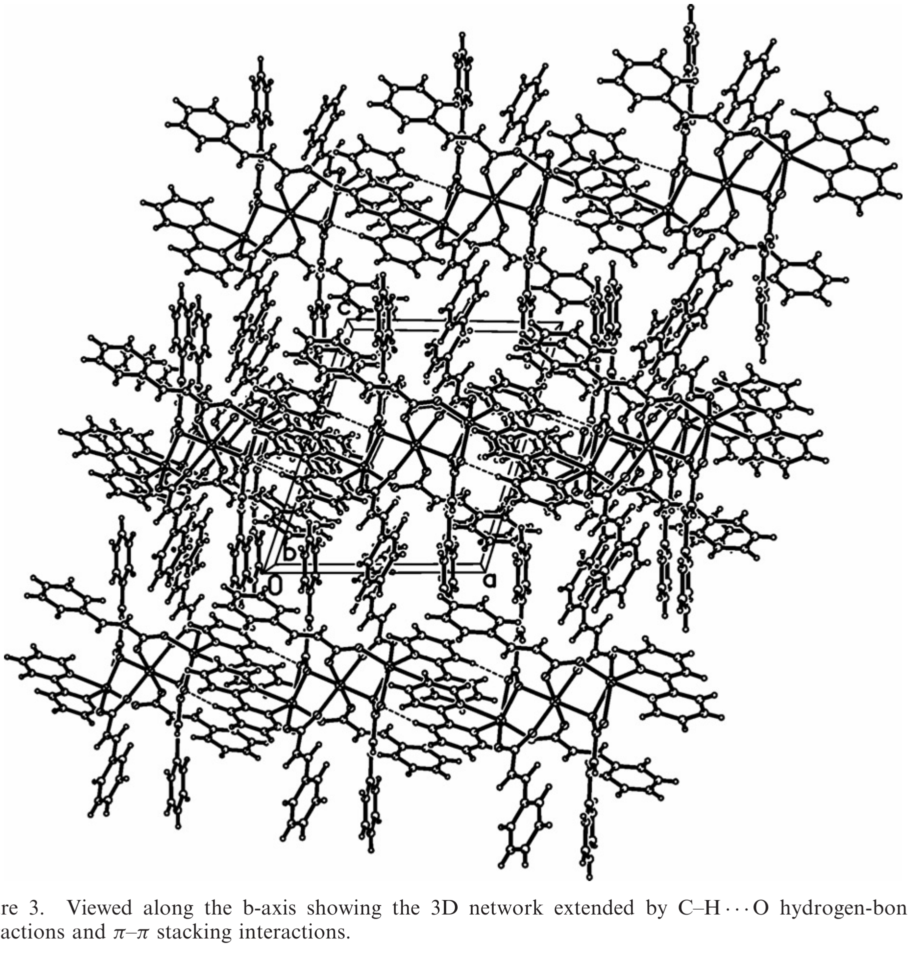


Figure 3. Viewed along the b-axis showing the 3D network extended by C–H ··· O hydrogen-bonding interactions and π–π stacking interactions.

1.0 M NaOH afforded **1** under ambient conditions. It is very difficult to obtain **1** using other manganese(II) salts with cinnamatic acid and 2,2-bipyridine at the same conditions. Compound **1** is stable in air at normal room temperature, but will decompose when the temperature is over 40°C. **1** dissolves in methanol, ethanol, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA) and water.

3.3. *XRD patterns, infrared spectra, and thermal analyses*

X-ray powder diffraction (XRD) data were collected on a Rigaku D_max/3b diffractomerter with CuKa radiation ($\lambda = 1.5418$ Å). The experimental XRD pattern agreed well with the simulated one generated on the basis of the single-crystal analysis, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.

The infrared spectrum of compound **1** shows bands at 3400 and 3020 cm^{-1} attributed to $\nu_{\mathrm{O–H}}$ of lattice water molecules and the unsatuated $\nu_{\mathrm{=C–H}}$ stretching vibrations of cinnamate groups, respectively; and the absorptions of 1640 should be assigned $\nu_{\mathrm{C–O}}$ stretching vibrations of cinnamate carboxylate groups. Comparison to the characteristic carboxylate group stretching vibrations bands (1700 cm^{-1}) of free cinnamatic acid, the $\nu_{\mathrm{C–O}}$ stretching vibrations peak shifted due to coordination [18]. Strong absorptions bands, located at 1580, 1565, 1554, 1400 cm^{-1}, belong to C–C stretching vibrations of the phenyl groups.

TG analysis showed a weight loss of 1.40% between 41 and 55°C, attributed to loss of lattice water molecules corresponding well to the calculated value of 1.30%. The framework of **1** is stable below ca 136°C. Upon further heating, the sample lost weight gradually and the total weight loss summed up to 82.25% from 136 to 600°C, suggesting sublimation of the 2,2-bipyridine groups and cinnamate fragments (calculated value: 83.22%). The residue collected at 600°C was identified as MnO by powder X-ray diffraction patterns.

Supplementary data

Crystallographic data (excluding structure factors) for the structure in this article have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 611985 ($C_{74}H_{60}Mn_3N_4O_{13}$). Copies of the data can be obtained on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033 or Email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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