The Structure of the Mixed-metal Cluster Anion $[FeOs_3H(CO)_{13}]^-$ as its $[N(PPh_3)_2]^+$ Salt †

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The mixed-metal cluster anion $[FeOs_3H(CO)_{13}]^-$ has been prepared by the reaction of $[N(PPh_3)_2]_2[Fe_3(CO)_{11}]$ with $[Os_3(CO)_{12}]$. The compound crystallises in the triclinic space group $P\bar{1}$, with a = 9.184(1), b = 15.223(2), c = 19.152(2) Å, α = 107.75(1), β = 102.81(1), γ = 93.67(1)°, and Z = 2. The four metal atoms define a tetrahedron with two carbonyl ligands semi-bridging between the iron atom and two of the osmium atoms, and the hydride lying along an osmium–osmium edge. The cation has the usual bent geometry with an angle P–N–P of 146.3(7)°.

Structural determinations for several transition-metal cluster anions having the stoicheiometry $[M_xM'_{(4-x)}H(CO)_{13}]^-$ (where M, M′ = Os, Fe, or Ru) have been reported in the literature. In particular, the cluster $[Fe_4H(CO)_{13}]^-$ adopts the interesting ' butterfly ' arrangement of metal atoms, with one of the carbonyl groups acting as an unusual four-electron donor ligand and interacting with all four iron atoms.[1] By contrast, the osmium analogue $[Os_4H(CO)_{13}]^-$ adopts a more conventional tetrahedral framework of metal atoms, with one carbonyl group lying along one edge of the tetrahedron, bonded in a μ fashion.[2]

The structural determination of $[FeOs_3H(CO)_{13}]^-$, reported in this paper, was undertaken to investigate whether a mixed-metal cluster of this type would exhibit a geometry intermediate between these extremes.

Results and Discussion

Single-crystal *X*-ray work shows there are discrete cations and anions, the $[N(PPh_3)_2]^+$ cations having the common bent geometry with an angle P–N–P of 146.3(7)°. In the $[FeOs_3H(CO)_{13}]^-$ anion the metal atoms are in a distorted tetrahedral arrangement, with two carbonyl ligands from the iron atom interacting with two osmium atoms of the basal triangle in a semi-bridging manner.[3] A PLUTO plot of the anion is shown in Figure 1.

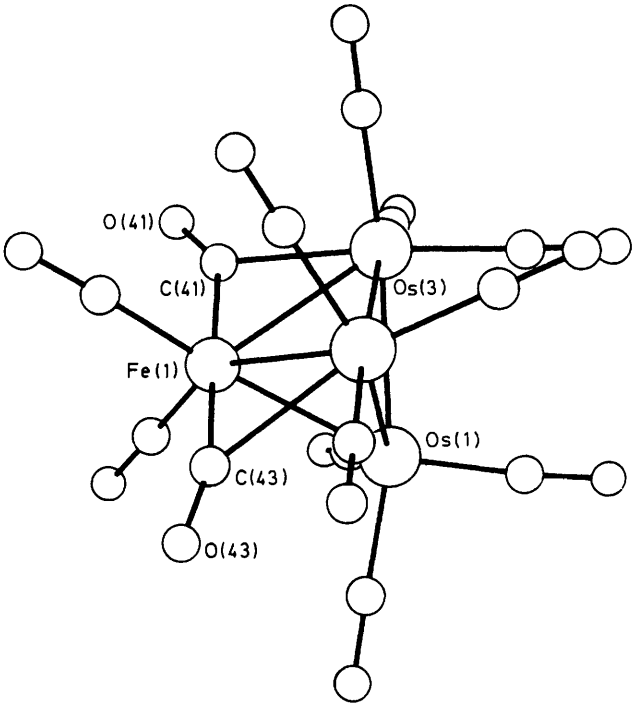

Figure 1. Molecule of $[FeOs_3H(CO)_{13}]^-$ showing part of the labelling scheme

Metal–metal bond distances are entirely typical with Os(1)–Os(2) 2.921(2), Os(1)–Os(3) 2.756(2), and Os(2)–Os(3) 2.822(2) Å. The hydride is thought to lie along the long Os(1)–Os(2) edge, although its position was not located directly. Large angles to *cis* carbonyls [*viz.* Os(1)–Os(2)–C(23) 108.1(4), Os(2)–Os(1)–C(13) 112.1(4)°] are also indicative of steric repulsion by a hydride lying along Os(1)–Os(2).[4,5] Osmium–iron distances are Fe(1)–Os(1) 2.694(3), Fe(1)–Os(2) 2.655(2), and Fe(1)–Os(3) 2.741(3) Å. Each osmium atom bears three terminal carbonyl ligands with average Os–C and C–O distances of 1.89(2) and 1.15(2) Å respectively.

Bonded to the iron atom are two terminal carbonyl ligands and two carbonyls which are semi-bridging, C(41) to Os(3) [2.256(13) Å] and C(43) to Os(2) [2.485(16) Å], with angles Os(3)–C(41)–O(41) 132.0(12) and Os(2)–C(43)–O(43) 125.0(11)°. For these two semi-bridging carbonyls the iron–carbon distance also differs substantially, Fe(1)–C(41) 1.902(16) and Fe(1)–C(43) 1.779(22) Å. The iron–carbon distances for the two terminal carbonyl ligands actually have distances intermediate between those of the semi-bridging ones, but no comparable carbon–osmium interactions are found.

Churchill *et al.*[6] have recently reported the structure of the neutral analogue, $[FeOs_3H_2(CO)_{13}]$, whose structure is much more symmetrical than that of the anion reported in this work. In $[FeOs_3H_2(CO)_{13}]$ the second hydride lies along another side of the Os_3 triangle, and the two semi-bridging carbonyls are much more similar in their

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† Bis(triphenylphosphine)iminium 1,2;1,3-di-μ-carbonyl-1,1,2,2,2,3,3,3,4,4,4-undecacarbonyl-2,4-μ-hydrido-*tetrahedro*-irontriosmate(3 *Fe–Os*)(3 *Os–Os*).

Supplementary data available (No. SUP 23769, 48 pp.): H-atom co-ordinates, thermal parameters, structure factors, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Bond lengths (Å)

Os(1)–Os(2)	2.921(2)	Fe(1)–C(42)	1.725(14)	Os(1)–C(11)	1.881(14)	Fe(1)–C(43)	1.779(22)
Os(1)–Fe(1)	2.694(3)	Fe(1)–C(44)	1.795(18)	Os(1)–C(13)	1.859(18)	C(11)–O(11)	1.144(18)
Os(1)–C(12)	1.868(19)	C(12)–O(12)	1.165(25)	Os(2)–Fe(1)	2.655(2)	C(13)–O(13)	1.173(23)
Os(2)–Os(3)	2.822(2)	C(21)–O(21)	1.139(22)	Os(2)–C(22)	1.885(17)	C(22)–O(22)	1.166(22)
Os(2)–C(21)	1.902(18)	C(23)–O(23)	1.130(16)	Os(2)–C(43)	2.485(16)	C(31)–O(31)	1.140(22)
Os(2)–C(23)	1.868(12)	C(32)–O(32)	1.149(19)	Os(3)–C(31)	1.921(18)	C(33)–O(33)	1.130(19)
Os(3)–Fe(1)	2.741(3)	C(41)–O(41)	1.167(19)	Os(3)–C(33)	1.892(15)	C(42)–O(42)	1.168(18)
Os(3)–C(32)	1.895(15)	C(43)–O(43)	1.159(27)	Fe(1)–C(41)	1.902(16)	C(44)–O(44)	1.147(24)
Os(3)–C(41)	2.256(13)	Os(1)–Os(3)	2.756(2)				

Table 2. Bond angles (°)

N(1)–P(1)–C(121)	110.3(5)	Os(1)–Fe(1)–C(42)	90.1(6)	Os(1)–Os(2)–C(43)	66.7(4)
Os(2)–Os(1)–Fe(1)	56.2(1)	Os(3)–Fe(1)–C(42)	123.3(6)	Fe(1)–Os(2)–C(43)	40.3(5)
Os(2)–Os(1)–C(11)	141.9(6)	Os(1)–Fe(1)–C(43)	81.3(6)	C(22)–Os(2)–C(43)	77.9(6)
Fe(1)–Os(1)–C(11)	90.1(5)	Os(3)–Fe(1)–C(43)	124.2(5)	Os(1)–Os(3)–Os(2)	63.1(1)
Os(3)–Os(1)–C(12)	163.1(5)	C(42)–Fe(1)–C(43)	93.8(8)	Os(2)–Os(3)–Fe(1)	57.0(1)
C(11)–Os(1)–C(12)	97.8(7)	Os(2)–Fe(1)–C(44)	105.3(4)	Os(2)–Os(3)–C(31)	95.9(5)
Os(3)–Os(1)–C(13)	100.0(7)	C(41)–Fe(1)–C(44)	85.1(7)	Os(1)–Os(3)–C(32)	100.6(5)
C(11)–Os(1)–C(13)	93.9(7)	C(43)–Fe(1)–C(44)	95.8(8)	Fe(1)–Os(3)–C(32)	114.6(4)
Os(1)–Os(2)–Os(3)	57.3(1)	Os(1)–C(12)–O(12)	178.8(16)	Os(1)–Os(3)–C(33)	87.6(6)
Os(3)–Os(2)–Fe(1)	60.0(1)	Os(2)–C(21)–O(21)	179.6(16)	Fe(1)–Os(3)–C(33)	139.4(6)
Os(3)–Os(2)–C(21)	90.9(5)	Os(2)–C(23)–O(23)	177.6(13)	C(32)–Os(3)–C(33)	91.8(6)
Os(1)–Os(2)–C(22)	114.5(4)	Os(3)–C(32)–O(32)	179.0(15)	Os(2)–Os(3)–C(41)	97.9(4)
Fe(1)–Os(2)–C(22)	117.5(4)	Os(3)–C(41)–Fe(1)	82.0(5)	C(31)–Os(3)–C(41)	92.2(6)
Os(1)–Os(2)–C(23)	108.1(4)	Fe(1)–C(41)–O(41)	146.0(12)	C(33)–Os(3)–C(41)	169.0(5)
Fe(1)–Os(2)–C(23)	147.7(5)	Os(2)–C(43)–Fe(1)	75.0(7)	Os(1)–Fe(1)–Os(3)	60.9(1)
C(22)–Os(2)–C(23)	94.6(6)	Fe(1)–C(43)–O(43)	160.0(12)	Os(1)–Fe(1)–C(41)	97.8(4)
Os(3)–Os(2)–C(43)	98.3(4)	P(1)–N(1)–P(2)	146.3(7)	Os(3)–Fe(1)–C(41)	54.6(4)
C(21)–Os(2)–C(43)	99.4(6)	Os(2)–Os(1)–Os(3)	59.5(1)	Os(2)–Fe(1)–C(42)	149.3(7)
C(23)–Os(2)–C(43)	167.2(7)	Os(3)–Os(1)–Fe(1)	60.4(1)	C(41)–Fe(1)–C(42)	87.0(8)
Os(1)–Os(3)–Fe(1)	58.7(1)	Os(3)–Os(1)–C(11)	89.8(5)	Os(2)–Fe(1)–C(43)	64.7(5)
Os(1)–Os(3)–C(31)	158.8(5)	Os(2)–Os(1)–C(12)	106.9(5)	C(41)–Fe(1)–C(43)	178.8(6)
Fe(1)–Os(3)–C(31)	108.5(5)	Fe(1)–Os(1)–C(12)	104.4(5)	Os(1)–Fe(1)–C(44)	171.4(4)
Os(2)–Os(3)–C(32)	163.7(5)	Os(2)–Os(1)–C(13)	112.1(4)	Os(3)–Fe(1)–C(44)	115.4(6)
C(31)–Os(3)–C(32)	100.3(7)	Fe(1)–Os(1)–C(13)	160.0(6)	C(42)–Fe(1)–C(44)	98.2(7)
Os(2)–Os(3)–C(33)	89.1(5)	C(12)–Os(1)–C(13)	94.5(9)	Os(1)–C(11)–O(11)	178.8(11)
C(31)–Os(3)–C(33)	95.5(7)	Os(1)–Os(2)–Fe(1)	57.5(1)	Os(1)–C(13)–O(13)	175.6(20)
Os(1)–Os(3)–C(41)	88.0(4)	Os(1)–Os(2)–C(21)	140.5(5)	Os(2)–C(22)–O(22)	178.9(13)
Fe(1)–Os(3)–C(41)	43.4(4)	Fe(1)–Os(2)–C(21)	87.4(4)	Os(3)–C(31)–O(31)	179.0(15)
C(32)–Os(3)–C(41)	79.1(5)	Os(3)–Os(2)–C(22)	171.8(5)	Os(3)–C(33)–O(33)	175.0(15)
Os(1)–Fe(1)–Os(2)	66.2(1)	C(21)–Os(2)–C(22)	96.8(7)	Os(3)–C(41)–O(41)	132.0(12)
Os(2)–Fe(1)–Os(3)	63.1(1)	Os(3)–Os(2)–C(23)	87.8(5)	Fe(1)–C(42)–O(42)	176.7(17)
Os(2)–Fe(1)–C(41)	114.2(4)	C(21)–Os(2)–C(23)	91.8(6)	Os(2)–C(43)–O(43)	125.0(11)
				Fe(1)–C(44)–O(44)	177.6(13)

bonding pattern. In its ligand distribution, $[FeOs_3H(CO)_{13}]^-$ thus describes a 14-vertex polyhedron and the electron is presumably delocalised around the metal cage. The neutral analogue $[FeOs_3H_2(CO)_{13}]$, a 15-vertex polyhedron, has a different ligand pattern, which manifests itself as a more symmetrical bonding of the semi-bridging carbonyls and both hydrides exert a considerable steric influence. It has been argued that ligand packing plays an important role in determining overall molecular geometry.[7] It is therefore, perhaps, not surprising that these geometries should differ. The geometries of $[FeOs_3H(CO)_{13}]^-$ and $[FeOs_3H_2(CO)_{13}]$ are illustrated in Figure 2.

Isostructural with $[FeOs_3H(CO)_{13}]^-$ are the species $[FeRu_3H(CO)_{13}]^-$,[8] $[Ru_4H_2(CO)_{13}]$,[9] $[FeRu_3H_2(CO)_{13}]$,[10] and $[FeOs_3H_2(CO)_{13}]$,[6] all having a tetrahedral metal framework with 11 terminal and two bridging carbonyl ligands. Further work on mixed-metal species, *viz*. $[Fe_2Os_2H(CO)_{13}]^-$ and $[Fe_3OsH(CO)_{13}]^-$, would help to rationalise geometries adopted by the series of compounds from $[Os_4H(CO)_{13}]^-$ to $[Fe_4H(CO)_{13}]^-$.

Experimental

Preparation of $[N(PPh_3)_2][FeOs_3H(CO)_{13}]$.—To $[N(PPh_3)_2]_2[Fe_3(CO)_{11}]$ (0.28 g, 0.179 mmol) and $[Os_3(CO)_{12}]$ (0.165 g, 0.179 mmol) was added freshly distilled bis(2-methoxyethyl) ether (30 cm³) and the mixture heated to reflux for 7 h. The solvent was removed *in vacuo* at 35 °C and the residue dissolved in dichloromethane (35 cm³). Aqueous $FeCl_3$ solution (ten-fold excess) was added while carbon monoxide was bubbled through the solution. The mixture was vigorously stirred for 10 min. The organic phase was separated and purified by t.l.c. $[N(PPh_3)_2][FeOs_3H(CO)_{13}]$ was obtained by elution with CH_2Cl_2–hexane (9 : 1 v/v), and recrystallised from the same solvent to give crystals which were suitable for single-crystal *X*-ray work. The i.r. spectrum in CH_2Cl_2 showed the following bands in the ν(CO) region: 2 078w, 2 037s, 2 013s, 1 997s, 1 964m, 1 940m, and 1 794w cm⁻¹. The $[FeOs_3H(CO)_{13}]^-$ anion is protonated by HBF_4–Et_2O in CH_2Cl_2 to give the neutral compound $[FeOs_3H_2(CO)_{13}]$.

Structure Determination of $[N(PPh_3)_2][FeOs_3H(CO)_{13}]$.—

Table 3. Atom co-ordinates (× 10^4)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	3(1)	4 137(1)	1 740(1)	C(113)	4 396(10)	−3 825(6)	109(5)
Os(2)	2 863(1)	4 581(1)	2 895(1)	C(114)	3 511(10)	−4 185(6)	491(5)
Os(3)	88(1)	4 074(1)	3 171(1)	C(115)	3 526(10)	−3 681(6)	1 235(5)
Fe(1)	1 429(2)	2 855(1)	2 219(1)	C(116)	4 426(10)	−2 816(6)	1 598(5)
C(11)	−1 806(16)	3 302(11)	1 352(9)	C(121)	5 498(8)	−503(4)	1 304(4)
O(11)	−2 895(12)	2 783(9)	1 109(7)	C(122)	4 298(8)	−792(4)	656(4)
C(12)	470(18)	4 030(11)	819(9)	C(123)	3 543(8)	−133(4)	407(4)
O(12)	765(19)	3 979(11)	248(8)	C(124)	3 988(8)	814(4)	807(4)
C(13)	−959(19)	5 180(11)	1 765(11)	C(125)	5 188(8)	1 103(4)	1 455(4)
O(13)	−1 603(17)	5 829(9)	1 818(10)	C(126)	5 942(8)	444(4)	1 703(4)
C(21)	3 931(18)	4 162(10)	3 676(9)	C(131)	8 142(10)	−1 459(5)	1 369(5)
O(21)	4 573(13)	3 916(8)	4 146(7)	C(132)	8 786(10)	−808(5)	1 106(5)
C(22)	4 552(17)	4 918(10)	2 575(8)	C(133)	10 176(10)	−902(5)	930(5)
O(22)	5 607(13)	5 116(9)	2 381(8)	C(134)	10 922(10)	−1 647(5)	1 018(5)
C(23)	2 928(16)	5 766(9)	3 582(9)	C(135)	10 278(10)	−2 297(5)	1 281(5)
O(23)	3 019(14)	6 487(8)	4 001(8)	C(136)	8 888(10)	−2 203(5)	1 457(5)
C(31)	928(18)	4 092(10)	4 189(9)	C(211)	7 254(10)	−1 279(5)	3 927(4)
O(31)	1 427(15)	4 117(10)	4 796(7)	C(212)	7 030(10)	−2 251(5)	3 661(4)
C(32)	−1 974(16)	3 678(10)	3 059(9)	C(213)	6 559(10)	−2 745(5)	4 096(4)
O(32)	−3 223(12)	3 448(9)	3 001(8)	C(214)	6 311(10)	−2 266(5)	4 797(4)
C(33)	−203(15)	5 341(10)	3 446(9)	C(215)	6 534(10)	−1 294(5)	5 064(4)
O(33)	−476(14)	6 078(7)	3 617(8)	C(216)	7 006(10)	−801(5)	4 628(4)
C(41)	−15(15)	2 514(9)	2 700(8)	C(221)	9 772(9)	−818(5)	3 332(5)
O(41)	−732(13)	1 902(7)	2 771(7)	C(222)	10 530(9)	−293(5)	3 005(5)
C(42)	427(20)	1 989(11)	1 403(10)	C(223)	12 016(9)	−398(5)	2 977(5)
O(42)	−186(18)	1 392(9)	844(8)	C(224)	12 744(9)	−1 028(5)	3 277(5)
C(43)	2 774(19)	3 198(10)	1 777(11)	C(225)	11 987(9)	−1 554(5)	3 604(5)
O(43)	3 526(14)	3 153(7)	1 359(8)	C(226)	10 500(9)	−1 449(5)	3 632(5)
C(44)	2 577(17)	2 145(11)	2 638(9)	C(231)	7 882(7)	559(5)	3 809(5)
O(44)	3 298(15)	1 667(10)	2 881(10)	C(232)	9 209(7)	1 099(5)	4 305(5)
P(1)	6 440(3)	−1 331(2)	1 668(2)	C(233)	9 248(7)	2 055(5)	4 644(5)
P(2)	7 842(3)	−670(2)	3 347(2)	C(234)	7 959(7)	2 470(5)	4 487(5)
N(1)	6 674(10)	−1 032(7)	2 550(5)	C(235)	6 631(7)	1 930(5)	3 991(5)
C(111)	5 312(10)	−2 546(6)	1 217(5)	C(236)	6 593(7)	975(5)	3 652(5)
C(112)	5 297(10)	−2 961(6)	472(5)				

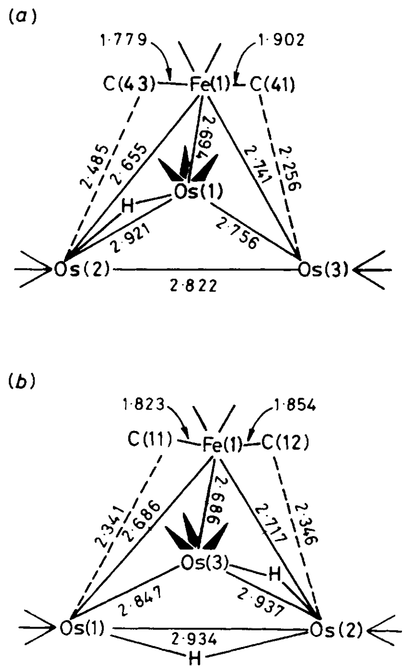

Figure 2. Geometries (with bond distances in Å) of (*a*) $[FeOs_3H(CO)_{13}]^-$ and (*b*) $[FeOs_3H_2(CO)_{13}]$

The complex was obtained as deep red-black glistening crystals. Many were irregularly shaped but some had a regular rhomboidal morphology. A rhomboid with approximate dimensions 0.23 × 0.15 × 0.10 mm was suitable for *X*-ray work.

Data collection was carried out on a STOE four-circle automatic diffractometer. Accurate cell dimensions were obtained by centring 44 strong reflections lying in the shell $15 \leqslant 2\theta \leqslant 25°$.

Intensities of 9 252 reflections lying in the hemisphere $+h$, $\pm k$, $\pm l$ having $5.0 \leqslant 2\theta \leqslant 50.0°$ were measured using graphite-monochromatised Mo-K_α radiation and an ω—2θ scan mode. During data collection, three standard reflections, measured after every 100 reflections, showed only random deviations about their mean values.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 324 azimuthal scan data from 31 reflections was applied. Using 300 of these data the *R* factor of 0.088 before correction was reduced to 0.023. Transmission factors ranged between 0.21 and 0.11. Lorentz and polarisation corrections were applied to the data and the structure was solved using 7 013 unique reflections having $F_o \geqslant 3\sigma(F_o)$.

Crystal data. $C_{49}H_{31}FeNO_3Os_3P_2$, $M = 1\,530.16$, Triclinic, space group $P\bar{1}$, $a = 9.184(1)$, $b = 15.223(2)$, $c = 19.152(2)$ Å, $\alpha = 107.75(1)$, $\beta = 102.81(1)$, $\gamma = 93.67(1)°$, $U = 2\,461.6(10)$ Å^3, $Z = 2$, $D_c = 2.06$ g cm^{-3}, $F(000) = 1\,440.0$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 81.09 cm^{-1}.

The positions for the three osmium atoms were found from the best *E*-map using the program EEES, the centrosymmetric direct methods option of SHELX.[11] Positions for all other non-hydrogen atoms were found during the following electron density difference syntheses. Atomic positions were refined by blocked-cascade least squares, with the entire anion and P and N atoms of the cation given anisotropic thermal parameters. During the final cycles of refinement the phenyl rings were constrained to be regular hexagons and hydrogen atoms were placed in idealised positions with C–H 1.08 Å and C–C–H 120°, giving a common isotropic thermal parameter to all hydrogens. Complex neutral-atom scattering factors were used for all atoms,[12] and unit weights employed throughout the refinement.

The values of R $(= \Sigma\Delta/\Sigma F_o,\ \Delta = |F_o - F_c|)$ and R' $[= (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}]$ converged at 0.049 and 0.052. Fractional atomic co-ordinates for the non-hydrogen atoms are given in Table 3, and selected bond distances and bond angles in Tables 1 and 2.

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