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[19. ABSTRACT]

The 2:1 mole ratio reaction of $\mathrm{InCl_3}$ and $\mathrm{P(SiMe_3)_3}$ in a toluene/THF mixture was investigated. Reaction appears to occur in a 1:1 mole fashion, since the products obtained are unreacted $\mathrm{InCl_3}$ (48.5% recovered) as $\mathrm{InCl_3{\cdot}2THF}$ and a fine powder which roughly analyzes to be $\mathrm{[Cl_2In_3P_3(SiMe_3)_2]_n}$. The latter was characterized by melting point and partial elemental analysis. The X-ray crystal structure of $\mathrm{InCl_3{\cdot}2THF}$ is reported. $\mathrm{InCl_3{\cdot}2THF}$ crystallizes in the orthorhombic space group *Pbcn* [(D_{2h}^{14}), No.60] with unit cell parameters of a = 10.802(1) Å, b = 10.101(1) Å, c = 13.083(1) Å, V = 1427.5(4) Å^3, and D_{calcd} = 1.700 g cm^{-3} for Z = 4 [R = 0.042 (R_w = 0.058)] and is an example of a neutral pentacoordinated bis-adduct of an indium(III) trihalide. The crystal structure consists of discrete monomeric units with no abnormally short intermolecular separations. The geometry about the indium atom approximates to trigonal bipyramidal with oxygen atoms of each of the THF molecules occupying axial positions [In-O = 2.257(9) Å, O-In-O = 178.5(3)°] while the three chlorine atoms (mean In-Cl = 2.321 Å) lie in the equatorial plane.

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X-RAY CRYSTAL STRUCTURE OF $InCl_3 \cdot 2THF$, A NEUTRALFIVE-COORDINATE BIS-ADDUCT OF AN In(III) TRIHALIDE

by

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X-Ray Crystal Structure of $InCl_3 \cdot 2THF$, a Neutral Five-Coordinate Bis-adduct of an In(III) Trihalide

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Abstract - The 2:1 mole ratio reaction of $InCl_3$ and $P(SiMe_3)_3$ in a toluene/THF mixture was investigated. Reaction appears to occur in a 1:1 mole fashion, since the products obtained are unreacted $InCl_3$ (48.5% recovered) as $InCl_3 \cdot 2THF$ and a fine powder which roughly analyzes to be $[Cl_2In_3P_3(SiMe_3)_2]_n$. The latter was characterized by melting point and partial elemental analysis. The X-ray crystal structure of $InCl_3 \cdot 2THF$ is reported. $InCl_3 \cdot 2THF$ crystallizes in the orthorhombic space group *Pbcn* [(D_{2h}^{14}), No.60] with unit cell parameters of a = 10.802(1) Å, b = 10.101(1) Å, c = 13.083(1) Å, V = 1427.5(4) Å^3, and D_{calcd} = 1.700 g cm^{-3} for Z = 4 [R = 0.042 (R_w = 0.058)] and is an example of a neutral pentacoordinated bis-adduct of an indium(III) trihalide. The crystal structure consists of discrete monomeric units with no abnormally short intermolecular separations. The geometry about the indium atom approximates to trigonal bipyramidal with oxygen atoms of each of the THF molecules occupying axial positions [In-O = 2.257(9) Å, O-In-O = 178.5(3)°] while the three chlorine atoms (mean In-Cl = 2.321 Å) lie in the equatorial plane.

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For some time our laboratory has been investigating convenient and facile routes to the formation of novel compounds containing Ga-As bonds.[1] In fact, one such compound with the empirical formula $(AsCl_3Ga_2)_n$ (**I**) can be easily converted into nanocrystalline GaAs itself.[2] Compound **I** results from the 2:1 mole ratio reaction of $GaCl_3$ and $As(SiMe_3)_3$. In related work, Barron and coworkers recently reported that the 1:1 mole ratio reaction of $InCl_3$ and $P(SiMe_3)_3$ at low temperature yields $[Cl_2InP(SiMe_3)_2]_x$ (**II**).[3] In that we have now begun to direct considerable attention to the production of compounds containing In-P bonds,[4-7] it was decided that the In/P analogue of the reaction leading to the formation of **I** should be investigated [i.e., the 2:1 reaction of $InCl_3$ and $P(SiMe_3)_3$], the goal being the possible isolation of new precursor $(PCl_3In_2)_n$. We report that though the 2:1 reaction of $GaCl_3$ and $As(SiMe_3)_3$ to produce **I** occurs cleanly and readily, the corresponding reaction of $InCl_3$ and $P(SiMe_3)_3$ affords $[Cl_2In_3P_3(SiMe_3)_2]_n$ (**III**) and unreacted $InCl_3$ (48.5% of the starting $InCl_3$) in a solvated form [$InCl_3 \cdot 2THF$ (**IV**)]. Compound **III** (characterized by melting point and partial elemental analysis) was isolated as a relatively unreactive fine orange powder. It is insoluble in hydrocarbon solvents, THF, and Et_2O, and air stable for several hours at room temperature. Complex **IV** has been previously synthesized and quite extensively characterized by Fairbrother *et. al*,[8] but no solid-state structure was ever obtained. Herein, we report the crystal structure of **IV** as it represents a novel example of a neutral pentacoordinated bis-adduct of an indium(III) trihalide.

EXPERIMENTAL

Synthesis

All manipulations were performed using general Schlenk techniques. Colorless crystals of **IV** were obtained by the 2:1 mole reaction of $P(SiMe_3)_3$ [9] and $InCl_3$ (purchased from Strem chemicals). In the dry box (Vacuum/Atmospheres HE-493 Dri-Lab containing an argon atmosphere), $P(SiMe_3)_3$ (0.250 g, 0.998 mmol) was dissolved in 25 cm^3 of anhydrous, degassed toluene (distilled from sodium/benzophenone ketyl) in a 100-cm^3 one-necked round-bottomed flask equipped with a Teflon valve and a micro-stirbar. A suspension of $InCl_3$ (0.441 g, 1.99 mmol) in 15 cm^3 of toluene and 15 cm^3 of anhydrous, degassed tetrahydrofuran (THF) (distilled from sodium/benzophenone ketyl) was slowly added drop-wise. Immediately upon addition, the reaction mixture became yellow-orange and quite turbid. The reaction mixture was stirred at room temperature for 2 days then allowed to settle undisturbed for 1 day. Decantation of the colorless mother liquor from the bright orange powder {$[Cl_2In_3P_3(SiMe_3)_2]_n$ **(III)**, 0.204g, 47% yield based on In, Mp = 200 to 260°(dec to black), Anal. Calcd (Found) for $C_6H_{18}Cl_2In_3P_3Si_2$: C,11.01 (11.40, 11.62); H,2.75 (2.59, 2.53); Cl, 10.83 (10.66, 10.91)} and subsequent cooling at -15° C for 3 days afforded crystals of **IV** (0.352g, 48.5% yield based on In) suitable for X-ray analysis.

X-ray structural solution and refinement

Crystallographic data are summarized in Table 1. The crystal used was a colorless block mounted inside a flame-sealed 0.6 mm thin-walled glass capillary under an inert argon atmosphere. Oscillation and Weissenberg photographs yielded preliminary unit cell parameters and space group information. X-ray intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer at 25° C using graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å). Lorentz and polarization corrections were applied as was an empirical absorption correction. The crystal structure was solved by direct methods. Initial coordinates for the indium and chlorine atoms were derived from an *E*-map. Carbon and oxygen atoms were located in a difference Fourier synthesis phased by these atoms. Several rounds of full-matrix least-squares adjustment of non-hydrogen atom positional and thermal parameters (at first isotropic, then anisotropic) followed. Hydrogen atoms were incorporated at their calculated positions (C-H = 1.05 Å) in the later iterations which converged (max. shift:esd = 0.02) at $R = 0.042$ ($R_w = 0.058$). A final difference Fourier synthesis revealed no unusual features (max. 0.56, min. -0.41 e/Å^3, both in the vicinity of the indium atom). Crystallographic calculations were performed using the Enraf-Nonius Structure Determination Package (SDP).[10] For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 11. Selected distances and angles are provided in Table 2. An ORTEP diagram showing the atom labeling scheme and solid-state conformation of **IV** is presented in Figure 1; the packing arrangement of molecules of **IV** in the crystal is illustrated in Figure 2. Full information concerning conditions for crystallographic data collection and structure refinement, atomic coordinates, positional parameters, anisotropic thermal parameters, and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Though the structural chemistry of five-coordinate aluminum and gallium compounds has been well examined, corresponding investigations of such indium compounds have remained more sparse.[12] Currently, there are seven pentacoordinate indium(III) trihalide bis-adducts which have been crystallographically characterized [*viz.*, $InX_3 \cdot L_2$: X = Cl; L = PPh_3 (**V**),[13] HMPA ($OP\{N(Me)_2\}_3$) (**VI**),[14] NMe_3 (**VII**),[15] $SPMe_3$ (**VIII**),[16] $SAsMe_3$ (**IX**)[16]: X = Br; L = $SPMe_3$ (**X**),[16] $SAsMe_3$ (**XI**)[16]]. Of these, it is interesting to note that five (**VII** - **XI**) were only reported within the last six years and **IV** is only the second such compound containing In-O bonds to be structurally characterized, the first being **VI**.

The crystal structure of **IV** consists of discrete monomeric units which have one of their In-Cl bonds lying on a crystallographic C_2 symmetry axis (see Fig. 1). In common with the other $InX_3 \cdot L_2$ adducts, the coordination geometry about the indium atoms is trigonal-bipyramidal with three chlorine atoms defining the equatorial plane and the oxygen atoms of the THF molecules occupying the axial sites. The O-In-O angle at 178.5(3)° in **IV** deviates only slightly from an exactly linear value and lies close to that of 178.0(2)° in **VI**. The In-O bond length of 2.257(9) Å in **IV** is significantly longer and thus weaker than the corresponding bonds in **VI** where they average 2.180 Å; this difference may be ascribed to the increased electron donating ability of the oxygen atom in the HMPA ligand. The mean In-Cl bond length at 2.321 Å in **IV** is shorter than that of 2.359 Å in **VI** as well as the corresponding lengths of 2.360 Å - 2.412 Å in **V**, **VII** - **IX**. The observed decrease in the equatorial bond lengths in **IV** vs. **VI** is correlated with the aforementioned lengthened axial bond distance in the former. Endocyclic torsion angles characterizing the conformation of the THF molecule are related by an approximate C_2 symmetry axis which passes through the oxygen atom and the midpoint of the C(3)-C(4) bond, and, accordingly, this ring is in a half-chair conformation. The mean bond angle subtended at the oxygen atom is 118° and thus the geometry about this atom lies closer to trigonal planar than to tetrahedral. X-ray crystallographic studies[16] on the series $InX_3{\cdot}L_2$ (X = Cl, Br; L = $SPMe_3$, $SAsMe_3$) have shown that in the solid state the angle subtended at the axial sulfur atom is dependent on intermolecular as well as intramolecular non-bonded interactions. The orientation of the In-O bond with respect to the THF ring in crystals of **IV** produces no unusually short intramolecular Cl...H non-bonded distances (min. Cl...H = 3.29 Å). Crystal packing requirements involving two equidistant intermolecular interactions between Cl(2) in the reference molecule and one of the hydrogen atoms at C(2) in neighboring molecules [Cl(2)...H(2) = 2.87 Å] apparently dictate the geometry at the oxygen atom in the solid state.

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References

1) For a general review see R. L. Wells,*Coord. Chem. Rev.* 1992, **112**, 273.

2) R. L.Wells, R. B.Hallock, A. T. McPhail, C. G. Pitt, and J. D. Johansen, *Chem. Mater.* 1991, **3**, 381.

3) M. D. Healy, P. E. Laibinis, P. D. Stupik, and A. R. Barron, *J. Chem. Soc., Chem. Commun.* 1989, 359.

4) R. L. Wells, A. T. McPhail, and M. F. Self, *Organometallics* 1992, **11**, 221.

5) R. L. Wells, A. T. McPhail, L. J. Jones,M. F. Self, and R. J.Butcher, *Organometallics* 992,**11**, 2694.

6) R. L. Wells, A. T. McPhail, and M. F. Self, *J. Coord. Chem.* **in press.**

7) R. L. Wells, A. T. McPhail, L. J. Jones, and M. F. Self, *J. Organomet. Chem.* **in press.**

8) F. Fairbrother, N. Flitcroft, and H. Prophet, *J. Less-Common Metals* 1960, **2**, 49.

9) G. Becker, and W. Holderich, *Chem. Ber.* 1975, **108**, 2484.

10) Enraf-Nonius Structure Determination Package (SDP 3.0), Enraf-Nonius, Delft, The Netherlands, 1985.

11) *International Tables for X-ray Crystallography*; The Kynoch Press, Birmingham, England, 1974, Vol IV.

12) (a) D. G. Tuck, In *Comprehensive Organometallic Chemistry;* G.Wilkinson, Ed; Pergamon Press: Oxford, England, 1982; Vol. 1, Chpt. 7, pp. 683 - 723. (b) D. G. Tuck, In*Comprehensive Coordination Chemistry;* G.Wilkinson, R. D.Gillard, and J. A. McCleverty, Eds; Pergamon Press: Oxford, England, 1987; Vol. 3, Chpt. 25.2, pp. 153 - 182.

13) M. V.Veidis, and G. J. Palenik, *J. Chem. Soc. D* 1969, 586.

14) S. P. Sinha, T. T. Pakkanen, T. A. Pakkanen, and L. Niinisto, *Polyhedron* 1982, **1**, 355.

15) R.Karia, G. R. Willey, and M. G. B. Drew, *Acta. Cryst. Sect. C. Cryst. Struct. Comm.* 1986, **C42**, 558.

16) W. T.Robinson, C. J. Wilkins, and Z. Zeying, *J. Chem. Soc., Dalton Trans.* 1988, 2187.

Figure captions

Fig. 1. ORTEP diagram (50% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of $InCl_3 \cdot 2THF$ (**IV**); primed atoms are related to the unprimed atoms by a crystallographic C_2 symmetry axis passing through In and Cl(2). Small circles represent hydrogen atoms.

Fig. 2. Packing arrangement of molecules of $InCl_3 \cdot 2THF$ (**IV**) in the crystal.

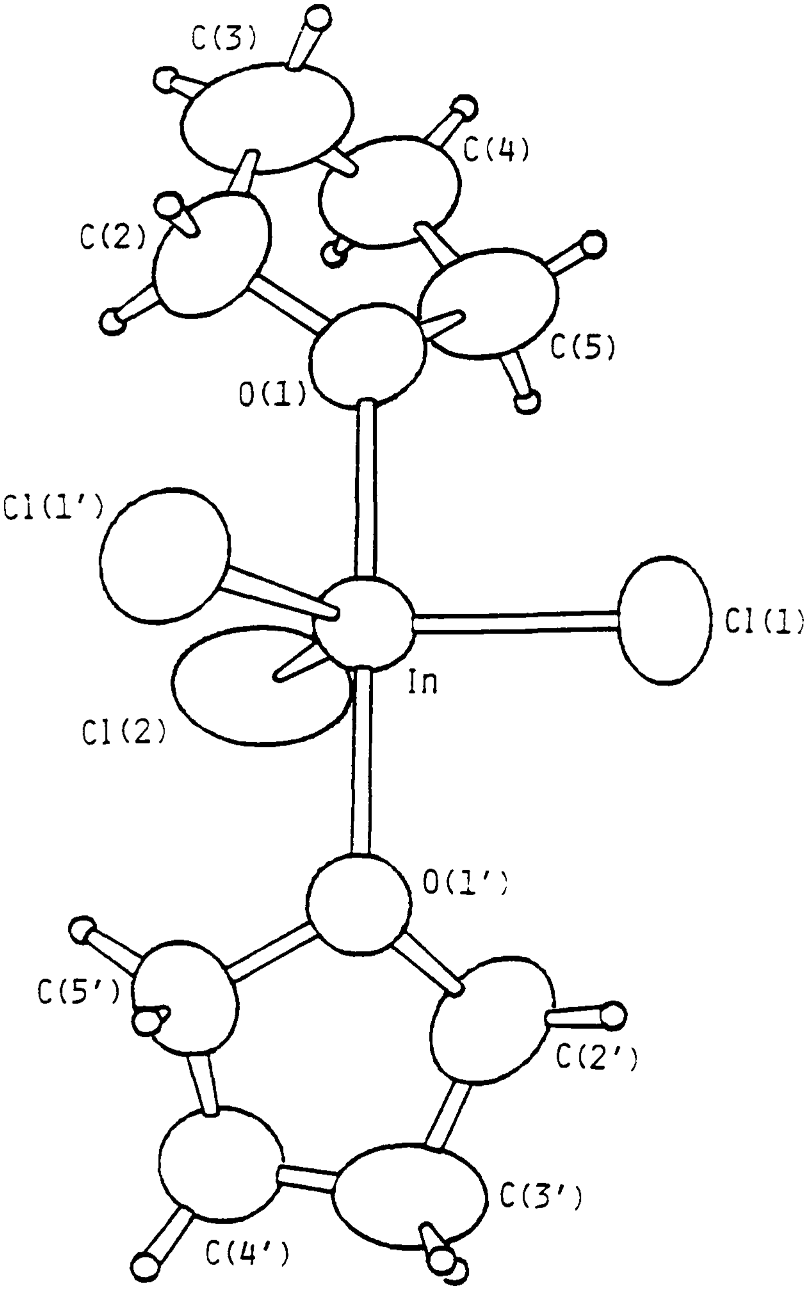

Fig. 1

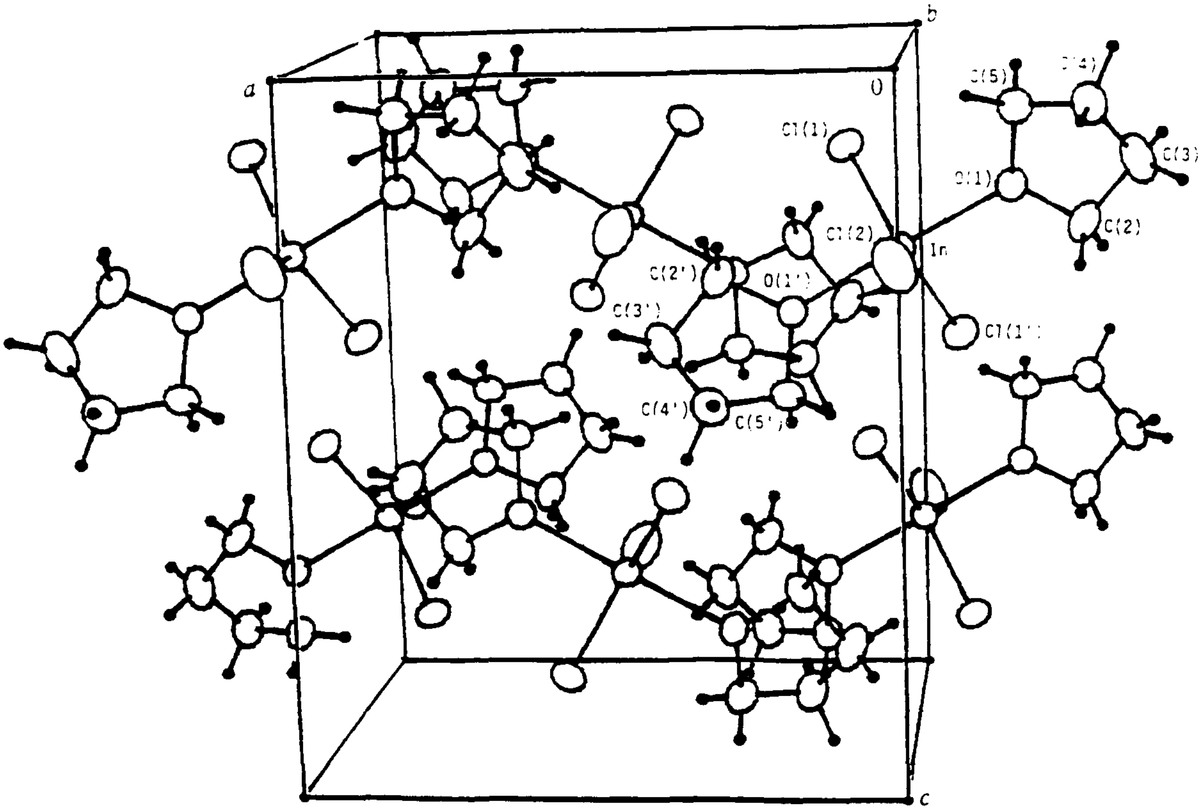

Fig. 2

Table 1. Crystallographic data for $InCl_3 \cdot 2THF$ (**IV**)

molecular formula	$C_8H_{16}Cl_3InO_2$
formula weight	365.39
crystal system	orthorhombic
space group	$Pbcn(D_{2h}^{14})$ - No.60
a(Å)	10.802(1)
b(Å)	10.101(1)
c(Å)	13.083(1)
no. of orientation refls.; θ(°) range	25; 36-40
V(Å^3)	1427.5(4)
Z	4
$D_{calcd.}$ (g cm^{-3})	1.700
μ(Cu-$K\alpha$ radiation, λ = 1.5418 Å)	186.9
temp. (°C)	25
crystal dimensions (mm)	0.16 x 0.18 x 0.20
$T_{max}:T_{min}$	1.00:0.71
scan type	ω-2θ
scanwidth (°)	0.80 + 0.14tanθ
θ_{max} (°)	75
intensity control refls.;	1 1 1, 1 2 2, 1 3 3, 1 1 4
variation; repeat time (hr)	<1% ; 2
total no. of refls. ($+h,+k,\pm l$) recorded	1471
no. of refls. retained [$I > 3.0\sigma(I)$]	537
no. of parameters refined	65
R (R_w)[a]	0.042 (0.058)
goodness-of-fit[b]	1.16
max. shift:esd in final least-squares cycle	0.02
final $\Delta\rho$(e/Å^3) max.;min.	0.56 ; -0.41

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[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $\Sigma w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized.

[b] Goodness-of-fit = $[\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Table 2. Interatomic Distances (Å) and Angles[a] (deg.) for $InCl_3 \cdot 2THF$ (**IV**), with ESD's in Parentheses

a) Bond Distances

In-Cl(1)	2.330(4)	O(1)-C(5)	1.49(2)
In-Cl(2)	2.312(5)	C(2)-C(3)	1.53(3)
In-O(1)	2.257(9)	C(3)-C(4)	1.45(3)
O(1)-C(2)	1.46(2)	C(4)-C(5)	1.50(2)

(b) Bond Angles

Cl(1)-In-Cl(1')	117.8(2)	In-O(1)-C(2)	122(1)
Cl(1)-In-Cl(2)	121.1(1)	In-O(1)-C(5)	122(1)
Cl(1)-In-O(1)	90.5(3)	C(2)-O(1)-C(5)	109(1)
Cl(1)-In-O(1')	90.3(3)	O(1)-C(2)-C(3)	104(1)
Cl(2)-In-O(1)	89.2(2)	C(2)-C(3)-C(4)	105(1)
O(1)-In-O(1')	178.5(3)	C(3)-C(4)-C(5)	104(1)
		O(1)-C(5)-C(4)	104(1)

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[a] Primed atoms are related to unprimed atoms by the following transformation: $-x$, y, $1/2 - z$.

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