pairs. The only lead atoms not situated on mirror planes, Pb(5), exhibit an oxygen coordination (five- or sixfold, depending on whether oxygen atoms at 3·5 Å are considered to be in the coordination sphere) which is too irregular to be described in terms of any conventional polyhedron.

The pentagonal pyramids around Pb(3) and Pb(4) share edges with the UO_6 octahedra and with each other, resulting in layers $(PbUO_6)_\infty$ perpendicular to **b**. The remaining three lead atoms, each with a different oxygen environment, are distributed between the layers, in such a way that the structure exhibits rather large 'voids' towards which the lone pairs from all five types of lead atoms appear to be directed (*cf.* Fig. 2).

We thank a referee for pointing out that the formula $2PbO.PbUO_4$ would be preferable to Pb_3UO_6, in line with the terminology used for solid-solution phases formed by PbO with compounds such as $PbSO_4$, described by the general formula nPbO.$PbSO_4$. This is certainly in accord with the mode of formation of Pb_3UO_6 and of the other discrete phase in the PbO–$PbUO_4$ system, $Pb_{11}U_5O_{26}$ or 6PbO.5$PbUO_4$ (Sterns, 1967). On the other hand, it is stated in the literature on phases in the PbO–$PbSO_4$ system, notably PbO.$PbSO_4$ (Sahl, 1970) and 2PbO.$PbSO_4$ (Sahl, 1981), that the structural principles of these phases, which contain no recognizable elements of the $PbSO_4$ (anglesite) structure, are better expressed by the formulae $Pb_2O(SO_4)$ and $Pb_3O_2(SO_4)$ respectively. In the former (lanarkite), OPb_4 tetrahedra, similar to those encountered in both forms of PbO, share two edges to form infinite chains of stoichiometry Pb_2O which are connected to discrete sulfate groups by longer Pb—O bonds. In $Pb_3O_2(SO_4)$, tetrahedra of the same kind share three edges resulting in chains of composition Pb_3O_2. A somewhat similar description, involving OPb_4 tetrahedra, is also possible for the Pb_3UO_6 ($2PbO.PbUO_4$) structure. The oxygen atoms O(3) and O(4) which do not participate in the octahedral oxygen environment of the uranium atoms are each surrounded tetrahedrally by four lead atoms (Fig. 2, Table 3) and the two tetrahedra share an edge, Pb(5)—Pb(5), 3·61 Å, forming the dimeric unit Pb_6O_2. The dimeric units include all lead atoms in the structure and are connected to the $(UO_5)_\infty$ chains of corner-sharing UO_6 octahedra by other, usually longer, Pb—O bonds. Considered in this way, the composition of the unit cell is $4Pb_6O_2.8UO_5$, corresponding to the formula Pb_3OUO_5 which may be structurally more informative than either Pb_3UO_6 or $2PbO.PbUO_4$.

Table 3. *Coordination around oxygen atoms* O(3) *and* O(4)

O(3)—Pb(1)	2·45 (1) Å	Pb(1)—O(3)—Pb(4)	100·1 (5)°
O(3)—Pb(4)	2·21 (1)	Pb(1)—O(3)—Pb(5)	104·7 (4) 2×
O(3)—Pb(5)	2·26 (1) 2×	Pb(4)—O(3)—Pb(5)	119·4 (3) 2×
O(3)—O(4)	2·87 (2)	Pb(5)—O(3)—Pb(5)	106·2 (5)
O(4)—Pb(2)	2·37 (1)	Pb(2)—O(4)—Pb(3)	109·0 (6)
O(4)—Pb(3)	2·28 (2)	Pb(2)—O(4)—Pb(5)	104·2 (4) 2×
O(4)—Pb(5)	2·36 (1) 2×	Pb(3)—O(4)—Pb(5)	118·8 (4) 2×
		Pb(5)—O(4)—Pb(5)	100·0 (5)

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The Structure of Atacamite and its Relationship to Spinel

BY J. B. PARISE* AND B. G. HYDE

Research School of Chemistry, The Australian National University, GPO Box 4, *Canberra, ACT* 2601, *Australia*

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Abstract. Atacamite, $Cu_2Cl(OH)_3$, $M_r = 213·6$, $F(000) = 408$, orthorhombic, *Pnma*, $a = 6·030$ (2), $b = 6·865$ (2), $c = 9·120$ (2) Å, $V = 377·5$ Å^3, $Z = 4$, $D_x = 3·76$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 117·8$ cm^{-1}, $T = 293$ K. Non-H atoms refined anisotropically to $R = 0·029$ for 399 observed data with $I > 3\sigma(I)$. (The structure refined less satisfactorily in the alternative space group $Pna2_1$.) Cu atoms are in

* Present address: The Department of Chemistry, New South Wales Institute of Technology, Broadway, Sydney, NSW 2006, Australia.

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characteristic distorted octahedral, (4+2)-coordination sites: Cu(1) is bonded to four hydroxyl groups [2×1·940 (2) and 2×2·017 (2) Å] and two Cl atoms [2·776 (2) Å] and Cu(2) to five hydroxyl groups [2×1·993 (2), 2×2·010 (3) and 2·358 (4) Å] and one Cl atom [2·750 (1) Å]. These Cu-centred octahedra are edge-linked as in the spinel structure: the $(OH)_3Cl$ group forms a squashed tetrahedron. Cl is bonded to three atoms of Cu [2·750 (1), 2×2·776 (2) Å] and three of H [2·10 (5), 2×2·22 (5) Å] arranged in a trigonal prism. O(1) is bonded to three atoms of Cu [2×1·940 (2), 2·358 (4) Å] and one H atom [0·95 (8) Å] arranged tetrahedrally; and O(2) similarly [1·993 (2), 2·010 (2) and 2·017 (2), and 0·87 (5) Å].

Introduction. The structure of atacamite, a copper hydroxychloride mineral, was first proposed by Brasseur & Toussaint (1942), and later corrected by Wells (1949) who noted that, in its idealized form, it could be derived from the *B*1 type of NaCl. While the positions of the H atoms were not discussed in these earlier studies the present report is concerned with their locations, with H bonding in the structure, and also with an alternative description of the structure, relating it to that of spinel (*Strukturbericht* symbol $H1_1$).

Experimental. Emerald-green crystals of atacamite from Mina La Farola, Chile, were kindly provided from the Adelaide Museum collection (sample No. 10550) by Dr Allan Pring. Several small prismatic crystals were examined by X-ray techniques, confirming their orthorhombic (*mmm*) symmetry, space group *Pnma* (No. 62), with absences $0kl$, $k+l=2n+1$; $hk0$, $h=2n+1$. Data were collected from a prismatic crystal 0·13 × 0·05 × 0·05 mm (Picker FACSI diffractometer, $3<2\theta<55°$, θ–2θ scans, 10 s background counts, scan rate 2° min^{-1}; three orthogonal reflections measured periodically showed no significant variation). The quoted unit-cell parameters are from 12 fully centred reflections with $38·9<2\theta<42·9°$ (h: 0→7; k: 0→8; l: 0→11). Of the 449 unique data with $I>0·0$, 50 with $I<3\sigma(I)$ were excluded from the structure solution and refinement. Absorption corrections, varying from 0·69 to 0·81, were applied ($\mu=117·8$ cm^{-1}). Wells' (1949) coordinates of non-H atoms were refined anisotropically, and used to phase a $\Delta\rho$ map which revealed the positions of two H atoms. Final refinement was with anisotropic thermal parameters for all except the H atoms: the function $\sum w(F_o-F_c)^2$ was minimized, with weights $w=[\sigma^2(F)+0·001F^2]^{-1}$, where σ is based on counting statistics. The maximum shift/e.s.d. ratio was 0·05 for the final cycle of refinement, and there were no peaks of chemical significance in the final $\Delta\rho$ map (−0·9 to 0·8 e Å^{-3}).

Analytical expressions for the scattering factors were taken from *International Tables for X-ray Crystallography* (1974), corrected for anomalous dispersion. Final discrepancy factors were, for 399 data with $I>3\sigma(I)$, $R=0·029$, $wR=0·039$, $S=1·38$. Calculations were carried out on a Digital Equipment VAX 11/750 using programs *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Atomic parameters are given in Table 1, and a list of selected bond lengths and angles in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43104 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional* (×10^4) *and thermal* (×10^3) *parameters for atacamite* $[Cu_2(OH)_3Cl]$

$U_{eq}=(U_{11}+U_{22}+U_{33})/3$, in units of Å^2; e.s.d.'s for these values estimated according to Schomaker & Marsh (1983).

	x	y	z	U/U_{eq}
Cu(1)	0	0	0	7 (1)
Cu(2)	1906 (1)	$\frac{1}{4}$	2553 (1)	7 (1)
Cl	3518 (2)	$\frac{3}{4}$	556 (1)	12 (1)
O(1)	1498 (8)	$\frac{1}{4}$	−18 (3)	11 (2)
O(2)	4406 (4)	651 (4)	2879 (2)	8 (2)
H(1)	3049 (85)	$\frac{1}{4}$	−148 (62)	3 (9)
H(2)	4331 (71)	−334 (84)	2279 (48)	3 (9)

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

O(1)—Cu(1)	1·940 (2)	O(2)—Cu(2)	1·993 (2)
O(1^{i})—Cu(1)	1·940 (2)	O(2^{vi})—Cu(2)	1·993 (2)
O(2^{ii})—Cu(1)	2·017 (2)	O(2^{vii})—Cu(2)	2·010 (2)
O(2^{iii})—Cu(1)	2·017 (2)	O(2^{viii})—Cu(2)	2·010 (2)
Cl^{iv}—Cu(1)	2·776 (1)	O(1)—Cu(2)	2·358 (4)
Cl^{v}—Cu(1)	2·776 (1)	Cl^{ix}—Cu(2)	2·750 (1)
O(1)—Cu(1)—O(1^{i})	180	O(2)—Cu(2)—O(2^{vi})	79·1 (1)
O(1)—Cu(1)—O(2^{ii})	96·0 (1)	O(2)—Cu(2)—O(2^{vii})	177·3 (1)
O(1)—Cu(1)—O(2^{iii})	84·0 (1)	O(2)—Cu(2)—O(2^{viii})	101·3 (1)
O(1)—Cu(1)—Cl^{iv}	101·1 (1)	O(2)—Cu(2)—O(1)	103·1 (1)
O(1)—Cu(1)—Cl^{v}	78·9 (1)	O(2)—Cu(2)—Cl^{ix}	85·5 (1)
O(1^{i})—Cu(1)—O(2^{ii})	84·0 (1)	O(2^{vi})—Cu(2)—O(2^{vii})	101·2 (1)
O(1^{i})—Cu(1)—O(2^{iii})	96·0 (1)	O(2^{vi})—Cu(2)—O(2^{viii})	177·3 (1)
O(1^{i})—Cu(1)—Cl^{iv}	78·9 (1)	O(2^{vi})—Cu(2)—O(1)	103·1 (1)
O(1^{i})—Cu(1)—Cl^{v}	101·1 (1)	O(2^{vi})—Cu(2)—Cl^{ix}	85·5 (1)
O(2^{ii})—Cu(1)—O(2^{iii})	180	O(2^{vii})—Cu(2)—O(2^{viii})	78·3 (1)
O(2^{ii})—Cu(1)—Cl^{iv}	84·4 (1)	O(2^{vii})—Cu(2)—O(1)	74·1 (1)
O(2^{ii})—Cu(1)—Cl^{v}	95·6 (1)	O(2^{vii})—Cu(2)—Cl^{ix}	97·2 (1)
O(2^{iii})—Cu(1)—Cl^{iv}	95·6 (1)	O(2^{viii})—Cu(2)—O(1)	74·1 (1)
O(2^{iii})—Cu(1)—Cl^{v}	84·4 (1)	O(2^{viii})—Cu(2)—Cl^{ix}	97·2 (1)
Cl^{iv}—Cu(1)—Cl^{v}	180	O(1)—Cu(2)—Cl^{ix}	168·7 (1)
Hydrogen bonds			
H(1)···O(1)	0·95 (8)	H(2)···O(2)	0·87 (5)
H(1)···Cl^{x}	2·10 (5)	H(2)···Cl^{xi}	2·22 (5)
O(1)···Cl^{x}	3·044 (2)	O(2)···Cl^{xi}	3·075 (3)
O(2)—H(2)···Cl^{x}	167 (4)	O(2)—H(2)···Cl^{x}	168 (4)

Symmetry operators: (i) px, py, pz; (ii) $\frac{1}{2}-x$, py, $z-\frac{1}{2}$; (iii) $x-\frac{1}{2}$, y, $\frac{1}{2}-z$; (iv) x, $y-1$, z; (v) $-x$, $1-y$, pz; (vi) x, $\frac{1}{2}-y$, z; (ix) $\frac{1}{2}-x$, $y-\frac{1}{2}$, $z+\frac{1}{2}$; (x) $1-x$, $1-y$, $-z$; (xi) x, $y-1$, z.

Discussion. *Framework.* Fig. 1, a stereoscopic drawing, shows the structure as a cross-linked array of Cu-centred octahedra. This is essentially Wells' (1949) description of atacamite, derived from the $B1$ (NaCl) type by emptying half the octahedrally coordinated cation sites (Wells, 1975).

The coordination about Cu(1) consists of four short bonds to O, with average bond length 1·98 Å, and approximately square-planar geometry (Table 2), and two longer bonds to Cl, 2·78 Å, completing the octahedron. These octahedra are joined *via* O(1)—Cl edges to form chains in the **b** direction [Fig. 1(*b*)]. In the **a** direction there are puckered chains of edge-shared squares centred on Cu(2), with four short bonds to O(2) of average length 2·00 Å. A fifth, longer bond to O(1), 2·36 Å, links the two chains; and the distorted octahedral geometry is completed by a Cl atom at 2·75 Å.

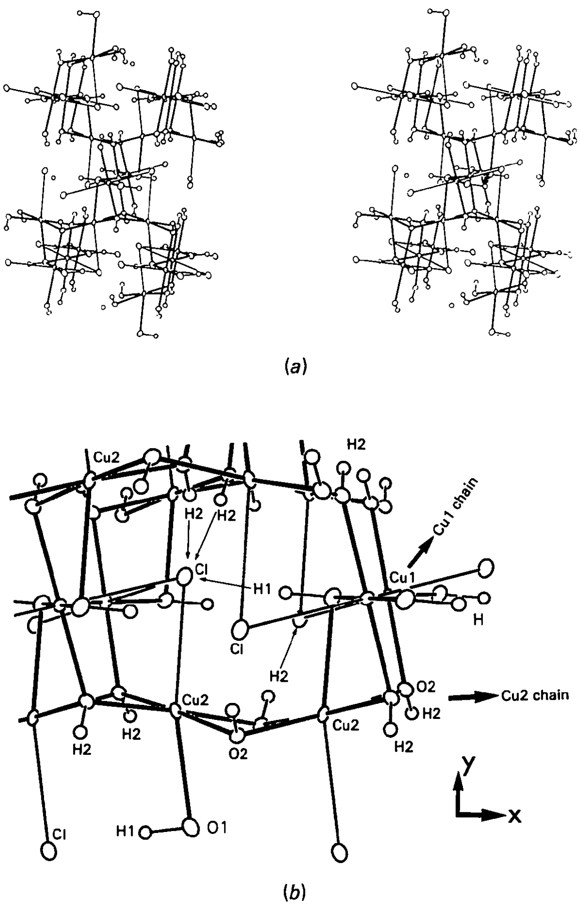

Fig. 1. (*a*) Stereoscopic *ORTEP* (Johnson, 1965) drawing of the structure of atacamite. Thinner lines represent Cu—Cl bonds. (*b*) A part of (*a*), enlarged: chlorine is in trigonal prismatic coordination Cu_3H_3 (thin arrows); Cu(1) is at the origin of the unit cell.

Fig. 1 also emphasizes an alternative description of the structure as consisting of a framework of $-[CuO_4]-$ squares (the heavier bonds in the figure) outlining narrow tunnels parallel to **b**. Within these tunnels reside Cl atoms, each bonded to three Cu atoms and three hydroxyl oxygens in a trigonal prismatic arrangement. Each O atom is bonded to one H and three Cu atoms arranged tetrahedrally.

Hydrogen bonding. Details of the hydrogen bonds in the structure are given in Table 2. Both H(1) and H(2) lie close to the straight lines O···Cl in O—H···Cl. The group $(OH)_3Cl$ is a tetrahedron, O_3Cl, with the two H(2) atoms just inside its O(2)···Cl edges, and H(1) just outside its O(1)···Cl edge (Fig. 2). The tetrahedron is squashed along its pseudo-threefold axis: $\angle$ OClO = 88° (instead of 60° for a regular tetrahedron). Its basal edges are long: $2 \times 4{\cdot}19$ and 4·33 Å for d(O···O) [*cf.* its other three edges: d(Cl···O) = 3·04 and $2 \times 3{\cdot}08$ Å]. This geometry is mainly a result of the relatively short distances d(O···O) = 2·54 Å in the shared edges of the $Cu(2)O_5Cl$ octahedra (in the rod parallel to **a**). Except for these long basal edges all other second-nearest-neighbour distances (anion and cation) appear to be close to, or slightly less than, the sums of the appropriate non-bonded radii. In particular, the three H···H distances of 2·9 (1) Å are close to $2r_0(\mathrm{H}) \simeq 2{\cdot}8$–$3{\cdot}3$ Å, according to the source (*cf.* Kitaigorodsky, 1973). ($2r_0 = d$ at the minimum in the potential-energy curve.)

The relationship to spinel. As Wells (1949, 1975) pointed out, the framework of edge-connected CuX_6 octahedra is derived from the $B1$ type by omitting alternate rows of cations parallel to [110] and [$\bar{1}$10] (of the f.c.c. unit cell), the directions alternating in adjacent (001) layers. Exactly the same octahedral framework exists in the spinel structure, in which additional cations (A in AB_2X_4) occupy tetrahedrally coordinated interstices. It is known that a tetrahedrally coordinated cation (*e.g.* Si, P) may in some circumstances be replaced by a group of H atoms (*e.g.* McConnell & Verhoek, 1963), a classic example being hydrogrossular in which some of the Si in grossular (garnet),

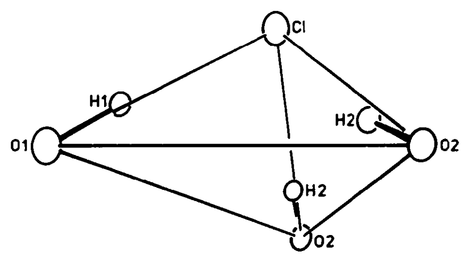

Fig. 2. The squashed O_3Cl tetrahedron in atacamite showing the arrangement of O—H···Cl bonds. The edges of the O_3 base are longer than the O···Cl edges (see text).

$Ca_3Al_2Si_3O_{12}$, is replaced by 4H, giving $Ca_3Al_2[Si_{3-x}(H_4)_x]O_{12} = Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$. The importance of this example is that complete substitution is possible; the accuracy of the 4H-for-Si substitution has been substantiated by complete structure determinations of $Ca_3Al_2(OH)_{12}$ (Cohen-Addad, Ducros, Durif, Bertaut & Delapalme, 1964; Cohen-Addad, Ducros & Bertaut, 1967; Foreman, 1968).

In the present instance a similar substitution occurs, but with a 3H group occupying the tetrahedral cation site in spinel, *i.e.* AB_2X_4 is here $(H_3)Cu_2(O_3Cl)$. This is best demonstrated by projecting the spinel structure on to (100) = (010) of its body-centred tetragonal (rather than its face-centred cubic) unit cell and, particularly as atacamite has two types of anions and Jahn–Teller distortions of the Cu-centred octahedra of anions, emphasizing the *cation* array and AX_4 [$=(H_3)(O_3Cl)$] tetrahedra. The AB_2 cation array in spinel is (the *Strukturbericht*) *C*15 (**$MgCu_2$**) type, with the *B* atoms forming a *C*9 array (of corner-connected tetrahedra), as shown in Fig. 3, and the *A* atoms (or AX_4 tetrahedra) centring its B_{12} truncated tetrahedral interstices. Figs. 4(*a*) and 4(*b*) show the corresponding (100) and (010) projections of atacamite. The first strongly resembles spinel (Fig. 3), and the second is a not very large topological distortion of it. The centre of mass of the 3H group [in the $(H_3)(O_3Cl)$ tetrahedron] is at 0·02 (1), 0·25 (1), 0·34 (1), which is only ~0·3 (1) Å from the ideal *A* atom site at 0, 0·25, 0·375.

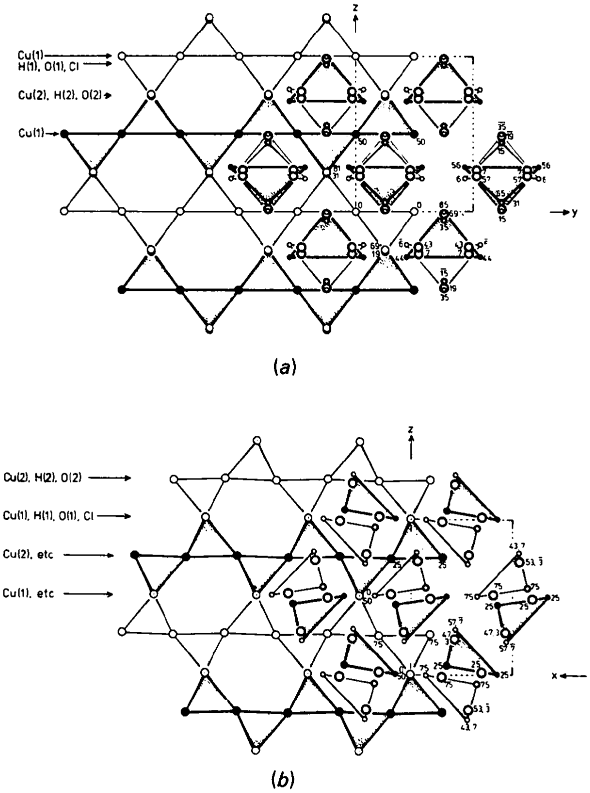

Fig. 4. The structure of atacamite, $Cu_2(OH)_3Cl$, projected on (*a*) (100) and (*b*) (010). The *C*9-like array of empty Cu_4 tetrahedra and the $(H_3)O_3Cl$ tetrahedra are emphasized. Compare Fig. 3. In order of decreasing size the circles represent the positions of the H, Cu, Cl and O atoms; heavier circles are H and Cl, lighter ones are Cu and O. Heights are in units of (*a*) *a*/100, (*b*) *b*/100.

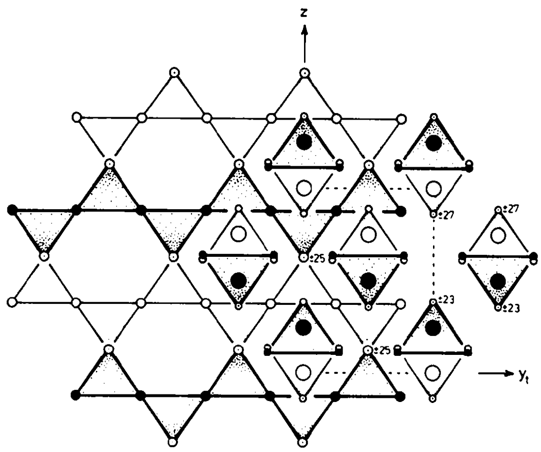

Fig. 3. The structure of $MgAl_2O_4$, spinel (Yamanaka & Takeuchi, 1983) projected on $(100)_t$ of the body-centred tetragonal unit cell [$=(110)_c$ of the f.c.c. cell]. Large circles are Mg, medium circles are Al and small circles are O atoms: open at $x = 0$, filled at $x = \frac{1}{2}$, and dotted at $x \simeq \pm\frac{1}{2}$ (heights in units of $a/100$). The *C*9-like array of empty, corner-connected Al_4 tetrahedra is shown on the left, and the MgO_4 tetrahedra on the right.

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