

Triaquamanganese sulfite revisited

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Orthorhombic $\text{Mn}(\text{SO}_3)(\text{H}_2\text{O})_3$ has been reinvestigated by single-crystal X-ray diffraction in two possible space groups, *viz.* $P2_12_12_1$ (with all atoms in general positions) and $Pnma$ (with the molecule bisected by a mirror plane). The results confirm the lower symmetry assigned in a previous single-crystal neutron diffraction study. However, the refinement of the $P2_12_12_1$ model requires the introduction of racemic twinning and soft positional and displacement restraints for the H atoms. The importance of a scrupulous report on symmetry absence violations as standard policy in crystallographic work is discussed.

Comment

$\text{Mn}(\text{SO}_3)(\text{H}_2\text{O})_3$ is known to crystallize in two polymorphic varieties, *viz.* a monoclinic form (Engelen & Freiburg, 1979; Johansson & Lindqvist, 1980) and an orthorhombic form (Baggio & Baggio, 1976; Engelen, 1983; Basso *et al.*, 1991; Gonschorek *et al.*, 1996). Both structures present the same local coordination scheme (SO_3 bound to three different cationic units *via* its three O atoms) but with a different three-dimensional connectivity (to be discussed below). While the structure of the monoclinic form is well established, that of the orthorhombic form still presents an apparent contradiction between the $Pnma$ symmetry originally determined and the $P2_12_12_1$ symmetry associated with an ordered distribution of its aqua H atoms.

X-ray studies could not distinguish definitively between the options ' $Pnma$ + splitting' and ' $P2_12_12_1$ + ordering'. As a result of 'real symmetry' or 'strong pseudosymmetry', both $Pnma$ and $P2_12_12_1$ treatments resulted in similar difference Fourier maps, from which it was almost impossible to differentiate genuine H atoms from eventual ghost images. A single-crystal neutron diffraction study (Gonschorek *et al.*, 1996) determined $P2_12_12_1$ as the correct space group, at least for the deuterated samples used. Unfortunately, this seemingly

accurate work ended up in a report impaired by a number of numerical inconsistencies, some of which affected relevant atomic coordinates involved in the 'hot' part of the structure, and rendered much of the reported geometry meaningless.¹

We present here the results of the structure refinement of a good X-ray data set in the two controversial space groups, namely (i) $P2_12_12_1$ and (ii) $Pnma$. Fig. 1 shows the corresponding ellipsoid plots and numbering schemes, while Tables 1 and 3 present relevant distances and angles. Some redundant values have been included in Table 3 in order to facilitate comparison with corresponding values in Table 1.

A simplified view of the structure as obtainable in a difference Fourier synthesis is shown in Fig. 2(a). The 'H-like' atoms drawn are the maxima clearly appearing in both centro- and non-centrosymmetric difference Fourier maps; the two maps look equivalent except for the presence of a mirror in $Pnma$ (Fig. 1b) *versus* a pseudo-mirror in $P2_12_12_1$ (Fig. 1a).

First, there is a clear distinction between atom O1W with its two well behaved H atoms and the remaining atoms O2W and O3W, each showing three plausible maxima in the Fourier maps. These 'proto-H atoms', in turn, fall into two categories, *viz.* (i) H2WA and H3WA (one for each aqua ligand), which do not present any possible 'steric collision' with other atoms in the structure and are in principle good candidates to be real H atoms, and (ii) other H atoms that do present steric hindrance problems [in $P2_12_12_1$: $\text{H2WB} \cdots \text{H3WC}(2-x, \frac{1}{2}+y, \frac{1}{2}-z) = 1.24 \text{ \AA}$ and $\text{H2WC} \cdots \text{H3WB}(x, 1+y, z) = 0.93 \text{ \AA}$; in $Pnma$: $\text{H2WB} \cdots \text{H2WB}(2-x, 2-y, 1-z) = 1.34 \text{ \AA}$ and $\text{H2WC} \cdots \text{H2WC}(x, \frac{5}{2}-y, z) = 1.04 \text{ \AA}$]. In $P2_12_12_1$, this problem could be overcome by the judicious choice of one H atom from each set (H2WB and H3WC, or H2WC and H3WB) as the correct partners of H2WA and H3WA. In $Pnma$, the existence of H2WB(C) would necessarily imply the existence of H3WB(C); in this case, only a split model is possible in the form of a 50:50 mixture of the two possible non-centrosymmetric solutions.

The *ab initio* analysis of systematic absences (and their violations) favoured $P2_12_12_1$ rather than $Pnma$ (Table 5). The strongest violation occurs for the multiply determined 041 reflection with an intensity $I \simeq 60\sigma$ in seven different measurements in the whole data set. Overall, the strong pseudosymmetry is apparent from the very low mean intensities of the offending reflections.

In order to test both hypotheses, three unrestrained refinements in the two possible space groups were performed, including two ordered models in $P2_12_12_1$ (one for each possible choice of the controversial H atoms, *viz.* H2WA, H2WB/H3WA, H3WC or H2WA, H2WC/H3WA, H3WB) and a disordered structure in $Pnma$, with a fully occupied H2WA and two half-occupied H2WB and H2WC sites. The results of both $P2_12_12_1$ refinements yielded significantly lower *R* factors

¹The coordinates for atoms O3 and D2 as reported by Gonschorek *et al.* (1996) are clearly in error, as confirmed by their calculated distances to the Mn cation (not presented in the paper), *viz.* $\text{Mn}-\text{O3} = 1.84 \text{ \AA}$ (expected *ca.* 2.20 Å) and $\text{Mn} \cdots \text{D2} = 1.58 \text{ \AA}$ (expected 2.65–2.85 Å). In fact, only a few of the reported bonds and angles can be derived precisely from the published coordinates.

(0.0199 and 0.0215 versus 0.0238), though at the cost of nearly twice as many parameters and with the need of a (nearly equi-populated) racemic twin model (0.45/0.55). In addition, the behaviour of the controversial H atoms during the completely free refinement was rather erratic and a smooth convergence could only be achieved when soft restraints were applied. In contrast, the *Pnma* model proved to be quite robust and, in spite of its slightly larger *R* factor, provided a sensible and stable solution even when severely over-refined.

Our conclusion is that $\text{Mn}(\text{SO}_3)(\text{H}_2\text{O})_3$ crystallizes in the non-centrosymmetric $P2_12_12_1$ space group, as confirmed by the lower *R* indices and the violations of the expected systematic absences in *Pnma*. In ordinary circumstances, without previous information or with only a medium-quality X-ray data set, it would be impossible to discriminate between the $P2_12_12_1$ and *Pnma* space groups and the latter would be normally preferred. This result alerts us to the fact that it might sometimes be easy to overlook annoying violations of systematic absences.

For the sake of completeness, a very brief description of the $P2_12_12_1$ structure of $\text{Mn}(\text{SO}_3)(\text{H}_2\text{O})_3$ follows. The basic structural unit consists of an Mn^{II} cation octahedrally coordinated to three water molecules and atoms O1, O2ⁱ and O3ⁱⁱ from three symmetry-related sulfite ions (Fig. 1a). The anion is bonded through each of its O atoms to a different cation in a μ_3 -mode to generate a double chain running along *b*, where both the cations and the anions are surrounded by aqua ligands (Fig. 2b). These good hydrogen-bond donors find an adequate number of acceptors to build up an extremely complex hydrogen-bonding network. The interactions are either inter-chain (entries 1–3 in Table 2) or intra-chain (entries 4–6) and connect each chain to six others (Fig. 3). This chain structure is the most conspicuous difference between the orthorhombic and monoclinic forms of $\text{Mn}(\text{SO}_3)(\text{H}_2\text{O})_3$. In fact, the latter presents a completely analogous cation coordination scheme but with a slightly different interconnectivity between polyhedra (Table 4), which leads to a tightly woven three-dimensional covalent structure. These packing differ-

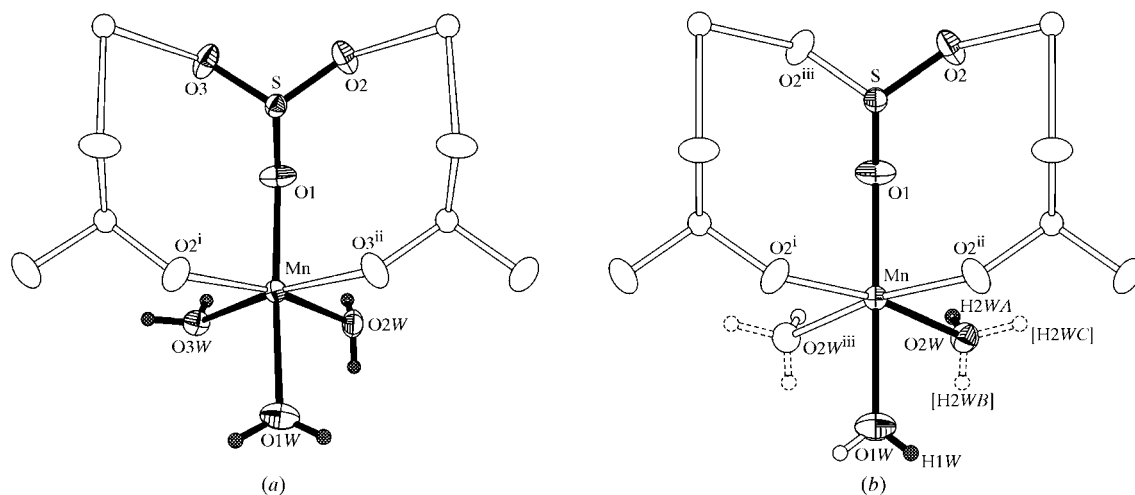


Figure 1 Displacement ellipsoid plots (50% probability level) of the Mn polyhedron in (a) the $P2_12_12_1$ and (b) the *Pnma* model. Symmetry-independent atoms are drawn as filled ellipsoids. The symmetry codes are as given in Tables 1 and 3.

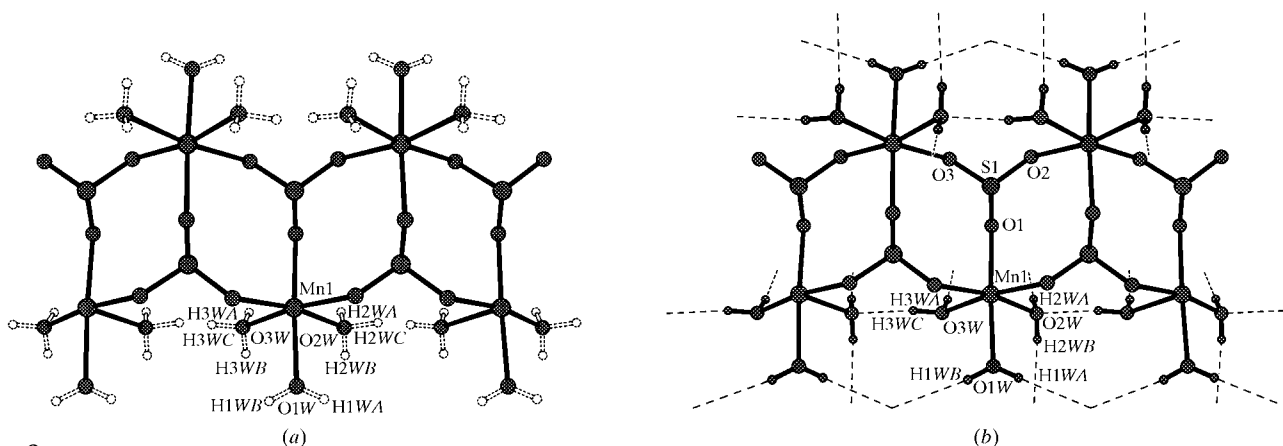


Figure 2 Schematic diagrams presenting (a) the possible H-atom positions and (b) their correct assignment in $P2_12_12_1$. Note the formation of chains along the horizontal *b* direction.

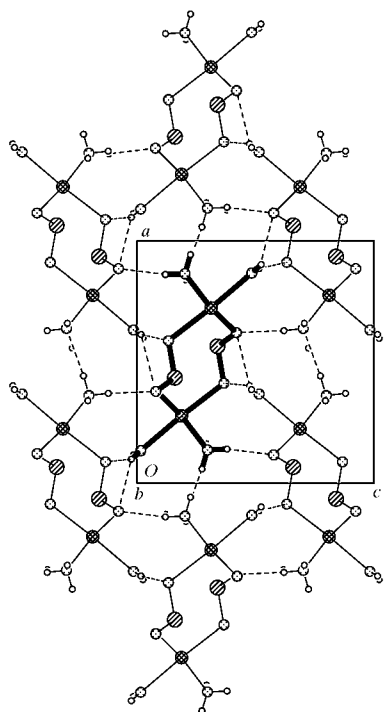


Figure 3

The packing in $P2_12_12_1$, viewed along the chain direction, showing a central chain (bold lines) connected to six different neighbours (thin lines). The inter-chain hydrogen-bonding interactions are indicated by broken lines.

ences, however, do not affect the compactness of the material, as the two structures differ in their crystal densities by less than 1%.

Experimental

The title compound was prepared as described by Baggio & Baggio (1976) by allowing equimolar aqueous solutions of $MnSO_4$ and Na_2SO_3 to diffuse slowly in a U-shaped tube through a much denser Na_2SO_4 solution, which acted both as a separation medium (avoiding initial mixing of the original solutions) and as a deterring agent (slowing down the diffusion rate). After a few weeks, colourless prisms adequate for X-ray diffraction analysis were observed at the glass walls.

Determination in $P2_12_12_1$

Crystal data

$Mn(SO_3)(H_2O)_3$
 $M_r = 189.05$
 Orthorhombic, $P2_12_12_1$
 $a = 9.7577$ (10) Å
 $b = 5.6319$ (6) Å
 $c = 9.5579$ (10) Å
 $V = 525.25$ (10) Å³

$Z = 4$
 $D_x = 2.391$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 2.86$ mm⁻¹
 $T = 295$ (2) K
 Prism, colourless
 $0.16 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)
 $T_{min} = 0.658$, $T_{max} = 0.804$

4391 measured reflections
 1190 independent reflections
 1152 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.021$
 $\theta_{max} = 27.9^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.052$
 $S = 0.97$
 1190 reflections
 99 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.26P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.28$ e Å⁻³
 $\Delta\rho_{min} = -0.29$ e Å⁻³
 Absolute structure: Flack (1983),
 424 Friedel pairs
 Flack parameter: 0.45 (4)

Table 1

Selected geometric parameters (Å, °) for (I) in $P2_12_12_1$.

Mn—O1	2.1673 (13)	Mn—O3W	2.242 (2)
Mn—O2 ⁱ	2.162 (2)	S—O1	1.5202 (13)
Mn—O3 ⁱⁱ	2.185 (2)	S—O2	1.522 (2)
Mn—O1W	2.1647 (14)	S—O3	1.533 (2)
Mn—O2W	2.236 (2)		
O1 ⁱ —Mn—O2	96.40 (10)	O3 ⁱⁱ —Mn—O1W	85.64 (11)
O1—Mn—O3 ⁱⁱ	94.40 (10)	O3 ⁱⁱ —Mn—O2W	93.30 (9)
O1—Mn—O1W	176.08 (8)	O3 ⁱⁱ —Mn—O3W	171.50 (9)
O1—Mn—O2W	89.43 (10)	O1W—Mn—O2W	86.66 (11)
O1—Mn—O3W	90.19 (10)	O1W—Mn—O3W	89.28 (10)
O2 ⁱ —Mn—O3 ⁱⁱ	95.58 (6)	O2W—Mn—O3W	79.58 (5)
O2 ⁱ —Mn—O1W	87.49 (11)	O1—S—O2	104.65 (14)
O2 ⁱ —Mn—O2W	168.96 (9)	O1—S—O3	104.21 (13)
O2 ⁱ —Mn—O3W	91.00 (9)	O2—S—O3	104.36 (8)

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

Table 2

Hydrogen-bond geometry (Å, °) for (I) in $P2_12_12_1$.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WA \cdots O1 ⁱⁱⁱ	0.79 (3)	2.44 (3)	3.227 (4)	172 (5)
O2W—H2WA \cdots O3 ^{iv}	0.79 (3)	1.90 (4)	2.686 (5)	171 (6)
O3W—H3WA \cdots O2 ^v	0.80 (3)	1.92 (3)	2.711 (4)	171 (3)
O1W—H1WB \cdots O1 ^v	0.77 (3)	2.42 (3)	3.134 (4)	155 (5)
O2W—H2WB \cdots O3W ^{vi}	0.79 (2)	2.04 (3)	2.830 (2)	176 (3)
O3W—H3WC \cdots O2W ^{vii}	0.81 (3)	1.99 (3)	2.766 (2)	158 (3)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (v) $-x + \frac{3}{2}, -y + 2, z + \frac{1}{2}$; (vi) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x, y - 1, z$.

Determination in $Pnma$

Crystal data

$Mn(SO_3)(H_2O)_3$
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 Orthorhombic, $Pnma$
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$Z = 4$
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 Prism, colourless
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Data collection

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4138 measured reflections
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Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.068$
 $S = 1.35$
 670 reflections
 59 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0226P)^2 + 0.7961P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.30$ e Å⁻³
 $\Delta\rho_{min} = -0.33$ e Å⁻³

Table 3
Selected geometric parameters (\AA , $^\circ$) for (I) in *Pnma*.

Mn—O1	2.166 (3)	Mn—O2W	2.2396 (19)
Mn—O2 ⁱ	2.1716 (18)	S—O1	1.519 (3)
Mn—O1W	2.167 (3)	S—O2	1.5289 (18)
O1—Mn—O2 ⁱ	95.34 (7)	O2 ⁱⁱ —Mn—O2W	92.15 (7)
O1—Mn—O2W	89.82 (8)	O1W—Mn—O2W	87.99 (9)
O2 ⁱ —Mn—O2 ⁱⁱ	95.39 (11)	O2W—Mn—O2W ⁱⁱⁱ	79.78 (10)
O2 ⁱ —Mn—O1W	86.58 (8)	O1—S—O2	104.38 (10)
O2 ⁱ —Mn—O2W	170.43 (8)	O2 ⁱⁱⁱ —S—O2	104.63 (15)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + 1$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $x, -y + \frac{3}{2}, z$.

Table 4
Hydrogen-bond geometry (\AA , $^\circ$) for (I) in *Pnma*.

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1W...O2 ^{iv}	0.72 (4)	2.47 (4)	3.062 (3)	141 (4)
O2W—H2WA...O2 ^v	0.80 (4)	1.91 (4)	2.698 (3)	167 (4)
O2W—H2WB...O2W ^{vi}	0.73 (6)	2.10 (6)	2.834 (4)	178 (7)
O2W—H2WC...O2W ^{vii}	0.93 (6)	1.89 (6)	2.759 (4)	154 (5)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + 1$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $x, -y + \frac{3}{2}, z$; (iv) $-x + \frac{3}{2}, -y + 2, z + \frac{1}{2}$; (v) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (vi) $-x + 2, -y + 2, -z + 1$; (vii) $x, -y + \frac{5}{2}, z$.

Table 5
Statistics of violations to (eventual) systematic absences.

	Along <i>a</i>	Along <i>b</i>	Along <i>c</i>
SO	<i>bcn</i> 2 ₁	<i>acn</i> 2 ₁	<i>abn</i> 2 ₁
<i>N</i> (tot)	140 135 133 10	239 238 233 6	144 148 138 8
<i>N</i> (σ)	81 95 36 1	216 209 211 1	57 99 82 0
$\langle I \rangle$	145.3 153.0 3.9 0.6	362.6 398.7 402.1 1.1	4.2 189.4 201.7 0.5
$\langle I/\sigma \rangle$	1 1 5.9 17.4 2.5 1.5	37.0 37.9 38.6 1.2	3.5 20.7 21.3 0.8

Notes: SO: eventual symmetry operations defining conditions among *hkl* indices; *N*(tot): total number of reflections to which the former condition applies; *N*(σ): subset of *N*(tot) with $I > 3\sigma(I)$ [number of violations to a $3\sigma(I)$ level]; $\langle I \rangle$: mean intensity of the group; $\langle I/\sigma \rangle$: mean intensity (in units of σ).

Owing to the real or strong pseudosymmetry presented by non-H atoms in both possible space groups, three plausible candidates for the two H atoms corresponding to each of the two controversial aqua molecules (O2W and O3W) clearly appeared in the difference

Fourier map (see Fig. 2*a*). In *P2₁2₁2₁*, the correct set was chosen through a combination of steric arguments and least-squares refinement, which was extremely sensitive to the correct choice (*R*/*wR* factors: 0.0199/0.0520 and 0.0215/0.0579). The model with lower *R* effectively seems to correspond to the set reported by Gonschorek *et al.* (1996). However, and in spite of the extremely accurate data set (*R*_{int} = 0.020), refinement of the H atoms in the non-centrosymmetric space group was not possible without the use of restraints [O—H = 0.80 (5) \AA and *U*_{iso}(H) = 0.06 (4) \AA^2]. The refinement also required an allowance for racemic twinning (0.45/0.55). In the *Pnma* refinement, the split H-atom positions and their *U*_{iso} values converged quite smoothly to reasonable values without the need for any external restraint.

For both determinations, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2005).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3010). Services for accessing these data are described at the back of the journal.

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