

Revision of the  $\text{Mg}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  crystal structure

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A revision is presented of the restrained Rietveld analysis of the crystal structure of magnesium perchlorate tetrahydrate,  $\text{Mg}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ , recently published by Robertson & Bish [(2010), *Acta Cryst.* **B66**, 579–584]. The actual symmetry of the material is shown to be  $C2/m$ . The corrected structure model is refined by the derivative difference method [Solovyov (2004). *J. Appl. Cryst.* **37**, 743–749], anisotropically for all non-H atoms and isotropically for two independent H atoms without restraints.

In the X-ray powder diffraction (XRPD) crystal structure analysis of  $\text{Mg}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  recently reported by Robertson & Bish (2010), the authors applied the charge-flipping algorithm and the restrained Rietveld refinement that gave a structure model in the  $C2$  space group. The resultant difference between the observed and calculated XRPD patterns was enormous, making the results quite dubious. A revision of the structure using the diffraction data from the supplementary materials of Robertson & Bish (2010) reveals that the actual symmetry of the material is  $C2/m$ . The  $C2/m$  structure model is refined without restraints using the derivative difference method (DDM; Solovyov, 2004) that gave a perfect fit of the calculated XRPD profile to the experiment (Fig. 1). The only notable residuals on the difference curve are due to parasitic reflections from the NiCr substrate of the high-temperature chamber.

The structure is refined anisotropically for all non-H atoms. The positions and isotropic displacement parameters of two independent H atoms are successfully refined without restraints, signifying an excellent quality of the model. The calculated XRPD intensities were corrected for the preferred orientation, the primary beam overflow and the finite sample thickness. The systematic peak shifts due to the sample surface displacement and the X-ray beam divergence were taken into account. The anisotropic peak broadening was refined using the model of Popa (1998). The refinement details and the resultant geometric parameters of the structure are listed in Tables 1 and 2. The respective data and parameter files for the DDM program (Solovyov, 2006) are included in the supplementary material.<sup>1</sup> The high-angle data interval after  $85^\circ 2\theta$  was excluded from the refinement as it was affected by strong parasitic peaks from the NiCr substrate.

The DDM refinement was also attempted in the  $C2$  space group both isotropically and anisotropically for the non-H atoms. The isotropic refinement resulted in a worse profile fit [ $R\text{-DDM} = 0.066$ ,  $R_{\text{Bragg}} = 0.027$ ,  $R(F) = 0.044$ ,  $\chi^2 = 4.11$ ], negative  $B_{\text{iso}}$  values of Mg and some O atoms, and the absence of convergence in the refinement of H positions. The anisotropic refinement in  $C2$  gave negligible improvements in the profile fit [ $R\text{-DDM} = 0.054$ ,  $R_{\text{Bragg}} = 0.009$ ,  $R(F) = 0.016$ ,  $\chi^2 = 3.36$ ] compared with that obtained for  $C2/m$  (Table 1). The resultant structural parameters of the  $C2$  model are listed in Table S1 and the refined atomic coordinates for  $C2/m$  and  $C2$  are compared in Table S2 of the supplementary material. The refined  $C2$  model features notably larger estimated standard uncertainties (e.s.u.);

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: KD5057). Services for accessing these data are described at the back of the journal.

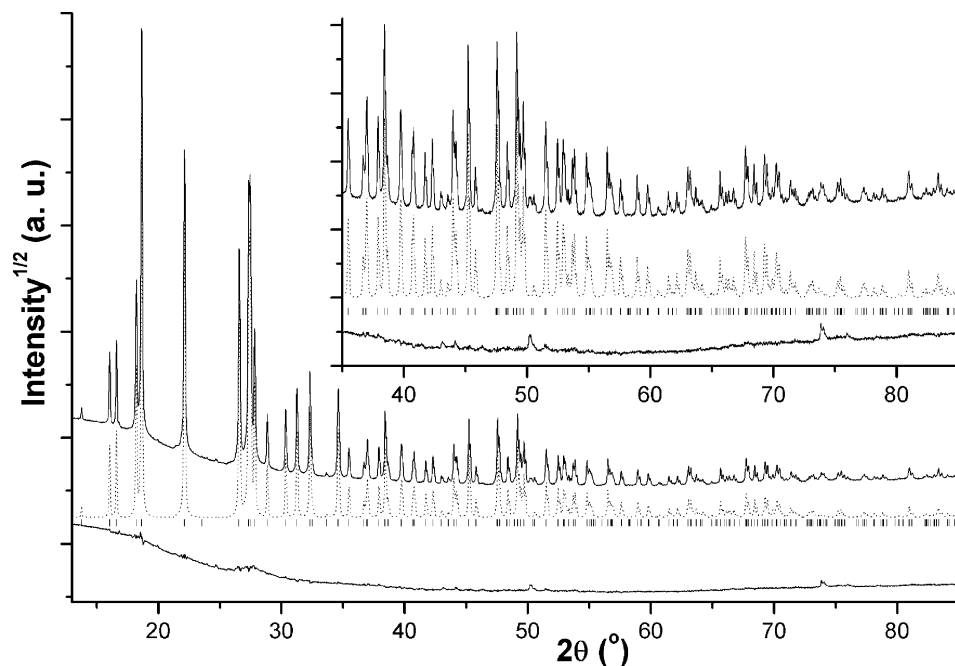
**Table 1**  
Experimental details.

Crystal data	
Chemical formula	Cl <sub>2</sub> H <sub>8</sub> MgO <sub>12</sub>
<i>M<sub>r</sub></i>	295.26
Crystal system, space group	Monoclinic, <i>C2/m</i>
Temperature (K)	348
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.4802 (2), 8.0016 (4), 5.9363 (2)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 112.3169 (8), 90
<i>V</i> (Å <sup>3</sup> )	504.46 (3)
<i>Z</i>	2
Radiation type	Cu <i>K</i> $\alpha$ , $\lambda$ = 1.5406, 1.5444 Å
Specimen shape, size (mm)	Flat sheet, 10 × 14
Data collection	
Specimen mounting	Ni–Cr plated copper front-loaded sample mount
Data collection mode	Reflection
Scan method	Step
2 $\theta$ values (°)	2 $\theta_{\min}$ = 10, 2 $\theta_{\max}$ = 85, 2 $\theta_{\text{step}}$ = 0.017
Refinement	
<i>R</i> factors and goodness of fit	<i>R</i> -DDM = 0.055, <i>R</i> -DDM <sub>exp</sub> = 0.016, <i>R</i> <sub>Bragg</sub> = 0.011, <i>R</i> ( <i>F</i> ) = 0.020, $\chi^2$ = 3.43
No. of data points	4417
No. of parameters	76
No. of restraints	0

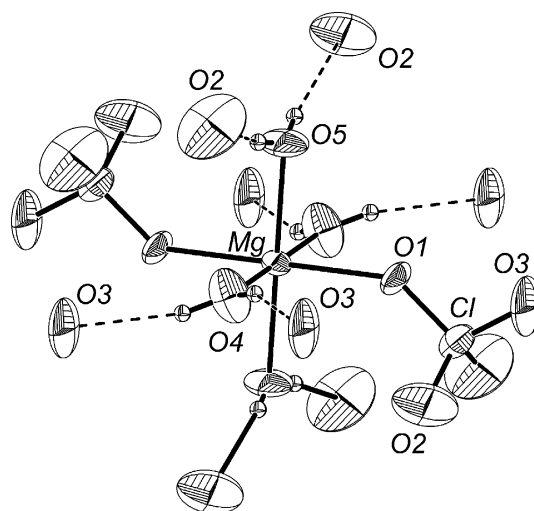
**Table 2**  
Selected geometric parameters (Å, °).

Cl–O1	1.440 (4)	Mg–O4	2.011 (4)
Cl–O2	1.397 (4)	Mg–O5	2.061 (6)
Cl–O3	1.423 (5)	O4–H1	0.83 (3)
Mg–O1	2.100 (3)	O5–H2	0.83 (3)
O1–Cl–O2	108.34 (15)	O1–Mg–O5 <sup>ii</sup>	93.22 (14)
O1–Cl–O3	107.2 (3)	Mg–O4–H1	126 (2)
O2–Cl–O2 <sup>i</sup>	113.3 (4)	H1–O4–H1 <sup>ii</sup>	109 (4)
O2–Cl–O3	109.72 (17)	Mg–O5–H2	104 (3)
O1–Mg–O5	86.78 (14)	H2–O5–H2 <sup>i</sup>	144 (4)

Symmetry code(s): (i) *x*,  $-y$ , *z*; (ii)  $-x$ , *y*,  $-z$ .



**Figure 1**  
Observed, calculated (dashed line) and difference XRPD profiles after DDM refinement.



**Figure 2**  
Ellipsoid plot of Mg(ClO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O crystal structure.

Table S2), much worse geometric parameters of the H<sub>2</sub>O groups (Table S1) and invalid displacement ellipsoids of some O atoms (Fig. S1). The differences in the atomic coordinates between the *C2/m* and *C2* models (Table S2) only slightly exceed 3 e.s.u. values mostly for the H atoms, which suggests that the differences are virtually insignificant considering the well known underestimation of the powder diffraction standard uncertainties.

An ellipsoid plot of the structure is shown in Fig. 2. The highly anisotropic displacement ellipsoids of O and Cl atoms are indicative of the structural disorder due to, apparently, the high-temperature transformation. The anisotropy of the O5 atom disorder explains the unexpectedly large value of the H2–O5–H2 angle since the H-atom positions in the structure result from the statistical averaging of H<sub>2</sub>O displacements.

The structural disordering revealed might be the reason for the erroneous space-group assignment by Robertson & Bish (2010) as the charge-flipping algorithm is normally started from the lowest symmetry. The example presented demonstrates that structure solutions involving the restrained Rietveld refinement must be validated with special care and all possible attempts should be made at the unrestrained refinement since the application of restraints disables the use of geometric and displacement parameters as the structure reliability indicators.

## References

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