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Assignment of a Space Group for $[Co(meen)_2(en)]Br_3 \cdot H_2O$

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In the preceding article [1] Marsh has suggested an alternative space group for the crystal structure of $[Co(meen)_2(en)]Br_3 \cdot H_2O$ (meen = *N*-methylethane-1,2-diamine), determined in these laboratories [2]. The compound was reported to crystallize in the centrosymmetric space group *I*2/*a* with eight formula units in the unit cell. The asymmetric unit in this setting is comprised of two unique halves of complex cations (each situated about a crystallographic two-fold axis), three bromide atoms in general positions, and two solvent water molecules of crystallization (each situated about a crystallographic two-fold axis). The two unique complex cations comprising the asymmetric unit are enantiomorphic, being related to each other by a pseudo-mirror plane. The presence of two closely related entities in the asymmetric unit poses the question as to whether a higher symmetry space group would be more appropriate [3]. However, an examination of interionic contacts in the lattice involving the bromide anions was thought to be consistent with the presence of three crystallographically unique bromide anions, i.e. *I*2/*a*. A satisfactory refinement in that space group, without problems with correlation effects, yielded final refinement details as listed in the original article [1] and in Table 1.

The application of a transformation matrix $[10\bar{1}, 010, 101]$ to the *I*2/*a* cell yields a metric cell and systematic absences consistent with the orthorhombic space group *Fddd*; this is the space group recommended by Marsh [1]. In this setting the asymmetric unit, by virtue of the higher crystallographic symmetry, is comprised of half a complex cation, a bromide anion and a water molecule, each situated on a crystallographic two-fold axis, and a bromide anion in a general position. The *Fddd* model was refined using the published coordinates [1] as a starting set. A full-matrix least-squares refinement based on *F* was performed with anisotropic thermal parameters for non-hydrogen atoms and hydrogen atoms included in the model at their calculated positions [4]. A weighting scheme of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ was introduced and the refinement continued until convergence. In all respects the refinement proceeded as for the original analysis [2]. Final refinement details for the *Fddd* setting are listed in Table 1.

On the basis of standard significance tests [5], it is evident that the refinement in the *I*2/*a* model results in a lower residual (Table 1), in particular for the R_g values (those recommended by Sheldrick [4]). However, it is noted that any differences in the residuals are not great and that both refinements yield chemically reasonable models for the structure of $[Co(meen)_2(en)]Br_3 \cdot H_2O$. The derived parameters for the *Fddd* model are available as Supplementary Material. It is worth emphasising that in both space groups the crystallographic results lead to the same chemical conclusions.

TABLE 1. Refinement details for $[Co(meen)_2(en)]Br_3 \cdot H_2O$

Space group	*I*2/*a* [a]	*Fddd*
R	0.038	0.039
g	0.0033	0.0075
R_w	0.041	0.044
R_g	0.053	0.060
No. of reflections	1693	1025
No. of refined parameters	186	94

[a] From ref. 2.

Supplementary Material

Tables of fractional atomic coordinates, thermal parameters, interatomic parameters and structure factor amplitudes are available from the author on request.

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