

## Validation of a Twinned Pseudo Symmetric Crystal using a Hierarchical Pathway

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An apparently monoclinic crystal of  $[\text{Mn}(\text{cyclam})(\text{NCO})_2]^+\cdot\text{ClO}_4^-$ , (cyclam is the tetradentate ligand 1,4,7,11-tetraazacyclotetradecane) was shown to be a 0.545(1) : 0.455 twin, space group  $C-1$ ,  $Z = 16$ , that is best described as a commensurate occupational and displacive modulation of a  $Z = 4$  idealised parent structure with space group  $A2/a$  and  $\mathbf{ap} = \mathbf{a}/2$ ,  $\mathbf{bp} = \mathbf{b}/2$ ,  $\mathbf{cp} = \mathbf{c}$ .

The quality of refinement is very pathway dependent. Success requires using constraints inspired by the pseudo symmetry. A hierarchical approach to solution and refinement obtained sequentially structures in space groups  $A2/a$ ,  $P2_1/n$ ,  $P-1$  and finally  $C-1$ . Major and minor components of the reflection intensities could be identified using irreducible representations of  $A2/a$  and  $P2_1/n$  to symmetrise the scattering density so that any reflection is associated with two symmetrised components. The  $h$  odd,  $k$  odd reflections are associated with a doubly degenerate irreducible representation, offering a choice for the creation of two  $C-1$  substructures that allowed identification of those parameter combinations worst determined and thus the best choice of constraints for optimising the refinement pathway.

Comparative refinement was used to show the correctness of the final structure solution and how appropriately chosen constrained refinement allowed escape from false minima.

**Keywords:** pseudo symmetry, twinning, constrained refinement