Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Space groups $P1$ and Cc: how are they doing?

Richard E. Marsh

The Beckman Institute, California Institute of Technology, Pasadena, CA 91125, USA

Correspondence e-mail: rmarsh@caltech.edu

Received 5 June 2009
Accepted 4 November 2009

A survey of recent entries in the Cambridge Structural Database suggests that the percentage of structures described in space groups of inappropriately low symmetry has decreased from about 10% in the early 2000s to less than 5% today for space group Cc, but that for space group $P1$ it remains close to 8%.

1. Introduction

This paper is an extension of four previous surveys (Marsh, 1997, 1999, 2004, 2005) of crystal structures which were reported in the Cambridge Structural Database (CSD; Allen *et al.*, 2002) as belonging to either space group $P1$ (Marsh, 1999, 2005) or to Cc (Marsh, 1997, 2004), but that should be revised to space groups of higher symmetry. At about the time of the two most recent surveys (which reflected results from the early 2000s), the majority of journals containing crystal-structure reports began to strongly encourage (or even to insist) that such reports be examined by structure-checking computer routines such as *PLATON* (Spek, 2003) or *checkCIF* before acceptance. The purpose of this paper is to examine how successful this policy has been in improving the reliability of crystallographic results.

2. Experimental

This survey was based on an examination of entries in the CSD dating from 2004 for space group Cc and from 2006 for $P1$, and ending with the Version 5.29 updates of August 2009. For most of the suspicious entries, CIFs could be recovered and the structural details (including the U^{ij} values and the refinement details) examined; in some cases only coordinates were available. With few exceptions (*e.g.* 'private communication') the original paper was also consulted. For a few entries, the higher-symmetry structure had already been reported in the CSD (with a different extension to the REFCODE); these entries are not included in the survey.

The 133 revised structures noted here, tabulated according to their REFCODES, and the accompanying references are available as supplementary material.[1] Individual CIFs, which include brief descriptions of the revisions, have been submitted to the CSD. (Included in the supplementary material are revisions to 11 structures originally described in space groups other than $P1$ or Cc; these 11 were reported as companion structures in the same papers that described $P1$ or Cc structures in need of revision.) The results of the survey are summarized in Table 1. While the statistical uncertainties of these relatively small numbers are large, the trends seem apparent: while the number of revisions has decreased noticeably for space group Cc, the decrease is less encouraging for $P1$.

3. Discussion

Until about the turn of the millenium, the frequencies of inappropriate space-group assignments were approximately 10% for both space groups $P1$ and Cc (Marsh, 1997, 1999); for Cc but not $P1$, the

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK5088). Services for accessing these data are described at the back of the journal.

Table 1
Revisions to structures originally described in space groups *P*1 (No. 1) and *Cc* (No. 9).

Space group	Year	Total No. of entries in CSD	No. of revisions
Cc	2004	311	22
Cc	2005	341	17
Cc	2006	343	13
Cc	2007	385	7
Cc	2008	139	7
*P*1	2006	286	18
*P*1	2007	337	29
*P*1	2008	94	10

frequency appears to have dropped slightly, to *ca* 8%, in the early 2000s (Marsh, 2004, 2005). The present survey indicates (Table 1) that the frequency for *Cc* is continuing to drop, and now appears to lie below 5% – an apparently encouraging sign as to the efficacy of journal policies concerning the checking of crystallographic results. However, the results for *P*1 suggest that the frequency remains at *ca* 8%. The reason for the apparent difference between the trends of the two space groups is a bit of a mystery. Perhaps it reflects a tendency for investigators to resort to *P*1 if they have trouble with the structure solution without checking if higher symmetry is available. Or, possibly, in some laboratories *P*1 may be chosen, at the beginning, as a default space group and an adequate search for higher symmetry is not always carried out.

Two groups of compounds warrant comment, and perhaps shed some light on the situation:

(i) The structures of the three compounds CIBJED, CIBKAA and CIBLOP were reported (Boyle *et al.*, 2007) in space groups *Cc*, $P\overline{1}$ and *P*1; they should be revised to *C*2/*c*, *C*2/*c* and $P\overline{1}$ (18 other structures were described in the same paper, all in appropriate space groups). In the CIFs supplied as supplementary material, the authors noted that all three of these questionable structures had been checked by *PLATON* and that the *ADDSYM* routine suggested that higher symmetries might be available. In all three cases the authors reported that they were unable to verify the higher symmetries. Indeed, in the case of CIBKAA they noted that they were able to find satisfactory solutions in each of the three space groups *P*1, *Cc* and $P\overline{1}$, but not in *C*2/*c*; they selected $P\overline{1}$ even though their success with *Cc* required the lattice symmetry and the glide planes necessary to change from $P\overline{1}$ to *C*2/*c*. There is no indication that any referee or editor followed up on the situation.

(ii) The two isostructural compounds SEWXUO and SEWYAV were described (Shiga *et al.*, 2006) in space group *P*1 even though, in both cases, the unit cells were effectively tetragonal – all three angles within 0.1° of 90.0° and the *a* and *b* axes equal within 0.002 Å. (These cell dimensions were included, as a footnote, in the original paper.) The appropriate space group is $P\overline{4}n2$. Again it is surprising that nobody along the line was curious enough about the situation to pursue it further.

Finally, we note one example where there were two distinct errors in the space-group assignment. The manganese complex POKLEH was described (Hureau *et al.*, 2008) in space group *P*1 with Z (= Z') = 4. However, the *c* axis should be halved: every molecule is related, atom for atom, to a neighboring molecule at $z + \frac{1}{2}$; in addition, the revised, smaller cell can be transformed to form a C-centered monoclinic lattice where pairs of molecules can again be matched, also within *ca* 0.01 Å, so as to comply with space group *Cc* (with Z' = 1).

All three of these examples derive from 'high-impact' journals which require evidence that crystal structure reports be checked before acceptance. It is not clear that such evidence was always provided; but it is clear that – in at least some cases – evidence for higher symmetry was present but not sufficiently examined.

For both space groups, about 80% of the revisions noted here involve the addition of a center of inversion (*P*1 to $P\overline{1}$; *Cc* to *C*2/*c*). As is well known in the crystallographic community, overlooking a center of symmetry can lead to important errors in molecular structure. The present revisions include two cases in which a sodium counter-cation was misinterpreted as a chloride ion, obviously leading to changes in the structures of the more important constituents. Reported aromatic C—C distances ranged from 1.07 (3) Å (a quadruple bond?) to 1.67 (3) Å (DOCXID); in a number of instances, H atoms needed to be either added or removed, because the peculiar C—C bond lengths led to a misinterpretation of hybridization by the positioning routine. Many solvent molecules were incorrectly identified. In some cases, drawings of the structure may be incorrect. For example, bond distances between a metal atom and a pair of its ligands which are equivalent in the correct space-group description may appear, in the incorrect description, to be so unequal that the longer distance does not lie below the bonding limit assigned by the graphics program.

Finally, we emphasize that, relative to other space groups, *P*1 and *Cc* are exceptionally prone to misinterpretation; the more common space groups such as $P2_1/c$, $P2_12_12_1$ and $P\overline{1}$ have far lower frequencies. Nevertheless, crystallography, for whatever purpose it is used, should not be comfortable with the present results. While recent journal policies appear to have led to some reduction in incorrect space-group assignments, further safeguards are needed if inappropriate assignments – which can lead to important errors in molecular structures – are to become a thing of the past.

Larry Henling and Mike Day were essential to this work. I thank them deeply.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Boyle, T. J., Sewell, R. M., Ottley, L. A. M., Pratt III, H. D., Quintana, C. J. & Bunge, S. D. (2007). *Inorg. Chem.* **46**, 1825–1835.

Hureau, C., Groni, S., Guillot, R., Blondin, G., Duboc, C. & Anxolabehere-Mallart, E. (2008). *Inorg. Chem.* **47**, 9238–9247.

Marsh, R. E. (1997). *Acta Cryst.* B**53**, 317–322.

Marsh, R. E. (1999). *Acta Cryst.* B**55**, 931–936.

Marsh, R. E. (2004). *Acta Cryst.* B**60**, 252–253.

Marsh, R. E. (2005). *Acta Cryst.* B**61**, 359.

Shiga, T., Okawa, H., Kitagawa, S. & Ohba, M. (2006). *J. Am. Chem. Soc.* **72**, 16426–16427.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.