

More Space-Group Corrections: From Triclinic to Centred Monoclinic and to Rhombohedral; Also From $P1$ to $P\bar{1}$ and From Cc to $C2/c$

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Abstract

We present 14 examples of crystal structures that were originally described as triclinic, but are properly described as either C -centred monoclinic (ten examples) or rhombohedral (four examples). There is also one example each of changes from $P1$ to $P\bar{1}$ and from Cc to $C2/c$.

1. Introduction

Following earlier papers (e.g. Baur & Tillmanns, 1986; Marsh & Herbstein, 1988; Baur & Kassner, 1992; Marsh & Bernal, 1995; Marsh, 1995, 1997; Herbstein, 1997), we report and discuss more cases in which crystal structures have been described in space groups of unnecessarily low symmetry.

2. Experimental

Identification of likely candidates for correction was by inspection of cell dimensions (particularly of the reduced cells) and atomic coordinates taken from published literature or from the October 1996 release of the CSD (Cambridge Structural Database, 1992); when a fit to higher symmetry was found, the cell and coordinates were transformed to the new setting and coordinates were averaged according to the demands of the higher symmetry. The quality of the fit of the revised structure to the reported (original) structure was assessed by calculating

$$\Delta(\text{fit}) = \left(\sum_{i=1}^n \{ [q_i - q_{\text{mean}}]^2 / (n-1) \} \right)^{1/2},$$

where q_{mean} is the averaged coordinate in the revised structure and q_i are the individual coordinate values in the reported structure; n is the number of coordinates which become equivalent in the revised structure, and is 2 or 3 in all the examples considered in this paper. We place $\Delta(\text{fit})$ in square brackets after the averaged

coordinates given in the tables of atomic coordinates, which have been deposited.† In the 14 examples where the lattice type has been changed, the $\Delta(\text{fit})$ values are approximately the same as the s.u.'s from the original structure refinement; however, in the two examples where a centre of inversion has been added the $\Delta(\text{fit})$ values are much larger, as expected.

For convenience, we remind the reader that the metric tensor (Niggli matrix) is given by [**a.a b.b c.c** **c.a a.b**] (abbreviated as [*ABCDEF*]), with standard ordering of the axes as $a < b < c$; the general background is given by Giacovazzo (1994), while specifics on the use of reduced cells to determine correct symmetries have been summarized by de Wolff (1983). The reduced cells and transformations were calculated using *BLAF* and other standard computer programs; references are given in Herbstein (1997).

3. Change from triclinic to centred monoclinic

3.1. *Tetrathiafulvene*, 2,5-bis(methylthio)-*p*-benzoquinone-bis(*N*-cyanoimine); $C_6H_4S_4C_{10}H_8N_4S_2$ (YAFZAG)

The crystal structure of this segregated-stack charge-transfer compound (abbreviated as TTF–DMeT–DCNQI) was reported (Mori & Inokuchi, 1992) to be triclinic [$a = 15.447$ (3), $b = 15.774$ (3), $c = 3.834$ (2) Å, $\alpha = 96.96$ (3), $\beta = 97.14$ (3), $\gamma = 82.24$ (3)°, $P\bar{1}$] with two crystallographically independent TTF molecules lying on centres of inversion at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(1, \frac{1}{2}, \frac{1}{2})$ and two independent DMeT–DCNQI molecules on centres of inversion at (1,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. That the structure may have been reported in a unit cell of too low symmetry was strongly suggested by the fact that suitably chosen pairs of atoms in the two purportedly independent TTF half-molecules have both their x and y coordinates separated by 0.5 and for the DMeT–DCNQI half-molecules pairs of x (and y) coordinates sum to 1.5.

The reduced cell has dimensions $a = 3.834$, $b = 15.446$, $c = 15.775$ Å, $\alpha = 82.24$, $\beta = 84.00$, $\gamma = 82.88$ ° and is Type (I). The Niggli matrix of this cell has the form $ABCDA/2A/2$ (de Wolff, 1983), and the vectors $[\bar{1}20]$, $[00\bar{1}]$ and $[0\bar{1}1]$ define a C -centred cell with $a = 30.655$, $b = 3.834$, $c = 20.534$ Å, $\alpha = 89.98$, $\beta = 130.81$, $\gamma = 90.01$ °. (The transformation from the original triclinic cell is $[201]$,

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF0003). Services for accessing these data are described at the back of the journal.

[00 $\bar{1}$] and [$\bar{1}10$].) In order to confirm the monoclinic symmetry of the structure, we obtained a listing of F values deposited with The Chemical Society of Japan (document no. 8995); for 35 randomly selected pairs of (triclinic) reflections of the types h,k,l and $h+l, k+l, \bar{l}$ (which, after transformation, should be equivalent for the C monoclinic setting), we find excellent agreement (Fig. 1). Similarly, a c glide plane for the monoclinic structure is confirmed by the systematic absence of triclinic reflections $hk0$ with $h+k$ odd. Thus, the correct space group is $C2/c$ (rather than Cc , because of the centre of inversion present in the original $P\bar{1}$).

The relationship between the monoclinic and triclinic coordinates is $x_M = 0.5x_T + 0.5y_T$, $y_M = 0.5x_T + 0.5y_T - z_T$ and $z_M = y_T$. After averaging the coordinates of equivalent atoms and incrementing the x_M and y_M coordinates by 0.25 (to place the origin at a conventional centre of symmetry), we arrive at the coordinates and $\Delta(\text{fit})$ values given in Table 1 of the supplementary data.† These $\Delta(\text{fit})$ values are, on average, approximately equal to the coordinate uncertainties reported by Mori & Inokuchi (1992). (We have omitted the H atoms, since their coordinates as obtained from the CSD lead to unsatisfactory distances and angles. The H-atom coordinates were not included in the original paper.) The TTF molecules are now centred at Wyckoff positions (a) 0,0,0 and the DMeT–DCNQI molecules at positions (c) $\frac{1}{4}, \frac{1}{4}, 0$. The structure has formal resemblances to that of bis(oxamide oximate)nickel(II)–oxamide oxime, which also has segregated stacks along [010] in space group $C2/c$ (Endres *et al.*, 1980; Herbstein & Marsh, 1982).

3.2. 1,5-Dibromotetracyclo[4.2.2.2^{2,5}0^{2,6}]dodecane, $C_{12}H_{16}Br_2$ (BAHZEP10)

This compound was reported to crystallize in space group $P\bar{1}$ with (non-reduced) cell dimensions $a = 6.609$ (2), $b = 7.318$ (2), $c = 7.485$ (2) Å, $\alpha = 69.08$ (2), $\beta = 62.24$ (1), $\gamma = 64.72$ (2)°, $Z = 1$ (Wiberg *et al.*, 1984; note that α was misprinted as 69.98° in a preliminary publication). The reduced cell has $a = 6.609$, $b = 7.318$, $c = 7.323$ Å, $\alpha = 88.83$, $\beta = 64.76$, $\gamma = 64.72$ °. This is an example of cadre (*Ib*) of Herbstein (1997), where the reduced cell has two equal edges and two equal angles (the Niggli matrix has the form $ABBDEE$). The vectors [011], [0 $\bar{1}1$] and [100] define a C -centred cell with $a = 10.458$, $b = 10.246$, $c = 6.609$ Å, $\alpha = 89.99$, $\beta = 126.69$, $\gamma = 89.96$ °, $Z = 2$. The transformed coordinates (Table 2 of the supplementary material†) are clearly compatible with space group $C2/m$. (Note that the y coordinates given by Wiberg *et al.*, 1984, Table VII, must be incremented by 0.5 to place the origin at a conventional centre of symmetry.) The symmetry of the molecule in the crystal is $2/m$ and not $\bar{1}$ as previously reported.

† See deposition footnote on p. 677.

3.3. 7,14-Dicarboethoxyacenaphth[1,2- k]fluoranthene tetracyanoquinodimethane, $C_{32}H_{22}O_4C_{12}H_4N_4$ (YAVNIS)

The triclinic cell previously reported (Plummer *et al.*, 1993) is reduced, Type (II), and has two equal edges and two equal angles [$a = 7.146$ (3), $b = 10.839$ (7), $c = 10.840$ (7) Å, $\alpha = 90.36$ (5), $\beta = 95.29$ (4), $\gamma = 95.34$ (4)°, $Z = 1$]; the two types of molecules lie on separate centres of symmetry in $P\bar{1}$. The vectors [011], [0 $\bar{1}1$] and [100] define a C -centred cell with $a = 15.281$, $b = 15.378$, $c = 7.146$ Å, $\alpha = 89.97$, $\beta = 97.55$, $\gamma = 89.99$ °, $Z = 2$. For the structure to be monoclinic and centrosymmetric, the only possible space group is $C2/m$ with both components lying on sites of $2/m$ symmetry. Unfortunately, neither the observed intensities nor the derived atomic coordinates seem to be available. However, the drawings of the structure (Figs. 2 and 3 of Plummer *et al.*, 1993) clearly suggest that both components indeed have $2m$ symmetry, with the symmetry directions [the C(18)–C(18*) axis of TCNQ and the C(6)–C(6*) axis of the substituted fluoranthene] being parallel to [0 $\bar{1}1$] of the triclinic cell – the b axis of the monoclinic cell; the ethoxy groups appear to lie on a perpendicular mirror plane. Thus, we have little doubt that this structure is properly described in $C2/m$. Professor Watson (1995) has commented that the structure was refined in the monoclinic cell (space group Cc , presumably a transcription error), but reported in the triclinic cell. The

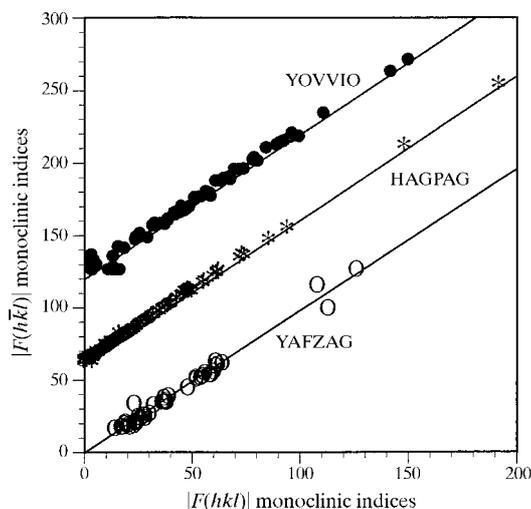


Fig. 1. Plots of $|F(h\bar{k}l)|$ against $|F(hkl)|$ (indices in the monoclinic cell) to demonstrate the presence of monoclinic symmetry. For YAFZAG $|F(h+l, k+l, -l)|$ is plotted against $|F(hkl)|$ (both triclinic indices); the correlation coefficient $R^2 = 0.9815$. For HAGPAG $1/2|F(h-k, -k, l-k)|$ is plotted against $1/2|F(hkl)|$ (both triclinic indices); the factor $1/2$ was introduced so that a single diagram could be used for all three plots); the correlation coefficient $R^2 = 0.9989$. For YOYVIO $|F(-k, h, l)|$ is plotted against $|F(hkl)|$ (both triclinic indices); the correlation coefficient $R^2 = 0.9834$. For clarity, successive plots have been shifted by 60 units along the vertical axis.

true symmetry of the structure can only be confirmed by access to appropriate experimental data.

3.4. *2-Acetylmethylidene-3-(2,4-dibromophenyl)-5-phenyl-2,3-dihydro-1,3,4-thiadiazole*, $C_{17}H_{12}Br_2N_2OS$ (HAGPAG)

This correction has been noted by Marsh (1995), but we discuss it again because the original authors had considered, but rejected, the possibility of higher symmetry. The structure was originally reported in a non-reduced cell [$a = 12.937$ (2), $b = 13.429$ (2), $c = 13.489$ (2) Å, $\alpha = 60.14$ (1), $\beta = 74.59$ (1), $\gamma = 58.70$ (1)°, space group, $Z = 4$],[†] with two molecules (*A* and *B*) in the asymmetric unit (Pandya *et al.*, 1993). Pandya *et al.* (1993) comment that ‘...molecules *A* and *B* are essentially identical. We checked carefully for higher symmetry..., especially since there is a pseudo-monoclinic *C*-centred cell that can be derived from the triclinic cell. However, normally equivalent reflections in the monoclinic cell did not have the same intensity, and the final structure showed that molecules *A* and *B* are not related by a monoclinic symmetry element’. Nevertheless, it has been shown (Marsh, 1995) that the vectors $[2\bar{1}0]$, $[010]$ and $[\bar{1}01]$ of the original cell give a *C*-centred monoclinic cell, with $a = 22.108$, $b = 13.429$, $c = 16.018$ Å, $\alpha = 90.02$, $\beta = 133.09$, $\gamma = 89.97^\circ$, $Z = 8$, with atomic coordinates consistent with space group *C2/c*. We also note that inspection of the triclinic coordinates given in Table 2 of Pandya *et al.* (1993) shows that for all pairs of corresponding atoms in the two molecules $x_A + x_B = 0.5$ and $z_A + z_B = 0.5$ [the signs of the *y* and *z* coordinates of *C*(10*B*) were obviously incorrect], strongly suggesting that the symmetry is higher than triclinic.

In order to check the Laue symmetry, we obtained the F_{obs} values from the CISTI Depository of Unpublished Data of the National Research Council of Canada and found excellent agreement between the intensities of pairs of reflections hkl and $h\bar{k}l$ in the monoclinic setting (hkl and $h - k, \bar{k}, l - k$ in the triclinic setting; Fig. 1). Similarly, a *c* glide plane in the monoclinic cell is indicated by the systematic absence of triclinic reflections of the type $h0l$ with $h + l$ odd (Fig. 2). Thus, the space group is *Cc* or *C2/c*, the latter being required because of the successful refinement in $P\bar{1}$. The *C2/c* coordinates were deposited with the CSD by Marsh (1995).

3.5. *3-(p-Chlorophenyl)-1-methyltriazene-1-oxide*, $C_7H_8N_3OCl$ (KORZIA)

This structure was described as triclinic, $a = 9.182$ (2), $b = 20.941$ (3), $c = 4.742$ (1) Å, $\alpha = 96.44$ (1), $\beta =$

[†] We remark that whenever a triclinic cell angle is greater than 120°, or less than 60°, the cell is certainly not reduced. A number of the triclinic cells cited here (HAGPAG, WEGTUX, BALFEZ and ENICCU) show this feature in their originally reported structures.

104.94 (3), $\gamma = 95.14$ (2)°, $Z = 4$ (Andreotti *et al.*, 1991). The space group reported by Andreotti *et al.* (1991) is *P1*; however, coordinates are given for only two independent molecules and these coordinates, when assigned to space group $P\bar{1}$, lead to entirely satisfactory packing distances. The authors also state that the structure was solved by ‘centrosymmetric direct methods’ and that there are ‘two molecules in the asymmetric unit’, so there can be little doubt that the space group was misprinted. (There are many, many other examples in the recent literature where the space group $P\bar{1}$ has been misprinted as *P1*, presumably owing to the inability of some word processors to produce an overline symbol.) Except for a cyclic permutation of axes, the original triclinic cell is reduced; after permutation the Niggli matrix has the form $ABCD - A/2 - A/2$, which suggests transformation to *C*-centred monoclinic.

We confirmed monoclinic symmetry from the structure factor listing given in the British Library Supplementary Publication No. 63154. We entered the 583 triclinic hkl reflections into our computer, transformed their indices in accordance with lattice character 27 and averaged the F_{obs} according to Laue symmetry *2/m*; the value of R_{merge} was 0.036 for 196 pairs of equivalent reflections – appreciably lower than the final *R* reported by the authors, 0.059. The *c* glide plane in *C2/c* (preferred over *Cc*, because of the successful refinement in $P\bar{1}$) should lead to the systematic absence of reflections $hk0$ with $h + k$ odd in the triclinic setting; of the 105 $hk0$ reflections in the listing [which, presumably, contained those reflections with $I > 3\sigma(I)$], only two violators (920 and 0,15,0) were present. Both were extremely weak. A further strong indication that the structure should be described in a unit cell of higher symmetry lies in the list of coordinates (CSD; they are

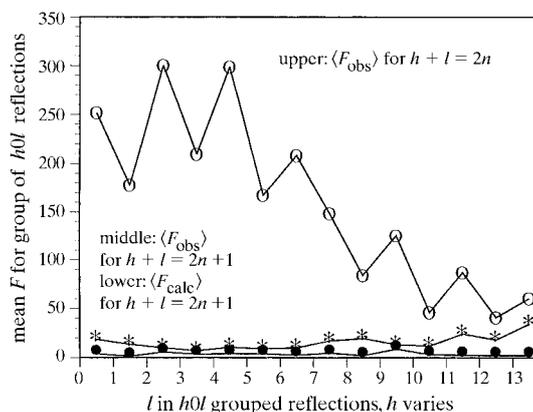


Fig. 2. Demonstration of the occurrence of a *c* glide plane in the monoclinic space group of HAGPAG. Triclinic indices are used in the figure and caption. The mean values of groups of $|F(\text{obs})|$ for $h0l$ ($h + l$ even) and $h0l$ ($h + l$ odd) reflections are shown. For the latter set of groups there appears to be a systematic error which increases in size as *l* increases; the mean values of $F(\text{calc})$ ($h + l$ odd) are very small for all values of *l*.

not contained in the original paper): both the x and the y coordinates of corresponding atoms in the two molecules differ, almost exactly, by 0.5. The vectors (201), (001) and $(\bar{1}\bar{1}\bar{1})$ applied to the original cell lead to a C -centred monoclinic cell ($a = 17.743$, $b = 4.742$, $c = 21.590$ Å, $\alpha = 90.07$, $\beta = 106.97$, $\gamma = 89.98^\circ$, $Z = 8$); the corresponding transformation of the coordinates ($x_M = 1/2x_T - 1/2y_T$; $y_M = -1/2x_T - 1/2y_T + z_T$; $z_M = -y_T$) leads to a structure which conforms very closely to space group $C2/c$. Averaging over the two purportedly independent molecules leads to the coordinates in Table 3 of the supplementary material.†

Andreotti *et al.* (1991) concluded that there were 'two slightly different types of molecule in the unit cell', but this is not correct, although the matching of coordinates which we obtain in our $C2/c$ description is noticeably worse than usual; the average $\Delta(\text{fit})$ value (Table 3 of the supplementary material†) is ~ 0.03 Å, while the s.u.'s in the bond lengths reported by Andreotti *et al.* (1991) ranged from 0.03 to 0.06 Å. The evidence summarized above shows that there can be no doubt that the correct space group is $C2/c$ and that the relatively poor matching was due to the quality of the data. The structure-factor listing contained only 583 entries; when merged according to Laue symmetry $2/m$, only 386 reflections for 109 parameters resulted (neglecting H atoms), with the hardly acceptable reflection/parameter ratio of 3.5.

3.6. (*Z*)-Acetophenone oxime, C_8H_9NO (FAKROY)

This structure was described in space group $P1$ (explicitly noted as 'azentrisch'), $Z = 4$, with $a = 7.075$ (5), $b = 7.281$ (8), $c = 15.194$ (5) Å, $\alpha = 75.69$ (5), $\beta = 76.71$ (4), $\gamma = 89.92$ (8)° (Gieren *et al.*, 1986b); the reduced cell has $a = 7.075$, $b = 7.281$, $c = 15.139$ Å, $\alpha = 103.47$, $\beta = 103.30$, $\gamma = 90.08^\circ$ [Type (II)]. The cell dimensions were measured with Mo $K\alpha$ from 8 reflections in the range $4.25 \leq \theta \leq 8.56^\circ$ and thus high accuracy is perhaps not to be expected; indeed, Gieren *et al.* (1986b) did ascribe 'die relativ schlechte Qualität der Meßdaten' to a slow solid-state E to Z transformation at room temperature. The Niggli matrix is 50.06 53.01 229.18 -25.67 -24.64 -0.07 , which can be taken to fit lattice characters 37 ($ABCD -A/2$ 0), 41 ($ABC -B/2$ E 0), 42 ($ABC -B/2 -A/2$ 0; orthorhombic) or 43 ($ABCDEF$; D and F have conditions). Such ambiguities owing to inaccuracies in cell dimensions can occur when a decision about the transformation type is based on cell dimensions alone (*cf.* Herbstein, 1997). The reduced cell of FAKROY can be described as belonging to cadre (Ib) of Herbstein (1997), with $a_{\text{red}}/2c_{\text{red}} = 0.23367$ and $\cos \beta = -0.23005$, and this favours lattice character 37; the ambiguity at this stage would have had to be eliminated by the study of intensity relations. We resolve the

problem here by considering the relations among (the published) coordinates; corresponding atoms in molecules 1 and 2, and in molecules 3 and 4, have essentially identical z coordinates and y coordinates differing by 0.5 (such relations were also noted by Gieren *et al.*, 1986b, who described them as pseudo-symmetric). The vectors $[10\bar{2}]$, $[\bar{1}00]$ and $[010]$ of the original cell define a C -centred cell with $a = 29.574$, $b = 7.075$, $c = 7.281$ Å, $\alpha = 90.08$, $\beta = 104.69$, $\gamma = 90.17^\circ$, $Z = 8$; the coordinate transformation $(00\frac{1}{2})$, $(\bar{1}0\frac{1}{2})$ and (010) leads to values that are compatible with space group Cc , with two crystallographically independent molecules per asymmetric unit. We note that Gieren *et al.* (1986b) reported that the intensity data had approximate $2/m$ Laue symmetry (but not pseudo-orthorhombic mmm symmetry) and that the structure has the approximate symmetry of space group Ia (an alternative setting of Cc). However, there is no indication that they attempted to refine a monoclinic model; if they had, they surely would have found that the structure conforms to Cc within the experimental s.u.'s (Table 4 of the supplementary material†). One consequence is that the four crystallographically independent molecules in the chiral $P1$ space group of the earlier report now become two groups of two racemic pairs in the achiral, but non-centrosymmetric, Cc space group.

The deviations of the angles α and γ from 90° are somewhat larger than usual, but by no means out of line with many other similar examples. Deviations of ~ 0.2 – 0.3° have been reported in FUPBIB (Huang *et al.*, 1988, corrected to $C2$ by Kapon & Reisner, 1989) and DIHCOM (Marsh, 1997). We must always bear in mind that these s.u.'s are measures of precision only and hence do not take into account many types of systematic error (Taylor & Kennard, 1986). The true symmetry of the lattice is determined far more reliably by the symmetry of the entire structure than by cell dimensions obtained from the setting angles of a few fiduciary reflections.

3.7. Bis(*L*-histidinato-*O,N,N'*)-bis(*L*-histidinato-*N,N'*)-(μ_2 -oxo)-divanadium(III) dihydrate, $C_{24}H_{32}N_{12}O_9V_2 \cdot 2(H_2O)$ (WEGFIX)

This structure was described in the reduced cell with $a = 10.100$ (1), $b = 10.100$ (1), $c = 10.646$ (1) Å, $\alpha = 62.54$ (1), $\beta = 62.52$ (1), $\gamma = 87.68$ (1)°, space group $P1$, $Z = 1$ (Kanamori *et al.*, 1993). Suspicion surely lurks in the equivalences $a = b$ and $\alpha = \beta$ [this is cadre (Ib) of Herbstein, 1997]. The indicated transformation to a C -centred monoclinic cell is $[110]$, $[\bar{1}\bar{1}0]$ and $[00\bar{1}]$ (de Wolff, 1983), yielding $a = 14.570$, $b = 13.991$, $c = 10.646$ Å, $\alpha = 90.01$, $\beta = 129.76$, $\gamma = 90.00^\circ$, $Z = 2$. Coordinate transformation and averaging according to space group $C2$ leads to the values in Table 5 of the supplementary material.† In this revised structure the bridging O1 atom lies on a crystallographic C_2 axis.

† See deposition footnote on p. 677.

3.8. *Tris(tetra-*n*-butylammonium) octadecatungstoperchlorate*, $3(C_{16}H_{36}N)^+(Cl_2O_{62}W_{18})^{3-}$ (WEGTUX)

This compound was described as having an α -Dawson (Dawson, 1953) mixed-valence tungstoperchlorate structure (Zhu *et al.*, 1993). The non-reduced triclinic cell was given as $a = 15.676$ (3), $b = 16.315$ (4), $c = 15.062$ (2) Å, $\alpha = 62.26$ (1), $\beta = 121.35$ (2), $\gamma = 118.74$ (2)°, $Z = 1$, space group $P1$. This cell contains three cations of composition $[N(n-C_4H_9)_4]^+$ and one anion of composition $[Cl_2O_{62}W_{18}]^{3-}$; two of the three anion charges originate from perchlorates and one is an unpaired electron 'somewhat delocalized over the W atoms in the anion network'. Alternatively stated, 'the anion contains randomly distributed W^V and W^{VI} in a 1:1.7 ratio' (Zhu *et al.*, 1993). The reduced cell has $a = 15.062$, $b = 15.064$, $c = 16.257$ Å, $\alpha = 62.62$, $\beta = 62.65$, $\gamma = 62.72$ ° and is clearly of cadre (Ib) of Herbstein (1997), with the Niggli matrix having the form AACDDE (de Wolff, 1983); the triclinic cell can be transformed to a C -centred monoclinic cell with $a = 25.726$, $b = 15.676$, $c = 16.257$ Å, $\alpha = 90.03$, $\beta = 122.56$, $\gamma = 89.99$ °. Transforming and averaging the coordinates according to space group $C2$ leads to the values in Table 6 of the supplementary material.† The asymmetric unit of the monoclinic cell consists of one cation located on a twofold axis $[N(1)]$, one cation at a general position $[N(2)]$ and one anion located on a twofold axis; the unit cell contains six cations and two anions.

In this example the matching of coordinates according to the higher symmetry space group ($C2$) is excellent, being within 0.005 Å, on average, for the W atoms and entirely satisfactory (0.03 Å) for the Cl, O and N atoms; however, it is unusually poor (up to 0.4 Å) for some of the C atoms (of the *n*-butyl groups). There are quite a number of unsatisfactory C—C bond lengths resulting from the coordinates we obtained from the CSD (coordinates were not given in the original paper), ranging from 1.11 to 1.75 Å; while misprints are possible, it seems more likely that the arrangements of the butyl groups, which are notorious for being disordered or highly fluxional, could not be well determined in the presence of W atoms. We also note that the crystal used had dimensions $2.5 \times 3.0 \times 2.5$ mm, with $\mu = 19.2$ mm⁻¹; absorption corrections were not mentioned.

3.9. (β -Cyclodextrin).0.94(3,5-dimethylbenzoic acid).9.1H₂O (YOVVIO) and (β -cyclodextrin).(4-tert-butyltoluene).8.5H₂O (KUTJUE)

These two isomorphous clathrate compounds, in which the β -cyclodextrin molecule (cyclomaltoheptaose) serves as the host species, were reported in space group $P1$ with $Z = 2$; the correct space group is $C2$. The cell dimensions reported for YOVVIO (Rontoyianni & Mavridis, 1994) are $a = 15.707$ (4), $b =$

15.694 (3), $c = 15.999$ (2) Å, $\alpha = 101.502$ (5), $\beta = 101.557$ (5), $\gamma = 103.805$ (4)°; for KUTJUE (Mavridis & Hadjoudis, 1992), $a = 15.562$ (4), $b = 15.564$, $c = 15.835$ (3) Å, $\alpha = 102.11$ (2), $\beta = 102.15$ (1), $\gamma = 103.64$ (2)°. Both cells are reduced (although a and b of YOVVIO should be interchanged to obtain the standard setting); the equality of two axes and two angles [cadre (Ib) of Herbstein, 1997] should immediately raise suspicion of higher symmetry. The Niggli matrix for both cells is of the form AACDDF, corresponding to lattice character 14 (de Wolff, 1983). The C -centred cells defined by the lattice vectors $[110]$, $[\bar{1}10]$ and $[001]$ have dimensions $a = 19.374$, $b = 24.711$, $c = 15.999$ Å, $\alpha = 89.96$, $\beta = 108.90$, $\gamma = 90.05$ ° (YOVVIO) and $a = 19.240$, $b = 24.467$, $c = 15.835$ Å, $\alpha = 89.98$, $\beta = 109.87$, $\gamma = 89.99$ ° (KUTJUE). We shall only discuss in detail the structure of YOVVIO as it appears to have been determined more precisely than that of KUTJUE. The F_{obs} values of some 9000 reflections (triclinic indices) were kindly supplied by Professor I. M. Mavrides and 77 randomly chosen pairs related by $(hkl)_M$ and $(h\bar{k}l)_M$ were plotted to obtain an excellent linear relationship (Fig. 1). Thus, the measured intensities conform to monoclinic symmetry.

The relationship between the monoclinic and triclinic coordinates is $x_M = (x_T + y_T)/2 - 0.57$, $y_M = (-x_T + y_T)/2$ and $z_M = z_T - 0.48$, the translations being needed to place the origin on a C_2 axis in space group $C2$. 75 of the 77 pairs of atoms in the two β -cyclodextrin molecules are matched across this C_2 axis within, on average, less than 0.015 Å. The two exceptions [O(49) and O(68) (CSD numbering)] are almost surely due to misprints, since distances and angles as calculated from the original (triclinic) coordinates are unsatisfactory. We believe that the x (triclinic) coordinate of O(49) should be 0.382 rather than 0.372, that the x coordinate of O(68) should be 0.7477 rather than 0.7577, and that the z coordinate of O(68) should be 0.0719 rather than 0.0919. Matching of the water molecules is less satisfactory, with an average mismatch of ~ 0.04 Å, and even worse for the enclathrated dimethylbenzoic acid molecules (where identification of equivalent atoms is difficult); the authors note that the water and benzoic acid molecules are 'extensively disordered'. Our listing of averaged coordinates (Table 7 of the supplementary material) does not include the enclathrated benzoic acid molecules.

In the case of KUTJUE the matching of coordinates is considerably less satisfactory, with average discrepancies of ~ 0.05 Å for the host molecules and even more for the water and butyltoluene molecules. The average coordinates are similar to those for YOVVIO (establishing the isomorphism of the two compounds) and we have not thought it worthwhile to report them. We note that Mavridis & Hadjoudis (1992) write 'if the transformation $a' = a + b$, $b' = b - a$, $c' = c$ is performed, a pseudo- C -centred dimeric layer is created'; we have shown that,

† See deposition footnote on p. 677.

for YOYVIO as well as for KUTJUE, the centring is exact and that these compounds join the other examples of 'packing-type CH' structures of β -cyclodextrin clathrates (Mentzafos *et al.*, 1991).

3.10. *2-Amino-4-methoxy-6-methyl-1,3,5-triazine, C₅H₈N₄O (JOGRUS)*

These crystals have already been described by Marsh (1995) as monoclinic; we expand the earlier discussion, because of the unusual feature that the Niggli matrix here does not provide a route to the determination of the correct symmetry. The compound crystallizes as needles (along [100]) in a metrically orthorhombic reduced cell with $a = 6.709$ (1), $b = 7.971$ (1), $c = 12.303$ (2) Å, $\alpha = \beta = \gamma = 90.0$ (1)°, $Z = 4$ (Lotz *et al.*, 1991; LKG). LKG reported that preliminary rotation and Weissenberg photographs showed 'extinction conditions' indicating Laue symmetry mmm and an orthorhombic unit cell. Intensities were then measured on a CAD-4 diffractometer, the authors noting that 'the compound crystallizes with $Z = 4$ formula units in the unit cell and has orthorhombic crystal symmetry'. LKG tried to solve the structure in each of 17 orthorhombic space groups, but failed. They then treated the crystal as triclinic and obtained a set of (non-hydrogen) atomic parameters (isotropic temperature factors) in space group $P\bar{1}$ with two molecules in the asymmetric unit, resulting in $R = 0.28$ and $wR = 0.27$; however, correlations between the two 'independent' molecules in their structure could not be suppressed and the structure was not refined.

The coordinates reported by LKG have two noteworthy features:

(i) the x values are identically zero for all atoms in one molecule and identically 1/2 for all atoms in the second molecule;

(ii) corresponding atoms in the two molecules are related, very closely, by $\Delta x = \Delta y = \Delta z = 0.5$, the body-centring condition.

The first feature, with both molecules lying in mirror planes, immediately defines the crystal symmetry as (at least) monoclinic, with a being the axis of symmetry. The second feature raises the question whether the cell is exactly body-centred or only approximately so; this question is more difficult to answer. The largest mismatch between corresponding atoms related by the centring is 0.11 Å, for C(5); in view of the refinement problems, this amount seems well within experimental error. Indeed, this mismatch is so small that all reflections with $h + k + l$ odd *must* have been extremely weak, which would result in extremely severe correlations between the two molecules, as was noted by the authors.

The authors report that they collected intensities out to $2\theta = 57^\circ$ for Mo $K\alpha$ radiation; of 1908 independent reflections, 1287 – well over 50% – had $I < 2\sigma(I)$. Thus,

reflections with $(h + k + l)$ odd could well have been systematically absent, in which case the correlations would have been complete, and refinement in $P\bar{1}$ impossible. Nor is it clear what diffraction symmetry was assumed when the intensities were collected. The entire sphere of reflection out to $2\theta = 57^\circ$ should contain about 6670 reflections (including those with $h + k + l$ odd), so perhaps only two octants were collected, an insufficient set for refinement of the presumed triclinic structure. In any event we are confident that the structure should be properly described as monoclinic, space group $I2/m$, with β coincidentally equal to 90.0 (1)°. Revised coordinates are now available in the CSD (JOGRUS01).

Another example with a metrically orthorhombic cell, but true symmetry monoclinic ($C_{16}H_{27}N_4O_3S^+ \cdot NO_3^-$, BAGPII) has been discussed by Baur & Tillmanns (1986). In both these cases with $\beta = 90^\circ$ twinning might be feared, but there is no evidence for it. KAs_2Se_2 is also metrically orthorhombic, but the true symmetry is monoclinic ($\beta = 107.88^\circ$; Kapon *et al.*, 1989).

4. Change from triclinic to rhombohedral

A number of interesting examples of the triclinic-to-rhombohedral correction have been reported. We particularly note cobaltocenyl-tetra(methylcarba)dodecaborane, $C_{18}H_{29}B_8Co$, which was first reported in space group $P1$ (three molecules in the asymmetric unit) by Grimes *et al.* (1979) and later revised to rhombohedral by Davies & Sinn (1986), despite a remark in the earlier paper that 'no evidence of monoclinic or higher symmetry was observed in precession photographs, in diffractometer-measured reflection intensities, or in the molecular packing in the unit cell'. The reduced cell has dimensions $a = 8.047$ (1), $b = 21.551$ (1), $c = 21.554$ (1) Å, $\alpha = 118.43$ (1), $\beta = 97.21$ (1), $\gamma = 97.13$ (1)°, which should surely have given rise to suspicion that the symmetry was too low. Another example is sodium *tert*-butoxide, C_4H_9NaO [$Na^+(OC(CH_3)_3)^-$], where the structure was originally solved in Cc (Greiser & Weiss, 1977) and later shown to be rhombohedral, $R3c$ (Davies *et al.*, 1982). The reduced triclinic cell has three equal axes and three equal angles, indicative of the need for reconsideration (this point is made in another way by Davies *et al.*, 1982). Four further examples follow.

4.1. *(-)-S-Cyclophosphamide or 2-bis(β -chloroethyl)-amino-2-oxo-1,3,2-oxazaphosphorinane, C₇H₁₅Cl₂N₂O₂P (CLEOZP10)*

This compound was reported to crystallize in a (non-reduced) triclinic cell with $a = 10.500$ (4), $b = 10.490$ (4), $c = 10.761$ (4) Å, $\alpha = 110.00$ (2), $\beta = 110.00$ (2), $\gamma = 108.90$ (2)°, $Z = 3$, space group $P1$ (Adamiak *et al.*, 1977).

The authors noted that 'it is remarkable that within the unit cell (= the asymmetric unit in this space group) three independent molecules are assembled which show identical conformations with torsion angles not deviating more than 3σ '. The near equalities $a = b$ and $\alpha = \beta$ should have suggested the need to search for a more symmetric lattice type. The vectors $[0\bar{1}0]$, $[111]$ and $[\bar{1}00]$ define the reduced cell with $a = 10.490$, $b = 10.500$, $c = 10.500$ Å, $\alpha = 109.02$, $\beta = 108.90$, $\gamma = 108.94^\circ$. This is effectively rhombohedral (*cf.* sodium *tert*-butoxide noted above); the corresponding hexagonal cell is formed from $[211]$, $[\bar{1}10]$ and $[001]$ ($a = 17.097$, $b = 17.078$, $c = 10.761$ Å, $\alpha = 89.99$, $\beta = 90.03$, $\gamma = 120.02^\circ$). It is convenient to convert the (triclinic) coordinates given in Table III of Adamiak *et al.* (1977) as follows: molecules 1 and 2, add 1.0 to x , y and z ; molecule 3, add 1.0 to y . The three molecules are now arranged in an equilateral triangle; after transforming to the hexagonal cell [$x_H = (x_T + y_T)/3$, $y_H = (-x_T + 2y_T)/3$ and $z_H = (-x_T - y_T + z_T)/3$] the corresponding atoms [*e.g.* P(1), P(2), P(3)] have effectively the same z_H coordinates. After moving the centroid (on the threefold axis) to the origin and averaging over equivalent atoms, we obtain the coordinates and $\Delta(\text{fit})$ values given in Table 8 of the supplementary material.† The space group is clearly $R\bar{3}$. We omit the H atoms from this table, since some are missing from the original table of coordinates and others are obviously misplaced.

We point out three peculiarities in the bond lengths: N(2,4,6)–C(6,13,20) being abnormally long at 1.58 Å, C(6,13,20)–C(7,14,21) (a formal single bond) abnormally short at 1.38 Å and C(7,14,12)–Cl(2,4,6) abnormally long at 1.93 Å (see Kaftory, 1983). (These distances are, of course, approximately the same as reported for all three molecules in the original triclinic description.) We note that several of the associated H atoms were missing or misplaced, which might have led to systematic errors in the positions of the C atoms. Bond lengths in the other β -chloroethylamino grouping are normal and the H atoms are in satisfactory positions.

4.2. Hexakis(μ_3 -(*N*-phenyl-*N'*,*N'*-oxapenta-1,5-diyl)thio-ureido)hexacopper(I), $C_{66}H_{78}N_{12}O_6S_6Cu_6$ (BALFEZ)

This is probably the most interesting of the present examples. The structure was originally described (Willemse *et al.*, 1981) in space group $P\bar{1}$, with four hexameric units in the cell located on separate centres of inversion, at (111) , $(11\frac{1}{2})$, $(\frac{11}{2}0)$ and $(\frac{111}{222})$. The authors noted that 'One of the four independent clusters has almost $D_{3d}(\bar{3}1m)$ symmetry, whereas the symmetry of the other three clusters is only approximately D_{3d} ' (note that the

correct Hermann–Mauguin symbol is $\bar{3}m$). The triclinic unit cell used by Willemse *et al.* [1981; $a = 10.487$ (9), $b = 28.961$ (8), $c = 29.579$ (12) Å, $\alpha = 120.72$ (3), $\beta = 103.69$ (5), $\gamma = 83.14$ (4)°, $Z = 4$] was not reduced and without reducing the cell (triclinic; $a = 10.487$, $b = 28.949$, $c = 28.956$ Å, $\alpha = 118.51$, $\beta = 97.03$, $\gamma = 96.92^\circ$) the presence of higher symmetry is not immediately apparent. The vectors $[011]$, $[\bar{1}0\bar{1}]$ and $[0\bar{1}0]$ describe an effectively rhombohedral cell with $a = 28.955$ Å, $\alpha = 118.56^\circ$; the triply primitive hexagonal cell ($[112]$, $[\bar{1}\bar{1}\bar{1}]$ and $[\bar{1}00]$) has $a = 49.768$, $b = 49.794$, $c = 10.487$ Å, $\alpha = 89.97$, $\beta = 89.94$, $\gamma = 119.98^\circ$, $Z = 12$. Coordinate transformation to this hexagonal cell ($x_H = 1/3y_T + 1/3z_T$, $y_H = 2/3y_T - 1/3z_T$ and $z_H = -x_T - 1/3y_T + 2/3z_T$) places the centre of molecule 1 at $(\frac{2}{3}\frac{1}{3}-\frac{2}{3})$ – a site of symmetry $\bar{3}$ in space group $R\bar{3}$ – and the other three molecules on sites of symmetry $\bar{1}$. After translating the four molecules to more convenient symmetry centres and averaging over the sets of three atoms that become equivalent in $R\bar{3}$, we obtain the coordinates and $\Delta(\text{fit})$ values in Table 9 of the supplementary material.† These $\Delta(\text{fit})$ values are, if anything, slightly smaller (on average) than the original coordinate s.u.'s reported by Willemse *et al.* (1981) and there can be no doubt that $R\bar{3}$ is the appropriate space group.

The coordinates of the atoms of the morpholino groups were not given by Willemse *et al.* (1981); we obtained them from the CSD [atom C(60) was missing and the coordinates of C(47) were obviously misprinted: its y (triclinic) coordinate should probably be incremented by 0.1]. The atoms of the phenyl rings were included in the refinement ('constrained to an ideal model'), but their coordinates are not available anywhere, neither in Willemse *et al.* (1981) nor in the CSD. We also note two other minor errors by Willemse *et al.* (1981):

(i) their stereogram in Fig. 1 (which clearly suggests threefold symmetry) is a view approximately along the shortest triclinic axis a rather than c ;

(ii) the coordination about copper is appreciably more pyramidal than planar, the four independent Cu atoms deviating by amounts ranging from 0.18 to 0.32 Å from the planes of the coordinating atoms (one N and two S).

This is an unusual structure type. We have searched the CSD for structures in space group No. 148 with $Z = 4$ (or $Z = 12$ in a hexagonal setting) and found only one other clear example in which one molecule is on a site of $\bar{3}$ symmetry, while the other three molecules are in general positions (as are the sub-units in BALFEZ). That example is tris(dimethylammonium) hexabromobismuthate (McPherson & Meyers, 1968; DMEABI10), where the BiBr_6^{3-} anions occupy two sets of crystallographically independent $\bar{3}$ positions, while the $(\text{CH}_3)_2\text{NH}_2^+$ cations occupy two sets of general positions.

† See deposition footnote on p. 677.

4.3. *Bis(N,N-diethylnicotinamide)copper(II) dichloride*, $C_{20}H_{28}N_4O_2CuCl_2$ (ENICCU)

This compound was described in a non-reduced cell with $a = 10.453$ (5), $b = 14.242$ (6) (corrected from 12.242), $c = 15.476$ (7) Å, $\alpha = 122.9$ (1), $\beta = 116.9$ (1), $\gamma = 75.8$ (1)°, $Z = 3$, space group (Rubinchik *et al.*, 1977*a,b,c*). The reduced cell has $a = 10.453$, $b = 14.226$, $c = 14.242$ Å, $\alpha = 114.25$, $\beta = 104.20$, $\gamma = 104.04$ ° and a metric tensor of type 24 (de Wolff, 1983); the indicated rhombohedral cell has $a = 14.24$ Å, $\alpha = 114.21$ °. The vectors $[02\bar{1}]$, $[\bar{1}1\bar{1}]$ and $[100]$ of the original cell give the corresponding (obverse) hexagonal cell with $a = 23.916$, $b = 23.909$, $c = 10.453$ Å, $\alpha = 89.90$, $\beta = 89.97$, $\gamma = 120.02$ °, $Z = 9$. The transformed and averaged coordinates for space group are given in Table 10 of the supplementary material.† The channel nature of the structure is clear from its projection down c . (Incidentally, the reference in the CSD is incorrect, as is the ‘two-dimensional chemical connectivity’ drawing, which is of the *cis* rather than the *trans* compound; otherwise the entry is correct. We have encountered other errors of this type in the CSD.)

4.4. *3-(2'-Phenyl-2,4'-bithiazole-4-carboxamido)propyl-dimethylsulfonium iodide*, $C_{18}H_{20}N_3OS_3I$ (BORYEM)

Although the results of this correction have already been given briefly (Marsh, 1995), a more extended discussion is warranted owing to the complexity of the transformation. This compound was reported to crystallize in a non-reduced cell with $a = 5.434$ (1), $b = 26.129$ (2), $c = 26.314$ (3) Å, $\alpha = 120.24$ (1), $\beta = 97.86$ (1), $\gamma = 86.06$ (1)°, $Z = 6$, space group $P\bar{1}$ (Kuroda *et al.*, 1982). The authors noted that ‘the three independent molecules in an asymmetric unit are related by a pseudo-threefold symmetry of rotation along the crystallographic a axis ([their] Fig. 3). As the phenyl and bithiazole rings are slightly rotated with respect to each other, the molecule is chiral depending on the sense of rotation. The unit cell contains [an] equal number of molecules of [each] optical antipode (space group $P\bar{1}$) and all the three molecules arranged around a pseudo-threefold axis have the same chirality’. The vectors $[112]$, $[\bar{1}1\bar{1}]$ and $[\bar{1}00]$ form a cell with $a = 45.146$, $b = 45.151$, $c = 5.434$ Å, $\alpha = 89.95$, $\beta = 90.04$, $\gamma = 120.00$ °, strongly suggestive of a rhombohedral cell expressed in hexagonal axes. Transformation of the coordinates given by Kuroda *et al.* (1982) turned out to be somewhat intricate, since two of the purportedly independent cations [(1) and (2)] belong to one chirality group, while cation (3) belongs to the other; accordingly, we first inverted cation (3) through the origin of the triclinic cell and then translated it by -1.0 units along c ; the three cations were now of the same chirality and related by a

3_1 axis parallel to a (the hexagonal c axis). Coordinates in $R\bar{3}$ could now be generated by the appropriate transformation ($x_H = 1/3y_T + 1/3z_T$, $y_H = 2/3y_T - 1/3z_T$ and $z_H = -x_T - 1/3y_T + 2/3z_T$), followed by translation to an appropriate origin and averaging over the three cations (and iodide ions). The $\Delta(\text{fit})$ values during this averaging were typical of our other examples, averaging less than 0.01 Å for the I and S atoms and less than 0.02 Å for C, N and O. The coordinates (referred to a rhombohedral unit cell) were deposited with the CSD (Marsh, 1995; BORYEM01).

5. Insertion of a missing centre of symmetry

5.1. *[Tetra-(μ-benzoato)bis(pyridine-N-oxide)copper(II)]*, $[(Cu^{II})_2(\mu-O_2C-C_6H_5)_4(ONC_5H_5)_2]$, $C_{38}H_{30}N_2O_{10}Cu_2$

This compound was described in a non-reduced triclinic cell with dimensions $a = 9.262$ (4), $b = 10.697$ (2), $c = 10.881$ (3) Å, $\alpha = 59.60$ (2), $\beta = 74.83$ (3), $\gamma = 72.80$ (2)°, $Z = 1$. The space group was given explicitly as $P1$ and the structure was solved in this space group; nevertheless, the phrase ‘the structure of compound (1) shows a clear centre of symmetry’ (or minor variants thereof) appears three times in the text (Yang *et al.*, 1997). A comparison of coordinates of paired atoms (see Fig. 1 of Yang *et al.*, 1997) shows that these are related by a centre of symmetry at $x = 0.108$ (3), $y = 0.069$ (3), $z = 0.956$ (2). We give coordinates of 9 out of 26 non-H atoms of the asymmetric unit of the centrosymmetric ($P\bar{1}$) cell in Table 11 of the supplementary material;† $P1$ coordinates of the atoms of two (out of four) phenyl groups are missing from Table 2 of Yang *et al.* (1997), as well as those of the 10 C atoms from two pyridine-*N*-oxide groups. We have not been able to retrieve the missing information. Comparison of bond lengths related by the centre shows appreciable discrepancies and further refinement in $P\bar{1}$ is clearly necessary. Sixteen similar examples have been discussed by Marsh (1995).

We note that the cell reported by Yang *et al.* (1997), with α less than 60°, is clearly not reduced. The reduced cell results from the transformation matrix $[\bar{1}00/0\bar{1}0/0\bar{1}1]$ and has the dimensions $a = 9.262$, $b = 10.697$, $c = 10.725$ Å, $\alpha = 61.05$, $\beta = 88.31$, $\gamma = 72.80$ °, $Z = 1$.

5.2. *(E)-Acetophenone oxime*, C_8H_9NO (FAKRIS01)

There are two polymorphs (Gieren *et al.*, 1986*a*). The triclinic α -form, $P\bar{1}$ with $Z = 4$ (FAKRIS), was reported in the reduced cell and does not transform to higher symmetry; it does not concern us further here. The monoclinic β -form, space group Cc with $Z = 16$ (FAKRIS01), shows the relationships $x_i = -x_j$, $y_i = y_j$, $z_i = \frac{1}{2} - z_j$ between the coordinates of corresponding atoms for molecules $i = 1, j = 3$, and for molecules $i = 2$,

† See deposition footnote on p. 677.

$j = 4$. This is one of the relationships between symmetry-related atoms in space group $C2/c$. Most of the mismatches are very large compared with the formal s.u.'s and some are larger than 0.1 \AA , which is not unusual in such situations. Symmetrizing the structure so as to conform to $C2/c$ led to more reasonable molecular dimensions and we are confident that the revised coordinates (Table 12 of the supplementary material†) are more reliable than the earlier ones; nevertheless, further refinement in $C2/c$ is desirable.

6. Discussion

The present collection of space-group corrections illustrates neatly a point often made in the past (*e.g.* Marsh & Bernal, 1995). In one type of error ('Category 1' errors) the Laue group has been determined incorrectly. The possibility of such an error (*e.g.* triclinic instead of C -centred monoclinic, or rhombohedral) can be checked as soon as cell dimensions have been measured, using the tools of the reduced cell and the Niggli matrix, although confirmation that the symmetry is truly in error can only be obtained, before the structure has been determined, from comparison of intensities of possibly related reflections. After the structure is known, then relations between coordinates of purportedly independent atoms are a prime diagnostic tool in demonstrating symmetry which is too low. In this type of error the changes in coordinates are small and the molecular dimensions derived by the original investigators are effectively unchanged (Schomaker & Marsh, 1979). However, the crystallographic symmetries imposed on the structures and, usually, on the component molecules, are altered.

In the second type of error ('Category 2' errors), the Laue symmetry has been determined correctly, but a non-centrosymmetric space group has been chosen rather than the corresponding centrosymmetric space group (as in the last two of our examples; *cf.* Marsh, 1986). In this situation, the only way of showing which space group is to be preferred is by considering the relations between coordinates of purportedly independent atoms. Here the changes in coordinates can be comparatively large (say, up to ten times the least-squares s.u.'s) and further refinement in the centrosymmetric space group is needed to obtain reliable molecular dimensions. In this regard, we wish to emphasize that the large correlations arising from the refinement of an approximately centrosymmetric model in a non-centrosymmetric space group (the correlations that give rise to the distorted coordinates) relate primarily to the antisymmetric aspects of the model – deviations from centrosymmetry. The symmetric aspects should be perturbed only slightly, so that the symmetrizing of the structure should lead to quite reliable

average coordinates. We have found this to be so in almost all the structures we have studied; the revised centrosymmetric structure giving bond lengths and angles in agreement with standard values within the normal errors of $\sim 0.02 \text{ \AA}$ and $\sim 0.2^\circ$.

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† See deposition footnote on p. 677.

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