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Recognizing the (False Symmetry) Triclinic (*aP*) to (True Symmetry) Centred Monoclinic (*mC*) Pathology

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Abstract

Some fifty-odd published examples of corrections from (false symmetry) triclinic to (true symmetry) centred monoclinic (*aP* to *mC*) are analysed to see whether the need for correction of symmetry should have been obvious to the original investigators. We conclude that about two-thirds of the examples were transparent in that special features of the dimensions of the reduced triclinic cell should have aroused the suspicions of the investigator. For the other third, calculation of the metric tensor would have indicated the possibility of symmetry higher than triclinic. However, it should always be remembered that the true symmetry of a crystal is revealed by intensity rather than by metric relationships, or by other techniques such as optical microscopy.

1. Introduction

Some fifty-odd crystal structures have been reported in which the space group has been corrected from (false symmetry) triclinic (*aP*) to (true symmetry) centred monoclinic (*mC*). In how many of these examples may one say (with the benefit of hindsight), that there were clear signs of the possible occurrence of higher symmetry, which should then have been pursued? We wish particularly to consider whether correction could have been made at the stage where the unit cell had been determined as triclinic, the investigators then having proceeded to solve the crystal structure under the assumption that this symmetry was correct. This point of view is somewhat different from that of previous studies, mainly by Marsh, Bauer, Parthé and co-workers, where *published* structure reports were scrutinized for evidence of higher symmetry undetected by the original investigators. Thus, we emphasize the analysis of the information provided by the measured cell dimensions, whereas others have focused attention on relationships among atomic coordinates,† which are, of course, not available at the stage we are considering. We stress that cell dimensions *alone* do not provide conclusive evidence of higher symmetry, but only indications of possible existence. Once the omens have been understood it is incumbent on the investigator to determine the correct symmetry by standard methods, such as the study of intensity relations. Also, cell dimensions are potentially important indicators because atomic coordinates are now often relegated to databases and are not immediately available to the reader for checking. Remarkably and regrettably, some quite detailed descriptions of crystal structures have appeared with coordinates, but without mention of cell dimensions and space group (O'Bannon, Carroll & Dailey, 1991) or even without cell dimensions, space group and coordinates (Birkett *et al.*, 1993).

2. Background to analysis of database of *aP* to *mC* space-group corrections

The material for our analysis originates from the triclinic to centred monoclinic corrections reported in the literature. Baur & Kassner (1992; BK92) give information on 25 such corrections. Marsh (1995; M95) has given an additional 24 and Marsh & Bernal (1995; MB95) two more. We added four further examples, two (Dunitz & Shearer, 1960; Kapon, Reisner & Marsh, 1989: KRM89) not included in the Baur–Kassner and Marsh surveys, and the others analysed in a companion paper (Herbstein & Marsh, 1997; HM97), using published data. Some fifty-odd examples are thus available for study; we do not give a more precise number because some examples fall away for various reasons. In Fig. 1 we show a histogram of the years of publication of the original (*i.e.* incorrect) reports; the epidemic appears to have peaked some 10 years ago, but analysis of its symptoms may help to produce a diagnostic to reduce recurrence.

We give a very brief and incomplete background to reduced cells, which were introduced into crystallography by Niggli (1928). Their calculation and application to the determination of crystal symmetry were discussed by Santoro & Mighell (1970) and Mighell & Rodgers (1980). These results were clearly summarized by de Wolff (1983; see particularly Table 9.3.1) and by Baur & Tillmanns (1986; BT86), who give references to earlier

† Among the computer programs available for checking relationships among atomic coordinates are *MISSYM* (Le Page, 1987), *ACCMM* (Mika, Hauck & Funk-Kath, 1994), *PARST* (Nardelli, 1995, 1996) and *BUNYIP* (Hester & Hall, 1996).

work. More recently, the earlier literature has been surveyed and put into context by Macicek & Yordanov (1992). We shall not repeat this material, but only remind the reader that the metric tensor (Niggli matrix) is given by **[a.a b.b c.c/b.c c.a a.b]** (conveniently abbreviated as [*A B C/D E F*]), with standard ordering of the axes as $a \leq b \leq c$. A type (I) triclinic cell is defined as having the product $T(= DEF)$ positive, from which it follows that two of the opposing cell corners have all angles acute and one of these corners is taken as the origin in the standard setting; alternatively, two angles are obtuse and one acute for a different choice of axial directions. A type (II) triclinic cell is defined as having T zero or negative and it follows, as above, that the origin can be chosen at a corner with angles 90° or obtuse (alternatively, one obtuse and two acute). The Niggli reduced cell has $a + b + c$ = abs. min. (which defines the Buerger cells) *and* the deviation ($D = [|\pi/2 - \alpha| + |\pi/2 - \beta| + > |\pi/2 - \gamma|]$), $\{|\cos\alpha| + |\cos\beta| + |\cos\gamma\}$ and $\{|\cos\alpha \cos\beta \cos\gamma|\}$ relative maxima among the Buerger cells (Gruber, 1989).

3. Procedure used for triclinic to centred monoclinic corrections

The procedure followed here for space-group determination [*cf.* Fig. 5 of Mighell & Rodgers (1980), the nine recommendations of BT86 (p. 110) and the nine recommendations of Marsh (1995)] involves taking the triclinic unit-cell dimensions as reported and checking whether this original cell was reduced. If not, then the original cell is transformed to the reduced cell. Parenthetically, we note here that BT86 found that ~27% of the 297 published triclinic cells in a sample investigated by them had not been reduced according to the definition of *International Tables for Crystallography* (1983, Vol. A; ITC83) or some other definition. We have used *TRACER* (Lawton, 1969), *PARST* (Nardelli, 1983) and *BLAF* (Version 4.1; Macicek & Yordanov, 1992) for cell reduction, but a number of other programs [*NEWLAT* (Mugnoli, 1985), *DELOS* (Burzlaff & Zimmerman, 1985), *LEPAGE* (Spek, 1988) and *NIST*LATTICE* (Karen & Mighell, 1991*b*)] are available. The metric tensor of the reduced cell was calculated and compared with the 44 lattice characters given in Table 9.3.1 of ITC83 (de Wolff, 1983) in order to identify whether the lattice possibly had symmetry higher than triclinic. The transformation matrix to a higher symmetry cell (in this paper, specifically a *C*- or *I*-centred monoclinic cell) is also given in Table 9.3.1; as these corrections have generally been published, we only give a reference unless discussion is required. For convenience, we have excerpted in our Table 1 the forms of the metric tensors, lattice characters and transformation matrices needed in this paper. We have not checked atomic coordinates for conformation to the higher symmetry because this has already been done for the *published* structures considered in this paper; however, appraisal of the atomic coordinates (when available) is an essential step in investigating any suspect structure and has been carried out here (or elsewhere) for the structures we correct and/or discuss.

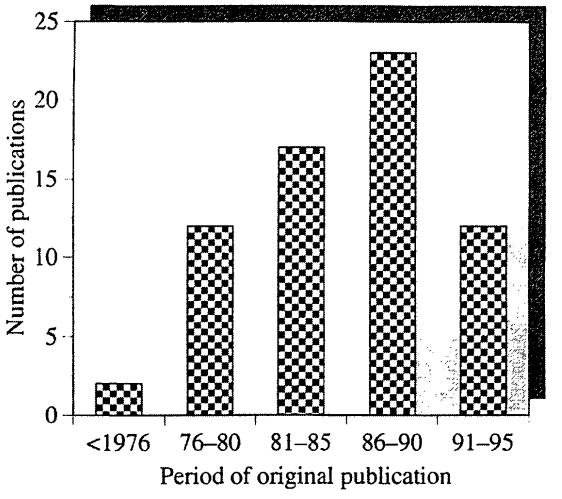

Fig. 1. Number of publications with triclinic unit cells which can be transformed to centred monoclinic cells plotted against the year in which the publication appeared.

Table 1. *The parameters D, E and F for the lattice characters encountered in this paper, and the transformation matrices from triclinic, Bravais type aP, to centred monoclinic, mC*

This material has been extracted from Table 9.3.1 of ITC83.

No.	Type	*D*	*E*	*F*	Transformation
$A = B$, no conditions on C					
10	(I)	*D*	*D*	*F*	$110/1\bar{1}0/00\bar{1}$
14	(II)	*D*	*D*	*F*	$110/\bar{1}10/001$
17	(II)	*D*†	*E*	*F*	$1\bar{1}0/110/\bar{1}0\bar{1}$
$B = C$, no conditions on A					
20	(I)	*D*	*E*	*E*	$011/01\bar{1}/\bar{1}00$
25	(II)	*D*	*E*	*F*	$011/0\bar{1}1/100$
No conditions on A, B and C					
27	(I)	*D*	*A*/2	*A*/2	$\bar{1}20/\bar{1}00/0\bar{1}1$
28	(I)	*D*	*A*/2	2*D*	$\bar{1}00/\bar{1}02/010$
29	(I)	*D*	2*D*	*A*/2	$100/1\bar{2}0/00\bar{1}$
37	(II)	*D*	$-A/2$	0	$\bar{1}02/100/010$
39	(II)	*D*	0	$-A/2$	$\bar{1}2\bar{0}/\bar{1}00/00\bar{1}$
41	(II)	$-B/2$	*E*	0	$0\bar{1}2/0\bar{1}0/\bar{1}00$
43	(II)	*D*‡	*E*	*F*	$\bar{1}00/\bar{1}\bar{1}2/0\bar{1}0$

† $2|D + E + F| = A + B$. ‡ In addition to $2|D + E + F| = A + B$, $|2D + F| = B$.

The original cell reported as triclinic was determined from photographic or, more usually, diffractometer measurements. The latter, on which we concentrate, have provided most of the results discussed here; computer analysis of area-detector data will presumably be analogous to the use of photographs. The unit cell *initially* obtained from the diffractometer output of measurements of ω, 2θ, χ and φ for (say) 25 reflections

will depend, among other factors, on the nature and initial orientation of the crystal and the scan ranges used. The values obtained for the cell dimensions are subject to errors (often considerably underestimated by the original authors) and this may make it difficult to decide whether two cell edges or angles are indeed significantly different, or different from special values such as 90 or 120°. Nevertheless, cell-dimension errors prevented us from identifying a lattice character in only one example out of fifty-odd. When the triclinic to monoclinic transformations are carried out, we deliberately do not initially require that $\alpha = \gamma = 90°$, as the deviations give an independent assessment of the accuracy of the original measurements. A different method of determining metric symmetry – that of converse transformation analysis – has been developed by Karen & Mighell (1991*a*,*b*) which includes the possibility of taking experimental error into account; however, we have not used this method during the preparation of the present paper.

Original and reduced cells often have very similar dimensions and thus very similar metric tensors. However, as has been emphasized many times in the past, only the *reduced* cell is uniquely defined and the metric tensor of a non-reduced triclinic cell has no significance in the present context. The orientations of the axes of original and reduced cells with respect to a standard set of axes (for example, the diffractometer axes) are different. It is instructive to show the geometrical relationships between the original and reduced triclinic cells and the ensuing *C*-centred monoclinic cell and we use published results for methyl 8-isopropyl-3,3a,8,8a-tetrahydroindeno[2,1-*c*]pyrazole-8a-carboxylate ($C_{15}H_{18}N_2O_2$; CEMBOL; Toupet & Messager, 1984; Marsh & Herbstein, 1988) for this purpose [details are also entered into (deposited) Table C, which is defined below†]. This is #19 in Table 1 of the listing of BK92, whose serial numbers we use for identification of the crystals; we have added compound names, CDF refcodes and references so that the present paper will be self-contained.

$C_{15}H_{18}N_2O_2$ was reported to be type (I) triclinic with $a = 5.791$ (4), $b = 15.503$ (4), $c = 15.954$ (5) Å, $\alpha = 82.24$ (5), $\beta = 79.35$ (6), $\gamma = 79.13$ (5)°, $P\bar{1}$, $Z = 4$. This cell is not reduced, but reduction [transformation matrix $(100/1\bar{1}0/10\bar{1})$] gives a cell of dimensions $a = 5.791$, $b = 15.493$, $c = 15.935$ Å, $\alpha = 82.34$, $\beta = 79.72$, $\gamma = 79.33°$, which are very close to those of the original cell, but with a different orientation. The metric tensor of the reduced cell [33.54 240.02 253.92/32.93 16.46 16.61]) could be taken to approximate to the form [*A B C/A A/2 A/2*]. However, this does not correspond to any of the reduced forms of Table 9.3.1. We therefore try the less restrictive form [*A B C/D A/2 A/2*], which corresponds to lattice character #27 for a type (I) cell, with transformation matrix $(\bar{1}20/\bar{1}00/0\bar{1}1)$ from the reduced cell to a *C*-centred monoclinic cell (Table 1). This transformation was given by Marsh & Herbstein (1988) from the *original* cell to a cell with $a = 30.450$, $b = 5.791$, $c = 20.690$ Å, $\alpha = 90.07$, $\beta = 131.09$, $\gamma = 90.11°$, $Z = 8$. Multiplication of the two matrices $(\bar{1}20/\bar{1}00/0\bar{1}1)$ and $(100/1\bar{1}0/10\bar{1})$ gives the present transformation matrix from the original to the monoclinic cell as $(1\bar{2}0/\bar{1}00/01\bar{1})$. This cell has the same edges as that given by Marsh & Herbstein, but with α and γ acute instead of obtuse. The relation between original and reduced triclinic cells is shown in Fig. 2, as well as the relation between these two cells and the final monoclinic cell. The final monoclinic cell is obtained by ascribing the deviations of α and γ from 90° to errors in the original measurements. The space group of the monoclinic cell is obtained by analysis

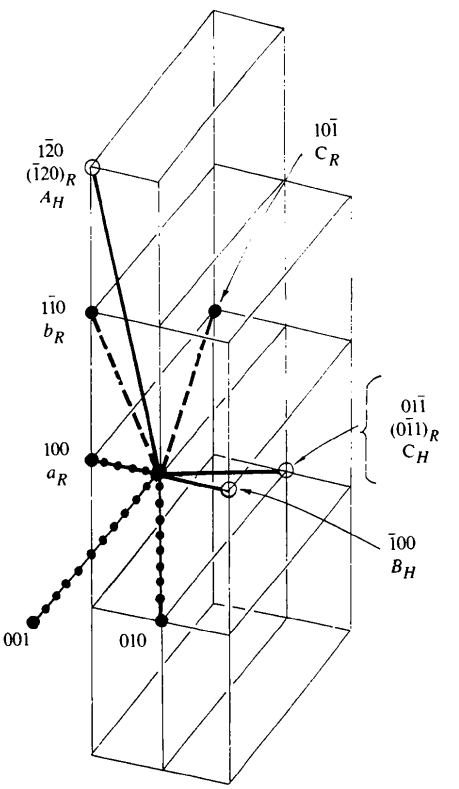

Fig. 2. The relation between original, reduced and *C*-centred monoclinic cells for CEMBOL (#19). The axes of the original cell are identified by chain (– • – • – • –) lines and indices of lattice points are given in terms of this basis as 100 *etc.* The background framework is drawn in terms of the unit cells of the original lattice and also that of the reduced cell. The axes of the reduced cell are identified by dashed lines and indices of lattice points are given in terms of this basis as a_R or $(100)_R$ *etc.* The present monoclinic cell (denoted by A_H, B_H, C_H) is obtained by applying the transformation matrix $(1\bar{2}0/\bar{1}00/01\bar{1})$ to the original triclinic cell or the transformation matrix $(\bar{1}20/\bar{1}00/0\bar{1}1)$ to the reduced cell. The cell given by Marsh & Herbstein (1988) has vectors A_{MH} and C_{MH} in opposite directions to A_H and C_H, while B_H and B_{MH} coincide. The second group of monoclinic vectors has not been shown to avoid overloading the diagram.

† A list of data for triclinic unit cells has been deposited with the IUCr (Reference: CF0002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of intensities of reflections (if available) or from symmetry relations between atomic coordinates.

4. Analysis of published triclinic to centred monoclinic corrections

We now analyse the fifty-odd published examples of triclinic to centred monoclinic corrections (most $P\bar{1}$ to $C2/c$) in terms of the procedure noted above. We find that the reduced cells fall into two 'cadres'. In the first of these the reduced cell dimensions show special relationships between pairs of parameters, such as equality to two axes or their mutual orthogonality [however, there is an additional requirement (see below) for a reduced cell with one angle 90° to have higher symmetry]. The second cadre comprises examples where the reduced cell dimensions do not show the special relationships between parameters found in cadres (I*a*) and (I*b*), but the metric tensor corresponds to one of the lattice characters of Table 9.3.1. The cadres are discussed separately; the complete results are given in three deposited tables [A (18 entries), B (14 entries) and C (18 entries)].† A typical entry from each of these deposited tables is given for illustration in Table 2. Special features are discussed in each section.

We begin with two reports of historical interest. The first example of a triclinic to monoclinic correction that we have found (through Bürgi & Dunitz, 1992) is for cyclododecane, which was originally described as triclinic by Müller (1933; ***a* = 7.84**, b = 5.44, ***c* = 7.82 Å**, α = **81.7**, β = 64.0, γ = **81.0**°, Z = 1, $P\bar{1}$) and corrected to C-centred monoclinic by Dunitz & Shearer (1960), their measurements giving a = 13.27 (1), b = 8.28 (1), c = 5.44 (1) Å, β = 99.5 (2)°, Z = 2, space group $C2/m$, transformation matrix (110/001/1$\bar{1}$0). Allowing for the limited precision of Müller's measurements, these fit into our Cadre (I*b*) (see Table B of deposited material†). The second concerns the low-temperature polymorph of benzil, which crystallizes in space group $P3_121$ (Z = 3) at room temperature (Brown & Sadanaga, 1965; Gabe, Le Page, Lee & Barclay, 1981) and undergoes a first-order transformation on cooling (T_c = 83.5 K). The crystal structure of the low-temperature polymorph was reported as triclinic, with (at 80 K) $a = b$, $\alpha = \beta$, $P1$, Z = 12. Tolédano (1979) pointed out that this triclinic cell could be transformed into a C-centred monoclinic cell with Z = 24. Tolédano also summarized the physical properties favouring a monoclinic cell and discussed the physics of the transformation. More recent work (More, Odou & Lefebvre, 1987) has shown that the original diffraction patterns were incorrectly interpreted because of transformation-induced twinning and that the space group of the low-temperature phase is monoclinic ($P2_1$, Z = 6) and not triclinic.

† See deposition footnote on p. 970.

Table 2. *A single example is given for each cadre*

The cell type is not given explicitly as it can be inferred from the value of T (= DEF). Type (I) $T > 0$; type (II) $T \leq 0$.

Cadre (I*a*). Data for triclinic unit cells where the reduced cell has one angle = 90° and (edge1)/{2(edge2)} = |cos(included angle)|.

The example is CEMBOL (#13), with dimensions of the reduced triclinic cell as a = 6.897 (3), b = 12.016 (4), c = 22.537 (6) Å, α = 104.92 (3), β = **89.96 (3)**, γ = 106.62 (3)° [note that β is set to 90° (see text) and the cell is type (II); however, we give here the value of β as reported]. The metric tensor (in the form *A B C/D E F*) is 47.57 144.38 507.92/69.63 0 23.70. $|a_{red}/2b_{red}| = 0.28700$; $\cos\gamma = -0.28602$. The lattice character is #39 and the transformation to centred monoclinic has been discussed by MS79 and BT86.

Cadre (I*b*). The reduced cell has two equal cell edges and two equal angles.

The example is DOBKOU (#84), with dimensions of the reduced triclinic cell as a = 7.587 (2), b = **14.239 (5)**, c = **14.274 (5)** Å α = 110.07 (2), β = 91.30 (2), γ = 91.39 (2)° (we assume here that $b = c$, despite the difference of 5u in their values, and that $\beta = \gamma$, despite the difference of 3u). The lattice character is #25; the transformation to centred monoclinic is given by Schaefer (1986).

Cadre (II). Data for reduced triclinic unit cells which do not show the special features of cadres (I*a*) and (I*b*), but the metric tensor corresponds to a lattice character in Table 9.3.1 of ITC83.

The example is K[B(SO_3Cl)$_4$], with dimensions of the original cell as a = 10.513 (9), b = 10.838 (7), c = 10.965 (11) Å, α = 99.21 (3), β = 135.48 (3), γ = 97.15 (3)°. The reduced cell has a = 8.147 (41), b = 10.513 (9), c = 10.836 (49) Å, α = 82.87 (18), β = 67.93 (53), γ = 70.68 (19)°, and is type (I). The metric tensor (in the form *A B C/D E F*) is 66.37 110.52 117.43/14.14 33.17 28.34; hence, we have *A B C/D A*/22*D* and the lattice character is #28.

4.1. *Cadre (I): special features in the dimensions of the reduced cell*

The criteria for 'special' are:

Cadre (I*a*): one angle = 90° and (edge1)/{2(edge2)} = |cos(included angle)|.

Cadre (I*b*): equality of two cell edges and of two angles (*e.g.* *a*,*a*,*c*,α,α,γ).

We have highlighted the special features below.

4.1.1. *Cadre (Ia): the reduced cell has one angle = 90° and (edge1)/{2(edge2)} = |cos(included angle)|.* When the reduced cell has two mutually orthogonal axes the cell is type (II) [see p. 739 of ITC83, condition 4(*c*)]; this gives the metric tensor of the reduced cell with the form [*A B C/D* 0 *A*/2] [condition 5(*e*)] when β = 90°. The lattice character is #39. It is illuminating to use a simple graphical solution based on the orthogonality of two of the axes. If there is a transformation to a C-centred monoclinic cell, then one of the two orthogonal axes must be the monoclinic b axis. If $|a_{red}| = |B_{mono}|$ then $a_{red}/2b_{red} = |\cos\gamma|$ (analogous expressions can be set up for the other alternative and for other choices of axes). If this solution holds, then the transformation matrix from the reduced cell to the axes of the monoclinic cell is ($\bar{1}\bar{2}$0/$\bar{1}$00/00$\bar{1}$). We discuss #13 in some detail (see Fig. 3) and then point out similarities found in the other examples. Finally, in this cadre we note examples where equalities

between cell edges or values of 60° for angles can introduce additional complications.

#13: [(3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioximato)copper(II) perchlorate hemi(methanol); AEIBCU] was reported in a type (II) triclinic cell with a = 6.897 (3), b = 12.023 (4), c = 22.647 (6) Å, α = 100.81 (3), β = 98.69 (3), γ = 106.73 (3)°, $P\bar{1}$, Z = 4 (Bertrand, Smith & Vanderveer, 1977). Reduction of the cell gives a = 6.897 (3), b = 12.016 (4), c = 22.537 (6) Å, α = 104.92 (3), β = **89.96 (3)**, γ = 106.62 (3)° (transformed to type (II) cell, but we have deliberately not set $\beta = 90°$ in the list of cell dimensions). Now 6.897/(2 × 12.016) = 0.28700 = cos 73.32°, *i.e.* $a_{red}/2b_{red} = |\cos\gamma|$ and transformation to C-centred monoclinic can be made as shown in Fig. 3. Marsh & Schomaker (1979) obtained the C-centred monoclinic cell with A_M = 23.028, B_M = 6.897, C_M = 22.537 Å, α = 90.04, β = 105.57, γ = 90.06°, $C2/c$, Z = 8. Marsh & Schomaker (1979) remarked that 'the reported cell dimensions provide no clear clue, and discovery of the monoclinic lattice would have required systematic search for orthogonal axes'. We comment that calculation of the metric tensor for the reduced cell gives the orthogonal axes sought.

$[NEt_4]_4[Ni_6(\eta^2\text{-}\mu^6\text{-}In_2Br_5)_2(CO)_{10}].Me_2CO$: This cluster compound has been discussed by MB95. The reduced cell has a = 13.174, b = 13.198, c = 26.485 Å, α = 75.72, β = 88.95, γ = 60.22° (error estimates deliberately omitted; Z = 2), and the metric tensor is 173.56 174.19 701.47/86.20 6.39 86.35, which approximates to $AAC/A/2EA/2$; this 'reduced form' does not appear in Table 9.3.1. The *reported* cell dimensions thus indicate that the crystals are triclinic; however, the atomic coordinates of the two purportedly independent units (I) and (II) are related by $x_I = 1/2 - x_{II}$; $z_I - 1/2 = z_{II}$. The transformation programs are apparently quite fault-tolerant as MB95 obtained a C-centred monoclinic cell without difficulty, a result confirmed now by *BLAF*. MB95 commented 'large errors in the measured cell dimensions – several times larger than the indicated precisions – presumably led the authors to assume a triclinic rather than a monoclinic unit cell, whereas the structure obeys monoclinic symmetry well within the e.s.d.'s of the coordinates'. This is the only example we have found where the (measured) metric tensor did not lead to a clear conclusion; it is not included in the deposited tables.

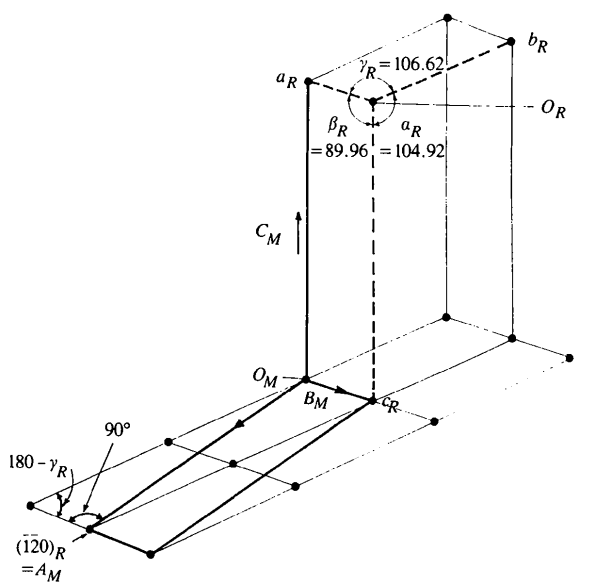

Fig. 3. This diagram illustrates the relationships found in cadre (*la*). The origin and axes of the reduced cell of AEIBCU (#13) are denoted by O_R, a_R *etc.* and broken lines. The origin and axes of the monoclinic cell derived here are shown by full lines and O_M, A_M *etc.* The centring in the C plane is also shown. The origins of reduced and monoclinic cells have been separated for convenience.

MATCCU-02 (#40) and GAKKOS (#41): We treat these two examples together. The cell reported for tetramethylammonium trichlorocuprate at 323 K (#40) was triclinic, but not reduced (Willett, Bond, Haije, Soonieus & Maaskant, 1988). The reduced cell obtained using *BLAF* has a metric tensor of the form $[A\,B\,B/B/2\,E\,0]$ (Table A†), which does not correspond to any of the lattice characters of Table 9.3.1. The cell reported for polymorph B of bis(2,2′-bis-2-thiazoline)-bis(thiocyanato)iron(II), $Fe(C_6H_8N_2S_2)_2(NCS)_2$ (#41), was triclinic but not reduced (Ozarowski, McGarvey, Sarkar & Drake, 1988). The reduced cell obtained using *BLAF* has a metric tensor of the form $[A\,B\,B/B/2\,E\,0]$ (Table A), which does not correspond to any of the reduced forms of Table 9.3.1.

Marsh (1988) commented that in both #40 and 41 'the original triclinic cells show three coplanar lattice vectors – [100], [010] and [110] – that are equal in length and subtend angles of 120° (within experimental error). It is probable that this coincidence caused difficulties in the computer-directed cell reduction process'. Marsh (1988) derived C-centred monoclinic unit cells for both compounds.

The reduced cells obtained above for #40 and #41 are analogous (apart from nomenclature of the axes), with each having two mutually orthogonal axes. We take #40 as an example. Either [010] or [001] of the reduced cell can be the unique monoclinic axis (both $b_{red}/2c_{red}$ and $c_{red}/2b_{red} \simeq \cos 60°$), with a trial showing that the first of these is correct. The bc plane of the direct lattice was checked for possible orthogonal axes and C-centring and a monoclinic cell obtained which agreed with that given by Marsh. It was the unusual relations among atomic coordinates that prompted Marsh to study these two compounds; we note that the unusual values of the cell parameters (two equal cell edges, two mutually orthogonal axes) should have provided 'hints of trouble'. However, the fundamental property in each of these examples is the orthogonality of two axes *and* the cosine relation noted above, with equality of two axes serving only to complicate the situation.

† See deposition footnote on p. 970.

4.1.2. *Cadre (Ib) (equality of two cell edges and two angles).* The general treatment for conventionally ordered ($a \leq b \leq c$) reduced cells with dimensions $a,a,c,\alpha,\alpha,\gamma$ is illustrated. As noted in BT86 (and elsewhere), the equality of two cell edges immediately suggests a centred cell and these examples can be solved graphically in a simple manner. The metric tensors have the form $[AAC/DDF]$. If the cell is type (I), then the lattice character is #10 and the transformation matrix to a *C*-centred monoclinic cell is $(110/1\bar{1}0/00\bar{1})$; if the cell is type (II), then the lattice character is #14 and the transformation matrix to a *C*-centred monoclinic cell is $(110/\bar{1}10/001)$. We show the second situation in Fig. 4 and discuss some examples below; crystals belonging to cadre (*Ib*) are listed in Table B (deposited).†

DOBKOU (#84): The triclinic cell of the tetrameric copper cluster bis(*p*-toluidine)bis(acetonitrile)tetraiodocopper was reduced after reorienting the reported cell (Rath, Holt & Tanimura, 1985). Schaefer (1986) has given the transformation matrix from the *original* cell to a *C*-centred monoclinic cell and shown that systematic absences and relationships between pairs of coordinates are compatible with the space group *C*2/*c*. This monoclinic cell is essentially isomorphous with that reported for the tetrameric copper cluster bis(*p*-chloroaniline)bis(acetonitrile)tetraiodocopper by Rath, Holt & Tanimura (1985), thus showing, in common with many other examples, that replacement of methyl by chloro has only a minor effect on the crystal structure.

α-$NaSbS_2$ (#206) was reported (Kanishcheva, Kuznetsov & Batog, 1979) as having a reduced triclinic cell (Table B). The metric tensor ([33.97 33.93 46.69/ −15.86 −15.85 −0.04]) has the form $[AAC/DDF]$, where F is indistinguishable from zero. However, $b_{red}/2c_{red} = 0.42624$, while $\cos\alpha = -0.39843$. Thus, the condition for *C*-centring described above in cadre (I*a*) is not fulfilled and it is coincidental that F is so close to zero. The lattice character is #14. A monoclinic cell was reported in an almost simultaneous publication (Olivier-Foucade, Phillipot & Maurin, 1978) and this has a = 8.232 (3), b = 8.252 (7), c = 6.836 (3) Å, α = 90.00 (1), β = 124.28 (2), γ = 90.00 (3)°, *C*2/*c*, Z = 4. This example has also been discussed by Cenzual, Gelato, Penzo & Parthé (1991). A similar example is provided by FEBMUU [disodium(μ^2-oxo)bis(μ^2-xanthoperine-*N,O,O'*)-bis(dioxomolybdenum) dimethyl sulfoxide tetrahydrofuran solvate (Burgmayer & Stiefel, 1986); note that the space group of the triclinic cell is misprinted as $P\bar{1}$ instead of $P1$ in Table 1 of M95]. In these examples the decisive feature is the pairwise equality of two edges and two angles [cadre (I*b*)] and not the mutual near-orthogonality of the a and b axes [cadre (I*a*)]. A particularly interesting example is $KAsSe_2$ (KRM89), because the metric tensor of the reduced cell has the form *AACDDF* and fulfils the conditions for lattice character 16 (transformation to *F*-centred orthorhombic), which include those for lattice character 14 (transformation to *C*-centred monoclinic). This situation was noted by KRM89 who commented that 'no symmetry element appropriate to an orthorhombic space group is present', and transformed cell and coordinates to *C*-centred monoclinic.

4.1.3. *Cadre (II): triclinic unit cells which do not show the special features of cadres (Ia) and (Ib) in the reduced cell dimensions but the metric tensor corresponds to a reduced form in Table 9.3.1 of ITC83.* Silver trimetaphosphate trihydrate (#2) – the crystals are described as triclinic, with original cell dimensions a = 7.800 (5), b = 7.796 (5), c = 9.276 (5) Å, α = 115.15 (5), β = 115.15 (5), γ = 88.93 (5)°, $P\bar{1}$, Z = 2 (Bagieu-Beucher, Durif & Guitel, 1975); this cell is not reduced and is therefore not included in cadre (I*b*), despite the equality of a pair of edges and a pair of angles. The correction to *I*2/*m via* the reduced cell (which retains equal axes but not equal angles) has been discussed in detail by BT86. The *C*-centred monoclinic cell has a = 11.13, b = 10.92, c = 9.276 Å, α = 90.0, β = 126.5, γ = 90.0°, Z = 4.

$K[B(SO_3Cl)_4]$ (#38) was reported (Mairesse & Drache, 1978) in a type (II) triclinic cell which was not reduced. The non-centrosymmetric space group $P1$ was chosen after statistical analysis of the intensity distribution; nevertheless, it was noted that the 'two independent anions are mirror images of each other'. Correction to *Cc* has been made by Marsh & Schomaker (1980). The crystal data are given in Table 2 and Table C (deposited).†

† See deposition footnote on p. 970.

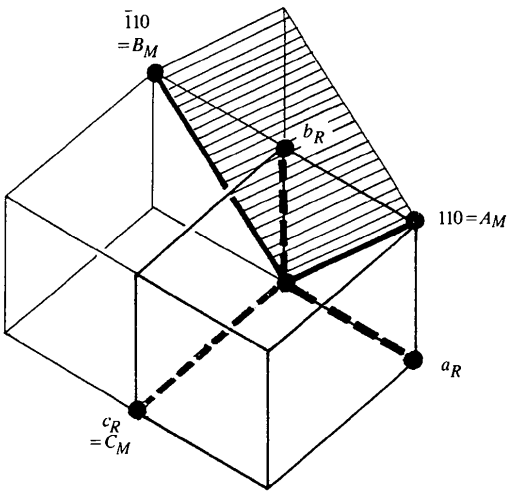

Fig. 4. A diagram of two conjoined reduced unit cells with $a \leq b \leq c$ and dimensions $a,a,c,\alpha,\alpha,\gamma$ (γ obtuse) are shown, the axes being designated by a_R,b_R,c_R [$(NH_4)_2Ce(PO_3)_5$ (#6) is used for illustration; see BT86 for discussion]. The axes (A_M *etc.*) of the corresponding *C*-centred monoclinic cell are shown emphasized, with indices of lattice points given in terms of the reduced cell.

† See deposition footnote on p. 970.

HAGPAG (x). 2-Acetylmethylidene-3-(2,4-dibromophenyl)-5-phenyl-2,3-dihydro-1,3,4-thiadiazole ($C_{17}H_{12}Br_2N_2O_5$) has been reported in a triclinic non-reduced cell with two molecules (*A,B*) in the asymmetric unit (Pandya *et al.*, 1993). The reduced cell is given in Table C (deposited) and can be transformed (M95) into a cell with $a = 22.108$, $b = 13.429$, $c = 16.018$ Å, $\alpha = 90.02$, $\beta = 133.09$, $\gamma = 89.97°$. Pandya *et al.* (1993) remarked '...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, nominally 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'. We show in an accompanying paper (HM97) that HAGPAG does have monoclinic symmetry, as judged from relations among (triclinic) structure factors and atomic coordinates.

5. Discussion and conclusions

A current mantra reminds one that apparent metrical symmetry must be validated by other means, such as intensity relationships. We have encountered one example of a crystal that is metrically centred monoclinic, but actually triclinic; this is the triclinic polymorph of $Li_4P_2O_7$ (Daidouh, Veiga, Pico & Martinez-Ripoli, 1997), where the authors drew attention to a pseudo-monoclinic centred cell. This polymorph fits into our cadre (I*a*) with $\beta_{red} = 90.01°$, $a_{red}/2b_{red} = 0.36488$, $|\cos \gamma_{red}| = 0.36397$. We have encountered three examples of metrically orthorhombic cells which are actually monoclinic $[C_{16}H_{27}H_4O_3S^+.NO_3^-$ (BT86), $KAsSe_2$ (KRM89) and JOGRUS (M95; also discussed by HM97)]. It is also worth noting that the real symmetry of an (apparently) single crystal can often only be revealed by optical means (Kahr & MacBride, 1992).

The examples analysed above fall into two cadres – those which have been found to have special features in the dimensions of the *reduced* triclinic cell [cadres (I*a*) and (I*b*)] and those without such special features, but with a metric tensor corresponding to one of the entries of Table 9.3.1 [cadre (II)]. We conclude, with the benefit of hindsight, that the need to investigate the possibility of higher symmetry should have been apparent for the crystals in cadre (I). However, suspicions about the possibility of higher symmetry should also have been aroused for the crystals in cadre (II) *after* cell reduction *and* calculation of the metric tensor. Clearly, calculation of the metric tensor is an essential step as soon as the cell dimensions have been measured during a crystal structure investigation. Remarkably, this has not always been done when the triclinic to monoclinic correction has been made for published structures, even though such a recommendation is of long standing in the literature. Here, however, the investigator also has the opportunity to search for special relationships among coordinates of atoms purportedly unrelated by crystallographic symmetry and this strategy has the advantage, as R. E. Marsh has so often emphasized, that it relies on the overall symmetry of the structure rather than on cell dimensions determined from a few (perhaps too few) arbitrarily chosen reflections.

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