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How to Avoid Unnecessarily Low Symmetry in Crystal Structure Determinations

BY WERNER H. BAUR

Department of Geological Sciences, Box 4348, *University of Illinois at Chicago, Illinois* 60680, *USA*

AND EKKEHART TILLMANNS*

Institut für Geowissenschaften, Postfach 3980, *Universität Mainz, D*-6500 *Mainz, Federal Republic of Germany*

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Abstract

A check of recent volumes of *Acta Crystallographica* and *Crystal Structure Communications* shows that about 3% of all recently published crystal structures were described with too low symmetry. Three categories of error are recognized: (1) both Laue class and crystal system are wrong; (2) only the Laue class is wrong; (3) Laue class and crystal system are correct, but an inversion center is missing. Category (1) cases can be most easily diagnosed by calculating the reduced cell and its Niggli matrix. Category (3) cases are most easily recognized during full-matrix least-squares refinement from singularities, high correlations between parameters and poor convergence. The omission of an inversion center will not result in a singular matrix when all atoms in the centrosymmetric cell are in special positions which become general positions in the noncentrosymmetric cell. Once the refinement is completed structures with a missing inversion center can be recognized by unusually high e.s.d.'s, especially for the highly correlated parameters, and by large distortions of observed bond distances and angles from accepted values. Such distortions often show up as splitting of the centrosymmetrically related atomic positions into positions whose average is close to the true centrosymmetric positions. A mechanical application of the *R*-ratio test should be avoided; it can easily lead to wrong conclusions. Proof of higher symmetry must be obtained from the diffraction data. The presence of more than one effective formula per asymmetric unit should always be reason to check for higher symmetry. Cases in all three categories can be checked for the occurrence of higher symmetry by searching for regularities in bond lengths and angles or in the positional coordinates of the atoms. The most systematic way for such searches is the simple, but powerful method of topological analysis of crystal structures. For six structures which previously had been described with too low symmetry higher-symmetry descriptions are provided.

Introduction

In the last several years it was pointed out repeatedly that a number of published crystal structure determinations had been performed with space groups of incorrectly low symmetry. Examples have been given by Marsh and co-workers [Marsh & Schomaker

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* Present address: Mineralogisches Institut, Universität Würzburg, Am Hubland, D-8700 Würzburg, Federal Republic of Germany.

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(1981) for cases from *Inorganic Chemistry*; Marsh & Herbstein (1983) for occurrences in *Acta Crystallographica*; and also, among many others, by Baur & Tillmanns (1970), and by Jones (1984)]. Schomaker & Marsh (1979) recognized two categories: (1) the structure has been described with the wrong Laue symmetry; (2) the Laue symmetry is correct but an inversion center has been omitted. In the second case refinement by full-matrix least-squares methods results either in singular matrices or in high correlation coefficients between related parameters. Convergence is poor and atomic positions can be severely misdetermined. These effects do not occur when the refinement is based on the wrong Laue class. What happens then is that the structure is described by too many parameters but is otherwise essentially correct.

The wrong Laue symmetry may be assigned more easily when the reciprocal lattice has not been surveyed photographically and the investigator or the computer programs of an automated single-crystal diffractometer fail to examine the crystal symmetry properly. Description of a structure in the correct Laue class with omission of an inversion center can result in deviations of mean and individual bond lengths from accepted values. Bond lengths might seem to be significantly different in chemically equivalent moieties which in reality are related by the missing centers of symmetry. Most papers reporting corrections of crystal structures which had been determined in wrong space groups do not describe the techniques an investigator can use to avoid such pitfalls. We wish to remedy this situation by presenting such techniques. In the process we give descriptions of higher symmetry for six previously published crystal structures.

Reduced bases and lattice characters

Any attempt to avoid assignment of an incorrect Laue symmetry should begin with the determination of the reduced cell of the lattice. This is an old topic (see Seeber, 1831) which was dealt with by Niggli (1928) and has been summarized by de Wolff (1983) in Vol. A of the new *International Tables for Crystallography* (1983).

Three vectors **a**, **b**, **c** describing a primitive unit cell are called a reduced basis if they define a right-handed system and if the parameters of the metric tensor (reduced form)

$$\begin{matrix} \mathbf{a}.\mathbf{a} & \mathbf{b}.\mathbf{b} & \mathbf{c}.\mathbf{c} \\ \mathbf{b}.\mathbf{c} & \mathbf{c}.\mathbf{a} & \mathbf{a}.\mathbf{b} \end{matrix} \qquad (1)$$

satisfy certain requirements leading to the following two conditions:

(*a*) Of all possible lattice vectors, none is shorter than **a**; of all those not parallel to **a**, none is shorter than **b**; of all those not lying in the **a**, **b** plane none is shorter than **c**.

(*b*) The three angles between the basis vectors are either all acute (type I cell) or all obtuse (type II cell). Condition (*a*) is essential since it defines the lengths of **a**, **b** and **c** uniquely, and limits all three angles to values between 60 and 120°. Condition (*b*) is a convention. The reduced form (1), also often referred to as a Niggli matrix (see Niggli, 1928), makes it possible to assign the given reduced cell to one of 44 different lattice characters. The lattice characters allow a much finer differentiation between lattice types than is provided by the Bravais lattices. Tables of the 44 lattice characters have been given by Niggli (1928), Mighell, Santoro & Donnay (1969), Mighell & Rodgers (1980) and de Wolff (1983), among others. It is important to make sure that both the main conditions and the special conditions [not listed here, but see Mighell, Santoro & Donnay (1969)] for reduction are satisfied. Failure to do this caused much discussion in the past. A number of computer programs exist which perform this operation [for instance *REZE* by Biedl (1967) and *NBS*AIDS*80 by Mighell, Hubbard & Stalick (1981)]. This latter program also assigns the Niggli matrix found for a particular cell to one of the 44 lattice characters by comparing its numerical relationships with those of the various lattice characters. Other methods of finding a higher metric symmetry of a lattice exist. Le Page (1982) describes a method to search systematically for twofold axes. This approach is purely geometrical and has the advantage of not depending on the reduced cell, since in some cases small differences in lattice constants (of the order of magnitude of the experimental error) can lead to different reduced cells. The *B*-matrix algorithm (Santoro, Mighell & Rodgers, 1980) has been coded for computers (Himes & Mighell, 1982; Mugnoli, 1984). This method is completely general and consists of testing various cells for rational coefficients in the transformation matrices.

The topic of finding reduced cells and describing them uniquely has been confused by the existence of various algorithms, definitions and conventions. We do not wish to give an historical survey, but are simply following the definitions given by Mighell *et al.* in Vol. I of the old *International Tables for X-ray Crystallography* (1969) and by de Wolff (1983) in Vol. A of the new *International Tables for Crystallography* (1983). It should be kept in mind that the definitions given in the first and second editions of Vol. I of the old *International Tables for X-ray Crystallography* (1952, 1965) are different from those used currently.

Inspection of the Niggli matrix of the reduced cell helps in identifying cases where both Laue class and crystal system are wrong. It cannot help in cases where the Laue class is wrong, but the crystal system is correct. Herbstein & Marsh (1982) described three such cases. They are possible when there are two Laue classes within one crystal system, as in the tetragonal, trigonal, hexagonal and cubic systems.

Topological analysis of crystal structures

The cases where a structure has been described in the wrong Laue class and the wrong crystal system can be diagnosed not only by investigating the Niggli matrix of the reduced cell, but also by analyzing the topology of the crystal structure. Topological analysis (Baur, Tillmanns & Hofmeister, 1983) is also useful when the Laue class is correct but the presence of an inversion center has been overlooked, and when there is more than one Laue class in a crystal system.

Such analysis consists of a study of the topological symmetry of the various atomic environments in a crystal structure. It can show either that the topology of the arrangement does not allow the structure to be described in a space group of higher symmetry or that the arrangement allows a higher symmetry. In the first case the analysis gives a proof that the structure is already described by the highest admissible symmetry. Such proof was given by Tillmanns, Hofmeister & Baur (1983) for $Ba_2Ti_9O_{20}$ (space group $P\bar{1}$), where earlier studies had suggested monoclinic symmetry. In the second case the diffraction evidence must be evaluated in order to ascertain whether or not a higher space-group symmetry is actually realized. The same restriction applies of course to cases where a higher Laue symmetry is suggested by the metric symmetry of a reduced cell. Topological analysis can be applied to test for higher symmetries in other Laue classes within other crystal systems. However, it appears that in such cases use of the Niggli matrix leads to an answer more quickly.

Comparison of observed and empirically derived bond lengths

It is always instructive to compare the results of a new crystal structure determination with data available from the literature. In practice this means that the newly determined bond distances and angles should compare well with those found previously for similar moieties. Such comparisons are particularly called for when one is trying to determine whether or not a given structure has an inversion center.

When studying inorganic compounds with ionic or partly ionic bonds (an area of expertise of the present authors) we recommend to check whether the mean bond lengths in the various coordination polyhedra have values close to those obtained by adding the appropriate effective ionic radii, tabulated as a function of formal ionic charge and of coordination number (Shannon, 1976). One can do even better and compare the observed individual anion–cation distances within coordination polyhedra with those predicted from empirical relations which are based on the bond-strength differences of various anions in these structures. Bond lengths in ionic or partly ionic structures can be represented by the equation (Baur, 1970, 1971):

$$d(A\text{–}X)_{\text{ind}} = [d(A\text{–}X)_{\text{mean}} + b\,\Delta p(X)]\ \text{Å}, \quad (2)$$

where $d(A\text{–}X)_{\text{mean}}$ and b are empirically derived values for the mean bond lengths and the slopes of the dependence of the individual bond lengths $d(A\text{–}X)_{\text{ind}}$ on $p(X)$ for given pairs of A and X in a given coordination. The difference $\Delta p(X)$ between the individual $p(X)$ and the mean $p(X)$ for the coordination polyhedron is:

$$\Delta p(X) = p(X)_{\text{ind}} - p(X)_{\text{mean}}. \quad (3)$$

Numerical values for $d(A\text{–}X)_{\text{mean}}$ and b of equation (2) based on regression calculations are given for a number of common elements in Baur (1981). The predictions of bond distances in inorganic substances by the use of equation (2) for tightly bound tetrahedral groups are good to about ±0·01 Å.

Statistics of reported and reduced cells

In order to see how prevalent the use of reduced cells is in the literature we searched systematically through Vols **10** (1981) and **11** (1982) of *Crystal Structure Communications* and Vols B**31** (1975) and C**39** (1983) of *Acta Crystallographica.* The computations were performed using the program *REZE* (Biedl, 1967) and the program *NBS*AIDS*80 (Mighell *et al.*, 1981). The results for all triclinic cells encountered there are shown in Table 1. The definition of Mighell *et al.* (1969) for a reduced cell has been used in only about 29% of all triclinic cases. In another 42% some other definition was used, but the cell vectors reported are the three shortest ones possible. In an additional 29% of the published triclinic structures, the reduction algorithm showed that the true cell had shorter cell vectors than originally reported. In four of these cases an inspection of the Niggli matrix of the reduced cell indicated that the lattice had monoclinic symmetry and was centered. These are the cases where we considered it useful to investigate the crystal structure itself or the diffraction pattern for signs of higher symmetry.

There are a number of additional cases where the reduced basis is close to higher symmetry but with deviations larger than the usual experimental errors in lattice-constant determination. We have not investigated them, but in at least one case where an angle differed by as much as 0·3° from 90°, higher symmetry is indicated (Marsh, 1984*a*), and is entered in Table 1.

The monoclinic cells (Table 2) were not compared with their reduced bases because conventionally the unique axis is *b*, and also because the centered cells are usually described in their centered and not in their primitive setting. In 28% of the studied cases the shortest monoclinic cell vectors had not been

Table 1. *Results of checking the triclinic lattices of all crystal structures published in Acta Crystallographica Vol.* **B31** (1975) (*AC*, **B31**), *Crystal Structure Communications Vol.* **10** (1981) (*CSC*, **10**), *Crystal Structure Communications Vol.* **11** (1982) (*CSC*, **11**) *and Acta Crystallographica Vol.* C**39** (1983) (*AC*, C**39**)

The cells which were reported in reduced form in the original papers are subdivided into those reduced according to *International Tables* (1983) (*IT*) and those reduced to any other convention. Those originally reported in not reduced cells are subdivided into those where the identification of shorter cell vectors did not lead to a higher metric symmetry and those where it did. The latter cases all lead to centered cells, all but one of which are monoclinic.

	AC, **B31**	*CSC*, **10**	*CSC*, **11**	*AC*, **C39**	Σ	% of Σ
All cases considered	72	43	67	115	297	100·0
Reduced after *IT*	8	18	27	34	87	29·3
Other definitions	39	13	23	50	125	42·1
Not reduced	24	12	16	28	80	26·9
Higher metric symmetry detected	1	0	1	3	5	1·7
Higher overall symmetry confirmed	1	0	1	3	5	1·7

Table 2. *Results of checking monoclinic lattices of structures published in Crystal Structure Communications Vol.* **10** (1981) (*CSC*, **10**), *Crystal Structure Communications Vol.* **11** (1982) (*CSC*, **11**) *and Acta Crystallographica Vol.* C**39** (1983) (*AC*, C**39**)

In the last case only those cells were considered where the monoclinic angle was $>115°$. We are including here also the two cases with $\beta < 115°$ [Jaber *et al.* (1983) and Haller *et al.* (1983)] which had been identified by Marsh (1983, 1984*d*). Only those instances are considered in which shorter lattice vectors were identified or a higher metric symmetry was encountered. The latter cases all lead to orthorhombic cells, which in all but one case are centered.

	CSC, **10**	*CSC*, **11**	*AC*, **C39**	Σ	% of Σ
All cases considered	150	199	29	278	100·0
Shorter cell vectors found	21	36	22	78	28·1
Higher metric symmetry detected	3	2	3	8	2.9
Higher overall symmetry confirmed	1	0	3	4	1·4

used. In an additional 3% of the reported monoclinic structures we found metrically orthorhombic cells, centered in all but one case.

Although our check of the literature data may not have been completely exhaustive because of mistakes and oversights made by us, on balance it appears that in about 30% of all triclinic cases the vectors used to describe the cell were not the three shortest ones possible. In an even larger proportion of cases the standard reduced cell was not determined. Therefore in all these instances it was impossible to test for the occurrence of higher metric symmetries by inspection of the Niggli matrix. For about 2% of all these structures possible higher metric symmetries are indicated. This of course is not a proof that the structures really have higher symmetries, but it should be taken as sufficient reason to have a closer look at them.

As we shall show below, all originally triclinic cases of higher metric symmetry were found to have monoclinic or orthorhombic crystal structures (five out of five). For the originally monoclinic cases four out of eight of the structures could be proven to be of higher symmetry. Our sample is too small to provide a sufficient statistical base, but it seems reasonable to estimate that about 1 to 2% of all published triclinic and monoclinic structures may have been described with too low symmetry. This estimate is made simply on the basis of a systematic search and evaluation of the metric symmetry of the unit cells. In addition we have to take into account the cases where an inversion center has been omitted. We also assume a similar error ratio for orthorhombic, trigonal, tetragonal, hexagonal and cubic crystal classes, that is inversion centers have to be added, the metric symmetry changed to a different system, or the Laue class changed within the same crystal system in similar proportions as for triclinic and monoclinic crystals. Based on the relative numbers of these cases as documented by Marsh and co-workers it appears that the number of crystal structure descriptions in unnecessarily low symmetry may conservatively be estimated as at least 3% of all published crystal structures. Depending on the estimate of how many structures are published annually, this could mean that several hundred incorrectly described structures are published each year.

The fact that we chose *Acta Crystallographica* and *Crystal Structure Communications* as a base for our search does not imply that crystal structures of too low symmetry are not published in other periodicals. We shall quote a few such cases, encountered by chance in other journals.

Examples of testing of higher metric symmetries

In this section we will treat chronologically the cases identified in Tables 1 and 2 as having metric symmetries which exceed the originally reported crystal symmetries. Thus, by definition we have not made any attempt to identify wrong Laue classes within the same crystal system, nor have we tried to look systematically for missing inversion centers.

(*a*) *Silver trimetaphosphate monohydrate*, $Ag_3P_3O_9.H_2O$

The crystal structure of this compound has been described in space group $P\bar{1}$, with $Z = 2$, by Bagieu-Beucher, Durif & Guitel (1975), see Table 3. The cell, as reported, is not reduced. The Niggli matrix as calculated from the reduced cell clearly corresponds to lattice character case No. 17 (Mighell *et al.*, 1969). The right angles calculated for the monoclinic setting deviate from 90° by less than one e.s.d. Inasmuch as $C2/m$ (or in a different setting $I2/m$) is one of the minimal non-isomorphic supergroups of $P\bar{1}$ (*International Tables for Crystallography*, 1983) space group $I2/m$ is the obvious choice for investigating the potentially higher symmetry of $Ag_3P_3O_9.H_2O$. A direct transformation of the positional coordinates of all 16 atoms in the asymmetric unit reveals that five of them can be located in positions $x0z$ [$(4i)$] with site symmetry m, one in $\tfrac{1}{2}y0$ [$(4h)$] with symmetry 2, while the remaining ten can be combined pairwise in five general positions [$8(j)$]. The mean shift necessary to change from the triclinic to the monoclinic coordinates amounts to an average of only one-third of the e.s.d.'s of the transformed coordinates derived from those reported in Bagieu-Beucher *et al.* (1975). In no instance is the shift larger than one e.s.d. Therefore, in this case we can state that well within the reported random errors the crystal structure of $Ag_3P_3O_9.H_2O$ conforms to space-group symmetry $I2/m$. In retrospect one sees that the original cell constants correspond to a primitive setting of a centered unit cell ($a = b$, $\alpha = \beta$).

Bagieu-Beucher *et al.* (1975) remark that the ring phosphate P_3O_9 has a chair configuration and possesses a pseudo mirror plane. This clue could also have led to the discovery of the $I2/m$ symmetry. When we perform a topological analysis of $Ag_3P_3O_9.H_2O$ (Table 3) along the lines suggested by Baur *et al.* (1983) it becomes clear that the O-atom types B, C and D occur pairwise. Also the O environments of atoms P(1) and P(2) are topologically equivalent, as are those of atoms Ag(1) and Ag(2). When we compare the corresponding interatomic distances with each other in detail [for instance around Ag(1) and Ag(2)] we see that they are equal within 2 e.s.d.'s. Thus we get the five pairs of atoms which are independent in the description in $P\bar{1}$, but are symmetrically and topologically equivalent in $I2/m$.

The Niggli matrix is also very close to lattice character case 16, orthorhombic F, and somewhat close to case 15, tetragonal I. Although the maximal deviations of the angles from 90° (0·32° for case 16, 1·1° for case 15) are outside the normal range of error, similar errors have been reported before (Marsh, 1984*a*). The topological analysis, however, assures us that higher than monoclinic symmetry does not exist here: in space group $I2/m$ all atoms are differently coordinated. Therefore, in an orthorhombic F-centered or a tetragonal I-centered space group with a higher multiplicity of the general position all atoms would have to occupy special positions. This is not possible for P(1, 2) which is tetrahedrally coordinated by four topologically different O atoms (Table 3); therefore, it cannot reside in any special position.

Thus there are three independent ways to arrive at the suspicion that $Ag_3P_3O_9.H_2O$ could have a higher symmetry: the numerical values of the original cell constants, the Niggli matrix of the reduced cell, and the topological analysis of the atomic environments in the crystal structure. The confirmation of a higher symmetry comes in this case from a transformation and an analysis of positional coordinates.

(*b*) *Bis(benzoylaziridine)dibromozinc*(II), $ZnBr_2(C_9H_9NO)_2$

Faure, Loiseleur, Bartnik, Lesniak & Laurent (1981) reported the crystal structure of $ZnBr_2(C_9H_9NO)_2$ in space group $P2_1$, with $Z = 2$ (Table 4). The number of formula units per cell equals the number of asymmetric units, but as we shall see below the molecule is symmetric within itself. The

Table 3. *Cell constants, transformation and Niggli matrices, positional coordinates* ($\times 10^4$) *in space group* $I2/m$ *of* $Ag_3P_3O_9.H_2O$, *together with topological analysis*

The numbers in square brackets are the coordinate shifts (averaged when two atoms are involved) needed to obtain $I2/m$ symmetry. Numbers in parentheses are e.s.d.'s derived from those reported by Bagieu-Beucher *et al.* (1975) in their Table 1.

Cell as reported by Bagieu-Beucher *et al.* (1975) for structure in $P\bar{1}$

$a = 7{\cdot}800$ (5) Å $\alpha = 115{\cdot}15$ (5)°
$b = 7{\cdot}796$ (5) $\beta = 115{\cdot}15$ (5)
$c = 9{\cdot}276$ (5) $\gamma = 88{\cdot}93$ (5)

Transformation matrix to reduced cell

$0\,\bar{1}\,0/1\,0\,0/0\,1\,1$

Reduced cell

$a = 7{\cdot}796$ (5) Å $\alpha = 114{\cdot}26$ (5)°
$b = 7{\cdot}800$ (5) $\beta = 114{\cdot}65$ (5)
$c = 9{\cdot}239$ (5) $\gamma = 91{\cdot}07$ (5)

Niggli matrix of reduced cell

60·78	60·84	85·36
−29·61	−30·04	−1·14

This corresponds to case 17, monoclinic I centered

$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{c}\cdot\mathbf{c}$
$-\lvert\mathbf{b}\cdot\mathbf{c}\rvert$	$-\lvert\mathbf{a}\cdot\mathbf{c}\rvert$	$-(\mathbf{a}\cdot\mathbf{a}-\lvert\mathbf{b}\cdot\mathbf{c}\rvert-\lvert\mathbf{a}\cdot\mathbf{c}\rvert)$

Transformation matrix from reduced cell to monoclinic I-centered

$\bar{1}\,0\,\bar{1}/\bar{1}\,\bar{1}\,0/0\,1\,1$

Unit cell in monoclinic I-centered setting

$a = 9{\cdot}326$ (6) Å $\alpha = 90{\cdot}01$ (5)°
$b = 10{\cdot}925$ (7) $\beta = 106{\cdot}50$ (5)
$c = 9{\cdot}276$ (5) $\gamma = 90{\cdot}03$ (5)

Direct transformation from original $P\bar{1}$ cell of Bagieu-Beucher *et al.* (1975) to monoclinic I cell

$\bar{1}\,\bar{1}\,\bar{1}/1\,\bar{1}\,0/0\,0\,1$

The inverse of this matrix needed for coordinate transformation of the original parameters to those in the monoclinic setting (monoclinic to original)

$-\tfrac{1}{2}\,-\tfrac{1}{2}\,-\tfrac{1}{2}/-\tfrac{1}{2}\,-\tfrac{1}{2}\,-\tfrac{1}{2}/0\,0\,1$

Coordinates in space group $I2/m$ (multiplied by 10^4)

	x	y	z
Ag(1, 2)	8244[1] (1)	1705[1] (1)	8893[0] (1)
Ag(3)	5000[0] (1)	3183[-] (1)	0[1] (1)
P(1, 2)	4208[1] (3)	1329[1] (2)	6962[1] (3)
P(3)	2051[-] (3)	0[2] (2)	8034[-] (3)
O(*L*12)	4976[-] (7)	0[1] (6)	7062[-] (8)
O(*L*13, *L*23)	3150[2] (7)	1131[2] (6)	8066[2] (8)
O(*E*11, *E*21)	3275[0] (8)	1574[2] (7)	5399[6] (8)
O(*E*12, *E*22)	5380[4] (8)	2225[3] (6)	7745[1] (8)
O(*E*31)	1651[-] (8)	0[2] (6)	9470[-] (8)
O(*E*32)	840[-] (8)	0[1] (6)	6594[-] (8)
H_2O	1853[-] (8)	0[2] (6)	2778[-] (8)

Table 3 (*cont.*)

Topological analysis of atomic environments in $Ag_3P_3O_9.H_2O$

O-atom environments (= O-atom types)

Label	Number of such atoms	Number of neighbors P	Ag[5]	Ag[8]	CN
A	1	2	0	0	2
B	2	2	0	1	3
C	2	1	1	1	3
D	2	1	2	1	4
E	1	1	2	0	3
F	1	1	0	2	3
G	1	0	2	0	3

Cation environments with labels for the O atoms as defined above

	O-atom types						
P(1)	1*A*	1*B*	1*C*	1*D*			
P(2)	1*A*	1*B*	1*C*	1*D*			
P(3)		2*B*			1*E*	1*F*	
Ag(1)			1*C*	2*D*	1*E*		1*G*
Ag(2)			1*C*	2*D*	1*E*		1*G*
Ag(3)		2*B*	2*C*	2*D*		2*F*	

originally reported cell is not reduced. However, the reduced cell has almost the same dimensions as the reported cell. This can happen when the metric symmetry of the lattice is actually higher than assumed. The Niggli matrix clearly points to a centered orthorhombic cell. Inspection showed the presence of a mirror plane; therefore, of the two centered orthorhombic space groups ($C222_1$ and $Cmc2_1$) which had to be investigated (because both are minimal non-isomorphic supergroups of $P2_1$), the latter is the correct choice. We chose the *A* setting (Table 4). Three of the atoms are on the mirror plane [Zn, Br(1) and Br(2)]; all others can be combined pairwise. The shifts in positional coordinates needed to attain orthorhombic symmetry are on average one-half an e.s.d. for the non-hydrogen atoms. All but two are below one e.s.d.; the other two are below two e.s.d.'s. Therefore, the pseudo mirror plane mentioned by Faure *et al.* (1981) as passing through the Zn and Br atoms is, within the limits of error of the structure determination, a real mirror. Neither *Crystal Data Determinative Tables* (1984) nor the Cambridge Data Base [Allen *et al.* (1979) (1982 release)] have pointed out that this structure has been described with too low symmetry.

Table 4. *Cell constants, transformation and Niggli matrices and positional coordinates* ($\times 10^4$) *of* $ZnBr_2(C_9H_9NO)_2$ *in space group* $A2_1ma$ *as transformed from the values of Faure et al.* (1981); *for explanations see Table* 3

(*a*) Unit cells

	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
Original	7·781 (3)	10·746 (4)	11·823 (3)	90	109·22 (3)	90
Reduced	7·781 (3)	10·746 (4)	11·822 (3)	90	109·21 (3)	90
Orthorhombic *A*	10·746 (4)	22·328 (6)	7·781 (3)	90·01 (3)	90	90

(*b*) Transformation matrices

Original to reduced	1 0 0	0 $\bar{1}$ 0	$\bar{1}$ 0 $\bar{1}$
Original to orthorhombic *A*	0 1 0	$\bar{1}$ 0 $\bar{2}$	$\bar{1}$ 0 0
Orthorhombic *A* to original	0 0 $\bar{1}$	1 0 0	0 $-\frac{1}{2}$ $\frac{1}{2}$

(*c*) Niggli matrix of reduced cell

60·54	115·48	139·76
0	−30·27	0

Lattice character case 36, orthorhombic *C* (or *A*)

a · a	b · b	c · c
0	$\frac{-\mathbf{a}\cdot\mathbf{a}}{2}$	0

(*d*) Coordinates in space group $A2_1ma$ (multiplied by 10^4)

	x	*y*	*z*
Zn	9442[-] (2)	0[0] (-)	17[-] (3)
Br(1)	9991[-] (2)	0[1] (2)	2904[-] (3)
Br (2)	1087[-] (2)	0[1] (2)	7972[-] (3)
N(1, 2)	8250[0] (10)	645[5] (5)	9180[30] (20)
C(1, 10)	8235[15] (20)	800[10] (15)	7475[15] (50)
C(2, 11)	8465[5] (10)	1268[3] (10)	8692[3] (30)
C(3, 12)	7450[0] (20)	1705[5] (10)	9090[10](20)
O(1, 2)	6445[5] (10)	1510[0] (5)	9525[5] (20)
C(4, 13)	7660[20] (20)	2355[0] (5)	8865[20] (20)
C(5, 18)	8745[5] (10)	2568[3] (10)	8222[18] (20)
C(6, 17)	8875[15] (20)	3190[5] (10)	8035[20] (30)
C(7, 16)	7940[10] (20)	3568[3] (10)	8437[18] (30)
C(8, 15)	6825[5] (20)	3340[5] (10)	9065[10] (20)
C(9, 14)	6685[35] (20)	2735[0] (10)	9270[15] (30)

(*c*) 1-[(4-*Cyclooctylamino*-3-*pyridyl*)*sulfonyl*]-3-*ethylurea hydrogen nitrate*, $C_{16}H_{27}N_4O_3S^+.NO_3^-$

This structure has been reported in space group $P2_1/c$ with $Z = 4$ (Dupont, Lewinski, Stadnicka & Delarge, 1981). The Niggli matrix of the reduced cell points to lattice character case 40, orthorhombic *C* (Table 5). The molecule itself is asymmetric, and the number of molecules in the unit cell does not exceed the number of asymmetric units in $P2_1/c$. The only *C*-centered minimal non-isomorphic supergroup of $P2_1/c$ is *Cmca*. The multiplicity of the general position in *Cmca* is 16, but there are only 8 molecules in this *C*-centered cell, which has twice the volume of the primitive monoclinic cell. The maximal non-isomorphic subgroups of *Cmca* are $C222_1$, *Cmc*2, *Abm*2 and *Aba*2. There the general position is eightfold, but none of these space groups has inversion centers as $P2_1/c$ does, which means there are no glide planes normal to the 2_1 axes. Consequently in this case the metric symmetry is fortuitously close to orthorhombic, but the crystal structure itself is not of higher symmetry. The structure has already been described in the highest possible symmetry.

(*d*) *Cobalt*(II) *chloride phosphate*, Co_2PO_4Cl

The crystal structure of Co_2PO_4Cl was determined in space group $C2/c$ with $Z = 8$ by Nord & Stefanidis (1981). The Niggli matrix of the reduced cell points to a higher metric symmetry and the possibility of a higher crystal symmetry (lattice character case 8, Table 6). Indeed, when Nord & Stefanidis (1980) were dealing previously with twinned crystals of this compound, they could not decide between mono-

Table 5. *A monoclinic case where the metric symmetry points to orthorhombic, but the crystal symmetry nevertheless is monoclinic*: $C_{16}H_{27}N_4O_3S^+.NO_3^-$ (*Dupont et al.*, 1981)

(*a*) Unit cells

	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
Original	18·397 (3)	5·283 (1)	22·893 (3)	90	113·73 (5)	90
Reduced	5·283 (1)	18·397 (3)	22·882 (3)	113·66 (5)	90	90
Orthorhombic *C*	18·397 (3)	41·915 (5)	5·283 (1)	90	90	90·04 (5)

(*b*) Transformation matrices

Original to reduced	$0\,1\,0$	$1\,0\,0$	$\bar{1}\,0\,\bar{1}$
Original to orthorhombic *C*	$\bar{1}\,0\,0$	$\bar{1}\,0\,\bar{2}$	$0\,\bar{1}\,0$

(*c*) Niggli matrix of reduced cell

27·91	338·45	523·59
−168·94	0	0

Lattice character case 40, orthorhombic *C*

$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{b}\cdot\mathbf{b}$	$\mathbf{c}\cdot\mathbf{c}$
$\dfrac{-\mathbf{b}\cdot\mathbf{b}}{2}$	0	0

Table 6. *Cell constants, transformation and Niggli matrices and toplogical analysis of* Co_2PO_4Cl (*Nord & Stefanidis*, 1981) *and* Fe_2PO_4Cl (*Anderson, Rea & Kostiner*, 1976)

(*a*) Unit cells

	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
Co_2PO_4Cl						
Original, monoclinic *C*	13·514 (2)	9·132 (2)	9·220 (2)	90	132·90 (2)	90
Reduced	8·155 (2)	8·155 (2)	8·167 (2)	105·32 (2)	111·21 (2)	111·90 (2)
Orthorhombic *I*(?)	9·220 (2)	9·900 (2)	9·132 (2)	90	90	89·88 (2)
Monoclinic *I*	9·900 (2)	9·132 (2)	9·220 (2)	90	90·12 (2)	90
Fe_2PO_4Cl						
Original, monoclinic *C*	13·677 (1)	9·217 (1)	9·326 (1)	90	132·53 (1)	90
Reduced	8·246 (1)	8·246 (1)	8·292 (1)	104·90(1)	111·35 (1)	112·05 (1)
Orthorhombic *I*(?)	9·326 (1)	10·079 (1)	9·217 (1)	90	90	89·54 (1)
Monoclinic *I*	10·079 (1)	9·217 (1)	9·326 (1)	90	90·46 (1)	90

(*b*) Transformation matrices

Original to reduced	$\frac{1}{2}\,-\frac{1}{2}\,0$	$-\frac{1}{2}\,-\frac{1}{2}\,0$	$-\frac{1}{2}\,\frac{1}{2}\,\bar{1}$
Original to orthorhombic	$0\,0\,1$	$1\,0\,1$	$0\,1\,0$
Original to monoclinic *I*	$1\,0\,1$	$0\,\bar{1}\,0$	$0\,0\,\bar{1}$

(*c*) Niggli matrices

Co_2PO_4Cl: Niggli matrix of reduced cell

66·50	66·50	66·70
−17·60	−24·10	−24·81

Lattice character case 8, orthorhombic *I*

$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{a}\cdot\mathbf{a}$
$-\lvert\mathbf{b}\cdot\mathbf{c}\rvert$	$-\lvert\mathbf{a}\cdot\mathbf{c}\rvert$	$-(\lvert\mathbf{a}\cdot\mathbf{a}\rvert-\lvert\mathbf{b}\cdot\mathbf{c}\rvert-\lvert\mathbf{a}\cdot\mathbf{c}\rvert)$

Fe_2PO_4Cl: Niggli matrix of reduced cell

68·00	68·00	68·76
−17·58	−24·89	−25·53

Lattice character case 17, monoclinic *I*

$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{c}\cdot\mathbf{c}$
$-\lvert\mathbf{b}\cdot\mathbf{c}\rvert$	$-\lvert\mathbf{a}\cdot\mathbf{c}\rvert$	$-(\mathbf{a}\cdot\mathbf{a}-\lvert\mathbf{b}\cdot\mathbf{c}\rvert-\lvert\mathbf{a}\cdot\mathbf{c}\rvert)$

(*d*) Topological analysis of atom environments in Co_2PO_4Cl (and Fe_2PO_4Cl)

O- and Cl-atom environments

		Number of neighbors				
Label	Number of such atoms	P	Co(1)	Co(2) in 2	Co(3) in $\bar{1}$	CN
A	1	1	1	1	1	4
B	1	1	1	0	0	2
C	1	1	1	1	0	3
D	1	1	1	0	1	3
Cl	1	0	2	1	1	4

Cation environments using the labels of the anions defined above

	Anion atom types				
P	*A*	*B*	*C*	*D*	
Co(1)	*A*	*B*	*C*	*D*	2Cl
Co(2) in 2	2*A*		2*C*		2Cl
Co(3) in $\bar{1}$	2*A*			2*D*	2Cl

clinic and orthorhombic symmetries. Even though the structure has now been solved and refined in space group $C2/c$ the question still remains because of the higher metric symmetry of the lattice. Topological analysis can, with the help of symmetry arguments, settle it (Table 6*d*). There are four different O-atom types present in Co_2PO_4Cl. Atoms *C* and *D* are not equivalent despite the fact that both have coordination number 3, because *D* coordinates to Co(3) which resides in position 4(*a*) with site symmetry $\bar{1}$, while atom *C* coordinates to Co(2) [in 4(*e*), site symmetry 2]. Therefore O atom *C* is a neighbor to its equivalent atom in the coordination octahedron around Co(2), while *D* is opposite to its equivalent atom in the coordination around Co(3). The cell constants and the volumes of the monoclinic and the orthorhombic *I*-centered cells are identical. If Co_2PO_4Cl were orthorhombic the space group would have to be *Ibam*, *Ibca* or *Imma*, which are all minimal non-isomorphic supergroups of $C2/c$. There are 8 equivalent positions in $C2/c$ and 16 in the orthorhombic space groups. The three different Co atoms in space group $C2/c$ would have to occupy the same 16-fold general position in an orthorhombic cell. However, this is impossible because all three are topologically different (Table 6*d*). Therefore, we would have to consider special positions for them. In *Ibca* all eightfold positions have site symmetries 2 and $\bar{1}$, and no fourfold positions are present. This is incompatible with the topology of Co(1); therefore *Ibca* can be ruled out. In space groups *Imma* and *Ibam* Co(1) could in principle be accommodated in an eightfold position with site symmetry *m*, but all fourfold positions have symmetries 222, $2/m$ or *mm*2, which cannot be reconciled with the particular environment around Co(2). Thus Co_2PO_4Cl is correctly described in space group $C2/c$ and, as in the previous example, the metric symmetry is fortuitously almost orthorhombic. Actually Co_2PO_4Cl is isostructural with Fe_2PO_4Cl (Anderson, Rea & Kostiner, 1976) and here the deviation from the orthorhombic symmetry is more pronounced: *γ* differs by 0·46° from the right angle (Table 6*a*).

(*e*) *Bis*(*N^1-isopropyl-2-methyl-1,2-propanediamine*)-*disalicylatocopper*(II), $[Cu(C_7H_{18}N_2)_2(C_7H_5O_3)_2]$

This compound has been described in space group $P2_1/c$ with $Z = 2$ (Pajunen & Pajunen, 1982). The Cu atom is at an inversion center and the whole complex is therefore centrosymmetric. This case is very similar to (*c*) and thus another case of fortuitously approaching a higher metric symmetry.*

(*f*) *Bis*[*bis*(*acetone S-methylisothiosemicarbazone*)-*chlorocobalt*(II)] *tetrachlorocobaltate*(II), $[CoCl(C_5H_{11}N_3S)_2]_2[CoCl_4]$

This structure has been described in $P\bar{1}$ with $Z = 2$ (Gostojić, Divjaković, Leovac, Ribár & Engel, 1982). The formula already contains the acetone *S*-methylisothiosemicarbazone complex around the Co atom twice. The cell constants as reported are reduced, but the Niggli matrix apparently had not been calculated, because it corresponds to lattice character case 29, monoclinic *C* (Table 7). The monoclinic angles α and γ are equal to 90° within much less than one e.s.d. A further clue is provided by the original *y* coordinates of the atoms which are pairwise equal to each other for 22 pairs of atoms. This includes all of the atoms but Co(3), which is in a special position with site symmetry 2 in $A2/a$. For the same pairs of atoms the *z* coordinates complement each other to 0·5000. Since $A2/a$ is a minimal non-isomorphic supergroup of $P\bar{1}$ and the twofold axes and the glide plane are recognizable in the projection parallel to [001] of the triclinic description of Gostojić *et al.* (1982), the higher symmetry is appropriate. The shifts necessary to obtain $A2/a$ symmetry are on average 0·6 of one e.s.d. calculated from the values given by the original authors. The shift exceeds one e.s.d. only 6 times; once it is 1·4 e.s.d.

(*g*) *μ-Oxo-bis*[(*1,1,1,5,5,5-hexafluoro-2,4-pentanedionato*)*oxo*(*2,4-pentanedionato*)*molybdenum*(V)], $[Mo_2(C_5HF_6O_2)_2(C_5H_7O_2)_2O_3]$

The crystal structure of this compound has been described by Kamenar, Korpar-Čolig & Penavić (1982) in space group $P2_1/c$ with $Z = 2$. The case is analogous to (*c*) and (*e*) because here as well the structure is monoclinic, while the lattice appears to be orthorhombic.*

Table 7. *Cell constants, transformation and Niggli matrices and positional coordinates* ($\times 10^4$) *of* $[CoCl(C_5H_{11}N_3S)_2]_2[CoCl_4]$ *in space group* $A2/a$ *as transformed from the values of Gostojić et al.* (1982); *for explanations see Table* 3

(*a*) Unit cells

	a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)
Original and reduced	9·088 (4)	10·106 (5)	24·910 (20)	89·56 (6)	89·04 (9)	63·29 (4)
Monoclinic *A*	24·910 (20)	18·055 (9)	9·088 (4)	89-99 (4)	90·96 (9)	89·99 (6)

(*b*) Transformation matrices

Original to monoclinic *A*	0 0 1	$\bar{1}$ 2 0	$\bar{1}$ 0 0
Monoclinic *A* to original	0 0 $\bar{1}$	0 $\frac{1}{2}$ $-\frac{1}{2}$	1 0 0

(*c*) Niggli matrix of reduced cell

82·59	102·13	620·51
1·93	3·79	41·28

Lattice character case 29, monoclinic *C* (or *A*)

$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{b}\cdot\mathbf{b}$	$\mathbf{c}\cdot\mathbf{c}$
$\frac{\mathbf{a}\cdot\mathbf{c}}{2}$	$\mathbf{a}\cdot\mathbf{c}$	$\frac{\mathbf{a}\cdot\mathbf{a}}{2}$

(*d*) Coordinates in space group $A2/a$ (multiplied by 10^4)

	x	*y*	*z*
Co(1, 2)	972[1] (1)	1871[0] (0)	4456[2] (2)
Co(3)	2500[0] (1)	9756[-] (1)	0[2] (2)
Cl(1, 2)	186[0] (1)	1474[1] (2)	5483[2] (3)
Cl(3, 4)	2204[1] (2)	5412[1] (2)	6946[1] (4)
Cl(5, 6)	3238[1] (1)	4092[0] (2)	5633[2] (4)
S(*A*, *D*)	944[0] (1)	2167[0] (2)	9496[3] (3)
S(*B*, *C*)	2435[1] (1)	2189[1] (2)	7405[5] (5)
N(*A*1, *D*1)	1111[1] (3)	1711[1] (5)	2326[6] (9)
N(*A*2, *D*2)	674[3] (3)	2819[0] (4)	1918[13] (10)
N(*A*3, *D*3)	640[4] (3)	2875[1] (4)	3465[6] (9)
N(*B*1, *C*1)	1532[1] (3)	2354[7] (5)	5709[7] (10)
N(*B*2, *C*2)	1865[3] (3)	1180[4] (5)	6086[7] (10)
N(*B*3, *C*3)	1441[2] (3)	933[5] (5)	5190[1] (9)
C(*A*1, *D*1)	916[3] (4)	2201[1] (6)	1417[11] (11)
C(*A*2, *D*2)	1151[2] (5)	1218[3] (7)	9237[0] (14)
C(*A*3, *D*3)	486[1] (4)	3490[2] (6)	4016[13] (12)
C(*A*4, *D*4)	344[2] (5)	4173[0] (7)	3124[5] (15)
C(*A*5, *D*5)	458[1] (5)	3542[3] (7)	5638[4] (14)
C(*B*1, *C*1)	1890[1] (4)	1913[0] (6)	6306[0] (12)
C(*B*2, *C*2)	2257[1] (6)	3130[2] (7)	7808[19] (16)
C(*B*3, *C*3)	1387[1] (4)	227[3] (6)	4967[10] (12)
C(*B*4, *C*4)	1755[6] (6)	9641[2] (7)	5593[14] (16)
C(*B*5, *C*5)	944[5] (5)	9974[6] (7)	3951[20] (14)

(*h*) *Trineptunium dodecafluoride monohydrate*, $Np_3F_{12}.H_2O$

This structure has been refined in space group *P*1 with $Z = 2$ (Cousson, Abazli, Pagès & Gasperin, 1983). The number of formula units exceeds the number of asymmetric units in the cell. The reported unit cell is not reduced; reduction and inspection of the Niggli matrix clearly leads to character case 10, monoclinic *C* (Table 8). Inspection of the transformed atomic parameters and a topological analysis reveal the presence of a mirror plane, and a new refinement of the structure in space group *Cm* (Cousson & Gasperin, 1985) confirmed that $Np_3F_{12}.H_2O$ has monoclinic symmetry. Actually the structure almost conforms to space group $C2/m$, but a refinement in $C2/m$ gives an *R* of 0·089, while in *Cm* an *R* of 0·045 is obtained (Cousson & Gasperin, 1985).

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* Two tables containing details for this case and for cases (*g*), (*i*), (*j*), (*k*), (*l*) and (*m*) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42453 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 8. *A case from Acta Crystallographica Vol.* C39 (1983) *for which a corrected crystal structure description has been published*: $Np_3F_{12}.H_2O$ (*Cousson et al.*, 1983)

(*a*) Unit cells

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Original	8·455 (8)	8·858 (9)	8·396 (10)	113·83	116·64	58·03
Reduced	8·396 (10)	8·405 (9)	8·455 (8)	63·39	63·36	88·55
Monoclinic *I*	9·427 (10)	11·729 (12)	8·455 (8)	90·00	95·63	90·08

(*b*) Transformation matrices

Original to reduced	0 0 1	$\bar{1}$ 1 0	$\bar{1}$ 0 0
Original to monoclinic *I*	0 $\bar{1}$ $\bar{1}$	$\bar{1}$ 1 $\bar{1}$	1 0 0

(*c*) Niggli matrix of reduced cell

70·49	70·64	71·49
31·83	31·83	1·79

Lattice character case 10, monoclinic *C* (or *I*)

a · a	**a · a**	**c · c**
b · c	**b · c**	**a · b**

(*i*) *N-Methylacetamide hemihydrochloride*, $C_3H_7NO.\frac{1}{2}HCl$

Jaber, Guilhem & Loiseleur (1983) described the structure of this compound in space group $C2$ ($Z = 8$); that is with two formula units in the asymmetric unit. Marsh (1983) pointed out that the structure within its stated errors fits into space group *Fdd*2. The unit cell as reported does not show any signs of higher symmetry, but the reduced cell and the Niggli matrix point clearly to character case 16, orthorhombic *F*. Another clue is given by the z coordinates of the corresponding atoms in the two crystallographically independent molecules in the $C2$ description: they add up to 0·5000 within ±0·0005, thus indicating the presence of an additional symmetry element (twofold axis or screw axis, mirror or glide plane) at $z = 0·25$.*

(*j*) 8,5′-*Anhydro*-8-*hydroxy*-9-*β*-D-*ribofuranosyladenine* (8,5′-*O-cyclo-A*) *monohydrate*, $C_{10}H_{11}N_5O_4.H_2O$

Sugio, Mizuno, Kitamura, Hamada, Ikehara & Tomita (1983) determined this structure in space group $P2_1$ with $Z = 4$ (twice as many formula units as asymmetric units). Marsh (1984*b*) showed that it fits an orthorhombic cell and space group $P2_12_12_1$, because two additional 2_1 axes relate the independent molecules in $P2_1$ to each other. Sugio, Mizuno, Kitamura, Hamada, Ikehara & Tomita (1984) rerefined the structure successfully in the higher symmetry. The originally not reduced cell in the monoclinic setting does not show obvious signs of being orthorhombic, but the reduced cell and the Niggli matrix point unequivocally to lattice character case 32, orthorhombic *P*. Another clue comes from the x coordinates in the monoclinic description: they add up for pairs of atoms to 0·500.*

(*k*) 2-*Amino*-3,5-*dibromo-N-cyclohexyl-N-methylbenzenemethanamine-salicylic acid* (1:1), $C_{14}H_{20}Br_2N_2.C_7H_6O_3$

Shimizu, Nishigaki, Nakai & Osaki (1983) published the structure of this compound in space group $P\bar{1}$. Both Marsh (1984*c*) and Shimizu, Nishigaki, Nakai & Osaki (1984) showed that it could equally well be described in $C2/c$. Marsh (1984*c*) proved it by demonstrating that the triclinic structure coincided within the reported uncertainties with the monoclinic description. Shimizu *et al.* (1984) proved it by rerefining the structure in the higher symmetry. The original unit cell is not reduced, but gives a clue to higher symmetry by the near equality of cell constants b and c. The Niggli matrix points to lattice character case 10. Another indication is provided by the x coordinates in the original triclinic description: they add up to 0·500.*

(*l*) *Diamminebis*(*dimethylglyoximato*)*cobalt*(III) *tetracyanonickelate*(II) *hexahydrate*, $[Co(C_4H_7N_2O_2)_2(NH_3)_2]_2[Ni(CN)_4].6H_2O$

Solans, Font-Altaba, Bermejo & Alvarez (1983) described this compound in space group $P\bar{1}$ ($Z = 1$). Marsh (1984*a*) pointed out that the atomic coordinates for this structure are consistent within the reported e.s.d.'s with space group *Immm*. An editorial note in Marsh's (1984*a*) paper states that Solans *et al.* (1983) had investigated both $P\bar{1}$ and *Immm*, and preferred the former 'according to e.s.d.'s and thermal coefficients obtained in both space groups'. The comparison of formula units and asymmetric units is in this case not diagnostic because the molecules are in the mirror plane in the orthorhombic description. In addition two cell angles deviate by 0·18 and 0·30° from 90°. This deviation is larger than for any case of suspected higher symmetry which we have seen so far. However, the shift necessary to symmetrize the structure in *Immm* is on average only 0·6 of the corresponding e.s.d.'s as estimated from the values of Solans *et al.* (1983), while the maximum shift is $2·1\sigma$. For nine pairs of atoms both the x and the z coordinates are equal to each other in the triclinic setting. We consider this significant. We agree with Marsh (1984*a*) that the proper description should be orthorhombic and the cell constants have most likely been mismeasured.*

(*m*) *Octahydro*-1,3,5,7-*tetranitro*-1,3,5,7-*tetrazocine* (*HMX*) *and N,N-dimethylformamide* (*DMF*) *complex*, $C_4H_8N_8O_8.C_3H_7NO$

Haller, Rheingold & Brill (1983) found a second HMX-DMF complex crystallizing with $Z = 12$ in space group $C2/c$, while the previously known one crystallized in $R\bar{3}c$ (Cobbledick & Small, 1975).

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* See deposition footnote.

* See deposition footnote.

Marsh (1984*d*) pointed out that they are almost certainly identical, and should both be described in $R\bar{3}c$. A check of the reduced cell and the Niggli matrix could have avoided this error (Table 8). Several clues could have led in this case to further checking. There are a number of near equalities between z coordinates of related atoms among themselves and more importantly with certain x coordinates. The number of formula units is larger than the number of asymmetric units. Also the knowledge that $R\bar{3}c$ is a minimal non-isomorphic supergroup of $C2/c$, coupled with knowing that $Z = 12$, is significant.*

Table 9. *Cell constants, transformation and Niggli matrices and positional coordinates* ($\times 10^4$) *of* $(NH_4)_2Ce(PO_3)_5$ *in space group Cc as transformed from the values of Rzaigui et al.* (1983); *for explanations see Table* 3

(*a*) Unit cells

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Original	7·241 (5)	13·314 (8)	7·241 (5)	90·35 (5)	107·50 (5)	90·28 (5)
Reduced	7·241 (5)	7·241 (5)	13·314 (8)	90·28 (5)	90·35 (5)	107·50 (5)
Monoclinic *C*	8·563 (6)	11·679 (7)	13·314 (8)	89·96 (5)	90·53 (5)	90·00 (5)

(*b*) Transformation matrices

Original to reduced	0 0 1	1 0 0	0 1 0
Original to monoclinic *C*	1 0 1	1 0 $\bar{1}$	0 1 0

(*c*) Niggli Matrix of reduced cell

52·43	52·43	177·26
−0·47	−0·59	−15·77

Lattice character case 14, monoclinic *C*

$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{c}\cdot\mathbf{c}$
$-\lvert\mathbf{b}\cdot\mathbf{c}\rvert$	$-\lvert\mathbf{b}\cdot\mathbf{c}\rvert$	$-\lvert\mathbf{a}\cdot\mathbf{b}\rvert$

(*d*) Toplogy of O-atom environments

	Number of such	Number of neighbors				
Label	atoms	P[4]	Ce[8]	N(1)/N(2)[9+2]	N(3)/N(4)[10]	CN
A	4	2	0	0	1	3
B	2	2	0	0	0	2
C	10	1	1	1	1	4
D	4	1	0	1	1	3
E	4	2	0	2	0	4
F	4	1	1	1	0	3
G	2	1	1	0	1	3

(*e*) Cation environments using the labels of the anions defined above

	Anion atom types						
P(1)	*A*	*B*	*C*	*D*			
P(8)	*A*	*B*	*C*	*D*			
P(2)	*A*				*E*	2*F*	
P(9)	*A*				*E*	2*F*	
P(3)	*A*		2*C*		*E*		
P(10)	*A*		2*C*		*E*		
P(4)	*A*		*C*	*D*	*E*		
P(6)	*A*		*C*	*D*	*E*		
P(5)		*B*	*C*		*E*		*G*
P(7)		*B*	*C*		*E*		*G*
Ce(1)			5*C*			2*F*	*G*
Ce(2)			5*C*			2*F*	*G*
N(1)			5*C*	2*D*	2*E*	2*F*	
N(2)			5*C*	2*D*	2*E*	2*F*	
N(3)	2*A*		5*C*	2*D*			*G*
N(4)	2*A*		5*C*	2*D*			*G*

Table 9 (*cont.*)

(*f*) Coordinates in space group *Cc* (multiplied by 10^4)

	x	y	z
Ce(1, 2)	0[0] (1)	−955[15] (1)	0[0] (0)
P(1, 8)	3066[1] (3)	−762[0] (2)	8066[1] (1)
P(2, 9)	3294[3] (3)	−1203[4] (2)	5892[2](1)
P(3, 10)	6680[1] (3)	−1056[1] (2)	5778[1] (1)
P(4, 6)	7959[1] (3)	−1958[1] (2)	7632[1] (1)
P(5, 7)	5782[2] (3)	−3920[2] (2)	7809[0] (1)
N(1, 2)	5130[5] (8)	−2055[10] (6)	73[8] (7)
N(3, 4)	6713[17] (8)	1198[3] (6)	8013[5] (7)
O(*L*12, 89)	3177[12] (8)	−1499[1] (5)	7050[5] (4)
O(*L*15, 78)	2350[5] (8)	394[3] (5)	7659[6] (5)
O(*E*11,81)	6954[1] (8)	3618[6] (5)	8726[5] (5)
O(*E*12, 82)	4643[4] (8)	−520[5] (6)	8480[2] (5)
O(*L*23, 910)	4941[1] (8)	−563[3] (5)	5817[2] (5)
O(*E*21, 92)	2098[9] (8)	−363[4] (5)	5582[0] (5)
O(*E*22, 91)	3348[2] (8)	−2331[8] (5)	5384[1] (5)
O(*L*34, 610)	7172[1] (8)	−1009[9] (5)	6923[2] (4)
O(*E*31, 101)	7623[0] (8)	−177[5] (6)	5264[9] (5)
O(*E*32, 102)	6663[4] (8)	−2247[6] (6)	5397[2] (5)
O(*L*45, 67)	6448[2] (8)	−2668[4] (5)	7914[5] (6)
O(*E*41, 61)	8439[0] (8)	−1360[6] (6)	8555[2] (5)
O(*E*42, 62)	4115[4] (8)	2372[2] (6)	7077[3] (5)
O(*E*51, 71)	9828[3] (8)	997[9] (6)	6883[7] (5)
O(*E*52, 72)	5055[6] (8)	−4206[6] (6)	8787[8] (5)

The following three cases are not from our statistical sample, but we thought it worthwhile to comment on them.

(*n*) *Diammonium cerium pentametaphosphate*, $(NH_4)_2Ce(PO_3)_5$

Rzaigui, Ariguib, Averbuch-Pouchot & Durif (1983) report this compound to crystallize in space group $P1$ with $Z = 2$. They state that from first inspections by film techniques the unit cell seemed to be monoclinic or possibly orthorhombic, but that a closer inspection of the intensities of the reflexions showed that these two possibilities were incorrect and that the unit cell is triclinic despite its unusual dimensions (Table 9). A cyclic exchange of the lattice constants gives the reduced cell in standard setting and the Niggli matrix corresponds to character case No. 14, monoclinic *C*. The right angles in the calculated monoclinic cell deviate by less than one e.s.d. from 90°. The atomic parameters of pairs of atoms transformed from triclinic to monoclinic setting obey the symmetry of the mirror plane to better than two e.s.d.'s for all atoms except Ce. There is a significant difference between the positions of the mirror plane calculated from the Ce-atom parameters ($y = 0{\cdot}0955$) and from all the other atom pairs ($y = 0{\cdot}0936 \pm 0{\cdot}0006$). We cannot resolve this discrepancy without inspection and possibly refinement of the diffraction data. But it cannot be assumed without further proof that this structure is really the first evidence for the existence of crystallographically independent infinite PO_3 chains as thought by Rzaigui *et al.* (1983).

(*o*) *Shakhovite*, $Hg_4Sb(OH)_3O_3$

Shakhovite has been described as a new mineral from mercury deposits at Kelyansk, Buryat ASSR, and Kaidarkansk, Kirghiz SSR, by Vasiliev, Lavren-

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* See deposition footnote.

Table 10. *Cell constants, transformation and Niggli matrices and positional coordinates* ($\times 10^4$) *of shakhovite in space group Im as transformed from the values of Palchik et al.* (1984); *corresponding values reported by Tillmanns et al.* (1982) *are also listed in braces*

(*a*) Unit cells

a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Original					
4·855 (1)	5·415 (2)	8·249 (2)	106·42 (2)	104·18 (2)	98·75 (2)
Monoclinic					
4·855 (1)	15·077 (5)	5·415 (2)	89·95 (2)	98·75 (2)	90·00 (2)
{4·871 (1)	15·098 (3)	5·433 (1)	90	98·86 (2)	90}

(*b*) Transformation matrix

Original to monoclinic *I*	$\bar{1}\,0\,0$	$\bar{1}\,\bar{1}\,\bar{2}$	$0\,\bar{1}\,0$

(*c*) Niggli matrix of reduced cell

$$\begin{array}{ccc} 23\cdot57 & 29\cdot32 & 68\cdot05 \\ -12\cdot63 & -9\cdot81 & -4\cdot00 \end{array}$$

Lattice character case 43, monoclinic *I*

$$\begin{array}{ccc} \mathbf{a}\cdot\mathbf{a} & \mathbf{b}\cdot\mathbf{b} & \mathbf{c}\cdot\mathbf{c} \\ -\dfrac{\mathbf{b}\cdot\mathbf{b}-|\mathbf{a}\cdot\mathbf{b}|}{2} & -\dfrac{\mathbf{a}\cdot\mathbf{a}-|\mathbf{a}\cdot\mathbf{b}|}{2} & -|\mathbf{a}\cdot\mathbf{b}| \end{array}$$

(*d*) Coordinates in space group *Im* ($\times 10^4$)

	x	y	z
Hg(2, 3)	0[1] (4)	1183[-] (2)	0[3] (4)
{Hg(1)	0	1184·5 (3)	0}
Hg(1, 4)	−3605[1] (4)	−7806[1] (2)	−5160[5] (4)
{Hg(2)	3607 (2)	7804·2 (4)	5170 (1)}
Sb	−4250[-] (6)	0[46] (3)	−4936[-] (6)
{Sb	4169 (2)	0	4882 (2)}
O(6)	−2240[-] (90)	0[97] (30)	−1330[-] (80)
{O(1)	2220 (30)	0	1360 (20)}
O(4, 5)	−1930[-] (60)	−950[55] (25)	−5960[25] (60)
{O(2)	1800 (20)	954 (7)	5900 (20)}
O(1, 3)	−6670[05] (70)	−950[55] (30)	−3900[40] (65)
{O(3)	6530 (20)	959 (8)	3870 (20)}
O(2)	−6800[-] (60)	0[50] (25)	−8350[-] (60)
{O(4)	6530 (30)	0	8330 (20)}

tiev & Palchik (1980). Based on a microprobe analysis and powder and single-crystal X-ray work they give the chemical formula $Hg_8Sb_2O_{13}$ and a triclinic unit cell with $a = 5{\cdot}47$, $b = 4{\cdot}85$, $c = 16{\cdot}5$ Å, $\alpha = 101$, $\beta = 75$ and $\gamma = 82°$. An independent investigation of chemical composition, unit cell and crystal structure of this mineral using a sample from Moschellandsberg, Rheinland-Pfalz, Germany, revealed a monoclinic body-centered unit cell (Table 10) and a chemical composition of $Hg_4Sb(OH)_3O_3$ (Tillmanns, Krupp & Abraham, 1982). With the exception of the c axis, which should be 8·25 Å instead of 16·5 Å, the unit cell given by Vasiliev *et al.* (1980) corresponds to a primitive, though not reduced, setting of the monoclinic body-centered cell. Another description of the crystal structure has been published recently by Palchik, Antipin, Vasiliev, Potekhin & Struchkov (1984) without reference to the earlier structure determination. The mineral is reported to have triclinic symmetry, space group $P1$ and the chemical composition Hg_4SbO_6. The lattice constants of the triclinic cell (Table 10) are close (deviations <0·02 Å) to the dimensions of the reduced cell calculated from the body-centered cell given by Tillmanns *et al.* (1982) and the Niggli matrix corresponds to character case 43, monoclinic body centered.

A transformation of coordinates from space group $P1$ to Im is also given in Table 10. The parameter shifts needed for achieving monoclinic symmetry are, however, mostly larger than the standard deviations, up to 15 e.s.d.'s for Sb. Interatomic distances which are equivalent in the monoclinic description assume rather different values in $P1$. Thus the distances Hg(2)–O(6) and Hg(3)–O(6) in $P1$ are 2·04 (4) and 2·28 (4) Å, while the equivalent Hg(1)–O(1) value given by Tillmanns *et al.* (1982) is 2·16 (1) Å. There is also an appreciable difference between the transformed positional parameters and the coordinates given by Tillmanns *et al.* (1982), apart from the fact that both structures differ in absolute configuration. Refinement in both configurations employing the intensity data of Tillmanns *et al.* (1982) led to $R = 0{\cdot}049$ for the configuration chosen by these authors, while the configuration preferred by Palchik *et al.* (1984) gave $R = 0{\cdot}065$. A refinement in space group $I1$ employing hkl and $h\overline{kl}$ data showed that the largest deviation from monoclinic symmetry was less than two e.s.d.'s in the case of atoms O(3*a*) and O(3*b*) [=O(3) in *Im*]; for all other atoms the deviations were <1·0 e.s.d. Most physical and chemical properties reported by Vasiliev *et al.* (1980) for their samples of shakhovite are identical to those of the sample from Moschellandsberg. We believe, therefore, that both samples are of the same species and that the true space group of shakhovite is *Im*.

(*p*) *Calcium sulfite tetrahydrate*, $CaSO_3.4H_2O$

Matsuno, Takayanagi, Furuhata, Koishi & Ogura (1983, 1984) determined the crystal structure of $CaSO_3.4H_2O$ in space group $C2/c$ with $Z = 12$. The combination of $C2/c$ with twelve formula units per cell should always raise suspicion [see (*m*) above]. In this instance lattice character 9 (rhombohedral) follows from an inspection of the Niggli matrix (Table 11). The positional coordinates in the monoclinic description display numerous similarities and special values. The transformation to rhombohedral reduces the number of atoms in the asymmetric unit from seventeen to eight. Since one of the sulfite groups was described by Matsuno *et al.* (1983, 1984) as disordered, we rerefined the structure with isotropic temperature factors using space group $R\bar{3}c$ after appropriate averaging. The resulting R is 0·090 for 612 F_{obs}, as compared with 0·102 obtained by Matsuno *et al.* (1983). However, even in the rhombohedral description the disordering of the sulfite group around S(2) cannot be avoided. In a recent paper Cohen & Zangen (1984) have shown that $Ca_3(SO_3)_2SO_4.12H_2O$ forms solid solutions with $CaSO_3.4H_2O$. Apparently the sulfate group can replace completely the disordered sulfite group around S(2). Cohen & Zangen (1984) have reported cell constants for different amounts of substitution of

Table 11. *Cell constants, transformation and Niggli matrices, positional coordinates (with mean deviation from monoclinic setting given in square brackets) and temperature factors of* $CaSO_3.4H_2O$ *as refined by us from the structure factors of Matsuno et al.* (1983) *after transformation to space group* $R\bar{3}c$

(*a*) Unit cells

a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)
Original					
19·385 (11)	11·192 (4)	11·449 (10)	90	124·34 (4)	90
Reduced					
11·192 (5)	11·192 (5)	11·449 (10)	60·76 (4)	60·76 (4)	60·00 (4)
Rhombohedral					
11·192 (5)	11·192 (5)	28·360 (21)	90·00 (4)	90·02 (4)	120·00 (4)

(*b*) Transformation matrices

Original to reduced	$-\frac{1}{2}\,\frac{1}{2}\,0$	$-\frac{1}{2}\,-\frac{1}{2}\,0$	0 0 1
Original to rhombohedral	$-\frac{1}{2}\,\frac{1}{2}\,0$	$0\,\bar{1}\,0$	1 0 3

(*c*) Niggli matrix of reduced cell

125·26	125·26	131·08
62·59	62·59	62·63

Lattice character case 9, rhombohedral

$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{a}\cdot\mathbf{a}$	$\mathbf{c}\cdot\mathbf{c}$
$\frac{\mathbf{a}\cdot\mathbf{a}}{2}$	$\frac{\mathbf{a}\cdot\mathbf{a}}{2}$	$\frac{\mathbf{a}\cdot\mathbf{a}}{2}$

(*d*) Coordinates in $R\bar{3}c$ and U_{eq} (both $\times 10^4$)

	x	*y*	*z*	U_{eq} (Å^2)
Ca(1, 2)	7938[2] (2)	0[–]	2500[–]	49 (5)
S (1)	0[–]	0[–]	1728[2] (1)	42 (6)
S(2)	0[–]	0[–]	0[–]	298 (13)
O(1, 2, 3)	6668[2] (5)	2100[7] (5)	1367[4] (2)	73 (11)
O(8, 11, 13)	6584[6] (7)	9918[7] (7)	1842[2] (2)	327 (17)
O(9, 10, 12)	651[3] (6)	4935[3] (6)	5781[2] (2)	187 (13)
O(4)	0[8]	0[8]	5498[8] (8)	314 (52)
O(5, 6, 7)	850[21] (20)	1376[64] (19)	229[2] (6)	241 (40)

sulfate for sulfite. Each of these sets of cell constants can be transformed with the same precision to the rhombohedral setting as the cell constants reported by Matsuno *et al.* (1983) can. Interestingly, Shiino, Yasue & Arai (1982) have already described $CaSO_3.4H_2O$ rhombohedrally.

Examples of higher symmetries by addition of an inversion center

We made no effort to search the literature systematically for cases where an inversion center might have been omitted in a crystal structure determination. The examples discussed below were stumbled upon in the reading of the literature and are useful for a discussion of the principles involved.

(*q*) *Diiron*(II) *diphosphate*, $Fe_2P_2O_7$

The crystal structure of $Fe_2P_2O_7$ was determined by Stefanidis & Nord (1982) in space group $P1$, with $Z = 1$. Shortly thereafter Hoggins, Swinnea & Steinfink (1983) published a structure determination of the same compound in a centrosymmetric triclinic setting. Stefanidis & Nord chose the noncentrosymmetric space group because the statistical $N(z)$ test after Howells, Phillips & Rogers (1950) gave an unequivocally acentric result. Hoggins *et al.* (1983), however, report that their data agree closely with a centrosymmetric distribution. It is unlikely that $Fe_2P_2O_7$ exists in two modifications with essentially identical cell constants, but one with, the other without an inversion center. More likely is that Stefandis & Nord have omitted the weak reflections [smaller than $2\sigma(I)/I$] from the $N(z)$ test. Marsh (1981) has shown that such deletion of weak reflections biases the statistical tests towards acentric distributions. Hoggins *et al.* (1983) in their paper took note of the work of Stefanidis & Nord (1982) and argued for a centrosymmetric structure on the basis of their statistical tests, and because of the high correlations between related parameters and the nonpositive-definite temperature factors encountered when they refined the structure in the noncentrosymmetric space group.

We show that the noncentrosymmetric strucure is also unlikely because of internal crystal-chemical evidence. In the $P1$ structure the two crystallographically independent phosphate groups have widely different mean P–O bond distances: 1·516 and 1·556 Å (Table 12). The mean P–O distance in a large number of P_2O_7 groups in precisely determined crystal structures, however, is close to 1·531 Å (Baur, 1974). There is no reason for the mean distances of the two phosphate groups in $Fe_2P_2O_7$ to be different since the bonding situation for both of them is identical; that is their environments are topologically equivalent. Moreover, when we calculate the individual P–O distances according to equation (2) and compare them with the observed values we get individual deviations (Δ) ranging up to 0·044 Å, while the mean deviation amounts to 0·022 Å. Such large values for Δ are unusual (Baur, 1974) and exceed the e.s.d.'s of the P–O bond lengths appreciably. The agreement between the calculated values and those from the centrosymmetric refinement is much better (mean Δ of 0·012 Å). In addition a comparison of the P–O bond lengths averaged for the two independent groups in the $P1$ refinement with the individual bond lengths of the centrosymmetric refinement shows that they are very similar to each other. The split P–O values in the two groups in the noncentrosymmetric case are an artifact of the noncentrosymmetric refinement of a centrosymmetric structure. The only exception to this is the P–O(4) bond length: O(4) is in a general position in $P1$, but in a special position in $P\bar{1}$: the angle P–O(4)–P is 180° by symmetry. In the noncentrosymmetric description it has been moved arbitrarily out of the centrosymmetric position and both P–O(4) distances have become longer. One could argue that all the effects mentioned here are small. However, they are real and should not be neglected in the course of a crystal structure determination.

Table 12. *Observed* P–O *distances* (Å) *in* $Fe_2P_2O_7$ (*as calculated from the coordinates of the original authors*) *in space group* $P1$ (*Stefanidis & Nord*, 1982) *and in space group* $P\bar{1}$ (*Hoggins et al.*, 1983), *compared with the calculated values according to the method of Baur* (1970, 1974); O *atoms* O(1) *and* O(7), O(2) *and* O(6), *as well as* O(3) *and* O(5) *become identical in the centrosymmetric description*

	$P1$	Calculated	$P\bar{1}$	Average $P1$
P(1)–O(1)	1·522 (9)	1·522	1·527 (4)	1·524
P(1)–O(2)	1·540 (10)	1·522	1·511 (5)	1·511
P(1)–O(3)	1·540 (10)	1·522	1·516 (4)	1·511
P(1)–O(4)	1·623 (10)	1·579	1·554 (1)	1·599
Mean	1·556	1·531	1·527	1·536
P(2)–O(4)	1·574 (12)	1·579		
P(2)–O(5)	1·480 (11)	1·522		
P(2)–O(6)	1·483 (9)	1·522		
P(2)–O(7)	1·525 (9)	1·522		
Mean	1·516	1·531		

(*r*) *Dicalcium potassium heptahydrogentetrakis-(phosphate) dihydrate*, $Ca_2KH_7(PO_4)_4.2H_2O$

Recently the crystal structure of $Ca_2KH_7(PO_4)_4.2H_2O$ was determined both by X-ray and by neutron diffraction (Prince, Takagi, Mathew & Brown, 1984). The X-ray refinement is reported in space group $P\bar{1}$. The structure has several hydrogen bonds which are apparently across centers of symmetry, but are too long to be symmetrical hydrogen bonds with the H atom residing in the central special position. In addition the K atom seems to be close to, but still clearly out of another special position on a center of symmetry. In order to answer the question whether the structure is disordered, or truly noncentrosymmetric a neutron diffraction study was undertaken: the positions of the H atoms should be more clearly visible by this method. The authors refined the neutron diffraction data four different ways (Table 13). They preferred in their discussion model (3), because model (4) had one nonpositive-definite anisotropic temperature-factor matrix. On the basis of Hamilton's (1965) *R*-ratio test the authors point out that each of the successive models shows a highly significant improvement in the fit relative to the next more restrictive model. Therefore, they consider $P1$ to be the correct space group of $Ca_2KH_7(PO_4)_4.2H_2O$.

Just as we could calculate the individual P–O distances in $Fe_2P_2O_7$ using equation (2), we can calculate them in $Ca_2KH_7(PO_4)_4.2H_2O$ (Table 14). The P(2) phosphate group is not affected by the rearrangement of the H atoms in $P1$ relative to $P\bar{1}$; therefore the predicted distances around P(2) and P(2′) in $P1$ are identical and the same as for P(2) in $P\bar{1}$. However, the observed individual P(2)–O distances are diverging here similarly as in $Fe_2P_2O_7$, and likewise without any reason, because the bonding topologies for all three phosphate groups [P(2) and P(2′) in $P1$; P(2) in $P\bar{1}$] are identical. Moreover, the Δ values for all phosphate groups in the noncentrosymmetric refinement are large (mean Δ 0·032 Å; maximum Δ 0·068 Å), while for the centrosymmetric refinement they are much smaller (mean Δ 0·006 Å; maximum Δ 0·013 Å; that is less than the mean Δ in the noncentrosymmetric case). We would argue that by the same token by which a model without nonpositive-definite temperature factors is preferable over one which exhibits them, a model in which bond distances conform with accepted values is preferable to a model with strange unexplained deviations from reasonable values. The mean P–O bond distances, as well as the individual ones show in the $P1$ refinement the same kind of splitting as was observed in $Fe_2P_2O_7$ (compare Tables 12 and 14); the mean P–O distance observed for well determined acidic phosphate groups is 1·536 Å (Baur, 1974). On crystal-chemical grounds the centrosymmetric refinement results are to be preferred: the space group of $Ca_2KH_7(PO_4)_4.2H_2O$ is more likely to be $P\bar{1}$ than $P1$. That means the hydrogen bonds are really disordered since their ordering results in PO_4 groups which do not correctly reflect in their bond lengths the ordered bond-strength distribution.

Table 13. *Summary of refinement of* $Ca_2KH_7(PO_4)_4.2H_2O$ (*from Prince et al.*, 1984)

The temperature factors (TF) were constrained in model (3) to be related by a center of symmetry between those atoms which were crystallographically equivalent in $P\bar{1}$.

Model	Number of observations	Number of parameters	*wR*
(1) $P\bar{1}$–K on center	1381	170	0·070
(2) $P\bar{1}$–K split	1381	173	0·067
(3) $P1$–TF's constrained	1383	227	0·060
(4) $P1$–TF's unconstrained	1379	323	0·052

Where does this leave the results of Hamilton's *R*-ratio test? It is instructive to reread Hamilton (1965) and to realize that twenty years ago the data sets were much smaller than today. All the examples used in that paper for the application of the *R*-ratio test had degrees of freedom (= number of observations minus number of refined parameters) ranging from 16 to 527. In most modern single-crystal structure determinations several thousand F_{obs} are used and the degrees of freedom usually exceed 1000. The higher this number is, the closer we get to the limit in which any improvement in the *R* ratio will be judged to be significant by this test. Prince (1982) has pointed out that passing a test for significance is a necessary, but by no means sufficient condition for inferring the need for a model with more parameters. A model with more parameters that violates the laws of nature is not a better model no matter what the results of the significance test are. We must judge the soundness of additionally introduced parameters by their chemical or physical reasonableness. In a way we can call this a happy circumstance, because we are thrown back to making sense out of the results of our crystal structure determinations. Whenever we

Table 14. *Observed* P–O *distances* (Å) *in* $Ca_2KH_7(PO_4)_4.2H_2O$ (*Prince et al.*, 1984) *in* $P1$ (*neutron*) *and* $P\bar{1}$ (*X-ray*), *compared with the calculated values* (*Baur*, 1970, 1974)

	Observed for $P1$	Calculated for $P1$	Observed for $P\bar{1}$	Calculated for $P\bar{1}$	Observed average for $P1$
P(1)–O(11)	1·564 (9)	1·530	1·553 (1)	1·556	1·557
P(1)–O(12)	1·567 (9)	1·499	1·514 (1)	1·506	1·520
P(1)–O(13)	1·575 (9)	1·585	1·539 (2)	1·545	1·537
P(1)–O(14)	1·464 (9)	1·530	1·535 (2)	1·537	1·534
Mean	1·543	1·536	1·535	1·536	1·537
P(1′)–O(11′)	1·549 (9)	1·581			
P(1′)–O(12′)	1·472 (9)	1·514			
P(1′)–O(13′)	1·499 (9)	1·505			
P(1′)–O(14′)	1·604 (9)	1·545			
Mean	1·531	1·536			
P(2)–O(21)	1·461 (9)	1·504	1·497 (1)	1·504	1·495
P(2)–O(22)	1·499 (8)	1·504	1·498 (1)	1·504	1·498
P(2)–O(23)	1·529 (9)	1·568	1·565 (1)	1·568	1·567
P(2)–O(24)	1·583 (10)	1·568	1·581 (1)	1·568	1·583
Mean	1·518	1·536	1·535	1·536	1·536
P(2′)–O(21′)	1·528 (9)	1·504			
P(2′)–O(22′)	1·496 (9)	1·504			
P(2′)–O(23′)	1·606 (9)	1·568			
P(2′)–O(24′)	1·583 (10)	1·568			
Mean	1·553	1·536			

get unreasonable results, such as nonpositive-definite temperature factors or inexplicable bond lengths and angles we should have the courage to discard the results of an automatic application of the R-ratio test.

(*s*) 1,8-*Octanediamine dihydrobromide*, $C_8H_{20}N_2.2HBr$

The crystal structure of $C_8H_{20}N_2.2HBr$ was recently described by Brisson & Brisse (1984) in space group *Pba*2 (1305 reflexions considered as observed, $R = wR = 0\cdot037$, least-squares refinement in block-diagonal approximation). The corresponding centrosymmetric space group *Pbam* was also considered, but rejected because of Hamilton's R-ratio test: wR was found to be 0·047 for 1305 reflexions; that is higher than in the noncentrosymmetric case. We were intrigued by the fact that $\sigma(z)$ is in Å about four times as large as $\sigma(x)$ and $\sigma(y)$. Therefore we refined the structure by full-matrix least squares using F_{obs} (Supplementary Publication No. SUP 39048) in several ways: in space groups *Pbam* and *Pba*2, with unit weights and individual weights derived from counting statistics, based on all 1546 F_{obs} and on the 1305 F_{obs} with $I > 1\cdot96\sigma(I)$, and finally with either isotropic or anisotropic temperature factors for the non-hydrogen atoms. We shall confine our discussion mostly to the refinements closest to the one performed by Brisson & Brisse (1984): 1305 F_{obs}, anisotropic temperature factors for the heavy atoms only and individual weights. However, we did not attempt a block-diagonal approximation. The refinement in the centrosymmetric space group *Pbam* resulted in an $R = 0\cdot037$; the final parameters are listed in Table 15. The refinement in the noncentrosymmetric space group *Pba*2 gave $R = 0\cdot032$. In our refinements the e.s.d.'s of the positional coordinates were consistently higher by about 25%, when compared with Brisson & Brisse's (1984) results. This is most likely due to the fact that block-diagonal refinements are more optimistic in their estimate of the random errors than full-matrix refinements. The errors in the centrosymmetric refinement are isotropic. The C–H and N–H distances range in the centrosymmetric refinement from 0·58 to 1·27 Å, while the angles H–C–H and H—N—H spread from 86 to 117°. For our noncentrosymmetric refinement the corresponding figures are 0·52 to 1·77 Å and 79 to 137°. However, the most telling point is that the noncentrosymmetric refinements are rather different from each other and from the noncentrosymmetric refinement reported by Brisson & Brisse (1984) in the values of the z positional coordinates: these differ by amounts of up to 0·02, which is four times the already anomalously large standard deviation in z. An instance in which adding or subtracting a few F_{obs} to the data set, or changing the weighting scheme, gives a formally significantly different refinement result means that the refinement is not stable. We prefer the centrosymmetric description of the crystal structure of $C_8H_{20}N_2.2HBr$.

We cannot perform a meaningful R-ratio test according to Hamilton (1965) because the data set from SUP 39048 is incomplete for space group *Pba*2: it contains only $F(hkl)$ with positive h, k and l, whereas for the R-ratio test to be done properly we would need the separated Friedel pairs for the refinement in *Pba*2, and the averaged Friedel pairs for the centrosymmetric refinement. Strictly speaking the available data set is only proper for the centrosymmetric refinement; for the noncentrosymmetric refinement it corresponds to about one half of the needed data because dispersion effects (Br is present) make the Friedel pairs inequivalent (*International Tables for X-ray Crystallography*, 1974).

This case is instructive, because it shows that very large correlation coefficients (>0·9) in the least-squares refinement do not always occur when switching from a centrosymmetric to a noncentrosymmetric space group. In the structure of $C_8H_{20}N_2.2HBr$ all heavy atoms are in special positions on mirror planes in *Pbam*. When the structure is described and refined in *Pba*2 the special positions of *Pbam* become general positions in the lower-symmetry space group. The H atoms are in general positions, but do not contribute sufficiently to the scattering to give rise to strong correlations. The only effect of using *Pba*2 is visible in the correlations between the z coordinates and the $U(33)$ thermal parameters: they range from 0·8 to 0·9, which is small enough not to cause singular matrices, but large enough to give convergence problems (as demonstrated by the large e.s.d.'s of the z coordinates and their sensitivity to weighting schemes

Table 15. *Final atomic coordinates for* $C_8H_{20}N_2.2HBr$ *in Pbam* ($\times 10^5$ *for* Br, $\times 10^4$ *for* N *and* C, $\times 10^3$ *for* H), *and* U_{eq} ($\times 10^4$ *for* Br, $\times 10^3$ *for* N *and* C) *and* U_{iso} ($\times 10^2$ *for* H)

	x	*y*	*z*	U_{eq}, U_{iso} (Å^2)
Br(1)	21721 (3)	20242 (4)	00000	510 (4)
Br(2)	87510 (3)	6167 (3)	00000	446 (3)
N(1)	6197 (3)	4035 (3)	5000	48 (3)
N(2)	2333 (3)	−1516 (3)	5000	48 (3)
C(1)	5431 (3)	3758 (4)	5000	62 (4)
C(2)	5381 (3)	2815 (4)	5000	62 (4)
C(3)	4613 (3)	2476 (4)	5000	61 (4)
C(4)	4578 (4)	1520 (4)	5000	69 (5)
C(5)	3815 (4)	1157 (5)	5000	66 (4)
C(6)	3803 (3)	208 (4)	5000	69 (5)
C(7)	3036 (3)	−165 (4)	5000	59 (4)
C(8)	3052 (4)	−1104 (5)	5000	67 (4)
H(1)	518 (3)	400 (3)	672 (12)	0 (1)
H(2)	572 (3)	253 (4)	326 (15)	3 (2)
H(3)	439 (3)	272 (4)	692 (15)	2 (1)
H(4)	483 (4)	116 (5)	328 (18)	4 (2)
H(5)	351 (3)	138 (4)	678 (16)	2 (2)
H(6)	407 (3)	3 (4)	299 (12)	0 (1)
H(7)	267 (4)	16 (4)	673 (16)	3 (2)
H(8)	335 (3)	−127 (4)	339 (14)	2 (2)
HN(11)	648 (4)	365 (4)	284 (16)	3 (2)
HN(12)	622 (4)	440 (4)	500	5 (3)
HN(21)	202 (2)	−140 (3)	318 (12)	0 (1)
HN(22)	257 (5)	−199 (4)	500	9 (3)

and number of F_{obs} used in the refinement). Of course the e.s.d.'s of the $U(33)$ parameters are also large. If the R-ratio test, which we cannot perform, were to indicate a significant improvement in R for the noncentrosymmetric refinement, we would still prefer the centrosymmetric description of this structure because of the correlation and convergence problems in *Pba*2.

Clues and checks for higher symmetries

To achieve the highest possible symmetry for a given structure we have to either

Category (1): change both the Laue class and the crystal system; or
Category (2): change the Laue class, but retain the crystal system; or
Category (3): add a center of symmetry, but retain both Laue class and crystal system.

For all three categories it is true that a too low symmetry might be suspected when there is more than one formula unit per asymmetric unit. Unfortunately, a formula unit is generally not identical to a molecule or a standard chemical formula. One molecule can effectively be composed of two formula units when it is located on a symmetry element. Also there are many cases in which we cannot doubt that there is more than one formula unit per asymmetric unit and the symmetry of the structure is still not too low, because the different independent molecules have significantly different conformations.

Once we suspect higher symmetry, we can look for additional symmetry elements by checking for near equalities in bond lengths and bond angles of unrelated molecules, or look for positional coordinates of atoms in general with values close to special numbers such as zero, one quarter or the like; or we can inspect the coordinates of the various atoms for special relationships, such as equalities, constant sums, constant differences or similar instances. A systematic way to search for higher symmetries is the simple, but powerful method of topological analysis of crystal structures (Baur *et al.*, 1983).

Cases of category (1) can be diagnosed by calculating the reduced base and the Niggli matrix. They are the simplest ones to find, because we do not have to look at the details of the crystal structure in order to recognize them. We have to study only the metric symmetry of the lattice.

Category (2) cases are most difficult to identify because no special method is known to us for recognizing them. We have to use the general methods valid for all three categories.

Category (3) cases are easiest to recognize at the time the crystal structure is being determined. During full-matrix least-squares refinement structures in which inversion centers have been omitted can be recognized from singular matrices, high correlations between parameters and difficulties in attaining convergence. The occurrence of either of these can be made less obvious by block-matrix refinement, in which the related parameters are put into different blocks, but this of course does not solve the problem, it only hides it. After the fact, once the refinement is completed, omitted centers of symmetry make their presence known by unusually high e.s.d.'s, especially for the highly correlated parameters, and by large distortions of observed bond distances and angles from accepted values. These effects can be relatively subtle, as in the examples reported above, or they can be very large as in the case of $Zn_3(BO_3)_2$, where the bond lengths were up to 0·2 Å off their accepted values in a refinement in *Ic*, but became quite normal when refined subsequently in space group *I*2/*c* (Baur & Tillmanns, 1970).

When comparing R values of centrosymmetric and noncentrosymmetric refinements one should also be careful about what is considered a comparable refinement. Marsh (1981) has pointed out that it may be misleading to compare them when both were refined with anisotropic temperature factors, because two isotropic atoms in a slightly noncentrosymmetric array can closely approximate in their $|F|$ values a pair of anisotropic atoms in a centrosymmetric array. This is particularly obvious because of the splitting effect observed by us. A meaningful comparison could then be made between a centrosymmetric refinement with anisotropic temperature factors and a noncentrosymmetric refinement with isotropic temperature factors.

Singular matrices are unlikely to be encountered when omitting an inversion center in a crystal structure in which all atoms, or at least all heavy atoms are on special positions, which become general positions in the lower-symmetry space group. Difficulties in attaining convergence and/or the occurrence of certain classes of parameters with large e.s.d.'s can give a clue to this condition. When convergence problems are due to the use of an inefficient least-squares algorithm a more efficient method can be used and constraints can be introduced (see ch. 9 of Prince, 1982).

Proof that a structure has been described in too low symmetry does not come from the clues discussed here, but from evaluating the diffraction evidence anew. For cases such as those analyzed above, where the indications came from the unit-cell metric, confirming evidence consists in showing that the structure can be described in a higher symmetry within one or two e.s.d.'s of the original determination. In this context it is advisable to study carefully the subgroup and supergroup relations of the space groups in question (see the new *International Tables for Crystallography*, 1983). If the lower symmetry was due to a missing inversion center it is best to refine the structure again in the higher symmetry. However, because of the splitting effect demonstrated above, one can get a good approximation of the more highly symmetric structure also by averaging the positional parameters of related atoms.

Last but not least it should be remembered that even reasonable people can reasonably disagree over the correct interpretation of a particular diffraction experiment. On purpose we have limited ourselves in this discussion to the crystallographic aspects of the problem. However, when the diffraction evidence is ambiguous, the decision between various possible symmetries for a particular crystal structure will come from additional information from one or the other kind of spectroscopic measurements.

Recommendations

It would be preferable if crystal structure descriptions of too low symmetry were recognized before publication. This could be be achieved if authors of structural papers would follow the points listed here:

(1) explore reciprocal space by photographic methods before or while using an automatic diffractometer (1, 2);

(2) if the number of formula units per asymmetric unit exceeds one, look for excess symmetry in bond lengths, coordinates and topology (1, 2, 3);

(3) always calculate the reduced cells and inspect their Niggli matrices (inspect the Niggli matrix not only after a preliminary orientation matrix is available after a peak search in a computer-controlled diffractometer, but also after the final refinement of lattice constants and orientation matrix has been made) (1);

(4) inspect carefully the correlation coefficients from the least-squares refinements (3);

(5) be suspicious of large e.s.d.'s for whole classes of parameters (3);

(6) follow up on deviations of bond lengths and angles from commonly accepted values (3);

(7) perform Hamilton's (1965) R-ratio test on the proper data sets with separated Bijvoet pairs when choosing between centrosymmetric and noncentrosymmetric space groups in the presence of anomalous scatterers (3);

(8) compare corresponding models with each other when applying the R-ratio test; for instance realize that a centrosymmetric model with anisotropic temperature factors is analogous to a slightly noncentrosymmetric model with isotropic temperature factors (3);

(9) do not accept Hamilton's (1965) R-ratio test as proof of lower symmetry if bond lengths and/or thermal parameters are suspect (3).

The numbers in parentheses given above indicate the category of symmetry change which can be checked for by each of the above listed items. If one or several of the above nine items are applicable, the diffraction evidence should be checked again for signs of higher symmetry.

Previously we have pointed out that in some cases the evidence for lower or higher symmetry could be ambiguous. However, we suggest that whenever there is reason to consider two or more symmetries for a given crystal structure, such fact should be stated in the paper, the evidence for the final choice should be explicitly presented, and when the case is sufficiently ambiguous, the full description in two or more space groups should be given in the paper. If the authors are not explicit about documenting any of these items we would hope that editors and referees will request relevant information along these lines from them.

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