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Use of software to search for higher symmetry: space group *C*2

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From a search of the October 2000 release of the Cambridge Structural Database we find coordinate data for approximately 1500 entries under space group No. 5: *C*2 or, occasionally, *A*2, *I*2 or *B*112. Software designed to detect cases of missed higher symmetry identified 144 entries for detailed inspection. Of these, 50 should, we believe, be revised to space groups of higher symmetry. The most common revision is to space group $C2/m$, which entails adding a center of inversion and usually results in important changes in bond lengths and angles.

1. Experimental

A survey of the October 2000 release of the Cambridge Structural Database (Allen & Kennard, 1993) was carried out for space group No. 5 using the program *PLATON/ADDSYM* (Spek, 2001). This program checks cell dimensions and atom coordinates, within default tolerances, for missed symmetry and suggests the appropriate higher symmetry group. This automatic search provided a list of 144 possible candidates for the revision of a space group. These 144 candidates were then examined manually; many chiral compounds with approximately centrosymmetric structures within the distance tolerances used were examined carefully and rejected as noncentrosymmetric. If it seemed appropriate, coordinates were transformed and averaged according to the alternative symmetry and the feasibility of the resulting structure was assessed. In 50 cases (Table 1) we became convinced that the structure should be revised to one of higher symmetry. The original paper was always consulted; in most cases, the authors make no comment concerning the possibility of higher symmetry. In all cases we found satisfactory interatomic distances and angles for the revised description. In two instances (ENCOCL01 and TARFUN) we obtained a listing of observed structure factors and re-refined the structure in the revised space group; in both cases our final *R* was marginally smaller than that reported for the original refinement in the lower symmetry (with many more parameters).[1] A listing of revised coordinates has been submitted as supplementary material;[2] in most cases, H atoms are omitted as unreliable. Unfortunately, in most cases no structure factors

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[1] In the case of TARFUN, the authors attempted refinement in $C2/m$ and obtained a large *R* – 0.165 – and 'unreasonable atomic displacement parameters'. We had no such difficulties, which might have been caused by incorrect atom multiplicities when the structure was transformed from *C*2 to $C2/m$.

[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0095). Services for accessing these data are described at the back of the journal.

Table 1
Structures originally described in space group No. 5 which are more properly described in higher symmetries.

Included are the ‘Refcodes’ assigned by the Cambridge Structural Database (Allen & Kennard, 1993), the revised space group, and the formula unit.

Refcode	Space group	Formula unit	Reference
AFUMCO01	$C2/c$	$C_8H_{20}Co_2O16\cdot 2H_2O$	Porollo *et al.* (1997)
APONCU	$C2/c$	$C_{38}H_{34}CuN_4O_2$	Shnulin *et al.* (1977)
BUPRIN	$Fdd2$	$C_{15}H_{22}N_2O_4$	Buchanan & Sim (1983)
CACBUD	$C2/m$	$C_{13}H_{30}NBr\cdot C_7H_6O_3\cdot H_2O$	Sawada *et al.* (1998)
CIDVOA	$C2/m$	$C_{12}H_{16}N_2O_8Cr$	Cooper *et al.* (1984)
COBTAO	$C2/m$	$C_{17}H_{19}O_3S_3Cr_2Mn$	Pasynskii *et al.* (1984)
COJJAM	$C2$	$C_{78}H_{60}P_4F_{18}Ge_2Pt_2Hg\cdot 2C_7H_8$	Bochkarev *et al.* (1984)
ENCOCL01	$C2/m$	$C_6H_{21}N_5Cl_3Co\cdot 0.5H_2O$	Johnston & Freeman (1975)
FABZIR	$C2/c$	$C_{18}H_{22}N_2O_4W$	Wong *et al.* (1998)
FILGIQ	$Fdd2$	$C_8H_{22}N_6O_4CoCl\cdot 0.5H_2O$	Cai *et al.* (1998)
FOWFIG	$C2/m$	$C_6H_4O_3PCl$	Cattani-Lorente *et al.* (1987)
GIDKIN	$C2/m$	$C_8H_{18}N_4O_4S_2Fe_2$	Glidewell *et al.* (1988)
GIHNUG	$C2/c$	$C_{26}H_{28}N_2O_8S_2Cu$	Chan *et al.* (1985)
HANLIR	$C2/c$	$C_{12}H_{14}N_2\cdot 3C_9H_5N_4Br$	Hünig *et al.* (1998)
HIRDOB	$C2/c$	$C_{66}H_{48}N_{18}Os_2CrCl\cdot 8H_2O$	Otsuka *et al.* (1999)
HIWNAC	$C2/c$	$C_8H_{28}N_8S_4Cl_6Pb$	Mousdis *et al.* (1998)
JOBBUX	$C2/m$	$C_{24}H_{46}N_8Na_2$	Andrews *et al.* (1991)
JOGHES	$I222$	$C_{19}H_{25}N_8O_{11}P\cdot 6H_2O$	Krishnan *et al.* (1991)
JOSXAQ	$R32$	$C_{78}H_{66}N_{20}Tb\cdot 3ClO_4\cdot H_2O$	Su *et al.* (1998)
JULLOR	$C2/c$	$C_{20}H_{28}O_4P_2$	Hitchcock *et al.* (1992)
KACPOT	$C2/m$	$C_{26}H_{58}P_2Mn_2$	Jones *et al.* (1988)
LAHWAS	$C2/m$	$C_{20}H_{24}S_4Pt\cdot 2BF_4$	Loeb & Smith (1993)
MAHXUO	$C2/m$	$C_4H_6N_2Cl_4W$	Manteghetti *et al.* (1999)
MEHXBO	$C2/m$	$C_{12}H_{36}B_6N_6$	Nöth & Pommerening (1980)
NEZBOJ	$Fdd2$	$C_{20}H_{20}S_{16}Cu_2I_2$	Ramos *et al.* (1997)
NIJGIW	$Fdd2$	$C_{20}H_{28}O_6$	Chai *et al.* (1997)
NOGMUR	$Fdd2$	$C_{28}H_{34}P_2SiRu$	Wada *et al.* (1997)
NOQZUO	$I222$	$C_{28}H_{72}N_8O_2Zn_6$	Malik *et al.* (1997)
NUFYOC	$Aba2$	$C_8H_{32}N_{22}O_4Ni_2Mn$	Rajendiran *et al.* (1998)
NUHJOP	$C2/m$	$C_{22}H_8F_9N_4ORe$	Tse *et al.* (1998)
PEMGAP	$C2/c$	$C_{16}H_{24}O_2Yb$	Jiang *et al.* (1993)
PIJLUP	$C2/c$	$C_{10}H_{26}N_2Mg$	Viebrock & Weiss (1994)
PIZZON	$C2/c$	$C_{12}H_{15}O_9PS$	Despax *et al.* (1994)
RENPAB	$C2/m$	$C_6H_{18}N_2\cdot HfF_6$	Tkachev *et al.* (1996)
RULYIG	$R32$	$C_{36}H_{80}P_2Ga_2$	Malik *et al.* (1996)
RUMDUY	$C2/m$	$C_{32}H_{28}N_6O_{14}Nd_2$	Niu *et al.* (1997)
SAPACU	$P3_121$	$C_{32}H_{30}N_2O_8Cu_2$	Hämäläinen *et al.* (1978)
SIPWAP	$F222$	$C_{40}H_{40}N_4O_4Br_2Cu_2\cdot C_3H_6O$	Haddleton *et al.* (1998)
TARFUN	$C2/m$	$C_{20}H_{14}N_2$	Preut *et al.* (1992)
TIWXOM	$C2/m$	$C_5H_7N_2\cdot C_4O_4\cdot 2H_2O$	Karle *et al.* (1996)
VALTIL	$Fdd2$	$C_{12}H_{30}N_2O_6Ni\cdot C_{14}H_8O_4S_2$	Ramalingam *et al.* (1987)
VIHYIU	$C2/m$	$C_8H_{22}Cl_4P_2W$	Harlan *et al.* (1990)
WEVZAY	$C2/m$	$C_{36}H_{30}P_2Au\cdot C_{12}H_4N_4\cdot C_4H_{10}O$	Alonso *et al.* (1993)
XETCMO01	$C2/c$	$C_{20}H_{40}N_4O_3S_8Mo_2$	Lin & Chen (1985)
YEDVOS	$C2/m$	$C_6H_4S_4\cdot C_4H_{22}B_{18}Cr$	Forward *et al.* (1994)
YINCUT	$C2/m$	$H_8B_6NCs\cdot H_2O$	Franken & Preetz (1995)
ZEPWUM	$C2/m$	$C_{36}H_{38}Fe_3\cdot 3CF_3O_3S$	Barlow *et al.* (1995)
ZEVQEW	$R\bar{3}c$	$C_{18}H_{38}N_2O_6Cl_4\cdot H_{14}O_6$	MacGillivray & Atwood (1995)
ZICZIU	$C2/m$	$C_{24}H_{24}S_{16}\cdot C_{12}H_4N_4$	Tanabe *et al.* (1995)
ZIFKII	$I222$	$C_{24}H_{16}N_4S_{20}RbZn$	Mori *et al.* (1995)

are available, thus precluding proper rerefinement and corroboration of H-atom positions.

2. Discussion

Of the 50 changes in space group listed in Table 1, the majority involve the addition of a center of inversion (space groups $C2/m$, $C2/c$ or $R\bar{3}c$). In such cases the near-singularities associated with refining a centrosymmetric (or nearly so) structure in a non-centrosymmetric space group are expected to be severe and the resulting description in $C2$ is expected to be distorted. This was, almost invariably, the case. In most instances the $C2$ description involved two chemically identical species – either entire molecules or halves of individual molecules – which should have equivalent geometries; however, the coordinates derived for space group $C2$ typically lead to disparities of 0.1 Å or more in the face of formal s.u.'s of, perhaps, 0.01 Å. (A particularly serious example is VIHYIU, where the C—C distances within the *t*-butyl group are 1.27, 1.62 and 1.85 Å, according to the C2 coordinates, but become 1.56, 1.56 and 1.57 when the coordinates are averaged according to $C2/m$.) In most cases it was this marked improvement in the molecular geometry that convinced us that the change in space group is appropriate, even when the revised space group $C2/c$ requires the systematic absence of reflections $h0l$ with l odd. Only in the case of GIHNUG were such absences noted (along with a ‘pseudo’ center of inversion); in that case, it seems likely that the authors failed to realise that there are two distinct types of inversion centers in $C2/c$. In the other examples, we presume there were weak violations of the extinction condition – perhaps caused by double reflection – that steered the user, or his computer program, away from $C2/c$. In several instances the original choice of space group $C2$ was apparently made on the basis of intensity statistics favoring an acentric distribution of atoms; such statistics are notoriously unreliable, particularly when the structure contains a small number of heavy atoms (Hargreaves, 1955) or when the weak intensities have been deleted from the data set (Marsh, 1981). It is also likely that some authors, after searching unsuccessfully for a solution in the correct centrosymmetric space group ($C2/m$ or $C2/c$), were able to find a satisfactory solution in $C2$ (or, perhaps, $P1$), but then failed to notice that this solution was compatible with the higher symmetry.

A few entries in Table 1 deserve special note:

2.1. COJJAM

Here, the $C2$ description includes two molecules in the asymmetric unit, arranged to form an almost exact face-centered array; this face-centered structure can be transformed to a new C-centered cell, again with space group $C2$, half the size of the original. Presumably there were a small number of apparent violations to the face-centering conditions (h, k, l all even or all odd) that seemed to require the larger cell. However, once again this situation – the attempt to develop and refine a superstructure on the basis of weak superlattice reflections – leads to high correlations and, perhaps, singularities in the refinement procedure (Schomaker & Marsh, 1979). The scatter among chemically equivalent bond lengths was strikingly improved when the near-singularities were removed, *i.e.* when the structure was converted to the smaller cell.

2.2. JOSXAQ

This terbium compound, whose structure we have revised to space group $R32$, is isostructural with the corresponding europium compound JOSTEQ, whose structure was originally reported in $R3$ (Su *et al.*, 1998). We include revised coordinates for both compounds in the supplementary material.

2.3. ZIFKII

After the structure of this Rb–Zn compound is transformed to space group $I222$, it becomes apparent that it is isostructural with the corresponding Cs–Zn (ZIFKEE) and Cs–Co (ZIFKAA) compounds described in the same paper (Mori *et al.*, 1995). However, it appears that the coordinates of the Rb and Zn atoms have been interchanged. In the structure as reported in $C2$, the Rb atom is bonded, approximately tetrahedrally, to four N atoms (of thiocyanate groups) at 1.93–2.01 Å, while the Zn atom has, as its closest neighbors, eight S atoms (also of thiocyanate groups) at 3.61–3.71 Å. These would be surprising coordination groups for both atoms, and at odds with the structures of the Cs–Zn and Cs–Co compounds. Moreover, the displacement parameters $B_{\rm iso}$ are reported as 3.5 for Zn and 5.0 for Rb, also suggesting that the atom identities have been interchanged.

There are a few further examples, not included in Table 1, which warrant special discussion

2.4. DUYVOI (Aumann *et al.*, 1986) [$C_{21}H_{16}N_2OS$]

Here, the two molecules in the asymmetric unit of space group $C2$ are nearly identical, except for the position of the terminal methyl group of the ethoxy substituent. The authors reported that they attempted refinement, in space group $C2/c$, of a model with these methyl groups disordered, but that the refinement led to unrealistic C—C distances; they also note that 38 reflections $h0l$ with l odd were weak but not absent. However, in the final $C2$ model (as well as in $C2/c$) there is an unsatisfactory contact, at 2.85 Å, between one of these methyl groups and its symmetry-related mate, which suggests that disorder is needed whichever the space group. Symmetrizing the structure according to $C2/c$ leads to a marked improvement in bond lengths in other parts of the molecule, but further study would be needed to resolve the situation.

2.5. GIVKIF (Zhou *et al.*, 1998) [$C_{24}H_{42}Fe_2O_{16}VCl\cdot 3H_2O$]

The cell dimensions and atom coordinates reported for this compound agree closely with the trigonal space group $R32$; however, this transformation would require disorder between the V atom and the two Fe atoms (which would be related by a C_3 axis in $R32$). The compound was synthesized from a 1:2 ratio of VCl_3 and $FeCl_3$; there seems to be no further confirmation of the stoichiometry of the crystalline material. The IR spectrum showed a single broad peak at 609 cm^{-1}, which the authors interpreted as a combination of V—Cl and Fe—Cl stretching frequencies. While it is probable that the structure should be described in $R32$, the stoichiometry of the compound seems questionable.

2.6. KEGPOB (Ozaki *et al.*, 1990) [$C_{17}H_{28}CoN_2O_5Na\cdot 1.5C_4H_8O$]

This structure probably should be revised to orthorhombic, space group $F222$. However, the coordinate agreement between equivalent atoms is poor, with mismatches as large as 0.5 Å for two pairs of methyl groups. The authors note that the quality of the diffraction data was low, with a large number of poorly measured weak intensities; they also reported disorder of methyl and ethyl groups and of the solvent molecules (tetrahydrofuran). The final R was very high, 0.17. Clearly, better data must be obtained if a reliable structure is to be found.

2.7. PEGGAJ [$C_{108}H_{96}N_{18}Ni_3\cdot 6ClO_4$]

The original authors (Krämer *et al.*, 1993) noted that this structure has approximate rhombohedral symmetry, but they rejected the space group $R32$ since the averaging of intensities according to the additional threefold symmetry was poor. However, the crystals decayed in the X-ray beam and cracked easily and the number of significant intensities was small – 2721 for 599 parameters. Averaging the coordinates according to the space group $R32$ leads to noticeable improvement in the bond lengths and angles. Confirmation of the space group must await further investigation.

2.8. QADPAM (Bernal *et al.*, 1997) [$C_6H_{16}CoN_4O_4F\cdot 11.5H_2O$]

Here, the authors say: ‘Examination of the systematic absences clearly show(s) the absence of any glide planes’. Nevertheless, they note that the derived structure (in $C2$) has a *pseudo* inversion center at *ca* 1/4, 0, 1/4 and they describe it as a ‘kryptoracemate’. The coordinates correspond very closely – within r.m.s. deviations of *ca* 0.08 Å – to space group $C2/c$ with the exception of one water molecule (or fluoride ion), lying on a C_2 axis, which is unpaired across the inversion center. In addition, the interatomic distances and angles, as well as the $B_{\rm iso}$ values, become appreciably more reasonable when the structure is symmetrized in $C2/c$. Are the apparent violations to the glide-plane absences ($h0l$, l odd) real? If so, what is their origin? There is no evidence that the fluoride ions and water molecules (which the authors were not able to distinguish between) are responsible for lowering the symmetry; their coordinates (except for the unpaired atom) obey the symmetry of $C2/c$ as well as do those of the main molecules. Is the problem associated with the loss of water of crystallization which apparently occurred during data collection? In any event, we are reluctant to assert that the space group should be revised; but we point out that the atom coordinates presently available are unreliable, due to the near-singularities that were surely present, and that any detailed discussion of the molecular structure should focus on the average of the two independent molecules (in $C2$) rather than on either molecule separately. For a discussion on near singularities see Dunitz (1979). Near singularities are often successfully handled using similarity constraints and restraints.

2.9. DAVQAS (Vankatraman *et al.*, 1999) [$C_{12}H_{15}N_3S$], MNIURC10 (Ginell & Parthasarathy, 1981) [$C_5H_5N_3{\cdot}H_2O$], and TAKZEK (Coiro & Mazza, 1991) [$2C_{12}H_{25}O_4S{\cdot}H_{12}MgO_6$]

In these three compounds, all or most of the atoms lie on approximate mirror planes that would be exact if the space group were $C2/m$; in each case the authors fully realised the ambiguity and carried out refinements in both $C2$ and $C2/m$. In the case of DAVQAS, the two refinement results were equivalent and the authors chose to report the structure as completely ordered in $C2$ rather than as slightly disordered in $C2/m$. For TAKZEK and MNIURC10, refinement in $C2$ produced slightly lower R values which, on the basis of the Hamilton (1964) test, led the authors to reject $C2/m$; we note though that this 'significance test' is unreliable in such cases, where the additional parameters in $C2$ can accommodate experimental errors of many kinds. In any event, in cases such as these, where the decision between a centrosymmetric or a non-centrosymmetric space group results in deciding whether atoms lie exactly or only approximately in a crystallographic mirror plane, the interatomic distances and angles are effectively unable to help in the choice; they are insensitive to small deviations from co-planarity.[3] Thus, the choice between space groups is less clear. It is also less important, unless the out-of-plane atomic displacement parameters – which couple closely with the out-of-plane positional coordinates – are of interest.

2.10. COPARS (Pauling *et al.*, 1970) and DASTCA10 (Elder *et al.*, 1980)

These two compounds – *trans*-[MCl$_2$(diars)$_2$]ClO$_4$, with M = Co (COPARS) or Tc (DASTCA10) and diars = o-$C_6H_4[As(CH_3)_2]_2$ – are isostructural, space group $C2$. While the two structures conform closely to space group $C2/m$, both sets of authors reported significantly poorer refinement results in $C2/m$ than in $C2$; our attempts to re-refine the structure of DASTCA10 in $C2/m$ were also unsatisfactory. It is primarily the ClO_4 group that appears unable to accommodate $C2/m$. In both cases the refinements in $C2$ presented some problems, presumably due to near-singularities; for COPARS, the authors constrained the cation to lie on the mirror plane.

So we add a word of caution: lacking (in most cases) the primary intensity data necessary to carry out a re-determination of the structure, we may be treading on thin ice when we assert that all 50 structures listed in Table 1 should be revised. In those cases where only the Laue symmetry is changed, the coordinate shifts necessary to achieve the higher symmetry are almost invariably no larger than the reported s.u.'s; in these instances, the ice seems firm. However, when centers of symmetry need to be added, the shifts are far larger; our conviction that these corrections are warranted lies primarily in the striking improvement in molecular geometry that invariably occurs. Should we fear that we have included cases similar to COPARS and DASTCA10, where the deviations from centrosymmetry are small but real? If the deviations are small enough, the near-singularities in the refinement routine may lead to surprising molecular dimensions. However, these near-singularities are reflected in large uncertainties in the antisymmetric terms – the differences between pseudo-equivalent bond lengths and angles, rather than their sums (or average values). So, to the extent that it is the molecular geometry that is of most interest, it is the average structure – the structure compatible with the centrosymmetric space group – that should be preferred. If details concerning the differences between *pseudo*-related molecules are wanted, it might be necessary to resort to techniques other than diffraction.

However, the purpose of this paper is not only to note the prevalence of incorrect space-group assignments in the crystallographic literature (which has been documented many times previously), but to emphasize that there are now available easy-to-use computer tools such as the program *MISSYM* (Le Page, 1987, 1988) or its extended version *PLATON*/*ADDSYM* (Spek, 2001) that are readily available to check for the possibility of higher symmetry. Surely it should become standard procedure to check every structure for such a possibility. While some journals (including the International Union of Crystallography journals) routinely carry out such checks on every published paper, it is far more sensible that the checking be performed as early as possible – preferably while the crystal is still available, in case that additional experimental evidence is needed. Facilities and software for this purpose are freely available from various sources. (This checking seems particularly necessary because of the apparent tendency for direct-methods routines to provide structure solutions in non-centrosymmetric space groups while failing in the corresponding correct centrosymmetric groups.)

A final word of caution is needed: as is always the case, such symmetry-checking programs must be used carefully and the results examined thoughtfully. As we have noted, only one-

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[3] In the case of TAKZEK, two O atoms of the sulfate group, as well as two coordinated water molecules, lie on opposite sides of the mirror plane, rather than in it. Thus, the S—O and Mg—O distances can provide some clue as to the proper description. In $C2$ the S—O distances are distinctly different, at 1.391 and 1.479 Å; in $C2/m$ they are equivalent, at 1.435 Å. The Mg—O distances are 2.065 and 2.084 Å in $C2$, 2.075 Å in $C2/m$. The ordered, $C2$ description of DAVQAS results in peculiar bond lengths within the cyclopentane ring.

third of the possible candidates for revision that we found in our initial survey were, in fact, incorrect; the remaining two-thirds apparently show only pseudosymmetry. However, such pseudosymmetry may be interesting in its own right, particularly in the many cases where chiral compounds crystallize in nearly centrosymmetric structures.

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