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22 Space-group changes

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This paper reports 22 examples of space-group changes from low to higher symmetry. The revisions involve 15 crystal structures that were originally described in space group $P2_1$, six in $P\bar{1}$ and one in $P1$. The relevance of higher-symmetry elements is discussed in connection with the crystallography, the molecular dimensions and, when possible, the spectroscopic properties.

1. Introduction

Recently, many crystal structures have been revised to space groups of higher symmetry (Baur & Tillmanns, 1986; Cenzual *et al.*, 1991; Herbstein & Marsh, 1998; Marsh, 1995, 1999; Marsh & Spek, 2001). The percentage of possible revisions was evaluated (Baur & Tillmanns, 1986) to be about 3% of all the published structures (~245 000), so that up to 7000 structures may be incorrect. In addition, some crystal structures are reported to have higher symmetry than the true symmetry. This occurs, for example, when all the weak intermediate-layer lines are systematically lost during a peak search, which results in a subcell of the correct unit cell (see *e.g.* Galdecki *et al.*, 1999; Connick *et al.*, 1996). The detection of the true crystal symmetry is important for several reasons:

(i) the theory of occurrence of three-dimensional space groups;

(ii) the second-order non-linear optics which demand non-centrosymmetric space groups;

(iii) the IR and NMR spectroscopy in the solid state;

(iv) the correct attribution of isomorphism.

2. Data retrieval and methods

Version 5.22 of the CSD (Cambridge Structural Database; Allen & Kennard, 1993) was used (December 2001, 245 000 entries). We focused on crystal structures that contain (*a*) two molecules per asymmetric unit or (*b*) only one molecule but have a molecular symmetry element such as a mirror plane or twofold axis. We examined over 5000 crystal structures; 340 were shown to be metrically orthorhombic, but orthorhombic symmetry is only really present in 18 of these structures. A centre of symmetry must be added to another four space groups. The space-group changes reported here belong to two categories: (i) an increase in the Laue symmetry (18 examples) and (ii) a change from non-centrosymmetric to centrosymmetric (four examples). For structures in which the Laue class was changed we used firstly our own local (written by DAC) programs *CLASS.FOR* or *CELL.FOR*, which classify the crystal structure among the 44 metric classes (Mighell &

Rodgers, 1980). If the crystal structure was metrically different from that reported in the literature, the following three tests were applied:

(i) Our program *FSCC.FOR* read the original cell, space group and coordinates[1] and applied a low isotropic displacement factor ($U = 0.02$ Å^2) to all atoms, to give h, k, l and F_c for at least 10000 reflections distributed over the complete reflection sphere and at high θ angles. The Miller indices were then transformed according to the matrix found by *CLASS.FOR* or *CELL.FOR* to give a reflection data file NAME.HKL, which is adapted for use with *SHELXL* (Sheldrick, 1997) and retains the structure factors F_c. Then, *LAUE.EXE* (Farrugia, 1997) or *ORDRIFL.EXE* (Nardelli, 2001) was used to merge the equivalent reflections using the new Miller indices. If $R_{\rm int}$ on F_o was lower than 5% the structure was accepted for subsequent analysis.

(ii) The second test was carried out in real space. The atomic shifts[2] necessary to achieve the higher symmetry (reported in square brackets in Tables 1–22 of the supplementary material[3]) were compared with the s.u. values averaged over (now) equivalent atoms (reported in parentheses in Tables 1–22 of the supplementary material[3]). The atomic shift and the s.u. value must be similar.

(iii) A structure-factor calculation was performed using *SHELXL* (Sheldrick, 1997), which reads the file NAME.HKL, and the coordinates that had been transformed to the new space group and averaged. If the space-group change is correct the R factor must be less than 3%.

We have found that test (i) is the most important and severe. Moreover, the four structures that belong to category (ii) were discovered by consideration of the spread of chemically equivalent distances.

We have also used *PARST.FOR* (Nardelli, 1983, 1995, 1996). The 22 revised structures after space-group revisions are listed in Table 1,[3] together with the CSD Refcode.

3. Category (i): increase in Laue symmetry

3.1. From $P2_1$ (No. 4) to $C222_1$ (No. 20)

Within this space-group change, the b axis of $P2_1$ becomes the c axis of $C222_1$. Since the z coordinate origin is now fixed, an origin shift along c is needed during this change. Moreover, an origin shift along the a and b axes is necessary whenever the original authors have chosen (in $P2_1$) the origin on the 2_1 axis that meets the other two perpendicular screw axes instead of choosing the origin on the 2_1 axis that meets the two perpendicular twofold axes.

3.1.1. BARJAF. Space group $C222_1$ can accommodate this chiral Co(II) complex that now lies on a twofold axis along b. The earlier paper noted that 'the molecule presents a remarkable non-crystallographic twofold pseudosymmetry around the axis containing Co(II), the midpoint of the C(6)—C(7) bond and C(14) [C15 in the CSD]'. Even so, the dioxolane ring remains distributed over two equally populated conformations related by this twofold crystallographic axis: the *endo*-C atom connecting the dioxolane O(1) and O(2) is still split into C(13) and C(14), and the methyl C(15) lies on the crystallographic binary axis. We believe that this disorder is not due to refinement in the improper $P2_1$ space group but is real. In $P2_1$ the chemically equivalent distances N(4)—O(5) = 1.186 (15) Å and N(3)—O(8) = 1.272 (16) Å are the most disparate, whereas in $C222_1$ this distance becomes 1.229 Å.

3.1.2. CLAECU. The twofold crystallographic axis along b passes through Cu(1), the midpoint of the ethylenediamine C—C and the two chloroacetato ligands. We note that the original paper stated 'the molecules have pseudo C_2 symmetry'.

3.1.3. QANXOS. This Co(III) complex possesses a twofold crystallographic axis parallel to a passing through Cl(1), Co(1) and Cl(2), while the perchlorate anion lies on the crystallographic twofold axis parallel to b. These twofold axes relate atom pairs well within their s.u. values, but the deviations of the perchlorate anion from the averaged values are slightly greater because of its disorder, in which the four O atoms are duplicated by the twofold axis parallel to b.

3.1.4. SAZPAK. In $P2_1$ there are two independent [Ni(en)(5′GMPH)$_2$(H$_2$O)$_2$](en)·6.5H$_2$O molecules (5′GMPH is guanosine 5′-monophosphate) in the asymmetric unit. In $C222_1$ there are two half molecules in the asymmetric unit: one on the twofold axis along a and the other on the twofold axis along b. The original paper states that the complex does not possess a twofold axis, although the authors had verified the presence of a crystallographic twofold axis passing through Ni in the inosine analogue [Ni(en)(5′IMPH)$_2$(H$_2$O)$_2$]·13H$_2$O (SAZNUC) published in the same work. The two independent ethylenediamine molecules in $P2_1$ are related by a twofold axis along b, so that the water molecules are related by twofold axes along a or b, with one water molecule on the twofold axis along b.

3.1.5. YAKVIPI. The space-group transformation shows that the two independent organic molecules in $P2_1$ are related, within the s.u. values, by an additional 2_1 axis along a of space group $C222_1$. Moreover, two water molecules (O11, O17) are related by a twofold axis along b, and the other two water molecules (O14, O18) lie on two distinct twofold axes along b.

3.2. From $P2_1$ (No. 4) to $Cmc2_1$ (No. 36)

This space-group change was discussed by Marsh (1990) for KAFFEC and by Herbstein (1991) for VEXPET. Here, the b axis of $P2_1$ becomes the c axis of $Cmc2_1$. Since the origin is

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[1] Three sets of atomic coordinates and numbering schemes may be reported in the literature for each compound: *i.e.* the sets (i) in the original publication, (ii) in the Cambridge Structural Database system (CSD) and sometimes (iii) in the Internet archives. Because the three sets may be different, the CSD system will be followed here.

[2] We define the shift necessary to achieve the higher symmetry as one half of the distance between the two equivalent atoms when they are brought as near as possible to each other by the added symmetry elements (lost in the original paper).

[3] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0613). Services for accessing these data are described at the back of the journal.

Table 1
Structures originally described in space groups that are more properly described in higher symmetries.

Included are Refcode, original space group, revised space group, original (Z) and new (Z') number of formula units per cell.

Refcode	Original space group	Revised space group	$Z \rightarrow Z'$	Formula unit	Atomic shifts† ($\times 10^3$ Å) min $\leftrightarrow$max	TMD‡(Å)	$R_{\rm int}$§ (%)	Transformation vectors	Coordinate transformations¶	Reference
BARJAF	$P2_1$	$C222_1$	2→4	$C_{15}H_{16}CoN_4O_8$	7↔31	N—O = 1.186 ↔ 1.272 → 1.229 Co—N = 2.055 ↔ 2.11 → 2.081	4.1	$[00\bar{1}]$ [201] $[0\bar{1}0]$	$x' = (x/2 - z) + 3/4$; $y' = x/2 - 1/4$; $z' = -y + 0.5059$	Minardi *et al.* (1999)
CLAECU	$P2_1$	$C222_1$	2→4	$C_{10}H_{20}Cl_2CuN_2O_4$	2↔5	C—Cl = 1.775 ↔ 1.785 → 1.780 Cu—N = 2.037 ↔ 2.039 → 2.038	2.1	[101] $[10\bar{1}]$ [010]	$x' = (x + z)/2 + 3/4$; $y' = (x - z)\ /2$; $z' = y - 0.2243$	Ahlgrén *et al.* (1978)
QANXOS	$P2_1$	$C222_1$	2→4	$[C_{16}H_{32}Cl_2{\cdot}CoN_4]^+ ClO_4^-$	2↔14	C—N = 1.468 ↔ 1.499 → 1.484 C—C = 1.497 ↔ 1.512 → 1.505	2.0	[101] $[10\bar{1}]$ [010]	$x' = (x + z)/2 + 1/4$; $y' = (-x - z)/2 + 3/4$; $z' = y + 0.0717$	House *et al.* (1999)
SAZPAK	$P2_1$	$C222_1$	4→8	$C_{22}H_{38}N_{12}NiO_{18}P_2{\cdot}C_2H_8N_2{\cdot}6.5H_2O$	7↔56	C—C = 1.333 ↔ 1.435 → 1.383 C—O = 1.385 ↔ 1.463 → 1.423	2.8	$[\bar{1}0\bar{1}]$ $[10\bar{1}]$ $[0\bar{1}0]$	$x' = -(x + z)/2 + 1$; $y' = (x - z)/2 + 1/2$; $z' = -y + 0.0080$	Fiol *et al.* (1989)
YAKVIP	$P2_1$	$C222_1$	4→8	$[C_5H_7N_2O_5Na(H_2O)_{2.5}]_n{\cdot}1.5n(H_2O)_2\ (n = 1)$	3↔8	C—C = 1.524 ↔ 1.543 → 1.533 Na—O = 2.407 ↔ 2.418 → 2.411	1.0	[100] [102] $[0\bar{1}0]$	$x' = x - z/2$; $y' = z\ /2$; $z' = -(y + 0.3857)$	Davis *et al.* (1991)
BOGPIW	$P2_1$	$Cmc2_1$	2→4	$[C_7H_5FeO_4S]^+{\cdot}[AsF_6]^-$	5↔30	C—C = 1.287 ↔ 1.388 → 1.336 C—C = 1.326 ↔ 1.390 → 1.357	3.2	[101] $[10\bar{1}]$ [010]	$x' = (x + z)/2 + t$††; $y' = (x - z)/2 + 3/4$; $z' = y - 1$	Hartmann *et al.* (1982)
NOVHUB	$P2_1$	$Cmc2_1$	2→4	$[C_{60}H_{54}Cu_2N_3O_3P_4]^+{\cdot}[NO_3]^-{\cdot}CH_3OH$	1↔17	C—C = 1.344 ↔ 1.375 → 1.359 C—C = 1.377 ↔ 1.401 → 1.391	2.9	$[10\bar{1}]$ [101] [010]	$x' = (x - z)/2 + 1/4$; $y' = (x + z)/2 + 1/4$; $z' = y$	Ruina *et al.* (1997)
NOHNED	$P2_1$	$P2_12_12_1$	4→4	$C_{22}H_{26}N_2O_6$	1↔12	C—N = 1.309 ↔ 1.334 → 1.322 C—N = 1.267 ↔ 1.274 → 1.270	1.9	[100] [010] [001]	$x' = x$; $y' = y - 0.8780$; $z' = z - 1/4$	Casellato, Tamburini *et al.* (1997)
NOHNED01					2↔17	C—N = 1.282 ↔ 1.316 → 1.300 C—O = 1.394 ↔ 1.427 → 1.410	1.7	[100] [010] [001]	$x' = x$; $y' = y{-}0.8785$; $z' = z - 1/4$	Brianese *et al.* (1999)
QELPUS	$P2_1$	$P2_12_12_1$	4→4	$C_{28}H_{32}Cl_2N_2Pd_2{\cdot}H_2O$	2↔79	C—C = 1.310 ↔ 1.450 → 1.380 C—C = 1.302 ↔ 1.410 → 1.352	1.8	[100] [010] [001]	$x' = x + 3/2$; $y' = y + 1.0777$; $z' = z + 3/4$	Gül & Nelson (2000)
APLSOL	$P2_1$	$P4_3$	4→4	$C_{15}H_{19}BrO_2$	6↔77	C—C = 1.286 ↔ 1.456 → 1.370 C—C = 1.491 ↔ 1.604 → 1.546	3.7	[001] [100] [010]	$x' = z + 1$; $y' = x + 1$; $z' = y$	McMillan *et al.* (1976)
DOQZAK	$P2_1$	$P4_3$	4→4	$C_{17}H_{20}NO_5V$	1↔13	C—N = 1.404 ↔ 1.431 → 1.417 C—C = 1.425 ↔ 1.449 → 1.438	1.3	[100] $[00\bar{1}]$ [010]	$x' = x - 1/2$; $y' = -z + 1$; $z' = y$	Rajac *et al.* (2000)

Table 1 (continued)

Refcode	Original space group	Revised space group	$Z \to Z'$	Formula unit	Atomic shifts† ($\times 10^3$ Å) min ↔max	TMD‡(Å)	$R_{\rm int}$§ (%)	Transformation vectors	Coordinate transformations¶	Reference
BAMUBR	$P\bar{1}$	$C2/c$	2→4	$2[C_{16}H_{36}N]^{+} \cdot [UO_2Br_4]^{2-}$	7↔62	C−C = 1.512 ↔ 1.581 → 1.547 C−C = 1.572 ↔ 1.634 → 1.603	2.1	$[0\bar{1}1]$ $[0\bar{1}\bar{1}]$ $[110]$	$x' = (x - y + z)/2 + 3/4$; $y' = (x - y - z)/2 + 1/4$; $z' = x + 1/2$ ‡‡	Di Sipio *et al.* (1977)
FARNER	$P\bar{1}$	$C2/c$	2→4	$C_{10}H_{24}Cl_4N_4O_2U$	0↔34	C−O = 1.258 ↔ 1.301 → 1.278 C−N = 1.323 ↔ 1.359 → 1.341	1.4	$[0\bar{2}1]$ $[00\bar{1}]$ $[110]$	$x' = (x - y)/2 + 1/4$; $y' = (x - y)/2 - z + 1/4$; $z' = x$	Du Preez *et al.* (1986)
FARNIV	$P\bar{1}$	$C2/c$	2→4	$C_{10}H_{24}Br_4N_4O_2U$	0↔35	C−O = 1.265 ↔ 1.310 → 1.288 U−O = 2.197 ↔ 2.230 → 2.213	1.0	$[0\bar{2}1]$ $[00\bar{1}]$ $[110]$	$x' = (x - y)/2 + 1/4$; $y' = (x - y)/2 - z + 1/4$; $z' = x$	Du Preez *et al.* (1986)
HIMFUE	$P\bar{1}$	$I2/a$	4→8	$C_{26}H_{43}F_3O_3P_2Pd$	2↔23	C−C = 1.501 ↔ 1.567 → 1.534 C−C = 1.387 ↔ 1.424 → 1.405	1.4	$[0\bar{1}1]$ $[\bar{1}00]$ $[1\bar{1}\bar{1}]$	$x' = (-y + z)/2 + 1/4$; $y' = -x - (y + z)/2 + 3/4$; $z' = -(y + z)/2 + 3/4$	Van der Boom *et al.* (1998)
HORBIZ	$P\bar{1}$	$I2/a$	4→8	$C_{47}H_{63}NO_6Si$	2↔25	C−C = 1.492 ↔ 1.517 → 1.505 C−C = 1.469 ↔ 1.494 → 1.481	2.1	$[\bar{1}11]$ $[100]$ $[01\bar{1}]$	$x' = (y + z)/2$; $y' = x + (y + z)/2$; $z' = (y - z)/2$	Comins *et al.* (1999)
PEJVAB	$P\bar{1}$	$I2/m$	1→2	$C_8H_{12}S_8Tc_2$	1↔6	Tc−S = 2.390 ↔ 2.392 → 2.390 C−S = 1.836 ↔ 1.838 → 1.837	1.7	$[11\bar{1}]$ $[00\bar{1}]$ $[\bar{1}10]$	$x' = (x + y)/2$; $y' = -(x + y)/2 - z + 1$; $z' = (-x + y)/2$	Tisato *et al.* (1993)
SIXFIO	$P1$	Ia	2→4	$[C_{23}H_{25}NPPd]^{+} \cdot [PF_6]^{-}$	1↔36	Pd−C = 2.194 ↔ 2.262 → 2.228 Pd−C = 2.060 ↔ 2.100 → 2.078	1.3	$[0\bar{1}1]$ $[\bar{1}00]$ $[1\bar{1}\bar{1}]$	$x' = -(y - z)/2 + 1/2$; $y' = -x - (y + z)/2 + 1.5295$; $z' = -(y+z)/2 + 1/2$	Crociani *et al.* (1998)
BIHJUX	$P2_1$	$P2_1/m$	2→2	$[C_{23}H_{37}CeN_3O_9]^{3+} \cdot 3Cl^{-} \cdot H_2O$	51↔264	C−C = 1.295 ↔ 1.658 → 1.469 C−O = 1.313 ↔ 1.655 → 1.460	–	[100] [010] [001]	$x' = x$; $y' = y - 0.0288$; $z' = z$	Casellato *et al.* (1999)
BIHLIN	$P2_1$	$P2_1/m$	2→2	$[C_{23}H_{37}DyN_3O_9]^{3+} \cdot 3Cl^{-} \cdot H_2O$	59↔227	C−N = 1.270 ↔ 1.572 → 1.417 C−C = 1.250 ↔ 1.546 → 1.396	–	[100] [010] [001]	$x' = x$; $y' = y - 0.0288$; $z' = z$	Casellato *et al.* (1999)
ZEXBUZ-01	$P2_1$	$P2_1/m$	2→2	$C_{33}H_{57}ClO_6Zr$	9↔91§§	C−C = 1.345 ↔ 1.450 → 1.394 C−C = 1.335 ↔ 1.417 → 1.375	–	[100] [010] [001]	$x' = x$; $y' = y - 0.2093$; $z' = z$	Casellato, Fregona & Graziani (1997)
PYRHSB	$P2_1$	$P2_1/a$	4→4	$[C_5H_6N]^{+} \cdot [SbCl_6]^{-}$	20↔118 ¶¶	Sb−Cl = 2.206 ↔ 2.437 → 2.321 Sb−Cl = 2.274 ↔ 2.440 → 2.355	–	[100] [010] [001]	$x' = x + 1/4$; $y' = y + 0.0277$; $z' = z$	Porter & Jacobson (1972)

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† Only the shifts of the non-H atoms are reported. ‡ The distances in the column labelled TMD are the most disparate pair in the lower-symmetry group and the corresponding value in the higher-symmetry group. § $R_{\rm int}$ is defined as $\sum[F_o(h) - F_o(h')]/\sum F_o(h)$(mean) ($h$ and h' are the Miller indices of equivalent reflections). ¶ When there is more than one residue, the coordinate transformations are strictly valid for the most populated residue. †† $t = -3/4$ for the $[C_7H_5FeO_4S]^{+}$ cation and $t = 1/4$ for the $[AsF_6]^{-}$ anion. ‡‡ Only for the tetra-*n*-butylammonium cations. §§ *tert*-Butyl groups are not considered because of their high thermal motion. ¶¶ Excluding the pyridinium cation because it is disordered.

arbitrary along both of these axes, no origin shift is needed during this change. However, an origin shift along *a* and *b* is needed whenever the original authors have chosen (in $P2_1$) the origin on the 2_1 axis at the intersection of the *n*-glide with the *b*-glide instead of at the intersection of the *m*-plane with the *c*-glide.

3.2.1. BOGPIW. Atoms Fe(1), S(1), O(1), O(2) and C(2) of the $[C_5H_5Fe(CO)_2SO_2]^+$ cation lie on the mirror plane (*m*-plane) at $x = 0$, while As(1), F(1) and F(5) of the octahedral AsF_6^- anion lie on the *m*-plane at $x = 1/2$. The deviations from the *m*-plane are greater than the formal s.u. values for C(2), O(2), F(1) and F(5) because they have large anisotropic displacement parameters (ADPs). However, even if the distances in $P2_1$ and $Cmc2_1$ space groups remain almost equal, some distances become more realistic in the latter space group. For example the most disparate C—C (cyclopentadienyl) distances, which range from 1.287 (16) to 1.388 (14) Å, become 1.336 Å. The distances in the Cp ring remain shorter than normal {1.421 (3) Å, *e.g.* in (μ-CH_2)-$[CpMn(CO)_2]_2$; Clemente *et al.*, 1982}, probably because of the large libration around the ring-centroid–metal-atom axis. We ascribe the rather high deviations from the *m*-plane to the high ADPs of these atoms rather than to a real loss of the *m*-plane. The As—F distances are practically unchanged after the revision and are comparable to those of other AsF_6^- anions (Cameron *et al.*, 2000).

3.2.2. NOVHUB. The orthorhombic cell contains four formula units of $[C_{60}H_{54}Cu_2N_3O_3P_4]^+\cdot NO_3^-\cdot CH_3OH$. This arrangement is possible because the *m*-plane at $x = 0$ passes through the two (CH_2) groups, the μ^2-nitrato and the ionic nitrate, thus the two Cu atoms and the other atoms of the molecule are related by this *m*-plane. A particular disorder situation has been found for the methanol molecule. The original monoclinic cell has two methanol molecules, thus the new orthorhombic cell must contain four methanols that are constrained to lie on the *m*-plane at $x = 1/2$. However, the methanol is not situated in the *m*-plane, but this plane lies perpendicular to the C—O bond, so that the C atom is mirrored with the O atom.

3.3. From $P2_1$ (No. 4) to $P2_12_12_1$ (No. 19)

3.3.1. NOHNED and NOHNED01. Two refinements are reported for this compound: a preliminary communication (Casellato, Tamburini *et al.*, 1997) and a final publication (Brianese *et al.*, 1999). The change in space group reveals that the two independent molecules in the asymmetric unit are related by a 2_1 screw axis along *a*. Seven C atoms in the preliminary communication and three H atoms in the final publication lack their corresponding equivalent atoms since they are not reported in the CSD file. The double refinement of this compound provides an opportunity to verify the statistical law that the atomic shifts must be comparable to their s.u. values. It appears that the shifts in z' coordinates of six atomic pairs in the final publication are nearly twice their s.u. values, so we can conclude that the change of the space group is real but the final refinement is less accurate than the first refinement. Finally, we note that this compound was reported in the preliminary communication with $0.1(CHCl_3)$ solvate, but was subsequently reported as unsolvated.

3.3.2. QELPUS. The two organometallic molecules present in the asymmetric unit of space group $P2_1$ are indeed related by a 2_1 screw axis along *c* and the two water molecules by a 2_1 screw axis along *a*. The differences between equivalent distances are greater than expected for a change between two non-centrosymmetric space groups, but this chiral Pd(II) complex is nearly centrosymmetric, except, of course, for the asymmetric C atoms. The refinement thus involves a nearly centrosymmetric structure in a non-centrosymmetric space group, which produces difficulties and incorrect distances if suitable precautions are not taken, *e.g.* by using constraints (Watkin, 1994; Marsh & Spek, 2001).

3.4. From $P2_1$ (No. 4) to $P4_3$ (No. 78)

3.4.1. APLSOL. The crystal structure of this chiral molecule was described in space group $P2_1$ with $Z = 4$. In the new space group the atoms of molecule *A* are crystallographically related to the chemically equivalent atoms of molecule *B* by a 4_3 axis along c' (the old *b* axis in the monoclinic system), and thus the tetragonal 4_3 axis is coincident with the 2_1 monoclinic axis. Some atoms, especially those in the exterior of the molecule [C(3), C(5), C(6), C(7), C(9), C(10), C(12), C(31), O(11)] are needed to be shifted by 1–3 times their reported s.u. value, possibly because of the high ADPs (the structure was refined anisotropically but the parameters are not reported in the original publication). Irregularities are also present in the equivalent distances that involve these atoms in molecules *A* (first) and *B* (second):

C(3)—C(13) = 1.60 (2)–1.49 (2),
C(5)—C(6) = 1.46 (3)–1.29 (3),
C(6)—C(7) = 1.37 (3)–1.42 (3),
C(10)—C(13) = 1.43 (2)–1.52 (2),
C(3)—C(9) = 1.53 (4)–1.63 (3),
C(6)—C(12) = 1.54 (4)–1.49 (2),
C(28)—C(31) = 1.45 (3)–1.53 (3) Å.

The distances in $P4_3$ are much more regular, *e.g.* the C(sp^3)—C(sp^3) distance C(3)—C(13) becomes 1.55 Å and the phenyl C(5)—C(6) distance becomes 1.37 Å.

3.4.2. DOQZAK. The structure of this vanadium(V) complex was described as monoclinic, space group $P2_1$, with $Z = 4$; the two independent molecules are in fact related by a 4_3 screw axis along *c*. For the averaging, no atoms needed to be shifted by as much as their reported s.u. values with the exception of nine H atoms, probably because they were located in a difference Fourier map. The original paper states ‘the crystal system was confirmed to be monoclinic by suitable checking of the Laue symmetry’, but if this check is carried out with the original (monoclinic) Miller indices, it is not possible to discover the 4/*m* Laue symmetry.

3.5. From $P\bar{1}$ (No. 2) to $C2/c$ (No. 15)

This change is the most commonly reported (Marsh & Schomaker, 1979; Marsh & Herbstein, 1988; Marsh, 1984, 1989*a*,*b*, 1991, 1995; Herbstein, 1997; Herbstein & Marsh, 1998), probably because it is easy to detect.

3.5.1. BAMUBR. The crystal structure of this uranyl complex was originally reported in a non-reduced triclinic cell, space group $P\bar{1}$, with an asymmetric unit that contains two tetra-*n*-butylammonium cations and a highly symmetric $[UO_2Br_4]^{2-}$ anion. The Niggli reduced cell ($a = 11.500$, $b = 11.520$, $c = 17.077$ Å, $\alpha = 78.62$, $\beta = 78.69$, $\gamma = 79.25°$) has $a \simeq b$ and $\alpha \simeq \beta$, which immediately suggests a monoclinic *C*-centred cell. The two tetra-*n*-butyl-ammonium cations are related by a diagonal *n*-glide, while U(1), Br(3) and Br(4) are placed on a twofold axis that gives a perfectly linear Br(3)—U(1)—Br(4) group [179.74 (8)° in the old cell]. Br(1) is related to Br(2) and O(1) to O(2) by this binary axis. The earlier paper states 'the four Br atoms are arranged around the linear uranyl group [O(1)—U(1)—O(2) = 179.4 (2)°] to form a distorted to square bipyramidal octahedral coordination polyhedron'. In the more symmetrical $C2/c$ cell the $[UO_2Br_4]^{2-}$ anion becomes a little more regular [O(1)—U(1)—O(2) = 179.8°], but the angle Br(1)—U(1)—Br(2) = 177.7° is still very different from 180°. Also the spread of the C—C and C—N distances is slightly reduced, but the improvement is low because the change is between two centrosymmetric space groups.

3.5.2. FARNER and FARNIV. In the triclinic ($P\bar{1}$) description there are two independent half molecules of UCl_4L_2 (L = *N*,*N*,*N*′,*N*′-tetramethylurea) in the asymmetric unit. In $C2/c$, the two U atoms are placed in the Wyckoff position 4(*c*), while the L ligands are related by a *c*-glide perpendicular to *b*. The original paper states 'molecules *A*, with the U atom at the corners of the (triclinic) cell, are independent from molecules *B*, with the U atom at the centre. This feature, of the two independent molecules in the unit cell, is the first reported for trans-octahedral molecules of the type UX_4L_2 (X = Cl, Br; L = monodentate neutral oxygen donor ligand)'. This statement and the interpretation of IR spectra should now be reconsidered. In fact, the paper states 'the broad nature of the C═O peaks and even clear splitting of it in the case of the chloride can be interpreted in terms of the two different molecules (and uranium surroundings) found in the unit cells'. Finally, we note that a metrically orthorhombic cell ($a = 28.211$, $b = 16.807$, $c = 8.514$ Å, $\alpha = 90.09$, $\beta = 90.00$, $\gamma = 90.04°$), with a volume four times the original triclinic cell, is present in the lattice but does not possess *mmm* Laue symmetry. FARNIV (UBr_4L_2) is isomorphous and isostructural with FARNER and thus presents the same features; the only difference is that the metrically orthorhombic cell does not exist since the γ' angle is now 90.42°, which is too far from 90°.

3.6. From $P\bar{1}$ (No. 2) to $I2/a$ (No. 15)[4]

3.6.1. HIMFUE. The new space group $I2/a$ reveals that the two independent molecules (in $P\bar{1}$) are related by a twofold axis along *b*. The coordinate shifts (1/4, 3/4, 3/4) are necessary to place the origin on the *a*-glide; in fact the centre of symmetry that was chosen as the origin in the triclinic description does not correspond to the conventional origin in $I2/a$ (*i.e.* that at $\bar{1}$ on the *a*-glide). This structure was determined with very high accuracy, as is evident from the almost perfect overlap of the two independent molecules (including H atoms); this accuracy is explained by the low-temperature data collection.

3.6.2. HORBIZ. The space-group revision shows that the two independent molecules in $P\bar{1}$ are related in $I2/a$, almost within the s.u. values (excepting a few H atoms), by the 2_1 axis along *b* at $x = 1/2$ and $z = -1/4$. No translation of the origin is necessary since the centre of symmetry chosen as the origin in $P\bar{1}$ corresponds to a conventional origin in $I2/a$. The phenyl rings have very short and very long C—C bonds that cannot be corrected because the change is between two centrosymmetric space groups. The original authors noted the monoclinic *C*-centred cell but refined the structure using the rotational twin software *SMART–SAINT–ASTRO* (see http://pubs.acs.org).

3.7. From $P\bar{1}$ (No. 2) to $I2/m$ (No. 12)

3.7.1. PEJVAB. Space-group revision shows that the Tc(IV) ion and the ethene-1,2-dithiolato moiety (S3, S4, C3, C4) lie on the *m*-plane at $y = 0$. Since the space group is centrosymmetric there is, perpendicular to this *m*-plane, a twofold axis passing through the midpoint of vectors C(1)—C(2*a*), C(2)—C(1*a*), S(1)—S(2*a*) and S(2)—S(1*a*). Thus, the complex possesses exact C_{2h} and not exact C_i point-group symmetry as originally stated. The increment by 1.0 of the y' coordinates was applied to bring the molecule onto the mirror plane at $y = 0$ instead of at $y = -1$. No other origin translation is necessary since the centre of symmetry chosen in $P\bar{1}$ was already chosen on the *m*-plane. We note that C(3) lies out of the *m*-plane by 2.36 times its s.u., a value slightly higher than expected. This value is surely a result of the high ADPs of C(3) (see Fig. 1 of the original publication).

3.8. From $P1$ (No. 1) to Ia (No. 9)

3.8.1. SIXFIO. The new space group Ia (a non-standard setting of Cc) shows that the two independent Pd(II) complexes in $P1$ are related by the *c*-glide at $y = 1/4$, while the two independent PF_6^- anions in $P1$ are related by the *c*-glide at $y = 3/4$. Thus, Ia provides the natural explanation for the near identity of the two molecules that was observed by the original authors. This change has also been reported in Cc by Spek on his Internet site.

4. Category (ii): from non-centrosymmetric to centrosymmetric

4.1. From $P2_1$ (No. 4) to $P2_1/m$ (No.11)

We report here three examples of crystal structures that can be revised from $P2_1$ to $P2_1/m$ and one that can be revised from $P2_1$ to $P2_1/a$. Although the latter change is rather common (Marsh, 1997; Baur & Kassner, 1992), the former is less so but

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[4] We prefer to use the $I2/a$ variant of $C2/c$ because it gives the three shortest translations of the monoclinic lattice.

has sometimes been reported (Marsh, 1986*a*,*b*; Cenzual *et al.*, 1991).

4.1.1. BIHJUX. This Ce(III) complex has a mirror plane passing through Ce(III), Cl1, N(2), O(4), O(6), O(7) and C(10). The $P2_1/m$ space group is generated by placing this mirror plane at $y = 0.2500$ and consequently shifting all the other atoms. We note that Cl(3) lacks an equivalent atom even if it does not lie on the mirror plane. Moreover, the original paper reports that Cl(3) was refined with an occupation factor of about 0.40 or 0.60 (but 0.50 in the Internet archives at http://pubs.acs.org). The situation is complicated by the circumstance that Cl(3) is split into Cl(3) and Cl(4) [Cl(3*A*) and Cl(3*B*) in *Internet Archives*] where Cl(4) is, instead, the mirror image of Cl(2) and should have the same occupancy as Cl(2). Since the Cl(3) atom is also split in BIHMAG [the Lu(III) derivative that has space group $P2_1/n$ (Casellato *et al.*, 1999)], forms a normal hydrogen bond Cl(3)$\cdots$H(4)—C(7) and shows normal van der Waals contacts, we are inclined to think that Cl(3) is really present in the crystal. Several explanations are possible:

(i) A refinement in $P2_1/m$ might reveal that Cl(4) has a normal (1.0) occupation factor [so balancing exactly the charge of Ce(III)] or that the partially occupied Cl(3) atom is indeed a water molecule. This latter possibility is suggested by the short contact Cl(2)$\cdots$Cl(3)$^{\rm i}$ = 3.21 Å [(i) $-x+1$, $y+\frac{1}{2}$, $-z+1$], which is too short for two Cl^- ions but acceptable for a $Cl^-\cdots H—O—H$ hydrogen bond.

(ii) The mirror image of Cl(3) has been incorrectly omitted from the coordinate table.

Finally, the unusual bond distances[5] become more realistic: for instance C(20)—C(21) = 1.658 (28) Å becomes 1.469 Å and C(21)—O(4) = 1.313 (25) Å is now 1.460 Å.

4.1.2. BIHLIN. This Dy(III) complex[5] is isomorphous with the analogous Ce(III) compound described above and behaves similarly. In light of the recovered *m*-plane, the original detailed discussion of the ^{1}H NMR spectra of these complexes in solution deserves reconsideration. In fact, the presence of the *m*-plane in solution may itself account for the observed 'resonance spectral degeneracy' (*i.e.* the presence in the proton spectra of only 'eight resonances'). Such degeneracy is usually observed in other symmetric compounds, for instance, in symmetrical anhydrides (Valle *et al.*, 1986; Crisma *et al.*, 1997). Nevertheless, the earlier paper states 'this spectral degeneracy indicates that a dynamic process is occurring in solution on the NMR time scale which averages the signals of pairs of atoms'.

4.1.3. ZEXBUZ01. The chemically equivalent bond lengths of this Zr(IV) complex in $P2_1$ are disparate. For example, the heptanedionato C—C bonds range from 1.335 (15) to 1.450 (12) Å. Much greater differences are present in the *tert*-butyl groups, but these differences are also the result of very high ADPs and will be excluded from further discussion. This structure can be described as monoclinic, $P2_1/m$, since the molecule possesses a mirror plane coincident with the 2,2,6,6-tetramethyl-3,5-heptanedionato ligand, parallel to the x and z axes and bisecting the b axis at $y = 0.4593$. To obtain the $P2_1/m$ coordinates, the origin must be shifted along **b** by 0.2093, thus bringing the Zr atom onto the mirror plane. The new structural description leads to more reasonable molecular geometry, *e.g.* the heptanedionato distances now range from 1.375 to 1.414 Å. The coordinates of two H atoms have been recalculated from the symmetrized coordinates because the original coordinates were unrealistic. Surprisingly, the structure of this same complex was published in $P2_1/m$ in 1995 (*ZEXBUZ:* Jardin *et al.*, 1995), but this paper was not cited by the later authors (Casellato, Fregona & Graziani, 1997). The ZEXBUZ coordinates can be obtained from our coordinates through the transformation $1-x'$, $\frac{1}{2}-y'$, $\frac{1}{2}-z'$ if $y' > 0.2500$ and $1-x'$, y', $\frac{1}{2}-z'$ if $y' < 0.2500$. Therefore we can obtain a realistic evaluation of the scatter of the same bond length when the centre of symmetry goes unrecognized. Excluding the *tert*-butyl groups, the greatest difference is always observed in the heptanedionato C—C bond ($\Delta d = 1.450$–$1.382 = 0.068$ Å).

4.2. From $P2_1$ (No. 4) to $P2_1/a$ (No. 14)

4.2.1. PYRHSB. The structure of this compound was described in $P2_1$ with $Z = 4$; however, the two $SbCl_6^-$ anions are related by an inversion centre at (0.2500, 0.4723, 0.0000) or by a glide plane a parallel to xz and passing through $y = 0.2223$. The pyridinium rings deserve mention, since they cannot be simply averaged as the two $SbCl_6^-$ because there is disorder over two positions, probably with the same occupation factors (although no ADPs or occupation factors are reported). Similar situations were described by Marsh (1986*a*), who remarks 'a particular bothersome situation arises when the choice is between a disordered structure in the centrosymmetric space group and an ordered (or more ordered) structure in the non-centrosymmetric space group'. However, Marsh concludes that it is better to choose the centrosymmetric description even though disorder may result. In our revision, the Sb—Cl bonds become more regular (2.32–2.36 Å) as do the Cl—Sb—Cl angles (88.76–91.04°). It is remotely possible that only the $SbCl_6^-$ groups form a centrosymmetric atomic array, while the pyridinium rings form a non-centrosymmetric structure. The structure factor table is required to achieve a definitive result.

5. Conclusions

The present work has been undertaken to identify new types of space-group changes. Thus we report, for the first time to our knowledge, two space-group changes from $P2_1$ to $P4_3$. Here a 4_3 axis is incorrectly treated as a 2_1 axis with the consequent doubling of the number of molecules in the asymmetric unit. Furthermore, the space-group changes $P2_1 \rightarrow C222_1$, $P2_1 \rightarrow Cmc2_1$ and $P2_1 \rightarrow P2_12_12_1$ are also uncommon and suggest that space group $P2_1$ must be treated with great care, especially when $Z = 4$. These changes also

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[5] For calculating bond distances for both BIHJUX and BIHLIN it is important not to use the cell parameters reported in the *Abstract* of the original paper because they are different from those reported in the CSD file, on the Internet site and in Table 1 of the original paper.

suggest that the space-group change $P2_1 \rightarrow P2_1/m$ is not the only possibility. Our results confirm that the omission of a centre of symmetry produces manifestly unsatisfactory structural data (Ermer & Dunitz, 1970; Schömaker & Marsh, 1979; Marsh, 1986*a*,*b*, 1995, 1999). In fact, the atomic shifts (Table 1) are as high as 0.264 Å (in BIHJUX), but occasionally may be much larger (Marsh, 1989*b*). As expected, the atomic shifts are lower for space-group changes that belong to category (i), but the shifts reach 0.079 Å for QELPUS, because this chiral compound is nearly centrosymmetric. Further, we have detected four examples (BIHJUX, BIHLIN, FARNER, FARNIV) where an incorrect space-group assignment questions the interpretations of IR or NMR spectra, with consequent erroneous determination of the molecular structure in solution.

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