

30 Space-group corrections : two examples of false polymorphism and one of incorrect interpretation of fine details of IR spectra

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A full description of the changes in crystal structures reported for all 30 cases listed in Table 1 of the paper are provided below.

1. Category A: change in Laue group

1.1. *ABPZCU01: cis-diaqua-(2,2-bipyridyl-N,N')-copper sulfate, triclinic polymorph, [C₁₀H₁₂CuN₂O₂]²⁺ SO₄²⁻ (Chattopadhyay *et al.*, 2000)*

This structure was reported in space-group $P\bar{1}$ (No. 2), $Z = 2$, with $a = 6.9630(10)$, $b = 9.8040(10)$, $c = 9.8190(10)$ Å, $\alpha = 78.900(10)$, $\beta = 77.680$, $\gamma = 78.050^\circ$. The equivalence of b with c and of β with γ suggest a C-centered monoclinic cell. However, in order for the β angle to be much closer to 90° we have transformed the triclinic cell to the I -body centered cell, space-group $I2/a$ (No. 15), with $a = 6.963$, $b = 12.469$, $c = 14.854$ Å, $\alpha = 89.95$, $\beta = 101.01$, $\gamma = 90.30^\circ$, $Z = 4$. The transformation matrix is $(100, 01\bar{1}, \bar{1}11)$, coordinate transformations : $x' = x + 1/2y + 1/2z + 1/4$; $y' = 1/2y - 1/2z + 1/4$; $z' = 1/2y + 1/2z + 1/4$. The $[\text{Cu}(2,2'\text{-bipy})_2(\text{OH}_2)_2]^{2+}$ cation now lies on a twofold axis along b and the same is true for the SO_4^{2-} anion. Moreover, the transformation matrix $(0\bar{1}\bar{1}, 01\bar{1}, 100)$ leads to a C-centered cell, space-group $C2/c$, with $a = 15.152$, $b = 12.469$, $c = 6.963$ Å, $\alpha = 90.30$, $\beta = 105.80$, $\gamma = 89.91^\circ$. This C-centered cell immediately reveals that the claimed triclinic polymorph is in fact the already known ABPZCU (Tedenac *et al.*, 1976).

1.2. *AZCDCO : Dinitro-(1,4,7,10-tetra-azacyclododecane) cobalt(III) chloride monohydrate, [C₈H₂₀CoN₆O₄]⁺ Cl⁻ ·H₂O (Iitaka *et al.*, 1974)*

This Co(III) complex was reported as monoclinic, space-group $P2_1$ (No.4), with $a = 7.627(5)$, $b = 13.003(10)$, $c = 7.616(5)$ Å, $\beta = 102.75(10)^\circ$, $Z=2$. The Niggli matrix has the form (A,A,C,0,0,F) and corresponds to the lattice character 13 (Orthorhombic- oC) of Table 9.2.5.1 pp 753 (de Wolff, 2002). Transforming the axes by the lattice vectors $[101]$, $[\bar{1}01]$, $[0\bar{1}0]$ and shifting the origin to $(-1/4,$

1/4, 0) gives an orthorhombic C-centered cell, space-group $Cmc2_1$ (No. 36), with dimensions: $a = 9.515$, $b = 11.909$, $c = 13.003$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.08^\circ$, $Z = 4$. The coordinate transformations are : $x' = 1/2x + 1/2z + 1/4$; $y' = -1/2x + 1/2z - 1/4$; $z' = -y$. The molecule now possesses an exact mirror plane, passing through Co(1), N(4), N(10), N(13), N(16), O(19) water oxygen and Cl(1) anion, and not only an approximate mirror plane as the original authors reported. 1148 F_o values were taken from the supplementary material of *Inorg. Chem.* and were averaged according to Laue symmetry mmm ; $R(\text{int})$ (on I) was 0.0365 for 491 pairs of equivalent reflections; the total number of independent reflections in $Cmc2_1$ is 654. The new space-group requires the additional reflection condition $(h,0,l)$ absent for $l(h)$ odd, in the monoclinic setting this condition becomes (h,k,h) absent for k odd. Only two reflections of this type are present, one (131) is reported as unobserved by the original authors, while the other (474) has $F_o = 15$, that is four times the threshold value. All non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms were included in calculated position. The final $(R(F))$ index was 0.0289 ($(R(F)) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$), for all the 654 reflections and 118 variables. The $(R(F))$ index obtained by the previous authors was 0.026 but for 277 parameters. Since $Cmc2_1$ contains mirror and glide planes, the original authors' discussion of absolute configuration is irrelevant.

1.3. **BETWUS: 3',6'-O-(1,1,3,3-tetraisopropyl-disiloxane-1,3-diyl)-neoplanocin A**, $C_{23}H_{39}N_5O_4Si_2$ (Yamazaki *et al.*, 1982)

The crystal structure of this antitumor and antibiotic drug has been described as monoclinic, space-group $P2_1$, with $a = 8.953$ (1), $b = 34.638$ (4), $c = 8.957$ (1) Å, $\beta = 94.41(1)^\circ$, $Z = 4$. The Niggli matrix has the form (A,A,C,0,0,F) and correspond to the lattice character 13 (Orthorhombic- oC) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact this structure is better described in the orthorhombic system, space-group $C222_1$ (No. 20). The vectors $[\bar{1} 01]$, $[101]$, $[010]$ define an orthorhombic C-centered cell with $a' = 13.142$, $b' = 12.168$, $c' = 34.638$ Å, $\alpha = 90.00$, $\beta' = 90.00$, $\gamma' = 89.97^\circ$, $Z = 8$. The corresponding coordinate transformations are: $x' = 1/2(-x+z) - 1/4$, $y' = 1/2(x+z) + 1/4$, $z' = y - 0.4016$. In the original description there are two independent molecules in the asymmetric unit, now in $C222_1$, the two molecules are related by a screw axis along b .

1.4. **DAMLIM : (R*,R*)-4,4'-bi(1-t-butylcyclohexen-3-one), triclinic polymorph**, $C_{20}H_{30}O_2$ (Arain *et al.*, 1985)

This compound was reported (see supplementary material or CSD) as triclinic, space-group $P\bar{1}$ (No.2), with $a = 5.7713(7)$, $b = 11.758(2)$, $c = 15.264(2)$ Å, $\alpha = 68.75(2)$, $\beta = 79.09(1)$, $\gamma = 89.98(2)^\circ$, $Z = 2$. The Niggli matrix has the form (A,B,C,D, $-A/2,0$) and corresponds to the lattice character 37 (Monoclinic- mC) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact transforming the axes by $[11\bar{2}]$, $[100]$, $[010]$ gives a I -body centered cell, space-group $I2/a$ (No.15), with dimensions: $a = 27.869$, $b = 5.771$, $c = 11.758$ Å, $\alpha = 90.02$, $\beta = 91.43$, $\gamma = 90.01^\circ$. The coordinate transformations are : $x' = -1/2z + 1/2$; $y' = x + 1/2z$; $z' = -y - 1/2z + 1$. The molecule now lies on a twofold axis passing between the C(1) and C(7) atoms. The bond distances remain unchanged. Three years later the same authors (Arain, *et al.*, 1988) published the same compound but in space-group

C2/c, thus the CCDC has archived it as the monoclinic polymorph with Refcode DAMLIM01. However, the lattice vectors $[10\bar{2}]$, $[\bar{1}00]$, $[010]$ transform the triclinic polymorph DAMLIM into the monoclinic polymorph DAMLIM01.

1.5. FAXPID: N-(3-Aminopropyl)-N'-3-(anthracen-9-ylmethyl) amino propyl-ethane-1,2-diamino)-chloro-copper chloride monohydrate, $[\text{C}_{23}\text{H}_{32}\text{ClCuN}_4]^+\text{Cl}^-\cdot\text{H}_2\text{O}$ (Bernardo *et al.*, 1999)

This compound was reported as triclinic, space-group $P\bar{1}$ (No. 2), with $a = 13.307(1)$, $b = 13.305(1)$, $c = 16.538(2)$ Å, $\alpha = 104.94(1)$, $\beta = 111.67(1)$, $\gamma = 102.76(1)^\circ$, $Z = 4$. The Niggli matrix has the form (A,A,C,D*,E,F) with the supplementary condition $2|D+E+F| = A+B$, and corresponds to the lattice character 17 (Monoclinic-*mC*) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact the vectors $[011]$, $[110]$, $[\bar{1}0\bar{1}]$ describe a body-centered cell, space-group $I2/a$ (No.15), with dimensions: $a = 18.6300(18)$, $b = 16.610(2)$, $c = 16.972(3)$ Å, $\alpha = 90.00$, $\beta = 108.020(9)$, $\gamma = 90.01(1)^\circ$. The coordinate transformations are : $x' = -1/2x + 1/2y + 1/2z$; $y' = 1/2x + 1/2y - 1/2z + 1/2$; $z' = -1/2x + 1/2y - 1/2z + 1/2$. The new space-group reveals that two independent molecules in the asymmetric unit are related by a twofold axis along b . The mean shift (0.018 Å, hydrogen atoms included) is so low that we have inserted also the hydrogen atoms in the FAXPID.CIF file.

1.6. GADFOG: Calcium bis(phenoxyphenicillin) dihydrate, $2(\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_5\text{S})^-\text{Ca}^{2+}\cdot 2\text{H}_2\text{O}$ (Cole *et al.*, 1987).

This six-coordinate calcium complex was described as monoclinic, space-group $P2_1$ (No. 4), with $a = 10.057(7)$, $b = 29.178(18)$, $c = 6.508(2)$ Å, $\beta = 108.84(4)^\circ$, $Z = 2$. The Niggli matrix has the form (A,B,C,0,0, $-A/2$) and corresponds to the lattice character 38 (Orthorhombic-*oC*) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact transforming the axes by $[201]$, $[001]$, $[0\bar{1}0]$ and shifting the origin to $(0,0,-0.2084)$ gives a C-centered cell, space-group $C222_1$ (No.20), with dimensions $a = 19.036$, $b = 6.508$, $c = 29.178$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 89.96^\circ$. The coordinate transformations are : $x' = 1/2x - 1/2$; $y' = -1/2x + z - 1/2$; $z' = -y - 0.2084$. The two purportedly independent penicillin V molecules and the two coordinated water molecules O(1) and O(2) are related by a twofold axis along a , while the Ca^{2+} cation lies on this axis. The atomic shifts necessary to achieve the more symmetric space-group are within the s.u. for almost all the atoms with exception of the three pairs: C(4)–C(20) (0.039 Å), C(7)–C(23) (0.051 Å) and C(14)–C(30) (0.083 Å).

1.7. GOHPAU: tris(methyltriethylammonium) bis(dicarbonyl-(4,4',5,5'-tetracyano-2,2'-bi-imidazole-N,N')-iridium), dicyano-(4,4',5,5'-tetracyano-2,2'-bi-imidazole-N,N')-platinum acetonitrile solvate, $[\text{C}_{12}\text{N}_8\text{MY}_2]^- [\text{C}_7\text{H}_{18}\text{N}]^+\cdot\text{CH}_3\text{CN}$, M = 2/3 Ir, 1/3 Pt, Y = 2/3 O, 1/3 N (Rasmussen *et al.*, 1988)

This structure was described as monoclinic, space-group $P2_1$ (No. 4), with $a = 13.412(12)$, $b = 6.874(5)$, $c = 13.409(17)$ Å, $\beta = 111.21(8)^\circ$, $Z = 2$. The Niggli matrix has the form (A,B,B,D,0,0) and corresponds to the lattice character 23 (Orthorhombic-*oC*) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact the lattice

vectors $[\bar{1}0\bar{1}]$, $[\bar{1}01]$, $[010]$ define an orthorhombic C cell with $a = 15.151$, $b = 22.132$, $c = 6.874$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 89.99^\circ$. The original papers remarks that “the anions follow the symmetry of $P2_1/m$, the cations require $P2_1$ ”. Also now two space-groups are possible: $Cmcm$ (No.63) and $Cmc2_1$ (No.36) because the anions follow exactly the symmetry of $Cmcm$ while the $[\text{NEt}_3\text{Me}]^+$ cations require the symmetry of $Cmc2_1$, unless they are disordered. The original paper does not mention any disorder of the cation but we believe that it must be disordered because it presents the following very short contact: $\text{C}(17)\cdots\text{C}(21)$ ($-x+1$, $+y+1/2$, $-z+1$) = 2.084(2). However, we have followed in this discussion the $Cmc2_1$ space-group and prepared the GOMPAU.CIF file according to this less symmetric space-group, but choosing the origin in such a way that the z coordinate is very near to $3/4$ for almost all the atoms that are then described also in $Cmcm$. The coordinate transformations are : $x' = -1/2x - 1/2z + 3/4$; $y' = -1/2x + 1/2z - 1/4$; $z' = y + 0.6270$. The anion is perpendicular to the mirror plane at $x = 1/2$ that passes through Pt and the midpoint between C(1) and C(7) atoms. Also the CH_3CN solvent molecule lies on this mirror plane. The N(9), C(13), C(17) and C(19) atoms of the $[\text{NEt}_3\text{Me}]^+$ cation lie on the mirror plane at $x = 0$ and C(14) is mirrored with C(15) and C(16) with C(18). The more symmetric $Cmcm$ space-group requires that a twofold axis at $z = 3/4$ passes through the $[\text{NEt}_3\text{Me}]^+$ cation, this requires that only the three atoms C(17), C(18) and C(19) should be disordered, a realistic situation. Of course, the short contact remains and now it is: $\text{C}(17)\cdots\text{C}(21)$ ($-x+1/2$, $-y-1/2$, $+z+1/2$) = 2.072(2) Å. However, the structure factors table is required to ascertain the disordered of the cation and the ambiguity between $Cmc2_1$ and $Cmcm$.

1.8. **GULDOG: 4-(2-Chloro-4,5-dimethoxybenzylidene)-2-methyl-5-oxazolone, $\text{C}_{13}\text{H}_{12}\text{ClNO}_4$ (Haasbroek *et al.*, 1998)**

This compound was described as monoclinic, space-group $P2_1/c$ (No.14), with $a = 9.148(2)$, $b = 22.938(2)$, $c = 6.707(1)$ Å, $\beta = 111.50(2)^\circ$, $Z = 4$. The Niggli matrix has the form (A,B,C,0,0,-A/2) and corresponds to the lattice character 38 (Orthorhombic- oC) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact the lattice vectors $[001]$, $[201]$, $[010]$ define a C -centered cell, space-group $Cmca$ (No. 64), with $a = 6.707(1)$, $b = 17.023(4)$, $c = 22.938(2)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 89.99(1)^\circ$. The coordinate transformations are : $x' = -1/2x + z - 1/2$; $y' = 1/2x$; $z' = y - 1/2$. The original paper reports: “except for the methyl protons, all the atoms lie in the same plane”, this molecular plane becomes the crystallographic mirror plane perpendicular to a of the new space-group $Cmca$, thus now all the atoms, with the exception of two hydrogen atoms for each methyl group, lie in the Wyckoff position 8(f).

1.9. **HOPFUN : Inosine 5'-monophosphate nonahydrate, $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_8\text{P}\cdot 9\text{H}_2\text{O}$, (Bera, *et al.*, 1998)**

This structure was solved in space-group $P2_1$, (No.4), with $a = 8.650(1)$, $b = 21.900(1)$, $c = 12.370(1)$ Å, $\beta = 110.38(9)^\circ$, $Z = 4$. The Niggli matrix has the form (A,B,C,0,0,-A/2) and corresponds to the lattice character 38 (Orthorhombic- oC) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact the lattice vectors $[102]$, $[100]$, $[010]$ transform the monoclinic cell to an orthorhombic C -centered cell, space group $C222_1$ (No.20), with $a = 23.191(1)$, $b = 8.650(1)$, $c = 21.900(1)$, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 89.91(8)$, $Z = 8$. The origin shift is $\Delta x = 1/4$, $\Delta y = 1/4$, $\Delta z =$

0.3399, and the coordinate transformations are : $x' = 1/2z - 1/4$; $y' = x - 1/2z - 1/4$; $z' = y - 0.3399$. The two inosine 5'-monophosphate (5'-IMP) molecules are related by a twofold axis running along x , well within the s.u., in fact the atomic shifts range from 0.002 Å for the P(1)–P(2) pair to 0.025 Å for the C(6)–C(16) pair. The change in space-group does not affect the chirality of the molecules but makes exactly equivalent the two purportedly independent 5'-IMP molecules, whereas the original paper reports: “*the two independent 5'-IMPs adopt slightly different conformation*”. Although the crystal contains a large number of water molecules, both ordered and disordered, almost all respect the symmetry of the $C22_1$ space-group. The pairing and the atomic shifts are : O(17)–O(18) = 0.009, O(27)–O(29) = 0.012, O(19)–O(20) = 0.025, O(22)–O(24) = 0.027, O(26)–O(37) = 0.052, O(28)–O(30) = 0.058, O(31)–O(33) = 0.075, O(32)–O(34) = 0.127 Å, while O(21) and O(23) lie on a twofold axis along a and b , respectively. Only the O(25), O(35) and O(36) water molecules have no symmetry related counterpart so they are reported in the HOPFUN.CIF file with site occupation factor of 0.5. Thus, 10.5 water molecules for each 5'-IMP are now present and not 9 as reported in the original paper. However, the number and the position of the water molecules must be re-refined because some short contacts between water molecules are present in the original and of course in this revised version.

1.10. NEJBAF: catena-((μ_2 -Acetato-O,O')-(acetato-O,O')-(pyridine)-zinc(II)), (C₁₈H₂₂N₂O₈Zn₂)_n (Singh *et al.*, 1997)

This compound was reported as triclinic, space-group $P\bar{1}$ (No.2), with $a = 8.626(2)$, $b = 8.868(3)$, $c = 28.871(8)$ Å, $\alpha = 90.17(2)$, $\beta = 90.02(2)$, $\gamma = 99.02^\circ$, $Z = 4$. However, setting α and β to 90° and reorienting the cell axes (transformation matrix [100], [00 $\bar{1}$], [010], no origin shift), we obtain a monoclinic cell with $a = 8.626$, $b = 28.871$, $c = 8.868$ Å, $\beta = 99.02^\circ$, space-group $P2_1/n$ (No. 14), $Z = 4$. The coordinate transformations are : $x' = x$; $y' = -z$; $z' = y$. The coordinates of the two purportedly independent molecules in $P\bar{1}$ can be matched across a n -glide plane of $P2_1/n$. Shifts range from 0.00 Å for Zn(1)–Zn(3) or Zn(2)–Zn(4) pairs to 0.041 Å for C(4)–C(22) pair. Since the shifts are low, there is no significant variation in bond lengths and angles. Before atomic pairing, O(8), C(7), C(8) and O(16) atoms must be shifted by -1 along b of the triclinic cell for bringing them inside the same molecule.

1.11. NEJBOT: bis(pyridine)-tetra-aqua-iron(II) diacetate, [C₁₀H₁₈FeN₂O₄]²⁺ 2(C₂H₃O₂)⁻ (Singh *et al.*, 1997)

This compound was reported as triclinic, space-group $P\bar{1}$ (No. 2), with $a = 7.999(2)$, $b = 8.002(2)$, $c = 8.401(2)$ Å, $\alpha = 69.79(2)$, $\beta = 69.69(2)$, $\gamma = 74.94^\circ$, $Z = 2$. Relationships between coordinates of purportedly independent atoms show that the true space-group is $I2/m$ (No. 12). The transformation matrix is [11 $\bar{1}$], [$\bar{1}$ 10], [001] without origin shifts, and the coordinate transformations are : $x' = 1/2x + 1/2y$; $y' = -1/2x + 1/2y$; $z' = 1/2x + 1/2y + z$. The atomic shifts are very low: O(1)–O(2) = 0.002, C(2)–C(4) = 0.003, C(1)–C(5) = 0.002, O(3)–O(4) = 0.003 Å. The cation is in Wyckoff position 2(a), symmetry $2/m$, while the two carbon atoms of the acetate anion are in Wyckoff position 4(i), symmetry m . There is no variation in bond lengths and angles.

1.12. PAJVUR: *trans*-(1,4,8,11-tetra-azacyclotetradecane)-dioxo-rhenium hexa-fluorophosphate, [C₁₀H₂₄N₄O₂Re]⁺ (PF₆)⁻ (Luna *et al.*, 1992)

The structure of this complex, *trans*-[ReO₂(cyclam)]⁺ (PF₆)⁻, was reported as triclinic, space-group $P\bar{1}$ (No.2), with $a = 5.533(1)$, $b = 11.899(3)$, $c = 13.622(3)$ Å, $\alpha = 89.78(2)$, $\beta = 78.33(2)$, $\gamma = 76.51(2)^\circ$, $Z = 2$. The Niggli matrix has the form (A,B,C,D,A/2,A/2) and corresponds to the lattice character 27 (Monoclinic-*mC*) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact the transformation matrix $[\bar{1} \ 11]$, $[100]$, $[01\bar{1}]$ define a monoclinic cell, space-group $I2/a$ (No.15), with $a = 17.257$, $b = 5.533$, $c = 18.053$ Å, $\alpha = 89.94$, $\beta = 98.14$, $\gamma = 90.01^\circ$. The coordinate transformations are : $x' = 1/2y + 1/2z$; $y' = x + 1/2y + 1/2z$; $z' = 1/2y - 1/2z$. The new space-group reveals that the two purportedly independent molecules are related by a twofold axis along b (the old triclinic a axis). The Re(V) ion is at Wyckoff 4(*a*) position, while the P atom is at Wyckoff 4(*d*) position. The reflection condition (in $P\bar{1}$) $0kl$ absent for $k+l = \text{odd}$ was not recognized. We have checked this by obtaining the supplementary data from *Inorg. Chem.* containing 4992 F_o values. There are 240 reflections $0kl$ with $k+l = \text{odd}$. They are all very weak with $F_o < 3\sigma(F_o)$ (only eight reflections have: $3\sigma(F_o) < F_o < 5\sigma(F_o)$), but this is due to the unreasonably small value of $\sigma(F_o)$ rather than to the (small) value of F_o . The 4752 reflections were merged according to Laue symmetry $2/m$, giving 2500 F_o values with an $R(\text{int})$ of 6.5 % on F_o and an $R(\text{int})$ of 12.1% on I . Final full-matrix refinement was based on 129 parameters and 1 restraint (the total sum of the population of the 11 independent disordered fluorine atoms was restrained to be 3.00). The final R factor ($R(F)$) was 0.0771, slightly greater than the ($R(F)$) factor (0.063) obtained by the original authors, but now with fewer parameters. Although the molecular geometry is practically unchanged, as happens when the space-group change concerns two centrosymmetric space-groups, a clear improvement in the distances must be noted, for example the two Re–O distances 1.77 and 1.78 Å become 1.75 Å and the four Re–N distances 2.09, 2.12, 2.13, 2.15 Å become 2.12 and 2.14 Å. The revised distances are in excellent accordance with those found in the analogous compound *trans*-[ReO₂(cyclam)]⁺ Cl⁻·2(BPh₃·H₂O) (Blake, 1988).

This complex presents two IR bands at 809 cm⁻¹ and 776 cm⁻¹. The original authors suggest to attribute the two observed absorptions to the single asymmetric stretching of the [ReO₂]⁺ group associated with each one of the two (purportedly) inequivalent sets of molecules. In light of the recovered twofold axis the original discussion on the IR spectra requires reconsideration.

1.13. POFXUD: Bis(μ_4 -N,N-Diethylcarbamato-O,O',O'',O''')-tetrakis(μ_3 -N,N-diethylcarbamato-O,O',O'')-hexakis(μ_2 -N,N-diethylcarbamato-O,O')-hexairon at 213 K, C₆₀H₁₂₀Fe₆N₁₂O₂₄ (Dell'Amico *et al.*, 1994)

This compound was reported in space-group $C2/c$ (No.15), $Z = 4$, but $\beta = 90.001(7)^\circ$ suggests an orthorhombic cell. Moreover, the original paper reports "*Refinements in the orthorhombic supergroups of the space group C2/c were unsuccessful*". However, the true space-group of this compound is $Ccca$ (No. 68), (transformation matrix = identity, no origin shifts). In $C2/c$ description the molecule lies on the twofold axis, in $Ccca$ other twofold axes, perpendicular to the original one, must be added, thus the molecule has exact $D_2 = 222$ symmetry, the three twofold axes meet at (0,0,1/4), Wyckoff position 4(*a*). The relations between

coordinates agree with *Ccca* within the reported s.u., maximum shift is 0.061 Å for the C(5)–C(25) pair.

Probably, during the supergroup refinements, the original authors have not tested the space-group *Ccca* because it requires additional systematic absences that apparently were not recognized.

1.14. *QIPBEW*: Bis(2,2'-bis(p-tolylphosphino)-1,1-binaphthyl)-palladium(0) benzene solvate at -90 °C, C₉₆H₈₀P₄Pd·2C₆H₆ (Alcazar-Roman *et al.*, 2000)

This Pd(0) complex, benzene solvate, was described as monoclinic, space-group *P2*₁ (No. 4), with $a = 16.743(7)$, $b = 19.458(6)$, $c = 16.859(5)$ Å, $\beta = 119.57(3)$, $Z = 2$. The Niggli matrix has the form (A,B,C,0,0,-A/2) and corresponds to the lattice character 38 (Orthorhombic, *oC*). In fact, the transformation vectors [102] [100] [010] lead to a *C*-centered orthorhombic cell, space-group *C222*₁ (No. 20), with parameters $a = 29.327$, $b = 16.743$, $c = 19.458$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 89.80^\circ$. The coordinate transformations are : $x' = 1/2z - 1/2$; $y' = x - 1/2z - 1/2$; $z' = y - 0.3389$. The Pd atom lies on Wyckoff position 4(*b*), thus the two halves of the complex are related by a twofold axis running along *y*, well within the s.u. . Also the two benzene rings (C(9)···C(102)) and (C(109)···C(114)) are related by another twofold axis along *y*. The (C(103)···C(108)) and (C(115)···C(120)) benzene rings are related by a twofold axis running along *x*.

Further, we note that the tests used by the original authors as systematic absences, packing considerations, analysis of intensity distribution or successful solution of the structure are not adapted to distinguish between *P2*₁ and *C222*₁.

1.15. *WERBIE* : bis(4-amino-N-2-thiazolylbenzenesulfonamide-N)-dichloromethanol-copper(II), C₁₉H₂₂Cl₂CuN₆O₅S₄ (Casanova *et al.*, 1994).

This structure was reported as triclinic, space-group *P* $\bar{1}$ (No.2), with $a = 7.564(6)$, $b = 11.044(6)$, $c = 16.344(7)$ Å, $\alpha = 108.43(1)$, $\beta = 102.99(1)$, $\gamma = 90.31(1)^\circ$, $Z = 2$, (in the experimental section it is reported *P1*, but the abstract and CSD report *P* $\bar{1}$). The Niggli matrix has the form (A,B,C,D,-A/2,0) and corresponds to the lattice character 37 (Monoclinic-*mC*) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact the triclinic cell can be transformed to an *I* centered monoclinic cell, space-group *I2/a* with $a = 30.123(13)$, $b = 7.564(6)$, $c = 11.044(6)$ Å, $\alpha = 90.31(1)$, $\beta = 91.27(1)$, $\gamma = 90.30(1)^\circ$. The transformation matrix is [112], [$\bar{1}$ 00], [0 $\bar{1}$ 0], and the coordinate transformations are : $x' = 1/2z - 1/4$; $y' = x - 1/2z - 1/4$; $z' = y$. The new space-group reveals that the molecule is located on the twofold axis along *b* and the methanol molecule is disordered about this axis. The relatively large deviation of α and γ angles from 90° might give rise to suspicions about the space-group change, but similar errors have been already discussed (Marsh *et al.*, 2002; Herstein *et al.* 2002). However, we have obtained the F_o table (Document no. CSD 57014) from the *Fachinformationszentrum* (Karlsruhe). The Miller indices of the 3855 F_o reflections were transformed and the intensities averaged according to Laue symmetry *2/m*, yielding $R(\text{int})$ on *I* of 0.073. Final full-matrix least-squares refinement was based on 173 variables for 2077 reflections; the final R factor ($R(F)$) was 0.0543 for all data. The R factor obtained by the original authors was 0.0564, but for 328 variables. The space-group *I2/a* requires the additional reflection condition of $h0l$ absent for $h(l)$ odd. In the original indexing this condition becomes $0kl$ absent for k odd. The

reflection list contains only 18 of these reflections, with F_o values ranging from 3.00 to 4.00. Only two reflections, $0\bar{1}5$ ($F_o = 6.0$) and $0\bar{7}7$ ($F_o = 5.0$), violate this condition (largest $F_o = 184.0$ for $\bar{2}\bar{1}3$). The bond distances undergo very little changes.

1.16. WOHHOO: catena-(tetrakis(μ_2 -4-aminobenzoato)-diaqua-dicadmium(II) tetrahydrate, ($C_{28}H_{28}Cd_2N_4O_{14}$) $_n \cdot 4n(H_2O)$ (Hauptmann *et al.*, 2000)

The structure of this polymeric complex was reported in $P\bar{1}$ (No.2), with $a = 6.2028(7)$, $b = 8.253(1)$, $c = 17.592(2)$ Å, $\alpha = 94.295(1)$, $\beta = 100.153(1)$, $\gamma = 112.072(4)^\circ$, $Z=1$. The Niggli matrix has the form (A,B,C,D,A/2,A/2) and corresponds to the lattice character 27 (Monoclinic- mC) of Table 9.2.5.1 pp 753 (de Wolff, 2002). In fact the triclinic cell can be converted (transformation matrix $[\bar{1}\bar{2}0]$, $[100]$, $[111]$, no origin shift) into a monoclinic cell, space-group $C2/c$ (No. 15), with dimensions: $a = 15.296$, $b = 6.203$, $c = 17.815$, $\alpha = 90.00$, $\beta = 106.20$, $\gamma = 90.00^\circ$, $Z=2$. The coordinate transformations are : $x' = -1/2y + 1/2z$; $y' = x - 1/2y - 1/2z$; $z' = z$. The twofold axis along b passes through the Cd(II) cation and the O(5) water molecule, whereas the two purportedly independent p -aminobenzoate anions and the two O(6) and O(7) water molecules are related by this twofold axis. No significant variations in the molecular dimensions occur.

1.17. XATYOG : 4-ferrocenylmethylene-2-phenyl-4H-oxazol-5-one, $C_{20}H_{15}FeNO_2$ (Ponikwar *et al.*, 2000)

This compound was reported as triclinic, space-group $P\bar{1}$ (No. 2), with $a = 7.252(3)$, $b = 10.391(2)$, $c = 20.662(2)$, $\alpha = 82.53(1)$, $\beta = 89.90(2)$, $\gamma = 89.71(3)^\circ$, $Z = 4$. However, setting β and γ to 90° and reorienting the cell axes (transformation matrix $[010]$, $[100]$, $[00\bar{1}]$, no origin shift) , we obtain a monoclinic cell with $a = 10.391$, $b = 7.252$, $c = 20.662$, $\beta = 97.47^\circ$, space-group $P2_1/n$ (No. 14), $Z = 4$. The coordinate transformations are : $x' = y$; $y' = x$; $z' = -z$. The two independent molecules in $P\bar{1}$ are related to each other by the n -glide of $P2_1/n$, well within their s.u. . Since the atomic shifts are so low, there is no significant variation in bond lengths and angles.

1.18. ZOSLIC: bis((μ_2 -chloro)-diaqua-(2,4-pentanedione-O,O')-magnesium, diaqua-bis(2,4-pentanedione-O,O')-magnesium dichloride), $1/2[C_{10}H_{24}Cl_2Mg_2O_8]^{2+} 1/2[C_{10}H_{20}MgO_6]^{2+} 2Cl^-$ (Di Noto *et al.*, 1995)

We have correctly written the formula of the second cation with 20 hydrogen atoms instead of 18 reported by CSD file. Our formulae do not agree also with that reported by the original authors, see later.

This compound is a rare example of incorrect $P2_1/c$ space-group. In fact, it was reported as monoclinic, space-group $P2_1/c$, $Z = 4$ [$a = 7.835(2)$, $b = 18.169(4)$, $c = 13.303(3)$ Å, $\beta = 90.70(2)^\circ$], but can be transformed to orthorhombic, space-group $Pmna$ (No.53), without origin translation but with reorientation of cell axes obtaining: $a = 13.303(3)$, $b = 7.835(2)$, $c = 18.169(4)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 89.30(2)^\circ$. The large deviation of the γ angle (i.e. the old β angle) from 90° is explained by the dramatic deterioration of the crystal under the X-ray beam and

by misalignment problems due to the abundant coating resin used to protect the crystal from the contact with air.

In the new space-group the centrosymmetric [(*acac*)Mg(H₂O)₂Cl₂(H₂O)₂Mg(*acac*)]²⁺ cation (hereafter called A²⁺) [*acac* = 2,4 pentanedione, CH₃–CO–CH₂–CO–CH₃, i.e. the *acac* ligand must be neutral for electrostatic balancing] lies at Wyckoff 4(*h*) position, namely all the atoms of this A²⁺ cation, with the exception of the four water molecules, lie on the mirror plane at *x* = 0, thus this A²⁺ cation possesses 2/*m* molecular symmetry.

The Mg(2)²⁺ ion contained in [Mg(*acac*)₂(H₂O)₂]²⁺ cation (hereafter called B²⁺) lies at Wyckoff 2(*c*) position, namely also the B²⁺ cation presents 2/*m* molecular symmetry. The Cl(2)[−] anion lies on the twofold axis along *b* at position 4(*g*), while the second anion, Cl(3)[−], lies on the twofold axis along *a* at position 4(*e*). Thus, the exact content of the unit cell is: 2A²⁺, 2B²⁺, 8 Cl[−] and the moiety formula is consequently 0.5 A²⁺, 0.5 B²⁺, 2 Cl[−] i.e. C₁₀H₂₂ClMg_{1.5}O₇ · 2Cl[−]. This formula does not agree with the empirical formula, C₁₀H₂₁Cl₃Mg_{1.5}O₇ reported in the original work, the difference being one hydrogen atom. This is due to the particular bonding mode of the *acac* ligand, in fact it is bonded to Mg²⁺ as neutral ligand, an unique situation not reported before. This is consistent both with the presence of two Cl[−] anions in the moiety formula and with the average C–C distance (1.47 Å) of the chelate ring, that is significantly longer than the analogous C–C distances (mean 1.406 Å) found in ionic *acac*[−] coordinated to Mg²⁺ as determined from six compounds taken from the CSD file. Also the C=O distances (mean 1.22 Å) are significantly shorter than the analogous C–O distances (mean 1.268 Å) found in the same six compounds.

Moreover, we must note that the ¹H NMR study and the empirical formula reported in the original work are in agreement. In fact, the NMR study has established that the ligand is present in both the complex cations as [CH₃–CO–CH–CO–CH₃][−] + 1/2H⁺ (only half H⁺ is bonded to one or to the other oxygen atom) thus decreasing the charge of each cation to 1+, thus the moiety formula should be 0.5A⁺, 0.5B⁺, 2Cl[−] but so the electrostatic balancing is not respected. However, the NMR study was carried out in solution and not in solid state.

The atomic coordinates averaged according to the space-group *Pmna* (which requires the additional reflection conditions (*h,0,l*) absent for *l+h* odd) shows shifts of about 0.08 Å; only the Cl(2)[−] anion requires a larger shift of 0.23 Å. The shifts are somewhat larger than usual, surely because the dramatic decay of the crystal under the X-ray beam.

2. Category B: add a center of symmetry

2.1. *KENBIO* : *tris*((μ₂-cyano)-tetracarbonyl-rhenium), C₁₅N₃O₁₂Re₃ (Calderazzo *et al.*, 1989)

This structure was reported in space-group *Pna2*₁ (No. 33), *Z* = 4, and here is revised to *Pnma* (No. 62), *Z* = 4. Transformation matrix [1̄ 00], [001], [010], with origin shifts : Δ*x* = −0.5000; Δ*y* = 0.0928, Δ*z* = 0.0000. The coordinate transformations are : *x*' = −*x* + 1/2; *y*' = *z* − 0.0928; *z*' = *y*.

The molecule has a mirror plane running through the Re2 atom and the two carbonyl groups C(5)–O(5) and C(7)–O(7). The largest deviation from *Pnma* is presented by the O(6)–O(8) pair (0.245 Å). Moreover, the added mirror plane requires that carbon and nitrogen atoms of the CN groups are interchangeable or better are positional disordered, a normal situation considering that the CN groups

form bridges between the three Re atoms. The original authors say: “...*the distinction between carbon and nitrogen atoms in the bridging CN groups was difficult. Some attempts were made by refining the interchanged C and N positions.... The results are substantially identical within the limits of error....*”. They also say: “*the accuracy of the light atom positions is not good, as indicated by the high values of their positional e.s.d.'s.*” This is usually found when the center of symmetry goes unrecognised.

2.2. **NUYGAP** : 2-(4'-cyanophenylthio)-5-methylthiadiazole, $C_{10}H_7N_3S_2$, (Ettorre et al., 1998)

This structure was reported in space-group $P2_1$ (No. 4), $Z = 2$, but can be transformed to $P2_1/m$ (No. 11), after an origin shift $\Delta y = 0.4651$, the coordinate transformations are : $x' = x$; $y' = y - 0.4651$; $z' = z$. The maximum deviation is 0.098 Å for the C(3)–C(3) pair. In the new description the 5-methyl-thiazole ring lies on the mirror passing also through S(1), C(4), C(7), C(10) and N(3) atoms. Now the dihedral angle between the two aromatic rings is exactly 90.00° and not 91.0(4)° as reported in the original publication. Although this space-group change adds a center of symmetry to the structure, the molecular geometry is not substantially varied.

2.3. **QOXPOI**: trans-bis(μ_2 -Chloro)-dichloro-dicarbonyl-di-platinum(II) at 203 K, $C_2Cl_4O_2Pt_2$ (Bagnoli et al., 2001)

This compound was reported in space-group $P4_2$ (No.77), $Z = 2$, and is here revised to $P4_2/m$ (No. 84), $Z = 2$, with a shift of origin $\Delta z = 0.2660$. The coordinate transformations are : $x' = x$; $y' = y$; $z' = z - 0.2660$. This change requires that the added mirror plane passes through all the atoms of the molecule, whose symmetry becomes $2/m$ rather than 2. The deviations from the added mirror plane for the five atoms Pt(1), Cl(1), Cl(2), O(1) and C(1) are respectively: 0.00, +0.12, +0.12, -0.18 and -0.07 Å. The revised bond lengths are unchanged, while two bond angles become more regular, viz. Pt(1)–C(1)–O(1) changes from 176.25 to 179.70° and Cl(2)–Pt(1)–Cl(1)^I ($I = -x+1, -y, -z$) from 173.60 to 179.26°. The original paper states “*the point symmetry of the molecule being C_2 , rather than C_{2h} , the Cl(2) atom is 0.228 Å out of the plane defined by Pt, Cl(1), Cl(1'), C and O*” but these distortions are typical for the “add a center” situation.

2.4. **SEYJAH** : Dihydro-1H-pyrrolizine-3,5(2H,6H)-dione, $C_7H_9NO_2$ (Bandoli et al., 1989)

This structure was reported and refined in space-group $P2_1$ (No. 4), $Z=2$, with a non reduced cell [$a = 7.737(4)$, $b = 6.993(4)$, $c = 7.110(4)$ Å, $\beta = 117.89(3)^\circ$] but is here revised to a conventional reduced cell with space-group $P2_1/m$ (No.11). The original authors report some difficulties in the refinement: “*No straightforward explanation can be given for the anomalously short C(1)–C(7) and C(6)–C(7) distances. The anomaly is likely to be associated with a poor location of the C(7) atom, due to the very large C(1)–C(7)–C(6) angle (134.0(8)°) and, in the final difference Fourier map, to some residuals of electron density (up to 0.6 e Å⁻³) in the immediate vicinity of the C(7) atom. On the other hand, the amplitudes of atomic vibration derived from the thermal vibration tensors U_{ij} are particularly large for the C(1), C(7) and C(6) atoms (especially their U_{22}*

component perpendicular to the pyrrolizine ring)". These difficulties can be overcome changing the space-group from $P2_1$ to $P2_1/m$ and considering that the nearly planar molecule is disordered over the mirror plane at $y = 1/4$. In fact, a mean plane calculation reveals that almost all the atoms lie, within $\pm 0.1 \text{ \AA}$, on the plane at $y = 1/4$, while C(7), C(6) and C(1) atoms deviate slightly more by +0.29, -0.15, -0.12 \AA , respectively. Thus, the molecule is nearly planar or at least it is non-planar in a manner that the least-squares method is not able to ascertain for the presence of near-singularities in the normal matrix and the distortions to the molecular geometry which result. It is thus possible to transform this structure to a conventional reduced cell with space-group $P2_1/m$ (No.11) using the transformation matrix $[00\bar{1}]$, $[010]$, $[101]$, without any origin shift. The coordinate transformations are : $x' = x - z$; $y' = y$; $z' = x$. The new cell, with dimensions $a = 7.110(4)$, $b = 6.993(4)$, $c = 7.678(4) \text{ \AA}$, $\beta = 117.04(4)^\circ$, presents all the atoms on the mirror plane at $y = 1/4$, of course with the exception of the C(7), C(6) and C(1) atoms. In fact, the C(7) atom appears unable to accommodate $P2_1/m$ because its hybridization must be very near to sp^3 , also the other two atoms C(6) and C(1) appear to suffer to a smaller extent of the same problem. However, these difficulties are easily overcome considering that the C(7), C(6) and C(1) atoms are disordered across the mirror plane at $y = 1/4$. Thus, we have prepared a SEYJAH.CIF file with half the C(7), C(6) and C(1) atoms in the downward direction with respect to the mirror plane and the other half atoms in the upward mirrored position. The short distances and the large angle found in $P2_1$ can be easily explained as due to the disordered atoms across the mirror plane, while the spurious peak can be interpreted as the disordered mirrored position of the C(7) atom.

Finally, we note that there is no improvement in the molecular geometry on going from $P2_1$ to $P2_1/m$ because coordinates cannot be averaged, thus for obtaining an accurate molecular geometry a new refinement in space-group $P2_1/m$ is necessary. The starting model is that reported in our SEYJAH.CIF file and the instructions reported by Spek (1993) should be followed.

2.5. XIHBOF : Dichloro-(S-methyl β -N-((2hydroxyphenyl) ethylidene)dithiocarbazato)-bis-(triphenylphosphine)-rhenium(V), $C_{38}H_{33}Cl_2N_2P_2ReS_2$, (Mevellec *et al.*, 2002)

The structure of this rhenium(V) complex was reported as monoclinic, space-group Cc (No.9) but can be converted to $C2/c$ (No.15), the transformation matrix is $[\bar{1} 0 0]$, $[010]$, $[00\bar{1}]$ and the coordinate transformations are : $x' = -x$; $y' = y$; $z' = -z$. This space-group change imposes to the Re(V) complex to lie on the twofold axis along b , with Re(1) and C(1) atoms on this axis. However, the hydrazido ligand does not possess a twofold molecular axis and then must be disordered.

However, it was already disordered in the original Cc model, in fact the original authors stated: "A relevant anomaly was encountered in the refinement of 3. A Fourier difference map revealed maxima in the vicinity of the hydrazido ligand, indicating a second complete image of the ligand". The Cl(1) atom was eliminated from the input stream because the original Re-Cl(1) distance (2.312 \AA) is significantly shorter than the analogous Re-Cl distances accepted in literature (2.39-2.41 \AA , see GIDSOB and ZEWDUA01 compounds) and the shift of the pair Cl(1)-Cl(2) (0.48 \AA) is considerably high. The other shifts are in the range 0.027

Å for the pair C(10)–C(28) to 0.251 Å for the pair N(3)–N(4)?. These shifts are slightly larger than the expected values when the center of symmetry goes unrecognized because the original authors, in order to reduce the refinement difficulties due to ill conditioning of the least-squares matrix, have treated the phenyl rings as rigid idealized hexagons, thus transferring all the errors on the free atoms.

2.6. ZEQSOD01: 1,1'-bis(Diphenylthiophosphoryl)ferrocene, C₃₄H₂₈FeP₂S₂ (Pilloni *et al.*, 1997)

This compound was reported as monoclinic, space-group *Cc* (No. 9). Surprisingly, the structure of the same complex has been published two years before as *C2/c* (No. 15) (Fang *et al.*, 1995, CSD Refcode = ZEQSOD), but this paper was not cited by the later authors. The cell parameters and the atomic coordinates indicate, without doubt, that the complex is always the same, although the colour reported for ZEQSOD is orange-red while that of ZEQSOD01 is yellow, but this may be due to the thinness of the latter crystal. Moreover, the right F(000) value is 1280 as reported for ZEQSOD and not 1272 as reported for ZEQSOD01. The ZEQSOD01 coordinates, changed according to the transformation (1–*x*, 1–*y*, 1/2–*z*), can be compared to those of ZEQSOD. This comparison reveals that the deviations range from 0.004 Å for the S(1)–S(1)' pair to 0.060 Å for the C(15)–(C15)' pair. Since we are dealing with the same compound and the deviations are small we do not prepare the corresponding ZEQSOD01.CIF file.

Finally, we note that the original authors say '*the molecule is centrosymmetric with the inversion center at the Fe ion*' but they have not realized that the molecule has crystallographically imposed inversion symmetry.

2.7. ZUXBUP: bis(η⁶-benzene)-chromium hydroxide trihydrate, [(η⁶-(C₆H₆)₂Cr)⁺ [OH][–] · 3H₂O (Braga *et al.*, 1996, 1997)

This structure was reported in space-group *Aba2* (No. 41), *Z* = 4, but can be transformed to *Cmca* (No. 64), *Z* = 4, after reorientation (transformation matrix, [001], [010], [100] and origin shifts Δ*x* = –0.2887, Δ*y* = 0.5000, Δ*z* = 0.0000. The coordinate transformations are : *x*' = –*z* + 0.2887; *y*' = *y* – 1/2; *z*' = *x*. The symmetrizing involves shift of 0.07 Å for the oxygen atoms and no shifts larger than 0.05 Å for benzene ring. The organometallic cation [(η⁶-(C₆H₆)₂Cr)⁺ lies on a site of symmetry 2/*m* rather than symmetry 2, while the two oxygen atoms are related by a twofold axis along *b*, thus there is a complete mixing of OH[–] and H₂O. The spread in bond lengths disappears on going to *Cmca*, in fact the Cr–C distances range from 2.10 to 2.18 Å in *Aba2* while they range from 2.13 to 2.14 Å in *Cmca*. Similarly for the C–C distances in the benzene ring, 1.38–1.43 Å, against 1.40–1.41 Å. Since *Cmca* is a centrosymmetric space-group there is no polar axis in the structure (Braga *et al.*, 1997).

3. Category C: Change in Laue group and add a center of symmetry

3.1. GEWLEZ : *mer,trans*-trichloro-phenylimido-bis(trimethylphosphine)-rhenium, C₁₂H₂₃Cl₃NP₂Re (Park *et al.*, 1995)

This compound has been described as monoclinic, space-group $P2_1$ (No. 4), with $a = 10.053(1)$, $b = 10.844(1)$, $c = 10.058(2)$ Å, $\beta = 113.45(2)^\circ$, $Z = 2$. The Niggli matrix has the form (A,A,C,0,0,F) and corresponds to the lattice character 13 (Orthorhombic, oC). In fact, the lattice vectors $[101]$, $[10\bar{1}]$, $[010]$ and the origin shifts $(0,0,1/4)$ define an orthorhombic C -centered cell, space-group $Cmcm$ (No.63), with dimensions: $a = 11.0341(10)$, $b = 16.8137(20)$, $c = 10.844(10)$ Å, $\alpha = 90.00$, $\beta = 90.00(9)$, $\gamma = 90.03(2)^\circ$. The coordinate transformations are : $x' = 1/2x + 1/2z$; $y' = 1/2x - 1/2z$; $z' = y - 1/4$. We note that the original authors state: “*a statistical analysis of intensities suggested a non centrosymmetric space group*”, but such analysis is unreliable when an heavy atom is present (Hargreaves, 1955; Marsh, 1981). The molecule lies at Wyckoff position (4c), symmetry mm , in fact the twofold axis along b , passing through Cl(3), Re(1), N(1), C(1), and C(4), produces a very symmetric molecule with point group C_{2v} . The original paper reports: “*the bond angle of Re-N-C (158(2)°) is considerably distorted from linearity, compared to other related complexes*”, now it becomes exactly 180° .

3.2. YAXKOX: (μ_3 - η^4, η^4 -Buta-1,3-dien-1,4-diyl)-(μ_2 -hydrido)-tris(η^4 -cyclo-octa-1,5-diene)-tri-iridium, (C_8H_{12})₃C₄H₄HIr₃, (Muller *et al.*, 1993)

We immediately note that this structure was published without the coordinates of the two cyclo-octa-1,5-diene ligands bonded to Ir2 and Ir3, thus our analysis will be necessarily incomplete.

This structure was solved in space-group $P2_1$ (No. 4), with $a = 7.430$, $b = 25.998$, $c = 7.441$ Å, $\beta = 98.461^\circ$, $Z = 2$. The Niggli matrix has the form (A,A,C,0,0,F) and corresponds to the lattice character 13 (Orthorhombic, oC). In fact, the lattice vectors $[\bar{1}01]$, $[101]$, $[010]$ (No origin shifts) transform the monoclinic cell to orthorhombic, space-group $Cmcm$ (No. 63), with dimensions $a = 11.2624$, $b = 9.711$, $c = 25.998$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 89.91^\circ$. The coordinate transformations are : $x' = -1/2x + 1/2z$; $y' = 1/2x + 1/2z$; $z' = y$. The point symmetry of the molecule is $m2m$. In fact, one mirror plane is coincident with the buta-1,3-diene ligand and the other one passes midway and parallelly to the (formally) double bonds of cyclo-octa-1,5-diene. Also the μ -H atom should respect the $m2m$ symmetry, one possibility is that it lies on the mirror plane at $x = 0$ but split above and below the mirror plane at $y = 1/4$. There is a distinct improvement in molecular geometry on going from $P2_1$ to $Cmcm$. For example, the six C–C single bond distances of the cyclo-octa-1,5-diene ligand range from 1.48 to 1.72 Å and the two (formally) C=C distances are 1.41 and 1.47 Å. In the revised structure there are two independent C–C distances of 1.54 and 1.62 Å, and one C=C distance of 1.39 Å. Similarly, the three C–C distances in the buta-1,3-diene, C(2)–C(3)=1.42, C(1)–C(3)=1.50, C(1)–C(4)=1.48 Å become 1.44, 1.50, 1.44 Å in $Cmcm$. This structure apparently contains very large solvent accessible voids (% filled space 32.3%), but this is due to the lack of the two cyclo-octa-1,5-diene ligands.

4. Category D: add a center of symmetry and systematic absences

4.1. KIRWAJ: bis(1,4-dimethyl-9-triptycyl)ethyne chloroform solvate, C₄₆H₃₄·2CHCl₃, (Toyota *et al.*, 2000)

This compound has been described in space-group $P2_1$ (No.4), $Z=2$, but can be transformed to $P2_1/n$ (No. 14), after an origin shift of $(1/4, 0.2368, 3/4)$ but without permutation of cell axes. The organic molecule appears to be centrosymmetric in their Fig. 3. The coordinate transformations ($x' = x-1/4$; $y' = y-0.2368$; $z' = z-3/4$) show that the midpoint of the acetylenic bond is located on a center of symmetry in space-group $P2_1/n$. The added center of symmetry shows that the shifts inside the organic molecule range from 0.005 Å for the C(45)–C(46) pair (C(45)–C(46) is the acetylenic bond) to 0.045 Å for the C(43)–C(44) pair, mean shift 0.024 Å. The C–C distances of the benzene rings range, in $P2_1$, from 1.35 to 1.43 Å, now in $P2_1/n$ they range from 1.38 to 1.40 Å. Similarly, for the C(sp³)–C(sp²) distances, 1.49–1.55 against 1.52–1.55 Å. The geometry of the acetylenic bond remains unchanged, $-C\equiv C- = 1.19$ Å and $C(21)-C(45)-C(45)^I = 170.8^\circ$, ($I = -x, 2-y, -z$). The chloroform molecules are disordered in such a way that in the asymmetric unit of $P2_1$ there are four solvent molecules instead of only two. Despite this, all the atoms of solvent molecules can be paired, but the shifts are high, namely: $C(47)-C(49) = 0.16$, $Cl(1)-Cl(9)? = 0.16$, $Cl(4)?-Cl(13) = 0.10$, $Cl(7)?-Cl(11) = 0.10$ Å and $C(48)?-C(50)? = 0.22$, $Cl(2)?-Cl(10) = 0.10$, $Cl(5)-Cl(14) = 0.08$, $Cl(8)-Cl(12) = 0.11$ Å. We have included in the KIRWAJ.CIF file two $CHCl_3$ molecules with site occupation factor = 0.5, of course the precision is not high.

4.2. WACSAU : tris(1,2-di-imidobenzene)-technetium(VII) pertechnetate, $[C_{18}H_{18}N_6Tc]^+ [TcO_4]^-$ (Gerber *et al.*, 1992)

This compound was reported in space-group $Pna2_1$ (No.33), $Z = 4$ [$a = 13.869(4)$, $b = 12.799(5)$, $c = 10.851(3)$ Å], but can be transformed to $Pnna$ (No.52) after an origin shifts of $\Delta x = 1/4$, $\Delta y = 0$, $\Delta z = 0.2442$ and cyclic permutation of cell axes giving $a = 13.869(4)$, $b = 10.851(3)$, $c = 12.799(5)$ Å. The coordinate transformations are : $x' = x - 1/4$; $y' = -z$; $z' = y - 0.2442$. The Tc(1) atom of $[Tc(pda)_3]^+$ cation ($H_2pda = 1,2$ -diaminobenzene) lies at Wyckoff position $4(d)$, namely on the twofold axis along a , however the cation presents a molecular symmetry very near to C_{2v} , even if the space-group $Pnna$ does not possess mirror planes. The shifts range from 0.025 Å for N(5)–N(6) pair to 0.118 Å for C(15)–C(16) pair, while the mean shift is 0.068 Å, which is typical for the “add a center” situation. The C(sp²)–N distances varied from 1.28 to 1.41 Å, now from 1.34 to 1.35 Å ($C_{ar}-NH_2 = 1.355$ Å, Allen *et al.*, 1987). Similarly, the six Tc–N distances ranged from 1.98 to 2.04 Å, now they are all equal to 2.01 Å. The large spread of C–C distances in the three benzene rings, 1.27–1.54 Å, is somewhat reduced in $Pnna$ model, 1.33–1.50 Å, but this still wide range is due to the significant decay (up to 15%) of the crystal during data collection, this affects principally the position of C(2), C(3) and C(9) atoms and their terrible ellipsoids (see Fig. 3 of the original work). A new fast data collection if possible at low temperature is clearly needed.

The situation of the $[TcO_4]^-$ pertechnetate group requires some comments. The new space-group $Pnna$ imposes to the Tc(2) atom of $[TcO_4]^-$ anion to lie on the center of symmetry at (0,0,0). Since the $[TcO_4]^-$ group cannot be centrosymmetric because it possesses a tetrahedral geometry, disorder of this group is necessary to place it on the center of symmetry. Also the original authors noted this disorder but they determined only one of all the possible positions of oxygen atoms. However, this only position is not reliable because the interatomic distance $N(4)\cdots O(1) = 1.71$ Å is very short also for a very strong $N-H\cdots O$ hydrogen bond.

For all these reasons, the coordinates of the disordered $[\text{TcO}_4]^-$ group are not reported in the WACSAU.CIF file. The disorder is not altered but explained by the change of space-group.

5. Category D: add systematic absences

5.1. *QUJXEY* : bis(n-propylamine)dichloropalladium(II), $(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{PdCl}_2$ (Casellato *et al.*, 1999)

This structure was reported in $P2_1/c$ (No. 14), with $a = 7.542(2)$, $b = 8.437(2)$, $c = 8.929(2)$ Å, $\beta = 92.65^\circ$, $Z = 2$. The original authors remark that “*the molecular complex is centrosymmetric with the palladium atom in a quasi regular square planar configuration (the N(1)-Pd-Cl(1) angle is of $87(1)^\circ$).*” However, we will show that this complex possesses $2/m$ symmetry and thus it presents a perfect regular planar configuration with Cl–Pd–N angles of 90° , Cl–Pd–Cl and N–Pd–N angles of 180° . In fact, the reflection condition ‘ hkl absent for $k+l$ odd’ was not recognized by the original authors, probably because this condition is due to a non conventional cell of type A. Reorienting the cell axes according to the lattice vectors $[001]$, $[0\bar{1}0]$, $[100]$ a conventional monoclinic C type cell with parameters $a = 8.929(2)$, $b = 8.437(2)$, $c = 7.542(2)$ Å, $\beta = 92.65^\circ$ is obtained. The corresponding coordinate transformations, $x' = z - 1/2$; $y' = -y + 1/2$; $z' = x$, show that the space group is space-group $C2/m$ (No.12). These transformations place the Pd(1) atom on Wyckoff position $2(a)$ (symmetry $2/m$) of space-group $C2/m$, the Cl(1) atom on Wyckoff position $4(g)$ (symmetry 2) and all the other atoms on the mirror plane perpendicular to the twofold axis, Wyckoff position $4(i)$. The deviations of the atoms from the mirror plane are 0.10(N(1)), $-0.03(\text{C}(1))$, $-0.07(\text{C}(2))$ and 0.22 Å (C(3)). Further, we note that, although this space-group change, from $P2_1/c$ (No. 14) to $C2/m$ (No.12), involves a decrease in the number of space-group, $A12/m1$ ($C2/m$, 12) is a minimal non-isomorphic supergroup of $P2_1/c$. Hydrogen atoms has been recalculated because the position of H(1N) is the same as N(1), moreover N(1) atom was moved inside the fundamental molecule.

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