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Some errors from the crystallographic literature, some amplifications and a questionable result

Frank H. Herbstein,[a]* Shengzhi Hu[b] and Moshe Kapon[a]

[a]Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel, and [b]Department of Chemistry, Xiamen University, Xiamen, People's Republic of China

Correspondence e-mail: chr03fh@tx.technion.ac.il

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Dedicated to Dr R. E. Marsh (Caltech), teacher and friend, on the occasion of his 80th birthday

The space groups of $\{[\mathrm{Mo_2(O_2CCH_3)_4}(\text{'linker'})]_n\}$ are corrected from $P\bar{1}$ to $C2/m$ for 'linker' = pyrazine and 1,4-diazabicyclo[2.2.2]octane (dabco) and from $P\bar{1}$ to $C2/c$ for 'linker' = 4,4′-bipyridine. Also, {[tris-(2-pyridylmethyl)amine]-BrV(μ-O)VBr[tris-(2-pyridylmethyl)amine]}Br·H_2O is corrected from $P\bar{1}$ to $C2/c$. These Laue class changes allow more reliable crystallochemical comparisons to be made among families of related structures. Space groups are corrected for 4-methyl-2,6-bis(4-methylbenzylidene)cyclohexanone, 2,6-bis(4-dimethylaminobenzylidene)cyclohexanone, K[Cr(tetramethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate)]·H_2O and {bis(11,-11-dimethyl-3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene)-(tetracyanoethylene)}. The conflicting reports for Cu(H_2O)(phenanthroline)$_2(X)_2$, where $X = \mathrm{ClO_4}$, NO_3 and BF_4, are resolved. Three related examples of open framework host–guest structures with space groups '*Cc* or *C*2/*c*' are discussed. Adding centers to 2,2′-bi-1*H*-imidazolium dipicrate and {tris(2,2′-bi-1*H*-imidazole)bis[2-(2-1*H*-imidazolyl)-1*H*-imidazolium]bis(iodide)} corrects discrepancies of up to 0.38 Å between chemically similar hydrogen-bond distances. Wrongly identified atoms are corrected in θ-[bis(ethylenedithio)-tetrathiafulvalene]$_2$ (CsCd)(SCN)$_4$ and (purported) diaquadihydroxotetrakis(*m*-nitrobenzenesulfonate)discandium(III). The reported difference between the crystal structure of $\mathrm{(CH_3NH_3)_4YbCl_7}$ and those of the other members of this family of $\mathrm{(CH_3NH_3)_4}MX_7$ (M = In, Fe, V; X = Cl, Br) structures is pointed out in the context of possibly different $\mathrm{N-H\cdots Cl}$ hydrogen bonding in the Yb structure.

1. Introduction

Some of the crystal structures reported in the crystallographic and chemical literature have incorrectly assigned space groups or errors of other kinds. Despite the relatively small number of such occurrences – perhaps 1000 or so among the 244455 unique organic and metal-organic compounds reported in the Cambridge Structural Database (CSD) by July 2002 – considerable effort has been devoted to their correction. Most often, such corrections are 'one of a kind' and are important only in the context of the particular crystal structure being considered. There are, however, some situations where the corrections allow clarification of the relations within a group of structures that resemble one another chemically and/or crystallographically, or make possible a more detailed discussion of the revised packing. A group of chemically related framework structures provides new examples of the 'centrosymmetric–non-centrosymmetric' ambiguity. We also revise a number of 'one of a kind' space groups. Finally, one intriguing example, apparently faultless but with internal contradictions, appears to suggest a new type of $\mathrm{N-H\cdots Cl}$

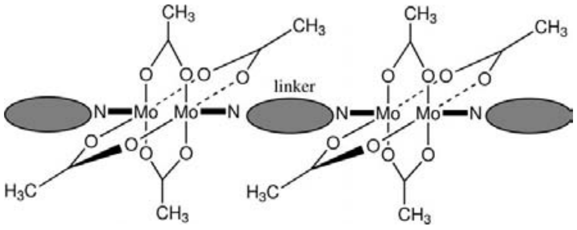
hydrogen bonding without parallel examples in the literature; however, caution requires re-examination of this crystal structure before accepting such an unprecedented conclusion.

Appropriate references to the literature are given in an earlier paper (Marsh *et al.*, 2002).[1] Structure determinations are generally referenced through their CSD Refcodes (Allen *et al.*, 1991). We follow as much as possible the arrangement pattern used by Marsh *et al.* (2002): *i.e.* Category *A*, change in Laue class; Category *B*, add a center of symmetry; and Category *C*, add a center of symmetry and systematic absences. A new category, *D*, establishes details of crystal structure. Revised crystal data are appended as deposited CIFs[2] and have been submitted to the CSD.

2. Category A: change in Laue class

2.1. Linear chain compounds of molybdenum(II) acetate linked by pyrazine, 1,4-diazabicyclo[2.2.2]octane ('dabco') or 4,4′-bipyridine

Handa *et al.* (1995) have presented three examples under this heading with dimolybdenum tetraacetate moieties linked by the linear molecules pyrazine, 1,4-diazabicyclo[2.2.2]octane (dabco) or 4,4′-bipyridine (see schemes for these and other formulae).



The pyrazine and 'dabco' compounds are isomorphous and were reported in space group $P\bar{1}$, $Z = 1$ {ZIXQOM, *catena*-[(μ^2-pyrazine-1,4-diyl)tetrakis(μ^2-acetato-*O*,*O*′)-dimolybdenum(II)] $[Mo_2(O_2CCH_3)_4(pyrazine)]_n$ and ZIXRAZ, *catena*-[(μ^2-(1,4-diazabicyclo[2.2.2]octane)-1,4-diyl)tetrakis-(μ^2-acetato-*O*,*O*′)-dimolybenum(II)] $[Mo_2(O_2CCH_3)_4(dabco)]_n$}. The third compound [a tetrahydrofuran (THF) solvate] was also reported in $P\bar{1}$ but with $Z = 2$ {VINBAV10, *catena*-[(4,4′-bipyridine)-1,4-diyl]tetrakis(μ^2-acetato-*O*,*O*′)dimolybdenum(II) $[Mo_2(O_2CCH_3)_4(4,4'\text{-bipyridine})]_n\cdot m\text{THF}$)}. Relevant cell dimensions are given in Table 1.

The isomorphous structures can be transformed from $P\bar{1}$ to $C2/m$, $Z = 2$. The dabco C atoms are disordered over at least two orientations and we have not attempted to reproduce their values. The $Mo_2(O_2CCH_3)_4$ moiety is located about Wyckoff position *c* $(0, \frac{1}{2}, 0)$ with $2/m$ symmetry and the linking molecule (pyrazine or dabco) about Wyckoff position *d* $(0, \frac{1}{2}, \frac{1}{2})$, also with $2/m$ symmetry. Linked molecules are packed in parallel chains in the unit cell [see Figs. 1 and 4 of Handa *et al.* (1995)].

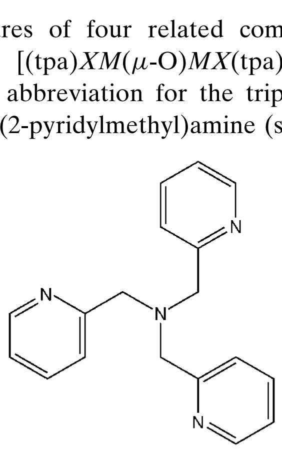
Table 1
Reduced and revised cell dimensions (Å, °) for the three compounds ZIXQOM, ZIXRAZ and VINBAV10.

REFCODE	*a*	*b*	*c*	*α*	*β*	*γ*
Reduced cells						
ZIXQOM	7.628	8.178	8.253	60.36	84.97	79.69
ZIXRAZ	7.864	8.091	8.882	62.93	84.11	76.95
VINBAV10	12.348	14.425	8.472	66.60	72.99	69.96
Revised cells						
ZIXQOM *C*2/*m*, *Z* = 2	8.178	14.347	7.628	89.93	100.31	90.06
ZIXRAZ *C*2/*m*, *Z* = 2	8.091	15.818	7.864	89.99	103.05	90.03
VINBAV10 *C*2/*c*, *Z* = 4	23.20	8.472	14.801	89.96	118.41	89.98

The triclinic cell of VINBAV10 can be transformed to space group $C2/c$, $Z = 4$. The r.m.s. deviations of paired atoms from the glide plane in $C2/c$ are 0.007 Å in *x*, 0.006 Å in *y* and 0.004 Å in *z*. The B_{equiv} values for the atoms listed range from 2.4 to 5.3 Å^2. The THF atoms have B_{equiv} values ranging from 8.3 to 16 Å^2 and are not listed. Handa *et al.* (1995) remark that '...the crystal consists of two crystallographically independent [polymeric] chains...with no remarkable structural difference...' (copied by CSD). In fact, there is only one *independent* polymeric chain in the monoclinic cell, the two chains in Fig. 3 of Handa *et al.* (1995) being related by symmetry operations of the monoclinic space group. Supplementary data are in BCSJ 68041.[3] Three other linked-chain structures of molybdenum acetate have been reported {$[Mo_2(O_2CCH_3)_4(tmed)]_n$ (Kerby *et al.*, 1990), $[Mo_2(O_2CCH_3)_4(N,N'\text{-dimed})]_n$ and $[Mo_2(O_2CCH_3)_4(pda)]_n$ (Eichhorn *et al.*, 1991)} but these are not relevant in the present context because the chains are zigzag rather than linear.

2.2. Compounds of the general formula [(tpa)*XM*(*μ*-O)*MX*(tpa)]*Y*$_2$

Crystal structures of four related compounds with the general formula [(tpa)*XM*(μ-O)*MX*(tpa)]Y_2 are known, where tpa is the abbreviation for the tripodal tetradentate amine ligand tris-(2-pyridylmethyl)amine (see Scheme 2).



tpa is tris(2-pyridylmethyl)amine

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[1] Unfortunately we earlier omitted reference to the Nardelli (1996) paper in which he showed that the 1995 update of the *PARST* program (Nardelli, 1995) provides efficient detection of missed symmetry.

[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0053). Services for accessing these data are described at the back of the journal.

[3] BCSJ *XXXXX* indicates that the supplementary data can be obtained from the offices of the Chemical Society of Japan.

Table 2
Comparison of crystal data for four compounds with general formula $[(\mathrm{tpa})XM(\mu\text{-O})MX(\mathrm{tpa})]Y_2$.

Name	a, α	b, β	c, γ	Z	Space group	Cation symmetry	Angle $M-(\mu-\mathrm{O})-M$
GAMTUJ	11.321 (1), 90	14.805 (1), 97.82 (1)	12.658 (1), 90	2	$P2_1/c$	$\bar{1}$	180
SONHOS	12.244 (6), 77.42 (1)	12.299 (2), 83.15 (2)	13.370 (2), 81.41 (3)	2	$P\bar{1}$	$\bar{1}$†	180
WIHSAH	16.308 (2), 90	17.178 (3), 111.81 (1)	16.575 (2), 90	4	$C2/c$	$C_2(2)$	174.7 (5)
ZIXRED‡	11.505 (5), 103.73 (2)	11.509 (5), 103.71 (2)	16.348 (7), 93.26 (3)	2	$P\bar{1}$	No imposed symmetry	175.3 (2)
ZIXRED, transformed cell	15.804, 90	16.730, 110.21	16.348, 90	4	$C2/c$	$C_2(2)$	175.3 (2)

† Two cations at independent centers of symmetry. ‡ The cell reported was reduced.

The following combinations have been reported:

(i) GAMTUJ $X = \mathrm{NCS}$, $M = \mathrm{Cr}$, $Y = \mathrm{ClO_4}$ (Gafford *et al.*, 1988);

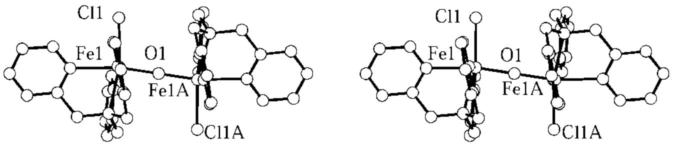
(ii) SONHOS $X = \mathrm{O}$, $M = \mathrm{V}$, $Y = \mathrm{ClO_4}$ (Toftlund *et al.*, 1991);

(iii) WIHSAH $X = \mathrm{Cl}$, $M = \mathrm{Fe}$, $Y = \mathrm{ClO_4}$ (Hazell *et al.*, 1994);

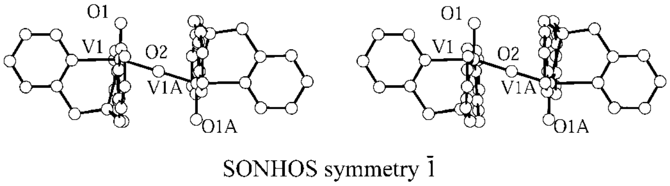
(iv) ZIXRED $X = \mathrm{Br}$, $M = \mathrm{V}$, $Y = \mathrm{Br}, \mathrm{H_2O}$ (Kanamori *et al.*, 1995).

The crystal data are compared in Table 2. The ZIXRED structure was transformed from $P\bar{1}$ to $C2/c$; the equality of two cell edges and two angles in the original (reduced) cell could have suggested the need to check possible higher symmetry (Herbstein, 1997). The r.m.s deviations of the paired atoms from the glide plane in $C2/c$ are 0.002 Å in all three coordinates, indicating that the dimensions calculated in the triclinic cell can be used without change, especially after averaging. Supplementary data are in BCSJ 68047.

WIHSAH and ZIXRED have similar cation structures, and the crystal structures are also closely related despite the difference between the anions $\mathrm{ClO_4}$ and $(\mathrm{Br{\cdot}H_2O})$, while GAMTUJ and SONHOS have different crystal structures although both have centrosymmetric cations and the same perchlorate anions. Despite the difference in symmetry of the two pairs of cations, their overall shape is very similar, as is shown by comparison of the stereoviews of Fig. 1.



WIHSAH symmetry 2



SONHOS symmetry $\bar{1}$

Figure 1
Stereoviews of the cations $[(\mathrm{tpa})\mathrm{OV}(\mu\text{-O})\mathrm{VO}(\mathrm{tpa})]^{2+}$ [symmetry C_i; Toftlund *et al.* (1991)] and $[(\mathrm{tpa})\mathrm{ClFe}(\mu\text{-O})\mathrm{FeCl}(\mathrm{tpa})]^{2+}$ [symmetry $C_2(2)$; Hazell *et al.* (1994)].

2.3. QADZOK: 4-methyl-2,6-bis(4-methylbenzylidene)cyclohexanone, $C_{23}H_{24}O$

This compound, abbreviated as MBMCH, was reported (Kawamata *et al.*, 1998) as monoclinic, space group $P2_1$, $Z = 2$ [$a = 11.332$ (4), $b = 8.067$ (4), $c = 11.312$ (4) Å, $\beta = 119.2$ (3)°]. The near equality of a and c and the closeness of β to 120° could have aroused suspicion about the possibility of higher symmetry. Indeed, the $10\bar{1}$, 101 and 010 lattice nodes form an essentially orthogonal cell with $a = 19.531$, $b = 11.459$, $c = 8.067$ Å, $\alpha = \gamma = 90.00$, $\beta = 89.88°$, $Z = 4$, space group $Cmc2_1$ (No. 36); the molecule has a mirror plane (Wyckoff position a).

2.4. QAFBAA: 2,6-bis(4-dimethylaminobenzylidene)cyclohexanone, $C_{24}H_{28}N_2O$

This compound, abbreviated as DMABCH, was reported (Kawamata *et al.*, 1998) as orthorhombic, space group $Pca2_1$, $Z = 4$ [$a = 9.291$ (3), $b = 21.838$ (3), $c = 9.647$ (3) Å]. Transforming the axes by (010, 100, $00\bar{1}$) and shifting the origin to ($\frac{1}{4}$, $\frac{3}{4}$, 0.0) gives a C-centered cell, space group $Cmc2_1$ (No. 36), the molecule now having a mirror plane (Wyckoff position a).[4]

The revised coordinates are compatible with this arrangement to within a maximum deviation of 0.11 Å. The implication of this revision is that the hkl reflections with $h + k = 2n + 1$ in the original primitive-cell indexing must have been very weak and are now considered to be absent. Document BCSJ 71060 lists 1233 F_{obs} values, the largest being reflection 201 with $F_{\mathrm{obs}} = 262.1$. There are 64 reflections that violate the C-centering condition, with F_{obs} values ranging from 2.3 to 4.3. There is little doubt that $Cmc2_1$ is the correct space group.

3. Category B: adding a center

3.1. $\mathrm{K[Cr(tmdta)]{\cdot}H_2O}$, where tmdta is tetramethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate

This compound was reported as triclinic [$a = 9.674$ (5), $b = 12.942$ (3), $c = 6.994$ (1) Å, $\alpha = 99.26$ (2), $\beta = 108.92$ (2), $\gamma = 87.40$ (2)°, $Z = 2$, space group $P1$] (Kanamori *et al.*, 2001). The mean values of $x_1 + x_2$, $y_1 + y_2$ and $z_1 + z_2$ are 1.34002,

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[4] There is no change of Laue class. The discussion has been placed here for convenience.

Table 3
Cell dimensions for [Cu(H_2O)(phenanthroline)$_2$](X)$_2$, where X = ClO_4, NO_3, BF_4.

All compounds have $Z = 4$. The perchlorate was transformed from triclinic to monoclinic.

X	a	b	c	β	Space group	Reference
NO_3	22.58 (2)	7.23 (1)	16.59 (2)	123.6 (1)	$C2/c$	Nakai & Deguchi (1975)
NO_3	22.640 (5)	7.254 (2)	16.604 (3)	123.76 (2)	Cc	Catalan *et al.* (1995)
BF_4	19.099 (6)	8.100 (3)	16.177 (5)	100.54 (5)	$C2/c$	Nakai & Noda (1978)
ClO_4	19.101, 19.177 (2)	8.182, 8.1994 (0)	16.261, 16.246 (1)	100.20, 100.10 (1)	*C*-centered†, Cc	Wang *et al.* (1990), Le *et al.* (2001)

† No coordinates.

1.18627 and 0.03487, where subscripts 1 and 2 refer to corresponding atoms in the two purportedly independent molecules. After shifts of origin by $\Delta x = -0.67000$, $\Delta y = -0.59313$ and $\Delta z = -0.01743$, the arrangement is centrosymmetric. The Flack parameter (Flack & Bernardinelli, 1999, 2000) was reported (for $P1$) as 0.05 (3); of course, there is no such parameter in $P\bar{1}$.

3.2. {Bis(11,11-dimethyl-3,4:8,9-dibenzobicyclo[4.4.1]-undeca-3,8-diene)–(tetracyanoethylene)}

This molecular compound was reported as triclinic [$a = 9.409$ (5), $b = 13.743$ (5), $c = 7.519$ (5) Å, $\alpha = 104.391$ (5), $\beta = 95.457$ (5), $\gamma = 93.973$ (5)°, $Z = 1$, space group $P1$] (Taniguchi *et al.*, 1998). The mean values of $x_1 + x_2$, $y_1 + y_2$ and $z_1 + z_2$ are 0.8300, 0.1667 and 0.2009, where subscripts 1 and 2 refer to corresponding atoms in the two purportedly independent molecules and the two halves of tetracyanoethylene. After shifts of origin by $\Delta x = -0.4150$, $\Delta y = -0.08335$ and $\Delta z = -0.10045$, the arrangement is centrosymmetric. The Flack parameter was reported (for $P1$) as 1.99 (254); of course, there is no such parameter in $P\bar{1}$.

For completeness, we add that compound 8 of Taniguchi *et al.* (1998) was reported in space group $R3$, $Z = 6$; inspection of the CIF shows that this is a typographical error and that the space group used in the structure analysis was $R\bar{3}$.

3.3. NUXTIJ tetrakis(μ^3-phenylsulfido)tricarbonylmanganese {$Mn_4(SPh)_4(CO)_{12}$}

This cubane-type cluster compound was reported (Onaka & Katukawa, 1996) as *A*-centered monoclinic ($a = 16.544$, $b = 22.081$, $c = 11.529$ Å, $\beta = 108.28°$, $Z = 4$, Flack parameter not given), with space group Aa. Inspection of the coordinates shows that pairs of atoms have the same y coordinates, a sure sign of a twofold axis along [010]. After an origin shift of $\Delta x = 0.19373$, $\Delta y = 0$ and $\Delta z = -0.28413$ (obtained from the more precise coordinates of the Mn and S atoms) and a transformation $(001/0\bar{1}0/100)$ to the conventional *C*-centered cell, the revised coordinates fit space group $C2/c$ within experimental error.

For completeness, we add that compound 3 of Onaka & Katukawa (1996) was reported in space group $P1$, $Z = 2$; inspection of the table of coordinates shows that this is a typographical error and that the space group used in the structure analysis was $P\bar{1}$.

3.4. [Cu(H_2O)(phenanthroline)$_2$](X)$_2$, where X = ClO_4, NO_3, BF_4

In this family of compounds, the tetrafluoroborate and perchlorate are isomorphous, while the nitrate has a similar but somewhat different structure (Table 3). The tetrafluoroborate has been reported (Nakai & Noda, 1978) as monoclinic ($C2/c$, $Z = 4$, $R_F = 0.083$), but the perchlorate was originally reported as triclinic [$P1$, $Z = 2$, $a = 8.182$ (2), $b = 10.389$ (2), $c = 16.261$ (5) Å, $\alpha = 99.38$ (2), $\beta = 89.97$ (2), $\gamma = 113.18$ (2)° (Wang *et al.*, 1990), coordinates not available]. In fact, the triclinic cell of the perchlorate transforms to a *C*-centered monoclinic cell, similar to that of the tetrafluoroborate. The perchlorate has been independently reported, this time in a *C*-centered monoclinic cell but with space group Cc (Le *et al.*, 2001). The coordinates (those of the perchlorate anion are missing, presumably owing to unresolved disorder), after an origin shift of $\Delta x = -0.3485$, $\Delta y = 0$, $\Delta z = -0.2275$, fit the requirements of $C2/c$ within about 0.05 Å.

The nitrate has been reported twice (Nakai & Deguchi, 1975, APENCU; Catalan *et al.*, 1995, APENCU01) with similar unit-cell dimensions (Table 3). Nakai & Deguchi (1975) refined their data in space group $C2/c$ to $R_F = 0.118$. Catalan *et al.* (1995) refined in both $C2/c$ ($R_F = 0.0470$ for 187 variables; nitrates disordered[5] and coordinated water 'poorly fitted') and Cc ($R_F = 0.0424$ for 341 variables; nitrates ordered, coordinated water 'showed an improved mode'). Reflection statistics also favored the non-centrosymmetric space group. However, our examination of the coordinates given by Catalan *et al.* (1995) shows that $C2/c$ is the correct space group. We conclude that all three coordination complexes crystallize in space group $C2/c$.

3.5. Three related examples of 'Cc or $C2/c$?'

3.5.1. Introduction. Open framework structures with cavities are obtained when $M(NO_3)_2$ (M = Ni, Cu) is reacted in solution with suitable ligand–guest combinations (Biradha & Fujita, 2000). Compound 4 (we retain the Biradha–Fujita numbering) is obtained with 1,4-bis(4-pyridyl)benzene as ligand and benzene as guest, while compounds 5–8 are obtained with 1,4-bis(4-pyridyl)anthracene as ligand and nitrobenzene and cyanobenzene as guests. The crystal structures (Table 4) were all determined at 193 K. The full reci-

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[5] In $C2/c$ there will be only one crystallographically independent nitrate.

Table 4
Crystal data [at 193 K; Biradha & Fujita (2000)] for five structures; $Z = 4$ for all five structures.

	4†	5‡	6§	7¶	8††
a (Å)	16.854 (2)	13.636	13.810	13.645	13.792
b (Å)	15.626 (2)	24.875	24.700	24.777	24.529
c (Å)	19.144 (2)	15.217	15.286	15.457	15.515
β (°)	114.785 (2)	99.60	101.98	99.56	101.44
V (Å^3)	4577.5 (10)	5089.0	5100.3	5153	5144.8
Reported space group	*Cc*	*Cc*	*Cc*	*C*2/*c*	*C*2/*c*
Unique reflections	7210	6895	9892	4543	6148
wR_2 (on F^2, all data)	0.2178	0.2176	0.2386	0.1859	0.2104
Approximate no. of non-H parameters, restraints	556, 86	712	712	375	375

† $C_{43}H_{54}NiN_6O_{13}$ (guest benzene). ‡ $C_{60}H_{42}NiN_8O_{10}$ (guest nitrobenzene). § $C_{60}H_{42}CuN_8O_{10}$ (guest nitrobenzene). ¶ $C_{62}H_{37}NiN_8O_6$ (guest cyanobenzene). †† $C_{62}H_{37}CuN_8O_6$ (guest cyanobenzene).

procal lattice sphere was measured (graphite-monochromated Mo $K\alpha$) for all five structures; thus many Friedel pairs must have been measured although it is not clear what averaging process was applied to obtain 'unique' from 'measured' reflections. $R_{(\mathrm{int})}$ was 0.03, 0.06, 0.09 and 0.09 for structures 4, 5, 6 and 8, respectively, but 0.2088 for structure 7 (*C*2/*c*). We note some outstanding points regarding the refinements of 4, 5 and 6. The Flack parameter was given as 0.00 (no s.u.) for these structures. From the results it is clear that the benzene rings of the guest molecules were eventually adjusted to be regular hexagons of side 1.39 Å, but how this could affect the refinement process was not explained. As the nitrate anions are ligated to the metal atoms in compounds 5–8, the frameworks are neutral, as are the enclathrated guest molecules. The situation in 4, described as a 'doubly interpenetrated three-dimensional hydrogen-bonded network', is somewhat more complicated, but the double network and enclathrated benzene are both neutral.

3.5.2. Compound 4: ({Ni[1,4-bis(4-pyridyl)benzene]$_2$-(H$_2$O)$_2$}(benzene)·5MeOH·2(NO$_3$)$_2$) at 193 K, $C_{43}H_{54}N_6$-NiO_{13} (Biradha & Fujita, 2000). The crystal structure was reported in space group *Cc* (Table 4). The C—C bond lengths in the two purportedly independent 1,4-bis(4-pyridyl)benzene ligands *A* and *B* vary from 1.340 (10) to 1.483 (12) Å and those in the nitrate anions from 1.112 (14) to 1.345 (14) Å. Projection of the structure along [010] suggests that there is a twofold axis through Ni with centers of symmetry at the center of the included benzene ring and between the two nitrates. This was confirmed by analysis of pairwise related atomic coordinates after an origin shift of $\Delta x = -0.12751$, $\Delta y = 0$ and $\Delta z = -0.21501$.[6] The revised space group is *C*2/*c*, with the origin placed at the center of the benzene ring of 1,4-bis(4-pyridyl)benzene-*A*. Although the overall description of the structure is little altered, the detailed molecular dimensions are changed to conform to the revised symmetry. The authors remark that this crystal structure was also refined in *C*2/*c*, where one methanol is disordered, but 'solving the structure in a non-centrosymmetric space group resulted in a lower *R* factor and no disorder' [of methanol]. The difference in *R* factors is not given but cannot be large as it stems from the difference between ordered and disordered positions for a C and an O atom. The arguments for preferring a centrosymmetric to a non-centrosymmetric space group (when a choice is required) can be summarized in one quotation: 'In cases where diffraction data do not provide a clear choice between a centrosymmetric and a non-centrosymmetric space group, it is better to opt for the centrosymmetric description even though disorder may result' (Marsh, 1986). This point of view has been elaborated further (Marsh, 1994, 1995).

3.5.3. Compounds 5–8: {[*M*(1,4-bis(4-pyridyl)anthracene)$_2$(NO$_3$)$_2$]·2(guest)} at 193 K [5, 6 *M* = Ni, Cu, guest = nitrobenzene; 7, 8 *M* = Ni, Cu, guest = cyanobenzene; $C_{60}H_{42}MN_8O_{10}$ (guest nitrobenzene) and $C_{62}H_{37}MN_8O_6$ (guest cyanobenzene)] (Biradha & Fujita, 2000). The crystal data are summarized in Table 4. There are no standard criteria for gauging the degree of resemblance among closely similar structures. Here, the pairs 5/7 and 6/8 (same metal, different guests) are closest if the angle β is the criterion, while the pairs 5/6 and 7/8 (same guest, different metals) are closest if cell volumes decide the issue.

In 7 and 8 (the *C*2/*c* structures), the origin is between the two nitrate anions (for example, between O3*A* at −0.1950, −0.0198, −0.0687 (*i.e.* 0.9313 − 1) and its centrosymmetric congener. In 7, the Ni atom is on the twofold axis [Wyckoff position *e* $(0, y, \frac{3}{4})$ with $y = -0.0030$ (6)], and the center of the 1,4-bis(4-pyridyl)anthracene *A* ligand is at Wyckoff position *c* $(\frac{1}{4}, \frac{1}{4}, 0)$ and similarly for the Cu atom and ligand center of 8. If the origin of 5 is shifted by $\Delta x = 0.61663$, $\Delta y = -0.5$ and $\Delta z = 0.37004$, the Ni atom has the same coordinates as that in 7 and pairwise averaging of coordinates shows that the *framework* conforms to space group *C*2/*c*. However, the guest nitrobenzene molecules and the nitrate anions do not. The same procedure can be applied to 6 ($\Delta x = 0.61700$, $\Delta y = -0.5$ and $\Delta z = 0.37038$), yielding a *framework C*2/*c* structure very similar to that of 8, but with discrepant guest nitrobenzene molecules and nitrate anions. There appear to be systematic errors in the coordinates of the nitrates in both structures: the N—O distances range from 1.12 to 1.49 Å and the O—N—O angles from 77 to 127°, while the U_{equiv} values range from 0.028 to 0.198 Å^2; furthermore, the coordinates of the guest molecules have been adjusted, Thus we suggest that these discrepancies must be established more firmly before they can be considered real effects. Biradha & Fujita (2000) have remarked 'The crystal structures of . . . 5 and 6 were refined in centrosymmetric space groups also. However . . . the nitrobenzene molecules in 5 and 6 were disordered. Solving the structures [of 5 and 6] in a non-centrosymmetric space group . . . the *R* factor remained the same but the guest molecules are not disordered.' There is no mention of the nitrates.

We have shown here that the frameworks of these four structures do not differ, while there are obvious systematic

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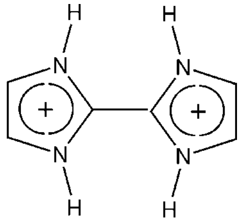
[6] The origin shifts can be obtained by averaging over all the pairwise related atoms, but the precision of the coordinates of the metal atoms is considerably higher than that of the other atoms and so it seems better to use the metal-atom shifts.

errors in the location of the nitrate anions. In addition, as has been argued above and previously, the inherently questionable location of the nitrobenzene molecules in 5 and 6 (ordered or disordered) is best set out in a disordered and centrosymmetric description, strong evidence to the contrary not having been advanced.

4. Category C: add a center and systematic absences

4.1. RUDRAJ: 2,2′-bi-1*H*-imidazolium dipicrate, $[(C_6H_8N_4)^{2+}\cdot 2(C_6H_2N_3O_7)^{-}]$

This compound was reported (Akutagawa *et al.*, 1996) in space group $P2_1$, $Z = 2$, with cell dimensions $a = 23.522$ (3), $b = 5.459$ (3), $c = 8.781$ (4) Å, $\beta = 96.66$ (7)° (a was misprinted as 25.522), $R = 0.0402$ (block diagonal approximation). H-atom positions were determined from difference syntheses. The revised coordinates fit space group $P2_1/a$ with r.m.s. deviations of about 0.03 Å in x, y and z. Supplementary data are in BCSJ 69054. The reflection condition '$h0l$ present for h even' was missed.

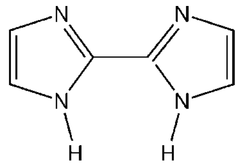


$(C_6H_8N_4)^{2+}$ or H4BIM^{2+}

The description of the crystal structure given by Akutagawa *et al.* (1996) needs revision because of the change of space group; the original diagrams can form a basis for such a description provided the consequences of the change in space group are taken into account. The cation is situated about the center of symmetry at the origin and is hydrogen bonded to two (centrosymmetrically related) picrate anions. There are only dispersion forces between these three-moiety units. In space group $P2_1$, the largest differences between 'equivalent' distances in the two purportedly independent picrate anions are 0.18 Å for C—O and 0.12 Å for C—C.

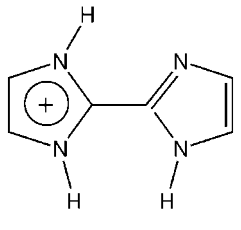
4.2. RUDREN: {tris(2,2′-bi-1*H*-imidazole)bis[2-(2-1*H*-imidazolyl)-1*H*-imidazolium]bis(iodide), $[3(C_6H_6N_4)\cdot 2(C_6H_7N_4)^{+}\cdot 2(I^{-})]$}

This compound was reported (Akutagawa *et al.*, 1996) in space group $P2_1$, $Z = 2$, with cell dimensions $a = 29.422$ (8), $b = 12.304$ (3), $c = 5.071$ (4) Å, $\beta = 94.06$ (3)°, $R = 0.0528$ (block diagonal approximation; H-atom positions not determined; Flack parameter not given). The revised coordinates fit space group $P2_1/a$ with r.m.s. deviations from $P2_1/a$ of about 0.08, 0.05 and 0.07 Å in x, y and z, respectively. Supplementary data are in BCSJ 69054. The reflection condition '$h0l$ present for h even' was missed.



$C_6H_6N_4$ or H2BIM^0

The formula has been drawn with a mirror plane but a centrosymmetric conformation is also possible.



$(C_6H_7N_4)^{+}$ or H3BIM^{+}

The change of space group requires a somewhat revised description of the packing. We use the following abbreviations: [2-(2-1*H*-imidazolyl)-1*H*-imidazolium] is (H3BIM$^+$) and (2,2′-bi-1*H*-imidazole) is (H2BIM^0). In formal terms, there are two structural units, *A* and *B*, which alternate along [010]. Here *A* is the neutral

$$[I(^{-})(H3BIM^{+})(H2BIM^{0})(\bar{1})(H2BIM^{0})(H3BIM^{+})I(^{-})]$$

moiety located about the crystallographic center of symmetry at $0, \frac{1}{2}, 0$ and *B* is the neutral (H2BIM^0) molecule located about the crystallographic center of symmetry at 0, 0, 0. It is also possible for *A* to have an alternative structure:

$$[I(^{-})(H2BIM^{0})(H3BIM^{+})(\bar{1})(H3BIM^{+})(H2BIM^{0})I(^{-})].$$

The first of these possibilities [proposed by Akutagawa *et al.* (1996)] seems more likely as iodide ions are usually found near positive centers. Distinction between them would be best based on determination of H-atom positions, although determination of precise moiety dimensions could perhaps suffice.

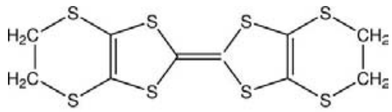
There is a large difference of 0.38 (17) Å between the N11···N41 [2.969 (12) Å] and N23···N33 [2.585 (12) Å] hydrogen bonds, which are purportedly independent in $P2_1$ but related by a center of symmetry in $P2_1/a$. Akutagawa *et al.* (1996) suggest that the shorter of these links may be a symmetrical hydrogen bond, but this remains to be demonstrated. The presence of the variously charged species is shown by comparison of infrared spectra [Fig. 5 of Akutagawa *et al.* (1996)], but the current errors in interatomic distances do not allow for unequivocal confirmation of the (apparently reasonable) hydrogen-bonding scheme proposed.

RUDRAJ and RUDREN are excellent examples of what can (and does) happen when a center of symmetry is erroneously omitted. Further refinement is desirable.

5. Category D: establishing details of crystal structures

5.1. Compounds with formula θ-[bis(ethylenedithio)tetrathiafulvalene]$_2$ (M^1M^2)(SCN)$_4$

The crystal structures of a number of compounds of formula θ-(BEDT-TTF)$_2$(M^1M^2)(SCN)$_4$[(M^1M^2) $S_{20}N_4C_{24}H_{16}$)] [bis(ethylenedithio)tetrathiafulvalene is abbreviated as (BEDT-TTF) or (ET)] have been reported (Mori *et al.*, 1995). Marsh & Spek (2001) have discussed the RbZn compound (ZIFKII), where 'it appears that the coordinates of the Rb and Zn atoms have been interchanged.' These corrections (and some others) had earlier been made by Mori *et al.* (1996, 1998).



ET or BEDT-TTF

The Cs and Cd atoms have also possibly been interchanged in the (Cs/Cd) compound [ZIFLAB; triclinic $P\overline{1}$, *R*-factor for 1450 reflections, Mo $K\alpha$, 0.12; Mori *et al.* (1995)]. Cs and Cd were placed on inversion centers, with Cs^+ reported to have square-planar coordination of four N atoms, [d(Cs—N) = 2.33, 2.36 (3) Å], while the nearest atom to Cd was N with d(Cs—N) = 3.50 (2) Å and there was also coordination of S about Cd [d(Cs—S) = 3.62, 3.64 (1) Å]. We have entered the 1450 reflections given in BCSJ 68014 and repeated the refinement. Interchanging Cs and Cd at an early stage of the refinement reduced R by 0.01. The refinement was stopped at $R = 0.11$, but satisfactory convergence was not obtained because of non-positive definite atomic displacement parameters (ADPs) for C and N atoms of the organic and isothiocyanate moieties. In the revised structure, Cd and Cs both have octahedral coordination with d(Cd—N) = 2.30, 2.40 Å, d(Cd—S) = 2.79 Å and d(Cs$\cdots$S) = 3.62, 3.63, 3.86 Å. These distances are in good agreement with values extracted from the CSD and the metal coordination is no longer anomalous. However, *conclusive* crystallographic evidence for the change is lacking.

5.2. (Purported) diaquadihydroxotetrakis(*m*-nitrobenzenesulfonate)discandium(III) {[$Sc_2(OH)_2(O_2NC_6H_4SO_3)_4$-$\cdot 2H_2O$]}

This crystal structure was reported [Tateyama *et al.*, 1988*a* (SAKCAI), 1988*b* (SAKCAI10)] in a monoclinic unit cell [$a = 28.90$ (2), $b = 10.251$ (4), $c = 5.981$ (1) Å, $\beta = 94.68$ (3)°, space group Pn, $Z = 2$ (*i.e.* two independent Sc atoms in the unit cell)]. 4507 reflections with $|F_o| > 3\sigma|F_o|$ were used in the structure refinement, which gave $R = 0.074$ (the inverse sense of chirality gave the same R factor); the x and z coordinates of Sc(1) were held fixed at 0.7500 and 0.2500, respectively.[7] The authors noted two unusual features of their results:

(i) Sc(1) has a normal atomic displacement parameter ($B_{eq} = 1.23$ Å^2, from BCSJ 8796), while that for Sc(2) is $B_{eq} = 8.19$ Å^2.

(ii) The values of d(Sc—O) about Sc(1) range from 2.031 (7) to 2.095 (8) Å, while those around Sc(2) are in the range 2.307 (10) to 2.556 (10) Å.

The non-equivalence of Sc(1) and Sc(2) rules out space groups $P2/n$ and $P2_1/n$.

We first describe possible explanations for these effects and then give results for further refinement of the structure. As the compound was synthesized from Sc_2O_3 and sodium *m*-nitrobenzenesulfonate, one could infer that Sc(2) is really Na^+. This could account for the large ADP and also for the difference between the two groups of Sc—O (*sic*) distances as the ionic radius for octahedral Na^+ is 0.3 Å larger than that of octahedral Sc^{3+}. Thus the correct formula of the compound would be {[$NaSc(O_2NC_6H_4SO_3)_4\cdot 4H_2O$]}. Tateyama *et al.* (1988*a*,*b*) measured the crystal density as 1.79 (3) g cm^{-3}. The calculated values for the 'Sc_2' and 'NaSc' formulae are 1.811 (1.82 given in the paper) and 1.774. No definite conclusion can be drawn. CHN chemical analyses were also reported: the measured values are (wt%) C = 30.11, H = 2.48, N = 5.86; the calculated values for the two formulae are C = 29.76, H = 2.29, N = 5.78 and C = 30.39, H = 2.55, N = 5.91. The 'NaSc' formula is marginally favored but the difference is very small. Unfortunately, the Sc content was not determined directly.

The suggestion that Sc(2) is really Na^+ can be checked by repeating the structure analysis using the 4507 F_{obs} values from BCSJ 8796. A full refinement was carried out, including H atoms. The final R_F factor was 0.05 compared with 0.074 for the 1988 refinement; the Flack parameter was 0.002 (65), while the earlier refinement showed the same R_F value for both configurations. The ADPs of Sc and Na show the latter to be less tightly bound than the former. H atoms on the O atoms of the moieties formerly described as hydroxyl and now as water could not be identified with certainty and do not provide evidence favoring any one formulation. The two sets of metal–ligand distances now conform to standard values. This compound shows local symmetry with the Sc (Na) atoms at local approximate centers of symmetry.

5.3. The $(CH_3NH_3)_4MX_7$ (M = In, Fe, V, Yb; X = Cl, Br) family of structures

Four compounds of formula $(CH_3NH_3)_4MX_7$ (M = In, Fe, V; X = Cl, Br) have isomorphous structures, space group $P2/n$, $Z = 4$ (Table 5). There is a hydrogen-bonded arrangement of two independent $(CH_3NH_3)^+$ cations, two independent octahedral $(MX_6)^-$ anions centered at Wyckoff positions a $(0,0,0;\ \frac{1}{2},0,\frac{1}{2})$ and d $(0,0,\frac{1}{2};\ \frac{1}{2},0,0)$, and two independent Cl^- anions at Wyckoff positions e $(\frac{3}{4},y,\frac{3}{4};\ \frac{1}{4},-y,\frac{1}{4})$ and f $(\frac{3}{4},y,\frac{1}{4};\ \frac{1}{4},-y,\frac{3}{4})$ on twofold axes. This arrangement was first described in detail by Knop *et al.* (1987) for $(CH_3NH_3)_4InCl_7$, the structure of which had been determined earlier by Schlimper & Ziegler (1972).

This structural harmony is disturbed by the results reported for the 'extremely hygroscopic and instable in air' {$(CH_3NH_3)_4YbCl_7$} by Czjzek *et al.* (1992) (FOXTIV10).

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[7] Four-circle diffractometer; Mo $K\alpha$, 2θ scan range 3–65°; 6721 independent reflections measured; $-43 \le h \le 43$, $0 \le k \le 15$, $0 \le l \le 9$; absorption and extinction not corrected; no details given about possible use of Friedel pairs; block-diagonal refinement; H atoms not included in structure factor calculations.

Table 5
Cell dimensions for compounds of formula $(CH_3NH_3)_4[M^{III}X_6]^{3-}$ X^-.

The first four compounds all crystallize in space group *P*2/*n* with *Z* = 4. FOXTIV10 was reported as monoclinic, *Z* = 2, space group *P*2, but can be transformed to the pseudo cell given in the table.

Compound	*a*	*b*	*c*	*β*	Refcode (Reference†)
$(CH_3NH_3)_4[In^{III}Cl_6]^{3-}$ Cl^-	16.113	7.446	16.163	103.75	FUVCEE (1)
$(CH_3NH_3)_4[Fe^{III}Cl_6]^{3-}$ Cl^-	15.998 (3)	7.292 (1)	16.056 (3)	103.57 (2)	TOQCUX (2)
$(CH_3NH_3)_4[V^{III}Cl_6]^{3-}$ Cl^-	15.968 (4)	7.295 (3)	16.030 (4)	103.60 (3)	YUDFUY (3)
$(CH_3NH_3)_4[In^{III}Br_6]^{3-}$ Br^-	16.727	7.722	16.838	103.14	HXBRIN (4)
$(CH_3NH_3)_4[Yb^{III}Cl_6]^{3-}$ Cl^- ‡	16.205	7.605	16.351	104.44	FOXTIV10 (5)

† References: (1) Knop *et al.* (1987); (2) James *et al.* (1996); (3) Halepoto *et al.* (1995). These authors do not mention the earlier work in references (1), (4) or (5); (4) Khan & Tuck (1981); (5) Czjzek *et al.* (1992). ‡ Transformed pseudo cell.

These authors gave a monoclinic cell *a* = 9.972, *b* = 7.605, *c* = 12.866 Å, *β* = 90.53°, *Z* = 2, space group *P*2, although it was stated that 'Weissenberg photographs revealed orthorhombic symmetry'. The authors remark: 'No systematic absences were observed for the Yb compound, in contrast to the In compound. We therefore conclude that the asymmetric space group is the correct one for the title compound.' No reasons were given for selection of space group *P*2 from the three alternatives *P*2, *Pm* or *P*2/*m*. Refinement of the structure in *P*2 (anisotropic displacement parameters) using 1464 independent absorption-corrected reflection intensities collected at 273 K by an *ω*-scan technique with Mo *Kα* radiation (Nicolet four-circle diffractometer, $R_{\rm merge} = 0.0474$) gave *R* = 0.072; the Flack parameter was not reported, N(1) and C(3) were refined isotropically; no H atoms were found. The *P*2 monoclinic cell can be transformed into a monoclinic *pseudo* cell with *Z* = 4 (Table 5) and the reported structure is similar, but not identical, to the four isomorphous structures noted above. The structure given for $(CH_3NH_3)_4YbCl_7$ has the remarkable feature that there are two N—H···Cl hydrogen bonds with *d*(N···Cl) values of 2.80 and 2.77 Å, about 0.5 Å shorter than the usual value of 3.2–3.3 Å [the lower limit found for *d*(N—H···Cl) is about 3.0 Å]. This difference was mentioned but not discussed by Czjzek *et al.* (1992). We used the CSD to survey *d*(N—H···Cl) values in the range 2.7–2.9 Å and found 15 such values but checking showed all to be caused by errors of various kinds (details deposited).[8] Thus, the unusually short distances reported for FOXTIV10 are (so far) unique. Although it is difficult to envisage a rationale for such shortened hydrogen bonds, the structure determination appears to meet the usual criteria of correctness.

Other possible descriptions of the reported crystal structure can be considered. One is that the crystals are indeed orthorhombic, as indicated by the Weissenberg photographs. This would require an error of 0.5° in the value of *β*, which seems unlikely although there are precedents (some quoted by Marsh *et al.*, 2002). After setting *β* = 90°, the *P*2 cell was transformed to *Pba*2 (No. 32) by (100 00$\bar{1}$ 010); the coordinate pairs are Yb1, 2; Cl1, 2; Cl3, 7; Cl5, 6; Cl4, 8; N1, 2; N3, 4; C1, 2; C3, 4. The short N···Cl distances remain essentially unchanged. Change of space group implies that systematic absences were missed. Our attempt to retrieve the measured *F*-values was not successful. There are so many unresolved problems with this structure that redetermination appears essential to confirm, or otherwise, its unusual features.

6. Discussion

Chemically similar compounds often, but not always, crystallize in structures that are similar (which we call 'isostructural') or very similar (which we call 'isomorphous'). At present, we are hardly able to account for such subtle differences. One requirement is to establish whether apparent differences are indeed real or due to factors such as a wrong space group. The structures of ZIXQOM and ZIXRAZ are confirmed as isomorphous but changed from triclinic to monoclinic. A similar change is made for isostructural VINBAV10. Real differences are shown for the group of GAMTUJ, SONHOS, WIHSAH and ZIXRED. However, the differences reported among the family of $[Cu(H_2O)(phenanthroline)_2](X)_2$ structures and within a family of framework structures are here ascribed to errors. Space groups for the triclinic ZIFLAB (Cs/Cd) and monoclinic $\{[NaSc(O_2NC_6H_4SO_3)_4{\cdot}4H_2O]_n\}$ structures were correct, but metal atoms were probably wrongly identified in the first of these compounds and certainly in the second. A paradox appears in the group of $(CH_3NH_3)_4MX_7$ (*M* = In, Fe, V; *X* = Cl, Br) structures because the apparently faultless chemically similar $(CH_3NH_3)_4YbCl_7$ structure differs from the other four that have been reported as isomorphous. Furthermore, the occurrence of surprisingly short N···Cl hydrogen bonds in $(CH_3NH_3)_4YbCl_7$ suggests that the validity, or otherwise, of these features needs to be established by a redetermination of the structure. In addition, a number of space-group errors are corrected.

Crystal structure determination based on modern measuring instruments and computational tools is a remarkably powerful technique, but not without its pitfalls. Most structures reported are without significant blemish, but a few (not negligible in number) are only first approximations to the correct detailed structures. Lack of detail, or incorrect detail, can be the source of misleading conclusions.

We are grateful to Dr R. E. Marsh (Pasadena) for his interest and for information about a number of the structures

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[8] Another example of misleading information in the CSD is given by Dalhus & Görbitz (2000). These authors searched for occurrences of organic racemates in space groups containing only proper symmetry elements. 139 hits were found initially, but only 17 survived critical scrutiny.

discussed, to Professor H. D. Flack (Geneva) for discussion of the Flack parameter, and to Professor Hatsumi Mori (Tokyo) for helpful correspondence.

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