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Three Incorrect Space Groups in *Inorganica Chimica Acta*, Volume 142*

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Three crystal structures reported in Volume 142 (1988) of *Inorganica Chimica Acta* were almost surely described in space groups of unnecessarily low symmetry. In two cases the decrease in symmetry resulted in a lowering of Laue symmetry (from *mmm* to $2/m$); since in such cases there is no inherent problem in refinement [1], the reported molecular geometries are essentially correct and reformulation in the higher symmetry results in only minor adjustments. In the third case, however, a center of symmetry went unrecognized; as a result, the earlier refinement led to some peculiar bond lengths and angles.

(1) Bismuth Hexacyanoferrate(III) tetrahydrate, $BiFe(CN)_6 \cdot 4H_2O$

The crystal structure of this compound was described [2] as monoclinic, space group $P2_1/m$, with $a = 7.420(1)$, $b = 13.678(2)$, $c = 7.421(1)$ Å, $\beta = 119.76(1)°$, $Z = 2$. It is properly described as orthorhombic, space group *Cmcm*. The lattice vectors [101], $[10\bar{1}]$, and [010] describe a C-centered cell with $a' = 7.447$, $b' = 12.837$, $c' = 13.678$ Å, $\alpha' = \beta' = 90.0°$, $\gamma' = 90.01°$, $Z = 4$; the corresponding transformations $x' = (x + z)/2$, $y' = (x - z)/2$, $z' = y$ result in coordinates that are in accord with *Cmcm* within the reported e.s.d.s. (There are four misprints in the original list of coordinates (Table I, ref. 2): the x coordinates of C(1), C(2) and O(3) and the z coordinate of C(2) must be presumed to be negative rather than positive if the bond distances and angles in Table 2 are to be reproduced.) After appropriate averaging over equivalent atoms, the *Cmcm* coordinates of Table 1 result.

TABLE 1. $BiFe(CN)_6 \cdot 4H_2O$: Coordinates, Space Group *Cmcm*

Atom	Site	x	y	z
Bi	4(c)	0.5	−0.1763	0.25
Fe	4(a)	0.0	0.0	0.5
C(1)	8(f)	0.0	−0.1370	0.5583
C(2,3)	16(g)	0.1875	−0.0480	0.4121
N(1)	8(f)	0.0	−0.2185	0.5936
N(2,3)	16(g)	0.2975	−0.0750	0.3610
O(1)	8(f)	0.5	0.1575	0.4023
O(2,3)	8(m)	0.2625	0.2130	0.25

Since the original (monoclinic) values of a and c are effectively equal and β is close to 120°, the earlier authors [2] investigated the possibility that the cell is hexagonal; but they rejected this hexagonal cell and the corresponding orthohexagonal (orthorhombic) cell since the necessary intensity equivalences were absent. The true orthorhombic cell described here is rotated by about 60° from the conventional orthohexagonal cell; it results only from the condition that $a = c$ (monoclinic cell), and hence that [101] is perpendicular to $[10\bar{1}]$. With the revision of the structure, the compound is indeed isomorphous with the lanthanide compounds $LnCo(CN)_6 \cdot 4H_2O$ described by Hulliger *et al.* [3, 4].

(2) $(+)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$

The structure of this compound was described [5] as monoclinic, space group $P2_1$, with $a = 8.084(14)$, $b = 8.527(2)$, $c = 32.706(21)$ Å, $\beta = 104.32(10)°$, $Z = 4$. It is properly described as orthorhombic, space group $P2_12_12_1$. The vectors [100], [010] and [101] describe a cell with $a' = 8.084$, $b' = 8.527$, $c' = 31.690$ Å, $\alpha' = \gamma' = 90.0°$, $\beta' = 90.01°$, $Z = 4$. The necessary coordinate transformations are $x' = x - z + 0.75$, $y' = y - 0.0475$, $z' = z + 0.25$, the translations being necessary to place the origin at its conventional point. After transforming and averaging over pairs of atoms in the two independent molecules of $P2_1$, the $P2_12_12_1$ coordinates of Table 2 result.

The earlier authors noted that the two independent molecules in their $P2_1$ description had "essentially identical" conformations although "the packing environment of the two molecules is different", and hence concluded that the conformation was an energy minimum "over which packing forces have no control". In the revised, $P2_12_12_1$ description, all molecules are identical, not only in conformation but also in environment, and there is no reason to conclude that the environment would be unimportant in determining the molecular conformation.

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*The authors of refs. 2, 5 and 6 have been given the opportunity to publish replies alongside this paper. D. F. Mullica and E. L. Sappenfield's reply is thus published immediately following (*Inorg. Chim. Acta, 157* (1989) 3).

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TABLE 2. $(+)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$: Coordinates, Space Group $P2_12_12_1$

Atom	*x*	*y*	*z*
Fe	0.5312	0.0404	−0.1758
P	0.4027	−0.0590	−0.1212
O(6)	0.220	0.146	−0.214
O(7)	0.643	0.252	−0.114
C(6)	0.338	0.108	−0.198
C(7)	0.568	0.238	−0.147
C(1)	0.676	0.044	−0.233
C(2)	0.779	0.070	−0.197
C(3)	0.768	−0.063	−0.170
C(4)	0.658	−0.172	−0.190
C(5)	0.602	−0.106	−0.228
C(8)	0.510	0.386	−0.165
C(9)	0.282	0.078	−0.088
C(10)	0.128	0.126	−0.104
C(11)	0.038	0.240	−0.082
C(12)	0.102	0.308	−0.046
C(13)	0.255	0.260	−0.030
C(14)	0.345	0.144	−0.052
C(15)	0.243	−0.204	−0.134
C(16)	0.130	−0.252	−0.103
C(17)	0.013	−0.368	−0.113
C(18)	0.010	−0.434	−0.153
C(19)	0.123	−0.386	−0.184
C(20)	0.239	−0.270	−0.174
C(21)	0.538	−0.163	−0.083
C(22)	0.510	−0.318	−0.072
C(23)	0.611	−0.390	−0.042
C(24)	0.739	−0.306	−0.023
C(25)	0.768	−0.150	−0.034
C(26)	0.667	−0.079	−0.065

(3) $[Li(THF)_2]_2(\mu$-$Cl)_4(\eta^5$-$C_5H_5)Nd \cdot THF$

The structure of this compound was described [6] as orthorhombic, space group *Pna*2_1, with a = 16.814(4), b = 18.931(4), c = 10.504(2) Å, Z = 4. (The cell dimensions listed here are cyclically permuted from those given in ref. 6; without this permutation, the bond lengths and angles cannot be reproduced.) It is highly probable that the correct space group is *Pnam*.

The *Pnam* structure, Table 3 (which is here described in the conventional setting *Pnma*), is derived by placing the Nd, Li, and several other atoms on the added mirror plane at y = 0.25 and averaging the coordinates of the remaining pairs of atoms (which are approximately related by this mirror plane). The shifts necessary to achieve the higher symmetry range up to about 0.4 Å – much larger than in the previous two examples, but not atypical of the distortions caused when an effectively centrosymmetric structure is refined in a non-centrosymmetric space group [1, 7]. Other indications of the near-singularities in the earlier, *Pna*2_1 refinement include highly disparate and often unrealistic e.s.d.s (ref. 6, Table 2) and unusual interatomic distances, such as Li–Cl distances ranging from 2.17(6) to 2.55(7) Å (ref. 6, Table 3) and C–O from 1.33(3) to 1.58(3) Å (as calculated from the published coordinates). Many of these surprises disappear when the structure is symmetrized (Li–Cl, 2.33 and 2.37 Å; C–O, 1.39–1.45 Å). However, final confirmation and refinement of the *Pnma* model should be based on the observed diffraction intensities, which apparently are not available.

TABLE 3. $[Li(THF)_2]_2(\mu$-$Cl)_4(\eta^5$-$C_5H_5)Nd \cdot THF$: Coordinates, Space Group *Pnma*. Cell Dimensions: a = 16.816, b = 10.504, c = 18.931 Å

Atom	*x*	*y*	*z*
Nd	0.2220	0.25	0.5405
Cl(3,4)	0.2952	0.0772	0.4494
Cl(1,2)	0.1098	0.0762	0.5858
O(1)	0.1256	0.25	0.4386
C(11,14)	0.0948	0.1360	0.4052
C(12,13)	0.0608	0.1802	0.3378
O(2)	0.0257	0.25	0.7235
C(21,24)	0.0321	0.1403	0.7692
C(22,23)	0.0796	0.1805	0.8310
O(3)	−0.0759	0.25	0.5934
C(31)	−0.1007	0.25	0.5230
C(32)	−0.1883	0.25	0.5219
C(33)	−0.2141	0.25	0.5983
C(34)	−0.1428	0.25	0.6379
O(4)	0.3246	0.25	0.2933
C(41,44)	0.3095	0.1454	0.2506
C(42,43)	0.2754	0.1878	0.1836
O(5)	0.4657	0.25	0.3966
C(51,54)	0.5100	0.1414	0.4098
C(52,53)	0.5756	0.1810	0.4538
Li(1)	0.0308	0.25	0.6240
Li(2)	0.3494	0.25	0.3893
C(1,2)	0.2761	0.1834	0.6742
C(3,5)	0.3344	0.1422	0.6166
C(4)	0.3705	0.25	0.5972

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