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More Space-Group Changes*

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Abstract

Revised structures are reported for 19 crystalline compounds, based on space groups of higher symmetry than originally reported. In four cases the Laue symmetry is changed, one from $\bar{1}$ to $2/m$ and three from $2/m$ to mmm ; in the remaining fifteen a center of symmetry has been added. For eight of these latter compounds we have obtained F values and carried out least-squares refinements in the centrosymmetric space groups, with more satisfactory results than originally reported.

Introduction

We present here revised crystal structures for nineteen additional (Marsh & Herbstein, 1983, and references therein) compounds for which the original descriptions were based on space groups of unnecessarily low symmetry. In four cases the crystal class is revised, one from triclinic to monoclinic and three from monoclinic to orthorhombic; in the remaining fifteen, centers of symmetry are added. As noted earlier (Schomaker & Marsh, 1979), the increases in Laue symmetry have involved no significant changes in the structural parameters; the additional symmetry elements have become crystallographically exact rather than approximate and, usually, unrecognized. On the other hand, the additions of centers of symmetries have removed inherent singularities associated with refining a centrosymmetric structure in a non-centrosymmetric space

group, and highly significant parameter changes usually resulted. For eight of the non-centrosymmetric-to-centrosymmetric cases we have been able to obtain the original F data and carry out successful refinements. Details follow.‡

Category 1: changes in Laue group

Methyl 8-isopropyl-3,3a,8,8a-tetrahydroindeno[2,1-c]-pyrazole-8a-carboxylate, $C_{15}H_{18}N_2O_2$

The structure of this compound was reported as triclinic, space group $P\bar{1}$, $Z = 2$ (Toupet & Messenger, 1984a; the correct value for Z is 4); the cell dimensions were subsequently corrected to: $a = 5.791$ (4), $b = 15.503$ (4), $c = 15.954$ (5) Å, $\alpha = 82.24$ (5), $\beta = 79.35$ (6), $\gamma = 79.13$ (5)° (Toupet & Messenger, 1984b). The structure is better described in $C2/c$.

The vectors $[-1,2,0]$, $[-1,0,0]$, $[0,-1,1]$ define a C -centered cell with $a' = 30.450$, $b' = 5.791$, $c' = 20.690$ Å, $\alpha' = 90.07$, $\beta' = 131.09$, $\gamma' = 90.11$ °, $Z = 8$; the corresponding transformation $x' = \frac{1}{2}(y+z)$, $y' = -x - \frac{1}{2}(y+z)$, $z' = z$ leads to coordinates that are compatible with $C2/c$ within the reported e.s.d.'s. The $C2/c$ coordinates, averaged over molecules A and B , are given in Table 1.

The c -glide plane of $C2/c$ requires the absence of reflections $0kl$ with $(k+l)$ odd in the triclinic system. The supplementary table of F 's (SUP 38963) contains

‡ Lists of observed and calculated structure factors for nine of the compounds, and anisotropic thermal parameters for ten of the compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44411 (76 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. $C_{15}H_{18}N_2O_2$: coordinates ($\times 10^4$ for x' and z' , $\times 10^3$ for y'), space group $C2/c$

Numbers in square brackets are displacements of the individual atoms, as earlier described in space group $P\bar{1}$, from the averaged values given here; numbers in parentheses are (averaged) e.s.d.'s for the individual atoms.

	x'	y'	z'
O(1)	3870 1 (2)	-61 2 (1)	6590 3 (4)
O(2)	3796 1 (2)	-439 1 (1)	6256 0 (4)
N(1)	2458 2 (2)	-209 0 (1)	4190 0 (4)
N(2)	2914 0 (2)	-321 2 (1)	4604 2 (4)
C(1)	2585 5 (3)	48 0 (1)	4376 3 (6)
C(2)	3214 2 (3)	73 0 (1)	4785 1 (5)
C(3)	3463 4 (3)	-175 1 (1)	5160 4 (6)
C(4)	3856 0 (3)	-237 0 (1)	4983 1 (5)
C(5)	3626 0 (3)	-92 1 (1)	4209 8 (5)
C(6)	3298 2 (3)	90 2 (1)	4140 6 (5)
C(7)	3052 4 (3)	253 0 (1)	3492 2 (6)
C(8)	3140 6 (3)	231 1 (2)	2929 5 (6)
C(9)	3449 1 (3)	49 0 (2)	2968 4 (6)
C(10)	3695 3 (3)	-114 2 (2)	3612 10 (6)
C(11)	4522 1 (3)	-203 2 (1)	5741 7 (6)
C(12)	4692 4 (3)	51 0 (2)	6020 8 (6)
C(13)	4893 3 (4)	-297 1 (2)	5566 9 (6)
C(14)	3724 5 (3)	-206 2 (1)	6078 0 (5)
C(15)	4058 3 (4)	-494 2 (2)	7122 10 (6)

Table 2. 2,2',4,4'-Tetraaminodiphenyl at 153 K: coordinates ($\times 10^4$), space group $Fdd2$

Numbers in square brackets are shifts in the original (Bb) positions of individual atoms, necessary to satisfy the twofold axis in $Fdd2$. E.s.d.'s in the individual atoms are about 0.0005 in x' , 0.0003 in y' and 0.0020 in z' (Gridunova *et al.*, 1983).

	x'	y'	z'
N(1),(4)	2909 3	-1127 0	523 23
N(2),(3)	-86 3	-625 2	-3105 5
C(1),(7)	469 4	-157 5	43 17
C(2),(8)	628 0	-540 2	-1500 15
C(3),(9)	1465 7	-852 1	-1352 22
C(4),(10)	2123 2	-771 1	322 32
C(5),(11)	1995 3	-382 1	1818 8
C(6),(12)	1168 3	-82 1	1692 37

entries for only 14 such reflections [there are entries for 136 reflections $Ok\bar{l}$ with $(k+l)$ even]. All 14 $F(\text{obs.})$ values are quite small; moreover, the $F(\text{cal.})$ values based on the $P\bar{1}$ structure are much smaller, averaging only 24% as large as $F(\text{obs.})$. Thus, the $P\bar{1}$ structure does little better than $C2/c$ in explaining the weak violations of the glide plane, which may be due to other effects such as twinning or double reflection. In any event, the fact that the coordinates show the symmetry of $C2/c$ within their e.s.d.'s (Table 1) leaves no doubt that $C2/c$ is the appropriate space group.

2,2',4,4'-Tetraaminodiphenyl, $C_{12}H_{14}N_4$, at 153 K

Crystals of this compound have been reported as monoclinic, space group Bb , with $a = 6.089$ (2), $b = 13.517$ (3), $c = 13.635$ (3) Å, $\gamma = 102.89$ (2)°, $Z = 4$ (Gridunova, Shklover, Struchkov & Chayanov, 1983). The authors noted that a metrically orthorhombic cell could be chosen but pursued refinement in Bb to an R of 0.068 for 686 reflections with $F^2 > 2\sigma(F^2)$. The orthorhombic space group $Fdd2$ is to be preferred.

The vectors $[0,0,-1]$, $[1,2,0]$, $[1,0,0]$ define a cell with $a' = 13.635$, $b' = 26.353$, $c' = 6.089$ Å, $\alpha' =$

89.87 , $\beta' = \gamma' = 90^\circ$, $Z = 8$. The corresponding transformations $x' = -z + 0.3750$, $y' = \frac{1}{2}y - 0.1627$, $z' = x - \frac{1}{2}y$ (the translations are necessary to place the origin on a twofold axis) yield coordinates for atom pairs that are compatible with space group $Fdd2$ within the reported e.s.d.'s. The $Fdd2$ coordinates, and the shifts necessary to achieve that symmetry, are given in Table 2.

The change in space group requires that the molecule have an exact twofold axis, but does not otherwise significantly change the description of the structure.

Terpin

The crystal structure of terpin, *trans*-4-(1-hydroxyisopropyl)-1-methylcyclohexan-1-ol monohydrate ($C_{10}H_{20}O_2 \cdot H_2O$), was described as monoclinic, space group Cc , with $a = 10.912$ (3), $b = 22.791$ (4), $c = 10.705$ (2) Å, $\beta = 120.64$ (2)°, $Z = 8$ (Ho, Cheng, Peng, Chen & Tsau, 1986). It is properly described as orthorhombic, space group $Fdd2$. The vectors $[1,0,2]$, $[0,-1,0]$, $[1,0,0]$ describe a cell with $a' = 18.421$, $b' = 22.791$, $c' = 10.912$ Å, $\alpha' = \beta' = \gamma' = 90.00^\circ$, $Z = 16$; the corresponding coordinate transformations $x' = \frac{1}{2}(z - 0.2024)$, $y' = -y + 0.1250$, $z' = x - z/2$ lead to a structure that conforms quite closely to the symmetry of $Fdd2$. Since in a few cases [most notably, C(8) and the water molecule O(13)] the additional symmetry element—a twofold axis—relating the two independent molecules in Cc was not quite satisfied within three e.s.d.'s, we have obtained the original data in order to confirm that $Fdd2$ is appropriate.

Values of F_o for 1663 reflections coded as 'observed' were recovered from SUP 43195;* none was of the type $(2h, k, -h)$ with $(2h+k) \neq 4n$ (in the monoclinic indexing) that would be forbidden by the additional d -glide plane of $Fdd2$. Reindexing and averaging according to Laue symmetry mmm led to an R for averaging of 0.029. Refinement in $Fdd2$ converged routinely to an R of 0.0259 for 927 averaged reflections, compared to 0.047 for 1665 reflections in the Cc description (Ho *et al.*, 1986). Final parameters are given in Table 3.

There are no major changes in the bond distances and angles reported by Ho *et al.* (1986).

Dithia[3.3.1]propellane

The structure of this compound was described (Herbstein, Ashkenazi, Kaftory, Kapon, Reisner & Ginsburg, 1986) in space group Cc [$a = 6.626$ (3), $b = 41.077$ (20), $c = 6.600$ (3) Å, $\beta = 120.11$ (5)°, Z

* SUP 43195 contained an interesting, systematic set of misprints that was obviously computer generated: whenever the slowest-moving index l changed from an odd to an even value, the first four (and only the first four) subsequent reflections showed l to have been decremented rather than incremented. This complicated the data-entry process.

Table 3. *Terpin*: final coordinates and U_{eq} values ($\times 10^4$), space group *Fdd2*

	x	y	z	U_{eq} *(Å ²)
C(1)	-237 (1)	2863 (1)	306 (3)	395 (6)
C(2)	237 (1)	2194 (1)	150 (3)	431 (6)
C(3)	529 (2)	1958 (1)	28 (3)	450 (7)
C(4)	1018 (1)	2118 (1)	1099 (3)	431 (6)
C(5)	1009 (1)	2782 (1)	1268 (3)	486 (7)
C(6)	246 (2)	3028 (1)	1390 (3)	500 (7)
C(7)	-1003 (1)	3128 (1)	383 (3)	435 (6)
C(8)	-976 (2)	3796 (1)	269 (4)	609 (8)
C(9)	-1418 (2)	2953 (2)	1522 (4)	635 (9)
O(10)	-1431 (1)	2911 (1)	-632 (-)	445 (4)
C(11)	1781 (2)	1887 (2)	909 (4)	638 (9)
O(12)	731 (1)	1874 (1)	2210 (2)	468 (5)
O(13)	408 (1)	723 (1)	1827 (3)	727 (7)
H(1)	-12 (11)	3018 (9)	-406 (21)	2.3 (5)
H(2,1)	-548 (13)	2083 (10)	-538 (25)	4.1 (6)
H(2,2)	-496 (13)	1999 (10)	893 (26)	4.1 (6)
H(3,1)	528 (12)	1522 (12)	-56 (23)	3.9 (6)
H(3,2)	736 (11)	2093 (9)	-690 (23)	2.5 (5)
H(5,1)	1332 (13)	2908 (10)	1938 (25)	3.6 (5)
H(5,2)	1274 (14)	2970 (11)	529 (26)	3.9 (6)
H(6,1)	273 (13)	3472 (11)	1435 (25)	4.8 (6)
H(6,2)	28 (13)	2899 (10)	2144 (21)	3.0 (5)
H(8,1)	-725 (15)	3976 (13)	909 (29)	5.6 (8)
H(8,2)	-728 (16)	3909 (13)	-538 (30)	6.1 (8)
H(8,3)	-1468 (13)	3941 (10)	243 (24)	3.6 (6)
H(9,1)	-1419 (15)	2508 (14)	1559 (30)	7.0 (9)
H(9,2)	-1206 (17)	3105 (15)	2238 (33)	6.6 (9)
H(9,3)	-1928 (17)	3104 (14)	1409 (32)	6.8 (8)
H(10)	-1242 (15)	3022 (12)	-1206 (28)	4.2 (8)
H(11,1)	2007 (15)	2045 (11)	179 (27)	4.3 (7)
H(11,2)	1757 (13)	1463 (12)	850 (25)	4.8 (7)
H(11,3)	2084 (15)	2025 (12)	1509 (29)	4.8 (7)
H(12)	670 (15)	1527 (12)	2106 (27)	4.8 (8)
H(13,1)	613 (17)	431 (14)	1901 (34)	6.4 (10)
H(13,2)	-41 (19)	658 (15)	1863 (39)	8.0 (11)

* $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$, B_{iso} values are given for H atoms.

= 8] and refined to an R of 0.057 ($wR = 0.062$) for 1164 reflections and 241 parameters. Space group *Fdd2* is to be preferred. The vectors [1,0,2], [0,1,0] and [-1,0,0] define an effectively orthogonal cell ($a' = 11.419$, $b' = 41.077$, $c' = 6.626$ Å, $\alpha' = \gamma' = 90$, $\beta' = 90.02^\circ$, $Z = 16$) and the corresponding coordinate transformations $x' = (z - 0.0385)/2$, $y' = y + 1/8$, $z' = -x + z/2$ lead to a structure in *Fdd2* that we have refined (based on the original data) to an R of 0.0441 ($wR = 0.0423$) for 577 *mmm*-averaged reflections and 121 parameters. The revised coordinates are given in Table 4.

Category 2: center of symmetry added, structure re-refined

Guanidinium pentacarbonatocerate tetrahydrate

The structure of this compound, $[\text{C}(\text{NH}_2)_3]_6[\text{Ce}(\text{CO}_3)_5 \cdot 1.4\text{H}_2\text{O}]$, was described (Voliotis, Rimsky & Faucherre, 1975; VRF) in space group *Bb* [monoclinic, first setting, $a = 16.05$ (3), $b = 16.63$ (3), $c = 13.14$ (3) Å, $\gamma = 108.10$ (22)°, $Z = 4$] and refined to an R of 0.072 for 4059 reflections with $I > 2\sigma(I)$. However, the results of this refinement were manifestly unsatisfactory: bond lengths were disparate [for example, C—O bonds in the carbonato groups ranged from 1.114 (24) to 1.549 (23) Å and C—N bonds in the guanidine groups from 1.153 (28) to 1.577 (38) Å],

Table 4. *Dithia*[3.3.1]propellane: coordinates ($\times 10^5$ for S, $\times 10^4$ for C, $\times 10^3$ for H) and U_{eq} values ($\times 10^4$) after refinement in *Fdd2*

	x'	z'	z'	U_{eq} *(Å ²)
S(1)	32806 (17)	40587 (4)	62715 (-)	828 (5)
S(2)	15645 (17)	48118 (4)	9977 (40)	849 (5)
C(1)	1738 (4)	4348 (1)	3806 (9)	555 (13)
C(2)	1857 (7)	4252 (2)	5996 (12)	742 (19)
C(3)	3886 (6)	4249 (2)	4026 (13)	742 (18)
C(4)	2877 (4)	4346 (1)	2711 (10)	527 (13)
C(5)	3009 (6)	4637 (2)	1352 (15)	726 (18)
C(6)	972 (6)	4631 (2)	3254 (11)	673 (17)
C(7)	1969 (6)	4097 (2)	2220 (11)	676 (17)
H(21)	183 (6)	445 (2)	686 (12)	9 (2)
H(22)	122 (9)	407 (2)	667 (19)	18 (4)
H(31)	448 (7)	408 (2)	348 (16)	11 (3)
H(32)	425 (5)	443 (1)	438 (9)	6 (2)
H(51)	358 (5)	480 (1)	204 (11)	8 (2)
H(52)	326 (6)	458 (2)	25 (14)	9 (3)
H(61)	17 (5)	457 (1)	290 (8)	5 (1)
H(62)	99 (5)	480 (2)	462 (11)	9 (2)
H(71)	216 (4)	387 (1)	266 (9)	6 (2)
H(72)	150 (6)	414 (1)	104 (12)	8 (2)

* See footnote, Table 3.

and the U_{ij} matrices for many of the atoms were non-positive-definite. Space group *B2/b* is to be preferred.

Full-matrix refinement in *B2/b* (we describe the structure in the more conventional second setting, *C2/c*) converged at an R of 0.067 for 4058 reflections recovered from SUP 31066, compared to 0.072 for the *Bb* model. The final *C2/c* coordinates are given in Table 5. The U_{ij} 's for all atoms are entirely reasonable. A summary of bond lengths and angles for both the *Bb* and the *C2/c* refinements is given in Table 6; the *C2/c* results are obviously more believable.

VRF selected the non-centrosymmetric space group *Bb* over *B2/b* (*C2/c*) because of a 'very strong' piezoelectric effect; nevertheless, they noted that the crystal morphology was centrosymmetric (*2/m*). Furthermore, Voliotis & Rimsky (1975) report that the isomorphous thorium compound (whose structure was similarly described in space group *Bb*; see Category 3) also showed holohedral morphology but an inconclusive test for piezoelectricity. It is surprising that the cerium compound could show strong piezoelectricity, since even the *Bb* description of the structure is very close to centrosymmetric. In any event, it is clear that the diffraction data are explained much better in space group *C2/c*; if the structure is indeed slightly distorted from centrosymmetric, these diffraction data are unable to arrive at a unique, correct structure because of their insensitivity to such distortions (Marsh, 1986).

Anthra[2,1,9,8-*hijkl*]*benzo*[*naphtho*[2,1,8,7-*stuv*]-*pentacene*, $\text{C}_{38}\text{H}_{18}$

The structure of this compound (Fujisawa, Oonishi, Aoki, Ohashi & Sasada, 1982; FOAOS) was described in space group *Pa* [monoclinic, $a = 31.276$ (4), $b = 3.7818$ (4), $c = 21.663$ (3) Å, $\beta = 124.22$ (1)°, $Z = 4$] and refined to $R = 0.073$ for 2619 reflections with

Table 5. Guanidinium pentacarbonatocerate tetrahydrate: coordinates and U_{eq} values ($\times 10^4$), space group $C2/c$

Cell dimensions: $a = 16.05$ (3), $b = 13.14$ (3), $c = 16.631$ (3) Å, $\beta = 108.10$ (22)°.

	x	y	z	U_{eq} *(Å ²)
Ce	5000	2742 (0.6)	2500	154 (1)
C(1.3)	3345 (5)	3732 (6)	2068 (5)	262 (18)
C(2)	5000	562 (8)	2500	210 (25)
C(4.5)	5010 (5)	2789 (8)	783 (4)	321 (16)
C(6.8)	3210 (5)	3897 (7)	-1338 (5)	324 (19)
C(7.11)	1124 (5)	5345 (7)	-38 (5)	346 (20)
C(9.10)	3717 (6)	6234 (7)	1011 (6)	402 (21)
O(11.33)	2602 (4)	4190 (5)	1845 (4)	399 (17)
O(12.32)	3412 (3)	2794 (5)	1944 (3)	395 (15)
O(13.31)	4055 (3)	4213 (4)	2470 (3)	276 (13)
O(21.23)	4341 (3)	1073 (4)	2037 (3)	284 (13)
O(22)	5000	-410 (6)	2500	342 (22)
O(41.52)	5568 (3)	2238 (5)	1360 (3)	348 (12)
O(42.51)	4526 (4)	3383 (5)	1057 (3)	485 (17)
O(43.53)	4944 (4)	2715 (6)	12 (3)	457 (14)
W(1.4)	3016 (4)	6593 (6)	-1150 (4)	618 (20)
W(2.3)	1355 (4)	6735 (5)	-2460 (5)	597 (19)
N(61.82)	3073 (5)	3132 (6)	-873 (5)	495 (5)
N(62.83)	3987 (4)	4333 (6)	-1144 (5)	407 (20)
N(63.81)	2540 (5)	4229 (6)	-1974 (5)	387 (20)
N(71.113)	1419 (5)	5640 (6)	762 (4)	415 (19)
N(72.112)	1480 (5)	4539 (6)	-285 (5)	484 (22)
N(73.111)	493 (5)	5858 (6)	-578 (4)	401 (19)
N(91.103)	3962 (5)	6197 (6)	1841 (5)	498 (22)
N(92.102)	3791 (6)	5421 (6)	566 (5)	472 (22)
N(93.101)	3408 (6)	7087 (6)	621 (5)	542 (23)

$$* U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 6. Guanidinium pentacarbonatocerate tetrahydrate: a summary of bond distances (Å) and bond angles (°) from the revised $C2/c$ refinement and from the original Bb refinement

No.*		Ce—O	C—O	C—N	O—C—O	N—C—N
	<i>C2/c</i>	5	8	9	8	9
	<i>Bb</i>	10	15	18	15	18
Value (avg.)	<i>C2/c</i>	2.442	1.279	1.323	120.0	120.0
	<i>Bb</i>	2.448	1.287	1.355	119.8	119.7
E.s.d. (avg.)	<i>C2/c</i>	0.006	0.012	0.013	0.9	0.9
	<i>Bb</i>	0.016	0.025	0.033	1.7	2.1
Scatter (r.m.s.)	<i>C2/c</i>	0.012	0.026	0.013	2.4	1.0
	<i>Bb</i>	0.035	0.132	0.102	6.0	6.7
Range	<i>C2/c</i>	2.430–	1.255–	1.314–	117.2–	118.2–
		2.458	1.313	1.337	123.2	121.6
	<i>Bb</i>	2.388–	1.114–	1.153–	110.7–	108.6–
		2.488	1.549	1.577	130.2	131.5

* Number of independent values.

Table 7. $C_{38}H_{18}$: coordinates and U_{eq} values, space group $P2_1/a$

	x($\times 10^4$)	y($\times 10^4$)	z($\times 10^4$)	U_{eq} *(Å ² $\times 10^4$)
C(1)	-170 (1)	1449 (10)	-2041 (2)	420 (8)
C(2)	-355 (1)	1367 (10)	-1588 (2)	477 (9)
C(3)	-60 (1)	2583 (11)	-858 (2)	493 (9)
C(4)	427 (1)	3930 (11)	-561 (2)	454 (9)
C(5)	641 (1)	4073 (10)	-985 (2)	384 (7)
C(6)	1140 (1)	5392 (10)	-705 (2)	391 (8)
C(7)	1340 (1)	5550 (9)	-1128 (2)	364 (8)
C(8)	1836 (1)	7058 (10)	-859 (2)	403 (9)
C(9)	2028 (1)	7150 (9)	-1280 (2)	379 (8)
C(10)	1749 (1)	5740 (9)	-2031 (2)	327 (7)
C(11)	1953 (1)	5736 (9)	-2470 (2)	338 (7)
C(12)	2503 (1)	6220 (9)	-2162 (2)	370 (7)
C(13)	2896 (1)	5404 (10)	-1424 (2)	395 (8)
C(14)	3411 (1)	6151 (10)	-1139 (2)	433 (9)
C(15)	3548 (1)	7662 (10)	-1584 (2)	449 (9)
C(16)	3174 (1)	8204 (10)	-2348 (2)	414 (8)
C(17)	3310 (2)	9447 (11)	-2837 (2)	514 (9)
C(18)	2954 (1)	9608 (11)	-3582 (2)	500 (9)
C(19)	2432 (1)	8558 (10)	-3903 (2)	435 (8)
C(20)	2067 (2)	8456 (11)	-4683 (2)	495 (9)
C(21)	1579 (2)	7223 (11)	-4987 (2)	503 (9)
C(22)	1417 (1)	6095 (10)	-4519 (2)	420 (8)
C(23)	908 (1)	4853 (10)	-4821 (2)	463 (9)
C(24)	751 (1)	3920 (10)	-4375 (2)	430 (9)
C(25)	1087 (1)	4214 (9)	-3585 (2)	375 (8)
C(26)	912 (1)	3515 (9)	-3103 (2)	352 (8)
C(27)	420 (1)	2070 (9)	-3380 (2)	388 (8)
C(28)	232 (1)	1784 (9)	-2937 (2)	373 (8)
C(29)	-274 (1)	350 (10)	-3222 (2)	435 (9)
C(30)	-463 (1)	222 (10)	-2797 (2)	468 (9)
C(31)	336 (1)	2827 (9)	-1739 (2)	364 (8)
C(32)	537 (1)	2983 (9)	-2185 (2)	342 (7)
C(33)	1035 (1)	4345 (9)	-1892 (2)	341 (7)
C(34)	1231 (1)	4550 (9)	-2347 (2)	332 (7)
C(35)	1602 (1)	5325 (9)	-3260 (2)	341 (7)
C(36)	1767 (1)	6271 (9)	-3741 (2)	373 (8)
C(37)	2281 (1)	7482 (9)	-3431 (2)	401 (8)
C(38)	2652 (1)	7342 (9)	-2640 (2)	367 (8)

	x($\times 10^3$)	y($\times 10^3$)	z($\times 10^3$)	B_{iso} (Å ²)
H(2)	-73 (1)	40 (10)	-184 (2)	4.2 (8)
H(3)	-22 (1)	256 (9)	-58 (2)	4.1 (8)
H(4)	64 (1)	488 (10)	-1 (2)	4.4 (8)
H(6)	136 (1)	629 (8)	-17 (2)	1.8 (6)
H(8)	203 (1)	805 (9)	-38 (2)	3.0 (7)
H(9)	237 (1)	832 (8)	-106 (2)	2.4 (6)
H(13)	281 (1)	425 (10)	-107 (2)	4.0 (8)
H(14)	369 (1)	548 (8)	-61 (2)	2.5 (6)
H(15)	394 (1)	842 (9)	-133 (2)	3.8 (8)
H(17)	367 (1)	1007 (9)	-263 (2)	3.6 (8)
H(18)	306 (1)	1030 (9)	-395 (2)	4.1 (8)
H(20)	218 (1)	930 (10)	-503 (2)	4.8 (9)
H(21)	130 (1)	706 (11)	-560 (2)	6.0 (10)
H(23)	65 (1)	471 (10)	-541 (2)	4.7 (8)
H(24)	40 (1)	314 (10)	-456 (2)	4.3 (8)
H(27)	18 (1)	116 (8)	-397 (2)	2.2 (6)
H(29)	-49 (1)	-48 (10)	-380 (2)	4.3 (8)
H(30)	-80 (1)	-61 (9)	-297 (2)	4.0 (8)

* See footnote, Table 5.

$F_o \geq 3\sigma(F_o)$. The space group $P2_1/a$ was originally considered, but was abandoned because the structure obtained by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) in that space group did not refine properly and because the 030 reflection 'had weak but significant intensity' on 200-h Weissenberg photographs. We had no difficulty in refining in $P2_1/a$.

After averaging the coordinates of molecules *A* and *B* (FOAOS, Table 2), we obtained rapid convergence in $P2_1/a$, to an *R* of 0.069 for 2618 reflections in the Supplementary Material (the reflection 211, with a very large F_c value, had no F_o value listed). The number of parameters in the full matrix was 416, including anisotropic U 's for the C atoms, isotropic B 's for H, and an isotropic extinction parameter [final value,

0.53 (3) $\times 10^{-6}$]. The earlier *Pa* refinement was 'block diagonal' and included 829 parameters (no extinction).

Since our $P2_1/a$ parameters (Table 7) are considerably more precise than those from the *Pa* refinement of FOAOS (the e.s.d.'s are approximately one-half as large), we list the revised C—C bond lengths in Table 8. FOAOS found appreciable differences in the dimensions of the two independent molecules in *Pa*: corresponding bond lengths differed by an r.m.s. amount of 0.029 Å (about 2σ) and the difference in the C(10)—C(11)—C(12) angles was so great, at 7.8°, as to prompt speculation that the two molecules used different types of distortion to relieve the H(9)···H(13) contacts. In $P2_1/a$ the two molecules are equivalent,

Table 8. $C_{38}H_{18}$: bond lengths (Å), space group $P2_1/a$

C(1)–C(2)	1.392 (6)	C(17)–C(18)	1.352 (6)
C(1)–C(30)	1.432 (6)	C(18)–C(19)	1.426 (6)
C(1)–C(31)	1.427 (5)	C(19)–C(20)	1.410 (6)
C(2)–C(3)	1.387 (6)	C(19)–C(37)	1.407 (5)
C(3)–C(4)	1.375 (6)	C(20)–C(21)	1.359 (6)
C(4)–C(5)	1.411 (6)	C(21)–C(22)	1.429 (6)
C(5)–C(6)	1.408 (5)	C(22)–C(23)	1.418 (6)
C(5)–C(31)	1.430 (5)	C(22)–C(36)	1.404 (5)
C(6)–C(7)	1.372 (5)	C(23)–C(24)	1.353 (6)
C(7)–C(8)	1.434 (5)	C(24)–C(25)	1.422 (5)
C(7)–C(33)	1.443 (5)	C(25)–C(26)	1.450 (5)
C(8)–C(9)	1.345 (5)	C(25)–C(35)	1.413 (5)
C(9)–C(10)	1.448 (5)	C(26)–C(27)	1.410 (5)
C(10)–C(11)	1.414 (5)	C(26)–C(24)	1.411 (5)
C(10)–C(34)	1.431 (5)	C(27)–C(28)	1.384 (5)
C(11)–C(12)	1.464 (5)	C(28)–C(29)	1.443 (5)
C(11)–C(35)	1.429 (5)	C(28)–C(32)	1.422 (5)
C(12)–C(13)	1.397 (5)	C(29)–C(30)	1.345 (6)
C(12)–C(38)	1.419 (5)	C(31)–C(32)	1.419 (5)
C(13)–C(14)	1.391 (6)	C(32)–C(33)	1.410 (5)
C(14)–C(15)	1.381 (6)	C(33)–C(34)	1.425 (5)
C(15)–C(16)	1.406 (6)	C(35)–C(36)	1.444 (5)
C(16)–C(17)	1.424 (6)	C(36)–C(37)	1.424 (5)
C(16)–C(38)	1.418 (5)	C(37)–C(38)	1.431 (5)

and the H(9)···H(13) distance is 2.06 (5) Å. An even more uncomfortable contact seems to exist between H(24) and H(27), at 1.91 (5) Å.

The very weak 030 reflection, even if it represents a true violation of $P2_1/a$, is surely unable to adequately break the inherent singularity so as to allow an unambiguous choice among the immense number of ways of distorting the centrosymmetric $P2_1/a$ structure into a non-centrosymmetric Pa structure.

$As_2O(SO_4)_2$

This compound forms monoclinic crystals with cell dimensions $a = 6.650$ (1), $b = 6.671$ (2), $c = 16.612$ (4) Å, $\beta = 94.34$ (2)°, $Z = 4$ (Mercier & Douglade, 1982; MD). On the basis of Weissenberg and precision photographs the authors report "the systematic extinctions $h0l$, $l = 2n + 1 \dots$ characteristic of the space groups Pc and $P2_1/c$ ". Since the As–As vectors on the Patterson map were not compatible with space group $P2_1/c$, the structure was described in Pc and refined to an R of 0.044 for 1066 reflections with $I > 2.5\sigma(I)$ (out of 2563 reflections surveyed). However, the list of 1066 reflections deposited with SUP 36737 contains none of the type $0k0$ with k odd, and the structure is better described in $P2_1/c$.

The $P2_1/c$ structure is derived by incrementing the coordinates (Table 1, MD) by $\Delta x = 0.30$, $\Delta y = 0.25$, $\Delta z = 0.04$. Initial refinement in $P2_1/c$ with all atoms anisotropic (as in MD) converged at an R of 0.048 for 118 parameters – slightly higher than the 0.044 for 233 parameters reported by MD. However, the structure-factor listing suggested that extinction was important, and introduction of an isotropic extinction parameter [final value, $2.34(10) \times 10^6$] led to convergence at $R = 0.038$. The final $P2_1/c$ parameters are given in Table 9.

As usual, the centrosymmetric $P2_1/c$ structure has led to smaller e.s.d.'s (by factors of $\frac{1}{2}$ to $\frac{1}{3}$) and to more

Table 9. $As_2O(SO_4)_2$: final parameters ($\times 10^4$), space group $P2_1/c$

	x	y	z	$U_{eq}^*(\text{Å}^2)$
As(1,4)	3012 (2)	2660 (2)	351 (1)	159 (2)
As(2,3)	1849 (2)	1227 (2)	2069 (1)	185 (2)
S(1,3)	–1474 (4)	2257 (4)	711 (1)	173 (5)
S(2,4)	2757 (4)	5740 (4)	1756 (2)	206 (5)
O(1,2)	3255 (11)	1198 (11)	1225 (4)	209 (15)
O(11,32)	283 (12)	2436 (15)	170 (4)	358 (21)
O(12,31)	–661 (13)	1205 (16)	1472 (5)	437 (23)
O(13,33)	–2920 (14)	950 (14)	312 (5)	444 (22)
O(14,34)	–2249 (18)	4137 (14)	884 (6)	588 (29)
O(21,42)	2889 (14)	5089 (11)	891 (4)	334 (28)
O(22,41)	1855 (18)	3971 (12)	2217 (6)	539 (48)
O(23,43)	1310 (14)	7270 (14)	1743 (5)	411 (22)
O(24,44)	4700 (15)	6198 (24)	2076 (6)	746 (41)

* See footnote, Table 5.

Table 10. α - KHo_2F_7 : coordinates and U_{eq} values ($\times 10^5$ for Ho, $\times 10^4$ for K and F), space group $C2/m$

	x	y	z	$U_{eq}^*(\text{Å}^2)$
Ho(1)	50000	24075 (8)	0	796 (10)
Ho(2,5)	75946 (6)	0	67845 (6)	702 (11)
Ho(3,4)	237 (3)	76275 (6)	68185 (3)	681 (8)
K(1,3)	2338 (3)	0	6526 (4)	209 (7)
K(2,4)	2621 (3)	0	195 (4)	136 (6)
F(1,2)	1018 (4)	2348 (7)	9160 (5)	134 (8)
F(3,8)	1170 (4)	2361 (7)	2369 (5)	125 (9)
F(4,18)	3955 (6)	5000	2494 (7)	136 (16)
F(5,10)	3954 (7)	0	9257 (7)	140 (14)
F(6,9)	3867 (6)	5000	6179 (7)	111 (12)
F(7,11)	1632 (4)	3331 (7)	4999 (4)	169 (10)
F(12,13)	1742 (4)	3294 (6)	7405 (5)	143 (9)
F(14,15)	4956 (7)	0	2632 (8)	168 (14)
F(16)	5000	3213 (10)	5000	192 (15)
F(17,19)	3951 (6)	5000	9128 (8)	130 (14)

* See footnote, Table 5.

regular geometry. Of particular note are the SO_4 tetrahedra: for the Pc refinement these tetrahedra were 'very deformed' (MD), with O–S–O angles ranging from 97 (3) to 133 (3)° and O–O contacts from 2.19 (4) to 2.66 (4) Å, while the $P2_1/c$ refinement leads to ranges of 105.7 (5)–117.5 (6)° and 2.33 (1)–2.47 (1) Å. Typically, the largest angles are between the short S–O(terminal) bonds and the smallest are between the longer S–O(bridge) bonds, a trend that tends to equalize the O–O distances.

α - KHo_2F_7

The structure of this room-temperature phase was described in space group Cm [monoclinic, $a = 14.287$ (6), $b = 8.004$ (3), $c = 11.950$ (4) Å, $\beta = 125.33$ (3)°, $Z = 8$] and refined to an R of 0.033 for 976 reflections with $I \geq 3.3\sigma(I)$ (Le Fur, Aléonard, Gorius & Roux, 1982; LAGR). It can be better described and refined in $C2/m$.

Symmetrizing the coordinates (Table 1, LAGR) so as to correspond to $C2/m$ required shifts no larger than 0.1 Å. Two cycles of full-matrix least squares with all atoms anisotropic, as in LAGR, led to convergence at an R of 0.025 for the 978 reflections recovered from SUP 36529; two more cycles including an isotropic extinction parameter [final value, $0.24(1) \times 10^{-6}$] converged at $R = 0.020$. The number of parameters

was 105, compared with 203 for the *Cm* refinement of LAGR. The *C2/m* coordinates (Table 10) led to appreciably more regular coordination within the HoF_8 polyhedra and to e.s.d.'s about one-third as large as those reported earlier.

It is probable that the structure of the high-temperature phase, as represented by the erbium compound $\beta\text{-KEr}_2\text{F}_7$, should also be described in a centrosymmetric space group (*Pnam*) rather than the non-centrosymmetric *Pna2*₁, reported by Aléonard, Le Fur, Gorius & Roux (1980) (see Category 3).

2-Piperidinotricyclo[5.2.2.0^{2,6}]undecan-9-one,
 $\text{C}_{16}\text{H}_{25}\text{NO}$

The structure of this compound was described (Nirmala & Sake Gowda, 1982; NS) in space group *Cc* [$a = 24.28$ (4), $b = 8.76$ (6), $c = 14.03$ (2) Å, $\beta = 108.00$ (9)°, $Z = 8$] and refined to an *R* of 0.063 for 1165 visually measured reflections. Questionable features of this structure include single-bond C—C distances that range from 1.379 to 1.719 Å (as calculated from the coordinates in Table 1 of NS; values given in the paper itself are averages over the two independent molecules) and non-positive-definite B_{ij} matrices for two atoms (SUP 36391).

The two independent molecules are related by an approximate 2₁ axis, and NS carried out preliminary refinement in space group *C2/c* but apparently were unable to reduce *R* below 0.18. At this stage refinement was continued in *Cc* (there is no mention as to how the inherent singularity was removed), and refinement was continued to $R = 0.112$. An absorption correction was then introduced, and *R* was reduced to 0.063.

Our experiences have been somewhat different. Refinement in *C2/c* was quite satisfactory,* proceeding quickly to $R = 0.104$ (with no negative U_{ij} eigenvalues). Our final *R* is considerably higher than the 0.063 reported by NS for their *Cc* refinement. However, we note the following: (1) the *Cc* parameters (NS, Table 1 and SUP 36391) led, on our computer, to an *R* of 0.13 rather than 0.063; (2) six cycles of refinement in *Cc* led to $R = 0.084$, but to negative U_{ij} eigenvalues for 23 of the 36 atoms and little sign of convergence. It is possible that the absorption corrections noted by NS were applied to the $F(\text{cal.})$ values rather than to $F(\text{obs.})$. We further note that the intensities were estimated visually, and SUP 36391 contained only 1115 reflections out of a total of about 3000 within the $\text{Cu } K\alpha$ sphere; there were 325 parameters in the *Cc* model, 163 in the *C2/c*. It is probable that the accuracy and number of the intensity data are not adequate for a

Table 11. $\text{C}_{16}\text{H}_{25}\text{NO}$: coordinates and U_{eq} values ($\times 10^4$), space group *C2/c*

	x	y	z	U_{eq} *(Å ²)
O(1)	2705 (2)	4112 (7)	2353 (4)	581 (21)
N(1)	3879 (2)	2524 (6)	4040 (4)	166 (16)
C(1)	3015 (3)	3872 (8)	4164 (6)	272 (23)
C(2)	3659 (3)	3421 (7)	4723 (5)	167 (20)
C(3)	3752 (3)	2651 (8)	5762 (5)	275 (18)
C(4)	4283 (3)	3355 (9)	6482 (5)	335 (30)
C(5)	4246 (3)	4992 (8)	6154 (6)	398 (26)
C(6)	4029 (3)	4979 (7)	5011 (5)	246 (20)
C(7)	3652 (3)	6297 (8)	4461 (6)	332 (25)
C(8)	3400 (4)	5929 (12)	3325 (6)	527 (28)
C(9)	3000 (3)	4585 (9)	3202 (6)	306 (18)
C(10)	2784 (3)	5084 (8)	4740 (6)	359 (22)
C(11)	3120 (4)	6630 (9)	4839 (7)	434 (24)
C(12)	4500 (3)	2035 (7)	4415 (5)	224 (21)
C(13)	4709 (3)	1436 (8)	3593 (6)	293 (21)
C(14)	4348 (4)	76 (8)	3067 (6)	409 (24)
C(15)	3701 (3)	501 (9)	2731 (6)	390 (25)
C(16)	3529 (3)	1171 (8)	3610 (6)	276 (21)

* See footnote, Table 5.

Table 12. $\text{Cd}_2\text{As}_3\text{I}$: final parameters ($\times 10^4$), space group *C2/c*

	x	y	z	U_{eq} *(Å ²)
I	0	3736 (1)	2500	241 (3)
Cd(1,2)	2451 (1)	1444 (1)	2900 (2)	221 (2)
As(1,3)	1243 (2)	472 (1)	-307 (2)	151 (2)
As(2)	5000	2905 (2)	2500	129 (3)

Secondary extinction: $g = 1.41$ (5) $\times 10^{-6}$.

* See footnote, Table 5.

conclusive choice of space group. In these circumstances, there seems no reason to abandon the higher symmetry.

The *C2/c* parameters (Table 11) lead to entirely satisfactory geometry; the bond lengths are not far from those reported in Fig. 3 (NS) as the average of the two independent molecules in *Cc*. Of particular note is the bridgehead distance C(2)—C(6), now at 1.61 (1) Å and, hence, significantly longer than the remaining C(*sp*³)—C(*sp*³) bonds.

$\text{Cd}_2\text{As}_3\text{I}$

The structure of this compound (Rebbah, Leclaire, Yazbeck & Deschanvres, 1979; RLYD) was described in space group *Cc* [monoclinic, $a = 8.436$ (1), $b = 9.594$ (2), $c = 7.952$ (2) Å, $\beta = 100.65$ (2)°, $Z = 4$] and refined to an *R* of 0.087 for 1843 reflections with $I > 3\sigma(I)$ and, apparently, 51 parameters. It is better described in *C2/c*. The *C2/c* coordinates can be obtained from Table 1 of RLYD by shifting the origin by $\Delta x = -0.24$, $\Delta z = 0.21$ so that I and As(2) lie on twofold axes, and then averaging Cd(1) with Cd(2) and As(1) with As(3). Full-matrix refinement of this model quickly converged at $R = 0.074$ for 1842 reflections (recovered from SUP 34482) and 30 parameters. Final parameters are given in Table 12.

The interatomic distances differ by as much as 0.023 Å (compared with an e.s.d. of 0.002 Å) from the values reported in Table 2 of RLYD. The revised values are essentially identical to the values obtained by

* In entering $F(\text{obs.})$ values into our computer, we found it necessary to reverse the signs of all the h (or l) indexes in SUP 36391; otherwise, many reflections would have been outside the Cu sphere of data.

averaging pairs of distances in Cc that become equivalent in $C2/c$.

$Tl(C_4H_8O_2)^+ \cdot TlBr_4^-$

The structure of this 1,4-dioxane complex of thallium was described (Jeffs, Small & Worrall, 1983; JSW) in space group $Cmc2_1$ [orthorhombic, $a = 10.31$ (1), $b = 8.560$ (5), $c = 15.55$ (2) Å, $Z = 4$] and refined to an R of 0.057 for 604 reflections with $I > 3\sigma(I)$. More satisfactory refinement can be attained in $Cmcm$.

Describing the structure in $Cmcm$ involves incrementing the z coordinates (JSW, Table 1) by about 0.064, so that the Tl atoms and Br(3) lie on a mirror plane, and averaging coordinates of the remaining pairs of atoms. Full-matrix refinement, based on the 604 reflections included in SUP 38631, quickly converged at an R of 0.0577 for 37 parameters, essentially the same as reported by JSW for 48 parameters in $Cmc2_1$. However, the structure factors showed a curious anomaly: the $F(\text{obs.})$ values for the $0kl$ reflections were consistently larger in magnitude than the $F(\text{cal.})$ values. (The same phenomenon applied to the $Cmc2_1$ model of JSW.) A plot of F_o/F_c vs h suggested that the $F(\text{obs.})$ values for the $0kl$ reflections should be multiplied by about 0.86; after this was done, further least-squares refinement led to an R of 0.040.

We have no idea as to the source of this apparent systematic error. Data were collected on a Stoe diffractometer and scaling was done layer-by-layer, but the layers were reported to be along k rather than h . Other experimental errors such as absorption or misalignment could hardly have resulted in such a peculiar discontinuity, and the lattice dimensions do not suggest that twinning would have been a problem. We can imagine no structural explanation, and a difference map was uninteresting. In any event, the anomaly is so distinct that we feel it appropriate to consider the additional parameter—a scale factor for the $0kl$ data—as legitimate.

Final parameters are given in Table 13; some interatomic distances, together with the earlier values reported by JSW, are given in Table 14. Of particular note are the Tl(1)—Br(1,2) and Tl(2)—O(1,2) distances; in the latter case, the $Cm2_1$ refinement had led not only to severely disparate distances but to an unreasonable difference in the e.s.d.'s—due, surely, to the problem of near singularity (Ermer & Dunitz, 1970).

$(DENC)_4Cu_4Cl_6O$

The structure of this tetranuclear Cu^{II} complex ($DENC = N,N$ -diethylnicotinamide) was described (El-Toukhy, Cai, Davies, Gilbert, Onan & Veidis, 1984; ECDGOV) in space group $I4_1$ [tetragonal, $a = 15.213$ (3), $c = 22.864$ (4) Å, $Z = 4$]. It is better described in $I4_1/a$.

Table 13. $Tl(C_4H_8O_2)^+ \cdot TlBr_4^-$: final parameters ($\times 10^4$), space group $Cmcm$

	Position	x	y	z	U_{eq} (Å ²)
Tl(1)	4(c)	5000	3242 (2)	2500	415 (3)
Tl(2)	4(c)	5000	8258 (2)	2500	513 (4)
Br(1,2)	8(f)	5000	4897 (3)	3853 (1)	576 (6)
Br(3)	8(g)	2987 (2)	1478 (3)	2500	729 (7)
O(1,2)	8(f)	5000	9375 (30)	4213 (11)	941 (64)
C(1,2)	16(h)	6165 (17)	9395 (29)	4728 (11)	835 (56)

* See footnote, Table 5.

Table 14. $Tl(C_4H_8O_2)^+ \cdot TlBr_4^-$: interatomic distances (Å)

	$Cmcm^a$	$Cmc2_1^b$	
Tl(1)—Br(1,2)	2.536 (3)	2.576 (17)	2.498 (18)
—Br(3)	2.567 (3)	2.564 (5)	
Tl(2)—Br(1,2)	3.565 (3)	3.570 (18)	3.559 (20)
—Br(3 ^h)	3.450 (3)	3.454 (6)	
—Br(3 ^h)	3.437 (3)	3.439 (5)	
—O(1,2)	2.83 (2)	3.28 (22)	2.71 (6)

Symmetry code: (i) $x, 1 + y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} + y, z$.

References: (a) this investigation; (b) Jeffs, Small & Worrall (1983).

The starting model in $I4_1/a$ was obtained by placing the central O atom on a site of $\bar{4}$ symmetry ($0, \frac{1}{2}, \frac{1}{2}$) and averaging the coordinates of other pairs of atoms (Table II, ECDGOV) accordingly. Observed structure factors for 2461 reflections with $I > 2\sigma(I)$ were recovered as Supplementary Material; they included two measurements (hkl and $k\bar{h}l$) for most forms. These were averaged to yield 1352 independent reflections; the R factor for averaging was 0.05. (This averaging is appropriate for either space group, $I4_1$ or $I4_1/a$). Of the 104 reflections of the type $h0l$, l odd that lay within the quadrant of data surveyed and which would be systematically absent for space group $I4_1/a$, only 9 were recorded; all 9 were among the very weakest in the table, and obviously lay very close to the 2σ threshold. Full-matrix refinement of coordinates and anisotropic U 's for the Cu, Cl, O, N and C atoms, and with the H atoms in assumed positions (as in ECDGOV), led to a final R of 0.063 for the 1352 averaged reflections, compared to an R of 0.069 for 2461 (unaveraged) reflections reported for the $I4_1$ refinement. Final heavy-atom coordinates are given in Table 15.

Bond lengths to the Cu^{II} atom are given in Table 16. While these values are somewhat more regular than reported for the $I4_1$ refinement (which showed, for example, two independent Cu—O distances at 1.875 and 1.930 Å), the range of Cu—Cl distances remains large, as does the range of Cl—Cu—Cl angles in the equatorial plane [104.8 (8), 118.8 (7) and 133.6 (9)°]; the trigonal bipyramidal geometry of the Cu^{II} atom is severely distorted. However, the unusual bond lengths found by ECDGOV (Supplementary Material) within the DENC ligand have disappeared; for example, the C—C distances in the pyridine rings, which varied from 1.27 (2) to 1.52 (2) Å in the $I4_1$ description, now lie in the range 1.363 (12)—1.386 (11) Å.

Table 15. $(DENC)_4Cu_4Cl_6O$: coordinates and U_{eq} values ($\times 10^3$), space group $I4_1/a$

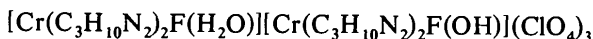
	x	y	z	$U_{eq}^*(\text{\AA}^2)$
Cu	856 (0.7)	1936 (0.7)	1725 (0.5)	678 (3)
Cl(1,2)	60 (1)	595 (1)	1402 (1)	725 (5)
Cl(3,4)	0	2500	-31 (1)	718 (7)
O(1)	0	2500	1250	577 (21)
N(1,13)	1686 (4)	1302 (4)	2237 (3)	652 (17)
C(2,14)	1374 (5)	731 (5)	2609 (3)	713 (22)
C(3,15)	1883 (6)	270 (5)	3008 (3)	684 (22)
C(4,16)	2767 (6)	441 (6)	3012 (4)	819 (25)
C(5,17)	3105 (5)	1035 (6)	2626 (4)	830 (25)
C(6,18)	2552 (5)	1454 (5)	2243 (3)	691 (21)
C(7,19)	1489 (6)	-460 (6)	3362 (4)	834 (26)
N(8,20)	1162 (5)	-310 (5)	3876 (3)	904 (22)
C(9,21)	1151 (8)	545 (8)	4142 (4)	1282 (39)
C(10,22)	295 (11)	1026 (8)	4065 (6)	1803 (55)
C(11,23)	766 (6)	-1027 (7)	4207 (4)	1116 (31)
C(12,24)	1382 (8)	-1489 (8)	4589 (4)	1350 (39)
O(2,3)	1510 (6)	-1188 (4)	3141 (3)	1384 (27)

* See footnote, Table 5.

Table 16. $(DENC)_4Cu_4Cl_6O$: bond lengths (\AA) to the Cu^{II} atom, space group $I4_1/a$

Cu—O(1)	1.901 (1)	Cu—Cl(3,4)	2.414 (3)
—Cl(1,2)	2.486 (2)	—N(1,13)	1.973 (6)
—Cl(1,2)'	2.346 (2)		

Category 3: center of symmetry added, no further refinement



The structure of this 1,3-propanediamine complex of Cr^{III} (Solans, Font-Altaba, Briansó, Solans, Casabó & Ribas, 1982; SFBSCR) was described in space group $P1$ [triclinic, $a = 10.710$ (4), $b = 9.047$ (3), $c = 8.785$ (3) \AA , $\alpha = 111.25$ (3), $\beta = 100.44$ (2), $\gamma = 86.60$ (2) $^\circ$, $Z = 1$] and refined to $R = 0.064$ for 3138 reflections with $I > 2.5\sigma(I)$. Since the structure is very nearly centrosymmetric, there is no reason not to describe it in $P\bar{1}$. The $P\bar{1}$ model (Table 17) is derived by symmetrizing pairs of atoms in molecules A and B [$x' = \frac{1}{2}(x_A - x_B)$, etc.; SFBSCR]; the resulting center of symmetry is at about $x = 0.275$, $y = 0.218$, $z = 0.660$, which becomes the origin in $P\bar{1}$.

In $P\bar{1}$, the perchlorate group B lies on a center of symmetry (the Cl atom is at $0, \frac{1}{2}, 0$), and hence must be disordered. However, it was already disordered in the $P1$ model, in such a way that every half-atom except O(1) is associated with a second, centrosymmetrically related half-atom. Except for this O(1) and for the O(3) atoms of perchlorate groups A and C , no atom needs to be moved by as much as 0.1\AA to achieve the symmetry of $P\bar{1}$.

The averaged $P\bar{1}$ structure leads to effective equality among chemically equivalent bond lengths: Cr—N 2.094 (10), N—C 1.498 (4), C—C 1.526 (12), Cl—O 1.395 (16) \AA (ordered ClO_4 group only), where the numbers in parentheses are scatter e.s.d.'s. In contrast, there were significant disparities in the $P1$ structure, with Cr—N ranging from 2.01 to 2.16 \AA . In the $P\bar{1}$ description the OH and the OH_2 ligands are equivalent by symmetry; no attempt was made to distinguish

Table 17. $[\text{Cr}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{F}(\text{H}_2\text{O})][\text{Cr}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{F}(\text{OH})](\text{ClO}_4)_3$: coordinates ($\times 10^4$), space group $P\bar{1}$ Numbers in square brackets are shifts from the $P1$ coordinates (Solans *et al.*, 1982) necessary to achieve the symmetry of $P\bar{1}$.

	x	y	z
Cr	-2368 [2]	726 [4]	940 [2]
F	-660 [34]	500 [5]	1738 [0]
O	-4181 [9]	922 [22]	130 [6]
N(1A,5B)	-1861 [48]	611 [20]	-1280 [55]
C(2A,4B)	-2462 [16]	-576 [48]	-2904 [68]
C(3A,3B)	-2354 [31]	-2258 [12]	-2868 [44]
C(4A,2B)	-3100 [61]	-2600 [18]	-1720 [96]
N(5A,1B)	-2546 [44]	-1749 [31]	71 [37]
N(6A,10B)	-2212 [76]	3200 [31]	1845 [7]
C(7A,9B)	-1456 [10]	3936 [6]	3543 [110]
C(8A,8B)	-2044 [46]	3652 [6]	4860 [74]
C(9A,7B)	-1954 [90]	1907 [0]	4732 [20]
N(10A,6B)	-2842 [48]	906 [22]	3225 [33]
Cl(A,C)	4889 [3]	3108 [15]	-2850 [36]
O(1A,1C)	6013 [31]	3101 [7]	-1752 [90]
O(2A,4C)	4533 [75]	4638 [51]	-2695 [13]
O(3A,3C)	3855 [209]	2438 [132]	-2588 [186]
O(4A,2C)	5122 [46]	2272 [57]	-4476 [58]
Cl(B)	0 [4]	5000 [17]	0 [1]
O(1B)*	-637 [-]	6102 [-]	1555 [-]
O(2B,5B)	-138 [6]	3544 [6]	-155 [64]
O(3B,4B)	1386 [8]	5586 [80]	834 [96]
O(7B,6B)	-304 [26]	5772 [54]	-1081 [71]

* Atom O(1B) was treated as ordered in $P1$, and has no centrosymmetrically-related counterpart (see text).

between them in the $P1$ refinement. The very short O...O distance between these ligands, 2.41 \AA , suggests a symmetric hydrogen bond with the H atom lying on (or symmetrically disordered across) a center of symmetry ($-\frac{1}{2}, 0, 0$).

1-Methyl-1-thioniacyclohexane iodide, $\text{C}_6\text{H}_9\text{S}^+\text{I}^-$

The structure of this compound was described (Gerdil, 1974) in space group $Pna2_1$ [orthorhombic, $a = 18.038$ (8), $b = 6.611$ (5), $c = 7.420$ (5) \AA , $Z = 4$]. No coordinate needs to be shifted by more than 0.05 \AA to attain the symmetry of $Pnam$, and while we were unable to obtain a listing of F values, we have no doubt that the $Pnam$ description is preferable. The $Pnam$ coordinates (averaged where necessary) are given in Table 18.

Gerdil (1974) noted that the derived structure was unreliable because of ill conditioning of the least-squares matrix. This ill conditioning surely arose from attempts to refine a closely centrosymmetric structure in a non-centrosymmetric space group, and would disappear in $Pnam$.

Trimethylphosphineallylchloroplatinum(II), $\text{C}_6\text{H}_{14}\text{PClPt}$

The structure of this compound (Zanotti, Del Pra & Scrivanti, 1982) was described in space group $Pna2_1$ [orthorhombic, $a = 11.867$ (5), $b = 10.567$ (5), $c = 7.941$ (4) \AA , $Z = 4$]. The reported coordinates correspond to a nearly exact mirror plane at $z = 0.01$, and the correct space group is surely $Pnam$. The $Pnam$ coordinates can be obtained from the values in Table 1 of Zanotti *et al.* (1982) by setting z to 0.0 for Pt, Cl, P, and C(1)—C(4), to 0.20 for C(5,6), and by averaging x

Table 18. 1-Methyl-1-thioniacyclohexane iodide: coordinates ($\times 10^4$), space group $Pnam$

	<i>x</i>	<i>y</i>	<i>z</i>
C(1,5)	1302	6291	4365
C(2,4)	1970	7685	4185
C(3)	1940	8971	2500
C(6)	419	3360	2500
S	1318.2	4538	2500
I	849.5	1439.7	7500

and *y* of C(5) and C(6). Attempts to refine the structure in the non-centrosymmetric $Pna2_1$ may well have been responsible for "the very large e.s.d.'s of the bond lengths and angles" and "the remarkable disorder of the $P(CH_3)_3$ group."

Dicarbonyl(η^5 -cyclopentadienyl)- μ_3 -(phenylphosphinidene)-bis(tributylphosphanetricarbonyl)iron-manganese(Fe-Fe), $C_{43}H_{64}Fe_2MnO_8P_3$

The structure of this compound (Schneider, Zsolnai & Huttner, 1982) was described in space group $P2_1$ [monoclinic, $a = 16.83$ (1), $b = 12.60$ (2), $c = 22.14$ (2) Å, $\beta = 91.40$ (6)°, $Z = 4$] and refined to an R of 0.059 for 4048 independent reflections with $I \geq 6\sigma(I)$. It should surely be described in $P2_1/c$. After the origin is shifted to $y = -0.259$, $z = -0.250$ and atoms are appropriately paired, only small adjustments are necessary to achieve the symmetry of $P2_1/c$ (Table 19). The maximum adjustments are 0.02 Å for Fe, Mn and P, 0.15 Å for the C and O atoms of the phenyl, cyclopentadienyl and carbonyl groups, and 0.23 Å for the *tert*-butyl groups; these values are typical of the distortions created when a centrosymmetric structure is refined in a non-centrosymmetric space group.

The averaged $P2_1/c$ coordinates lead to much more reasonable molecular geometry. In Table 20 we list the ranges and scatter e.s.d.'s for the various types of chemically equivalent bond lengths; whereas these values are unreasonably large for the $P2_1$ structure, for the $P2_1/c$ structure they are entirely compatible with the expected e.s.d.'s. While we have not been able to obtain a listing of F 's to confirm the absence of reflections $h0l$ with l odd, we are confident that the $P2_1/c$ description is to be preferred.

Spiro[isoindoline-4-(3,4,5,6-tetrahydro-2,2,7,7-tetramethyl-3-carbomethoxy)-3'-(2',2',5',5'-tetramethyl-4'-methylenecarbomethoxy)pyrrole] dihydrate, $C_{24}H_{38}N_2O_4 \cdot H_2O$

The structure of this compound (Bocelli, 1982) was described in space group Cc [$a = 18.943$ (3), $b = 11.318$ (2), $c = 24.376$ (3) Å, $\beta = 94.5^\circ$, $Z = 8$] and refined to an R of 0.080 for 2949 reflections with $I > 2\sigma(I)$. However, the two purportedly independent molecules are related by a nearly exact center of symmetry, and there can be little doubt that the

Table 19. $C_{43}H_{64}Fe_2MnO_8P_3$: coordinates ($\times 10^4$ for Mn, P and Fe; $\times 10^3$ for C and O), space group $P2_1/c$

Numbers in square brackets are shifts from the $P2_1$ coordinates (Schneider *et al.*, 1982) necessary to attain the symmetry of $P2_1/c$.

	<i>x</i>	<i>y</i>	<i>z</i>
Mn(1,2)	6504 [4]	4854 [13]	4529 [3]
P(1,5)	7508 [10]	4154 [3]	3962 [0]
P(2,4)	9106 [6]	6268 [12]	2834 [4]
P(3,6)	6518 [6]	2478 [11]	2714 [2]
Fe(1,3)	8396 [2]	5233 [2]	3460 [3]
Fe(2,4)	7526 [8]	3586 [6]	2962 [4]
C(112,512)	758 [6]	242 [0]	474 [1]
C(113,513)	794 [2]	171 [3]	517 [2]
C(114,514)	874 [8]	178 [2]	531 [1]
C(115,515)	919 [4]	254 [8]	504 [3]
C(116,516)	886 [4]	325 [1]	462 [1]
C(111,511)	805 [3]	319 [0]	448 [2]
C(211,431)	900 [2]	771 [0]	294 [3]
C(212,432)	910 [6]	812 [0]	359 [1]
C(213,433)	922 [12]	932 [0]	360 [0]
C(214,434)	925 [8]	980 [0]	424 [2]
C(221,421)	896 [3]	620 [8]	200 [2]
C(222,422)	812 [4]	640 [14]	178 [1]
C(223,423)	799 [12]	622 [2]	107 [1]
C(224,424)	856 [6]	688 [16]	71 [1]
C(231,411)	1018 [2]	604 [11]	286 [3]
C(232,412)	1060 [0]	612 [9]	348 [4]
C(233,413)	1151 [2]	592 [3]	344 [6]
C(234,414)	1172 [1]	480 [6]	327 [3]
C(311,621)	556 [4]	284 [8]	304 [5]
C(312,622)	485 [4]	216 [16]	284 [10]
C(313,623)	412 [4]	238 [14]	324 [10]
C(314,624)	379 [2]	330 [11]	317 [8]
C(321,631)	664 [8]	105 [0]	288 [0]
C(322,632)	662 [8]	76 [4]	356 [0]
C(323,633)	670 [12]	-47 [2]	361 [6]
C(324,634)	676 [12]	-78 [6]	429 [4]
C(331,611)	632 [6]	237 [2]	189 [1]
C(332,612)	608 [8]	342 [0]	158 [1]
C(333,613)	582 [8]	320 [8]	92 [2]
C(334,614)	562 [10]	424 [6]	58 [0]
C(1,4)	594 [4]	366 [6]	453 [2]
O(1,4)	555 [2]	292 [2]	456 [2]
C(2,5)	590 [1]	538 [4]	392 [0]
O(2,5)	544 [5]	575 [16]	359 [2]
C(711,811)	607 [3]	532 [12]	539 [2]
C(712,812)	680 [3]	472 [12]	549 [2]
C(713,813)	744 [8]	530 [0]	521 [2]
C(714,814)	708 [4]	622 [2]	494 [0]
C(715,815)	625 [3]	625 [7]	505 [3]
C(11,33)	763 [1]	622 [0]	339 [2]
O(11,33)	720 [1]	693 [0]	335 [5]
C(12,31)	910 [2]	422 [2]	330 [1]
O(12,31)	962 [2]	364 [0]	320 [5]
C(13,32)	882 [2]	569 [1]	416 [4]
O(13,32)	909 [2]	598 [4]	460 [1]
C(21,41)	687 [5]	463 [0]	275 [0]
O(21,41)	641 [5]	526 [2]	258 [3]
C(22,42)	801 [4]	362 [3]	225 [3]
O(22,42)	836 [3]	362 [4]	182 [1]
C(23,43)	810 [12]	247 [0]	322 [1]
O(23,49)	846 [5]	173 [2]	335 [3]

structure should be described in $C2/c$. The $C2/c$ coordinates (Table 21) can be obtained by translating the origin to $x = 0.110$, $z = 0.669$ and averaging; no atom needs to be moved by more than 0.2 Å.

Bocelli (1982) reports significant differences – up to 0.180 (15) Å – between equivalent bonds in the two molecules, and notes that the two molecules appear to have somewhat different conformations. These differences are surely the result of the problems associated with refining a centrosymmetric structure in a non-centrosymmetric space group – problems which were masked by the block-diagonal refinement in Cc . The $C2/c$ parameters of Table 21 lead, of course, to bond lengths and angles that are essentially the averages of

Table 20. $C_{43}H_{64}Fe_2MnO_8P_3$: average lengths, scatter *e.s.d.*'s and ranges (Å) for chemically equivalent bonds

Bond type	No.	<i>d</i> (av.)	$P2_1^a$ E.s.d.*	Range	No.	<i>d</i> (av.)	$P2_1^b$ E.s.d.*	Range
Fe-Fe	2	2.753	0.003	2.751-2.756	1	2.755	—	—
Fe-P(Mn)	4	2.326	0.010	2.313-2.334	2	2.326	0.003	2.323-2.328
Mn-P	2	2.305	0.022	2.289-2.321	1	2.305	—	—
Fe-P(Bu)	4	2.261	0.012	2.250-2.277	2	2.260	0.007	2.255-2.265
Fe-C	12	1.787	0.055	1.694-1.865	6	1.787	0.008	1.773-1.795
Mn-C(O)	4	1.784	0.060	1.706-1.851	2	1.787	0.012	1.779-1.795
Mn-C(ep)	10	2.175	0.068	2.113-2.327	5	2.174	0.032	2.147-2.226
P-C(Bu)	12	1.850	0.032	1.790-1.892	6	1.845	0.010	1.820-1.859
P-C(Ph)	2	1.883	0.073	1.832-1.935	1	1.890	—	—
C-O	16	1.16	0.05	1.07-1.25	8	1.15	0.01	1.13-1.17
C-C(Ph)	12	1.40	0.13	1.17-1.58	6	1.39	0.02	1.37-1.41
C-C(ep)	10	1.44	0.10	1.31-1.59	5	1.44	0.02	1.41-1.47
C-C(Bu)	34	1.56	0.11	1.32-1.83	17	1.54	0.02	1.50-1.60

References: (a) Schneider *et al.* (1982), (b) present work.

* $\{\sum[d-d(av.)]^2/N-1\}^{1/2}$.

Table 21. $C_{24}H_{38}N_2O_4 \cdot H_2O$: coordinates ($\times 10^4$), space group $C2/c$ Numbers in square brackets are shifts from the Cc coordinates (Bocelli, 1982) necessary to achieve the symmetry of $C2/c$.

	<i>x</i>	<i>y</i>	<i>z</i>
O(1,1)	4288 81	3928 30	-463 51
O(2,2)	4123 43	3213 100	384 36
O(3,3)	2701 18	1827 11	-1348 118
O(4,4)	2567 7	591 17	-650 10
N(1,1)	4822 5	872 12	-1678 118
N(2,2)	2282 34	-2766 26	-1626 26
C(1,1)	4714 18	-244 44	-1372 14
C(2,2)	4694 18	1883 48	-1315 18
C(3,3)	4274 18	1350 14	-862 16
C(4,4)	4092 13	68 16	-1001 19
C(5,5)	3357 18	38 34	-1342 111
C(6,6)	3051 27	-1190 24	-1388 14
C(7,7)	3254 30	-2088 34	-1058 10
C(8,8)	3853 13	-2006 42	-622 10
C(9,9)	4048 14	-738 27	492 10
C(10,10)	2826 21	-3179 41	-1194 10
C(11,11)	2460 22	-1565 37	-1810 18
C(12,12)	4578 2	-1226 28	-1800 16
C(13,13)	5389 16	-567 44	-1017 7
C(14,15)	4264 17	2839 71	-1674 0
C(15,14)	5394 4	2429 7	-1086 32
C(16,16)	4090 4	1850 20	-389 9
C(17,17)	4196 4	3102 38	-211 42
C(18,18)	4314 114	4480 19	620 87
C(19,19)	2832 2	826 12	-1064 4
C(20,20)	2252 150	2682 42	-1096 28
C(21,22)	1800 18	-772 5	-1811 59
C(22,21)	2715 42	-1610 74	-2387 115
C(23,24)	2460 12	-3645 34	-712 2
C(24,23)	3284 18	-4156 20	-1440 26
O \bar{H} (1,2)	1162 2	4190 40	2776 4

Table 22. β - KEr_2F_7 : coordinates ($\times 10^4$) from Table 1 of Aléonard *et al.* (1980), symmetrized in accordance with space group $Pnam$ Numbers in square brackets are shifts necessary to achieve the symmetry of $Pnam$. Cell dimensions: $a = 11.820$, $b = 13.333$, $c = 7.816$ Å; $Z = 8$.

	<i>x</i>	<i>y</i>	<i>z</i>
Er(1)	-58	7420	2500 11
Er(2,3)	2563 6	3365 7	238 2
Er(4)	2096	622	7500 4
K(1)	839	950	2500 86
K(2)	4343	687	2500 280
F(1)	1616	4204	2500 2
F(2,12)	1692 52	1992 29	9138 98
F(3,4)	2814 17	5022 6	5150 7
F(5)	2431	2338	2500 11
F(6)	3647	4044	2500 52
F(7)	3124	3374	7500 54
F(8,13)	4270 18	2670 10	34 44
F(9,14)	869 18	3771 72	9230 20
F(10)	3764	1245	7500 11
F(11)	245	886	7500 153

given in Table 22; we have been unable to obtain a structure-factor listing to confirm them.

Guanidinium pentacarbonatothorate tetrahydrate

As noted earlier (Category 2), the structure of this compound was reported (Voliotis & Rimsky, 1975) to be isomorphous with the corresponding cerium compound (Voliotis, Rimsky & Faucherre, 1975), and was refined in space group Bb [monoclinic, first setting, $a = 16.15$ (3), $b = 16.70$ (3), $c = 13.23$ (3) Å, $\gamma = 108.41$ (22)°, $Z = 4$] to an R of 0.062 for 11 601 reflections. We have already shown that the cerium compound is better described in space group $B2/b$ (we refined it in the more conventional $C2/c$), and there is no reason to believe that the thorium compound should not also be described in $B2/b$. Approximate coordinates in $B2/b$ are obtained by placing the Th atom on a twofold axis ($x = 0.5$, $y = 0.25$, $z = 0.2740$) and averaging the coordinates of other atoms related, in pairs, either by this axis or by a center of symmetry. The resulting values are close to those we reported for the cerium compound (see Table 5). In view of the isomorphism of the two compounds, we have not carried out a re-refinement of the thorium structure.

the values reported by Bocelli (1982), and are considerably more reasonable than the individual values.

Although the compound was named as a dihydrate, the reported structure corresponds to a 1 : 1 ratio of organic moiety to water (formula: $C_{24}H_{38}N_2O_4 \cdot H_2O$) and hence is a monohydrate.

 β - KEr_2F_7

As noted earlier (Category 2), the structure of this high-temperature phase should probably be described in the centrosymmetric space group $Pnam$ rather than the non-centrosymmetric $Pna2_1$, reported by Aléonard, Le Fur, Gorius & Roux (1980). These authors noted strong correlations during the $Pna2_1$ refinement, and no deviations from $Pnam$ are greater than 0.22 Å. Symmetrized coordinates for the $Pnam$ representation are

Final comments

We emphasize once again the difference—in terms of structural ramifications—between space-group errors that fall into Category 1 and those that fall into Categories 2 or 3. The consequences of a Category 1 error—describing a structure in a Laue group of unnecessarily low symmetry—are relatively minor: symmetry properties of the structure may go unrecognized, and e.s.d.'s will be somewhat increased because of the introduction of unnecessary parameters, but the resulting atomic coordinates and U 's should conform to the higher symmetry within the e.s.d.'s (barring systematic errors that might somehow conform to the lower symmetry but not to the higher). Errors in Categories 2 and 3—failure to recognize a center of symmetry—are much more serious. In almost all the examples reported here, the original non-centrosymmetric description led to unreasonable structural features: large variations in chemically equivalent distances, distorted coordination, non-positive-definite U_{ij} 's, or the like; these features disappeared after refinement in the centrosymmetric space group. Indeed, such distortions are often a clue that an alternative, centrosymmetric space group should be investigated.

Other clues that a higher-symmetry space group might be appropriate are: (1) molecular symmetry that is not used by the reported space group; (2) more than one molecule per asymmetric unit; (3) cell dimensions that might be compatible with a higher symmetry; (4) suggestive values of, or relationships between, the atom coordinates. In our experience, the most useful clues by far are those of type (4). Coordinate equivalences within their e.s.d.'s are completely reliable indicators of an incorrect Laue group (Category 1), whereas cell dimensions (which, despite high precision, may be of questionable accuracy) are not. When a center of symmetry has been overlooked, coordinate equivalences may be much less exact (within 0.2 or 0.3 Å, perhaps), and proof of the centrosymmetric model may require further refinement of the structure—and, hence, access to the observed intensities. Of the 50 or 60 non-centrosymmetric structures we have examined where a centrosymmetric model was suggested by such coordinate equivalences, the centrosymmetric structure was proved correct (by further refinement) in perhaps 85% of the cases, 5% were definitively non-centrosymmetric, and 10% were inconclusive.

Computational details

Our least-squares refinements were based on full-matrix minimization of the quantity $\sum w(F_o^2 - F_c^2)^2$. None of the Supplementary Tables contained values for $\sigma(F)$; accordingly, we chose functional representations for the weights w . The function we used in most cases was that suggested by Hughes (1941): $w = 1/F_o^2$ for $F \geq 4F_m$, $w = 1/(F_o)(4F_m)$ for $F_o \leq 4F_m$, with F_m equal to the

lowest F_o value retained by the original authors. We have invariably found this function to do an adequate job of representing experimental errors in diffractometer data, mimicking counting statistics for the stronger reflections and increasing the uncertainties of the weaker reflections for which background counts become appreciable. In the case of $C_{16}H_{25}NO$, where intensities were estimated from photographs, we used $w = 1/F_o^4$ or $1/(F_o)^2(4F_m)^2$ to more closely approximate the pattern of visual estimates. In no case did we find unusual patterns of weighted discrepancies that might have indicated the weights to have been inappropriate; in all cases refinement converged within three cycles (maximum shift to e.s.d. 0.1). All calculations were carried out on a VAX-11/750 under the CRYM (Duchamp, 1977) system of programs.

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Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (R. O. Gould, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland). As far as practicable books will be reviewed in a country different from that of publication.

Acta Cryst. (1988). B44, 88

Protein engineering. Edited by D. L. OXENDER and C. F. FOX. Pp. xvii+365. New York: Alan R. Liss, 1987. Price £22.00.

Crystallography is today a source of data for many other sciences, the science of protein structure being a notable example. For anyone interested in the wealth of detail of the structure of proteins, as it is currently known, this is a superb text, full of information, excellently set out. Protein engineering – the book's title – is not the sole subject matter of the book: it deals with protein structure quite thoroughly, and only after that with protein engineering as it is now developing, based on that foundation of detailed structural understanding.

This is a multi-author production: 100 authors, to be exact; and it is an almost wholly American treatise, since only four of the authors are from outside the US (they are British). The average length of each contribution is hardly more than ten pages, so none of them are very comprehensive; nonetheless, the coherence of the subject matter throughout the book is impressive and the range of topics is not only extensive but is systematically and elegantly handled. The presentation is well conceived. Initial essays outline methods for the determination of protein structure (including 20 pages on the use of NMR); then follow contributions on the underlying principles such as the effects of hydrophobic interactions, folding, stability and so on; and this then leads to the section on the deliberate modification of proteins. At the end of the book, a collection of over 30 colour plates, including stereo-pictures, serves both to clarify points made in the text and to add examples from several very recently determined protein structures.

X-ray crystallographic results are present at every turn, as one would expect. The specific procedures of the crystallographic method, and its theory, are laid out in highly abbreviated but very readable form in ten pages, written by W. A. Hendrickson.

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The magic of minerals. By O. MEDENBACH and H. WILK. Pp. 205. Berlin: Springer-Verlag, 1986. Price DM 98.00.

The English edition of the German book *Zanberwelt der Mineralien* (published in 1977) is a superb product of Springer Verlag's excellent production standards. For a mineralogist there are exceptional reproductions of museum-quality specimens, with clear morphology, a similarly high quality of reproduction of colours (which is very difficult) and a normal text, suitable for such an artistic book, addressed not only to scientific people but also to those interested in general knowledge. Turning every page of the book gives one a new excitement; a rhombohedral glassy-lustre crystal of rose rhodochrosite, of 34 × 39 mm, reproduced on a full page of the book (300 × 270 mm, involving a ×16 magnification), shows very rare good morphology of a Colorado specimen; quartz on marble (40 × 46 mm original size); smoky, amethyst, or rose quartz; the exceptional amethyst rosette (90 × 103 mm original size); or the crystal-clear sceptre quartz present a series of beautiful natural crystals of trigonal specimens. Calcite, ankerite, aragonite, nice twins of gypsum; the colours and form of cuprite, with small crystals of malachite, or overgrowth; the rare pyrite on calcite, or the exceptional crystals of apophyllite; and so on, surprising every time, as one encounters each photograph. Olaf Medenbach has portrayed special specimens and produced exceptional photographs, following Hauy's description of crystals as 'the flowers of the mineral kingdom' – because of the beauty and colouration of many of their clusters.

The text of the book is divided into two parts: a general mineralogy, and a specific description for every one of the mineral species illustrated on the adjacent pages. The general mineralogy, accurate and well written, gives the crystalline nature of matter, the structure of minerals, the symmetry of the external forms and physical properties, the occurrence and origin and the mineral names. The latter is a simple classification of the minerals. The specific descriptions of the mineral species reflect a clearly gemmological and historical influence. They are in good harmony with the aesthetic quality of the photographs and the minerals described are limited to the ones reproduced.

Finally, it seems imperative to draw attention to the exceptional photography of diamond, showing the trigonal markings and the rounded corners of the octahedron ... together with tourmaline, emerald, morganite, topaz ... all gem specimens!

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