for evaluating proposed models and perhaps a basis for proposing new ones. But it does not directly provide data about the types of interactions and bonding at the enzyme receptor site which are important for activity.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A27, 157–165.

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, edited by J. A. IBERS & W. C. HAMILTON, Table 2.2B. Birmingham: Kynoch Press.

DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. ELIEL & N. ALLINGER, pp. 271–383. New York: John Wiley.

FULLERTON, D. S., ROHRER, D. C., AHMED, K., KITATSUJI, E., DEFFO, T. & FROM, A. (1982). In *Current Topics in Membranes and Transport*, edited by F. BONNER & A. KLINZELLER. New York: Academic Press.

FULLERTON, D. S., YOSHIOKA, Y., ROHRER, D. C., FROM A. H. L. & AHMED, K. (1979). *J. Med. Chem.* 22, 529–533.

HAMILTON, W. C. (1959). *Acta Cryst.* 12, 609–610.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KARLE, I. L. & KARLE, J. (1969). *Acta Cryst.* B25, 434–442.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN* 77. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MESSERSCHMIDT, A., HÖHME, E. & LINDIG, C. (1981). *Cryst. Struct. Commun.* 10, 629–635.

REPKE, K. R. & DITTRICH, F. (1982). In *Current Topics in Membranes and Transport*, edited by F. BONNER & A. KLINZELLER. New York: Academic Press.

REPKE, K. R. & PORTIUS, H. J. (1966). *Sci. Pharm. Proc.* 1, 39–57.

ROHRER, D. C., DUAX, W. L. & FULLERTON, D. S. (1976). *Acta Cryst.* B32, 2893–2895.

ROHRER, D. C. & FULLERTON, D. S. (1980). *Acta Cryst.* B36, 1565–1568.

ROHRER, D. C. & FULLERTON, D. S. (1983). *Acta Cryst.* C39. To be published.

ROHRER, D. C., FULLERTON, D. S., YOSHIOKA, K., FROM, A. H. L. & AHMED, K. (1979). *Advances in Chemistry: Computer Assisted Drug Design*. Vol. 112, edited by R. E. CHRISTOFFERSON & E. C. OLSON, pp. 257–279. Washington, DC: American Chemical Society.

ROHRER, D. C. & SMITH, G. D. (1980). '*FITMOL*' in *PROPHET Molecules*, edited by W. P. RINDONE & T. KUSH. Cambridge, MA: Bolt Beranek and Newman, Inc.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.

THOMAS, R., BOUTAGY, J. & GELBART, A. (1974). *J. Pharmacol. Exp. Ther.* 191, 219–231.

THOMAS, R., BROWN, L., BOUTAGY, J. & GELBART, A. (1980). *Circ. Res. Suppl.* I, 46, 167–172.

WEEKS, C. M., CODY, V., POKRYWIECKI, S., ROHRER, D. C. & DUAX, W. L. (1974). *AFIPS Natl Comput. Conf. Expo. Conf. Proc.* 43, 469–472.

WEINTRAUB, H. J. R. & HOPFINGER, A. J. (1975). *Int. J. Quantum Chem. Quantum Biol. Symp.* 2, 203–208.

YOSHIOKA, K., FULLERTON, D. S. & ROHRER, D. C. (1978). *Steroids*, 32, 511–517.

Some Additional Changes in Space Groups of Published Crystal Structures*

BY RICHARD E. MARSH AND FRANK H. HERBSTEIN†

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA

Abstract

Revised structures are reported for ten crystalline compounds, based on space groups of higher symmetry than originally deduced. For two of them the Laue symmetry is changed, from $2/m$ to $\bar{3}m$. For the remaining eight a center of symmetry has been added; for six of these we have been able to obtain F values and carry out least-squares refinements in the higher-symmetry space groups, with more satisfactory results than originally reported.

One of the most essential results of a successful crystal-structure analysis is the determination of the space group, for it is the space group that defines the

inherent symmetry properties of the structure. In recent years we have noted a relatively large number of structures that have been reported with space groups of unnecessarily low symmetry (Marsh & Schomaker, 1979, 1980, 1981; Schomaker & Marsh, 1979a; Marsh, 1980; Herbstein & Marsh, 1982). We separate these structures into two categories: (1) those for which the reported space group has a lower Laue symmetry than that of the structure itself; (2) those for which the reported space group lacks a center of symmetry which is present in the structure. For category (2), the problem of refinement is inherently singular (Ermer & Dunitz, 1970); even if the singularity is somehow masked (perhaps by performing block-matrix rather than full-matrix least-squares refinement, or by beginning with a model that is sufficiently far from centro-symmetric), large errors in atomic parameters can result. For category (1), no such problem arises and the refinement should proceed normally, if inefficiently (Schomaker & Marsh, 1979b); however, the true symmetry of the structure may go unrecognized, and correlation with the results of other physical measurements may be confusing (Herbstein & Marsh, 1982).

We report here revised structures for ten additional compounds, described in space groups of higher symmetry than originally reported. Two of them fall into category (1), the revised structures having Laue symmetry $\bar{3}m$ rather than $2/m$. The other eight fall into category (2). For six of these latter cases we have been able to obtain, as Supplementary Material, the original sets of F values and have carried out successful least-squares refinements in the higher-symmetry space groups; the resulting structures are appreciably improved in terms of molecular geometry and, usually, of the agreement index R. Details follow.

Category 1 – changes in Laue group

1. *Diammonium hexaaquachromium*(III) *penta-fluoride*, $(NH_4)_2[Cr(H_2O)_6]F_5$

The structure of this compound was described as monoclinic, space group $C2/c$, with $a = 11.997$ (1), $b = 6.928$ (1), $c = 13.574$ (2) Å, $\beta = 90.0°$, $Z = 4$ (Massa, 1977). Massa recognized that the cell is metrically hexagonal ($a \simeq \sqrt{3}b$) but selected the monoclinic description on the basis of Weissenberg and precession photographs. Refinement in $C2/c$ converged at $R = 0.042$ for 791 independent reflections with net intensities greater than zero.

The vectors $[\frac{1}{2}, -\frac{1}{2}, 0]$, $[0,1,0]$, $[0,0,1]$ describe a hexagonal cell with $a' = 6.927$, $b' = 6.928$, $c' = 13.574$ Å, $\alpha' = \beta' = 90.0$, $\gamma' = 120.01°$, $Z = 2$; the corresponding transformations $x' = 2x$, $y' = x + y$, $z' = z + \frac{1}{2}$ lead to a set of atomic coordinates that are compatible, well within the reported e.s.d.'s, with the symmetry of the trigonal space group $P\bar{3}c1$. Atomic

Table 1. $(NH_4)_2[Cr(H_2O)_6]F_5$. *Atomic coordinates* ($\times 10^4$ *for* Cr, F, O, N; $\times 10^3$ *for* H) *symmetrized and averaged so as to correspond to space group* $P\bar{3}c1$

Numbers in parentheses are standard deviations estimated from Table 2 of Massa (1977); numbers in square brackets are mean deviations of the individual atoms from the symmetrized positions.

	Wyckoff position	x	y	z
Cr	2(b)	0	0	0
F(1)	4(d)	6667 (3) [0]	3333	277 (1)[–]
F(2,3)	6(f)	2795 (2) [0]	2795	2500 (1) [1]
O(1,2,3)	12(g)	2616 (2) [2]	1634 (3) [3]	856 (2) [1]
N	4(d)	6667 (5) [7]	3333	3264 (2) [–]
H(1)	4(d)	667 (4) [3]	333	389 (2) [–]
H(2,3,4)	12(g)	686 (3) [6]	450 (3) [8]	305 (2) [4]
H(5,7,10)	12(g)	362 (3) [1]	200 (3) [9]	64 (2) [2]
H(6,8,9)	12(g)	256 (3) [3]	109 (3) [4]	136 (2) [1]

coordinates corresponding to this space group are listed in Table 1; they were symmetrized by averaging the transformed coordinates of equivalent atoms. The anisotropic U's reported by Massa are also in good agreement with the higher symmetry: no U_{ij} term needs to be changed by more than 0.0008 Å^2 to satisfy the symmetry conditions of $P\bar{3}c1$.

We do not know what features of the Weissenberg and precession photographs led Massa to choose Laue symmetry $2/m$ rather than $\bar{3}m$. Whatever these features, they are not reflected in the *structure* derived by Massa, which clearly shows the symmetry of $P\bar{3}c1$ within experimental error. We see no reason why this structure should be described in a lower-symmetry space group.

2. RbGa₇

The structure of this intermetallic compound was described in the monoclinic space group $C2/m$, with $a = 11.432$ (3), $b = 6.603$ (2), $c = 10.259$ (3) Å, $\beta = 111.85$ (2)°, $Z = 4$ (Belin, 1981). It can be better described in the rhombohedral space group $R\bar{3}m$.

The base vectors $[\frac{1}{2}, \bar{\frac{1}{2}}, 1]$, $[\frac{1}{2}, \frac{1}{2}, 1]$, $[0,0,1]$ describe a cell that is rhombohedral within the reported errors: $a' = b' = 10.255$, c' ($= c$) $= 10.259$ Å, $\alpha' = \beta' = 37.54$, $\gamma' = 37.56°$ ($Z = 2$). The corresponding coordinate transformations $x' = x - y$, $y' = x + y$, $z' = \frac{1}{2} - 2x + z$ (which include a shift of origin by $\frac{1}{2}$ in z) lead to a set of atomic coordinates that are compatible, well within the reported e.s.d.'s, with the symmetry of $R\bar{3}m$. These coordinates, as obtained by averaging the transformed parameters of symmetry-related atoms, are given in Table 2.

The corresponding hexagonal cell can be derived from the lattice vectors $[0,\bar{1},0]$, $[\frac{1}{2},\frac{1}{2},0]$, $[1,0,3]$ of the original monoclinic cell; its dimensions are $a_H = 6.603$, $b_H = 6.601$, $c_H = 28.566$ Å, $\alpha_H = 90.04$, $\beta_H = 90.00$, $\gamma_H = 120.01°$. The hexagonal axis c_H is the approxi-

Table 2. $RbGa_7$. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic B's* (Å^2) *symmetrized and averaged so as to correspond to space group* $R\bar{3}m$

Numbers in parentheses are standard deviations in the individual, unaveraged parameters as estimated from Table 1 of Belin (1981); numbers in square brackets are mean deviations of the individual values from their averages.

	Wyckoff position	x	y	z	B_{eq}
Ga(1,2)	6(h)	1825 (3) [2]	1825	5789 (3) [2]	1·36 (7) [1]
Ga(3,5)	6(h)	2169 (3) [1]	2169	7980 (3) [3]	0·83 (6) [1]
Ga(4)	2(c)	4560 (4) [2]	4560	4560	0·73 (7) [–]
Rb	2(c)	1947 (4) [3]	1947	1947	1·71 (7) [–]

mate view direction in the right-hand half of Fig. 1 of Belin (1981); the $\bar{3}$ symmetry can be clearly seen in the lower right-hand corner of this drawing, but is lost elsewhere because of the perspective associated with a finite viewing distance in the drawing.

Category 2 – non-centrosymmetric to centrosymmetric

3. Tin(II) *fluoroiodide*

The structure of Sn_2IF_3 (Vilminot, Granier, Al Oraibi & Cot, 1978; VGOC) was described in the orthorhombic space group $C222_1$, with $a = 13·502$, $b = 4·371$, $c = 9·340$ Å, $Z = 4$, and was refined to an R of 0·041 for 130 reflections with $\sigma(I)/I < 0·30$ (out of a total of 523 independent reflections that were measured). The resulting structure conforms very closely to space group $Ccmm$, and none of the 130 retained reflections is of the type $0kl$ with l odd that would violate the conditions for the additional glide plane.

Reformulating the structure in $Ccmm$ ($Cmcm$ is the conventional setting) required incrementing the z coordinates by 0·25, but no other shift larger than 0·09 Å. An initial structure-factor calculation resulted in an R of 0·046 for the 130 reflections, and two full-matrix least-squares cycles (anisotropic for Sn and I, isotropic for F, as in VGOC) reduced it to 0·025. The number of parameters was 16, compared with 21 for the $C222_1$ refinement of VGOC. Final $Ccmm$ parameters are given in Table 3. In view of the considerable improvement in R and the reduced number of parameters, there can be no doubt that the structure should be described in $Ccmm$ rather than in $C222_1$.

4. $Pb_3Mn_7O_{15}$

The structure of this compound was described in the orthorhombic space group $Cmc2_1$, with $a = 17·28$ (1), $b = 9·98$ (1), $c = 13·55$ (1) Å, and refined to an R of 0·047 for 904 reflections with $I > 1·5\sigma(I)$ (Darriet,

Devalette & Latourrette, 1978; DDL). It can be better described in $Cmcm$.

Reformulating the structure in $Cmcm$ involves shifting the origin by about 0·25 in z and symmetrizing the positions of some atoms or pairs of atoms; the symmetrizing shifts ranged up to about 0·2 Å. [We presume that the y coordinate of O(3) was misprinted, and should be 0·406 rather than 0·706; otherwise, both the reported interatomic distances and the Figures are in error.] Refinement in $Cmcm$ (anisotropic for Pb, isotropic for Mn and O, as in DDL) quickly converged at an R of 0·045 for the 904 reflections in the supplementary table; the number of parameters was 69 compared with 124 for the $Cmc2_1$ refinement of DDL. The $Cmcm$ parameters are given in Table 4.

As expected, the Pb–O and Mn–O distances are considerably more regular in the $Cmcm$ description; they have changed by amounts ranging up to 0·25 Å. The only surprise in the parameters is a large U_{33} term for Pb(3), 0·108 (3) Å^2, which suggests that the atom may be disordered between two arrangements of the sort shown in Fig. 4(a) of DDL; the somewhat enlarged B's of O(6,8) and O(13) suggest that these

Table 3. Sn_2IF_3. *Atomic coordinates* $(\times 10^4)$ *and thermal parameters* (Å^2), *space group* $Ccmm$

The anisotropic Gaussian has the form $\exp[-2\pi^2(10^{-4})(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	3620 (2)	0	4359 (2)	265 (11)	345 (15)	215 (11)	0	−59 (13)	0
I	167 (2)	0	2500	344 (22)	228 (21)	232 (17)	0	0	0
F(1)	2085 (9)	0	5380 (15)	$B = 1·48$ (27)					
F(2)	2887 (19)	0	2500	$B = 2·63$ (57)					

Table 4. $Pb_3Mn_7O_{15}$. *Atomic coordinates* $(\times 10^4)$ *and isotropic B's* (Å^2) *for the* $Cmcm$ *description*

	x	y	z	B
Pb(1)	1938 (1)	1905 (2)	2500	0·88 (3)*
Pb(2)	1318 (1)	1377 (1)	7500	0·98 (4)*
Pb(3)	0	2614 (2)	2500	3·11 (19)*
Pb(4)	0	3935 (2)	7500	1·10 (6)*
Mn(1)	1680 (3)	0	0	0·6 (1)
Mn(2,7)	840 (2)	2532 (4)	−4 (4)	0·8 (1)
Mn(3,8)	1670 (2)	4965 (4)	1480 (3)	0·3 (1)
Mn(4)	2500	2500	0	0·4 (1)
Mn(5)	0	0	0	0·6 (1)
Mn(6)	0	5000	0	0·9 (1)
O(1,4)	2444 (11)	869 (18)	807 (15)	0·8 (3)
O(2)	2410 (19)	4077 (34)	2500	1·8 (6)
O(3,12)	778 (12)	4162 (21)	9205 (17)	1·5 (4)
O(5,7)	0	1654 (29)	9253 (24)	1·2 (5)
O(6,8)	0	3327 (36)	4310 (30)	2·3 (6)
O(9,14)	3339 (11)	1769 (20)	9186 (17)	1·2 (3)
O(10,11)	824 (11)	806 (18)	754 (15)	1·0 (3)
O(13)	875 (21)	4265 (37)	2500	2·5 (6)
O(15)	1729 (16)	3558 (31)	7500	1·3 (5)
O(16,17)	1674 (11)	1727 (21)	9274 (17)	1·2 (3)

$$*B_{eq} = \frac{8\pi^2}{3}(U_{11} + U_{22} + U_{33}).$$

atoms may also be involved in the disorder. While it is conceivable that an ordered structure in $Cmc2_1$ might be appropriate, it is clear that the *particular* structure derived by DDL is less satisfactory than the *Cmcm* structure. Moreover, it seems quite certain that no decision concerning the presence or absence of the additional mirror plane (and, hence, a center of symmetry) can be made without considering the weak reflections (Marsh, 1981), and these reflections were deleted from the data set. The data at hand point strongly toward the *Cmcm* description.

5. CeS₂ prepared at 1773 K and 5·5 GPa

Crystals of this phase were identified as orthorhombic, with $a = 8\cdot103$ (2), $b = 16\cdot221$ (2), $c = 4\cdot093$ (1) Å and $Z = 8$ (Yanagisawa, Kanamaru & Kume, 1979). Refinement was by block-diagonal least squares, based on 688 reflections. The authors reported that 'R decreased to 0·084 in the case of $Pn2_1a$, while it remained at 0·35 for *Pnma*'. A disturbing feature of the derived structure, apparent only from the Supplementary Publication, was non-positive-definite U matrices for three of the six atoms in the asymmetric unit, including one of the two Ce atoms.

Reformulating the structure in *Pnma* involved incrementing the y coordinates by about 0·25 so that S(3) and S(4) lie on a mirror plane while Ce(1) and Ce(2), and S(1) and S(2), are related by a 2_1 axis parallel to **c**; the symmetrizing shifts ranged up to about 0·1 Å. Full-matrix refinement converged at 0·095 – somewhat higher than the 0·084 reported for $Pn2_1a$, but far lower than the 0·35 reported earlier for *Pnma*. All the U_{ij} values are reasonable. Final *Pnma* parameters are given in Table 5.

It is apparent from the lists of observed and calculated structure factors that neither the $Pn2_1a$ nor the *Pnma* structure does a satisfactory job of explaining the observed intensities. A difference map, in *Pnma*, showed features ranging from −7·5 to 9·0 e Å⁻³ in positions that seemed to be related, in a complex manner that we do not understand, to the coordinates of the various atoms. Systematic errors may be present in the data. It also seems possible that the crystal was a

composite, particularly in view of the close metric relationships between the cell edges and the known existence of other polymorphs, including a pseudo-cubic monoclinic phase with cell dimensions and structural motif closely related to the orthorhombic phase discussed here.

Since neither the $Pn2_1a$ nor the *Pnma* structure satisfactorily explains the observations, simple statistical tests for distinguishing between the two are unreliable. In the present case, the non-positive-definite U matrices obtained in the $Pn2_1a$ structure can presumably help to compensate for any experimental problems that may have arisen, and the difference between the R values is probably of little significance. It is our personal prejudice that the *Pnma* formulation is to be preferred, but conclusive proof one way or the other must await further experiments.

6. α-SrSiO₃

The structure of this atmospheric-pressure phase compound was described in space group $C2$, with $a = 12\cdot323$ (5), $b = 7\cdot139$ (2), $c = 10\cdot873$ (5) Å, $\beta = 111\cdot58$ (4)°, $Z = 12$, and was refined to an R of 0·053 for 730 reflections with $F_o \geq 3\sigma(F_o)$ (Machida, Adachi, Shiokawa, Shimada & Koizumi, 1982). There can be little doubt that it should be described in $C2/c$.

The supplementary table of 730 structure factors contained none of the type $h0l$ with l odd that would be extinguished by the c glide of $C2/c$. An initial structure-factor calculation in $C2/c$ (which required an origin shift $\Delta y = 0\cdot26$, $\Delta z = 0\cdot25$ and an averaging of symmetry-related coordinates) led to an R of 0·10; after two cycles of full-matrix least-squares refinement convergence was attained at $R = 0\cdot042$ for 30 parameters – conclusively better than the R of 0·053 for 60 parameters in the $C2$ refinement. The $C2/c$ parameters are given in Table 6.

Bond distances and angles are appreciably more regular for the $C2/c$ structure than for the $C2$ model. The ranges of bond distances drop from 1·48–1·85 to 1·56–1·67 Å in the SiO₄ tetrahedra and from 2·39–2·82 to 2·47–2·74 Å in the SrO₈ dodecahedra, and the range of O—Si—O angles from 97–129 to 105–127°.

Table 5. CeS₂. *Atomic coordinates* (×10⁴) *and equivalent isotropic U's* (Å² ×10⁴) *from refinement in space group Pnma*

	x	y	z	U_{eq}*
Ce(1,2)	1276 (2)	−1116 (1)	2270 (3)	87 (1)
S(1,2)	1251 (12)	671 (3)	2455 (16)	106 (9)
S(3)	1127 (16)	2500	6450 (26)	182 (17)
S(4)	3370 (16)	2500	1685 (27)	213 (18)

* $\frac{1}{3}\sum U_{ii}$.

Table 6. α-SrSiO₃. *Atomic coordinates* (×10⁴) *and isotropic B's* (Å²); *C2/c refinement*

	x	y	z	B
Sr(1,3)	871 (1)	2599 (1)	4993 (1)	0·09 (1)
Sr(2)	2500	7500	5000	0·30 (2)
Si(1,3)	0	6696 (5)	2500	0·40 (5)
Si(2,4)	1236 (2)	435 (4)	2477 (3)	0·59 (4)
O(1,6)	0	1311 (13)	2500	0·54 (14)
O(2,7)	470 (6)	5668 (10)	3866 (7)	0·84 (10)
O(3,8)	1080 (6)	8119 (10)	2509 (7)	0·72 (11)
O(4,9)	1231 (6)	938 (10)	1038 (6)	0·61 (10)
O(5,10)	2185 (5)	976 (10)	3848 (6)	0·50 (10)

Table 7. *8,9,10-Trinorbornadiene*.2AgNO₃. *Atomic coordinates* (×10⁴) *and isotropic B's* (Å²) *from Cmcm refinements*

	x	y	z	B
Ag	1734 (2)	2508 (12)	2500	2·68 (4)*
C(1)	0	3473 (115)	2500	2·8 (11)
C(2,3)	0	1741 (68)	1357 (31)	2·4 (7)
C(4,5)	675 (13)	446 (41)	1842 (17)	1·4 (4)
N	2148 (20)	5000	5000	3·0 (7)
O(1)	1430 (19)	5000	5000	4·1 (7)
O(2,3)	2506 (17)	4331 (30)	4012 (15)	3·4 (4)
H(1)	439	4302	2500	5·0
H(2,3)	0	2061	475	5·0
H(4,5)	1027	−205	1230	5·0

$$* \, B_{eq} = \frac{8\pi^2}{3}\,(U_{11} + U_{22} + U_{33}).$$

7. C₇H₈.2AgNO₃

The structure of this 8,9,10-trinorbornadiene–silver nitrate complex was described in space group $Cmc2_1$, with $a = 17\cdot670$ (3), $b = 6\cdot065$ (2), $c = 10\cdot135$ (14) Å, $Z = 4$, and refined to an R of 0·090 for 298 observed reflections recorded on precession films (Baenziger, Haight, Alexander & Doyle, 1966; BHAD). It can be better described in $Cmcm$.

Recasting the structure in $Cmcm$ involves shifting the origin by about 0·25 in z, so that the 8,9,10-trinorbornadiene molecule lies on a site of symmetry mm and the NO₃ group on a twofold axis. Least-squares refinement quickly converged at an R of 0·085, assuming (as in BHAD) anisotropic U_{ij}'s for Ag, isotropic B's for C, N, and O, and chemically reasonable positions (C—H = 0·95 Å) for the H atoms. Final parameters are given in Table 7.

The resulting geometry is considerably more satisfactory than reported by BHAD for the $Cmc2_1$ structure. The Ag atom is bonded to two C atoms at 2·35 (2) Å and two O atoms at 2·33 (2) Å, the nitrate group is closely equilateral with N—O distances of 1·26 (4) Å, and the 8,9,10-trinorbornadiene molecule has C—C single-bond lengths of 1·54 (5) Å and a double-bond length of 1·33 (3) Å; angles in the 8,9,10-trinorbornadiene molecule range from 96 to 109°, compared with the range 90–126° reported by BHAD.

8. C₁₃H₁₀N₄S.HgCl₂

This compound, a 1:1 adduct between anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide and mercury(II) chloride, was described in the monoclinic space group $C2$, with $a = 25\cdot717$ (10), $b = 6\cdot476$ (6), $c = 11\cdot476$ (8) Å, $\beta = 102\cdot79$ (3)°, $Z = 4$, and was refined to an R of 0·060 for 1134 reflections with $F_o^2 >$

$3\sigma(F_o^2)$ (Kozarek & Fernando, 1973; KF). Space group $C2/m$ was initially rejected because it 'requires that the molecule has mirror symmetry. Since this seemed unlikely, the refinement was carried out in the space group $C2$. The successful refinement in this space group clearly showed that there was no mirror plane.'

In fact, the reported structure has an approximate mirror plane: none of the y coordinates in Table I of KF differs by more than 0·24 Å from 0·0, and the two benzene rings that were refined as rigid groups are oriented nearly parallel to **b**. We have reformulated the structure in $C2/m$ and carried out a successful refinement to an R of 0·045; since our results include an additional surprise – the presence of solvent – we describe them in some detail.

An initial least-squares refinement in $C2/m$, based on the coordinates in Tables I and II of KF but appropriately symmetrized, led to an R of 0·062 for 1132 reflections. However, a difference map showed regions of appreciable electron density (up to 3·5 e Å⁻³) in an otherwise empty area around the position $(0,0,\frac{1}{2})$. These regions formed a planar but distorted hexagon, about 4 Å along the long diagonal and 3 Å along the other two. To represent them, we introduced two sets of atoms, one in special positions on twofold axes and the other in general positions. We assigned them the form factor of nitrogen, and included both a population factor and an isotropic B among their refinable parameters. The population factors converged at 1·00 (7) and 0·98 (4); their B's, while large, are comparable to those of many of the phenyl C atoms. Final parameters are given in Table 8.

Table 8. C₁₃H₁₀N₄S.HgCl₂. *Final atomic coordinates* (×10⁴) *and isotropic B's* (Å²), *C2/m model*

	x	y	z	B
Hg(1)	1950 (0·3)	0	−488 (0·8)	3·58 (1)†
Cl(1)	1537 (3)	0	1345 (5)	5·91 (12)†
Cl(2)	1294 (2)	0	−2236 (5)	5·98 (13)†
S(1)	2862 (2)	0	588 (4)	3·80 (10)†
C(1)	3190 (6)	0	−561 (15)	3·3 (3)
N(1)	2964 (5)	0	−1740 (12)	3·4 (3)
N(2)	3364 (6)	0	−2264 (13)	3·9 (3)
N(3)	3813 (6)	0	−1446 (14)	4·2 (3)
N(4)	3719 (6)	0	−362 (14)	4·4 (3)
C(2)	3325 (8)	0	−3537 (19)	5·1 (5)
C(3,7)	3284 (11)	1793 (53)	−4057 (27)	15·6 (10)
C(4,6)	3224 (14)	1767 (60)	−5451 (32)	17·4 (11)
C(5)	3249 (15)	0	−5886 (35)	11·6 (10)
C(8)	4354 (9)	0	−1701 (20)	5·9 (5)
C(9,13)	4585 (11)	−1841 (52)	−1616 (24)	14·7 (9)
C(10,12)	5207 (13)	−1750 (53)	−1762 (27)	15·9 (10)
C(11)	5310 (14)	0	−2110 (32)	10·8 (9)
X(1)*	0	2907 (60)	5000	16·2 (18)
X(2)*	492 (6)	814 (28)	4747 (14)	10·9 (8)

* Solvent atoms: see text.

$$† \, B_{eq} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i{}^* a_j{}^* (\mathbf{a}_i . \mathbf{a}_j).$$

We have no idea what the solvent material might be. The two independent distances around the hexagon are 1·05 and 1·92 Å, both with formal e.s.d.'s of about 0·04 Å, and the angles are 90 (2) and 135 (2)°. A benzene molecule is a possibility, although there is no mention of the presence of benzene during the synthesis (KF). [The C—C distances within the benzene rings of the ligand molecule are also unsatisfactory, as noted by KF: our final values range from 1·25 (5) to 1·64 (4) Å.] We see no reasonable way to accommodate any of the solvents water, acetone, and ethanol that were specified in the synthetic and crystallization procedures. It is probable that, whatever the solvent, disorder occurs, and is responsible for the large B factors and unsatisfactory geometries of both the ligand benzene rings and the solvent.

The density calculated for our final model, containing the three additional N atoms per mercury complex, is 2·023 Mg m^{-3} compared with 1·874 Mg m^{-3} calculated for the unsolvated material; the measured density is 1·95 (5) Mg m^{-3} (KF).

9. $K_4[Pt_2(H_2P_2O_5)_4]$·2H$_2$O

The structure of this coordination complex was described in the tetragonal space group $P\bar{4}b2$, with $a =$ 13·335 (1), $c = 7·989$ (1) Å, and was refined to an R of 0·0356 for 1055 reflections with $I_o > 2·5\sigma(I_o)$ (Filomena Dos Remedios Pinto, Sadler, Neidle, Sanderson, Subbiah & Kuroda, 1980).* The atomic coordinates (not published in the original paper, but kindly furnished by Professor Dr G. Bergerhoff of Bonn, West Germany) strongly suggest that the structure should be described in space group $P4/mbm$.

In order to describe the structure in $P4/mbm$, only the coordinates of the bridging diphosphate groups need to be adjusted; the $P\bar{4}b2$ coordinates of the Pt, K, and water atoms are equally compatible with $P4/mbm$. We list in Table 9 the $P4/mbm$ coordinates, including the shifts necessary to achieve the higher symmetry. That these symmetrizing shifts are appreciably larger than would be expected from the formal e.s.d.'s can surely be ascribed to the problem of near-singularity associated with the refinement of an approximately centrosymmetric model in a non-centrosymmetric space group (Ermer & Dunitz, 1970). They are smaller than the symmetrizing shifts necessary in most of the other non-centrosymmetric-to-centrosymmetric examples reported here.

We were unable to obtain F_o values, and hence could not carry out refinement in $P4/mbm$; we believe that such a refinement would have been successful. We note that the closely related compound $K_4[Pt_2(H_2P_2O_5)_4]$·

* The space group is incorrectly given as $P4b2$, and the number of formula units per cell should be 2 and not 1.

Table 9. $K_4Pt_2(H_2P_2O_5)_4$·2H$_2$O. Atomic coordinates ($\times 10^4$) for P4/mbm description

Numbers in parentheses are e.s.d.'s in the symmetrized positions as obtained from the table of $P\bar{4}b2$ parameters; numbers in square brackets are the shifts necessary to achieve the higher symmetry.

	Wyckoff position	x	y	z
Pt	4(e)	0	0	3169 (<1)
P(1,2)	16(l)	3847 (2) [10]	3697 (2) [6]	3135 (4) [1]
O(1,3)	16(l)	4198 (6) [20]	2677 (6) [3]	2526 (12) [26]
O(2,4)	16 (l)	2850 (6) [53]	3945 (7) [29]	2152 (9) [79]
O(5)	8(j)	3507 (6)	6596 (5)	5000 (17) [16]
K(1)	4(g)	2245 (2)	7245	0
K(2)	4(h)	1135 (2)	6135	5000
H$_2$O	4(h)	3987 (6)	8987	5000

Br]·3H$_2$O is nearly isostructural, and was successfully refined in $P4/mbm$ (Che, Herbstein, Schaefer, Marsh & Gray, 1982).

10. Isobutyl 4-(4-phenylbenzylideneamino)cinnamate, IBPBAC

This compound forms monoclinic crystals with $a =$ 20·115 (2), $b = 5·589$ (1), $c = 37·816$ (4) Å, $\beta =$ 97·47 (1)°, and $Z = 8$ (Leadbetter, Mazid & Malik, 1980; LMM). It was described in space group Cc and refined to an R of 0·059 for 1791 reflections with $I > 2\sigma(I)$ – about 50% of the measured reflections. LMM noted that 'space group Cc rather than $C2/c$ was indicated by the intensity statistics and confirmed later by the structure determination.' The reported structure does, in fact, conform quite closely to $C2/c$, and it seems likely that the misleading intensity statistics resulted from the neglect of the weak reflections (Marsh, 1981).

Molecules 1 and 2 (LMM) are related by an approximate 2_1 axis at $x = 0·3014$, $z = 0·5430$; in order to describe the structure in the conventional setting of $C2/c$, the atomic coordinates (Table II, LMM) must be decremented by $\Delta x = -0·0514$, $\Delta z =$ $-0·2930$. After this origin shift, averaging of pairs of 2_1-related atoms leads to the coordinates in Table 10. We note that atoms C(15) and C(16) of molecule 1 must be paired with atoms C(19) and C(18) of molecule 2, and vice versa, and that the y coordinate of C(28) must have been misprinted: the value $-1·3123$ gives bond lengths in agreement with those in Table V of LMM, whereas the tabulated value $-1·1323$ does not.

The structure reported by LMM is surprising in that corresponding bond lengths in the two structurally distinct molecules show differences ranging up to 0·31 Å with an r.m.s. difference of 0·06 Å, compared with reported e.s.d.'s of 0·01–0·02 Å; bond lengths in

Table 10. *IBPBAC. Atomic coordinates* $(\times 10^4)$ *corresponding to space group C2/c*

Values in square brackets are shifts in the reported values (Table II, LMM) necessary to achieve the higher symmetry. The r.m.s. values of these shifts are 0·0014 (=0·028 Å) in x, 0·0060 (=0·033 Å) in y, and 0·0008 (=0·030 Å) in z.

	x	y	z
C(1)	2480 [25]	−13500 [84]	1658 [11]
C(2)	1900 [3]	−13894 [68]	1429 [2]
C(3)	1712 [20]	−12302 [48]	1153 [4]
C(4)	2102 [0]	−10290 [1]	1102 [1]
C(5)	2686 [6]	−9954 [72]	1338 [4]
C(6)	2868 [8]	−11552 [103]	1612 [6]
C(7)	1914 [10]	−8622 [24]	806 [1]
C(8)	1239 [20]	−8089 [34]	687 [12]
C(9)	1062 [2]	−6513 [1]	408 [10]
C(10)	1552 [7]	−5425 [71]	242 [3]
C(11)	2226 [22]	−5952 [10]	355 [4]
C(12)	2405 [13]	−7508 [72]	636 [1]
C(13)	1434 [14]	−3707 [69]	−56 [2]
N(1)	864 [18]	−2854 [28]	−158 [3]
C(14)	798 [2]	−1281 [28]	−462 [12]
C(15)	398 [33]	720 [66]	−458 [4]
C(16)	286 [8]	2222 [25]	−750 [1]
C(17)	580 [6]	1725 [23]	−1060 [3]
C(18)	978 [18]	−289 [23]	−1062 [0]
C(19)	1086 [5]	−1786 [56]	−765 [6]
C(20)	472 [16]	3254 [64]	−1380 [7]
C(21)	42 [14]	5008 [66]	−1438 [2]
C(22)	24 [16]	6434 [44]	−1768 [9]
O(1)	−494 [4]	7946 [26]	−1804 [17]
O(2)	413 [9]	6317 [92]	−1978 [10]
C(23)	−560 [16]	9467 [165]	−2118 [51]
C(24)	−1178 [12]	10221 [319]	−2232 [28]
C(25)	−1190 [42]	11990 [104]	−2544 [8]
C(26)	−1765 [25]	8600 [22]	−2256 [9]

the benzene rings range from 1·32 (1) to 1·46 (1) Å, with an r.m.s. spread of 0·036 Å from the mean. These problems can almost surely be blamed on the near-singularities associated with refinements of centro-symmetric structures in non-centrosymmetric space groups (Ermer & Dunitz, 1970). The shifts necessary to attain the symmetry of $C2/c$ show an r.m.s. value of 0·05 Å (Table 10), and result in a molecular structure that is far more reasonable; for example, the benzene C—C distances now show an r.m.s. spread of only 0·012 Å from the mean of 1·386 Å.

We have not been able to obtain a table of observed F's, but we have essentially no doubts that the structure should be formulated in $C2/c$ rather than Cc.

Computational details

The least-squares refinements which we carried out for examples 3 through 8 were based on minimization of the quantity $\sum w(F_o^2 - F_c^2)^2$. Since the supplementary tables of F values did not include e.s.d.'s, we assigned weights according to the expression originally devised by Hughes (1941) for refinements based on F (rather

than F^2) values from visual data; we have found this expression to be quite satisfactory for F^2 refinements on diffractometer data (Marsh & Schomaker, 1979). In all cases convergence was rapid and the values of $\sqrt{w}(F_o^2 - F_c^2)$ showed no severe outliers. Lacking experimental e.s.d.'s, we can report no meaningful values for the goodness-of-fit. We report the Gaussian parameter B_{ij} or U_{ij} in the same form as used by the original authors.

Summary

For compounds 1 and 2, the structures originally reported conform to the higher-symmetry space groups within the experimental errors, and we have seen no reason to examine the experimental intensities (which surely must reflect the same symmetry). On the other hand, for compounds 3 through 10, where the change in space group involves the addition of a center of symmetry, the parameter shifts necessary to attain the higher symmetry are substantial. For compounds 3–8 we were able to obtain the original F values, and have shown by additional refinements that the centro-symmetric descriptions are indeed preferable. For compounds 9 and 10, however, we were unable to obtain the F values, and our preference for the centrosymmetric descriptions is based only on inference: the deviations from centrosymmetry are well within the range expected for refinement of a centro-symmetric structure in a non-centrosymmetric space group.

References

Baenziger, N. C., Haight, H. L., Alexander, R. & Doyle, J. R. (1966). *Inorg. Chem.* **5**, 1399–1401.

Belin, C. (1981). *Acta Cryst.* B**37**, 2060–2062.

Che, C.-M., Herbstein, F. H., Schaefer, W. P., Marsh, R. E. & Gray, H. B. (1982). *J. Am. Chem. Soc.* In the press.

Darriet, B., Devalette, M. & Latourrette, B. (1978). *Acta Cryst.* B**34**, 3528–3532.

Ermer, O. & Dunitz, J. (1970). *Acta Cryst.* A**26**, 163.

Filomena Dos Remedios Pinto, M. A., Sadler, P. J., Neidle, S., Sanderson, M. R., Subbiah, A. & Kuroda, R. (1980). *J. Chem. Soc. Chem. Commun.* pp. 13–15.

Herbstein, F. H. & Marsh, R. E. (1982). *Acta Cryst.* B**38**, 1051–1055.

Hughes, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.

Kozarek, W. J. & Fernando, Q. (1973). *Inorg. Chem.* **12**, 2129–2131.

Leadbetter, A. J., Mazid, M. A. & Malik, K. M. A. (1980). *Mol. Cryst. Liq. Cryst.* **61**, 39–60.

Machida, K., Adachi, G., Shiokawa, J., Shimada, M. & Koizumi, M. (1982). *Acta Cryst.* B**38**, 386–389.

Marsh, R. E. (1980). *J. Cryst. Mol. Struct.* **10**, 163–166.

Marsh, R. E. (1981). *Acta Cryst.* B**37**, 1985–1988.

Marsh, R. E. & Schomaker, V. (1979). *Inorg. Chem.* **18**, 2331–2336.

MARSH, R. E. & SCHOMAKER, V. (1980). *Acta Cryst.* B36, 219–220.

MARSH, R. E. & SCHOMAKER, V. (1981). *Inorg. Chem.* 20, 299–303.

MASSA, W. (1977). *Z. Anorg. Allg. Chem.* 436, 29–38.

SCHOMAKER, V. & MARSH, R. E. (1979a). *Acta Cryst.* B35, 1094–1099.

SCHOMAKER, V. & MARSH, R. E. (1979b). *Acta Cryst.* B35, 1933–1934.

VILMINOT, S., GRANIER, W., AL ORAIBI, Z. & COT, L. (1978). *Acta Cryst.* B34, 3308–3309.

YANAGISAWA, Y., KANAMARU, F. & KUME, S. (1979). *Acta Cryst.* B35, 137–139.

Book Review

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

Extended linear chain compounds. Vols. 1 and 2. Edited by JOEL S. MILLER. Pp. XVI + 481 and XVI + 517. New York and London: Plenum, 1982. Prices US$52.50 and 55.00 respectively.

Contents: Vol. 1: (1) The Solution Properties of One-Dimensional Metal Chain Complexes (Alan L. Balch); (2) Mass Spectrometry of Low-Dimensional Materials (F. E. Saalfeld, J. J. DeCorpo, and J. R. Wyatt); (3) The Synthesis, Structure, Electrical Conduction Properties, and Theory of Divalent, Tetravalent, and One-Dimensional Partially Oxidized Tetracyanoplatinate Complexes (Jack M. Williams, Arthur J. Schultz, Allan E. Underhill, and Kim Carneiro); (4) Linear Chain Bis(oxalato)platinate Salts (Allan E. Underhill, David M. Watkins, Jack M. Williams, and Kim Carneiro); (5) A Comprehensive Review of Linear Chain Iridium Complexes (Arthur H. Reis Jr); (6) Highly Conductive Halogenated Low-Dimensional Materials (Tobin J. Marks and Davida W. Kalina); (7) Structural Aspects of Iodine-Containing Low-Dimensional Materials (Phillip Coppens); (8) Linear Chain Platinum Haloamines (Heimo J. Keller); (9) Optical Properties of Linear Chain Haloamine Platinum Complexes (Dan S. Martin Jr); Vol. 2: (1) An Added Dimension – Two-Dimensional Analogs of One-Dimensional Materials (Martin B. Dines and Matt Marrocco); (2) The Electronic Structure of Semiconducting Polymers (C. B. Duke); (3) Band Structures of One-Dimensional Inorganic, Organic, and Polymeric Conductors (Myung-Hwan Whangbo); (4) Quasi-One-Dimensional Conductors: The Peierls Instability, Pressure and Fluctuation Effects (D. Jerome and H. J. Schulz); (5) Optical Properties of One-Dimensional Systems (D. B. Tanner); (6) Super-structures and Phase Transitions in One-Dimensional Inorganic and Organic Materials (Hayao Kobayashi and Akiko Kobayashi); (7) X-ray, Neutron, and Electron Scattering Studies of One-Dimensional Inorganic and Organic Conductors (Seiichi Kagoshima); (8) Photo-conductive Properties of Organic Assemblies and a Comparison with Dark Conductors (Jerome H. Perlstein and Paul M. Borsenberger); (9) Cation-Radical Salts of Tetrathiotetracene and Tetraselenotetracene: Synthetic Aspects and Physical Properties (I. F. Schegolev and E. B. Yagubskii); (10) Structural Aspects of One-Dimensional

Conductors Based on Tetrathiafulvalene and Tetrathiatetracene (Rimma P. Shibaeva); (11) Metal Complexes of Tetrathiafulvalene and Related Compounds (Allen R. Seidle).

'Low-dimensional' systems in the sense of chain or layer compounds with electrically or magnetically strongly interacting atoms or molecules within the chains or layers are attracting growing interdisciplinary interest in the scientific community of chemists, solid-state physicists and crystallographers. This conclusion can at least be drawn from the number of monographs related to this subject. The present series endeavours to cover '...all aspects of the diverse linear chain substances...' (quotation from the editor's preface to the first volume) within three volumes by a number of review articles. As long as the whole series has not appeared, it cannot be judged to what extent that ambitious objective will be attained.

The first two volumes present twenty papers. Each contribution covers its subject independently and can therefore be studied at the reader's choice. From the formal point of view most articles offer an introduction and a conclusion. All papers have a list of the notations used and of the references at the end. Although related topics are put together within each of the single volumes (*e.g.* five review articles on linear-chain platinum or iridium compounds in Vol. 1), there is no real specialization. Each volume contains a subject index.

The substances in question belong predominantly to the two classical families of linear-chain conductors, *i.e.* columnar platinum and iridium complexes of the Krogmann-salt type and stacked organic charge-transfer complexes or cation-radical salts based on tetrathiafulvalene (TTF, and analogues) and tetrathialenes, especially tetrathiatetracene (TTT). Semiconducting polymers, however, and miscellaneous organometal complexes are also dealt with, as well as the role of halogens as doping agents and as polyhalide counterions.

The spectrum of contributions to these two volumes certainly covers the most interesting physical properties very well (*i.e.* electric, magnetic, optical, phase transitions) – and the theoretical models for their explanation. In view of the intimate connection between the physical properties and the atomic or molecular arrangement in these substances an impressive amount of detailed structural and crystal-chemical information and arguments is woven into the