## Some Incorrect Space Groups in *Inorganic Chemistry*, Volume 16

*Sir:*

It is the purpose of this paper to point out that seven crystal structure analyses published in Volume 16 of *Inorganic Chemistry* (1977) were almost certainly described in space groups of unnecessarily low symmetry. In two instances the decrease in symmetry resulted in a change of Laue symmetry (from $2/m$ to $\bar{1}$); since in such cases there is no inherent problem in refinement,[1] the reported molecular geometries are essentially correct, and our reformulations in the higher symmetry result in only minor adjustments. In the remaining five instances, however, the decrease in symmetry involved removing a center of symmetry without changing the Laue group. In such instances, singularities or near-singularities in the least-squares matrices—sometimes noticed by the original authors—led to refinement problems[2] and the resulting structures are in all instances unsatisfactory in some aspects. For four of these latter cases we have carried out successful least-squares refinements in the higher symmetry space groups and have arrived at structures with improved agreement indexes and no unsatisfactory features.[3]

**Dichlorobis(4-vinylpyridine)zinc(II).**[3] The crystal structure of this compound was described in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 7.501$ (4) Å, $b = 7.522$ (5) Å, $c = 14.482$ (6) Å, $\alpha = 90.41$ (4)°, $\beta = 90.53$ (4)°, and $\gamma = 105.29$ (5)°. If one chooses [110], [$\bar{1}$10], and [001] as base vectors, one obtains a $C$-centered lattice with cell dimensions $a' = 9.115$ Å, $b' = 11.942$ Å, $c'$ (=$c$) $= 14.482$ Å, $\alpha' = 89.93°$, $\beta' = 90.77°$, and $\gamma' = 89.83°$. While the deviations of $\alpha'$ and, particularly, $\gamma'$ from 90° seem to be significantly larger than the reported esd's (about 0.04°), convincing evidence of monoclinic symmetry comes from the atomic coordinates (Table III, ref 3). Within the reported errors, all the atom positions[4] conform to the symmetry of the monoclinic space group $C2/c$. The Zn atom lies on a twofold axis at $x' = 0$, $z' = \frac{1}{4}$ while the remaining atoms are related to one another, in pairs, by this same axis. Averaged values of the coordinates of each pair of atoms, transformed to the $C$-centered monoclinic cell and symmetrized about the twofold axis, are given in Table I; also listed are the shifts necessary to symmetrize the transformed parameters. Compared to the reported esd's, these shifts are satisfactorily small for all the parameters except for $\beta'_{12}$ and $\beta'_{23}$ of the Zn atom.

The $c$-glide plane of space group $C2/c$ requires the systematic absence of reflections $h0l$ with $l$ odd or, in the triclinic setting used in ref 3, of $hhl$ with $l$ odd. Of 59 such reflections included in the supplementary table of structure factors for this paper,[3] all but six are reported as unobserved. The six observed reflections are very weak, the strongest being $11\bar{1}$ ($20\bar{1}$ in the monoclinic setting) with $F_o = 9.3$. The triclinic structure reported in ref 3 fails to explain the intensities of these six reflections: $F_c$ for $11\bar{1}$ is only 0.7, and $R$ for all six is 0.86.

We have not made a statistical analysis of the reported $F_o$ values of reflections that would be equivalent in space group $C2/c$ ($hkl$ and $khl$ in the triclinic setting), but the agreement looks to be very good. Of course, the nearly exact $C2/c$ symmetry of the reported structure must be reflected in similar symmetry of the $F_o$'s.

The change in space group has no significant effect on the structural results other than to impose exact, rather than approximate, $C_2$ symmetry on the molecule.

**Cu(II) Complex of 3,9-Dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione Dioxime.**[5] The structure of this compound was reported in space group $P\bar{1}$ with four molecules in a unit cell of dimensions $a = 6.897$ (3) Å, $b = 12.023$ (4) Å, $c = 22.646$ (7) Å, $\alpha = 100.81$ (3)°, $\beta = 98.69$ (3)°, and $\gamma = 106.73$ (3)°.

It, too, can be described in space group $C2/c$. The vectors [120], [100], and [$\bar{1}\bar{1}\bar{1}$] describe a unit cell of dimensions $a' = 23.028$ Å, $b'$ (=$a$) $= 6.897$ Å, $c' = 22.537$ Å, $\alpha' = 90.04°$, $\beta' = 105.57°$, and $\gamma' = 90.06°$; in this case, the angles $\alpha'$ and $\gamma'$ are within 2 esd's of 90°. Transformation of the coordinates of the atoms (Table I, ref 4) according to the expressions $x' = \frac{1}{2}(y - z)$, $y' = x - \frac{1}{2}(y + z)$, $z' = -z$ shows that, with two exceptions, the atoms of molecule A are related, well within experimental error, to those of molecule B by one or another of the symmetry elements of space group $C2/c$. The exceptions are O2 of unit A, which is missing from the table, and C1 of unit A, whose $z$ coordinate of 0.1101 is probably a misprint of 0.1001 (otherwise, the reported bond length C1–C2 is seriously in error). Transformation of the $\beta$'s ($\beta'_{11} = \frac{1}{4}(\beta_{22} + \beta_{33}) - \frac{1}{2}\beta_{23}$, $\beta'_{22} = \beta_{11} - \beta_{12} - \beta_{13} + \frac{1}{4}(\beta_{22} + \beta_{33}) + \frac{1}{2}\beta_{23}$, $\beta'_{33} = \beta_{33}$, $\beta'_{12} = \frac{1}{2}(\beta_{12} - \beta_{13}) + \frac{1}{4}(\beta_{33} - \beta_{22})$, $\beta'_{13} = \frac{1}{2}(\beta_{33} - \beta_{23})$, $\beta'_{23} = \frac{1}{2}(\beta_{33} + \beta_{23}) - \beta_{13}$) leads to equally impressive agreement between the two units with the following exceptions: (1) the $\beta$'s of O2(A), like its coordinates, are missing; (2) the $\beta_{11}$ term of O1(A) is anomalously small and perhaps is misprinted; (3) the $\beta_{22}$ term of O1(B) is anomalously large and perhaps is misprinted; (4) the $\beta$'s for atoms C7–C11 seem to have been cyclically permuted, for either unit A or unit B. (The $\beta$'s of C9(A), for example, closely match those of C8(B).) Since atoms C8 and C11 lie at the periphery of the molecule and would be expected to have the largest $\beta$'s, it is likely that it is the parameters of unit A that have been permuted.

We have not, in this case, obtained the list of structure factors and confirmed the equivalence of reflections related by the $2/m$ Laue symmetry ($hkl$ and $\bar{h}, k + h, l + h$) or the systematic absences characteristic of the $c$ glide ($0kl$ with $k + l$ odd). Nevertheless, the essentially exact symmetry relationship between the coordinates of the two molecules leaves no reasonable doubt that the structure should be formulated in space group $C2/c$ rather than in $P\bar{1}$.

In the following four cases, in which the structures were originally described in noncentrosymmetric space groups but can be better described in centrosymmetric ones, we have carried out least-squares refinements in the higher symmetries based on the original experimental data.

Lists of observed and calculated structure factors were obtained from the American Chemical Society as supplementary material. Since these lists did not include standard deviations, weights were assigned according to expressions 1 and 2, where $F_{min}$ is the smallest value reported for an

$$w^{-1} = F_o^2 \quad \text{for } F_o \geq 4F_{min} \tag{1}$$

$$w^{-1} = 4F_oF_{min} \quad \text{for } F_o \leq 4F_{min} \tag{2}$$

"observed" reflection. This expression does a reasonable job of mimicking the pattern of variances $\sigma^2(F_o^2)$ (=$1/w$) expected for counter data; it may be recognized as the function originally suggested by Hughes[6] to express the variances in $F_o$, rather than $F_o^2$, for film data. For counter data, the tailing function (eq 2) tends to account for the increased impact of background counts on the accuracies of the weaker reflections, but no provision is made for instrumental errors which might increase the variances of the very strong reflections. In all instances the weighted residuals $w^{1/2}(F_o^2 - F_c^2)$ seemed to be essentially independent of $F_o$ and of $(\sin \theta)/\lambda$, and we believe this weighting function to be a reasonable one.

Our refinements were by full-matrix minimization of the quantity $\sum w(F_o^2 - F_c^2)^2$, carried out on an IBM 370-3032 computer under the CRYM system of programs. Atomic form factors, including corrections for anomalous dispersion, were as specified by the original authors. We invariably attained convergence, for any particular model, in two least-squares cycles. The $R$ index we report is the quantity $\sum ||F_o| - |F_c||/\sum|F_o|$, and the goodness-of-fit is $[\sum w(F_o^2 - F_c^2)^2/(n -$

**Table I.** Parameters of Dichlorobis(4-vinylpyridine)zinc(II),[3] Transformed[a] So As To Conform to Space Group $C2/c$

| | $x'$ | $y'$ | $z'$ | $\beta'_{11}$ | $\beta'_{22}$ | $\beta'_{33}$ | $\beta'_{12}$ | $\beta'_{13}$ | $\beta'_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Zn | 0.0 [2.4] | −56.2 | 2500.0 [0.2] | 213.4 | 99.1 | 65.6 | 0.0 [17.8] | 62.0 | 0.0 [6.4] |
| Cl(1, 2) | 2084 [0] | 886 [0] | 2482 [0] | 266 [1] | 138 [−1] | 100 [1] | −108 [18] | 84 [0] | −6 [5] |
| N(1, 2) | 40 [5] | −1137 [5] | 1403 [2] | 196 [−7] | 104 [9] | 64 [1] | 9 [4] | 33 [−2] | 10 [1] |
| C(2a, 2b) | 916 [6] | −964 [2] | 678 [0] | 206 [2] | 126 [0] | 70 [0] | 5 [15] | 48 [−1] | 10 [3] |
| C(3a, 3b) | 918 [9] | −1655 [5] | −66 [4] | 245 [0] | 136 [−8] | 66 [0] | 56 [−1] | 35 [−5] | −9 [9] |
| C(4a, 4b) | 28 [3] | −2576 [7] | −98 [−2] | 259 [−23] | 124 [3] | 68 [−2] | 70 [15] | −52 [3] | −35 [9] |
| C(5a, 5b) | −862 [13] | −2757 [0] | 654 [6] | 274 [3] | 134 [1] | 82 [0] | −59 [9] | 16 [−9] | −21 [10] |
| C(6a, 6b) | −834 [8] | −2035 [0] | 1374 [4] | 242 [−4] | 124 [2] | 76 [−2] | −66 [2] | 46 [−3] | −19 [−2] |
| C(7a, 7b) | 138 [5] | −3282 [−1] | −947 [13] | 338 [13] | 156 [8] | 145 [−14] | 16 [11] | −160 [6] | −44 [4] |
| C(8a, 8b) | −487 [7] | −4159 [−9] | −1010 [0] | 384 [−20] | 250 [7] | 143 [10] | 58 [−1] | −130 [34] | −59 [2] |

$a$ The new parameters were transformed from those in Table III of ref 3 according to the expressions $x' = \frac{1}{2}(x + y)$, $y' = \frac{1}{2}(-x + y)$, $z' = z$, $\beta'_{11} = \frac{1}{4}(\beta_{11} + \beta_{22} + \beta_{12})$, $\beta'_{22} = \frac{1}{4}(\beta_{11} + \beta_{22} - \beta_{12})$, $\beta'_{33} = \beta_{33}$, $\beta'_{12} = \frac{1}{2}(-\beta_{11} + \beta_{22})$, $\beta'_{13} = \frac{1}{2}(\beta_{13} + \beta_{23})$, $\beta'_{23} = \frac{1}{2}(-\beta_{13} + \beta_{23})$; parameters of symmetry-related atoms were then averaged. Numbers in square brackets are the shifts necessary to symmetrize the transformed parameters. All values are $\times 10^4$. The original $x$ coordinate of C(4b) was presumed to be 0.2538 rather than 0.2438.

**Table II.** Results of Least-Squares Refinement of Parwelite

| | $b$ | $c$ | $(1)^e$ | $(2)^f$ | $(3)^g$ |
|---|---|---|---|---|---|
| $p^a$ | 170 | | 87 | 102 | 134 |
| $R$ | 0.048 | 0.062 | 0.055 | 0.052 | 0.042 |
| GOF$^d$ | | 17.1 | 13.9 | 12.7 | 10.3 |

$a$ Number of parameters. $b$ Earlier model;[7] space group $Aa$; all atoms isotropic. $c$ Initial $A2/a$ model before refinement. $d$ Goodness-of-fit. $e$ Refined $A2/a$ model; all atoms isotropic. $f$ Sb, As, Si anisotropic; "M", O isotropic. $g$ Sb, As, Si, "M" anisotropic; O isotropic.

$p)]^{1/2}$ for $n$ observations and $p$ parameters; since the weights are on an arbitrary scale, the absolute value of the goodness-of-fit is without significance. We have tabulated final coordinates and $U$'s, $\beta$'s, or $B$'s from our refinements in the same units as were used in the original papers.

**Parwelite.**[7] The structure of this complex oxide, of empirical formula $(Mn,Mg,Ca)_5SbAsSiO_{12}$, was described in the monoclinic space group $Aa$ with eight formula units in a cell with dimensions $a = 10.048$ Å, $b = 19.418$ Å, $c = 9.735$ Å, and $\beta = 95.83°$. It was refined to $R = 0.048$ for 1665 independent reflections and 170 parameters, including isotropic $B$'s for each of the 40 atoms in the asymmetric unit and ten population parameters. The authors noted high correlations in the refinement procedure and "were forced to perform two blocked-matrix refinements, alternating between atoms related by pseudocentrosymmetry". We have reformulated the structure in the centrosymmetric space group $A2/a$ and have obtained rapid convergence to $R = 0.042$ for the same 1665 observations but with only 134 parameters.

In order to transform the atomic coordinates listed in Table III of ref 7 so as to conform with space group $A2/a$, we incremented the values of $x$ and $z$ by 0.2500 so as to translate the origin of the unit cell to a center of symmetry. The atom positions were then symmetrized: M(1) and M(2) were shifted slightly so as to lie on centers of symmetry; M(3), M(4), M(7), and M(8) were moved onto twofold axes, and the remaining atoms were adjusted so as to be related, in pairs, by a twofold axis. The required shifts, while generally small, reached 0.1 Å or more for O(1), O(6), O(9), O(10), O(20), and O(23) and more than 0.05 Å for M(1), M(2), M(3), and M(8). Besides the atomic coordinates and temperature factors, we refined the compositional parameters associated with sites "M", as in the earlier work. We also attempted, in an initial cycle, to refine a secondary extinction parameter; however, the indicated shift was to a negative, and hence unrealistic, value, and this parameter was removed from subsequent cycles. The earlier workers[7] reported a very small and marginally significant value ($c = 1.7$ (8) $\times 10^{-8}$).

The $U$'s and $B$'s were adjusted in three stages: (1) isotropic for all atoms; (2) anisotropic for Sb, As, and Si and isotropic for O and M; (3) anisotropic for Sb, As, Si, and M and isotropic for O. The progress of these three refinements is summarized in Table II, and final parameters from refinement (3) are listed in Table III. Compared with our starting, symmetrized model, no coordinate shift was as large as 3.0 esd; as indicated earlier, however, the symmetrizing operation involved much larger shifts.

The general features of the structure we find are as reported for the earlier structure in space group $Aa$, but the details of

**Table III.** Atomic Parameters$^a$ for Parwelite, Space Group $A2/a$, Refinement (3)

| atom | $P^b$ | $x^c$ | $y^c$ | $z^c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Sb(1, 2) | | 24933 (6) | −460 (3) | 24947 (6) | 98 (3) | 128 (3) | 103 (2) | 4 (2) | −7 (2) | 1 (2) |
| As(1, 2) | | 18359 (8) | 25483 (4) | 29369 (8) | 139 (4) | 171 (4) | 135 (4) | −1 (3) | −21 (3) | 6 (3) |
| Si(1, 2) | | 49334 (23) | 12043 (10) | 25398 (25) | 92 (10) | 140 (10) | 106 (10) | −1 (8) | −17 (8) | 2 (8) |
| M(1) | 0.81 (2) | $^1/_2$ | 0 | $^1/_2$ | 119 (12) | 217 (12) | 131 (12) | 17 (8) | −16 (8) | −28 (8) |
| M(2) | 0.90 (2) | 0 | 0 | 0 | 100 (11) | 213 (11) | 133 (11) | 2 (7) | −6 (7) | −40 (7) |
| M(3) | 0.90 (2) | $^1/_4$ | 11018 (9) | $^1/_2$ | 197 (12) | 143 (11) | 175 (12) | 0 | −88 (8) | 0 |
| M(4) | 0.95 (2) | $^3/_4$ | 14234 (9) | $^1/_2$ | 116 (10) | 164 (10) | 138 (11) | 0 | −14 (7) | 0 |
| M(5, 6) | 0.84 (1) | 49343 (14) | 10337 (6) | 74725 (15) | 111 (7) | 140 (7) | 129 (7) | −2 (5) | −23 (5) | −7 (5) |
| M(7) | 0.93 (2) | $^1/_4$ | 13091 (9) | 0 | 107 (10) | 198 (10) | 123 (11) | 0 | −21 (7) | 0 |
| M(8) | 0.83 (2) | $^3/_4$ | 12603 (10) | 0 | 181 (12) | 147 (11) | 160 (12) | 0 | −56 (8) | 0 |
| M(9, 10) | 0.58 (1) | 51209 (14) | 25461 (8) | 46761 (14) | 117 (8) | 152 (9) | 121 (8) | 10 (6) | −28 (6) | −3 (6) |

| atom | $x^d$ | $y^d$ | $z^d$ | $B$, Å$^2$ | atom | $x^d$ | $y^d$ | $z^d$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1, 6) | 3894 (6) | 668 (3) | 3248 (6) | 1.01 (9) | O(13, 18) | 5617 (6) | 1631 (3) | 3836 (6) | 1.16 (9) |
| O(2, 5) | 8458 (6) | 688 (3) | 3789 (6) | 0.92 (9) | O(14, 17) | 8259 (5) | 2411 (3) | 3785 (6) | 1.37 (9) |
| O(3, 4) | 1385 (5) | 353 (3) | 3818 (6) | 0.92 (9) | O(15, 16) | 1454 (6) | 1779 (3) | 3588 (6) | 1.39 (10) |
| O(7, 12) | 3457 (6) | 614 (3) | 8803 (6) | 1.04 (9) | O(19, 24) | 5750 (6) | 1896 (3) | 8581 (6) | 1.23 (10) |
| O(8, 11) | 6399 (6) | 432 (3) | 8842 (6) | 1.19 (9) | O(20, 23) | 8289 (6) | 2179 (3) | 8709 (6) | 1.46 (10) |
| O(9, 10) | 8971 (6) | 722 (3) | 8206 (6) | 1.06 (9) | O(21, 22) | 891 (5) | 1629 (3) | 8692 (6) | 0.98 (9) |

$a$ Estimated standard deviations, in parentheses, refer to the last digit. The anisotropic Gaussian factor has the form $\exp[(-2\pi^2)(10^{-4})\cdot(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. $b$ Site population: $PMn^{2+} + (1-P)Mg^{2+}$ (see Table IV, ref 7). $c \times 10^5$. $d \times 10^4$.

**Table IV.** Ranges of Metal-Oxygen Distances in the Coordination Polyhedra in Parwelite

| central atom | coord no. | M-O range, A | |
|---|---|---|---|
| | | *a* | *b* |
| Sb | 6 | 1.92-2.13 | 1.946-2.058 |
| As | 4 | 1.60-1.77 | 1.659-1.700 |
| Si | 4 | 1.58-1.71 | 1.605-1.672 |
| M(1) | 6 | 1.95-2.47 | 2.014-2.333 |
| M(2) | 6 | 2.01-2.42 | 2.067-2.391 |
| M(3) | 6 | 2.07-2.57 | 2.105-2.463 |
| M(4) | 6 | 2.13-2.43 | 2.141-2.416 |
| M(5, 6) | 6 | 2.07-2.24 | 2.112-2.230 |
| M(7) | 4 | 2.04-2.15 | 2.050-2.081 |
| | (2)[c] | (2.86-2.89) | (2.889) |
| M(8) | 8 | 2.19-2.72 | 2.197-2.618 |
| M(9, 10) | 5 | 2.02-2.28 | 2.039-2.263 |
| | (1)[c] | (2.75-2.93) | (2.850) |

[a] Earlier structure;[7] space group *Aa*; reported esd's, 0.01-0.02 A. [b] Present structure; space group *A2/a*; esd's, ~0.006 A. [c] These longer distances were not noted in the earlier work.

the various interatomic distances are quite different, possibly in ways that would be interesting in relation to the structural discussion already given.[7] We shall not go into such details, however, restricting ourselves to two rather general points. (1) The coordination polyhedra about the various metal atoms (see Table IV) are considerably more regular. (2) The pattern of the *U*'s and *B*'s, particularly for the oxygen atoms, is much improved. The earlier authors reported isotropic *B* values ranging from 0.3 to 3.3 and commented that "this doubtless arises from the relatively low data-to-variable parameter ratio and the high correlations inherent in the crystal structure...and...can only be improved through collection of a much larger data set". Invoking the higher symmetry has removed the correlations, and we find *B* values that range only between 0.9 and 1.5.

We believe that our description of the structure—which provides a more regular arrangement of atoms and better concordance among observed and calculated structure factors while being based on fewer parameters—is an undeniable improvement over the earlier structure and that the space group is in fact *A2/a* rather than *Aa*. One might conceivably argue that our presumption of anisotropic "temperature" factors for the heavier atoms creates an inherently different model and hence gives us an unfair advantage, so to speak, over the earlier refinement. However, the anisotropies are small and, in view of the compositional disorder associated with the M sites, hardly unreasonable. We further note that attempts to refine such anisotropic parameters for the earlier *Aa* model (which would have increased the parameter list to 236) almost certainly would have led to chaos because of

additional near-singularities in the least-squares matrix. In *A2/a* full anisotropy (194 parameters) presumably would still refine satisfactorily and give an even lower *R* and probably a lower GOF—but we have refrained.

*catena*-**Bis[μ-bis(2-aminoethyl)amine]-bis(μ-thiocyanato)-bis(isothiocyanato)dicadmium(II).**[8] The structure of this compound was derived and refined in the triclinic space group *P*1, with two molecules in a unit cell of dimensions *a* = 12.46 Å, *b* = 9.07 Å, *c* = 7.52 Å, α = 121.8°, β = 123.4°, and γ = 83.9°. (A more conventional choice would have been the reduced cell, based on the vectors [011], [101], and [00$\bar{1}$] and having dimensions *a'* = 8.18 Å, *b'* = 10.42 Å, *c'* = 7.52 Å, α' = 93.6°, β' = 109.6°, and γ' = 102.8°.) Block-diagonal refinement led to an *R* index of 0.049 for 1741 reflections. The authors attempted, unsuccessfully, to find a structure consistent with space group *P*$\bar{1}$, with the two molecules related to one another by a center of symmetry. We find, instead, that each molecule lies *on* a center of symmetry and that the space group is indeed *P*$\bar{1}$. Details follow.

The *x* coordinates of all the atoms were decremented by approximately 0.25 so as to place the two cadmium atoms at centers of symmetry (0, $^1/_2$, $^1/_2$ and $^1/_2$, $^1/_2$, $^1/_2$); the coordinates of the remaining atoms were then symmetrized, in pairs, about these centers. This symmetrizing step required a shift of about 0.04 Å in the position of Cd(2) relative to Cd(1) and shifts ranging up to 0.25 Å for the lighter atoms. The anisotropic *B*'s were averaged in pairs. Hydrogen atoms were assigned as described.[8] Least-squares refinement converged to *R* = 0.037 for the 1741 reflections. Final parameters are given in Table V and bond lengths in Table VI.

The earlier refinement,[8] in space group *P*1, was by block-diagonal least squares, and accordingly the singularities inherent in the refinement of a centrosymmetric structure in an acentric space group[2] would not have been immediately obvious. However, convergence was undoubtedly slow (if, indeed, convergence was obtained: "Refinement was terminated after six cycles..."), and the resulting structure was quite distorted. For example, the two Cd-S distances, at 2.80 and 2.93 Å, differed by more than 10 esd's, as did some of the Cd-N distances (2.25-2.44 Å). The structure we have derived in *P*$\bar{1}$ is reasonable in all aspects. The spread among chemically equivalent S-C, N-C, and C-C bond lengths is well within the esd's, and variations among the Cd-N distances can be easily correlated with the nature of the various ligands. Since the *P*$\bar{1}$ model yields a considerably improved agreement index and is based on approximately half as many parameters as the earlier *P*1 model, there can be no doubt that it is a more appropriate description of the structure.

**(Malonato)diaquacalcium(II).**[9] The structure of this compound was described in the monoclinic space group *C*2,

**Table V.** Final Parameters for *catena*-Bis[μ-bis(2-aminoethyl)amine]-bis(μ-thiocyanato)-bis(isothiocyanato)dicadmium(II)[a]

| atom | *x* | *y* | *z* | *B*₁₁ | *B*₂₂ | *B*₃₃ | *B*₁₂ | *B*₁₃ | *B*₂₃ |
|---|---|---|---|---|---|---|---|---|---|
| Cd(1) | 0 | $^1/_2$ | $^1/_2$ | 1.89 (2) | 2.61 (2) | 2.63 (2) | 0.66 (3) | 1.97 (3) | 3.38 (3) |
| Cd(2) | $^1/_2$ | $^1/_2$ | $^1/_2$ | 1.86 (2) | 3.62 (2) | 1.97 (2) | 1.55 (3) | 2.07 (3) | 3.57 (3) |
| S(1, 2) | 14 (1) | 2839 (2) | 544 (3) | 1.97 (5) | 4.66 (7) | 2.88 (7) | 0.24 (8) | 2.67 (9) | 2.50 (11) |
| S(3, 4) | 3042 (1) | 1124 (2) | -4165 (3) | 2.80 (6) | 4.74 (7) | 2.19 (6) | 0.95 (9) | 2.48 (9) | 2.91 (11) |
| N(1, 2) | 2729 (4) | 3860 (7) | 2964 (10) | 2.38 (18) | 5.57 (27) | 4.07 (26) | 1.34 (33) | 3.70 (35) | 5.56 (43) |
| N(3, 4) | 4726 (4) | 2840 (6) | 1158 (9) | 3.47 (21) | 5.01 (24) | 2.82 (24) | 3.19 (36) | 3.93 (38) | 3.68 (39) |
| N(5, 8) | 283 (4) | 2676 (5) | 5513 (9) | 2.35 (16) | 3.58 (18) | 3.64 (23) | 2.45 (27) | 2.83 (32) | 5.21 (33) |
| N(6, 9) | -2249 (3) | 3311 (5) | 2446 (8) | 1.89 (14) | 2.46 (16) | 2.12 (17) | 1.31 (24) | 2.18 (25) | 2.98 (27) |
| N(7, 10) | 5607 (4) | 2964 (6) | 6175 (8) | 2.16 (16) | 3.46 (19) | 2.18 (19) | 1.03 (27) | 1.59 (27) | 3.11 (30) |
| C(1, 2) | 1622 (4) | 3446 (6) | 1995 (10) | 2.56 (20) | 3.01 (21) | 3.02 (25) | 1.34 (30) | 3.05 (36) | 3.49 (36) |
| C(3, 4) | 4019 (4) | 2123 (6) | -1034 (10) | 2.44 (19) | 3.02 (20) | 2.69 (24) | 1.93 (30) | 3.57 (36) | 3.21 (36) |
| C(5, 10) | -978 (5) | 1245 (6) | 3419 (12) | 2.94 (20) | 2.72 (21) | 4.82 (32) | 2.01 (32) | 3.93 (41) | 4.83 (43) |
| C(6, 9) | -2130 (4) | 2058 (7) | 3196 (11) | 2.41 (19) | 3.69 (23) | 3.54 (29) | 1.42 (32) | 3.24 (38) | 5.16 (43) |
| C(7, 11) | 6962 (4) | 2392 (6) | 9625 (9) | 2.01 (17) | 2.60 (19) | 2.14 (21) | 1.37 (28) | 2.04 (30) | 2.53 (32) |
| C(8, 12) | 6603 (5) | 3739 (7) | 8944 (10) | 3.28 (22) | 3.27 (22) | 2.16 (23) | 0.54 (35) | 1.97 (36) | 3.25 (36) |

[a] From our refinement in space group *P*$\bar{1}$; all coordinates except those of Cd(1) and Cd(2) are ×10⁴; the Gaussian factor is of the form exp[−¹/₄(*B*₁₁*h*²*a*\*² + ... + *B*₂₃*klb*\**c*\*)].

Table VI. Bond Lengths (Å) in *catena*-Bis[μ-bis(2-aminoethyl)amine]-bis(μ-thiocyanato)-bis(isothiocyanato)dicadmium(II)[a]

| | | |
|---|---|---|
| Cd(1)–S(1, 2) | 2.865 (2) | 2.80, 2.93 |
| Cd(1)–N(5, 8) | 2.294 (5) | 2.30, 2.31 |
| Cd(1)–N(6, 9) | 2.403 (5) | 2.38, 2.42 |
| Cd(2)–N(1, 2) | 2.367 (6) | 2.36, 2.38 |
| Cd(2)–N(3, 4) | 2.322 (6) | 2.27, 2.44 |
| Cd(2)–N(7, 10) | 2.334 (5) | 2.25, 2.44 |
| S(1, 2)–C(1, 2) | 1.643 (7) | 1.61, 1.67 |
| S(3, 4)–C(3, 4) | 1.636 (7) | 1.59, 1.67 |
| N(1, 2)–C(1, 2) | 1.136 (9) | 1.12, 1.17 |
| N(3, 4)–C(3, 4) | 1.144 (10) | 1.12, 1.17 |
| N(5, 8)–C(5, 10) | 1.480 (9) | 1.46, 1.54 |
| N(6, 9)–C(6, 9) | 1.477 (8) | 1.43, 1.54 |
| N(6, 9)–C(7, 11) | 1.475 (9) | 1.42, 1.56 |
| N(7, 10)–C(8, 12) | 1.472 (9) | 1.46, 1.49 |
| C(5, 10)–C(6, 9) | 1.507 (8) | 1.45, 1.61 |
| C(7, 11)–C(8, 12) | 1.498 (9) | 1.48, 1.56 |

[a] The first column of values is from our refinement in space group $P\bar{1}$; the right-hand column is from the earlier refinement[8] in $P1$.

with four molecules in a unit cell of dimensions $a$ = 13.955 Å, $b$ = 6.855 Å, $c$ = 6.835 Å, and $\beta$ = 106.28°. Least-squares refinement led to $R$ = 0.029 for 748 reflections with $I > \sigma(I)$. The final coordinates (Table I, ref 9) correspond quite closely to space group $C2/m$; indeed, the authors reported that "An attempt was made to refine the structure in space group $C2/m$.... Three cycles of full-matrix least-squares led to unacceptably high discrepancy indices of 0.19 and 0.26 for $R_1$ and $R_2$, respectively." We have experienced no such difficulty in refining in $C2/m$.

Symmetrizing the coordinates and anisotropic temperature parameters so as to conform to $C2/m$ resulted initially in $R$ = 0.035 (rather than the 0.19 noted above), and one least-squares cycle reduced it to 0.033. A difference map then showed that the hydrogen atoms attached to O(6) had been positioned incorrectly; it also suggested very strongly that O(6) is disordered across the mirror plane at $y$ = 0. Such a disorder explains the very large $\beta_{22}$ term (Table I, ref 9) and also results in a reasonable hydrogen-bonding pattern. Our final least-squares refinement was based on such a disordered model and included 74 parameters: coordinates and anisotropic $\beta$'s for the eight Ca, O, and C atoms, coordinates and isotropic $B$'s for the four H atoms, a scale factor (final value 0.993 (2)), and an extinction parameter (1.38 (13) × 10⁻⁶). Our final $R$ index was 0.024 for 748 reflections and 74 parameters, compared to 0.029 for 90 parameters in the earlier investigation.

Our parameters are listed in Table VII and bond distances and assorted angles in Table VIII. Once again the structure is considerably more regular than that reported for the refinement in the lower symmetry. Other aspects of the structure

are approximately as discussed earlier with the exception of the hydrogen bonding; whereas the earlier investigators reported that only the water molecule O(5) forms hydrogen bonds, we find that O(6) does as well.

We have no explanation for the failure of the earlier investigators to obtain a satisfactory structure in $C2/m$. We suspect an error in the use of the computer program, noting again that we obtained an $R$ of 0.035 for, presumably, the same model that led to an $R$ of 0.19 earlier.[10]

**Disodium Di-μ-hydroxo-dizinc(II) Molybdate, NaZn(OH)(MoO₄).**[11] This compound forms orthorhombic crystals with unit cell dimensions $a$ = 7.850, $b$ = 9.292, and $c$ = 6.148 Å. Block-diagonal least-squares refinement in space group $Pna2_1$ led to $R$ = 0.038 for 843 reflections with intensities greater than $3.0\sigma$. Surprising features of the resulting structure include a rather wide range of Mo–O distances, from 1.67 to 1.79 Å, within the MoO₄ tetrahedra and anisotropic $\beta$'s, notably for O(1), O(2), and O(3), that differ wildly from one atom to another. The authors reported systematic absence of reflections $h0l$ with $h$ odd and $0kl$ with $k + l$ odd and stated that "these absences fix the space group unequivocally as $Pna2_1$". However, the centrosymmetric space group $Pnam$ ($Pnma$ is its standard setting) is also consistent with these absences, and we have attained satisfactory refinement in it.

Reformulating the structure in $Pnam$ involved incrementing the $z$ coordinates of all the atoms by about 0.09 followed by symmetrizing so that Zn lies on a center of symmetry, Mo, Na, O(3), O(4), and O(5) lie on mirror planes, and O(1) and O(2) are related to one another across a mirror; the symmetrizing shifts ranged up to 0.17 Å. Initial refinement reached convergence at $R$ = 0.036 for 46 parameters, compared to $R$ = 0.038 for 73 parameters in the earlier work; the goodness-of-fit was 3.3. At this point a difference map, calculated in hopes of confirming the location of the hydrogen atom, showed severe features, reaching –2.2 e/Å³, in the vicinities of the oxygen atoms because, following the earlier study,[11] the atomic form factor of F⁻ was being used for the oxygen atoms. Accordingly, we carried out further refinements based on form factors[12] for O⁻ and, to achieve total charge balance, for Mo²⁺ rather than Mo⁶⁺. The resulting $R$ index was 0.026, and a subsequent difference map had its largest peak, 0.8 e/Å³, in the position proposed for the hydrogen atom.[11] Final refinement, including coordinates and an isotropic $B$ for this hydrogen atom, converged at $R$ = 0.025 and a goodness-of-fit of 2.0.

Atomic parameters are given in Table IX and some interatomic distances in Table X. The distances are more regular than those obtained in $Pna2_1$, and the $\beta$'s are much more reasonable.

**Red Isomer of Bis[$N$-isobutyl(5-chloro-$\alpha$-phenyl-2-hydroxybenzylidine)aminato]copper(II).**[13] Finally, although we have not carried out the definitive least-squares refinement

Table VII. Positional Parameters[a] and $\beta$'s[b] for Ca(C₃H₂O₄)(H₂O)₂

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | $M^c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 2227.0 (4) | 0 | 1231.4 (7) | 27.4 (3) | 61 (1) | 86 (1) | 0 | 21.0 (4) | 0 | 4 |
| O(1, 2) | 3231 (1) | 1600 (2) | –908 (2) | 49 (1) | 70 (2) | 169 (3) | 15 (1) | 55 (1) | 14 (2) | 8 |
| O(3, 4) | 3519 (1) | 1606 (2) | –5830 (2) | 52 (1) | 86 (3) | 112 (3) | –1 (1) | 11 (1) | 13 (2) | 8 |
| O(5) | 1245 (1) | 0 | 3614 (3) | 38 (1) | 95 (4) | 124 (4) | 0 | 33 (2) | 0 | 4 |
| O(6) | 863 (2) | 364 (7) | –1770 (4) | 38 (2) | 158 (19) | 163 (6) | –15 (3) | 2 (2) | 46 (6) | 4 |
| C(1) | 3532 (2) | 0 | –1407 (3) | 23 (1) | 82 (4) | 65 (4) | 0 | 7 (2) | 0 | 4 |
| C(2) | 4297 (2) | 0 | –2638 (3) | 21 (1) | 106 (5) | 96 (5) | 0 | 15 (2) | 0 | 4 |
| C(3) | 3754 (2) | 0 | –4921 (3) | 24 (1) | 99 (5) | 98 (5) | 0 | 23 (2) | 0 | 4 |

| | $x$ | $y$ | $z$ | $B$, Å² | $M$ | | $x$ | $y$ | $z$ | $B$, Å² | $M$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H(2) | 472 (1) | 112 (3) | –229 (3) | 1.5 (3) | 8 | H(6) | 93 (4) | 139 (9) | –237 (9) | 5.2 (16) | 4 |
| H(5) | 136 (2) | 100 (4) | 443 (4) | 5.8 (7) | 8 | H(6') | 31 (3) | 0 | –216 (7) | 5.7 (12) | 4 |

[a] Values are × 10⁴ for Ca, O, and C and × 10³ for H. [b] The form of the anisotropic Gaussian factor is $\exp[-10^4(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Multiplicity—number of atoms per unit cell.

**Table VIII.** Bond Distances (A) and Angles (deg) in
$Ca(C_3H_2O_4)(H_2O)_2$

| | this work | ref 9 |
|---|---|---|
| | Distances | |
| Ca-O(1, 2) | 2.540 (2) | 2.520, 2.555 |
| -O(1.2)$^a$ | 2.411 (1) | 2.397, 2.424 |
| -O(3, 4)$^b$ | 2.543 (2) | 2.516, 2.563 |
| -O(5) | 2.404 (2) | 2.408 |
| -O(6) | 2.389 (3) | 2.384 |
| C(1)-O(1, 2) | 1.255 (2) | 1.313, 1.194 |
| -C(2) | 1.533 (3) | 1.541 |
| C(2)-C(3) | 1.532 (3) | 1.537 |
| C(3)-O(3, 4) | 1.261 (2) | 1.238, 1.281 |
| C(2)-H(2) | 0.95 (2) | 1.05, 1.05 |
| O(5)-H(5) | 0.87 (3) | 0.85, 0.81 |
| O(6)-H(6) | 0.83 (7) | |
| -H(6') | 0.78 (5) | |
| O(5)···O(34)$^a$ | 2.745 (2) | 2.748, 2.755 |
| H(5)···O(34)$^a$ | 1.88 (3) | 1.94, 1.92 |
| O(6)···O(34)$^c$ | 2.923 (4) | 3.04, 3.05 |
| H(6)···O(34)$^c$ | 2.13 (6) | |
| O(6)···O(5)$^d$ | 2.869 (4) | 3.091 |
| H(6')···O(5)$^d$ | 2.12 (5) | |
| | Angles | |
| O(12)-C(1)-O(12)$^e$ | 121.7 (1) | 121.9 |
| C(2)-C(1)-O(12) | 119.1 (1) | 118.9, 119.2 |
| C(1)-C(2)-C(3) | 109.7 (2) | 109.4 |
| C(1)-C(2)-H(2) | 110 (1) | 110, 110 |
| C(3)-C(2)-H(2) | 110 (1) | 109, 109 |
| H(2)-C(2)-H(2)$^e$ | 107 (2) | 109 |
| C(2)-C(3)-O(34) | 119.2 (1) | 114.8, 124.2 |
| O(34)-C(3)-O(34)$^e$ | 121.6 (1) | 121.0 |
| H(5)-O(5)-H(5)$^e$ | 104 (3) | 107 |
| H(6)-O(6)-H(6') | 110 (5) | |

$^a$ $^1/_2 - x, ^1/_2 - y, \bar{z}$.  $^b$ $x, y, z + 1$.  $^c$ $^1/_2 - x, ^1/_2 - y, \bar{z} - 1$.
$^d$ $\bar{x}, \bar{y}, \bar{z}$.  $^e$ $x, \bar{y}, z$.

(the number of $F_0$ values is reported to be 5194), we are confident that the structure of this compound should be described in space group $P\bar{1}$ rather than $P1$. As in the case of *catena*-bis[$\mu$-bis(2-aminoethyl)amine]-bis($\mu$-thiocyanato)-bis(isothiocyanato)dicadmium(II),[8] the authors' attempts to derive a structure in $P\bar{1}$ were apparently predicated on the assumption that the two molecules in the unit cell would be related to one another by a center of symmetry; instead, each of the molecules is itself centrosymmetric. The description of the structure in $P\bar{1}$ entails incrementing the $x$, $y$, and $z$ coordinates (Table IIIc, ref 13) by approximately 0.25 and then averaging the parameters of the equivalent ligands (A and B; C and D). Shifts necessary to achieve the centric structure are approximately of the same amount as those noted in the previous four examples, reaching a maximum of about 0.2 Å.

The earlier authors reportedly carried out full-matrix least-squares refinement to convergence; however, the number of parameters, 664, reported in Table IIIc is so large as to suggest that, in fact, the full matrix was not collected. (In addition, full-matrix refinement in $P1$ would at least have resulted in singularities due to the polarity of the assumed

space group, i.e., the lack of a fixed origin of coordinates; no such singularities were noted.) The resulting molecular geometry was quite unsatisfactory, pairs of chemically equivalent distances differing by as much as 50 esd's (Table IV, ref 13). We have no doubt that refinement in space group $P\bar{1}$ would proceed normally and would lead to more satisfactory results.

**Conclusions.** Approximately 200 crystal structure analyses were reported in Volume 16 (1977) of *Inorganic Chemistry*. Of these, we have noted seven that were reported in space groups of unnecessarily low symmetry; there may well be a few more that we have missed. For the two cases in which the assumed space group, $P\bar{1}$, has a different Laue symmetry than the correct space group, $C2/c$, the derived molecular parameters were correct within their esd's. In the remaining five, however, the Laue groups were correct, but centers of symmetry were overlooked; in these cases, the derived results were seriously in error. And while five, or seven, out of 200 is not a large percentage, it is large enough to cause concern. How can these errors be avoided?

In these days of automation, the identification of the correct lattice type is often left entirely to a computer, and the true lattice symmetry may not be noted if the software tolerances are inappropriate. Preliminary precession or Weissenberg photography should provide adequate safeguards against this sort of error. Yet, in one of the two instances noted in which the lattice symmetry was incorrectly assigned,[3] preliminary photographs *were* prepared, so the incorrect assignment of lattice type cannot be blamed on the automatic indexing features of diffractometer software. For the Zn compound[3] a hint of higher symmetry lies in the near equality of the $a$ and $b$ axes and of the angles $\alpha$ and $\beta$. For the Cu compound,[5] however, the reported cell dimensions provide no clear clue, and discovery of the monoclinic lattice would have required a systematic search for orthogonal axes.[14]

In four of the five instances in which a center of symmetry was overlooked, the authors were well aware of the space group ambiguities and indeed searched, without success, for centrosymmetric descriptions of the structures. In fact, the structures *were* closely centrosymmetric; the difficulty lay in recognizing the presence of the centers of symmetry. In such cases, full-matrix least-squares refinement should result in near-singularities and, accordingly, in chaotic parameter shifts and standard deviations. Indeed, in one of the five instances[7] the least-squares matrix was blocked into two separate submatrices, specifically to circumvent such singularities. In at least two, and probably three, other instances the matrix was blocked because of the large number of parameters; although refinement convergence is essentially unattainable in such cases, the singularities are otherwise well masked. In one instance,[9] however, a reportedly full-matrix refinement apparently failed to adequately signal any difficulty.

We can offer no simple way to avoid the types of errors exposed above. To us, the clearest clue that something was amiss invariably lay in the table of atomic coordinates: values suspiciously close to 0, $^1/_4$, or the like or pairs of chemically equivalent atoms with interesting numerical relationships. But we suspect that these clues will not always be clear. Our only

**Table IX.** Atomic Parameters for $NaZn(OH)MoO_4$$^a$

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | M |
|---|---|---|---|---|---|---|---|---|---|---|
| Zn | 0.5 | 0 | 0.5 | 50.6 (7) | 39.6 (5) | 46.2 (10) | 14.4 (11) | 18.3 (17) | -3.7 (14) | 4 |
| Mo | 0.12379 (5) | 0.17058 (5) | 0.25 | 25.6 (4) | 22.7 (3) | 54.6 (7) | 9.8 (9) | 0 | 0 | 4 |
| Na | 0.36433 (5) | 0.3104 (3) | 0.75 | 110 (5) | 38 (3) | 151 (7) | 9 (6) | 0 | 0 | 4 |
| O(1, 2) | 0.1140 (4) | 0.2785 (3) | 0.0153 (4) | 92 (4) | 38 (2) | 64 (5) | 57 (6) | -9 (11) | 5 (5) | 8 |
| O(3) | 0.4529 (7) | 0.4480 (6) | 0.25 | 68 (7) | 85 (7) | 277 (20) | 86 (10) | 0 | 0 | 4 |
| O(4) | 0.8691 (5) | 0.4357 (4) | 0.75 | 26 (4) | 34 (3) | 44 (6) | 1 (7) | 0 | 0 | 4 |
| O(5) | 0.3125 (5) | 0.0617 (5) | 0.25 | 58 (4) | 51 (8) | 72 (8) | 0 | 0 | 4 |
| H | 0.783 (13) | 0.457 (10) | 0.75 | 4 (2)$^b$ | | | | | | 4 |

$^a$ Anisotropic Gaussian parameters are of the form $\exp(-\beta_{11}h^2 - ... - \beta_{23}kl) \times 10^4$.  $^b$ Isotropic.

**Table X.** Interatomic Distances for NaZn(OH)MoO$_4$

| | this work | ref 11 |
|---|---|---|
| Zn–O(1, 2)$^a$ | 2.246 (3) | 2.219, 2.264 |
| –O(4)$^b$ | 1.943 (3) | 1.882, 1.988 |
| –O(5) | 2.204 (3) | 2.135, 2.325 |
| Mo–O(1, 2) | 1.758 (3) | 1.669, 1.790 |
| –O(3)$^c$ | 1.736 (6) | 1.747 |
| –O(5) | 1.794 (4) | 1.755 |
| Na–O(1, 2)$^d$ | 2.571 (4) | 2.562, 2.623 |
| –O(1, 2)$^e$ | 2.680 (4) | 2.633, 2.799 |
| –O(3) | 2.664 (6) | 2.692 |
| –O(4)$^c$ | 2.287 (5) | 2.360 |
| –O(5)$^f$ | 2.716 (5) | 2.712 |
| O(4)–H | 0.71 (10) | |
| O(4)···O(3)$^g$ | 2.749 (6) | |
| H···O(3)$^g$ | 2.05 (10) | |

$^a$ $1/2 + x, 1/2 - y, 1/2 - z.$  $^b$ $3/2 - x, -1/2 + y, 1 - z.$  $^c$ $-1/2 + x, 1/2 - y, z.$  $^d$ $x, y, 1 + z.$  $^e$ $1/2 + x, 1/2 - y, 1 + z.$  $^f$ $1/2 - x, 1/2 + y, 1 - z.$  $^g$ $1 - x, 1 - y, 1/2 + z.$

suggestion is that extreme caution be maintained at all stages of a crystal structure analysis and that undue haste be avoided, even when the pressures of competition or the availability of sophisticated automation make haste seem an end in itself.

**Registry No.** Dichlorobis(4-vinylpyridine)zinc(II), 17501-34-7; (3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioximato)-copper(II) perchlorate·$^1/_2$ methanol, 62197-90-4; parwelite, 12420-60-9; *catena*-bis[μ-bis(2-aminoethyl)amine]-bis(μ-thiocyanato)-bis(isothiocyanato)dicadmium(II), 60840-52-0; (malonato)diaquacalcium(II), 18923-49-4; disodium di-μ-hydroxo-dizinc(II) molybdate, 61231-78-5; bis[*N*-isobutyl(5-chloro-α-phenyl-2-hydroxybenzilidine)aminato]copper(II), 61129-02-0.

**References and Notes**

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(4) An apparent exception is C(4). However, the x coordinate of C(4b) is undoubtedly misprinted; otherwise, the C–C distance would be unrealistic. Its correct value is probably 0.2538 rather than 0.2438.
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(10) Dr. Howard Einspahr has brought to our attention a recent paper describing a second, independent X-ray diffraction study of this compound (B. Briggman and Å. Oskarsson, *Acta Crystallogr., Sect. B*, **33**, 1900 (1977)). Refinement in C2/*m* converged at $R = 0.032$ for 992 reflections, and "a few cycles of refinement in the space group C2 did not significantly improve the structural model". Atom O(6) was treated as a single, highly anisotropic atom rather than as disordered; otherwise, the resulting structure is essentially identical with what we find. All atomic coordinates agree with our values within 3 esd's except for the z coordinates of O(6) and H(6), which were undoubtedly influenced by the way in which O(6) was treated.
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(15) Contribution No. 5986.

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# Additions and Corrections

## 1977, Volume 16

**Kenneth R. Poeppelmeier and John D. Corbett***: Metal–Metal Bonding in Reduced Scandium Halides. Synthesis and Characterization of Heptascandium Decachloride (Sc$_7$Cl$_{10}$). A Novel Metal-Chain Structure.

Pages 1108 and 1109. The Sc2–C15 distance, Figure 1 and Table II, should be 2.611 (3) Å rather than 2.44 Å.

Page 1110. In the Discussion, paragraph 3, last sentence, the bond order for a 3.15 Å Sc–Sc bond should be 0.4, not 0.6 as printed—John D. Corbett

## 1979, Volume 18

**Howard W. Turner, Richard A. Andersen,** * **Allan Zalkin,*** **and David H. Templeton***: Chloro-, Methyl-, and (Tetrahydroborato)tris((hexamethyldisilyl)amido)thorium(IV) and -uranium(IV). Crystal Structure of (Tetrahydroborato)-tris((hexamethyldisilyl)amido)thorium(IV).

Page 1222. The last sentence in the second paragraph of the first column should read: "...shows two single absorptions at δ 4.17 and 73.6...." The second sentence in the first complete paragraph in the second column should read: "...quartet centered at δ −101, $J_{HB}$ = 79 Hz, and a singlet at δ −1.87."—Richard A. Andersen

**Donald J. Darensbourg*** **and Allen H. Graves**: Steric Contributions to the Solution Dynamics Involving Phosphorus Ligand Dissociation in Substituted Derivatives of Molybdenum Hexacarbonyl.

Page 1258. The second reaction in Scheme I should be



o = $^{12}$CO, ● $^{13}$CO
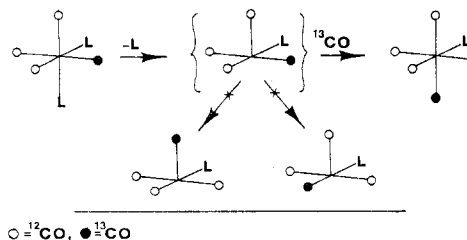
clearly indicating that no rearrangement of the [Mo(CO)$_4$L] intermediate was observed on the time scale of $^{13}$CO addition.—Donald J. Darensbourg