

ATP on the basis of potential-energy calculations (Perahia, Pullman & Saran, 1972).

Potassium and water coordinates

Each of the four non-equivalent K^+ ions is six-coordinated but with significant differences (Table 7). $K(2)$, $K(3)$ and $K(4)$ are coordinated by O atoms of the α and β phosphate groups forming the UDP dimer (Fig. 2). $K(1)$ is coordinated by two O(2) atoms of the uracil, and O atoms of four water molecules. The water molecules are either three- or four-coordinated (Table 7) and provide a hydrogen-bonded network. As a result the structure has large hydrophilic cavities containing water and K^+ ions, alternating with hydrophobic regions (Fig. 4).

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The Crystal Structure of Bis(tetraethylammonium) Tetrachlorodioxouranate(VI): Correction from $P\bar{1}$ to $P2_1/n$

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Abstract

Bois, Nguyen & Rodier [*Acta Cryst.* (1976). **B32**, 1541–1544] refined the structure of $[(C_2H_5)_4N^+]_2(UCl_4O_2)^{2-}$

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$(UCl_4O_2)^{2-}$ in space group $P\bar{1}$, $Z = 2$, to $R = 0.048$, but it very nearly has symmetry $P2_1/n$. We find that refinement in $P2_1/n$ hardly changes R and renders both ions substantially more symmetrical. Including (but not refining) the hydrogen positions and isotropic Gaussian amplitudes, letting all the heavy-atom Gaussians become anisotropic, and accounting for secondary extinction reduces R to 0.040 and further regularizes the ions. Finally, allowing for the presence of two minor twin components (4.4% and 7.1%) brings R to 0.035, still further regularizes the bond lengths and angles, and

explains pretty well the 37 apparent violations of the $P2_1/n$ extinctions. Of the final averages (U—Cl 2.670, U—O 1.758, N—C 1.515, and C—C 1.488 Å; and N—C—C 116.3°) those of the cation differ markedly from the original values, surely in consequence of including the H's.

The $P\bar{1}$ structure (Bois, Nguyen & Rodier, 1976; 'BNR') reported for $[(C_2H_5)_4N]_2UCl_4O_2$, 'TEACLOU', attracted our attention for two reasons. First, the great ranges of the distances and angles in the cation (N—C 1.50–1.62, C—C 1.30–1.64 Å; C—N—C 109–130, N—C—C 101–120°) seemed inconsistent with the care evidently taken in the experimental work, which included the preparation of a spherical crystal of suitable size. Second, the reported structure differs so little from $P2_1/n$ symmetry as to suggest error in the space-group assignment. The average deviation of the atomic coordinates reported by BNR from positions consistent with $P2_1/n$ is about three times the e.s.d.'s of these coordinates (see Table 1). Taken individually, these deviations are not very large; taken together at face value — there are 74 such parameter comparisons — they would make a compelling but (we are convinced) false statistical case against the higher symmetry. The deviations in bond lengths and angles from $P2_1/n$ symmetry are similarly small or great, depending on the point of view, but here the scale of comparison is uncertain because of the lack of the positional covariances, not reported by BNR, and because of our inability to reproduce even approximately the BNR angle and distance e.s.d.'s, which seem to be too large by a factor of about two.

The list of structure factors, obtained from The Executive Secretary, International Union of Crystallography, includes 36 weak $h0l$ reflections with $(h + l)$ odd and a single $0k0$ with k odd that violate the extinctions of space group $P2_1/n$ and forced BNR to seek a triclinic structure, when, after having frozen their data collection in a monoclinic mode, they failed to find a $P2$, Pm , or $P2/m$ structure. However, the reported intensities of these reflections are by no means explained by the triclinic structure of BNR. The worst are 100, 010, and 001, for which the mean $|F_o - |F_c||$ is about 12σ . Indeed, these F_o 's are all roughly equal to each other and to 2.5 times their F_c 's. For the remaining 34 $h0l$ reflections with $(h + l)$ odd, the r.m.s. deviation between F_o and F_c is 7.5σ .

Some exploratory calculations based on $P2_1/n$ (see Table 2, columns II and III) increased our conviction that the symmetry is monoclinic, despite the apparent space-group violations. The observations by Staritzky & Singer (1952, p. 538, not mentioned by BNR, although they reference SS for other crystal data and for the chemical preparation) that the compound 'commonly form[s] twins, either simple or repeated with

{110} as the twinning plane' suggested a possible source for these violations, and observations that we have made confirm the twinning and lead to a qualitative explanation of the reported intensities of most of the $h0l$ reflections with $(h + l)$ odd. Our final model, based on $P2_1/n$ with small amounts of two orientations of twin components, seems good [Tables 1, 2 (column IV), and 3].* It has led to significant improvement in agreement and in approximate non-crystallographic molecular symmetry; it has also reduced the total weighted variance for the forbidden reflections (excluding 100, 010, and 001) by 56%. We must dismiss the reported intensities of 100, 010, and 001 as aberrant as they cannot be explained by our twinning model; they may represent genuine error in estimating the backgrounds of reflections that lie so close to the main beam ($2\theta \sim 4^\circ$).

Some of the details follow.

Constraint to $P2_1/n$ and check refinement in $P\bar{1}$

We note that we obtained a slight *decrease* in R , compared with the value reported by BNR, in refinement (II), in $P2_1/n$ [Table 2 (columns I and II)]. Here the only change from BNR's $P\bar{1}$ model was to add the constraints necessary for $P2_1/n$ symmetry, thereby reducing the number of parameters from 149 to 75. To confirm that this decrease was no more than an accident of the particular computer programs, to assure that additional refinement in $P\bar{1}$ would not lead to results convincingly better than any we obtained in $P2_1/n$, and to verify that, in contrast to the centric \rightarrow acentric case, no difficulty in refinement arises when the symmetry of a structure is allowed to decrease to a subgroup of different Laue symmetry (Schomaker & Marsh, 1979), we continued the refinement in $P\bar{1}$. There was indeed no apparent difficulty. Convergence was substantially complete in one full-matrix step, and brought slight decreases in R (0.0474 to 0.0466), R' (0.0531 to 0.0505), and the goodness of fit (3.34 to 3.20). While conventional significance tests (*e.g.* Hamilton, 1965) might suggest that these improvements are overwhelming evidence that the space group actually is $P\bar{1}$, we contend that such tests can be misleading. In this case the twin components indeed do reduce the overall symmetry of the crystal specimen. However, the truly overwhelming *statistical* evidence, with goodness of fit ~ 3.3 and some 2000 degrees of freedom, is that both models are enormously unsatisfactory for unknown reasons which if corrected might well reverse the judgment. In any event, the improve-

* Lists of structure factors and hydrogen parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34219 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *The $P2_1/n$ average of the BNR structure and the scatter in that average compared with the TWINS- $P2_1/n$ results*

For each atom parameter, the first line gives the BNR average, the e.s.d. of this average in parentheses, *i.e.* $\sqrt{2}$ times the mean BSR e.s.d., and the e.s.d. of a single 'P1' value, from the difference between the two transformed values obtained on assuming $P2_1/n$ equivalence ($\sigma = |A|/\sqrt{2}$), all (except the B's) multiplied by 10^3 (U), 10^4 (Cl), or 10^3 (O, N, and C), and the second line gives the TWINS- $P2_1/n$ values, multiplied by 10^4 except for U(10^5). Note that the second B value in the first line for each C atom is a TWINS average^c.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}^a	β_{22}^b	β_{33}	β_{12}	β_{13}, B^c	β_{23}
U	0 (0)	0 (0)	0 (0)	770 (7)14	810 (7)42	415 (7)21	0 (7)0	-30 (7)14	-65 (14)21
	0 (0)	0 (0)	0 (0)	835 (4)	901 (4)	464 (2)	-11 (11)	-70 (4)	-49 (8)
Cl(1)	7749 (3)23	1398 (4)0	161 (4)15	89 (3)0	110 (5)4	133 (5)23	53 (4)64	18 (3)25	20 (6)16
	7754 (2)	1413 (2)	172 (2)	93 (2)	112 (2)	121 (2)	22 (4)	8 (3)	-16 (4)
Cl(2)	6381 (3)1	2749 (4)8	4753 (4)4	109 (4)3	98 (4)4	130 (5)5	17 (4)6	0 (4)3	-10 (6)11
	6381 (2)	2757 (2)	4732 (2)	116 (2)	100 (2)	111 (2)	24 (4)	0 (4)	-18 (4)
O	28 (1)4	15 (1)1	135 (1)0	22 (1)8	31 (2)20	5 (1)1	-1 (1)4	-2 (1)1	4 (2)7
	302 (6)	137 (6)	1339 (4)	173 (8)	193 (9)	44 (3)	-4 (1)4	-45 (8)	-45 (11)
N	3 (1)2	481 (1)0	250 (1)4	14 (1)4	11 (2)0	6 (1)2	4 (1)3	1 (1)6	-2 (1)1
	26 (6)	4758 (6)	2517 (5)	103 (6)	103 (10)	60 (4)	-6 (1)2	-21 (8)	-22 (10)
C(1)	146 (1)2	450 (2)1	222 (1)12		6.9 (4)·1			7.0 (3)	
	1435 (9)	4427 (11)	2198 (8)	103 (10)	237 (15)	112 (9)	-7 (2)1	38 (16)	-61 (21)
C(2)	197 (1)10	538 (2)1	133 (1)1		7.8 (4)·2			7.7 (4)	
	1970 (11)	5291 (10)	1324 (8)	214 (16)	212 (18)	90 (8)	-139 (25)	56 (19)	4 (18)
C(3)	-33 (1)2	399 (2)8	354 (1)8		7.6 (4)1·6			6.4 (3)	
	-284 (9)	3926 (10)	3471 (8)	150 (12)	190 (15)	81 (8)	-34 (2)3	7 (1)5	51 (18)
C(4)	-28 (1)10	247 (2)11	336 (1)2		7.7 (4)1·1			7.4 (4)	
	-232 (9)	2480 (9)	3352 (9)	182 (14)	124 (12)	148 (11)	6 (2)2	53 (20)	36 (19)
C(5)	-100 (1)12	446 (2)6	164 (1)16		6.9 (4)2·0			6.4 (3)	
	-945 (10)	4414 (10)	1644 (8)	185 (14)	151 (11)	83 (8)	-58 (2)3	-66 (17)	0 (16)
C(6)	-238 (1)3	439 (1)1	190 (1)2		7.2 (4)·1			6.7 (3)	
	-2389 (9)	4419 (10)	1884 (8)	121 (10)	172 (12)	124 (10)	4 (2)0	-77 (17)	-42 (19)
C(7)	-21 (1)1	629 (2)1	278 (2)9		8.4 (4)·6			6.8 (3)	
	-198 (10)	6200 (10)	2771 (8)	196 (14)	146 (13)	99 (9)	-38 (2)3	4 (1)8	-28 (18)
C(8)	77 (1)4	680 (2)8	353 (2)1		7.8 (4)2·5			7.6 (3)	
	755 (10)	6814 (11)	3516 (8)	189 (14)	218 (17)	94 (8)	-148 (2)6	-25 (1)7	-103 (19)

(a) Gaussian attenuation factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ or $\exp[-B(\sin \theta/\lambda)^2]$. This is not a genuine temperature factor; because there are indeed numerous reported measurements of the temperature factor and thermal amplitudes of vibration *per se*, it is important to refrain from usual misnomers. Accordingly, we also refer to B's, β 's, and U's as Gaussian amplitudes.

(b) For BNR.

(c) $(8\pi^2/3)(U_{11} + U_{22} + U_{33})$ for TWINS- $P2_1/n$.

ments are very small compared with those obtained by making allowance for the twinning in $P2_1/n$.

The scatter in bond lengths and angles in our $P1\bar{1}$ refinement is, like the agreement indexes, slightly smaller than obtained by BNR. We surmise that these decreases are consequences of refining on F^2 rather than on F , of including the imaginary component f'' for uranium (which BNR presumably omitted – their amplitudes for U, like ours when at first we omitted f'' , differ from our final values in the right sense), and perhaps of obtaining more complete convergence.

Finally, we note that all refinements of $P1\bar{1}$, ours as well as those of BNR, are somewhat suspect because they are based on the single quadrant of experimental data that BNR collected. Intensity comparisons between two quadrants of data could have provided more straightforward proof of the correct Laue symmetry. Moreover, careful inspection of BNR's diffraction photographs should have revealed the twinning that we propose, and preliminary examination of the crystal

with a polarizing microscope would at least have given sufficient warning of its presence.

Further refinement in $P2_1/n$

More elaborate refinement in $P2_1/n$ improves both agreement and approximate molecular symmetry, as summarized in Table 2 (column III) but of course leaves the odd $h0l$'s unexplained.

Experimental

Our treatment of the twinning was based on microscopic and goniometric observations and precession photographs.

TEACLOU was prepared in 3–4M HCl by the recipe of Staritzky & Singer (SS, 1952), except that uranyl acetate, first boiled in HCl to remove most of the

Table 2. *Refinement synopsis; bond length (Å) and angle (°) averages and agreement statistics for several treatments*

	I ^a	II ^b	III ^c	IV ^d
U—O	1.765 [7] ^e	1.760	1.751	1.758
U—Cl	2.670 [14]	2.669[4]	2.668 [2]	2.670 [1]
N—C	1.556 [42]	1.546 [28]	1.516 [22]	1.515 [9]
C—C	1.499 [107]	1.511 [28]	1.481 [30]	1.488 [26]
X—U—Y	90.0 [15]	90.0 [15]	90.0 [11]	90.0 [11]
C—N—C	109.2 [52]	109.5 [26]	109.4 [28]	109.5 [25]
N—C—C	114.0 [71]	112.8 [14]	116.3 [20]	116.3 [13]
R ^f	0.048	0.047	0.040	0.035
R' ^f	—	0.053	0.040	0.035
Goodness of fit	—	3.3	2.5	2.2
g ^g	—	0.0	1.45 (8)	1.24 (6)

(a) The P1̄ BNR model.

(b) P2₁/n, full-matrix least-squares refinement with the CRYM system (Duchamp, Trus & Westphal, 1969) by the BNR 'rules', except that the residuals minimized are of F_o² rather than of F_o; no allowance for secondary extinction or the H's; Cl, N, O, and U anisotropic, but C isotropic. Form factors: for C, N, O, and Cl from *International Tables for X-ray Crystallography* (1962) pp. 202–203; f, f', and f'' for U from Cromer & Waber (1965), Cromer (1965), and *International Tables for X-ray Crystallography* (1962) p. 216. Weights: 1/σ²(F_o²), as transformed from the BNR data.

(c) P2₁/n with secondary extinction, H's included in F_c but not refined (f_H from Stewart, Davidson & Simpson, 1965; symmetrical positions to give, initially, C—H = 1.05 Å, H—C—H = 108°, and staggered CH₃'s; B 8.0 for CH₂, 9.0 for CH₃); anisotropic Gaussians for all atoms except H; otherwise like II.

(d) TWINS-P2₁/n. Like III with unchanged H parameter values, but with two twin components added [final fractions: X = 0.0445 (14), Y = 0.0706 (14)].

(e) Scatter e.s.d.'s in square brackets, for a single value, i.e. one of the eight N—C's in (I), estimated from the dispersions of the indicated groups. For X—U—Y and C—N—C, these e.s.d.'s were calculated for n degrees of freedom (3 and 6, but 6 and 12 in case I) rather than n - 1, in view of the geometric constraints. For C—N—C in case I, however, n - 1 = 11 was used.

(f) $R = \sum |F_o - |F_c|| / \sum F_o$, $R' = [\sum w(F_o^2 - |F_c|^2)^2 / \sum wF_o^4]^{1/2}$.

(g) The secondary-extinction parameter, in Larson's formulation (1967, equation 3) × 10⁶.

acetate as acetic acid, replaced uranyl chloride. The crystals obtained on cooling or by evaporation at room temperature were always unsuitable. Dr Edward J. Valente then obtained generous amounts of fine-looking crystals of suitable size by recrystallization from dilute HCl on evaporation in a refrigerator. (We thank him.)

Long searches with the petrographic microscope, however, revealed no untwinned crystals, while qualitatively confirming the optical properties reported by SS. Several of the better crystals were mounted and examined on our optical goniometer (at least some of the faces of each gave badly imperfect signals) and by Weissenberg or precession photography. The best, mounted along c*, was studied by precession pictures down a and down b. Many of the spots of high h or l have single weak satellites, all of which can be assigned to a minor twin component rotated by 90° about c*; the rest of the spots are assigned as unresolved superpositions from both main crystal and twin, or as

belonging solely to one of these. This done, all the features of the photographs come into agreement with the BNR unit cell [a = 9.997 (5), b = 10.064 (5), c = 12.914 (5) Å; α = 90.00 (5), β = 90.69 (5), γ = 90.00 (5)°] and symmetry P2₁/n, as well as our eyes could tell.

The main net of the picture down a has the mm symmetry required for a monoclinic structure, whereas the minor net has only a twofold axis and shows the monoclinic angle; the c* axes of the two nets are coincident. Correspondingly, the main net of the picture down b shows the monoclinic angle while the minor net has mm symmetry. The difference in spacing between a* and b*, though small, is unmistakable. Most of the violations of P2₁/n recorded by BNR correspond to reflections that can be seen actually to lie on the minor net of one picture, with relative intensities that agree well with their counterparts on the other picture, while others evidently are too weak to be located precisely on our pictures or even seen at all. The forbidden first-order reflections 100, 010, and 001 were not recorded (beam stop).

The observed twinning seems structurally altogether reasonable, since the deviation from tetragonality is so slight (the crystal becomes tetragonal at 354 K; SS). The invariance of c* suggests that (001) is the composition plane, but we are uncertain of this because we do not understand what we see under crossed Nicols in the goniometer: there is a region of poor extinction through one pair of {110} faces, marked by a few

Table 3. *Bond lengths (Å) and angles (°) in the TWINS-P2₁/n structure^{a, b}*

U—O	1.758	Cl(1)—U—Cl(2)	90.2
U—Cl(1)	2.670	Cl(1)—U—O	90.6
U—Cl(2)	2.670	Cl(2)—U—O	88.8
N—C(1)	1.510	C(1)—N—C(3)	107.4
N—C(3)	1.524	C(1)—N—C(5)	109.7
N—C(5)	1.520	C(1)—N—C(7)	114.5
N—C(7)	1.506	C(3)—N—C(5)	109.9
C(1)—C(2)	1.526	C(3)—N—C(7)	108.7
C(3)—C(4)	1.465	C(5)—N—C(7)	106.6
C(5)—C(6)	1.480	N—C(1)—C(2)	114.4
C(7)—C(8)	1.480	N—C(3)—C(4)	116.9
		N—C(5)—C(6)	117.4
		N—C(7)—C(8)	116.6

(a) Rough e.s.d.'s calculated from the least-squares (CRYM) positional e.s.d.'s by ignoring all covariances, averaging over all appropriate groups of atoms and all (hypothetical) directions: U—O 0.005, U—Cl 0.002, C—N 0.011, C—C 0.014 Å; O—U—Cl 0.02, Cl—U—Cl 0.06, C—N—C 0.7, N—C—C 0.8°. For example:

$$\sigma_{N-C}^2 = (\sigma_{N,x}^2 + \sigma_{N,y}^2 + \sigma_{N,z}^2 + \sigma_{C,x}^2 + \sigma_{C,y}^2 + \sigma_{C,z}^2) / 3,$$

the carbon values being averages over C(1), C(3), C(5), and C(7).

(b) Torsion angles (°), in the order C(1)NC(1)C(2), C(1)NC(3)C(4), C(1)NC(5)C(6), C(1)NC(7)C(8); C(3)NC(1)C(2), ... C(7)NC(5)C(6), C(7)NC(7)C(8): —, —60, 168, —51; —173, —, 50, 69; 67, 59, —, —173; —52, 175, —67, —. The approximate S₄ axis bisects angles C(1)NC(7) and C(3)NC(5).

fringes perpendicular to the spindle axis (\mathbf{c}) and seemingly restricted to a small volume in one quadrant of the crystal. In any case, the twinning law we observe on the precession photographs (90° rotation about \mathbf{c}^*) would be equivalent to the law expressed by SS ($\{110\}$ as the twinning plane) if β were more nearly equal to 90° ; but the difference seems real and unmistakable, and we are left puzzled.

The 'TWINS' calculations

A twinning model, consistent with our precession photographs, was then adopted in order to explain the space-group violations in BNR's table, as follows.

Hand calculations for about 50 reflections, chosen for their relatively large residuals in the least-squares calculations, showed that a few per cent each of two minor twin components rotated by $+90^\circ$ and -90° about \mathbf{c}^* would substantially reduce these residuals, but that adding the obvious fourth twin component, rotated by 180° , would not. Least-squares adjustment of the fractions X and Y of the two minor twins together with the parameters of the $P2_1/n$ model was then achieved through a cyclic procedure that finds best values of X and Y from the weights, F_o 's, and current F_c 's, calculates corrected F_o^2 's $\{[1/(1-X-Y)]/(F_{ohkl}^2 - XF_{ckhl}^2 - YF_{ckhl}^2)\}$, reads these into two or three cycles of normal full-matrix least squares, finds new X and Y values, and so on. Approximate convergence required four tours of this circuit, but surely would have been immediate if it had been convenient to include X and Y in the full-matrix refinement. Final parameters are listed in Table 1, agreement criteria in Table 2 (column IV), and all the bond lengths and angles in Table 3.

The convergence led to eventual increases of X and Y by more than 50% of their initial values along with appreciable readjustments of the parameters of the structure. Some of these readjustments can be understood in terms of recovery from the previous partial simulation of a superposition of the structures of the two twins upon the main crystal [the anion tips a little more away from exact alignment with \mathbf{c} , and there are decreases in the β 's that had helped the O's (β_{11} and β_{22}) and Cl's (β_{33}) to cover for their twin counterparts], but the reasons for the others are less evident.

Some of the differences between the final *TWINS* parameter values and the original $P2_1/n$ averages of the BNR values are large, and in general they are considerable: expressed in terms of average ratios of absolute parameter difference to the relevant σ 's from the *TWINS* structure they are 13 for U (β 's only); 4.5 for Cl, 5 for O, and 3 for N (β 's and positions); and 4 (positions) and 2 (β 's) for C. Each class of shifts includes some as great as 10σ . As may be seen for the combinations represented in Table 2, some were not

affected by the *TWINS* refinement while others were affected by it as well as the other changes, especially the addition of the H's.

A difference map calculated at the end of the *TWINS* refinement shows nothing much but noise, of the same amplitude level close to the ions as in the spaces between them. In view of this and the fact that none of the H distances or angles had changed by more than a few hundredths of an ångström or a few degrees (*i.e.* all remained well within the range commonly found after *refinement* of the H's), we chose not to make the occasional adjustments of hydrogen positions or amplitudes (especially the latter, and usually to presupposable anisotropy) that the map seemed to suggest. Such adjustments and some more refinement circuits, or a full least-squares refinement including the H parameters, would probably bring some small changes in the carbon positions, but these would not rival the large changes already effected by the H's.

The tetraethylammonium ion

As already implied, we believe it likely that the ions have in fact a rather high degree of bond-length and bond-angle symmetry, and we regard the increases in such symmetry as significant points in favor of our treatment of the data. This improvement is most notable for the TEA bond lengths and angles, which are much more uniform in our final structure than in the original (Table 2). The C-N bond length is notably greater, the C-C less, and the N-C-C angle greater than is normal for amines and hydrocarbons. Is this characteristic of the tetraethylammonium ion? Unfortunately, our extensive but incomplete search, while turning up several reports each of S_4 , D_{2d} , and disordered TEA's, has revealed no reasonably precise determinations of the lengths and angles, but only the refrain '...agree with the normal values'. We did not know, and have not been able to ascertain, what the 'normal values' are. The *TWINS* TEA values agree well, it may be noted, with the N-C-C and r_{N-C} averages found for the tetra-*n*-butylammonium ion by Templeton & Zalkin in several salts, for example, the 115.7° and 1.517 \AA in tetra-*n*-butylammonium tribromo(quinoline)nickelate(II) (Horrocks, Templeton & Zalkin, 1968).

The torsion angles of the C-N bonds are rather close to the ideal values for the S_4 staggered conformation, as of course they were already in the $P1$ structure, *not* to the impossible T_d mistakenly given in the BNR abstract.

Afterword

This note should be taken for what it really is, a cautionary reflection on the marvelous automated

stampede of contemporary chemical crystallography. It exposes one of the occasional mishaps but hardly disposes of the problems seen. They, in varying degrees, require separate reinvestigation and review.

Some will argue that the mishap was harmless: after all, the reported structure is essentially correct, as far as we know, except for the symmetry and the divergent lengths and angles. We can understand, but hardly agree.

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Disordered Structure of an $(\text{O}_2\text{NO} \cdot \text{H} \cdot \text{ONO}_2)^-$ Ion. A Neutron Diffraction Study of *trans*-Dichlorotetrakis(pyridine)rhodium(III) Hydrogendinitrate

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Abstract

Three dimensional single-crystal neutron diffraction data have been collected for *trans*-dichlorotetrakis(pyridine)rhodium(III) hydrogendinitrate, $[\text{Rh}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2]\text{H}(\text{NO}_3)_2$, at 298 K. The unit cell is orthorhombic, space group *Pbcn* with four formula units. $a = 7.529$ (5), $b = 21.717$ (6), $c = 14.717$ (7) Å. The structure comprises $\text{RhPy}_4\text{Cl}_2^+$ cations and orientationally disordered symmetric $(\text{O}_2\text{NO} \cdot \text{H} \cdot \text{ONO}_2)^-$ anions. Contrary to earlier X-ray findings the hydrogen bond within the hydrogendinitrate ion is very short, 2.46 (2) Å. The structure was refined to a final *R* value of 0.031.

Introduction

Recently both neutron and X-ray diffraction studies have reported evidence for the hydrogendinitrate ion,

$(\text{O}_2\text{NO} \cdot \text{H} \cdot \text{ONO}_2)^-$, in several crystals. Some controversy has surrounded the interpretation of hydrogen bonding in the hydrogendinitrate ion and it has been suggested that the ion exists in two forms. In tetraphenylarsonium hydrogendinitrate, the $\text{H}(\text{NO}_3)_2^-$ ions have been found with a planar conformation (Faithful & Wallwork, 1967). In caesium hydrogendinitrate, the anion is non-planar and the two nitrate groups lie in nearly orthogonal planes (Williams, Dowling, Gunde, Hadzi & Orel, 1976; Rozière, Rozière-Bories & Williams, 1976). In both salts, the nitrate groups are orientationally disordered and the hydrogendinitrate ions consist of two NO_3^- groups linked by a very short and possibly symmetric hydrogen bond of 2.43–2.47 Å.

Here we wish to report two other examples of the $\text{H}(\text{NO}_3)_2^-$ ion observed in *trans*-dichlorotetrakis(pyridine)rhodium hydrogendinitrate.