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A Note on the Structure Determinations of Putrescinium Monohydrogenphosphate Dihydrate

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Kamoun and Jouini [*J. Solid State Chem.* **89**, 67 (1990)] recently reported an X-ray structure of putrescinium monohydrogenphosphate dihydrate which is practically identical to that determined earlier [M. Jaskólski, M. Alejska, and M. Wiewiórowski, *J. Crystallogr. Spectrosc. Res.* **16**, 31 (1986)] except for the axial lengths which are systematically and significantly lower than those in the earlier report. A redetermination of the unit-cell constants shows that the original report was correct.

In a recent paper, Kamoun and Jouini (KJ) (*1*) reported the X-ray structure of putrescinium monohydrogenphosphate dihydrate [$NH_3^+(CH_2)_4NH_3^+ \cdot HPO_4^{2-} \cdot 2H_2O$, systematic name: 1,4-butanediammonium hydrogenphosphate dihydrate]. We point out here that, aside from an evident mistake in unit-cell parameters, this structure duplicates the results of an earlier (marginally more precise) structure determination by Jaskólski, Alejska, and Wiewiórowski (JAW) (*2*), although Kamoun and Jouini did not reference the earlier paper.

Putrescinium monohydrogenphosphate dihydrate crystallizes in the monoclinic $P2_1/c$ space group with $Z = 4$. The unit-cell parameters reported by KJ disagree with those measured by JAW. While the values for β are consistent, the axial lengths determined by KJ are systematically and significantly shorter (Table I). In order to resolve this discrepancy we redetermined the unit-cell constants for a crystal with dimensions $0.25 \times 0.42 \times 0.45$ mm ($T = 293$ K). The experiments were carried out two times: (I) on a Syntex $P2_1$ diffractometer (Eulerian geometry) (*3*) and (II) on a KM-4 diffractometer (κ geometry) (*4*). Graphite-monochromated Cu$K\alpha$ radiation was used to obtain accurate setting angles for 15 reflections with $28 < 2\theta < 48°$ (I) and for 25 reflections with $13 < 2\theta < 48°$ (II). In both cases the unit-cell parameters were calculated by a least-squares fit of those setting angles and are reported in Table I. They are fairly close to the original values of JAW and strongly indicate that the values of KJ are affected by a systematic error (e.g., instrumental missetting or incorrect λ). Pairwise comparisons of the axial lengths determined by JAW and in I and II result in deviations within 7.5σ. This result indicates that the standard deviations used in these comparisons may be underestimated by three times

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TABLE I

UNIT-CELL CONSTANTS FOR THE CRYSTALS OF PUTRESCINIUM MONOHYDROGENPHOSPHATE DIHYDRATE DETERMINED IN SEVERAL STUDIES

	a (Å)	*b* (Å)	*c* (Å)	*β* (°)
KJ[a]	6.541(1)	16.648(3)	9.175(1)	95.74(1)
JAW[b]	6.5932(4)	16.776(1)	9.2375(7)	95.772(6)
I[c]	6.5983(8)	16.800(3)	9.251(2)	95.79(1)
II[c]	6.5946(8)	16.776(3)	9.240(1)	95.81(1)

[a] Ref. (*1*).
[b] Ref. (*2*).
[c] This study (see text).

or more. This is consistent with the conclusion of Taylor and Kennard (*5*) that cell-length e.s.d.'s from routine determinations may be underestimated by a factor of 5. When the axial lengths of KJ are compared with the results of I, II, and JAW, the analogous deviations range from 30σ to 50σ. Averaging the results of I, II, and JAW gives $a = 6.595$, $b = 16.784$, $c = 9.243$ Å, which are higher by, respectively, 0.83, 0.82, and 0.74% (average, 0.80%) than the corresponding values of KJ.

To further verify the measurements of the cell parameters, the density of the present crystals has been carefully determined by the flotation method in a $CH_2Cl_2/CHCl_3$ mixture. The result, $D_m = 1.451 \pm 0.002$ g · cm^{-3}, is in excellent agreement with the value of $D_x = 1.450(2)$ g · cm^{-3} calculated using the averaged parameters above. We do not find any explanation why KJ, using the same crystal form at the same temperature, measured $D_m = 1.498$ g · cm^{-3}.

That the crystals used by JAW and KJ have identical structures, as expressed in fractional coordinates, has been confirmed in a half-normal probability plot (*6*) represented in Fig. 1. The 39 points in this plot represent absolute differences between the corresponding fractional coordinates of non-H atoms (symmetry transformed, if necessary) as reported by JAW and KJ (three errors in Table III of KJ had to be corrected). The plot has negligible departures from linearity (correlation coefficient, 0.988) and the best line through the points has an intercept of 0.048 and a slope of 1.543. This suggests that the two sets of fractional coordinates do not differ in a systematic way and that their standard deviations are 1.5 times too small. It was not possible to compare the temperature factors in a similar way because the expression for the anisotropic temperature factor given by KJ is evidently incorrect. [Also in JAW, the exponent in the temperature-factor expression (Table II of JAW) should include $2\pi^2$.]

The hydrogen-bond pattern determined by KJ is identical to that described earlier, although the table in which it is characterized (Table IV of KJ) contains numerous errors [e.g., N. . .O for N(1)–H(1N1). . .O(2) should read 3.039 Å, not 2.691 Å; e.s.d.'s for parameters involving H atoms of O(W1)

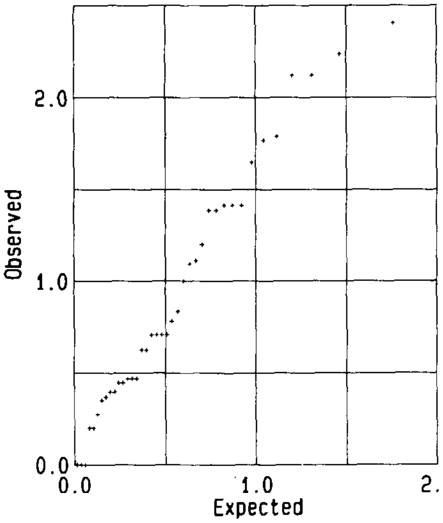

FIG. 1. Half-normal probability plot (*6*) of 39 fractional coordinates (x_{ij}; $i = 1, 2, 3$; $j = 1 \ldots 13$) of non-H atoms determined by JAW and KJ. The *observed* values, calculated as $|x_{ij}^{JAW} - x_{ij}^{KJ}|/[\sigma^2(x_{ij}^{JAW}) + \sigma^2(x_{ij}^{KJ})]^{1/2}$, are plotted against those *expected* for a normal distribution.

are incorrect; O(W1)–H(2W1)...O(W2) is incorrectly represented as O(W1)–H(2W1)...O(2), etc.]. When the O...O and N...O distances given by KJ are multiplied by the factor 1.008 determined above, they are in excellent agreement with the values reported by JAW with all deviations well below 2σ. In this light, the discussion of the hydrogen bonds presented by KJ which consists in classifying them as strong [O(N)...O < 2.73 Å] or weak [O(N)...O > 2.73 Å] misses its point. [This point is rather unclear anyway because the classification criterion (2.73 Å) does not differentiate between O...O and N...O bridges.] For instance, the statement by KJ that the putrescinium moiety participates in two strong hydrogen bonds is incorrect because there is a typographic error in one of those bonds, which is actually quite long (see above), while the other, when scaled by 1.008, has N...O of 2.715(3) Å, i.e., is on the borderline of the classification by KJ.

References

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