

The lighter carbon and oxygen atoms have a very small contribution to the higher-order reflections, and the Fourier synthesis does not give accurate coordinates for these atoms. Further three-dimensional work is therefore planned. The other two projections are badly resolved and are not suitable for further structure analysis.

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photographs and performing some of the calculations.

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X-ray studies of molecular overcrowding. I. Some crystallographic data. By G. FERGUSON and G. A. SIM, *Chemistry Department, The University, Glasgow, W. 2, Scotland*

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With a view to obtaining detailed information about the effect on the molecular geometry of the close approach of neighbouring groups structural analysis of a number of substituted benzoic acids is at present in progress. As a preliminary to this work lattice parameters and space groups were determined and are presented in Table 1. In the case of *o*-chlorobenzoic acid and *o*-bromobenzoic

acid the diffraction conditions allow the space group to be either $Cc-C_2^2$ or $C2/c-C_{2h}^2$. The successful refinement of the structure based on the centrosymmetrical choice indicates $C2/c$ as the true space group.

Full details of the structure determinations will be published in due course.

Table 1. *Crystallographic data for some substituted benzoic acids*

Molecular formulae	<i>o</i> -chlorobenzoic acid $C_7H_5O_2Cl$	<i>o</i> -bromobenzoic acid $C_7H_5O_2Br$	2-chloro-5-nitro-benzoic acid $C_7H_4O_4NCl$	4-chloro-3-nitro-benzoic acid $C_7H_4O_4NCl$
<i>a</i> (Å)	14.73 ± 0.03	14.82 ± 0.04	5.86 ± 0.02	7.41 ± 0.02
<i>b</i> (Å)	3.90 ± 0.02	4.10 ± 0.02	5.13 ± 0.02	5.70 ± 0.02
<i>c</i> (Å)	25.50 ± 0.05	25.90 ± 0.05	26.65 ± 0.05	19.12 ± 0.04
β	112° 40'	118° 15'	97° 54'	100° 30'
<i>U</i> (Å ³)	1351	1386	794	794
<i>z</i>	8	8	4	4
Mol. wt.	156.6	201.0	201.6	201.6
<i>D_m</i> (g.cm. ⁻³)	1.544	1.929	1.678	1.687
<i>D_x</i> (g.cm. ⁻³)	1.539	1.926	1.687	1.686
Space group	$C2/c-C_{2h}^6$	$C2/c-C_{2h}^6$	$P2_1/c-C_{2h}^2$	$P2_1/c-C_{2h}^2$

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Unit cell and space group of L-proline monohydrate. By V. SASISEKHARAN, *Department of Physics, University of Madras, Madras-25, India.*

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Crystals of L-proline are highly hygroscopic. Therefore there has been considerable difficulty in growing single crystals suitable for X-ray diffraction studies. When grown from a saturated solution in a closed container, the crystals occur as a white powder or take up a feather-like formation, but no large enough single crystals appear at room temperature. The powder pattern obtained from this material was found to be very much different from that of the original compound thereby showing that the compound was a hydrated form of proline. The unit-cell dimensions and space group of the original dry powder have already been reported (Wright & Cole, 1949). Successful single crystals of the hydrated compound were grown by the author from a solution of the dry

material in ethyl alcohol by controlling the percentage of alcohol and the temperature at which the compound was crystallised. Single crystals of the monohydrate were obtained by dissolving the substance in 70% ethanol and keeping the solution at a constant temperature of 45 °C.

The crystals obtained were needle-shaped, transparent, birefringent and approximately rectangular in cross section. The needles were elongated along [001] and bounded by faces of the form {110}. As the crystals were unstable when exposed to the atmosphere, considerable care was taken to protect the crystals by enclosing them in Lindemann-glass tubes at 45 °C. Even then the crystals were stable for only a few days.

Oscillation, rotation, Weissenberg and precession X-ray photographs were taken about the needle axis, using Cu $K\alpha$ radiation. The unit cell was found to be monoclinic with the dimensions

$$a = 20.73 \pm 0.04, \quad b = 6.34 \pm 0.01, \quad c = 5.20 \pm 0.01 \text{ \AA}; \\ \beta = 93^\circ 40' \pm 02'.$$

Complete examination of the zero, first and second layer photographs showed the following systematic absences:

- hkl reflections — only $h+k$ even present
- $h0l$ reflections — only l even present
- $0k0$ reflections — only k even present.

The three monoclinic space groups, C_s^3-Cm , C_2^2-C2 and C_2^2-C2/m are consistent with the above X-ray data. On the other hand, the first and last possibilities, viz., Cm and $C2/m$ are ruled out, since the compound L-proline is asymmetric. Hence the space group is deduced to be C_2^2-C2 .

The density of the compound was determined by the flotation method using benzene-bromoform mixtures. The observed density was 1.324 g.cm.^{-3} . On the basis

of the above unit cell, with four molecules per cell, the calculated densities for the free L-proline, the monohydrate and the dihydrate are 1.129, 1.307 and 1.483 g.cm.^{-3} respectively. It will be seen that the observed density agrees best with the calculated value for the monohydrate. The slight discrepancy in the two values is to be attributed to the hygroscopic nature of the crystal, and the consequent error in the measurement. Thus the compound is identified to be L-proline monohydrate.

The point group could not be determined uniquely from morphological data, as complete data could not be obtained. The above space group assignment was however confirmed from the [001] Patterson projection which showed concentrations of peaks (Harker interactions) along $y=0$ and $\frac{1}{2}$, as required by the space group.

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Reference

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The crystal structure of PuNi.* By DON T. CROMER and R. B. ROOF, JR., *University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.*

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The Pu-Ni phase diagram published by Wensch & Whyte (1951) shows the existence of six binary compounds. The structures of PuNi_2 , PuNi_3 and $\text{Pu}_2\text{Ni}_{17}$ have been reported by Coffinberry & Ellinger (1956) and the PuNi_3 structure has been reported by Cromer & Olsen (1959). The structure of PuNi is the subject of the present note. The structure of PuNi_4 , the remaining compound of the series, is currently being studied.

A Pu-Ni alloy containing 75 at. % Pu was heated to 1150°C. , well above the liquidus for that composition, and then thermally cycled between 445 and 475°C. for about three months. Because PuNi is formed by a peritectic reaction, non-stoichiometric ratios of Pu and Ni were required in order to avoid the formation of the next higher Ni containing compound, PuNi_2 . The specimen was crushed and fragments were examined with a precession camera. In spite of the prolonged heat treatment, good quality PuNi single crystals were impossible to find. Finally, however, one crystal of usable quality was found.

The crystal was found to be orthorhombic with

$$a = 3.59 \pm 0.01, \quad b = 10.21 \pm 0.02, \quad c = 4.22 \pm 0.01 \text{ \AA},$$

as measured from precession photographs (Mo $K\alpha$, $\lambda = 0.7107 \text{ \AA}$). The photographs showed the following systematic extinctions: hkl absent if $h+k=2n+1$ and $h0l$ absent if $l=2n+1$. These extinctions are characteristic of space groups $Cmcm$ or $Cmc2_1$. The space group and axial ratios suggested that the structure was of the TII

type (space group $Cmcm$) and cursory examination of the intensities showed that this was indeed the case. In the TII structure there are four formula units per unit cell with the larger atom (Pu in this case) in the set $4c$, with $y \approx 0.14$, and the smaller atom in the same set with $y \approx 0.42$. The calculated density of PuNi is thus 12.9 g.cm.^{-3} .

In order to define the y parameters more precisely, intensities of the $0kl$ zone were visually estimated from a precession photograph taken with Zr filtered Mo radiation. These intensities were corrected for the Lorentz-

Table 1. Observed and calculated $0kl$ structure factors for PuNi

k	l	F_o	F_c	k	l	F_o	F_c
0	2	287	-310	6	4	0	44
0	4	137	163	6	5	58	66
2	0	0	-11	8	0	91	80
2	1	237	-207	8	1	149	-147
2	2	0	13	8	2	81	-69
2	3	116	137	8	3	101	103
2	4	0	-12	8	4	40	48
2	5	69	-79	10	0	124	-108
4	0	277	-269	10	1	103	-84
4	1	186	168	10	2	101	93
4	2	203	207	10	3	83	61
4	3	112	-102	10	4	61	-64
4	4	93	-119	12	0	0	-11
4	5	38	51	12	1	104	84
6	0	72	70	12	2	0	11
6	1	162	171	12	3	74	-66
6	2	58	-62	14	0	106	83
6	3	108	-117				

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