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# Structure of Urea–Oxalic Acid (1/1), $CH_4N_2O.C_2H_2O_4$, Determined by Neutron Diffraction*

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**Abstract.** $M_r = 150{\cdot}1$, monoclinic, $C2/c$, $a = 13{\cdot}0625\ (7)$, $b = 6{\cdot}6437\ (2)$, $c = 6{\cdot}8478\ (3)$ Å, $\beta = 92{\cdot}474\ (6)°$, $U = 593{\cdot}72$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}68$ g cm$^{-3}$, $\lambda = 1{\cdot}275$ Å, $\mu = 1{\cdot}49$ cm$^{-1}$, $T = 295\ (1)$ K. Final $R = 6{\cdot}2\%$ for 757 independent observed reflexions. The crystal structure contains urea and oxalic acid molecules, held together by a two-dimensional hydrogen-bonding network. The neutron diffraction experiment provides a more accurate description of the geometry of the hydrogen bonds than the corresponding X-ray experiment [Harkema & ter Brake (1979). *Acta Cryst.* B**35**, 1011–1013].

**Introduction.** Urea and oxalic acid can form two different addition compounds with ratio 1:1 or 2:1. The crystal structure of these compounds has been determined by X-ray diffraction (Harkema & ter Brake, 1979; Harkema, Bats, Weijenberg & Feil, 1973). Both compounds have been studied in our laboratory in order to obtain accurate electron densities. To obtain more accurate hydrogen parameters a neutron diffraction experiment was carried out, the results of which are presented here.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$)

| | $x$ | $y$ | $z$ | $U_{eq}$* |
|---|---|---|---|---|
| C(1) | 0 | 7861 (3) | 2500 | 276 (5) |
| C(2) | 2135 (1) | 1654 (2) | 4651 (2) | 257 (4) |
| N(1) | 762 (1) | 6853 (2) | 3414 (2) | 395 (4) |
| O(1) | 0 | 9752 (3) | 2500 | 347 (7) |
| O(2) | 1330 (1) | 2345 (3) | 3678 (3) | 334 (5) |
| O(3) | 2309 (1) | −86 (3) | 5001 (3) | 395 (5) |
| H(1) | 1328 (3) | 7634 (6) | 4095 (6) | 499 (11) |
| H(2) | 836 (3) | 5356 (5) | 3362 (7) | 558 (13) |
| H(3) | 856 (2) | 1193 (5) | 3246 (5) | 422 (9) |

* Defined according to Willis & Pryor (1975).

**Experimental.** A crystal suitable for neutron diffraction work ($1{\cdot}9 \times 4{\cdot}1 \times 4{\cdot}2$ mm) was prepared by slow evaporation of a solution of 8 g urea and 84 g oxalic acid dihydrate in 220 ml of water at 313 K (Dalman, 1934); neutron data collected on a four-circle diffractometer at the HFR reactor at Petten, wavelength of 1·275 Å obtained after diffraction from the (311) planes of the copper crystals of a double monochromator; $\omega$–$2\theta$ step scans (0·0625° step$^{-1}$); results processed by the procedure of Lehmann & Larsen (1974); reflexions with $\theta < 65°$ (approx. 3750), equivalents averaged, $R_{int} = 4{\cdot}5\%$, insignificant reflexions [$I < \sigma(I)$] omitted, 757 independent reflexions; index range $h \pm 18$, $k$ 0–9, $l$ 0–9; reference reflexion

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Table 2. *Bond distances* (Å) *and angles* (°)

| | Neutron | X-ray | | Neutron | X-ray | | Neutron | X-ray |
|---|---|---|---|---|---|---|---|---|
| C(1)–N(1) | 1·333 (1) | 1·332 (1) | O(1)···O(2′) | 2·552 (3) | 2·553 (1) | N(1)–H(2) | 1·000 (4) | 0·84 (2) |
| C(1)–O(1) | 1·256 (3) | 1·261 (2) | N(1)···O(3′) | 3·035 (2) | 3·030 (1) | O(2)–H(3) | 1·020 (4) | 0·91 (2) |
| C(2)–C(2″) | 1·537 (2) | 1·537 (1) | C(2)–O(3) | 1·200 (2) | 1·206 (1) | N(1)···O(2) | 3·089 (2) | 3·085 (1) |
| C(2)–O(2) | 1·304 (2) | 1·306 (1) | N(1)–H(1) | 1·002 (4) | 0·81 (2) | | | |

| | Neutron | X-ray | | Neutron | X-ray | | Neutron | X-ray |
|---|---|---|---|---|---|---|---|---|
| N(1)–C(1)–N(1‴) | 119·7 (2) | 120·0 (1) | O(2)–C(2)–O(3) | 125·6 (2) | 125·8 (1) | H(1)–N(1)–H(2) | 117·5 (5) | 115 (3) |
| N(1)–C(1)–O(1) | 120·2 (1) | 120·0 (1) | N(1)–H(1)···O(3′) | 162·9 (6) | 158 (2) | C(2)–O(2)–H(3) | 110·5 (3) | 106 (1) |
| C(2″)–C(2)–O(2) | 112·2 (1) | 112·1 (1) | C(1)–N(1)–H(1) | 118·6 (3) | 124 (2) | O(1)···H(3′)–O(2′) | 169·7 (7) | 165 (2) |
| C(2″)–C(2)–O(3) | 122·2 (2) | 122·1 (1) | C(1)–N(1)–H(2) | 123·7 (4) | 122 (2) | N(1)–H(2)···O(2) | 165·7 (7) | 164 (2) |

measured every 25 reflexions, no significant variation detected. Cell constants and starting parameters for the refinement taken from the X-ray work (Harkema & ter Brake, 1979). Absorption corrections made by *ACXR* (Harkema, 1976), transmission factors 0·580–0·775, absorption coefficient determined experimentally; refinement by full-matrix least squares on $F$ (Busing, Martin & Levy, 1962), with weights $w = [\sigma(F_o) + 0{\cdot}01\,|F_o|]^{-2}$, where $\sigma(F_o)$ is the e.s.d. of the structure factor ($F_o$) obtained from counting statistics; scattering lengths from *International Tables for X-ray Crystallography* (1974); number of parameters refined 75 (scale factor, isotropic extinction parameter, positional and anisotropic thermal parameters of all atoms). The asymmetric unit contains one half molecule of urea and one half molecule of oxalic acid, the other halves being generated by a twofold axis and an inversion center respectively. Final $R = 6{\cdot}2\%$, $R_w = 6{\cdot}6\%$; shift-to-error ratio in final least-squares cycle $< 0{\cdot}06$; largest correction for extinction ($yF_c$), $y = 0{\cdot}62$.

**Discussion.** Final atomic positions and equivalent isotropic thermal parameters are given in Table 1.* The numbering of the atoms is shown in Fig. 1. Bond distances and angles are collected in Table 2 and compared with the corresponding X-ray values (Harkema & ter Brake, 1979). The neutron diffraction experiment confirms the compound to be an addition compound and not a salt. The acidic proton is attached to the oxalic acid molecule. Details of the geometry of the hydrogen bonds are included in Table 2. Comparison of neutron and X-ray results shows only minor differences as far as bond distances and angles of the heavy atoms are concerned. The largest differences are found in the C–O bond lengths, possibly as a result of asphericity shifts (Coppens, 1975). Bond lengths involving H atoms are significantly shorter in the X-ray experiment, due to the polarization of the electron density caused by chemical bonding.

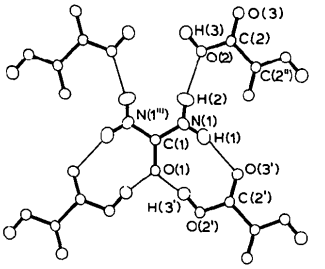


Fig. 1. Part of the crystal structure of urea–oxalic acid (1:1). Primed atoms are related to the unprimed ones by a translation along **b**. N(1‴) is related to N(1) by a twofold rotation around the axis passing through C(1) and O(1). There is an inversion center between C(2) and C(2″).

Comparison of the thermal parameters shows somewhat higher values for the neutron parameters. The mean values for the ratio $U_{ii}$(neutron)/$U_{ii}$ (X-ray) for the heavy atoms are: 1·01 (2), 1·19 (5), and 1·05 (3) for $U_{11}$, $U_{22}$ and $U_{33}$, respectively.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39524 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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