On peut aussi apprécier la force relative des complexes par comparaison des énergies de destruction de réseau (Artiga, Gaultier, Haget & Nguyen-Ba-Chanh, 1977). Elles sont déduites avec une bonne approximation des chaleurs de dissolution et d'informations complémentaires concernant la quinhydrone (Suzuki & Seki, 1953). Ramenées à l'unité de volume, elles expriment la densité d'énergie d'interactions et par conséquent, rendent compte valablement de la cohésion du complexe cristallisé.

Elles sont respectivement: 101 cal $Å^{-3}$ pour le complexe 2:1 naphtoquinone–naphtohydroquinone, 126 cal $Å^{-3}$ pour le complexe 1:1 naphtoquinone–hydroquinone, 180 cal $Å^{-3}$ pour le complexe 1:1 benzoquinone–hydroquinone.

Ces résultats confirment les conclusions de l'analyse radiocristallographie: la naphtoquinone-1,4 forme avec les molécules aromatiques des complexes faibles, plus faibles que la benzoquinone.

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The Crystal Structure of Guanidinium Hydrogen Oxalate Monohydrate

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$C(NH_2)_3HC_2O_4.H_2O$ crystallizes in space group $P2_1/c$ with $a = 6\cdot70$ (1), $b = 10\cdot55$ (1), $c = 10\cdot21$ (2) Å, $\beta = 103\cdot8$ (1)°, $Z = 4$, $d_o = 1\cdot60$, $d_c = 1\cdot58$ g cm^{-3} and λ(Cu $K\alpha$) = 1·5418 Å. There are infinite two-dimensional hydrogen-bonded sheets ~3·2 Å apart parallel to $(\bar{1}01)$ which are held together by less dense hydrogen bonding from water molecules within the sheets to oxalate ions of the next sheet. All the H atoms are involved in hydrogen bonding. One of the oxalate O atoms accepts three hydrogen bonds.

Introduction

This structural investigation was undertaken as part of a study of hydrogen bonding in simple guanidinium salts. Often in these compounds there is multiple hydrogen bonding where O atoms may accept up to four hydrogen bonds (Adams & Ramdas, 1976).

Experimental

Colourless needle-shaped crystals were obtained by crystallization from an aqueous solution containing the correct proportions of oxalic acid and guanidinium carbonate. The density was determined by flotation. Oscillation and Weissenberg photographs were used to determine the cell parameters and space group. The crystal needle axis was shown to be coincident with a; the major faces observable were (011), $(01\bar{1})$, $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$. Film packs (0–4kl and $h0l$–$h5l$) were used to collect intensities. The films were examined by the SRC Microdensitometer Service, Harwell, and the intensities corrected for Lorentz–polarization effects and put on a common scale. No correction for absorption was made (crystals were ~0·25 × 0·08 × 0·08 mm).

Structure determination

All reflections that had been too weak to be observed by the microdensitometer were given intensities of 0·75 of the minimum observed value. A Wilson plot gave a

Table 1. *Fractional atomic coordinates and their standard deviations*

	x	y	z
C(1)	0·762 (1)	0·9975 (6)	0·0081 (7)
C(2)	0·747 (1)	0·8563 (6)	−0·0277 (6)
C(3)	1·207 (1)	0·8810 (6)	0·4125 (7)
N(1)	1·130 (1)	0·7969 (6)	0·3172 (7)
N(2)	1·304 (1)	0·8448 (6)	0·5339 (6)
N(3)	1·182 (1)	1·0038 (6)	0·3836 (7)
O(1)	0·8222 (10)	0·7749 (5)	0·0521 (5)
O(2)	0·6858 (9)	1·0743 (5)	−0·0805 (5)
O(3)	0·6433 (9)	0·8309 (5)	−0·1524 (5)
O(4)	0·8604 (8)	1·0234 (5)	0·1268 (5)
O(5)	0·6304 (9)	0·9153 (5)	0·3005 (5)
H(1)	1·050 (17)	0·823 (9)	0·232 (10)
H(2)	1·091 (17)	0·708 (10)	0·344 (9)
H(3)	1·322 (17)	0·745 (10)	0·565 (9)
H(4)	1·369 (17)	0·905 (9)	0·581 (9)
H(5)	1·214 (18)	1·087 (10)	0·430 (10)
H(6)	1·127 (18)	1·010 (10)	0·322 (11)
H(7)	0·493 (16)	0·943 (9)	0·278 (9)
H(8)	0·737 (16)	0·931 (9)	0·256 (9)
H(9)	0·657 (18)	0·746 (10)	−0·185 (9)

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

C(1)–C(2)	1·53 (1)	O(2)–C(1)–O(4)	126·3 (6)
C(1)–O(2)	1·232 (8)	C(2)–C(1)–O(4)	115·4 (5)
C(1)–O(4)	1·263 (8)	C(2)–C(1)–O(2)	118·2 (6)
C(2)–O(1)	1·208 (8)	O(1)–C(2)–O(3)	122·9 (6)
C(2)–O(3)	1·325 (8)	C(1)–C(2)–O(3)	114·6 (5)
C(3)–N(1)	1·325 (9)	C(1)–C(2)–O(1)	122·5 (6)
C(3)–N(2)	1·312 (9)	N(1)–C(3)–N(2)	121·1 (6)
C(3)–N(3)	1·330 (9)	N(1)–C(3)–N(3)	118·8 (6)
N(1)–H(1)	0·94 (10)	N(2)–C(3)–N(3)	120·0 (6)
N(1)–H(2)	1·03 (11)		
N(2)–H(3)	1·09 (11)		
N(2)–H(4)	0·85 (10)		
N(3)–H(5)	1·00 (11)		
N(3)–H(6)	0·65 (10)		
O(3)–H(9)	0·97 (11)		

Table 3. *Deviations* (Å) *of atoms from least-squares planes*

(i) Plane through C(3), N(1), N(2), N(3)

$$6{\cdot}4208x + 0{\cdot}0725y - 5{\cdot}1658z = 5{\cdot}6786$$

C(3)	0·003	H(2)	−0·40
N(1)	−0·001	H(3)	−0·05
N(2)	−0·001	H(4)	0·18
N(3)	−0·001	H(5)	−0·03
H(1)	−0·08	H(6)	−0·03

(ii) Plane through C(1), C(2), O(1), O(2), O(3), O(4)

$$6{\cdot}3741x + 0{\cdot}5594y - 5{\cdot}3262z = 5{\cdot}3866$$

C(1)	−0·012	O(3)	−0·010
C(2)	0·003	O(4)	−0·006
O(1)	0·010	H(9)	0·20
O(2)	0·015		

The 'heavy' atoms of both the guanidinium and oxalate groups are planar within experimental error. The angle between planes (i) and (ii) is 2·9°.

low overall temperature factor of 0·8 Å^2. An $N(z)$ test confirmed that the data had a centric distribution. The 100 reflections with $E > 1{\cdot}63$ were used to solve the structure with *MULTAN* (Germain, Main & Woolfson, 1971). An E map computed with the set of phases with the highest combined figure of merit enabled all of the non-hydrogen atoms to be located. Isotropic least-squares refinement with the 755 observed reflections reduced R to 0·17; the use of anisotropic thermal parameters with the omission of the 002, 014, 12$\bar{1}$, 202, 21$\bar{2}$ and 212 reflections (considered to be suffering from extinction) reduced R to 0·11. The H atoms were located from a difference map: they were constrained to have thermal parameters equal to those of the atoms to which they were bound. Refinement terminated at R = 0·085.* Unit weights were used. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations, apart from the structure solution, were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Positional parameters are in Table 1.

Discussion

All the C–N distances in the guanidinium group are essentially equal and the ion is planar. In the hydrogen oxalate ion C(1)–O(2) and C(1)–O(4) are almost equivalent whereas C(2)–O(1) is typical for >C=O and C(2)–O(3) is a usual C–OH length (Table 2). Again this ion is planar (Table 3) like almost all oxalates although this is not a condition imposed by symmetry [ammonium oxalate monohydrate is an

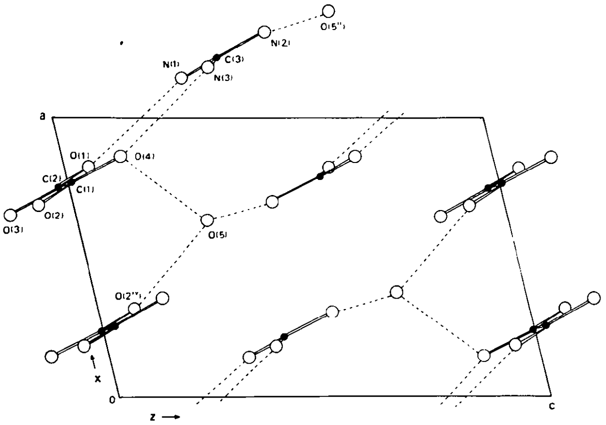

Fig. 1. Projection of the structure on to (010) from y = 0·7 to 1·2. Part of the hydrogen-bonding scheme is shown.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33154 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Hydrogen-bonding geometry*

A–H···B	H···B	A···B
N(1)–H(1)···O(1)	2·15 Å	2·997 (9) Å
N(1)–H(2)···O(4^{i})	1·99	2·940 (9)
N(2)–H(3)···O(2^{i})	1·82	2·892 (9)
N(2)–H(4)···O(5^{ii})	2·25	3·017 (9)
N(3)–H(5)···O(1^{iii})	2·01	2·936 (9)
N(3)–H(6)···O(4)	2·34	2·975 (9)
O(5)–H(7)···O(2^{iv})	2·09	2·698 (7)
O(5)–H(8)···O(4)	1·97	2·850 (9)
O(3)–H(9)···O(5^{v})	1·71	2·639 (8)

Symmetry code

(i) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(ii) $2-x, 2-y, 1-z$
(iii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$
(iv) $1-x, 2-y, -z$
(v) $x, 1\frac{1}{2}-y, -\frac{1}{2}+z$

exception, being twisted by 28° (Jeffrey & Parry, 1952)]. All angles involving H atoms on either ion [except for H(6), which was not located accurately] are within 1σ of 120°.

The ions and water molecules are arranged in almost coplanar fashion parallel to ($\bar{1}01$) (Figs. 1 and 2): the angle between the guanidinium and oxalate groupings is only 2·9°. Within these planes there is a very high degree of hydrogen bonding (Table 4), whereas the layers are held together by a much looser hydrogen-bonding scheme only involving bonds from water to an oxalate O(4). Nevertheless, these structural layers are closely packed at ~3·2 Å apart. The O–H···O bonds range from 2·64 to 2·85 Å while the N–H···O bonds are between 2·89 and 3·02 Å.

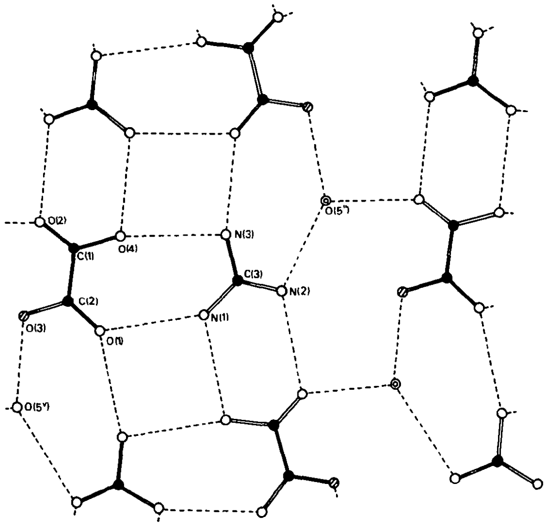

Fig. 2. Projection of one layer of the structure on to ($\bar{1}01$). The hydrogen bonds holding the layers together are shown.

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