photographs confirmed that the crystals are orthorhombic with,

$$a = 6 \cdot 290 \pm 0 \cdot 003, \quad b = 9 \cdot 318 \pm 0 \cdot 005, \quad c = 15 \cdot 39 \pm 0 \cdot 01 \text{ Å}.$$

These give $0 \cdot 674 : 1 : 1 \cdot 652$ for the axial ratios. Taking the density to be $1 \cdot 548$ g.cm.$^{-3}$ (the mean of the two values, $1 \cdot 542$ and $1 \cdot 553$ g.cm.$^{-3}$ given by Groth), the unit cell contains 4 molecules of $C_6H_8O_7.H_2O$ per unit cell (density calculated $= 1 \cdot 546$ g.cm.$^{-3}$).

The only systematic absences were $h00$ absent when $h$ is odd, $0k0$ when $k$ is odd and $00l$ when $l$ is odd. The space group is therefore $D_2^4-P2_12_12_1$. This space group is not consistent with the crystal class quoted by Groth. Quite apart from the absent reflexions, the class $mmm$ is unlikely to be correct with a unit cell containing only 4 molecules as it would mean that each molecule of citric acid *and* the molecule of water would have to possess some element of symmetry.

### Potassium citrate monohydrate

Crystals of this substance are monoclinic, with

$$a = 7 \cdot 06 \pm 0 \cdot 03, \quad b = 11 \cdot 72 \pm 0 \cdot 05, \quad c = 13 \cdot 69 \pm 0 \cdot 07 \text{ Å};$$
$$\beta = 112 \cdot 0°.$$

The density determined by flotation is $2 \cdot 00$ g.cm.$^{-3}$, giving 4 molecules of $C_6H_5O_7K_3.H_2O$ per unit cell (density calculated $= 2 \cdot 050$ g.cm.$^{-3}$). Systematic absences were $h0l$ when $l$ is odd and $0k0$ when $k$ is odd. The space group is therefore $C_{2h}^5-P2_1/c$.

### Sodium citrate dihydrate

Groth gives this substance as monoclinic prismatic (2/m), with $a:b:c = 0 \cdot 8923 : 1 : 1 \cdot 3647$, $\beta = 115°55'$. X-ray photographs gave

$$a = 11 \cdot 23 \pm 0 \cdot 05, \quad b = 12 \cdot 501 \pm 0 \cdot 002, \quad c = 15 \cdot 82 \pm 0 \cdot 08 \text{ Å};$$
$$c \sin \beta = 15 \cdot 262 \pm 0 \cdot 003 \text{ Å}, \quad \beta = 104°22'.$$

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If the same $c$ axis is chosen as that of Groth we get $c' = 16 \cdot 98$ Å and $\beta' = 115°49'$, giving axial ratios of $a:b:c' = 0 \cdot 898 : 1 : 1 \cdot 358$. The density determined by flotation is $1 \cdot 84$ g.cm.$^{-3}$ and there are 8 molecules of $C_6H_5O_7Na_3.2H_2O$ per unit cell (density calculated $= 1 \cdot 823$ g.cm.$^{-3}$). Systematic absences were: $hkl$ when $(k+l)$ is odd, $h0l$ when $h$ or $l$ is odd and $0k0$ when $k$ is odd. There are two space groups available $C_s^4-Aa$ and $C_{2h}^6-A2/a$. If the classification given by Groth is correct then the latter space group is the appropriate one.

### Sodium citrate pentahydrate

This compound is given by Groth as rhombic bisphenoidal (222) with axial ratios $a:b:c = 0 \cdot 6208 : 1 : 0 \cdot 2431$. X-ray photographs confirmed that the crystals are orthorhombic with

$$a = 6 \cdot 41 \pm 0 \cdot 03, \quad b = 16 \cdot 36 \pm 0.08, \quad c = 26 \cdot 31 \pm 0 \cdot 10 \text{ Å}.$$

These give axial ratios $b:c:a = 0 \cdot 6218 : 1 : 0 \cdot 2436$. The density determined by flotation is $1 \cdot 70$ g.cm.$^{-3}$, which differs appreciably from the value given by Groth ($1 \cdot 857 - 1 \cdot 859$ g.cm.$^{-3}$). The calculated density, using the above unit-cell dimensions and assuming 8 molecules of $C_6H_5O_7Na_3.5H_2O$ per unit cell, is $1 \cdot 68$ g.cm.$^{-3}$. It would appear that the density given by Groth is a misprint and should really refer to the dihydrate, for which he does not give any density. Systematic absences were $h0l$ when $l$ is odd and $hk0$ when $(h+k)$ is odd. These are characteristic of two space groups, $C_{2v}^9-P2_1cn$ and $D_{2h}^{16}-Pmcn$. Neither of these space groups is in the class 222 quoted by Groth.

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# The atomic scattering factors of Au+ and Hg++. By W. G. Henry, *Division of Applied Chemistry, National Research Council, Ottawa, Canada*

Total atomic scattering factors, $f$, for coherent radiation have been calculated for Au$^+$ and Hg$^{++}$ by the numerical integration (Scarborough, 1950) of the integral (James & Brindley, 1931)

$$f = \int_0^\infty P^2(r) \frac{\sin \mu r}{\mu r} \, dr,$$

where $\mu = 4\pi \sin \theta/\lambda$ and $P^2(r)$ is the radial charge density.

The radial charge density $P^2(r)$ has been determined by the method of the self-consistent field, without exchange, for Hg$^{++}$ by Hartree & Hartree (1935) and for Au$^+$ by Henry (unpublished work). The effect on the

scattering factor of including exchange is small (Brindley & Ridley, 1938). Results are given in Table 1.

Table 1. *Atomic scattering factors*
(Integration error $\pm 0 \cdot 02$)

| $\dfrac{\sin \theta}{\lambda} \times 10^{-8}$ | Au$^+$ | Hg$^{++}$ | $\dfrac{\sin \theta}{\lambda} \times 10^{-8}$ | Au$^+$ | Hg$^{++}$ |
|---|---|---|---|---|---|
| 0·0 | 78·00 | 78·00 | 0·7 | 37·46 | 37·98 |
| 0·1 | 74·26 | 74·71 | 0·8 | 33·66 | 34·38 |
| 0·2 | 66·32 | 67·21 | 0·9 | 30·52 | 31·20 |
| 0·3 | 58·35 | 59·18 | 1·0 | 27·62 | 28·23 |
| 0·4 | 51·62 | 52·27 | 1·1 | 25·27 | 25·86 |
| 0·5 | 46·07 | 46·65 | 1·2 | 23·28 | 23·36 |
| 0·6 | 41·42 | 41·97 | | | |

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# On the crystal and molecular structure of fluorene. By GEORGE M. BROWN and MARLYN H. BORTNER, *Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.*

According to the X-ray analysis of crystalline fluorene by Iball (1936), the two six-membered rings in the fluorene molecule are each tilted up about 20° out of the plane of the five-membered ring. In contrast, recent stereochemical (Weisburger *et al.*, 1950) and ultra-violet spectroscopic (Merkel & Wiegand, 1947, 1948) studies on fluorene and an X-ray analysis (Fenimore, 1948) of the closely related bifluorene (dibiphenylene-ethylene) molecule indicate a uniplanar structure for the fluorene carbon skeleton. Since the details of the fluorene structure are of some interest from the point of view of valence theory and chemical reactivity (Lothrop, 1939) and in relation to carcenogenicity of fluorene derivatives (Miller *et al.*, 1949; Sandin *et al.*, 1952), a new X-ray analysis of fluorene has been undertaken in this laboratory.

Crystals of fluorene have been found to be orthorhombic, of space group *Pna* or *Pnam*, with four molecules per unit cell, and with $a = 8.50$, $b = 5.71$, $c = 19.00$ Å, in essential agreement with the data of Iball. With the use of the Weissenberg multiple-film technique and Cu $K\alpha$ radiation, data have been obtained for the zero and higher layers for rotations about the three principal axes. In all, 210 reflections have been recorded and their intensities estimated visually, the number being limited so far because of difficulties in preserving the volatile crystal specimens. Limited success in preserving the crystals was attained by coating them with diluted colorless nail polish.

The distribution of peaks in a Patterson projection [010] strongly suggested space group *Pnam*. The planar model below (similar to Iball's first trial structure and to Fenimore's model for half the bifluorene molecule) was adopted. Satisfactory preliminary agreement between calculated and observed structure factors for the reflec-

tions of the three principal zones was obtained for a structure having the model molecule oriented parallel to $z$ with the point $O$ at $x/a = 0.353$, $y/b = 0.431$, $z/c = 0.250$, with an angle of 30.5° between the line $OP$ and the $y$ axis. The reliability factor $\Sigma(||F_o| - |F_c||) \div \Sigma|F_o|$ was 0.22. The value of $B$ in the temperature factor was $4.6 \times 10^{-16}$ cm$^2$.

Electron-density projections [100], [010], and [001] were computed using X-RAC. The [100] projection shows each molecule, but not each atom, resolved. In the [010] projection carbons 2, 3, 7, 8, 10, 11, 12, and 13 are clearly resolved, and their positions show the approximate correctness of the angular orientation of the benzene nuclei as given in the model. In the [001] projection, each molecule is seen edgewise as one link in a zigzag chain. The shape and distribution of contours in this projection are consistent only with a structure in which deviations from uniplanarity are no more than trivial.

The essential correctness of the proposed planar structure of fluorene is regarded as established. The process of refinement is being carried out, and efforts are being made to record more of the 1090 reflections theoretically accessible using Cu $K\alpha$ radiation, in the hope of achieving a very accurate structure determination.

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