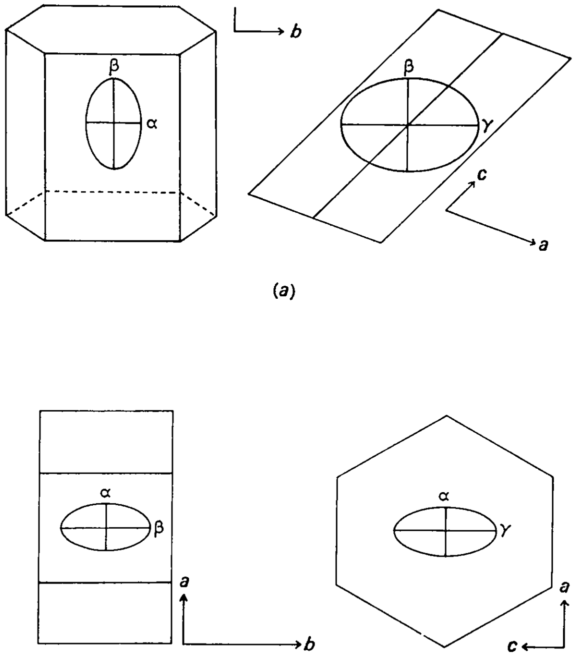

(a)

(b)

Fig. 1. Common habit, the indicatrix and chosen crystallographic axis of (*a*) uric acid (*b*) uric acid dihydrate. The differences between the principal optic axes are exaggerated five times.

The observed density 1·844 g.cm^{-3} gives $Z = 3{\cdot}985$ molecules of $C_5H_4N_4O_3$, molecular weight 168·11, per unit cell. $D_{calc} = 1{\cdot}851$ g.cm^{-3}. The monoclinic crystals thus consist of pure anhydrous uric acid.

The orthorhombic form

Under conditions mentioned above, uric acid can crystallize in an orthorhombic form which disintegrates when allowed to dry in air and is converted into a polycrystalline aggregate of the monoclinic form. This conversion has been followed by powder diffraction and no detectable intermediate crystalline form has been observed. However, stable crystals of the orthorhombic form were found in some rare human bladder stones and on the inside of hatched eggshells of hens.

The most common crystal habit in relation to principal optical directions and corresponding crystallographic axes is shown in Fig. 1(*b*).

Optical Biaxial negative

$\gamma = 1{\cdot}728 \pm 0{\cdot}003$
$\beta = 1{\cdot}691 \pm 0{\cdot}003$
$\alpha = 1{\cdot}508 \pm 0{\cdot}003$
$2V_{obs} = 40{\cdot}4° \pm 0{\cdot}6°$
$2V_{calc} = 44° \pm 4°$
$B = 0{\cdot}22$

Weissenberg and rotation photographs taken with Cu $K\alpha$ radiation showed that the unit cell was orthorhombic. The systematic absences varied between different, optically untwinned crystals, without any change of the unit-cell dimensions. Consistent absences for all crystals were $hk0$ when k was odd. In addition $h00$ and $00l$ were absent when h and l were odd, but because of the small number of reflexions these absences could not be regarded as trustworthy. The $h0l$ reflexions when h was odd were very few and varied moreover in intensity. So did, to even greater extent, the $0kl$ reflexions when $k+l$ was odd. These variations can probably be assigned to changes in the water content. Hence the space group could not be determined with certainty.

The lattice parameters were

$a = 7{\cdot}40 \pm 0{\cdot}01$ Å
$b = 17{\cdot}55 \pm 0{\cdot}01$
$c = 6{\cdot}35 \pm 0{\cdot}005$
$V = 825{\cdot}7$ Å^3

The observed density 1·650 g.cm^{-3} gives four formula units with a molecular weight of 204·96. As this crystal form (1) was formed in water solution,(2) disintegrated upon drying and (3) converted into anhydrous uric acid, it is probable that it contains water. The calculated molecular weight for uric acid with two H_2O (204·15) is in good agreement with the observed value. The calculated density = 1·643 g.cm^{-3}. Thus it seems likely that the orthorhombic unit cell contains four formula units of $C_5H_4N_4O_3 . 2H_2O$. Further support for this concept was gained in measuring the weight loss after heating a sample of this compound to 105 °C for five hours.

The crystal structure of uric acid is now under investigation.

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A three-dimensional refinement of the structure of crocoite, $PbCrO_4$.

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Introduction

A complete determination of the crocoite structure and two-dimensional refinement have already been carried out (Quareni & De Pieri, 1964). By means of this early study it was possible to refine the lead and chromium parameters and to determine the positions of the oxygen atoms. The purpose of the present work was to confirm the previous determination of the structure and to refine the atomic parameters, particularly the parameters of the oxygen atoms which the two-dimensional refinement could not determine very accurately.

Experimental

The material was taken from a sample of crocoite from Dundas (Tasmania). The photographs were obtained from a crystal which was ground to a small sphere having a radius $R = 0{\cdot}0088$ cm. The linear absorption coefficients for the crocoite are 1169 cm^{-1} (Cu $K\alpha$) and 512 cm^{-1} (Mo $K\alpha$), so that $\mu R = 10{\cdot}28$ and 4·51 respectively.

Equi-inclination multiple-film integrated Weissenberg photographs about the *b* axis were taken from zero to the fifth level with Cu $K\alpha$ radiation and the sixth level with Mo $K\alpha$. For the *hk*0 and 0*kl* reflexions the approximate scale factors were obtained by the Wilson method; the remaining observations were correlated with these.

Of the 747 possible reflexions, 656 gave measurable intensities. The integrated intensities were measured by a Hilger microdensitometer and corrected for absorption using the figures of Evans & Ekstein (1952). The non-linear behaviour of Ilford Industrial G film was corrected by the formula $D_{corr} = D(1 + 0{\cdot}1\ D)$ (Mammi, Bardi & Bezzi, 1963). The square roots of these intensities, corrected for the Lorentz and polarization effects, gave the observed structure factors.

The refinement

The refinement was carried out by the method of least squares. The analytical form of Forsyth & Wells (1959) of the scattering factors was used in this analysis. We took account of the anomalous scattering of the Pb atom by changing *C* in the Forsyth & Wells expression from 20·89 to 14·89, to correspond to the $\Delta f'$ value of the real part of the dispersion correction reported in *International Tables for X-Ray Crystallography* (1962). No ionization was assumed for any of the atoms, and even if this assumption is not true it will not affect the accuracy of the final atomic parameters.

The initial *R* index was 0·165 using the positional parameters, isotropic temperature factors for Cr and O and anisotropic temperature factors for Pb which we found in the two-dimensional refinement. The examination of the $F_o - F_c$ values after the first stage of the least-squares refinement showed a better absorption correction and a new scaling to be necessary.

For this purpose *B* and *K* factors were obtained by the Wilson method for each level. These positive *B* values increased from zero to the sixth level. Each F_o of each level was corrected by the formula $F_{\text{corr}} = KF_o \exp(B \sin^2 \theta/\lambda^2)$. By this method it is possible, for a spherical sample, to correct for absorption because the expressions for the absorption and for the thermal vibration are both exponential functions of θ. However, the final *B* values will be not very accurate; for this reason the temperature factors were held constant and the coordinates and the scale factor alone allowed to vary. After a number of cycles of least-squares refinement *R* dropped to 0·085 and the work was discontinued since the shifts in the atomic parameters were below the standard deviation.

Description of the structure

The final atomic coordinates based on this three-dimensional refinement are shown in Table 1 as fractions of the unit-cell edges with the corresponding standard deviations. The interatomic distances in crocoite are given in Table 2. The chromium atom is surrounded by a tetrahedron of oxygen atoms at an average distance of 1·65 Å with bond

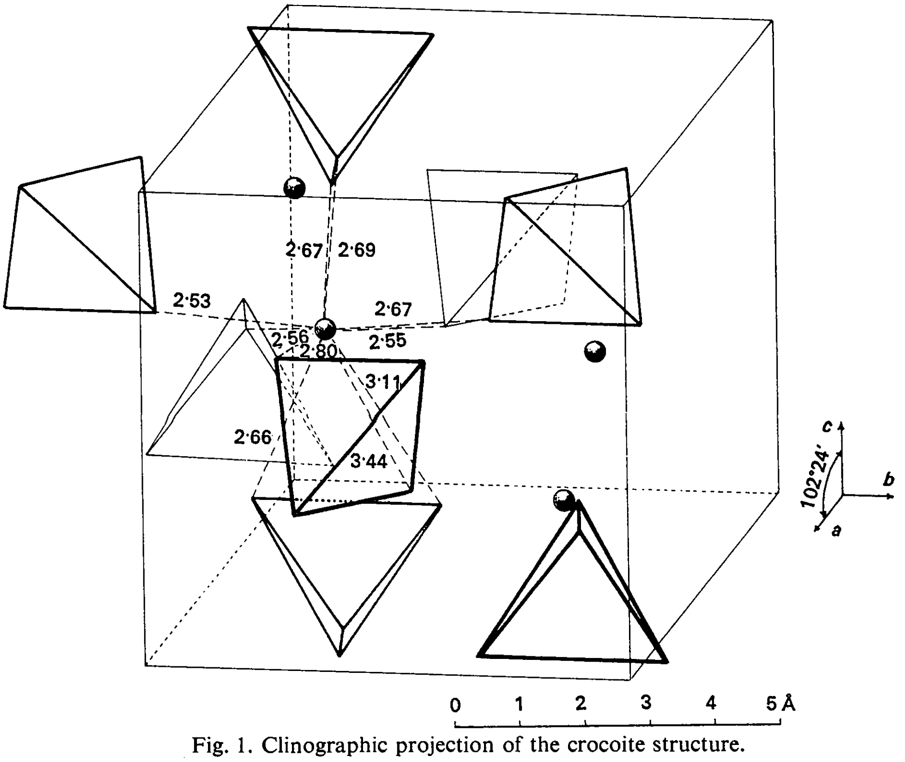

Fig. 1. Clinographic projection of the crocoite structure.

Table 1. *Final positional parameters with standard deviations*

Atom	x	$10^3\sigma(x)$	y	$10^3\sigma(y)$	z	$10^3\sigma(z)$
Pb	0·2218	0·0	0·1450	0·0	0·3974	0·0
Cr	0·2010	0·5	0·1651	0·6	0·8800	0·5
O(1)	0·0354	2·9	0·0989	3·5	0·6944	3·0
O(2)	0·1247	3·1	0·3461	3·0	0·9869	3·2
O(3)	0·2534	3·1	0·4982	3·6	0·4540	3·4
O(4)	0·3887	2·7	0·2173	3·4	0·7810	2·9

Table 2. *Interatomic distances with standard deviations*

Distance	Value	σ	Distance	Value	σ
Cr–O(1)	1·61 Å	0·02 Å	Pb–O(1)	2·67 Å	0·02 Å
Cr–O(2)	1·67		Pb–O(2)	3·11	
Cr–O(3)	1·66		Pb–O(3)	2·66	
Cr–O(4)	1·67		Pb–O(4)	2·68	
O(1)–O(2)	2·68	0·03	Pb–O(1′)	2·56	
O(2)–O(3)	2·73		Pb–O(2′)	2·53	
O(2)–O(4)	2·75		Pb–O(3′)	2·67	
O(1)–O(3)	2·64		Pb–O(4′)	2·55	
O(3)–O(4)	2·78		Pb–O(1″)	3·44	
O(1)–O(4)	2·61		Pb–O(2″)	2·80	
Pb–Cr(1)	3·49	0·00			
Pb–Cr(2)	3·32				
Pb–Cr(3)	4·15				
Pb–Cr(4)	3·72				
Pb–Cr(5)	3·94				
Pb–Cr(6)	3·95				
Pb–Cr(7)	3·87				

angles varying from 105·7° to 113·1° (Table 3). The distortion of this tetrahedron is now seen to be less than it appeared in the two-dimensional analysis. The lead atom is surrounded by seven CrO_4 tetrahedra. The Pb–Cr distances are in the range 3·32 Å to 4·15 Å. The lead atom is also surrounded by ten oxygen atoms with Pb–O distances ranging from 2·53 to 3·44 Å, all the other distances Pb–O are more than 4·03 Å. Fig. 1 shows a clinographic projection of the crocoite structure.

Table 3. *Bond angles in the tetrahedron CrO_4 with standard deviations*

Angle	Value	σ
O(1)–Cr–O(4)	105·7°	1·3°
O(1)–Cr–O(2)	109·6°	
O(1)–Cr–O(3)	107·9°	
O(2)–Cr–O(4)	110·5°	
O(2)–Cr–O(3)	109·9°	
O(3)–Cr–O(4)	113·1°	

The orthorhombic (Collotti, Conti & Zocchi, 1959) and the monoclinic modifications of $PbCrO_4$ have very similar interatomic distances. The distance Cr–O in the orthorhombic modification is 1·65 Å, corresponding exactly to the average value found in crocoite. This confirms the evidence for multiple bonds in the CrO_4^{2-} ion (Pauling, 1948). The spacial arrangement of the atoms is quite similar in the two modifications. This is seen in Fig. 2, which shows the distances and the angles of the lead atoms and the CrO_4 tetrahedra with respect to their centers of symmetry.

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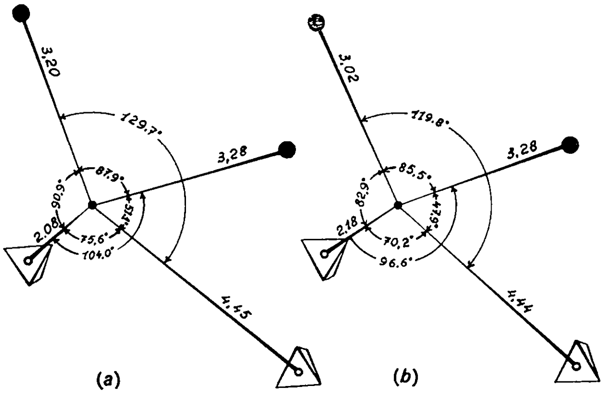

Fig. 2. Schematic representation of the Pb atoms and the CrO_4 tetrahedra with respect to their centres of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, 0) for the orthorhombic modification (*a*) and at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) for crocoite (*b*).

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