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The Structure of Crystalline Chromous Acetate Revealing Paired Chromium Atoms

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Crystals of chromous acetate are monoclinic with space group $C2/c$. The unit cell, of dimensions $a = 13{\cdot}15$, $b = 8{\cdot}55$, $c = 13{\cdot}94$ Å, $\beta = 117° 0'$, contains four $Cr_2(CH_3COO)_4.2H_2O$ molecules. Projections of the structure on two crystallographic planes are given and from these it is inferred that chromous and cupric acetate are isostructural.

The most striking feature of the structure is the close approach of 2·64 Å between the two chromium atoms in a molecule, which, as in the case of the cupric acetate structure, suggests direct interaction between such atoms.

Introduction

The unusual structural features found in cupric acetate, $Cu_2(CH_3COO)_4.2H_2O$ (van Niekerk & Schoening, 1953), have led us to examine the crystal structures of the acetates of the other transition elements in an endeavour to determine whether these compounds show similar features. Althongh preliminary work on the acetates of cobalt, nickel and zinc reveal no unexpected results, the structure of chromous acetate, $Cr_2(CH_3COO)_4.2H_2O$, which is briefly described in this paper, is strikingly similar to that of cupric acetate.

Preparation*

Crystals of chromous acetate, in the form of needles and prisms, were prepared from sodium acetate and chromous chloride solutions under an atmosphere of oxygen-free nitrogen in an apparatus similar in principle to that of Hatfield (1950). Initial conditions (a pH of 1–2 and a temperature of 70–80° C.) were so chosen that no acetate precipitated on mixing the solutions. After adjusting the pH to a value where precipitation just began, the solution was slowly cooled to 0–5° C. A typical analysis follows:

	Calculated for $Cr(CH_3COO)_2.H_2O$	Found
Cr''	27·65 %	25·15 %
Cr	27·65	26·02
C	25·5	25·2
H	4·25	4·48
CH_3COO	62·7	60·45

Owing to the low solubility of the salt and its susceptibility to oxidation, the purity could not be improved upon in the present apparatus. The above analysis seems to indicate one molecule of water of crystallization, confirming the work of Peligot (1844), whereas Hatfield (1950) and others assume that no water of crystallization is present.

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Crystal data

The crystals, which are reddish in colour, are unstable, becoming black on exposure to the atmosphere. They were stored in nitrogen-filled glass tubes, which were broken under xylol whenever specimens suitable for X-ray examination were required. They were cut and mounted under xylol into thin-walled glass capillaries, which were then sealed. Most of the crystals are in the form of hollow needles with fairly well developed {110} prism faces, the angles between such faces being 72° 21′ and 107° 39′. In some cases four apparently octahedral faces occasionally develop at one end of the needles. Two of these four faces are of the form {111}. The remaining two are (001) and (101) faces, the angle between them being 61° 18′.

It is interesting to note that the crystals can be referred to a face-centred or a body-centred lattice in which the axial lengths are almost identical. If *abc* (*hkl*) and *ABC* (*HKL*) refer to the face- and body-centred cells respectively, then $h = H+L$, $k = -K$ and $l = -L$, and the monoclinic angles are 117° 0′ and 125° 0′ respectively. During this investigation a *C*-face-centred cell has been retained throughout. Its dimensions, as determined from rotation and Weissenberg photographs, are as follows:

$$a = 13{\cdot}15,\ b = 8{\cdot}55,\ c = 13{\cdot}94 \text{ Å},\ \beta = 117° 0'.$$

These values are very similar to the corresponding ones for cupric acetate:

($a = 13{\cdot}15$, $b = 8{\cdot}52$, $c = 13{\cdot}90$ Å, $\beta = 117° 0'$).

Assuming four $Cr_2(CH_3COO)_4.2H_2O$ molecules in a cell with the above dimensions, the calculated density is 1·78 g.cm.$^{-3}$, in good agreement with the measured value 1·79 g.cm.$^{-3}$.

Systematic extinctions occur only for hkl with $h+k$ odd, $h0l$ with h odd and l odd and $0k0$ with k odd. The space group is therefore either Cc or $C2/c$. By analogy with the corresponding copper compound, and considering the successful structural analysis, the correct space group is $C2/c$.

Preliminary estimate of the structure

Using the multiple-film technique, zero-layer Weissenberg photographs were taken of suitable crystal specimens rotating about the a and b axes. In order to avoid confusion, filtered Cu $K\alpha$ radiation was used for the a-axis rotation, as our Weissenberg instrument recorded, in addition to the zero-layer reflexions, also first-layer reflexions when Mo $K\alpha$ radiation was used. The intensities of the reflexions were estimated visually and corrected for Lorentz and polarization factors. In view of the small size of the crystals used, absorption and extinction corrections were neglected.

By comparing these films with corresponding ones taken with cupric acetate it was immediately evident that the two compounds are structurally very similar. This point is illustrated in Fig. 1, where the $P(u, 0, w)$

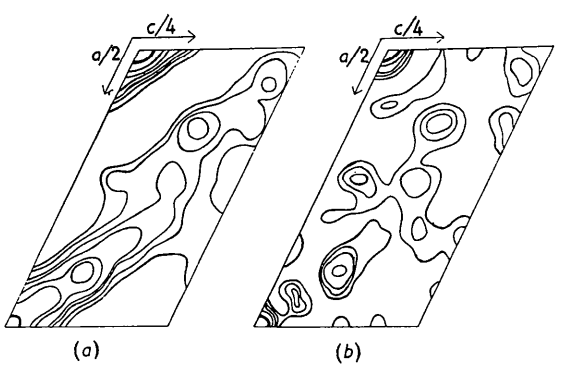

Fig. 1. $P(u, 0, w)$ projection of (*a*) chromous acetate, (*b*) cupric acetate.

projections of chromous and cupric acetate are shown. The increased resolution in the case of the cupric acetate projection is accounted for by the fact that in this case it was possible to use Cu $K\alpha$ radiation so that more weak spectra were recorded. In the case of chromous acetate the method used for mounting the crystals, together with the fact that Mo $K\alpha$ radiation was used, restricted the number of spectra that were recorded for such exposure times as were experimentally practicable.

Projection of the structure on two crystallographic planes

Because of the similarity, it was decided to use the atomic co-ordinates previously obtained for cupric acetate during the preliminary investigations of chromous acetate. With these co-ordinates the $F(h0l)$ values were calculated and the $\sigma(x, z)$ projection shown in Fig. 2 was obtained. The f values used for chromium

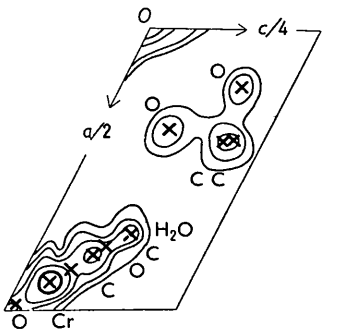

Fig. 2. $\sigma(x, z)$ projection with contours drawn at arbitrary intervals. Crosses show the positions of corresponding atoms found for cupric acetate. Origin of projection is as in *International Tables*.

are those given in *International Tables*. For carbon the values obtained by Robertson (1935) were used. For oxygen proportionately reduced values were used. The observed and calculated structure factors are listed under Table 1. The agreement is good and leads to an R factor of 0·17 when the absent spectra are not taken into account. Because of this agreement, and since the majority of the atoms on this projection are not resolved, further refinement of this projection was not considered feasible.

Again using as atomic co-ordinates those obtained for cupric acetate, the $\sigma(y, z)$ projection for chromous acetate was similarly evaluated (Fig. 3). For reasons pointed out earlier, the observed $F(0kl)$ values were in this case estimated from films taken with Cu $K\alpha$ radiation, so that absorption effects probably influenced these intensities appreciably. Nevertheless, it was possible to correlate the two projections and there were no inconsistencies. Considering the inaccuracy of the intensities, the agreement between the observed and calculated $F(0kl)$ values (see Table 1) is satis-

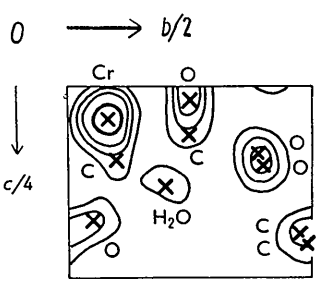

Fig. 3. $\sigma(y, z)$ projection. Contours, crosses and origin are as for Fig. 2.

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	147	+169	$\bar{6}06$	108	−117	025	70	−76
400	31	−57	$\bar{6}08$	59	−64	026	< 22	− 6
600	28	−35	$\bar{6}$,0,10	< 24	+28	027	145	−121
800	63	−85	$\bar{6}$,0,12	< 27	+35	028	106	−75
10,0,0	< 27	−35	$\bar{6}$,0,14	< 29	+64	029	80	−79
12,0,0	50	−55	$\bar{6}$,0,16	63	+83	0,2,10	< 30	−11
14,0,0	< 46	−28	802	< 24	−19	0,2,11	< 30	− 3
002	188	+190	804	< 27	−25	0,2,12	< 30	−33
004	< 15	−11	806	81	+72	0,2,13	< 27	+35
006	< 18	−22	808	63	+106	0,2,14	44	−38
008	88	−86	$\bar{8}02$	69	−77	0,2,15	27	+37
0,0,10	< 25	−48	$\bar{8}04$	< 27	−40	041	< 20	−10
0,0,12	56	−73	$\bar{8}06$	62	−52	042	36	−76
0,0,14	55	−56	$\bar{8}08$	< 22	− 4	043	54	−68
0,0,16	< 34	−16	$\bar{8}$,0,10	< 24	+45	044	45	+28
202	307	+275	$\bar{8}$,0,12	52	+88	045	110	−90
204	330	+246	$\bar{8}$,0,14	101	+92	046	73	+68
206	59	+39	$\bar{8}$,0,16	63	+55	047	123	−104
208	< 25	− 2	$\bar{10}$,0,2	111	−117	048	< 29	+20
2,0,10	36	−53	$\bar{10}$,0,4	59	−44	049	44	−41
2,0,12	52	−76	$\bar{10}$,0,6	< 24	+42	061	38	−21
$\bar{2}$02	161	+124	$\bar{10}$,0,8	< 25	+42	062	150	−133
$\bar{2}$04	97	−108	$\bar{10}$,0,10	83	+106	063	62	−34
$\bar{2}$06	< 18	−18	$\bar{10}$,0,12	88	+79	064	40	−73
$\bar{2}$08	88	−87	$\bar{10}$,0,14	52	+44	065	< 29	+33
$\bar{2}$,0,10	118	−130	$\bar{10}$,0,16	< 31	+12	066	< 30	+28
$\bar{2}$,0,12	< 28	−21	12,0,2	55	−76	067	< 27	+34
$\bar{2}$,0,14	< 31	−20	$\bar{12}$,0,2	< 24	+ 1	068	< 30	+46
$\bar{2}$,0,16	< 34	+15	$\bar{12}$,0,4	< 25	+ 3	069	< 26	−14
402	221	+195	$\bar{12}$,0,6	< 27	+65	0,6,10	40	+66
404	256	+232	$\bar{12}$,0,8	56	+84	0,6,11	< 25	+ 6
406	126	+140	$\bar{12}$,0,10	80	+79	0,6,12	39	+55
408	28	+27	$\bar{12}$,0,12	119	+70	081	31	+27
4,0,10	< 28	0	$\bar{14}$,0,2	< 31	+27	082	< 25	− 3
$\bar{4}$02	113	−105	$\bar{14}$,0,4	< 29	+70	083	31	+45
$\bar{4}$04	< 15	−23	$\bar{14}$,0,6	42	+71	084	< 25	+ 2
$\bar{4}$06	100	−104	$\bar{14}$,0,8	95	+89	085	43	+75
$\bar{4}$08	< 21	−35	$\bar{14}$,0,10	52	+29	086	< 24	−10
$\bar{4}$,0,10	57	−62	$\bar{14}$,0,12	< 31	−10	087	55	+74
$\bar{4}$,0,12	28	−39				088	< 29	+ 5
$\bar{4}$,0,14	< 29	+41	020	134	+98	089	23	+45
$\bar{4}$,0,16	< 32	+55	040	< 20	−37	0,8,10	34	+29
602	< 20	−14	060	206	−151	0,10,1	< 22	+22
604	80	+89	080	53	− 8	0,10,2	< 22	+41
606	116	+116	021	34	−40	0,10,3	39	+35
608	127	+124	022	60	−59	0,10,4	< 20	+ 8
6,0,10	< 31	+55	023	62	−84	0,10,5	< 18	+47
$\bar{6}$02	< 18	−10	024	< 19	+ 7	0,10,6	55	−19
$\bar{6}$04	80	−96						

factory, giving an R factor of 0·26 when absent spectra are excluded.

That the atomic co-ordinates found for the cupric acetate structure fit the present structure remarkably well is further shown by the positions of the crosses on the two projections described above. These crosses represent the positions of the relevant atoms of cupric acetate when plotted on the two chromous acetate projections.

Because of poor resolution, long exposure times and difficulties in mounting suitable crystal specimens, no further attempt was made to refine the structure. From this investigation it is therefore concluded that the atomic co-ordinates and the interatomic distances in the structure of chromous acetate are indeed very similar to corresponding ones previously described by van Niekerk & Schoening (1953) for cupric acetate. Furthermore, the projections confirm the existence of one water molecule for every chromium atom in the structure.

Description of the structure

The most outstanding feature of this binuclear molecule, $Cr_2(CH_3COO)_4.2H_2O$, is the short Cr–Cr distance (2·64 Å), indicating direct interaction between the two metal atoms in a molecule. Each pair of metal atoms is bridged by the four acetate groups in such a manner that four oxygen atoms, arranged approximately at the corners of a square, form the nearest neighbours of a chromium atom (1·97 Å). Perpendicularly above and below the plane of the square lie a water molecule at a distance of 2·20 Å and a chromium

atom at a distance 2·64 Å. Four such oxygen atoms, a water molecule and a chromium atom thus form a distorted octahedron about each of the two chromium atoms in a molecule.

As in the case of cupric acetate, apart from van der Waals forces, hydrogen bonds again appear to be the main forces between the molecules. Each chromous acetate molecule is linked by eight such bonds (2·82 and 2·89 Å) to four neighbouring molecules at different levels. For further details about the atomic arrangement, reference should be made to the paper describing the structure of cupric acetate.

Discussion of the bonds

When the paper on cupric acetate was sent for publication, no reliable magnetic data were available, so that only the interatomic distance suggested a direct Cu–Cu bond. Shortly afterwards Bleaney & Bowers (1952) published a paper containing detailed magnetic measurements, and suggested interaction between the copper atoms. These two independent determinations make it certain now that a bond does exist between the copper atoms. From the remarkable similarity between the chromous and cupric acetate structures, it seems reasonable to infer that a direct bond also exists between the two chromium atoms.

The configuration around the chromium atom described in this paper disagrees with the tetrahedral co-ordination proposed by King & Garner (1950) to explain the diamagnetism they observed for chromous acetate.

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The Crystal Structure of a *cyclo*Nucleoside

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X-ray analysis has been used to discover the nature of a chemical rearrangement undergone by certain nucleoside derivatives to form *cyclo*nucleosides. Crystals of the iodide of 2′:3′-*iso*propylidene, 3:5′-*cyclo*adenosine are orthorhombic with $a = 5{\cdot}4$, $b = 15{\cdot}4$, $c = 18{\cdot}1$ Å. The space group is $P2_12_12_1$ and there are four molecules in the unit cell. The y and z atomic coordinates were determined by use of the heavy-atom method applied to the (100) projection; x coordinates by use of 'higher layer projection' techniques. The purine ring system is planar and makes an angle of 90° with the puckered furanose ring to which it is joined by a β glycosidic linkage.

Crystals of 5′ iodo, 2′:3′ *iso*propylidene uridine are orthorhombic, $P2_12_12_1$, with $a = 5{\cdot}42$, $b = 15{\cdot}4$, $c = 16{\cdot}7$ Å, and the unit cell contains four molecules. This substance has been examined in the (100) projection only, and shows by contrast a normal covalent iodide structure.

Introduction

In recent years, one of the projects undertaken in this laboratory has been the investigation of the crystal structures of nucleic acid constituents and their derivatives. It has consisted mainly in the detailed investigation of pyrimidines and purines, with particular interest in their tautomeric forms, but it was also intended that more complex units (i.e. nucleosides and nucleotides) should be examined.

The structures of 2-amino,4-methyl-6 chloropyrimidine and 2-amino,4-6 dichloropyrimidine (Clews & Cochran, 1948), 5-bromo,4-6 diaminopyrimidine and 4-amino, 2-6 dichloropyrimidine (Clews & Cochran, 1949), adenine hydrochloride hemihydrate (Broomhead, 1948; Cochran, 1951) and guanine hydrochloride monohydrate (Broomhead, 1951) have been reported.

The present study of certain nucleoside derivatives is part of this programme, and also provides the solution of a specific chemical problem. An account of part of this more recent work, mainly from a chemical standpoint, has already been published (Clark, Todd &

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