Acta Cryst. (1970). B26, 673

The Crystal Structure of a Basic Chromium Acetate Compound, $[OCr_3(CH_3COO)_6.3H_2O]^+Cl^-.6H_2O$, having Feeble Paramagnetism*

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(*Received* 13 *March* 1969)

The crystal structure of $[OCr_3(CH_3COO)_6.3H_2O]^+Cl^-.6H_2O$ has been determined from three-dimensional diffractometer data using Cu $K\alpha$ radiation. The configuration of the complex cation consists of three chromium atoms linked to a central oxygen atom in a planar configuration. Each chromium atom is coordinated octahedrally by the central oxygen atom, one from each of four acetate groups and a water molecule. The acetate groups link the vertices of the three octahedra in the complex cation. The anions and those water molecules not included in the cations are disordered and lie in channels along the twofold axes. Their structure is ill-defined, but a reasonable model can be presented in which the cations are linked by a system of hydrogen bonds into zigzag layers perpendicular to the c axis.

Introduction

The chemistry of a number of polynuclear basic chromium and iron carbonato compounds was studied by Weinland (1919). This particular compound was given the formula $[Cr_3(OH)_2(CH_3COO)_6]Cl.8H_2O$, and others were described in which one, two or all three metal atoms were replaced by ferric ion. The acetate groups were also replaced by other carbonato ions such as formate, propionate, benzoate. There were reported, in addition, a variety of anions and hydrates.

The magnetic properties of some thirty of these crystalline materials were studied by Welo (1928) in a paper which was quite remarkable for that time. The magnetic susceptibility *versus* temperature measurements, which led to a large negative Curie–Weiss temperature, were interpreted in terms of intramolecular magnetic dipole interactions involving coupled clusters of paramagnetic ions. Although Welo's model is certainly incorrect, this structural concept corresponds remarkably with the actual structure of the chromium complex. Some twenty years later Kambe (1950) postulated a quantum mechanical explanation also assuming triangular clusters of paramagnetic ions but with antiferromagnetic exchange. Independently, Abragam, Horowitz & Yvan (1952) used the same model to explain the temperature dependence of the susceptibilities and specific heats at low temperatures. Further experimental measurements on this Cr_3 compound and the corresponding Cr_2Fe compound have been reported by Wucher & Gijsman (1954), Gijsman, Karantassis & Wucher (1954) and Wucher & Wasscher (1954). Owing to the large negative value of θ in the Curie–Weiss relationship, χ changes only slightly with temperature. It is believed that the magnetic exchange interactions are confined within small clusters of the metal ions and tend to conceal each other, hence the name 'feeble paramagnetism' (Bates, 1961).

Following the preliminary reports of the structure of the complex cation by Chang & Jeffrey (1965) and Figgis & Robertson (1965), Uryû & Friedberg (1965) made a theoretical investigation of the possibility of accounting for the paramagnetic properties on the basis of a model with the observed symmetry of the complex cation.

Experimental

Material, originally prepared by Dr A. Weiss of the Physics Department, Carnegie–Mellon University, was recrystallized by slow evaporation of aqueous solution. Dark green orthorhombic crystals were obtained as needles, thin plates and prisms. The prisms which had a pseudo-hexagonal morphology were used in this investigation. Two chemical analyses gave: Cr, 21·5 and 21·7; Cl, 4·9 and 5·2; C, 21·3; H, 4·93; O, 38·6; H_2O, 20·1 and 19·9; acetate, 48·8; calculated for the formula $[OCr_3(CH_3COO)_6.3H_2O]^+Cl^-.6H_2O$: Cr, 21·6; Cl, 4·9; C, 19·9; H, 4·98; O, 48·6; H_2O, 22·5; acetate, 48·9. Only the oxygen results were in substantial disagreement with the formula. The space group was determined from the systematic extinctions ($h00$) absent h odd, ($0k0$) absent k odd. The unit-cell dimensions were measured with Cu $K\alpha$ radiation on a General Electric single-crystal orienter and XRD-3 diffractometer using a $\cos^2\theta$ extrapolation of the principal axial 2θ values.

* Work done mainly at the Crystallography Laboratory, University of Pittsburgh, and supported by the U.S. Army Research Office, Contract No. DA-ORD-D-31-124-G786.

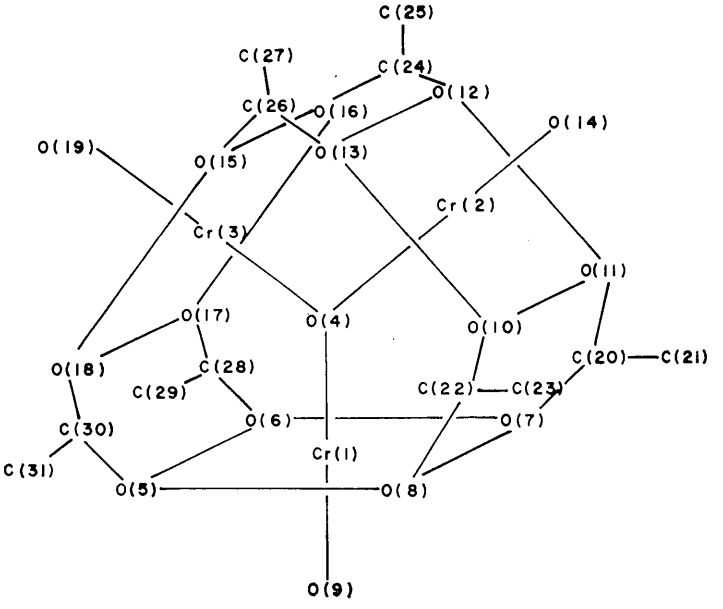
The density was measured by flotation in a mixture of carbon tetrachloride and bromoform.

Crystal data

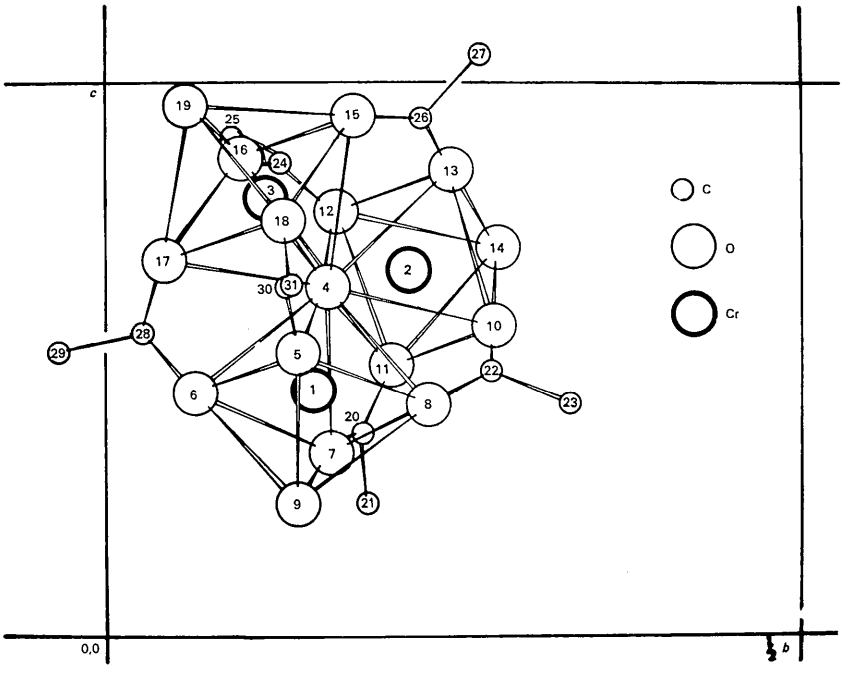
trans-μ_3-Oxo-tris{bisacetatoaquochromium(III)} chloride hexahydrate, $[OCr_3(CH_3COO)_6 . 3H_2O]^+Cl^- . 6H_2O$. Orthorhombic:

$a = 13{\cdot}677 \pm 0{\cdot}01$ Å
$b = 23{\cdot}141 \pm 0{\cdot}018$
$c = 9{\cdot}142 \pm 0{\cdot}007$
Space group $P2_12_12$
μCu $K\alpha = 112{\cdot}7$ cm^{-1}

$V = 2893{\cdot}44 \pm 0{\cdot}04$ Å^3
$D_x = 1{\cdot}662 \pm 0{\cdot}003$ g.cm^{-3}
$D_m = 1{\cdot}654 \pm 0{\cdot}008$ g.cm^{-3}
$Z = 4$
Formula wt. = 723·907

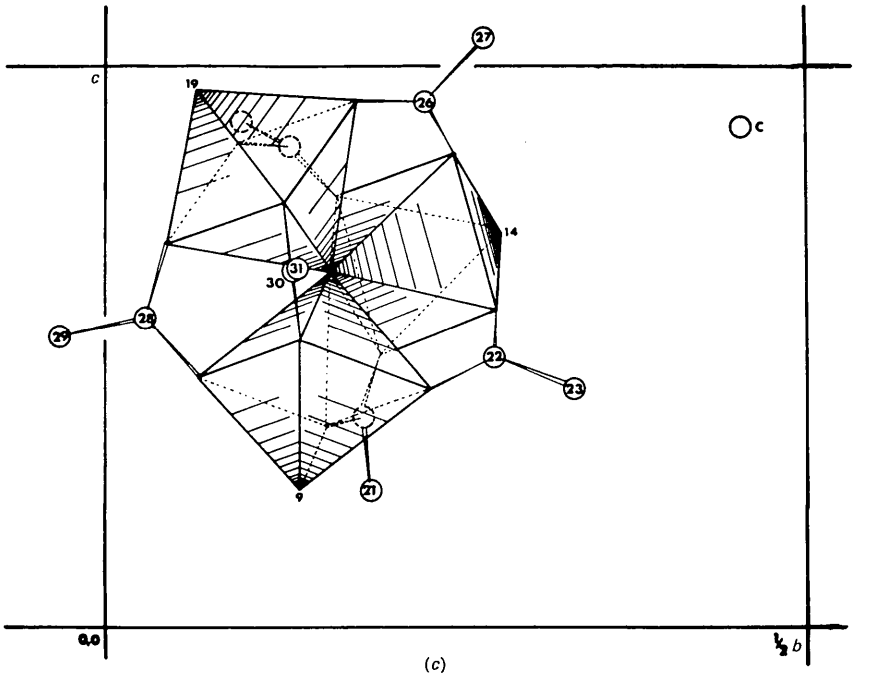


(*a*)



(*b*)

Fig. 1. (*a*) Diagrammatic representation of the complex cation $[OCr_3(CH_3COO)_6 . 3H_2O]^+$. (*b*) Actual view of the complex cation in the direction of the *a* axis.



(*c*)

(*c*) Coordination octahedra of the chromium ions.

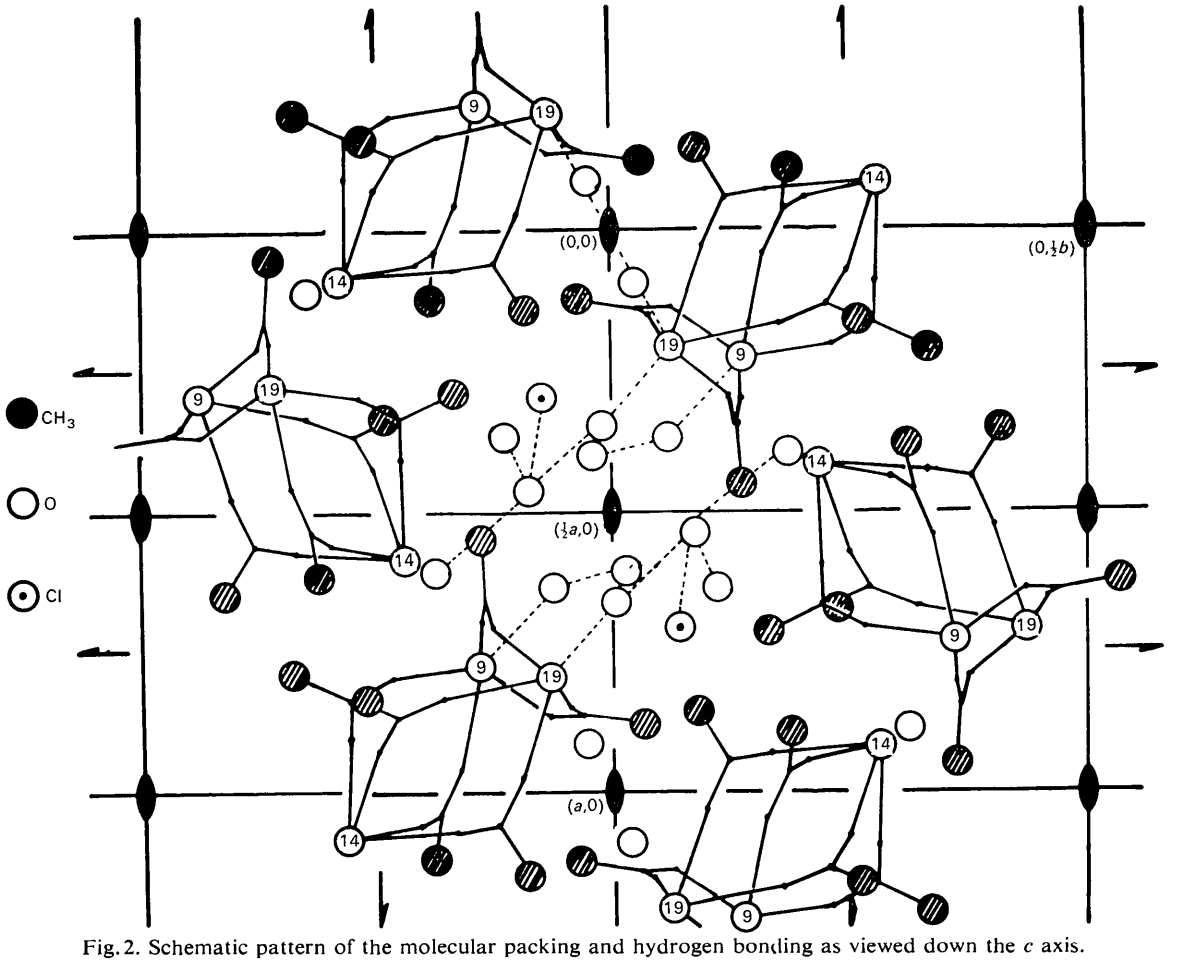


Fig. 2. Schematic pattern of the molecular packing and hydrogen bonding as viewed down the *c* axis.

Table 1. *Fractional atomic coordinates and thermal parameters in* $[OCr_3(CH_3COO)_6 . 3H_2O]^+Cl^- . 6H_2O$

The temperature factor is expressed as $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

Numbers in parentheses here and in the succeeding Tables are estimated standard deviations in the least significant digits.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factors Observed	Assumed O	Assumed Cl
The ordered cationic structure												
Cr(1)	0·1685 (2)	0·1496 (1)	0·4440 (3)	302 (14)	101 (5)	549 (31)	−16 (6)	−7 (17)	−27 (9)			
Cr(2)	0·0203 (2)	0·2188 (1)	0·6637 (3)	276 (14)	117 (5)	671 (31)	0 (6)	−12 (16)	7 (10)			
Cr(3)	0·1578 (2)	0·1149 (1)	0·7917 (3)	330 (15)	111 (5)	714 (33)	15 (6)	−30 (18)	1 (10)			
O(4)	0·1127 (8)	0·1610 (4)	0·6386 (12)	32 (6)	6 (2)	82 (13)	5 (3)	−17 (7)	3 (4)			
O(5)	0·2997 (7)	0·3187 (7)	0·5137 (14)	14 (5)	31 (3)	95 (5)	3 (3)	−3 (7)	6 (6)			
O(6)	0·1410 (10)	0·0643 (4)	0·4416 (13)	73 (8)	3 (1)	92 (15)	−7 (3)	10 (9)	5 (4)			
O(7)	0·0480 (11)	0·1599 (6)	0·3343 (14)	62 (8)	21 (3)	83 (14)	11 (4)	−26 (9)	4 (6)			
O(8)	0·2068 (12)	0·2314 (4)	0·4238 (17)	84 (10)	6 (2)	149 (19)	−0 (3)	38 (13)	−1 (5)			
O(9)	0·2308 (10)	0·1373 (5)	0·2469 (12)	57 (7)	18 (2)	41 (12)	0 (3)	−13 (8)	−2 (4)			
O(10)	0·0968 (8)	0·2768 (5)	0·5561 (16)	27 (6)	17 (2)	138 (20)	−0 (3)	19 (9)	−8 (6)			
O(11)	0·4415 (9)	0·2935 (6)	0·5192 (16)	33 (6)	23 (3)	131 (18)	−8 (4)	14 (10)	1 (6)			
O(12)	0·4303 (10)	0·3347 (5)	0·2310 (14)	65 (8)	11 (2)	98 (14)	−13 (3)	−5 (10)	18 (5)			
O(13)	0·0794 (12)	0·2478 (6)	0·8429 (13)	63 (9)	24 (3)	76 (14)	6 (4)	−22 (10)	−26 (6)			
O(14)	0·4183 (9)	0·2185 (5)	0·2984 (16)	42 (6)	17 (2)	131 (17)	−16 (3)	−6 (9)	−7 (5)			
O(15)	0·1749 (11)	0·1811 (6)	0·9312 (15)	69 (9)	21 (3)	83 (16)	14 (4)	−42 (11)	−12 (6)			
O(16)	0·0255 (9)	0·0951 (5)	0·8727 (15)	50 (7)	17 (2)	97 (16)	−9 (3)	23 (9)	6 (5)			
O(17)	0·1549 (11)	0·0419 (6)	0·6797 (16)	66 (8)	15 (2)	122 (18)	5 (4)	−28 (11)	10 (5)			
O(18)	0·2983 (13)	0·1274 (7)	0·7549 (17)	59 (10)	28 (3)	109 (18)	12 (5)	6 (11)	14 (6)			
O(19)	0·2101 (11)	0·0659 (6)	0·9508 (13)	60 (8)	20 (2)	58 (14)	4 (4)	−9 (9)	8 (5)			
C(20)	0·4656 (12)	0·3157 (8)	0·6343 (16)	37 (8)	20 (3)	39 (16)	7 (4)	16 (10)	−2 (6)			
C(21)	0·3947 (16)	0·3090 (13)	0·7655 (27)	44 (11)	38 (7)	126 (28)	1 (7)	32 (15)	−14 (11)			
C(22)	0·1668 (12)	0·2788 (7)	0·4687 (15)	37 (8)	16 (3)	31 (15)	−4 (4)	−4 (9)	5 (5)			
C(23)	0·2107 (15)	0·3352 (6)	0·4168 (23)	67 (12)	5 (2)	150 (26)	−2 (4)	−34 (16)	−2 (7)			
C(24)	0·4457 (11)	0·3778 (7)	0·1569 (20)	25 (7)	18 (3)	126 (20)	6 (4)	−11 (11)	−14 (7)			
C(25)	0·3592 (13)	0·4096 (10)	0·1018 (28)	15 (8)	23 (4)	193 (33)	2 (5)	−12 (14)	5 (10)			
C(26)	0·1378 (15)	0·2297 (7)	0·9378 (21)	69 (12)	8 (2)	105 (22)	−4 (4)	−15 (14)	−2 (7)			
C(27)	0·1719 (21)	0·2680 (12)	0·0614 (28)	94 (17)	27 (5)	150 (33)	3 (8)	−53 (22)	−8 (10)			
C(28)	0·1391 (12)	0·0295 (6)	0·5418 (19)	47 (9)	9 (3)	106 (21)	8 (4)	−30 (12)	−30 (6)			
C(29)	0·3730 (24)	0·4673 (8)	0·4875 (42)	130 (22)	8 (3)	298 (56)	−1 (4)	−24 (32)	16 (10)			
C(30)	0·3424 (13)	0·1323 (6)	0·6307 (20)	40 (9)	8 (2)	108 (22)	5 (4)	−0 (11)	11 (6)			
C(31)	0·4507 (14)	0·1373 (8)	0·6398 (23)	41 (9)	19 (3)	128 (26)	−8 (4)	−15 (13)	−13 (8)			
The disordered water/anionic structure												
O(32)	0·365 (2)	0·056 (1)	0·233 (3)	224 (36)	25 (5)	301 (53)	34 (10)	236 (38)	19 (11)	0·9 (1)	0·9	0·0
O(33)	0·399 (1)	0·184 (1)	0·013 (2)	94 (12)	33 (4)	145 (22)	−6 (5)	−56 (13)	−18 (7)	1·2 (1)	0·9	0·0
O(34)	0·038 (2)	0·415 (1)	0·991 (4)	80 (16)	59 (9)	353 (58)	−37 (9)	26 (24)	−93 (18)	1·0 (1)	0·9	0·0
Cl(35)	0·114 (1)	0·486 (1)	0·475 (2)	77 (10)	22 (3)	215 (28)	−2 (4)	13 (13)	6 (7)	0·6 (0)	0·2	0·5
O(36)	0·096 (3)	0·015 (1)	0·162 (2)	303 (55)	72 (13)	100 (23)	−86 (22)	77 (28)	−41 (13)	1·1 (1)	0·9	0·0
O(37)	0·375 (2)	−0·002 (1)	0·865 (3)	102 (20)	42 (8)	293 (51)	1 (10)	−63 (26)	−26 (17)	1·0 (1)	0·9	0·0
O(38)	0·091 (10)	0·393 (3)	0·701 (7)	1321 (310)	54 (16)	459 (140)	−43 (55)	664 (181)	−33 (36)	0·9 (1)	0·9	0·1
O(39)	0·204 (3)	0·426 (2)	0·782 (6)	67 (29)	17 (8)	283 (93)	−5 (10)	71 (43)	−17 (20)	0·4 (1)	0·1	0·1

Table 2. *Structure factors for* $[OCr_3(CH_3COO)_6 . 3H_2O]^+Cl^- . 6H_2O$

* Indicates unobserved reflections.

Table 2 (*cont.*)

	FOBS	FCAL
24	123	74
25	299	279
1, K, 4		
0	843	984
1	711	685
2	610	670
3	278	301
4	737	633
5	214	227
6	765	697
7	1017	1020
8	360	400
9	374	352
10	121	148
11	889	788
12	73	102
13	369	363
14	813	865
15	550	435
16	438	449
17	137	79
18	161	165
19	199	149
20	48	31
21	57	77
22	189	153
23	303	264
24	130	184
25	127	162
2, K, 4		
0	1132	1169
1	675	570
2	513	515
3	667	637
4	793	864
5	316	229
6	873	763
7	824	642
8	567	670
9	831	844
10	187	208
11	360	388
12	1097	1052
13	361	277
14	463	445
15	40*	96
16	186	143
17	179	129
18	155	195
19	164	142
20	189	178
21	367	276
22	170	183
23	266	209
24	144	109
25	106	94
3, K, 4		
0	668	578
1	530	548
2	883	748
3	344	517
4	503	471
5	182	160
6	845	951
7	156	166
8	506	491
9	361	324
10	964	965
11	95	144
12	825	760
13	142	124
14	384	361
15	124	91
16	174	227
17	42*	52
18	391	301
19	175	71
20	407	346
21	167	133
22	123	126
23	70	29
24	214	209
4, K, 4		
0	531	639
1	676	698
2	390	353
3	164	141
4	299	279
5	175	174
6	119	129
7	322	293
8	732	836
9	924	844
10	714	629
11	38*	107
12	615	565
13	359	292
14	220	274
15	111	134
16	313	395
17	299	213
18	263	301
19	106	135
20	375	321
21	390	312
22	406	398
23	159	151
24	125	119
5, K, 4		
0	775	661
1	161	128
2	805	851
3	292	259
4	140	157
5	176	179
6	36*	56
7	780	735
8	357	329
9	383	331
10	387	475
11	841	797
12	151	69
13	173	109
14	356	381
15	389	349
16	356	356

	FOBS	FCAL
17	94	124
18	216	192
19	445	376
20	155	156
21	195	154
22	87	86
23	244	225
6, K, 4		
0	189	200
1	369	371
2	377	366
3	590	406
4	280	195
5	635	573
6	86	115
7	315	256
8	415	445
9	479	461
10	423	460
11	493	423
12	41*	60
13	697	640
14	187	191
15	171	190
16	184	162
17	372	393
18	39*	57
19	184	171
20	114	71
21	189	175
22	212	173
23	48	57
7, K, 4		
0	237	193
1	703	687
2	295	271
3	419	396
4	313	261
5	294	224
6	388	369
7	472	399
8	528	456
9	278	168
10	293	298
11	350	219
12	323	278
13	400	403
14	350	320
15	473	388
16	258	222
17	260	253
18	79	87
19	205	150
20	115	86
21	135	99
22	132	173
8, K, 4		
0	327	268
1	350	363
2	257	200
3	313	344
4	401	461
5	406	435
6	242	255
7	375	327
8	350	317
9	288	242
10	199	154
11	40*	72
12	38*	280
13	120	142
14	274	316
15	280	263
16	303	261
17	221	187
18	319	281
19	81	66
20	139	72
21	258	200
9, K, 4		
0	157	202
1	396	366
2	205	143
3	570	510
4	154	82
5	374	421
6	248	307
7	153	160
8	241	257
9	185	142
10	384	384
11	63	89
12	240	248
13	333	312
14	246	259
15	236	221
16	298	296
17	98	118
18	303	287
19	167	158
20	299	268
10, K, 4		
0	63	77
1	269	211
2	117	112
3	115	119
4	72	139
5	77	103
6	282	261
7	180	201
8	531	571
9	410	351
10	300	232
11	144	108
12	35	69
13	195	243
14	171	178
15	132	120
16	201	271
17	364	261
18	241	252
11, K, 4		
0	213	227
1	234	204

	FOBS	FCAL
2	110	162
3	107	164
4	268	199
5	307	331
6	309	305
7	336	292
8	206	207
9	194	186
10	106	173
11	451	385
12	95	59
13	26	21
14	130	166
15	186	107
16	163	128
12, K, 4		
0	210	158
1	316	315
2	263	319
3	220	171
4	229	278
5	267	186
6	120	95
7	330	355
8	243	200
9	371	315
10	320	244
11	129	138
12	61	91
13	269	224
14	114	78
13, K, 4		
0	157	117
1	350	306
2	129	96
3	313	221
4	62	113
5	154	189
6	186	123
7	276	235
8	221	215
9	115	104
10	203	164
11	91	39
12	104	72
14, K, 4		
0	76	104
1	33*	126
2	32*	74
3	234	292
4	301	252
5	234	221
6	286	240
7	162	149
8	59	69
0, K, 5		
0	239	178
1	460	355
2	128	83
3	809	790
4	975	886
5	126	115
6	89	85
7	269	220
8	313	222
9	188	130
10	106	125
11	751	763
12	147	181
13	604	630
14	329	342
15	225	236
16	446	445
17	483	393
18	175	137
19	309	244
20	74	35
21	138	150
22	285	290
23	32*	34
24	29*	14
1, K, 5		
0	574	532
1	556	514
2	763	753
3	103	88
4	210	256
5	435	348
6	596	465
7	532	527
8	304	299
9	515	556
10	334	324
11	571	562
12	227	241
13	152	164
14	428	411
15	433	440
16	362	335
17	271	295
18	172	174
19	288	220
20	200	196
21	174	171
22	86	108
23	224	206
2, K, 5		
0	486	517
1	31*	222
2	423	372
3	390	329
4	207	267
5	275	252
6	328	406
7	1038	1078
8	393	321
9	801	668
10	192	183
11	281	246
12	647	672
13	39*	77
14	283	260
15	140	88
16	195	252

	FOBS	FCAL
17	178	181
18	479	466
19	143	149
20	147	54
21	344	334
22	163	178
23	312	285
3, K, 5		
0	107	92
1	559	503
2	147	81
3	623	436
4	727	626
5	335	281
6	750	753
7	128	133
8	256	201
9	743	762
10	885	854
11	319	352
12	490	419
13	151	128
14	228	241
15	73	71
16	76	138
17	240	163
18	281	154
19	201	232
20	361	334
21	266	191
22	121	123
23	135	173
4, K, 5		
0	367	330
1	508	440
2	452	437
3	445	443
4	413	411
5	540	607
6	686	625
7	506	402
8	799	719
9	934	849
10	190	115
11	168	157
12	352	307
13	149	164
14	42*	77
15	213	203
16	390	350
17	95	121
18	326	287
19	228	177
20	150	108
21	168	178
22	331	310
23	229	212
5, K, 5		
0	787	787
1	81	106
2	930	906
3	497	410
4	37*	52
5	376	281
6	369	337
7	335	407
8	503	420
9	277	225
10	238	253
11	503	397
12	373	278
13	263	245
14	476	365
15	196	168
16	585	535
17	40*	48
18	123	166
19	257	164
20	308	272
21	287	263
22	219	194
6, K, 5		
0	140	143
1	273	288
2	244	260
3	138	155
4	468	473
5	114	179
6	195	207
7	221	194
8	463	379
9	279	221
10	456	382
11	270	227
12	174	232
13	485	338
14	40*	134
15	99	79
16	196	159
17	421	359
18	140	123
19	265	275
20	92	127
21	25	44
7, K, 5		
0	214	163
1	477	422
2	41*	117
3	385	375
4	118	100
5	181	242
6	265	230
7	233	305
8	457	378
9	133	152
10	277	207
11	267	188
12	153	127
13	332	284
14	375	363
15	485	434
16	371	343
17	325	292
18	127	165
19	157	143
20	101	87

	FOBS	FCAL
8, K, 5		
0	32	80
1	173	168
2	240	95
3	467	448
4	129	136
5	294	378
6	334	127
7	388	343
8	110	111
9	41*	50
10	212	213
11	214	204
12	196	224
13	182	147
14	159	170
15	278	246
16	202	190
17	211	215
18	279	184
19	123	89
9, K, 5		
0	32	30
1	284	351
2	260	232
3	316	200
4	55	119
5	198	217
6	237	323
7	71	44
8	78	64
9	307	267
10	206	264
11	203	159
12	128	73
13	315	338
14	231	193
15	204	141
16	36*	92
17	168	175
18	162	141
10, K, 5		
0	190	174
1	302	189
2	41*	84
3	86	62
4	345	372
5	300	216
6	285	221
7	352	307
8	618	582
9	180	151
10	245	224
11	237	258
12	155	196
13	140	92
14	125	95
15	301	244
16	183	210
17	110	108
11, K, 5		
0	230	244
1	122	115
2	414	379
3	193	212
4	38*	45
5	236	205
6	231	240
7	39*	130
8	285	245
9	283	263
10	321	275
11	342	296
12	124	64
13	181	112
14	143	141
15	68	61
12, K, 5		
0	160	162
1	216	225
2	236	261
3	85	151
4	286	299
5	36*	24
6	150	125
7	284	246
8	282	279
9	233	193
10	299	250
11	285	282
12	160	166
13, K, 5		
0	83	19
1	411	354
2	71	63
3	156	155
4	33*	19
5	144	152
6	204	178
7	31*	31
8	182	186
9	219	234
14, K, 5		
0	30*	38
1	116	136
2	157	216
3	264	201
0, K, 6		
0	462	384
1	579	487
2	146	125
3	1090	1005
4	641	665
5	226	329
6	138	137
7	235	279
8	125	58
9	177	95
10	404	424
11	434	507

	FOBS	FCAL
12	295	289
13	271	201
14	38*	67
15	191	55
16	175	199
17	111	130
18	34	97
19	290	265
20	96	126
21	200	195
22	102	63
1, K, 6		
0	492	414
1	758	706
2	206	179
3	553	469
4	358	240
5	595	546
6	334	346
7	499	440
8	38*	80
9	485	402
10	220	181
11	311	381
12	188	226
13	200	160
14	122	111
15	106	132
16	182	109
17	28	14
18	217	269
19	214	233
20	36*	39
21	320	295
22	218	279
2, K, 6		
0	1275	1195
1	427	346
2	1101	1081
3	265	170
4	167	93
5	448	450
6	491	491
7	45	166
8	198	163
9	39*	33
10	80	49
11	160	69
12	167	201
13	217	166
14	283	296
15	40*	53
16	210	323
17	154	155
18	131	167
19	37*	62
20	289	249
21	204	88
22	179	184
3, K, 6		
0	1144	1137
1	269	232
2	358	320
3	795	666
4	868	900
5	483	466
6	173	158
7	233	173
8	269	299
9	358	292
10	185	156
11	311	317
12	112	202
13	422	382
14	157	130
15	107	58
16	61	66
17	122	103
18	283	241
19	119	124
20	106	115
21	64	35
4, K, 6		
0	394	342
1	644	711
2	911	826
3	715	648
4	46	61
5	405	450
6	424	482
7	276	230
8	238	160
9	262	268
10	41*	118
11	421	399
12	174	207
13	114	91
14	280	277
15	276	299
16	313	345
17	186	207
18	210	184
19	136	143
20	212	167
21	109	107
5, K, 6		
0	330	366
1	632	585
2	248	214
3	471	345
4	365	331
5	579	581
6	301	244
7	495	450
8	142	93
9	328	332
10	158	112
11	89	81
12	327	379
13	39*	26
14	350	318
15	39*	59
16	107	48
17	120	132
18	135	74
19	134	134

	FOBS	FCAL
20	173	191
6, K, 6		
0	41*	83
1	339	323
2	248	249
3	568	465
4	201	227
5	447	396
6	284	237
7	490	514
8	155	181
9	79	156
10	184	209
11	71	130
12	313	258
13	125	117
14	235	108
15	215	243
16	207	187
17	216	158
18	149	166
19	125	99
20	169	204
7, K, 6		
0	383	394
1	382	388
2	220	220
3	223	179
4	204	275
5	409	418
6	164	196
7	201	205
8	391	253
9	169	244
10	208	237
11	231	194
12	157	176
13	207	180
14	63	37
15	37*	82
16	32	31
17	34*	13
18	178	230
19	51	28
8, K, 6		
0	38	100
1	342	300
2	453	391
3	218	217
4	95	121
5	306	215
6	312	344
7	137	187
8	71	58
9	133	130
10	80	104
11	184	196
12	96	74
13	218	162
14	123	71
15	202	153
16	171	216
17	296	242
9, K, 6		
0	335	345
1	177	175
2	163	146
3	170	227
4	400	357
5	112	94
6	159	182
7	58	139
8	397	286
9	39*	51
10	249	207
11	77	96
12	128	135
13	245	189
14	34*	53
15	117	128
16	95	104
10, K, 6		
0	98	48
1	415	359
2	246	213
3	350	267
4	145	78
5	169	178
6	329	297
7	274	266
8	156	201
9	181	121
10	126	106
11	78	64
12	56	71
13	207	203
14	135	88
11, K, 6		
0	136	72
1	263	251
2	149	227
3	275	262
4	382	373
5	264	339
6	236	254
7	290	265
8	163	153
9	172	200
10	197	191
11	199	133
12	189	197
12, K, 6		
0	138	72
1	353	327
2	56	51
3	277	307
4	257	263
5	106	121
6	194	241
7	262	247
8	164	138
9	64	53

	FOBS	FCAL
13, K, 6		
0	109	163
1	195	178
2	30*	17
3	141	89
4	197	216
0, K, 7		
0	432	432
1	39*	39
2	249	227
3	198	223
4	226	234
5	186	184
6	171	95
7	528	464
8	54	50
9	463	381
10	313	336
11	307	284
12	435	396
13	193	228
14	271	183
15	70	31
16	119	143
17	203	165
18	298	282
19	163	106
20	268	271
1, K, 7		
0	244	204
1	49	74
2	417	363
3	427	446
4	412	283
5	466	473
6	477	458
7	375	370
8	203	189
9	325	250
10	241	214
11	104	147
12	416	448
13	190	132
14	341	245
15	257	257
16	246	280
17	195	179
18	190	191
19	152	160
20	298	272
2, K, 7		
0	121	75
1	146	133
2	347	371
3	93	140
4	272	181
5	221	193
6	358	355
7	326	282
8	371	313
9	317	266
10	330	321
11	467	398
12	156	188
13	76	146
14	310	258
15	308	319
16	297	301
17	185	175
18	118	143
19	373	326
20	64	47
3, K, 7		
0	269	237
1	40*	58
2	286	357
3	286	252
4	145	158
5	543	451
6	202	198
7	195	147
8	173	137
9	286	261
10	157	154
11	374	362
12	196	157
13	608	545
14	457	465
15	137	163
16	298	284
17	425	341
18	74	88
19	73	46
4, K, 7		
0	135	107
1	114	46
2	260	137
3	348	277
4	445	425
5	738	213
6	59	100
7	280	214
8	192	210
9	274	259
10	191	119
11	361	370
12	204	186
13	472	398
14	356	371
15	471	392
16	173	226
17	72	147
18	210	229
19	156	132
5, K, 7		
0	231	184
1	303	323
2	139	201
3	340	292
4	40*	152
5	114	115
6	131	129

	FOBS	FCAL
7	192	160
8	284	242
9	77	125
10	60	100
11	232	161
12	470	429
13	321	320
16	331	295
14	270	234
15	357	322
17	169	100
18	248	153
6, K, 7		
0	359	377
1	168	149
2	39*	153
3	46	58
4	169	170
5	434	385
6	444	419
7	433	442
8	323	283
9	319	301
10	382	345
11	159	96
12	442	397
13	223	199
14	272	215
15	207	272
16	171	178
17	144	132
7, K, 7		
0	42*	30
1	197	101
2	127	118
3	203	195
4	188	176
5	351	290
6	76	43
7	40*	68
8	269	233
9	446	451
10	276	279
11	265	244
12	282	243
13	171	169
14	236	216
15	97	89
16	178	124
8, K, 7		
0	111	111
1	250	221
2	139	135
3	244	259
4	43*	74
5	240	183
6	310	279
7	321	353
8	373	309
9	104	46
10	314	287
11	374	405
12	118	81
13	113	84
14	105	97
15	191	161
9, K, 7		
0	318	311
1	180	173
2	299	349
3	115	169
4	158	141
5	156	179
6	40*	104
7	135	79
8	188	181
9	203	226
10	272	239
11	274	301
12	111	113
13	403	359
10, K, 7		
0	228	174
1	171	151
2	149	160
3	197	164
4	189	172
5	137	75
6	100	136
7	149	102
8	142	121
9	187	192
10	213	222
11	186	208
11, K, 7		
0	33*	60
1	153	191
2	34*	46
3	117	148
4	303	301
5	87	59
6	239	241
7	177	111
8	136	129
12, K, 7		
0	63	63
1	69	73
2	97	128
3	178	154
0, K, 8		
0	486	440
1	302	284
2	202	157
3	135	152
4	154	167
5	153	175
6	105	107
7	190	138
8	74	74
9	642	558

	FOBS	FCAL
10	211	222
11	207	212
12	46	29
13	130	116
14	130	155
15	189	209
16	223	190
17	136	124
18	256	232
1, K, 8		
0	191	163
1	315	276
2	259	325
3	88	116
4	188	85
5	84	130
6	143	209
7	196	226
8	67	110
9	39*	53
10	160	226
11	421	366
12	244	230
13	38*	79
14	116	77
15	214	246
16	228	191
17	74	85
18	245	269
2, K, 8		
0	221	227
1	679	630
2	132	137
3	125	208
4	97	168
5	347	299
6	75	61
7	217	246
8	212	309
9	257	195
10	350	379
11	158	162
12	313	338
13	306	296
14	171	169
15	33*	49
16	208	163
17	114	106
3, K, 8		
0	75	48
1	492	529
2	341	339
3	286	312
4	316	330
5	236	183
6	40*	53
7	347	301
8	137	139
9	134	117
10	204	144
11	255	240
12	37*	25
13	179	211
14	467	457
15	73	95
16	187	265
17	85	37
4, K, 8		
0	324	312
1	372	386
2	30	30
3	355	249
4	253	277
5	372	311
6	234	96
7	245	274
8	208	177
9	291	239
10	109	91
11	215	217
12	177	200
13	238	193
14	112	40
15	112	98
16	233	258
5, K, 8		
0	205	188
1	184	179
2	486	471
3	477	395
4	275	268
5	161	162
6	372	301
7	73	99
8	245	190
9	106	83
10	224	198
11	267	199
12	158	152
13	303	272
14	74	49
15	331	310
6, K, 8		
0	589	506
1	219	137
2	194	202
3	213	205
4	291	295
5	248	155
6	366	301
7	199	239
8	320	238
9	436	430
10	218	237
11	220	172
12	35*	57
13	152	168
14	112	74
7, K, 8		
0	397	343
1	304	256
2	356	355

	FOBS	FCAL
3	141	131
4	305	239
5	157	100
6	193	230
7	237	201
8	205	188
9	114	110
10	64	114
11	335	338
12	263	288
13	124	103
8, K, 8		
0	119	116
1	346	307
2	222	241
3	124	97
4	165	150
5	241	263
6	219	204
7	36*	83
8	310	332
9	251	207
10	318	320
11	31*	50
9, K, 8		
0	70	51
1	257	252
2	240	230
3	366	350
4	118	122
5	141	140
6	141	102
7	369	351
8	115	77
9	136	115
10, K, 8		
0	209	133
1	130	135
2	39	75
3	129	166
4	309	260
5	407	373
6	211	197
0, K, 9		
0	645	682
1	83	32
2	224	236
3	34	79
4	304	289
5	129	98
6	130	98
7	76	58
8	126	83
9	128	53
10	36*	65
11	159	166
12	123	142
13	316	312
14	292	217
1, K, 9		
0	173	140
1	191	241
2	330	346
3	322	321
4	136	92
5	42*	73
6	174	245
7	111	99
8	145	170
9	152	119
10	217	178
11	327	301
12	189	165
13	155	159
14	48	25
2, K, 9		
0	144	103
1	310	303
2	275	225
3	301	254
4	337	224
5	258	273
6	313	280
7	93	95
8	133	176
9	229	224
10	283	216
11	56	67
12	76	87
13	221	162
14	207	200
3, K, 9		
0	314	263
1	334	234
2	153	114
3	202	168
4	225	182
5	461	347
6	132	114
7	436	465
8	279	236
9	157	128
10	153	152
11	74	47
12	224	186
13	63	100
4, K, 9		
0	57	26
1	124	113
2	351	317
3	339	202
4	376	293
5	387	313
6	200	206
7	94	105
8	36*	57
9	329	310
10	106	121
11	128	114
12	185	101

	FOBS	FCAL
13	134	130
5, K, 9		
0	77	101
1	266	248
2	278	195
3	247	278
4	277	248
5	188	164
6	305	233
7	84	117
8	256	249
9	245	213
10	73	103
11	335	291
12	34	45
6, K, 9		
0	544	487
1	245	235
2	137	149
3	189	163
4	190	119
5	36*	123
6	83	107
7	26	52
8	262	261
9	33*	52
10	79	118
7, K, 9		
0	32	57
1	236	213
2	332	334
3	126	99
4	199	204
5	64	67
6	94	65
7	33*	81
8	113	64
8, K, 9		
0	64	40
1	389	375
2	95	84
3	100	159
4	211	237
5	156	124
0, K,10		
0	514	528
1	67	23
2	277	230
3	112	63
4	57	43
5	34*	19
6	228	183
7	206	197
8	36	19
9	265	244
1, K,10		
0	235	256
1	174	156
2	204	177
3	193	182
4	105	135
5	313	263
6	68	95
7	152	146
8	243	285
9	99	139
2, K,10		
0	36*	65
1	212	228
2	90	84
3	215	225
4	195	175
5	181	239
6	200	111
7	283	260
8	164	112
9	215	167
3, K,10		
0	131	139
1	33*	13
2	221	224
3	103	24
4	35*	86
5	44	73
6	137	113
7	269	232
8	144	115
4, K,10		
0	102	108
1	34*	62
2	96	34
3	142	196
4	88	130
5	301	255
6	176	200
7	259	212
5, K,10		
0	154	140
1	93	95
2	33*	92
3	82	133
4	70	90

Although the absorption coefficient for Cu radiation was largely due to fluorescence, the size of the unit cell and the diffuse scattering were such that no advantage could be obtained by using a shorter wave-length radiation. Initially the intensity data were eye-estimated from multiple-film taken with a Weissenberg camera. This gave 3586 independent structure amplitudes of which 433 were observed zero, which is 95 per cent of the reflections within the Cu $K\alpha$ reflection sphere. Later, another set of data was taken on a Picker four-circle automatic diffractometer. This gave 2794 independent structure amplitudes of which 138 were unobserved. These intensities were corrected for absorption using the absorption program of Busing & Levy (1957).

Determination and general description of the structure

The positions of the three chromium atoms were determined from the Harker sections of a three-dimensional Patterson synthesis. The interpretation is not unambiguous (Buerger, 1960) in this space group, due to choices involving translations of **b**/2. One in which the three chromium atoms formed an equilateral triangle with reasonable interatomic distances was tested and confirmed by seeking and finding the non-Harker Cr–Cr vectors in the synthesis. No peaks corresponding to Cr–Cl vectors could be found. However, the chromium positions alone gave reasonably good structure factor agreement and an R value of 0·33 with no other atoms included.

A three-dimensional Fourier synthesis based on the chromium phases revealed sixteen atoms (Nos. 4–19) of height appropriate to those of oxygen atoms around the three chromiums (Nos. 1, 2, 3) in the configuration shown in Fig. 1. The Cr–O distances ranged from 1·91 to 2·05 Å and the coordination around each chromium atom was approximately octahedral. The second Fourier synthesis phased with the three chromium and sixteen oxygen atoms per asymmetric unit revealed the carbon atoms of the acetate groups. These are atom Nos. 20–31 in Figs. 1 and 2. A third Fourier synthesis was computed including these atoms in the phase calculations, in order to locate the remaining chloride ion and six water oxygen atoms. Eight diffuse

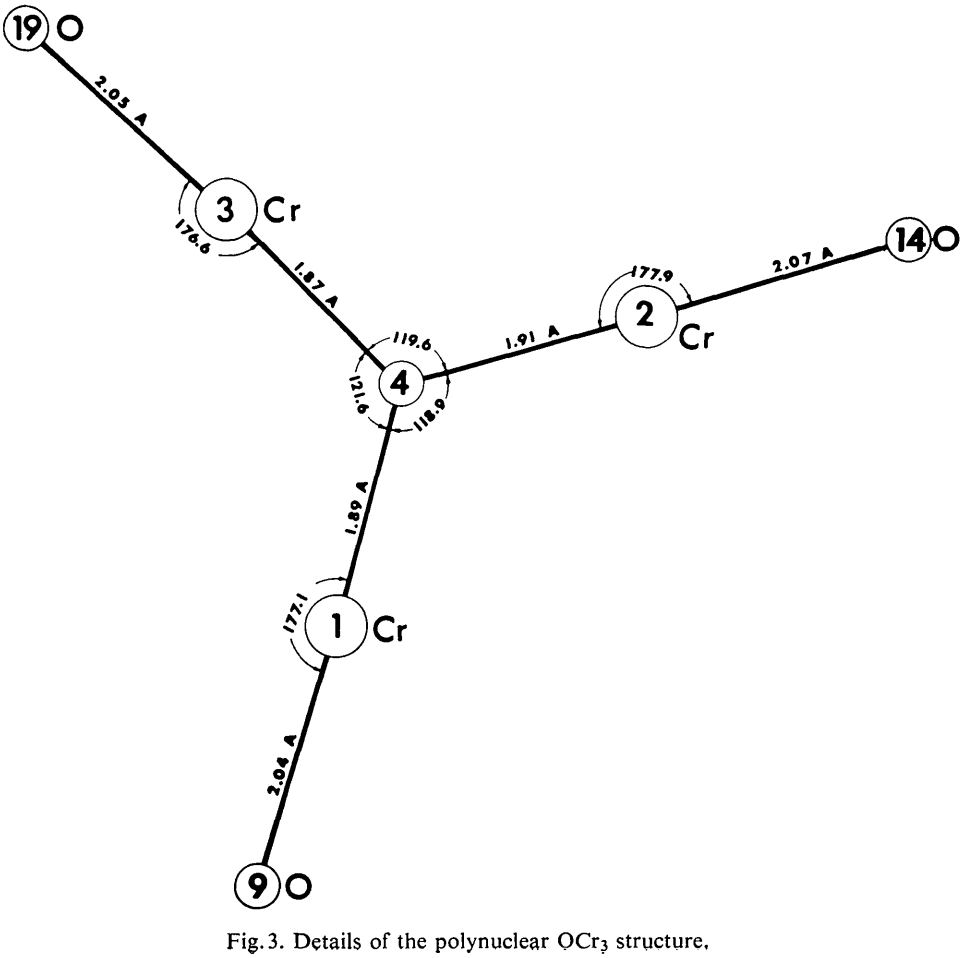


Fig. 3. Details of the polynuclear OCr_3 structure.

Table 3. *Interatomic distances and angles in* $[OCr_3(CH_3COO)_6 . 3H_2O]^+$

Cr–O distances and angles

i	*j*	*d*(*ij*)
Cr(1)	O(4)	1·95 Å
Cr(1)	O(5)	1·92
Cr(1)	O(6)	2·01
Cr(1)	O(7)	1·94
Cr(1)	O(8)	1·97
Cr(1)	O(9)	2·01
Cr(2)	O(4)	1·86
Cr(2)	O(10)	1·97
Cr(2)	O(11)	2·01
Cr(2)	O(12)	2·00
Cr(2)	O(13)	1·95
Cr(2)	O(14)	2·04
Cr(3)	O(4)	1·86
Cr(3)	O(15)	2·01
Cr(3)	O(16)	2·01
Cr(3)	O(17)	1·97
Cr(3)	O(18)	1·97
Cr(3)	O(19)	2·02

i	*j*	*k*	∠(*ijk*)
O(4)	Cr(1)	O(5)	94·6°
O(4)	Cr(1)	O(6)	94·0
O(4)	Cr(1)	O(7)	97·0
O(4)	Cr(1)	O(8)	93·4
O(5)	Cr(1)	O(6)	92·8
O(5)	Cr(1)	O(8)	84·8
O(5)	Cr(1)	O(9)	83·3
O(6)	Cr(1)	O(7)	87·5
O(6)	Cr(1)	O(9)	86·0
O(7)	Cr(1)	O(8)	93·4
O(7)	Cr(1)	O(9)	85·1
O(8)	Cr(1)	O(9)	86·5
O(4)	Cr(2)	O(10)	93·9
O(4)	Cr(2)	O(11)	99·2
O(4)	Cr(2)	O(12)	91·8
O(4)	Cr(2)	O(13)	94·0
O(10)	Cr(2)	O(11)	88·1
O(10)	Cr(2)	O(13)	88·0
O(10)	Cr(2)	O(14)	87·9
O(11)	Cr(2)	O(12)	89·0
O(11)	Cr(2)	O(14)	82·9
O(12)	Cr(2)	O(13)	93·7
O(12)	Cr(2)	O(14)	86·5
O(13)	Cr(2)	O(14)	84·0
O(4)	Cr(3)	O(15)	94·5
O(4)	Cr(3)	O(16)	96·2
O(4)	Cr(3)	O(17)	95·4
O(4)	Cr(3)	O(18)	96·3
O(15)	Cr(3)	O(16)	92·7
O(15)	Cr(3)	O(18)	83·3
O(15)	Cr(3)	O(19)	84·9
O(16)	Cr(3)	O(17)	88·7
O(16)	Cr(3)	O(19)	85·3
O(17)	Cr(3)	O(18)	93·2
O(17)	Cr(3)	O(19)	85·2
O(18)	Cr(3)	O(19)	85·2

Distances and angles in acetato groups

i	*j*	*d*(*ij*)	*i*	*j*	*k*	∠(*ijk*)
O(7)	C(20)	1·29 Å	O(7)	C(20)	O(11)	127·8°
O(11)	C(20)	1·22	O(8)	C(22)	O(10)	119·8
O(8)	C(22)	1·29	O(12)	C(24)	O(16)	131·1
O(10)	C(22)	1·25	O(13)	C(26)	O(15)	122·2
O(12)	C(24)	1·22	O(6)	C(28)	O(17)	125·0
O(16)	C(24)	1·29	O(5)	C(30)	O(18)	123·7
O(13)	C(26)	1·25				
O(15)	C(26)	1·24	O(7)	C(20)	C(21)	114·6
O(6)	C(28)	1·22	O(11)	C(20)	C(21)	117·2
O(17)	C(28)	1·31	O(8)	C(22)	C(23)	117·8
O(5)	C(30)	1·23	O(10)	C(22)	C(23)	122·4
O(18)	C(30)	1·29	O(12)	C(24)	C(25)	117·1
			O(16)	C(24)	C(25)	111·4
C(20)	C(21)	1·55	O(13)	C(26)	C(27)	121·4
C(22)	C(23)	1·51	O(15)	C(26)	C(27)	116·3
C(24)	C(25)	1·48	O(6)	C(28)	C(29)	120·7
C(26)	C(27)	1·51	O(17)	C(28)	C(29)	114·1
C(28)	C(29)	1·47	O(5)	C(30)	C(31)	120·9
C(30)	C(31)	1·49	O(18)	C(30)	C(31)	115·9

First neighbor O···O distances

i	*j*	*d*(*ij*)	*i*	*j*	*d*(*ij*)
O(4)	O(5)	2·85 Å	O(19)	O(15)	2·72 Å
O(4)	O(6)	2·90	O(19)	O(16)	2·73
O(4)	O(7)	2·92	O(19)	O(17)	2·70
O(4)	O(8)	2·86	O(19)	O(18)	2·62
O(4)	O(10)	2·79			
O(4)	O(11)	2·95	O(6)	O(7)	2·74
O(4)	O(12)	2·77	O(11)	O(12)	2·81
O(4)	O(13)	2·78	O(16)	O(17)	2·78
O(4)	O(15)	2·85			
O(4)	O(16)	2·88	O(5)	O(8)	2·63
O(4)	O(17)	2·84	O(10)	O(13)	2·72
O(4)	O(18)	2·86	O(15)	O(18)	2·64
O(9)	O(5)	2·62	O(5)	O(6)	2·85
O(9)	O(6)	2·74	O(7)	O(8)	2·85
O(9)	O(7)	2·68	O(10)	O(11)	2·76
O(9)	O(8)	2·73	O(12)	O(13)	2·87
			O(15)	O(16)	2·90
O(14)	O(10)	2·78	O(17)	O(18)	2·87
O(14)	O(11)	2·68			
O(14)	O(12)	2·77			
O(14)	O(13)	2·67			

peaks of height appropriate for oxygen atoms with large temperature factors were obtained, but there was no indication of the position of the chloride ions.

The notation for the structure as shown in the Figures and referred to in the Tables is as follows: the chromium atoms are 1, 2, 3; the central oxygen atom is 4; the three oxygen octahedra are respectively (4, 5, 6, 7, 8, 9), (4, 10, 11, 12, 13, 14), (4, 15, 16, 17, 18, 19); the twelve oxygen atoms and twelve carbons atoms of the six acetate groups are (7, 11, 20, 21), (8, 10, 22, 23), (12, 16, 24, 25), (13, 15, 26, 27), (17, 6, 28, 29,), (18, 5, 30, 31). The three water molecules contained in the complex correspond therefore to oxygen atoms 9, 14 and 19. The remaining eight electron density peaks were numbered 32 to 39.

As shown in Fig. 2, the complex cations are grouped around channels along the twofold axes in the **c** direction. The water molecules which are not part of the complex and the disordered anions lie within these channels.

Since no further interpretation was possible by inspection of the Fourier synthesis, least-squares refinement was attempted. Successive cycles of full-matrix anisotropic calculations gave the atomic parameters shown in Table 1 and an R value of 0·128. As expected, the cationic atoms refined normally, while oxygen atoms placed in positions 32 to 39 showed abnormally large temperature factors. The occupation factors of these atoms were also allowed to vary and some of them exceeded unity. These results confirmed those of the Fourier syntheses and suggested that the anions were distributed over the hydrate water sites, but not necessarily in equal ratios. On the basis of the nearest neighbour geometry of these atoms, which is discussed

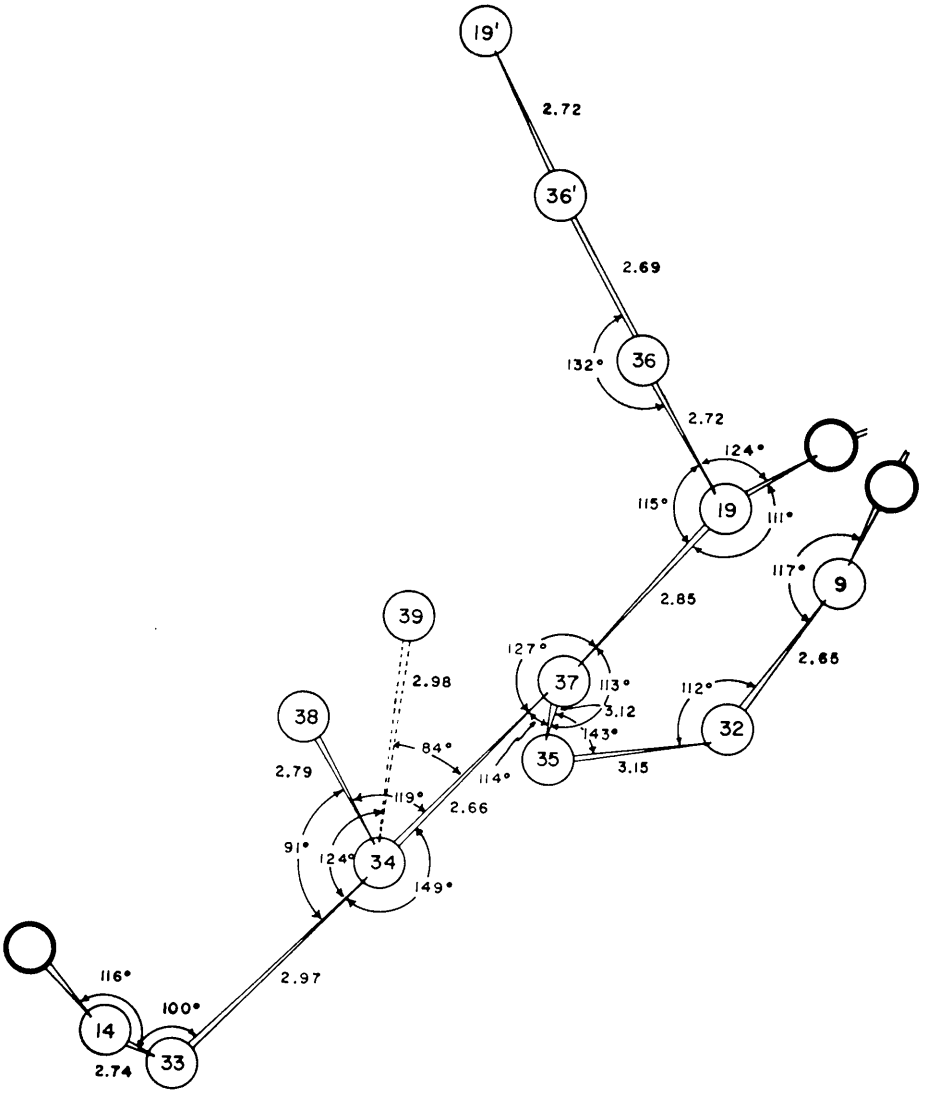


Fig. 4. Details of the hydrogen bonding structure viewed down the c axis.

later, a model was proposed with the assumed occupancy factors also given in Table 1. The structure factor agreement for this model ($R=0{\cdot}13$) was not significantly inferior to that obtained when the occupancy factors were allowed to vary. The structure factors corresponding to the model are given in Table 2. Clearly there is no unique solution for this part of the structure, since there is no way of distinguishing from the diffraction data between this and the many other possible ways of distributing the anions and water molecules to give a similar electon density distribution.

This structure is probably identical with that reported briefly by Figgis & Robertson (1965) for the compound $[Cr_3 . (CH_3COO)_6 . O . 3H_2O]Cl . 2H_2O$. They also failed to locate the anions. Since they did not measure the crystal density or report a chemical analysis, the water content in the crystal they used was not determined other than from their interpretation of their Fourier syntheses. The possibility of variable hydration cannot be excluded, but the discrepancy between calculated and observed density of the crystals we examined corresponds to less than 0·2 mole of H_2O per formula unit.

The configuration of the cation

The important interatomic distances and angles are given in Table 3. The structure around the central oxygen atom (4) is shown in Fig. 3. Within experimental error, the chromium atoms form an equilateral triangle at the center of which lies the oxygen atom. The mean Cr–O(4) distance is significantly shorter, by about 0·1 Å, than those to the water oxygen atoms, 9, 14 and 19. The small departure from non-linearity of the O–Cr–OH_2 bonds shows that the octahedra around the chromium atoms are slightly distorted by the steric requirements of the acetate groups. The least-squares plane containing the chromium atoms, central oxygen atom (4) and water oxygen atoms (9, 14, and 19) is found to be $0{\cdot}718X+0{\cdot}666Y+0{\cdot}203Z=4{\cdot}80$, with X, Y, and Z in Ångstrom units. The chromium atoms and O(4) are below the plane by 0·02 Å and the water oxygen atoms are above the plane by 0·025 Å. The acetate groups are planar with a mean and greatest deviation from planarity of 0·01 and 0·04 Å respectively. The C–CH_3 bond lengths vary from 1·47 to 1·55 Å, with a mean of 1·50 Å. The C–O bonds vary from 1·22 to 1·31 Å with a mean of 1·26 Å. The C–C–O angles are systematically less than the O–C–O angles with mean values of 117° *versus* 125°. There is a systematic trend for each acetate group to have one long and one short C–O bond differing by 0·07 Å, which implies that the structure of the cation in the crystal may be $[OCr_3(CH_3COOH)_3(CH_3COO)_3(OH)_3]^+$ or some intermediate form. In the absence of information concern-

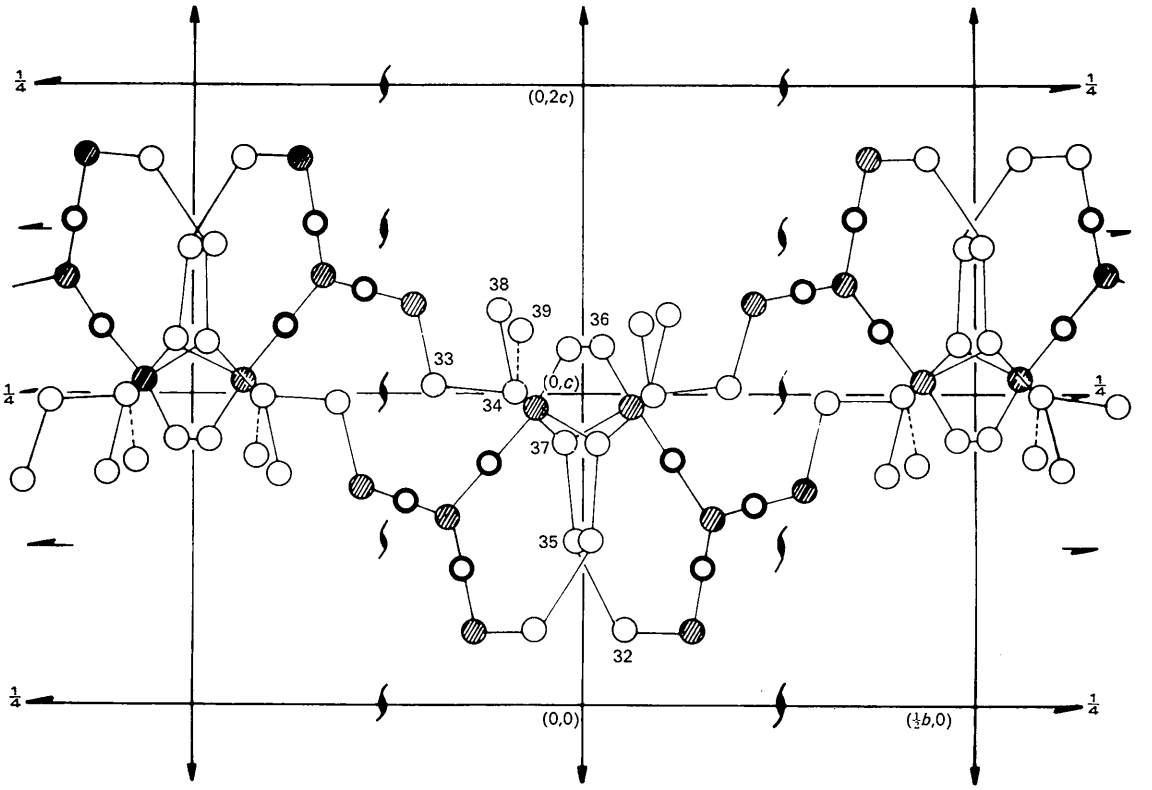


Fig. 5. The layered packing structure as viewed down the *a* axis.

ing the hydrogen atom positions it is not possible to resolve this ambiguity.

The nearest neighbour distances of the [CrO_6] octahedra additional to those given in Fig. 3 are shown in Table 3. Excluding the central Cr–O(4) bonds, the Cr–O distances range from 1·92 to 2·04 Å, with a mean of 1·985 Å. The angles subtended by the ligands at the chromium atom vary from 82 to 99°.

The central oxygen atom which is a common vertex of the three octahedra (see Fig. 1) has twelve second neighbour oxygen atoms (5 to 18, excluding 9, 14 and 19) at distances between 2·77 and 2·95 Å. No information is available concerning the location of the hydrogen atoms and the hydrogen-bonding of the water molecules. The O–O distances involving oxygen atoms 9, 14 and 19 lie in the range 2·62 to 2·78 Å, and are indistinguishable in length from the non-bonded distances of 2·63 and 2·90 Å, which form the edges of the octahedra.

The water anion structure

The complex cations form a pseudo-hexagonal packing arrangement, with well-defined electron density peaks, surrounding channels in which the atomic structure is much more diffuse. These channels contain the anions and the hydration water molecules, for which the nearest neighbour environment less than 3·2 Å is shown in Fig. 4. (This is the same view as in Fig. 2, where the hydrogen-bond interactions are dotted lines.) The anions would be expected to lie at minima in the electrostatic potential of the cations close to the center of the channels (*i.e.* near the twofold axes along **c**, shown at ($\frac{1}{2}a$, 0) or (a, 0) in Fig. 2). Positions (35) and (39) are the more obvious choices since their nearest neighbours are about 3 Å away; however, the low electron density of these peaks, particularly that at 39, shows that these sites can only be occupied partially by the ions. With water molecules at the six other positions, a loosely packed arrangement of hydrogen-bonded atoms is obtained which links the cations through their water oxygen atoms, 9, 14 and 19, into zigzag layers perpendicular to the c axis. This is shown in Fig. 5. In this anion/water structure, four-coordination is rare and most atoms have only one, two, or three nearest neighbours at hydrogen-bond O...O or O...Cl^- distances. The hydrophobic methyl groups of the acetato residues, which surround and penetrate into the channels, appear to leave no space available for the development of a complete four-coordinated water/anion structure. This, we believe, is an important structural factor giving rise to the observed disorder, which is envisaged as space-averaged, with the chloride ions at position 35 in about half of the crystal unit-cells and at 39 in a lesser proportion. In the remainder of the crystal, the anions alternate with the water molecules, as suggested by the assumed occupancy factors given in Table 1. The resulting adjustments in geometry would cause a space-averaged variation in atomic positions and a corresponding increase in the apparent temperature factors. Although the least-squares refinement suggested positions 33 and 36 particularly for partial occupancy by the chloride ions, the geometry shown in Fig. 4 indicates that most of the oxygen atoms in the main chain near the center of the hydration channel can be involved in this exchange, particularly that at position 38, where the electron density distribution is especially diffuse. A strongly exposed rotation photograph about the c axis showed diffuse layer lines intermediate between the zero and first, and this is consistent with this model since the chloride ions are disordered within the hydrogen-bonded layers parallel to (001) as shown in Fig. 5. Since it is probable that the cations are hydrated in aqueous solution by hydrogen-bonding through their water molecules, the formation of an ordered array in the initial stages of crystallization is likely to proceed by the alignment of the cations into layers through the two main hydrogen-bonded chains 19–36–36′–19′, and 19–37–34–33–14. The anions and additional water molecules would then attach themselves to these layers. However, the presence of the methyl groups of the cations interferes with the development of the four-coordinated tetrahedral type of structure usually associated with water molecules and chloride ions. In consequence, the anion/water structure is comparatively loosely bound and will have residual hydrogen atoms not involved in hydrogen-bonding. Under these circumstances, 'mistakes' can often occur and the structure can vary from one part of the crystal to another without a significant loss in lattice energy. Consequently the water/anion structure is semi-amorphous despite the well-ordered cationic structure in the crystal. There is an interesting analogy here with the disordered water which separates the comparatively well-structured arrangement of protein molecules in a crystal.

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