CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA

The Crystal Structure of Dichlorotetraaquochromium(III) Chloride Dihydrate: Primary and Secondary Metal Ion Hydration

BY IAN G. DANCE AND HANS C. FREEMAN

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trans-$[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$ crystallizes with a monoclinic unit cell, $a = 12.053$, $b = 6.840$, $c = 11.640$ Å., $\beta = 94° 10'$, which contains four formula units according to the symmetry of space group C2/c. All atoms other than the hydrogen atoms have been located by X-ray methods. The octahedral complex ions are very slightly distorted from D_{4h} symmetry, with Cr–O distances 2.004 and 2.006 Å. and Cr–Cl = 2.289 Å. Hydrogen-bonded "cages" of water molecules and chloride ions link the octahedra in chains. Estimated standard deviations of metal–light atom bond lengths are *ca.* 0.005 Å.

Introduction

The coordination chemistry of a number of crystalline chloroaquochromium(III) hydrates has been well described[1] but only one, violet hexaaquochromium(III) chloride, has been examined crystallographically.[2]

The "Bjerrum-green" dichlorotetraaquochromium(III) chloride dihydrate, presumably the *trans* isomer,[1c] crystallizes from neutral aqueous solution and belongs to the series of crystalline hydrates $[CrCl_2(OH_2)_4]Cl \cdot 0$-, 2-, and $6H_2O$. The crystal structure determination of this compound was motivated by an interest in the bonding geometry of water molecules in highly hydrated compounds of metal ions. The question arises whether the stability of excessively hydrated salts[3] such as $MgCl_2 \cdot 12H_2O$ is primarily due to the influence of the metal ion on its second coordination sphere or to the formation of hydrogen-bonded clusters of water molecules as in the clathrate hydrates. The present compound was chosen in order to study the bonding relationships between primarily and secondarily coordinated water molecules in a system in which the other ligands and anions, being monatomic, have limited capacities as hydrogen-bond acceptors and, being nonhydrogenic, cannot be hydrogen-bond donors.

Experimental

The commercially available salt was recrystallized from water. The hygroscopic crystals were sealed into capillary tubes for the X-ray measurements. The crystals so obtained were almost invariably either multiple or so fragile that fracture during mounting was unavoidable. Only one single crystal was ever mounted, and from this three-dimensional intensity data were recorded photographically using Mo Kα radiation: the (monoclinic) lattice layers *h*0*l* through *h*7*l* and the first four layers about the [310] axis were obtained. Very slightly fractured crystals were employed to record 0*kl* and *hk*0 data. The intensities were estimated visually. The maximum crystal dimension was 0.22 mm. and the mean dimensions were approximately 0.10 mm. Absorption corrections were considered unnecessary with Mo Kα radiation.

The structure factor and Fourier calculations were made with the Silliac computer at Sydney; the least-squares refinement was performed with the program ORXLS[4] on an IBM 7090 computer.

Results

Unit Cell and Space Group.—The unit cell is monoclinic and contains four $[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$ units (formula weight 266.48): $a = 12.053$ Å., $b = 6.840$ Å., $c = 11.640$ Å., $\beta = 94° 10'$, $V = 957.0$ Å.^{3}, $D_x = 1.849$ g. cm.$^{-3}$, $\sigma(a) = 0.002_2$ Å., $\sigma(b) = 0.001_8$ Å., $\sigma(c) = 0.001_7$ Å., $\sigma(\beta) = 3'$, $Z = 4$, D_m[5] $= 1.835$ g. cm.$^{-3}$. Systematic reflection absences are characteristic of the space groups Cc and C2/c; the latter was shown to be correct by structure solution.

Determination of the Structure.—The structure is composed of centrosymmetric $[CrCl_2(OH_2)_4]^+$ units linked by Cl^- ions and water molecules. The nonligand chloride ion is designated Cl(1), the chlorine coordinated to chromium as Cl(2). The oxygen atoms of the two independent ligand ("primary") water molecules are O(1) and O(2), while the uncoordinated ("secondary") water oxygen atom is O(3).

Conventional Patterson and Fourier analysis employing 1416 observed reflections yielded the chromium, chlorine, and oxygen positions. The scattering factors used for chromium, Cl(1), Cl(2), and oxygen were, respectively, those for Cr^0 (Freeman and Watson[6]), Cl^- and Cl^0 (Dawson[7]), and O^0 (Berghuis, *et al.*[8]). Dispersion corrections were applied[9] to the chromium and chlorine scattering factors.

The full-matrix least-squares method, with minimization of $\sum_{hkl} w(hkl)[|F_o(hkl)| - |F_c(hkl)|]^2$, was used in the refinement of the structure. Initially, individual weights were assigned to the structure factors according to error estimates derived statistically from the relatively numerous photographic intensity data. The 510 unobserved reflections, estimated with Hamilton's[10] statistics, were included with the 1416 observed reflections. After three refinement cycles with isotropic

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TABLE I

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR $[Cr^{III}Cl_2(OH_2)_4]Cl\cdot H_2O$[a]

• 0	0	
2	82.22	88.24
4	63.04	49.65
6	21.82	24.33
8	-13.74	14.15
10	-36.91	40.46
12	101.02	91.38
14	18.88	22.91
16	36.56	38.01
18	33.34	33.90
• 0	2	
0	-33.55	40.10
1	-105.98	90.03
2	-155.83	117.70
3	30.07	47.60
4	-49.92	47.84
5	51.11	50.60
6	-37.49	37.85
7	-23.53	25.91
8	-20.41	21.73
9	-21.62	24.19
10	-66.08	63.47
11	41.29	44.69
12	-5.10	10.50
13	-39.93	42.93
14	-43.82	44.83
16	-21.77	23.05
17	13.03	17.15
18	-16.97	21.26
19	-4.13	18.12
21	-2.90	17.04
• 0	4	
0	81.79	76.19
1	-84.73	79.33
2	109.36	96.68
3	-1.10	2.90X
4	67.85	51.48
5	-12.70	13.53
6	-25.64	26.89
7	-11.15	14.81
8	27.69	30.81
9	-20.07	25.09
10	26.68	28.49
11	51.10	50.13
12	13.34	15.93
13	-22.73	25.40
14	42.32	39.45
16	35.39	35.25
• 0	6	
0	-79.25	70.49
1	-4.44	5.82X
2	-3.68	2.97X
3	22.19	23.71
4	-23.76	25.07
5	-17.99	18.03
6	-59.26	56.90
7	28.67	31.27
8	-29.90	31.22
9	-18.59	21.60
12	-49.30	45.91
• 0	8	
0	18.45	20.66
1	14.03	17.30
2	42.93	42.44
4	14.60	17.67
5	-29.64	30.53
6	24.71	24.52
7	18.41	19.56
8	1.89	14.70
10	30.29	29.51
14	19.77	22.33
• 0	10	
0	-8.99	12.87
4	-28.13	28.21
8	-29.65	27.81
• 0	12	
0	18.89	16.91
• 1	1	
-19	-26.46	23.39
-18	-22.69	22.56
-17	-19.73	16.78
-15	-18.45	19.76
-14	17.09	18.16
-13	-39.96	40.94
-12	15.83	19.62
-11	-43.36	42.75
-10	-29.38	33.87
-9	-3.51	5.53X
-8	76.65	75.39
-7	-89.56	83.02
-6	-87.06	80.66
-5	-60.74	56.16
-4	-51.03	54.22
-3	-53.41	49.68
-1	-123.82	112.86
0	24.12	23.20
1	-116.10	99.53
2	-69.09	60.39
3	-5.55	7.42
4	171.48	151.49
5	-118.73	106.72
6	-30.62	31.95
7	-53.65	55.03
8	-9.59	9.66
9	-27.81	31.25
10	2.03	7.12X
11	-44.71	47.51
13	-34.63	36.17
14	-39.12	40.74
16	34.38	33.06
17	-33.40	30.36
19	-17.27	16.05
• 1	3	
-21	25.87	24.33
-17	30.75	30.97
-16	17.02	20.24
-15	34.30	33.75
-13	11.58	15.19
-12	13.98	17.09
-11	7.27	10.67
-10	-5.78	5.66X
-9	90.27	89.88
-8	-10.52	13.28
-7	-20.02	21.77
-6	-38.15	39.09
-5	89.29	84.39
-4	12.84	15.76
-3	113.35	104.67
-2	-16.17	15.73
-1	45.82	43.62
0	64.33	64.21
1	10.79	16.14
2	22.22	27.90
3	146.63	128.81
4	17.49	17.78
5	-26.23	29.98
6	-20.18	22.65
7	60.83	56.75
8	-5.71	9.49
9	66.40	70.09
10	-51.67	31.81
11	22.56	26.84
12	10.45	16.77
15	55.46	49.11
• 1	5	
-15	-24.15	22.32
-12	18.13	17.42
-11	-29.02	26.67
-10	33.62	34.73
-9	-7.40	6.43X
-8	-32.64	34.33
-7	-77.73	74.11
-6	7.90	9.22
-5	-32.55	30.58
-4	-5.18	7.45
-3	-58.49	62.05
-2	-70.87	65.11
-1	-23.97	21.27
0	4.37	7.19
1	-49.97	48.60
2	48.56	43.49
3	13.50	15.26
4	-20.49	23.99
5	-64.03	57.56
6	38.51	36.92
7	-31.61	32.47
8	24.10	26.43
9	-49.75	49.77
10	-35.33	37.20
11	-20.38	19.27
13	-40.23	39.71
• 1	7	
-13	23.67	25.49
-8	-29.97	31.07
-7	37.48	37.26
-6	15.07	17.93
-5	56.74	54.11
-4	-7.20	5.39X
-3	9.59	4.86X
-2	-4.49	4.05X
-1	61.41	58.86
0	4.64	8.99
1	10.51	13.13X
2	36.24	37.29
3	2.88	4.20X
4	-25.82	24.31
5	27.92	26.04
6	10.32	5.90X
7	37.24	35.83
11	47.79	47.05
• 1	9	
0	-11.97	12.28
• 2	0	
-18	-35.90	35.99
-16	16.02	23.19
-14	-57.48	55.96
-12	-47.25	49.83
-10	-32.25	35.91
-8	-42.93	42.57
-6	-125.91	108.71
-4	117.90	110.02
-2	-130.47	106.25
0	-116.36	73.52
2	-87.13	83.19
4	-100.47	91.40
6	-169.72	139.68
8	44.89	50.45
10	-53.61	56.20
12	-31.58	32.70
16	-18.08	21.87
18	-48.39	44.43
• 2	2	
-21	-5.08	20.86
-18	-2.76	16.86
-17	26.69	25.63
-16	27.87	27.67
-15	-20.46	22.58
-12	35.89	35.71
-11	23.39	24.60
-10	75.72	72.73
-9	-22.74	24.24
-8	93.03	81.74
-7	-45.93	45.07
-6	10.20	12.14
-5	69.40	69.26
-4	53.29	49.87
-3	-84.20	82.97
-2	-90.50	103.07
-1	33.11	33.43
0	20.06	11.00
1	86.08	84.93
2	102.33	102.14
3	-8.36	7.30
4	171.97	152.14
5	-42.82	43.48
6	75.23	68.02
7	57.82	64.73
8	104.97	102.06
9	-57.67	59.67
10	4.82	7.08X
11	-4.36	7.03X
12	5.56	6.29X
13	20.62	23.15
15	27.03	26.77
18	9.14	17.03
19	19.92	20.79
20	31.84	28.63
• 2	4	
-17	15.05	18.11
-15	-30.26	30.71
-13	-31.68	33.41
-14	-23.79	24.01
-12	-8.96	6.94X
-11	4.13	6.56X
-10	-57.68	59.06
-9	2.01	5.30X
-8	-26.12	27.67
-7	-15.65	18.10
-6	-17.27	15.99
-5	68.77	64.85
-4	-69.87	64.74
-3	-67.07	62.90
-2	-46.67	42.90
-1	.54	2.42X
0	-27.97	26.94
1	-7.02	8.79
2	-110.87	94.10
3	-7.78	8.84
4	-42.90	41.62
5	-32.34	35.57
6	-24.19	26.59
7	69.42	71.20
8	-53.09	57.83
9	-26.74	30.39
10	-18.78	20.48
11	7.45	10.00
14	-44.38	44.13
17	-17.76	17.76
19	17.06	16.40
20	-19.51	16.78
• 2	6	
-14	27.53	29.39
-13	22.39	21.63
-12	30.83	32.09
-11	-16.56	19.04
-10	17.09	21.34
-9	11.94	15.29
-8	42.56	42.58
-7	-16.50	13.92
-6	63.71	63.19
-5	-3.42	4.37X
-4	-20.71	22.19
-3	-11.46	11.41
-2	35.97	35.54
-1	32.66	32.71
0	37.50	35.31
1	-13.89	11.88
2	11.35	11.69
3	36.66	36.40
4	45.95	46.33
5	-15.89	17.40
6	79.91	72.89
7	-2.06	6.47X
8	-.20	6.93X
9	-12.60	15.52
10	31.42	33.17
12	26.33	27.75
13	-15.29	17.29
• 2	8	
-4	-43.30	38.86
-2	-16.04	16.98X
-1	8.82	16.89X
0	-40.01	38.93
• 2	12	
0	-18.53	14.96
• 3	1	
-15	17.99	18.15
-14	-37.44	39.24
-13	56.88	57.63
-12	44.59	45.96
-11	22.40	23.81
-10	-26.14	28.79
-9	47.54	45.39
-8	8.17	8.48
-7	69.81	65.80
-6	40.40	41.00
-5	36.82	35.44
-4	39.31	40.15
-3	21.77	21.69
-2	-130.03	122.76
-1	152.16	140.46
0	99.47	97.01
1	36.10	38.61
2	-87.50	85.63
3	78.28	71.99
4	-25.00	29.34
5	93.81	85.61
6	31.17	32.04
7	42.69	41.49
8	38.42	39.79
9	22.80	24.00
10	-44.98	47.09
11	64.44	65.71
12	47.29	51.20
13	10.38	8.67X
14	-18.13	17.71
15	19.74	20.26
17	25.41	25.54
• 3	3	
-17	-22.31	20.94
-15	-40.63	40.73
-14	-15.52	17.68
-12	-10.72	7.04X
-11	-73.46	72.80
-10	-20.09	23.07
-9	-26.08	25.82
-8	35.74	35.06
-7	-7.59	4.72X
-6	16.92	21.26
-5	-52.58	51.22
-4	52.32	57.32
-3	-115.33	106.26
-2	-3.33	5.52
-1	21.38	20.17
0	-30.50	35.48
1	-156.01	140.44
2	-72.31	70.14
3	-59.89	58.47
4	-12.22	13.68
5	-9.02	11.02
6	-22.30	25.74
7	-39.10	38.94
8	37.38	40.12
9	-70.68	59.44
10	15.60	19.75
11	20.46	24.85
12	13.28	16.11
13	-58.04	55.76
15	-26.57	27.69
• 3	5	
-14	18.20	17.42
-13	43.91	43.22
-12	-20.38	22.14
-10	13.99	15.16
-9	43.34	45.26
-8	30.18	30.96
-7	10.82	9.50
-6	-28.60	28.61
-5	39.66	40.01
-4	-2.75	3.69X
-3	19.75	20.42
-2	29.42	31.26
-1	95.09	83.43
0	-53.83	54.58
1	27.94	26.55
2	8.52	11.30X
3	62.67	59.99
4	36.76	38.28
5	21.36	22.36
6	-23.54	23.00
7	39.93	41.07
8	5.91	6.31X
9	-1.30	6.72X
10	27.11	29.70
11	47.68	47.04
12	-29.72	27.78
15	23.56	25.02
• 3	7	
-13	-27.39	30.20
-12	-27.68	24.47
-7	-40.31	38.57
-6	5.42	7.51X
-5	-2.12	6.64X
-4	3.45	5.64X
-3	-39.70	38.94
-2	25.48	25.73
-1	-61.70	56.56
0	-42.45	40.89
1	-41.01	39.78
3	-9.97	10.55
4	-5.53	5.68X
5	-44.57	40.91
6	-3.07	6.87X
8	-2.89	14.45X
10	31.94	32.64
11	-30.65	33.56
• 3	9	
0	-7.09	11.30
• 4	0	
-20	40.85	38.00
-16	14.49	20.05
-14	19.13	21.54
-12	20.90	25.79
-10	-39.82	39.49
-8	135.99	123.22
-6	85.68	79.57
-4	130.96	122.33
-2	146.45	139.93
0	75.71	62.35
2	-165.10	161.36
4	94.82	91.98
6	13.95	17.52
8	51.44	49.23
10	87.34	84.62
12	71.22	72.89
14	-17.41	22.49
16	42.79	41.52
• 4	2	
-18	-24.54	24.50
-16	-10.72	16.21
-15	12.79	16.02
-14	-16.94	17.91
-13	-8.15	7.26X
-12	-15.15	17.76
-11	-36.53	40.48
-10	-71.07	66.73
-9	45.96	45.98
-8	-27.01	29.59
-7	-45.12	45.40
-6	-108.23	99.33
-5	3.82	3.68X
-4	-66.46	67.68
-3	62.57	61.50
-2	-40.45	42.96
-1	5.77	9.03
0	20.33	26.88
1	-65.29	66.69
2	-81.35	78.16
3	74.34	74.54
4	-7.31	9.39
5	-64.19	63.25
6	-95.38	90.64
7	-16.96	18.76
8	-69.88	70.84
9	30.12	32.65
10	-48.84	50.04
11	2.03	6.16X
12	-7.48	13.30
13	-20.83	22.49
14	-30.06	38.68
15	34.29	36.39
17	-14.57	14.79
18	-18.47	20.68
• 4	4	
-20	13.39	13.65
-18	18.00	13.74
-16	32.65	31.19
-12	11.05	11.44
-11	-12.60	12.98
-10	33.17	36.10
-9	58.85	56.09
-8	19.09	22.88
-7	-33.19	39.07
-6	58.46	58.75
-4	117.46	109.17
-3	-6.65	7.53
-2	37.95	40.52
-1	-13.19	16.52
0	43.08	42.91
1	-55.35	56.80
2	37.24	37.75
3	74.36	70.44
4	-13.92	16.75
5	-22.78	27.48
6	25.39	28.91
7	12.97	13.51
8	70.64	70.99
9	12.27	13.62
10	21.89	22.89
12	41.50	44.26
13	-34.06	35.14
14	35.69	38.38
15	21.01	22.89
17	-11.70	19.68
• 4	6	
-14	-29.65	26.72
-12	-25.28	26.45
-11	-10.35	14.51
-8	-60.27	57.03
-7	-14.43	19.10
-6	-17.58	17.55
-5	29.82	32.75
-4	-10.25	4.97X
-3	-18.50	18.24
-2	-48.15	46.76
-1	25.34	28.45
0	-39.15	40.44
1	-15.15	15.36
2	5.16	4.27X
3	-4.33	4.55X
4	-74.86	70.79
5	-17.12	17.91
6	-31.13	30.66
7	12.39	11.15
8	-11.51	7.32X
9	-17.14	15.27
10	-34.42	35.23
• 4	8	
-6	36.60	37.05
-2	41.03	38.12
0	15.79	16.89
• 4	10	
0	-23.26	20.12
• 5	1	
-19	-24.41	25.15
-17	-16.01	17.70
-16	33.61	32.94
-15	-26.45	25.29
-13	-24.27	24.67
-12	-5.59	8.24X
-11	-18.64	22.90
-9	-48.41	50.81
-8	1.32	5.94X
-7	-89.41	85.93
-6	-95.79	95.34
-5	-22.18	24.16
-4	81.57	84.43
-3	-87.38	89.48
-2	4.35	12.19
-1	-62.12	58.77
0	28.32	35.75
1	-22.41	26.58
2	43.13	43.80
3	-60.74	62.07
4	36.31	38.52
5	-91.59	91.64
6	-99.72	96.22
7	-12.91	15.79
8	31.25	36.30
9	-57.57	59.53
10	-20.72	24.46
11	-39.35	40.84
12	-10.11	8.54X
13	14.41	13.62
15	-22.78	24.07
16	24.13	22.60
17	-28.83	25.62
18	-19.35	14.80
• 5	3	
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-13	20.85	22.13
-12	15.90	15.95
-11	45.97	46.21
-10	-10.33	11.97
-9	43.52	45.25
-8	7.87	10.11
-7	5.21	4.50X
-6	-3.97	4.24X
-5	127.50	115.76
-4	11.65	13.94
-3	-5.44	10.07
-2	-15.50	17.77
-1	33.56	33.69
0	29.15	33.26
1	80.35	76.22
2	-39.27	39.95
3	59.51	57.79
4	13.53	15.51
5	-3.55	8.07X
6	-8.96	9.94
7	101.56	105.39
8	.03	6.07X
9	3.74	5.61X
10	-9.32	9.25
11	17.15	17.48
12	11.50	12.95
13	39.90	41.87
14	-19.17	16.43X
15	24.57	24.27
19	33.35	29.65
• 5	5	
-15	-31.03	27.89
-12	16.00	18.27
-11	-40.12	39.77
-10	-32.19	31.32
-9	-30.15	30.19
-8	-29.55	30.35
-7	-53.60	53.48
-6	15.31	14.70
-5	1.58	14.79
-4	-33.58	35.64
-3	-45.64	46.22
-2	20.30	20.21
-1	-7.42	6.94
0	64.76	59.42
1	-52.73	49.36
2	-9.92	12.03
3	-30.30	35.75
4	-13.65	14.46
5	-30.00	35.77
6	17.12	17.95
7	-11.43	12.89
8	-47.26	45.90
9	-35.25	35.05
12	24.38	24.70
13	-19.01	21.54
17	-29.70	27.69
• 5	7	
-9	38.13	37.17
-7	28.21	30.65
-6	23.06	25.82
-5	8.92	6.79X
-4	-24.20	26.59
-3	12.56	16.40
-2	15.24	17.97
-1	44.78	44.56
0	8.61	13.37
1	-.87	5.79X
2	.07	6.01X
3	53.86	53.14
4	-15.52	18.41
5	36.60	37.63
6	22.79	24.17
8	-20.47	19.13
9	17.67	21.05
11	26.53	28.76
• 6	0	
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-18	-22.11	24.43
-14	-62.76	61.37
-12	25.27	29.90
-10	-24.33	25.29
-8	-33.09	34.87
-6	-40.53	40.84
-4	-52.58	51.90
-2	-239.79	206.12
0	-18.64	22.45
2	-65.55	61.78
4	-33.43	30.01
6	8.22	12.82
8	14.51	17.00
10	-106.36	102.00
12	-9.06	10.70X
14	-40.17	39.79
16	-34.61	31.55
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-18	16.73	15.92
-16	34.82	35.18
-15	-22.15	21.56
-14	15.08	19.19
-13	29.11	30.39
-12	58.00	55.63
-11	-23.78	25.20
-10	7.52	12.93
-9	-7.71	5.61X
-8	13.62	17.99
-7	33.12	34.51
-6	7.70	11.02
-5	20.36	21.85
-4	58.68	66.40
-3	-48.27	50.63
-2	39.29	45.05
-1	75.29	80.58
0	159.54	156.27
1	-48.65	50.49
2	77.76	78.72
3	-33.27	36.40
4	50.59	48.76
5	24.52	27.92
6	12.38	15.51
7	8.34	10.83
8	35.38	40.45
9	-35.54	39.70
10	-12.47	18.88
11	47.15	48.08
12	46.88	46.87
13	-13.17	16.03X
14	28.01	28.26
15	-11.40	15.86X
16	25.07	24.24
20	20.98	20.37
• 6	4	
-18	-23.56	22.72
-16	-22.52	21.66
-13	34.32	35.85
-12	-25.26	26.44
-11	-23.52	23.37
-10	-28.35	28.46
-9	-1.46	5.75X
-8	2.01	5.46X
-7	-9.13	11.01X
-6	-59.37	61.35
-4	-62.72	63.79
-3	-53.58	55.32
-2	-41.69	42.85
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2	-48.07	49.25
3	14.07	14.74
4	13.94	15.29
5	11.48	12.99
6	-41.34	43.46
7	7.05	5.94X
8	-29.24	32.21
9	-49.01	52.46
10	-16.98	17.08
11	27.51	31.39
12	-46.15	47.35
13	-11.83	11.90
14	-31.18	31.79
18	-19.04	19.27
• 6	6	
-14	39.36	37.02
-11	-13.84	13.03
-10	29.64	30.74
-9	22.40	25.27
-8	33.98	35.91
-7	-13.40	13.82
-6	1.36	8.76X
-5	21.81	22.54
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-1	8.60	5.17X
0	12.05	15.42
1	-17.67	17.46
2	46.79	43.77
3	15.63	18.78
4	39.71	39.87
5	-26.63	27.88
6	15.08	17.35
7	17.45	17.47
10	41.22	40.34
• 6	8	
0	-34.64	35.23
• 6	10	
0	19.01	19.41
• 6	12	
0	-9.51	17.58
• 7	1	
-17	19.69	17.59
-15	31.12	30.23
-13	27.87	27.58
-12	24.91	25.09
-11	1.72	8.19X
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-9	49.16	49.89
-8	55.55	57.18
-7	22.94	25.92
-5	42.72	45.14
-4	-21.19	24.69
-3	89.23	90.50
-2	-16.69	19.05
-1	79.93	82.48
0	33.62	40.21
1	20.43	20.27
2	-85.14	85.39
3	82.96	81.27
4	62.76	67.25
5	24.39	26.17
6	8.69	11.94
7	21.91	24.48
8	-7.58	7.45X
9	47.16	48.63
10	1.08	8.40X
11	34.02	36.56
12	23.56	25.62
14	-40.54	38.63
15	37.54	34.61
17	14.71	17.98
• 7	3	
-19	-25.20	23.93
-17	-21.21	20.07
-15	-13.24	14.80
-13	-12.00	11.78
-11	-52.41	48.05
-10	12.05	11.88
-9	22.45	22.06
-8	21.08	24.99
-7	-65.58	64.68
-6	-24.96	24.45
-5	-65.78	65.32
-4	-9.48	12.21
-3	-40.21	40.68
-2	-53.27	52.92
-1	-35.02	35.54
0	-10.28	9.98
1	-99.75	92.65
2	3.32	4.16X
3	36.58	40.70
4	34.75	33.96
5	-55.14	53.39
6	12.46	13.50
7	-52.03	52.94
8	24.47	27.84
9	-18.97	21.86
10	-19.66	23.53
11	-18.89	22.33
13	-57.16	53.25
14	-11.94	14.79
17	-20.70	23.28
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-17	22.56	20.86
-15	11.48	15.12
-14	-9.02	15.99
-13	20.71	19.92
-10	26.91	28.18
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-8	-12.08	14.85
-7	11.75	14.38
-6	.99	5.76X
-5	55.47	57.06
-4	35.56	36.66
-3	28.68	29.37
-2	-16.60	19.14
-1	47.06	48.44
0	-22.56	24.53
1	-3.54	4.51X
2	32.57	36.73
3	53.09	53.79
4	-24.83	26.40
5	14.33	14.82
6	-7.20	6.59X
7	41.71	45.03
8	31.16	34.99
9	22.59	22.04
11	38.99	38.14
15	22.92	17.75
• 7	7	
-10	21.96	23.87
-9	-26.84	27.09
-7	-40.29	42.67
-5	-13.22	16.45
-3	-55.28	57.28
-2	-14.68	19.21X
0	-23.80	25.88
2	27.98	24.69
3	-20.17	23.06
4	-8.19	19.32X
5	-25.91	29.54
9	-49.81	49.50
• 8	0	
-16	33.73	32.30
-14	16.40	17.06
-12	26.22	30.76
-10	44.41	44.80
-8	88.78	82.99
-6	-31.81	34.69
-4	73.27	71.13
-2	10.96	8.92
0	9.71	9.41
2	59.17	60.81
4	127.16	115.51
6	-9.27	15.43
8	79.83	76.87
10	26.41	31.07
16	38.41	35.81
• 8	2	
-18	-21.76	19.87
-15	-12.61	15.30
-14	-39.56	39.13
-12	-37.41	38.78
-11	14.08	17.32
-10	-45.02	46.69
-9	19.76	21.88
-8	-6.62	5.73X
-7	-37.38	39.22
-6	-44.50	47.22
-5	47.99	51.22
-4	26.09	29.20
-3	-30.05	31.27
-2	-40.79	44.21
-1	-39.22	40.03
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1	10.86	14.82
2	-100.20	101.98
3	19.07	21.45
4	-48.50	49.30
5	-42.26	45.46
6	-80.15	79.36
7	55.09	57.89
8	4.63	6.59X
9	-5.61	6.88X
10	-8.83	7.18X
11	-18.07	19.27
14	-27.22	27.19
16	-13.69	17.05
17	-20.06	16.28
18	-34.80	31.00
• 8	4	
-17	20.56	18.61
-12	38.76	38.31
-10	24.53	26.91
-9	6.72	6.71X
-8	32.25	35.13
-7	-40.44	41.83
-6	55.67	51.84
-5	46.14	50.95
-4	22.27	25.65
-3	-14.00	15.79
-2	1.59	4.35X
-1	10.81	10.89
0	52.16	53.38
1	12.91	15.67
2	16.74	19.99
3	21.60	23.02
4	33.96	36.54
5	-50.27	51.47
6	64.45	65.55
7	30.88	33.38
8	28.09	30.65
9	-14.12	15.34
10	14.53	18.48
12	35.97	37.39
16	9.49	15.94
18	20.62	17.75
• 8	6	
-14	-16.89	18.73
-10	-27.64	31.24
-8	-36.06	36.41
-6	9.36	17.10
-5	4.84	6.57X
-4	-41.18	40.79
-3	-27.86	30.28
-2	-26.34	26.58
-1	9.07	11.39
0	-12.94	14.43
1	-28.93	30.02
2	-41.62	43.56
3	14.09	17.80
4	-55.08	57.65
5	1.45	7.49X
8	-32.14	31.47
10	-20.40	21.46
• 8	10	
0	-29.53	25.81
• 9	3	
-20	9.07	20.78X
-17	21.21	22.12
-13	51.71	48.71
-11	14.92	15.86
-10	-19.72	20.29
-9	17.14	19.41
-8	4.36	6.75X
-7	32.03	32.54
-6	-13.26	17.36
-5	48.43	48.69
-4	13.74	16.80
-3	-17.69	20.97
-2	11.61	12.81
-1	98.15	96.56
0	27.24	29.24
1	33.53	34.62
2	-10.65	12.90
3	22.45	26.05
4	8.94	10.19
5	42.60	43.81
6	-24.89	28.19
7	47.96	47.46
8	-1.38	7.08X
9	-18.84	22.71
11	54.83	50.88
13	18.72	19.24
15	8.00	16.94
• 9	1	
-15	-33.96	31.88
-14	-32.55	29.81
-13	-17.09	19.90
-12	15.08	19.94
-11	-38.82	40.25
-10	-12.85	18.22X
-9	-40.15	40.14
-8	-7.27	7.69X
-7	-17.06	20.59
-6	3.80	7.16X
-5	-10.79	12.73
-4	63.19	65.46
-3	-63.33	66.81
-2	-51.09	56.45
-1	-19.89	21.61
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1	-64.92	66.84
2	-17.50	19.63
3	-71.36	72.42
4	-34.08	35.05
5	-32.61	34.44
6	-18.14	21.89
7	-19.97	22.92
8	42.07	42.34
9	-47.82	46.74
10	-33.19	33.75
12	28.01	26.98
13	-22.33	23.54
15	-27.34	22.86
• 9	5	
-15	-28.72	26.03
-12	-18.09	17.59
-11	-35.03	33.10
-10	-14.78	14.75
-8	22.32	22.65
-7	-23.06	21.41
-5	-9.16	10.92
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-1	-17.68	19.67
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1	-59.15	60.37
2	-33.82	33.90
3	-22.16	24.69
4	10.81	14.00
5	-30.87	32.26
6	-11.32	12.56
9	-36.22	36.97
10	33.51	32.22
13	-25.19	19.92
• 9	7	
-9	29.32	31.78
-5	27.69	31.23
-3	37.42	38.84
-2	31.33	33.30
-1	28.19	29.58
0	-8.73	10.86
3	38.79	40.62
7	18.34	20.56
8	-17.63	22.36
9	24.21	21.20
• 10	0	
-14	-14.51	16.73
-10	-79.54	72.98
-8	-27.68	29.55
-6	-62.36	62.29
-4	-59.31	59.60
-2	-28.85	33.64
0	59.99	59.24
2	-72.13	72.38
4	-4.14	8.27X
6	-49.60	49.97
8	-73.46	72.15
10	-50.35	50.21
12	13.49	16.37
14	-37.31	37.69
• 10	2	
-16	17.82	16.63
-14	11.04	14.65
-13	16.35	12.90
-12	31.65	31.22
-11	-23.11	24.36
-10	.27	7.30X
-9	-30.97	31.52
-8	52.31	53.72
-7	-8.50	10.41
-6	33.89	38.49
-5	-22.54	25.09
-4	48.84	51.81
-3	3.44	4.88X
-2	28.17	33.04
-1	24.99	27.50
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1	-43.49	48.30
2	-7.92	4.91X
3	47.61	51.71
4	45.88	52.34
5	2.60	5.90X
6	28.64	32.62
7	-19.49	23.91
8	33.51	32.97
10	19.63	22.44
12	41.95	41.10
13	-28.75	30.04
16	20.39	19.43
• 10	4	
-14	-13.77	12.89
-12	-22.95	21.37
-11	-33.72	35.79
-10	-16.06	14.22
-9	22.63	23.51
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-6	-58.95	61.55
-5	8.26	9.02
-4	-14.39	20.28
-3	9.09	6.13X
-2	-29.16	31.20
-1	26.19	28.10
0	-24.12	26.04
1	-50.51	52.26
2	3.14	6.17X
3	20.45	23.44
4	-28.66	31.26
5	-20.01	22.53
6	-55.48	54.86
8	-19.90	21.09
10	-37.52	39.61
11	24.78	25.54
12	-25.83	28.72
13	-18.02	16.00
• 10	6	
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-7	-16.24	18.14
-5	16.18	20.68
-4	43.44	45.59
-3	-15.22	14.88
-2	34.90	36.75
-1	11.75	14.88
0	8.85	12.29
2	51.34	51.88
8	28.38	29.34
10	20.94	22.04
• 10	8	
0	-24.08	22.17
• 10	10	
0	17.62	16.11
• 11	1	
-13	10.74	16.21
-11	26.39	24.20
-9	46.91	47.66
-8	33.71	36.58
-7	19.74	19.60
-6	-51.18	52.05
-5	54.82	55.05
-4	11.92	12.42
-3	27.87	29.35
-2	-6.39	6.17X
-1	9.88	10.64
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1	29.64	32.21
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3	49.00	49.14
4	57.98	58.61
6	-36.90	38.41
7	52.16	52.21
8	13.23	15.19
9	30.92	30.62
13	20.80	23.47X
15	22.02	18.97
• 11	3	
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-11	-24.37	26.26
-9	-13.24	15.32
-8	-7.41	7.31X
-7	-73.25	71.06
-6	-16.46	20.17
-5	4.07	6.17X
-4	8.27	10.74
-3	-28.41	30.82
-2	-8.44	5.90X
-1	-34.22	35.44
0	25.54	26.72
1	-22.88	23.10
2	-.86	6.58X
3	-3.96	6.69X
4	5.73	6.84X
5	-81.54	79.64
6	-10.74	7.21X
9	-25.26	26.02
11	-32.05	31.78
• 11	5	
-13	24.91	24.41
-12	19.26	22.78
-11	17.61	17.94
-9	33.16	32.67
-6	16.60	17.49
-5	37.77	36.36
-4	-15.38	15.09
-3	2.20	7.21X
-2	-25.16	24.76
-1	32.53	31.19
0	19.27	20.82
1	20.90	21.98
3	50.79	50.43
5	31.19	33.38
7	35.35	34.97
10	-19.17	19.06
11	16.63	18.82
• 11	7	
-11	-27.48	22.39
-9	-19.62	25.78X
1	-36.56	34.80
3	-25.20	21.39
7	-21.01	22.54
• 12	0	
-16	32.24	30.03
-12	31.26	30.66
-10	19.31	20.59
-8	19.12	21.49
-6	12.10	12.40
-4	83.59	77.88
-2	-7.09	8.71X
0	57.81	59.68
2	37.99	41.62
4	13.79	16.44
8	65.26	62.52
12	31.77	31.38
14	26.64	27.96
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-14	-30.54	26.93
-13	15.25	15.70
-9	-14.18	14.71
-6	-38.12	39.13
-5	17.72	19.17
-4	-22.59	24.99
-3	-38.79	41.34
-2	-82.93	83.97
-1	31.84	35.61
0	-32.98	35.87
1	5.77	9.42
2	-30.99	34.36
3	-13.09	14.32
5	-.14	7.13X
6	-18.37	20.23
7	18.01	22.11
9	-36.13	37.51
10	-42.74	41.45
12	-25.85	24.82
14	-25.50	26.88
• 12	4	
-15	-15.60	13.80
-14	20.39	17.93
-13	15.15	15.10
-12	23.10	23.95
-8	32.66	34.48
-6	19.75	25.07
-5	25.76	29.27
-4	11.49	14.29
-3	-36.03	37.95
-2	36.50	39.74
-1	19.23	16.92
0	33.06	36.50
1	-12.67	14.47
4	43.45	45.02
6	21.54	23.41
7	29.97	30.93
9	-21.04	21.93
10	27.97	25.41
12	17.28	21.78
• 12	6	
-4	-40.56	41.80
-1	12.18	15.25
0	-36.40	36.61
2	-34.09	37.57
3	18.00	17.76
8	-29.59	26.85
• 13	1	
-15	-18.16	19.49
-12	20.02	19.18
-11	-23.18	22.18
-10	-22.86	24.42
-8	17.32	19.22
-7	-22.49	21.39
-6	4.14	8.66X
-5	-43.15	42.69
-3	-43.17	42.95
-2	-24.74	24.07
-1	-21.42	22.03
0	32.54	33.81
1	-48.43	46.00
2	-41.16	41.92
3	-7.14	8.48X
4	11.16	8.63X
5	-13.07	16.72
7	-29.62	28.21
9	-23.94	23.03
11	-13.37	15.00
12	23.78	20.20
13	-32.87	28.72
14	-18.82	15.24
• 13	3	
-9	36.29	33.63
-8	19.04	19.53
-7	23.72	23.96
-5	24.98	26.21
-4	21.84	22.69
-3	27.96	29.50
-2	-5.14	7.21X
-1	55.75	55.51
0	-6.30	10.93
1	-18.31	18.66
2	-19.63	21.13
3	40.35	41.20
5	24.01	24.37
7	13.28	17.16
8	19.23	19.03
9	21.29	17.60
11	41.20	38.42
• 13	5	
-11	-24.59	20.40
-7	-34.37	32.95
-6	-16.17	16.94
-5	-19.05	16.65
-3	-35.83	32.50
0	-23.30	25.27
1	-34.79	32.76
2	15.97	17.11
5	-26.46	23.86
7	-15.69	16.28
9	-29.02	26.78
• 13	7	
0	-18.04	18.07
• 14	0	
-14	-22.20	18.97
-12	-25.08	20.16
-10	-41.02	39.01
-8	12.46	15.27
-6	-39.26	37.61
-2	-11.89	16.34
0	-34.95	37.74
2	-69.05	67.26
6	-58.62	56.81
14	-25.64	27.14
• 14	2	
-12	21.41	20.93
-9	15.12	16.63
-8	33.25	30.74
-7	-22.80	23.51
-5	20.32	24.24
-4	33.18	33.73
-3	11.70	15.48
-2	24.00	26.14
0	36.70	38.47
2	16.60	16.94
3	20.77	19.47
4	45.61	45.15
5	-33.51	32.53
8	21.04	23.89
10	16.08	20.67
12	20.60	20.18
• 14	4	
-3	-13.74	15.27
-2	-27.88	28.63
0	-11.77	12.51
2	-29.47	29.18
3	25.10	26.34
4	-43.39	43.41
5	-19.93	17.63
6	-20.35	17.99
7	15.33	19.52
10	-20.51	15.46
• 14	6	
-6	33.61	31.73
-4	17.10	21.73
0	19.73	21.31
2	23.02	24.63
6	29.37	29.79
• 15	1	
-15	11.94	17.11
-13	25.16	24.72
-11	22.11	23.62
-6	-21.69	21.68
-5	25.29	22.84
-4	31.49	28.79
-2	-16.01	14.09
-1	36.40	33.24
0	17.48	18.91
1	38.63	36.32
3	24.34	25.88
5	18.62	19.75
6	-26.25	25.86
7	27.96	25.65
8	18.34	16.85
• 15	3	
-15	-26.81	23.91
-11	-18.97	17.64
-7	-20.25	19.26
-3	-47.58	44.01
-1	-12.61	14.33
1	-25.20	23.34
3	-31.62	31.79
5	-28.26	25.39
9	-35.14	32.02
• 15	5	
-9	16.10	21.27
-5	29.26	28.78
-2	21.00	19.53
-1	37.51	37.77
0	16.34	18.91
1	14.23	15.21
3	21.88	20.00
7	22.70	22.35
• 16	0	
-12	35.82	31.16
-8	29.22	27.73
-6	20.87	20.92
-4	19.19	23.54
-2	-10.15	16.72
0	47.62	47.97
4	31.51	28.43
6	34.69	33.71
8	24.20	25.85
12	28.01	27.92
• 16	2	
-10	-28.92	25.51
-8	-17.77	17.53
-6	-30.85	27.77
-4	-17.86	18.06
-2	-28.38	27.88
-1	18.63	19.30
1	-26.12	23.72
2	-24.27	20.83
6	-25.75	24.32
8	-22.07	23.37
10	-31.78	27.73
11	16.02	19.47
• 16	4	
-10	15.90	16.63
-8	22.11	23.16
-4	21.98	20.40
-2	20.01	22.18
-1	25.19	25.30
2	21.71	24.34
3	16.69	16.86
4	27.48	26.98
• 16	6	
-6	-24.24	23.98
0	-25.76	24.24
• 17	1	
-10	-11.08	21.50
-9	-15.84	16.06
-6	-13.75	29.52
-5	-15.50	13.61
1	-20.18	17.35
2	-19.82	17.91
4	23.88	20.35
5	-33.91	30.60
6	-9.72	13.91
7	-21.26	20.87
• 17	3	
-9	34.51	28.58
-5	22.29	20.75
-1	11.38	14.07
3	42.45	37.97
7	23.95	22.46
• 17	5	
-3	-19.75	20.17
1	-24.52	24.05
• 18	0	
-6	-33.79	32.60
-2	-37.89	33.83
0	-20.40	24.24
6	-28.22	26.63
• 18	2	
-8	21.78	23.15
-4	34.37	31.68
-2	10.22	17.60
0	18.54	19.43
4	16.05	16.65
8	28.17	25.45
• 18	4	
-2	-20.64	14.44
0	-14.97	17.65
2	-26.33	25.08
• 18	6	
0	15.60	17.80
• 19	1	
-7	18.69	18.23
-5	23.09	19.37
-3	17.63	16.20
-1	26.17	23.23
0	14.79	17.56
• 19	3	
-7	-15.73	15.59
-5	-16.68	16.41
-3	-27.98	23.47
1	-24.37	20.24
• 20	0	
-2	18.83	18.06
0	30.43	28.78
4	26.15	27.03
• 20	2	
3	13.63	21.11
• 20	4	
0	16.63	14.54
2	18.79	20.81
• 22	0	
-2	-21.84	18.98
• 22	2	
0	15.26	18.45

[a] Based on four formula units. Each group is headed by the values of h and k. Each line contains l, F_c, and F_o; $F(000) = 336.4$. Unobserved reflections are denoted by X.

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC VIBRATIONAL TENSOR COMPONENTS[a]

Atom	x (σ_x)	y (σ_y)	z (σ_z)	U_{11}, Å.^{2}	U_{22}, Å.^{2}	U_{33}, Å.^{2}	U_{12}, Å.^{2}	U_{23}, Å.^{2}	U_{31}, Å.^{2}
Cr	0.25	0.25	0.5	0.0122 (04)	0.0142 (06)	0.0106 (04)	−0.0028 (04)	0.0021 (04)	−0.0005 (03)
Cl(1)	0.5	0.55530 (30)	0.75	0.0177 (07)	0.0262 (10)	0.0176 (06)	...	...	0.0018 (05)
Cl(2)	0.31241 (12)	0.09139 (23)	0.66545 (11)	0.0292 (06)	0.0293 (08)	0.0175 (05)	−0.0026 (05)	0.0076 (05)	−0.0045 (04)
O(1)	0.39677 (30)	0.19494 (65)	0.43577 (33)	0.0154 (14)	0.0284 (22)	0.0202 (15)	−0.0015 (14)	0.0023 (15)	0.0029 (12)
O(2)	0.30266 (33)	0.50821 (62)	0.56459 (32)	0.0251 (17)	0.0224 (21)	0.0179 (15)	−0.0072 (15)	−0.0016 (14)	−0.0037 (13)
O(3)	0.58692 (34)	0.24894 (66)	0.56947 (37)	0.0255 (18)	0.0269 (23)	0.0275 (18)	0.0001 (17)	0.0019 (17)	0.0002 (14)

[a] The standard deviations (in parentheses) refer to the two least significant digits in the preceding quantities. The atomic temperature factors are $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + klb^*c^*U_{23} + lhc^*a^*U_{31})]$.

temperature factors, the weighted discrepancy residual converged to 0.127.

A re-examination of the data at this stage revealed that the individual weighting factors were not nearly as reliable as the structure factors themselves. Consequently a composite weighting function in terms of F_o was applied to all reflections in the further refinement.[11] Some unreliable observed structure factors and all unobserved reflections occurring at $\sin\theta/\lambda > 0.6$ Å.$^{-1}$ were removed from the calculations. Anisotropic temperature factors were introduced for all atoms. The refinement was completed after four further cycles of least squares, with the weighted and unweighted discrepancy residuals converging to 0.096 and 0.081, respectively.

The structure factors from the final cycle are listed in Table I. Reflections with $|F_c| \geq 80$ show mean ratios of $|F_c|/|F_o|$ increasing to 1.12 with $|F_o|$, and this may be a manifestation of slight extinction effects (for which corrections have not been made). An attempt to locate hydrogen atoms by a difference synthesis of 289 reflections with $\sin\theta/\lambda \leq 0.45$ and $|F_c| < 80$ showed a number of features of maximum electron density $\backsim +0.3$ e Å.$^{-3}$. None of these was at a position geometrically suitable for a hydrogen atom. It was concluded that the hydrogen atoms could not be located with the present data. In describing the structure, the existence of hydrogen bonds therefore had to be deduced from the contacts and relative orientations of suitable donor and acceptor sites. In all cases except one this could be done unambiguously.

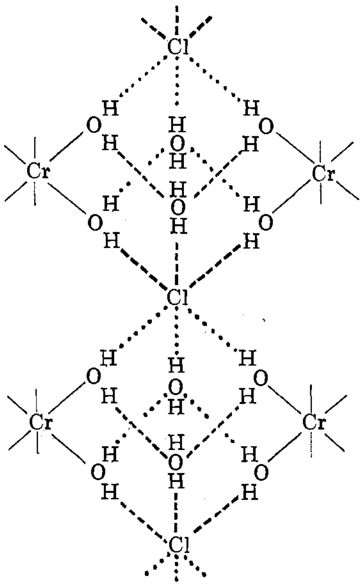
The final positional and thermal parameters are presented in Table II. The standard deviations given in parentheses are computed assuming that the structure factor discrepancies represent random errors.

Description of the Structure

The chromium atoms lie at the centers of symmetry ($^1/_4$, $^1/_4$, $^1/_2$), ($^3/_4$, $^1/_4$, 0), ($^1/_4$, $^3/_4$, 0), and ($^3/_4$, $^3/_4$, $^1/_2$), and the chloride ions Cl(1) at the special positions ($^1/_2$, y, $^3/_4$), ($^1/_2$, $\bar{y}$, $^1/_4$), (0, $^1/_2 + y$, $^3/_4$), and (0, $^1/_2 - y$, $^1/_4$) on twofold axes. Atoms in asymmetric units different from that of Table II are labeled by Roman superscripts defined according to the transformations listed in Table IV.

The structure is depicted in Figure 1. The Cr atoms are arranged in layers parallel to the ab plane and separated by $c/2$ = 5.82 Å. Each such layer is a quasi-hexagonal array in which every Cr atom is surrounded by four others at 6.93 Å. and two at 6.84 Å. The complex ions are linked only in chains, which lie along the [110] and [1$\bar{1}$0] directions in alternate layers. Each octahedral ion is linked to its neighbors in the chain *via* two secondary water molecules, each of which is the proton acceptor in two hydrogen bonds from primary waters of two octahedra.

Every primary water molecule forms two donor hydrogen bonds, one to a secondary water molecule and the other to a chloride ion. The chloride ions are situated midway between the sheets of octahedra. Each chloride ion is almost equidistant from four octahedra, accepting one hydrogen bond from a primary water molecule of each of them.



The chloride ions not only link the octahedra in lines similarly to the secondary water molecules, but also provide connections between the lines of octahedra in adjacent sheets. In addition, two secondary water molecules form donor hydrogen bonds to each chloride ion. The hydrogen bonds to the chloride ions provide virtually the only structure linkages along the c direction, this being compatible with the well-developed {001} habit observed during crystallization.

These links between the complexes result in the most distinctive feature of this structure—empty "cages" of water molecules and chloride ions occurring between the chromium atoms (Figure 2). Each cage consists

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(11) This function was constructed from weighted means of the standard deviations $\sigma_R(F)$ and $\sigma_S(F)$, where $\sigma_R(F)$ represented random errors and was calculated from multiple observations of individual reflections and $\sigma_S(F)$ took into account systematic errors and was calculated from the values of symmetrically equivalent reflections.

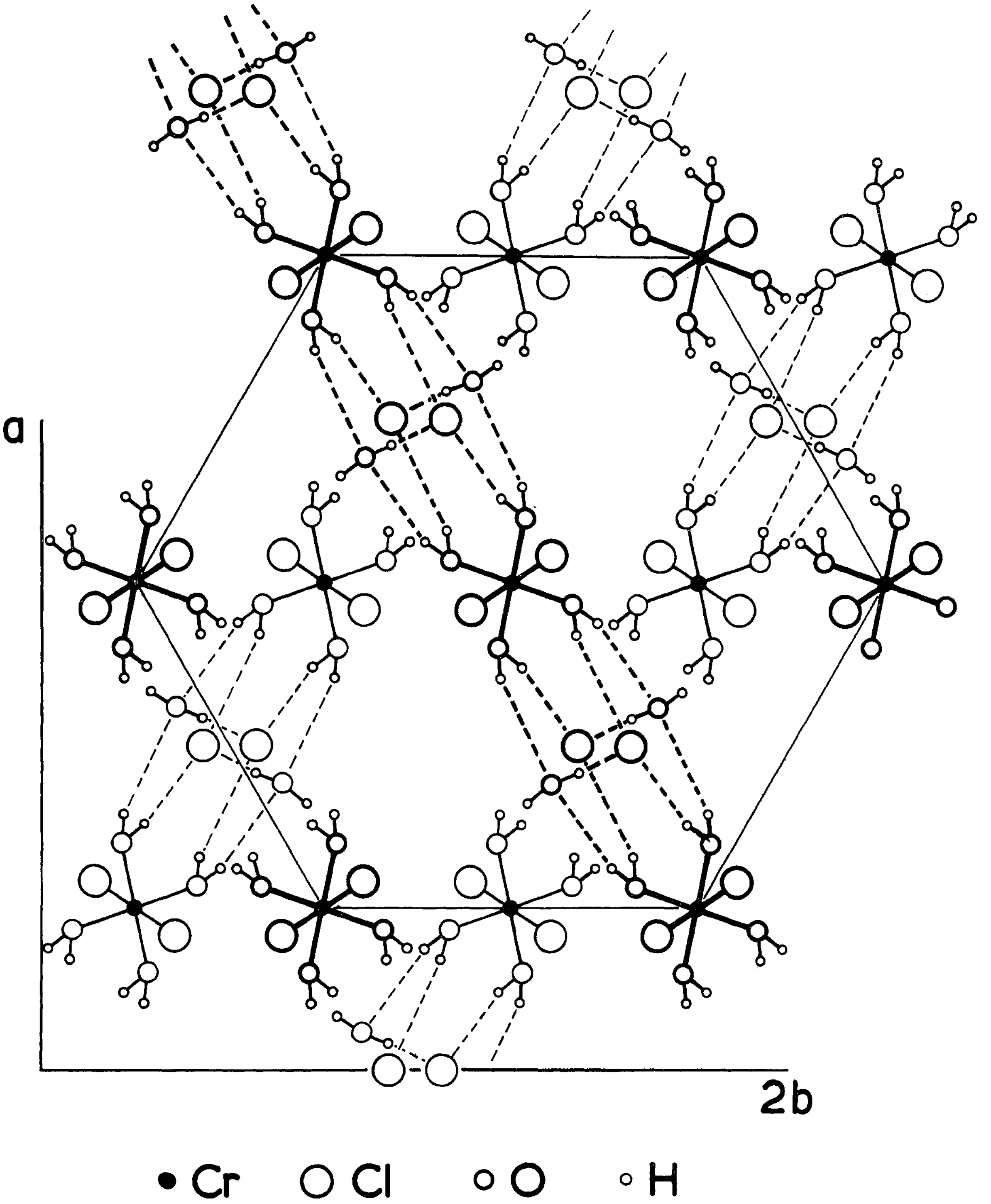
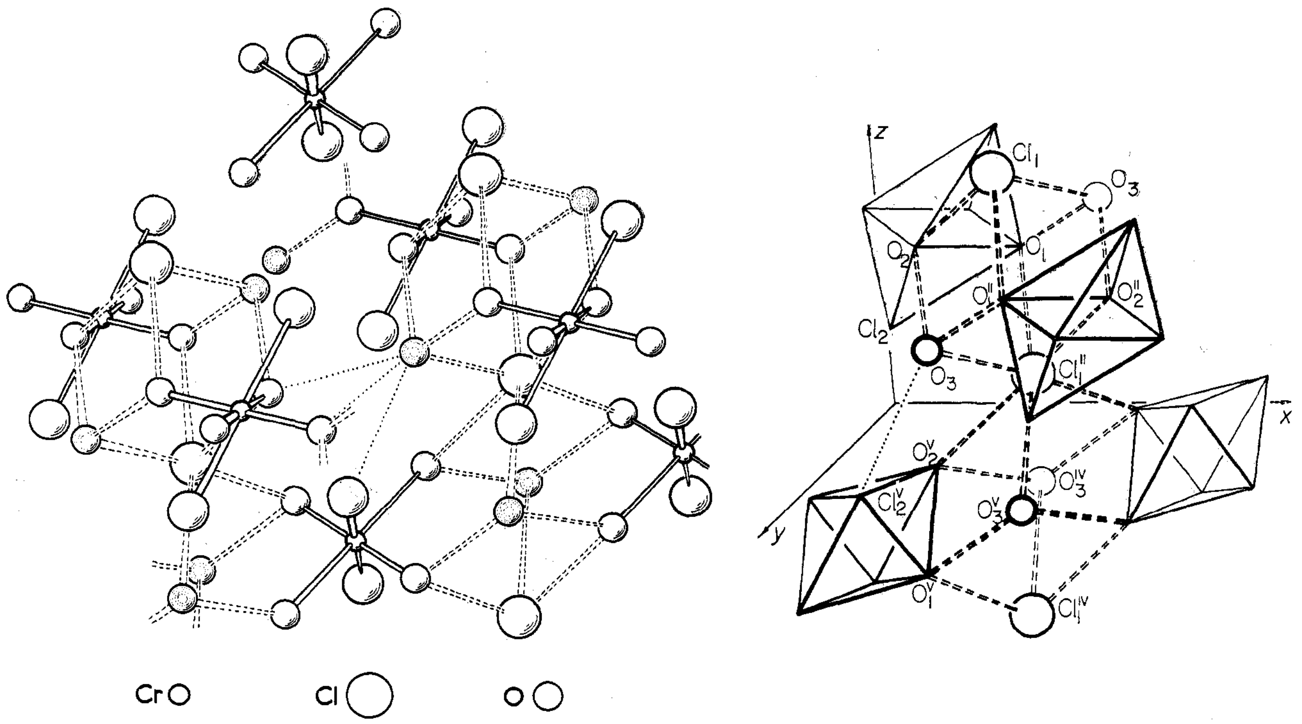


Figure 1.—Projection along the *z* axis. Broken lines are hydrogen bonds. The thickness of the line is proportional to the distance above the *xy* plane. The diagram is *not* to scale: the octahedra have been contracted for clarity.

of two atoms of each of the types O(1), O(2), O(3), and Cl(1), arranged in a centrosymmetric and approximately cubic form in which ten of the edges are hydrogen bonds and the other two are O(1)–O(2) edges of coordination octahedra. Each chloride ion is a common vertex for two cages in two different layers of octahedra.

Dimensions of Complex Ion.—The present analysis has confirmed the conclusions of King, Woods, and Gates[1c] that it is the *trans* coordination isomer which crystallizes first from solution. The sole, strictly crystallographic, symmetry element of the coordination octahedron is a center. The deviations from D_{4h} symmetry are small, being 2.5° from orthogonality in the Cr–O bonds and 2° in the inclination of the Cr–Cl bond from the normal to the plane of the oxygen atoms. Interatomic distances and angles are listed in Table III.

The lengths for the chlorine–chromium(III) (2.289 Å.) and water–chromium(III) bonds (2.004, 2.006 Å.) appear to be the most accurate values yet recorded.



(a) (b)

Figure 2.—Atomic arrangement of $[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$. (a) Secondary water molecules O(3) are shaded. Broken double lines represent hydrogen bonds, broken single lines are close contacts with secondary water molecules. (b) Key to atoms involved in "cage" formation.

TABLE III

INTERATOMIC DISTANCES AND BOND ANGLES IN THE $[CrCl_2(OH_2)_4]^+$ CATION[a]

Atoms	Distance l, Å.	$\sigma(l)$,[b] Å.
Cr—Cl(2)	2.289	0.0014
Cr—O(1)	2.006	0.004
Cr—O(2)	2.004	0.004
Cl(2)···O(1)	3.013	0.004
Cl(2)···O(2)	3.082	0.004
O(1)···O(2)	2.894	0.006
Cl(2)···O(1′)[c]	3.074	0.004
Cl(2)···O(2′)[c]	3.003	0.004
O(1)···O(2′)[c]	2.776	0.006
Atoms	Angle θ, deg.	$\sigma(\theta)$, deg.
Cl(2)—Cr—O(1)	88.8	0.2
Cl(2)—Cr—O(2)	91.5	0.2
O(1)—Cr—O(2)	92.4	0.2

[a] Calculated without taking into account the differential thermal motion of the atoms. [b] Standard deviations calculated by assuming r.m.s. isotropic errors for atomic positions [D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953). [c] Atoms ′ at $^1/_2 - x, {}^1/_2 - y, 1 - z$.

Comparable values for Cr(III)–OH_2 are 2.02 Å. in potassium *trans*-bis(oxalato)diaquochromate(III) trihydrate[12] and 1.94 Å. in potassium chrome alum, $K(OH_2)_6 \cdot Cr(OH_2)_6 \cdot (SO_4)_2$.[13] In chromous acid, $HCrO_2$ or $DCrO_2$,[14] the Cr–O distance is (1.979 ± 0.005) Å. For Cr(III)–Cl, the value 2.32 Å. has been reported in CrOCl[15] and distances of 2.347, 2.342, and 2.340 (s.d. ∽ 0.002 Å.) occur in anhydrous $CrCl_3$.[16] The chlorine atoms Cl(2) in the present structure are each bonded to only one chromium atom. This explains why these bonds are significantly shorter than the corresponding ones in $CrCl_3$, where the number of chlorine–neighbor interactions is larger.

Details of Hydrogen-Bond System

Table IV is a list of all hydrogen bonds and the shortest nonbonded contacts in the structure. For reasons to be discussed later (see Related Structures), corresponding data for $CoCl_2(OH_2)_4 \cdot 2H_2O$ are also shown.

Bonding of Ligand Water Molecules.—Two pseudomirror planes are associated with each complex and its environment. They are normal to the CrO_4 plane and bisect the O–Cr–O angles. The angles and distances about the primary water molecules O(1) and O(2) are therefore remarkably similar.

The angle between the two hydrogen bonds formed by each primary water molecule is small (O(1), 88°; O(2), 87°). If the H–O–H angles are about 105–110°, then the hydrogen bonds must be considerably bent, as is common in the hydrogen bonds of metal salt hydrates.[17] The three atoms to which each primary water molecule is bonded have a flattened pyramidal, but not a planar, arrangement. The angle between the water–chromium bond and the plane of the two hydrogen bonds is 42° for O(1) and 44° for O(2).

Environment of Secondary Water Molecule.—The

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(12) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **4**, 35 (1951).

(13) G. E. Bacon and W. E. Gardner, *Proc. Roy. Soc.* (London), **A246**, 78 (1958).

(14) W. C. Hamilton and J. A. Ibers, *Acta Cryst.*, **16**, 1209 (1963).

(15) H. E. Forsberg, *Acta Chem. Scand.*, **16**, 777 (1962).

(16) B. Morosin and A. Narath, *J. Chem. Phys.*, **40**, 1958 (1964).

(17) W. C. Hamilton, *Ann. Rev. Phys. Chem.*, **13**, 28 (1962).

TABLE IV

HYDROGEN BONDS AND SHORT CONTACTS

$[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$			$[CoCl_2(OH_2)_4] \cdot 2H_2O$	
Atoms	Distance l, Å.	$\sigma(l)$, Å.	Atoms[a]	Distance Å.
Hydrogen Bonds				
O(1)—H···O(3)	2.701	0.006	$O_p \cdots O_s$	2.69
O(2)—H···O(3″)	2.696	0.006		
O(1)—H···Cl(1″)	3.088	0.004	$O_p \cdots Cl$	3.18
O(2)—H···Cl(1)	3.110	0.004		
O(3)—H···Cl(1)	3.198	0.005	$O_s \cdots Cl$	3.31
Bifurcated Hydrogen Bond				
O(3″)—H···O(1^{vi})	3.043	0.006	$O_s \cdots O_p$	3.12
O(3″)—H···O(2^{vii})	3.082	0.006		
Shortest Nonbonded Contacts				
O(3″)···Cl(2^{v})	3.407			
O(2^{v})···Cl(2′)	3.57			
O(3)···Cl(2‴)	3.70			
O(3)···Cl(2)	3.73			
O(3″)···O(1)	3.81			

Atoms	Angle,[b] deg.	Atoms	Angle, deg.
Angles at Hydrogen-Bonded Atoms			
Cr—O(1)···O(3)	119.6	Co—O_p—O_s	115
Cr—O(2)···O(3″)	118.8		
Cr—O(1)···Cl(1″)	124.6	Co—$O_p \cdots Cl$	124
Cr—O(2)···Cl(1)	123.9		
O(3)···O(1)···Cl(1″)	87.7	$O_s \cdots O_p \cdots Cl$	89
O(3″)···O(2)···Cl(1)	87.3		
O(1)···O(3)···O(2″)	100.6	$O_p \cdots O_s \cdots O_p$	100
O(1)···O(3)···Cl(1)	99.4	$O_p \cdots O_s \cdots Cl$	106
O(2″)···O(3)···Cl(1)	100.1		
O(2)···Cl···O(1″)	84.1		
O(2)···Cl···O(3)	75.3		
O(1″)···Cl···O(3)	74.6		
Angles at Atoms in Bifurcated Hydrogen Bond			
Cl(1″)···O(3″)···O(1^{vi})	134	$Cl \cdots O_s \cdots O_p$	119
Cl(1″)···O(3″)···O(2^{vii})	133		
O(1″)···O(3″)···O(1^{vi})	85	$O_p \cdots O_s \cdots O_p$	86
O(2)···O(3″)···O(2^{vii})	82		
O(1″)···O(3″)···O(2^{vii})	127	$O_p \cdots O_s \cdots O_p$	131
O(2)···O(3″)···O(1^{vi})	125		
Cr—O(1′)···O(3^{viii})	105	Co—$O_p \cdots O_s$	97
Cr—O(2)···O(3^{viii})	104		
Cl(1^{ix})···O(1′)···O(3^{viii})	121	$Cl \cdots O_p \cdots O_s$	132
Cl(1)···O(2)···O(3^{viii})	122		
O(3′)···O(1′)···O(3^{viii})	95	$O_s \cdots O_p \cdots O_s$	94
O(3″)···O(2)···O(3^{viii})	98		

[a] (See section on Related Structures.) The octahedral $[CoCl_2(OH_2)_4]$ complex possesses C_{2h} symmetry. The *four* equivalent primary oxygen atoms are here labeled O_p and the secondary water molecules O_s. [b] Standard deviations of all angles are 0.3°. Code for symmetry-related atoms:

Superscript	Position	Superscript	Position
None	$x, \quad y, \quad z$	v	$x, \quad 1-y, \quad -1/2+z$
′	$1/2-x, \quad 1/2-y, \quad 1-z$	vi	$x, \quad 1+y, \quad z$
″	$1-x, \quad 1-y, \quad 1-z$	vii	$1/2-x, \quad 1\,1/2-y, \quad 1-z$
‴	$1/2+x, \quad 1/2+y, \quad z$	viii	$-1/2+x, \quad 1/2+y, \quad z$
iv	$1-x, \quad y, \quad 1/2-z$	ix	$-1/2+x, \quad -1/2+y, \quad z$

secondary water molecule participates in two acceptor hydrogen bonds of moderate strength from primary water molecules (2.701, 2.696 Å.) and one slightly weaker donor hydrogen bond to a chloride ion (3.198 Å.). The environment of O(3) is unusual in that the directions of the three hydrogen bonds are half-way between being mutually orthogonal and tetrahedral, as is indicated by the inter-hydrogen-bond angles of 99, 100, and 101°. Substantial bending of all O(3)–H bonds from the direct lines between the hydrogen-bonded atoms must therefore be expected.

Participation of the other hydrogen atom of the secondary water molecule in a donor hydrogen bond is not clearly apparent from the heavy-atom geometrical relationships. The three possible contacts (marked as single broken lines in Figure 1) are to primary water molecules O(1) (3.04 Å. distant) and O(2) (3.08 Å.), and chromium-coordinated chlorine Cl(2) (3.41 Å.). These distances are at the upper limits for O—H···O and O—H···Cl hydrogen-bond interactions.[17,18] The bond angles reveal that the Cl(2) is geometrically quite unsuitable as a hydrogen-bond acceptor. The atoms O(1) and O(2) of a neighboring complex are virtually equivalent as acceptors. If the O–H bond of the secondary water molecule is directed midway between O(1) and O(2) in a weak bifurcated hydrogen bond, then the water molecule is almost regularly tetrahedral.

The water O(3) in the present structure is analogous to the noncoordinated water molecule W4 in the structure of $[Mg(OH_2)_6]_3[Ce(NO_3)_6]_2 \cdot 6H_2O$.[19] In the presence of the large oxyanion, W4 accepts two hydrogen bonds from water molecules coordinated to magnesium and donates a weaker hydrogen bond to a nitrate group. Its second hydrogen atom is located symmetrically with respect to two nitrate oxygens too distant for hydrogen bonding. Baur,[20] however, concludes that no hydrogen bond exists in a similar situation in $MgSO_4 \cdot 4H_2O$, where the hydrogen atom has been located by neutron diffraction.

Related Structures.—The recently determined crystal structures of the isomorphous *trans*-$[CoCl_2(OH_2)_4] \cdot 2H_2O$[21] and *trans*-$[NiCl_2(OH_2)_4] \cdot 2H_2O$[22] are, in spite of the stoichiometric difference, remarkably closely related to that of $[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$. In $[CoCl_2(OH_2)_4] \cdot 2H_2O$ the coordination octahedra are linked in sheets by hydrogen-bonded cages of distorted cubic shape. These cages consist of two pairs of primary water molecules, two secondary water molecules, and—in place of the chloride ions of $[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$—two metal-coordinated atoms of nearby octahedra. The corresponding geometrical features are compared in Table IV.

The close resemblance between the cages in the two structures extends to the hydrogen-bond schemes for the secondary water molecules. In complete analogy with the proposed bifurcated hydrogen bond in $[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$, a weak bifurcated hydrogen bond from the secondary to two primary water molecules is postulated in $[CoCl_2(OH_2)_4] \cdot 2H_2O$. There it provides the only binding between adjacent sheets of cage-linked octahedra.

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Conclusion.—The features of secondary hydration which the structure of this compound has in common with those of two compounds $[MCl_2(OH_2)_4]\cdot 2H_2O$ are (i) the strong hydrogen bonding with the primary hydration sphere, and (ii) the ion–water association in cage formation. The secondary water–chloride ion hydrogen bonds appear to be relatively weak links in this structure. Continued existence of such cages when the solid is dissolved in water would provide a mechanism for the $[CrCl_2(OH_2)_4]^+\cdot Cl^-$ ion-pair association suspected to occur in aqueous hydrochloric acid solution.[23]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA 15213

Configurational and Vicinal Contributions to the Optical Activity of the Isomers of Tris(alaninato)cobalt(III)[1]

BY BODIE E. DOUGLAS AND SHOICHI YAMADA

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Four isomers of $[Co(L\text{-}ala)_3]$ (and the corresponding isomers of the D-alanine complex) have been isolated and characterized using circular dichroism (CD) data. Lifschitz's original assignment of the α' isomer as the opposite configuration to that of the α isomer (Δ) has been confirmed. The new β' isomer has been assigned as the opposite spiral configuration (Δ) to that of the β isomer (Λ). The vicinal and configurational contributions to the CD have been separated and demonstrated to be additive.

Introduction

Lifschitz[2] isolated three isomers from the reaction of $Co(OH)_3$ with *d*-alanine.[3] He designated the red isomer as β and the two violet isomers α and α'. He believed α and β to be geometrical isomers. The α and α' isomers were believed to represent the two spiral configurations (right and left) of the chelate rings. This was supported by the optical rotatory dispersion (ORD) curves of these isomers which indicated opposite configurations, although the ORD curves were not quite mirror images, as indeed, the isomers are not mirror images since the ligands are all *d*. He believed the β isomer to be a racemic mixture, unresolved because of its very low solubility.

The assignments of α-tris(glycinato)cobalt(III) as the 1,2,6 (peripheral) isomer and the β complex as the 1,2,3 (facial) isomer have been made based on absorption spectra,[4,5] infrared spectra,[6] and the study of model compounds.[7,8] Corresponding assignments were made of the α and β isomers of tris(alaninato)cobalt(III).[9]

Lifschitz's assumption concerning the configuration of α'-tris(alaninato)cobalt(III) seemed uncertain because this isomer, unlike the α and β isomers, is very soluble in water. This seemed inconsistent with the formulation of this as a neutral complex. He found that a cryoscopic molecular weight in water indicated that α' was a monomer. Swift[10] found the conductivity of the α' isomer to be low enough for a neutral complex, but it was still possible that one chelate ring was opened with another group, *e.g.*, H_2O, coordinated.

It has now been possible to isolate these three isomers (α, α', and β) as well as a fourth isomer, β', for the cobalt(III) complexes of D- and L-alanine. The study of the circular dichroism (CD) of these complexes makes it possible to assign their configurations and to separate the configurational and vicinal contributions to the optical activity as for other amino acid complexes.[11]

Experimental

The L- and D-alanine were purchased from Nutritional Biochemicals Corporation, Cleveland, Ohio. All other chemicals were reagent grade.

α- and β-Tris(glycinato)cobalt(III).—α- and β-$[Co(gly)_3]$ were

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