858. *The Crystal Structure of Di-μ-hydroxobistetramminedicobalt*(III) *Chloride Tetrahydrate.*

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The crystal structure of di-μ-hydroxobistetramminedicobalt(III) chloride tetrahydrate has been determined by three-dimensional techniques. The crystals contain binuclear cations in which the cobalt atom has a distorted octahedral co-ordination. These cations are arranged in layers separated from each other by two anion layers containing chloride ions and water molecules. The chlorine–oxygen hydrogen bond system is discussed and the probable configuration of the bridging hydroxyl group deduced.

In recent years some attention has been paid to the mutual interaction of metal ions held in close proximity by bridging groups in bi- and poly-nuclear complexes. These bridges may be halide, amido-, hydroxide, oxide, or alkylthio-ions. Although hydroxide is frequently found in this context little appears to be known about the structural behaviour of this ion or the complexes containing it. The spectra of complexes containing hydroxide bridges have been investigated by Schäffer,[1] and the paramagnetic susceptibilities by Earnshaw and Lewis.[2] It appears from their work that interaction between the metal ions, where possible, is slight except in the case of single hydroxyl bridges, and decreases as the number of bridging hydroxyl groups increases. Accordingly, the crystal structure of di-μ-hydroxobistetramminedicobalt(III) chloride tetrahydrate has now been determined. This complex represents the limiting case in which metal–metal interaction is not possible, directly or through the bridging group. It was chosen for the simplicity of the complex ion and the quality of its crystals.

Di-μ-hydroxobistetramminedicobalt(III) chloride tetrahydrate was first prepared by Werner [3] in 1907 and given the possible constitution (A). It readily crystallises as red

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[1] Schäffer, *J. Inorg. Nuclear Chem.*, 1958, **8**, 149.

[2] Earnshaw and Lewis, *J.*, 1961, 396.

[3] Werner, *Ber.*, 1907, **40**, 4437, 4820.

TABLE 1.

Observed structure amplitudes and calculated structure factors for (*hkl*), rounded from the computer figures used in calculating *R*.

h k l	$5F_o$	$5F_c$
0.0.1	159	216
2	34	45
3	188	−236
4	70	−22
6	109	117
7	120	105
9	93	−83
10	191	−205
11	78	−62
0.1.0	224	252
1	199	187
2	193	−178
3	211	151
4	126	−104
5	99	132
6	154	111
7	226	224
9	55	21
10	93	−96
11	62	−63
−1	165	163
−2	148	−158
−3	325	−358
−4	128	−153
−5	133	−107
−6	179	186
−7	81	70
−8	123	125
−9	70	−60
−10	42	−44
−11	96	−94
−12	76	79
0.2.0	54	55
1	116	93
2	149	−141
3	194	−181
4	135	−163
5	107	−67
6	120	91
7	51	21
8	79	72
9	60	−36
11	77	−75
−1	250	227
−2	175	−96
−3	275	184
−4	79	−35
−5	106	85
−6	133	113
−7	185	208
−8	81	70
−10	83	−68
−11	88	−98
0.3.0	534	574
1	93	124
2	77	−4
3	195	−152
4	36	−24
6	123	109
9	106	−116
10	152	−176
11	54	−75
−1	206	237
−2	45	0
−3	68	−45
−4	32	−27
−7	86	98
−10	148	−134
−11	60	−73
0.4.0	250	247
1	75	23
2	160	−124
3	46	−71
4	123	−66
5	146	93
6	141	163
7	180	156
−1	157	159
−2	60	−91
−3	317	−275
−4	113	−156
−5	128	−70
−6	148	107
−7	95	132
−8	126	106
−11	73	−64
0.5.0	38	95
1	95	21
2	145	−103
3	138	−156
4	161	−142
−1	200	149
−2	71	8
−3	82	−14
−4	64	−31
−5	52	20
−6	132	128
−7	168	173
−8	86	90
−10	63	−74
−11	80	−90
0.6.0	224	207
1	43	77
2	57	−15
3	114	−60
6	73	42
−1	144	146
−6	54	−18
−7	80	59
0.7.0	136	104
1	34	−28
2	99	−92
3	68	−77
5	86	73
6	83	119
7	81	89
−1	54	97
−3	179	−133
−4	43	−99
−5	73	−53
−6	57	18
−7	70	90
−8	88	90
0.8.2	114	−93
3	93	−133
4	88	−91
−6	73	72
−7	68	122
−8	68	81
0.9.0	82	107
−1	77	93
1.0.1	45	43
2	96	−131
3	310	−436
4	269	−351
5	40	49
6	57	62
7	134	111
8	56	−33
9	63	17
10	108	−114
1.1.0	254	310
1	257	319
2	94	−83
3	64	−74
4	172	−162
5	92	54
6	87	−32
7	64	−22
9	96	−88
10	96	−106
1.2.0	82	81
3	148	−137
6	185	176
7	65	75
8	120	85
9	100	−80
10	82	−89
1.3.0	202	118
1	45	−4
2	129	−136
3	325	−356
4	186	−225
6	96	93
7	86	72
8	61	−19
10	89	−92
1.4.0	242	261
1	206	162
2	137	−71
3	121	−171
4	148	−96
5	101	63
8	53	−38
9	72	−94
1.5.0	60	55
2	71	−67
3	95	−84
6	113	86
7	59	76
8	84	45
1.6.0	87	20
1	84	−20
2	73	−105
3	200	−182
4	87	−113
6	55	51
1.7.0	142	142
1	111	73
2	93	−64
3	77	−127
4	67	−33
5	78	62
1.8.3	57	−83
4	35	−7
1.−1.1	64	74
2	63	66
3	193	−245
4	78	−60
5	0	5
6	254	270
7	116	116
8	99	87
9	95	−86
10	120	−131
11	71	−78
1.−2.2	61	−34
3	34	−48
4	144	−141
7	51	−21
9	104	−91
10	85	−115
11	104	−126
1.−3.1	59	62
2	76	−68
3	180	−233
4	216	−250
5	37	7
6	40	36
7	86	66
8	52	19
9	77	46
10	65	−59
1.−4.2	84	48
3	155	−111
4	47	−107
5	46	23
6	183	187
7	88	138
8	63	59
1.−5.1	228	198
3	70	−94
4	135	−129
5	55	−44
6	63	48
8	109	17
1.−6.1	118	48
2	97	−40
7	73	53
1.−7.2	102	117
2	138	49
3	89	−23
1.−8.1	182	146
3	91	−64
4	85	−99
5	77	−55
6	65	25
1.−9.1	64	57
2	61	−25
3	116	92
1.0.−3	163	−227
−4	50	27
−5	95	−57
−6	389	355
−7	305	268
−8	212	156
−9	94	−91
−10	75	−75
−11	54	−50
1.−1.−1	123	120
−2	159	−165
−3	272	−306
−4	165	−188
−5	46	−17
−6	36	25
−7	231	205
−8	35	5
−9	78	42
−10	84	−76
−11	42	29
1.−2.−1	266	267
−2	91	−49
−3	234	154
−4	52	6
−5	53	−8
−6	55	−0
−7	171	120
−8	26	27
−9	116	−95
−10	94	−91
−11	101	−105
1.−3.−1	43	38
−2	53	−49
−3	80	−32
−4	73	13
−5	65	−3
−6	327	253
−7	183	217
−8	157	105
−9	114	−73
−10	37	−61
−11	82	−56
1.−4.−1	61	82
−2	139	−150
−3	311	−243
−4	157	−154
−5	33	−26
−6	104	116
−7	158	132
−8	43	−1
−10	111	−67
1.−5.0	313	301
−1	214	129
−2	100	−23
−3	91	−8
−4	80	−7
−5	77	10
−7	115	78
−9	74	−79
1.−6.0	92	79
−4	36	−8
−6	138	131
−7	98	138
−8	96	50
−9	51	−24
1.−7.0	161	102
−2	51	−99
−3	144	−122
−4	69	−97
−5	32	−14
−6	89	79
−7	67	63
1.−8.0	151	178
−1	97	59
−2	58	−38
−4	48	−13
1.−9.0	26	62
−3	37	−27
1.1.−2	110	−73
−3	164	92
−4	70	−35
−6	55	34
−7	178	149
−8	114	90
−9	202	−148
−10	97	−98
−11	119	−124
1.2.−1	91	73
−2	137	−127
−3	206	−183
−4	172	−150
−6	101	−55
−7	225	170
−8	25	63
−9	112	60
−10	78	−46
1.3.−1	128	139
−2	128	77
−3	197	−119
−5	59	−20
−6	98	190
−7	240	229
−8	171	130
−10	74	−64
−11	35	−39
1.4.−1	285	200
−3	80	−65
−4	147	−102
−5	92	−93
−6	83	41
−7	122	148
−8	139	87
−9	146	−109
−10	90	−123
−11	88	−82
1.5.−1	93	44
−2	107	−70
−3	136	−158
−4	177	−121
−6	89	−4
−7	162	113
−8	68	106
−9	60	15
−10	56	−46
−11	14	−24
1.6.−1	58	80
−2	108	58
−3	92	−29
−4	48	−46
−5	36	−4
−6	107	72
−7	109	129
−8	88	96
−9	52	8
−10	39	−39
1.7.−1	67	123
−2	64	48
−3	62	−37
−4	81	−95
−5	82	−89
−6	42	−5
−7	38	89
−8	80	66
−9	66	−43
1.8.−1	66	49
−2	77	−29
−3	76	−109
−4	124	−108
−7	91	89

TABLE 1. (*Continued.*)

h k l	$5F_o$	$5F_c$
2.0.1	135	153
2	151	−167
3	89	−87
4	174	−150
5	126	125
6	112	79
7	192	176
8	30	1
9	55	−42
10	54	−84
11	21	−30
2.1.0	225	−221
1	33	4
2	116	−126
3	231	−259
4	176	−189
5	81	−64
6	88	77
7	53	32
8	62	56
9	63	−56
10	49	9
2.2.0	238	249
1	60	84
2	47	4
3	219	−253
4	57	−66
6	71	70
9	96	−107
10	93	−109
2.3.0	120	116
1	71	33
2	177	−151
3	113	−138
4	95	−60
5	138	106
6	108	131
7	143	153
9	48	−65
2.4.0	107	−15
1	46	−9
2	187	−140
3	194	−197
4	152	−143
6	71	71
7	53	62
2.5.0	151	111
1	64	82
2	58	−23
3	131	−108
6	50	42
2.6.0	76	57
2	78	−98
3	64	−81
5	77	75
6	71	109
2.7.2	120	−115
3	106	−135
4	84	−78
2.8.0	88	83
2.−1.1	94	135
2	32	22
3	293	−367
4	172	−159
6	72	68
7	67	54
8	72	−43
9	105	−106
10	133	−151
11	36	−28
2.−2.1	49	−24
2	38	−53
3	318	−338
4	190	−220
5	97	−74
6	122	109
7	60	48
8	89	72
9	69	−61
11	44	−38
2.−3.1	176	113
2	84	−17
3	58	−32
4	155	−107
5	88	58
6	80	75
7	134	112
10	65	−68
2.−4.0	350	290
1	146	170
2	58	11
3	228	−199
4	192	−180
7	61	35
8	51	−17
9	53	−72
10	121	−111
2.−5.0	74	50
3	336	−250
4	192	−221
5	88	−38
6	134	94
7	60	87
8	77	54
9	53	−28
2.−6.0	76	31
1	144	73
4	114	−78
6	80	90
7	84	87
2.−7.0	170	134
1	80	105
3	65	−74
2.−8.0	76	52
3	116	−126
4	90	−147
5	61	−35
6	57	57
2.−9.1	76	73
3	71	−33
2.0.−2	66	−93
−3	301	−465
−4	214	−266
−5	155	−138
−6	168	155
−7	110	88
−8	170	162
−9	92	−103
−11	69	−54
−12	93	84
2.−1.−2	144	178
−3	173	−212
−4	114	−83
−5	43	−66
−6	101	102
−7	181	152
−8	29	13
−9	116	−99
−10	160	−156
−12	55	−46
2.−2.−2	87	−37
−3	108	11
−4	190	−156
−5	144	100
−6	122	111
−7	241	251
−8	77	66
−9	53	27
−10	50	−31
−12	30	−31
2.−3.−1	167	109
−2	135	−91
−3	254	−255
−4	184	−184
−5	103	−68
−6	103	71
−7	80	90
−8	107	82
−9	73	−60
−11	58	−29
2.−4.−1	96	129
−2	134	41
−3	217	−137
−6	140	126
−7	132	135
−9	118	−135
−10	115	−124
2.−5.0	86	50
−1	64	36
−2	113	−53
−3	67	−91
−4	133	−72
−5	113	58
−6	107	163
−7	209	191
−9	49	−27
2.−6.0	76	31
−1	121	55
−2	128	−64
−3	125	−140
−4	145	−111
−6	51	38
−7	55	68
−8	42	17
2.−7.0	162	134
−1	64	85
−2	67	7
−3	84	−42
−4	51	−11
−6	104	79
−7	55	83
2.−8.0	78	52
−2	66	−63
−3	63	−77
−4	44	−36
−5	66	46
−6	97	134
2.−9.0	33	60
−1	48	25
−2	74	−59
−3	50	−96
−4	66	−73
2.1.−1	108	117
−2	71	−31
−3	104	23
−4	230	−233
−5	109	96
−6	165	117
−7	238	243
−8	127	90
−10	63	−46
−11	38	−56
2.2.−1	44	42
−2	175	136
−3	83	−42
−4	152	−120
−5	51	−89
−6	56	−3
−7	128	111
−9	53	−45
−11	45	−20
2.3.−1	84	70
−3	338	−313
−4	210	−242
−5	181	−134
−6	115	68
−7	78	90
−8	139	129
−12	36	34
2.4.−1	158	100
−2	50	39
−3	52	−89
−4	209	−182
−6	166	146
−7	169	178
−8	105	102
−10	90	−69
2.5.−1	60	66
−2	101	67
−4	130	−115
−5	42	−89
−6	47	2
−7	76	68
2.6.−1	50	36
−3	179	−121
−4	109	−149
−5	109	−98
−8	71	83
2.7.−1	87	90
−3	37	−56
−4	105	−120
−6	79	81
−7	80	112
−8	72	81
2.8.−1	54	70
−2	49	51
−4	95	−102
−5	44	−81
3.0.0	126	149
1	158	185
2	125	−125
3	65	−81
4	148	−126
7	72	48
9	78	−78
3.1.0	50	71
3	53	−63
4	79	51
6	171	160
7	111	98
8	70	63
9	68	−57
3.2.0	73	59
1	118	−94
2	117	−126
3	184	−188
4	116	−126
6	117	113
7	126	126
3.3.0	185	182
1	137	109
2	131	−90
3	77	−106
4	112	−85
5	74	51
6	57	81
7	68	54
8	54	−46
3.4.0	81	89
2	69	−67
3	49	−39
4	54	19
6	120	119
7	70	89
3.5.0	49	18
1	112	−65
2	47	−88
3	90	−93
4	58	−68
6	72	79
3.6.0	108	110
1	58	38
2	62	−46
3	41	−73
4	52	−30
3.7.0	45	77
3	3	−49
3.−1.1	61	−58
0	53	84
2	142	−163
3	237	−250
4	171	−202
6	107	97
7	186	169
10	42	−53
3.−2.0	94	100
3	115	−119
4	63	2
5	45	−7
6	228	166
7	140	137
8	63	56
9	79	−74
10	56	−74
3.−3.0	80	114
1	184	123
2	109	−60
3	69	−94
4	119	−103
5	59	−49
7	49	36
8	45	3
9	86	−74
10	41	−52
3.−4.0	43	13
1	44	−20
2	123	−102
3	190	−192
4	170	−166
5	47	−32
7	139	118
9	36	−14
10	32	−24
3.−5.1	53	86
2	53	−9
3	151	−95
6	141	112
7	118	138
8	60	43
9	58	−63
3.−6.3	98	−102
4	105	−106
5	62	−56
6	46	12
8	46	11
3.0.−3	65	−37
−4	269	−252
−6	71	88
−8	64	37
−9	152	−133
−10	126	−111
−11	161	−152
3.−1.−3	216	−310
−4	162	−191
−5	61	−31
−6	313	289
−7	106	118
−8	132	112
−10	61	−54
−11	55	−60
3.−2.−3	337	−299
−4	238	−272
−5	65	−42
−6	52	−24
−7	57	51
−8	62	−5
−9	91	52
−10	115	−76
3.−3.−3	40	−26
−4	199	−145
−5	72	6
−7	73	58
−9	99	−77
−10	92	−107
−11	104	−100
3.−4.−3	246	−194
−4	149	−158
−6	265	207
−7	90	141
−8	120	84
−9	59	−33
−10	52	−55
−11	38	−40
3.−5.−3	324	−265
−4	220	−195
−6	62	55
−7	63	43
−10	91	−53
3.−6.−4	108	−54
−5	63	29
−7	82	43
3.−7.−3	119	−100
−4	62	−72
−6	134	112

TABLE 1. (*Continued.*)

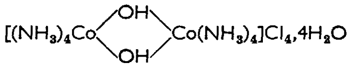
h k l	$5F_o$	$5F_c$
−7	49	102
−8	85	52
3.−8.0	98	58
−3	183	−161
−4	83	−110
−6	58	52
3.−9.0	87	88
−1	69	67
−2	46	−2
−3	42	−66
−4	36	−25
3.1.−1	40	23
−2	91	−99
−3	279	−198
−4	311	−278
−5	66	−56
−6	112	−75
−7	100	73
−8	64	0
−9	91	74
−10	99	−84
3.2.−1	39	61
−2	106	80
−3	204	−177
−4	136	−145
−5	82	−39
−6	206	176
−7	62	94
−8	90	76
−9	63	37
−10	60	−43
−11	64	−65
3.3.−1	207	179
−2	58	69
−3	72	−63
−4	233	−203
−5	96	−116
−6	86	78
−7	62	79
−8	63	30
−9	135	−93
−10	82	−104
−11	130	−126
3.4.−1	88	61
−2	88	−64
−3	126	−154
−4	242	−198
−5	75	−95
−6	63	−9
−7	109	73
−9	58	20
−10	72	−66
−11	57	−63
3.5.−1	49	75
−2	82	48
−3	89	−61
−4	70	−93
−5	63	−10
−6	98	82
−7	77	74
−8	54	53
−9	66	42
−10	54	−27
3.6.−1	91	124
−2	63	84
−4	90	−121
−5	92	−99
−6	50	18
−8	44	15
−9	72	−27
3.7.−1	91	70
−3	69	−93
−4	148	−131
−5	67	−95
−6	46	−2
4.0.0	42	19
1	54	−37
2	111	−116
3	117	−96
4	101	−70
6	134	108
7	77	68
8	73	56
4.1.0	197	225
2	53	20
3	90	−101
6	85	80
4.2.0	186	163
1	55	34
2	100	−86
3	49	−33
5	134	117
6	116	121
7	110	117
4.3.0	58	63
2	143	−123
3	90	−99
4	89	−69
5	41	27
6	95	95
4.4.0	162	129
2	58	−5
4.5.0	97	85
4.1.−1	94	110
−2	110	109
−3	38	−27
−4	57	−68
−5	59	−67
−6	43	4
−7	70	64
−8	49	−27
−10	117	−132
−11	87	−84
4.2.−1	118	115
−2	56	−38
−3	188	−199
−4	109	−133
−5	150	−147
4.3.−1	190	170
−2	85	1
−3	79	−95
−4	157	−131
−6	109	92
−7	130	131
4.4.−1	142	133
−2	104	82
−3	69	−10
−4	102	−83
−5	49	−57
−7	89	66
4.5.−1	66	71
−3	110	−83
−4	58	−87
−5	126	−93
4.6.−1	161	122
−3	50	−57
−4	75	−70
−6	69	42
−7	61	78
4.7.−2	64	74
−4	60	−82
4.0.−3	34	−64
−4	156	−185
−5	54	61
−6	86	75
−7	133	160
−8	69	64
−9	40	47
−10	75	−70
−11	105	−121
4.−1.−4	106	−194
−5	114	−143
−6	76	61
−7	36	14
−8	81	94
−9	74	−66
−10	70	−61
4.−2.−3	78	−102
−4	46	−71
−5	54	−56
−6	47	61
−7	57	48
−9	49	−46
−10	137	−140
−11	79	−87
4.−3.−1	68	63
−2	97	−74
−3	31	−78
−4	154	−135
−5	61	43
−6	50	74
−7	115	113
−9	75	59
−10	70	−55
−11	55	−77
4.−4.0	85	118
−1	117	92
−2	131	−107
−3	193	−207
−4	165	−179
−5	104	−74
−6	61	22
−7	49	18
−8	49	36
−9	66	−32
−10	46	−80
−11	78	−75
4.−5.0	216	213
−1	76	104
−2	88	8
−3	150	−102
−4	53	−78
−5	48	8
−6	112	85
−7	49	50
−9	82	−75
−10	98	−127
4.−6.0	82	57
−2	86	−66
−3	78	−109
−4	124	−87
−5	70	36
−6	56	93
−7	106	75
−9	57	24
4.−7.0	40	75
−1	78	40
−2	97	−67
−3	103	−131
−4	116	−111
−5	46	−32
−7	38	1
4.−8.0	121	115
−1	45	64
−2	45	−7
−3	90	−64
−6	78	62
4.−9.0	61	47
−1	29	3
−2	58	−59
−3	77	−96
−4	64	−54
−5	29	43
4.−1.1	103	93
2	119	−111
3	75	−8
4	57	−32
5	136	111
6	139	115
4.−2.1	44	61
3	128	−132
4	70	−69
6	91	79
7	82	70
9	52	−59
4.−3.1	61	−55
2	71	−90
3	120	−110
4	79	−73
5	69	−33
6	118	97
7	81	90
4.−7.1	85	51
2	49	−10
3	47	−11
6	42	55
7	75	82
4.−8.1	37	68
2	51	−29
3	48	−63

TABLE 2.

Atomic co-ordinates (× 10^4) and standard deviations (× 10^4).

	x/a	*σ(x)*	*y/b*	*σ(y)*	*z/c*	*σ(z)*
Co	139	6·1	99	3·8	1484	2·9
Cl(1)	3500	11·9	6615	7·6	568	5·7
Cl(2)	8430	13·2	6918	7·6	4627	5·5
N(1)	942	39	2757	27	1723	16
N(2)	9273	40	7473	23	1433	19
N(3)	2608	45	339	26	3225	19
N(4)	7970	37	29	21	2431	17
O(1)	1978	29	223	20	314	14
O(2)	5954	134	3153	20	2495	18
O(3)	3336	50	6932	31	4024	22

prismatic needles with well-developed faces. The crystals are stable in air and in an *X*-ray beam.


$[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4,4H_2O$

(A)

Crystal Data.—$H_{34}Cl_4Co_2N_8O_6$. *M,* 501·7. Triclinic pinacoidal; $a = 6{\cdot}72 \pm 0{\cdot}03$,

$b = 7{\cdot}76 \pm 0{\cdot}03$, $c = 10{\cdot}06 \pm 0{\cdot}03$ Å, $\alpha = 92{\cdot}8° \pm 0{\cdot}2°$, $\beta = 106{\cdot}3° \pm 0{\cdot}2°$, $\gamma = 106{\cdot}5° \pm 0{\cdot}2°$. $U = 469{\cdot}2$ Å^3. $D_m = 1{\cdot}78 \pm 0{\cdot}01$ (by flotation), $Z = 1$, $D_c = 1{\cdot}776$, $F(000) = 260$. $\mu = 320$ cm.$^{-1}$ Space group, $P\bar{1}$ (C^1_i, No. 2). Cu-K_α radiation, single-crystal oscillation and Weissenberg photographs. Optically biaxial.

A three-dimensional Patterson function, sharpened to " point atoms at rest," was computed, from 1072 independent reflections. All the major peaks in the distribution could be interpreted on the assumption of cobalt and chlorine atoms, related by a centre of symmetry. Minor peaks suggested preliminary positions for the light atoms of the cation. The distribution contained no evidence to suggest the possibility of space group $P1$. A three-dimensional F_o synthesis, phased on the contributions of the three heavy and five light atoms whose parameters were deduced from the Patterson function, had regions of high electron density in possible positions for the water molecules.

Seven cycles of least-squares refinement were evaluated by using a block diagonal approximation to the normal matrix. The weighting function $\sqrt{w} = |F_o|/F_*$ if $|F_o| < F_*$; if not, $\sqrt{w} = F_*/|F_o|$ was used, F_* being given a value of 28·0 on an absolute scale. Anisotropic temperature parameters were introduced after the third cycle. After the refinement the reliability index was 0·154. At no stage in the refinement was it possible to deduce hydrogen atom positions from three-dimensional difference syntheses.

Table 1 gives the observed and the calculated structure factors based on the final atomic co-ordinates that are listed in Table 2. Thermal parameters are given in Table 3. The standard deviations recorded are minimum values deduced from the block-diagonalised normal matrix. The atomic co-ordinates given in Table 4 are referred to a set of orthogonal axes X', Y', Z' with their origin at the cell origin, and defining the least-squares best plane through the metal, bridging hydroxyl groups, and peripheral nitrogen atoms. The transformation matrix from the orthogonal co-ordinates a, b', and c^* (in Å) to these co-ordinates is:

$$\begin{pmatrix} 0{\cdot}2231 & 0{\cdot}0867 & -0{\cdot}9709 \\ 0{\cdot}9717 & 0{\cdot}0600 & 0{\cdot}2286 \\ -0{\cdot}0781 & 0{\cdot}9944 & 0{\cdot}0709 \end{pmatrix}$$

TABLE 3.

Thermal parameters ($\times 10^4$). The temperature factor T is equal to $\exp. -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	193	81	49	9	21	−12
Cl(1)	341	174	107	−21	113	101
Cl(2)	638	192	73	1	196	222
N(1)	497	327	92	−44	72	281
N(2)	622	102	94	20	113	−134
N(3)	581	180	68	−8	103	364
N(4)	371	121	101	78	385	299
O(1)	321	240	75	−43	−9	37
O(2)	518	149	190	18	334	−397
O(3)	929	570	233	227	870	902

TABLE 4.

Atomic co-ordinates (Å) referred to a set of orthogonal axes defining the least-squares best plane through the cobalt, bridging hydroxyl groups, and peripheral nitrogen atoms.

	X'	Y'	Z'		X'	Y'	Z'
Co	1·4660	0·0208	0·0025	O(1)	0·0145	−1·2336	−0·0516
Cl(1)	0·0979	−2·8208	2·7720	O(2)	−3·0604	−3·3334	2·4900
Cl(2)	−4·7691	−2·4890	5·1172	O(3)	−4·9276	−5·7789	5·4215
N(1)	−1·5543	0·0387	1·9620				
N(2)	1·5855	0·1395	1·9389				
N(3)	2·8383	−1·4400	0·0229				
N(4)	2·7422	1·4859	0·0213				

Some interatomic distances and angles are listed in Table 5, together with standard deviations deduced from the formulæ of Cruickshank[4] and Darlow.[5]

TABLE 5.

Some interatomic distances (Å) and angles.

(Numbers in parentheses are standard deviations.)

Co–Co′	2·932 (0·005)	Cl(1)–O(1)	3·24 (0·02)	N(2)–Co–N(4)	85·7° (0·9)
Co–O(1)	1·911 (0·015)	Cl(1)–O(1)′	3·68 (0·02)	N(2)–Co–O(1)	96·5° (0·8)
Co–O(1)′	1·913 (0·015)	Cl(1)–O(2)	3·21 (0·02)	N(2)–Co–O(1)′	88·9° (0·8)
Co–N(1)	1·96 (0·02)	Cl(2)–O(2)	3·24 (0·02)	N(3)–Co–N(4)	95·8° (1·0)
Co–N(2)	1·95 (0·02)	Cl(2)–O(3)	3·32 (0·03)	N(3)–Co–O(1)	92·5° (0·9)
Co–N(3)	2·00 (0·03)	Cl(2)–O(3)′	3·38 (0·03)	N(3)–Co–O(1)′	171·9° (0·9)
Co–N(4)	1·95 (0·02)	O(1)–Co–O(1)′	79·9° (0·5)	N(4)–Co–O(1)	171·5° (0·9)
Co–Cl(1)	4·20 (0·01)	N(1)–Co–N(2)	174·1° (0·7)	N(4)–Co–O(1)′	92·0° (0·8)
Co–Cl(1)′	4·223 (0·01)	N(1)–Co–N(3)	87·9° (1·0)	Co–O(1)–Co′	100·1° (0·5)
Co–Cl(1)″	4·32 (0·01)	N(1)–Co–N(4)	89·4° (0·8)	Cl(1)–O(1)–Co	106·7° (0·6)
Co–Cl(2)	4·31 (0·01)	N(1)–Co–O(1)	88·9° (0·7)	Cl(1)–O(1)–Co′	107·6° (0·6)
Co–Cl(2′)	4·16 (0·01)	N(1)–Co–O(1)′	94·5° (0·7)	Cl(1)–O(2)–Cl(2)	113·9° (0·6)
				Cl(2)–O(3)–Cl(2)′	96·7° (0·8)

The crystal is made up of binuclear complex cations, simple chloride anions, and water of crystallisation not associated with the metal atoms.

In the cation two cobalt atoms, 2·93 Å apart, are bound to a pair of oxygen atoms equidistant from each metal, and 1·23 Å from the line between their centres. Four nitrogen atoms of ammine groups complete an irregular octahedral co-ordination sphere around each metal atom. The bonded distances within the cation are only slightly longer than the sum of covalent radii. The angle made by the metal–oxygen linkages at the cobalt atom is 79·9°, considerably less than the octahedral angle. The nitrogen atoms N(1) and N(2)′ are displaced towards nitrogen atoms N(3) and N(4)′, respectively. If this were entirely a mutual repulsion effect between N(1) and N(2)′, it would be expected that the displacement would be towards either N(3) and N(3)′, or N(4) and N(4)′. The cation, together with some neighbouring atoms, is shown in Fig. 1, projected on to, and perpendicular to, the plane of the cation, as defined as for the co-ordinates in Table 4.

The cations are arranged in layers parallel to the (010) plane at $y = 0$ with the plane of the cation almost parallel to the crystal plane. The cation layers are separated by two layers at heights $\frac{1}{3}b$ and $\frac{2}{3}b$, containing both chloride ions and water molecules (Fig. 2a and b). Each cation has eight chloride ions as nearest neighbours at between 4·16 and 4·31 Å from the cobalt atoms. The water molecules each have two shorter oxygen–chlorine contacts and the hydroxyl group one, all being between 3·21 and 3·38 Å. Similar short contacts, said to be oxygen–chlorine hydrogen bonds, were observed by Vainshtein[6] (using electron diffraction) in cobalt(II) and manganese(II) chloride dihydrate, and by Levy and Peterson[7] (using neutron-diffraction techniques) in copper(II) chloride dihydrate. Levy and Peterson further demonstrated that the hydrogen atoms lie approximately on the line between atomic centres at about 1 Å from the oxygen. In all three salts the short contact distances give approximately tetrahedral angles at the oxygen atoms.

The short oxygen–chlorine vectors observed in our structure have very similar characteristics to those in the metal(II) chloride dihydrates and are believed to be hydrogen bonds, the adjacent layers of the structure being held together by a network of weak hydrogen bonds. The positions, relative to the cation, of the four best-established hydrogen bonds are shown in Fig. 1 [Cl(1)—O(1), Cl(1)—O(2), O(2)—Cl(2), and Cl(2)—O(3)].

If we assume, from Levy and Peterson's observations, that the hydroxyl-hydrogen lies

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[4] Cruickshank, *Acta Cryst.*, 1953, **6**, 385.

[5] Darlow, *Acta Cryst.*, 1960, **13**, 683.

[6] Vainshtein, *Doklady Akad. Nauk S.S.S.R.*, 1952, **83**, 722.

[7] Levy and Peterson, *J. Chem. Phys.*, 1957, **26**, 220.

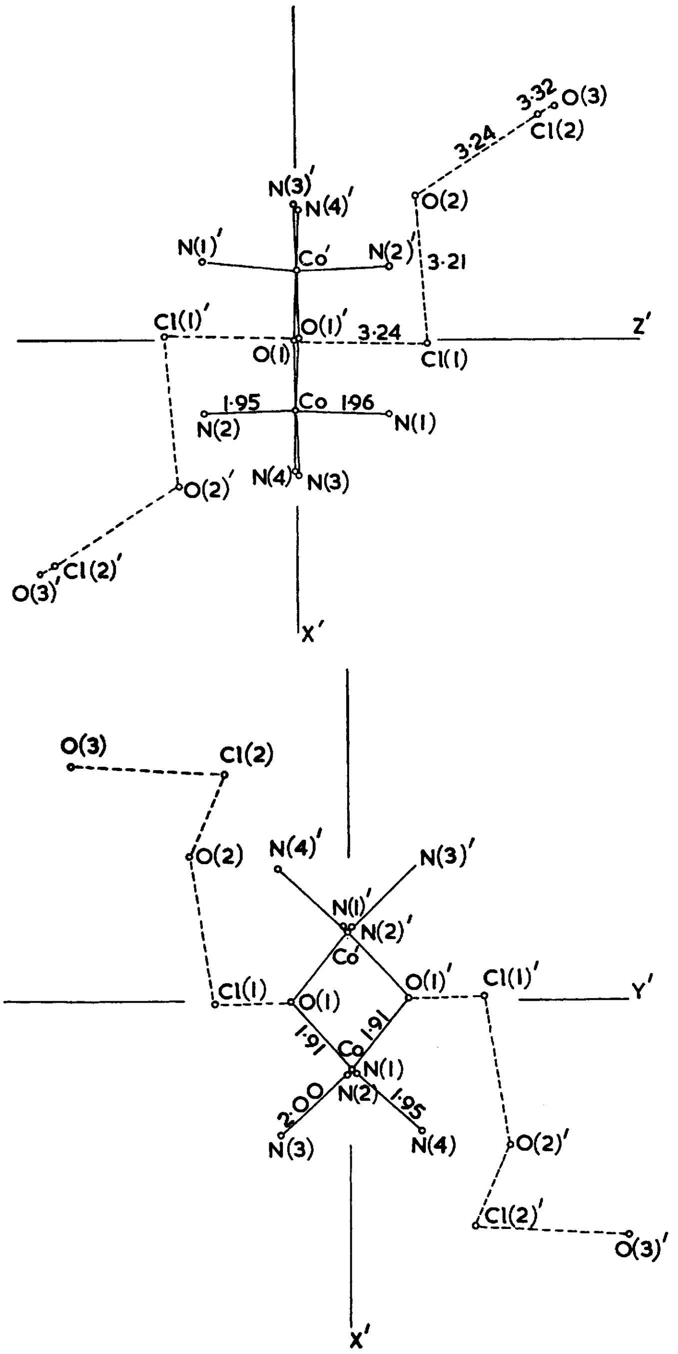

FIG. 1. The binuclear cation projected on to, and perpendicular to, the bent plane through the metal atoms, bridging groups, and peripheral nitrogen atoms, together with part of the hydrogen-bond system. Some interatomic distances are given (in Å).

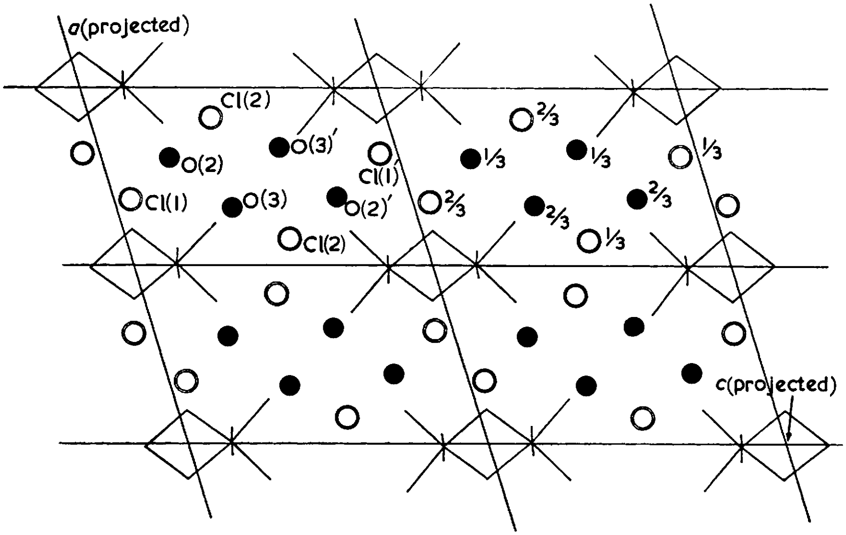

FIG. 2a.

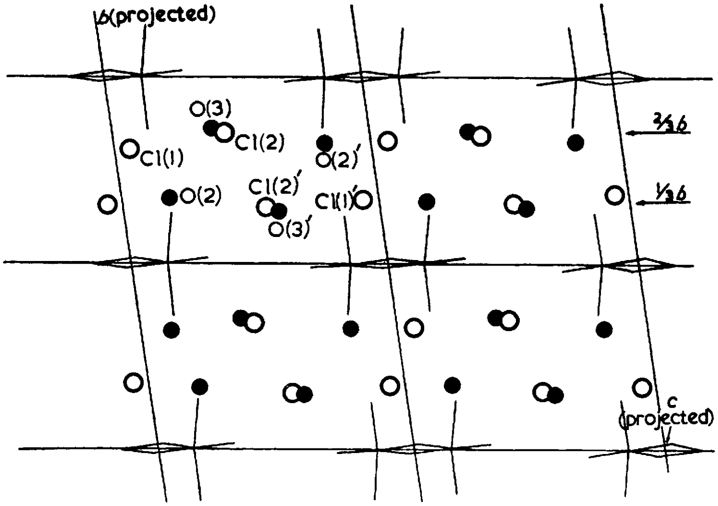

FIG. 2b.

FIG. 2. A schematic representation of the structure projected (a) on to the (100) plane and (b) on to the (010) plane.

along the oxygen–chlorine vector, which also is consistent with the displacements of N(1) and N(2)′, the oxygen atom is forming three bonds in a pyramidal array with apex angles of 100°, 108°, and 106°, of which the first is the Co–O(1)–Co′ bond angle. In the pyramidal hydronium ion H_3O^+, the apex angles have been reported as 112° in hydronium perchlorate [8] and 117° in hydronium chloride.[9] It is suggested that in our complex the oxygen atom has an approximately tetrahedral configuration, the lone pair of electrons occupying the fourth position in the tetrahedron. The Co–O(1)–Co′ angle is strained because of the necessary compromise with the O(1)–Co–O(1)′ angle which is expected to be 90°. It is probable that this configuration persists in similar compounds of chromium, *e.g.*, di-μ-hydroxybisdi-1,10-phenanthrolinedichromium(III) iodide tetrahydrate, in which there is, by magnetic criteria, little interaction between the unpaired *d*-electrons of the two bridged metal ions. The tetrahedral configuration at the oxygen atom does not permit p–d_π bonding between the metal and the oxygen, as suggested by Orgel and Dunitz [10] for the M–O–M bridged system. The behaviour of the hydroxyl group in cations with a triple hydroxyl bridge is probably similar, but for cations such as $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ a model shows that on steric grounds alone the M–O–M′ angle must be at least 140°.

Experimental.—Preparation. Dr. C. Schäffer of Copenhagen kindly supplied a sample of the compound prepared by Werner's method.[3]

X-*Ray photography.* The unit-cell dimensions were obtained from zero-layer Weissenberg photographs about the *a*-, *b*-, and *c*-axes, calibrated by means of the powder diffraction pattern of a copper wire. The angles were checked by optical goniometric measurements. The *X*-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg film about the needle axis obtained from crystals about 0·015 cm. thick. Similar intensity measurements from photographs about the *b*-axis were used only to obtain an approximate common scale for the observations (method of Rollett and Sparks [11]). The intensities were corrected for Lorentz and polarisation factors. No absorption or extinction corrections were applied.

Calculations. These were carried out on a Ferranti " Mercury " computer. Structure factors and cycles of least-squares refinement were calculated by using the " SFLS " programme of Rollett and Mills.[12] Atomic scattering factors for nitrogen, oxygen, and chlorine were as given by Berghuis *et al.*,[13] and for cobalt as given by Thomas and Umeda.[14] For Fourier syntheses Mills's general Fourier synthesis programme [12] was used, and for interatomic distances and angles Sparks's programme.[12]

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[10] Orgel and Dunitz, *J.*, 1953, 2594.

[11] Rollett and Sparks, *Acta Cryst.*, 1960, **13**, 273.

[12] Rollett and Mills, " Computing Methods and the Phase Problem in X-ray Analysis," Pergamon Press, London, 1961, p. 107.

[13] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[14] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.