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Redetermination of the Crystal Structure of Chloropentamminecobalt(III) Dichloride

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The crystal structure of $[Co(NH_3)_5Cl]Cl_2$ has been redetermined from three-dimensional counter data at room temperature. The crystals are orthorhombic (*Pnma*) with lattice constants $a=13{\cdot}26$, $b=10{\cdot}34$, both $\pm 0{\cdot}01$, and $c=6{\cdot}72\pm 0{\cdot}005$ Å. The structure is made up of molecular ions, $Co(NH_3)_5Cl^{2+}$ and Cl^- ions, separated by ordinary van der Waals distances. There is no evidence for a *trans* distortion of the Co–N bond by the Co–Cl bond. The four independent Co–N distances were found to be: $1{\cdot}962\pm 0{\cdot}004$, $1{\cdot}964\pm 0{\cdot}006$, $1{\cdot}978\pm 0{\cdot}006$ and $1{\cdot}998\pm 0{\cdot}006$ Å. The nitrogen associated with the longest Co–N distance appears to be involved in a N–Cl intermolecular hydrogen bond.

Introduction

We have been interested in the bond length changes that occur with *trans*-directing ligands in transition metal complexes. In some cases substantially different bond lengths have been found than would be expected from the sum of the covalent radii, *e.g.* in Pt(II) complexes with phosphines (Messmer & Amma, 1966; Messmer, Amma & Ibers, 1967). The previous X-ray investigation of chloropentamminecobalt(III) dichloride $[Co(NH_3)_5Cl]Cl_2$ reported a significantly shorter Co–N distance *trans* to the halogen compared with the other four Co–N distances (Shigeta, Komiyama & Kuroya, 1963). However, these results were based on only two-dimensional data and incomplete refinements. Further, these results have been used in the interpretation of the optical spectra of single crystals of Co(III) complexes (Wentworth & Piper, 1965). To clarify the situation regarding bond lengths in $Co(NH_3)_5Cl^{2+}2Cl^-$, we decided to reinvestigate the crystal structure by using counter data.

Experimental

$[Co(NH_3)_5Cl]Cl_2$ was prepared by the method of Hynes, Yanowski & Schiller (1938). Single crystals suitable for diffraction purposes were grown by slow evaporation of a warm, concentrated aqueous solution. A crystal 0·18 mm × 0·20 mm × 0·33 mm was selected for X-ray diffraction intensity data. Since the absorption factor (μ) for this crystal with Mo $K\alpha$ radiation is only 27 cm^{-1}, no corrections were made for absorption.

Preliminary precession and Weissenberg data were used to establish the probable space groups. Calibrated precession photographs were used to find the cell constants. The crystals are orthorhombic with cell constants ($\lambda=0{\cdot}7107$ Å) $a=13{\cdot}26$, $b=10{\cdot}34$, both $\pm 0{\cdot}01$ and $c=6{\cdot}72$, $\pm 0{\cdot}005$ Å. The observed systematic absences (for $0kl$, $k+l=2n+1$, for $hk0$, $h=2n+1$) specified the possible space groups as *Pnma* or $Pn2_1a$. The structure analysis established the space group as *Pnma* (*vide infra*). There are four $[Co(NH_3)_5Cl]Cl_2$ entities per cell and the X-ray density is 1·81 $g.cm^{-3}$.

A total of 1011 independent pieces of *hkl* intensity data were collected with Zr-filtered Mo $K\alpha$ radiation on a Picker diffractometer with a General Electric single-crystal orienter. Backgrounds were estimated by stationary counting for 20 seconds at ±0·67° 2θ from the peak maximum. The peaks were then scanned for 40 seconds by a θ–2θ scan and the integrated intensity was simply taken as the total counts from the scan minus the sum of the two background counts. This assumes a linear variation in background through the peak. The stability of the generator and counting circuitry was checked by examining a standard reference peak every two hours.

Structure determination and refinement

Initially space group *Pnma* (*International Tables for X-ray Crystallography*, 1952) was assumed. *Pnma* has an eightfold set of general positions; hence, cobalt, one chlorine atom, and at least one of the nitrogen atoms in the asymmetric unit must be in special positions. In this space group there are three sets of fourfold special positions, two of which are centers of symmetry and one of which has mirror symmetry. With the molecule ion, $Co(NH_3)_5Cl^{2+}$, it is not possible to place the cobalt, chlorine or nitrogen atoms on centers of symmetry; but Co, Cl and at least one nitrogen atom can be placed on the mirror at $y=\frac{1}{4}$. An unsharpened three-dimensional Patterson* vector map indicated that not only cobalt, Cl(1) and one nitrogen N(1), but also N(2) and N(3) were in special positions; and N(4) and Cl(2) were in general positions. Cl(2) is the ionic chlorine, *i.e.* not directly bonded to the cobalt atom. The appropriate coordinates for all the atoms were found from this Patterson function. This assignment of atomic

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* Patterson and Fourier calculations performed with Sly–Shoemaker–van den Hende Fourier Program ERFR2 for the IBM 7090 computer.

Table 1. *Observed and calculated structure factors*

$$F(c)=10\,F(\text{calc})$$

$$F(\text{calc})_{\text{absolute}}=\frac{F(\text{calc})}{\text{Scale factor}}$$

Non-observed reflections were not included in the refinement and are listed separately at the end of the listing. A few reflections that are obviously due to bookkeeping errors and poor background measurements are not listed. $F(c)$ min. ~ 10.

	F(O)	F(C)
H00		
2	96	104
4	244	-268
6	50	53
8	173	169
10	63	70
12	17	-15
H10		
2	260	-265
4	28	25
6	134	139
8	226	232
12	66	-62
H20		
0	161	-156
2	184	-194
4	270	-241
6	132	128
8	18	-18
10	217	-220
12	39	41
H30		
2	135	127
4	72	-67
6	80	-85
8	157	-161
10	15	-7
12	32	31
H40		
0	455	625
2	63	57
4	170	-165
6	71	69
8	131	128
10	29	33
12	20	-15
H50		
2	237	-219
4	30	-20
6	127	129
8	194	200
12	68	-65
H60		
0	175	-186
2	143	-138
4	63	-61
6	141	140
8	36	-32
10	201	-197
12	27	29
H70		
2	110	114
6	84	-82
8	120	-120
12	30	30
H80		
0	292	296
2	29	27
4	92	-85
6	61	59
8	77	76
H90		
2	87	-81
6	64	64
8	108	108
10	5	3
H100		
0	98	-96
2	85	-80
4	27	-25
6	94	91
8	21	-21
10	130	-128
H110		
2	93	96
6	67	-69
8	90	-90
12	28	34
H120		
0	175	175
2	18	19
4	65	-65
6	21	20
8	53	49
10	14	12
H130		
2	30	-32
4	7	1
6	29	30
8	53	53
H140		
0	32	-31
2	34	-36
4	21	-22
6	37	39
10	37	-60
H150		
2	49	50
6	31	-37
8	45	-47
12	17	21
H160		
0	94	99
2	19	13
4	42	-47
8	18	30
10	18	20
H170		
2	28	-29
6	22	23
8	33	35
H180		
0	18	-16
6	17	18
H01		
1	113	120
2	101	-73
3	129	129
4	236	-239
5	58	-49
6	21	12
7	87	-83
8	226	239
9	82	80
10	45	-47
11	60	59
12	174	-171
H11		
0	258	-258
1	65	-57
2	42	-31
3	32	-30
4	154	157
5	105	105
6	130	125
7	131	132
8	80	-78
9	96	100
10	109	-112
11	16	9
12	4	-1
H21		
1	205	-220
2	301	334
3	105	93
4	35	-33
5	17	10
6	139	-136
7	84	-83
8	24	27
9	4	4
10	65	64
11	23	23
12	9	4
H31		
0	122	116
1	22	16
3	15	-10
4	68	-72
5	86	-83
6	74	-71
7	96	-96
8	52	53
9	84	-85
10	75	75
11	18	-17
12	5	-2
H41		
1	73	67
2	31	-17
3	101	101
4	160	-155
5	20	-18
6	12	-10
7	63	-63
8	171	174
9	59	59
10	40	-36
11	49	46
12	138	-137
H51		
0	236	-218
1	61	-55
2	33	-33
3	48	-45
4	155	149
5	78	75
6	112	112
7	114	111
8	69	-68
9	82	79
10	102	-101
12	5	-3
H61		
1	168	-162
2	282	278
3	65	65
4	21	18
5	37	36
6	133	-132
7	61	-58
8	15	-13
9	14	-13
10	57	52
12	27	26
H71		
0	95	99
1	18	18
2	6	12
3	12	10
4	72	-73
5	50	-49
6	67	-64
7	78	-74
8	38	40
9	65	-62
10	70	65
H81		
1	33	32
2	13	11
3	68	68
4	83	-80
5	9	1
6	23	-19
7	37	-37
8	99	98
9	36	34
10	22	-23
11	30	28
12	89	-86
H91		
0	97	-88
1	24	-21
2	8	-8
3	13	-14
4	74	68
5	45	44
6	47	49
7	58	59
8	36	-35
9	45	45
10	50	-50
11	4	8
H101		
1	95	-95
2	165	162
3	33	34
4	19	13
5	25	23
6	83	-84
7	35	-37
8	16	-13
10	33	33
12	26	20
H111		
0	80	82
1	20	17
2	15	15
3	21	19
4	63	-66
5	28	-27
6	59	-57
7	55	-55
8	32	32
9	40	-40
10	59	57
H121		
1	19	24
2	7	-8
3	35	36
4	54	-52
5	13	-6
7	24	-21
8	67	67
9	25	25
12	59	-59
H131		
0	41	-39
4	31	32
5	24	23
7	29	28
H141		
1	37	-43
2	67	70
H151		
0	38	42
4	28	-34
H161		
4	26	-33
H171		
4	25	26
H02		
0	121	-122
1	226	-251
2	55	64
3	313	-324
4	280	290
5	174	177
6	95	102
7	97	102
8	62	-67
9	81	-80
10	22	-28
11	19	-18
12	27	-24
H12		
2	144	145
3	104	103
4	141	140
5	245	247
6	48	-43
7	15	18
8	20	-19
9	54	-54
10	60	62
11	43	-44
12	78	79
H22		
0	178	-156
1	178	-157
2	35	-33
3	87	80
4	97	-88
5	136	140
6	148	-147
7	88	-89
9	77	-74
10	78	76
11	101	102
H32		
1	33	-25
2	79	-77
3	76	-72
4	98	-97
5	167	-166
6	21	16
9	26	23
10	54	-56
11	21	25
12	62	-61
H42		
0	77	-68
1	173	-165
2	56	54
3	215	-210
4	206	203
5	141	137
6	63	65
7	57	58
8	49	-50
9	78	-78
10	8	-11
12	18	-20
H52		
1	59	-53
2	132	128
3	83	78
4	109	109
5	196	198
6	43	-41
7	22	21
8	26	-26
9	58	-58
10	53	52
11	44	-45
12	73	74
H62		
0	30	-32
1	47	-47
2	6	-6
3	100	103
4	90	-91
5	93	94
6	129	-127
7	102	-99
8	12	15
9	71	-69
10	80	78
11	97	97
H72		
1	19	17
2	73	-70
3	59	-57
4	68	-67
5	119	-118
6	18	16
9	30	25
10	41	-42
11	23	23
12	48	-51
H82		
0	35	-31
1	95	-92
2	37	37
3	104	-104
4	112	110
5	88	84
6	29	28
7	18	20
8	29	-29
9	60	-60
H92		
1	13	-14
2	60	58
3	35	35
4	55	54
5	95	94
6	17	-14
7	10	13
9	24	-29
10	34	34
11	29	-24
12	44	42
H102		
0	12	-11
1	21	-21
3	61	62
4	55	-55
5	56	58
6	78	-79
7	65	-64
9	49	-46
10	55	54
11	65	65
H112		
1	28	34
2	55	-59
3	42	-42
4	47	-47
5	86	-87
6	23	18
9	29	30
10	28	-26
11	24	22
12	37	-40
H122		
0	31	-30
1	60	-61
2	16	18
3	69	-69
4	68	69
5	49	48
6	14	21
7	25	22
9	31	-30
H132		
1	8	-3
2	22	27
4	23	25
5	46	44
H142		
4	15	-21
5	30	30
H152		
5	44	-45
H162		
3	42	-45
4	42	41
H03		
2	65	62
3	39	-45
4	27	-29
5	235	253
6	77	-82
7	133	133
8	51	-56
9	145	-147
10	37	-36
11	131	-126
12	9	-12
H13		
0	82	78
1	84	80
2	32	36
3	231	226
4	23	-21
5	18	8
6	11	-9
7	88	-97
10	17	21
11	89	87
H23		
1	121	113
3	231	-223
4	10	15
5	181	-183
6	45	45
7	110	109
8	73	71
9	10	13
10	40	38
H33		
0	62	-61
1	28	-30
2	27	-28
3	148	-143
4	12	12
6	8	-2
7	48	50
9	21	-22
10	17	-13
11	66	-67
H43		
1	41	39
2	46	42
3	50	-48
4	27	-27
5	170	173
6	64	-66
7	109	110
8	40	-43
9	105	-109
10	34	-31
11	104	-102
H53		
0	67	64
1	86	86
2	33	33
3	196	192
4	9	-15
7	94	-92
10	25	22
11	77	80
H63		
1	132	130
3	181	-178
5	180	-174
6	38	37
7	75	73
8	63	60
9	37	36
10	35	30
H73		
0	50	-50
1	37	-37
2	27	-23
3	113	-110
7	52	48
11	56	-58
H83		
1	44	42
2	22	22
3	39	-37
4	21	-19
5	91	88
6	42	-41
7	72	73
8	27	-25
9	62	-65
10	18	-20
11	66	-63
H93		
0	35	33
1	39	40
2	23	22
3	94	92
7	42	-41
11	43	44
H103		
1	84	84
2	7	-4
3	112	-111
5	110	-110
6	25	23
7	46	45
8	41	38
9	26	28
H113		
0	35	-37
1	34	-38
2	19	-16
3	86	-86
4	5	9
7	51	50
H123		
4	8	-8
5	63	62
6	32	-24
H133		
0	16	15
3	43	43
4	6	0
H143		
1	35	34
3	53	-53
5	43	-47
H153		
3	39	-46
H04		
0	120	-128
1	198	210
2	44	48
3	151	167
4	97	104
5	133	-142
6	26	-26
7	130	-139
8	48	-51
9	25	-28
10	21	17
11	16	14
H14		
1	205	205
2	45	47
4	29	33
5	62	-68
6	20	20
9	102	103
10	41	39
11	50	52
H24		
0	82	-82
3	32	-29
4	48	52
5	36	-39
6	69	-73
7	121	121
9	118	118
10	70	73
11	63	-66
H34		
1	146	-147
2	35	-35
4	22	-23
5	21	25
6	24	-23
7	9	-14
9	73	-74
10	37	-34
11	34	-35
H44		
0	93	-95
1	152	155
2	42	42
3	113	113
4	83	83
5	119	-120
6	29	-26
7	97	-100
8	40	-41
9	15	-16
10	22	19
H54		
1	172	173
4	31	30
5	72	-73
6	15	15
9	94	96
10	32	33
11	49	50
H64		
0	50	-51
3	65	-60
4	28	27
5	30	-27
6	60	-62
7	123	123
9	104	104
10	64	62
11	65	-66
H74		
1	113	-110
2	31	-31
4	19	-16
5	35	32
6	14	-12
9	62	-62
10	26	-26
11	33	-30
H84		
0	57	-55
1	90	88
2	37	30
3	59	57
4	54	54
5	81	-82
6	19	-20
7	57	-56
8	25	-25
10	13	17
H94		
4	22	19
5	30	-33
6	8	14
10	12	20
9	54	53
11	28	26
H104		
0	30	-32
3	43	-42
4	17	15
6	38	-40
7	85	83
9	71	68
10	37	40
11	47	-46
H114		
1	83	-82
2	26	-25
5	39	41
9	52	-51
H124		
0	37	-34
1	57	58
3	42	45
4	32	34
5	47	-48
H134		
1	45	43
2	7	5
4	17	10
5	10	-14
H154		
1	36	-44
H164		
1	30	36
3	26	35
H174		
1	26	29
H05		
1	108	114
2	23	-19
4	40	39
5	64	-68
7	33	-31
8	164	-173
9	83	85
10	20	-22
11	45	45
H15		
0	160	158
1	68	-70
2	38	38
3	70	-72
5	22	19
6	17	-16
7	83	85
8	32	30
9	36	38
10	50	54
11	39	-43
H25		
1	110	-112
2	143	-148
3	35	34
4	74	79
5	39	36
6	99	103
7	21	-20
8	13	16
9	43	-46
H35		
0	119	-117
1	47	50
2	30	-32
3	41	44
5	20	-19
7	62	-61
9	24	-26
10	39	-42
11	28	32
H45		
1	82	81
2	33	-33
4	28	28
5	43	-44
7	23	-24
8	139	-145
9	66	68
10	17	-22
11	31	34
H55		
0	138	137
1	63	-60
2	32	34
3	70	-68
4	21	-20
6	20	-16
7	75	80
8	29	30
9	34	37
10	45	48
11	41	-40
H65		
1	104	-103
2	133	-132
3	35	35
4	40	50
5	51	51
6	91	94
8	26	25
9	50	-49
H75		
0	92	-87
1	42	41
2	24	-28
3	42	40
5	15	-17
7	52	-53
8	16	-17
9	23	-20
10	35	-36
11	30	26
H85		
1	43	44
2	34	-34
4	16	17
5	23	-22
8	93	-95
9	42	41
11	13	19
H95		
0	78	80
1	5	-30
3	32	-33
7	44	45
8	16	17
9	23	22
10	23	25
H105		
1	68	-67
2	85	-86
3	22	24
4	28	29
5	37	37
6	64	62
9	31	-34
H115		
0	63	-62
1	32	35
3	36	39
5	9	-11
7	45	-44
10	35	-32
H125		
1	28	31
4	15	13
5	13	-22
8	58	-60
H145		
2	39	-40
3	14	12
H06		
0	178	181
3	55	-54
4	144	-154
5	50	-51
6	16	-16
7	15	18
8	52	53
9	14	-3
11	53	-54
H16		
2	78	-78
3	44	45
4	28	-31
5	62	65
6	57	60
7	16	17
8	60	64
9	30	-32
11	12	-17
H26		
1	48	48
2	29	-29
3	56	57
6	97	100
8	7	7
9	42	40
10	85	-77
11	35	31
H36		
2	53	52
3	37	-37
4	17	17
5	49	-52
6	47	-45
7	12	-15
8	45	-45
9	29	27
H46		
0	141	144
3	39	-42
4	118	-124
5	45	-45
8	43	42
11	41	-47
H56		
2	74	-74
3	48	43
4	30	-32
5	64	59
6	61	57
8	71	61
9	32	-28
H66		
0	6	-4
1	41	44
2	34	-30
3	62	54
4	22	14
6	108	93
9	30	27
10	85	-74
11	31	27
H76		
2	58	48
3	33	-26
4	18	16
5	39	-42
6	34	-38
8	40	-37
9	22	23
H86		
0	100	91
2	11	-10
3	26	-24
4	83	-78
5	27	-31
8	28	27
11	32	-33
H96		
2	51	-38
3	33	30
5	33	35
6	30	31
8	41	35
H106		
1	28	29
2	22	-21
3	38	36
5	6	1
6	65	62
10	56	-53
H116		
2	48	44
5	39	-31
6	32	-33
8	33	-34
H126		
0	66	62
3	24	-18
4	48	-53
5	19	-17
8	19	20
H156		
2	20	26
H07		
1	40	-38
2	46	-44
3	50	53
4	91	-92
6	15	16
7	30	-34
8	53	56
10	26	-29
H17		
4	99	98
6	68	69
8	22	-24
10	35	-38
H27		
1	22	-24
2	103	101
3	39	40
4	35	33
6	47	-49
7	45	-44
8	20	19
9	29	27
10	31	33
H37		
4	78	-79
6	55	-53
8	20	18
H47		
1	31	-34
2	29	-28
3	47	48
4	74	-76
7	32	-31
8	39	42
10	27	-25
H57		
4	94	88
6	66	64
8	24	-23
10	39	-39
H67		
1	21	-20
2	101	97
3	36	33
4	34	34
6	49	-49
7	39	-36
10	32	29
H77		
0	18	12
4	68	-64
6	48	-43
8	19	17
10	16	23
H87		
3	34	34
4	55	-49
7	20	-23
8	28	25
11	15	11
H97		
4	52	52
6	38	38
H107		
2	70	68
4	23	24
H117		
4	49	-51
6	36	-35
H127		
4	32	-33
H137		
4	30	28
H08		
0	74	-76
1	57	-56
2	28	-25
3	59	-57
4	50	47
5	34	34
6	21	23
8	22	-27
9	49	-48
10	41	-39
H18		
2	51	51
4	21	22
5	34	34
6	42	-38
8	39	-38
H28		
0	42	44
1	36	-33
2	22	23
4	24	-24
5	62	58
6	17	-20
8	18	20
10	39	36
11	43	40
H38		
2	36	-35
4	16	-16
5	26	-26
6	31	29
8	31	30
H48		
0	64	-60
1	48	-47
2	19	-20
3	49	-47
4	38	37
5	30	29
6	21	16
8	23	-23
9	47	-43
10	30	-31
H58		
2	50	51
4	26	21
5	34	31
6	36	-37
8	37	-36
H68		
0	50	48
1	24	-22
2	19	22
3	16	16
4	31	-29
5	46	45
6	24	-25
10	38	37
H78		
2	33	-29
5	16	-22
6	27	24
8	30	28
H88		
1	44	-32
3	29	-31
4	25	23
5	20	21
9	31	-31
11	7	-0
H98		
2	31	32
4	22	11
6	29	-25
H108		
4	23	-23
6	16	-19
10	30	28
H118		
4	21	-16
6	27	20
H128		
4	22	20
H09		
1	18	-24
2	40	43
3	25	-25
6	43	-40
7	26	25
9	47	-46
11	32	-31
H19		
2	20	26
3	28	22
7	30	-32
H29		
1	55	56
3	30	-32
6	12	16
7	28	28
8	30	35
H39		
0	42	-41
2	22	-22
H49		
2	34	36
3	25	-24
6	36	-34
7	23	22
9	38	-38
H59		
2	25	23
3	25	23
7	31	-31
H69		
1	51	52
3	33	-29
6	17	16
7	24	22
8	39	33
H89		
9	23	-26
H010		
1	39	36
3	26	29
6	28	-26
7	31	-35
H110		
1	37	33
H210		
4	19	32
7	22	32
H410		
1	28	30
3	18	23
6	23	-22
7	16	-28
H510		
1	31	32
H610		
7	35	32
H011		
3	21	-19
H111		
3	27	-25
H211		
3	16	15
H311		
3	20	21

Table 1 (*cont.*)

```
   F(O)F(C)
* H  1  0 *  * H  2  2 *  * H  2  3 *    9  10  10    8  10  -4    7  10  -1    3  10  11    7  10  -1    1  10  -5    2  10 -13  * H  8  7 *    1  10   2    5  10  15    5  10   9
 10  10   1    3  10  10    2  10   9   10  10  14  * H  6  4 *    8  10  -3    6  10   6  * H  3  6 *    6  10   4    3  10   4    5  10  -2    3  10   7    8  10 -20    8  10 -15
* H  5  0 *  * H  3  2 *   11  10  -7  * H 10  3 *    1  10 -17  * H  0  5 *    7  10 -15    1  10 -12    7  10   5    5  10   2    6  10   1    5  10  19   10  10  -4  * H  5  9 *
 10  10   0    7  10  -6  * H  3  3 *    4  10  -1    2  10   1    3  10   7   10  10 -17   10  10   8    9  10  -6    7  10   6    9  10   2    7  10   1  * H  1  9 *    4  10 -12
* H  8  0 *    8  10  -6    5  10 -16  * H 11  3 *    8  10  -4    6  10  -9  * H  9  5 *   11  10  13   10  10 -14    9  10   8  * H  9  7 *    8  10 -21    4  10 -12    5  10  -9
 10  10   4  * H  4  2 *    8  10  -6    5  10  -6  * H  7  4 *  * H  1  5 *    2  10  21  * H  4  6 *  * H  9  6 *   10  10  25    0  10 -11    9  10 -11    5  10 -10    6  10 -11
* H  7  0 *   11  10  -6  * H  5  3 *    6  10   1    3  10  -0    4  10 -12    4  10  -7    1  10 -10    1  10  -1  * H  4  7 *    1  10   3  * H 10  8 *    6  10  -9  * H  6  9 *
 10  10  -4  * H  7  2 *    5  10   3    8  10  -7    7  10  -9  * H  2  5 *    5  10   8    2  10 -11    7  10   6    5  10  -3    2  10   4    0  10  36    8  10  13    2  10  -9
* H  9  0 *    7  10  -4    6  10 -12    9  10   4    8  10  -8   10  10   8    6  10  -4    6  10  -6    9  10 -17    6  10   7    3  10  -4    1  10 -13  * H  2  9 *    4  10 -13
  4  10  -2    8  10   3    3  10   6   10  10  -9  * H  8  4 *   11  10 -10  * H 10  5 *    7  10  13   10  10  -7    9  10   4    5  10   5    2  10  16    2  10  -4  * H  7  9 *
* H 11  0 *  * H  8  2 *    9  10   4  * H  1  4 *    9  10  -4  * H  3  5 *    7  10  -6    9  10  -6  * H 10  6 *  * H  5  7 *    7  10  -5    3  10  13    4  10 -11    3  10 -15
  4  10  10   10  10  -0  * H  6  3 *    3  10  -7   11  10  -4    4  10 -10    8  10  13   10  10 -11    0  10  -8    1  10   6    8  10 -14    5  10  29    5  10 -10    4  10  12
 10  10   1   11  10   3    2  10  -6    7  10   7  * H  9  4 *    6  10   5   10  10   1  * H  5  6 *    4  10  12    2  10   4  * H 10  7 *    7  10  -9    9  10  16    5  10   7
* H  3  1 *  * H  9  2 *    4  10   2    8  10   2    2  10  15    8  10 -21  * H 11  5 *    1  10  -5    7  10  -8    3  10  -6    1  10 -13    8  10  15  * H  3  9 *    6  10   3
  2  10   3    3  10  -7   11  10  10  * H  2  4 *    3  10  -1  * H  4  5 *    4  10   9    7  10  13    8  10  -3    5  10   5    3  10  22    9  10  -8    1  10 -19    7  10  23
* H  5  1 *  * H 10  2 *  * H  7  3 *    1  10   9    7  10   5    3  10  12    6  10  15   10  10 -11    9  10  16    7  10  -6    5  10   6  * H 11  8 *    3  10 -15    8  10 -11
 11  10   5    2  10  -3    4  10  10    2  10  -0    8  10  -2    6  10   0  * H  0  6 *  * H  6  6 *  * H 11  6 *    9  10 -12  * H 11  7 *    1  10   4    4  10  10  * H  8  9 *
* H  6  1 *    8  10  10    5  10 -12    8  10  -9  * H 10  4 *  * H  5  5 *    1  10 -16    5  10   3    1  10   0  * H  6  7 *    1  10  -8    2  10 -27    5  10   9    1  10 -10
 11  10  11  * H 11  2 *    3  10  -7  * H  3  4 *    1  10 -13    5  10  15    2  10  -3    7  10  -8    3  10 -17    5  10   9    2  10  -0    3  10 -11    6  10   3    3  10 -19
* H  7  1 *    7  10  -4    9  10 -10    3  10  -8    2  10   1  * H  6  5 *   10  10  -3    8  10  -1    4  10  18    8  10   3    3  10   1    5  10 -19    6  10   3    4  10  -3
 11  10  -3    8  10  15   10  10 -11    8  10 -11    5  10 -18    7  10 -11  * H  1  6 *  * H  7  6 *    7  10 -13  * H  7  7 *    5  10   3    7  10   2    7  10  25    5  10   5
* H 10  1 *  * H  0  3 *  * H  9  3 *  * H  4  4 *    8  10  -2   10  10   3    1  10   1    1  10  -8  * H  2  7 *    2  10  -8  * H  8  8 *    8  10  26    8  10 -12    8  10 -10
  9  10 -11    1  10  13    4  10  -2   11  10   5  * H 11  4 *   11  10 -17   10  10 -12    7  10 -15    5  10  10    3  10   2    2  10 -13    9  10  10    9  10  17
 11  10   5  * H  1  3 *    5  10   2  * H  5  4 *    3  10   9  * H  7  5 *  * H  2  6 *    8  10   8  * H  3  7 *    5  10   4    6  10   9   10  10  -2  * H  4  9 *
* H 11  1 *    0  10   5    6  10  -4    3  10 -12    4  10 -11    6  10  10    4  10  -5   11  10  13    0  10   6    7  10   4    7  10  -7  * H  0  9 *    1  10 -13
 11  10   2    9  10  11    0  10   5    7  10   3    6  10  -2  * H  8  5 *    5  10   4  * H  8  6 *    1  10 -14    9  10   5  * H  9  8 *    4  10  -0    4  10  -2
```

Table 2. *Atom positional and temperature parameters and errors*

$\sigma' = \sigma \times 10^5$

Positional parameters

	x/a	$\sigma'\ (x/a)$	y/b	$\sigma'\ (y/b)$	z/c	$\sigma'\ (z/c)$
Co	0·1046	7	0·2500	—*	0·1797	12
Cl(1)	−0·0257	13	0·2500	—*	−0·0393	26
Cl(2)	0·3524	10	0·0011	12	0·1587	17
N(1)	0·2161	50	0·2500	—*	0·3691	91
N(2)	0·1993	49	0·2500	—*	−0·0442	85
N(3)	0·1023	32	0·0603	36	0·1773	60
N(4)	0·0084	51	0·2500	—*	0·4052	95

Thermal parameters

Anisotropic temperature factors of the form
$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right];\ \sigma'=\sigma\times 10^5].$

	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Co	0·0024	6	0·0028	5	0·0091	15	0·0	—*	−0·0001	7	0·0	—*
Cl(1)	0·0033	12	0·0053	13	0·0143	38	0·0	—*	−0·0019	15	0·0	—*
Cl(2)	0·0039	9	0·0049	9	0·0134	22	−0·00007	6	−0·0001	10	0·0008	12
N(1)	0·0038	41	0·0052	48	0·0153	132	0·0	—*	−0·0010	60	0·0	—*
N(2)	0·0036	41	0·0060	50	0·0129	126	0·0	—*	−0·0003	57	0·0	—*
N(3)	0·0042	29	0·0033	27	0·0167	96	0·0002	24	−0·0010	39	−0·0001	44
N(4)	0·0044	44	0·0067	54	0·0136	142	0·0	—*	0·0021	61	0·0	—*

Scale factor = 0·23724 ± 0·00031
To put F(calc) on absolute scale

$$F(\text{calc})_{\text{absolute}} = \frac{F(\text{calc})}{\text{Scale factor}}$$

* Parameter constrained by symmetry requirements.

positions was confirmed by a three-dimensional electron density map. The structure was refined by full-matrix least squares on the IBM 7090 computer (Busing, Martin & Levy, 1962) including anisotropic temperature factors. Atomic scattering factors for neutral nitrogen, Co^{3+} and Cl^- (*International Tables for X-ray Crystallography*, 1962) were used. Real and imaginary dispersion corrections were applied to Co^{3+} and Cl^- (Cromer, 1965). We minimized the function $\Sigma w(F_o-F_c)^2$ and the observations were weighted on counting statistics and a 4% intensity factor (Busing & Levy, 1957). Atomic parameter shifts for the last cycle of refinement were less than 4×10^{-6} of a cell edge. The final disagreement index R ($R=\Sigma\,|F_o|-|F_c|/\Sigma\,|F_o|$), weighted R ($\Sigma\, w(F_o-F_c)^2/\Sigma\, wF_o^2$) and standard error ($[\Sigma\, w(F_o-F_c)^2/(NO-NV)]^{\frac{1}{2}}$ where $NO=1011$ and $NV=49$) were found to be 0·054, 0·082 and 0·80, respectively. A final three-dimensional difference map did not give any indications of the ammonia hydrogen atoms and was, in general, rather featureless.

An attempt was made to refine the structure in the lower symmetry space group by distorting the molecule slightly to remove the constraints imposed by the centrosymmetric space group. It was found that the atoms that would be symmetry-related in the higher symmetry space group were strongly correlated $\geqslant 0{\cdot}9$, and y coordinates of those atoms that would be in the mirror plane at $y=\frac{1}{4}$ in *Pnma* refined to the same y value in $Pn2_1a$. Hence, we feel the correct space group is *Pnma* and not $Pn2_1a$. Final observed and calculated structure factors are listed in Table 1. Final atomic coordinates, temperature factors and e.s.d.'s are listed in Table 2.

Results and discussion

Interatomic distances, angles and their standard deviations were calculated from the refined parameters, the variance–covariance matrix and the unit-cell dimensions. The Busing & Levy (1964) Function and Error program was used to obtain these and other functions of the parameters.

Distances, angles and the respective errors are listed in Table 3. Root mean square thermal displacements along the principal axes of the thermal ellipsoids and the angle these axes make with an orthogonal coordinate system on the molecule ion are also listed in Table 4. The orientation of the molecular ions $\mathrm{Co(NH_3)_5Cl^{2+}}$ in the unit cell and the molecular packing can be seen in Figs. 1 and 2.

Of the five Co–N distances in the $\mathrm{Co(NH_3)_5Cl^{2+}}$ molecular ion two are symmetry related [Co–N(3), Co–N(3′)] at 1·962 ± 0·004 Å and the other three are independent at [Co–N(1)] 1·964 ± 0·006 Å, [Co–N(2)] 1·978 ± 0·006 Å, and [Co–N(4)] 1·998 ± 0·006. We do not believe the differences between 1·962, 1·964 and 1·978 are statistically significant, not only because the differences are less than 3σ but also because their thermal motions are very similar (*vide infra* and Table 3). However, we believe the difference between the Co–N(4) distance and the other Co–N distances is real. An examination of the r.m.s. atomic amplitudes of motion along the principal axes of the thermal ellipsoid and the angles these ellipsoids make with the Co–Cl(1), Co–N(3′) and Co–N(4) directions (Table 4) shows that these directions are to a good approximation the principal axes for all the non-hydrogen atoms in the $\mathrm{Co(NH_3)_5Cl^{2+}}$ molecular ion. Further, the smal-

Table 3. *Interatomic distances and bond angles, and deviations from least-squares planes*

Intramolecular distances and errors

Co—Cl(1)	2·286 ± 0·002 Å
Co—N(1) apex	1·964 ± 0·006
Co—N(2)	1·978 ± 0·006
Co—N(3)	1·962 ± 0·004
Co—N(3′)	1·962 ± 0·004
Co—N(4)	1·998 ± 0·006
Cl(1)–N(1)	> 4
Cl(1)–N(2)	2·989 ± 0·007
Cl(1)–N(3)	2·987 ± 0·004
Cl(1)–N(4)	3·065 ± 0·007
N(1)–N(2)	2·827 ± 0·009
N(1)–N(3)	2·800 0·006
N(1)–N(4)	2·768 ± 0·010
N(2)–N(3)	2·791 ± 0·006
N(2)–N(4)	3·977 ± 0·009
N(3)–N(4)	2·796 ± 0·006
N(3)–N(3′)	3·924 ± 0·008

Intramolecular bond angles and errors

N(1)–Co–N(3)	91·0 ± 0·1 °
N(1)–Co–N(4)	88·6 ± 0·3
N(1)–Co–N(2)	91·6 ± 0·3
Cl(1)–Co–N(2)	88·7 ± 0·2
Cl(1)–Co–N(3)	89·0 ± 0·1
Cl(1)–Co–N(4)	91·1 0·2
Cl(1)–Co–N(1)	179·7 ± 0·2
N(3)–Co–N(2)	90·2 ± 0·1
N(3)–Co–N(4)	89·8 ± 0·1
N(4)–Co–N(2)	179·8 ± 0·3

Intermolecular distances and errors

Co—Cl(2)	4·179 ± 0·001 Å	Cl(2)–N(3′)	3·554 ± 0·005 Å
Cl(1)–Cl(2)	5·801 ± 0·002	Cl(2)–N(3)	3·396 ± 0·004
N(1)–Cl(2)	3·458 ± 0·005	Cl(2)–N(4)	3·333 ± 0·005
N(2)–Cl(2)	3·559 ± 0·005	Cl(2)–N(2)	3·364 ± 0·004
Cl(2)–N(3)	3·379 ± 0·005	Cl(2)–Cl(1)	3·997 ± 0·002
Cl(2)–N(1)	3·387 ± 0·004	All others	> 4

Equations of best least-squares planes of the form $Ax+By+Cz-D=0$.

(*a*) Through Co, N(2), N(3), N(3′), N(4)

A	−0·7703
B	−0·0000
C	−0·6376
D	+1·8496

Deviations from this plane

Co	−0·0006 Å	N(3′)	0·0333 Å
N(2)	0·0033	N(4)	0·0036
N(3)	0·0333		

(*b*) Through Co, Cl(1), N(1), N(3), N(3′)

A	0·6537
B	−0·0000
C	−0·7566
D	+0·0193

Deviations from this plane

Co	+0·0010 Å	N(3)	−0·0065 Å
Cl(1)	−0·0011	N(3′)	−0·0065
N(1)	−0·0065		

(*c*) Plane through Co, Cl(1), N(1), N(2), N(4) is exact by symmetry requirements.

lest r.m.s. amplitude of motion for all the atoms but N(4) is in the Co–N(4) direction (approximately half that of the other two directions), but for N(4) the smallest r.m.s. amplitude (approximately half the other two) is in the Co–Cl(1) direction. An examination of Fig. 1 shows that the Co–Cl(1) direction is almost parallel to the N(4)–Cl(2) direction. Also Table 3 shows that the N(4)–Cl(2) intermolecular distance is the shortest N–Cl intermolecular distance. These facts lead us to believe that N(4) is involved in a weak hydrogen bond to Cl(2) and this hydrogen bonding is what makes the Co–N(4) bond significantly longer than the other four Co–N distances. This hydrogen bond might involve two of the three hydrogen atoms on N(4) or a statistical disordering of these hydrogen atoms, but the answer to this question seems to be outside the limits of our data.

Hence, our average Co–N distance for comparison with other structures is 1·968 Å with a total spread of

Table 4. *Root mean square displacements of atoms along the principal axes* (1,2,3) *of the thermal ellipsoids, and angles between these principal axes and the* Co–Cl (α), Co–N(3′) (β) *and* Co–N(4) (γ) *directions*

	Axis	$(r^2)^{\frac{1}{2}}$	α	β	γ
Co	1	0·1074 0·0031 Å	90·0°	180·0°	90·0°
	2	0·1023 ± 0·0033	5·4	90·0	95·4
	3	0·0493 ± 0·0085	95·4	90·0	174·6
Cl(1)	1	0·1655 ± 0·0051	177·5	90·0	92·5
	2	0·1471 ± 0·0058	90·0	0·0	90·0
	3	0·0913 ± 0·0075	87·5	90·0	177·5
N(1)	1	0·2368 ± 0·0319	90·0	180·0	90·0
	2	0·1374 ± 0·0323	2·0	90·0	87·9
	3	0·0329 ± 0·0169	88·0	90·0	178·0
N(2)	1	0·2081 ± 0·0228	159·0	90·0	69·0
	2	0·1855 ± 0·0210	90·0	0·0	90·0
	3	0·0780 ± 0·0531	111·0	90·0	159·0
N(3)	1	0·2107 ± 0·0149	87·1	176·1	87·4
	2	0·1777 0·0139	3·0	87·1	89·2
	3	0·1299 ± 0·0170	89·0	92·6	177·2
N(4)	1	0·1864 ± 0·0196	83·8	90·0	173·8
	2	0·1290 ± 0·0218	90·0	0·0	90·0
	3	0·0786 ± 0·0423	173·8	90·0	96·2

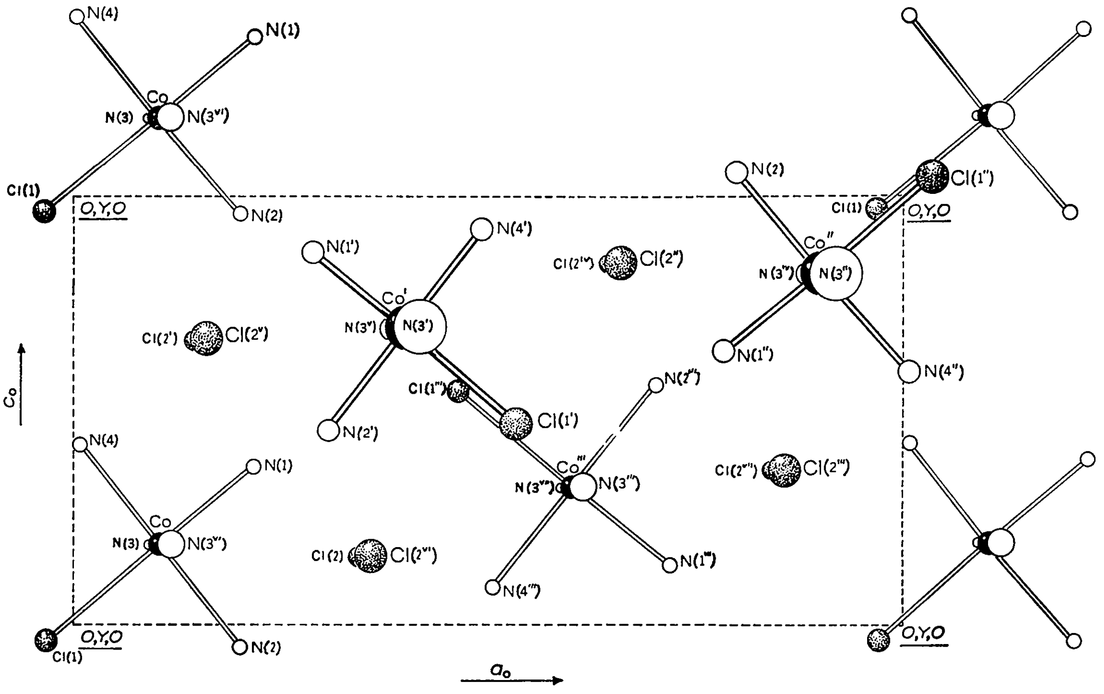

Fig. 1. Projection of the structure of $Co(NH_3)_5Cl^{2+}2Cl^-$ onto (010). The Co, Cl(1), N(1), N(2), N(4) atoms all lie in the mirrors at $y=\frac{1}{4}$, $\frac{3}{4}$. The molecule ions with the larger atoms correspond to molecules with atoms at $y=\frac{3}{4}$.

±0·01 Å or less and individual standard deviations of ±0·006 Å or less. This distance is in good agreement with the results of Palenik (1964) who found an average Co–N distance from five Co–N distances of 1·968 with a spread of ±0·008 Å and an individual standard error of ±0·007 Å in azidopentaminecobalt(III) azide, $[N_3Co(NH_3)_5][N_3]_2$. In contrast to the results of Shigeta, Komiyama & Kuroya (1963), we do not observe a significant '*trans*' effect due to the chlorine substituent.

Stanko & Paul (1967) have also determined the geometry of the molecular ion $Co(NH_3)_5Cl^{2+}$ in $[Co(NH_3)_5Cl]^{2+}[SiF_6]^{2-}$ but their standard errors were three to five times larger than ours. However, there is general agreement within the larger standard deviations. There might be some Co–N bond elongation in $[Co(NH_3)_5\text{-}Cl]^{2+}[SiF_6]^{2-}$ due to the presence of the highly electronegative fluorine atoms.

The cobalt–chlorine distance of 2·281±0·004 Å is only slightly longer, but nevertheless significantly longer, than the 2·21 Å expected from the sum of the covalent radii (Pauling, 1960).

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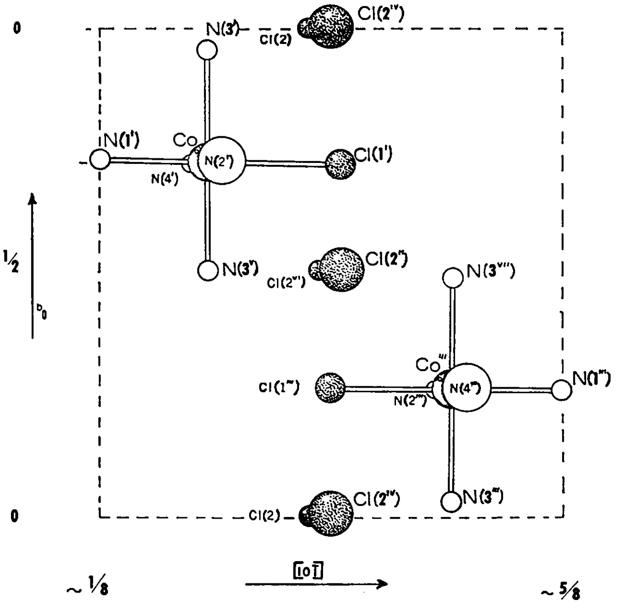

Fig. 2. View of the structure of $Co(NH_3)_5Cl^{2+}2Cl^-$ in the [110] direction to show the reversed Co–Cl directions in adjacent molecules.

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Weak Reflexions in the X-ray Diffraction Pattern of Magnetite, Fe_3O_4

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Synthetic polycrystalline specimens of magnetite, Fe_3O_4, were studied by X-ray diffraction. Several weak reflexions were observed which have not hitherto been reported for magnetite. These reflexions can be indexed on the spinel (f.c.c.) structure as 531, 551–711, 662 and 753. Addition of Ti^{4+} ions to the lattice results in a systematic shift of these reflexions with composition, showing that they are not simply due to a second phase. Structure-factor calculations confirm the presence of the four extra lines.

Introduction

A number of X-ray diffraction studies have been made on both natural and synthetic samples of magnetite. Basta (1957) has made an accurate determination of the cell size of natural magnetite and Rooksby (1961) has studied synthetic material. The *X-ray Powder Data File* card number 7–322 is based on Rooksby's work. Both authors publish a list of *d* values.

In the course of an investigation of the magnetic properties of the magnetite-ulvöspinel solid-solution series, X-ray powder pictures were made of synthetic