length as the condensation of the chromates increases is undoubtedly significant, and may be compared with similar increases noted for sulphates (Cruickshank & Robinson, 1966).

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The Crystal Structure of (+)D-(*N*,*N*,*N'*,*N'*-Tetrakis-(2'-aminoethyl)-1,2-diaminoethane) cobalt(III) Hexacyanocobaltate(III) Dihydrate

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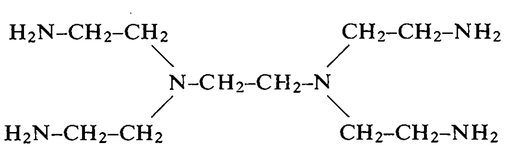
(+)D-(*N*,*N*,*N'*,*N'*-Tetrakis(2'-aminoethyl)-1,2-diaminoethane)cobalt(III) hexacyanocobaltate(III) dihydrate, (+)D-[Co(penten)] $[Co(CN)_6].2H_2O$, forms orthorhombic crystals with $a=15{\cdot}471$, $b=16{\cdot}036$, $c=9{\cdot}253$ Å and four formula units in the unit cell, in space group $P2_12_12_1$. The structure has been refined by least-squares methods with anisotropic temperature factors. The structure consists of complex cations, $[Co(penten)]^{3+}$, complex anions, $[Co(CN)_6]^{3-}$ and water molecules. The central cobalt atom of the cation is bonded octahedrally to the six nitrogen atoms of a penten molecule. Three out of the five chelate rings form a girdle about the cobalt atom. Approximately at right angles to the girdle and to one another are two other five-membered chelate rings. All the five-membered chelate rings are not planar. Their conformations are not the same, two of them being enantiomeric with the other three. The absolute configuration of the complex ion, (+)D-$[Co(penten)]^{3+}$ can be designated as skew chelate pairs, $\Lambda\Delta\Lambda$. When applied to this case, the method of ring pairing, together with the octant rule, correctly predicted the sign of the circular dichroism band.

Introduction

N,*N*,*N'*,*N'*-Tetrakis(2'-aminoethyl)-1,2-diaminoethane (I), penten, can function as a sexidentate, giving complexes structurally related to those derived from ethylenediaminetetra-acetic acid (EDTA) (Wiekliem & Hoard, 1959).



(I)

Recently the cobalt(III) complex, $[Co(penten)]Br_3$, was resolved and the optical properties were examined by Yoshikawa, Fujii & Yamasaki (1967). They confirmed the previous results (Schwarzenbach & Moser, 1953: Emmenegger & Schwarzenbach, 1966). However, the absolute configuration proposed by Yoshikawa, Fujii & Yamasaki (1967) and by Gollogly & Hawkins (1966) is enantiomeric with that proposed by Emmenegger & Schwarzenbach (1966) and by Mason & Norman (1965). Therefore it was highly desired to establish the absolute configuration of the complex ion, $[Co(penten)]^{3+}$. In this paper, the result of the crystal structure analysis of [Co(penten)] $[Co(CN)_6].2H_2O$ and the relationship between the absolute configuration of optically active complexes and their optical rotatory dispersion and circular dichroism spectra will be given.

Experimental

Crystals of $(+)_{D}$-[Co(penten)]$\mathrm{Br_3}$ were kindly supplied by Professor K. Yamasaki of Nagoya University. The crystals for X-ray work were grown by the diffusion method. Two small beakers, one containing a solution of $(+)_{D}$-[Co(penten)]$\mathrm{Br_3}$ and the other a solution of $\mathrm{K_3[Co(CN)_6]}$, were put side by side in a large beaker, and distilled water was poured very carefully into the beakers along their walls until the level reached about 3 cm above the tops of two small beakers. After two weeks single crystals grew on the upper part of the wall of the beaker containing $(+)_{D}$-[Co(penten)]$\mathrm{Br_3}$ solution. Orange-red crystals in the form of irregular rhombs were obtained. For the purpose of X-ray analysis a crystal of maximum dimensions 0·18 mm was used. Three-dimensional Weissenberg data were collected with Fe $K\alpha$ radiation ($\lambda = 1{\cdot}937$ Å) rotating the crystal about its a and b axes. 1243 independent reflexions were recorded. Intensities were measured visually and converted to $|F|$ by applying Lorentz and polarization corrections. No corrections were made for absorption.

Table 1. *Observed and calculated structure amplitudes* (×2·5)

H	FO	FC
K,L= 0 0		
2	130	153
4	33	20
6	87	63
8	210	215
10	102	98
14	51	53
K,L= 1 0		
3	68	83
4*	13	8
5	88	90
6	132	132
7	55	52
8	194	215
9	27	16
10	90	78
11	182	190
12	178	195
13	75	73
14	107	103
15	63	60
K,L= 2 0		
0	122	122
1	490	468
2	409	463
3	77	83
4*	6	16
5	369	378
6	207	209
7	30	26
8	92	88
9	126	114
10	32	20
11	24	13
12	70	83
13*	10	7
14	30	38
K,L= 3 0		
1	114	108
2	123	117
3	193	190
4	95	80
5	220	237
6	218	221
7	202	207
8*	7	10
9	40	40
10	247	242
11	94	91
14	141	127
K,L= 4 0		
0	58	40
1	158	165
2	318	320
3	230	218
4	328	314
5*	12	11
6	308	317
7	205	182
8	112	92
9	114	116
10	166	150
11	47	42
12	28	25
13	60	88
14*	0	3
15	83	104
K,L= 5 0		
1	264	264
2	230	234
3	20	11
4	38	22
5	200	213
6	125	138
7	83	89
8	58	50
9	116	116
10	150	154
11	60	41
12	95	70
13	68	61
14	113	106
K,L= 6 0		
0	250	278
1	203	211
2	25	5
3	170	178
4	203	190
5	258	246
6	35	32
7	168	175
8	73	68
9	31	35
10	25	35
11	117	124
12	78	106
13	50	78
K,L= 7 0		
1	118	132
2	125	127
3	178	171
4	267	252
5	189	193
6	158	132
7	65	63
8	118	108
9	173	187
10*	17	7
11*	17	7
12	138	118
13	43	30
K,L= 8 0		
0	104	103
1	23	14
2	81	81
3	45	29
4	150	149
5	173	180
6	23	20
7	40	43
8	55	58
9	136	140
10	43	50
11*	14	29
12*	12	7
13	61	67
K,L= 9 0		
1	89	82
2	104	206
3	287	306
4	115	116
5	62	54
7	133	120
8	60	51
9	42	22
10	79	70
11	124	109
12*	22	19
13	56	68
K,L= 10 0		
0	75	80
1	164	181
3	81	73
K,L= 11 0		
1	83	86
2	39	45
3	217	245
K,L= 12 0		
0	129	137
1	95	102
2	69	77
3	83	85
K,L= 13 0		
2	43	43
3	42	54
K,L= 14 0		
0	95	106
2	42	40
3	69	80
K,L= 15 0		
3	27	28
K,L= 16 0		
0*	7	0
2	55	89
K,L= 0 1		
1	55	52
2	180	172
3	99	80
4	43	37
5	25	35
6	167	165
7	53	45
8	81	84
9	167	73
10	273	274
11*	16	0
12	57	57
13	53	47
14	130	140
15*	16	2
K,L= 1 1		
0*	12	7
1	330	383
2	405	480
3	147	150
4	134	143
5	51	52
6	119	124
7	159	174
8	60	59
9	85	90
10	122	139
11*	10	5
12	53	59
13	54	54
14	33	31
15*	4	12
K,L= 2 1		
0*	16	5
1	165	161
2	74	71
3	42	41
4	120	131
5	106	108
6	97	94
7	140	135
8	120	108
9	136	130
10	103	92
11	131	124
12	135	137
13	124	102
14	63	50
15	25	22
K,L= 3 1		
0	354	426
1	120	119
2	45	65
3	131	135
4	199	230
5	130	135
6	85	74
7	112	111
8	142	159
9	73	80
10	125	127
11	139	135
12	31	33
13	46	33
14	35	37
15*	18	24
K,L= 4 1		
0	24	12
1	147	133
2	156	142
3	101	116
4	208	198
5	123	112
6	169	156
8	268	265
9	33	37
10	47	57
11	55	64
12	84	100
14	52	42
15	39	54
K,L= 5 1		
0	279	309
1	76	64
2	101	102
3	290	290
4	173	181
5	251	257
6	70	60
7	97	95
8	117	95
9	75	74
10*	21	27
11	105	97
12	114	123
13	112	110
14	37	30
K,L= 6 1		
0*	19	16
1	216	221
2	202	189
3	296	290
5	140	118
6	85	82
7	198	196
8	30	32
9	57	59
10	93	100
11	129	131
12	48	53
13	49	40
K,L= 7 1		
0*	13	5
1	113	107
2	214	216
3	87	79
4	134	120
5	130	127
6	174	165
7	30	16
8*	17	23
9	47	44
10	72	58
11	112	115
12	50	49
13	59	59
K,L= 8 1		
0	54	63
1	190	202
2	47	45
3	59	71
4	86	84
5	204	198
6	131	131
7	107	98
8	44	47
9	81	76
10	99	97
11*	17	19
12	48	54
13	49	56
K,L= 9 1		
0	24	32
1	117	127
2	101	98
3	147	143
4	66	56
5	79	63
6	98	75
7	178	168
8	50	43
9	93	79
10	30	17
11	51	29
12	50	55
13	50	40
K,L= 10 1		
0	67	45
1	154	157
2	93	98
3	63	67
K,L= 11 1		
0	156	173
1	48	43
2	143	157
3	83	93
K,L= 12 1		
0	37	36
1	82	90
2	68	91
3	77	78
K,L= 13 1		
0	40	36
1	126	147
2	31	41
3	48	62
K,L= 14 1		
0*	12	21
3	96	109
K,L= 15 1		
0	86	89
2*	15	27
K,L= 16 1		
0	28	40
1	30	43
K,L= 0 2		
0	451	514
1	221	202
2	267	270
3	100	98
4	289	314
5	166	153
6*	9	1
8	99	98
9*	16	8
10	42	44
11	27	27
13*	16	21
14	70	72
15*	12	22
K,L= 1 2		
0	77	72
1*	16	12
2	94	92
3	80	84
4	111	130
5	97	97
6	23	20
7	59	71
8	86	91
9	40	53
10	40	55
11	125	151
12	131	162
13	46	42
14	48	51
15	44	51
K,L= 2 2		
0	53	20
1	212	222
2	172	173
3	268	261
4	305	310
5	197	211
6	198	213
7	128	142
8	81	83
9	65	80
10	34	31
11	38	30
12	75	78
13	50	58
14*	5	15
15	30	40
K,L= 3 2		
0	138	104
1	78	68
2	136	131
3	80	71
4	104	84
5	170	150
6	196	207
7	144	138
8	67	46
9	132	131
10	178	190
11	116	118
12	27	25
13	51	30
14	59	82
K,L= 4 2		
0	126	127
1	214	183
2	183	184
3	84	80
4	34	23
5	138	116
6	197	189
7	93	85
8	117	108
9	190	173
10	129	121
11	34	35
12	23	22
13	97	103
14	24	24
K,L= 5 2		
1	162	162
2	100	96
3	71	73
4	132	116
5	229	230
6	215	208
7	87	82
8	44	28
9	144	136
10	122	115
11	79	70
12	49	52
13	89	82
14	79	92
K,L= 6 2		
0	110	117
1	41	47
2	204	197
3	250	247
4	121	139
5	210	192
6	46	45
7	98	100
8	41	42
9	69	69
10	77	96
11	79	81
12*	16	28
13	25	23
14	30	45
K,L= 7 2		
0	70	73
1	71	75
2	148	143
3	119	112
4	127	119
5	164	160
6	74	63
7	84	83
8	158	155
9	95	89
10	83	80
11	40	40
12	108	100
13	65	59
K,L= 8 2		
0	145	157
1	85	84
2	86	78
3	49	44
4	171	160
5	102	91
6	90	96
7	106	100
8	80	72
9	61	44
10	23	41
11	34	30
12*	6	15
13	23	30
K,L= 9 2		
0	33	28
1	172	175
2	104	104
3	173	169
4	112	107
5	93	88
6	78	71
7	156	157
8	51	41
9*	21	18
10	27	21
11	92	88
12	24	29
K,L= 10 2		
0	62	66
1	128	136
2	57	65
3	79	88
K,L= 11 2		
0	135	136
1	157	156
2	33	42
3	140	152
K,L= 12 2		
0	150	169
1	64	76
2	80	95
3	42	42
K,L= 13 2		
0	28	25
1	103	111
2	53	57
3	45	58
K,L= 14 2		
0	54	63
1	62	75
2	71	74
3	40	51
K,L= 15 2		
0*	9	22
1	40	51
2*	19	21
K,L= 0 3		
1	104	104
2*	25	31
3	134	127
4	70	50
5	60	51
6	201	210
7	34	24
8	24	29
9	26	20
10	127	143
11	80	97
12	96	103
13*	21	12
14	60	74
K,L= 1 3		
0	218	234
1	257	260
2	201	203
3	305	308
4	237	225
5	111	133
6	138	162
7	109	112
8	65	60
9	71	73
10	96	104
11*	17	17
12	32	35
13	32	35
14	40	50
K,L= 2 3		
0*	12	10
1	100	107
2	24	18
3	56	46
4	123	117
5	181	191
6	110	106
7	119	120
8	80	60
9	144	149
10	79	87
11	129	120
12	50	50
13	78	78
14*	17	23
K,L= 3 3		
0	91	88
1	78	65
2	28	22
3	103	104
4	255	249
5	184	178
6	95	100
7	140	145
8	131	127
9	113	109
10	56	53
11	80	72
12	30	26
13*	13	14
14*	20	20
K,L= 4 3		
0	34	23
1	54	54
2	67	77
3	140	130
4	152	140
5	63	62
6	81	80
7	130	123
8	180	186
9	125	124
10	61	64
11	41	40
12	113	105
13	86	67
14*	15	24
K,L= 5 3		
0	116	121
1	171	184
2	57	55
3	94	98
4	205	210
5	187	181
6	24	26
7	75	73
8	55	44
9	44	31
10	43	31
11	64	76
12	91	93
13	34	32
14	31	38
K,L= 6 3		
0	159	164
1	117	113
2	52	44
3	106	93
4	76	80
5	22	9
6	75	73
7	184	157
8	120	120
9	40	43
10	84	89
11	110	127
12	40	52
13	39	47
K,L= 7 3		
0	71	60
1	120	126
2	102	192
3	45	45
4	62	60
5	112	108
6	172	157
7*	17	20
8	34	25
9	36	32
10	30	32
11	80	77
12	37	38
13	42	50
K,L= 8 3		
0*	13	21
1	166	150
2	120	124
3	37	31
4	159	137
5	120	117
6	174	178
7	94	89
8	79	75
9	82	85
10	101	110
11	20	23
12	34	42
K,L= 9 3		
0*	21	13
1	24	32
2	94	88
3	112	114
4	46	35
5	43	30
6	102	89
7	94	83
8	92	84
9	82	55
10	59	50
11	35	20
12	28	17
K,L= 10 3		
0	159	153
1	107	118
2	106	126
3	29	41
K,L= 11 3		
0	105	104
1	27	10
2	88	100
3	62	59
K,L= 12 3		
0	139	141
1	102	111
2	95	111
3	87	92
K,L= 13 3		
0	36	33
1	85	86
2	35	45
3	45	44
K,L= 14 3		
1	57	56
2	34	37
3	75	80
K,L= 15 3		
0	112	124
1	43	52
3	36	51
K,L= 5 4		
0	70	75
1	69	59
2	106	103
3	61	57
4	66	78
5	169	161
6	195	197
7	77	69
8	63	52
9	165	156
10	128	140
11	114	114
12*	20	10
13	40	49
K,L= 6 4		
0*	21	18
1	133	138
2	70	78
3	201	196
4	82	78
K,L= 0 4		
0	446	521
1	260	265
2	116	115
3	81	87
4	82	101
5	120	131
6	57	47
7	150	157
8	147	151
10	80	67
11	36	37
12*	14	12
13*	12	21
14*	20	22
K,L= 1 4		
0	151	158
1	46	50
2	83	80
3	84	81
4	85	92
5	150	174
6	107	101
7	120	139
8	150	173
9	111	107
10	65	70
11	109	118
12	75	79
13	72	70
K,L= 2 4		
0	98	99
1	359	367
2	79	68
3	130	137
4	121	115
5	181	196
6	169	171
7	182	190
8	80	72
9	80	88
10*	21	15
11	34	35
12*	9	6
13	34	32
K,L= 3 4		
0	73	57
1	134	96
2	47	47
3	113	114
4	96	108
5	59	51
6	110	108
7	175	147
8	95	95
9	81	73
10	124	122
11	91	95
12	70	65
13	44	40
K,L= 4 4		
0	148	141
1	91	74
2	200	202
3	99	133
4	115	108
5	153	155
6	247	234
7	107	86
8	90	86
9	105	94
10	28	20
11*	13	26
12	28	23
13	48	44
K,L= 6 4		
5	114	101
6	91	91
7	137	136
8	36	39
9	37	40
10	49	45
11	31	32
12*	20	24
13	22	35
K,L= 7 4		
0	77	80
1	90	86
2	98	96
3	101	102
4	182	173
5	121	111
6	99	89
7	39	40
8	139	124
9	149	166
10	60	52
11*	10	7
12	87	60
K,L= 8 4		
0	109	106
1	31	25
2	108	113
3	67	60
4	196	201
5	132	129
6	72	74
7*	11	10
8	54	63
9	46	57
11*	4	12
12*	14	38
K,L= 9 4		
0	107	99
1	55	55
2	99	93
3	140	139
4	174	171
5	43	36
6	88	73
7	85	70
8	99	86
9	27	20
10	57	59
11	73	82
K,L= 10 4		
0	52	54
1	97	106
2	35	36
3	56	57
K,L= 11 4		
0	87	87
1	54	51
2	104	114
3	121	117
K,L= 12 4		
0	126	121
1	57	52
2	71	78
3	31	29
K,L= 13 4		
0*	10	7
1	36	41
2	86	94
3	67	67
K,L= 14 4		
0	43	50
1	60	67
2	48	52
3	48	50
K,L= 0 5		
1	141	138
2	101	101
3	139	138
4	68	72
6	157	161
7	79	76
8	62	56
9	56	62
10	154	162
12	73	79
13	62	65
K,L= 1 5		
0	133	132
1	270	282
2	140	139
3	160	159
4	111	121
5	143	160
6	118	136
7	45	55
8*	10	5
9	95	106
10	46	53
11*	13	17
12	24	33
13*	19	22
K,L= 2 5		
0	58	60
1	118	112
2	51	51
4	75	57
5	141	129
6	32	29
7	169	170
8	65	66
9	130	130
11	126	137
12	37	41
K,L= 3 5		
0	234	231
1	182	185
2	59	62
3	136	141
4	97	107
5	135	136
6	157	166
7	191	187
8	89	95
9	23	22
10	58	51
11	81	91
12	41	40
K,L= 4 5		
0*	13	11
1	64	66
2	122	139
3	36	41
4	79	73
5	80	75
6	126	126
7	73	67
8	124	117
9	106	101
10	84	84
11	57	57
12	86	87
K,L= 5 5		
0	130	129
1	132	128
2	131	120
3	191	182
4	164	154
5	170	167
6*	16	17
7	74	73
8	54	43
9*	12	11
10	49	50
11	57	51
12	73	89
K,L= 6 5		
0	195	199
1	61	58
2	57	56
3	63	66
4	114	121
5	83	76
6*	9	17
7	134	137
8	107	114
9	74	74
10	29	29
11	65	80
12*	12	20
K,L= 7 5		
0	44	24
1	113	112
2	121	121
3	86	85
4	209	193
5	134	125
6	175	156
7	34	30
8	47	49
9	26	33
10	24	18
11	29	31
K,L= 8 5		
0	125	122
1	41	32
2	95	94
3	53	60
4	134	130
5	43	36
6	141	135
7	40	34
8	68	67
9	30	26
10	77	102
K,L= 9 5		
0	71	67
1	115	119
2	92	84
3	107	104
4	47	42
5	81	75
6	94	83
7	102	87
8	56	56
9	22	28
10	67	82
K,L= 10 5		
0	43	36
1	45	46
2	171	178
3	44	55
K,L= 11 5		
0	136	131
1	44	40
2	90	106
3	40	30
K,L= 12 5		
0	113	119
1*	12	10
2	56	52
3	94	90
K,L= 13 5		

Table 1 (*cont.*)

H	FO	FC
0*	16	21
1	93	91
2	33	41
3	47	51
K,L= 0 6		
0	147	136
1	108	107
2	86	100
3	192	200
4	75	78
5	50	57
6	128	134
7	96	94
8	114	126
9	43	46
10*	15	24
11	77	76
K,L= 1 6		
0	62	52
1	60	57
2	27	34
3	42	41
4	70	82
5	63	64
6	51	51
7	85	70
8	59	66
9	94	91
10	55	51
11	108	113
K,L= 2 6		
0*	26	27
1	213	208
2	54	40
3	178	180
4	70	50
5	126	122
6	57	40
7	102	103
8	95	90
9	72	74
10*	20	12
11	42	47
K,L= 3 6		
0	64	74
1	53	52
2	51	54
3	42	42
4	110	122
5	42	40
6	63	57
7	56	51
8	83	90
9	97	96
10	85	90
11	80	95
K,L= 4 6		
0	97	90
1	130	127
2	156	154
3	50	52
4	129	130
5	117	103
6	72	70
7	70	76
8	84	87
9	115	110
10	85	69
11	23	30
K,L= 5 6		
0	40	43
1	75	72
2	92	97
3	75	77
4	95	91
5	75	81
6	71	59
7	98	93
8	43	36
9	75	65
10	37	32
11	58	72
K,L= 6 6		
0	27	25
1	97	98
2	120	120
3	155	148
4	95	91
5	97	104
6	40	44
7	51	51
8	31	30
9	68	85
10	92	111
K,L= 7 6		
0	50	63
1	44	38
2	189	177
3	37	30
4	78	74
5	112	105
6	92	82
7	51	58
8	52	44
9	40	47
10	41	54
K,L= 8 6		
0	69	61
1	57	48
2	82	59
3	91	92
4	51	40
5	42	44
6	65	79
7	36	41
8	50	65
9*	17	13
K,L= 9 6		
0	145	143
1	43	31
2	107	106
3	40	46
4	105	110
5	99	102
6	80	55
7	82	55
8	47	48
K,L= 10 6		
0	45	45
1	98	77
2	19	34
3	31	23
K,L= 11 6		
0	141	122
1*	10	24
2	75	83
3	51	55
K,L= 12 6		
0	94	43
1	59	62
2	33	30
K,L= 0 7		
1*	18	5
2	38	40
3	142	131
4	45	44
5	35	30
6	99	93
7*	9	0
8	56	57
9*	21	32
10	46	51
K,L= 1 7		
0	150	148
1	101	156
2	32	26
3	166	162
4	46	60
5	82	87
6	66	70
7	52	54
8	24	33
9	83	61
10	35	47
K,L= 2 7		
0*	14	18
1	24	17
2	86	94
3	26	24
4	61	67
5	92	81
6	45	47
7	39	38
8*	21	25
9	77	74
10*	18	19
K,L= 3 7		
0	103	97
1	126	125
2	70	71
3	149	140
4	39	35
5	42	44
6	97	90
7	74	70
8	26	18
9	64	67
10	67	92
K,L= 4 7		
0	82	71
1	80	79
2	73	89
3	32	35
4	81	90
5	60	61
6	53	54
8	40	10
9	58	59
K,L= 5 7		
0*	11	20
1	120	110
2	84	54
3	86	85
4	40	44
5	61	51
6	32	34
7	35	30
8	89	65
9	25	36
K,L= 6 7		
0	194	189
1	23	29
2	47	51
3	52	62
4	71	70
5	49	41
6	36	42
7	57	80
8	34	47
K,L= 7 7		
0	55	53
1	105	92
2	58	55
3	29	32
4	80	79
5	31	30
6	42	29
7	35	43
8	49	61
K,L= 8 7		
0	71	72
1*	10	24
2	96	105
3	52	61
4	63	60
5	31	35
6	55	71
K,L= 9 7		
1	77	73
2	31	19
3	80	62
4*	17	4
5	50	62
6	53	72
K,L= 10 7		
0	131	121
2	87	80
3	74	88
K,L= 0 8		
0*	8	28
1	172	165
2	123	119
3	47	45
4	24	7
5*	7	4
6	31	36
7	90	90
8	27	17
K,L= 1 8		
0	37	29
1*	19	13
2*	15	14
3*	13	10
4	81	65
5	69	67
6	59	71
7	48	50
8*	19	25
K,L= 2 8		
1	176	158
2	61	54
3	85	82
4	25	26
5	67	54
6	39	49
7	56	62
K,L= 3 8		
0	101	101
1	31	33
2	34	26
3	50	40
4	71	73
5	48	42
6*	21	23
7	39	43
K,L= 4 8		
0	117	108
1	112	99
2	59	54
3	49	43
4	77	75
5	28	28
6	74	75
7	30	39
K,L= 5 8		
0	27	25
1	42	44
2	100	97
3	96	88
4*	21	17
5	31	29
6	55	62
K,L= 6 8		
0*	15	32
1	61	61
2	23	23
3	75	75
4*	14	25
5	60	68
6*	10	29
K,L= 7 8		
0	77	76
1	107	101
2	80	77
3	39	38
4	71	80
5	56	72
K,L= 8 8		
3*	20	47
K,L= 0 9		
2*	21	17
3	70	67
K,L= 1 9		
0	151	151
1	99	97
2*	13	5
3	46	40
4	76	91
K,L= 2 9		
0	23	20
1*	18	14
2	79	81
3	29	36
K,L= 3 9		
0	52	45
1	84	78
2	94	104
3	46	50
K,L= 4 9		
0	43	30
1	73	73
2	46	40

Crystal data

$(+)_{D}$-$\mathrm{[Co(C_{10}H_{28}N_6)]\ [Co(CN)_6].2H_2O}$, M.W.540·39

Orthorhombic, $a = 15{\cdot}471 \pm 0{\cdot}004$, $b = 16{\cdot}036 \pm 0{\cdot}005$, $c = 9{\cdot}253 \pm 0{\cdot}003$ Å

$U = 2295{\cdot}6$ Å^3, $D_m = 1{\cdot}551$ g.cm^{-3}, $Z = 4$, $D_x = 1{\cdot}564$ g.cm^{-3}, $F(000) = 1128$.

Linear absorption coefficient for Fe $K\alpha$ radiation $\mu = 38{\cdot}29$ cm^{-1}.

Absent reflexions, $h00$ for h = odd, $0k0$ for k = odd, $00l$ for l = odd. Space group $P2_12_12_1$ (D_2^4, No. 19).

Structure analysis

In order to obtain a trial structure, a three-dimensional Patterson function was calculated. Coordinates of the two kinds of cobalt atoms were determined from the prominent peaks in the Patterson function. These coordinates were used to calculate the structure factors. The reliability index for these F_c's was 0·35. A three-dimensional electron density map was then calculated with all the terms, the phases of which were calculated on the basis of the cobalt atoms. The resulting map showed, in addition to two large cobalt peaks, smaller peaks corresponding to six cyano groups in the complex anion and six nitrogen atoms in the complex cation. Positions of these lighter atoms were then included in the calculation of the structure factors. Successive Fourier syntheses of electron density revealed the positions of all other lighter atoms.

The atomic positions and isotropic temperature factors were refined by the least-squares method with a block-diagonal program *HBLS* written by Dr Ashida.

A weighting scheme, $\omega=0{\cdot}3$ for $|F_o|$'s smaller than 2·00 and $\omega=1$ for all other $|F_o|$'s, was employed, and the scattering factors for Co, N, C and O were those listed in *International Tables for X-ray Crystallography* (1962). After several refinement cycles the structure converged with $R=0{\cdot}100$. Three further cycles of least-squares were calculated in anisotropic modes. R then reduced to 0·091. Difference synthesis revealed four-

Table 2. *Final atomic parameters* ($\times 10^4$) *and estimated standard deviations*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	4783	3816	4894	25	24	46	−1	4	2
	2	2	3	1	1	3	3	4	4
Co(2)	2344	2258	405	28	24	51	−1	−4	6
	2	2	3	1	1	3	3	4	4
N(1)	1630	507	597	28	20	142	−12	−41	−5
	11	11	22	9	9	32	16	29	29
N(2)	3030	4043	721	13	16	89	6	−5	30
	10	10	18	7	8	24	14	23	23
N(3)	3692	1869	−1936	43	46	68	23	−19	28
	13	13	20	11	12	25	20	29	29
N(4)	1029	2630	−2011	80	25	68	47	44	20
	15	12	20	14	10	25	23	33	27
N(5)	3634	1814	2733	37	22	80	−19	7	8
	12	11	20	10	9	26	17	28	26
N(6)	935	2755	2508	38	58	77	−19	45	−4
	12	15	20	10	12	26	21	28	33
N(7)	5913	3223	4839	8	12	82	−16	−3	−1
	9	9	19	6	7	23	12	23	25
N(8)	5478	4765	4222	3	28	34	−13	15	−13
	9	10	16	6	9	20	13	19	21
N(9)	3793	4565	5153	7	16	63	16	3	39
	9	9	17	6	7	22	12	23	24
N(10)	3959	2889	5276	12	17	77	14	−10	−8
	9	10	18	6	8	23	13	23	26
N(11)	4983	3963	7007	8	33	51	−22	12	−26
	9	11	16	7	9	21	15	20	23
N(12)	4608	3573	2803	16	17	32	−8	11	−17
	10	10	16	7	8	19	14	21	20
C(1)	1904	1137	463	20	3	80	−19	−16	9
	12	12	21	8	8	27	17	28	28
C(2)	2781	3378	543	10	24	61	16	−9	22
	12	13	22	8	10	27	17	28	28
C(3)	1839	8017	3920	43	14	11	49	−6	−12
	14	12	20	12	10	23	20	28	24
C(4)	3424	7488	3845	14	31	42	−5	32	−17
	13	13	21	9	12	25	18	26	28
C(5)	3169	1973	1849	21	11	9	1	−16	11
	12	11	19	9	9	22	17	25	23
C(6)	1450	2573	1719	49	29	13	26	−6	−10
	16	14	21	13	12	23	22	30	28
C(7)	4953	5565	4468	21	42	76	−21	59	6
	13	15	23	10	12	29	20	30	32
C(8)	3971	5343	4264	50	16	75	44	54	70
	15	13	23	13	10	31	21	35	29
C(9)	6298	4778	5110	14	26	158	−4	−77	−37
	12	13	29	9	11	40	17	35	39
C(10)	6641	3864	5121	33	49	100	12	−15	−17
	14	16	27	11	13	33	23	36	44
C(11)	3013	4099	4579	35	39	108	36	−10	−18
	14	15	27	11	13	34	21	35	36
C(12)	3024	3186	5195	25	24	70	−47	−26	9
	12	13	24	9	10	28	18	31	32
C(13)	4963	4280	1848	70	17	11	−24	10	12
	17	13	20	15	9	22	24	33	24
C(14)	5693	4690	2649	29	29	49	3	49	9
	14	14	22	10	11	28	20	31	29
C(15)	3681	4803	6756	38	17	32	−14	25	−43
	14	13	21	11	10	25	19	29	27
C(16)	4125	4147	7734	24	18	74	11	−24	−2
	13	13	23	10	11	29	18	30	29
O(1)	4089	6103	723	65	99	181	1	28	14
	13	15	23	12	15	33	24	35	42
O(2)	355	9345	1474	56	42	89	8	−23	16
	11	11	17	10	9	22	18	26	23

teen positions out of twenty eight hydrogen atoms of the penten molecule. Positions of the missing hydrogen atoms were supplied by calculation. After inclusion of the hydrogen atoms a final set of least-squares calculations was carried out, but the parameters of hydrogen atoms were not varied. Temperature factors of the hydrogen atoms were assumed to be isotropic and were given the same values as those of the atoms to which the hydrogen atoms were attached. In the last cycle of least-squares, all the parameter shifts were well within the corresponding standard deviations. Table 1 gives the observed and calculated structure factors.

The *R* value was 0·083 for all the 1243 observed reflexions. The atomic parameters are listed in Table 2, together with their estimated standard deviations.

Determination of the absolute configuration

An equi-inclination Weissenberg photograph was taken, with Cu $K\alpha$ radiation, of the first layer line around the *a* axis. Calculation showed that the series of re-

Table 3. *Determination of the absolute configuration*

Indices			$F_c^2(hkl)$	Observed relations	$F_c^2(h\bar{k}$
1	1	3	8138	<	10644
1	2	3	1779	>	1271
1	3	3	362	<	1761
1	4	3	516	>	101
1	5	3	4198	≃	4204

Table 4. *Interatomic distances and angles within the complex ions with their estimated standard deviations*

(*a*) $(+)_D$-$[Co(penten)]^{3+}$

Co(1)–N(7)	1·990 Å 14	N(7)—C(10)	1·548 27
Co(1)–N(8)	1·965 16	N(8)—C(7)	1·535 27
Co(1)–N(9)	1·962 14	N(8)—C(9)	1·512 25
Co(1)–N(10)	1·989 15	N(8)—C(14)	1·498 25
Co(1)–N(11)	1·993 15	N(9)—C(8)	1·519 26
Co(1)–N(12)	1·993 15	N(9)—C(11)	1·516 27
C(7)—C(8)	1·570 31	N(9)—C(15)	1·541 25
C(9)—C(10)	1·558 32	N(10)–C(12)	1·525 24
C(11)–C(12)	1·571 32	N(11)–C(16)	1·517 25
C(13)–C(14)	1·502 32	N(12)–C(13)	1·539 26
C(15)–C(16)	1·548 29		

N(7)—Co(1)–N(8)	83·2° 6	N(7)—Co(1)–N(9)	169·0 6	N(7)—Co(1)–N(10)	102·2 6
N(7)—Co(1)–N(11)	86·9 6	N(7)—Co(1)–N(12)	90·1 6	N(8)—Co(1)–N(9)	89·5 6
N(8)—Co(1)–N(10)	170·2 6	N(8)—Co(1)–N(11)	97·7 6	N(8)—Co(1)–N(12)	85·3 6
N(9)—Co(1)–N(10)	86·3 6	N(9)—Co(1)–N(11)	85·9 6	N(9)—Co(1)–N(12)	97·6 6
N(10)-Co(1)–N(11)	90·8 6	N(10)-Co(1)–N(12)	86·5 6	N(11)-Co(1)–N(12)	175·5 6
Co(1)–N(7)—C(10)	108·5 12	Co(1)–N(8)—C(7)	108·1 11	Co(1)–N(8)—C(9)	107·3 12
Co(1)–N(8)—C(14)	111·6 12	Co(1)–N(9)—C(8)	107·2 11	Co(1)–N(9)—C(11)	106·0 12
Co(1)–N(9)—C(15)	110·9 11	Co(1)–N(10)-C(12)	111·5 11	Co(1)–N(11)-C(16)	108·8 11
Co(1)–N(12)-C(13)	111·4 11	C(7)—N(8)—C(9)	110·6 15	C(7)—N(8)—C(14)	109·2 15
C(8)—N(9)—C(11)	111·1 15	C(8)—N(9)—C(15)	109·8 14	C(9)—N(8)—C(14)	110·0 14
C(11)–N(9)—C(15)	111·7 14	N(7)—C(10)–C(9)	112·0 16	N(8)—C(7)—C(8)	107·7 17
N(8)—C(9)—C(10)	106·1 17	N(8)—C(14)–C(13)	110·3 17	N(9)—C(8)—C(7)	107·3 16
N(9)—C(11)–C(12)	109·0 17	N(9)—C(15)–C(16)	110·2 16	N(10)-C(12)–C(11)	108·5 16
N(11)–C(16)–C(15)	105·2 16	N(12)–C(13)–C(14)	108·0 15		

Table 4 (*cont.*)

(*b*) $[\mathrm{Co(CN)_6}]^{3-}$

Co(2)–C(1)	1·922 Å 19	N(1)—C(1)	1·103 26
Co(2)–C(2)	1·925 21	N(2)—C(2)	1·145 26
Co(2)–C(3)	1·919 20	N(3)—C(3)	1·156 28
Co(2)–C(4)	1·914 20	N(4)—C(4)	1·174 29
Co(2)–C(5)	1·903 18	N(5)—C(5)	1·118 26
Co(2)–C(6)	1·908 22	N(6)—C(6)	1·121 29

C(1)—Co(2)-C(2)	174·6° 8	C(1)—Co(2)-C(3)	92·2 8	C(1)—Co(2)-C(4)	90·0 8
C(1)—Co(2)-C(5)	89·7 8	C(1)—Co(2)-C(6)	88·5 9	C(2)—Co(2)-C(3)	91·7 9
C(2)—Co(2)-C(4)	94·0 9	C(2)—Co(2)-C(5)	86·6 8	C(2)—Co(2)-C(6)	88·0 9
C(3)—Co(2)-C(4)	85·3 8	C(3)—Co(2)-C(5)	90·3 8	C(3)—Co(2)-C(6)	173·8 9
C(4)—Co(2)-C(5)	175·6 8	C(4)—Co(2)-C(6)	88·5 9	C(5)—Co(2)-C(6)	95·9 9
Co(2)-C(1)—N(1)	174·8 18	Co(2)-C(2)—N(2)	175·5 18	Co(2)-C(3)—N(3)	174·6 18
Co(2)-C(4)—N(4)	172·1 18	Co(2)-C(5)—N(5)	177·5 18	Co(2)-C(6)—N(6)	178·9 20

flexions 113, 123, 133, 143 and 153 were most suitable for the determination. The differences in intensity between the reflexions and the counter-reflexions were clearly observable in this series as shown in Table 3. Comparison of the observed and calculated differences shows that $(+)_{\mathrm{D}}$-$[\mathrm{Co(penten)}]^{3+}$ has the absolute configuration illustrated in Fig. 1.

Description of the structure and discussion

The structure is essentially ionic, consisting of $(+)_{\mathrm{D}}$-$[\mathrm{Co(penten)}]^{3+}$, $[\mathrm{Co(CN)_6}]^{3-}$ and water molecules. The configuration of the complex ion $(+)_{\mathrm{D}}$-$[\mathrm{Co(penten)}]^{3+}$ is illustrated in Fig. 1. The interatomic distances and bond angles within the complex ions are listed in Table 4. The cobalt atom is surrounded by six nitrogen atoms at distances 1·96–1·99 Å. These Co–N distances are similar to those reported for other amine complexes. However, the coordination octahedron is distorted. The angles for N(7)–Co(1)–N(10) and N(9)–Co(1)–N(12) are 102·2° and 97·6° respectively; these would be 90° if the octahedron were regular.

The N(11)–Co(1) and Co(1)–N(12) bonds are not collinear, but make an angle of 175·5°. Likewise the angles N(8)–Co(1)–N(10) and N(7)–Co(1)–N(9) are 170·2 and 169·0° respectively. Five five-membered chelate rings are formed in the complex cation. Roughly speaking, three of the five chelate rings form a girdle about the cobalt atom. Approximately at right angles to the girdle and to one another are two other five-membered chelate rings. The C–C and C–N distances are normal as shown in Table 4. The N–Co–N angle in the chelate ring is always less than 90°. The angle N(8)–Co(1)–N(9) of 89·5° is somewhat larger than the average value of other N–Co–N angles, 85·2°. This may be the result of multiple ring formation at N(8) and N(9). All the chelate rings are not planar. Table 5

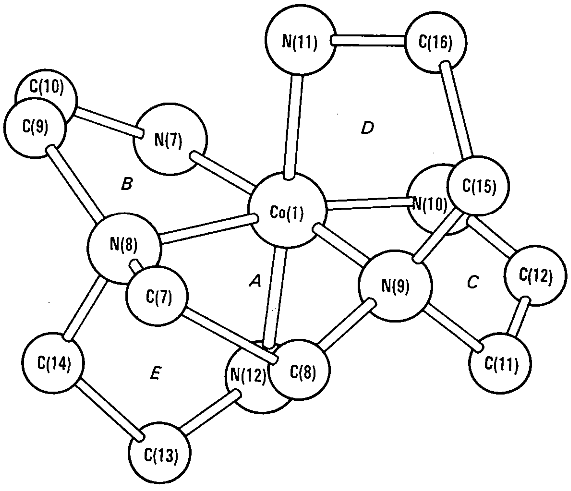


Fig. 1. A perspective drawing of the complex ion, $(+)_{\mathrm{D}}$-$[\mathrm{Co(penten)}]^{3+}$.

lists the deviation of the carbon atoms from the plane formed by the central cobalt atom and the two nitrogen atoms. The deviations are not symmetrical with respect to the plane unlike the case of the structure of $[Co(en)_3]^{3+}$ salts. The conformation of each chelate ring is also listed in Table 5. The conformation of the unique ring *A* is *δ*. The conformations of the rings *B*, *C*, and *E* are all *λ*, whereas that of the ring *D* is *δ*. Thus the complex cation, as a whole, does not have a twofold axis through the midpoint of the *C–C* bond of ring *A* and the central cobalt atom, as in the structurally related EDTA complex (Wiekliem & Hoard, 1959). The conformations of these chelate rings are determined primarily by the non-bonded hydrogen interactions within the ligand, but it may also be affected by the packing of the neighbouring ions. The distortion of the chelate rings *B* and *C* is most noticeable. The two carbon atoms are both on the same side of the plane defined by Co and the two nitrogen atoms. This is clearly a result of the constraints attending multiple, as well as fused, ring formation. Nevertheless, the dispositions of bonds around the tertiary nitrogen atoms N(8) and N(9) are nearly regular tetrahedral as seen in Table 4.

Table 5. *Deviations of the carbon atoms from the plane formed by the central cobalt atom and the two nitrogen atoms*

Ring	Atom	Shift	Ring conformation
A	C(7)	−0·211 Å	*δ*
	C(8)	0·468	
B	C(9)	−1·003	*λ*
	C(10)	−0·715	
C	C(11)	0·806	*λ*
	C(12)	0·334	
D	C(15)	0·082	*δ*
	C(16)	0·676	
E	C(13)	0·205	*λ*
	C(14)	−0·340	

The six CN groups in the complex ion $[Co(CN)_6]^{3-}$ are arranged at the apices of a slightly distorted octahedron around the metal atom, with an average Co–C distance of 1·92 Å. The C–N distances are in the range 1·10–1·17 Å and correspond to the normal triple bond. The C–N bonds are nearly collinear with the Co–C bonds.

The most striking feature of the packing of the complex ions is that they and the water molecules are in layers parallel to the plane (001). A projection of the structure along the *c* axis is shown in Fig. 2. The cobalt atoms are all approximately in the planes $z=0,\frac{1}{2}$. Broken lines indicate some close contacts. The complex ion $[Co(penten)]^{3+}$ is so oriented that the three chelate rings which form a girdle around the cobalt atom are approximately parallel to the plane (001). The complex anion, $[Co(CN)_6]^{3-}$ lies with one of its NC–Co–CN bonds nearly parallel to (001).

The shortest contacts between the complex cations and anions occur between the nitrogen atom of $[Co(CN)_6]^{3-}$ and the terminal nitrogen atom of $[Co(penten)]^{3+}$. They are listed in Table 6 and are also indicated by broken lines in Fig. 2. The tertiary nitrogen atoms of penten have no such neighbours but have only usual van der Waals contacts.

Table 6. *Interatomic distances less than* 3·5 Å *outside the complex ions*

N(1)–N(11)	3·483 26	N(1)--O(2)	2·833 25
N(2)–N(12)	3·199 23	N(4)—O(1)	2·926 30
N(3)–N(10)	3·082 25	N(6)--O(1)	3·493 33
N(4)–N(7)	2·958 25	N(6)--O(2)	3·371 28
N(4)–N(12)	3·015 26	N(7)--O(1)	3·439 30
N(5)–N(10)	2·960 24	C(13)–O(1)	3·386 32
N(5)–N(12)	3·198 27	C(15)–O(2)	3·356 28
N(6)–N(7)	2·913 30	C(16)–O(2)	3·164 30
N(6)–N(11)	3·156 31	O(1)—O(2)	2·912 27
N(1)–C(13)	3·447 30		
N(1)–C(14)	3·350 31		
N(2)–C(13)	3·191 28		
N(2)–C(16)	3·246 26		
N(4)–C(13)	3·482 32		

Two water molecules are held together by a weak hydrogen bond to form a pair, with an O---O distance of 2·91 Å. Each oxygen atom is bonded to the nitrogen atoms of the CN group in $[Co(CN)_6]^{3-}$. Thus the complex anions are held together by these water molecules, forming a two-dimensional network parallel to (001). The complex cations are arranged between these networks.

Absolute configuration and optical properties

The absolute configuration of the complex ion, $(+)_D$-$[Co(penten)]^{3+}$ can be designated as skew chelate pairs, $\Lambda\Delta\Lambda$, (*IUPAC Information Bulletin*, 1968). It is now possible to correlate the octant sign (Hawkins & Larsen, 1965; Gollogly & Hawkins, 1966) or the net chirality (Legg & Douglas, 1966) of the complex ion $(+)_D$-$[Co(penten)]^{3+}$ with the circular dichroism spectra, since the absolute configuration has been established by X-ray analysis. The net chirality of $(+)_D$-$[Co(penten)]^{3+}$ is Λ or its octant sign is +. The circular dichroism spectra of this complex ion in aqueous solutions shows a positive Cotton effect in the longer wavelength band in the region of the octahedral T_{1g} absorption $({}^1A_{1g} \rightarrow {}^1T_{1g})$. Accordingly, it may be concluded that both the ring-pairing method to deduce the net chirality of the complex ion and the method of octant sign are applicable to a series of sexidentate complexes and the sign of the longer wavelength circular dichroism spectra can be empirically correlated with the net chirality of the complex ion. The complex ion also shows a positive circular dichroism band in the region of octahedral T_{2g} absorption ($^1A_{1g} \rightarrow {}^1T_{2g}$). This transition is magnetically forbidden and should be optically inactive according to the definition of rotatory strength. Under the digonal field, however, the energetic splitting of the octahedral $^1T_{1g}$ and $^1T_{2g}$ states might

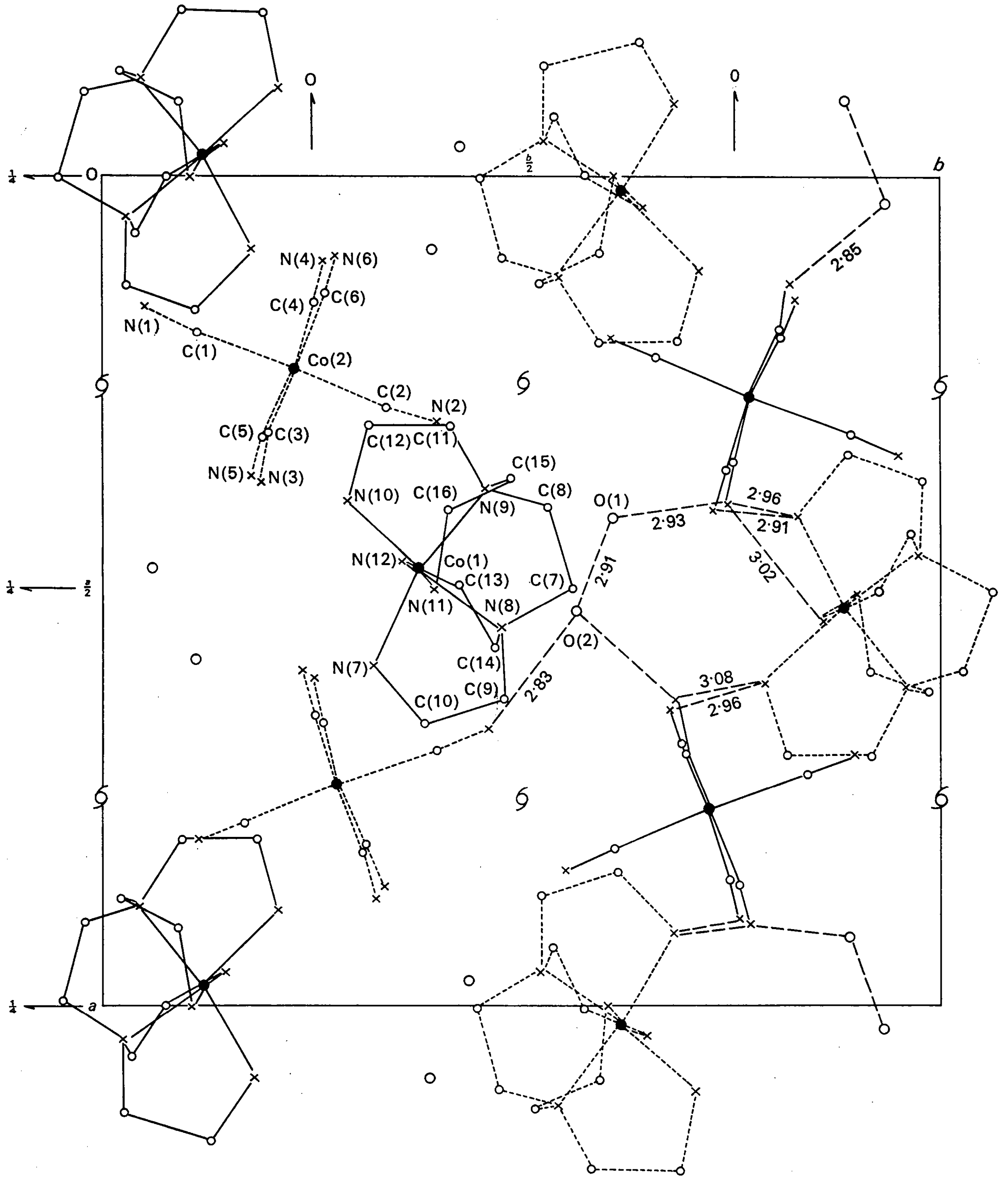


Fig. 2. A projection of the structure along the c axis. Broken lines indicate some close contacts. Full and broken lines indicate complex ions where the central cobalt atoms are at approximate heights ½ and 0 respectively.

enable the two states to mix to some extent, the former being magnetically allowed. Thus the transition in the region of octahedral T_{2g} absorption becomes optically active and this may explain the fairly large circular dichroism band observed in this region.

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Die Kristallstruktur von monoklinem Siliziumphosphat $\mathrm{SiP_2O}A_7\mathrm{III}$: Eine Phase mit [SiO$_6$]-Oktaedern

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SiP$_2$O$_7$ (*A*III modification) crystallizes in space group $P2_1/c$ with four formula units in the cell with the dimensions $a=4·73$, $b=6·33$, $c=14·71$ Å, $\beta=90·1$°. The crystal structure has been determined by three-dimensional X-ray analysis, the final R index being 0·07. Two PO$_4$-tetrahedra are linked almost symmetrically (plane of symmetry) forming a staggered P$_2$O$_7$ group with a P–O–P angle of 139·2°. The averaged P–O bond lengths to the bridge oxygen atom and to the terminal oxygen atoms are 1·589 and 1·506 Å respectively. The average Si–O distance of a slightly deformed SiO$_6$-tetrahedron is 1·763 Å.

Einleitung

Silizium ist in den Silikaten bekanntlich tetraedrisch von je vier Sauerstoffatomen umgeben. 1935 schlossen jedoch Levi & Peyronel aufgrund der Isotypie von kubischem SiP$_2$O$_7$ mit ZrP$_2$O$_7$ auf oktaedrische Koordination des Siliziums gegenüber Sauerstoff im kubischen Siliziumdiphosphat. Grosse Beachtung fand die Synthese einer mit Rutil, TiO$_2$ isotypen Modifikation des Siliziumdioxids bei sehr hohem Druck und hoher Temperatur durch Stishov & Popova (1961), die nach ihrer Entdeckung in Meteoritenkratern als Stishovit bezeichnet wurde (Chao, Fahey & Littler, 1962). Seitdem bemüht man sich in zahlreichen Laboratorien intensiv, petrographisch wichtige Silikate durch Anwendung extrem hoher Drucke bei gleichzeitigem Erhitzen in Phasen mit oktaedrisch koordiniertem Silizium umzuwandeln. So gelang Ringwood, Reid & Wadsley (1967) bei 120 kb und 900°C die Umwandlung von Kalifeldspat KAlSi$_3$O$_8$ in eine Phase, die nach diesen Autoren [SiO$_6$]-Oktaeder enthalten soll, und Ringwood (1967) berichtete über die Synthese einer Granatphase der Zusammensetzung Mg$_3$(AlMg$_{0,5}$ Si$_{0,5}$) [SiO$_4$]$_3$ bei etwa 100 kb und 900°C, bei der ein Teil des Siliziums oktaedrisch koordiniert sein soll. Das starke Interesse an solchen Phasen beruht darauf, dass derartige Druck- und Temperaturbedingungen in grossen Erdtiefen vorliegen.

Trotz dieses lebhaften Interesses an der Oktaeder-Koordination des Siliziums liegen bisher nur von Stishovit (Stishov & Belov, 1962; Preisinger, 1962) und dem Hochdruck-Kalifeldspat (Ringwood, Reid & Wadsley, 1967) Angaben über die Abmessungen der [SiO$_6$]-Gruppe vor, die sich zudem noch widersprechen. Die vorliegende Arbeit gibt genauere Angaben über Atomabstände und Valenzwinkel von [SiO$_6$]-Oktaedern in SiP$_2$O$_7$.

Nach Liebau, Bissert & Köppen (1968) lassen sich die mindestens acht Phasen der Zusammensetzung SiO$_2$.P$_2$O$_5$ aufgrund ihrer Röntgen-Pulverdiagramme in zwei Gruppen einteilen, die als *A*- bzw. *B*-Phasen bezeichnet wurden. Die Phase SiP$_2$O$_7$*A*I ist die von Levi & Peyronel beschriebene kubische Phase, SiP$_2$O$_7$*A*III ist eine monokline Modifikation, deren Struktur in der vorliegenden Arbeit beschrieben wird. Eine Kristallstrukturbestimmung einer weiteren mono-