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The Absolute Configuration of the $(+)_{546}$-β-Oxalato[(6*R*,8*S*)-dimethyl-2,5,9,12-tetraazatridecane]cobalt(III) Ion, $(+)_{546}$-β-[Co(ox)(*N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet)]$^+$

Shigenobu Yano, Keizo Furuhashi, and Sadao Yoshikawa

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Tokyo 113

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The crystal and molecular structure of $(+)_{546}$-β-[Co(ox)(*N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet)]$^+$ has been determined from three-dimensional intensity data collected by counter methods. The structure has been refined by least-squares techniques to an *R* factor of 5.9% for 838 reflections above the background. The red violet crystals are orthorhombic, with a space group of $P2_12_12_1$, with $Z=4$ ($D_m=1.501$, $D_c=1.505$ g/cm^3), and with cell constants of $a=14.175(5)$, $b=18.591(2)$ and $c=7.747(4)$ Å. The complex ion has the Δ absolute configuration, which was determined by the Bijvoet method. The quadridentate ligand, *N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet, is coordinated to the Co *via* 4 N atoms in the *cis*-β configuration, yielding two terminal 5-membered chelate rings with the λ conformation and a central 6-membered ring with a chair conformation (both C–CH$_3$ groups are equatorial). The secondary N atoms have *R* chirality except for one terminal N atom, the absolute configuration of which is *S*. The N(*S*)–CH$_3$ group in the "out-of-plane" 5-membered ring is equatorial, whereas the N(*R*)–CH$_3$ group in the other ring has an axial disposition.

In recent years, metal complexes containing six-membered β-diamine with *C*-methyl groups have been under investigation.[1] However, only two complexes have been structurally elucidated by X-ray analysis. Kobayashi *et al.*, reported that each 2,4-pentanediamine chelate ring in the {Co[(*R*,*R*)-2,4-pentanediamine]$_3$}$^{3+}$ ion takes a skew-boat conformation, with both methyl groups in an equatorial position.[2] On the other hand, in the $(+)_{470}$-β-[Co(NO$_2$)$_2$(4-methyl-3,7-diazanonane-1,9-diamine)]$^+$ ion, the central six-membered chelate ring of the tetramine adopts a chair conformation, with an equatorial methyl group.[3] Thus, there are two probable conformations for the central 2,4-pentanediamine moiety of the tetramine in the [Co(ox)(*N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet)]$^+$ ion, where *N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet is (6*R*,8*S*)-6,8-dimethyl-2,5,9,12-tetraazatridecane.

Our present ligand, *N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet, has two *N*-methyl groups, it is of interest in elucidating the stereochemistry of this system.

The crystal structure of $(+)_{546}$-[Co(ox)(*N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet)]ClO$_4$, isolated by Dr. Fujio Mizukami,[4] has been determined by X-ray structure analysis in oder to establish the stereochemical configuration of the complex ion.

Experimental

The crystals of $(+)_{546}$-β-[Co(ox)(*N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet)]ClO$_4$ were kindly supplied by Dr. Fujio Mizukami of the National Chemical Laboratory for Industry. The systematic absences observed on Weissenberg photographs are *h*00 for *h* odd, 0*k*0 for *k* odd, and 00*l* for *l* odd, all consistent with the $P2_12_12_1$ space group. The precise lattice conatsnts were obtained by the least-squares analysis of the 2θ angles of the reflections carefully measured on a Rigaku-Denki four-circle automatic X-ray diffractometer by the use of Mo$K\alpha$ radiation $\lambda=0.7107$ Å). The values are $a=14.175(5)$, $b=18.591(2)$, and $c=7.747(4)$ Å. The calculated density of 1.505 g/cm^3 for the four formula units in the unit cell agrees well with the density of 1.501 g/cm^3 measured by the floatation method in a mixture of carbon tetrachloride and dibromoethane. The crystal used in the data collection was an irregularly shaped plate with the approximate dimensions of $0.4\times0.25\times0.3$ mm. The crystal was mounted with the c axis approximately parallel to the instrument axis. The intensity data ($2\theta\leqq60°$) were collected by the ω-2θ scan technique, using Mo$K\alpha$ radiation monochromated by a LiF crystal. The scan speed was 2°/min in 2θ, and the stationary-crystal, stationary-counter background counts of 10 s were taken at each end of the scan. As a general check on the electronic and crystal stability, the intensities of four standard reflections were monitored every 50 reflections during the collection of the intensity data, no significant variation was noted. A total of 838 indepent reflctions larger than 3σ were used for the structure determination, where σ is given by $|F|/2I_0[I_P+(B_1+B_2)(T_P/2T_B)^2]^{1/2}$ (I_P and I_0 are the total intensity and the net intensity respectively; B_1 and B_2 are the background counts, T_P and T_B are the times required for the measurements of the peak and background intensities).

Determination and Refinement of the Structure

In order to obtain a trial structure, a three-dimentional Patterson function was calculated. The coordinates of the cobalt and chlorine atoms were determined from the prominent peaks in the Patterson function. The remaining non-hydrogen atoms were located from a Fourier map phased by the heavy atoms. The conventional *R* value ($\sum||F_o|-|F_c||/\sum|F_o|$) was 0.561 at this stage. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[5] Refinement was carried out with a block-diagonal least-squares method in the isotropic mode. A weighting scheme, $\omega=1$ if $F_o\geq10.0$ and otherwise $\omega=0.2$, was employed. After several cycles of the refinement, the *R* value was reduced to 0.175 ($R'=(\sum\omega(|F_o|-|F_c|)^2/\sum\omega F_o^2)^{1/2}=0.196$). When the least-squares calculations were continued with anisotropic thermal parameters, the *R* and *R*′ values reached 0.076 and 0.082 respectively. Differential synthesis showed no abnormal features except for the ambiguity in the positions of the hydrogen atoms. At this stage, the idealized positions of the hydrogen atoms were calculated using a C–H distance of 1.08 Å and H–C–H angles of 109°28′. These hydrogen atoms were included in the subsequent

Table. 1. Observed and calculated structure factors($\times 2$)

K	FO	FC
H,L= 0 0		
6	215	211
10	47	46
H,L= 1 0		
4	91	92
7	79	77
8	93	96
9	69	66
13	20	20
14	103	103
15	46	47
18	45	49
22	39	42
H,L= 2 0		
7	152	154
12	42	48
14	43	41
16	31	24
17	51	52
H,L= 3 0		
1	66	67
3	30	42
4	241	245
6	96	98
7	29	27
8	256	260
9	153	150
10	124	119
11	32	31
12	36	33
13	40	46
14	66	67
15	67	64
17	44	47
18	27	30
21	31	36
H,L= 4 0		
3	75	79
8	99	98
11	81	81
12	26	25
14	23	27
H,L= 5 0		
2	24	22
7	131	129
8	117	120
12	51	46
13	106	102
17	60	66
H,L= 6 0		
0	233	229
5	90	82
7	54	55
8	52	46
9	58	61
11	95	96
12	61	58
15	52	50
16	31	34
H,L= 7 0		
1	46	43
2	45	48
5	47	52
7	57	50
8	63	55
9	30	30
10	111	109
11	64	67
12	28	23
13	49	52
14	42	47
15	43	38
16	33	31
17	46	43
18	36	32
H,L= 8 0		
1	26	25
3	38	25
4	86	91
7	54	56
8	88	91
9	51	51
12	105	105
20	30	27
H,L= 9 0		
2	64	68
3	37	41
6	101	102
7	49	47
8	45	45
9	27	26
10	73	74
14	56	53
15	29	31
H,L= 10 0		
0	117	115
3	32	33
5	71	67
6	82	82
7	75	79
9	69	70
10	30	33
11	36	38
12	31	35
13	32	28
16	23	22
H,L= 11 0		
1	69	74
2	75	78
3	84	83
4	26	27
5	41	45
11	26	20
H,L= 12 0		
0	41	40
3	46	45
5	30	31
11	32	28
13	32	32
19	32	27
H,L= 13 0		
1	84	77
3	55	58
5	49	55
6	29	26
8	22	22
H,L= 14 0		
1	37	37
5	35	32
9	36	33
17	25	21
H,L= 15 0		
1	35	33
2	59	52
3	32	27
5	42	37
H,L= 16 0		
0	40	39
7	28	20
12	28	21
H,L= 17 0		
2	42	35
6	37	33
H,L= 19 0		
6	31	36
H,L= 0 1		
6	89	91
7	37	31
9	86	85
10	70	66
11	50	55
12	89	88
13	63	60
14	34	36
16	28	27
H,L= 1 1		
4	235	227
5	124	125
6	67	70
7	67	62
8	61	60
9	38	41
10	45	39
11	49	51
13	42	38
14	35	33
16	88	88
20	36	32
H,L= 2 1		
0	110	113
1	76	73
4	147	143
5	76	69
6	105	107
9	112	115
10	62	61
13	36	37
14	27	27
15	57	50
H,L= 3 1		
0	200	199
1	66	54
2	151	144
6	100	109
7	149	145
8	24	26
9	71	75
10	57	56
11	44	43
12	36	35
14	29	33
15	56	56
18	23	25
20	33	22
H,L= 4 1		
0	43	46
2	61	63
3	61	58
4	180	181
5	146	139
6	38	28
8	94	101
9	110	110
10	33	33
11	40	39
12	84	88
13	34	36
16	34	39
17	23	20
H,L= 5 1		
0	44	49
2	50	53
4	118	119
8	46	47
10	54	68
11	30	31
13	48	42
14	47	47
15	54	56
18	33	33
19	25	26
H,L= 6 1		
0	52	40
2	80	89
5	115	122
6	62	63
7	47	51
10	53	55
11	25	27
12	54	57
15	27	25
16	40	36
18	33	29
H,L= 7 1		
1	29	29
3	39	33
6	47	48
8	85	81
9	80	73
10	47	48
11	36	35
12	46	50
13	51	56
16	28	27
H,L= 8 1		
1	27	19
3	35	40
4	30	20
5	75	75
6	109	113
7	52	55
9	44	51
10	80	80
11	47	39
14	37	36
15	31	26
H,L= 9 1		
0	40	54
1	39	51
2	56	37
3	59	55
4	144	144
5	34	28
7	53	46
8	63	66
12	65	68
13	40	36
16	24	20
H,L= 10 1		
0	38	40
1	48	44
2	106	106
3	43	42
4	31	21
6	55	57
8	49	50
10	44	41
11	46	50
13	55	51
15	27	19
H,L= 11 1		
0	55	54
1	70	64
2	24	29
3	70	67
4	61	69
5	33	37
10	30	31
11	43	45
12	32	34
H,L= 12 1		
0	65	58
1	38	41
2	45	47
4	32	33
7	24	19
8	39	40
9	31	28
11	34	39
H,L= 13 1		
1	56	53
3	46	50
5	35	34
7	53	48
11	31	35
H,L= 14 1		
4	26	33
7	29	31
8	29	24
9	29	26
H,L= 15 1		
3	44	43
H,L= 17 1		
0	48	47
8	35	39
H,L= 0 2		
4	72	73
5	28	25
8	61	53
9	77	72
10	43	46
11	159	164
14	43	45
15	28	35
17	50	50
H,L= 1 2		
6	31	32
8	49	47
9	77	72
11	102	105
12	57	54
14	61	58
15	33	38
16	29	22
19	26	25
H,L= 2 2		
1	74	75
2	65	58
3	123	118
5	125	123
7	60	66
9	76	79
11	83	79
12	22	16
13	68	69
14	65	63
17	30	34
18	28	32
19	23	20
21	24	23
H,L= 3 2		
0	146	145
4	205	201
7	109	96
8	108	102
9	42	48
10	38	40
11	48	44
12	70	75
13	33	25
14	44	45
15	23	28
16	29	31
20	37	32
H,L= 4 2		
0	39	46
1	87	89
2	79	74
3	86	94
4	29	24
5	62	61
6	143	151
7	112	106
8	27	29
10	69	69
13	19	18
14	63	65
18	48	48
H,L= 5 2		
1	65	69
2	57	59
3	58	54
5	62	59
7	52	52
8	92	91
9	49	54
10	21	20
11	41	45
12	48	51
13	36	40
14	31	32
16	49	47
H,L= 6 2		
0	24	29
1	75	72
2	115	120
3	99	101
4	23	22
5	65	61
6	72	68
7	65	67
8	21	27
9	42	47
10	50	53
11	22	22
14	28	36
17	25	30
18	36	35
H,L= 7 2		
0	147	141
4	78	75
6	76	78
7	97	93
8	50	52
9	52	54
10	49	46
11	57	60
15	46	48
19	33	27
H,L= 8 2		
0	23	17
1	114	117
2	37	38
3	68	72
4	36	47
5	98	100
7	79	73
9	65	65
15	42	33
H,L= 9 2		
0	34	38
2	58	49
3	80	79
5	70	68
6	37	38
7	81	80
8	24	17
11	45	48
13	27	26
15	42	36
H,L= 10 2		
1	64	59
2	86	86
3	57	58
6	39	34
7	66	75
9	59	63
10	38	41
12	24	24
15	30	27
H,L= 11 2		
0	87	85
1	47	53
2	26	36
3	28	28
5	29	28
6	21	16
7	25	35
8	66	68
9	29	33
12	44	37
H,L= 12 2		
2	69	70
6	74	74
10	51	52
13	32	29
14	50	44
H,L= 13 2		
0	40	37
4	40	42
8	53	56
12	41	47
H,L= 14 2		
2	51	46
6	47	53
H,L= 16 2		
3	29	24
5	39	31
H,L= 0 3		
3	32	35
7	65	59
10	82	77
13	94	96
15	71	70
H,L= 1 3		
1	75	73
3	88	88
7	42	42
8	35	35
9	103	107
10	96	96
11	92	98
12	42	48
13	102	97
H,L= 2 3		
1	30	35
5	24	22
6	93	87
7	90	91
9	49	51
10	64	68
11	94	97
12	91	91
13	48	43
14	40	38
15	39	39
H,L= 3 3		
2	244	237
3	109	104
4	73	60
5	171	168
6	171	176
9	42	39
10	87	91
H,L= 4 3		
1	54	55
4	136	137
5	53	55
8	81	79
10	26	19
12	60	65
16	59	55
H,L= 5 3		
0	23	25
2	222	227
3	142	138
4	70	72
6	139	136
7	76	83
H,L= 6 3		
0	134	134
2	33	32
6	52	50
7	73	78
8	65	60
11	35	35
12	36	44
H,L= 7 3		
0	67	67
1	133	133
2	135	140
3	114	118
6	72	75
7	81	83
10	39	42
15	43	47
H,L= 8 3		
1	111	108
2	72	82
3	78	82
4	45	40
5	76	84
6	80	78
7	90	88
H,L= 9 3		
1	81	89
3	56	54
4	64	66
7	76	78
9	45	48
13	35	31
H,L= 10 3		
0	70	75
2	52	53
5	84	92
6	57	63
8	37	33
9	63	57
H,L= 11 3		
10	63	57
13	39	33
H,L= 12 3		
0	46	49
8	64	66
H,L= 13 3		
10	45	42
H,L= 0 4		
1	38	32
8	109	106
11	119	119
12	101	102
H,L= 1 4		
1	87	83
4	78	80
5	50	44
6	68	62
8	31	28
9	82	79
10	96	94
11	40	36
13	41	41
H,L= 2 4		
0	79	71
1	40	49
7	48	50
8	74	74
11	76	81
12	58	60
13	33	37
H,L= 3 4		
0	98	95
2	90	80
3	139	134
4	122	120
5	63	69
6	55	50
7	41	45
8	36	30
9	95	92
13	48	46
H,L= 4 4		
3	45	51
4	48	57
5	61	64
6	36	40
7	89	82
9	53	51
10	48	42
15	41	39
17	29	23
H,L= 5 4		
1	120	125
2	28	25
3	44	47
4	59	49
5	130	128
7	51	47
8	43	44
10	46	43
13	50	55
H,L= 6 4		
1	37	31
3	37	42
4	81	79
7	44	47
8	36	39
9	69	70
10	39	33
13	47	40
H,L= 7 4		
1	54	56
2	78	86
3	44	42
4	52	58
5	72	78
6	100	97
7	51	50
9	39	34
10	76	77
H,L= 8 4		
0	69	72
1	68	72
2	26	22
3	37	40
4	73	72
5	51	51
8	56	58
9	60	62
H,L= 9 4		
1	43	47
3	34	36
6	68	64
10	62	62
12	32	21
H,L= 10 4		
0	45	41
1	43	46
2	78	80
4	67	70
5	32	29
7	38	37
9	42	35
10	31	27
12	46	41
H,L= 11 4		
0	62	63
2	32	36
3	27	25
8	55	50
11	45	37
H,L= 12 4		
1	45	46
2	60	63
6	58	52
H,L= 13 4		
0	47	45
H,L= 14 4		
3	32	28
6	45	43
H,L= 17 4		
0	32	28
H,L= 18 4		
3	25	17
H,L= 0 5		
1	69	76
2	167	166
9	35	30
10	82	82
13	38	34
14	53	56
H,L= 1 5		
0	200	201
1	78	75
2	64	56
3	39	43
4	78	77
5	62	64
8	71	74
12	49	56
19	19	13
H,L= 2 5		
1	80	80
2	88	87
3	80	84
4	49	44
5	52	47
6	67	68
8	32	33
9	45	51
10	66	70
11	26	21
14	46	46
15	42	40
H,L= 3 5		
1	94	87
2	56	56
3	61	67
4	59	59
5	85	79
7	78	80
8	52	45
9	41	41
11	59	58
13	30	34
17	23	26
H,L= 4 5		
1	54	59
3	56	59
5	68	70
7	81	76
9	70	69
11	47	48
H,L= 5 5		
1	39	48
2	35	32
3	96	91
5	74	66
7	91	97
9	57	59
11	63	70
H,L= 6 5		
2	52	57
3	42	39
5	67	66
6	77	83
7	49	43
9	51	54
10	41	39
13	45	47
H,L= 7 5		
0	45	37
2	29	33
3	40	37
4	83	87
5	50	48
7	52	53
8	75	70
H,L= 8 5		
2	59	63
4	53	38
14	44	48
H,L= 9 5		
0	71	72
2	42	37
4	80	86
5	47	41
8	57	63
9	36	36
H,L= 10 5		
2	71	72
6	51	53
H,L= 11 5		
0	65	67
1	44	47
3	47	52
4	46	43
H,L= 12 5		
3	54	56
9	24	24
H,L= 13 5		
1	53	48
5	44	38
H,L= 14 5		
3	40	37
5	23	24
H,L= 15 5		
0	24	24
H,L= 0 6		
0	243	244
1	135	130
3	104	107
5	70	70
8	57	57
9	59	58
13	31	23
H,L= 1 6		
1	103	96
2	151	151
3	36	33
4	45	44
6	61	61
8	32	29
9	61	53
H,L= 2 6		
0	93	97
1	138	141
2	45	42
3	93	88
4	55	56
5	58	58
6	47	47
7	70	71
8	65	65
14	22	22
H,L= 3 6		
0	58	58
1	72	69
2	39	40
3	41	41
4	63	58
5	71	77
6	46	51
8	66	69
9	68	64
10	52	54
12	38	40
15	32	34
19	23	19
H,L= 4 6		
1	49	47
2	76	77
3	51	49
4	43	39
5	75	79
6	67	76
7	67	68
9	46	43
11	36	37
H,L= 5 6		
0	40	38
3	49	48
4	74	77
5	53	57
7	71	71
8	52	53
16	28	29
H,L= 6 6		
2	45	48
4	43	46
H,L= 7 6		
6	58	61
10	47	43
11	46	45
H,L= 9 6		
6	50	51
10	48	35
11	49	52
H,L= 10 6		
4	53	54
10	22	13
H,L= 11 6		
0	23	22
H,L= 12 6		
3	39	41
H,L= 14 6		
3	36	28
H,L= 0 7		
3	81	81
7	74	73
H,L= 1 7		
1	51	47
2	47	47
4	38	29
9	30	27
11	29	30
H,L= 2 7		
1	60	57
3	67	65
7	66	66
8	48	44
11	45	45
H,L= 3 7		
2	74	75
6	75	74
14	45	45
H,L= 4 7		
0	73	74
4	78	83
8	76	82
H,L= 5 7		
1	48	41
2	65	62
3	43	50
6	78	86
10	61	61
H,L= 6 7		
0	50	56
2	41	39
4	62	66
5	53	61
8	47	45
9	43	36
H,L= 7 7		
3	48	52
7	48	50
H,L= 8 7		
3	53	61
5	53	54
11	44	37
H,L= 9 7		
1	49	50
5	50	50
H,L= 10 7		
1	47	48
H,L= 0 8		
1	56	55
2	38	28
3	56	61
9	51	51
11	43	44
13	61	69
H,L= 1 8		
1	52	50
H,L= 2 8		
1	68	67
5	65	62
6	57	56
10	50	57
H,L= 3 8		
3	54	53
4	69	70
8	70	66
12	46	46
H,L= 4 8		
2	83	78
H,L= 5 8		
0	86	83
4	64	64
H,L= 6 8		
2	73	77
H,L= 7 8		
4	43	38
H,L= 8 8		
0	47	43
H,L= 9 8		
0	A6	41
H,L= 11 8		
0	51	47
H,L= 1 9		
0	39	38
1	40	33
4	60	68
8	47	48
H,L= 3 9		
1	43	42
4	34	31
5	44	43
H,L= 4 9		
0	48	49
H,L= 5 9		
3	46	45
5	43	38
H,L= 4 10		
5	39	33
H,L= 6 10		
0	43	43
1	35	31
H,L= 7 10		
3	30	23
H,L= 0 Q		

Table 2. Final atomic parameters

(a) Final positional parameters ($\times 10^4$) and their estimated standard devations (in parentheses).

Atom	*x*	*y*	*z*
Co	5578(1)	3774(1)	1491(2)
N(1)	6363(7)	4236(6)	3320(15)
N(2)	4795(9)	4632(6)	1719(16)
N(3)	4750(7)	3221(7)	3117(12)
N(4)	6431(9)	2885(7)	1382(19)
O(1)	4831(7)	3466(6)	−498(15)
O(2)	6368(7)	4244(6)	−182(13)
O(3)	4853(8)	3549(8)	−3324(16)
O(4)	6576(9)	4283(8)	−3028(13)
C(1)	6179(10)	4977(10)	3247(27)
C(2)	5077(10)	5059(9)	3166(21)
C(3)	3721(8)	4575(8)	1683(21)
C(4)	3395(11)	3965(12)	3043(27)
C(5)	3695(11)	3235(11)	2724(21)
C(6)	5091(13)	2435(11)	2989(25)
C(7)	6079(17)	2481(7)	2942(30)
C(N1)	7412(10)	4107(8)	3324(24)
C(N4)	6418(16)	2425(11)	−146(29)
C(C3)	3224(13)	5296(11)	1799(27)
C(C5)	3252(11)	2623(14)	4062(25)
C(8)	5175(10)	3702(9)	−1911(15)
C(9)	6151(12)	4078(8)	−1743(20)
Cl	5268(3)	945(2)	7146(7)
O(5)	4708(10)	1132(8)	8666(18)
O(6)	4636(9)	956(9)	5565(23)
O(7)	5962(11)	1482(8)	6812(23)
O(8)	5623(14)	279(10)	7313(24)

(b) Final thermal parameters ($\times 10^4$) and their estimated standard deviations (in parentheses) in the form:
$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	34(0)	24(0)	31(1)	−2(0)	0(1)	−3(1)
N(1)	37(6)	20(4)	36(19)	8(4)	0(10)	−18(8)
N(2)	48(6)	25(4)	62(21)	16(4)	−13(11)	−20(9)
N(3)	35(5)	36(4)	47(17)	13(4)	−17(8)	−1(7)
N(4)	33(8)	32(5)	37(21)	2(5)	0(13)	4(11)
O(1)	51(6)	33(4)	92(19)	−8(4)	21(10)	0(7)
O(2)	40(6)	37(4)	42(16)	−24(4)	15(8)	0(7)
O(3)	63(7)	78(7)	83(20)	−18(6)	−65(11)	7(11)
O(4)	68(8)	66(6)	31(18)	−4(6)	8(10)	10(9)
C(1)	21(7)	43(7)	185(41)	−13(6)	−16(17)	15(17)
C(2)	31(8)	40(6)	97(30)	16(6)	−19(13)	−20(13)
C(3)	11(5)	34(5)	81(28)	−1(4)	−16(13)	15(12)
C(4)	28(8)	61(9)	213(48)	3(7)	15(17)	0(19)
C(5)	17(8)	50(8)	113(29)	0(6)	10(14)	0(14)
C(6)	43(10)	52(8)	152(38)	14(7)	77(16)	22(15)
C(7)	75(17)	23(4)	198(54)	13(6)	−35(25)	6(12)
C(N1)	40(8)	30(5)	130(32)	5(6)	0(17)	−13(13)
C(N4)	93(16)	36(7)	145(40)	26(9)	11(22)	−10(15)
C(C3)	46(9)	53(8)	155(43)	7(8)	−20(18)	2(17)
C(C5)	46(8)	74(15)	63(42)	−49(10)	13(15)	−23(20)
C(8)	27(7)	42(6)	105(21)	6(7)	−10(10)	1(12)
C(9)	66(10)	17(4)	68(29)	10(6)	−19(15)	−8(10)
Cl	65(3)	34(1)	248(11)	−4(1)	14(5)	14(3)
O(5)	113(11)	60(6)	146(23)	44(7)	43(15)	−4(13)
O(6)	56(8)	68(7)	343(41)	0(6)	−58(17)	27(14)
O(7)	87(9)	63(7)	236(36)	1(6)	−15(16)	−6(13)
O(8)	117(14)	82(9)	313(42)	48(10)	6(25)	10(16)

Table 3. Reflexions used to determine the absolute configuration (Δ) ($\times 10$)

h	*k*	*l*	$\lvert F_c(hkl)\rvert$	$\lvert F_c(h\bar{k}l)\rvert$	Observed relationship
1	3	1	570	466	>
1	8	1	304	241	>
2	1	1	376	287	>
3	1	1	194	316	<
3	2	1	706	710	<
3	3	1	555	440	>
4	2	1	333	280	>
4	3	1	138	201	<
4	4	1	975	865	>
4	5	1	737	609	>
5	6	1	506	544	<
6	1	1	525	463	>
6	3	1	247	285	<
10	2	1	513	493	>

refinement, but their positional and isotropic thermal parameters (given the value of $B=3.5$) were not refined. The final refinement converged at the *R* value of 0.059 ($R'=0.064$). The observed and calculated structure factors all listed in Table 1. Table 2 summarizes the final values of the positional and thermal parameters. The absolute configuration of the complex was determined by using the absorption-edge technique.[6] An equi-inclination Weissenberg photograph of the 1st-layer about c axis was taken with Cu*Kα* radiation. Some Bijvoet pairs, *hkl* and $h\bar{k}l$, were found to show appreciable differences in intensity. These pairs and the observed inequality relationships are listed in Table 3, in which the structure amplitudes calculated on the basis of the Δ configuration of the complex are also given.

Description and Discussion of the Structure

There are four complex and four perchlorate ions per unit cell. Figure 1 gives a stereoscopic pair of view of the contents of a unit cell of this structure. The absolute configuration of the complex ion is represented by a perspective drawing in Fig. 2. The cobalt atom is situated at the center of a slightly distorted octahedron. The tetramine ligand, $(H_3C)NH-(CH_2)_2-NH-CH(CH_3)-CH_2-CH(CH_3)-NH-(CH_2)_2-NH(CH_3)$, is coordinated to the cobalt atom in the Δ-*cis*-β geometry. Each conformation of the three chelate rings for the tetramine is present in Fig. 3. The central $-HN(2)-C(3)H(CH_3)-C(4)H_2-C(5)H(CH_3)-N(3)H-$ atoms and the cobalt atom form a six-membered chelate ring with a chair conformation, both of the C–CH$_3$ groups being equatorial. The $H_3C(N1)-N(1)H-C(1)H_2-C(2)H_2-$

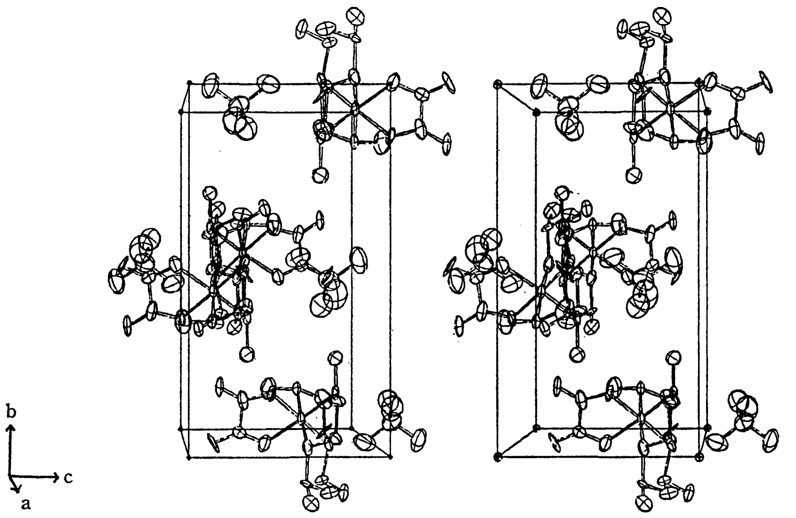

Fig. 1. Stereoscopic view of the unit cell contents.

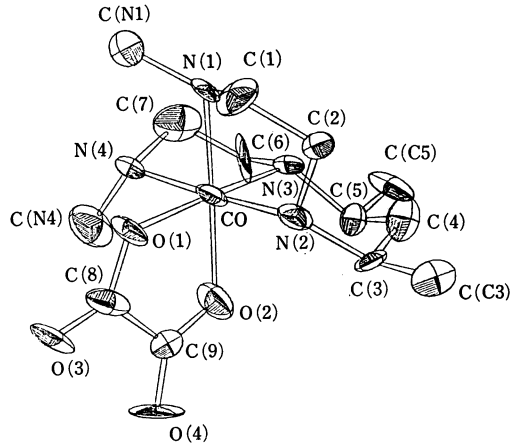

Fig. 2. A perspective drawing of the complex ion showing 50% probability ellipsoids of thermal motion.

Table 4. Interatomic non-bonded distances within the molecular and their standard deviations (in parentheses) less then 3.5 Å

C(N1)-Co	3.03(2) Å	C(N4)-Co	3.05(2) Å
C(N1)-C(1)	2.38(3)	C(N4)-C(6)	3.07(3)
C(N1)-N(4)	3.06(2)	C(N4)-C(9)	3.33(3)
C(N1)-O(2)	3.10(2)	C(N4)-O(1)	2.98(3)
		C(N4)-O(2)	3.38(3)

N(2)H- fragment participates in the five-membered chelate ring with a λ gauche conformation, and the methyl group is equatorial. The other five-membered ring is composed of the -HN(3)-C(6)H_2-C(7)H_2-N(4)-H-C(N2)H_3 fragment with a metal atom and also has a λ conformation, but the methyl group is axial with respect to the chelate ring. Among the secondary nitrogen atoms, N(1)—N(4), the N(1) has *S* chirality, while the absolute configurations of the remainder are *R*. The two outer chelate rings have similar gauche conformations. The ring carbon atoms, C(1) and C(2), lie at −0.53 and 0.21 Å respectively from the plane formed by N(1), Co, and N(2). The corresponding deviations of C(7) and C(6) from the plane of N(4), Co, and N(3) are −0.41 and 0.33 Å. Close contacts between the *N*-methyl carbon atoms and other atoms in the complex (less than 3.5 Å) are listed in Table 4. These are similar values between the two *N*-methyl groups.

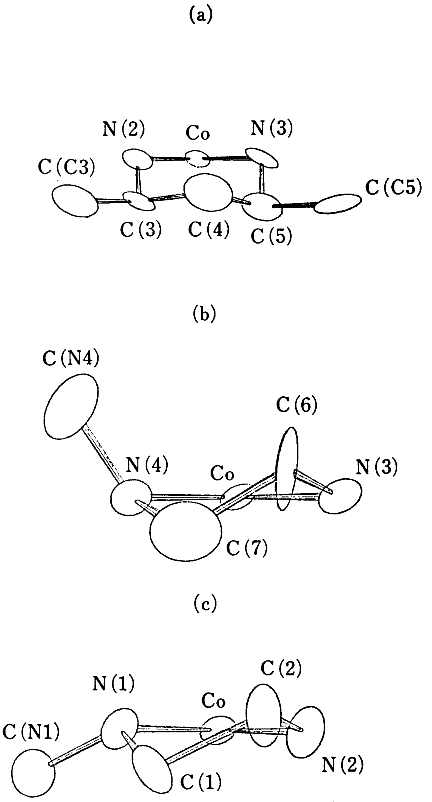

Fig. 3. A perspective drawing of the chelate rings; (a) central six-membered ring, (b) in-plane five-membered ring, and (c) out-of-plane five-membered ring.

Four isomers can exist with respect to the orientation of the two *N*-methyl groups in relation to the *Δ-cis-β*

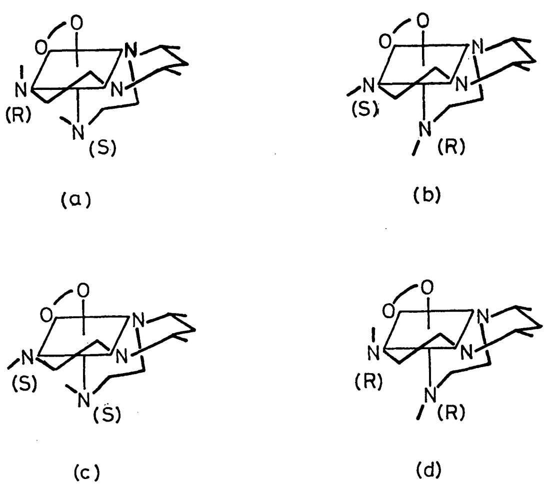

Fig. 4. Possible isomers of Δ-β-[Co(ox)(*N,N′*-Me$_2$-*R,S*-2,3″,2-tet)]$^+$.
(a) (N1(*S*), N4(*R*)), (b) (N1(*R*), N4(*S*)), (c) (N1(*S*), N4(*S*)), (d) N1(*R*), N4(*R*)).

form. They are (N1(*S*), N4(*R*)), (N1(*R*), N4(*S*)), (N1(*S*), N4(*S*)), and (N1(*R*), N4(*R*)), as shown in Fig. 4. The (N1(*S*), N4(*R*)) isomer to involve a smaller interaction than the other three forms, according to the molecular model study. This structural feature was supported by the present X-ray analysis. It is noteworthy that one *N*-methyl group has an axial orientation with that the equatorial orientation of the *N*-methyl group is preferable to the axial situation. This stereochemical feature can be attributed to severe steric interactions on the metal ion.

All the N–Co–N angles in five-membered chelate rings are less than 90°, and they have an average value of 86.0°. The N–Co–N angle in the central six-membered chelate ring is 91.7°. The bond distances and angles are given in Tables 5 and 6 respectively. The four Co–N distances are not significantly different from one another, and the average value (2.01 Å) is quite usual.

Absolute Configuration and Circular Dichroism. The stereochemical features which can contribute to the circular dichroism (CD) of a dissymmetric metal complex have been classified as follows: (1) a distribution of chelate rings about the metal ion (configurational effect), (2) the puckered dissymmetric conformation of individual chelate rings (conformational effect), and (3) the presence of asymmetric groups on the ligands, such as asymmetric carbon or asymmetric nitrogen atoms (vicinal effect). The latter two effects are considered to make minor contributions as compared with the configurational effect.

TABLE 5. BOND DISTANCES AND THEIR STANDARD DEVIATIONS (IN PARENTHESES)

Co –N(1)	2.00(2) Å	O(2)–C(9)	1.29(3) Å
Co –N(2)	1.95(2)	O(3)–C(8)	1.22(4)
Co –N(3)	2.01(2)	O(4)–C(9)	1.22(4)
Co –N(4)	2.05(2)	C(1)–C(2)	1.57(4)
Co –O(1)	1.96(2)	C(3)–C(4)	1.62(4)
Co –O(2)	1.92(2)	C(3)–C(C3)	1.52(4)
N(1)–C(1)	1.40(4)	C(4)–C(5)	1.44(5)
N(1)–C(N1)	1.51(4)	C(5)–C(C5)	1.66(5)
N(2)–C(2)	1.43(4)	C(6)–C(7)	1.40(5)
N(2)–C(3)	1.53(3)	C(8)–C(9)	1.56(4)
N(3)–C(5)	1.53(4)	Cl –O(5)	1.46(3)
N(3)–C(6)	1.54(4)	Cl –O(6)	1.52(3)
N(4)–C(7)	1.51(4)	Cl –O(7)	1.43(3)
N(4)–C(N4)	1.46(5)	Cl –O(8)	1.34(4)
O(1)–C(8)	1.28(3)		

TABLE 6. BOND ANGLES AND THEIR STANDARD DEVIATIONS (IN PARENTHESES)

N(1)–Co–N(2)	84.3(9)°
N(1)–Co–N(3)	95.8(9)
N(1)–Co–N(4)	92.7(9)
N(1)–Co–O(1)	170.9(10)
N(1)–Co–O(2)	87.6(8)
N(2)–Co–N(3)	91.7(9)
N(2)–Co–N(4)	176.8(11)
N(2)–Co–O(1)	90.2(9)
N(2)–Co–O(2)	91.2(9)
N(3)–Co–N(4)	87.6(9)
N(3)–Co–O(1)	91.6(9)
N(3)–Co–O(2)	175.7(10)
N(4)–Co–O(1)	92.9(10)
N(4)–Co–O(2)	89.7(10)
O(1)–Co–O(2)	85.2(8)
C(1)–N(1)–C(N1)	110(2)
C(2)–N(2)–C(3)	109(2)
C(5)–N(3)–C(6)	108(2)
C(7)–N(4)–C(N4)	111(3)
N(1)–C(1)–C(2)	106(2)
N(2)–C(2)–C(1)	105(2)
N(2)–C(3)–C(4)	109(2)
N(2)–C(3)–C(C3)	114(2)
C(4)–C(3)–C(C3)	117(2)
C(3)–C(4)–C(5)	118(2)
N(3)–C(5)–C(4)	106(2)
N(3)–C(5)–C(C5)	104(2)
C(4)–C(5)–C(C5)	115(3)
N(3)–C(6)–C(7)	105(2)
N(4)–C(7)–C(6)	112(2)
O(1)–C(8)–O(3)	123(2)
O(1)–C(8)–C(9)	115(2)
O(3)–C(8)–C(9)	121(2)
O(2)–C(9)–O(4)	125(2)
O(2)–C(9)–C(8)	114(2)
O(4)–C(9)–C(8)	121(2)
O(5)–Cl –O(6)	109(2)
O(5)–Cl –O(7)	111(2)
O(5)–Cl –O(8)	110(2)
O(6)–Cl –O(7)	105(2)
O(6)–Cl –O(8)	108(2)
O(7)–Cl –O(8)	114(2)

The CD spectrum of Δ-β-[Co(ox)(*N,N′*-Me$_2$-*R,S*-2,3″,2-tet)]$^+$ is shown in Fig. 5. The above results suggest the following conclusion: when the oxalato cobalt(III) complexes of 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and its derivatives give two circular dichroism bands with opposed signs in the first absorption region,

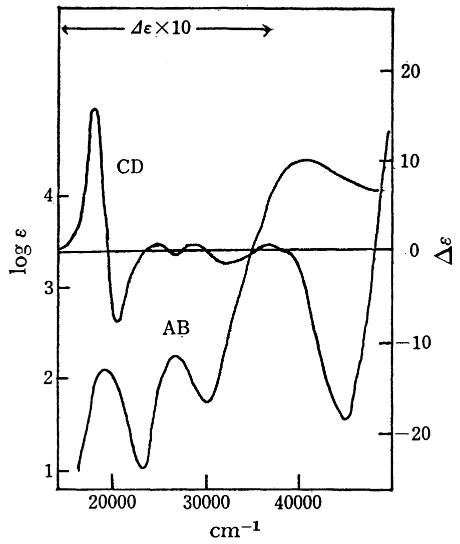

Fig. 5. Absorption (AB) and CD spectra of Δ-β-[Co(ox)(N,N'-Me_2-R,S-2,3″,2-tet)]$^+$.

an enantiomer which has a lawer-energy negative Cotton effect and a higher-energy positive one should be assigned the Δ configuration.

The calculation of the lattice constants, the Fourier synthesis the least-squares analysis, and drawings of the crystal or molecular structures were carried out on a HITAC 8700/8800 computer at the Computer Center of this University, using the RSCL3, ANSFR-2, HBLS-4, and ORTEP⁷⁾ programs of the UNICS system respectively.

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