CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201,
AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS AT CHICAGO CIRCLE, CHICAGO, ILLINOIS 60680

The Structure and Absolute Configuration of $(-)_{546}$-*cis,trans,cis*-Bis(diaminopropionato)cobalt(III) Bromide, $[Co(C_3H_7N_2O_2)_2]Br$

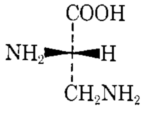
BY CHUI FAN LIU AND JAMES A. IBERS

Received December 27, 1968

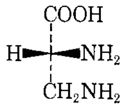
One of the two *cis* isomers of bis(L-diaminopropionato)cobalt(III) bromide, $[Co(C_3H_7N_2O_2)_2]Br$, was examined by X-ray methods. The red crystals belong to space group D_2^3-$P2_12_12$ of the orthorhombic system ($a = 11.76 \pm 0.02$, $b = 7.49 \pm 0.02$, $c = 5.91 \pm 0.02$ Å). The density of 2.21 g/cm³ calculated for two formula weights per unit cell agrees well with the measured value of 2.19 ± 0.01 g/cm³. X-Ray data were collected by the equiinclination Weissenberg method, and intensities of 450 independent reflections were estimated visually. The structure was refined by least-squares methods to a conventional R factor of 0.070. The absolute configuration of the complex was determined by least-squares refinements of the two mirror image structures. The complex is monomeric and contains two ligands per complex. Molecular symmetry 2 is imposed on the cation by crystallographic requirements. Coordination around the central Co atom is that of a distorted octahedron. The carboxyl groups are *cis* to each other as are the terminal amine groups. The α-amino groups occupy *trans* positions. The C_2 axis helicity of the ethylenediamine part of the molecule is Λ while the helicity of the α-amino acid ring is Δ.

Introduction

Recently the complexes of cobalt(III) with 2,3-diaminopropionic acid have been prepared.[1] In these



L-2,3-diaminopropionic acid



D-2,3-diaminopropionic acid

complexes the diaminopropionic acid acts as a tridentate ligand, and, owing to steric considerations, the ligand is constrained to occupy a triangular face of the cobalt(III) octahedron. In this fashion the 1:2 complex of cobalt(III) and diaminopropionic acid may exist in five geometric isomers, and four of these should be resolvable into D and L forms. The five possible geometric isomers are depicted in Figure 1. All of these isomers have been isolated, and, where possible, the configurations have been assigned by the use of absorption, ORD, and CD spectra, as well as by chemical means. These complexes are labeled according to the convention that the carboxyl groups are designated first, then the α-amino group, and last the β-amino group. Thus, the five isomers may be named *trans,cis,cis* (A), *cis,cis,trans* (B), *cis,trans,cis* (C), *cis,cis,cis* (D), and *trans,trans,trans* (E). Unambiguous differentiation of the isomers B and C was not possible by the chemical and spectral methods used. Since this is a complete series of isomers whose ORD and CD spectra are significant in correlating structures of other complexes, definitive assignments of these structures are highly desirable. In this paper we describe the detailed determination of the structure and absolute configuration of an isomer that proves to be the L-*cis,trans,cis* isomer (isomer C of Figure 1).

Collection and Reduction of X-Ray Data

The red crystals of what proved to be L-*cis,trans,cis*-bis(diaminopropionato)cobalt(III) bromide were examined by precession, Weissenberg, and optical methods and were found to belong to the orthorhombic system. Systematic extinctions are $h00$, for h odd, and $0k0$, for k odd. These extinctions are characteristic of the space group D_2^3-$P2_12_12$. The lattice dimensions are $a = 11.76 \pm 0.02$, $b = 7.49 \pm 0.02$, and $c = 5.91 \pm 0.02$ Å at 27°, as determined from precession photographs taken with Mo Kα radiation (λ 0.7107 Å). The calculated density of 2.21 g/cm³ with two molecules per unit cell agrees satisfactorily with the value of 2.19 ± 0.01 g/cm³ obtained by flotation of the crystals in chloroform–bromoform solutions. Intensity data were collected at room temperature using the multiple-film equiinclination Weissenberg technique from a crystal of approximate dimensions 0.4 × 0.2 × 0.1 mm with the short dimension of the crystal along the spindle axis. Zirconium-filtered Mo Kα radiation was employed. Integrated exposures of the layers $hk0$ through $hk7$ were made. Four hundred and fifty independent reflections accessible within the angular range of $2\theta_{\mathrm{Mo}} \leq 56°$ were estimated visually. The usual Lorentz–polarization factor was applied, and the data were then corrected for absorption. For the absorption correction the 12 crystal faces were indexed by optical goniometry and their dimensions were carefully measured. These crystal faces are of the forms $\{011\}$, $\{001\}$, $\{110\}$, and $\{100\}$. With a linear absorption coefficient of 58.21 cm^{-1} the transmission coefficients were found to range from about 0.128 to 0.514.[2]

Solution of the Structure

A complete trial structure was readily found from the usual combination of Patterson and difference Fourier maps. With two molecules in space group $P2_12_12$ the cobalt atoms may be placed in the special positions (2a) while the bromine atoms may be placed in the

---

(1) W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).

(2) In addition to various local programs for the CDC 6400 computer local modifications of the following programs were used in this work: Zalkin's FORDAP Fourier program, Busing and Levy's ORFLS and ORFFE least-squares and error function programs, Johnson's ORTEP thermal ellipsoid plotting program, and Burnham's GNABS absorption program.

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $(-)_{546}$-*cis,trans,cis*-BIS(DIAMINOPROPIONATO)COBALT(III) BROMIDE

Atom	x	y	z	B,[a] Å^2
Co	$^1/_2$	$^1/_2$	0.1171 (4)	
Br	0	$^1/_2$	0.3735 (3)	
C(1)	0.3222 (13)[b]	0.3465 (21)	−0.0920 (21)	1.01 (25)
C(2)	0.3636 (13)	0.2343 (23)	0.1041 (28)	1.72 (29)
C(3)	0.3144 (16)	0.3069 (34)	0.3069 (27)	2.22 (36)
N(1)	0.4853 (11)	0.2410 (15)	0.1111 (20)	1.19 (22)
N(2)	0.3761 (11)	0.4921 (43)	0.3434 (19)	2.03 (25)
O(1)	0.3871 (8)	0.4873 (27)	−0.1068 (15)	1.41 (20)
O(2)	0.2390 (9)	0.3141 (18)	−0.2047 (17)	1.61 (23)
N(1)H(1)	0.516	0.182	0.260	
N(1)H(2)	0.522	0.183	−0.025	
N(2)H(1)	0.321	0.598	0.322	
N(2)H(2)	0.410	0.500	0.507	
C(2)H(1)	0.336	0.097	0.087	
C(3)H(1)	0.223	0.329	0.286	
C(3)H(2)	0.329	0.220	0.451	

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk)]$. The root-mean-square amplitudes of vibration (in Å) for Co and Br are: 075 (20), 129 (10), and 155 (11); and 155 (9), 167 (7), and 207 (6). The anisotropic thermal parameters for cobalt are: β_{11}, 0.00246 (23); β_{22}, 0.0045 (7), β_{33}, 0.0095 (15); β_{12}, 0.0020 (7). Those for Br are: β_{11}, 0.0059 (3); β_{22}, 0.0103 (7); β_{33}, 0.0137 (15); β_{12}, −0.0010 (7). [b] The figures in parentheses are standard deviations and refer to least significant digits.

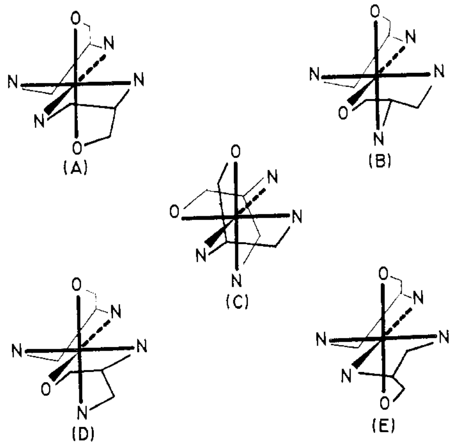


Figure 1.—The five geometrical isomers of the bis(2,3-diaminopropionato)cobalt(III) ion: (A) *trans,cis,cis*, (B) *cis,cis-trans*, (C) *cis,trans,cis*, (D) *cis,cis,cis*, (E) *trans,trans,trans*. (A), (B), and (C) require two ligands of the same absolute configuration—L in the above representations; (D) and (E) require that the two ligands have opposite absolute configurations.

other special positions (2b). Thus the cation is required crystallographically to possess symmetry 2.

The trial structure was refined by the least-squares procedure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was based on observed film intensities. When the observed intensity is lower than 20, the reflection is assigned $w = I_o^2/(4F^2)$, where I_o is the observed intensity and $|F|$ is the observed structure amplitude. When the observed intensity is greater than 20, the reflection is assigned $w = 100/F^2$. The values of I_o ranged from 2 to 210, with 2 barely visible.

The atomic scattering factors for the neutral atoms from the usual tabulation[3] were used. The values of $\Delta f'$ and $\Delta f''$ for cobalt and bromine were those of Cromer[4] and were included in the calculated structure factors.[5] The initial refinement with individual isotropic thermal parameters assigned to all atoms converged to a conventional R_1 factor ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.123 and a weighted R factor R_2 ($R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o)^{1/2}$) of 0.172. At this point idealized positions of the hydrogen atoms were calculated[6] by using the N–H distance of 1.03 Å, C–H distance of 1.11 Å, and H–N–H and H–C–H angles of 109° 28′. These hydrogen atoms were introduced into the refinement while their positional and thermal parameters were held constant. This refinement converged to values of $R_1 = 0.086$ and $R_2 = 0.102$. Since the space group involved is polar, it was necessary to attempt to distinguish between the two possible mirror image structures. Accordingly, a refinement for each of the two mirror image structures was carried out with all of the centrosymmetric zonal reflections omitted. The original trial structure refined to values of $R_1 =$ 0.081 and $R_2 = 0.093$ while the mirror image structure refined to values of $R_1 = 0.074$ and $R_2 = 0.085$, a significant improvement. Refinement of the latter structure with the full set of data converged at $R_1 = 0.081$ and $R_2 =$ 0.094. A difference Fourier map at this point revealed electron density no higher than 1.7 e$^-$/Å^3 (65% of a carbon atom in this structure) in the vicinity of the heavy atoms. A further refinement was carried out in which the Co and Br were allowed to vibrate anisotropically. This refinement converged to $R_1 = 0.070$ and $R_2 = 0.084$. A difference Fourier map after this refinement showed the highest electron density to be 1.2 e$^-$/Å^3 in the vicinity of the Br atom. The final $|F_c|$ values are based on the parameters from this refinement. These parameters are given in Table I. Table II lists the final values of the observed and calculated structure amplitudes (×10) in electrons.

---

(3) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(4) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(5) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(6) D. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) IN ELECTRONS FOR $[Co(C_3H_7N_2O_2)_2]Br$

K	H	FO	FC
*****	L =	0	*****
0	4	709	780
0	6	861	896
0	8	891	887
0	10	433	498
0	12	337	323
0	14	192	137
0	16	261	268
0	18	166	116
1	3	524	531
1	4	183	182
1	5	309	315
1	7	90	74
1	8	201	195
2	0	840	733
2	1	464	432
2	2	1166	1144
2	3	209	180
2	4	314	332
2	6	424	492
2	8	553	610
2	10	491	486
2	12	148	188
2	14	198	189
2	16	154	148
2	18	119	167
3	1	239	210
3	2	97	86
3	5	334	326
3	9	250	255
3	11	155	134
4	0	1236	1194
4	1	252	233
4	2	1050	433
4	3	290	288
4	4	464	491
4	6	586	576
4	8	688	706
4	10	393	408
4	12	198	177
4	14	216	218
4	16	165	170
5	3	175	189
5	5	148	151
5	10	137	175
6	0	784	733
6	2	361	363
6	4	411	386
6	6	311	334
6	8	331	339
6	10	289	289
6	12	223	205
7	1	140	131
8	0	425	425
8	2	422	456
8	4	197	208
8	6	367	335
8	8	360	325
8	10	234	242
10	0	257	235
10	2	200	185
10	4	167	176
12	0	214	209
*****	L =	1	*****
0	3	216	200
0	5	150	148
0	6	71	77
0	8	112	134
1	3	648	670
1	4	543	543
1	5	577	570
1	6	563	577
1	7	464	474
1	8	383	393
1	9	339	377
1	10	280	302
1	11	305	319
1	12	181	189
1	13	162	160
1	14	171	193
1	15	104	112
1	16	109	126
2	0	373	328
2	1	372	345
2	2	166	142
2	3	112	97
2	4	144	139
2	5	148	167
2	6	147	154
2	8	88	88
2	9	77	94
3	0	765	799
3	1	725	695
3	2	466	458
3	3	574	625
3	4	633	628
3	5	436	439
3	6	383	392
3	7	403	421
3	8	455	451
3	9	399	406
3	10	180	171
3	11	210	216
3	12	211	224
3	13	141	173
3	14	147	141
3	15	109	126
3	16	113	121
4	0	137	101
4	1	109	86
4	2	133	112
5	0	385	363
5	1	460	445
5	2	483	469
5	3	492	427
5	4	332	327
5	5	326	320
5	6	367	422
5	7	338	296
5	8	223	188
5	9	269	265
5	10	270	282
5	11	218	220
5	12	148	136
7	0	298	307
7	1	377	393
7	2	311	310
7	3	262	238
7	4	295	287
7	5	312	288
7	6	212	207
7	7	254	251
7	8	230	264
7	9	203	202
7	10	111	118
7	11	162	182
9	0	156	201
9	1	156	170
9	2	193	176
9	3	195	215
9	4	114	185
*****	L =	2	*****
0	3	1043	1307
0	4	157	139
0	5	958	941
0	6	139	132
0	7	621	649
0	9	482	485
0	11	259	266
0	13	398	397
0	15	167	208
1	3	238	244
1	4	223	222
1	5	63	47
1	8	138	146
1	9	99	136
2	0	177	133
2	1	439	438
2	2	246	205
2	3	778	864
2	4	202	172
2	5	820	861
2	6	73	71
2	7	355	389
2	9	202	217
2	11	407	410
2	13	262	259
3	1	100	82
3	2	271	251
3	3	189	157
3	4	204	213
3	5	62	59
3	6	65	78
3	7	122	46
3	8	102	156
3	9	76	84
3	10	114	68
4	1	728	730
4	2	67	77
4	3	723	752
4	4	67	61
4	5	765	786
4	7	537	508
4	9	309	299
4	11	330	316
4	13	297	279
4	15	189	166
5	0	354	342
5	1	108	101
5	4	107	76
5	8	84	113
6	1	273	272
6	2	84	88
6	3	541	565
6	5	427	424
6	7	230	223
6	9	216	226
6	11	191	195
6	13	224	224
6	15	162	116
7	1	141	142
7	4	93	87
8	1	296	332
8	3	371	362
8	5	367	362
8	7	266	275
8	9	152	170
8	11	195	192
*****	L =	3	*****
0	3	197	204
0	6	163	145
1	2	543	555
1	3	585	562
1	4	670	642
1	5	433	431
1	6	390	403
1	7	337	321
1	8	355	346
1	9	321	326
1	10	214	206
1	11	236	234
1	12	224	208
1	13	141	147
1	14	161	192
1	15	165	122
1	16	141	93
2	0	273	255
2	1	255	225
2	2	179	180
2	3	47	60
2	4	147	144
2	5	108	130
2	7	135	132
2	8	145	171
3	0	488	476
3	1	494	463
3	2	493	476
3	3	386	391
3	4	430	434
3	5	428	432
3	6	527	546
3	7	245	248
3	8	192	184
3	9	230	252
3	10	236	242
3	11	200	193
3	12	190	209
3	13	148	146
3	14	134	141
4	5	132	148
4	6	158	62
5	0	293	301
5	1	328	308
5	2	325	321
5	3	398	393
5	4	418	443
5	5	224	239
5	6	231	251
5	7	246	277
5	8	251	232
5	9	193	183
5	10	168	149
5	11	161	177
5	12	196	183
5	13	139	131
5	14	145	131
7	0	207	223
7	1	236	248
7	2	275	296
7	3	238	207
7	4	272	263
7	5	259	257
7	6	236	235
7	7	158	159
7	8	209	204
7	9	136	142
7	10	99	135
7	11	144	130
*****	L =	4	*****
0	2	661	740
0	4	415	389
0	6	623	591
0	7	98	110
0	8	514	503
0	10	383	359
0	12	201	191
0	14	153	153
0	16	134	158
1	1	138	132
1	2	116	119
1	3	203	196
1	4	71	98
1	5	128	139
1	8	107	96
2	0	618	648
2	2	531	504
2	4	427	423
2	6	355	322
2	8	440	405
2	10	314	299
2	12	155	181
2	14	125	107
2	16	118	137
3	1	99	116
3	2	137	142
3	3	73	85
3	4	54	41
3	5	150	164
3	6	95	128
3	8	67	49
3	9	100	81
4	0	648	678
4	2	565	564
4	4	372	370
4	6	354	390
4	8	479	452
4	10	294	288
4	12	153	141
4	14	162	167
4	16	142	124
5	0	123	133
6	0	382	364
6	2	314	319
6	4	213	213
6	6	267	285
6	8	233	221
6	10	212	221
6	12	163	143
8	0	370	379
8	2	270	262
8	4	205	223
8	6	195	219
8	8	240	249
8	10	170	173
*****	L =	5	*****
0	3	117	122
0	4	153	155
0	5	110	63
1	2	332	351
1	3	249	256
1	4	265	252
1	5	295	291
1	6	286	267
1	7	276	264
1	8	233	230
1	9	241	254
1	10	171	163
1	11	164	190
1	12	126	116
2	0	62	26
2	1	94	89
2	2	47	55
2	3	86	113
2	5	130	142
2	6	110	148
3	0	256	293
3	1	362	375
3	2	301	299
3	3	335	369
3	4	237	221
3	5	133	143
3	6	213	209
3	7	308	298
3	8	226	214
3	9	305	276
3	10	139	136
4	0	132	143
4	7	109	111
4	8	151	149
5	0	280	256
5	1	296	300
5	2	227	203
5	3	187	177
5	4	208	205
5	5	221	220
5	6	213	171
5	7	174	167
5	8	172	169
5	9	179	201
5	10	186	165
5	11	137	142
7	0	177	192
7	1	251	262
7	2	154	168
7	3	127	149
7	4	91	124
7	5	131	155
7	6	133	149
7	7	166	197
7	8	98	120
7	9	143	145
*****	L =	6	*****
0	3	400	414
0	5	408	392
0	7	322	329
0	9	201	191
0	11	193	208
0	13	131	147
0	15	175	144
2	1	239	249
2	3	341	356
2	5	317	320
2	7	211	196
2	9	170	168
2	11	172	152
2	13	189	171
3	0	135	144
3	1	54	86
3	3	103	85
3	6	68	46
4	1	309	330
4	3	317	324
4	5	317	339
4	7	316	254
4	9	223	175
4	11	166	164
4	13	173	146
6	0	112	112
6	1	143	162
6	3	238	240
6	5	212	213
6	7	153	140
8	1	164	190
8	3	191	201
8	5	170	183
8	7	124	152
*****	L =	7	*****
0	3	136	127
0	6	93	20
0	7	71	73
0	8	94	66
1	1	137	158
1	2	193	225
1	3	178	195
1	4	252	276
1	5	154	173
1	6	187	169
1	7	126	105
1	8	135	138
1	9	186	144
1	10	124	96
3	0	187	198
3	1	165	143
3	2	194	188
3	3	177	162
3	4	256	216
3	5	157	152
3	6	263	242
3	7	113	120
5	0	111	96
5	1	157	129
5	2	143	153
5	3	141	121
5	4	241	214
5	5	170	135
5	6	108	119
5	7	129	112
5	8	94	98

TABLE III

POSSIBLE A–H···B BONDS

A	H	B	A–H, Å	H···B, Å	A···B, Å	A–H···B, deg
N(1)	N(1)H(1)	Br ($^1/_2 + x$, $^1/_2 - y$, $1 - z$)	1.03	2.57	3.54	155
N(1)	N(1)H(2)	Br ($^1/_2 + x$, $^1/_2 - y$, $-z$)	1.03	2.49	3.39	149
N(2)	N(2)H(1)	O(2) ($^1/_2 - x$, $^1/_2 + y$, $-z$)	1.03	1.90	2.89	159
N(2)	N(2)H(2)	O(1) (x, y, $1 + z$)	1.05	2.30	3.25	150

Discussion of the Structure

The crystal structure consists of the packing of separated bis(diaminopropionato)cobalt(III) and bromide ions. The structure of the complex is depicted by a perspective drawing in Figure 2. As would be expected all of the hydrogen atoms on the nitrogen atoms appear to enter into hydrogen bonds. These interactions are listed in Table III. The remaining three hydrogen atoms on the carbon atoms do not appear to form hydrogen bonds. The intermolecular contacts appear to be normal, with the possible exception of an O(2)–C(3) nonbonded interaction of 3.02 Å.

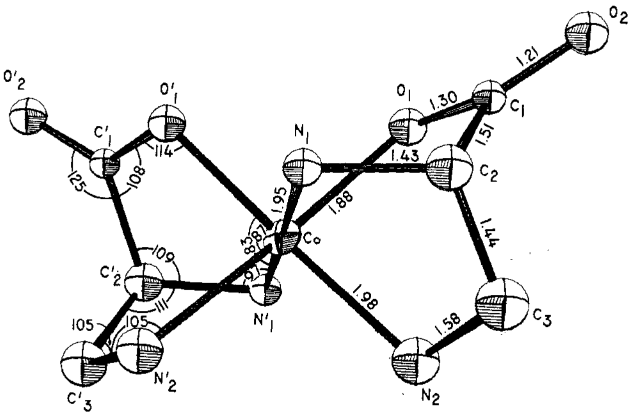


Figure 2.—A perspective drawing of the $Co(C_3H_7N_2O_2)_2$ cation. A crystallographic twofold axis relates the primed and unprimed atoms.

The geometric arrangement of the donor groups is *cis,trans,cis* according to the convention noted earlier. Table IV summarizes the bond distances and bond angles of the complex. The objective of the present study was the determination of the absolute configuration of the cation; we did not expect accurate determinations of light atom–light atom distances because of the use of film data and the presence of the heavy cobalt and bromine scatterers. Nevertheless it is worthwhile making a limited number of comparisons of the derived distances with those in the literature. The Co–N distances are comparable to those found for the *trans*-dichlorobis(*l*-propylenediamine)cobalt(III) ion[7] (1.94–2.02 (6) Å). The fact that we find the Co–O distance to be slightly shorter than the Co–N distances is consistent with the usual covalent radii. The distance of 1.44 (2) Å between the α-carbon and the β-carbon atoms

TABLE IV

INTERATOMIC DISTANCES AND ANGLES

Atoms	Distance, Å	Atoms	Angle, deg
Co–O(1)	1.876 (9)	O(1)–Co–N(1)	83 (1)
Co–N(1)	1.95 (1)	O(1)–Co–N(2)	87 (1)
Co–N(2)	1.98 (1)	N(1)–Co–N(2)	85 (1)
C(2)–C(3)	1.44 (2)	Co–N(1)–C(2)	97 (1)
C(2)–N(1)	1.43 (2)	N(1)–C(2)–C(1)	109 (1)
C(3)–N(2)	1.58 (4)	N(1)–C(2)–C(3)	111 (1)
C(1)–O(2)	1.21 (2)	C(2)–C(1)–O(1)	108 (1)
C(1)–O(1)	1.30 (2)	C(2)–C(1)–O(2)	125 (1)
C(1)–C(2)	1.51 (2)	C(3)–N(2)–Co	106 (1)
Co–Co	5.91	C(2)–C(3)–N(2)	105 (1)
Co–Br	4.74	Co–O(1)–C(1)	114 (1)
		O(2)–C(1)–O(1)	127 (1)
		C(3)–C(2)–C(1)	107 (1)

---

[7] Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

is significantly shorter than that of a paraffin C–C bond. However, it is within the range of α-carbon–β-carbon distances found in bis(β-aminobutyrato)copper(II) dihydrate[8] (1.49 (3) Å) and bis(histidinato)nickel(II)[9] (1.47 Å). The distances among the atoms in the carboxyl group are all similar to the distances found in other α-amino acid–metal complexes.[8-12] The α-carbon–α-nitrogen distance of 1.43 (2) Å is very close to the range of 1.44–1.52 Å quoted by Blount, *et al.*,[13] for this type of bond in peptide–copper complexes. The β-carbon–β-nitrogen distance of 1.58 (4) Å is possibly significantly longer than that of 1.49 (2) Å found in (β-alaninyl-L-histidinato)copper(II) dihydrate.[10] The difference between the two carbon–nitrogen distances (α-carbon–α-amine and β-carbon–β-amine) in the present structure of 0.15 (3) Å may be significant but may also be an indication that we have underestimated the standard deviations on the light atom–light atom distances. All of the bond angles are consistent with those found in ethylenediamine and α-amino acid complexes.

2,3-Diaminopropionic acid acts as a tridentate ligand and forms a rigid fused-ring chelate system in which the absolute configuration of the ligand uniquely determines the absolute configuration of the complex. This determination has resulted in the absolute configuration of the complex and the ligands. This assignment of the absolute configuration of the ligand corresponds to that made by Karrer and Schlosser[14] on the basis of chemical correlation with *l*-serine. The absolute configuration of the complex is of interest in that the fused-ring system introduces ambiguity into the simple helical model generally employed in designating optical isomers. According to the currently accepted convention the chirality of the complex can be defined by the helicity of the chelate rings viewed along a C_2 or pseudo-C_2 axis. The central atoms and the two donor atoms of a bidentate ligand define a plane. Two such planes in a *cis*-bis-bidentate complex define a twofold axis and a helix. When the helix is right-handed the complex is labled Δ. The mirror image is labeled Λ. Viewed down the twofold axis of the present complex, the two ethylenediamine rings form a left-handed helix, and from this standpoint the complex may be labeled Λ. On the other hand, the α-amino acid part of the complex gives rise to a conventional Δ absolute configuration. The β-amino acid moieties give chelate rings which cannot be designated as either Δ or Λ. Thus the simple helical model seems inadequate in assigning a label to the absolute configuration of the compound. Clearly, a different model or at least a modification of the simple model is needed. At this point one is again forced to rely on optical rotation data and merely label the compound (+) or (−) at a particular wavelength. Therefore, the compound studied is designated as $(-)_{546}$-*cis,trans,cis*-bis(L-diaminopropionato)cobalt(III) bromide.

The conformations of the chelate rings are also of interest. The conformation of a chelate ring can be labeled according to the following convention. When an ethylenediamine chelate ring is viewed along the axis through the two nitrogen atoms the sequence of bonds N–C–C–N defines a helix. When this system is right handed, the conformation is labeled δ; the mirror image is labeled λ. According to this convention, the ethylenediamine rings in the present complex assume δ conformations instead of the λ conformation usually found for a Λ complex. This is due to the fact that the carboxyl group which otherwise would occupy an equatorial position is coordinated and, therefore, is required to be in an axial position. The conformation of the α-amino acid chelate ring is λ, again due to the rigid fused-ring system. The same factor is responsible for the boat conformation of the six-membered β-amino acid rings.

Acknowledgment.—C. F. L. wishes gratefully to acknowledge the financial assistance of the National Institutes of Health through a special postdoctoral fellowship and a research grant (GM-14254).

---

(8) R. F. Bryan, R. J. Poljak, and D. Tomia, *Acta Cryst.*, **14**, 1125 (1961).

(9) K. A. Fraser, H. A. Long, R. Candlin, and M. M. Harding, *Chem. Commun.*, 344 (1965).

(10) H. C. Freeman and J. T. Szymanski, *Acta Cryst.*, **22**, 406 (1967).

(11) H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *ibid.*, **17**, 1463 (1964).

(12) R. D. Gillard, R. Mason, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 155 (1966).

(13) J. F. Blount, K. A. Fraser, H. C. Freeman, J. T. Szymanski, and C. H. Wang, *Acta Cryst.*, **22**, 396 (1967).

(14) P. Karrer and A. Schlosser, *Helv. Chim. Acta*, **6**, 411 (1923).