The Structure and Absolute Configuration of Bis(ethylenediamine)trimethylenediaminecobalt(III) Bromide

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The structure of the dextrorotatory ($\lambda = 589$ nm) enantiomer of bis(ethylenediamine)trimethylenediaminecobalt(III) bromide ([Co-(III)en$_2$tn]Br$_3$) has been determined by X-ray diffraction using visually estimated three-dimensional photographic data. The crystals are orthorhombic with space group $P2_12_12_1$ and with $a = 18.629$ Å, $b = 10.774$ Å, and $c = 8.719$ Å. The structure was determined from the Patterson function and was refined by least squares methods to an R-value of 7.15 %. Its absolute configuration was found to be Λ, *i.e.* similar to that of the dextrorotatory enantiomer of the tris-(ethylenediamine)cobalt(III) ion, using the effect of the anomalous scattering of Cu$K\alpha$-radiation on the cobalt and bromine atoms.

The absolute configuration and the conformation of chelate coordination compounds — in particular tris(diamine)chelates of Co(III)[1-4] and Cr(III)[5-7] — and the relation between these properties and the chiroptical properties (ORD and CD) have been the object of considerable theoretical interest and experimental investigation.[8]

The discovery of the strong dependence of the rotatory strength of comparable bands in the visible absorption spectrum of tris(diamine) chelates upon the size and conformation of the chelate rings [9] prompted a series of investigations of the structures of such complexes. In this laboratory special interest [10] has been devoted to the series [Co en$_n$tn$_{3-n}$]$^{3+}$ ($n = 0$, 1, 2, and 3), and the present paper supplements the structures and absolute configurations of the "pure" complexes (*i.e.* $n = 0$ and 3) determined by Saito *et al.*[1,3] by those of one of the "mixed" complexes ($n = 2$) in the form of the bromide of the dextrorotatory ** enantiomer.

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** The optical rotation at 589 nm (in aqueous solution at 25°C), however, happens to be small. Its sign is, of course, of no significance in the theoretical discussion, the important feature being the strong positive circular dichroism at *ca.* 500 nm.[10]

EXPERIMENTAL

The crystals were reddish-yellow, well developed needles with the crystallographic c-axis along the needle axis. To facilitate correction for the high absorption cylindrical shape was attained for two crystals (A) and (B). (A) was rolled on wet emery paper until it became a nearly perfect cylinder of length 0.70 mm and diameter 0.10 mm. It appeared to be a single crystal and was used in the intensity recording. (B) was ground into a very coarse cylinder of length 0.43 mm and diameter 0.10 mm while mounted on the glass rod. It was used for the initial scaling of the layers, its axis being approximately along the a-axis.

Both crystals were mounted on a Weissenberg camera in equi-inclination setting. The reflections were recorded on 3 films in stack, the $hk0$ to $hk3$-zones twice for different exposure times and the other zones once. An exposure scale for a single strong reflection provided the means for estimating the intensities visually. The records of each reflection were averaged as well as possible by means of a specially constructed slide rule. Correction for absorption [11] and spot elongation [12] were applied manually and for the Lorentz and polarisation factor by computer. 1383 reflections were recorded in the hkl and $-hkl$ octants for $l = 0 - 6$.

The anomalous dispersion of Co and Br for copper radiation gives rise to a fairly large background. As the R index of 0.0715 shows, the measurements were sufficiently accurate despite this disadvantage.

26 powder lines were measured together with a NaCl standard and the crystal axes calculated by a least squares procedure incorporating the orthorhombic symmetry.

As the calculated specific gravity of 1.901 g cm^{-3} is in good agreement with the value of 1.80 g cm^{-3} for a related compound,[1] it was not measured experimentally.

CALCULATIONS

The first calculations were done by the X-ray 63 system at the North European University Computing Centre in Copenhagen and the last at the University of Århus.

A search for vector correlations solved the Patterson synthesis for the Co and Br atoms. Their atomic coordinates were refined to an R index of 0.291 by the full matrix least squares program ORFLS using isotropic temperature factors and used for a Fourier synthesis which yielded the positions of all N and C atoms. The Co, Br, N, and C atom positions were refined isotropically to an R index of 0.233. When the Co and Br atoms were refined anisotropically and the N and C atoms isotropically, the R index became stationary at 0.131.

An attempt to introduce anomalous dispersion of Co and Br failed, possibly due to large parameter correlations and the rather awkward (now improved) handling of anomalous dispersion by the least squares program.

At this stage Mrs. R. G. Hazell of the University of Aarhus kindly offered to execute refinements using her own program. This includes least squares refinement of the atomic parameters, two weighting parameters and an extinction parameter. It yielded a stationary R index of 0.0715 for one absolute configuration and 0.1080 for the other in refining the Co, Br, N, and C atoms. Adopting the former, supposed hydrogen atoms and anisotropic temperature factors for Co, Br, N, and C were introduced. The R index dropped to 0.0661, but as the N and C temperature factors appeared improbable, the atom parameters giving the R index of 0.0715 were recognized as the most reliable. However, the structure factor table reproduced as Table 6 corresponds to the R index of 0.0661.

CRYSTAL DATA

Space group $P2_12_12_1$ (orthorhombic, No 19).
Cell axes $a = 18.629$ Å, $\sigma = 0.025$ Å; $b = 10.774$ Å, $\sigma = 0.009$ Å; $c = 8.179$ Å, $\sigma = 0.007$ Å.
Cell angles $\alpha = \beta = \gamma = 90°$.

Systematic extinction $h00$ (h odd), $0k0$ (k odd), $00l$ (l odd).
Cell content $Z = 4$ formula units.
Calculated specific gravity $\varrho = 1.901$ g cm^{-3}.
Linear absorption $\mu = 170.8$ cm^{-1}.
X-Ray wavelength $\lambda = 1.5418$ Å (weighted average of $CuK\alpha_1$ and $CuK\alpha_2$).
Equalities of structure factors for the indices

$$hkl = h\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}\bar{k}l$$
$$\bar{h}\bar{k}\bar{l} = \bar{h}kl = h\bar{k}l = hk\bar{l}$$

Atomic coordinates, temperature factors, bond lengths and angles are given in Tables 1 − 5. Structure factors are given in Table 6 and a list of selected Bijvoet pairs are given in Table 7.

Table 1. Atomic coordinates in fractions of the unit cell. Standard errors in parentheses, corresponding to last digits.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Br$_1$	− 0.05876	(15)	0.59046	(23)	− 0.54303	(36)		
Br$_2$	0.08122	(13)	0.90481	(22)	− 0.48826	(32)		
Br$_3$	0.16761	(14)	0.53935	(23)	− 0.46667	(34)		
Co	0.09946	(18)	0.68325	(30)	0.02866	(47)		
N$_1$	0.1636	(10)	0.7359	(17)	0.2043	(23)	2.00	(0.35)
N$_2$	0.1347	(9)	0.8184	(17)	− 0.1097	(22)	1.81	(0.35)
N$_3$	0.0211	(9)	0.7817	(15)	0.1225	(22)	1.53	(0.34)
N$_4$	0.0290	(10)	0.6430	(17)	− 0.1496	(24)	2.37	(0.39)
N$_5$	0.0662	(10)	0.5428	(17)	0.1623	(22)	2.13	(0.35)
N$_6$	0.1698	(9)	0.5695	(15)	− 0.0753	(20)	1.77	(0.33)
C$_1$	0.2400	(14)	0.7750	(23)	0.1700	(31)	2.78	(0.51)
C$_2$	0.2390	(14)	0.8881	(24)	0.0637	(34)	3.92	(0.57)
C$_3$	0.2120	(13)	0.8628	(21)	− 0.1054	(30)	2.41	(0.49)
C$_4$	− 0.0463	(12)	0.7605	(21)	0.0454	(33)	2.82	(0.46)
C$_5$	− 0.0308	(13)	0.7372	(22)	− 0.1345	(31)	2.42	(0.47)
C$_6$	0.1153	(13)	0.4306	(23)	0.1299	(31)	2.87	(0.51)
C$_7$	0.1414	(12)	0.4342	(21)	− 0.0505	(31)	2.77	(0.46)

Table 2. Mean square vibration amplitudes, u_{ij}, in Å$^2 \times 10^{-4}$. Standard errors in parentheses.

Atom	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
Br$_1$	629	(17)	278	(12)	500	(18)	− 8	(12)	64	(13)	− 19	(11)
Br$_2$	422	(14)	376	(13)	374	(17)	69	(11)	− 35	(11)	− 25	(11)
Br$_3$	407	(13)	432	(13)	311	(15)	20	(11)	3	(10)	19	(10)
Co	237	(19)	172	(17)	233	(23)	− 4	(14)	− 2	(15)	3	(15)

Table 3. Interatomic bond distances in Å, standard errors in parentheses.

Atoms	Distance		Atoms	Distance	
$Co-N_1$	1.953	(19)	C_1-C_2	1.497	(36)
$Co-N_2$	1.958	(18)	C_2-C_3	1.496	(36)
$Co-N_3$	1.961	(17)	C_4-C_5	1.520	(37)
$Co-N_4$	2.009	(20)	C_6-C_7	1.554	(36)
$Co-N_5$	1.967	(19)			
$Co-N_6$	1.986	(17)			
N_1-C_1	1.510	(31)			
N_2-C_3	1.518	(29)			
N_3-C_4	1.424	(29)			
N_4-C_5	1.513	(31)			
N_5-C_6	1.538	(31)			
N_6-C_7	1.564	(28)			

Table 4. Selected interatomic non-bonding distances in Å, standard errors in parentheses. Asterisk denotes that the distance is within a $Br-Co$ prism (*cf.* Discussion).

Atoms	Distance		Atoms	Distance	
Br_1-Br_2	4.2982	(41)	Br_2-N_2 *	3.383	(18)
Br_1-Br_3	4.3003	(42)	Br_2-N_4	3.474	(19)
Br_2-Br_3	4.2991	(40)	Br_2-N_5	3.432	(18)
Br_1-N_2	3.486	(18)	Br_3-N_1 *	3.425	(19)
Br_1-N_3	3.462	(17)	Br_3-N_6 *	3.218	(17)
Br_1-N_5 *	3.391	(18)	Br_3-N_6	3.367	(17)
Br_2-N_1 *	3.463	(19)			

Table 5. Bond angles in degrees. Middle atom symbol indicates apex.

Ring No.	Atoms	Angle	σ(Angle)	Atoms	Angle	σ(Angle)
1	N_1-Co-N_2	90.2	0.8	N_2-Co-N_3	94.2	0.7
2	N_3-Co-N_4	85.1	0.8	N_4-Co-N_5	91.8	0.8
3	N_5-Co-N_6	88.3	0.7	N_6-Co-N_1	95.2	0.7
1	$Co-N_1-C_1$	121.4	1.5	N_1-Co-N_3	90.6	0.8
1	$Co-N_2-C_3$	122.6	1.4	N_3-Co-N_5	90.0	0.7
2	$Co-N_3-C_4$	113.4	1.4	N_5-Co-N_1	90.4	0.8
2	$Co-N_4-C_5$	106.1	1.4	N_2-Co-N_4	87.7	0.8
3	$Co-N_5-C_6$	108.8	1.4	N_4-Co-N_6	89.3	0.7
3	$Co-N_6-C_7$	107.3	1.2	N_6-Co-N_2	89.4	0.7
1	$N_1-C_1-C_2$	108.8	2.0			
1	$N_2-C_3-C_2$	113.4	2.0			
2	$N_3-C_4-C_5$	106.7	1.8			
2	$N_4-C_5-C_4$	109.2	1.9			
3	$N_5-C_6-C_7$	109.3	1.9			
3	$N_6-C_7-C_6$	104.3	2.0			
1	$C_1-C_2-C_3$	113.1	2.1			

Table 6. Observed and calculated structure amplitudes of all observed reflections.

Table 6. Continued.

h	k	l	Fobs	Fcal
12	1	4	257	261
-12	1	4	312	296
13	1	4	291	229
-13	1	4	291	234
14	1	4	456	456
-14	1	4	416	437
15	1	4	183	212
-15	1	4	229	245
16	1	4	181	233
-16	1	4	256	269
17	1	4	244	301
-17	1	4	244	298
0	2	4	575	544
1	2	4	510	436
-1	2	4	414	361
2	2	4	614	588
-2	2	4	567	555
3	2	4	305	264
-3	2	4	357	321
4	2	4	224	225
-4	2	4	259	256
5	2	4	236	224
-5	2	4	216	203
6	2	4	352	320
-6	2	4	366	381
7	2	4	502	553
-7	2	4	574	602
8	2	4	324	321
-8	2	4	274	240
10	2	4	245	279
-10	2	4	298	276
11	2	4	378	389
-11	2	4	469	466
12	2	4	257	244
-12	2	4	185	186
13	2	4	261	242
-13	2	4	347	304
15	2	4	183	172
-15	2	4	183	140
17	2	4	168	183
-17	2	4	241	226
1	3	4	323	297
-1	3	4	259	245
2	3	4	430	416
-2	3	4	452	454
3	3	4	650	633
-3	3	4	535	535
5	3	4	293	280
-5	3	4	293	268
6	3	4	387	384
-6	3	4	457	442
7	3	4	602	623
-7	3	4	527	554
8	3	4	351	336
-8	3	4	339	290
10	3	4	483	488
-10	3	4	412	424
11	3	4	384	393
-11	3	4	444	436
12	3	4	183	189
-12	3	4	183	169
14	3	4	330	354
-14	3	4	263	287
15	3	4	182	201
-15	3	4	182	200
0	4	4	316	313
1	4	4	359	335
-1	4	4	328	297
2	4	4	529	551
-2	4	4	479	468
3	4	4	406	407
-3	4	4	414	437
4	4	4	218	217
-4	4	4	154	196
5	4	4	752	756
-5	4	4	814	845
6	4	4	673	652
-6	4	4	606	594
7	4	4	264	261
-7	4	4	355	275
8	4	4	534	546
-8	4	4	492	522
9	4	4	485	462
-9	4	4	469	452
10	4	4	223	227
-10	4	4	258	237
11	4	4	290	289
-11	4	4	378	336
12	4	4	264	295
-12	4	4	264	264
13	4	4	188	206
-13	4	4	188	182
14	4	4	188	216
-14	4	4	188	180
0	5	4	848	877
1	5	4	600	590
-1	5	4	588	562
2	5	4	358	369
-2	5	4	328	298
3	5	4	845	906
-3	5	4	937	938
4	5	4	436	444
-4	5	4	421	400
5	5	4	357	364
-5	5	4	396	405
6	5	4	440	410
-6	5	4	363	374
7	5	4	249	242
-7	5	4	295	319
8	5	4	358	397
-8	5	4	335	348
9	5	4	364	350
-9	5	4	374	367
11	5	4	187	177
-11	5	4	187	200
12	5	4	189	212
-12	5	4	189	156
13	5	4	182	200
-13	5	4	182	208
0	6	4	383	348
1	6	4	419	398
-1	6	4	419	428
2	6	4	364	357
-2	6	4	405	416
3	6	4	388	365
-3	6	4	356	294
4	6	4	174	203
-4	6	4	249	277
5	6	4	442	454
-5	6	4	378	392
6	6	4	256	288
-6	6	4	357	342
8	6	4	326	330
-8	6	4	369	375
10	6	4	266	228
-10	6	4	188	194
11	6	4	323	333
-11	6	4	372	341
13	6	4	306	322
-13	6	4	397	351
14	6	4	379	344
-14	6	4	379	344
0	7	4	337	322
1	7	4	389	365
-1	7	4	396	403
2	7	4	255	216
-2	7	4	286	307
3	7	4	374	348
-3	7	4	316	326
4	7	4	181	210
-4	7	4	181	225
8	7	4	228	222
-8	7	4	266	288
9	7	4	372	334
-9	7	4	293	306
0	8	4	186	232
1	8	4	186	225
-1	8	4	186	205
3	8	4	295	311
-3	8	4	396	395
4	8	4	463	434
-4	8	4	350	339
0	9	4	319	339
1	9	4	182	226
-1	9	4	288	296
3	9	4	223	236
-3	9	4	223	238
4	9	4	314	276
-4	9	4	286	303
8	9	4	355	409
-8	9	4	410	440
0	10	4	242	288
2	10	4	241	265
-2	10	4	293	317
3	10	4	288	321
-3	10	4	291	291
4	10	4	164	233
-4	10	4	236	264
1	0	5	262	253
2	0	5	427	451
3	0	5	695	671
5	0	5	389	402
6	0	5	104	64
7	0	5	435	425
9	0	5	294	270
10	0	5	371	360
11	0	5	322	306
13	0	5	316	328
14	0	5	221	225
15	0	5	126	134
16	0	5	237	203
0	1	5	283	267
1	1	5	292	278
-1	1	5	219	211
2	1	5	592	563
-2	1	5	592	578
3	1	5	315	282
-3	1	5	196	193
4	1	5	270	234
-4	1	5	323	284
5	1	5	552	563
-5	1	5	611	598
6	1	5	299	279
-6	1	5	211	214
7	1	5	610	645
-7	1	5	538	594
8	1	5	543	539
-8	1	5	543	551
9	1	5	297	288
-9	1	5	341	345
10	1	5	396	405
-10	1	5	353	328
11	1	5	350	361
-11	1	5	381	369
12	1	5	259	286
-12	1	5	259	268
13	1	5	224	257
-13	1	5	184	175
14	1	5	180	187
-14	1	5	180	179
16	1	5	167	220
-16	1	5	236	278
0	2	5	633	581
1	2	5	608	527
-1	2	5	596	530
2	2	5	790	783
-2	2	5	878	815
3	2	5	871	821
-3	2	5	881	841
5	2	5	470	446
-5	2	5	390	376
6	2	5	613	627
-6	2	5	672	646
7	2	5	362	377
-7	2	5	433	426
8	2	5	167	158
-8	2	5	291	215
9	2	5	444	412
-9	2	5	370	332
10	2	5	251	270
-10	2	5	356	347
11	2	5	316	286
-11	2	5	316	259
12	2	5	182	180
-12	2	5	182	123
14	2	5	311	283
-14	2	5	383	339
15	2	5	348	383
-15	2	5	388	345
0	3	5	820	783
1	3	5	664	579
-1	3	5	673	603
2	3	5	636	575
-2	3	5	602	558
3	3	5	644	624
-3	3	5	657	626
4	3	5	308	323
-4	3	5	282	266
5	3	5	222	197
-5	3	5	157	149
6	3	5	257	253
-6	3	5	333	311
7	3	5	261	271
-7	3	5	261	237
8	3	5	346	329
-8	3	5	432	433
9	3	5	389	417
-9	3	5	355	360
11	3	5	481	562
-11	3	5	464	491
12	3	5	375	416
-12	3	5	468	496
14	3	5	238	280
-14	3	5	306	301
15	3	5	169	149
-15	3	5	169	155
16	3	5	161	188
-16	3	5	161	202
0	4	5	245	242
1	4	5	310	305
-1	4	5	341	341
2	4	5	358	349
-2	4	5	400	351
4	4	5	230	246
-4	4	5	348	318
5	4	5	442	449
-5	4	5	426	437
6	4	5	385	344
-6	4	5	350	352
8	4	5	283	290
-8	4	5	356	331
9	4	5	256	268
-9	4	5	314	314
10	4	5	181	206
-10	4	5	259	260
12	4	5	315	311
-12	4	5	288	316
13	4	5	179	183
-13	4	5	179	200
14	4	5	335	328
-14	4	5	343	353
0	5	5	281	269
1	5	5	450	502
-1	5	5	394	448
2	5	5	269	255
-2	5	5	269	237
3	5	5	271	242
-3	5	5	297	265
4	5	5	395	404
-4	5	5	380	385
7	5	5	383	427
-7	5	5	383	411
11	5	5	262	243
-11	5	5	221	265
12	5	5	219	218
-12	5	5	179	141
13	5	5	350	374
-13	5	5	341	359
14	5	5	164	147
-14	5	5	199	193
0	6	5	365	340
1	6	5	179	167
-1	6	5	237	226
2	6	5	283	276
-2	6	5	296	290
3	6	5	254	266
-3	6	5	198	238
4	6	5	359	371
-4	6	5	311	311
5	6	5	182	182
-5	6	5	158	191
6	6	5	286	289
-6	6	5	258	272
8	6	5	489	498
-8	6	5	548	537
9	6	5	387	384
-9	6	5	303	336
10	6	5	311	314
-10	6	5	254	285
11	6	5	360	357
-11	6	5	350	334
12	6	5	169	213
-12	6	5	268	267
0	7	5	259	250
2	7	5	386	394
-2	7	5	365	358
3	7	5	466	483
-3	7	5	466	502
5	7	5	445	474
-5	7	5	429	487
6	7	5	482	551
-6	7	5	487	547
7	7	5	268	277
-7	7	5	262	278
8	7	5	179	182
-8	7	5	179	156
10	7	5	170	229
-10	7	5	240	249
11	7	5	165	181
-11	7	5	230	205
0	8	5	513	577
1	8	5	288	281
-1	8	5	180	183
3	8	5	285	292
-3	8	5	339	315
4	8	5	180	183
-4	8	5	254	216
5	8	5	223	233
-5	8	5	283	257
7	8	5	171	173
-7	8	5	203	182
8	8	5	373	423
-8	8	5	336	374
9	8	5	199	185
-9	8	5	258	228
2	9	5	240	202
-2	9	5	170	151
4	9	5	207	146
-4	9	5	237	198
5	9	5	283	318
-5	9	5	328	355
6	9	5	158	164
-6	9	5	158	134
1	0	6	640	675
2	0	6	322	277
3	0	6	572	587
4	0	6	267	263
6	0	6	378	372
7	0	6	174	157
8	0	6	257	208
9	0	6	351	395
10	0	6	170	163
11	0	6	405	445
12	0	6	329	334
13	0	6	183	204
0	1	6	121	59
1	1	6	310	267
-1	1	6	310	263
2	1	6	525	528
-2	1	6	497	480
3	1	6	367	380
-3	1	6	407	405
4	1	6	313	300
-4	1	6	343	328
5	1	6	228	226
-5	1	6	303	279
6	1	6	577	587
-6	1	6	561	550
8	1	6	290	258
-8	1	6	290	254
9	1	6	188	184
-9	1	6	267	263
10	1	6	191	190
-10	1	6	256	230
11	1	6	191	192
-11	1	6	191	213
12	1	6	274	239
-12	1	6	326	284
14	1	6	364	351
-14	1	6	353	337
15	1	6	237	234
-15	1	6	278	269
0	2	6	144	153
-1	2	6	283	240
2	2	6	504	460
-2	2	6	449	426
5	2	6	206	242
-5	2	6	225	230
7	2	6	514	564
-7	2	6	591	600
1	2	6	261	245
8	2	6	312	264
-8	2	6	185	199
11	2	6	257	299
-11	2	6	303	362
13	2	6	182	174
-13	2	6	182	245
0	3	6	162	127
2	3	6	432	398
-2	3	6	449	427
3	3	6	394	381
-3	3	6	314	320
4	3	6	364	378
-4	3	6	244	282
6	3	6	341	326
-6	3	6	314	325
7	3	6	322	306
-7	3	6	264	259
8	3	6	268	289
-8	3	6	268	259
10	3	6	419	427
-10	3	6	357	354
11	3	6	326	288
-11	3	6	355	324
1	4	6	304	270
-1	4	6	304	274
2	4	6	353	345
-2	4	6	177	255
3	4	6	377	356
-3	4	6	395	368
4	4	6	342	279
-4	4	6	326	296
5	4	6	564	585
-5	4	6	668	652
6	4	6	313	305
-6	4	6	253	253
8	4	6	428	450
-8	4	6	428	435
12	4	6	300	287
-12	4	6	255	273
13	4	6	170	191
-13	4	6	170	186
0	5	6	770	776
1	5	6	296	254
-1	5	6	184	198
2	5	6	374	338
-2	5	6	295	300
3	5	6	503	502
-3	5	6	564	547
4	5	6	187	202
-4	5	6	187	192
5	5	6	190	225
-5	5	6	269	221
6	5	6	270	277
-6	5	6	270	269
7	5	6	191	238
-7	5	6	270	281
8	5	6	269	290
-8	5	6	269	253
9	5	6	366	382
-9	5	6	353	389
1	6	6	136	203
-1	6	6	193	250
2	6	6	406	391
-2	6	6	406	413
4	6	6	170	187
-4	6	6	191	219
5	6	6	330	326
-5	6	6	330	305
7	6	6	189	182
-7	6	6	189	214
11	6	6	287	323
-11	6	6	313	316
0	7	6	133	131
1	7	6	266	315
-1	7	6	298	358
3	7	6	235	256
-3	7	6	235	240
4	7	6	166	153
-4	7	6	188	173
1	8	6	321	318
-1	8	6	196	256
4	8	6	247	279
-4	8	6	172	230
0	9	6	216	236
1	9	6	158	140
-1	9	6	147	194

Table 7. Observed and calculated structure amplitudes of Bijvoet pairs.

HKL	F_{obs}	F_{calc}	HKL	F_{obs}	F_{calc}
5 2 1	1285	1300	9 1 3	711	732
−5 2 1	1184	1266	−9 1 3	767	782
1 3 1	727	722	1 8 3	517	509
−1 3 1	804	829	−1 8 3	417	444
2 1 2	718	702	3 3 4	650	633
−2 1 2	644	617	−3 3 4	535	535
1 3 2	542	508	7 2 6	514	564
−1 3 2	452	441	−7 2 6	591	600
1 6 2	421	443	5 4 6	564	585
−1 6 2	500	510	−5 4 6	668	652

DISCUSSION

The following compounds similar to the title compound have been investigated: Abbreviations: en = ethylenediamine, tn = trimethylenediamine, l-pn = l-propylenediamine, R,R-2,4-ptn = R,R-2,4-diaminopentane.

$(-)$D − [Co tn₃]Br₃.H₂O   space group $P2_1$ compound   (I)[1]
        [Co l-pn₃]Br₃ $P6_2$ (II)[2]
        [Co en₃]Cl₃.H₂O $P3c1$ or $P\bar{3}c1$ (III)[3]
$(+)_{546}$ − [Co(R,R-2,4-ptn)₃]Cl₃.H₂O $P2_12_12_1$ (IV)[4]

Fig. 1 and Tables 3 and 5 show that the Co − N configuration in the present compound is roughly octahedral. The N − Co − N angle in the tn-ring is nearly 90°, as would be expected, and that of the en-rings smaller than 90°, probably
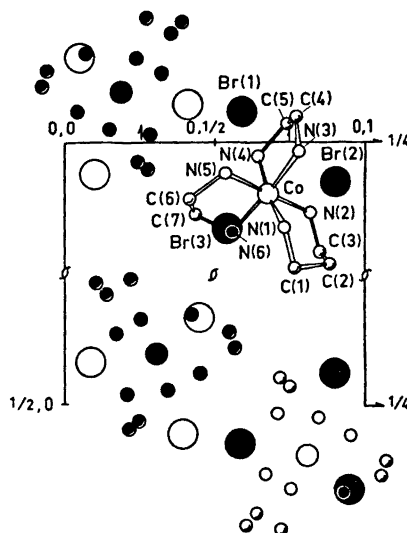

Fig. 1. The structure projected on the a-b plane. Open circles: atoms whose z coordinate is close to 0. Filled-in circles: atoms whose z coordinate is close to $\frac{1}{2}$. Large circles: Br. Medium circles: Co. Small unshaded circles: N. Small shaded circles: C.

due to strain although the difference is not marked. The Co − N distances (mean 1.972 Å) do not differ significantly mutually and are in accordance with those of the compounds (I), (II), and (III). The en-rings are slightly twisted pentagons while the tn-ring is a (distorted) chair, as in (I). The C − C distances are in the normally expected range and do not differ significantly. Most of the N − C distances are 1 − 2 standard deviations larger than normal, except the $N_3 − C_4$ distance which is slightly shorter. The lengthening may be due to the non-inclusion of hydrogen in the refinement. The $C_1 − C_2 − C_3$ angle is larger than, but within 2.2 standard errors of the tetrahedral angle of 109°. All the N − C − C angles are in tolerable agreement with the tetrahedral angle. So are the Co − N − C angles (mean 108.6°) in the en-rings, in agreement with (III), whereas in the tn-ring they are much larger (mean 122°), comparable to the mean value 117.4° of (I). A measure of the twist in the en-rings is the

angle between the $N-N$ vector and the $C-C$ vector which is 5.6° in ring 2 and 7.7° in ring 3.

The temperature factors of the N and C atoms are not much different from each other, being 1.5 to 2.4 for N and 2.4 to 3.9 for C. It will be noted that the value for C_2 is the largest, which would be expected since this atom is comparatively free to swing. The axes of the vibration ellipsoids of the Co and Br atoms lie close to the crystallographic axes. This may be significant but might also be caused by some systematic effect in the data collection or in the refinement.

Common to this and the mentioned structures is the feature of a quasi-regular triangular prism of halogen ions surrounding a Co(III) ion bonded octahedrally to 3 bidentate ligands. The Br triangle does not differ significantly from a regular one with a base length of 4.299 Å in accordance with (I) and (II). Ten $Br-N$ non-bonding distances were shorter than the sum of their van der Waals radii (3.5 Å), indicating probable $Br-H$ hydrogen bonds. The Br triangles are tilted with respect to the z-axis.

In lack of the present conclusive determination of the absolute configuration predictions [10] have been based upon the purely empirical "solubility criterion" or upon a semiempirical criterion concerning the sign of the rotatory strength of the "first" visible absorption band (ca. 500 nm). The first criterion is notorious for – admittedly infrequent – failure, the second criterion seems not yet quite unambiguously applicable.[13] In the present case, however, the predictions based upon both criteria agree with the result of the X-ray investigation in that the enantiomer exhibiting a positive circular dichroism within the absorption band at ca. 500 nm has the Λ absolute configuration.

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