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Absolute Configuration of (−)$_{589}$-2,2′-Bipiperidine: Crystal Structure of (−)$_{546}$-*trans*-Dinitrobis((−)$_{589}$-2,2′-bipiperidine)cobalt(III) *d*-3-Bromocamphor-9-sulfonate Tetrahydrate, (−)$_{546}$-*trans*-[Co(NO$_2$)$_2$((−)$_{589}$-2,2′-bpp)$_2$](*d*-BCS)·4H$_2$O

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The crystal structure of (−)$_{546}$-[Co(NO$_2$)$_2$((−)$_{589}$-2,2′-bpp)$_2$](*d*-BCS)·4H$_2$O has been determined from three-dimensional X-ray counter data. The complex forms monoclinic crystals with $a = 28.975$ (5) Å, $b = 7.853$ (2) Å, $c = 17.831$ (2) Å, $\beta = 101.35$ (1)°, and $Z = 4$, in space group *C*2. The structure was refined by least-squares methods with anisotropic temperature factors to an R value of 0.042 for 3864 independent reflections with $F_o > 3[\sigma(F_o)]$. Six nitrogen atoms of the diamine and nitro groups are bonded nearly octahedrally to the central cobalt atom. The complex cation has approximate twofold symmetry. The absolute configurations around the asymmetric carbon atoms are both *R* for (−)$_{589}$-2,2′-bipiperidine, and the conformations of the two five-membered chelate rings are both λ. The four six-membered heterocycles involving the secondary nitrogen atoms adopt the chair conformation. The absolute configurations about the four secondary nitrogen atoms are all *S*. It seems that the water molecules of crystallization play an important role in the diastereomeric discrimination of the complex cation by *d*-BCS. The relationship between the absolute configuration about the secondary nitrogen atom and the circular dichroism has been examined for the derived *trans*-dichloro complex.

Introduction

In recent years, the stereochemistry of octahedral metal complexes containing *N*-alkyl-group-substituted polyamines has been of much interest. Although the diamines with aliphatic heterocyclic rings belong to N-alkylated polyamines, there is very limited information concerning their stereochemical behavior toward transition-metal ions.[2]

Recently racemic 2,2′-bipiperidine (2,2′-bpp), which has two six-membered heterocyclic rings, was separated from the meso form in this laboratory. Several attempts to resolve this racemic compound were carried out, but no tendency to resolve into optical isomers was observed. However, we succeeded in optical resolution of the racemic diamine through its *trans*-dinitrobis(diamine)cobalt(III) complex, by using the resolving agent ammonium *d*-3-bromocamphor-9-sulfonate (NH$_4$-*d*-BCS). The optically active (−)$_{589}$-2,2′-bpp was recovered from the complex. These results will be dealt with in detail in a subsequent paper.[3] The work reported here represents, so far as we know, the first X-ray structure determination of a tetragonal cobalt(III) complex having a resolving reagent as a counteranion.

Our purpose in undertaking the X-ray structure determination was fourfold: to determine the absolute configuration about asymmetric carbon centers of (−)$_{589}$-2,2′-bpp, to elucidate the conformation of the piperidine ring, to clarify the interaction between the complex cation and the resolving reagent, and to establish relationships between CD curves and configuration at asymmetric secondary nitrogen centers involving heterocyclic rings.

Experimental Section

The preparation of (−)$_{546}$-*trans*-[Co(NO$_2$)$_2$((−)$_{589}$-bpp)$_2$](*d*-BCS)·4H$_2$O will be dealt in a subsequent paper.[3]

Crystal Data. Weissenberg photographs indicated a monoclinic unit cell with systematic extensions for *hkl*, $h + k = 2n + 1$. Of the three possible space groups *Cm*, *C*2, and *C*2/*m*, space group *C*2 was chosen because of the optical activity of the compound. The unit cell dimensions were obtained by least-squares refinement of 50 high-angle reflections centered on a Rigakudenki four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 28.975$ (5) Å, $b = 7.853$ (2), Å, $c = 17.831$ (2) Å, and $\beta = 101.35$ (1)°. With $Z = 4$ and the molecular weight of this complex, the calculated density is 1.45 g cm^{-3} compared with a measured density of 1.47 g cm^{-3} obtained by flotation in a dibromoethane–carbon tetrachloride mixture.

Intensity Data Collection. The crystal used in the data collection was a yellow prism with the approximate dimensions 0.26 × 0.19 × 0.16 mm. The crystal was mounted with the *b* axis approximately parallel to the instrument axis. Diffraction data were collected on a Rigakudenki four-circle automated diffractometer. The θ–2θ scan method was employed with a scanning rate of 3° min^{-1}. Stationary-crystal, stationary-counter background counts of 8 s were taken on each side of the scan. A unique data set (*hkl*) was first collected, for 2θ less than 55°, by using Mo Kα radiation monochromated by a graphite crystal. The takeoff angle was 1.2°. Three standard reflections were monitored every fifty reflections and showed only a 1–3% random variation in intensity, for which no correction was made. For determination of the absolute configuration of (−)$_{589}$-2,2′-bipiperidine, the Bijvoet pair data set ($h\bar{k}l$), with 2θ values between 15 and 20°, was then collected under the same conditions. A total of 5327 reflections were measured and the standard Lorentz and polarization corrections applied. Of the 5327 reflections collected, 3864 had $F_o > 3[\sigma(F_o)]$ and were considered observed. An absorption correction ($\mu = 16.2$ cm^{-1}) was applied.

Solution and Refinement of the Structure. The initial positions of the Co and Br were determined from a Patterson synthesis, and the positions of the remaining nonhydrogen atoms were determined by successive structure factor and electron density map calculations. Isotropic followed by anisotropic least-squares refinement gave values of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.062$ and $R' = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.082$. Atomic scattering factors were taken from ref 4. A weighting scheme

$$1/w = \sigma c^2 + (0.015|F_o|)^2$$

was employed, where σc defined as $\sigma c = (\bar{N})^{1/2}$ is a counting statistics error with Gaussian distribution function $P(N) = (^1/_2\bar{N})^{1/2} \exp[-(N - \bar{N})^2/2\bar{N}]$.

The absolute configuration of the ligand in the complex cation, originally solved as *R*,*R* around the asymmetric carbon atoms, was determined by using the absorption-edge technique.[5] Some reflections with indices ***hkl*** and $\boldsymbol{h\bar{k}l}$ were collected. The inequality relationships that were observed for some Bijvoet pairs of ***hkl*** and $\boldsymbol{h\bar{k}l}$ are shown in Table I.[6] Accordance between the observed and calculated difference indicates that the absolute configuration of the ligand is correct

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Table II. Final Atomic Positional Parameters

atom	x	y	z	atom	*x*	*y*	*z*
Co	9 631 (3)	6 018 (13)	30 159 (4)	H(1)	156 (2)	260 (9)	337 (3)
O(1)	10 537 (17)	−10 720 (65)	16 705 (25)	H(2)	157 (2)	157 (8)	185 (3)
O(2)	12 771 (16)	−25 929 (65)	26 697 (27)	H(3)	193 (2)	466 (10)	273 (3)
O(3)	10634 (17)	37 262 (64)	37 433 (28)	H(4)	198 (2)	438 (9)	185 (3)
O(4)	4 449 (16)	24 520 (75)	38 836 (31)	H(5)	279 (2)	358 (9)	273 (3)
N(1)	15 920 (16)	16 005 (66)	30 040 (26)	H(6)	255 (2)	189 (8)	214 (3)
N(2)	7 447 (16)	20 639 (69)	20 960 (27)	H(7)	245 (2)	252 (8)	382 (3)
N(3)	3 351 (16)	−5 929 (68)	29 588 (29)	H(8)	277 (2)	90 (8)	344 (3)
N(4)	11 570 (17)	−6 821 (66)	39 925 (27)	H(9)	201 (2)	−34 (9)	272 (3)
N(5)	11 201 (18)	−12 368 (68)	23 793 (28)	H(10)	202 (2)	−17 (9)	370 (3)
N(6)	8 019 (17)	24 869 (71)	36 252 (28)	H(11)	71 (2)	117 (9)	167 (3)
C(1)	15 896 (20)	24 809 (82)	22 609 (34)	H(12)	103 (2)	435 (9)	237 (3)
C(2)	20 093 (22)	36 929 (94)	23 392 (38)	H(13)	99 (2)	307 (8)	81 (3)
C(3)	24 810 (23)	27 401 (96)	26 082 (41)	H(14)	123 (2)	486 (9)	115 (3)
C(4)	24 704 (22)	16 630 (100)	33 128 (40)	H(15)	40 (2)	523 (10)	38 (3)
C(5)	20 309 (20)	5 115 (97)	31 949 (36)	H(16)	51 (2)	603 (8)	130 (3)
C(6)	11 180 (20)	33 326 (87)	20 106 (33)	H(17)	11 (2)	267 (9)	73 (3)
C(7)	10 203 (23)	40 448 (95)	12 043 (39)	H(18)	−14 (2)	433 (9)	106 (3)
C(8)	5 357 (25)	48 420 (114)	9 819 (37)	H(19)	32 (2)	401 (8)	240 (3)
C(9)	1 635 (25)	36 910 (118)	11 741 (46)	H(20)	4 (2)	219 (9)	212 (3)
C(10)	2 910 (21)	30 000 (99)	19 811 (39)	H(21)	12 (2)	29 (10)	314 (3)
C(11)	4 066 (22)	−20 481 (85)	35 161 (37)	H(22)	55 (2)	−298 (8)	327 (3)
C(12)	−637 (25)	−27 140 (107)	36 590 (43)	H(23)	−24 (2)	−150 (8)	385 (3)
C(13)	−3 792 (25)	−32 555 (114)	29 198 (50)	H(24)	−3 (2)	−370 (8)	404 (3)
C(14)	−4 079 (25)	−19 243 (117)	22 909 (45)	H(25)	−66 (2)	−354 (8)	302 (3)
C(15)	677 (23)	−12 318 (100)	22 191 (39)	H(26)	−23 (2)	−438 (10)	272 (3)
C(16)	7 287 (23)	−14 188 (87)	42 305 (37)	H(27)	−57 (2)	−85 (8)	247 (3)
C(17)	8 643 (27)	−28 006 (99)	48 499 (39)	H(28)	−55 (2)	−232 (10)	177 (4)
C(18)	11 951 (26)	−20 542 (108)	55 346 (39)	H(29)	25 (2)	−213 (8)	205 (3)
C(19)	16 125 (24)	−10 987 (106)	53 135 (36)	H(30)	3 (2)	−25 (10)	181 (4)
C(20)	14 480 (22)	1 704 (91)	46 832 (35)	H(31)	129 (2)	−164 (8)	383 (3)
Br	14 982 (4)	0 (14)	1 759 (5)	H(32)	53 (2)	−40 (9)	448 (3)
S	16 945 (6)	24 076 (26)	−31 703 (9)	H(33)	100 (2)	−364 (9)	466 (3)
O(5)	14 792 (16)	34 376 (74)	−38 364 (24)	H(34)	52 (2)	−322 (9)	505 (3)
O(6)	21 867 (16)	20 282 (17)	−31 515 (25)	H(35)	126 (2)	−299 (10)	591 (4)
O(7)	14 137 (17)	9 184 (66)	−30 834 (26)	H(36)	95 (2)	−108 (8)	580 (3)
O(8)	20 973 (18)	35 778 (81)	4 081 (26)	H(37)	180 (2)	−197 (9)	513 (3)
O(21)	17 261 (23)	42 125 (90)	−9 348 (35)	H(38)	178 (2)	−50 (9)	572 (3)
C(22)	19 079 (22)	31 044 (102)	−2 249 (35)	H(39)	121 (2)	121 (9)	490 (3)
C(23)	18 233 (24)	12 762 (97)	−5 015 (36)	H(40)	168 (2)	80 (8)	455 (3)
C(24)	15 765 (24)	14 619 (94)	−13 329 (35)	H(41)	213 (2)	75 (10)	−45 (4)
C(25)	10 817 (23)	22 358 (105)	−13 660 (38)	H(42)	154 (2)	33 (10)	−162 (3)
C(26)	11 866 (22)	40 411 (100)	−10 472 (36)	H(43)	85 (2)	149 (10)	−101 (4)
C(27)	19 105 (29)	60 291 (106)	−8 803 (44)	H(44)	84 (2)	225 (8)	−192 (3)
C(28)	18 538 (22)	30 089 (87)	−15 670 (34)	H(45)	99 (2)	502 (10)	−142 (4)
C(29)	16 566 (22)	37 441 (91)	−23 701 (34)	H(46)	104 (2)	429 (10)	−54 (4)
C(30)	23 906 (23)	27 248 (112)	−14 714 (38)	H(47)	175 (2)	669 (10)	−49 (4)
O(9)	−5 060 (18)	35 782 (92)	44 879 (31)	H(48)	174 (2)	668 (9)	−140 (3)
O(10)	22 034 (21)	67 772 (78)	41 727 (33)	H(49)	223 (2)	609 (9)	84 (3)
O(11)	20 860 (19)	38 778 (79)	49 881 (32)	H(50)	124 (2)	419 (9)	−242 (4)
O(12)	−4 633 (19)	15 654 (93)	32 297 (33)	H(51)	181 (2)	475 (9)	−242 (3)
				H(52)	245 (2)	198 (10)	−184 (4)
				H(53)	254 (2)	228 (9)	−95 (3)
				H(54)	254 (2)	390 (10)	−152 (4)

as that originally determined, in agreement with the known absolute configuration of *d*-3-bromocamphor-9-sulfonic acid used in the optical resolution of the complex.

The effects of anomalous dispersion were introduced in F_c, and values of f' and f'' for Br, Co, S, and O were taken from Cromer's tabulation.[7] Least-squares refinement, allowing all the atoms except for hydrogen atoms to vibrate anisotropically, converged to R and R' values of 0.060 and 0.080.

The final structure of each bipiperidine has an *R*,*R* configuration around the asymmetric carbon atoms and an *S*,*S* configuration around the secondary nitrogen atoms. When the f'' values of Br, Co, S, and O atoms were reversed in sign in order to test the final structure, convergence was reached with $R = 0.067$ and $R' = 0.089$, which are significantly larger than the values 0.060 and 0.080 for the final structure. This result agreed with the earlier determination by using the absorption-edge technique.

At this stage, a difference Fourier synthesis revealed clear evidence of a considerable number of hydrogen atoms, thus justifying their inclusion in the structure. Idealized positions of the hydrogen atoms were calculated by assuming a tetrahedral coordination about carbon atoms and nitrogen atoms, with C–H and N–H bond distances of 1.08 Å. Further refinement was carried out including the contributions of isotropic hydrogen atoms. Refinement converged with $R = 0.042$ and $R' = 0.052$. A final difference Fourier synthesis still showed peaks at heights up to 0.8 e $Å^{-3}$ around the bromine atom, although the electron density did not rise above 0.4 e $Å^{-3}$ elsewhere. The final positional parameters along with their standard deviations are listed in Table II. Compilations of the anisotropic thermal parameters and observed and calculated structure factors are available.[6] All calculations were performed on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with Universal Program System UNICS III.[8]

Results and Discussion

Description of the Molecular Structure. A perspective drawing of the complex cation showing ellipsoids of thermal

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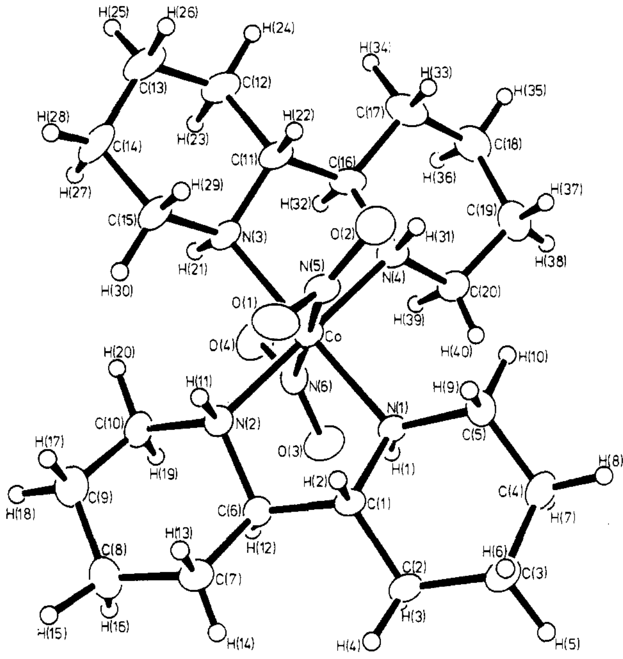

Figure 1. Perspective drawing of the complex cation $(-)_{546}$-*trans*-$[Co(NO_2)_2((-)_{589}\text{-}2,2'\text{-bpp})_2]^+$ and the numbering scheme for the atoms.

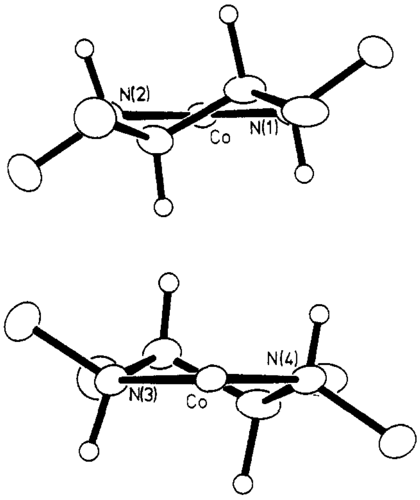

Figure 2. Perspective drawing of the chelate rings.

Table III. Bond Distances (Å)[a]

Co–N(1)	1.988 (5)	C(1)–C(2)	1.529 (9)
Co–N(2)	2.000 (5)	C(1)–C(6)	1.508 (8)
Co–N(3)	2.032 (5)	C(2)–C(3)	1.549 (9)
Co–N(4)	1.995 (5)	C(3)–C(4)	1.520 (11)
Co–N(5)	1.945 (6)	C(4)–C(5)	1.542 (9)
Co–N(6)	1.947 (6)	C(6)–C(7)	1.517 (9)
N(5)–O(1)	1.247 (7)	C(7)–C(8)	1.517 (10)
N(5)–O(2)	1.232 (7)	C(8)–C(9)	1.498 (12)
N(6)–O(3)	1.226 (7)	C(9)–C(10)	1.514 (11)
N(6)–O(4)	1.213 (8)	C(11)–C(12)	1.527 (10)
N(1)–C(1)	1.493 (8)	C(11)–C(16)	1.507 (9)
N(1)–C(5)	1.514 (8)	C(12)–C(13)	1.510 (11)
N(2)–C(6)	1.500 (8)	C(13)–C(14)	1.523 (12)
N(2)–C(10)	1.487 (8)	C(14)–C(15)	1.510 (11)
N(3)–C(11)	1.502 (8)	C(16)–C(17)	1.543 (10)
N(3)–C(15)	1.480 (8)	C(17)–C(18)	1.514 (10)
N(4)–C(16)	1.504 (9)	C(18)–C(19)	1.539 (11)
N(4)–C(20)	1.506 (8)	C(19)–C(20)	1.508 (10)
Br–C(23)	1.949 (8)	C(21)–C(22)	1.541 (9)
S–O(5)	1.470 (5)	C(21)–C(26)	1.542 (9)
S–O(6)	1.451 (5)	C(21)–C(27)	1.520 (11)
S–O(7)	1.450 (6)	C(21)–C(28)	1.570 (10)
S–C(29)	1.792 (7)	C(22)–C(23)	1.522 (11)
O(8)–C(22)	1.199 (8)	C(23)–C(24)	1.521 (9)
		C(24)–C(25)	1.548 (10)
		C(24)–C(28)	1.558 (10)
		C(25)–C(26)	1.535 (11)
		C(28)–C(29)	1.546 (8)
		C(28)–C(30)	1.547 (9)

[a] Estimated standard deviations in parentheses.

Table IV. Bond Angles (Deg)[a]

N(1)–Co–N(2)	84.7 (2)	Co–N(1)–C(1)	110.4 (3)
N(1)–Co–N(3)	174.5 (2)	Co–N(1)–C(5)	120.4 (4)
N)1)–Co–N(4)	96.2 (2)	N(1)–C(1)–C(2)	110.0 (5)
N(1)–Co–N(5)	88.1 (2)	N(1)–C(1)–C(6)	108.3 (5)
N(1)–Co–N(6)	91.6 (2)	N(1)–C(5)–C(4)	109.5 (6)
N(2)–Co–N(3)	95.1 (2)	C(1)–C(2)–C(3)	111.4 (6)
N(2)–Co–N(4)	174.4 (2)	C(2)–C(3)–C(4)	111.4 (6)
N(2)–Co–N(5)	91.2 (2)	C(3)–C(4)–C(5)	111.4 (5)
N(2)–Co–N(6)	87.1 (2)	C(1)–N(1)–C(6)	108.5 (5)
N(3)–Co–N(4)	84.6 (2)	Co–N(2)–C(6)	110.3 (3)
N(3)–Co–N(5)	86.5 (2)	Co–N(2)–C(10)	121.7 (4)
N(3)–Co–N(6)	93.9 (2)	N(2)–C(6)–C(1)	107.8 (5)
N(4)–Co–N(5)	94.4 (2)	N(2)–C(6)–C(7)	109.7 (5)
N(4)–Co–N(6)	87.4 (2)	C(2)–C(10)–C(9)	110.5 (5)
N(5)–Co–N(6)	178.2 (2)	C(6)–C(7)–C(8)	113.0 (6)
Co–N(5)–O(1)	120.5 (4)	C(7)–C(8)–C(9)	111.2 (7)
Co–N(5)–O(2)	120.4 (4)	C(8)–C(9)–C(10)	112.5 (6)
Co–N(6)–O(3)	119.4 (4)	C(6)–N(2)–C(10)	107.1 (5)
Co–N(6)–O(4)	120.7 (5)	C(22)–C(21)–C(26)	103.4 (5)
O(1)–N(5)–O(2)	119.1 (5)	C(22)–C(21)–C(27)	114.7 (5)
O(3)–N(6)–O(4)	119.8 (6)	C(22)–C(21)–C(28)	99.2 (5)
Br–C(23)–C(22)	110.5 (5)	C(26)–C(21)–C(27)	115.1 (6)
Br–C(23)–C(24)	117.5 (5)	C(26)–C(21)–C(28)	103.3 (5)
O(5)–S–O(6)	113.0 (3)	C(27)–C(21)–C(28)	118.8 (6)
O(5)–S–O(7)	111.9 (3)	C(21)–C(22)–C(23)	105.0 (5)
O(6)–S–O(7)	113.8 (3)	C(22)–C(23)–C(24)	103.9 (6)
O(5)–S–C(29)	108.4 (3)	C(23)–C(24)–C(25)	109.2 (6)
O(6)–S–C(29)	108.4 (3)	C(23)–C(24)–C(28)	99.6 (5)
O(7)–S–C(29)	105.3 (3)	C(25)–C(24)–C(28)	101.9 (6)
S–C(29)–C(28)	116.7 (5)	C(24)–C(25)–C(26)	103.5 (5)
O(8)–C(22)–C(21)	127.5 (7)	C(21)–C(26)–C(25)	104.5 (6)
O(8)–C(22)–C(23)	127.4 (7)	C(21)–C(28)–C(24)	94.0 (5)
		C(21)–C(28)–C(29)	110.1 (5)
		C(21)–C(28)–C(30)	112.4 (5)
		C(24)–C(28)–C(29)	115.1 (5)
		C(24)–C(28)–C(30)	114.7 (6)
		C(29)–C(28)–C(30)	109.7 (5)

[a] Estimated standard deviations in parentheses.

motion is given in Figure 1. The complex cation has approximate twofold symmetry. The cobalt atom is surrounded by six nitrogen atoms at the apices of a slightly distorted octahedron. The nitro groups are in trans positions. The absolute configurations around the asymmetric carbon centers, determined by the Bijvoet method,[5] are both *R* for each bipiperidine. The arrangement of the group around the secondary nitrogen atoms is an *S* configuration in the notation of Cahn, Ingold and Prelog.[9] This result agrees with the assignment made by analysis of the circular dichroism spectrum of the complex ion.[3] Each conformation of the two diamine chelate rings is presented in Figure 2. The conformations of the two five-membered chelate rings are both λ. The four six-membered heterocycles involving the secondary nitrogen atoms adopt the chair conformation. All *N*-methylene and *C*-methylene groups have equatorial orientations with respect to the chelate rings. A selection of intramolecular bond distances and angles are given in Tables III and IV. The Co–N bond lengths of Co–N(2) and Co–N(3) are 2.000 (5) and 2.032 (5) Å, respectively. These distances are slightly longer than the values of 1.988 (5) and 1.995 (5) Å for the other chelate bonds Co–N(1) and Co–N(4), respectively.

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These values are significantly long as compared with the reported values in *trans*-$[Co(NO_2)_2(en)_2]NO_3$,[10] the average Co–N(diamine) distance being 1.949 (2) Å, whereas in the complex ion *trans*-$[Co(Pip)_2(TPP)]^+$,[11] in which Pip and TPP represent the unidentate ligand piperidine in a trans position and the tetradentate ligand 5,10,15,20-tetraphenylporphinato anion, respectively, the average Co–N(Pip) distance is 2.060 (3) Å. The ring angles at the cobalt atom for the five-membered chelate rings, N(1)–Co–N(2) and N(3)–Co–N(4), are 84.7 (2) and 84.6 (2)°, respectively. These angles appear normal for Co(III) five-membered chelate rings and can be compared with the mean value of 84.8 (2)° for $(-)_{589}$-*cis*-$[Co(NO_2)_2(N^2\text{-Me-}(S)\text{-pn})_2]^+$,[12] where N^2-Me-(*S*)-pn represents (2*S*)-2-amino-4-azapentane. The Co–N(nitro group) distances are 1.945 (6) and 1.947 (6) Å, which are comparable with those observed in $(+)_{546}$-*trans*-dinitro(1,10-diamino-4,7-diazadecane)cobalt bromide[13] and $(+)_{589}$-*cis*-dinitrobis($(-)_{589}$-1,2-propylenediamine)cobalt chloride.[14] The average N–C and C–C distances of the bipiperidines, with the exception of C(1)–C(6) and C(11)–C(16), are 1.499 (8) and 1.523 (11) Å, respectively, which are comparable with the reported values in *trans*-$[Co(Pip)_2(TPP)]^+$, 1.497 (5) and 1.529 (7) Å, for the mean N–C and C–C distances of the piperidine, respectively. The bond distances C(1)–C(6) and C(11)–C(16) of the chelate ring carbon atoms are 1.508 (8) and 1.507 (9) Å, respectively, which are quite normal for Co(III) five-membered chelate rings. The average bond angle at the carbon and nitrogen atoms for the bipiperidines is 110.3°, which is as large as the idealized tetrahedral values of 109.5°. Therefore, a significant distortion of the bipiperidines does not appear to be induced as a result of coordination to the Co(III) atom.

The structure of the *d*-3-bromocamphor-9-sulfonate anion, which agrees with the known absolute configuration, is also shown in Figure 4. The C–C bond distances of the bromocamphor part appear from 1.52 (1) to 1.57 (1) Å, while in $(+)_{589}$-*cis*-$[CoClNH_3(en)_2](d\text{-BCS})_2{\cdot}H_2O$ these distances extend from 1.47 (4) to 1.67 (4) Å.[15] The other bond lengths of Br–C, O–C, S–O, and S–C bonds are comparable with the reported values. The bond angles of C(22)–C(21)–C(28), C(27)–C(21)–C(28), C(23)–C(24)–C(28), and C(21)–C(28)–C(24) are 99.2 (5), 118.8 (6), 99.6 (5) and 94.0 (5)°, respectively. These values indicate the significant distortions from the ideal tetrahedral structure as in some camphor derivatives.[16]

Some selected least-squares planes are given in Table V,[6] and intraionic close contacts are listed in Table VI.[6] The deviations from an ideal octahedron evidenced by the amine nitrogen atoms result in displacements of −0.097 and −0.095 Å from the equatorial plane for N(1) and N(3) and displacements of 0.096 and 0.096 Å for atoms N(2) and N(4). The dihedral angle between the planes defined by Co, N(1), N(2) and Co, N(3), N(4) is 8.2°. This distortion from ideal geometries and the elongation of the Co–N bond distances mentioned above may be attributed to the nonbonded interactions between the *N*-methylene groups of the other bipiperidine. In fact, the nonbonded distances of H(20)–H(30) and H(10)–H(40) are 1.99 and 2.12 Å, respectively.

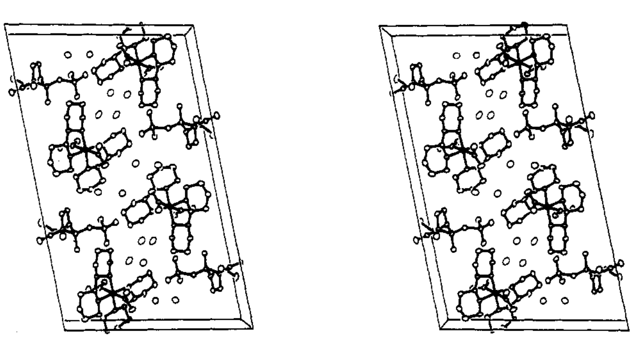

Figure 3. Stereoscopic illustration of the unit cell contents.

Description of the Unit Cell. A stereoview of the contents of one unit cell is presented in Figure 3. The unit cell consists of 4 complex cations, *d*-3-bromocamphor-9-sulfonate counterions, and the 16 waters of crystallization. The nitro groups of the complex cations and the sulfonate groups of *d*-3-bromocamphor-9-sulfonate anions form a hydrophilic sphere together with the water molecules. The hydrophilic sphere, in which hydrogen bonds of the type O–H···O probably exist, is surrounded by hydrophobic bipiperidine and bromocamphor residues.

There are two units of intermolecular hydrogen bonds. In the first unit (the A unit), hydrogen bonds of the type O–H···O probably exist between the O(4) atom of the nitro group and the water O(9) atom, the O–O distance being 3.01 Å. In the same manner, the O(9) atom is associated with the O(5) atom of the sulfonate group and the O(12) atom of the other water molecule at distances of 2.83 and 2.77 Å, respectively. The water O(12) atom is not only associated with the water O(9) atom but also linked to the O(7) atom of the sulfonate group, to which the O(5) atom linking to the water O(9) atom belongs. Furthermore the O(12) atom is linked to the H(21) atom of the bipiperidine by an N–H···O hydrogen bond at a distance of 1.99 Å. The second unit (the B unit) consists of the remaining two water molecules, the O(5) atom and the O(7) atom of the sulfonate group, and the H(31) atom of the bipiperidine. The water O(11) atom is associated with the sulfonate O(5) atom linking to the water O(9) atom in the A unit, the O(3) atom of the nitro group, and the O(10) atom of another water molecule. The water O(10) atom is linked to the O(6) atom of the sulfonate group at a length of 2.78 Å. Significantly, the water O(10) atom is also associated with the amine H(31) atom, while on the opposite side, the H(21) atom is linked to the water O(12) atom in the A unit, by an N–H···O hydrogen bond of distance 2.88 Å. These results are summarized in Figure 4. The network of hydrogen bonds along the *a* direction produce repeated stacking of A and B units. This network of hydrogen bonds seems to be very important in discriminating between the optical isomers (vide infra).

Four intramolecular hydrogen bonds are listed in Table VI.[6] Oxygen atoms of nitro groups are linked to hydrogen atoms of secondary amino groups. It seems that these interactions orient the two nitro groups nearly perpendicular to each other. The plane formed by Co, N(5), O(1) and O(2) makes a dihedral angle of 103.8° with the plane formed by Co, N(6), O(3), and O(4). At the same time these interactions probably assist in the formation of the intermolecular hydrogen bonds described above.

Diastereomeric Discrimination. The nitro groups of the complex cations, which form intramolecular hydrogen bonds with the N–H groups of the resulting asymmetric centers of the bipiperidines, are connected to the sulfonate groups of *d*-3-bromocamphor-9-sulfonate anions by the four water molecules of crystallization, via intermolecular hydrogen bonds. Moreover, the water molecules of crystallization also aid in

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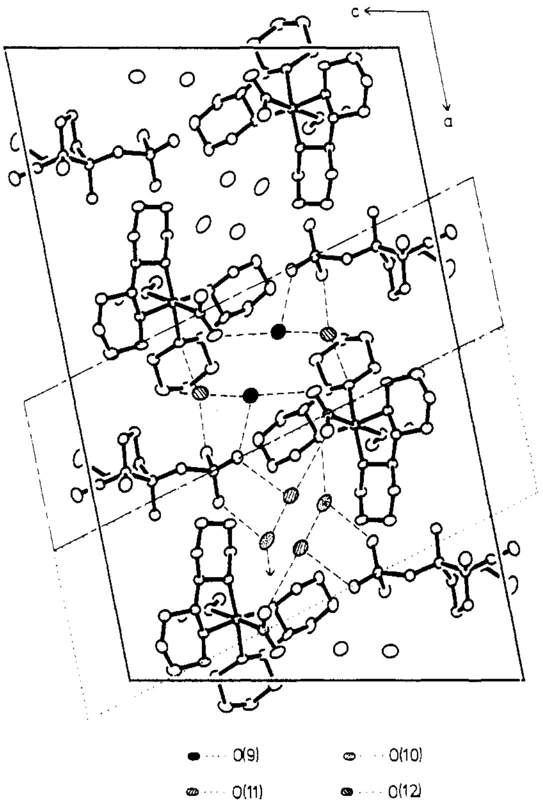

Figure 4. Unit cell contents viewed down the *b* axis. The hydrogen bonds are shown by broken lines. The dashed arrow indicates the hydrogen bond to the amine hydrogen atom at the other end. The A unit and the B unit are indicated by the chained line and the dotted line, respectively.

bringing the sulfonate groups into contact with the N–H groups of the bipiperidine by the intermolecular hydrogen bonds. In some cases complex cations can have special short contacts with resolving agents directly;[15] however, except for these hydrogen bonds through the four water molecules of crystallization, no significant intermolecular interactions between the complex cation and the *d*-3-bromocamphor-9-sulfonate anion were observed. This result implies that hydrogen bonds through the water molecules of crystallization play an important role in the diastereomeric discrimination in the present complex. Thus the existence of the water molecules of crystallization seems to be essential to discriminate the optical isomers. These features might be corresponding to the facts that no tendency to resolve into optical isomers was observed in the fractional recrystallization of the title complex from methanol.[3]

Absolute Configuration and Circular Dichroism. X-ray structure analysis and circular dichroism studies of *trans*-$[CoCl_2(N\text{-methyl-substituted diamine})_2]^+$ suggest the following empirical rule: The sign of the CD band near 22 000 cm^{-1} ($A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band) can be related to the configuration of the asymmetric nitrogen centers, as has been shown for *trans*-dichlorobis(diamine)cobalt(III) complexes of *N*-methyl- and *C*-methylethylenediamines.[17-19] When they give a positive Cotton effect in this region, they should be assigned to the *S* configuration around the asymmetric secondary nitrogen center. In accordance with the stereochemical studies, the five-membered chelate rings adopt preferably the λ-gauche conformation in these cases. In the CD spectrum of $(-)_{546}$-*trans*-$[CoCl_2((-)_{589}\text{-bpp})_2]^+$, which was derived from the crystals of the present work, a positive Cotton effect has been observed in this region (Figure 5). Consequently, the empirical rule appears to be applicable to the heterocyclic diamine containing the secondary nitrogen atoms, i.e., the bipiperidine.

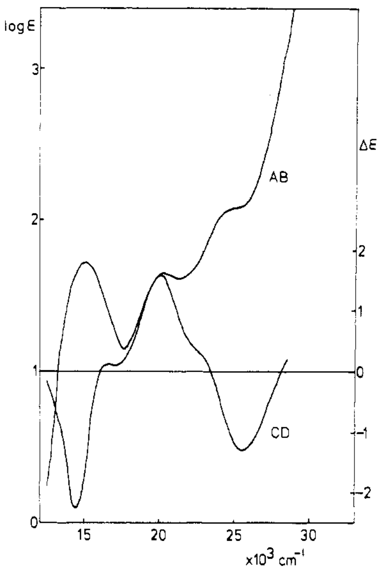

Figure 5. Absorption (AB) and CD spectra of $(-)_{546}$-*trans*-$[CoCl_2((-)_{589}\text{-}2,2'\text{-bpp})_2]Cl\cdot HCl\cdot{}^1/_2H_2O$ in methanol.

Conclusion

2,2′-Bipiperidine has two asymmetric carbon atoms and two secondary nitrogen atoms as the components of heterocycles. When this diamine coordinates to a metal ion, four asymmetric centers belong to the five-membered chelate ring. The absolute configuration of $(-)_{589}$-2,2′-bipiperidine, which was resolved through its cobalt(III) complex, was established by the present X-ray structure determination. The crystal structure of the title compound showed the importance of the water molecules of crystallization on the diastereomeric discrimination.

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Registry No. $(-)_{546}$-$[Co(NO_2)_2((-)_{589}\text{-}2,2'\text{-bpp})_2](d\text{-BCS})\cdot 4H_2O$, 80796-75-4; $(-)_{546}$-$[CoCl_2((-)_{589}\text{-}2,2'\text{-bpp})_2]Cl\cdot HCl$, 80781-27-7.

Supplementary Material Available: Listings of inequality relationships for Bijvoet pairs of *hkl* and *hk̄l* (Table I), least-squares planes (Table V), intra- and interionic close contacts (Table VI), final thermal parameters, and observed and calculated structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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