The Absolute Configuration of a Dissymmetric Pseudotetrahedral Coordination Compound Containing a Restricted Biphenyl. Molecular Structure of Δ-2,2′-Bis(salicylidenaminato)-$(+)_D$-(*R*)-6,6′-dimethylbiphenylcobalt(II)[1]

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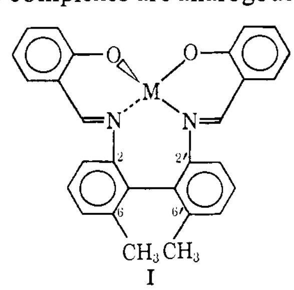
Abstract: The crystal and molecular structures of the dissymmetric molecule, Δ-2,2′-bis(salicylidenaminato)-$(+)_D$-(*R*)-6,6′-dimethylbiphenylcobalt(II), Δ-$Co(sal)_2$-(*R*)-bmp, have been determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group $P\,2_12_12_1$ with $a = 17.978$, $b = 11.206$, and $c = 11.628$ Å. For $Z = 4$ the measured and calculated densities are 1.35 ± 0.02 and 1.353 g/cm³, respectively. Counter data were collected for 1745 independent reflections by the stationary-crystal–stationary-counter technique. The structure was solved using Patterson and Fourier methods and refined by least-squares techniques to a conventional *R* value of 0.098. The absolute configuration was determined from a comparison of 18 (*hkl*), ($\bar{h}\bar{k}\bar{l}$) pairs and found to be *R* for the biphenyl moiety. The *R* configuration of the diamine uniquely establishes the Δ configuration for the complex as a whole as predicted by O'Connor, Ernst, and Holm. The structure consists of discrete molecules wherein the ligand atoms surround the cobalt atom in a highly distorted tetrahedral fashion. The average bond distances involving the cobalt atom are Co–N = 2.09 ± 0.01 Å, and Co–O = 1.90 ± 0.01 Å.

In 1958 Mislow and coworkers determined the absolute configuration of 2,2′-diamino-6,6′-dimethylbiphenyl (bmp) by partial assymmetric synthesis.[2] This molecule is a member of a configurationally related series of restricted biphenyls whose optical activity is of considerable interest.[3] Prior to the present work[4] no X-ray (Bijvoet) determination of the absolute configuration of any member of the restricted biphenyl series has been reported, although very recently the absolute configuration of a binaphthyl derivative has appeared[5] which was subsequently[6] chemically related to the biphenyl series confirming the original prediction.[2] Furthermore the ORD spectra of tetradentate Schiff base complexes derived from the hindered biphenyl- and binaphthyldiamines (*vide infra*) served to establish the absolute configuration in the former series.[7]

In 1957 Lyons and Martin[8] prepared copper(II) and beryllium(II) complexes [$Cu(sal)_2bmp$ and $Be(sal)_2bmp$] of the tetradentate ligand formed by the Schiff base reaction of salicylaldehyde, sal, on bmp. The expected distorted tetrahedral arrangement of ligand atoms was confirmed by a structure determination[9] of the nonrestricted biphenyl analog, $Cu(sal)_2bp$, bp = 2,2′-diaminobiphenyl. Recently O'Connor, Ernst, and Holm,[7] as part of an extensive series of investigations of diastereomeric four-coordinate complexes, have made use of these and similar ligands to prevent the racemization of dissymmetric metal complexes, for example, $M(sal)_2bmp$ shown in I, where M = Co(II), Ni(II), Zn(II), and Pd(II). These complexes are analogous to the bis-che-



I

late nickel(II) complexes, $Ni(A{-}B)_2$, which can exist in the Δ or Λ absolute configurations[10] but which are found to racemize rapidly on the nmr time scale. The present structure was undertaken to confirm the absolute configuration of bmp predicted by Mislow[2] and to show that it uniquely determines the configuration, Δ or Λ, of the coordination compound $Co(sal)_2bmp$. This structure is the first direct determination of the absolute configuration of a pseudotetrahedral coordination compound.

Experimental Section

Deep red, long plate-like orthorhombic crystals of Δ-2,2′-bis(salicylidenaminato)-$(+)_D$-(*R*)-6,6′-dimethylbiphenylcobalt(II), $Co(sal)_2bmp$, were grown from a chloroform–heptane mixture by slow evaporation under nitrogen.[11] An oscillation photograph and Weissenberg films of the *hl*0 through *hl*3 layers showed orthorhombic symmetry with systematic absences *h*00, $h = 2n + 1$, and 0*k*0, $k = 2n + 1$. Diffractometer data with a *c* axis mounting revealed the additional systematic absence for 00*l*, $l = 2n + 1$, uniquely determining the space group $P2_12_12_1$ (no. 19). The density was determined by flotation in methylene iodide–carbon tetrachloride giving 1.35 ± 0.02 g/cm³ compared with the calculated density

(1) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF 49(638)-1492.

(2) F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci, and K. Mislow, *J. Am. Chem., Soc.*, 80, 476 (1958); *cf.* K. Mislow, *Angew. Chem.*, 70, 683 (1958), and references therein.

(3) For a review of this and related work, see K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962).

(4) A preliminary account has appeared: L. H. Pignolet, R. P. Taylor, and W. DeW. Horrocks, Jr., *Chem. Commun.*, 1443 (1968).

(5) H. Akimoto, T. Shiori, Y. Jitaka, and S. Yamada, *Tetrahedron Letters*, 97 (1968).

(6) S. Yamada and H. Akimoto, *ibid.*, 3967 (1968).

(7) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 4561 (1968).

(8) F. Lyons and K. V. Martin, *ibid.*, **79**, 1273 (1957).

(9) T. P. Cheeseman, D. Hall, and T. N. Waters, *Proc. Chem. Soc.*, 379 (1963); *J. Chem. Soc., A*, 1396 (1966).

(10) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6104 (1967). Δ refers to right-hand and Λ to left-hand chirality with respect to the C_2 axis.

(11) We thank Dr. M. J. O'Connor for supplying the compound.

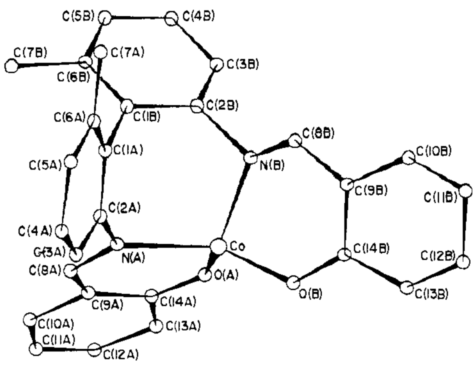


Figure 1. The Δ-2,2′-bis(salicylidenaminato)-(+)$_D$-(*R*)-6,6′-dimethylbiphenylcobalt(II) molecule.

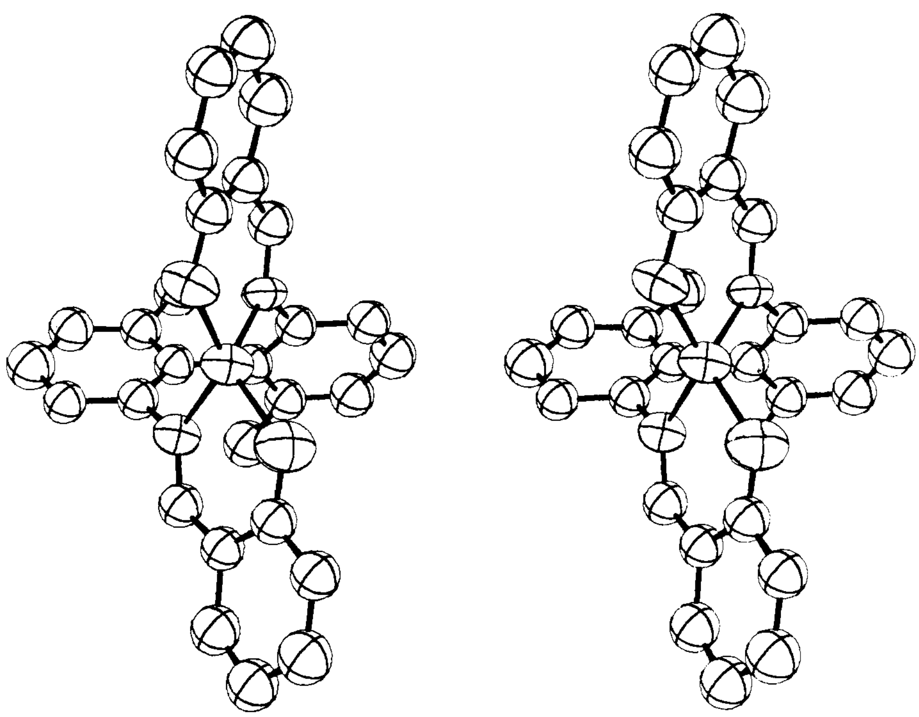


Figure 2. Stereoview of the molecule looking down the C_2 axis. The right-hand screw chirality Δ is clearly evident.

for $Z = 4$ of 1.353 g/cm^3. A crystal of approximate dimensions 0.70 × 0.26 × 0.28 mm was mounted on a quartz fiber with the *c* axis of the orthorhombic cell parallel to the spindle axis of the diffractometer. The unit cell dimensions were determined at room temperature on a General Electric XRD-5 instrument equipped with a manual goniostat, scintillation counter, and pulse height discriminator using unfiltered molybdenum radiation (λ 0.70926 Å for K α_1). Variations in the values obtained from measurement of the *h*00, 0*k*0, and 00*l* reflections at high 2θ were used to compute standard deviations yielding the following results: $a = 17.978 \pm 0.005$, $b = 11.206 \pm 0.002$, and $c = 11.628 \pm 0.003$ Å.

Intensities of 1745 independent reflections (1616 nonzero) were measured using zirconium-filtered molybdenum radiation out to $2\theta = 45°$ by 10-sec peak counts with a 10° take-off angle.[12] Small corrections in ϕ were made (<0.06°) during the collection of data by readjusting on four standard reflections after every 100 measurements. Only small changes (<10%) were noted in the intensities of the standard reflections throughout the course of data taking. Corrections for background were made from a general background curve in 2θ for values greater than 30° while individual 10-sec counts were measured for all other reflections at 2θ values of ±0.20° from the calculated value. After these corrections the intensities were assigned standard deviations $\sigma(I)$ where I = counts/sec except that, when any intensity was less than or equal to 2 counts/sec, it

$$\sigma(I) = [I + (0.08I)^2]^{1/2}$$

was assigned the standard deviation $\sqrt{2}$. Values for F_o were obtained from the intensities after correction[13] for Lorentz (*L*) and polarization (*p*) factors and were assigned standard deviations as follows.

$$\sigma(F_o) = \sigma(I)/2[(Lp)(I)]^{1/2}$$

The intensity of the 002 reflection ($\chi = 90°$) did not vary more than 18% with rotation of ϕ through 360°, indicating a small absorption error. The linear absorption coefficient for molybdenum radiation is 8.01 cm^{-1}. No absorption correction was applied since the structure was satisfactorily solved and refined (*vide infra*), and all the chemically significant information was revealed.

The cobalt atom was located in a three-dimensional Patterson map and refined by least squares to an *R* value[14] of 0.44. Using signs calculated for the cobalt atom, a three-dimensional Fourier map was computed and the coordinates of a few more atoms were disclosed. Several cycles of isotropic least-squares refinement and Fourier synthesis revealed the correct coordinates for all of the nitrogen, oxygen, and carbon atoms. The *R* factor at this time was 0.14. A Fourier difference map indicated some residual electron density around the atomic positions, and after several cycles of anisotropic least-squares refinement with the cobalt two nitrogen and two oxygen atoms treated anisotropically and the remaining nonhydrogen atoms treated isotropically (including anomalous dispersion on all nonhydrogen atoms), the *R* value dropped to 0.098 for all 1616 nonzero reflections. Atomic scattering factors and dispersion corrections were taken from the "International Tables."[15]

(12) The take-off angle had little effect on the width of the peaks, so a maximum value was arbitrarily chosen.

(13) Computations were performed on a CDC 6600 at the Institute for Defense Analysis, Princeton N. J., and IBM 7094 computer at the Princeton University Computer Center. The following computer programs were used for the operations indicated: instrumental setting, Zalkin's GONIO (a modification of a program written by D. W. Larsen); reduction of new data, Zalkin's INCORE; Patterson and Fourier syntheses, Zalkin's FORDAP; least-squares refinement, Zalkin's LS 250 (a modification of the Gantzel-Sparks-Trueblood full-matrix program which minimizes $\Sigma w|\Delta F|^2/\Sigma w|F_o|^2$, $w = 1/\sigma(F)$; interatomic distance and angle computation, Zalkin's DISTAN; calculation of least-squares planes, Chu's LSPLAN; molecular stereochemistry, Johnson's ORTEP.

(14) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, not including zero weight data.

Table I. Final Fractional Atomic Positional and Thermal Parameters for Co(sal)$_2$bmp[a]

Atom[b]	x	y	z	B, Å^2
Co	−0.1313 (1)	−0.0362 (2)	0.0185 (2)	...
N(A)	−0.1326 (6)	−0.2135 (10)	0.0517 (9)	...
N(B)	−0.2312 (6)	0.0023 (9)	0.0826 (9)	...
C(A)	−0.1067 (6)	−0.0588 (9)	−0.1388 (9)	...
O(B)	−0.0825 (5)	0.0957 (9)	0.0882 (9)	...
C(1A)	−0.2345 (8)	−0.2349 (12)	0.1860 (13)	5.0 (3)
C(2A)	−0.1599 (7)	−0.2460 (12)	0.1628 (12)	5.0 (3)
C(3A)	−0.1096 (7)	−0.2866 (12)	0.2441 (12)	5.3 (3)
C(4A)	−0.1359 (10)	−0.3116 (16)	0.3556 (15)	7.4 (4)
C(5A)	−0.2131 (9)	−0.2951 (16)	0.3808 (15)	6.5 (4)
C(6A)	−0.2631 (8)	−0.2577 (13)	0.2952 (13)	5.7 (3)
C(7A)	−0.3437 (9)	−0.2407 (16)	0.3243 (14)	7.5 (4)
C(8A)	−0.1104 (8)	−0.2945 (13)	−0.0206 (13)	5.4 (3)
C(9A)	−0.0837 (7)	−0.2667 (13)	−0.1338 (12)	5.0 (3)
C(10A)	−0.0582 (9)	−0.3710 (14)	−0.1971 (14)	6.5 (4)
C(11A)	−0.0309 (9)	−0.3630 (15)	−0.3045 (15)	6.7 (4)
C(12A)	−0.0324 (9)	−0.2498 (15)	−0.3551 (14)	6.9 (4)
C(13A)	−0.0559 (8)	−0.1466 (12)	−0.2993 (12)	5.6 (3)
C(14A)	−0.0832 (8)	−0.1551 (14)	−0.1896 (13)	5.2 (3)
C(1B)	−0.2892 (8)	−0.1934 (13)	0.0931 (12)	5.1 (3)
C(2B)	−0.2908 (8)	−0.0753 (13)	0.0514 (12)	5.1 (3)
C(3B)	−0.3433 (8)	−0.0360 (13)	−0.0287 (13)	5.6 (3)
C(4B)	−0.3960 (9)	−0.1155 (16)	−0.0624 (15)	6.9 (4)
C(5B)	−0.3961 (9)	−0.2354 (14)	−0.0276 (14)	6.6 (4)
C(6B)	−0.3421 (8)	−0.2723 (14)	0.4666 (13)	5.7 (3)
C(7B)	−0.3394 (9)	−0.4038 (16)	0.0769 (13)	7.6 (3)
C(8B)	−0.2473 (8)	0.1004 (14)	0.1346 (13)	5.6 (3)
C(9B)	−0.1934 (9)	0.1914 (14)	0.1610 (13)	5.5 (3)
C(10B)	−0.2257 (10)	0.2987 (16)	0.2079 (15)	7.3 (4)
C(11B)	−0.1798 (9)	0.3987 (15)	0.2308 (15)	6.9 (4)
C(12B)	−0.1041 (8)	0.3910 (14)	0.2013 (13)	5.8 (3)
C(13B)	−0.0730 (8)	0.2907 (14)	0.1556 (13)	6.1 (3)
C(14B)	−0.1158 (8)	0.1865 (13)	0.1328 (12)	5.2 (3)

	Anisotropic Thermal Parameters					
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	5.8 (1)	4.6 (1)	6.1 (1)	−0.0 (1)	1.4 (1)	−0.5 (1)
N(A)	5.3 (5)	4.6 (5)	5.7 (6)	−0.0 (5)	0.9 (6)	−0.2 (5)
N(B)	5.9 (6)	4.1 (5)	4.3 (5)	0.4 (4)	0.9 (5)	−0.9 (4)
O(A)	8.8 (7)	5.4 (5)	7.7 (6)	−0.6 (5)	1.8 (5)	0.3 (5)
O(B)	5.2 (5)	4.8 (5)	8.6 (6)	0.3 (4)	1.2 (5)	−0.5 (5)

[a] The numbers in parentheses here and in succeeding tables are the estimated standard deviations of the least significant digit(s). [b] The atom labeling conforms to Figure 1.

Table II. Comparison of Observed and Calculated Structure Factor Ratios for (hkl), $(\bar{h}\bar{k}\bar{l})$ Pairs[a]

hkl	R_{obsd}	R_{calcd}	hkl	R_{obsd}	R_{calcd}
114	3.1	2.3	252	1.3	1.3
115	0.66	0.59	254	1.8	2.3
163	0.69	0.70	311	0.85	0.83
165	1.4	1.6	313	0.69	0.67
225	0.65	0.60	315	1.5	1.5
232	0.73	0.70	322	1.6	1.5
237	0.70	0.63	337	1.7	1.8
243	0.57	0.64	422	0.60	0.62
244	0.52	0.60	822	0.79	0.79

[a] $R_{obsd} = (I_{hkl}/I_{\bar{h}\bar{k}\bar{l}})^{1/2}$ and $R_{calcd} = F_{hkl}/F_{\bar{h}\bar{k}\bar{l}}$ where I_{hkl} is intensity corrected for background; see text.

The isotropic thermal parameters have the form $\exp[-\beta(\sin^2\theta)/\lambda^2]$, while the anisotropic temperature factors were $\exp[-0.25(\beta_{11}b_1{}^2h^2 + \beta_{22}b_2{}^2k^2 + \beta_{33}b_3{}^2l^2 + 2\beta_{12}b_1b_2hk + 2\beta_{13}b_1b_3hl + 2\beta_{23}b_2b_3kl)]$ where b_i is the ith reciprocal axis. The hydrogen atoms were not located. On the final full-matrix least-squares cycle the largest variation of an atomic positional parameter was 0.000002 while the largest temperature factor change was 0.001; in all cases the shifts were smaller than the estimated standard deviations. The error in an observation of unit weight at the end was 1.85. The final electron density difference map indicated residual electron density comparable with that expected for the hydrogen atoms.

The absolute configuration was determined by measuring the intensities of 18 (hkl), $(\bar{h}\bar{k}\bar{l})$ pairs on a Picker four-circle automated X-ray diffractometer[16] using Ni-filtered Cu Kα_1 radiation (λ 1.5418 Å). Integrated intensities were measured by the θ–2θ scan technique using a scan rate of 1°/min. Each reflection was scanned once, with 10-sec background counts taken at each end of the scan. The background correction was made by assuming that the background for each reflection is the average of the background on either side of the peak in counts per second multiplied by the time required to scan through the peak. No absorption corrections were made. The (hkl), $(\bar{h}\bar{k}\bar{l})$ pairs measured were selected on the basis of a structure factor calculation assuming the Δ, R configuration of the complex and using $\Delta f''$ of 3.9 for the cobalt atom.[15] Those pairs having ratios R_{calcd} most different from one were used.

$$R_{calcd} = F_{hkl}/F_{\bar{h}\bar{k}\bar{l}}$$

These calculated ratios were then compared with the experimentally determined ratios $R_{exptl} = (I_{hkl}/I_{\bar{h}\bar{k}\bar{l}})^{1/2}$ where I_{hkl} is the intensity of the reflection corrected for background.

Results

The final atomic positional and thermal parameters are given in Table I. The observed and calculated

(15) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215 ff.

(16) We thank Professor S. J. Lippard of Columbia University for making this instrument available to us.

Table III. Intramolecular Bond Distances (Å) and Angles (Deg)

Atoms	Distance	Atoms	Distance
N(A)–Co	2.025 (10)	N(B)–Co	1.992 (10)
O(A)–Co	1.899 (10)	O(B)–Co	1.901 (9)
C(2A)–N(A)	1.435 (17)	C(2B)–N(B)	1.424 (16)
C(8A)–N(A)	1.293 (17)	C(8B)–N(B)	1.288 (17)
C(14A)–O(A)	1.302 (17)	C(14B)–O(B)	1.290 (16)
C(8A)–C(9A)	1.438 (19)	C(8B)–C(9B)	1.443 (20)
C(9A)–C(10A)	1.451 (20)	C(9B)–C(10B)	1.441 (22)
C(10A)–C(11A)	1.346 (21)	C(10B)–C(11B)	1.413 (23)
C(11A)–C(12A)	1.400 (22)	C(11B)–C(12B)	1.409 (21)
C(12A)–C(13A)	1.391 (20)	C(12B)–C(13B)	1.363 (20)
C(13A)–C(14A)	1.365 (19)	C(13B)–C(14B)	1.426 (20)
C(14A)–C(9A)	1.414 (19)	C(14B)–C(9B)	1.428 (20)
C(1A)–C(2A)	1.374 (18)	C(1B)–C(2B)	1.403 (19)
C(2A)–C(3A)	1.383 (18)	C(2B)–C(3B)	1.407 (18)
C(3A)–C(4A)	1.406 (21)	C(3B)–C(4B)	1.363 (20)
C(4A)–C(5A)	1.426 (23)	C(4B)–C(5B)	1.394 (22)
C(5A)–C(6A)	1.410 (20)	C(5B)–C(6B)	1.367 (20)
C(6A)–C(1A)	1.393 (19)	C(6B)–C(1B)	1.403 (19)
C(6A)–C(7A)	1.500 (21)	C(6B)–C(7B)	1.522 (22)
C(1A)–C(1B)	1.533 (19)		

Atoms	Angles	Atoms	Angles
Coordination Angles		Chelate Rings	
N(A)–Co–N(B)	97.4 (4)	Co–N(A)–C(2A)	115.3 (8)
N(A)–Co–O(A)	93.2 (4)	N(A)–C(2A)–C(1A)	118.8 (12)
N(A)–Co–O(B)	133.5 (4)	C(2A)–C(1A)–C(1B)	121.4 (12)
N(B)–Co–O(A)	127.0 (4)	C(1A)–C(1B)–C(2B)	122.6 (12)
N(B)–Co–O(B)	95.1 (4)	C(1B)–C(2B)–N(B)	118.3 (11)
O(A)–Co–O(B)	114.0 (4)	C(2B)–N(B)–Co	116.6 (8)
Chelate Rings			
Co–N(A)–C(8A)	123.9 (9)	Co–N(B)–C(8B)	124.3 (9)
N(A)–C(8A)–C(9A)	123.3 (12)	N(B)–C(8B)–C(9B)	123.4 (12)
C(8A)–C(9A)–C(14A)	127.8 (12)	C(8B)–C(9B)–C(14B)	125.4 (13)
C(9A)–C(14A)–O(A)	121.5 (12)	C(9B)–C(14B)–O(B)	125.3 (12)
C(14A)–O(A)–Co	128.7 (9)	C(14B)–O(B)–Co	124.6 (8)
Phenyl Rings			
C(1A)–C(2A)–C(3A)	122.7 (12)	C(1B)–C(2B)–C(3B)	122.5 (12)
C(2A)–C(3A)–C(4A)	117.9 (12)	C(2B)–C(3B)–C(4B)	116.9 (13)
C(3A)–C(4A)–C(5A)	119.7 (14)	C(3B)–C(4B)–C(5B)	123.3 (14)
C(4A)–C(5A)–C(6A)	120.7 (14)	C(4B)–C(5B)–C(6B)	118.0 (13)
C(5A)–C(6A)–C(1A)	117.7 (13)	C(5B)–C(6B)–C(1B)	122.5 (13)
C(6A)–C(1A)–C(2A)	121.2 (12)	C(6B)–C(1B)–C(2B)	116.5 (12)
Phenyl Rings			
C(9A)–C(10A)–C(11A)	122.1 (13)	C(9B)–C(10B)–C(11B)	119.7 (14)
C(10A)–C(11A)–C(12A)	116.1 (14)	C(10B)–C(11B)–C(12B)	118.2 (14)
C(11A)–C(12A)–C(13A)	124.6 (14)	C(11B)–C(12B)–C(13B)	122.6 (14)
C(12A)–C(13A)–C(14A)	118.9 (13)	C(12B)–C(13B)–C(14B)	121.7 (13)
C(13A)–C(14A)–C(9A)	119.5 (12)	C(13B)–C(14B)–C(9B)	117.0 (12)
C(14A)–C(9A)–C(10A)	118.6 (12)	C(14B)–C(9B)–C(10B)	120.8 (13)
Additional Angles			
C(5A)–C(6A)–C(7A)	119.7 (13)	C(5B)–C(6B)–C(7B)	117.5 (13)
C(6A)–C(1A)–C(1B)	117.4 (11)	C(6B)–C(1B)–C(1A)	120.9 (12)

structure factors may be obtained from ASIS–NAPS.[17] A comparison of R_{calcd} and R_{exptl} for the 18 (hkl), $(\bar{h}\bar{k}\bar{l})$ pairs is made in Table II. Figure 1 shows the molecular geometry and labeling scheme used throughout this paper. Table III lists the intramolecular distances and bond angles with standard deviations. Least-squares planes, deviations of atoms from these planes, and important angles between planes are given in Table IV. Figure 2 shows a stereoview of the molecule viewed down the C_2 axis.

(17) A list of observed and calculated structure factors has been deposited as Document No. NAPS-00579 with the ASIS National Publication Service, % CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. Copies may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Discussion

The absolute configuration of the complex is unambiguously shown to be Δ-Co(sal)$_2$-(*R*)-bmp. The right-hand screw chirality is clearly shown by the view down the "C_2" axis in Figure 2. Table III shows the excellent agreement between the (hkl), $(\bar{h}\bar{k}\bar{l})$ pair ratios observed and calculated assuming the Δ, *R* configuration for the complex. This assignment is consistent with Mislow's original determination[2] that (+)-2,2′-diamino-6,6′-dimethylbiphenyl corresponds to the *R* configuration. The results also substantiate the prediction of O'Connor, *et al.*,[7] that the *R*-bmp moiety fixes the Δ configuration for the complex.

The structure consists of discrete molecules of Δ-Co(sal)$_2$-(*R*)-bmp where the ligand atoms surround the co-

Table IV. Least-Squares Planes

Distance of atoms from plane, Å		Distance of atoms from plane, Å	
I. Plane through Salicylidene Phenyl Ring A; $0.922x + 0.161y + 0.352z + 2.426 = 0$		II. Plane through Salicylidene Phenyl Ring B; $0.199x - 0.340y + 0.919z - 0.292 = 0$	
C(9A)	0.010	C(9B)	0.009
C(10A)	−0.014	C(10B)	−0.016
C(11A)	0.016	C(11B)	0.013
C(12A)	−0.014	C(12B)	−0.004
C(13A)	0.010	C(13B)	−0.002
C(14A)	−0.008	C(14B)	−0.000
III. Plane through Chelate Ring A; $0.946x + 0.111y + 0.305z + 2.293 = 0$		IV. Plane through Chelate Ring B; $0.179x - 0.466y + 0.866z - 0.030 = 0$	
Co	0.080	Co	−0.078
O(A)	−0.086	O(B)	0.093
C(14A)	0.013	C(14B)	−0.041
C(9A)	0.063	C(9B)	−0.029
C(8A)	−0.023	C(8B)	0.005
N(A)	−0.047	N(B)	0.050
V. Plane through Biphenyl Phenyl Ring A; $0.167x + 0.950y + 0.265z + 2.619 = 0$		VI. Plane through Biphenyl Phenyl Ring B; $-0.604x + 0.248y + 0.758z - 3.395 = 0$	
C(1A)	−0.013	C(1B)	0.027
C(2A)	0.018	C(2B)	0.002
C(3A)	−0.006	C(3B)	−0.029
C(4A)	−0.011	C(4B)	0.028
C(5A)	0.015	C(5B)	0.003
C(6A)	−0.004	C(6B)	−0.031
C(7A)[a]	0.018	C(7B)[a]	−0.160

Angles between Planes

Planes	Angles (deg)
III–IV	67.6
V–VI	70.4
I–III	4.1
II–IV	7.9

[a] Atom not included in forming the plane.

balt atom in a highly distorted tetrahedral fashion as shown in Figures 1 and 2. The tetrahedron is flattened toward the vertical plane perpendicular to the plane of the paper in Figure 2. The cobalt, oxygen, and nitrogen atoms vibrate nearly perpendicular to the plane toward which the tetrahedron is flattened as revealed by their anisotropic thermal ellipsoids in Figure 2. The six angles at the cobalt atom are N(A)–Co–N(B), 97.4°; N(A)–Co–O(A), 93.2°; N(B)–Co–O(B), 95.1°; N(A)–Co–O(B), 133.5°; N(B)–Co–O(A), 127.0°; and O(A)–Co–O(B), 114.0°. The corresponding angles in the copper compound, Cu(sal)$_2$bp, are[9] 96, 94, 94, 151, 155, and 89°, respectively. The first three angles are largely determined by the coordinating requirements of the chelate rings and are in good agreement. The large differences in the latter three arise because the coordination in the cobalt compound is much closer to tetrahedral than in the copper complex. This is clearly seen in a comparison of the dihedral angle between the planes formed by the two salicylaldimine chelate rings. In the present case this angle is 67.6°, while in Cu(sal)$_2$bp it is only 41°.

Bis(salicylaldimine) complexes of cobalt(II) have a well-known tendency toward tetrahedral coordination[18] as evidenced by the geometry of bis(N-*n*-butylsalicylaldiminato)cobalt(II)[19] and bis(N-phenylsalicylaldiminato)cobalt(II).[18] The corresponding nickel(II) and copper(II) compounds have *trans* planar structures.[18] This tendency accounts in part for the difference in geometry of Co(sal)$_2$bmp and Cu(sal)$_2$bp. A further consideration is the steric effect produced by the methyl groups in the 6 and 6′ positions of bmp. This steric interaction (the two methyl carbon atoms are separated by only 3.41 Å, which is less than the sum of methyl van der Waals radii) results in a dihedral angle of 70.4° between the planes of the biphenyl rings, a considerable increase over the 57° angle found for the copper compound.[9]

In Co(sal)$_2$bmp the salicylaldimine (sal) chelate rings (O–C–C–C–N) are planar as seen by their least-squares planes. These planes make an average angle of 6° with the planes of the adjacent sal phenyl rings. Such planarity in the sal chelate rings is common for near-tetrahedral coordination found in bis(N-*sec*-alkylsalicylaldiminato)nickel(II) complexes.[18,20]

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