The Absolute Configuration of a Dissymmetric Pseudotetrahedral Co-ordination Compound containing a Restricted Biphenyl. The Molecular Structure of Δ-2,2′-bis(salicylideneaminato)-$(+)_D$-(*R*)-6,6′-dimethylbiphenylcobalt(II)

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MISLOW and his co-workers have determined the absolute configuration of 2,2′-diamino-6,6′-dimethylbiphenyl (bmp) by partial asymmetric synthesis.[1] This molecule is a member of a configurationally related series of restricted biphenyls, inherently dissymmetric chromophores, whose optical activity is of considerable interest.[2] Until now there has been no *X*-ray determination of the absolute configuration of any member of the restricted biphenyl series, although the absolute configuration of a binaphthyl derivative has been reported[3] and related chemically[4] to the biphenyl series, thus confirming the original determination.[1]

Lyons and Martin[5] have prepared copper(II) and beryllium(II) complexes of the tetradentate ligand formed by the Schiff base reaction of salicylaldehyde (sal) on bmp, $Cu(sal)_2bmp$ and $Be(sal)_2$ bmp. The expected distorted tetrahedral arrangement of ligand atoms was confirmed by a structure determination[6] of the non-restricted biphenyl analogue, Cu(sal)$_2$bp (bp = 2,2′-diaminobiphenyl).

Holm and his co-workers,[7] as part of an extensive series of investigations of diastereoisomeric four-co-ordinate complexes, have made use of these and similar ligands to prevent the racemization of dissymmetric metal complexes of the type M(sal)$_2$bmp, [M = Co^{II}, Ni^{II}, Zn^{II}, or Pd^{II}]. These complexes are analogous to the bischelate nickel(II) complexes, Ni(A-B)$_2$, which can exist in Δ or Λ absolute configurations[8] (Δ refers to right-hand and Λ to left-hand chirality with respect to the C-2 axis) but which are found to racemize rapidly on the n.m.r. time scale. A comparison[7] of the o.r.d. curves for nickel(II) Schiff-base complexes derived from the binaphthyl and biphenyl series gives further confirmation of Mislow's[1] original determination of absolute configuration in the latter series. The present structure of Co(sal)$_2$-(+)$_D$-bmp represents the first direct determination of the absolute configuration of a pseudotetrahedral co-ordination compound.

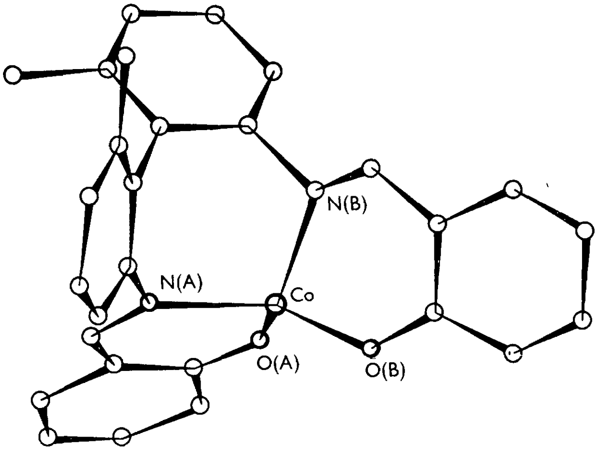

FIGURE. Δ-Co(sal)$_2$-(+)$_D$-(*R*)-bmp

The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 17{\cdot}978(5)$, $b = 11{\cdot}206(2)$, $c = 11{\cdot}628(3)$ Å, $U = 2342{\cdot}6$ Å^3, $M = 477{\cdot}4$, $D_m = 1{\cdot}35(2)$ (flotation), and $D_c = 1{\cdot}353$ for $Z = 4$. Intensities of 1745 independent reflections (1616 non-zero) were recorded with a GE XRD-5 manual goniostat using zirconium-filtered Mo-K_α radiation and the stationary crystal-stationary counter method. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares to R 0·098 with the cobalt, nitrogen, and oxygen atoms allowed anisotropic temperature factors while the carbon atoms were isotropically refined. The hydrogen atoms were not located. The intensities of 18 (hkl), $(\overline{hkl})$ pairs were measured on a Picker automated diffractometer† using nickel-filtered Cu-K_α radiation. The results were compared with ratios of structure factors calculated using $\Delta f''$ of 3·9 for the cobalt atom.[9]

The absolute configuration of the bmp moiety is *R*, confirming Mislow's determination.[1] The *R*-configuration of the diamine uniquely establishes[7] the Δ configuration for the complex as a whole and this is substantiated by the present work. The structure consists of discrete molecules of Δ-Co(sal)$_2$-(+)$_D$-(*R*)-bmp wherein the ligand atoms surround the cobalt atom in a highly distorted tetrahedral fashion (see Figure). The bond distances involving the cobalt atom are Co–N(A), 2·025(10); Co–N(B), 1·992(10); Co–O(A), 1·899(10); and Co–O(B), 1·901(9) Å; while the six angles at the cobalt atom are N(A)-Co-O(A), 93·2; N(B)-Co-O(B), 95·1; O(A)-Co-O(B), 114·0; N(A)-Co-O(B), 133·5; and N(B)-Co-(A), 127·0°. The corresponding angles in the copper compound[6] are 96, 94, 94, 89, 155, and 151° respectively. The first three angles, being largely determined by the bite requirements of the chelate rings, are in good agreement. The deviations in the latter three arise because the co-ordination in the cobalt compound is considerably closer to tetrahedral than in the copper complex. Thus the dihedral angle between the two salicylaldimine chelate rings is 67·6° in the present case but only 41° in the copper compound. Co(sal)$_2$bmp is, however, less tetrahedral than bis-(*N*-isopropylsalicylaldiminato)nickel(II)[10] where the corresponding dihedral angle is 81·5°. Two factors may contribute to the difference in co-ordination geometry between Co(sal)$_2$dmp and Cu(sal)$_2$dp. The first is the well-known tendency for cobalt(II) salicylaldimine complexes to attain tetrahedral co-ordination, even with *N*-aryl substituents.[11] The second is the geometry imposed by the biphenyl restriction resulting from the methyl groups in the 6 and 6′ positions. This steric interaction (the two methyl carbon atoms are separated by only 3·41 Å, 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.[6]

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