# Structural Studies of Asymmetric Hydrogenation. II*. The Crystal Structure of Methyl(*R*(+)-α-methylbenzylamine)-bis(dimethylglyoximato)cobalt(III) Benzene Solvate

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(Received January 28, 1977)

The structure of methyl(*R*(+)-α-methylbenzylamine)bis(dimethylglyoximato)cobalt(III) benzene solvate has been determined by X-ray crystal analysis. The crystal is orthorhombic; space group, $P2_12_12_1$; $Z=4$ with $a=14.074(1)$, $b=14.390(1)$, and $c=12.202(1)$ Å. The structure was deduced by the heavy-atom method and refined by the block-diagonal least-squares method to a final $R$ value of 0.063 for 1413 observed reflections. The symmetry of the bis(dimethylglyoximato)cobalt moiety has been lowered from $D_{2h}$ to $C_{2h}$ as a result of the steric repulsion from optically active amine. It is proposed that this deformation is a factor inducing the asymmetry in the hydrogenation catalyzed by the complex of bis(dimethylglyoximato)cobalt and the active amine.

It has recently been shown that the complexes of bis(dimethylglyoximato)cobalt (abbreviated to Co(dmg)$_2$ or cobaloxime) and optically active amine catalyze the asymmetric hydrogenation of olefins with the $CH_2$=CXY formula, where X and Y are nucleophilic and electrophilic substituents respectively.[2-7] The hydrogenation proceeds according to the scheme shown in Fig. 1. We explored the mechanism of inducing the asymmetry by analyzing the structures I, II, and III. In the first place, the title complex was chosen because it is the simplest crystallized complex of the methylcobaloxime and the asymmetric amine. The methyl group does not seem bulky enough to change the structural features of the Co(dmg)$_2$ moiety, and it can be expected that the effect of the optically active amine on the structure of Co(dmg)$_2$ will be revealed.

## Experimental

Dark red crystals of the title complex were obtained from a benzene solution. They are unstable in the air. The unit-cell dimensions were determined from zero-layer Weissenberg photographs, using Co$K\alpha$ radiation about the a and c axes. Spacing of 80 high-angle reflections ($\theta \geqq 70°$), calibrated with superposed silicon powder lines, were subjected to the least-squares treatment. The crystal data are summarized in Table 1.

Using a crystal with dimensions of $0.3\times0.2\times0.3$ mm, coated with nail enamel, the intensities for the layers from $hk0$ to $hk15$ and $0kl$ were collected on a Hilger-Watts linear diffractometer with Mo$K\alpha$ radiation. The balanced Y/Zr filter pair was used. Out of 3190 independent reflections ($3° \leqq 2\theta \leqq 55°$), 1418 were observed, those of $I<2.5\,\sigma(I)$ being regarded as unobserved. Only 65 reflections between 50° and 55°($2\theta$) had non-zero intensities. The usual Lorentz and polarization, but no absorption, corrections were made.

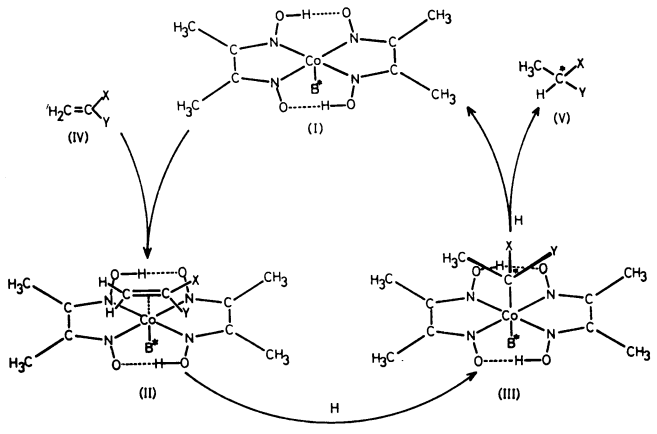


Fig. 1. The reaction path of the asymmetric hydrogenation, where B* is the optically active amine; (I) the catalyzer, (II) the π-complex, (III) the σ-complex, (IV) the substrate, and (V) the product.

* Part I of this series[1] deals with the crystal structure of β-cyanoethyl(D(−)-*erythro*-1,2-diphenyl-2-hydroxyethylamine)bis(dimethylglyoximato)cobalt(III).

## Structure Determination

The positions of the cobalt and the six coordinated atoms were obtained from the three-dimensional Patterson function. The other atoms were revealed on the first Fourier map phased with those seven atoms.

The structure was refined by the block-diagonal least-squares methods. After several cycles of the refinement, the five strongest reflections were excluded because they seemed to be affected by secondary extinction. All the hydrogen atoms were found on the three-dimensional difference Fourier map. The final refinement was performed including these hydrogen atoms, with isotropic temperature factors which were assumed to be equal to those of the directly bonded atoms. The weighting

Table 1. Crystal data

| | |
|---|---|
| Formula | $C_{17}H_{28}N_5O_4Co\cdot C_6H_6$ |
| F. W. | 503.5 |
| Crystal system | Orthorhombic |
| $a$ | 14.074(1) Å |
| $b$ | 14.390(1) |
| $c$ | 12.202(1) |
| Volume of a unit-cell | 2471.3 Å$^3$ |
| Systematic absences | $h00$, $h$ odd |
| | $0k0$, $k$ odd |
| | $00l$, $l$ odd |
| Space group | $P2_12_12_1$ |
| $Z$ | 4 |
| Density measured | 1.353 g/cm$^3$ |
| Density calculated | 1.353 g/cm$^3$ |
| $\mu$(Mo$K\alpha$) | 7.57 cm$^{-1}$ |

TABLE 2. FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^5$) FOR THE NON-HYDROGEN ATOMS

The anisotropic thermal parameters are of this form:

$$T=\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\right].$$

The estimated standard deviations are in parentheses.

| Atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 1869(1) | 2399(1) | 1149(1) | 0302(5) | 0336(6) | 0419(7) | 0050(17) | 0040(16) | 0068(19) |
| N(1) | 2453(6) | 3303(5) | 0267(7) | 0478(54) | 0210(48) | 0417(68) | 0029(84) | 0176(96) | 0202(89) |
| N(2) | 2411(6) | 1598(6) | 0097(8) | 0519(57) | 0512(64) | 0458(71) | 0273(102) | −0642(105) | −0229(117) |
| N(3) | 1217(7) | 1521(8) | 2010(9) | 0507(62) | 0682(72) | 0735(85) | 0225(113) | −0445(116) | −0009(135) |
| N(4) | 1298(6) | 3218(6) | 2185(8) | 0409(52) | 0338(52) | 0697(80) | 0445(91) | −0152(106) | −0307(108) |
| C(1) | 2903(7) | 3028(9) | −0562(10) | 0322(67) | 0833(86) | 0582(93) | 0024(120) | −0055(121) | 0534(150) |
| C(2) | 2926(8) | 2001(8) | −0655(9) | 0490(73) | 0479(61) | 0273(69) | 0432(110) | −0212(113) | 0142(107) |
| C(3) | 0738(7) | 1814(9) | 2831(11) | 0185(54) | 0621(78) | 0877(111) | 0261(113) | −0563(128) | 0004(162) |
| C(4) | 0757(7) | 2817(10) | 2916(10) | 0300(59) | 1111(115) | 0577(87) | 0494(139) | 0212(118) | −0151(170) |
| C(5) | 3450(8) | 3623(9) | −1368(10) | 0348(66) | 0744(83) | 0783(116) | −0117(120) | −0021(136) | 0546(162) |
| C(6) | 3341(9) | 1411(11) | −1526(11) | 0412(86) | 1142(115) | 0849(120) | −0020(156) | 0111(147) | −0401(191) |
| C(7) | 0231(10) | 1212(12) | 3626(11) | 0711(100) | 1190(117) | 0654(124) | −0735(184) | 0106(175) | 0443(205) |
| C(8) | 0213(11) | 3389(11) | 3780(12) | 0815(103) | 1259(121) | 0485(101) | 0337(190) | 0176(190) | −0279(214) |
| O(1) | 2404(6) | 4204(5) | 0453(7) | 0663(55) | 0411(46) | 0833(75) | 0037(86) | −0185(108) | 0115(105) |
| O(2) | 2282(6) | 0672(5) | 0184(7) | 0630(52) | 0262(41) | 0823(75) | 0025(76) | −0397(104) | −0339(95) |
| O(3) | 1291(7) | 0612(6) | 1837(8) | 0892(67) | 0546(55) | 0876(81) | −0363(104) | −0162(127) | 0103(113) |
| O(4) | 1401(6) | 4148(6) | 2117(7) | 0500(50) | 0687(57) | 0752(70) | 0287(92) | −0007(101) | −0308(112) |
| N(5) | 3142(6) | 2220(5) | 1999(6) | 0328(42) | 0437(52) | 0448(58) | −0059(105) | −0231(105) | −0033(87) |
| C(9) | 3493(8) | 2824(7) | 2875(10) | 0458(65) | 0241(59) | 0699(91) | −0131(95) | 0217(130) | 0066(116) |
| C(10) | 4570(7) | 2688(9) | 3052(10) | 0335(60) | 0682(84) | 0783(94) | −0073(147) | 0121(127) | 0288(180) |
| C(11) | 2984(6) | 2683(8) | 3981(8) | 0255(50) | 0633(66) | 0333(64) | 0007(119) | −0050(100) | −0105(147) |
| C(12) | 2804(9) | 1810(8) | 4393(10) | 0756(90) | 0303(63) | 0600(96) | −0098(122) | 0276(151) | 0079(131) |
| C(13) | 2395(10) | 1721(10) | 5404(13) | 0763(95) | 0629(95) | 1062(139) | −0334(161) | 0045(188) | 0502(188) |
| C(14) | 2141(7) | 2476(13) | 6008(9) | 0510(66) | 1198(101) | 0563(84) | 0435(211) | 0094(125) | 0382(281) |
| C(15) | 2346(10) | 3348(10) | 5597(11) | 0785(94) | 0761(100) | 0610(106) | 0383(165) | 0432(164) | −0397(174) |
| C(16) | 2786(9) | 3455(9) | 4594(11) | 0584(81) | 0720(91) | 0629(100) | −0002(141) | 0073(149) | −0375(163) |
| C(17) | 0730(6) | 2515(13) | 0194(8) | 0320(55) | 0734(75) | 0699(97) | 0045(170) | −0205(113) | 0651(219) |
| C(18) | 5561(10) | 4843(8) | 1688(13) | 0654(92) | 0289(63) | 1341(147) | 0494(137) | 0941(209) | 0028(164) |
| C(19) | 4604(12) | 5019(10) | 1673(13) | 1232(149) | 0654(89) | 0969(137) | −0043(200) | −0725(254) | 0278(196) |
| C(20) | 4122(9) | 5244(9) | 2579(14) | 0304(67) | 0455(71) | 1850(190) | 0194(126) | −0284(186) | 0863(210) |
| C(21) | 4638(11) | 5296(7) | 3544(11) | 1070(122) | 0237(58) | 0892(131) | −0012(146) | 0678(208) | 0214(141) |
| C(22) | 5570(9) | 5172(9) | 3579(11) | 0435(72) | 0640(79) | 0886(130) | −0519(133) | 0184(160) | 0299(168) |
| C(23) | 6048(9) | 4966(10) | 2651(13) | 0401(79) | 0818(98) | 1308(163) | −0364(153) | 0063(188) | 0764(224) |

TABLE 3. FRACTIONAL COORDINATES ($\times 10^3$) AND THERMAL PARAMETERS FOR HYDROGEN ATOMS

The estimated standard deviations are in parentheses.

| Atom | $x$ | $y$ | $z$ | $B$/Å$^2$ | Atom | $x$ | $y$ | $z$ | $B$/Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| H(N51) | 356(7) | 209(7) | 130(9) | 2.52 | H(21) | 413(9) | 558(8) | 427(10) | 4.42 |
| H(N52) | 308(8) | 163(7) | 223(9) | 2.52 | H(22) | 611(9) | 518(9) | 421(11) | 4.45 |
| H(9) | 349(8) | 343(8) | 258(10) | 3.32 | H(23) | 683(10) | 482(8) | 256(10) | 4.42 |
| H(101) | 473(8) | 215(7) | 330(9) | 3.52 | H(51) | 334(8) | 430(8) | −106(11) | 4.02 |
| H(102) | 489(8) | 283(7) | 242(10) | 3.52 | H(52) | 303(9) | 355(8) | −229(10) | 4.02 |
| H(103) | 472(8) | 314(7) | 355(10) | 3.52 | H(53) | 406(9) | 346(8) | −143(10) | 4.02 |
| H(12) | 294(8) | 121(8) | 408(10) | 3.62 | H(61) | 385(9) | 177(9) | −174(12) | 5.32 |
| H(13) | 219(9) | 101(9) | 568(11) | 4.72 | H(62) | 383(9) | 095(9) | −126(11) | 5.32 |
| H(14) | 192(8) | 228(9) | 662(10) | 5.42 | H(63) | 272(10) | 091(9) | −196(11) | 5.32 |
| H(15) | 230(9) | 395(9) | 609(12) | 5.52 | H(71) | 047(9) | 068(8) | 382(12) | 5.02 |
| H(16) | 309(9) | 418(8) | 429(10) | 4.82 | H(72) | −016(9) | 087(9) | 342(11) | 5.02 |
| H(171) | 040(8) | 212(8) | 037(10) | 4.22 | H(73) | 031(9) | 157(9) | 410(12) | 5.02 |
| H(172) | 094(7) | 264(9) | −059(9) | 4.22 | H(81) | −015(9) | 305(8) | 415(12) | 5.32 |
| H(173) | 033(9) | 304(8) | 042(10) | 4.22 | H(82) | 069(9) | 386(9) | 421(11) | 5.32 |
| H(18) | 583(9) | 454(8) | 106(11) | 4.42 | H(83) | 007(10) | 420(9) | 329(11) | 5.32 |
| H(19) | 419(9) | 494(8) | 107(11) | 4.42 | H(O1) | 187(9) | 433(8) | 151(10) | 4.42 |
| H(20) | 351(9) | 542(9) | 257(10) | 4.42 | H(O2) | 184(9) | 072(8) | 099(10) | 4.42 |

scheme of $w=(13.8/|F_o|)^2$ if $|F_o|>13.8$, $w=1.0$ if $13.8\geqq|F_o|\geqq4.6$, and $w=0.2$ if $|F_o|<4.6$ was employed. The final $R$ became 0.063 for 1413 observed reflections. At the final stage, no peaks higher than 0.03 $e$ Å$^{-3}$, except for the peaks of 0.05 $e$ Å$^{-3}$ around the cobalt atom, were observed on the difference map. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[8] The final atomic parameters and their standard deviations are given in Table 2 for non-hydrogen atoms and in Table 3 for hydrogen

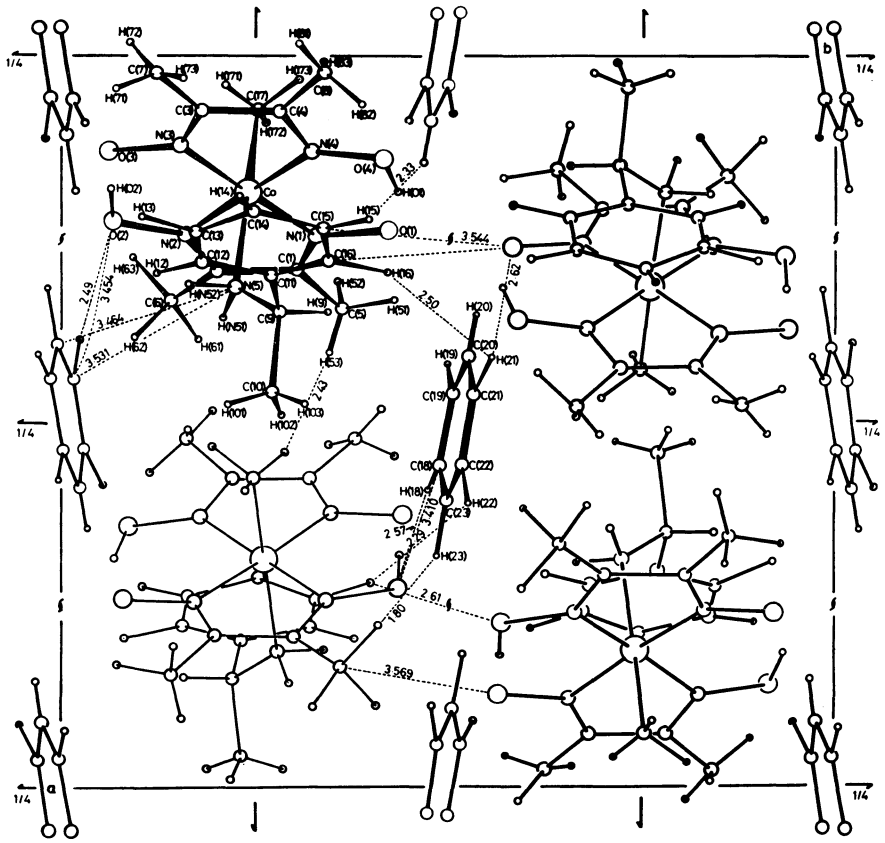

Fig. 2. Projection of the structure along the c axis and the interatomic distances between the Co-complexes and between the Co-complex and benzene. Along the c axis the contacts, 3.775 Å for C(14)···C(6), 2.77 Å for C(15)···H(52), and 2.30 Å for H(15)··· H(52), are observed.

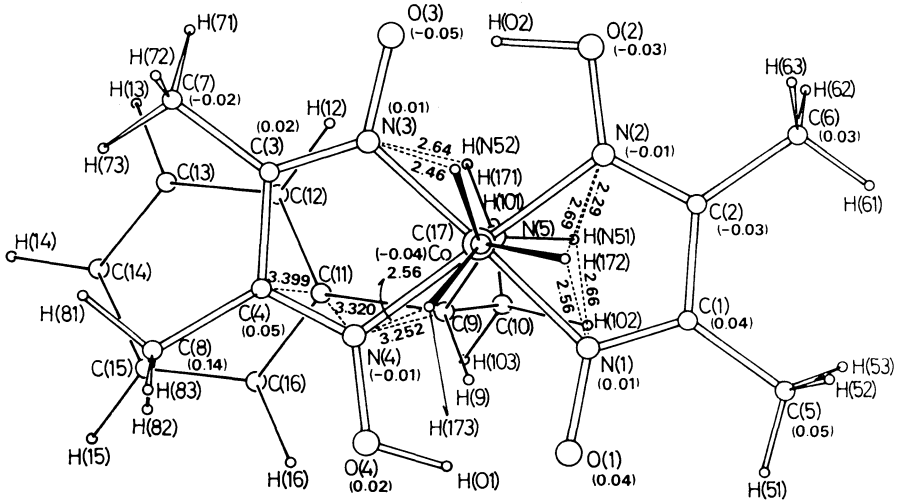


Fig. 3. Projection of the complex to the mean plane of four nitrogen atoms of $Co(dmg)_2$ and the short contacts between non-bonded atoms ($l$/Å), their threshold values being 3.400 Å for distances between the non-hydrogen atoms and 2.70 Å for those including hydrogen atoms. The deviations of the non-hydrogen atoms of $Co(dmg)_2$ from the plane are in parentheses.

atoms. A list of the observed and calculated structure factors is kept in the office of the Chemical Society of Japan (Document No. 7711).

The computation was done on the HITAC 8800 computer at the University of Tokyo and on the HITAC 8700 computer at Tokyo Institute of Technology. The programs, PROC for the data reduction and TLSU for the determination of the cell dimensions, were used. The other programs used were those in the UNICS Program System[9] with some modification.

## Description of the Structure

The crystal structure viewed along the c axis is shown in Fig. 2, in which the short interatomic distances are also given. There are no unusual short contacts between the Co-complexes, or between the Co-complex and the benzene molecule. The mean plane of the

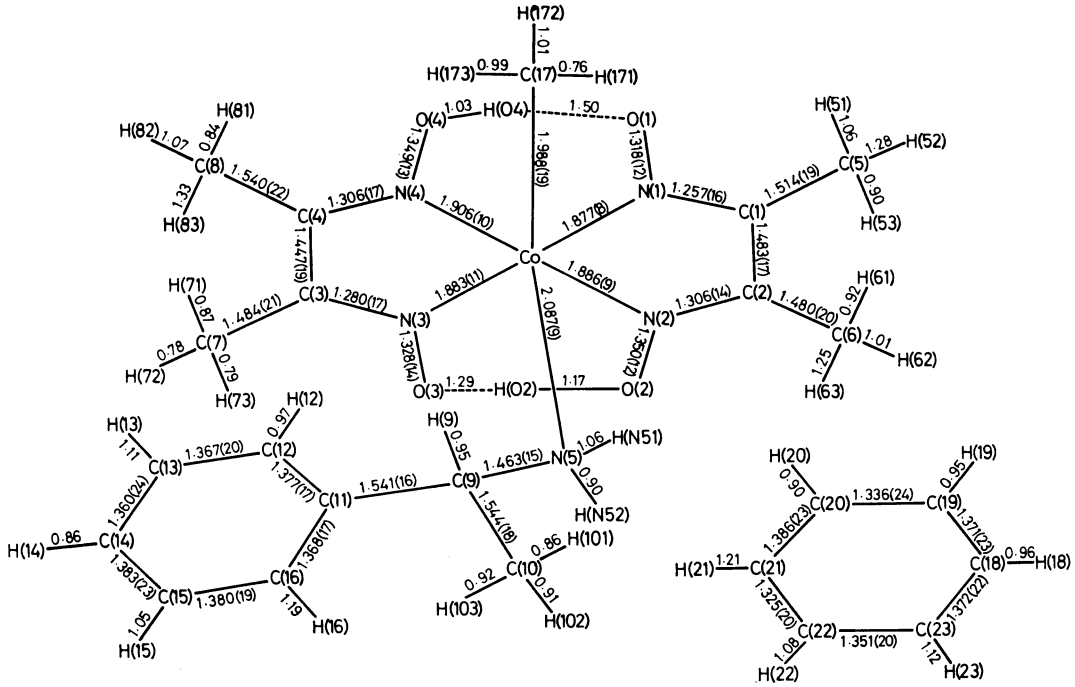


Fig. 4. Bond distances ($l$/Å). Their standard deviations are in parentheses, while those involving hydrogen atoms are 0.11—0.15 Å and are omitted for clarity.

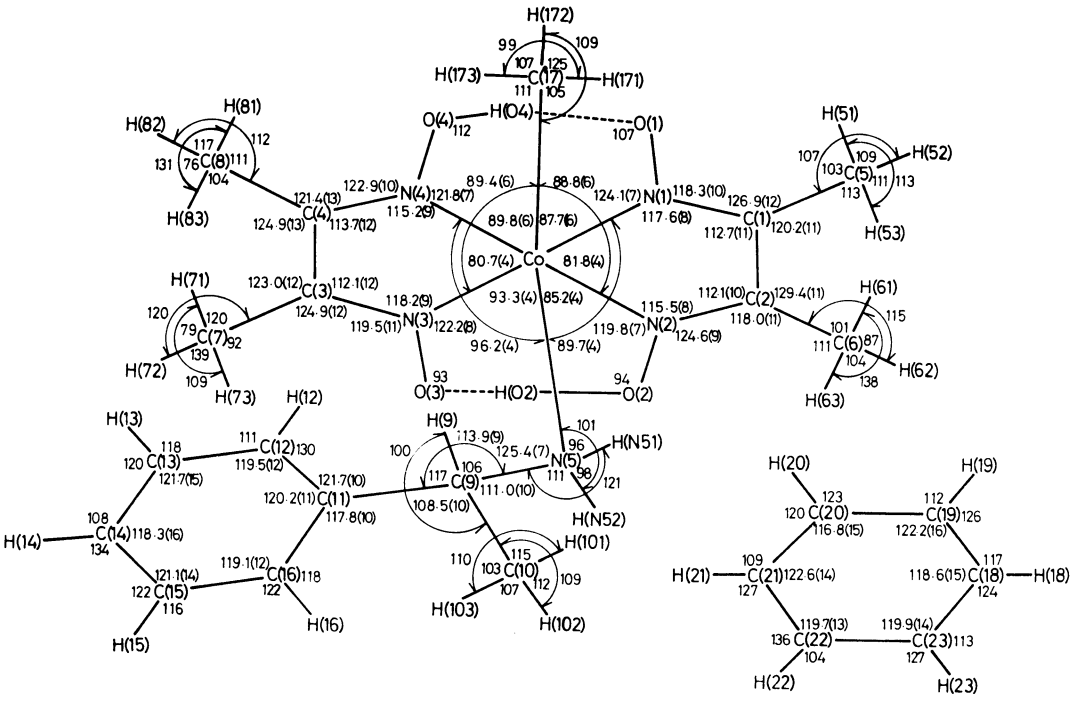


Fig. 5. Bond angles ($\phi$/°). Their standard deviations are in parentheses, while those involving hydrogen atoms are 6—14° and are omitted for clarity.

benzene ring is about at right angles to that of $Co(dmg)_2$ and to that of the phenyl ring of α-methylbenzylamine (abbreviated as mba).

The four nitrogen atoms in $Co(dmg)_2$ are coplanar within the limits of 0.01 Å, and the equation of the best plane is given by:

$$-0.8157X + 0.0781Y - 0.5731Z + 2.6438 = 0,$$

where $X$, $Y$, and $Z$ are the coordinates (in Å units) referred to the crystal axes. The deviations of the atoms from the plane and the distances between the non-bonded atoms in the complex are shown in Fig. 3. The C(8) atom over the phenyl ring is significantly out of the best plane, probably to avoid the short contact with the phenyl ring. The cobalt atom is slightly displaced from the plane toward mba. The short contact, N(4)···C(9), which is also observed in the complex reported in Part I (abbreviated as β-cne(dphyea)cobaloxime), seems to represent a fairly strong steric repulsion. The Co–N(5) bond makes an angle of 84° with the average plane.

The bond distances and angles are shown in Figs. 4 and 5 respectively. The $Co(dmg)_2$ moieties of aquomethylcobaloxime,[10,11] methylpyridinecobaloxime,[12] and methyl(3-*N*-methylimidazolyl)cobaloxime[12] have the $D_{2h}$ symmetry. Bigotto *et al.*[12] have suggested, on the basis of all the reported structures of the alkylcobaloxime complexes, that the standard values for Co–N, N–O, N–C, and C–$CH_3$ are 1.879, 1.343, 1.297, and 1.500 Å respectively. In the present complex, however, the bonds of Co–N, N–O, and N–C around N(2) and N(4) are longer than the standard lengths, whereas those around N(1) and N(3) are shorter except for Co–N(3). The hydrogen atoms, H(O1) and H(O2), do not exist at the mid-point of O···O, but come close to O(2) and O(4) respectively. The three angles of Co–N–O, Co–N–C and O–N–C around N(1) are in fair agreement with the corresponding angles of N(3), but are distinct from those of N(2), which, on the other hand, are close to those of N(4). These dimensions indicate that $Co(dmg)_2$ has a two-fold axis perpendicular to its plane and that the symmetry is approximately $C_{2h}$.

The Co–C distance coincides with those of the related methyl–Co(III) complexes.[10–14]

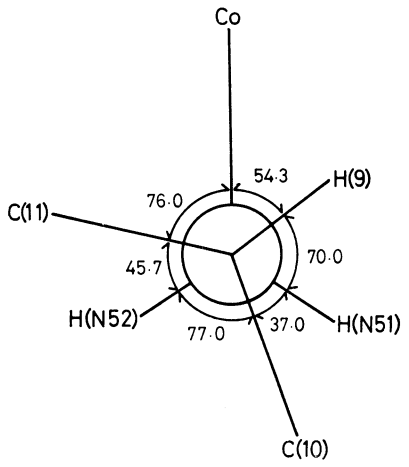


Fig. 6. Newman projection of mba along C(9)–N(5) with the angles ($\phi$/°) between the projected bonds.

The values of Co–N(5) and Co–N(5)–C(9) (2.087 Å and 125.4°) are nearly equal to those in β-cne(dphyea)-cobaloxime (2.08 Å and 126°), but significantly greater than the corresponding distance and angle of 2.001 Å and 119.5° in bis(aniline)cobaloxime chloride.[15] This is probably because of the steric repulsion between Co-$(dmg)_2$ and the pheny ring of mba; the 'trans-influence' suggested by Brückner and Randaccio[16] would also be included. The conformation of mba is a staggered form as shown in Fig. 6. The N(5)–C(9) length of 1.463 Å is close to the usual C–N(amine) distance (1.472±0.005 Å),[17] and the C(9)–C(11) value of 1.541 Å is slightly longer than the usual C–C(aromatic) bond (1.505±0.005 Å).[17] The phenyl ring is planar within an error of 0.02 Å, and makes an angle of 10° with the $Co(dmg)_2$ plane. The deviation of C(9) from the phenyl ring plane is 0.04 Å, C(9)–C(11) making an angle of 2.2° with the plane.

## Discussion

A fairly strong steric repulsion between $Co(dmg)_2$ and the axial ligand of the asymmetric amine was observed in the present complex. The $Co(dmg)_2$ moiety is deformed significantly, and its symmetry changes from $D_{2h}$ to $C_{2h}$ as a result of the repulsion. In order to explore the reaction mechanism, it is necessary to examine whether or not such a deformation can exist in the solution.

In conformation analysis to solve the problem, we made some simplifying assumptions which will not lead to any serious errors:

(1) The structure of $Co(dmg)_2$ has the $D_{2h}$ symmetry and the dimensions suggested by Bigotto *et al.*;[12]

(2) the dimensions and the conformation of mba are the same as those in the crystal, because the conformation around N(5)–C(9) is a stable staggered form and the rotation around C(9)–C(11) is prevented by the $Co(dmg)_2$ plane when the amine enters into coordination;

(3) the bond of Co–N(5) is perpendicular to the $Co(dmg)_2$ plane and has the same length as that in the crystal;

(4) the formulae and the parameters for the van der Waals energy are those proposed by Giglio,[18] because his parameters were deduced from the crystal of dimethylglyoxime;

(5) the parameters of the methyl groups of $Co(dmg)_2$ are the same as those of the nitrogen atom, because the methyl groups probably rotate freely around the C–$CH_3$ bonds.[19]

On such simplifications, the van der Waals energy was calculated by changing the rotation angle, $\phi$, around Co–N(5), as shown in Fig. 7. The minimum energy was obtained at the angle of −13°, which is in good agreement with the observed dihedral angle of N(4)–Co–N(5)–C(9), −17.6°, in the crystal. The N(4)···C(9) distance in the structure of the miniumm energy was 2.239 Å, which is shorter than that of the crystalline state. To avoid such short contact, N(5) should be driven toward N(2) and Co–N(4) should be lengthened, as observed in the crystal. It is reasonable to assume

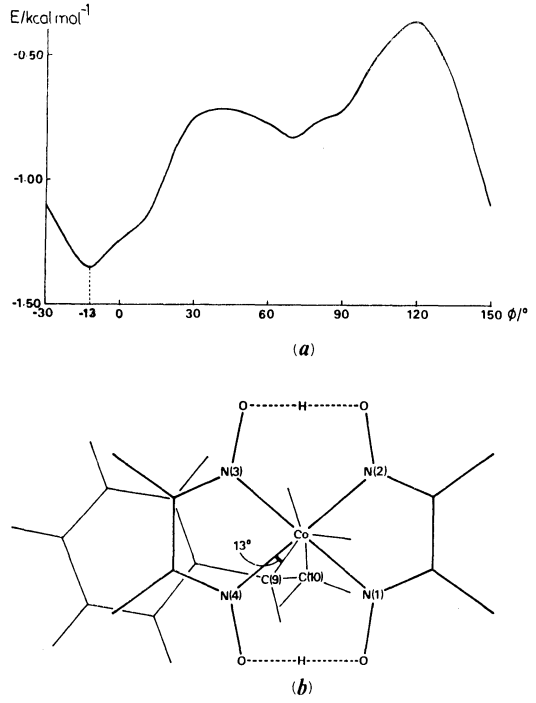


Fig. 7. (a) The variation of van der Waals energy, $E$, with the rotation angle, $\phi$, around Co–N(5), $Co(dmg)_2$ being fixed. The axial ligand of mba is rotated clockwise from the position in which the dihedral angle of N(4)–Co–N(5)–C(9) is zero. (b) The conformation with the minimum energy.

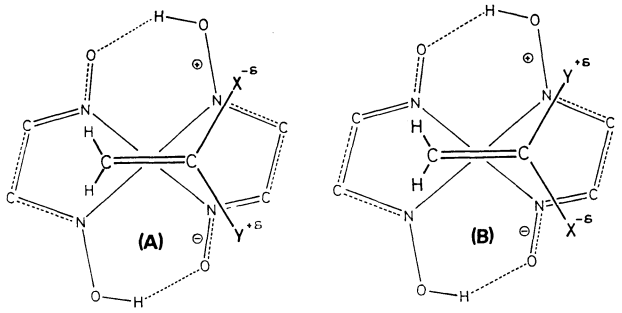


Fig. 8. Two possible ways in which the substrate approaches the active site of the catalyzer.

that such an elongation of Co–N(4) causes the change of the $\pi$-electron distribution and the geometry of dmg from $D_{2h}$ to $C_{2h}$. The negative charge in dmg is localized on the shorter bonds.

The hydrogenation proceeds when the substrate has the nucleophilic and electrophilic substituents adjacent to the C=C double bond.[2] These observations suggest that the electrostatic force controls the way in which the substrate comes close to the active site of the catalyzer. As shown in Fig. 8, the mode of approaching, (A), is more favorable than (B) in view of the electrostatic interaction, so that one configuration of the asymmetric carbon in the intermediate $\sigma$-complex (termed (III) in Fig. 1) should be preferable to the other. We propose that this is a factor for inducing the asymmetry in the hydrogenation. Besides the factor proposed above, some others, for example, the van der Waals force, probably affect the overall optical yield in the step of $\pi$-bond formation and in the following steps illustrated in Fig. 1. We intend to examine those factors and correlate the optical yield to each factor in further studies of this series.

The authors are grateful to Dr. Yoshiaki Ohgo and Professor Juji Yoshimura for kindly supplying the specimens and for their valuable discussions.

## References

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