Structural Studies of Asymmetric Hydrogenation. III. The Crystal Structure of (*R*)-1-(Methoxycarbonyl)ethyl(*R*)(+)-α-methylbenzylaminebis(dimethylglyoximato)cobalt(III)

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The structure of (*R*)-1-(methoxycarbonyl)ethyl(*R*)(+)-α-methylbenzylaminebis(dimethylglyoximato)cobalt-(III) has been determined by X-ray analysis. The crystal is monoclinic, the space group $P2_1$, $Z=2$ with $a=7.899(5)$, $b=16.397(2)$, $c=9.054(7)$ Å, and $\beta=90.98(7)°$. The structure was deduced by the heavy atom method and refined by the block-diagonal least-squares method to a final R value of 0.048 for 2146 observed reflections. The bis(dimethylglyoximato)cobalt moiety is twisted around its long axis, owing to the steric repulsion from the (*R*)-1-(methoxycarbonyl)ethyl group and the optically active amine. It is proposed that this twist is one of the factors inducing the asymmetry in the hydrogenation catalyzed by the complex of bis(dimethylglyoximato)cobalt and the active amine. At the step of Co–C bond cleavage the reaction proceeds mainly through inversion of the configuration.

The complexes of bis(dimethylglyoximato)cobalt (abbreviated to $Co(dmg)_2$ or cobaloxime) and optically active amine catalyze asymmetric hydrogenation of olefins.[1-6] The hydrogenation proceeds as follows:

$$H_2C{=}CXY + \underset{\underset{B^*}{|}}{Co(dmg)_2} \longrightarrow \underset{\underset{B^*}{|}}{\overset{H_2C{=}CXY}{\vdots}\,Co(dmg)_2} \longrightarrow \underset{\underset{B^*}{|}}{\overset{H_3CC^*XY}{|}\,Co(dmg)_2} \xrightarrow[\frac{1}{2}H_2]{} H_3CC^*HXY + \underset{\underset{B^*}{|}}{Co(dmg)_2}\ ,$$

where B* is the optically active amine. In order to clarify the mechanism of inducing asymmetry, several crystal structures of related complexes have been determined by X-ray analysis. In Part II of this series on the crystal structure of methyl(*R*)(+)-α-methylbenzylaminebis(dimethylglyoximato)cobalt(III) benzene solvate[7] (abbreviated to methyl complex), it has been shown that the $Co(dmg)_2$ moiety of the catalyzer is deformed by the steric repulsion from the optically active amine coordinated to the cobalt atom so that its symmetry changes from D_{2h} to C_{2h}. We proposed that this deformation is one of the factors inducing asymmetry in the reaction step of π-bond formation. The present study has been undertaken to disclose the mechanism of Co–C(σ) bond formation and its cleavage.

Experimental

Dark red crystals of the title complex were obtained from aqueous methanol solution. The unit cell dimensions were determined from zero layer Weissenberg photographs using Co$K\alpha$ radiation about b and c axes. Spacings of 40 high angle reflections ($\theta \geqq 60°$), calibrated with superposed silicon powder lines, were subjected to the least-squares treatment. The crystal data are summarized in Table 1.

With the use of a crystal of dimensions $0.2\times0.4\times0.3$ mm, the intensities for $3° \leqq 2\theta \leqq 60°$ were collected on a Hilger-Watts linear diffractometer with Mo$K\alpha$ radiation. The balanced Y/Zr filter pair was used. Out of 3055 accessible reflections, 2149 for which $I \geqq 3\sigma(I)$ were regarded as observed. The usual Lorentz and polarization, but no absorption, corrections were made.

Table 1. Crystal data

Formula	$C_{20}H_{32}N_5O_6Co$
F. W.	497.44
a	7.899(5) Å
b	16.397(2) Å
c	9.054(7) Å
β	90.98(7)°
V	1172(1) Å^3
Systematic absence	$0k0$, k odd
Space group	$P2_1$
Z	2
D_m	1.414 g/cm^3
D_x	1.409 g/cm^3
μ(Mo$K\alpha$)	8.05 cm^{-1}

Table 2. Part of observed and calculated intensity relations between hkl and $h\bar{k}l$

Indices			$\lvert F_c(hkl)\rvert^2$	Observed relations	$\lvert F_c(h\bar{k}l)\rvert^2$
1	1	−3	130	<	595
1	2	1	1183	>	511
1	3	−1	231	>	19
1	5	−1	595	<	1325
1	7	2	493	>	139
2	2	7	520	>	256
2	1	7	353	<	475
2	3	−4	92	<	346
2	4	−3	139	<	424
2	6	1	117	<	475
2	6	3	92	<	493
2	4	7	100	>	13
2	3	7	64	<	262

Structure Determination

The positions of the cobalt and six coordinated atoms were obtained from the three-dimensional Patterson function. The other atoms were revealed on the first

Table 3. Fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^5$) for the non-hydrogen atoms

The anisotropic thermal parameters are of the form;

$$T = \exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl).$$

Estimated standard deviations are in parentheses.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	1135(1)	2500	2740(1)	0852(9)	0143(2)	0529(6)	0126(14)	−0080(11)	0047(12)
N(1)	0514(6)	2298(3)	0752(6)	0803(81)	0244(26)	0731(62)	−0141(59)	0045(114)	−0072(52)
N(2)	2068(7)	1447(3)	2577(6)	1139(100)	0175(21)	0997(74)	0096(72)	0165(136)	0033(63)
N(3)	1869(7)	2748(3)	4675(5)	1184(94)	0292(26)	0546(56)	0196(70)	−0266(115)	0014(54)
N(4)	0253(7)	3559(3)	2892(6)	1073(93)	0155(19)	0750(64)	0214(67)	0017(122)	0107(56)
O(1)	−0328(6)	2843(3)	−0084(5)	1453(95)	0375(23)	0780(57)	0095(73)	−0706(119)	0171(58)
O(2)	2815(8)	1057(3)	3721(6)	2112(118)	0266(22)	1286(80)	0762(82)	−0051(154)	0502(66)
O(3)	2758(7)	2207(3)	5517(5)	1727(105)	0461(28)	0806(63)	0568(82)	−0528(131)	0345(62)
O(4)	−0609(7)	3939(3)	1779(5)	1481(95)	0256(21)	1022(67)	0324(71)	−0336(125)	0252(58)
C(1)	1102(9)	1637(5)	0185(8)	1022(119)	0320(32)	0964(92)	−0291(97)	0459(167)	−0113(84)
C(2)	1987(10)	1109(5)	1265(8)	1282(131)	0274(30)	1114(102)	0095(97)	0283(183)	−0286(86)
C(3)	1563(10)	3462(4)	5160(7)	1601(138)	0242(27)	0606(73)	−0043(95)	−0092(159)	−0166(70)
C(4)	0583(9)	3965(4)	4100(8)	1228(121)	0173(24)	1059(93)	0034(86)	0316(168)	−0146(74)
C(5)	0947(13)	1421(7)	−1443(9)	2355(202)	0558(50)	0903(105)	−0121(160)	0270(231)	−0545(119)
C(6)	2665(15)	0286(6)	0970(13)	3127(259)	0294(39)	2360(197)	0848(159)	1561(363)	−0444(140)
C(7)	2087(15)	3774(7)	6663(10)	3136(246)	0525(49)	0950(109)	0050(172)	−0876(265)	−0701(117)
C(8)	0052(13)	4814(6)	4356(11)	2489(216)	0262(35)	1626(141)	0044(131)	−0045(278)	−0329(110)
N(5)	3427(7)	2917(3)	1974(6)	0848(88)	0202(21)	0900(70)	−0010(68)	−0120(120)	0127(61)
C(9)	3607(9)	3595(4)	0915(7)	1178(115)	0197(24)	0805(79)	−0139(86)	−0101(155)	0122(71)
C(10)	5072(12)	3422(6)	−0090(9)	1993(165)	0349(36)	1155(106)	−0315(124)	1005(212)	−0254(100)
C(11)	3782(8)	4419(4)	1636(8)	0923(108)	0248(28)	1057(90)	−0017(87)	−0175(159)	−0194(81)
C(12)	4785(12)	4539(6)	2875(11)	2023(186)	0409(43)	1714(143)	0172(141)	−2122(271)	−0352(124)
C(13)	4984(15)	5325(6)	3480(13)	2833(247)	0397(46)	2408(193)	0038(166)	−2755(361)	−0707(151)
C(14)	4276(12)	5987(6)	2806(14)	1620(178)	0318(39)	3034(228)	−0005(125)	−0354(308)	−0566(151)
C(15)	3324(12)	5881(6)	1557(12)	1976(185)	0272(37)	2317(180)	0079(130)	−0321(289)	0057(126)
C(16)	3051(10)	5099(5)	0974(9)	1366(141)	0288(32)	1470(121)	−0001(105)	−0133(205)	0301(98)
C(17)	−0972(9)	1930(5)	3586(8)	1202(126)	0268(29)	0921(90)	0061(93)	0325(175)	0051(81)
C(18)	−1983(12)	1422(6)	2510(11)	1651(167)	0422(42)	1704(143)	−0676(137)	0659(249)	−0534(128)
C(19)	−2101(7)	2502(6)	4329(6)	0990(87)	0236(20)	0841(64)	−0225(137)	0039(120)	0183(122)
O(5)	−3325(6)	2827(4)	3772(6)	1116(88)	0500(30)	1471(81)	0494(80)	−0670(137)	0200(77)
O(6)	−1650(6)	2640(4)	5743(5)	1357(79)	0389(32)	0828(52)	0183(81)	0340(102)	−0111(67)
C(20)	−2663(13)	3201(7)	6555(10)	2117(188)	0576(52)	1290(125)	0364(160)	1358(250)	−0457(128)

Fourier map phased with these seven atoms.

The structure was refined by the block-diagonal least-squares method. After several cycles of refinement, the three strongest reflections were excluded because they seemed to be affected by secondary extinction. All the hydrogen atoms were found on the difference map. The final refinement was made including these hydrogen atoms with isotropic temperature factors. The weighting scheme, $w=(34.44/|F_o|)^2$ if $|F_o|>34.44$, $w=1.0$ if $34.44\geqq|F_o|\geqq8.61$, $w=0.3$ if $|F_o|<8.61$, was employed. The final R value became 0.048 for 2146 observed reflections. At the final stage, no peaks higher than 0.30 e Å^{-3}, except for the peaks of 0.45 e Å^{-3} around the cobalt atom, were found on the difference map. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[8]

The absolute configuration was determined from Weissenberg photographs using Cu$K\alpha$ radiation. The observed and calculated structure factors of 13 Bijvoet pairs are compared in Table 2.

Final atomic parameters and their standard deviations are given for non-hydrogen atoms and hydrogen atoms in Tables 3 and 4, respectively. A list of the observed and calculated structure factors is kept in the office of the Chemical Society of Japan (Document No. 7719). The computation was done on a HITAC 8800 computer at the University of Tokyo and a HITAC 8700 computer at this Institute.

Description of the Structure

Co(dmg)$_2$ Moiety. The equations of the mean planes of four nitrogen atoms and two dmg's, (I), (II), and (III), are given in Table 5, together with the deviations of atoms from the planes. Figure 1 shows the structure of the complex projected on plane (I) and the short contacts between the non-bonded atoms in the complex. The molecular coordinates, x and y, are taken in plane (I), where x is the projection of the line passing through the mid-points of N(1)···N(2) and N(3)···N(4) on the plane, y being perpendicular to x passing through the cobalt atom. Two arrows indicate

Table 4. Fractional coordinates ($\times 10^3$) and thermal parameters for hydrogen atoms
(Esd's are in parentheses)

Atom	x	y	z	B(Å^2)
H(O1)	−051(11)	346(6)	086(10)	3(2)
H(O2)	278(14)	184(7)	484(12)	4(3)
H(51)	051(13)	093(7)	−170(12)	5(3)
H(52)	137(12)	185(6)	−195(11)	3(2)
H(53)	227(15)	106(8)	−164(14)	6(3)
H(61)	196(15)	−009(7)	033(13)	6(3)
H(62)	358(16)	052(9)	016(15)	9(4)
H(63)	332(14)	−002(7)	140(13)	5(3)
H(71)	123(13)	422(7)	689(13)	5(3)
H(72)	225(14)	337(8)	718(14)	5(3)
H(73)	287(11)	405(6)	674(11)	3(2)
H(81)	−080(12)	497(6)	387(11)	4(2)
H(82)	−037(12)	498(7)	536(12)	4(2)
H(83)	093(13)	518(7)	409(12)	4(3)
H(N51)	414(11)	242(7)	143(9)	4(2)
H(N52)	389(12)	302(6)	273(10)	3(2)
H(9)	261(12)	367(6)	030(11)	3(2)
H(101)	490(12)	378(6)	−084(11)	3(2)
H(102)	520(18)	276(11)	−057(19)	10(5)
H(103)	565(17)	352(9)	063(16)	8(4)
H(12)	535(13)	410(7)	340(13)	5(3)
H(13)	555(16)	532(8)	431(15)	7(4)
H(14)	461(12)	657(6)	339(12)	4(2)
H(15)	261(12)	639(6)	109(11)	3(2)
H(16)	262(15)	508(8)	−001(14)	6(3)
H(17)	−034(12)	166(6)	432(11)	3(2)
H(181)	−260(11)	170(6)	199(10)	3(2)
H(182)	−135(12)	099(6)	206(11)	4(2)
H(183)	−255(16)	087(8)	290(15)	8(4)
H(201)	−346(12)	358(6)	597(10)	3(2)
H(202)	−306(17)	311(9)	726(14)	9(4)
H(203)	−224(15)	352(8)	738(13)	7(3)

the vectors normal to the planes of (II) and (III).

The Co(dmg)$_2$ moiety is significantly bent downward to avoid the short contact with the 1-(methoxycarbonyl)-ethyl group (abbreviated to mce group). The Co(dmg)$_2$ moiety in the methyl complex,[7] which contains the methyl group instead of the mce group and the same amine, is slightly bent in the opposite direction. The cobalt atom in the present complex is significantly displaced upward from the mean plane whereas that in the methyl complex is shifted downward (0.04 Å). Moreover, each dmg is inclined to the y direction. Contacts with the axial ligands, especially between C(18) and N(1) and between H(N51) and N(2), tilt the plane of (II), whereas contacts between C(9), C(11), and N(4), and between N(3), C(3), and O(6) tilt the plane of (III) in the opposite sense. A similar twist of Co(dmg)$_2$ is found in the crystal of 4-pyridyltributylphosphinecobaloxime.[9]

Bond distances and angles are shown in Fig. 2 and Table 6, respectively. In Table 7 the bond lengths in the Co(dmg)$_2$ moiety are compared with those in the methyl complex and the average distances suggested by Bigotto *et al.*[10] In regard to the bond lengths of N–C and C–CH$_3$ and three angles around the endo-cyclic carbon atom, the symmetry of C_{2h} holds good for the present complex.

However, four distances of Co–N are nearly the same and close to the value of Bigotto *et al.*[10] Two bonds of N(3)–O(3) and N(4)–O(4) are longer than N(1)–O(1) and N(2)–O(2). Two hydrogen atoms, H(O1) and H(O2), are bonded to O(4) and O(3), respectively.

Equivalence of four Co–N bonds might be caused

Table 5. Least-squares planes and deviations for equatorial ligands

X, Y, and Z in Å referred to **a**, **b**, and **c*** respectively.

(I) Co(dmg)$_2$ plane:
$-0.8635X-0.3853Y+0.3255Z+1.5507=0.$

(II) dmg plane:
$-0.8595X-0.4588Y+0.2252Z+1.9239=0.$

(III) dmg plane:
$-0.8585X-0.3307Y+0.3919Z+1.0370=0.$

	I	II	III
Co	0.041 (l/Å)	−0.132 (l/Å)	−0.080 (l/Å)
N(1)	−0.020*	0.010*	
N(2)	0.020*	−0.009*	
N(3)	−0.020*		0.001*
N(4)	0.020*		−0.001*
O(1)	−0.047	−0.011	
O(2)	0.109	0.025	
O(3)	−0.025		0.001
O(4)	0.026		−0.031
C(1)	−0.178	−0.016*	
C(2)	−0.115	0.016*	
C(3)	−0.113		−0.001*
C(4)	−0.089		0.001*
C(5)	−0.437	−0.102	
C(6)	−0.149	0.110	
C(7)	−0.205		0.028
C(8)	−0.184		−0.005

* Atoms included in the least-squares calculation.

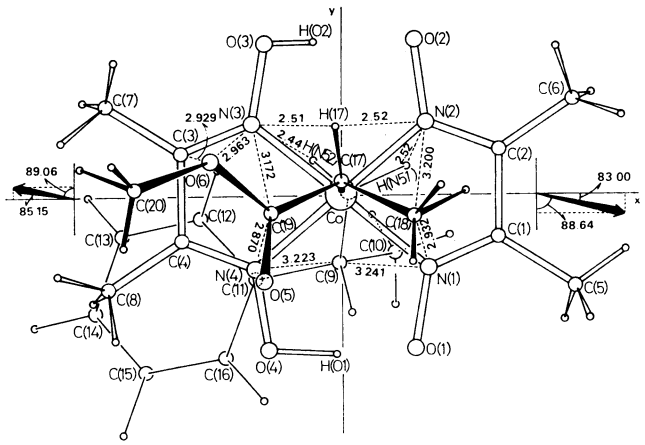

Fig. 1. Projection of the complex to the mean plane of four nitrogen atoms of Co(dmg)$_2$ and the short contacts between non-bonded atoms(l/Å), their threshold values being 3.400 Å for distances between the non-hydrogen atoms and 2.70 Å for those including hydrogen atoms.

Table 6. Bond angles (ϕ/°) (Esd's are in parentheses)
Angles including methyl hydrogens are omitted.

N(1)-Co-N(2)	81.9(2)	N(1)-Co-N(3)	176.1(2)
N(1)-Co-N(4)	98.1(2)	N(1)-Co-N(5)	87.3(2)
N(1)-Co-C(17)	94.4(3)	N(2)-Co-N(3)	99.0(2)
N(2)-Co-N(4)	178.7(2)	N(2)-Co-N(5)	86.0(2)
N(2)-Co-C(17)	86.2(3)	N(3)-Co-N(4)	80.8(2)
N(3)-Co-N(5)	89.1(2)	N(3)-Co-C(17)	89.4(3)
N(4)-Co-N(5)	92.7(2)	N(4)-Co-C(17)	95.1(3)
N(5)-Co-C(17)	171.7(3)	Co-N(1)-O(1)	122.6(4)
Co-N(1)-C(1)	116.0(5)	O(1)-N(1)-C(1)	121.0(6)
Co-N(2)-O(2)	122.8(5)	Co-N(2)-C(2)	116.4(5)
O(2)-N(2)-C(2)	120.7(6)	Co-N(3)-O(3)	121.9(4)
Co-N(3)-C(3)	117.5(5)	O(3)-N(3)-C(3)	120.4(6)
Co-N(4)-O(4)	123.6(4)	Co-N(4)-C(4)	117.7(5)
O(4)-N(4)-C(4)	118.6(6)	N(1)-C(1)-C(2)	113.6(7)
N(1)-C(1)-C(5)	124.0(7)	C(2)-C(1)-C(5)	122.4(7)
N(2)-C(2)-C(1)	111.6(7)	N(2)-C(2)-C(6)	122.5(8)
C(1)-C(2)-C(6)	125.9(8)	N(3)-C(3)-C(4)	113.0(6)
N(3)-C(3)-C(7)	124.9(8)	C(4)-C(3)-C(7)	122.1(7)
N(4)-C(4)-C(3)	110.9(6)	N(4)-C(4)-C(8)	124.1(7)
C(3)-C(4)-C(8)	125.0(7)	Co-N(5)-C(9)	124.2(4)
N(5)-C(9)-C(10)	109.5(6)	N(5)-C(9)-C(11)	113.8(6)
C(9)-C(11)-C(12)	122.0(7)	C(9)-C(11)-C(16)	120.0(7)
C(12)-C(11)-C(16)	117.8(8)	C(11)-C(12)-C(13)	120.5(9)
C(12)-C(13)-C(14)	120.9(11)	C(13)-C(14)-C(15)	119.2(12)
C(14)-C(15)-C(16)	120.7(10)	C(11)-C(16)-C(15)	120.8(8)
Co-C(17)-C(18)	115.7(6)	Co-C(17)-C(19)	112.4(6)
C(18)-C(17)-C(19)	109.4(7)	C(17)-C(19)-O(5)	125.5(9)
C(17)-C(19)-O(6)	113.1(8)	O(5)-C(19)-O(6)	121.5(9)
C(19)-O(6)-C(20)	117.2(8)		
Co-N(5)-H(N51)	111(6)	Co-N(5)-H(N52)	100(7)
C(9)-N(5)-H(N51)	103(6)	C(9)-N(5)-H(N52)	110(7)
H(N51)-N(5)-H(N52)	108(10)	N(1)-O(1)-H(O1)	102(4)
N(2)-O(2)-H(O2)	94(4)	N(3)-O(3)-H(O2)	92(7)
N(4)-O(4)-H(O1)	101(5)	O(1)-H(O1)-O(4)	172(10)
O(2)-H(O2)-O(3)	169(11)	N(5)-C(9)-H(9)	113(6)
C(10)-C(9)-H(9)	108(6)	C(11)-C(9)-H(9)	101(6)
C(11)-C(12)-H(12)	124(7)	C(13)-C(12)-H(12)	116(7)
C(12)-C(13)-H(13)	110(9)	C(14)-C(13)-H(13)	129(9)
C(13)-C(14)-H(14)	113(6)	C(15)-C(14)-H(14)	128(6)
C(14)-C(15)-H(15)	119(5)	C(16)-C(15)-H(15)	120(5)
C(15)-C(16)-H(16)	116(7)	C(11)-C(16)-H(16)	120(7)

Table 7. Bond lengths in $Co(dmg)_2$ (l/Å)

	Methyl complex	Present	Average value of Bigotto *et al.*		Methyl complex	Present	Average value of Bigotto *et al.*
Co-N(1)	1.877	1.888		N(2)-C(2)	1.306	1.312	1.297
Co-N(2)	1.886	1.885	1.879	N(3)-C(3)	1.280	1.275	
Co-N(3)	1.883	1.880		N(4)-C(4)	1.306	1.303	
Co-N(4)	1.906	1.877		C(1)-C(5)	1.514	1.519	
N(1)-O(1)	1.318	1.340		C(2)-C(6)	1.480	1.478	1.500
N(2)-O(2)	1.350	1.344	1.343	C(3)-C(7)	1.484	1.505	
N(3)-O(3)	1.328	1.358		C(4)-C(8)	1.540	1.474	
N(4)-O(4)	1.349	1.358		C(1)-C(2)	1.483	1.474	1.451
N(1)-C(1)	1.257	1.288		C(3)-C(4)	1.447	1.474	

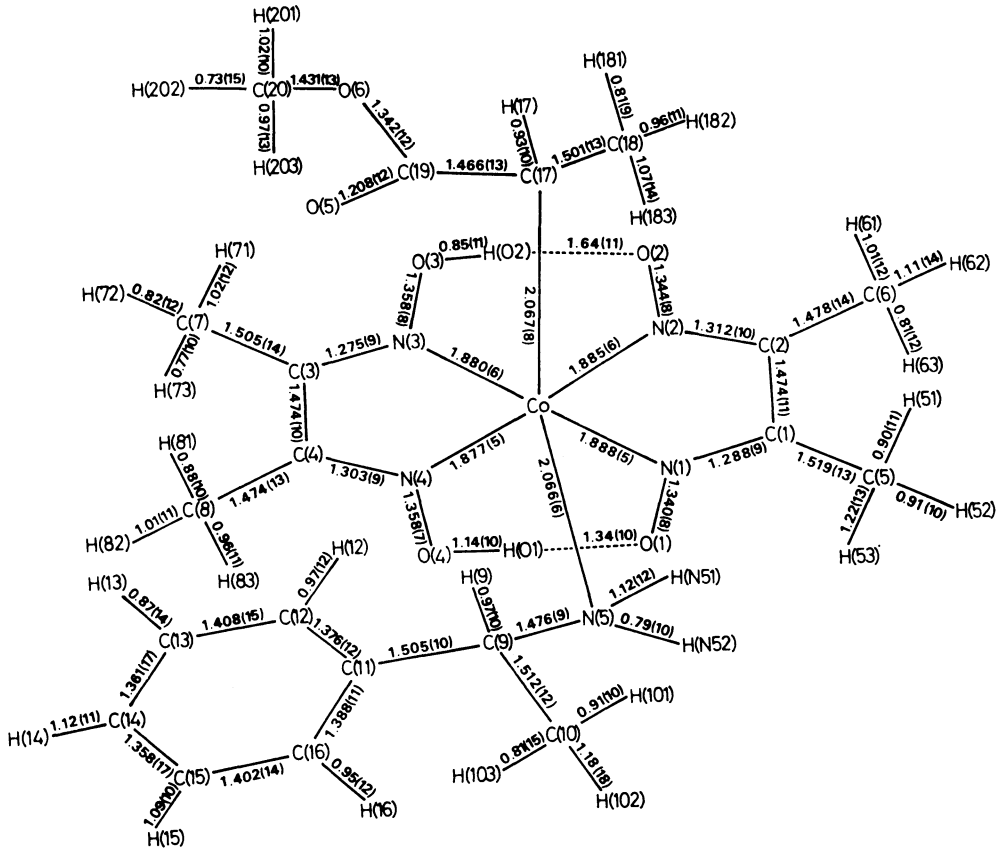

Fig. 2. Bond distances (l/Å). Their standard deviations are in parentheses.

Table 8. Various Co–C(sp^3) distances in cobaloxime complexes

	Co–C distance	Reference
$CH_3Co(dmg)_2(OH_2)$	1.990(5) Å	15
$CH_3Co(dmg)_2(py)$	1.998(5)	10
$CH_3Co(dmg)_2(nmeim)$	2.009(7)	10
$CH_3Co(dmg)_2(mba)$	1.988(19)	7
$(CH_2CO_2CH_3)Co(dmg)_2(py)$	2.04	11
(CH_2CH_2CN)-$Co(dmg)_2(dphyea)$	2.04	16
$(CH(CH_3)CO_2CH_3)$-$Co(dmg)_2(mba)$	2.067(8)	present

py: Pyridine, nmeim: 3-*N*-methylimidazole, dphyea: *erythro*-1,2-diphenyl-2-hydroxyethylamine.

Table 9. Characteristic dimensions of the amine

	Methyl complex	Present
Co–N(5)	2.087(9) Å	2.066(6) Å
N(5)–C(9)	1.463(15) Å	1.476(9) Å
C(9)–C(11)	1.541(16) Å	1.505(10) Å
N(4)–Co–N(5)	96.2(4)°	92.7(2)°
Co–N(5)–C(9)	125.4(7)°	124.2(4)°
Dihedral angle of N(4)–Co–N(5)–C(9)	17.6°	39.7°
Dihedral angle of Co–N(5)–C(9)–C(11)	76.0°	89.9°
Bending of C(9)–C(11) from the phenyl ring	2.2°	4.0°

by the steric repulsions between C(18) and N(1) and between C(19) and N(4). The highly negative O(5) and O(6) atoms would draw the positive H(O1) and H(O2) atoms toward O(4) and O(3), respectively, by electroattractive force. Thus in the step of σ-bond formation, not only the twist of $Co(dmg)_2$ but also slight changes of bond distance occur as a result of electrostatic force and the short contacts between the mce group and $Co(dmg)_2$.

1-(Methoxycarbonyl)ethyl Group. The Co–C(17) distance of 2.067 Å is significantly greater than the usual Co–C(sp^3) length. Various Co–C(sp^3) lengths so far determined in the cobaloxime complexes are summarized in Table 8. As the number of the bulky substituents bonded to the ligating carbon atom increases, the Co–C distance is lengthened. This can be interpreted by the steric repulsion between the substituents and the $Co(dmg)_2$ moiety. The C(17)–C(19) distance of 1.466 Å is significantly smaller than the corresponding one in propionic acid (1.50 Å) and slightly smaller than that in *O*-methyl-(Co–C)carboxymethylpyridinecobaloxime (1.48 Å).[11] Since C(17)–C(18) is shorter than the usual C(sp^3)–C(sp^3) single bond, this suggests that the hybridization of C(17) is modified by coordination. The other distances are in good agreement with the corresponding ones of *O*-methyl-(Co–C)carboxymethylpyridinecobaloxime. The angle of Co–C(17)–C(18), 115.7°, is greater than the tetrahedral angle, probably due to the steric repulsion from $Co(dmg)_2$. Three angles around the C(19) atom, 125.5, 121.5, and 113.1°, are close to those of propionic acid, 125, 122,

and 112°, respectively. Four atoms of C(17), C(19), O(5), and O(6) are coplanar within the limit of 0.001 Å, its plane making an angle of 27.5° with the plane (I) of $Co(dmg)_2$.

α-Methylbenzylamine Ligand. In Table 9, the characteristic dimensions of amine ligand (abbreviated to mba) are compared with those in the methyl complex. The $Co(dmg)_2$ plane is bent toward the amine so that the steric repulsion from the amine should be stronger than that of the methyl complex. To release this, rotation around Co–N(5) and N(5)–C(9) and bending of the phenyl group occur. Co–N(5) rotates from the stable conformation, in which the dihedral angle of N(4)–Co–N(5)–C(9) is 13°.[7] The conformation around N(5)–C(9) is shown in Fig. 3. The N(5)–C(9) bond rotates by about 15° from the conformation of

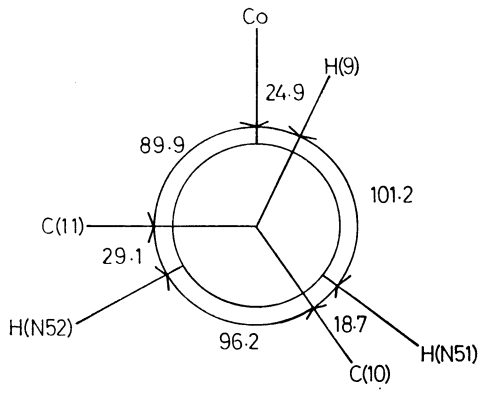

Fig. 3. Newman projection of mba along C(9)–N(5) with the angles (ϕ/°) between the projected bonds.

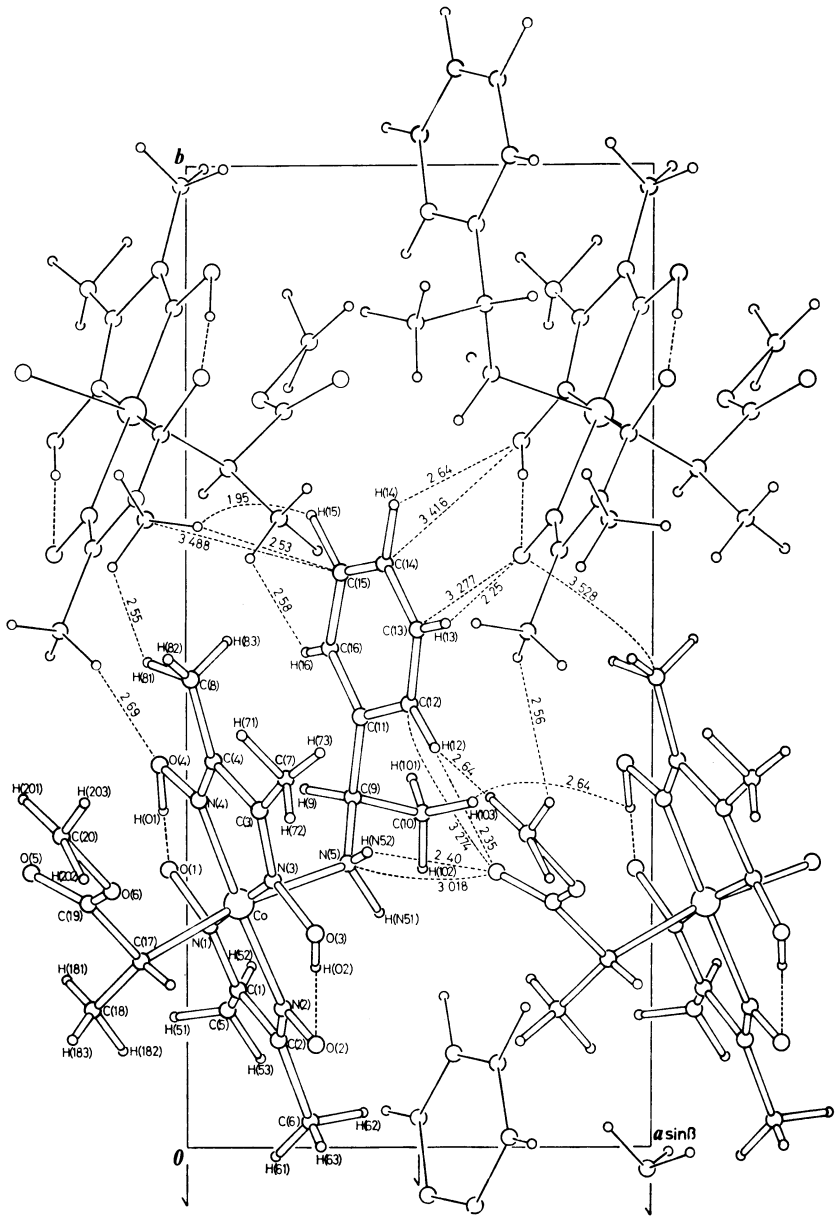

Fig. 4. Projection of the crystal structure along the c axis and short contacts between complexes. Along the c axis the contacts, 3.379 Å for O(3)···C′(5) and 3.580 Å for O(1)···C′(20) are observed.

the methyl complex to the unstable eclipsed form. On the other hand, the Co–N(5) distance is smaller than that in the methyl complex, probably by the effect of the *trans* ligand. The N(5)–C(9) and C(9)–C(11) lengths are in good agreement with the usual distances, 1.472±0.005 and 1.505±0.005 Å, respectively.[12]

Crystal Structure. The crystal structure viewed along the c axis is shown in Fig. 4, the short contacts also being given. There is a fairly short distance, 3.018 Å, between N(5) and O′(5) in the neighbouring complex along the a axis. Although this may be a hydrogen bond of N–H···O in view of N···O distance,[13] O′(5)···H(N52) is not so short and the angle of N(5)–H(N52)···O′(5) is 136°. Therefore, the interaction of N–H···O, if any, should be very weak.[14] Others are normal van der Waals contacts.

Discussion

The $Co(dmg)_2$ moiety is twisted as a 'propeller' by the steric repulsion with the mce group and mba ligand. The N(1) and N(4) atoms are shifted downward and upward, respectively, from the plane, to avoid the short contacts with the methyl of mce group and the asymmetric mba ligand. The carbonyl group with smaller van der Waals radius is located over N(4). If the absolute configuration of the mce group is *S*, as indicated by broken lines in Fig. 5, the methyl of mce group comes close to N(2), which is above the mean plane, giving rise to the strong steric repulsion. It is plausible that the σ-complex containing the *S*-mce group is less stable energetically than that having *R*-mce group, if the asymmetric amine has *R* configuration. We propose that this is one of the factors inducing asymmetry in the step of σ-bond formation of this hydrogenation reaction. This hypothesis, however, is based on the assumption that the *S*-mce group does not change seriously.

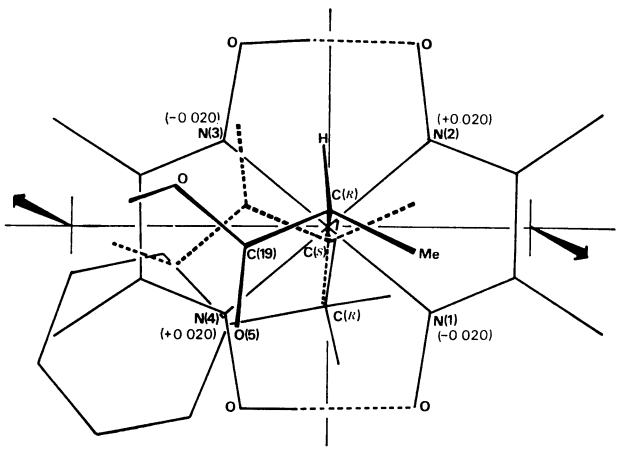

Fig. 5. A presumed conformation of σ-complex containing *S*-mce group (broken lines). The deviations of four nitrogen atoms from the mean plane are in parentheses.

As regards the mechanism of Co–C bond cleavage, the absolute configuration of the mce group was determined to be *R* by an anomalous dispersion method. The reaction product of (+)-methyl propionate-2-*d*, which was obtained by deuterogenation of this complex, was determined to have *S* configuration from the specific rotation.[6] It is, therefore, concluded that the Co–C bond cleavage proceeds mainly through inversion of configuration at the carbon atom.

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