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Structural Studies of Asymmetric Hydrogenation. V. The Crystal Structures of [(*S*)-1-Cyanoethyl][(*S*)(−)-*α*-methylbenzylamine]-bis(dimethylglyoximato)cobalt(III) at 293 K and 173 K

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The structure of [(*S*)-1-cyanoethyl][(*S*)(−)-α-methylbenzylamine]bis(dimethylglyoximato)cobalt(III) has been determined by X-ray analysis at 293 K and 173 K. The crystal is monoclinic, the space group being $P2_1$, $Z=2$, with $a=8.768(2)$, $b=13.356(2)$, $c=9.538(3)$ Å, and $\beta=96.73(3)°$ at 293 K, and $a=8.617(4)$, $b=13.222(4)$, $c=9.517(7)$ Å, and $\beta=96.26(7)°$ at 173 K. The structure was deduced by the heavy-atom method and was refined by the block-diagonal least-squares method to the final *R* values of 0.051 and 0.060 for 1878 and 1848 observed reflections at 293 K and 173 K respectively. The bis(dimethylglyoximato)cobalt moiety is twisted in the opposite way from that of [(*R*)-1-cyanoethyl][(*S*)(−)-α-methylbenzylamine]bis(dimethylglyoximato)cobalt(III). This supports the proposal that the asymmetry of the optically active amine is transferred into the substrate through the twist of the bis(dimethylglyoximato)cobalt moiety in the step of the σ-bond formation.

The serial crystal structures of the cobalt complexes have been determined by X-ray analysis[1–4] in order to clarify the mechanism of inducing asymmetry in the asymmetric hydrogenation of olefins.[5–10] In the crystal structures of [(*R*)-1-(methoxycarbonyl)ethyl][(*R*)(+)-α-methylbenzylamine]bis(dimethylglyoximato)cobalt(III)[3] and [(*R*)-1-cyanoethyl][(*S*)(−)-α-methylbenzylamine]bis(dimethylglyoximato)cobalt(III)[4] (hereafter abbreviated as the R-R ester complex and the R-S cyano complex respectively), it has been shown that the bis(dimethylglyoximato)cobalt moiety (hereafter abbreviated as $Co(dmg)_2$ or cobaloxime) is twisted around its long axis because of the steric repulsion from the substituted alkyl group and α-methylbenzylamine. To examine the twisting of the $Co(dmg)_2$ moiety more closely, we attempted to determine the structure of the title complex, the S-S cyano complex, the only change from the R-S cyano complex in the previous paper being the inversion of the absolute configuration of the cyanoethyl group.

Preliminary experiments revealed that the crystalline-state racemization of the cyanoethyl group also occurs and that the thermal expansion of the crystal is abnormally anisotropic.[11] Therefore, the crystal structures at 293 K and 173 K were determined.

Experimental

Dark red, plate-like crystals of the S-S cyano complex, whose preparation will be reported in detail elsewhere, were obtained from the mother liquor after the fractional precipitation of the R-S cyano complex had been carried out from a solution containing the cyano complex with the racemic cyanoethyl group. A crystal 0.20×0.25×0.45 mm³ in size was placed in a Rigaku four-circle diffractometer, Mo *Kα* radiation monochromated by graphite ($\lambda=0.71069$ Å) being used. The unit-cell dimensions were obtained by the least-squares method with 15 high-angle reflections ($2\theta>20°$). Their values before and after the intensity data collection are shown in Table 1. The average values in the last column were used in this work. The crystal data are summarized in Table 2. The intensity data were collected in the same manner as that used for the R-S cyano complex.[4] A total of 1878 independent reflections, $|F_0|\geqq 3\sigma(|F_0|)$, were obtained.

Table 1. The change in the unit-cell dimensions

	Start 1[a]	Start 2[b]	End[c]	Average[d]
a	8.768 (2) Å	8.768 (2)	8.774 (2)	8.771
b	13.356 (2) Å	13.380 (2)	13.427 (2)	13.404
c	9.538 (3) Å	9.533 (3)	9.520 (3)	9.527
β	96.73 (3)°	96.85 (3)	97.05 (4)	96.95
V	1109.2 (5) Å³	1110.4 (5)	1113.1 (5)	1111.8

a) 2 h after the initiation of the X-ray irradiation. The data collection was unsuccessful because the change was so fast. b) After 4 h, at which time the data collection was started. c) After the data collection, about 30 h later. d) The average values between Columns 2 and 3. The structure factors and bond distances and angles are calculated using these values.

Table 2. Crystal data

Formula	$C_3H_4NC_8H_{11}N(C_4H_7N_2O_2)Co$	
F.W.	464.48	
a	8.768(2) Å (293 K)	8.617(4) Å (173 K)
b	13.356(2)	13.222(4)
c	9.538(3)	9.517(7)
β	96.73(3)°	96.26(7)°
V	1109.2(5) Å³	1077.9(10) Å³
Systematic absences	0*k*0; *k* odd	
Space group	$P2_1$	
Z	2	
D_m	1.396 g/cm³	
D_c	1.391 g/cm³	
μ(Mo *Kα*)	8.79 cm⁻¹	

The experimental details at 173 K, using a crystal 0.15×0.15×0.59 mm³ in size, were the same as those for the R-S cyano complex. 1848 independent reflections, $|F_0|\geqq 3\sigma(|F_0|)$, were obtained. Corrections for Lorentz and polarization factors were made, but no correction for absorption was applied.

Structure Determination

The structure at 293 K was deduced by the heavy-atom method and refined by the block-diagonal least-

Table 3. Fractional coordinates, with their standard deviations, multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the hydrogen atoms at 293 K

Atom	*x*	*y*	*z*
Co	125(1)	2500(0)	2655(1)
N(1)	14(6)	2819(4)	4571(5)
N(2)	1784(5)	3392(4)	2941(5)
N(3)	265(5)	2177(4)	746(5)
N(4)	−1560(6)	1609(4)	2369(5)
O(1)	−1103(5)	2475(5)	5294(4)
O(2)	2589(5)	3673(4)	1885(4)
O(3)	1299(5)	2592(5)	−7(4)
O(4)	−2465(5)	1425(4)	3361(4)
C(1)	1061(7)	3412(5)	5171(6)
C(2)	2107(7)	3771(5)	4206(6)
C(3)	−739(7)	1528(5)	145(7)
C(4)	−1806(7)	1192(5)	1122(7)
C(5)	1159(9)	3723(6)	6696(7)
C(6)	3353(8)	4528(6)	4576(8)
C(7)	−779(10)	1209(6)	−1343(7)
C(8)	−3078(9)	465(6)	703(8)
N(5)	−1170(5)	3742(4)	2070(5)
C(9)	−2862(7)	3752(6)	1669(7)
C(10)	−3524(8)	4773(7)	1893(8)
C(11)	−3357(7)	3414(5)	173(6)
C(12)	−2624(8)	3713(7)	−963(7)
C(13)	−3157(10)	3446(8)	−2310(8)
C(14)	−4439(10)	2845(7)	−2555(9)
C(15)	−5175(8)	2559(8)	−1471(8)
C(16)	−4641(8)	2810(5)	−100(8)
C(17)	1521(8)	1283(5)	3212(7)
C(19)	1117(8)	826(5)	4459(7)
N(6)	821(8)	430(5)	5469(7)
C(18)	3213(9)	1410(7)	3200(11)
H(01)	−181(9)	171(7)	480(8)
H(02)	196(7)	292(4)	63(6)
H(51)	198(8)	336(6)	725(7)
H(52)	47(8)	338(6)	704(7)
H(53)	132(8)	448(6)	681(7)
H(61)	427(8)	412(6)	483(8)
H(62)	355(9)	511(7)	381(8)
H(63)	304(10)	496(8)	523(9)
H(71)	28(7)	111(5)	−149(6)
H(72)	−144(8)	172(6)	−190(7)
H(73)	−130(9)	49(6)	−157(7)
H(81)	−364(7)	57(5)	−21(6)
H(82)	−375(8)	36(5)	138(7)
H(83)	−272(6)	−25(5)	72(6)
H(N51)	−103(7)	407(5)	280(6)
H(N52)	−87(6)	406(4)	132(6)
H(9)	−340(6)	324(4)	235(5)
H(101)	−330(7)	495(5)	284(6)
H(102)	−465(7)	490(6)	168(6)
H(103)	−319(11)	535(8)	124(9)
H(12)	−182(6)	414(4)	−90(6)
H(13)	−266(8)	372(6)	−304(8)
H(14)	−468(6)	273(5)	−345(6)
H(15)	−606(7)	211(5)	−168(6)
H(16)	−513(8)	259(7)	71(7)
H(17)	146(9)	79(6)	246(7)
H(181)	390(10)	67(7)	343(8)
H(182)	349(11)	200(7)	409(9)
H(183)	350(10)	151(8)	227(9)

Table 4. Fractional coordinates, with their standard deviations, multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the hydrogen atoms at 173 K

Atom	*x*	*y*	*z*
Co	168(1)	2500(0)	2656(1)
N(1)	50(8)	2814(5)	4571(6)
N(2)	1878(7)	3405(4)	2908(6)
N(3)	311(7)	2168(5)	744(6)
N(4)	−1538(7)	1608(5)	2392(7)
O(1)	−1097(5)	2467(6)	5317(5)
O(2)	2688(6)	3687(4)	1860(5)
O(3)	1367(6)	2585(6)	−22(5)
O(4)	−2466(6)	1428(4)	3395(6)
C(1)	1134(9)	3422(6)	5162(8)
C(2)	2169(9)	3774(7)	4176(8)
C(3)	−709(9)	1517(6)	142(8)
C(4)	−1815(10)	1185(6)	1141(8)
C(5)	1244(10)	3727(7)	6669(8)
C(6)	3450(11)	4539(7)	4519(10)
C(7)	−746(12)	1183(7)	−1333(9)
C(8)	−3085(10)	454(7)	741(9)
N(5)	−1143(7)	3771(5)	2088(7)
C(9)	−2888(9)	3752(6)	1669(8)
C(10)	−3560(10)	4793(7)	1887(9)
C(11)	−3295(9)	3418(7)	139(8)
C(12)	−2540(11)	3790(8)	−956(10)
C(13)	−3006(10)	3555(8)	−2352(10)
C(14)	−4268(11)	2916(8)	−2637(10)
C(15)	−5070(9)	2566(10)	−1568(9)
C(16)	−4597(9)	2807(6)	−160(9)
C(17)	1560(10)	1266(7)	3195(8)
C(19)	1131(10)	805(7)	4456(9)
N(6)	815(9)	421(6)	5479(7)
C(18)	3289(12)	1415(9)	3258(13)
H(01)	−189(13)	193(9)	457(12)
H(02)	232(13)	314(9)	84(11)
H(51)	216(8)	357(6)	707(7)
H(52)	69(9)	333(6)	721(8)
H(53)	137(9)	439(7)	682(9)
H(61)	442(11)	434(8)	477(11)
H(62)	378(10)	498(7)	374(9)
H(63)	330(9)	497(6)	505(8)
H(71)	30(8)	108(5)	−159(7)
H(72)	−116(10)	162(7)	−201(9)
H(73)	−145(14)	58(10)	−169(12)
H(81)	−372(9)	61(6)	−11(8)
H(82)	−373(8)	39(5)	138(7)
H(83)	−278(11)	−24(7)	73(10)
H(N51)	−101(9)	421(6)	275(8)
H(N52)	−77(9)	405(6)	124(8)
H(9)	−341(9)	330(6)	222(8)
H(101)	−324(10)	498(7)	287(9)
H(102)	−482(9)	493(6)	162(8)
H(103)	−314(8)	533(6)	128(8)
H(12)	−177(8)	425(5)	−72(7)
H(13)	−243(8)	377(6)	−325(7)
H(14)	−464(9)	270(7)	−354(8)
H(15)	−579(10)	223(7)	−181(9)
H(16)	−515(8)	268(6)	55(7)
H(17)	180(12)	75(8)	233(10)
H(181)	405(15)	69(10)	349(13)
H(182)	352(11)	177(8)	426(10)
H(183)	357(9)	176(7)	226(9)

squares method. All the hydrogen atoms were found on a difference map. The final refinement was made with the anisotropic and isotropic temperature factors for non-hydrogen and hydrogen atoms respectively. The weighting scheme employed was: $w=0.2$ if $|F_0|>96.91$ and $|F_0|<9.69$ and $w=(0.00211F_0^2-0.22423|F_0|+6.97531)^{-1}$ if $9.69\leqq|F_0|\leqq96.91$. The final R value became 0.051 for 1878 reflections. No peaks higher than 0.30 eÅ^{-3}, except for a peak of 0.45 eÅ^{-3} around the cobalt atom, were found on the final difference map.

The structure at 173 K was refined by the block-diagonal least-squares method using the parameters of the structure at 293 K as the starting parameters. The weighting scheme employed was: $w=0.2$ if $|F_0|>154.32$ and $|F_0|<15.43$ and $w=(0.00117F_0^2-0.19947|F_0|+9.46501)^{-1}$ if $15.43\leqq|F_0|\leqq154.32$. The final R value became 0.060 for 1848 reflections. No peaks higher than 0.45 eÅ^{-3}, except for peaks of 0.55 eÅ^{-3} around the cobalt atom, were found on the final difference map. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[12] The final atomic coordinates and their standard deviations at 293 K and 173 K are given in Tables 3 and 4 respectively. Lists of the thermal parameters and the observed and calculated structure factors are kept in the Office of the Chemical Society of Japan (Document No. 8018). The computation was done on M-180 and M-160 computers at this Institute.

Description of the Structure

The equations of the mean planes for four nitrogen atoms and two dmg's are given in Table 5, together with the deviations of the atoms from the planes. The deviations are in good agreement between the two temperatures. The projection of the structure at 293 K on the plane (I) is shown in Fig. 1, in which the short contacts between the non-bonded atoms are also given. In Table 6, the short contacts at 173 K are compared with the corresponding ones at 293 K. The cyano and methyl groups are located over the gaps between the two dmg's. Such a conformation of the cyanoethyl group is also found in the R-S cyano complex,[4] although the locations of the methyl and cyano groups are exchanged because of the opposite configuration at C(17).

The four nitrogen atoms of Co(dmg)$_2$ are nearly coplanar, but the tetragon composed of them is slightly twisted in the opposite way from that of the R-S cyano complex. The twisting of the Co(dmg)$_2$ moiety will be discussed in detail in the following section. The diviation of the cobalt atom from the mean plane of Co(dmg)$_2$ is negligibly small. The oxygen atoms deviate downward to avoid the short contacts with the cyanoethyl group, whereas the carbon atoms deviate upward. These features are also observed in the R-S cyano complex.

The bond distances at 293 K are shown in Fig. 2, while they are compared with the corresponding ones at 173 K in Table 7. The bond angles at both temperatures are listed in Table 8. The Co–C(17) and Co–N(5) bonds at 293 K are longer by 0.011 Å, and shorter by 0.010 Å, respectively, than the corresponding ones at 173 K. This causes an increase in the bond angles of C(19)–C(17)–C(18) and Co–N(5)–C(9) at high temperatures. Considerable differences in the bond of N(5)–C(9) and the angle of N(2)–Co–C(17) are found

Table 5. Least-squares planes and deviations (l/Å) for equatorial ligands

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

(I) Co(dmg)$_2$ plane (293 K): $0.5806X-0.7619Y+0.2872Z+1.9444=0.$
(I′) Co(dmg)$_2$ plane (173 K): $0.5810X-0.7642Y+0.2802Z+1.8934=0.$
(II) dmg plane (293 K): $0.5741X-0.7783Y+0.2543Z+2.1319=0.$
(II′) dmg plane (173 K): $0.5765X-0.7789Y+0.2467Z+2.0748=0.$
(III) dmg plane (293 K): $0.5885X-0.7456Y+0.3126Z+1.8715=0.$
(III′) dmg plane (173 K): $0.5835X-0.7537Y+0.3023Z+1.8364=0.$

	(I)	(I′)	(II)	(II′)	(III)	(III′)
Co	−0.002	−0.005	0.049	0.044	0.042	0.028
N (1)	0.009[a]	0.011[a]	−0.005[a]	−0.006[a]		
N (2)	−0.009[a]	−0.011[a]	0.005[a]	0.006[a]		
N (3)	0.009[a]	0.011[a]			0.002[a]	−0.000[a]
N (4)	−0.009[a]	−0.011[a]			−0.002[a]	0.000[a]
O (1)	−0.062	−0.059	−0.083	−0.088		
O (2)	−0.103	−0.105	−0.069	−0.065		
O (3)	−0.042	−0.039			−0.050	−0.058
O (4)	−0.078	−0.089			−0.059	−0.062
C (1)	0.059	0.061	0.008[a]	0.010[a]		
C (2)	0.027	0.021	−0.008[a]	−0.010[a]		
C (3)	0.038	0.035			−0.004[a]	0.000[a]
C (4)	0.037	0.021			0.004[a]	−0.000[a]
C (5)	0.103	0.117	−0.001	0.012		
C (6)	−0.036	−0.040	−0.107	−0.102		
C (7)	0.039	0.052			−0.044	−0.018
C (8)	0.046	0.042			−0.022	−0.001

a) Atoms included in the least-squares calculation.

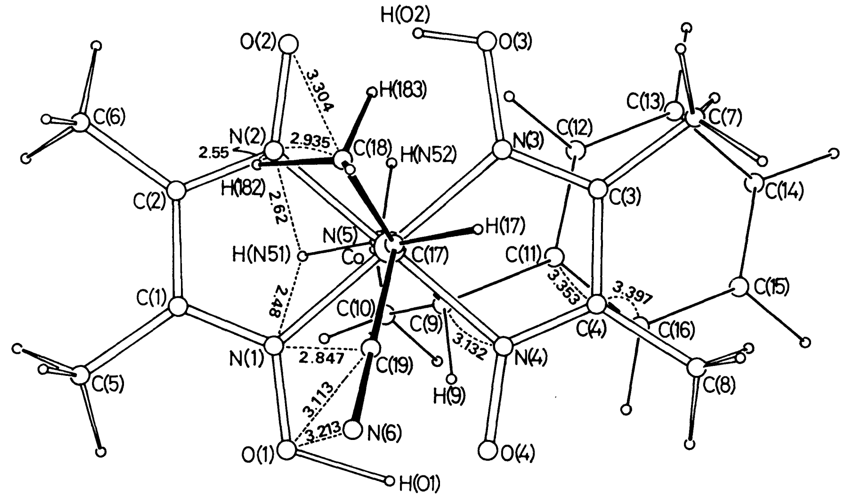

Fig. 1. Projection of the complex onto the mean plane of four nitrogen atoms of Co(dmg)$_2$ and the short contacts between non-bonded atoms (l/Å) at 293 K, their threshold values being 3.400 Å for the distances between the non-hydrogen atoms and 2.70 Å for those including hydrogen atoms.

TABLE 6. SHORT CONTACTS BETWEEN THE NON-BONDED ATOMS (l/Å)

	293 K	173 K
N (1) ··· C (19)	2.847 (9)	2.822 (11)
N (1) ··· N (6)	3.368 (9)	3.327 (11)
N (1) ··· H (N51)	2.48 (6)	2.63 (8)
N (2) ··· C (18)	2.934 (12)	2.902 (14)
N (2) ··· H (N51)	2.62 (6)	2.70 (8)
N (2) ··· H (182)	2.55 (10)	2.81 (10)
N (4) ··· C (9)	3.132 (9)	3.113 (10)
N (4) ··· C (19)	3.074 (9)	3.048 (11)
O (1) ··· C (19)	3.112 (10)	3.086 (12)
O (1) ··· N (6)	3.213 (10)	3.162 (11)
O (2) ··· C (18)	3.303 (12)	3.304 (14)
O (4) ··· C (19)	3.288 (9)	3.259 (11)
C (4) ··· C (11)	3.353 (9)	3.315 (12)
C (4) ··· C (16)	3.397 (10)	3.352 (12)

between 293 K and 173 K. These differences may be due to the positional changes of the C(17) and N(5) atoms. The other corresponding distances and angles are in good agreement with each other.

The Co(dmg)$_2$ moiety in the methyl[(R)(+)-α-methylbenzylamine]cobaloxime, methyl complex, has the C_{2h} symmetry as a result of the steric repulsion from the amine ligand.[2] For the R-R ester complex, the symmetry of C_{2h} holds good with regard to the bond lengths of N–C and C–CH_3 and three angles around the *endo*-cyclic carbon atoms in the Co(dmg)$_2$ moiety. Such a symmetry is no longer conserved for the two cyano complexes, however. This may indicate that the steric and electrostatic interactions between Co(dmg)$_2$ and the substituted alkyl group in the cyano complexes are stronger than those in the methyl and R-R ester complexes.

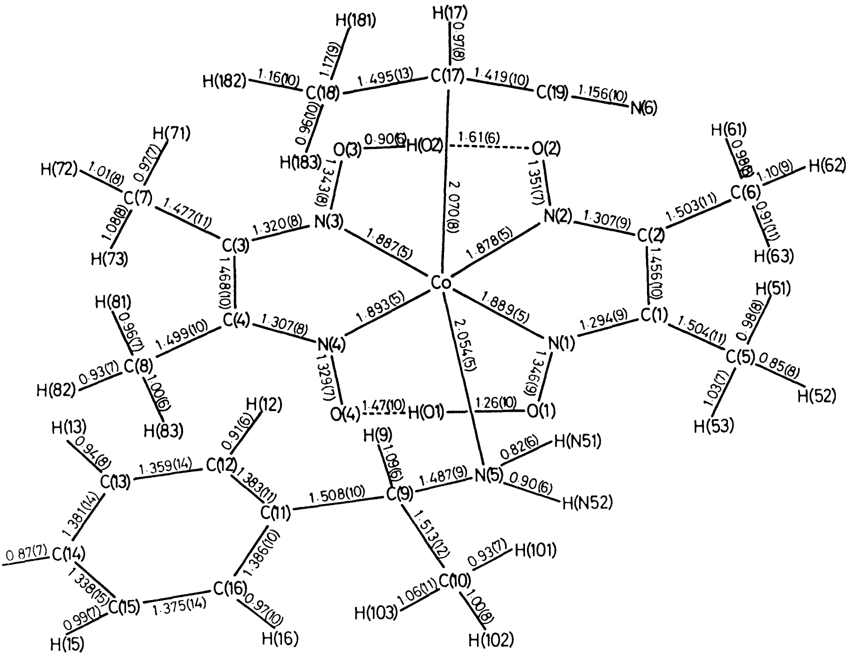

Fig. 2. Bond distances (l/Å) at 293 K. Their standard deviations are in parentheses.

Table 7. Bond distances (l/Å)
Esd's are in parentheses.

	293 K	173 K
Co–N(1)	1.889(5)	1.883(7)
Co–N(2)	1.878(5)	1.893(6)
Co–N(3)	1.887(5)	1.890(6)
Co–N(4)	1.893(5)	1.879(7)
Co–N(5)	2.054(5)	2.064(7)
Co–C(17)	2.070(8)	2.059(9)
N(1)–O(1)	1.346(9)	1.357(11)
N(1)–C(1)	1.294(9)	1.312(11)
N(2)–O(2)	1.351(7)	1.331(9)
N(2)–C(2)	1.307(9)	1.301(11)
N(3)–O(3)	1.343(8)	1.345(10)
N(3)–C(3)	1.320(8)	1.316(10)
N(4)–O(4)	1.329(7)	1.332(9)
N(4)–C(4)	1.307(8)	1.313(11)
C(1)–C(2)	1.456(10)	1.440(12)
C(1)–C(5)	1.504(11)	1.483(13)
C(2)–C(6)	1.503(11)	1.507(13)
C(3)–C(4)	1.468(10)	1.484(12)
C(3)–C(7)	1.477(11)	1.470(13)
C(4)–C(8)	1.499(10)	1.478(13)
N(5)–C(9)	1.487(9)	1.513(10)
C(9)–C(10)	1.513(12)	1.516(12)
C(9)–C(11)	1.508(10)	1.526(12)
C(11)–C(12)	1.383(11)	1.378(14)
C(11)–C(16)	1.386(10)	1.387(12)
C(12)–C(13)	1.359(14)	1.381(15)
C(13)–C(14)	1.381(14)	1.380(15)
C(14)–C(15)	1.338(15)	1.372(16)
C(15)–C(16)	1.375(14)	1.394(15)
C(17)–C(18)	1.495(13)	1.498(15)
C(17)–C(19)	1.419(10)	1.431(13)
C(19)–N(6)	1.156(10)	1.156(12)
O(1)–H(01)	1.26(10)	1.37(12)
O(2)–H(02)	1.61(6)	1.23(12)
O(3)–H(02)	0.90(6)	1.32(12)
O(4)–H(01)	1.47(10)	1.35(12)
C(5)–H(51)	0.98(8)	0.87(8)
C(5)–H(52)	0.85(8)	0.91(8)
C(5)–H(53)	1.03(7)	0.90(9)
C(6)–H(61)	0.98(8)	0.89(11)
C(6)–H(62)	1.10(9)	1.01(10)
C(6)–H(63)	0.91(11)	0.78(8)
C(7)–H(71)	0.97(7)	0.97(7)
C(7)–H(72)	1.01(8)	0.91(9)
C(7)–H(73)	1.08(8)	1.04(13)
C(8)–H(81)	0.96(7)	0.95(8)
C(8)–H(82)	0.93(7)	0.87(7)
C(8)–H(83)	1.00(6)	0.95(10)
N(5)–H(N51)	0.82(6)	0.86(8)
N(5)–H(N52)	0.90(6)	0.98(8)
C(9)–H(9)	1.09(6)	0.94(8)
C(10)–H(101)	0.93(7)	0.98(9)
C(10)–H(102)	1.00(8)	1.10(8)
C(10)–H(103)	1.06(11)	1.01(8)
C(12)–H(12)	0.91(6)	0.91(7)
C(13)–H(13)	0.94(8)	1.07(7)
C(14)–H(14)	0.87(7)	0.93(10)
C(15)–H(15)	0.99(7)	0.78(10)
C(16)–H(16)	0.97(10)	0.88(8)
C(17)–H(17)	0.97(8)	1.10(11)
C(18)–H(181)	1.17(9)	1.16(13)
C(18)–H(182)	1.16(10)	1.06(10)
C(18)–H(183)	0.96(10)	1.10(9)

The crystal structure viewed along the c axis is shown in Fig. 3, in which the short contacts are also given. There is a weak hydrogen bond between N(5) and N(6) in the unit of ($-x$, $0.5+y$, $1-z$). The N···N distances are 3.246 and 3.171 Å for 293 and 173 K respectively. The distance of H(N51)···N(6) and the angle of N(5)–H(N51)···N(6) are 2.45 Å and 164° for 293 K, and 2.32 Å and 177° for 173 K. Such a hydrogen bond is also observed in the crystal of the R-S cyano complex. The other contacts are not unusually short.

Discussion

In Part III of this series, concerning the structure of the R-R ester complex, we proposed that the twisting of the Co(dmg)$_2$ moiety, caused by the steric repulsion from the methoxycarbonylethyl group and the amine, is one of the factors inducing asymmetry in the step of σ-bond formation.[3] This proposal must now be examined in connection with the R-S and S-S cyano complexes.

In Table 9, the deviations of the atoms in the Co(dmg)$_2$ moiety from the mean plane composed of four nitrogen atoms and the bond distances of Co–C(17) and Co–N(5) are listed for the complexes determined in this serial study. (The *exo*-cyclic atoms are omitted for the sake of clarity.) For the cyano complexes, the values at both room and low temperatures are given, because they change considerably with the temperature. As the absolute configurations of α-methylbenzylamine are different between the cyano complexes and the other two, the latter complexes are replaced by their enantiomers in the following discussion. Figure 4 shows the structures and the numberings of the atoms for the S-S (enantiomer of R-R) ester and the R-S cyano complexes. The amine is located below the Co(dmg)$_2$ plane, whereas the methyl and the substituted alkyl groups are placed above.

The tetragons, composed of four nitrogen atoms in the S-S ester and R-S cyano (293 K) complexes, are twisted in the same manner. Moreover, the magnitude of the twisting is equal. The tetragon in the S-S cyano (293 K) complex, on the other hand, is twisted in the opposite way, and the magnitude of the twisting is smaller than those of the S-S ester and R-S cyano (293 K) complexes. The methyl of the substituted alkyl group comes close to N(1) in the two structures of S-S ester and R-S cyano complexes. The unusually short contact between the methyl group and N(1) causes N(1) to deviate downward from the plane. The deviation of N(1) from the plane brings about the twist of the tetragon in such a manner that N(3) deviates downward, too, and N(2) and N(4), upward, the cobalt atom being fixed as a center. This twisting is called "clockwise twisting" for the S amine, viewed down along the axis perpendicular to the mean plane of Co(dmg)$_2$. In Fig. 5, the "clockwise twisting" is drawn schematically, the arrows being directed from the lower nitrogen atom to the upper one in each dmg. Although the twisting was defined in the previous paper as the distortion around the long axis of Co(dmg)$_2$, the above notation is more convenient, since the substrate should approach

Table 8. Bond angles (ϕ/°)

Esd's are in parentheses. Angles including methyl and phenyl hydrogen atoms are omitted.

	(293 K)	(173 K)
N(1)–Co–N(2)	81.1(2)	82.1(3)
N(1)–Co–N(3)	179.2(2)	179.1(3)
N(1)–Co–N(4)	98.7(2)	98.3(3)
N(1)–Co–N(5)	89.3(2)	89.3(3)
N(1)–Co–C(17)	91.6(3)	91.4(3)
N(2)–Co–N(3)	98.4(2)	97.9(3)
N(2)–Co–N(4)	179.5(2)	179.5(3)
N(2)–Co–N(5)	85.3(2)	85.1(3)
N(2)–Co–C(17)	87.8(3)	92.6(3)
N(3)–Co–N(4)	81.8(2)	81.8(3)
N(3)–Co–N(5)	91.3(2)	91.6(3)
N(3)–Co–C(17)	87.8(3)	87.6(3)
N(4)–Co–N(5)	94.3(2)	94.5(3)
N(4)–Co–C(17)	88.1(3)	87.8(3)
N(5)–Co–C(17)	177.2(3)	177.4(3)
Co–N(1)–O(1)	122.9(5)	123.4(6)
Co–N(1)–C(1)	116.7(5)	116.0(6)
O(1)–N(1)–C(1)	120.5(6)	120.6(7)
Co–N(2)–O(2)	122.3(4)	123.2(5)
Co–N(2)–C(2)	117.3(5)	115.0(6)
O(2)–N(2)–C(2)	120.3(6)	121.7(7)
Co–N(3)–O(3)	123.2(4)	123.1(5)
Co–N(3)–C(3)	116.8(4)	117.4(5)
O(3)–N(3)–C(3)	120.0(6)	119.5(7)
Co–N(4)–O(4)	122.5(4)	122.5(5)
Co–N(4)–C(4)	116.2(5)	116.8(6)
O(4)–N(4)–C(4)	121.3(5)	120.6(7)
N(1)–C(1)–C(2)	113.1(6)	112.5(7)
N(1)–C(1)–C(5)	123.4(7)	123.2(8)
C(2)–C(1)–C(5)	123.5(7)	124.3(8)
N(2)–C(2)–C(1)	111.8(6)	114.4(8)
N(2)–C(2)–C(6)	123.3(7)	121.0(8)
C(1)–C(2)–C(6)	124.8(7)	124.5(8)
N(3)–C(3)–C(4)	111.8(6)	111.1(7)
N(3)–C(3)–C(7)	123.0(6)	123.8(8)
C(4)–C(3)–C(7)	125.2(6)	125.1(8)
N(4)–C(4)–C(3)	113.4(6)	112.8(7)
N(4)–C(4)–C(8)	123.8(6)	124.6(8)
C(3)–C(4)–C(8)	122.8(6)	122.5(8)
Co–N(5)–C(9)	125.4(4)	123.7(5)
N(5)–C(9)–C(10)	111.1(6)	109.4(7)
N(5)–C(9)–C(11)	113.9(6)	112.0(6)
C(9)–C(11)–C(12)	123.0(7)	122.7(8)
C(9)–C(11)–C(16)	119.2(6)	117.5(7)
C(12)–C(11)–C(16)	117.8(7)	119.4(8)
C(11)–C(12)–C(13)	121.6(9)	122.4(10)
C(12)–C(13)–C(14)	119.5(10)	117.9(10)
C(13)–C(14)–C(15)	119.7(9)	120.7(10)
C(14)–C(15)–C(16)	121.5(10)	121.2(11)
C(11)–C(16)–C(15)	119.8(8)	118.4(9)
Co–C(17)–C(18)	117.7(6)	117.2(7)
Co–C(17)–C(19)	110.8(5)	110.5(6)
C(18)–C(17)–C(19)	113.8(7)	111.7(8)
C(17)–C(19)–N(6)	177.8(8)	178.5(10)
N(1)–O(1)–H(O1)	116(4)	107(6)
N(2)–O(2)–H(O2)	102(2)	108(5)
N(3)–O(3)–H(O2)	105(4)	108(5)
N(4)–O(4)–H(O1)	115(4)	108(5)
O(1)–H(O1)–O(4)	133(7)	160(11)
O(2)–H(O2)–O(3)	160(6)	156(10)
Co–N(5)–H(N51)	101(4)	110(5)
Co–N(5)–H(N52)	113(4)	108(5)
C(9)–N(5)–H(N51)	105(4)	105(5)
C(9)–N(5)–H(N52)	100(4)	101(5)
H(N51)–N(5)–H(N52)	113(6)	109(7)
N(5)–C(9)–H(9)	109(3)	113(5)
C(10)–C(9)–H(9)	106(3)	107(5)
C(11)–C(9)–H(9)	106(3)	106(5)
Co–C(17)–H(17)	112(5)	117(6)
C(18)–C(17)–H(17)	92(5)	81(6)
C(19)–C(17)–H(17)	109(5)	117(6)

the Co atom along the axis perpendicular to the mean plane of Co(dmg)$_2$.

The asymmetric carbon atom, C(9), which comes most closely to Co(dmg)$_2$ among the atoms of the amine except for the coordinating amine group, comes near N(4). The steric repulsion between N(4) and C(9) should give rise to the twisting of the tetragon. The twisting is clockwise. In the two structures of the S-S ester and R-S cyano complexes, the steric repulsions of N(1)···C(18) and N(4)···C(9) result in the same twisting. On the other hand, the C(18) atom of the S-S cyano complex comes close to N(2). This causes a counterclockwise twisting of the tetragon. Because the repulsion of N(4)···C(9) would give a clockwise twisting, the Co(dmg)$_2$ moiety must have a more planar conformation than that of the R-S cyano complex. As the repulsion of N(2)···C(18) is stronger than that of N(4)···C(9), the tetragon shows the counterclockwise twisting.

The bond distance of Co–C(17) in the S-S cyano (293 K) complex is significantly longer than that of the R-S cyano (293 K) complex. Because the tetragon can not be twisted enough to avoid the short contact of N(2)···C(18), the Co–C(17) bond is lengthened. This may indicate that the strength of the Co–C bond is fairly weak.

At low temperatures, the Co–C(17) bonds in the R-S and S-S cyano complexes have the same distances, and the magnitude of the twisting in the R-S cyano complex becomes smaller than that at room temperature. As is shown in Table 10, the Co–C(sp^3) distance is lengthened with an increase in the number of the non-hydrogen substituents bonded to the coordinating carbon atom; that is, the Co–CH$_3$ and Co–CH$_2$R values are 2.00 and 2.04 Å respectively. As Table 10 shows, the Co–C(17) bond in the cyanoethyl complexes is estimated to have a distance between 2.04 and 2.067 Å, because the cyanoethyl group has two non-hydrogen substituents and the cyano and methyl groups are located over the gaps between two dmg's whereas the methoxycarbonyl

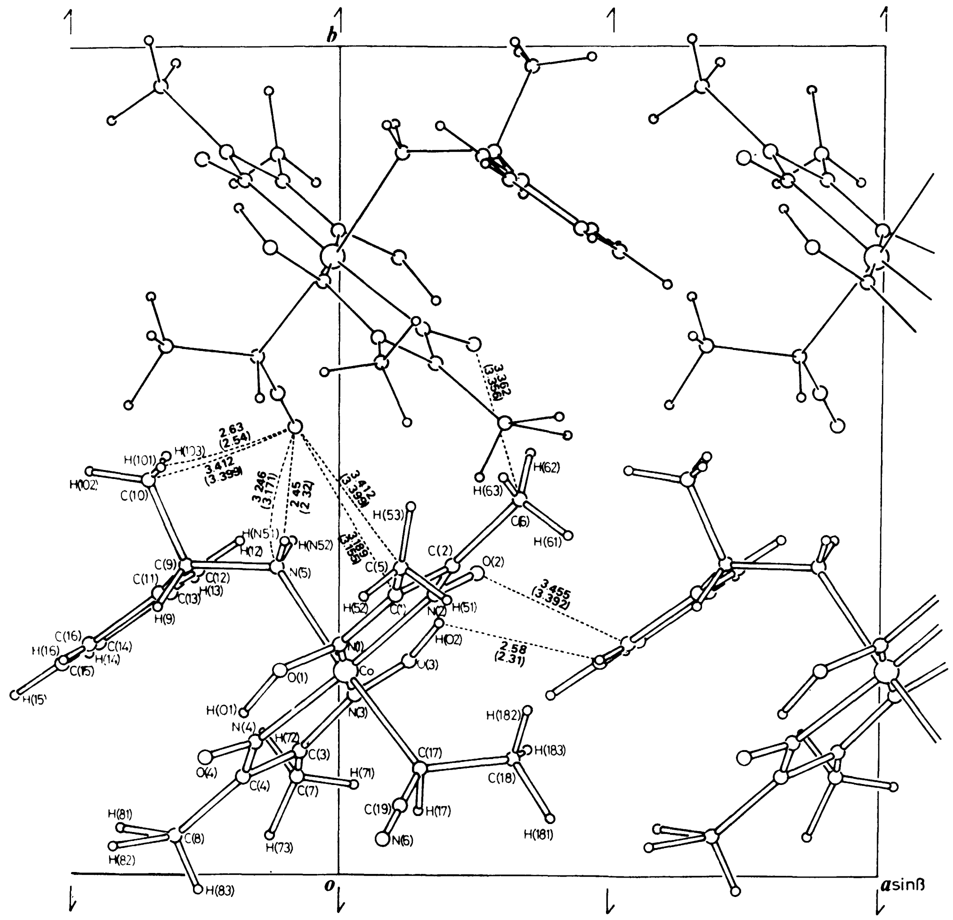

Fig. 3. Projection of the crystal structure along the c axis and the short contacts between complexes. The short contacts at 173 K are in parentheses.

TABLE 9. DEVIATIONS (l/Å) OF THE ATOMS FROM THE MEAN PLANE OF FOUR NITROGEN ATOMS, AND Co–C(17) AND Co–N(5) DISTANCES (l/Å), IN VARIOUS [SUBSTITUTED ALKYL] [α-METHYLBENZYLAMINE] COBALOXIMES

	Methyl	S-S ester[a]	R-S (293 K)	R-S (173 K)	S-S (293 K)	S-S (173 K)
Co	−0.04	0.041	0.008	0.003	−0.002	−0.005
N (1)	0.01	−0.020	−0.020	−0.014	0.009	0.011
N (2)	−0.01	0.020	0.020	0.014	−0.009	−0.011
N (3)	0.01	−0.020	−0.020	−0.014	0.009	0.011
N (4)	−0.01	0.020	0.020	0.014	−0.009	−0.011
C (1)	0.04	−0.178	0.029	0.033	0.059	0.061
C (2)	−0.03	−0.115	−0.007	0.019	0.027	0.021
C (3)	0.02	−0.113	0.003	0.012	0.038	0.035
C (4)	0.05	−0.089	0.107	0.053	0.037	0.021
Co–C (17)	1.988 (19)	2.067 (8)	2.036 (8)	2.056 (6)	2.070 (8)	2.057 (9)
Co–N (5)	2.089 (9)	2.066 (6)	2.088 (6)	2.070 (6)	2.054 (5)	2.064 (7)

a) The S-S ester is the enantiomer of the R-R ester complex.

and methyl groups in the S-S ester complex lie on the dmg rings. Therefore, the Co–C(17) distance of 2.057 Å at a low temperature seems to be a reasonable value. When the temperature is raised, the molecular packing in the crystal becomes loose and the strain in the molecule is released. For the R-S cyano complex, the tetragon composed of four nitrogen atoms is twisted to a greater extent and the Co–C bond becomes shorter, whereas the Co–C bond is lengthened for the S-S cyano complex. The abnormally anisotropic thermal expansion of the two cyano complexes may relate to the fact mentioned above. Because the reaction under investigation proceeds in solution, the conformation at room temperature may more closely resemble those in the intermediate state of the reaction.

It is noteworthy that the Co–N(5) bonds are altered

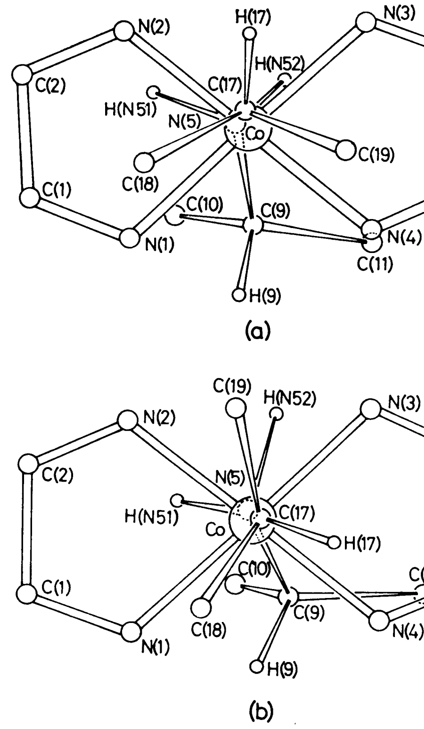

Fig. 4. Projections of the atoms around the Co atom onto the mean plane of four nitrogen atoms (a) for the S-S ester complex, the enantiomer of R-R,³⁾ and (b) for the R-S cyano complex.

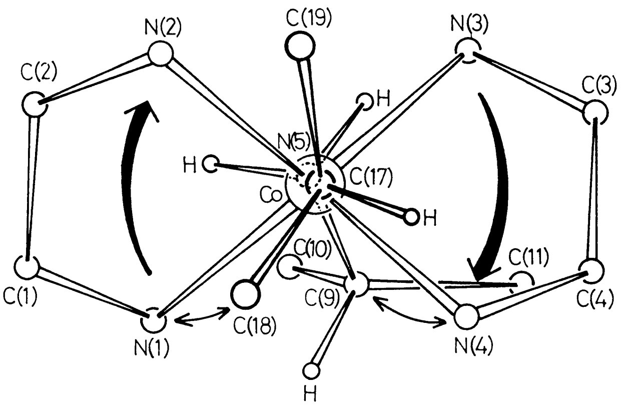

Fig. 5. Clockwise twisting of $Co(dmg)_2$ in the R-S cyano complex. The arrows are drawn from the lower nitrogen atoms to the upper ones in the Co-dmg rings. Such a twisting is brought about by the steric repulsions, N(1)···C(18) and N(4)···C(9).

in their lengths as the Co–C(17) distance in the cyano complexes is varied. All the sums of the Co–N(5) and Co–C(17) distances in both cyano complexes at low and room temperatures are nearly the same, the average value being 4.124 Å. This can be explained by the "trans influence" suggested by Brückner and Randaccio.¹⁶⁾

In summary, the tetragon of $Co(dmg)_2$ is twisted significantly and the Co–C bond is shortened for the R-S cyano complex, while the tetragon has a slightly twisted conformation and the Co–N bond is shortened for the S-S cyano complex. Table 11 shows the short interatomic distances between $Co(dmg)_2$ and the axial ligands for the two cyano complexes. Any distance of the R-S cyano complex is longer than the corresponding one of the S-S cyano complex. The repulsive energy of the former complex must be lower than that of the latter complex. The energy differences caused by the different lengths of the axial bonds, Co–C and Co–N, are considered to be compensated for the two cyano complexes, because the sums of the two bond distances are nearly the same.

Table 10. Co–C(sp^3) distances (l/Å) in various cobaloxime complexes

	Co–C distance	Ref.
$CH_3Co(dmg)_2(H_2O)$	1.990 (5)	13
$CH_3Co(dmg)_2(py)$	1.998 (5)	14
$CH_3Co(dmg)_2(nmeim)$	2.009 (7)	14
$CH_3Co(dmg)_2(mba)$	1.988 (19)	2
$(CH_2CO_2CH_3)Co(dmg)_2(py)$	2.04	15
$(CH_2CH_2CN)Co(dmg)_2(dphyea)$	2.04	1
$(CH(CH_3)CO_2CH_3)Co(dmg)_2(mba)$	2.067 (8)	3
$(CH(CH_3)CN)$- (293 K)	2.036 (8)	4
$Co(dmg)_2(mba)$ (173 K)	2.056 (6)	4
$(CH(CH_3)CN)$- (293 K)	2.070 (8)	present
$Co(dmg)_2(mba)$ (173 K)	2.057 (9)	present

py: pyridine, nmeim: 3-*N*-methylimidazole, dphyea: *erythro*-1,2-diphenyl-2-hydroxyethylamine, mba: α-methylbenzylamine.

Table 11. The short interatomic distances (l/Å) between $Co(dmg)_2$ and the axial ligands for the R-S and S-S cyano complexes

	R-S	S-S	Δ
C(9)···N(4)	3.176	3.132	0.044
C(18)···(N(1) or N(2))[a]	2.946	2.935	0.011
C(19)···(N(2) or N(1))[a]	2.863	2.847	0.016
C(19)···(O(2) or O(1))[a]	3.148	3.113	0.035
N(6)···(O(2) or O(1))[a]	3.284	3.212	0.071

a) The former atoms are for the R-S cyano complex, and the latter, for the S-S cyano complex.

In conclusion, the tetragon of the $Co(dmg)_2$ moiety is twisted because of the steric repulsion from the substituted alkyl group and the optically active amine. If the way of the twisting caused by the substituted alkyl group is in accord with that brought about by the amine, the tetragon is twisted and the steric repulsion between $Co(dmg)_2$ and the two axial ligands decreases. If both twistings are in the opposite way, on the other hand, the tetragon has a nearly planar conformation and the steric effect increases. The two σ-complexes have different repulsive energies, indicating that the two diastereomeric pathways in this reaction have different energies of activation in the "kinematically controlled asymmetric process."¹⁷⁾ This must be one of the factors inducing asymmetry in this asymmetric hydrogenation.

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