March, 1980] © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 627—634 (1980) 627

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

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(Received August 20, 1979)

The structure of [(*R*)-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 is $P2_1$; $Z=2$, with $a=8.665(2)$, $b=13.485(3)$, $c=9.584(3)$ Å and $\beta=96.95(3)°$ at 293 K, and $a=8.786(2)$, $b=13.500(2)$, $c=9.243(2)$ Å, and $\beta=98.09(3)°$ at 173 K. The structures were deduced by the heavy-atom method and refined by the block-diagonal least-squares technique to the final *R* values of 0.055 and 0.038 for 1940 and 1948 observed reflections at 293 K and 173 K respectively. The bis(dimethylglyoximato)cobalt moiety is twisted around its long axis because of the steric repulsion from the (*R*)-1-cyanoethyl group and the optically active amine. The degree of the twist is the same as that observed in the structure of [(*R*)-1-(methoxycarbonyl)ethyl][(*R*)(+)-*α*-methylbenzylamine]bis(dimethylglyoximato)cobalt(III). The conformation of the amine ligand was ascertained to be influenced by the substituted alkyl group through the bis(dimethylglyoximato)cobalt moiety.

The complexes of bis(dimethylglyoximato)cobalt (abbreviated to $Co(dmg)_2$ or cobaloxime) and optically active amine catalyze the asymmetric hydrogenation of olefins.[1–6] In order to clarify the mechanism of inducing the asymmetry, several crystal structures of related complexes have been determined by X-ray analysis.[7–9] In Part III of this series on the crystal structure of [(*R*)-1-(methoxycarbonyl)ethyl] [(*R*)(+)-*α*-methylbenzylamine] bis (dimethylglyoximato) cobalt(III) (abbreviated to the R–R ester complex), it has been shown that the $Co(dmg)_2$ plane is twisted around its long axis because of the steric repulsion from the (*R*)-1-(methoxycarbonyl)ethyl group and the optically active amine, *α*-methylbenzylamine.[9] We proposed in that paper that the twist is one of the factors inducing asymmetry in the reaction step of *σ*-bond formation.

To examine whether or not the twist exists in other complexes, we have determined the crystal structure of the title complex, the R–S cyano complex, in which the methoxycarbonyl group is replaced by the cyano group. Preliminary experiments revealed that the crystal changes its unit-cell dimensions upon X-ray exposure without the degradation of a single-crystal form. The change was proved to reflect the racemization of the cyanoethyl group.[10] When the crystal was cooled, it contracted in an abnormally anisotropic manner and the gradual change of its unit-cell dimensions upon X-ray exposure was no longer detectable below 173 K.[11] The crystal structures at 293 K and 173 K were determined to confirm the mechanism of the racemization, which has already been reported.[11,12] This paper will present the twist of the $Co(dmg)_2$ plane caused by the short contacts with the cyanoethyl group and the conformation of the amine ligand.

Experimental

Dark red plate-like crystals of the R–S cyano complex, whose preparation will be reported elsewhere, were obtained from an aqueous methanol solution. The selection of the crystal was carefully made on a microscope because the preliminary photographic technique could not be used. A crystal 0.14×0.20×0.60 mm in size was set up on a Rigaku four-circle diffractometer, Mo *Kα* radiation monochromated by graphite being used ($\lambda=0.71069$ Å). The unit-cell dimensions were obtained by means of the least-squares technique with 15 reflections ($2\theta>20°$). Their values before and after the 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. During the intensity-

Table 1. The change in the unit-cell dimensions

	Start 1[a]	Start 2[b]	End[c]	Average[d]
a/Å	8.665(2)	8.661(2)	8.657(2)	8.659
b/Å	13.485(3)	13.508(2)	13.540(2)	13.524
c/Å	9.584(3)	9.585(2)	9.581(2)	9.583
β/°	96.95(3)	97.07(3)	97.25(3)	97.16
V/Å^3	1111.6(5)	1112.8(4)	1114.0(4)	1113.4

a) Two 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 the data collection was started. c) After 30 h, at which the data collection was over. d) The average values between 'Start 2' and 'End'. The structure factors and bond distances and angles are calculated using these values.

Table 2. Crystal data

Formula	$C_3H_4NC_8H_{11}N(C_4H_7N_2O_2)_2Co$	
F.W.	464.48	
a/Å	8.665(2) (293K)	8.786(2) (173K)
b/Å	13.485(3)	13.500(2)
c/Å	9.584(3)	9.243(2)
β/°	96.95(3)	98.09(3)
V/Å^3	1111.6(5)	1085.5(4)
Systematic absences	$0k0$; k odd	
Space group	$P2_1$	
Z	2	
D_m/g cm^{-3}	1.388	
D_c/g cm^{-3}	1.388	
μ(Mo $K\alpha$)/cm^{-1}	8.79	

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*	Atom	*x*	*y*	*z*
Co	25(1)	2500(0)	2646(1)	H(O1)	192(13)	186(10)	68(11)
N(1)	1627(5)	1533(4)	2845(5)	H(O2)	−162(10)	327(7)	468(9)
N(2)	112(6)	2259(4)	4590(5)	H(51)	370(9)	43(6)	519(8)
N(3)	−1602(6)	3423(4)	2465(5)	H(52)	418(10)	108(7)	439(9)
N(4)	−16(5)	2740(4)	687(4)	H(53)	337(9)	−8(6)	372(8)
O(1)	2383(5)	1252(3)	1759(4)	H(61)	20(9)	147(6)	705(8)
O(2)	−924(5)	2644(5)	5377(4)	H(62)	161(7)	66(5)	680(6)
O(3)	−2426(5)	3649(4)	3473(5)	H(63)	187(10)	186(7)	730(9)
O(4)	996(5)	2317(4)	−91(4)	H(71)	−412(8)	439(6)	135(7)
C(1)	2043(8)	1214(5)	4088(6)	H(72)	−295(6)	500(4)	64(5)
C(2)	1112(7)	1602(5)	5130(6)	H(73)	−379(9)	441(7)	14(8)
C(3)	−1980(7)	3797(5)	1180(7)	H(81)	−88(7)	443(5)	−137(6)
C(4)	−966(8)	3428(6)	152(7)	H(82)	−62(7)	349(5)	−173(6)
C(5)	3274(8)	435(6)	4446(8)	H(83)	−223(6)	363(4)	−175(5)
C(6)	1222(9)	1329(7)	6650(7)	H(N51)	−117(8)	109(5)	380(7)
C(7)	−3308(10)	4486(6)	829(9)	H(N52)	−281(8)	168(6)	287(7)
C(8)	−1190(9)	3743(6)	−1323(7)	H(9)	−81(6)	67(4)	91(5)
N(5)	−1629(6)	1373(4)	2343(5)	H(101)	−384(6)	0(4)	184(6)
C(9)	−1969(8)	792(5)	1069(7)	H(102)	−227(8)	−60(5)	198(7)
C(10)	−2770(10)	−195(6)	1390(9)	H(103)	−301(7)	−57(5)	50(6)
C(11)	−2971(7)	1352(5)	−92(7)	H(12)	−465(7)	189(4)	91(5)
C(12)	−4330(8)	1800(6)	111(7)	H(13)	−633(7)	271(5)	−82(6)
C(13)	−5271(8)	2255(6)	−983(8)	H(14)	−555(7)	275(6)	−299(6)
C(14)	−4823(10)	2211(7)	−2324(8)	H(15)	−334(7)	161(5)	−342(6)
C(15)	−3503(10)	1731(8)	−2547(8)	H(16)	−171(7)	110(4)	−167(6)
C(16)	−2595(8)	1296(7)	−1449(8)	H(17)	157(9)	408(6)	222(8)
C(17)	1569(9)	3635(5)	2999(7)	H(181)	376(10)	296(7)	372(8)
C(19)	1327(8)	4202(6)	4256(8)	H(182)	326(9)	260(8)	201(8)
N(6)	1106(9)	4677(6)	5153(8)	H(183)	390(8)	398(5)	291(7)
C(18)	3245(10)	3453(7)	2957(11)				

data collection, the orientation matrix was redetermined if the intensities of three monitor reflections were significantly deteriorated. The intensities of the independent reflections with $2\theta \leqq 50°$ were measured with an $\omega/2\theta$ scan, a scanning rate of $8°(2\theta)\ \mathrm{min}^{-1}$, and a scan range of $(1.0+0.35\tan\theta)°$. Stationary background counts were accumulated for 5 s before and after each scan. A total of 1940 independent reflections, $|F_o| \geqq 3\sigma(|F_o|)$, were obtained.

For the experiment at low temperatures, the nitrogen-gas-flow method was used. The experimental details were the same as those at room temperature, using a crystal $0.15 \times 0.25 \times 0.40$ mm in size. 1948 independent reflections, $|F_o| \geqq 3\sigma(|F_o|)$, were obtained. Corrections for the 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 was refined by the block-diagonal least-squares technique. All the hydrogen atoms were found on the difference map. The final refinement was made with the anisotropic and isotropic temperature factors for non-hydrogen and hydrogen atoms respectively. The weighting scheme of $w=0.3$ if $|F_o|>70.79$ and $|F_o|<7.08$ and $w=(0.0023F_o^2-0.17906|F_o|+4.48559)^{-1}$ if $7.08 \leqq |F_o| \leqq 70.79$ was employed. The final R became 0.055 for 1940 reflections. No peaks higher than $0.25\ e\,\text{Å}^{-3}$, except a peak of $0.45\ e\,\text{Å}^{-3}$ around the cobalt atom, were found on the final difference map.

The procedure of the structure determination at 173 K was the same as that at 293 K. The weighting scheme of $w=0.2$ if $|F_o|>100.69$ and $|F_o|<7.55$ and $w=(0.00185F_o^2-0.19964|F_o|+6.40248)^{-1}$ if $7.55 \leqq |F_o| \leqq 100.69$ was applied. The final R was 0.038 for 1948 reflections. No peaks higher than $0.23\ e\,\text{Å}^{-3}$, except the peaks of $0.58\ e\text{Å}^{-3}$ 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.[13] The final atomic coordinates and their standard deviations at 293 K and 173 K are given in Tables 3 and 4 respectively. The 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. 8006). The computation was done on M-180 and M-160 computers at this Institute.

Description of the Structure

The equations of the mean planes of four nitrogen atoms and two dmg's are given in Table 5, together

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*	Atom	*x*	*y*	*z*
Co	22(1)	2500(0)	2613(1)	H(O1)	155(6)	215(4)	58(5)
N(1)	1665(4)	1569(3)	2760(4)	H(O2)	−172(7)	317(5)	470(6)
N(2)	122(4)	2174(3)	4604(4)	H(51)	385(6)	55(4)	526(6)
N(3)	−1637(4)	3407(3)	2461(4)	H(52)	369(5)	20(3)	342(5)
N(4)	−43(4)	2828(3)	630(4)	H(53)	325(6)	−3(4)	468(6)
O(1)	2376(4)	1337(3)	1605(4)	H(61)	109(7)	176(5)	730(6)
O(2)	−902(3)	2515(4)	5454(3)	H(62)	224(8)	98(5)	700(8)
O(3)	−2440(4)	3555(3)	3561(4)	H(63)	90(7)	40(5)	661(6)
O(4)	930(3)	2417(3)	−245(3)	H(71)	−392(4)	455(3)	165(4)
C(1)	2085(5)	1207(4)	4025(5)	H(72)	−300(6)	497(4)	43(6)
C(2)	1160(5)	1539(4)	5134(5)	H(73)	−421(6)	419(4)	5(5)
C(3)	−2019(5)	3823(4)	1174(5)	H(81)	−125(5)	450(3)	−161(4)
C(4)	−1047(5)	3489(4)	96(5)	H(82)	−59(5)	338(4)	−205(5)
C(5)	3392(6)	478(4)	4344(6)	H(83)	−215(5)	359(4)	−194(5)
C(6)	1342(6)	1178(4)	6673(5)	H(N51)	−102(5)	87(3)	287(5)
C(7)	−3358(6)	4492(4)	819(6)	H(N52)	−230(6)	166(4)	253(6)
C(8)	−1267(6)	3858(4)	−1442(5)	H(9)	−96(7)	68(5)	38(7)
N(5)	−1547(4)	1354(3)	2221(4)	H(101)	−347(6)	−11(4)	149(5)
C(9)	−1932(6)	847(4)	797(6)	H(102)	−213(6)	−53(4)	164(5)
C(10)	−2648(6)	−176(4)	992(7)	H(103)	−290(5)	−50(4)	9(5)
C(11)	−3030(5)	−1436(4)	−304(5)	H(12)	−449(5)	186(3)	109(4)
C(12)	−4370(5)	1866(4)	66(5)	H(13)	−620(5)	258(5)	−74(5)
C(13)	−5381(5)	2346(5)	−972(6)	H(14)	−584(5)	277(3)	−321(4)
C(14)	−5109(7)	2433(9)	−2395(6)	H(15)	−355(6)	195(4)	−368(5)
C(15)	−3782(7)	1980(5)	−2777(6)	H(16)	−212(7)	110(4)	−200(6)
C(16)	−2776(6)	1509(5)	−1744(6)	H(17)	183(7)	425(5)	221(6)
C(17)	1493(6)	3678(4)	3079(6)	H(181)	351(7)	308(5)	421(6)
C(19)	1204(6)	4177(4)	4417(6)	H(182)	328(6)	328(4)	205(5)
N(6)	992(6)	4587(4)	5427(5)	H(183)	395(6)	423(4)	319(5)
C(18)	3216(6)	3480(5)	3093(7)				

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

X, Y, and Z in Å are referred to $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}^*$ respectively.

(I) Co(dmg)$_2$ plane (293 K): $-0.6546X-0.7315Y-0.1909Z+2.7526=0.$
(I′) Co(dmg)$_2$ plane (173 K): $-0.6216X-0.7442Y-0.2445Z+2.8941=0.$
(II) dmg plane (293 K): $-0.6544X-0.7342Y-0.1807Z+2.7238=0.$
(II′) dmg plane (173 K): $-0.6160X-0.7548Y-0.2254Z+2.8549=0.$
(III) dmg plane (293 K): $-0.6536X-0.7170Y-0.2425Z+2.7704=0.$
(III′) dmg plane (173 K): $-0.6223X-0.7335Y-0.2733Z+2.8892=0.$

	(I)	(I′)	(II)	(II′)	(III)	(III′)
Co	0.008	0.003	0.021	0.034	0.072	0.041
N(1)	−0.020a)	−0.014a)	−0.014a)	−0.007a)		
N(2)	0.020a)	0.014a)	0.013a)	0.007a)		
N(3)	−0.020a)	−0.014a)			0.018a)	0.005a)
N(4)	0.020a)	0.014a)			−0.018a)	−0.005a)
O(1)	0.019	−0.024	0.035	−0.004		
O(2)	−0.105	−0.081	−0.118	−0.093		
O(3)	−0.160	−0.146			−0.076	−0.101
O(4)	0.095	0.007			0.026	−0.029
C(1)	0.029	0.033	0.023a)	0.011a)		
C(2)	−0.007	0.019	−0.022a)	−0.011a)		
C(3)	0.003	0.012			−0.030a)	−0.009a)
C(4)	0.107	0.053			0.030a)	0.004a)
C(5)	−0.007	0.060	−0.021	0.016		
C(6)	−0.058	−0.024	−0.089	−0.087		
C(7)	−0.104	−0.098			−0.166	−0.139
C(8)	0.139	0.084			−0.016	−0.005

a) Atoms included in the least-squares calculation.

with the deviations of the atoms from the planes. The projection of the structure at 293 K in the (I) plane is shown in Fig. 1, in which the short contacts between the non-bonded atoms are also given. The Co(dmg)$_2$ plane is twisted around its long axis, as is observed in the R–R ester complex. A fairly strong repulsion between N(1) and C(18) tilts the plane (II), whereas the contacts between N(4) and C(9) and between N(4) and C(11) tilt the plane (III) in the opposite sense. The deviations of the four nitrogen atoms at 293 K are the same as those of the R–R ester complex. However, the deviations of C(1), C(2), and C(3) are not so large. In the ester complex,

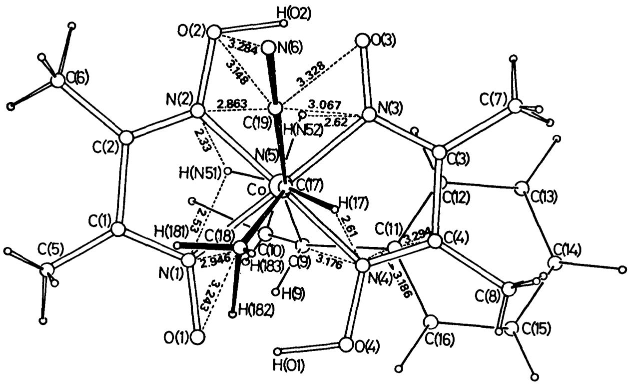

Fig. 1. Projection of the complex onto the mean plane of four nitrogen atoms of Co(dmg)$_2$ and the short contacts between non-bonded atoms (l/Å) at 293 K, their threshold values being 3.400 Å for distances between the non-bonded atoms and 2.70 Å for those including hydrogen atoms.

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

	293 K	173 K
N(1)···C(18)	2.946(12)	2.914(8)
N(1)···H(N51)	2.53(7)	2.56(5)
N(2)···C(19)	2.863(9)	2.880(7)
N(2)···H(N51)	2.33(7)	2.49(5)
N(3)···C(19)	3.067(11)	3.051(7)
N(3)···H(N52)	2.62(8)	2.44(6)
N(4)···C(9)	3.176(9)	3.163(7)
N(4)···C(11)	3.186(8)	3.245(6)
O(1)···C(18)	3.243(11)	3.244(8)
O(2)···C(19)	3.148(10)	3.142(7)
O(2)···N(6)	3·284(10)	3.257(8)
O(3)···C(19)	3.328(9)	3.296(6)
C(4)···C(11)	3.294(10)	3.266(7)

TABLE 7. BOND DISTANCES (l/Å) (e.d.s.'s are in parentheses)

	293 K	173 K		293 K	173 K
Co-N(1)	1.898(5)	1.904(4)	O(1)-H(O1)	1.34(13)	1.57(5)
Co-N(2)	1.883(5)	1.883(4)	O(2)-H(O2)	1.20(10)	1.28(7)
Co-N(3)	1.874(6)	1.893(4)	O(3)-H(O2)	1.37(10)	1.26(7)
Co-N(4)	1.901(5)	1.878(4)	O(4)-H(O1)	1.19(13)	0.94(5)
Co-N(5)	2.088(6)	2.070(6)	C(5)-H(51)	0.76(9)	0.89(6)
Co-C(17)	2.036(8)	2.056(6)	C(5)-H(52)	1.18(9)	1.00(5)
N(1)-O(1)	1.352(7)	1.348(5)	C(5)-H(53)	1.00(9)	0.77(6)
N(1)-C(1)	1.276(9)	1.273(7)	C(6)-H(61)	1.03(9)	1.01(6)
N(2)-O(2)	1.347(8)	1.355(7)	C(6)-H(62)	0.97(7)	0.85(7)
N(2)-C(2)	1.302(9)	1.296(7)	C(6)-H(63)	1.06(10)	1.12(7)
N(3)-O(3)	1.307(8)	1.331(6)	C(7)-H(71)	0.92(8)	0.97(4)
N(3)-C(3)	1.333(9)	1.316(6)	C(7)-H(72)	0.79(6)	0.82(6)
N(4)-O(4)	1.347(7)	1.374(6)	C(7)-H(73)	0.74(9)	1.04(6)
N(4)-C(4)	1.304(9)	1.302(6)	C(8)-H(81)	0.97(7)	0.88(5)
C(1)-C(2)	1.457(10)	1.466(7)	C(8)-H(82)	0.75(7)	1.09(5)
C(1)-C(5)	1.507(11)	1.510(8)	C(8)-H(83)	0.95(6)	0.92(5)
C(2)-C(6)	1.494(12)	1.491(8)	N(5)-H(N51)	0.86(7)	0.96(5)
C(3)-C(4)	1.485(10)	1.472(7)	N(5)-H(N52)	1.27(8)	0.86(6)
C(3)-C(7)	1.486(11)	1.482(7)	C(9)-H(9)	1.05(6)	1.00(7)
C(4)-C(8)	1.466(11)	1.493(7)	C(10)-H(101)	1.10(6)	0.92(5)
N(5)-C(9)	1.450(9)	1.480(7)	C(10)-H(102)	0.87(7)	0.85(6)
C(9)-C(10)	1.553(11)	1.539(8)	C(10)-H(103)	1.00(7)	0.94(6)
C(9)-C(11)	1.524(10)	1.524(7)	C(12)-H(12)	0.86(6)	0.96(4)
C(11)-C(12)	1.359(11)	1.398(7)	C(13)-H(13)	1.13(7)	0.84(7)
C(11)-C(16)	1.381(11)	1.384(8)	C(14)-H(14)	1.11(8)	1.03(5)
C(12)-C(13)	1.389(12)	1.375(8)	C(15)-H(15)	0.88(6)	0.89(5)
C(13)-C(14)	1.388(12)	1.374(14)	C(16)-H(16)	0.87(6)	0.85(6)
C(14)-C(15)	1.355(14)	1.405(14)	C(17)-H(17)	0.96(8)	1.18(6)
C(15)-C(16)	1.366(13)	1.364(10)	C(18)-H(181)	1.05(9)	1.17(6)
C(17)-C(18)	1.478(13)	1.536(9)	C(18)-H(182)	1.47(10)	1.01(6)
C(17)-C(19)	1.465(11)	1.461(8)	C(18)-H(183)	0.92(7)	0.96(10)
C(19)-N(6)	1.109(11)	1.123(8)			

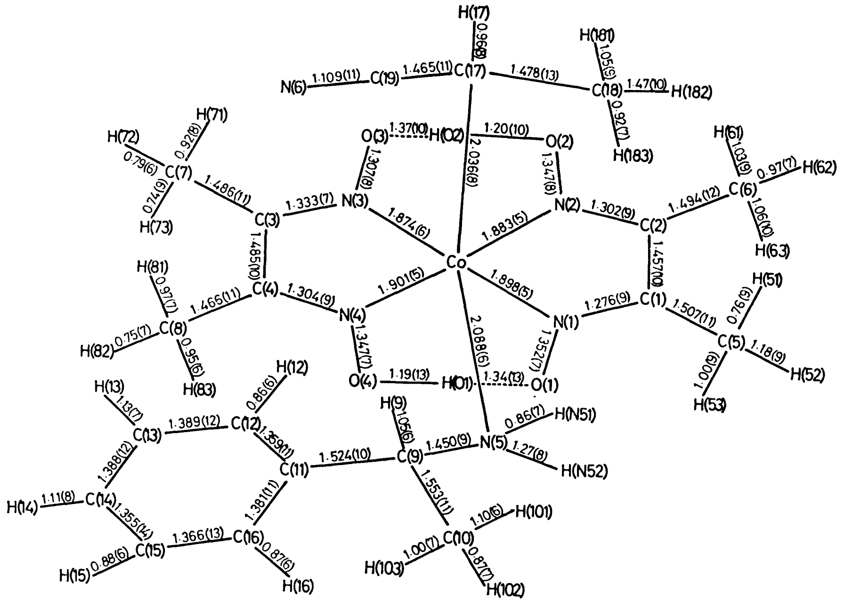

Fig. 2. Bond distances (*l*/Å) at 293 K. Their standard deviations are in the parentheses.

Table 8. Bond angles (ϕ/°) (e.s.d.'s are in parentheses)

	293 K	173 K		293 K	173 K
N(1)-Co-N(2)	81.0(2)	81.1(2)	N(4)-C(4)-C(3)	112.0(6)	112.3(4)
N(1)-Co-N(3)	178.1(2)	179.0(2)	N(4)-C(4)-C(8)	126.0(7)	125.5(5)
N(1)-Co-N(4)	98.1(2)	98.3(2)	C(3)-C(4)-C(8)	121.6(7)	122.2(4)
N(1)-Co-N(5)	89.5(2)	89.9(2)	Co-N(5)-C(9)	125.2(4)	124.4(3)
N(1)-Co-C(17)	92.7(3)	92.8(2)	N(5)-C(9)-C(10)	110.3(6)	111.0(4)
N(2)-Co-N(3)	98.3(3)	98.8(2)	N(5)-C(9)-C(11)	112.5(6)	113.3(4)
N(2)-Co-N(4)	178.8(2)	179.1(2)	C(9)-C(11)-C(12)	122.7(7)	122.0(5)
N(2)-Co-N(5)	87.3(2)	86.2(2)	C(9)-C(11)-C(16)	118.7(7)	120.5(5)
N(2)-Co-C(17)	91.2(3)	92.0(2)	C(12)-C(11)-C(16)	118.0(7)	117.5(5)
N(3)-Co-N(4)	82.7(2)	81.8(2)	C(11)-C(12)-C(13)	121.7(8)	120.6(5)
N(3)-Co-N(5)	88.8(2)	89.1(2)	C(12)-C(13)-C(14)	118.3(8)	121.7(7)
N(3)-Co-C(17)	89.1(3)	88.3(2)	C(13)-C(14)-C(15)	120.4(9)	117.8(10)
N(4)-Co-N(5)	93.4(2)	94.4(2)	C(14)-C(15)-C(16)	120.0(9)	120.4(8)
N(4)-Co-C(17)	88.1(3)	87.4(2)	C(11)-C(16)-C(15)	121.4(8)	122.0(6)
N(5)-Co-C(17)	177.2(3)	176.5(2)	Co-C(17)-C(18)	119.8(6)	117.2(4)
Co-N(1)-O(1)	122.3(4)	121.9(3)	Co-C(17)-C(19)	111.9(5)	110.8(4)
Co-N(1)-C(1)	116.4(5)	116.0(4)	C(18)-C(17)-C(19)	110.6(7)	111.2(5)
O(1)-N(1)-C(1)	121.1(5)	122.1(4)	C(17)-C(19)-N(6)	175.6(9)	177.9(6)
Co-N(2)-O(2)	122.7(4)	122.9(3)			
Co-N(2)-C(2)	117.0(5)	117.2(4)	N(1)-O(1)-H(O1)	107(5)	95(2)
O(2)-N(2)-C(2)	119.9(6)	119.7(4)	N(2)-O(2)-H(O2)	107(5)	106(3)
Co-N(3)-O(3)	124.1(5)	121.7(3)	N(3)-O(3)-H(O2)	106(4)	108(3)
Co-N(3)-C(3)	115.7(5)	116.1(3)	N(4)-O(4)-H(O1)	108(6)	91(3)
O(3)-N(3)-C(3)	120.0(6)	122.0(4)	O(1)-H(O1)-O(4)	155(11)	157(5)
Co-N(4)-O(4)	122.8(4)	122.9(3)	O(2)-H(O2)-O(3)	154(4)	156(6)
Co-N(4)-C(4)	116.3(5)	117.3(3)	Co-N(5)-H(N51)	89(5)	99(3)
O(4)-N(4)-C(4)	120.5(5)	119.9(4)	Co-N(5)-H(N52)	106(3)	96(4)
N(1)-C(1)-C(2)	113.7(6)	114.0(5)	C(9)-N(5)-H(N51)	118(5)	106(3)
N(1)-C(1)-C(5)	124.0(7)	123.0(5)	C(9)-N(5)-H(N52)	115(3)	115(4)
C(2)-C(1)-C(5)	122.1(6)	123.0(5)	H(N51)-N(5)-H(N52)	97(6)	116(5)
N(2)-C(2)-C(1)	111.8(6)	111.6(5)	N(5)-C(9)-H(9)	96(3)	110(4)
N(2)-C(2)-C(6)	120.9(7)	123.5(5)	C(10)-C(9)-H(9)	111(3)	103(4)
C(1)-C(2)-C(6)	127.3(7)	124.9(5)	C(11)-C(9)-H(9)	116(3)	110(4)
N(3)-C(3)-C(4)	112.8(6)	112.5(4)	Co-C(17)-H(17)	114(5)	125(3)
N(3)-C(3)-C(7)	122.7(7)	123.6(5)	C(18)-C(17)-H(17)	89(5)	77(3)
C(4)-C(3)-C(7)	124.4(7)	123.7(4)	C(19)-C(17)-H(17)	109(5)	111(3)

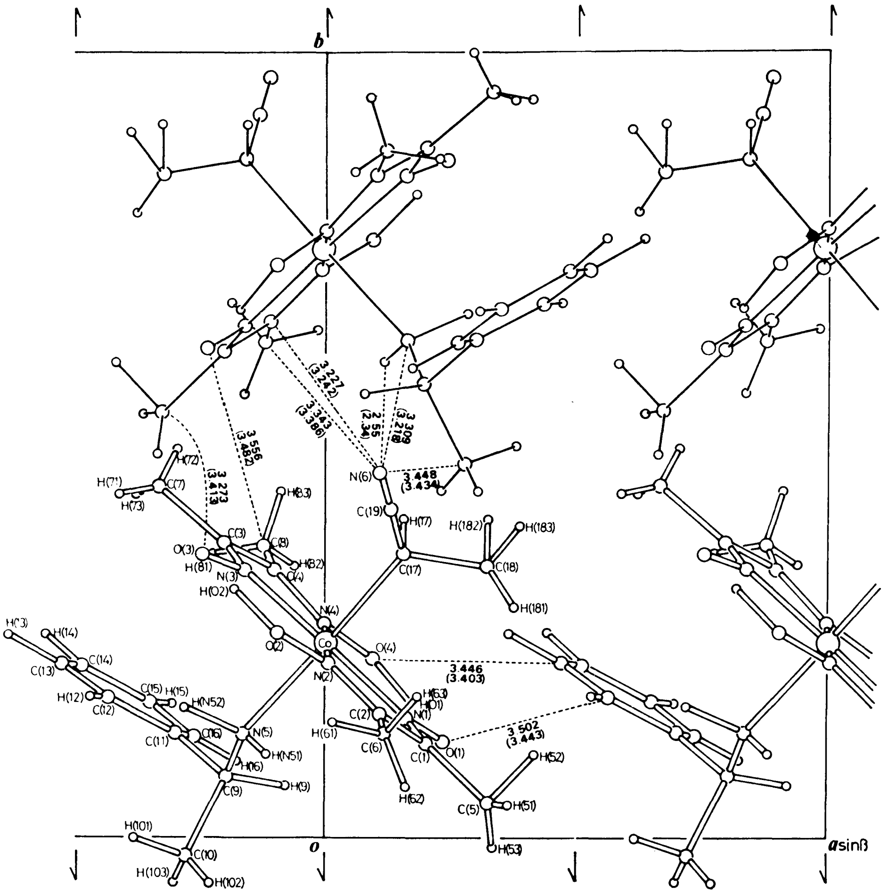

Fig. 3. Projection of the crystal structure along the c axis and short contacts bweteen complexes. The short contacts at 173 K are in the parentheses.

both of the methoxycarbonyl and methyl groups lie on the dmg planes. The carbon atoms of the dmg rings must deviate from the planes as a result of the steric repulsion from the methoxycarbonyl and methyl groups. The cyano and methyl groups in the present complex, on the other hand, are located over the gaps between the two dmg's. Therefore, only the nitrogen atoms should be affected by the steric repulsion from the cyanoethyl group.

The deviations of the atoms of the Co(dmg)$_2$ moiety from the plane (I′) at low temperatures becomes smaller than those at room temperature. The short contacts between the non-bonded atoms at 173 K are compared with the corresponding ones at 293 K in Table 6. The distances at 173 K are rather smaller than those at 293 K.

The deviation of the cobalt atom from the mean plane of Co(dmg)$_2$ is small at both temperatures. The Co atom in the methyl complex is shifted by 0.04 Å from its mean plane of Co(dmg)$_2$ toward the amine ligand, whereas the Co atom in the ester complex deviates toward the ester group by 0.04 Å. This indicates that the deviation of the Co atom from the mean plane of Co(dmg)$_2$ is affected by the relative bulkiness of the axial ligands.

The bond distances at 293 K are shown in Fig. 2, and 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 shorter by 0.02 Å and longer by 0.018 Å respectively than the corresponding ones at 173 K. The sums of the two bonds, however, are nearly equal at both temperatures. As the C(17) atom comes close to the cobalt atom at high temperatures, the angles of Co–C(17)–C(18) and Co–C(17)–C(19) become larger and the Co(dmg)$_2$ plane may be twisted more.

The three bonds around N(3), Co–N(3), N(3)–O(3), and N(3)–C(3), and the two bonds around N(4), Co–N(4), and N(4)–O(4) at 293 K have different distances from the corresponding ones at 173 K. The two angles around N(3), Co–N(3)–O(3), and O(3)–N(3)–C(3), have different values between the two temperatures. These differences may indicate that the resonance state of dmg is changed by the modified electronic state of Co, which is itself caused by the short Co–C distance at high temperatures.

The C(17)–C(18) distance at 293 K is significantly shorter then that at 173 K, probably because of the large thermal vibration of the C(18) atom. The other bond distances and angles are in fair agreement between the two temperatures.

The crystal structure viewed along the c axis is shown in Fig. 3, in which the short contacts are given. There is a short contact between N(5) and N(6) in the unit of $(-x, -0.5+y, 1-z)$. The N···N distances are 3.309 and 3.218 Å for 293 and 173 K respectively. The distanecs of H(N51)···N(6) and the angles of

Table 9. Characteristic dimensions of the amine in the various complexes

	Methyl	R-R ester	R-S(293 K)	R-S(173 K)	S-S(293 K)[a]	S-S(173 K)[a]	Average
Co-N(5)	2.087(9) Å	2.066(6)	2.088(6)	2.070(4)	2.054(5)	2.064(7)	2.072
N(5)-C(9)	1.463(15) Å	1.476(9)	1.450(9)	1.480(7)	1.487(9)	1.513(10)	1.479
C(9)-C(11)	1.541(16) Å	1.505(10)	1.524(10)	1.524(7)	1.508(10)	1.513(12)	1.519
N(4)-Co-N(5)	96.2(4)°	92.7(2)	93.4(2)	94.4(2)	94.3(2)	94.5(3)	94.3
Co-N(5)-C(9)	125.4(7)°	124.2(4)	125.2(4)	124.4(3)	125.4(4)	123.7(5)	124.8
N(4)···C(9)	3.252 Å	3.223(9)	3.176(9)	3.163(7)	3.132(9)	3.113(10)	3.177
N(4)-Co-N(5)-C(9)	17.6°	39.7	23.2	19.8	2.5	0.8	—
Co-N(5)-C(9)-C(11)	76.0°	89.9	77.4	78.3	79.7	80.2	78.3[b]
N(4)···C(11) or C(4)···C(11)	3.399 Å	3.340(9)	3.186(8)	3.245(6)	3.353(9)[c]	3.315(12)[c]	—
Bending of C(9)-C(11) from the phenyl ring	2.2°	4.0	4.0	2.9	3.3	4.8	3.5

a) Ref. 16. b) The value of the R-R ester is omitted. c) Distances of C(4)···C(11), the others being N(4)···C(11).

N(5)-H(N51)···N(6) are 2.55 Å and 149° for 293 K, and 2.34 Å and 152° for 173 K. This seems to be a weak hydrogen bond, judging from the previously reported N-H···N hydrogen bond.[14] The other contacts are not unusually short.

Discussion

In this serial study attempting to clarify the mechanism of inducing asymmetry, the distortion of the Co(dmg)$_2$ moiety has been examined for various substituted alkyl ligands. The optically acitve amine, α-methylbenzylamine, is kept unaltered except for its absolute configuration, because it seems necessary first to elucidate the effect of the substituted alkyl ligand on the Co(dmg)$_2$ moiety. For this purpose, it is assumed that the conformational change, if any, of the amine ligand is not seriously influenced by the intermolecular force or crystalline field, while it is influenced by the intramolecular force.

In Table 9, the characteristic dimensions and conformations of the amine in the crystal structures thus far determined are compared. As the crystals of the cyano complexes exhibit an abnormal thermal expansion, the values at 173 K are also listed. The Co-N(5) bond lengths range from 2.054 to 2.088 Å. Such variation seems to be brought about by the *trans* Co-C bond and will be discussed in detail in the following paper. The average length of N(5)-C(9) is in good agreement with the usual distance, 1.472± 0.005 Å.[15] The average distance of C(9)-C(11) is slightly longer than the usual one, 1.505±0.005 Å.[15] Bond distances, however, have relatively large variations. This may be due to the short contacts between the amine and the Co(dmg)$_2$ moiety.

The angles of N(4)-Co-N(5) and Co-N(5)-C(9) deviate from the right and tetrahedral angles respectively to avoid the short contact between N(4) and C(9). The average value of Co-N(5)-C(9)-C(11) is 78.3°. The torsion angle of the ester complex is significantly larger than the average value. This is due to the fact that the Co(dmg)$_2$ moiety is bent toward the amine. To avoid the short contacts between C(11)···N(4) and C(11)···C(4), the N(5)-C(9) bond rotates from the stable staggered form toward the eclipsed form.

The rotation around the Co-N(5) bond, that is, the torsion angle of N(4)-Co-N(5)-C(9), varies from 0.8° to 39.7°. In Part II of this series,[8] the most stable conformation was calculated to be 13°, and the potential energy curve against the torsion angle closely resembled a quadratic in the vicinity of 13°. For both cyano complexes, the deviations from the stable conformation are in the opposite direction, but are nearly equal. The energies should be practically the same for both complexes. The amine ligand in each cyano-complex crystal comes in contact with the cyanoethyl group of the neighbouring molecule. Such deviations in the opposite direction, therefore, should be brought about by the opposite configuration of the cyanoethyl group. The Co(dmg)$_2$ plane is bent toward the methyl group in the methyl complex, whereas it is bent toward the amine in the ester complex. The conformation around the Co-N(5) bond in the former complex is close to the stable one, whereas the bond in the latter rotates from the stable conformation to a considerable extent. These facts suggest that (i) the Co-N bond distance is apparently affected by the *trans* Co-C bond; (ii) although the conformation around the Co-N bond is affected by the crystalline field, the potential energy caused by such a conformation is nearly equal if the substituted alkyl group is the same except for its absolute configration, and (iii) the torsion angle of N(4)-Co-N(5)-C(9) depends on the bulkiness of the substituted alkyl group, showing 13+5 ° for the methyl group, 13±10° for the cyanoethyl group, and 13+27° for methoxycarbonyl group. The assumption mentioned above, therefore, holds good for the determined crystal structures. This seems to indicate that the difference in energy between the σ-complexes containing *R*- and *S*- substituted alkyl groups is attributable to the structure of the Co(dmg)$_2$ moiety or the Co-N and Co-C distances. These points will be discussed in detail in the following paper.

References

1) Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, **44**, 283 (1971).

2) Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, **44**, 583 (1971).

3) S. Takeuchi, Y. Ohgo, and J. Yoshimura, *Chem. Lett.*, **1973**, 265.

4) Y. Ohgo, S. Takeuchi, Y. Natori, and J. Yoshimura, *Chem. Lett.*, **1974**, 33.

5) Y. Ohgo, Y. Natori, S. Takeuchi, and J. Yoshimura, *Chem. Lett.*, **1974**, 709.

6) Y. Ohgo, Y. Natori, S. Takeuchi, and J. Yoshimura, *Chem. Lett.*, **1974**, 1327.

7) Y. Ohashi, Y. Sasada, Y. Tashiro, Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, **46**, 2589 (1973).

8) Y. Ohashi and Y. Sasada, *Bull. Chem. Soc. Jpn.*, **50**, 1710 (1977).

9) Y. Ohashi and Y. Sasada, *Bull. Chem. Soc. Jpn.*, **50**, 2863 (1977).

10) Y. Ohashi and Y. Sasada, *Nature*, **267**, 142 (1977).

11) Y. Ohashi, Y. Sasada, and Y. Ohgo, *Chem. Lett.*, **1978**, 457.

12) Y. Ohashi, Y. Sasada, and Y. Ohgo, *Chem. Lett.*, **1978**, 743.

13) "International Tables for X-Ray Crystallography," Vol. IV, The Kynoch Press, Birmingham (1974), p. 72.

14) G. C. Pimentel and A. L. McClillan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco and London (1960) p. 288.

15) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement," Special Publication No. 18, The Chemical Society, London (1965).

16) Y. Ohashi, Y. Sasada, S. Takeuchi, and Y. Ohgo, *Bull. Chem. Soc. Jpn.*, to be published.