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Preparations and Properties of Optically Active (Alkyl)bis(dimethylglyoximato)cobalt(III) Complexes

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Optically active alkyl cobalt complexes, $CH_3CHXCo(Hdmg)_2\cdot$Base [X=$COOCH_3$ or CN; Base=(*R*)- or (*S*)-1-phenylethylamine, H_2O, pyridine, or (1*R*,2*S*)-1,2-diphenyl-2-aminoethanol; Hdmg=dimethylglyoximate(1-)], have been prepared, and their spectroscopic and chiroptical data are given. The rotational contribution of the chiral alkyl moiety was shown to be considerably greater than that of the chiral amine moiety. This suggests that the rotational sign (in the longer-wave length region of about 546 to 589 nm) may be useful for deducing the chirality of the alkyl moiety.

Transition-metal alkyl complexes are important intermediates in various catalytic reactions. The reactions with chiral alkyl transition metal complexes can provide a clearer description of the elementary process of catalytic reactions, especially catalytic asymmetric reactions. Studies on the mechanism of asymmetric hydrogenation catalyzed by the bis(dimethylglyoximato)cobalt(II)–chiral amino alcohol system[1–5] prompted us to prepare optically pure (alkyl)bis(dimethylglyoximato)cobalt complexes which have chirality at the carbon coordinated directly to cobalt.

Two approaches are, in principle, possible in the preparation of such a complex. One is based on the stereospecific displacement of a labile group or atom of chiral-carbon compounds with metal complexes (1).[6] Another method is the resolution of diastereomeric complexes with a chiral ligand (L_1*) other than the alkyl group, followed by the displacement of the chiral ligand L_1* with an achiral ligand (L_2) (2). The optical purity gained by the former approach is completely dependent on the degree of stereospecificity of the reaction applied; also, there is no guarantee that the same stereospecificity will be afforded as in a model reaction. In fact, (−)-1-methylheptyl bromide ($[\alpha]_D$ −29°) reacts with bis(dimethylglyoximato)cobalt(I) anion to give bis(dimethylglyoximato)(1-methylheptyl)(pyridine)cobalt(III) of $[\alpha]_D$ +50°,[6a] while we could not detect the optical activity of the alkyl complex produced in a similar reaction with optically pure methyl 2-bromopropanoate. Therefore, the latter method (2) is considered to be favorable for obtaining optically pure alkyl complexes.

We wish here to report preparations and properties of some optically pure (alkyl)bis(dimethylglyoximato)cobalt complexes.

Results and Discussion

Bis(dimethylglyoximato)cobalt(II) was allowed to react with methyl acrylate or acrylonitrile in methanol under weakly acidic conditions under a hydrogen atmos-

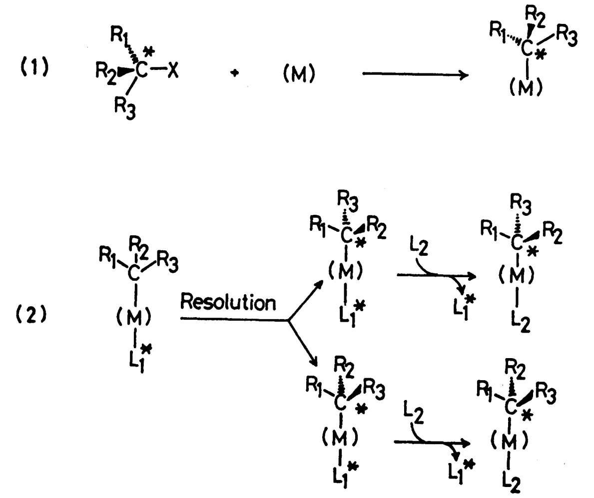

Fig. 1.

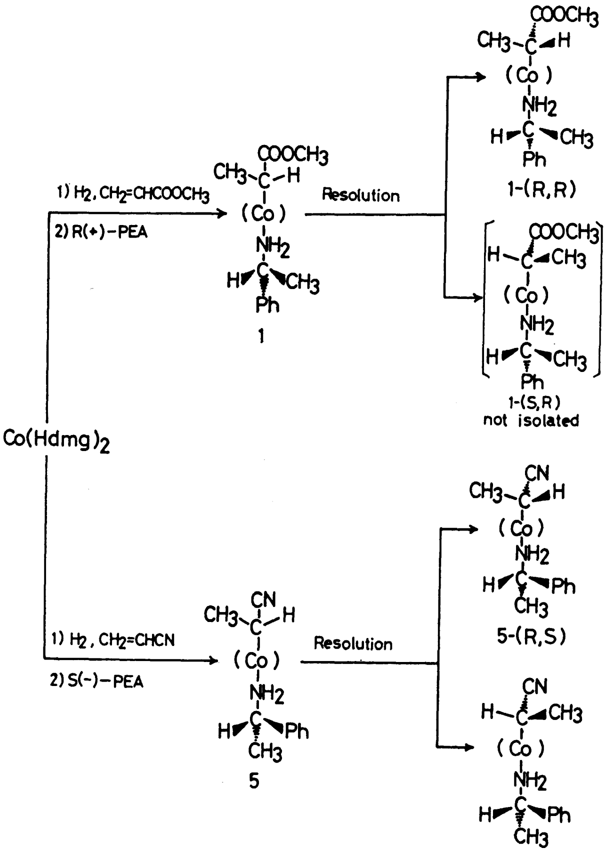

Fig. 2.

TABLE 1. ^{1}H NMR CHEMICAL SHIFTS OF DIASTEREOMERIC PAIRS OF 1-SUBSTITUTED ETHYL-(1-PHENYLETHYLAMINE)COBALOXIMES, CH_3CHX–$Co(Hdmg)_2 \cdot NH_2CH(CH_3)Ph$

Compound			Chemical shift, δ							
Substituent	Configuration		$C\underline{H}_3CHCo$	$C\underline{H}_3CNH_2$	$C\underline{H}Co$	$C\underline{H}_3$(Hdmg)	$OC\underline{H}_3$	$C\underline{H}NH_2$	NH_2	Ph
	Alkyl	Amine								
$COOCH_3$	*R*	*R*	0.32 (d, 3H)	1.22 (d, 3H)	1.96 (q, 1H)	2.20 and 2.24 (12H)	3.44 (s, 3H)	3.63 (q, 1H)	7.04 (m, 2H)	7.26 (m, 5H)
$COOCH_3$	*R*	*S*	0.32 (d, 3H)	1.22 (d, 3H)	1.94 (q, 1H)	2.20 and 2.24 (12H)	3.44 (s, 3H)	3.63 (q, 1H)	7.04 (m, 2H)	7.26 (m, 5H)
CN	*S*	*S*	0.48 (d, 3H)	1.25 (d, 3H)	1.98 (q, 1H)	2.25 (12H)		3.65 (q, 1H)	7.08 (m, 2H)	7.30 (m, 5H)
CN	*R*	*S*	0.48 (d, 3H)	1.25 (d, 3H)	1.96 (q, 1H)	2.25 and 2.27 (12H)		3.65 (q, 1H)	7.08 (m, 2H)	7.29 (m, 5H)

TABLE 2. MAIN IR ABSORPOTION BANDS OF DIASTEREOMERIC PAIRS OF 1-SUBSTITUTED ETHYL(1-PHENYLETHYLAMINE)COBALOXIMES

Compound			Spectral bands, $\tilde{\nu}$/cm^{-1}				
Substituent	Configuration		NH_2		CN	$COOCH_3$	C=N
	Alkyl	Amine	*asym*	*sym*			
$COOCH_3$	*R*	*R*	3313	3266		1685	1555
$COOCH_3$	*R*	*S*	3305	3250		1686	1556
CN	*S*	*S*	3320	3232	2200		1559
CN	*R*	*S*	3304	3235	2199		1560

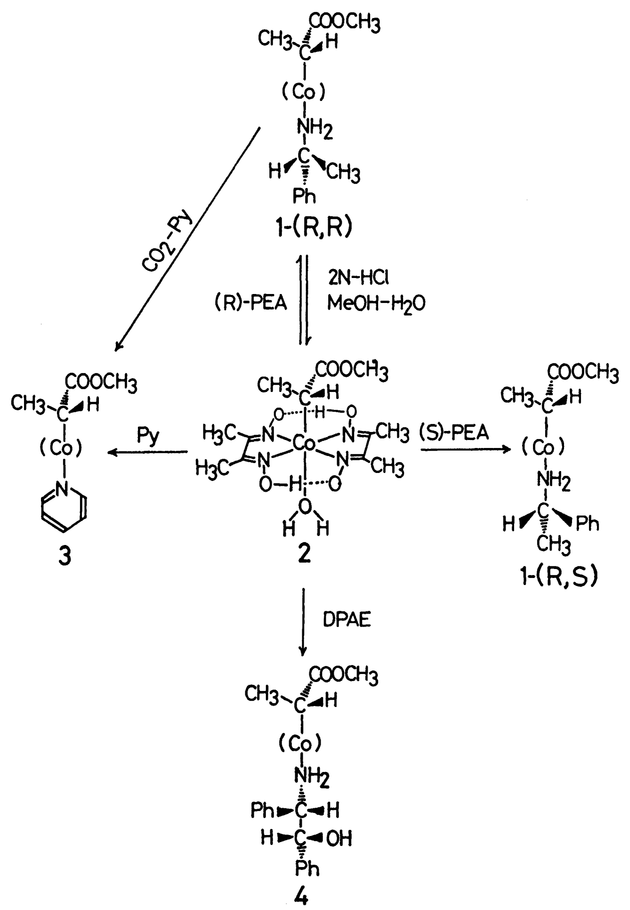

Fig. 3.

phere.[7] After neutralization, (*R*)- or (*S*)-1-phenylethylamine was added to give diastereomeric alkyl complexes with a chiral axial base (**1** or **5**; see Fig. 2). The repeated recrystallization of **1** from a mixture of methanol and water gave $(+)_{578}$-bis(dimethylglyoximato) [1-(methoxycarbonyl) ethyl] cobalt (III), **1**-(*R*,*R*), with $[\alpha]_{578}$ +211.3°. (*S*)-1-Phenylethylamine coordinated 1-cyanoethyl cobalt complexes were resolved into two diastereomers, **5**-(*R*,*S*) ($[\alpha]_{578}$ +55.85°) and **5**-(*S*,*S*) ($[\alpha]_{578}$ −60.13°). By the use of (*R*)-1-phenylethylamine, the enantiomer of the former, **5**-(*S*,*R*), was also obtained ($[\alpha]_{578}$ −55.6°).

The absolute configurations of cobalt-alkyl moieties of dextrorotating $(+)_{578}$-bis(dimethylglyoximato)-[1-(methoxycarbonyl)ethyl][(*R*)-1-phenylethylamine]-cobalt(III), dextrorotating $(+)_{578}$- and levorotating $(-)_{578}$-1-cyanoethylbis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III) were determined by the X-ray method to be (*R*), (*R*), and (*S*) respectively.[8–10]

The ^{1}H NMR spectra and main bands of the IR spectra of diastereomeric pairs of 1-(methoxycarbonyl)-ethyl and 1-cyanoethyl complexes are shown in Tables 1 and 2.

A diastereomeric difference appears in the ^{1}H NMR signals of the proton on the carbon attached to cobalt: the $\underline{H}C$–Co proton signal of the *R*–*S* complex (**1**-(*R*,*S*), **5**-(*R*,*S*)) appears in a somewhat higher field (0.02 ppm) than that of the corresponding *R*–*R* or *S*–*S* complex (**1**-(*R*,*R*) or **5**-(*S*,*S*)). The absorption bands due to the asymmetric stretching vibration of $-NH_2$ of the *R*–*R* or *S*–*S* complex appear at a higher frequency than that of the diastereomer, the *R*–*S* complex, while the other absorption bands are almost identical.

Aquabis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl] cobalt(III) was obtained in about a 60% yield by treating **1**-(*R*,*R*) with 2 mol dm^{-3} hydrochloric acid in aqueous methanol. The aqua ligand is so labile in this complex that the aqua complex is a useful intermediate in exchanging the axial ligand. Thus, the pyridine, (1*R*,2*S*)-1,2-diphenyl-2-aminoethanol, and (*S*)-1-phenylethylamine coordinated complexes were easily derived only by evaporating a methanol solution of an equimolar amount of the aqua complex and the axial base desired (Fig. 3). The pyridine complex (**3**) was also obtained in one step by treating **1**-(*R*,*R*) with CO_2

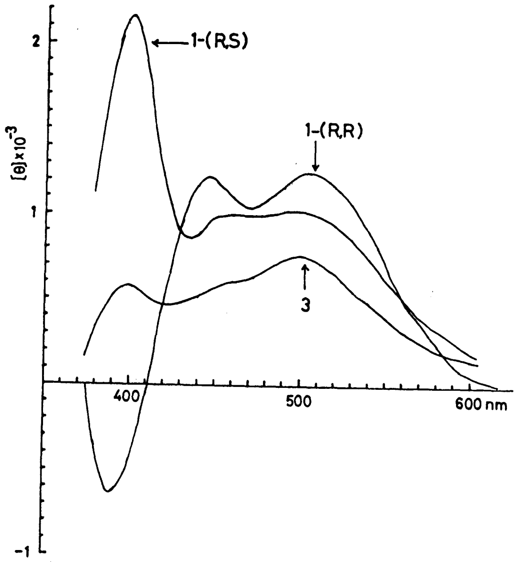

Fig. 4. CD spectra of 10^{-3} mol dm^{-3} dichloromethane solution of **1**-(*R*,*R*), **1**-(*R*,*S*), and **3**.

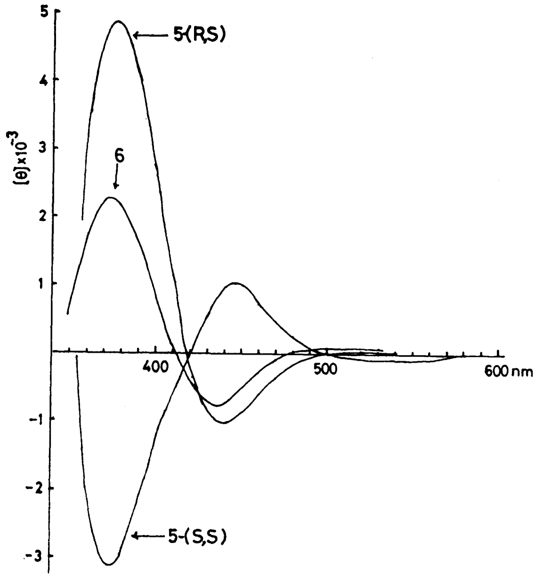

Fig. 5. CD spectra of 10^{-3} mol dm^{-3} dichloromethane solution of **5**-(*R*,*S*), **5**-(*S*,*S*), and **6**.

TABLE 3. SPECIFIC AND MOLECULAR ROTATION OF 1-SUBSTITUTED ETHYL COBALOXIMES, CH_3CHX–$Co(Hdmg)_2$-BASE, AND THEIR CONFIGURATIONS AT α-CARBON

	X	Axial base	Conf. at α-carbon	$[\alpha]^{RT}_{578}$	$[\Phi]^{RT}_{578}$[d)]
1-(*RR*)	$COOCH_3$	(*R*)-1-PEA[a)]	*R*[c)]	+211($CHCl_3$)	+1051
1-(*RS*)	$COOCH_3$	(*S*)-1-PEA	*R*	+161($CHCl_3$)	+801
2	$COOCH_3$	H_2O	*R*	+160(MeOH)	+631
3	$COOCH_3$	Pyridine	*R*	+167($CHCl_3$)	+760
4	$COOCH_3$	(1*R*,2*S*)-DPAE[b)]	*R*	+143($CHCl_3$)	+843
5-(*RS*)	CN	(*S*)-1-PEA	*R*[c)]	+55.85($CHCl_3$)	+259
5-(*SR*)	CN	(*R*)-1-PEA	*S*[c)]	−55.6($CHCl_3$)	−258
5-(*SS*)	CN	(*S*)-1-PEA	*S*[c)]	−60.13($CHCl_3$)	−279
6	CN	Pyridine	*R*	+52.2($CHCl_3$)	+220

a) 1-PEA: 1-phenylethylamine. b) (1*R*,2*S*)-DPAE: (1*R*,2*S*)-1,2-diphenyl-2-aminoethanol. c) These configurations were determined by the X-ray method.[3–5)] d) Molecular rotation.

TABLE 4. ESTIMATION OF PARTIAL CONTRIBUTION OF ALKYL AND AMINE PARTS FOR MOLECULAR ROTATION OF DIASTEREOMERIC 1-SUBSTITUTED ETHYL-(1-PHENYLETHYLAMINE)COBALOXIMES

Alkyl		Base	Parial contribution	
Substituent	Configuration		$[\Phi_{alkyl}]_{578}$	$[\Phi_{amine}]_{578}$
$COOCH_3$	*R*	(*R*)-1-PEA[a)]	+925.9	+125.1
$COOCH_3$	*R*	(*S*)-1-PEA[a)]	+925.9	−125.1
CN	*R*	(*S*)-1-PEA	+269.3	−9.9
CN	*S*	(*S*)-1-PEA	−269.3	−9.9

a) (*R*)-1-PEA: (*R*)-1-phenylethylamine.

and pyridine. 1-Cyanoethyl complex, **6**, was obtained by the same procedure. The structures of these complexes were characterized by IR, ^1H NMR, and/or elemental analyses.

No substantial racemization occurs during the ligand-exchange process: optical rotation did not decrease during 12 h under the conditions applied in ligand exchange, and the (*R*)-1-phenylethylamine complex, **1**-(*R*,*R*), regained through the aqua complex showed almost the same optical rotation ($[\alpha]_{578}$ +210°) as the original one.

The CD spectra of chiral 1-cyanoethyl and 1-(methoxycarbonyl)ethyl complexes are shown in Figs. 4 and 5 respectively. (*R*)-1-Cyanoethyl complexes (**5**-(*R*,*S*), **6**) have clear negative and positive Cotton effects at about 440 and 375 nm respectively; the (*S*)-1-cyanoethyl complex (**5**-(*S*,*S*)) also has clear but reverse Cotton effects at the corresponding wave lengths. However, the (*R*)-1-(methoxycarbonyl)ethyl complexes (**1**-(*R*,*R*), **1**-(*R*,*S*), **3**) give broad positive spectra, ranging from 600 to 400 nm, and the CD peak around 380 nm is greatly influenced by the chiral amine moiety rather than by the chiral alkyl. Thus, the configuration of the alkyl part can not simply be deduced from the sign of the Cotton effect.

The specific rotations and molecular rotations of the chiral alkyl-cobalt complexes prepared here are listed in Table 3. As may be seen from Table 3, the (*R*)-1-substituted alkyl complex and the (*S*)-1-substituted alkyl complex causes positive and negative rotation respectively. If the contribution from a chiral distortion of the inplane ligand is negligible, the molecular rotation of diastereomeric complex will be expressed by the sum of the partial contributions of the alkyl part ($[\Phi_{alkyl}]$)

and the amine part ($[\Phi_{\mathrm{amine}}]$):

$$[\Phi] = [\Phi_{\mathrm{alkyl}}] + [\Phi_{\mathrm{amine}}]. \tag{1}$$

The $[\Phi_{\mathrm{alkyl}}]$ and $[\Phi_{\mathrm{amine}}]$ values of the diastereomers are calculated (Table 4). From Table 4 it can be said that the partial contribution of the alkyl part is considerably greater than that of the amine part, and the calculated values of the partial contribution of the alkyl part, $[\Phi_{\mathrm{alkyl}}]$, are comparatively near to the molecular rotations of the corresponding pyridine complex, **3** or **6**, which has no chirality on the axial base. Thus, the rotational sign (in the longer-wavelength region of about 546 to 589 nm) can be useful for deducing the configuration of the 1-substituted alkyl metal complexes. Further studies on this respect are now under way.

Experimental

The IR spectra were recorded on a JASCO A-3 spectrometer. The NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer, using TMS as the internal standard. The optical rotations were measured on a Perkin-Elmer 241 polarimeter and a Carl Zeiss photoelectric precision polarimeter. The circular dichroism spectra were recorded on a JASCO J-40C spectrometer.

*Bis(dimethylglyoximato) [(*R*)-1-(methoxycarbonyl) ethyl] [(*R*)-1-phenylethylamine]cobalt(III), (**1**-(*R,R*)).* To a methanol (100 cm^3) solution of $Co(OCOCH_3)_2 \cdot 4H_2O$ (50 g) was added a hot solution of dimethylglyoxime (47 g) in methanol (400 cm^3) under a nitrogen atomosphere with stirring. The solution was stirred for 5—10 min. The reaction vessel was then connected to a hydrogen-gas burret. 22.5 cm^3 of methyl acrylate was added to the reaction vessel by means of a syringe. The reaction mixture was then stirred under a hydrogen atmosphere. After a theoretical amount of hydrogen had been absorbed, the reaction mixture was neutralized by an aqueous solution of sodium hydroxide (16 g) on cooling. To the resulting solution, 25.5 cm^3 of *R*(+)-1-phenylethylamine ($[\alpha]_D^{23}$ +38°) was added. The products were extracted with dichloromethane (2 dm^3) and washed several times with water. The dichloromethane solution was dried over anhydrous sodium sulfate and concentrated *in vacuo* to give a crystalline mass. The crude product was dissolved in methanol (370 cm^3) at room temerature. The solution was filtered, and then, to the filtrate, water (445 cm^3) was added gradually by means of a syringe on warming (30—35 °C). The solution was left standing overnight at room temperature. The dark red crystals thus deposited were collected by filtration; 25.4 g (1C-I). 1C-I (25.4 g) was recrystallized from methanol (240 cm^3) and water (288 cm^3) to give 15 g of crystals (1C-II), $[\alpha]_{578}$ +195.5° (*c* 0.404, chloroform). The recrystallization of 1C-II (14.9 g) from methanol (144 cm^3) and water (156 cm^3) gave 10.4 g of crystals (1C-III), $[\alpha]_{578}$ +211.3°, $[\alpha]_{546}$ +233,4° (*c* 0.407, chloroform). Found: C, 48.34; H, 6.33; N, 14.39%. Calcd for $C_{20}H_{32}N_5O_6Co$: C, 48.29; H, 6.48; N, 14.08%.

*Aquabis(dimethylglyoximato) [(*R*)-1-(methoxycarbonyl) ethyl]-cobalt(III), (**2**).* To a methanol (20 cm^3) solution of 4.5 g of **1**-(*R*, *R*) was added 2 mol dm^{-3} hydrochloric acid (9 cm^3), after which the solution was left standing for 2 h, and then 9 cm^3 of 6 mol dm^{-3} hydrochloric acid was added. The resulting complexes were extracted with three 100-cm^3 portions of dichloromethane. The extract was neutralized by adding an excess of solid potassium carbonate and 1 cm^3 of water. After 10 min, the dichloromethane solution was concentrated under a reduced pressure to give a crystalline mass. The crude product was dissolved in acetone (10 cm^3). In a few minutes crystals appeared which were collected by filtration; 1.7 g (48%). These are satisfactory enough for further syntheses. From the above filtrate another crop (0.9 g) of crystals was obtained by concentrating it, followed by treating the residue with acetone. The product was further purified by silica-gel column chromatography (Kiesel gel 60, Merck), using acetone–benzene as the eluent. Fractions giving a single spot on TLC [R_f 0.45, acetone (2)/benzene(1)] were collected and concentrated under reduced pressure to give a thick paste, which was then crystallized on addition of acetone. $[\alpha]_{578}$ +160° (*c* 0.206, methanol); IR(KBr): 3400 (OH), 1670 (ester), 1565 cm^{-1} (C=N); ^{1}H NMR (D_2O): δ 0.05 (d, 3H, $C\underline{H}_3CHCo$), 2.28 and 2.29 (CH_3 of Hdmg), 3.38 (s, 3H, $-COOCH_3$), 4.75 (broad, HOD); Found: C, 37.05; H, 5.89; N, 14.50%. Calcd for $C_{12}H_{23}N_4O_7Co$: C, 36.56; H, 5.88; N, 14.21%.

*Bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl](pyridine)-cobalt(III), (**3**).* *Method (A)*: 2.7 g of bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl][(*R*)-1-phenylethylamine]cobalt(III) ($[\alpha]_{578}$ +209°) was dissolved in methanol (30 cm^3), and pyridine (1.5 cm^3) was then added. Carbon dioxide was bubbled through the solution for 20 min, and then 15 cm^3 of water were added. The bubbling was continued for another 10 min. The reaction mixture was extracted with 200—250 cm^3 of benzene and washed several times with water. The benzene layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give a yellow crystalline powder; 2.14 g (87%). The crude product (1 g) was recrystallized from methanol (15 cm^3) and water (25 cm^3) to give leaflets (0.46 g), $[\alpha]_{578}$ +167°, $[\alpha]_{546}$ +198° (*c* 0.408, chloroform). The IR and ^{1}H NMR spectra were identical with those of the racemic compound.

Method (B): 8 g of bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl][(*R*)-1-phenylethylamine]cobalt(III) ($[\alpha]_{578}$ +196°) was dissolved in methanol (35 cm^3), and then 12 cm^3 of 2 mol dm^{-3} hydrochloric acid were added. After 1 h, pyridine (2.5 cm^3) was added to the solution. The resulting solution was left standing for another 30 min, extracted with 200 cm^3 of dichloromethane, and then washed with water. The dichloromethane layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give a yellow crystalline powder; 7 g (96%). The IR and ^{1}H NMR spectra were identical with those of the racemic compound.

*Mutarotation of Compound **3** in Methanol–Water*: To a methanol (5 cm^3) solution of the pyridine complex **3** (0.0303 g, 0.09 mmol) were added water (5 cm^3) and pyridine (0.021 g, 0.27 mmol). The optical rotational change of the above solution was followed. The change was very slow (see below):

Time/h	$\alpha_{578}/^\circ$
0.0	+0.31
0.5	+0.31
12.0	+0.30
20.0	+0.28
111.0	+0.175

*Bis(dimethylglyoximato) [(*R*)-1-(methoxycarbonyl) ethyl] [(*S*)-1-phenylethylamine]cobalt(III), (**1**-(*R,S*)).* 300 mg (0.76 mmol) of the *R*(+)-aqua complex (**2**) and 93 mg (0.76 mmol) of (*S*)-(−)-1-phenylethylamine were dissolved in methanol. The solution was concentrated *in vacuo* to dryness. The procedure was repeated three times. The IR and ^{1}H NMR spectra were shown in Tables 1 and 2. $[\alpha]_{578}^{21}$ +161°, $[\alpha]_{546}^{21}$

+186° (*c* 0.404, chloroform); Found: C, 47.97; H, 6.64; N, 13.93%. Calcd for $C_{20}H_{32}N_5O_6Co$: C, 48.29; H, 6.48; N, 14.08%.

*Bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl][(1*R*,-2*S*)-1,2-diphenyl-2-aminoethanol]cobalt(III), (**4**).* 250 mg (0.63 mmol) of the *R*(+)-aqua complex (**2**) and 135 mg (0.63 mmol) of (1*R*, 2*S*)-1,2-diphenyl-2-aminoethanol were dissolved in methanol. The solution was concentrated *in vacuo* to dryness. The procedure was repeated three times. ^{1}H NMR ($CDCl_3$): δ 0.25 (d, 3H, $\mathrm{C\underline{H}_3CHCOOCH_3}$), 1.95 and 1.98 ($\mathrm{CH_3(Hdmg)}$ and $\mathrm{CH_3C\underline{H}Co}$), 3.34 (s, 3H, $\mathrm{COOC\underline{H}_3}$), 4.46 (d, 1H, $\mathrm{\underline{H}COH}$), 6.84 (broad m, NH_2), 7.22 (m, 10H, Ph). $[\alpha]_{578}$ +143.3°, $[\alpha]_{546}$ +190° (*c* 0.30, chloroform).

*[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III), (**5**-(*R*,*S*)), and [(*S*)-1-Cyanoethyl]bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III), (**5**-(*S*,*S*)).* Acrylonitrile (8 cm^3) was added to a methanolic solution of bis(dimethylglyoximato)cobalt (II), prepared from Co $(OCOCH_3)_2 \cdot 4H_2O$ (25 g) and dimethylglyoxime (23.5 g) in methanol (250 cm^3). The reaction mixture was stirred under a hydrogen atmosphere at room temperature. After a theoretical amount of hydrogen had been absorbed, an aqueous solution of sodium hydroxide (8 g) and 13 cm^3 of (*S*)-1-phenylethylamine ($[\alpha]_D$ −39°) were successively added to the cooled reaction mixture. The resulting complexes were extracted with dichloromethane (1.5 dm^3) and washed several times with water. The dichloromethane solution was dried over anhydrous sodium sulfate and then concentrated under reduced pressure to give a crude product. It was dissolved in 150 cm^3 of methanol at room temperature. The solution was filtered, and 140 cm^3 of water were added by means of a syringe on warming (30—35 °C). The solution was then left standing overnight at room temperature. Dark red crystals deposited were collected by filtration; 26.7 g (5C-I), $[\alpha]_{578}$ +2°. 5C-I (25.3 g) was recrystallized from methanol (290 cm^3) and water (350 cm^3) to give 12.3 g of crystals (5C-II); $[\alpha]_{578}$ +32° (*c* 0.5, chloroform). 5C-II (11 g) was again recrystallized from methanol (140 cm^3) and water (200 cm^3) to give 6.68 g of crystals (5C-III); $[\alpha]_{578}$ +48.5°. 5C-III (6.68 g) was recrystallized from methanol (94 cm^3) and water (106 cm^3) to give 4.5 g of crystals (5C-IV); $[\alpha]_{578}$ +55.5° and $[\alpha]_{546}$ +60.5° (*c* 0.2, chloroform). Another experiment gave a constant rotation of $[\alpha]^{23}_{578}$ +55.85°, $[\alpha]^{23}_{546}$ +60.10°(*c* 0.188, chloroform). Found: C, 49.05; H, 6.45; N, 18.18%. Calcd for $C_{19}H_{29}N_6O_4Co$: C, 49.13; H, 6.29; N, 18.09%. From filtrates of 5C-I and 5C-II, 10 g of crystals (5F-I) ($[\alpha]_{578}$ −15.3°) and 2.5 g of crystals (5F-II) ($[\alpha]_{578}$ −47.7°) were obtained respectively. The repeated recrystallization of 5F-II (2 g) from methanol/water (1.2/1) gave 0.275 g of crystals with a constant rotation; $[\alpha]^{23.5}_{578}$ −60.13°, $[\alpha]^{23.5}_{546}$ −64.56° (*c* 0.158, chloroform). Found: C, 48.16; H, 6.34; N, 17.81%. Calcd for $C_{19}H_{29}N_6O_4Co$: C, 49.13; H, 6.29; N, 18.09%.

*[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(pyridine)cobalt(III), (**6**).* Pyridine (0.42 cm^3, 5.2 mmol) and water (6 cm^3) were added to a solution of [(*R*)-1-cyanoethyl]bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III), **5**-(*R*,*S*), (0.8 g, 1.7 mmol) in methanol (12 cm^3). Carbon dioxide was bubbled through the solution for 20 min at room temperature. The reaction mixture was then extracted with benzene (200 cm^3) and washed several times with water. The benzene layer was dried over anhydrous sodium sulfate and concentrated *in vacuo* to give 0.65 g of a crude product (89%). The crude product (0.65 g) was recrystallized from methanol (19 cm^3) and water (35 cm^3) to give orange leaflets (0.08 g), $[\alpha]^{22}_{578}$ +52.2°, $[\alpha]^{22}_{546}$ +59.2° (*c* 0.157, chloroform). The IR and ^{1}H NMR spectra were identical with those of the racemic compound.

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