Efficient Stereochemical Regulation of Octahedral Cobalt(III) Complexes by a Chiral Bidentate Ligand. Part 1. Effect of *N*-Alkyl Substitutions†

Morio Yashiro,[*,a] **Takashi Murata,**[b] **Sadao Yoshikawa**[b] **and Shigenobu Yano**[*,c]
[a] *Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*
[b] *Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*
[c] *Department of Chemistry, Faculty of Science, Nara Women's University, Kitauoya-nishi-machi, Nara 630, Japan*

A series of octahedral cobalt(III) complexes involving a tetradentate diaminedicarboxylate and a chiral diamine was prepared: $[\mathrm{CoL(am)}]^+$ where L = ethylenediamine-*N,N'*-diacetate (edda^{2-}), or its *N,N'*-dimethyl (dmedda^{2-}) and *N,N'*-diethyl (deedda^{2-}) derivatives; am = (1*R*),(2*R*)-cyclohexane-1,2-diamine (*R,R*-chxn), or its *N,N'*-dimethyl (*R,R*-dmchxn) and *N,N'*-diethyl (*R,R*-dechxn) derivatives. The complexes were separated into their diastereoisomers using cation-exchange column chromatographies, and characterized by elemental analyses, electronic absorption, circular dichroism and ^{13}C NMR spectroscopies. The crystal structure of a dominant product in the $[\mathrm{Co(edda)}(R,R\text{-dmchxn})]^+$ system, $(-)_{550}[\mathrm{Co(edda)}(R,R\text{-dmchxn})]\mathrm{ClO_4{\cdot}H_2O}$, has been established, and the stereochemistry determined to be Δ-sym-*cis*: orthorhombic, space group $P2_12_12_1$, a = 13.469(2), b = 19.184(3), c = 7.917(1) Å, Z = 4, R = 0.067, R' = 0.055. *N*-Alkyl substitutions on the edda ligand and those on the *R,R*-chxn ligand influence the stereochemistry of the cobalt(III) complexes in different ways. The former caused stereoselective formation of Λ-sym-*cis* forms, the latter preferential formation of Δ-sym-*cis* forms. High stereoselectivity was observed in the formation of $[\mathrm{Co(deedda)}(R,R\text{-chxn})]^+$, yielding a final product distribution of 96% Λ-sym-*cis* and 4% Δ-sym-*cis* forms, whereas $[\mathrm{Co(edda)}(R,R\text{-dechxn})]^+$ yielded 2% Λ-sym-*cis* and 98% Δ-sym-*cis* forms. The latter is due to steric interaction between *N*-alkyl substituents in the *R,R*-chxn chelate and acetate rings in the edda chelate, while the former is due to steric interaction between *N*-alkyl substituents in the edda chelate and NH in the *R,R*-chxn chelate. Such interactions are efficient in steric regulation of octahedral cobalt(III) complexes.

Chirality and the optical resolution of chiral compounds are becoming increasingly important in fields related to biology and medicine. It is often observed that a chiral chelate causes stereoselective formation of octahedral cobalt(III) complexes. Stereochemical regulation of octahedral cobalt(III) complexes by a chiral tetradentate ligand has been thoroughly studied, and the highly regulated complex systems have been applied to asymmetric reactions.[1-5]

Although some studies have reported the stereochemistry of cobalt(III) complexes involving a chiral bidentate ligand,[6-10] no remarkable stereochemical regulation has been observed. It can be expected that appropriate design of steric interactions between chelates will cause steric regulation around the metal centre. In order to shed light on this problem, we chose (1*R*),-(2*R*)-cyclohexane-1,2-diamine (*R,R*-chxn) as a chiral bidentate ligand, since the *R,R*-chxn chelate adopts the fixed λ-*gauche* conformation.[11] The rigidity in conformation will be useful in order to exert effective stereospecific interactions between chelates. In the present study, the stereochemical effect of *N*-alkyl substitutions in the formation of octahedral cobalt(III) complexes involving tetradentate ethylenediaminediacetate (edda^{2-}) and the chiral diamine *R,R*-chxn has been investigated. Since there is only limited information concerning the crystal structure of a mixed-ligand complex involving an edda-type chelate and a diamine,[12,13] the structure of one of the products has been determined by X-ray analysis, and stereoselective formation is discussed on the basis of it.

Experimental

Preparations.—The compound $\mathrm{H_2edda}$ was commercially available and used without further purification. The salts Ba(dmedda) and Ba(deedda) (dmedda = *N,N'*-dimethylethylenediamine-*N,N'*-diacetate, deedda = *N,N'*-diethylethylenediamine-*N,N'*-diacetate),[14] *R,R*-chxn,[15] and *R,R*-dmchxn[16] [*N,N'*-dimethyl-(1*R*),(2*R*)-cyclohexane-1,2-diamine] were prepared by reported procedures.

R,R-*dechxn*. A 20 g (0.18 mol) amount of *R,R*-chxn was dissolved in water (30 cm^3) and cooled in an ice-bath. Acetic anhydride (33 g, 0.32 mol) was added dropwise with stirring. After the addition had been completed, the mixture was stirred for 2 h. Then the reaction mixture was evaporated to dryness. Recrystallization from water–methanol gave colourless needles (yield 31.3 g). The resulting *N,N'*-diacetyl derivative (24 g, 0.12 mol) was treated with $\mathrm{LiAlH_4}$ (14 g, 0.37 mol) in tetrahydrofuran (thf, 250 cm^3), by a procedure reported for reduction of amides.[16] The required product was obtained by vacuum distillation, b.p. 105.5–107.0 °C (19 mmHg, *ca.* 2527 Pa), yield 10.3 g.

$[\mathrm{Co(edda)}(R,R\text{-chxn})]^+$ **1**. The method for the preparation of this complex is similar to reported procedures.[14]

To a solution of $\mathrm{Na_2(edda)}$ (0.01 mol, prepared from $\mathrm{H_2edda}$

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

and NaOH) in water (40 cm^3) a solution of $CoCl_2·6H_2O$ (2.38 g, 0.01 mol) in water (40 cm^3) and activated carbon (0.15 g) were added. Activated carbon was used to facilitate the formation of an equilibrium mixture of isomers.[17] To the solution, *R,R*-chxn (1.14 g, 0.01 mol) in water (50 cm^3) was added dropwise. During the addition air was bubbled through the mixture, and the aeration was continued for 9 h at room temperature. During the reaction, the pH of the solution was in the range 4–6.3. The reaction mixture was filtered and the filtrate poured onto a column of SP-Sephadex C-25 (Na^+ form, 800 × 50 mm). Washing with water removed a purplish material which was not adsorbed on the column.

Elution with 0.01 mol dm^{-3} NaCl aqueous solution produced a band containing 1 + products. The eluate from the band was then poured onto a column of Dowex 50W-X2 (100–200 mesh, Na^+ form, 800 × 50 mm). After washing with water (1 l), it was eluted with 0.1 mol dm^{-3} $NaClO_4$ aqueous solution. Three red bands (1 +) were developed (**1a**, **1b** and **1c**, respectively). The third band (**1c**) was of small amount and absorption spectroscopy indicated an asymmetrical-*cis* (asym-*cis*) isomer, so it was not isolated. Desalting of the eluted solution was accomplished by Sephadex G-15 gel chromatography. Concentration of each eluate from **1a** and **1b** gave microcrystals [Found: (for **1a**) C, 30.9; H, 5.4; N, 12.0. (for **1b**) C, 30.9; H, 5.3; N, 12.05. $C_{12}H_{24}ClCoN_4O_8·H_2O$ requires C, 31.0; H, 5.6; N, 12.1%]. **CAUTION**: Although these perchlorate salts are moderately stable, they are potential hazards and should therefore be handled with care and in small quantities.

[Co(dmedda)(*R,R*-chxn)]$^+$ **2**. The salt Ba(dmedda) (3.39 g, 0.01 mol) was dissolved in warm water (50 cm^3) and $CoSO_4·7H_2O$ (2.81 g, 0.01 mol) in water (20 cm^3) was added. The mixture was stirred for 1 h at 60 °C, then activated carbon (0.15 g) was added. A solution of *R,R*-chxn (1.14 g, 0.01 mol) in water (50 cm^3) was added dropwise, with air bubbling through the mixture. The aeration was continued for 9 h. During the reaction the pH of the solution was in the range 5–7. The reaction mixture was filtered and the filtrate subjected to column chromatography on SP-Sephadex C-25 and then Dowex 50W-X2, as described above. Two red bands (**2a** and **2b**) were developed on the latter column, in addition to a trace amount of a third band which is presumably an asym-*cis* isomer. Desalting of the eluted solution was accomplished by Sephadex G-15 gel chromatography. The main fraction (**2a**) was treated with Dowex 2X-8 (100–200 mesh, Cl^- form) and then filtered. Concentration of the filtrate gave microcrystals of the chloride salt (Found: C, 35.7; H, 7.1; N, 12.1. $C_{14}H_{28}ClCoN_4O_4·3.5H_2O$ requires C, 35.5; H, 7.45; N, 11.8%).

The complex [Co(deedda)(*R,R*-chxn)]$^+$ **3** was prepared similarly except that Ba(deedda) was used instead of Ba(dmedda). Two red bands (**3a** and **3b**) developed on the column of Dowex 50W-X2, in addition to a trace amount of a third band which is considered to be the asym-*cis* isomer. The main fraction (**3a**) was treated as described above and microcrystals of the chloride salt were obtained (Found: C, 38.5; H, 8.05; N, 11.5. $C_{16}H_{32}ClCoN_4O_4·3.5H_2O$ requires C, 38.3; H, 7.8; N, 11.2%).

The complex [Co(edda)(*R,R*-dmchxn)]$^+$ **4** was prepared similarly to **1** except that *R,R*-dmchxn was used instead of *R,R*-chxn. Two red bands (**4a** and **4b**) developed on the column of Dowex 50W-X2. Desalting of the eluted solution was accomplished by Sephadex G-15 gel chromatography, and concentration of the eluate from the main band gave microcrystals of the perchlorate salt **4b** (Found: C, 35.1; H, 6.2; N, 11.7. $C_{14}H_{28}ClCoN_4O_8$ requires C, 35.4; H, 5.9; N, 11.8%).

The complex [Co(edda)(*R,R*-dechxn)]$^+$ **5** was prepared similarly to **1**, except that *R,R*-dechxn was used instead of *R,R*-chxn. Two red bands (**5a** and **5b**) developed on the column of Dowex 50W-X2. Concentration of the eluate from the main band and addition of methanol gave microcrystals of the perchlorate salt **5b** (Found: C, 38.1; H, 7.0; N, 10.3. $C_{16}H_{32}ClCoN_4O_8·CH_3OH$ requires C, 38.2; H, 6.8; N, 10.5%).

Carbon-13 NMR spectroscopy indicated that the separation by column chromatography gave the pure diastereoisomer for each fraction.

Crystal Structure Determination of $(-)_{550}$[Co(edda) (*R,R*-dmchxn)]$ClO_4·H_2O$ **4b**.—*Crystal data.* $C_{14}H_{28}ClCoN_4O_8·H_2O$, $M = 492.8$, orthorhombic, space group $P2_12_12_1$, $a = 13.469(2)$, $b = 19.184(3)$, $c = 7.917(1)$ Å, $U = 2046$ Å^3, $D_m = 1.61$ g cm^{-3}, $Z = 4$, $D_c = 1.60$, $F(000) = 1032$. Red prism, approximate dimensions 0.18 × 0.17 × 0.33 mm, μ(Mo-Kα) = 10.7 cm^{-1}.

Data collection and processing. Rigakudenki AFC-2 four-circle automated diffractometer, θ–2θ mode, scan speed 2° min^{-1}, LiF monochromatized Mo-Kα radiation; 3395 reflections measured ($3 < 2\theta < 60°$), giving 2216 with $F_o > 3\sigma(F_o)$. The intensities were corrected for Lorentz and polarization factors. No absorption correction was made since the size of the crystal used was small.

Structure analysis and refinement. The structure was solved by the heavy-atom method, and refined by a block-diagonal least-squares method. The absolute configuration of the complex cation was determined on the basis of the known configuration of asymmetric carbons in the *R,R*-chxn moiety.[11] Anisotropic thermal parameters for non-hydrogen atoms were used in the refinement. Although the elemental analysis indicated that this compound contains no water of crystallization, the crystallography indicated the existence of one such molecule. Its existence is supported by the density of the crystal; the measured density is in good agreement with the calculated one including a water molecule. This difference is thought to arise from the fact that the water of crystallization is lost on drying *in vacuo* before the elemental analysis. Oxygen atoms in the perchlorate anion gave very large thermal parameters, indicating disorder of these atoms. Since this phenomenon is not important for the present study, no effort to determine their individual positions was made. Sixteen hydrogen atoms bound to carbon or nitrogen were located on Fourier difference maps. The remaining 12 were located by assuming a tetrahedral co-ordination with C–H and N–H bond distances of 10.9 Å. They were all included in the final refinement with the isotropic thermal parameters. The atomic scattering factors and values of f' and f'' were taken from ref. 18. The final indices were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.067$ and $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}} = 0.055$. The weighting scheme $1/w = \sigma_c{}^2 + (0.015|F_o|)^2$ was employed, where $\sigma_c = (\bar{N})^{\frac{1}{2}}$ is a counting statistics error with the Gaussian distribution function $P(N) = (\frac{1}{2}\bar{N})^{\frac{1}{2}}\exp[-(N - \bar{N})^2/2\bar{N}]$ where N is the count. When the coordinates were inverted in order to test the structure, convergence was reached with $R = 0.072$ and $R' = 0.059$. The final Fourier difference synthesis showed peaks at heights up to 0.76 e Å^{-3}. The final atomic coordinates for non-hydrogen atoms are listed in Table 3. All calculations were carried out on a HITAC M680H computer at the Computer Centre of University of Tokyo by use of the UNICS III[19] and ORTEP[20] programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Measurements.—Electronic absorption spectra were obtained on a Shimadzu UV-210 double-beam spectrophotometer, circular dichroism spectra on a JASCO J-500A spectropolarimeter. These measurements were made on aqueous solution, of concentration *ca.* 2 × 10^{-3} mol dm^{-3}. Fourier-transform ^{13}C NMR spectra in D_2O solutions were obtained on a JEOL PS-100 spectrometer (25 MHz) with $SiMe_4$ sealed in a capillary as an external reference.

Results and Discussion

Preparation of Complexes.—A series of mixed-ligand cobalt(III) complexes, [Co(edda)(*R,R*-chxn)]$^+$ **1**, [Co(dmedda)-

(R,R-chxn)]$^+$ **2**, [Co(deedda)(R,R-chxn)]$^+$ **3**, [Co(edda)(R,R-dmchxn)]$^+$ **4** and [Co(edda)(R,R-dechxn)]$^+$ **5** was prepared by air oxidation of aqueous solutions containing ligands and cobalt(III) ion in the presence of activated carbon. It was expected that using a charcoal catalyst would result in thermodynamic equilibrium.[17] They were separated into their diastereoisomers by cation-exchange column chromatographies. Electronic absorption and CD spectra are shown in Fig. 1 and corresponding numerical data in Table 1. Absorption spectra of **1a** and **1b** indicated that the complexes have *trans*-N_4O_2 geometries according to the shoulder in the first absorption region. The very simple ^{13}C NMR spectra (Table 2) also suggest that both complexes possess the *trans*-N_4O_2 geometry, with C_2 symmetry [symmetrical-*cis* (sym-*cis*)]. A small amount of an isomer **1c** (5%) in addition to the two sym-*cis* isomers **1a** and **1b** was obtained, which can be assigned a *cis*-N_4O_2 geometry (asym-*cis*) on the basis of electronic absorption spectroscopy.[12] Two diastereoisomers of sym-*cis* type are obtained for **2**–**5**. However, the asym-*cis* isomers were present only in trace amounts. The CD spectra of the two sym-*cis* isomers **1a** and **1b** indicated that they are nearly mirror images of each other. Similarly, the two isomers of **2**–**5** gave nearly inverted CD patterns. Absolute configurations of the complexes have been assigned on the basis of the crystallographic study.

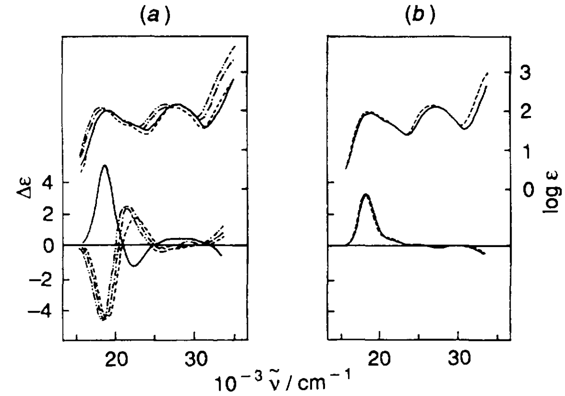


Fig. 1 Electronic absorption (upper) and CD spectra of the complexes: (*a*) (———) **1a**, (– – – –) **1b**, (–•–•–) **4b**, (–••–••–) **5b**; (*b*) (———) **2a**, (– – – –) **3a**

Table 1 Electronic absorption and CD spectral data

Complex	Absorption $10^{-3}\tilde{\nu}$/cm^{-1} (log ε)	CD $10^{-3}\tilde{\nu}$/cm^{-1} (Δε)
1a	18.87 (1.98)	18.52 (+5.17)
		22.22 (−1.56)
	27.78 (2.11)	26.74 (+0.24)
		28.74 (+0.21)
1b	18.87 (2.02)	18.52 (−4.94)
		22.22 (+1.69)
	27.78 (2.15)	26.74 (−0.28)
2a	18.76 (1.94)	18.15 (+3.34)
	27.17 (2.11)	27.25 (−0.09)
		29.76 (+0.08)
3a	18.62 (2.08)	17.95 (+3.38)
	26.88 (2.15)	27.25 (−0.11)
		29.50 (+0.04)
4b	18.69 (2.06)	18.24 (−5.03)
		21.51 (+2.37)
	27.03 (2.15)	25.77 (−0.36)
5b	18.18 (2.08)	18.01 (−5.18)
		21.00 (+2.49)
	26.67 (2.15)	25.77 (−0.54)

Table 2 The ^{13}C NMR spectral data obtained in D_2O*

Complex	δ							
1a	186.0	60.7	56.4	53.7	33.6	24.8		
1b	186.2	61.4	56.5	53.6	33.7	24.8		
2a	184.1	66.2	63.9	60.6	50.5	33.4	24.8	
2b	184.2	66.8	63.7	61.3	50.8	33.5	24.8	
3a	184.7	62.9	60.3	59.7	57.9	33.3	24.8	8.6
4b	185.6	68.8	56.8	53.8	36.4	30.5	25.2	
5b	185.7	67.4	57.0	53.8	46.7	30.7	25.1	13.9

* Chemical shifts are given in reference to $SiMe_4$.

Crystal Structure Analysis.—In order to establish the stereochemistry of the complex system, a crystal structure determination was carried out; [Co(edda)(R,R-dmchxn)]ClO_4 **4b** was chosen which gave good single crystals. The ORTEP drawing of the complex cation is shown in Fig. 2, atomic coordinates are listed in Table 3 and selected bond lengths and angles in Table 4. The stereochemistry is Δ-*trans*(O,O'). The five-membered chelate of R,R-chxn adopts a λ-*gauche* con-

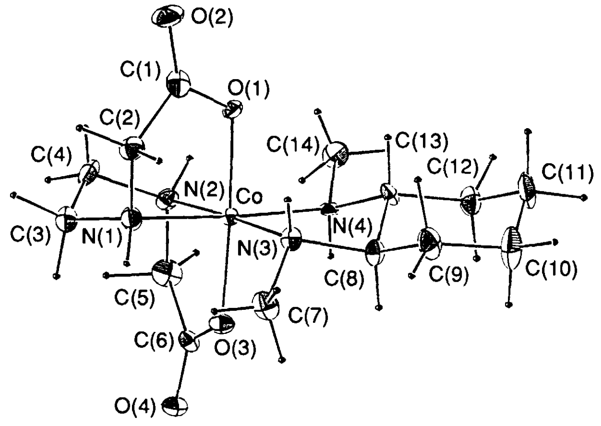


Fig. 2 An ORTEP drawing and atomic numbering scheme for the $(-)_{550}$[Co(edda)(R,R-dmchxn)]$^+$ cation of **4b**

Table 3 Atomic coordinates (× 10^4) of non-hydrogen atoms with estimated standard deviations (e.s.d.s) for complex **4b**

Atom	*x*	*y*	*z*
Co	150.3(6)	55.9(4)	938.6(11)
O(1)	−744(3)	17(3)	2796(5)
O(2)	−788(4)	−51(4)	5610(6)
O(3)	1081(3)	50(2)	−862(6)
O(4)	1896(4)	−653(3)	−2634(7)
N(1)	1221(4)	−47(3)	2626(7)
N(2)	190(4)	−973(3)	756(8)
N(3)	165(4)	1086(3)	1067(8)
N(4)	−975(4)	164(3)	−629(6)
C(1)	−335(5)	12(4)	4295(8)
C(2)	776(5)	172(4)	4271(10)
C(3)	1577(6)	−774(4)	2637(11)
C(4)	718(6)	−1243(4)	2291(10)
C(5)	682(6)	−1152(4)	−876(13)
C(6)	1284(5)	−550(4)	−1540(9)
C(7)	1159(5)	1439(4)	928(13)
C(8)	−517(5)	1359(3)	−309(10)
C(9)	−829(6)	2117(4)	40(13)
C(10)	−1601(7)	2339(4)	−1241(15)
C(11)	−2481(7)	1855(4)	−1285(14)
C(12)	−2159(6)	1096(4)	−1670(10)
C(13)	−1405(5)	871(4)	−348(10)
C(14)	−1756(6)	−382(4)	−656(11)
Cl	−1613(2)	−2568(1)	−1016(4)
O(5)	−955(6)	−2273(4)	175(13)
O(6)	−1720(13)	−3218(5)	−582(25)
O(7)	−1266(16)	−2505(10)	−2479(18)
O(8)	−2488(7)	−2263(9)	−850(25)
O(9w)	−648(6)	1644(4)	−5691(9)

formation, and the *N*-methyl substituents of the *R*,*R*-chxn chelate adopt equatorial orientations. The five-membered ring of the ethylenediamine moiety in the edda chelate adopts a δ-*gauche* conformation, and the two out-of-plane acetate rings of the edda chelate have envelope conformations. The absolute configurations of two nitrogens of the edda chelate [N(1) and N(2)] are both *R*, and those of the two nitrogens of the *R*,*R*-chxn chelate [N(3) and N(4)] are both *S*. Bond distances for Co–N(1), Co–N(2), Co–N(3) and Co–N(4) are 1.975(6), 1.979(5), 1.979(5) and 1.970(5) Å, respectively, which are normal for Co^{III}–N bond distances. The angle N(1)–Co–N(2) is 86.0(3)° and N(3)–Co–N(4) is 86.2(2)°, O(1)–Co–O(3) is 176.7(2)° and occupies axial positions of the N(4) plane.

Absolute Configuration and Circular Dichroism.—For tetragonal complexes of the type sym-*cis*-$[Co(L)L']^n$ (L = edda type ligand and L′ = two uni- or one bi-dentate ligand), the sign of the CD peak for the lowest-energy ^1E_g transition is expected to be negative for a Δ configuration. The stereochemistry of **4b** established by the X-ray analysis is consistent with this prediction on the basis of empirical rules. The complexes **1b**, **2b**, **3b** and **5b** show negative peaks and hence also might be expected to have Δ configurations. The diastereoisomers which give positive peaks at the same region (**1a**, **2a**, **3a**, **4a** and **5a**) are expected to adopt Λ configurations.

It has been reported that *N*-alkyl substituents in the $[Co(R_2edda)L']^n$ system (R = H, Me or Et)[12] cause a decrease in intensity of the CD peak. This is also observed in the present systems. On the other hand, substitution at the nitrogens of the *R*,*R*-chxn chelate cause no significant decrease in CD intensities.

Stereospecific Influence of N-*Alkyl Substitution.*—The formation ratios of the two sym-*cis* diastereoisomers of complexes **1**–**5** were determined from the absorbance at the maxima about 530 nm. For **1a**:**1b** the value was in good agreement with that determined from atomic absorption analysis for cobalt. The formation ratios are summarized in Table 5. The edda-*R*,*R*-chxn system with no alkyl substitution (**1**) gave two sym-*cis* forms in Λ:Δ ratio 60:40. Alkyl substitution at the nitrogens of the diamine chelate (**4** and **5**) cause preferential formation of the Δ-sym-*cis* diastereomer. Fig. 3(*ii*) shows the stereochemistry of the complexes. The acetate rings of edda would cause repulsion with the equatorially oriented *N*-alkyl groups (R^2) of the *R*,*R*-chxn moiety, which destabilizes the Λ configuration, and thus there is preferential formation of the Δ form. A high selectivity has been observed in $[Co(edda)(R,R\text{-dechxn})]^+$ **5** with Λ:Δ = 2:98.

Very interestingly, alkyl substitution at the nitrogens of the edda chelate (**2** and **3**) influence the Λ selectivity, in contrast to that at the nitrogens in the *R*,*R*-chxn chelate. A high selectivity has been observed in $[Co(deedda)(R,R\text{-chxn})]^+$ **3** with Λ:Δ = 96:4. A molecular model study indicates that interactions between the NR^1 groups of edda and the NH of *R*,*R*-chxn will cause preferential formation of the Λ form, while those between the acetate chelate rings of edda and NH of *R*,*R*-chxn will cause preferential formation of the Δ form. In the cases of **2** and **3**, the former interactions are effective and result in high Λ selectivity [Fig. 3(*i*)]. The selectivity increases with the bulkiness of the *N*-substituents on edda.

Conclusion

N-Alkyl substitution in the $[Co(edda)(R,R\text{-chxn})]^+$ system can

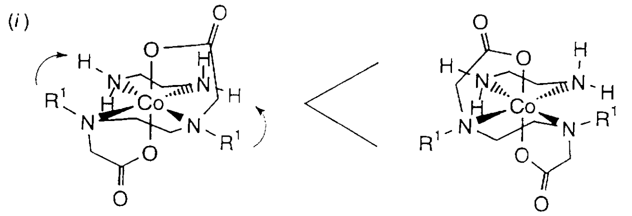
Table 4 Selected bond distances (Å) and angles (°) for complex **4b** with e.s.d.s in parentheses

Co–O(1)	1.902(4)	N(1)–C(3)	1.477(10)
Co–O(3)	1.899(4)	N(2)–C(4)	1.501(10)
Co–N(1)	1.975(6)	N(2)–C(5)	1.493(11)
Co–N(2)	1.979(5)	N(3)–C(7)	1.505(9)
Co–N(3)	1.979(5)	N(3)–C(8)	1.517(10)
Co–N(4)	1.970(5)	N(4)–C(13)	1.490(9)
O(1)–C(1)	1.309(8)	N(4)–C(14)	1.485(9)
O(2)–C(1)	1.212(8)	C(1)–C(2)	1.529(9)
O(3)–C(6)	1.298(9)	C(3)–C(4)	1.490(12)
O(4)–C(6)	1.213(9)	C(5)–C(6)	1.506(11)
N(1)–C(2)	1.493(9)	C(8)–C(13)	1.519(10)
O(1)–Co–O(3)	176.7(2)	Co–N(4)–C(13)	107.5(4)
O(1)–Co–N(1)	86.3(2)	Co–N(4)–C(14)	118.7(4)
O(3)–Co–N(2)	85.5(2)	C(13)–N(4)–C(14)	111.6(5)
N(1)–Co–N(2)	86.0(3)	O(1)–C(1)–O(2)	124.6(6)
N(3)–Co–N(4)	86.2(2)	O(1)–C(1)–C(2)	113.5(6)
Co–O(1)–C(1)	115.8(4)	O(2)–C(1)–C(2)	121.6(6)
Co–O(3)–C(6)	117.1(4)	N(1)–C(2)–C(1)	110.3(6)
Co–N(1)–C(2)	105.6(4)	N(1)–C(3)–C(4)	108.5(6)
Co–N(1)–C(3)	109.6(5)	N(2)–C(4)–C(3)	108.0(6)
C(2)–N(1)–C(3)	113.0(6)	N(2)–C(5)–C(6)	111.3(6)
Co–N(2)–C(4)	107.3(4)	O(3)–C(6)–O(4)	125.7(7)
Co–N(2)–C(5)	107.8(4)	O(3)–C(6)–C(5)	115.0(6)
C(4)–N(2)–C(5)	114.3(6)	O(4)–C(6)–C(5)	119.3(7)
Co–N(3)–C(7)	117.0(4)	N(3)–C(8)–C(13)	106.2(5)
Co–N(3)–C(8)	107.5(4)	N(4)–C(13)–C(8)	104.9(5)
C(7)–N(3)–C(8)	109.4(6)		

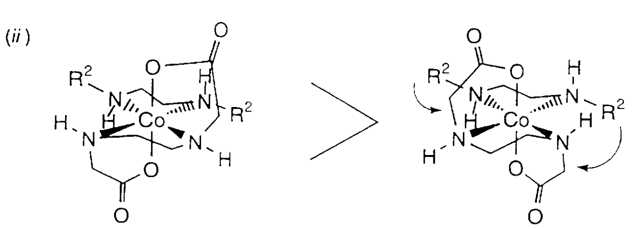
Table 5 Formation ratios of diastereoisomers of the *s-cis*-$[Co(R^1{}_2edda)(R,R\text{-}R^2{}_2chxn)]^+$ complex system *

(*i*) R^2 = H			
R^1	H	Me	Et
	1a:**1b**	**2a**:**2b**	**3a**:**3b**
Λ/Δ ratio	60:40	88:12	96:4
$\Delta G°$/kJ mol^{-1}	−0.97	−4.77	−7.61
(*ii*) R^1 = H			
R^2	H	Me	Et
	1a:**1b**	**4a**:**4b**	**5a**:**5b**
Λ/Δ ratio	60:40	11:89	2:98
$\Delta G°$/kJ mol^{-1}	−0.97	5.00	9.31

* $K = \exp(-\Delta G°/RT)$, T = 288 K.



(a) Δ - sym - *cis* (b) Λ - sym - *cis*



(a) Δ - sym - *cis* (b) Λ - sym - *cis*

Fig. 3 Two *s-cis*-type diastereoisomers of the complex systems (*i*) $[Co(R^1{}_2edda)(R,R\text{-chxn})]^+$ and (*ii*) $[Co(edda)(R,R\text{-}R^2{}_2chxn)]^+$. The cyclohexane moiety of the diamine chelate is omitted for clarity effect stereoselective formation concerning chirality about the octahedral metal centre. This substitution in the *R*,*R*-chxn chelate caused preferential formation of the Δ form, whereas those in the edda chelate caused preferential formation of the Λ form. The difference in stereoselectivity depending on substitutions of the two ligands is important because the stereochemistry of a complex can be regulated into a desired configuration using the same chiral source (*R*,*R*-chxn). This effective stereochemical regulation of octahedral complexes by a chiral bidentate ligand will be useful in constructing a chiral metal complex and also be a theoretical support of the role of chiral catalysts in highly selective asymmetric reactions.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (Nos. 63470035, 03555184 and 03241106), CIBA-GEIGY Foundation (Japan), Iwatani Naoji Foundation's Research, Nippon Itagarasu and Mitsubishi yuka kagaku Foundations.

References

1 R. G. Asperger and C. F. Liu, *Inorg. Chem.*, 1965, **4**, 1395; 1967, **6**, 796; R. C. Job and T. C. Bruice, *J. Am. Chem. Soc.*, 1974, **96**, 809.

2 S. Yoshikawa, M. Saburi and M. Yamaguchi, *Pure Appl. Chem.*, 1978, **50**, 915; M. Yamaguchi, S. Yamamatsu, T. Furusawa, S. Yano, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, 1980, **19**, 2010; M. Yamaguchi, S. Yano, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, 1980, **19**, 2016; *Bull. Chem. Soc. Jpn.*, 1980, **53**, 691; M. Yamaguchi, S. Yamamatsu, H. Oikawa, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, 1981, **20**, 3179; M. Yamaguchi, Y. Masui, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, 1982, **21**, 4138.

3 M. Ajioka, K. Matsuda, S. Yano and S. Yoshikawa, *J. Am. Chem. Soc.*, 1981, **103**, 2459; M. Yashiro, M. Ajioka, S. Yano, K. Toriumi, T. Ito and S. Yoshikawa, *Inorg. Chem.*, 1986, **25**, 1709.

4 F. Mizukami, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 472; S. Yano, A. Fujioka, M. Yamaguchi and S. Yoshikawa, *Inorg. Chem.*, 1978, **17**, 14; M. Yashiro, S. Yano, M. Ajioka and S. Yoshikawa, *Inorg. Chem.*, 1985, **24**, 3607.

5 S. Yano, S. Yaba, M. Ajioka and S. Yoshikawa, *Inorg. Chem.*, 1979, **18**, 2414.

6 L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, 1967, **6**, 1042; D. A. Buckingham, I. E. Maxwell and A. M. Sargeson, *Chem. Commun.*, 1969, 581; D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, A. M. Sargeson and H. C. Freeman, *Chem. Commun.*, 1969, 583.

7 M. Murakami and K. Takahashi, *Bull. Chem. Soc. Jpn.*, 1959, **32**, 308.

8 J. C. Dabrowiak and D. W. Cooke, *Inorg. Chem.*, 1975, **14**, 1305.

9 D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *J. Am. Chem. Soc.*, 1967, **89**, 5133.

10 F. P. Dwyer, T. E. MacDermott and A. M. Sargeson, *J. Am. Chem. Soc.*, 1963, **85**, 661.

11 S. Sato and Y. Saito, *Acta Crystallogr., Sect. B*, 1977, **33**, 860; A. Kobayashi, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B*, 1972, **28**, 2709; F. Marumo, Y. Utsumi and Y. Saito, *Acta Crystallogr., Sect. B*, 1970, **26**, 1492; M. Sato, Y. Yokoo, M. Yashiro, S. Yano, S. Yoshikawa, K. Kobayashi and T. Sakurai, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1392.

12 D. J. Radanovic, *Coord. Chem. Rev.*, 1984, **54**, 159.

13 S. Yano, T. Murata, M. Asami, M. Inoue, M. Yashiro, M. Kosaka and S. Yoshikawa, *Inorg. Chem.*, 1984, **23**, 4127; L. J. Halloran, R. E. Caputo, R. D. Willett and J. I. Legg, *Inorg. Chem.*, 1975, **14**, 1762.

14 J. I. Legg and D. W. Cooke, *Inorg. Chem.*, 1965, 4, 1576.

15 R. G. Asperger and C. F. Liu, *Inorg. Chem.*, 1965, **4**, 1492.

16 K. Kashiwabara, K. Hanaki and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2275.

17 L. N. Schoenberg, D. W. Cooke and C. F. Liu, *Inorg. Chem.*, 1968, 7, 2386; H. Takenaka and M. Shibata, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2133.

18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

19 T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, 1979, **55**, 69.

20 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

Received 15*th October* 1993; *Paper* 3/06188D