Efficient Stereochemical Regulation of Octahedral Cobalt(III) Complexes by a Chiral Bidentate Ligand. Part 2.[1] Remarkable Effect of the Chelate-ring Size in the Stereoselective Formation of sym-*cis*-(Ethylenediamine-*N*,*N'*-diacetato)-(pentane-2,4-diamine)cobalt(III)†

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The chiral diamine (2*R*),(4*R*)-pentane-2,4-diamine (2*R*,4*R*-ptn) has been found efficiently to regulate the stereochemistry of the cobalt(III) complex [Co(edda)(2*R*,4*R*-ptn)]$^+$ (edda = ethylenediamine-*N*,*N'*-diacetate). The product ratio Λ-sym-*cis*:Δ-sym-*cis* is 3:97. The stereoselectivity is surprisingly high in comparison with that for the analogous complex involving (1*R*),(2*R*)-cyclohexane-1,2-diamine (*R*,*R*-chxn), Λ-sym-*cis*:Δ-sym-*cis* = 60:40. It is discussed on the basis of crystal structure determinations carried out for both diastereoisomers of sym-*cis*-[Co(edda)(2*R*,4*R*-ptn)]$^+$. A notable difference was observed in the six-membered chelate ring of 2*R*,4*R*-ptn which adopts the chair conformation in Λ-sym-*cis*-[Co(edda)(2*R*,4*R*-ptn)]ClO$_4$·H$_2$O **1a** but the λ skew-boat conformation in Δ-sym-*cis*-[Co(edda)(2*R*,4*R*-ptn)]ClO$_4$ **1b**. The chair conformation in **1a** is due to steric repulsions between the chelates, which is the important factor for the preferential formation of **1b** over **1a**. Such steric repulsions between the chelates are remarkably efficient for the chiral six-membered chelate compared with those for the five-membered one. *N*-Alkyl substitutions on the edda ligand caused preferential formation of the Λ-sym-*cis* form, as is the case for the [Co(R$_2$edda)(*R*,*R*-chxn)]$^+$ system.

Chirality and the optical resolution of chiral compounds are important subjects in fields related to biochemistry and industry. Stereochemically regulated metal complexes formed by using a chiral tetradentate ligand are useful for the production of chiral compounds.[2-4]

We recently reported a successful regulation of the stereochemistry of an octahedral cobalt(III) complex by use of a chiral diamine, [Co(R$_2$edda)(*R*,*R*-R$_2$chxn)]$^+$, where R$_2$edda is *N*,*N'*-dialkylethylenediamine-*N*,*N'*-diacetate and *R*,*R*-R$_2$-chxn is *N*,*N'*-dialkyl-*R*,*R*-cyclohexane-1,2-diamine.[1] The stereochemistry is efficiently controlled by *N*-alkyl substitution of the ligand, and the high stereoselectivity could be explained by steric repulsions between the chelates. Therefore, it is important to design effective steric interactions between the chelates in order to achieve highly stereochemical regulation of a metal complex.

In the present study we wished to examine the effect of the chelate-ring size on the stereochemical regulation of an octahedral cobalt(III) complex. (2*R*),(4*R*)-pentane-2,4-diamine (2*R*,4*R*-ptn) was chosen as a chiral bidentate ligand, which forms a six-membered chelate, in contrast to *R*,*R*-chxn which forms a five-membered one. For the binary complex systems containing R$_2$edda and 2*R*,4*R*-ptn, the influence of the chiral diamine on the stereoisomer distribution of the complex has been investigated. In order to gain detailed information on the stereochemistry of the complexes elucidation of their crystal structures is indispensable.[1,5-7] Two diastereoisomers of the [Co(edda)(2*R*,4*R*-ptn)]$^+$ system gave single crystals suitable for X-ray analyses, therefore their crystal structures were determined. The observed stereoselectivity is discussed on the basis of these.

Experimental

Preparations.—The compound H$_2$edda was commercially available and used without further purification. The salts Ba(R$_2$edda) (R = Me or Et)[8] and 2*R*,4*R*-ptn[9] were prepared by reported procedures.

Λ-sym-*cis*-[Co(edda)(2*R*,4*R*-ptn)]ClO$_4$·H$_2$O **1a** *and* Δ-sym-*cis*-[Co(edda)(2*R*,4*R*-ptn)]ClO$_4$ **1b**. The method for the preparation of the complexes is similar to that reported previously.[1]

To an aqueous solution (40 cm^3) of CoCl$_2$·6H$_2$O (2.38 g, 0.01 mol) were added Na$_2$(edda) (0.01 mol, prepared from H$_2$edda and NaOH), 2*R*,4*R*-ptn (1.02 g, 0.01 mol), and activated carbon (0.15 g) and aerated for 12 h at room temperature. The pH of the solution changed from 6.3 to 4 during the reaction. The mixture was filtered and the filtrate poured onto a column of Dowex 50W-X2 (100–200 mesh, Na$^+$ form, 1000 × 50 mm outside diameter). After washing the column with water (1 l), the complexes were eluted with a 0.1 mol dm^{-3} NaClO$_4$ aqueous solution. Two main red bands (**1a** and **1b**) and a trace amount of a third red band were developed, and eluted in this order. All

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

species were considered to have +1 charges from the elution profiles. Absorption spectroscopy indicated that the third complex is of asymmetrical-*cis* (asym-*cis*) configuration, so it was not isolated. Each eluate from the first two bands was concentrated and desalted using Sephadex G-15 gel chromatography. Concentration of each solution gave microcrystals, which were filtered off (Found for **1a**: C, 28.9; H, 5.8; N, 12.4. $C_{11}H_{24}ClCoN_4O_8 \cdot H_2O$ requires C, 29.2; H, 5.8; N, 12.4. Found for **1b**: C, 30.0; H, 5.6; N, 12.7. $C_{11}H_{24}ClCoN_4O_8$ requires C, 30.4; H, 5.6; N, 22.9%). **CAUTION**: although these perchlorate salts are moderately stable, they are potential hazards and should therefore be handled with care and in small quantities.

Λ-sym-*cis- and* Δ-sym-*cis*-[Co(dmedda)(2*R*,4*R*-ptn)]ClO_4 **2a** *and* **2b** (*dmedda* = N,N′-*dimethylethylenediamine*-N,N′-*diacetate*). These complexes were prepared similarly to those above using Ba(dmedda) instead of Na_2(edda), and were separated on a cation-exchange column. Two main red bands (**2a** and **2b**, eluted in this order) and a trace amount of a third red band (asym-*cis*) were developed. Each eluate from the first two bands was treated by the procedures described above, and microcrystals were obtained.

Λ-sym-*cis- and* Δ-sym-*cis*-[Co(deedda)(2*R*,4*R*-ptn)]ClO_4 **3a** *and***3b** (*deedda* = N,N′-*diethylethylenediamine*-N,N′-*diacetate*). These complexes were prepared similarly to those above using Ba(deedda) instead of Na_2(edda), and were separated on a cation-exchange column. Two main red bands (**3a** and **3b**, eluted in this order) and a trace amount of a third red band (asym-*cis*) were developed. Each eluate from the first two bands was treated by the procedures described above, and microcrystals were obtained.

Carbon-13 NMR spectroscopy indicated that the separation by column chromatography gave pure diastereoisomers. Good elemental analyses were obtained for C, H and N.

Structure Determinations of Two Diastereoisomers of the [Co(edda)(2*R*,4*R*-ptn)]$^+$ *Complex*.—Crystal data and conditions for data collection are summarized in Table 1. Data for complex **1a** were measured on a Rigaku AFC-5 diffractometer. The intensities were corrected for Lorentz and polarization factors, and for absorption. The data for **1b** were measured on a Rigaku RASA-AFC-6B diffractometer. The intensities were corrected for Lorentz and polarization factors, but not for absorption. In each case graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) was employed.

Structure analysis and refinement. $(+)_{550,\mathrm{CD}}$[Co(edda)-(2*R*,4*R*-ptn)]$ClO_4 \cdot H_2O$ **1a**. The structure was solved by the heavy-atom method, and refined by full-matrix least squares. The absolute configuration of the cation was determined on the basis of known configurations of the asymmetric carbons in the diamine chelate.[10] Anisotropic thermal parameters for non-hydrogen atoms were used. A weighting scheme $w = (a|F_o|^2 + b|F_o| + c)^{-1}$ was employed, where a, b and c were calculated automatically. All hydrogen atoms bound to carbon and nitrogen atoms could be determined from a Fourier difference map. They were all included in the final refinement with isotropic thermal parameters. The final indices were $R = 0.046$ and $R' = 0.063$. The final Fourier difference synthesis showed peaks at heights up to 0.43 e Å^{-3}.

$(-)_{550,\mathrm{CD}}$[Co(edda)(2*R*,4*R*-ptn)]ClO_4 **1b**. The structure was solved by the heavy-atom method, and refined by block-diagonal least squares. The absolute configuration was determined as before.[10] Anisotropic thermal parameters for non-hydrogen atoms were used. The hydrogen atoms bound to carbon and nitrogen atoms were assumed to have tetrahedral coordinates. They were all included in the final refinement with isotropic thermal parameters. The final indices were $R = 0.065$ and $R' = 0.066$. Unit weights were employed. The final Fourier difference synthesis showed peaks at heights up to 0.92 e Å^{-3}.

Final atomic coordinates are listed in Table 2. All calculations were carried out on a FACOM M-380 computer at the Institute of Physics and Chemistry for **1a** and on a HITAC M-680H computer at the Computer Centre of University of Tokyo for **1b** using the UNICS III[11] and ORTEP[12] programs. Atomic scattering factors and values of f' and f'' were taken from ref. 13.

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

Measurements.—Spectroscopic measurements were conducted as reported previously.[1]

Results

Preparation of Complexes.—A series of mixed-ligand cobalt(III) complexes, [Co(edda)(2*R*,4*R*-ptn)]$^+$ **1**, [Co(dmedda)(2*R*,4*R*-ptn)]$^+$ **2** and [Co(deedda)(2*R*,4*R*-ptn)]$^+$ **3** were prepared by air oxidation of aqueous solutions containing the ligands and cobalt(II) ion in the presence of activated carbon. It was expected that using a charcoal catalyst would result in thermodynamic equilibrium.[14] They were each separated into two diastereoisomers by cation-exchange column chromatography. Absorption spectroscopy (Fig. 1 and Table 3) indicates that

Table 1 Crystal data and experimental conditions for complexes **1a** and **1b***

	1a	**1b**
Formula	$C_{11}H_{26}ClCoN_4O_9$	$C_{11}H_{24}ClCoN_4O_8$
M	452.73	434.72
Crystal size/mm	0.70 × 0.10 × 0.27	0 .76 × 0.39 × 0.33
a/Å	12.665(3)	10.050(5)
b/Å	18.984(6)	19.481(7)
c/Å	7.852(3)	8.860(2)
U/Å^3	1888(1)	1735
D_m/g cm^{-3}	1.59	1.65
D_c/g cm^{-3}	1.59	1.66
F(000)	944	904
μ/cm^{-1}	10.97	11.87
Scan speed/° min^{-1}	4	2
Standards	3 every 100	3 every 50
2θ limits/°	60	65
No. of data	3175	2189
No. of observed data [$|F_o| > 3\sigma(F_o)$]	2170	1988
R	0.046	0.065
R'	0.063	0.066

* Details in common: orthorhombic, space group $P2_12_12_1$; $Z = 4$; take-off angle 3°; θ–2θ scan.

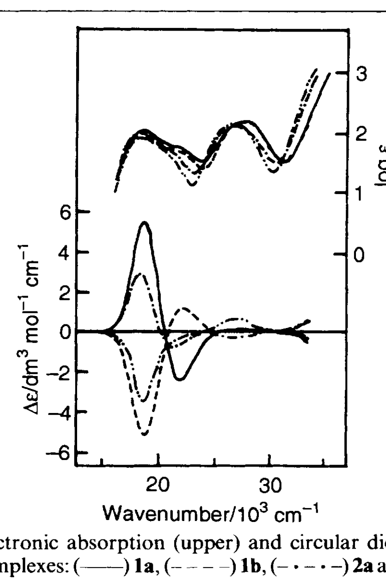


Fig. 1 Electronic absorption (upper) and circular dichroism spectra (lower). Complexes: (——) **1a**, (– – –) **1b**, (– · – · –) **2a** and (– ·· – ·· –) **2b**

Table 2 Atomic coordinates (× 10^4) of the non-hydrogen atoms of complexes **1a** and **1b** with estimated standard deviations (e.s.d.s)

	Complex **1a**			Complex **1b**		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Co	268.1(4)	248.3(3)	57.6(10)	18(1)	240(1)	1456(1)
O(1)	1210(3)	39(2)	1885(5)	1164(5)	265(4)	−239(6)
O(2)	1690(3)	−809(2)	3675(5)	1394(6)	−151(4)	−2573(6)
O(3)	−632(3)	390(3)	−1852(5)	−1123(5)	156(3)	3143(6)
O(4)	−670(3)	441(3)	−4653(4)	−1403(6)	−415(4)	5285(7)
N(1)	−46(3)	−767(2)	49(8)	−1062(7)	−443(4)	326(7)
N(2)	1377(4)	37(3)	−1624(6)	992(7)	−547(4)	2274(7)
N(3)	695(4)	1247(2)	161(8)	−1050(7)	997(4)	729(7)
N(4)	−902(4)	420(3)	1672(6)	1195(7)	880(4)	2487(8)
C(1)	1143(4)	−591(3)	2490(6)	734(8)	−81(5)	−1410(9)
C(2)	316(5)	−1073(4)	1677(8)	−650(9)	−374(6)	−1300(10)
C(3)	474(6)	−1083(4)	−1493(8)	−797(10)	−1125(5)	978(11)
C(4)	1547(5)	−729(3)	−1683(9)	684(10)	−1157(5)	1392(12)
C(5)	1014(4)	330(4)	−3276(6)	608(9)	−623(5)	3893(10)
C(6)	−177(4)	386(3)	−3304(6)	−730(7)	−292(5)	4150(8)
C(7)	348(8)	2525(3)	−59(16)	−2342(13)	2037(6)	1447(16)
C(8)	−154(5)	1798(3)	83(9)	−1167(10)	1586(5)	1801(10)
C(9)	−885(6)	1731(4)	1600(9)	154(16)	1990(5)	1844(10)
C(10)	−1558(5)	1082(4)	1683(8)	1408(11)	1552(5)	1763(10)
C(11)	−2425(5)	1044(4)	360(9)	2573(13)	1928(7)	2443(13)
Cl	1815(2)	2264(1)	4901(4)	23(4)	1637(1)	6483(3)
O(5)	1109(7)	2797(4)	5166(19)	−104(19)	2279(6)	5820(12)
O(6)	1422(7)	1699(5)	3891(10)	1098(14)	1280(7)	5841(13)
O(7)	2192(9)	1962(4)	6450(13)	217(29)	1730(7)	7940(11)
O(8)	2696(8)	2563(6)	4077(20)	−1082(14)	1235(9)	6382(29)
O(9w)	2264(3)	4137(3)	4078(7)			

Table 3 Electronic absorption and circular dichroism (CD) spectral data

Compound	Absorption $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1} (Δε/dm^3 mol^{-1} cm^{-1})
1a	18.52 (2.03)	18.76 (+5.51)
	27.55 (2.20)	21.73 (−2.42)
1b	18.62 (1.98)	18.76 (−5.18)
		21.97 (+1.21)
	27.55 (2.19)	27.78 (+0.17)
2a	18.52 (1.92)	18.52 (+2.92)
		21.28 (−0.79)
	26.88 (2.11)	26.74 (−0.28)
2b	18.18 (1.98)	18.52 (−3.48)
	26.67 (2.14)	27.02 (+0.70)
3a	18.42 (1.91)	18.24 (+2.84)
		21.00 (−0.63)
	26.46 (2.09)	26.52 (−0.30)
3b	18.18 (1.88)	18.52 (−1.73)
	26.32 (2.06)	27.02 (+0.32)

every complex adopts a *trans*-N_4O_2 geometry, in accord with the shoulder in the first absorption region. The very simple ^{13}C NMR spectra (Table 4) indicate that all complexes possess C_2 symmetry, suggesting symmetrical-*cis* (sym-*cis*) geometries.

The two diastereoisomers of each of complexes **1**–**3** show nearly inverted CD patterns: **1b**, **2b** and **3b**, which show negative peaks for the lowest-energy ^1E_g transition, are expected to have the Δ configurations, whereas **1a**, **2a** and **3a**, which show positive peaks for the corresponding transition, are expected to have the Λ configurations.[1,5] These assignments are supported by the following X-ray crystallographic studies.

Crystal Structure Analysis.—In order to establish the stereochemistry of the above complex system, X-ray crystallographic studies of $(+)_{550,\mathrm{CD}}$[Co(edda)(2*R*,4*R*-ptn)]$ClO_4\cdot H_2O$ **1a** and $(-)_{550,\mathrm{CD}}$[Co(edda)(2*R*,4*R*-ptn)]ClO_4 **1b** were carried out.

The ORTEP drawings of the complex ions are shown in Fig. 2. The established structures indicate that the stereochemistry of **1a** is of Λ-*trans*(*O*,*O′*) configuration, whereas that of **1b** is of Δ-*trans*(*O*,*O′*). The results are consistent with the predictions on the basis of empirical rules of electronic absorption and circular dichroism (CD) spectroscopy.

In the structure of complex **1b** the five-membered ring of the ethylenediamine moiety in the edda chelate is δ-*gauche*. Two acetate rings of the edda chelate, which link axial positions, adopt envelope conformations. The absolute configurations of two nitrogens of the edda chelate [N(1) and N(2)] are both *R*. The stereochemistry is very similar to that found in Δ-sym-*cis*-[Co(edda)(*R*,*R*-dmchxn)]$^+$ (dmchxn = *N*,*N′*-dimethylcyclohexane-1,2-diamine).[1] The conformation of the edda chelate in **1a** is quite similar to that in **1b**, with the exception that they are mirror images of each other.

A notable difference is observed in the conformation of the diamine chelate. The six-membered chelate ring of 2*R*,4*R*-ptn in complex **1b** adopts a λ skew-boat conformation with two methyl groups in equatorial orientations. In contrast, that in **1a** adopts a chair conformation with one methyl group equatorial and the other axial. The chair conformation will cause steric repulsion between the axial methyl group in the 2*R*,4*R*-ptn chelate and a ligand in the apical position. The skew-boat conformation will cause torsional angle strains, although the steric repulsion is released. Previous crystallographic studies indicated that the 2*R*,4*R*-ptn chelate favours the λ skew-boat conformation in octahedral complexes,[10,15] and the chair conformation has been found only in a planar complex.[16] The present result is the first example of the chair conformation for this chelate found in an octahedral complex.

The Co^{III}–N bond distances (Table 5) are normal, spanning the ranges from 1.968(4) to 1.977(5) Å for **1a** and from 1.935(8) to 1.987(8) Å for **1b**. The N(1)–Co–N(2) angles are 86.7(2) and 86.4(3)°, for **1a** and **1b**, respectively, normal for a five-membered ring. The angles N(3)–Co–N(4) are 91.2(2) and 90.3(3)°, respectively, considerably larger than those of the five-membered rings.

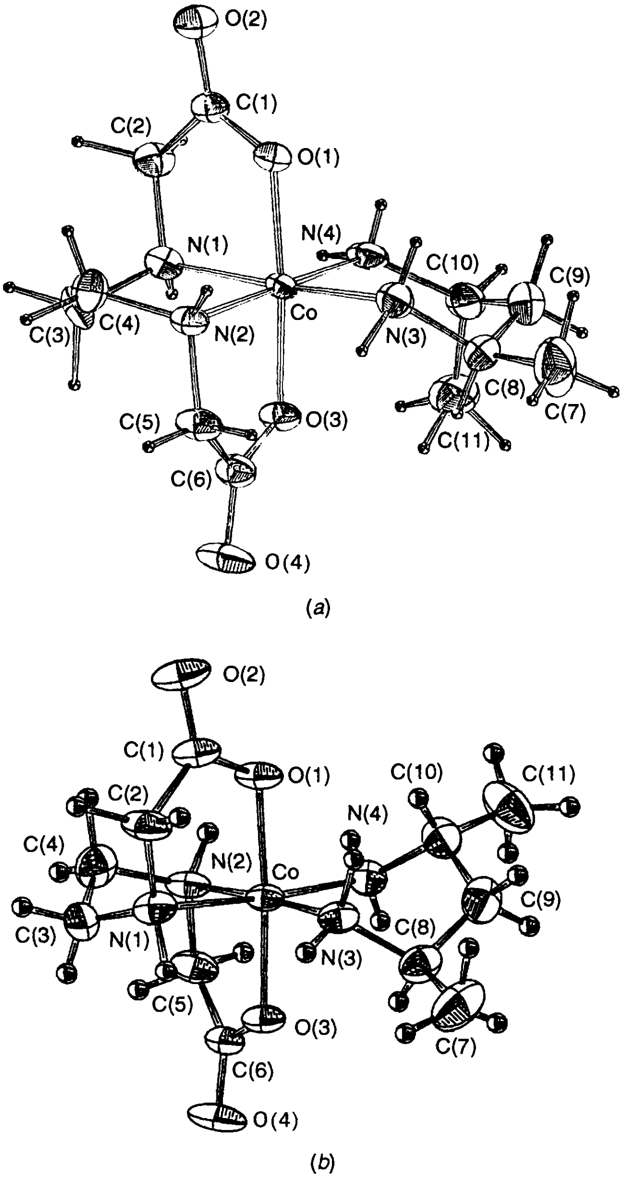
Discussion

Table 6 lists the distribution of diastereoisomers of binary cobalt(III) complex systems involving R_2edda and a chiral

Table 4 Carbon-13 NMR spectral data in D_2O*

	R_2edda					$2R,4R$-ptn		
		CH_2						
Complex	$>C{=}O$				CH_3	CH	CH_2	CH_3
1a	186.2	55.3	53.6			44.0	39.0	23.0
1b	185.7	56.0	53.6			45.1	39.4	23.2
2a	184.1	65.4	63.9		48.5	44.8	39.3	23.5
2b	183.5	66.4	63.8		47.9	45.3	39.1	23.2
3a	184.7	61.9	59.7	55.6	8.3	44.8	39.3	23.6
3b	184.2	62.4	59.0	55.0	8.2	44.9	38.5	23.0

* Chemical shifts (ppm) are given, referenced to $SiMe_4$.



(a)

(b)

Fig. 2 An ORTEP drawing of the complex cations of (*a*) **1a** and (*b*) **1b**

Table 5 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complexes **1a** and **1b**

	1a	**1b**
Co–O(1)	1.907(4)	1.893(7)
Co–O(3)	1.903(4)	1.891(7)
Co–N(1)	1.968(4)	1.987(8)
Co–N(2)	1.969(5)	1.957(8)
Co–N(3)	1.973(4)	1.935(8)
Co–N(4)	1.977(5)	1.946(8)
O(1)–Co–O(3)	175.4(2)	176.6(3)
O(1)–Co–N(1)	85.7(2)	87.2(3)
O(3)–Co–N(2)	85.9(2)	86.8(3)
N(1)–Co–N(2)	86.7(2)	86.4(3)
N(3)–Co–N(4)	91.2(2)	90.3(3)

Table 6 Formation ratio of Λ:Δ for the sym-*cis*- $[Co(R_2edda)(diamine)]^+$ complex system ($\Delta G°$/kJ mol^{-1} in parentheses[a])

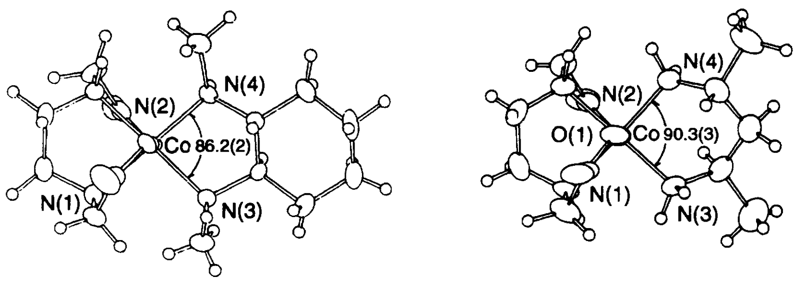
Diamine	R = H	Me	Et
$2R,4R$-ptn	3:97 (8.32)	66:34 (−1.59)	72:28 (−2.26)
R,R-chxn[1]	60:40 (−0.97)	88:12 (−4.77)	96:4 (−7.61)
R,R-dmchxn[1]	11:89 (5.00)		
R,R-dechxn[b,1]	2:98 (9.31)		

[a] $K = \Delta G°/RT$; $T = 288$ K. [b] N,N'-Diethyl-R,R-cyclohexane-1,2-diamine.

diamine. The ratios were determined from the absorbance of the eluate containing each isomer after separation by column chromatography. The sym-*cis*-$[Co(edda)(2R,4R\text{-ptn})]^+$ system **1** gave two forms with the ratio Λ-sym-*cis*:Δ-sym-*cis* = 3:97. The high selectivity is surprising, since a previous study indicated that the complex system involving edda and *R,R*-chxn instead of edda and 2*R*,4*R*-ptn shows no preferential formation between the two diastereoisomers (Λ-sym-*cis*:Δ-sym-*cis* = 60:40).[1] The chelate-ring size should be the important factor for the high selectivity observed for **1**. For the sym-*cis*-$[Co(edda)(R,R\text{-}R_2chxn)]^+$ system, *N*-alkyl substitutions on the diamine chelate cause preferential formation of the Δ-sym-*cis* over the Λ-sym-*cis* form. The high selectivity observed for **1** is comparable to that of the case using *R,R*-dechxn, for which Λ-sym-*cis*:Δ-sym-*cis* = 2:98.

Fig. 3 shows the crystal structures of the complex ions **1b** and Δ-sym-*cis*-$[Co(edda)(R,R\text{-dmchxn})]^+$,[1] viewed along the O(1)–Co–O(3) axes. The angle of the diamine chelate, N(3)–Co–N(4), is 86.2(2)° for *R,R*-dmchxn [Fig. 3(*a*)] whereas that for 2*R*,4*R*-ptn is 90.3(3)° [Fig. 3(*b*)]. The larger angle for the 2*R*,4*R*-ptn chelate causes steric repulsions between NH groups and the acetate rings of the edda chelate [Fig. 4(*i*)]. Such repulsions cause the Λ form to be thermodynamically unfavourable, which results in preferential formation of the Δ form. Their stereoselective influence is as effective as that of *N*-ethyl substitutions on the *R,R*-chxn chelate [Fig. 4(*ii*)].

Proton and ^{13}C NMR spectroscopies indicate that both complexes **1a** and **1b** have C_2 symmetry, suggesting rapid interconversion between the skew-boat and two chair conformations.[15,17,18] It has been reported that protons in the $CHCH_2CH$ fragment of the 2*R*,4*R*-ptn chelate are observed as a A_2B_2 pattern even for the case in which the contribution of the skew-boat conformation is dominant, although an AA′BB′ pattern is expected for this conformation.[18] The present complexes also show an A_2B_2 pattern for these protons. The J_{AB} value is 8.3 Hz for **1b** and 6.4 Hz for **1a**, respectively. The former



(*a*) (*b*)

Fig. 3 Perspective drawings of complex cations for (*a*) Δ-sym-*cis*-[Co(edda)(*R*,*R*-dmchxn)]$^+$ [1] and (*b*) **1b** viewed along the O(1)–Co–O(3) axes

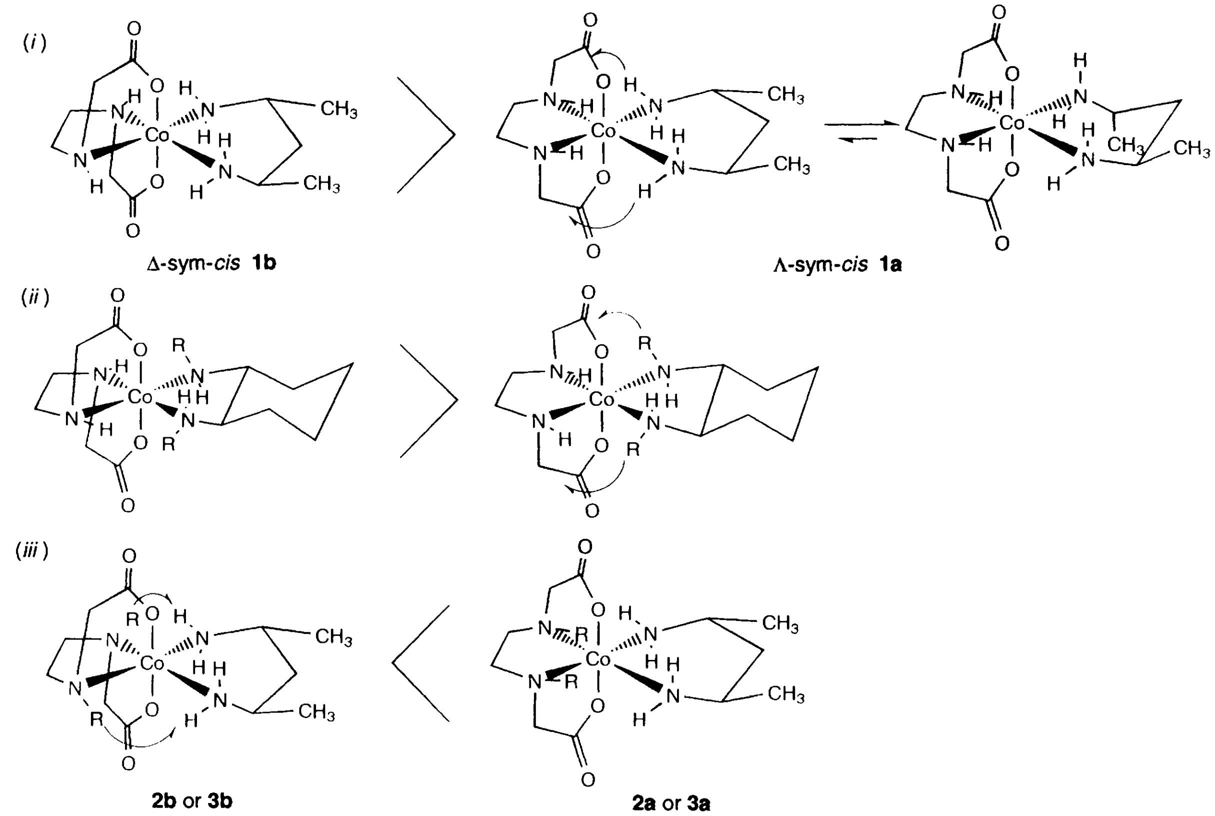


Fig. 4 Stereochemistry of the two diastereoisomers for (*i*) sym-*cis*-[Co(edda)(2*R*,4*R*-ptn)]$^+$, (*ii*) sym-*cis*-[Co(edda)(*R*,*R*-R$_2$chxn)]$^+$ and (*iii*) sym-*cis*-[Co(R$_2$edda)(2*R*,4*R*-ptn)]$^+$

value is in the range of those reported for the 2*R*,4*R*-ptn chelate in cobalt(III) complexes in which the diamine adopts the skew-boat conformation.[18] In contrast, the J_{AB} value for **1a** is significantly smaller. It is near to that reported for the chelate in a planar complex, in which the chair conformation of the diamine is dominant,[18] indicating that the diamine chelate in **1a** has a greater population of the chair conformation than has **1b**. This is in good agreement with the crystallographic study of **1a** where the diamine chelate is found to adopt the novel chair conformation. The skew-boat conformation in the Λ-sym-*cis* form would cause repulsions between the acetate rings of the edda chelate and NH groups of the diamine chelate [Fig. 4(*i*)]. One repulsion is partly released when the diamine chelate adopts the chair conformation. This could be clearly observed from the characteristic non-bonded distances between protons in **1a**. The distance between the proton on N(3) [H(1)] and that on C(5) [H(1)] is 1.98(10) Å, whereas the distances between the protons on N(4) [H(1) and H(2)] and that on C(2) [H(2)] are 2.53(12) and 2.97(12) Å. The unusual short distance for H(1)N(3) ··· H(1)C(5) reflects the unfavourable steric repulsions. On the other hand, the larger distances for H(1)N(4) ··· H(2)C(2) and H(2)N(4) ··· H(2)C(2) indicate the partial release of the steric repulsions due to the chair conformation of the 2*R*,4*R*-ptn chelate. The latter distances are not different from those between the corresponding protons in **1b**, which are in the range 2.79(13)–2.90(13) Å.* The chair conformation of the 2*R*,4*R*-ptn chelate in **1a** results in the short non-bonded distance between the axially oriented methyl group C(11) and the oxygen atom in the apical position O(3), which is 3.116(8) Å.

N-Alkyl substitutions of the edda ligand cause preferential formation of the Λ-sym-*cis* diastereoisomer (Table 6). The stereoselective influence of the alkyl groups increases in the order methyl < ethyl. A similar substitution effect has been observed in the [Co(R$_2$edda)(*R*,*R*-chxn)]$^+$ system. The results indicate that the observed stereoselectivity in the complex system involving 2*R*,4*R*-ptn could be interpreted in terms of steric repulsions between chelates [Fig. 4(*iii*)] as is the case with *R*,*R*-chxn.

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* In contrast, the corresponding C–N distances do not show any notable difference: N(3) ··· C(5) and N(4) ··· C(2) in complex **1a** are 3.236(8) and 3.226(9) Å, respectively, whereas N(3) ··· C(2) and N(4) ··· C(5) in **1b** are 3.246(13) and 3.236(13) Å, respectively.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, a grant from Mitsubishi Yukagaku Foundation, and Nippon Sheet Glass Foundation for Material Science.

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Received 25th *November* 1993; *Paper* 3/07022K