Diastereoselectivity of Octahedral Cobalt(II) Pybox Complexes

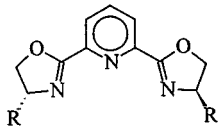
Christophe Provent,[a] Gérald Bernardinelli,[b] Alan F. Williams,*[a] and Nathalie Vulliermet[c]

Keywords: Cobalt / Chirality / N ligands / Coordination chemistry

The cobalt(II) complexes prepared with a series of enantiopure ligands (**1**–**3**) containing the bis(oxazolinyl)pyridine unit have been studied. The ligands form high spin octahedral complexes as shown by the X-ray crystal structure of the homochiral complex $[Co(R,R\text{-}\mathbf{1})_2](ClO_4)_2(CH_3CN)_3$. The diastereoselectivity of complex formation has been studied: equimolar mixtures of *RR* and *SS* ligands show mixtures of homochiral and heterochiral complexes for **2** and **3**, but the phenyl-substituted ligand **1** shows exclusive formation of the heterochiral species. This selectivity is correlated with structural and electronic properties of the complexes.

Introduction

The use of chiral ligands in coordination chemistry is becoming increasingly important.[1] When two or more chiral ligands are bound to the same ligand, diastereomers may be formed, and the selectivity for one or other diastereomer may be studied.[2–7] The bis(oxazolinyl)pyridine (pybox) family of ligands (Scheme 1) were first developed by Nishiyama and co-workers for enantioselective homogeneous catalysis,[8,9] and have also been used to generate chiral Lewis acid catalysts.[10] We have recently used these ligands for the enantioselective synthesis of helical complexes.[11] During this work it was observed that the phenyl derivative **1** showed significantly different behavior from the other ligands **2** and **3**, forming a cyclic trinuclear helicate rather than a linear dinuclear helicate. This difference could be attributed to intramolecular attractions between the phenyl substituents and the pyridine moiety.[12] It therefore seemed of interest to study the chemistry of simple, mononuclear octahedral complexes of the type $[ML_2]$ to see if these substituent effects were also observed in these simple systems. In this paper we report on the remarkable difference in diastereoselectivity observed with the three different ligands with cobalt(II).



1 R = Ph
2 R = Me
3 R = Bzl

Scheme 1. Ligands used in this work

Results

Synthesis of Complexes

The cobalt(II) complexes were prepared by adding two equivalents of ligand in acetonitrile to a solution of one equivalent of cobalt(II) perchlorate in acetonitrile at 20 °C (the heterochiral complex synthesis was carried out by mixing one equivalent of *R*,*R* ligand, one equivalent of *S*,*S* ligand and one equivalent of cobalt salt). The solutions were stirred for 30 minutes and then concentrated, before crystallization by diffusion of diethyl ether or *tert*-butyl methyl ether. The crystals prepared with $[Co(R,R\text{-}\mathbf{1})_2]^{2+}$ were of suitable quality for an X-ray structure determination. The complexes were characterized in solution by electrospray mass spectrometry (ESMS) and ^{1}H NMR spectroscopy. ESMS showed the exclusive formation of $[CoL_2]^{2+}$ with the base peak due to $[CoL_2]^{2+}$ and a weaker peak due to $\{[CoL_2](ClO_4)\}^+$. The ^{1}H NMR spectra are discussed below.

Crystal Structure of $[Co(R,R\text{-}\mathbf{1})_2](ClO_4)_2(CH_3CN)_3$

The X-ray crystal structure analysis of the orange crystals of $[Co(RR\text{-}\mathbf{1})_2](ClO_4)_2(CH_3CN)_3$ shows the expected octahedral ML_2 structure with the ligand acting as a meridional tridentate ligand (Figure 1). The cobalt(II) cation is coordinated by two pyridine-N atoms and four oxazoline-N atoms [av. Co-N(oxazoline) distance: 2.15 Å; av. Co-N(pyridine) distance: 2.06 Å]. The chelate bite angles are similar and close to 76°. The small bite angle results in considerable deviation of the angles at the cobalt atom from 90°, but the two pyridine rings are inclined at 93.2(8)°, close to the ideal value.

[a] Département de Chimie minérale, analytique, et appliquée, Université de Genève,
30 quai Ernest Ansermet, 1211 Genève 4, Switzerland
Fax: (internat.) + 41-22/702-6069
E-mail: Alan.Williams@chiam.unige.ch
[b] Laboratoire de Cristallographie aux rayons-X, Université de Genève,
24 quai Ernest Ansermet, 1211 Genève 4, Switzerland
[c] Département de Chimie physique, Université de Genève,
30 quai Ernest Ansermet, 1211 Genève 4, Switzerland

  1434–1948/01/0808–1963 $ 17.50+.50/0

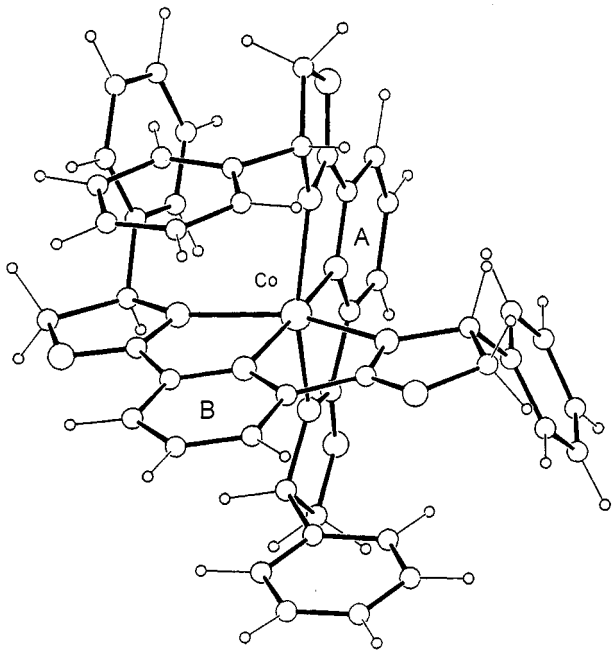


Figure 1. Structure of the cation $[Co(R,R\text{-}\mathbf{1})_2]^{2+}$; the stacking interaction is observed between the pyridine of ligand B and the phenyls of ligand A

The two ligands differ in the conformation of the phenyl substituents. Ligand A has the two phenyl rings oriented at roughly 90° to the oxazoline plane, in such a way as to lie almost parallel to the pyridine of ligand B [interplane angles: 3.7(7) and 3.0(7)°; interplane distances: 3.55(7) and 3.66(6) Å] indicating a stacking interaction similar to that observed in the circular trinuclear helicate.[11] The phenyl groups of ligand A are offset with respect to the coordinated pyridine of ligand B, as expected according to the model of Hunter and Sanders.[13] This orientation of ligand A, however, brings the phenyl rings close to those of ligand B. The geometry of this phenyl−phenyl interaction cannot be regarded as an edge-to-face interaction[14] since the hydrogen atoms are not directed toward the phenyl carbons. It may therefore be considered as a repulsion that prevents the phenyls of B from stacking with the pyridine of A. The phenyls of B are inclined at 17.9(9) and 31.1(1)° with respect to the pyridine of A, the interplane distances are longer, and the overlap is poor. The steric repulsion between the phenyls is shown by a CPK representation of the cation and by the slight deviations of the bis(oxazoline)pyridine units from planarity. The presence of the stacking interaction in one direction but not in the other reduces the molecular symmetry from D_2 to C_2.

Properties in Solution

Table 1 summarizes the electronic and CD transitions associated with the d-d bands in acetonitrile solution. The values are typical of high spin octahedral cobalt(II) with spin-allowed bands around 1100 nm and 470 nm. The ligand field as estimated by the d-d band positions decreases in the series **1** > **2** > **3**. The CD spectrum shows negative bands associated with the spin-allowed d-d bands for the *R*,*R* enantiomer of the ligand, although only the higher energy band falls completely within the range of the instrument. Two other weak CD bands are observed around 520 and 620 nm and are assumed to be associated with spin-forbidden or two-electron excitations. MLCT bands are observed around 340 nm as shoulders on ligand-based absorptions, at slightly higher energy than a strong CD signal (negative for the *R*,*R* isomer). The CD spectra of complexes of the *S*,*S* enantiomers of the ligands are the inverse of those of the *R*,*R* enantiomers.

The fast electronic relaxation times of high spin cobalt(II) allow the ^{1}H NMR spectra to be recorded at 20 °C in acetonitrile (Figure 2). The proton α to the nitrogen of the oxazoline lies closest to the metal center and has an NMR shift of δ = 86.3. The other peaks lie between δ = 0 and 40. The spectra show the two ligands to be equivalent and symmetric. The ^{1}H NMR spectra allow the investigation of the diastereoselectivity of complex formation. If an enantiopure ligand is used, only the homochiral complex is obtained, but if a racemic mixture of *R*,*R* and *S*,*S* ligands is used then the heterochiral *meso*-complex $[Co(R,R\text{-}\mathbf{L})(S,S\text{-}\mathbf{L})]^{2+}$ may also be formed. The two enantiomers of the homochiral complexes have identical spectra, but the heterochiral complex shows a different spectrum. Reaction of cobalt(II) with an equimolar amount of *R*,*R* and *S*,*S* ligands may thus be used to study the diastereoselectivity. The three ligands show very different behavior. Ligand **1** shows exclusive formation of the heterochiral complex $[Co(R,R\text{-}\mathbf{1})(S,S\text{-}\mathbf{1})]^{2+}$ with a spectrum totally different from $[Co(R,R\text{-}\mathbf{1})_2]^{2+}$ and no trace of the homochiral complex. Ligands **2** and **3**, on the other hand, show the presence of

Table 1. d-d absorption bands and circular dichroism of complexes in acetonitrile solution

	$[Co(R,R\text{-}\mathbf{1})_2]^{2+}$	$[Co(R,R\text{-}\mathbf{2})_2]^{2+}$	$[Co(R,R\text{-}\mathbf{3})_2]^{2+}$	$[Co(R,R\text{-}\mathbf{1})(S,S\text{-}\mathbf{1})]^{2+}$
d-d spectra: λ_{max}, ε				
$^4T_2(F) \leftarrow {}^4T_1$	1100(15)	1117(15)	1147(13)	1068(16)
$^4T_2(P) \leftarrow {}^4T_1$	463(56)	472(47)	475(36)	470(54)
CD spectra: λ_{max}, Δε				
	622(−0.053)	607(−0.03)	624(−0.07)	
	518(0.31)	527(0.09)	561(0.04)	
	459(−0.31)	468(−0.29)	472(−0.43)	
	368(−1.16)	365(−0.70)	359(−1.54)	

both complexes, with a heterochiral/homochiral ratio of 2 for **2** and 1 for **3**.

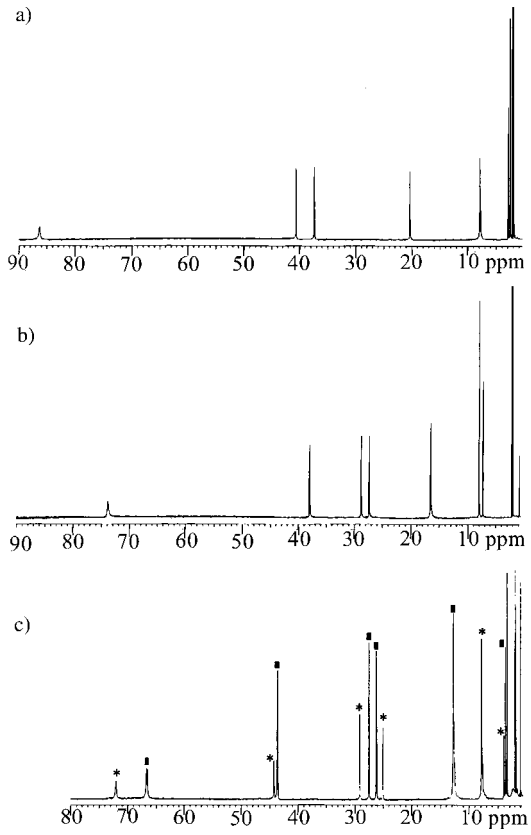


Figure 2. ^{1}H NMR spectra in [D$_3$]acetonitrile of (a) [Co(*R*,*R*-**1**)$_2$]$^{2+}$, (b) [Co(*R*,*R*-**1**) (*S*,*S*-**1**)]$^{2+}$, and (c) an equimolar mixture of cobalt(II), *R*,*R*-**2**, and *S*,*S*-**2**; the peaks due to the homochiral complex are marked with an asterisk, those of the heterochiral complex with a block

Cyclic voltammetry of [Co(*R*,*R*-**1**)$_2$]$^{2+}$ in acetonitrile showed three redox waves, two assigned to ligand reduction at −1.30 and −0.45 V, and a peak at +1.15V assigned to the Co^{III}/Co^{II} couple. This latter value is quite high, but may be understood in terms of the low donor strength of the oxazoline ligands, the π-acceptor properties of the ligand, and possible steric hindrance which prevents the shortening of the Co−N bond lengths associated with oxidation of Co^{II}.[15] The voltammogram for [Co(*R*,*R*-**2**)$_2$]$^{2+}$ is essentially identical, although for [Co(*R*,*R*-**3**)$_2$]$^{2+}$ no oxidation of Co^{II} was observed. For the heterochiral complex [Co(*R*,*R*-**1**)(*S*,*S*-**1**)]$^{2+}$ the ligand reduction potentials were unchanged but the Co^{III}/Co^{II} potential was significantly lower (+1.01 V) than for the homochiral complex.

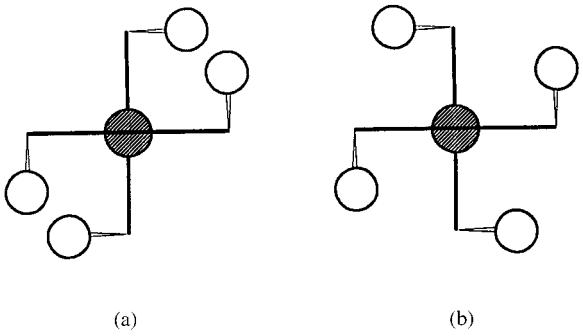
Discussion

The three ligands studied here all form octahedral complexes of the type ML$_2$ with cobalt(II), but show significant differences in their physical and chemical properties arising from the different substituents on the oxazoline ring. We assume that these effects are due to the size and shape of these substituents rather than from inductive electronic effects. The results suggest that the benzyl group of ligand **3** provides the greatest hindrance, resulting in the lowest ligand field strength and the absence of oxidation of Co^{II}. Logically one would expect the phenyl group to exert a steric effect similar to the benzyl, but it is in fact ligand **2** with a methyl substituent that is closer to the benzyl group in ligand field strength, although in this case oxidation to Co^{III} may be observed. The phenyl-substituted ligand **1** shows the strongest ligand field of the homochiral complexes. Furthermore, ligand **1** is unique in its diastereoselectivity, forming the heterochiral complex exclusively whereas **2** and **3** give mixtures, that for ligand **3** being essentially statistical.

Two features render the phenyl substituent unique: firstly, all atoms of the phenyl group lie in the same plane, and it is therefore possible to orient the substituent so that it lies parallel to the bisoxazolinyl plane of the second ligand in the complex of [Co(*R*,*R*-**1**)$_2$]$^{2+}$, as shown in Figure 1. Attempts to grow crystals of the other complexes were unfortunately unsuccessful, but modeling studies show that in the benzyl and methyl complexes the methylene hydrogens of the substituent must be directed towards the second ligand: this is not the case for the phenyl substituent. Secondly, the phenyl groups can actually give an attractive interaction with the pyridine of the second ligand. This was clearly established in the trinuclear silver complex,[11] and, on the basis of the crystal structure, appears to be the case here. The lesser interligand repulsion of **1** compared to **2** and **3** can therefore explain the higher ligand field. Intramolecular stacking interactions have previously been reported as enhancing the stability of 2:1 complexes.[16]

The diastereoselectivity may also be understood from an examination of the crystal structure of [Co(*R*,*R*-**1**)$_2$](ClO$_4$)$_2$. If we look along the pyridine−cobalt−pyridine axis, the ligand planes form a cross, with the substituents at right angles to the arms of the cross. In the homochiral complex, the substituents are directed into two diagonally opposed quadrants of the cross, and consequently may repel each other. In the heterochiral complex each substituent is directed into a different quadrant, and repulsion is avoided. It is now possible to obtain four π-stacking interactions between the pyridine and the phenyl groups. In consequence, the ligand field increases, and the cobalt(II) oxidation potential is lowered. Indeed, the first d-d band of the heterochiral complex moves to higher energy relative to the homochiral complex. This diastereoselectivity will be most marked for the phenyl-substituted ligand **1**, since it projects far enough out of the ligand plane for the substituents to repel each other in the homochiral complex (Scheme 2). For the smaller methyl-substituted ligand the extension is not sufficient, and the benzyl group is sufficiently flexible to be able to bend away from the other ligand.

This effect has been observed previously by Evans[10] for complexes of **1** with copper(II): the crystal structures of [Cu(*S*,*S*-**1**)$_2$]$^{2+}$ and [Cu(*R*,*R*-**1**)(*S*,*S*-**1**)]$^{2+}$, although they are affected by a Jahn−Teller distortion, show the repulsion of the phenyls in the homochiral complex that is absent in the



Scheme 2. Intraligand repulsion between substituents in the homochiral complex (a) and the heterochiral complex (b)

heterochiral complex. The greater stability of the heterochiral complex was shown by the nonlinear response of the enantioselectivity of reactions catalyzed by $[Cu(\mathbf{1})]^{2+}$ to the enantiomeric purity of ligand **1**: the selective formation and precipitation of $[Cu(R,R\text{-}\mathbf{1})(S,S\text{-}\mathbf{1})]^{2+}$ resulted in an enrichment of one enantiomer of the catalytically active species $[Cu(\mathbf{1})]^{2+}$ in solution. A similar nonlinear effect has been observed in other reactions catalyzed by oxazoline ligands.[17,18]

The remarkable difference in diastereoselectivity may thus be explained in terms of the properties of the substituent. The phenyl group which stood apart from the others in helicate chemistry[11] also shows different behavior in simple octahedral complexes. It is reasonable to suppose that this effect might influence the enantioselectivity of catalytic reactions using these ligands, and, indeed, Evans and coworkers[10] did observe that the enantioselectivity was highest for the phenyl-substituted ligand when compared with benzyl, isopropyl and *tert*-butyl substituents.

Experimental Section

General: The ligands were prepared according to the literature.[8,11,12] Diethyl ether was purified according to standard procedures. Other solvents (Fluka p.a.) were used without further purification. Hexaaquacobalt(II) perchlorate (Fluka) was used without purification. ^{1}H NMR spectra were recorded on a Varian Gemini-300 (at 300 MHz); shifts are given with reference to TMS. NMR solvents ([D$_3$]acetonitrile): Dr. Glaser AG Basel, isotopic purity > 99.80 atom%D. UV/visible spectra were recorded on a Cary/Varian spectrometer; 0.1 or 1 cm cell; 22 °C. CD spectra were recorded on a Jasco J-715 spectropolarimeter; 1 cm cell; 22 °C.

Cyclic Voltammetry: Electrochemical measurements were performed with a three-electrode system consisting of a platinum working electrode, a platinum counter-electrode and an Ag/AgCl reference electrode. All measurements were carried out under N_2 in degassed, freshly distilled solvent (acetonitrile), using 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte. Before measurement, the system was standardized with the Ru(bipy)$_3$(ClO$_4$)$_2$ complex and potentials are given with respect to the normal hydrogen electrode. A Bioanalytical System Model CV-50 W was used to record and process the data.

General Procedure for Complex Synthesis: An acetonitrile/dichloromethane solution (4:1) of enantiopure ligand (4.08×10^{-4} mol) was added dropwise to a solution of 2.04×10^{-4} mol of metal salt [Co(ClO$_4$)$_2$·6H$_2$O] in acetonitrile. The solution was stirred for 30 minutes at room temperature and then concentrated to 1−2 mL. The complex was crystallized from the acetonitrile solution by diffusion of diethyl ether or *tert*-butyl methyl ether. Yields were typically 75%. For the synthesis of heterochiral species, the acetonitrile/dichloromethane solution contained 2.04×10^{-4} mol of the *R*,*R* enantiomer and 2.04×10^{-4} mol of the *S*,*S* enantiomer.

[Co(*R*,*R*-1)$_2$(ClO$_4$)$_2$]: Yield 76%. $C_{46}H_{38}Cl_2CoN_6O_{10}.1/2H_2O$: calcd. C 54.94, H 3.91, N 8.36; found C 54.95, H 3.97, N 8.34. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, TMS): δ = 0.10 (2 H), 2.54 (8 H), 2.90 (4 H), 7.82 (8 H), 20.29 (4 H), 37.29 (4 H), 40.53 (4 H), 86.32 (4 H). − ES-MS (acetonitrile): *m*/*z* (%) = 399.0 (100) $[Co(\mathbf{1})_2]^{2+}$, 896.0 (15) $[Co(\mathbf{1})_2ClO_4]^+$. Very small peaks corresponding to the ligand and to the (complex + acetonitrile) were also observed. These last peaks are attributable to fragmentation in the spectrometer. Cyclic voltammetry: +1.14 V (Δ*E* = 105 mV), −0.43 V (Δ*E* = 75 mV), −1.30 V (Δ*E* = 80 mV).

[Co(*S*,*S*-1)$_2$](ClO$_4$)$_2$: Yield 69%. $C_{46}H_{38}Cl_2CoN_6O_{10}·H_2O$: calcd. C 54.45, H 3.97, N 8.28; found C 54.51, H 3.81, N 8.27. ^{1}H NMR spectrum and electrochemical data identical to [Co(*R*,*R*-1)$_2$(ClO$_4$)$_2$].

[Co(*R*,*R*-1)(*S*,*S*-1)](ClO$_4$)$_2$: Yield 75%. $C_{46}H_{38}Cl_2CoN_6O_{10}·H_2O$: calcd. C 54.45, H 3.97, N 8.28; found C 54.25, H 3.88, N 8.24. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, TMS): δ = 0.80 (2 H), 7.31 (4 H), 7.96 (8 H), 16.44 (8 H), 27.30 (4 H), 28.80 (4 H), 37.97 (4 H), 73.84 (4 H). − Cyclic voltammetry: +1.01 V (Δ*E* = 150 mV), −0.46 V (Δ*E* = 70 mV), −1.35 V (Δ*E* = 60 mV).

[Co(*R*,*R*-2)$_2$](ClO$_4$)$_2$: Yield 79%. $C_{26}H_{30}Cl_2CoN_6O_{10}$ (716.39): calcd. C 41.73, H 4.04, N 11.23; found C 41.14, H 4.11, N 11.08. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, TMS): δ = 3.96 (2 H), 7.80 (12 H), 25.08 (4 H), 29.20 (4 H), 44.18 (4 H), 72.20 (4 H). − ES-MS (acetonitrile): *m*/*z* (%) = 274.5 (100) $[Co(\mathbf{2})_2]^{2+}$, 648 (48) $[Co(\mathbf{2})_2ClO_4]^+$. − Cyclic voltammetry: +1.15 V (Δ*E* = 110 mV), −0.46 V (Δ*E* = 70 mV), −1.31 V (Δ*E* = 70 mV).

[Co(*S*,*S*-2)$_2$](ClO$_4$)$_2$: Yield 72%. $C_{26}H_{30}Cl_2CoN_6O_{10}$ (716.39): calcd. C 41.73, H 4.04, N 11.23; found C 41.36, H 3.97, N 11.14. − ^{1}H NMR spectrum and electrochemical data identical to [Co(*R*,*R*-2)$_2$](ClO$_4$)$_2$.

Equimolar mixture of Co(ClO$_4$)$_2$·6H$_2$O, *R*,*R*-2 and *S*,*S*-2: ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, TMS): two species. 33% of homochiral complex: δ = 3.96 (2 H), 7.80 (12 H), 25.08 (4 H), 29.20 (4 H), 44.18 (4 H), 72.20 (4 H). 66% of heterochiral complex: δ = 3.73 (2 H), 12.69 (12 H), 26.18 (4 H), 27.48 (4 H), 43.66 (4 H), 66.70 (4 H).

[Co(*R*,*R*-3)$_2$](ClO$_4$)$_2$ and [Co(*S*,*S*-3)$_2$](ClO$_4$)$_2$: Yield 80%. ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, TMS): δ = 0.24 (8 H), 3.96 (12 H), 5.64 (4 H), 16.52 (2 H), 17.40 (4 H), 22.89 (4 H), 30.10 (4 H, broad), 49.69 (4 H, broad), 66.00 (4 H). − Cyclic voltammetry: −0.43 V (Δ*E* = 73 mV), −1.24 V (Δ*E* = 74 mV). − ES-MS (acetonitrile): *m*/*z* (%) = 426.7 (100) $[Co(\mathbf{3})_2]^{2+}$, 952.0 (16) $[Co(\mathbf{3})_2ClO_4]^+$.

Equimolar Mixture of Co(ClO$_4$)$_2$·6H$_2$O, *R*,*R*-3 and *S*,*S*-3: ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, TMS): two species. ≈50% of homochiral complex: δ = 0.49 (8 H), 3.94 (12 H), 6.13 (4 H), 16.48 (2 H), 17.63 (4 H), 22.96 (4 H), 29.68 (4 H, broad), 50.58 (4 H, broad), 65.75 (4 H). ≈50% of heterochiral complex: δ = 5.66 (12 H), 6.79 (8 H), 6.89 (2 H), 17.13 (4 H), 20.91 (4 H, broad), 24.92 (4 H), 26.07 (4 H), 50.18 (4 H), 63.29 (4 H, broad).

Crystal Structure of $[Co(R,R\text{-}1)_2](ClO_4)_2\cdot 3MeCN$, $Co(C_{22}H_{19}N_3O_2)_2(ClO_4)_2(CH_3CN)_3$: Molecular mass = 1119.8, orange crystal 0.22 × 0.22 × 0.23 mm, monoclinic, $P2_1$, a = 10.907(1) Å, b = 21.717(3) Å, c = 11.879(1) Å, β = 112.768(8)°, V = 2594.5(5) (Å)^3, Z = 2, D_x = 1.43 g·cm^{-3}. Data collection, Stoe STADI4, Cu-K_α, graphite monochromator, T = 200 K, ω-2θ scan, 3° < 2θ < 110°, −11 < h < 11; 0 < k < 22; 0 < l < 12 and all antireflections of these. 6557 reflections measured, 6344 unique, 5159 observed ($|F_o| > 4\sigma(F_0)$], μ = 4.147 mm^{-1}, spherical absorption correction A* min., max = 1.862, 1.954. Structure solved by direct methods,[19] and refined by full-matrix least-squares with hydrogens in calculated positions using 687 parameters for 5159 reflections.[20] Final R value 0.057, R_w = 0.048, Flack absolute structure parameter = 0.00(1).[21,22]

Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149396. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Molecular Modeling: Calculations were carried out using the Universal force field 1.02[23] with charge equilibration.[24] A reasonable agreement between calculated structure and that observed for $[Co(RR\text{-}1)_2]^{2+}$ was obtained as judged by superposition of the structures, although the optimized Co−N bond lengths were too short (1.811 Å compared with the experimental average of 2.1190 Å).

Acknowledgments

This work was supported by the Swiss National Science Foundation. We thank Werner Kloeti (University of Geneva) for recording electrospray mass spectra.

[1] U. Knof, A. von Zelewsky, *Angew. Chem. Int. Ed.* **1999**, *38*, 302−322.
[2] K. Bernauer, S. Bourqui, D. Hugi-Cleary, R. Warmuth, *Helv. Chim. Acta* **1992**, *75*, 1288−1296.
[3] K. Bernauer, F. Gretillat, H. Stoeckli-Evans, R. Warmuth, *Helv. Chim. Acta* **1993**, *76*, 545−556.
[4] E. C. Constable, T. Kulke, M. Neuburger, M. Zehnder, *Chem. Commun.* **1997**, 489−490.
[5] G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862−1873.
[6] E. J. Enemark, T. D. P. Stack, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 996−998.
[7] J. M. Vincent, C. Philouze, I. Pianet, J.-B. Verlhac, *Chem. Eur. J.* **2000**, *6*, 3595−3599.
[8] H. Nishiyama, M. Kondo, T. Nakamura, K. Itoh, *Organometallics* **1991**, *10*, 500−508.
[9] H. Nishiyama, T. Nitoh, Y. Motoyama, K. Aoki, *Chem. Eur. J.* **1999**, *5*, 3509−3513.
[10] D. A. Evans, M. C. Kozlowski, J. A. Murry, C. S. Burgey, K. R. Campos, B. T. Connell, R. J. Staples, *J. Am. Chem. Soc.* **1999**, *121*, 669−685.
[11] C. Provent, S. Hewage, G. Brand, G. Bernardinelli, L. J. Charbonnière, A. F. Williams, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1287−1289.
[12] C. Provent, E. Rivara-Minten, S. Hewage, G. Brunner, A. F. Williams, *Chem. Eur. J.* **1999**, *5*, 3487−3494.
[13] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534.
[14] S. K. Burley, G. A. Petsko, *Science* **1985**, *229*, 23−28.
[15] C. Piguet, G. Bernardinelli, B. Bocquet, O. Schaad, A. F. Williams, *Inorg. Chem.* **1994**, *33*, 4112−4121.
[16] R. Wietzke, M. Mazzanti, J.-M. Latour, J. Pécaut, *Chem. Commun.* **1999**, 209−210.
[17] S. Kanemasa, Y. Oderaotoshi, S. Sakaguchi, H. Yamamoto, J. Tanaka, E. Wada, D. P. Curran, *J. Am. Chem. Soc.* **1998**, *120*, 3074−3088.
[18] S. Crosignani, G. Desimoni, G. Faita, S. Filippone, A. Mortoni, P. Righetti, M. Zema, *Tetrahedron Lett.* **1999**, *40*, 7007−7010.
[19] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, D. Germain, J. P. Declercq, M. M. Woolfson, Universities of York (England) and Louvaine-La-Neuve (Belgium) 1987.
[20] S. R. Hall, H. D. Flack, J. M. Stewart, *XTAL 3.2 User's Manual*, Universities of Western Australia, Geneva and Maryland **1992**.
[21] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876−881.
[22] H. D. Flack, G. Bernardinelli, *Acta Crystallogr., Sect. A* **1999**, *A55*, 908−915.
[23] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III, W. M. Skiff, *J. Am. Chem. Soc.* **1992**, *114*, 10024−10035.
[24] A. K. Rappe, W. A. Goddard III, *J. Phys. Chem.* **1991**, *95*, 3358.

Received October 13, 2000
[I00390]