Controlling helical chirality of cobalt complexes by chirality transfer from vicinal diamines
Controlling helical chirality of cobalt complexes by chirality transfer from vicinal diamines†

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Stereoselective cis–trans isomerism of a CoIII–N2O2 complex has been achieved by coordinating chiral vicinal diamines. The induced metal-centered helical chirality can be exploited for chirality amplification and asymmetric coordination chemistry.

There has been considerable fascination with asymmetric coordination chemistry since the discovery of metal-centered chirality by Alfred Werner in 1911.1 In particular, asymmetric octahedral metal complexes have received increasing attention in catalysis, material science, and pharmaceutics.2 Unlike well-established asymmetric control of carbon-centered chirality, controlling metal-centered chirality3v–c has proved to be challenging. In most examples, metal-centered chirality has been generated by stereoselective assembly of metals and chiral ligands.2v–c However, octahedral metal complexes can have a propeller-like helical arrangement with achiral ligands such as ethylenediamine (en) and 2,2′-bipyridine (bpy). The resulting octahedral M(en)3 or M(bpy)3 complexes exhibit helical chirality with ∆ and Λ configurations.1 Indeed, stereoselective generation of helical octahedral metal complexes with achiral ligands is a greater challenge than with chiral ligands, and only recently it has been shown that stereodiradical metal-centered chirality of M(bpy)3 can be controlled by chiral auxiliaries,3 chiral anions,4 and chiral catalysts,5 as well as long-range chiral induction.6 Given that the asymmetric coordination chemistry is still under development, it is highly desirable to expand such concepts to a wide range of stereodiradical metal complexes. Here we report stereoselective generation of metal-centered helical chirality of an unprecedented CoIII N2O2 complex by chirality transfer from chiral vicinal diamines.

The tetradentate N2O2 salen ligand is one of the well-known privileged ligands for developing stereoselective catalysts pioneered by Jacobsen and Katsuki.7 Most metal salen complexes show a trans configuration, but some cis-β metal salen complexes of TiIV, AlIII, and RuII have been reported and used for stereoselective catalysis.8 Such geometrical isomerization of metal salen complexes appears to originate from the nature of metals and ligands. In addition, we propose that the geometry conversion from trans to cis would be possible in metal salen complexes by coordinating a bidentate ligand due to the availability of the cis-binding site only in the cis configuration (Scheme 1). Interestingly, metal centers for the cis configuration become stereogenic while those for the trans configuration are achiral. Thus, stereoselective generation of metal-centered helical chirality can be studied during isomerization by chiral bidentate ligands. We have also studied the possibility of asymmetric coordination chemistry by substitution with an achiral ligand (Scheme 1). To the best of our knowledge, the stereoselective transition from an achiral trans to a chiral cis configuration in metal salen complexes has not yet been reported.

We prepared a salen-type ligand 3 by replacing an aldimine with a ketimine of 2,2′-dihydroxybenzophenone (1)9 because the ketimine structure is known to favor the formation of cis-β-CoIII complexes.10 A new N2O2 salen-type ligand (3) was prepared as illustrated in Scheme 2. When ethylenediamine was mixed with 2,2′-dihydroxybenzophenone (1) at 60 °C, 1:1 imine compound 2 was formed and precipitated out of a MeOH solution (85% yield). Unsymmetrical bisimine 3 was then synthesized by the reaction of 2 with 3,5-di-tert-butyl-2-hydroxybenzaldehyde in 84% yield. A [Co-3]OTs complex was

![Scheme 1](https://example.com/scheme1.png)
prepared by following the published procedure of \([\text{Co-salen}]^+\). When 1 equiv. of rac-dpen (rac-1,2-diphenylethylenediamine) was added to a methanolic solution of \([\text{Co-3}]^+\) at ambient temperature, several tert-butyl peaks were initially observed (see ESI†). To our surprise, when the solution was heated to 70 °C for 6 h, a remarkably clean \(^1\text{H}NMR\) spectrum resulted with only two sets of tert-butyl peaks in a 7:1 ratio (Scheme 2b and Fig. 1a). The major product was isolated in an 18:1 ratio by recrystallization in EtOH/pentane (Fig. 1b). When the major product was heated to 70 °C in methanol, the aforementioned 7:1 product ratio was obtained. Although the product ratio was expected to be 13:1 at 25°C, the aforementioned 7:1 product ratio was obtained. Even if the solution was heated to 70 °C, no minor product was observed when the pure major product was dissolved in CD\(_3\)OD or DMSO-\(d_6\) for 7 days at 25°C. The experimental data indicate that the thermodynamic products obtained at 70°C do not interconvert at ambient temperature due to the kinetic barrier.

The crystal structure of \([\text{Co-3-rac}]^+\) revealed the major compound as a cis-\(\beta\) octahedral complex (Fig. 2). The cis-\(\beta\)-[Co-3] were chiral with \(\Lambda\) and \(\Delta\) configurations (Scheme 2b). In principle, rac-dpen can chelate to cis-\(\beta\)-[Co-3] to form diastereomeric mixtures of \([\text{Co-3-(R,R)}\]dpen\]^+ and \([\text{Co-3-(R,R)}\]dpen\]^+ as well as \([\text{Co-3-(S,S)}\]dpen\]^+ and \([\text{Co-3-(S,S)}\]dpen\]^+. Interestingly, the unit cell consists of two octahedral \(\text{Co}^{III}\) complexes where \((R,R)\)dpen chelated to the \(\Delta\)-form of \([\text{Co-3}]^+\), and \(\text{dpen}\) chelated to the \(\Lambda\)-form of \([\text{Co-3}]^+\). The crystals of [Co-3-rac]dpen\]^+ were obtained in diastereomeric purity close to 100% as a racemate. Indeed, the \(^1\text{H}NMR\) spectrum of crystals dissolved in DMSO-\(d_6\) is identical to that of the major complex prepared from the solution (Fig. 1b). Because Co\(^{III}\) complexes are known to be kinetically inert to substitution, the solid-state structure (X-ray) and the major diastereomer in solution (\(^1\text{H}NMR\)) can be considered to be the same.

Computation can be used to help explain the selective chelation of dpen by cis-\(\beta\)-[Co-3]OTs. DFT computation shows that \(\Lambda\)-[Co-3-(R,R)-dpen\]^+ is more stable than \(\Lambda\)-[Co-3-(R,R)-dpen\]^+ by about 1.2 kcal mol\(^{-1}\) (Scheme 2b). This energy difference translates to an equilibrium ratio of about 5.6 for \(\Lambda\)-[Co-3-(R,R)-dpen\]^+ to \(\Lambda\)-[Co-3-(R,R)-dpen\]^+ at 70°C. It appears that steric hindrance between the phenyl group of dpen and the tert-butyl groups of 3 is responsible for the energy difference. Considering additional effects such as solvents and counter anions, the calculated value is in excellent agreement with the experimental results. Previously, cis-\(\alpha\) Zn\(^{II}\) complexes were used for recognition of chiral vicinal diamines. Although rigid C\(_2\) symmetric chiral ligands were used, the obtained stereoselectivity is moderate ranging from 2:1 to 5:1. It appears that the cis-\(\beta\) complex exhibits higher selectivity in diamine recognition than the cis-\(\alpha\) complex.

Since the chirality of \((R,R)\)dpen is selectively imprinted onto cis-\(\beta\)-[Co-3] with a \(\Delta\)-configuration, the helical contents of the Co\(^{III}\) complex can be verified by circular dichroism (CD) spectroscopy. Fig. 3 shows CD and UV-vis spectra of \([\text{Co-3-(R,R)}\]dpen\)OTs and \([\text{Co-3-(S,S)}\]dpen\)OTs. There are strong Cotton effects of the same amplitude but of opposite sign in \([\text{Co-3-(R,R)}\]dpen\)OTs and \([\text{Co-3-(S,S)}\]dpen\)OTs. The CD signal of \((R,R)\)dpen appears only at 250 nm, the CD signal at 300–700 nm is due to the metal-to-ligand-charge-transfer (MLCT) bands of \([\text{Co-3}]\)\(^{2+}\). Moreover, electronic CD calculation yielded simulated CD spectra that closely matched with the experimental CD spectra (ESI†). As observed in Fig. 3, the observed CD signals are in a good linear relationship with the
enantiomeric excess (ee) of dpen (ESI†). In principle, [Co-3]OTs can be used for sensing the enantiopurity of dpen.

In order to increase the observed stereoselectivity (7:1 with dpen), we used a more sterically bulky chiral diamine that may increase the energy difference between two helical isomers, based on the crystal and calculated structures. Indeed, when 1,2-bis(2,4,6-trimethylphenyl)ethylenediamine was used, only a single isomer was formed to any observable extent in $^1$H NMR spectra (Scheme 2b). Lastly, we studied asymmetric coordination chemistry of an octahedral cis-$\beta$-Co$^{III}$ complex by replacing the chiral diamine with an achiral ligand. Heating $\Delta$-[Co-3-(R,R)-dpen]OTs with an excess amount of ethylenediamine (en) gave a clean product of [Co-3-en]OTs, but the complex was CD inactive (Fig. 4). In contrast, when excess bipyridine (bpy) was used in the presence of trifluoroacetic acid (TFA), the dpen was cleanly replaced by bpy, and the resulting complexes were CD active (Fig. 4). Although we were not able to determine the structure and stereoselectivity of [Co-3-bpy]$^+$, the active CD spectra indicated that the helical chirality could be retained. We are currently exploring the asymmetric coordination chemistry of Co$^{III}$ complexes.

In summary, we have demonstrated stereoselective cis-\textit{trans} isomerization in a Co$^{III}$-N$_{2}$O$_{2}$ complex induced by a chiral vicinal diamine. (R,R)-Dpen chelates [Co-3]OTs to form $\Delta$-[Co-3-(R,R)-dpen]OTs selectively, as confirmed by $^1$H NMR spectra and X-ray structure analysis. DFT computation can be used to explain the origin of stereoselectivity. The cis-$\beta$-Co$^{III}$ complex exhibits strong CD signals, which were closely simulated by electronic TD-DFT calculations, due to the induced chirality. The metal-centered helical chirality was shown to be retained when the chiral diamine was replaced by an achiral bpy ligand. This work demonstrates chirality transfer from ligands to stereo-dynamic metal complexes and the asymmetric coordination chemistry of Co$^{III}$-salen-type complexes.

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