Redox-triggered helicity inversion in chiral cobalt complexes in combination with H^+ and NO^-_3 stimuli.

Autorzy

Janusz Gregoliński

Masahiro Hikita

Tatsuya Sakamoto

Hideki Sugimoto

Hiroshi Tsukube

Hiroyuki Miyake

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Three chiral ligands with variable denticity, H_2**L2**-H_2**L4**, conjugated by *N*,*N*′-ethylenebis[*N*-methyl-(*S*)-alanine] and an ortho-heterosubstituted aromatic amine, were newly synthesized as analogues of previously reported H_2**L1**. Four contracted-Λ_{oxo} cobalt(III) complexes $[Co(\mathbf{L})]^+$ with left-handed helical structure of $\Lambda_4\Delta_2$ configuration were prepared by one-electron oxidation of the corresponding contracted-Λ_{red} cobalt(II) complexes [Co(**L**)], which were generated from chiral ligands and $Co(ClO_4)_2{\cdot}6H_2O$ or $Co(CF_3SO_3)_2{\cdot}5.2H_2O$ in the presence of an organic base. Although the prepared cobalt(III) complexes were very inert and kinetically stable against protonation and NO_3^- complexation, cobalt(III) reduction in the presence of CF_3SO_3H and/or Bu_4NNO_3 allowed immediate changing of their three-dimensional structures from the contracted-Λ_{oxo} form to the extended-Λ $[Co(H_2\mathbf{L})Y_2]^{n+}$ (Y = solvent and/or anion, *n* = 0-2) form with left-handed helicity or to the extended-Δ $[Co(H_2\mathbf{L})(NO_3)]^+$ form with right-handed helicity via N- to O-amide coordination switching. Both extended forms were contracted to the original Λ_{oxo} form by oxidation of the cobalt(II) center in the presence of an organic base. Thus, redox reactions triggered dynamic helicity inversion of the chiral cobalt complexes, via multiple molecular motions consisting of relaxation/compression, extension/contraction, and helicity inversion motions in combination with deprotonation/protonation of amide linkages and NO_3^- anion complexation.

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