

# Dynamic helicity inversion in an octahedral cobalt(II) complex system *via* solvato-diastereomerism†

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The helical sense of a mononuclear Co(II) complex with an amino acid-based chiral tetradentate ligand was dynamically inverted by changing the solvent component.

Dynamic helicity induction and inversion often play important roles in biological DNA and protein systems.<sup>1</sup> Several artificial systems including acetylene-, silane- and amide-polymers,<sup>2</sup> bis-(metal porphyrin)s<sup>3</sup> and overcrowded alkenes<sup>4,5</sup> similarly form helical structures which respond well to external stimuli. Although labile transition metal complexes can offer characteristic helicity inversion based on their dynamic kinetics as well as their unique coordination geometry, redox activities, and spectroscopic/magnetic properties, the number of successful examples exhibiting helicity induction and subsequent inversion is still limited.<sup>6–9</sup> We recently demonstrated that the helicity of an octahedral Co(II) complex with a chiral tetradentate ligand **L** was dynamically inverted in CH<sub>3</sub>CN : CH<sub>2</sub>Cl<sub>2</sub> = 1 : 9 by simply adding NO<sub>3</sub><sup>–</sup> anion. When two NO<sub>3</sub><sup>–</sup> anions interacted respectively with the Co(II) centre and the amide hydrogen atom, the complex helicity changed from  $\Lambda$  to  $\Delta$  (Fig. 1).

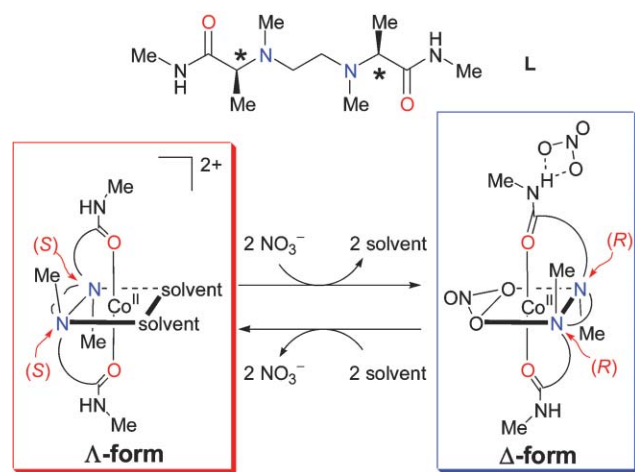


Fig. 1 Helicity inversion in L–Co(II) complex.

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† Electronic supplementary information (ESI) available: <sup>1</sup>H NMR titration experiments of NO<sub>3</sub><sup>–</sup> with L–Co(ClO<sub>4</sub>)<sub>2</sub> complex in CD<sub>3</sub>CN. See <http://dx.doi.org/10.1039/b506130j>

We report here that the helicity of the octahedral L–Co(II) complex can be dynamically inverted by changing the solvent component. The solvent is one of the most effective external stimuli, which provides solvation for the metal centre as well as hydrogen bonding and cation– $\pi$  interactions for ligand residues,<sup>10</sup> to significantly alter the helicity of the metal complex. The direction of the biological polyproline helix typically depends on the polarity of the medium employed.<sup>11,12</sup> The present L–Co(II) complex is demonstrated to exhibit “solvato-diastereomerism”, in which the nature of the solvent employed dynamically induces helicity inversion of the labile metal complex. This process resembles the “solvato-chromism” found in several coloured metal complexes.<sup>13,14</sup>

The <sup>1</sup>H NMR spectrum of the L–Co(NO<sub>3</sub>)<sub>2</sub> complex in CD<sub>3</sub>CN indicated the existence of three different species with independent C<sub>2</sub> symmetrical patterns {43% (red), 45% (green) and 12% (blue) in Fig. 2(b)}. Since one of the species {red in Fig. 2(b)} has a similar NMR spectrum to the  $\Lambda$  *cis*- $\alpha$  L–Co(ClO<sub>4</sub>)<sub>2</sub> complex<sup>9</sup> {Fig. 2(a)}, this can be assigned to the  $\Lambda$  form, in which the NO<sub>3</sub><sup>–</sup> anion does

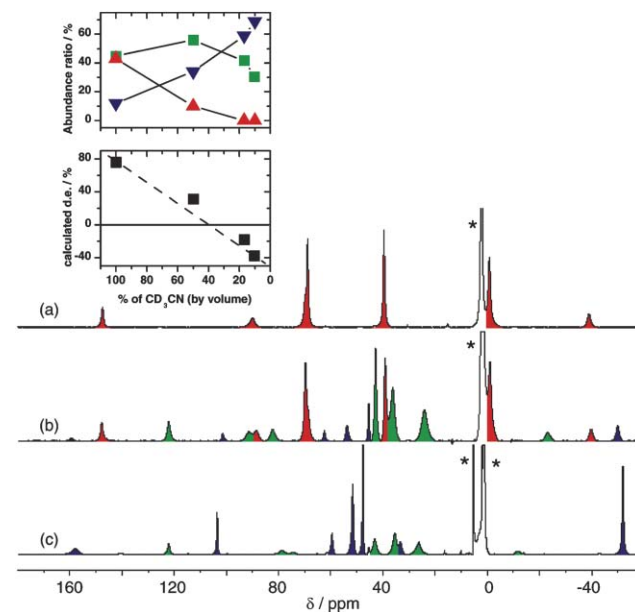
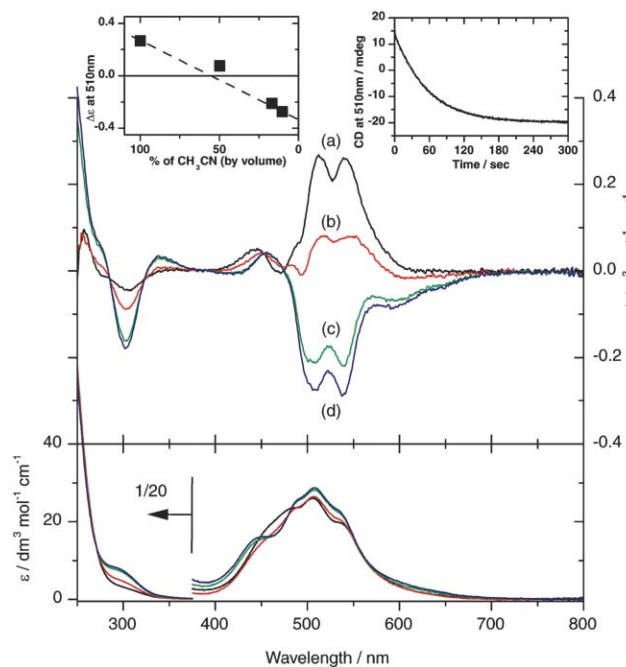


Fig. 2 <sup>1</sup>H NMR spectra of a 1 : 1 mixture of **L** and Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in CD<sub>3</sub>CN (a), a 1 : 1 mixture of **L** and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in CD<sub>3</sub>CN (b) and in CD<sub>3</sub>CN : CD<sub>2</sub>Cl<sub>2</sub> = 1 : 9 (c) at room temperature. [**L**] = [Co(II)] = 5 × 10<sup>–3</sup> mol dm<sup>–3</sup>. \*: Solvent and water signals. Inset: abundance ratio (upper) of each species in a 1 : 1 mixture of **L** and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and calculated de (%; positive indicates  $\Lambda$  form ascendancy) (lower) in several volumes of CD<sub>3</sub>CN in CD<sub>2</sub>Cl<sub>2</sub> at room temperature.

not coordinate directly to the Co(II) centre. In  $\text{CD}_3\text{CN} : \text{CD}_2\text{Cl}_2 = 1 : 9$  solution {Fig. 2(c)}, the species indicated by blue (69%) was found as the major component and the species marked by red ( $\sim 0\%$ ) and green (31%) decreased. Since the relative abundance ratio of the green-marked species was almost consistent (30–50%) in the range 100–10%  $\text{CD}_3\text{CN}$  in  $\text{CD}_2\text{Cl}_2$  {inset (upper) of Fig. 2}, this species was thought to be a steady-state intermediate for the transformation to the blue-marked species from red-marked ones.<sup>15</sup>

The CD spectrum of the  $\text{L-Co}(\text{NO}_3)_2$  complex has a positive signal in the range of the d–d transition (around 530 nm)<sup>16,17</sup> in  $\text{CH}_3\text{CN}$  {Fig. 3(a)}. The fact that its shape is similar to that observed in the  $\Lambda$  *cis*- $\alpha$   $\text{L-Co}(\text{ClO}_4)_2$  complex<sup>9</sup> suggests that the  $\text{L-Co}(\text{NO}_3)_2$  complex mainly exists in the  $\Lambda$  *cis*- $\alpha$  form in  $\text{CH}_3\text{CN}$ . The sign of the CD signal changed dramatically from positive to negative as the proportion of  $\text{CH}_2\text{Cl}_2$  increased {Fig. 3(a)–(b)–(c)–(d)}.<sup>18</sup> Thus, the nature of the solvent significantly inverted the helicity around the Co(II) centre from the  $\Lambda$  *cis*- $\alpha$  form to the  $\Delta$  *cis*- $\alpha$  form. The CD spectral changes at 510 nm correspond well with the ratio of  $\text{CH}_3\text{CN}$  to  $\text{CH}_2\text{Cl}_2$  {inset (left) in Fig. 3}. As reported earlier,<sup>9</sup> the  $\Delta$  *cis*- $\alpha$  Co(II) complex is stabilized by one  $\text{NO}_3^-$  anion coordinating with the Co(II) centre and the other hydrogen bonding with the amide hydrogen atom in  $\text{CH}_3\text{CN} : \text{CH}_2\text{Cl}_2 = 1 : 9$ . Since the  $\text{NO}_3^-$  anions act as more effective donors in the less polar solvent system, it can switch the helicity of the  $\text{L-Co}(\text{II})$  complex. As illustrated in the inset (right) of Fig. 3, the half time ( $t_{1/2}$ ) of the CD spectral inversion occurring



**Fig. 3** CD (upper) and absorption (lower) spectral changes of a 1 : 1 mixture of **L** and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN} : \text{CH}_2\text{Cl}_2 = 1 : 0$  (a, black), 1 : 1 (b, red), 1 : 5 (c, green) and 1 : 9 (d, blue) at room temperature.  $[\text{L}] = [\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ , 5 mm cuvettes. Inset (left): profiles of the CD amplitude at 510 nm versus the percentage of  $\text{CH}_3\text{CN}$  in  $\text{CH}_2\text{Cl}_2$  by volume. Inset (right): relaxation trace (510 nm) of  $\text{L-Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $50 \times 10^{-3} \text{ mol dm}^{-3}$ ) complex in  $\text{CH}_3\text{CN}$  by adding 9-fold volume of  $\text{CH}_2\text{Cl}_2$  at room temperature.  $\Delta\epsilon$  values were calculated per ligand concentration.

with addition of a 9-fold volume of  $\text{CH}_2\text{Cl}_2$  to the  $\text{CH}_3\text{CN}$  complex solution was estimated as 38 s, much faster than the half times observed in other solvent-induced helicity inversion processes: *i.e.*, Cr(III) complex ( $t_{1/2}$ : a few days)<sup>8</sup> and polyprolines ( $t_{1/2}$ : 50 min–a few hours),<sup>12</sup> and of the same order as the half time observed in the thermal helicity inversion process of sterically overcrowded alkenes ( $t_{1/2} = 18 \text{ s}$ ).<sup>5</sup>

Referring to these CD spectral changes, the blue- and green-marked species observed in the  $^1\text{H}$  NMR spectrum can be assigned to the  $\Delta$  and  $\Lambda$  forms, respectively (see Fig. 2). Based on the relative intensities of the  $^1\text{H}$  NMR signals of these species, the  $\Lambda : \Delta$  ratios were estimated as 76% de ( $\Lambda$ ) in  $\text{CD}_3\text{CN} : \text{CD}_2\text{Cl}_2 = 1 : 0$ , 32% de ( $\Lambda$ ) in  $\text{CD}_3\text{CN} : \text{CD}_2\text{Cl}_2 = 1 : 1$ , 18% de ( $\Delta$ ) in  $\text{CD}_3\text{CN} : \text{CD}_2\text{Cl}_2 = 1 : 5$  and 38% de ( $\Delta$ ) in  $\text{CD}_3\text{CN} : \text{CD}_2\text{Cl}_2 = 1 : 9$ . This profile {inset (lower) of Fig. 2} is similar to that observed in the CD spectral changes {see inset (left) of Fig. 3}.

The CD and  $^1\text{H}$  NMR spectra also indicated that both  $\text{L-Co}(\text{NO}_3)_2$  and  $\text{L-Co}(\text{ClO}_4)_2$  complexes prefer the  $\Lambda$  configuration (de > 95%) in  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$  and other polar solvents. Since the donor numbers (DN) of these solvents are comparable to that of the  $\text{NO}_3^-$  anion (23.3 for  $\text{CH}_3\text{OH}$ ; 17.0–19.5 for  $\text{H}_2\text{O}$ ; and 21.1 for the  $\text{NO}_3^-$  anion),<sup>13</sup> the solvent molecules can occupy the two vacant sites rather than the  $\text{NO}_3^-$  anion and stabilize the  $\Lambda$  form (see Fig. 1). When the less polar  $\text{CH}_2\text{Cl}_2$  (DN = 1.2<sup>13</sup>) was added to a  $\text{CH}_3\text{CN}$  solution (DN = 13.2<sup>13</sup>), however, the  $\text{NO}_3^-$  anions coordinated with the Co(II) centre and formed hydrogen bonds with the amide hydrogen.<sup>19,20</sup> Since the two tertiary amine nitrogens must detach to allow inversion of the chirality of the nitrogens, the mechanism may involve twisting<sup>21</sup> via a triangular prism geometry.

The nature of the employed solvent is known to lead to colour changes of some transition metal complexes, the so-called “solvato-chromism”.<sup>13</sup> The present study indicated that a labile Co(II) complex exhibited “solvato-diastereomerism”, in which the donor strength of the solvent molecules determined the helicity around the metal centre and gave the characteristic chirotopic behaviour.

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- 15 Titration experiments showed that two  $\text{NO}_3^-$  anions were required to give the green-marked species in  $\text{CD}_3\text{CN}$  (inset of Fig. S1†).
- 16 The absorption spectrum of the  $\text{L-Co}(\text{NO}_3)_2$  complex is somewhat complicated in  $\text{CH}_3\text{CN}$  due to the existence of three species. The major peaks around 510 and 540 nm are most likely d-d transitions for a high-spin  $\text{Co}(\text{II})$   $d^7$  octahedral species, though distinguishable shoulders appeared around 460, 600 nm. For more details see ref. 17.
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- 18 CD signals at 280–350 nm were also enhanced which could be assigned to a signal of the bound  $\text{NO}_3^-$  anion.
- 19 Addition of 11% of  $\text{CH}_3\text{OH}$  to the  $\text{L-Co}(\text{NO}_3)_2$  complex solution in  $\text{CH}_3\text{CN} : \text{CH}_2\text{Cl}_2 = 1 : 9$  could reswitch the helicity of the  $\text{Co}(\text{II})$  complex to the  $\Lambda$  form, which had a similar CD shape and intensity to the  $\text{L-Co}(\text{ClO}_4)_2$  complex in methanol.
- 20 The helicity inversion of a related chiral  $\text{Co}(\text{II})$  complex insufficiently occurred in high diluted solution ( $\sim 10^{-5} \text{ mol dm}^{-3}$ ). ESI-MS spectra of the  $\text{L-Co}(\text{NO}_3)_2$  complex measured in  $\text{CH}_3\text{CN} : \text{CH}_2\text{Cl}_2 = 1 : 9$  did not show the formation of polymeric species nor an  $\text{L}_2\text{-Co}(\text{NO}_3)_2$  complex.
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