Unexpected kinetic stability of a dinuclear helical complex

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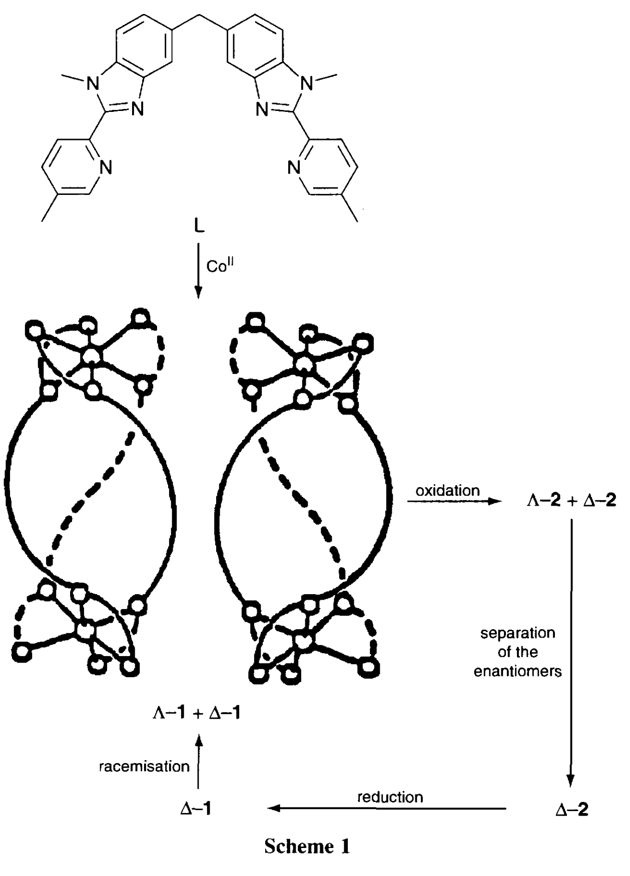
The circular dichroism spectrum of a chiral dinuclear cobalt(II) triple helix is reported, together with the kinetics of racemisation which are much slower than usual for cobalt(II).

Numerous examples of the formation of polynuclear helical complexes are now documented in the literature,[1,2] most of them being based on the self-assembly of labile metal atoms with polydentate ligands. Although the strategies for their synthesis are now well understood, little is known about the physicochemical properties of these complexes. In previous work,[3,4] we showed that the design of the ligand together with the choice of a suitable metal atom could lead to the formation of an inert dinuclear triple helix. By oxidation of the readily formed cobalt(II) complex $[Co_2L_3]^{4+}$ **1** (Scheme 1), we obtained the inert cobalt(III) complex $[Co_2L_3]^{6+}$ **2**, from which we were able to isolate the enantiomer $(-)_{589}$-$[Co_2L_3]^{6+}$, $(-)_{589}$-**2**. In this work, we report the reduction of the optically active dinculear triple helix of cobalt(III) to the cobalt(II) complex with retention of chirality, the CD spectrum and the kinetics of racemisation of the cobalt(II) complex.

Reduction of the perchlorate salt of **2** was effected with a slight excess of sodium dithionite in aqueous solution (acetate buffer, I = 0.1 mol dm^{-3}, pH = 4.8). The UV–VIS spectrum showed the reaction to be instantaneous, with the displacement of the $\pi \rightarrow \pi_{1,2}^*$ transition from 342 nm for **2** to 328 nm for **1**. Attempts to use hydrazine led to decomposition of the complex as shown by the electronic spectrum of the solution. The racemisation is slow at room temperature, and thus reduction of $(-)_{589}$-**2** gives $(-)_{589}$-**1** whose CD spectrum is shown in Fig. 1.



Scheme 1

The bands in the CD spectrum of $(-)_{589}$-**2** at 428 nm ($\Delta\varepsilon$ +3.23 dm^3 mol^{-1} cm^{-1}) and 492 (− 5.27) corresponding to the splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ in C_3 microsymmetry have disappeared and a new band appears at 475 nm ($\Delta\varepsilon$ −1.64 dm^3 mol^{-1} cm^{-1}) corresponding to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ d–d transition of Co^{II} which was found at 453 nm in $[Co(bpy)_3]^{2+}$.[5] The UV part of the spectrum shows a succession of negative and positive bands [λ = 371 nm, ($\Delta\varepsilon$ = −3.48 dm^3 mol^{-1} cm^{-1}), 353 (+12.1), 334 (−34.4), 309 (+33.3), 268 (−42.3)] which are attributed to the $\pi \rightarrow \pi_{1,2}^*$ transitions centred on the ligands.

The study of the spectra yields the following conclusions. Reduction of cobalt(III) to cobalt(II) has occurred as demonstrated by the changes observed in the d–d transitions. The general pattern of the $\pi \rightarrow \pi_{1,2}^*$ transitions has not changed after reduction (succession of absorptions with +, −, +, −, + signs). As the polarization of the transitions remains the same before and after reduction, the latter occurs with retention of configuration. Finally, a comparison of the d–d transitions of **1** and **2** with those of $[Co(bpy)_3]^{n+}$ (n = 2,3)[5,6] shows that the ligand fields of the cobalt complexes of L and bpy are quite similar. In this case the splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the cobalt(III) complex into A_2 and E transitions going from O_h to C_3 symmetry is nearly the same for $[Co(bpy)_3]^{3+}$ and **2**. A comparison of the CD spectra of $(-)_{589}$-**2** and of $(-)_{589}$-$[Co(bpy)_3]^{3+}$ whose absolute configuration is known allows the attribution of the Δ absolute configuration to $(-)_{589}$-**2**. As reduction occurs with retention of configuration, the absolute configuration of $(-)_{589}$-**1** is also Δ.

The racemisation process of $(-)_{589}$-**1** was followed by CD spectroscopy and polarimetry in aqueous solution (acetate buffer, I = 0.1 mol dm^{-3}, pH = 4.8). The kinetics are

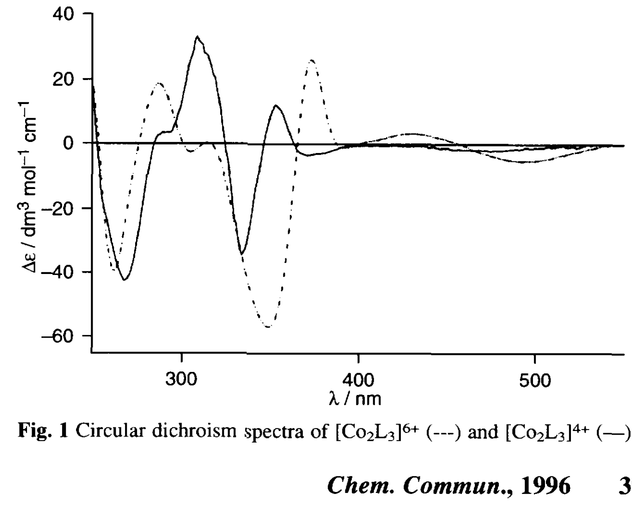
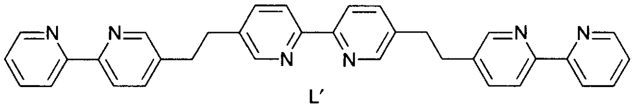
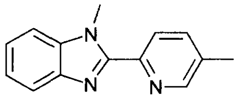


Fig. 1 Circular dichroism spectra of $[Co_2L_3]^{6+}$ (---) and $[Co_2L_3]^{4+}$ (—)

independent of the concentration and were satisfactorily fitted with a first-order rate law. The racemisation is surprisingly slow at room temperature [$k = 1.4(2) \times 10^{-5}\ \mathrm{s}^{-1}$ at 298 K] when compared with a mononuclear cobalt(II) complex with three bidentate units such as $[\mathrm{Co(phen)_3}]^{2+}$ for which the rate constant was found to be 9.6 s^{-1} at ambient temperature.[7] Preliminary kinetic results for *mer–fac* isomerisation of the mononuclear cobalt(II) complex with three non-symmetric bidentate units 5-methyl-2(2′-methylbenzimidazol)pyridine, (5-mpmb), which is the mononuclear ligand corresponding to L in **1** and **2**, show that the exchange rate in the complex is of the order of 10 s^{-1} at room temperature.[8] These results demonstrate that the kinetic stability of the dinuclear species compared to the mononuclear one, which can be taken as the ratio of their kinetic rates, is of the order of 10^6.



L′



5-mpmb

A similar, although less dramatic, increase in kinetic stability to racemisation was reported by Lehn and coworkers[9] who have shown that for the chiral trinuclear triple helix $[\mathrm{Ni_3L'_3}]^{6+}$, 23% of the optical activity was lost in 24 h, which, for a first-order mechanism, corresponds to a rate constant of $1.5 \times 10^{-6}\ \mathrm{s}^{-1}$. They compared it to the corresponding mononuclear $[\mathrm{Ni(bpy)_3}]^{2+}$ which racemises with a rate constant of $3.8 \times 10^{-4}\ \mathrm{s}^{-1}$.[10]

The effect of temperature on the racemisation of **1** was studied, and the rate constants gave the Eyring plot shown in Fig. 2, with activation parameters $\Delta H^\ddagger = +99(2)$ kJ mol^{-1} and $\Delta S^\ddagger = -6(7)$ J $\mathrm{mol}^{-1}\ \mathrm{K}^{-1}$. The activation process is thus dominated by the enthalpic factor which is over three times the value reported for $[\mathrm{Co(phen)_3}]^{2+}$,[7] and is responsible for the kinetic stability.

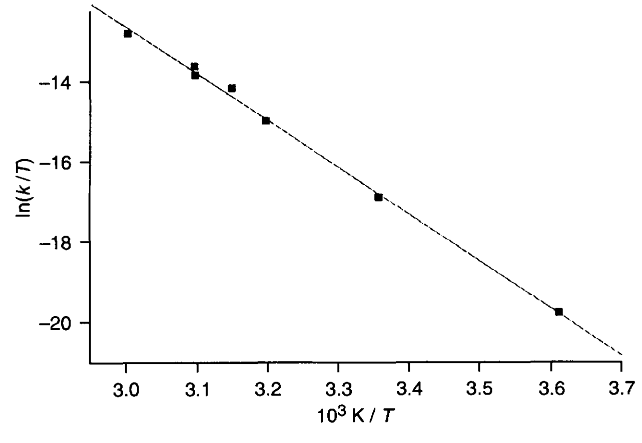


Fig. 2 Eyring plot of the racemisation reaction of $(-)_{589}$-$[\mathrm{Co_2L_3}]^{4+}$

The $\mathrm{Co^{II}}$–N distances in **1** are not significantly different from those in mononuclear cobalt(II) complexes[3] and the expected lability of the individual $\mathrm{Co^{II}}$–N bonds was confirmed by the observation that **1** is decomposed within the time of mixing in 1 mol dm^{-3} HCl. We conclude that the stability must therefore arise from the need to break or perturb several Co–N bonds in the same step. Addition of excess $\mathrm{Co^{II}}$ has no effect upon the racemisation rate so that a mechanism involving a rapid pre-equilibrium with loss of one cobalt ion [eqn. (1)] may be excluded.

$$\Delta\text{-}[\mathrm{Co_2L_3}]^{4+} \longleftrightarrow \Delta\text{-}[\mathrm{CoL_3}]^{2+} + \mathrm{Co}^{2+} \rightarrow \Lambda\text{-}[\mathrm{CoL_3}]^{2+} + \mathrm{Co}^{2+} \longleftrightarrow \Lambda\text{-}[\mathrm{Co_2L_3}]^{4+} \qquad (1)$$

Among the mechanisms for racemisation[11] which remain, the most probable seems to be a concerted Bailar twist which maintains the C_3 symmetry axis (the Ray–Dutt twist is impossible); complete dissociation of one ligand strand is equally possible. A one-end mechanism at one cobalt centre would be strongly disfavoured by the structural constraints arising from the second cobalt. In any mechanism, the degree of flexibility of the ligand will play an important rôle, and it may be significant that the more flexible ligand L′ used by Lehn and coworkers,[9] in which the bridging unit is an ethylene rather than a methylene, apparently results in a smaller kinetic stabilisation to racemisation, despite the greater number of nuclei in their triple helix.

We are currently carrying out further studies on the mechanism of racemisation. It seems, however, that polynuclear systems can possess very significant kinetic stability, and this offers interesting new perspectives for the resolution of enantiomers of complexes of labile metal ions, and the general stabilisation of polynuclear metal structures if substitution reactions require the simultaneous rupture of several metal ligand bonds. Such kinetic stabilisation is of course already well established in the chemistry of mononuclear macrocyclic complexes.

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