Synthesis, Structure and Resolution of a Dinuclear Co^{III} Triple Helix

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For the first time a helical dinuclear metal complex has been separated into enantiomers by transformation of a labile cobalt(II) triple-helical complex into the kinetically stable cobalt(III) complex $[Co_2(\mathbf{2a})_3]^{6+}$ which has been characterized structurally and resolved by chromatography.

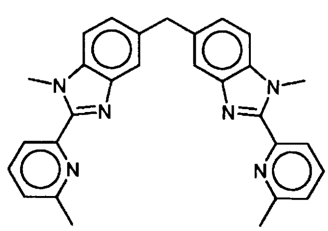
The synthesis of polynuclear helical complexes has been a major interest in the field of supramolecular chemistry.[1] Although these systems are preeminently chiral, the investigation of the physical properties associated with this chirality has been limited by the fact that virtually all helicates reported have been racemic mixtures. The exceptions have involved the use of chiral ligands[2,3] or in one case the spontaneous autoresolution of a triple helical complex upon crystallisation.[4] This difficulty is inherent in the synthetic strategy, which requires the use of kinetically labile metal ions for thermodynamically controlled self-assembly[5] to occur, with the regrettable consequence that the lability of the metal ions then prevents the separation of the enantiomers. A possible solution is to modify the lability of the metal ion by an electron transfer reaction after formation of the helix. The obvious choice was the oxidation of a labile Co^{II} complex into the related inert Co^{III} complex, but we were disappointed to observe that the triple-helical Co^{II} complex $[Co_2(\mathbf{1})_3]^{4+}$ could not be oxidised to $[Co_2(\mathbf{1})_3]^{6+}$.[6] More recently[7] we observed that the related complex $[Co_2(\mathbf{2a})_3]^{4+}$ could be oxidised, and here we report the synthesis of $[Co_2(\mathbf{2a})_3]^{6+}$, and its resolution into enantiomers. This is to our knowledge the first report of the resolution of a polynuclear helical complex.

Starting from the ligand bis[1-methyl-2-(5′-methyl-2′-pyridyl)benzymidazol-5-yl]methane (5-bismpmb, **2a**) (Scheme 1) $[Co_2(\mathbf{2a})_3]^{4+}$ was prepared by reaction with the stoichiometric amount of $Co(ClO_4)_2{\cdot}6H_2O$ in acetonitrile.[7] The complex was then oxidized with bromine in acetonitrile and crystallized from concentrated $LiClO_4$ in MeOH to obtain $[Co_2(\mathbf{2a})_3](ClO_4)_6{\cdot}4H_2O$, **3a** in 67% yield. The complex was characterized by elemental analysis, IR and ^1H and ^{13}C NMR spectroscopy. Slow diffusion of methanol into a concentrated solution of **3a** gave red crystals suitable for X-ray diffraction. The crystal structure† of **3a** shows the triple-helical cation $[Co_2(\mathbf{2a})_3]^{6+}$ and six perchlorate anions, two of which were slightly disordered. The residual electron density map suggested the presence of seven acetonitrile molecules (two atomic sites observed) and two molecules of water (one atomic site only observed); all solvent sites were disordered. The cation is a dinuclear triple helix formed by the three ligands wrapped around two octahedral Co^{III} cations. The Co–N distances show the expected decrease of *ca.* 0.2 Å in comparison with the cobalt(II) complex. The Co–Co distance increases slightly, passing from 8.85(5) Å in $[Co_2(\mathbf{2a})_3]^{4+}$ [7] to 9.146(6) Å in **3a**. Fig. 1 shows an ORTEP drawing of the cation; full details of the crystal structure will be published elsewhere.

All the signals in the ^1H NMR spectrum of **3a** were attributed by two dimensional (^1H–^1H) correlation spectroscopy. The most striking feature is the upfield shift of the isolated proton of the benzimidazole ring upon complexation ($\Delta\delta$ = 3.39 ppm), found at 4.29 ppm (wrt TMS). This is in agreement with the crystal structure where this proton is situated in the shielding zone of the neighbouring benzimidazole of a second ligand. Replacement of ligand **2a** by the ligand **2b** allowed the intramolecular diastereotopic effect[8] to be observed in this chiral complex; the complex $[Co_2(\mathbf{2b})_3]^{6+}$ displays a broad triplet at 1.70 ppm and a broad quadruplet at 4.94 ppm for the ABX_3 spin system of the ethyl groups. The presence of the two enantiomers was also evident in a solution containing a large excess of $Na_2Sb_2(d\text{-}C_4O_6H_2)_2{\cdot}5H_2O$ [9] in D_2O since the resonances due to the aromatic protons (apart from the isolated singlet of the benzimidazole, masked by the tartrate) were split into two equal signals. Finally Electron Spray Mass Spectroscopy showed the presence of the cations $[Co_2(\mathbf{2a})_3]^{6+}$ (m/z = 262.8) and $[Co_2(\mathbf{2b})_3]^{6+}$ (m/z = 249.0) with other peaks corresponding to adduct ions with up to 4 perchlorate anions.

An aqueous solution of **3a** was sorbed onto a Sephadex SP-C25 ion exchange resin and eluted with a 0.2 mol dm^{-3} aqueous solution of $Na_2Sb_2[(-)\text{-}C_4O_6H_2]_2{\cdot}5H_2O$ which allowed clear separation of the two enantiomers.[9] The two fractions were purified by absorption onto a cation exchange resin, elimination of antimonyl tartrate by washing, followed by elution with HCl (1 mol dm^{-3}); the enantiomers were isolated as chloride salts. The ^1H NMR spectra of the separated enantiomers in presence of an excess of $Na_2Sb_2[(-)\text{-}C_4O_6H_2]_2{\cdot}5H_2O$ showed that resolution had been achieved, but a precise determination of the optical purity could not be made because of the tendency of one of the enantiomers to precipitate in the NMR tube.

The circular dichroism spectrum of the first of the two enantiomers to be eluted from the column is shown in Fig. 2;



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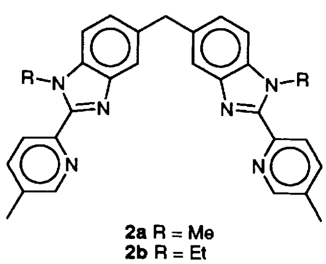

2a R = Me
2b R = Et

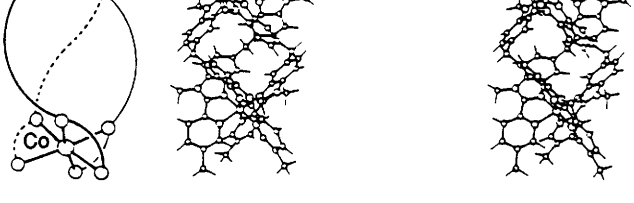

Fig. 1 Schematic view and ORTEP[11] stereoview of the cation $[Co_2(\mathbf{2a})_3]^{6+}$

the second enantiomer shows the expected inverted spectrum. The bands at wavelengths below 400 nm are due to ligand based transitions. The two bands at 429 nm ($\Delta\varepsilon = -1.08$) and 490 nm ($\Delta\varepsilon = 1.34$) lie in the tail of the ligand based transitions and are assigned to d–d transitions. In agreement with this the circular dichroism in this region is only one order of magnitude less than in the UV region, whereas the molar extinction coefficients are two orders of magnitude smaller; this assignment agrees with that previously made for $[Co(2,2'\text{-bipyridyl})_3](ClO_4)_3$.[10] The measured molar rotation for the first eluted enantiomer at 589 nm is $-10.8(10) \times 10^3$ deg mol^{-1} m^{-1} (1.12×10^{-4} mol dm^{-3} in acetonitrile). In the absence of more information about the excited states of the ligand it is not possible to deduce the absolute configuration from the sign of the CD spectrum.[10] It is however clear that the observed rotatory power of the complex is comparable with that of the two tris-bidentate cobalt units, and that the helical backbone itself does not contribute greatly.

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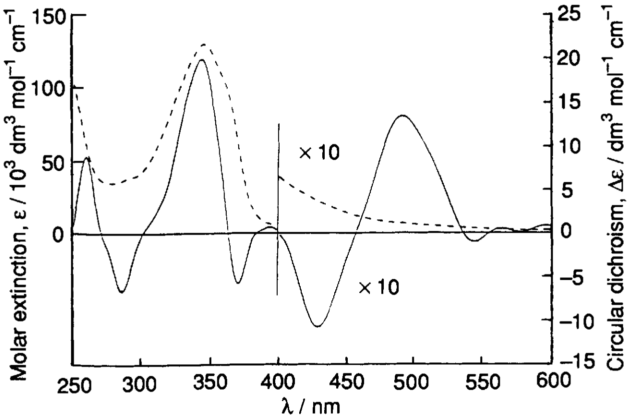

Fig. 2 Circular dichroism spectrum of one isomer of $[Co_2(\mathbf{2a})_3]^{6+}$ (full line) and electronic spectrum of the racemate (dashed line). The data for wavelengths above 400 nm have been multiplied by 10. ε and Δε are given per mol of dimer.

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Footnote

† *Crystal data* for **3a**: $Co_2C_{87}H_{78}N_{18}(ClO_4)_6(MeCN)_4(H_2O)_2$, red prisms. monoclinic, $P2_1/n$, $a = 12.687(2)$, $b = 41.585(2)$, $c = 21.486(5)$ Å, $\beta = 91.416(7)°$, $V = 11332(3)$ Å^3, $Z = 4$, $M_r = 2290.5$ g mol^{-1}, $\mu = 4.255$ mm^{-1}, $d_x = 1.34$ g cm^{-3}. Nonius CAD4 diffractometer with monochromated Cu-Kα radiation; ω-2θ scans. The structure was solved by direct methods and refined anisotropically to give $R = 0.127$, $R_w = 0.127$ for 4884 contributing reflections and 1235 variables [$6° < 2\theta < 100°$, $|F_0| > 4\sigma(F_0)$]. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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