Inorganic Chemistry
Communication
pubs.acs.org/IC

Enantioselective Synthesis of Tetranuclear Quadruple Helicates

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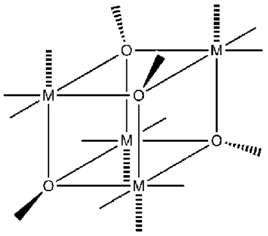
S Supporting Information

ABSTRACT: Quadruple helical structures are assembled around a tetranuclear cubane structure using four chiral tridentate ligands and two ligands coordinating diagonally across a face. Stereoselectivity in the complex formation is observed.

The synthesis of helical complexes of metal ions has attracted considerable attention in recent years,[1] but there have been relatively few examples of quadruple helices reported. While it is relatively easy to generate a double helix around a tetrahedral ion, or a triple helix around an octahedral ion, a quadruple helix requires a higher coordination number. There are a number of examples of quadruple helices formed around eight-coordinate ions[2,3] and one using a nine-coordinate ion with one site blocked by coordinated *N*,*N*-dimethylformamide.[4] A quadruple helical structure may be formed by twisting four ligands around two square-planar ions,[5] and quadruple helices have also been formed around linear metal–metal-bonded systems.[6] Finally, an unusual quadruple helix was reported by Lehn in which four essentially linear pyridinetetrapyridazinepyridine ligands were twisted into a bundle and held by 20 tetrahedrally coordinated silver ions. Although spontaneous resolution was observed for a chain polymer species,[3] none of the helicates reported so far has been resolved nor has an enantioselective synthesis appeared. In the present Communication, we report the first enantioselective synthesis of a quadruple helix.

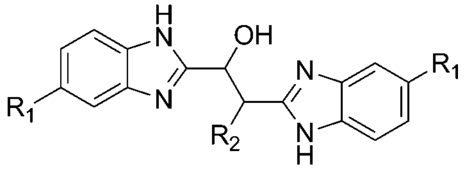
Rather than use a high-coordination-number metal ion, we have used a well-defined polynuclear center around which to form the helix. The use of polynuclear centers is less common than single metal ions but is gradually increasing and includes the Zn_4O centers used by Yaghi et al.[7] and dimetal tetracarboxylates of copper(II),[8] molybdenum(II),[9] and rhodium(II).[10] Bermejo et al. have prepared helicates containing multinuclear clusters with silver(I) and copper(I).[11] Polynuclear units offer a greater number of coordination sites and a more precise stereochemical control of binding sites. We have used the M_4O_4 cubane structure (Chart 1), which, for an octahedral metal M, offers 4 × 3 coordination sites as well as four possible covalent attachments to the oxygen atoms. Some hundreds of these compounds are known, and we have discussed their structures previously.[12,13] They form in high yield and show kinetic inertness even with labile metal ions.[14] The ligand **1** (Chart 2) forms a cubane $[M_4(\mathbf{1}\text{-H})_4]^{4+}$ with M = cobalt(II) and nickel(II), in which one alcohol function is deprotonated and bridges three metals and the second alcohol and two benzimidazoles occupy the free coordination sites of the metal ions.[13] This cubane structure is not helical, but we reasoned that blocking the four sites indicated by hashed lines in Chart 1 would allow the 12 remaining sites to template a helical structure using ligand **2**,[15] which, by virtue of its chirality, will favor either the *P* or *M* helix. Blockage of the sites may be achieved by the use of a ligand that binds across the diagonal of one of the cubane faces.[12] Suitable ligands are carboxylates[16] and diarylphosphinates.[17]

Chart 1. Structure of M_4O_4 Cubanes[a]



[a]The four coordination sites blocked by phosphinate or acetate are shown as hashed lines.

Chart 2. Ligands Used in This Work



R1 = H, R2 = OH : 1
R1 = H, R2 = H : 2
R1 = CH_3, R2 = H : 3

The reaction of ligand (*S*)-**2** with 1 equiv of cobalt(II) perchlorate, 1 equiv of diphenylphosphinic acid (dppH), and 2 equiv of triethylamine gave a solution that upon slow evaporation gave crystals of $[Co_4[(S)\text{-}\mathbf{2}\text{-H}]_4(dpp)_2](dpp)(ClO_4)\cdot 5MeOH$. The electrospray ionization mass spectrometry (ESI-MS) spectrum showed the principal peak at *m*/*z* 889, in agreement with the ion $[Co_4[(S)\text{-}\mathbf{2}\text{-H}]_4(dpp)_2]^{2+}$. The X-ray crystal structure (Figure 1) confirmed the existence of this ion and showed the alcohol function of ligand **2** to be deprotonated

Received: July 10, 2012
Published: August 8, 2012

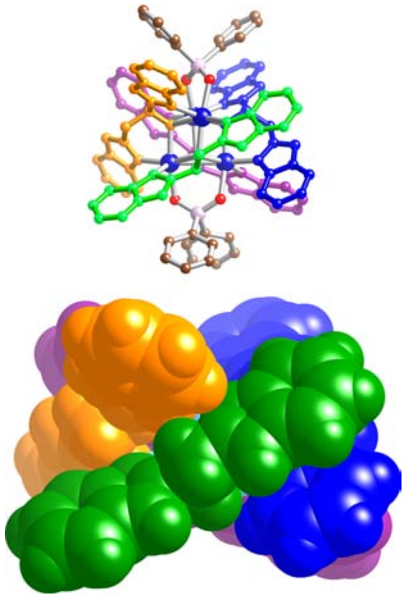


Figure 1. Structure of the cation $[Co_4[(S)\text{-}\mathbf{2}\text{-}H]_4(dpp)_2]^{2+}$. In the ball-and-stick representation (top), the four ligand strands are colored, while in the space-filling view (bottom), the dpp ligands have been removed.

and to bridge three cobalt ions. The dpp anions cap opposite faces of the cube, and the four ligands **2** are wrapped around the axis, joining the dpp anions in a quadruple helical structure. The four ligands are essentially identical and are oriented in alternating directions. They adopt a trans conformation. Inspection of a space-filling representation of the structure suggests a stacking between the phenyl groups of the dpp and the benzimidazole functions (Figure S1 in the Supporting Information, SI), implying that the dpp ligand does not merely occupy two coordination sites of the cube but also exerts a templating effect on the helix formation. The circular dichroism spectrum of the complex in a $MeOH/CH_2Cl_2$ solution is shown in Figure 2 and shows a strong structured band due to a d–d transition around 530 nm. If the enantiomeric ligand (*R*)-**2** was used, the circular dichroism was inverted, and the X-ray crystal structure showed the opposite helicity.

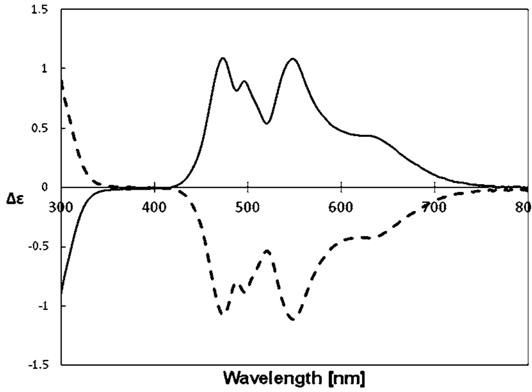


Figure 2. Circular dichroism spectra of $[Co_4[(S)\text{-}\mathbf{2}\text{-}H]_4(dpp)_2]^{2+}$ (full line) and $[Co_4[(R)\text{-}\mathbf{2}\text{-}H]_4(dpp)_2]^{2+}$ (dashed line).

If diphenylphosphinate was replaced by acetate, the complex $[Co_4[(S)\text{-}\mathbf{2}\text{-}H]_4(OAc)_2]^{2+}$ was obtained, giving crystals of composition $[Co_4[(S)\text{-}\mathbf{2}\text{-}H]_4(OAc)_2](OAc)_2(C_2H_5OH)_3(C_3H_7OH)_2$. The X-ray crystal structure (Figure 3) showed a quadruple helical structure, but the ligands now adopt a gauche conformation about the central C–C bond, giving an L-shaped appearance to the ligand. This arrangement is, however, topologically identical with that found for $[Co_4[(S)\text{-}\mathbf{2}\text{-}H]_4(dpp)_2]^{2+}$. The different conformation results in one of the benzimidazole groups being bent in toward the acetate, which would not be possible for the larger dpp anion. The conformations of the ligands are shown in Figure S2 in the SI.

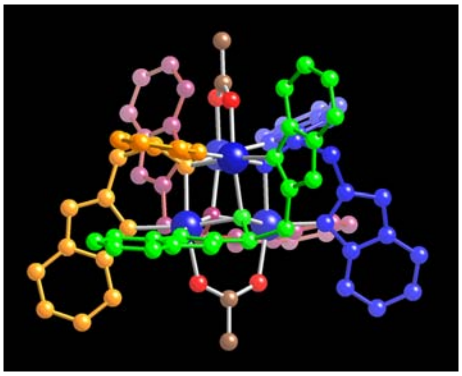


Figure 3. Structure of $[Co_4[(S)\text{-}\mathbf{2}\text{-}H]_4(OAc)_2]^{2+}$.

We investigated the stereoselectivity and kinetic inertness of these cubanes using the PIMMS method, which we presented previously.[14] Adding a methyl group at a remote position to give ligand **3** results in a ligand that is essentially identical with **2** in complexation properties but has a mass greater by 28 Da. If an equimolar mixture of (*S*)-**2** and -**3** is reacted with a stoichiometric amount of cobalt and dpp^-, the ESI-MS spectrum shows five signals corresponding to the expected complexes $[Co_4[(S)\text{-}\mathbf{2}\text{-}H]_{4-n}[(S)\text{-}\mathbf{3}\text{-}H]_n(dpp)_2]^{2+}$ ($n = 0$–4), with intensities roughly following the statistical distribution (Figure S3 in the SI). If an equimolar mixture of (*R*)-**2** and (*S*)-**3** is used, then the initial spectrum also shows all five peaks, but the intensities of $[Co_4[(R)\text{-}\mathbf{2}\text{-}H][(S)\text{-}\mathbf{3}\text{-}H]_3(dpp)_2]^{2+}$ and $[Co_4[(R)\text{-}\mathbf{2}\text{-}H]_3[(S)\text{-}\mathbf{3}\text{-}H](dpp)_2]^{2+}$ weaken (Figure S4 in the SI) and disappear completely after 3 days in solution, leaving only three peaks due to the *RRRR*, *RRSS*, and *SSSS* species. We may conclude from these experiments that there is a degree of stereoselectivity, and the relatively long period required to attain equilibrium confirms the kinetic inertness of the cubanes observed previously.[14] If the experiments are carried out using acetate instead of dpp^-, the same stereoselectivity is observed, although the spectra are somewhat complicated by overlapping signals due to the loss of acetic acid.

We were able to isolate the *RRSS* species $[Co_4[(R)\text{-}\mathbf{2}\text{-}H]_2[(S)\text{-}\mathbf{2}\text{-}H]_2(dpp)_2](ddp)_2\cdot 7MeOH$, and the structure of the cation is shown in Figure 4. In contrast to the enantiomerically pure sample, the ligands now adopt a gauche conformation. The structure may be regarded as a meso structure: if the cation is bisected perpendicularly to the helical axis, half has *P* chirality and the other half has *M* chirality. The ligand is twisted back on itself to give a V-shaped structure. We have analyzed the structures according to the method used previously[13] and find the geometrical parameters to be similar to those found for other cobalt(II) cubanes. All structures show a tetragonal distortion, but the complexes with dpp show an elongation along the helical axis with a concurrent shortening of the Co–

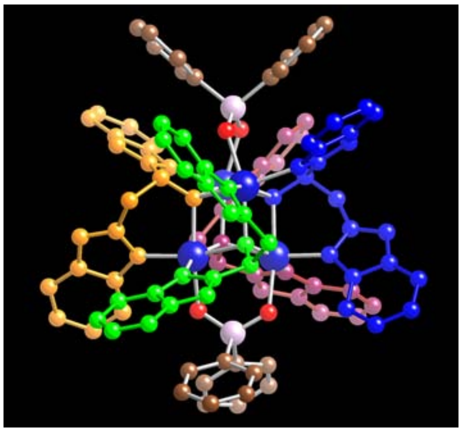


Figure 4. Structure of $[Co_4[(S)\text{-}\mathbf{2}\text{-}H]_2[(R)\text{-}\mathbf{2}\text{-}H]_2(dpp)_2]^{2+}$.

Co distance bridged by the dpp, while the only acetato-bridged complex shows a compression along the axis with an elongation of the Co−Co distances bridged by the acetate.

In conclusion, we have shown that 10 components can assemble rapidly in high yield to give a quadruple helix whose chirality is controlled by that of the ligand. The structures may be modified by the nature of the bridging ligands. There is a degree of stereoselectivity in the formation of complexes, a racemic mixture of ligands giving either enantiomerically pure helicates or a *meso*-helicate with two strands of each chirality. The slowness of ligand exchange suggests that these systems show the kinetic inertness observed for other cubane systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and full experimental details. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 868331−868334 contain the supplementary crystallographic material for this paper. These data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Swiss National Science Foundation for their support of this work. We are grateful to Dr. Sophie Michalet of the University of Geneva Mass Spectrometry Service for recording the MS spectra.

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