Metallotectons: using enantiopure tris(dipyrrinato)cobalt(III) complexes to build chiral molecular materials†

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Resolution of a tricarboxylic acid derived from a chiral tris(dipyrrinato)cobalt(III) complex provides a series of enantiopure metallotectons that crystallise as porous hydrogen-bonded networks.

Reliable supramolecular synthons,[1] such as cyclic hydrogen-bonded dimers of carboxylic acids, can be used to control the spacing and relative orientation of individual molecules in crystalline solids. This strategy has become one of the guiding principles of crystal engineering. Our group has sought to develop this method, combine it with the power of organic synthesis, and thereby create new crystalline molecular materials with predictable structures and properties.[2] In this strategy for purposeful construction, the individual molecular subunits have been called *tectons*.[3] Tectons have tended to be purely organic compounds that can engage in strong directional intermolecular interactions such as hydrogen bonds. Recently, however, we and others have begun to explore a complementary approach in which the tectons are coordination complexes of transition metals.[4–7] The unique geometries of such complexes, as well as their special catalytic, magnetic, and optoelectronic properties, expand the scope for developing useful new materials.
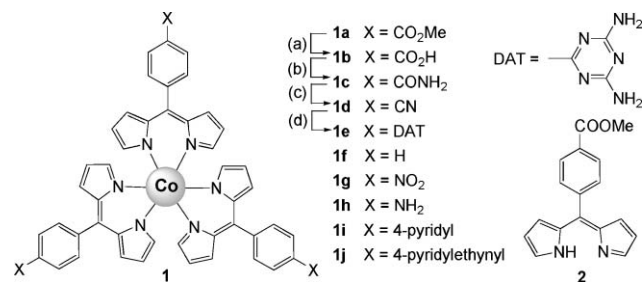
Although coordinative interactions have already been used in concert with hydrogen bonding to create crystalline hybrid inorganic–organic materials,[4–7] much of this work has involved grafting hydrogen-bonding groups onto simple ligands such as pyridines, nitriles, and carboxylic acids. Moreover, the coordinative interactions and the hydrogen bonds have frequently been formed in a single synthetic step, and discrete metallotectons have not been isolated. This approach has several drawbacks. Most notably, there is a lack of control over the coordination sphere of the metal and consequently over the ultimate structure and properties of the resulting material. Further disadvantages include (i) difficulties in identifying which factors determine the observed crystalline architecture, (ii) the need to crystallise under the same experimental conditions used in the synthesis, and (iii) the possibility that functional groups introduced to favour hydrogen bonding may coordinate to the metal instead.

To circumvent these problems, we sought to develop an alternative strategy based on robust preformed transition metal complexes decorated with substituents designed to induce the formation of hydrogen-bonded networks. Goldberg has demonstrated that metalloporphyrin-based networks can be constructed using this approach,[6] and Braga *et al.* have used substituted metallocenes in a similar way.[7]

The present report focuses on the use of tris(dipyrrinato)cobalt-(III) complexes (1) as metallotectons (Scheme 1).[8] The octahedral cobalt(III) core of these complexes is diamagnetic and kinetically inert, and the three monoanionic chelating dipyrrinato ligands are oriented in a chiral, propeller-like arrangement with D_3 symmetry. Diverse functional groups can be introduced on the periphery of these complexes, either during synthesis of the dipyrrin ligands or subsequently by reactions occurring after complexation has taken place. Such dipyrrinato complexes are attractive sources of metallotectons because they are robust enough to withstand conditions typically used in many functional group transformations, and their neutrality facilitates purification by conventional chromatography. Previously reported tris(dipyrrinato)cobalt(III) complexes include compounds **1a**, **1b**, and **1f–h**, which were reported by Dolphin *et al.*,[9] and complexes **1d** and **1i–j**, which were elegantly used by Cohen *et al.* as ligands for coordination polymers.[10,11]

The published synthesis of complex **1a** involves generating dipyrrin **2**, followed by reaction with [Co(py)$_4$Cl$_2$]Cl.[9] We modified this procedure by replacing [Co(py)$_4$Cl$_2$]Cl with commercially available Na$_3$[Co(NO$_2$)$_6$], which has been used to prepare related complexes.[11,12] As reported, triester **1a** is readily hydrolysed to give tricarboxylic acid **1b**.[9]

The presence of free carboxyl groups in chiral complex **1b** allowed us to resolve it *via* classical procedures involving the formation of diastereomeric salts with enantiomerically pure bases.

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Scheme 1 Structures of selected tris(dipyrrinato)cobalt(III) complexes and synthesis of complexes **1b–e**. Reaction conditions: (a) KOH (aq); (b) (i) oxalyl chloride, (ii) NH$_3$; (c) Tf$_2$O, pyridine; (d) dicyandiamide, KOH.

In testing various bases, we found that cinchonidine precipitated complex **1b** from THF as a crystalline salt. Optimisation of the resolution afforded the two enantiomers Δ- and Λ-**1b** in high yields and with ees of 100% (as determined by chiral HPLC). Despite the long tradition of resolving chiral organic compounds by forming diastereomeric salts, examples in which neutral transition metal complexes have been resolved by this method are rare.[13]

Resolved complexes Δ- and Λ-**1b** could be easily converted into enantiomerically pure derivatives Δ- and Λ-**1a** and **1c–e** by straightforward transformations (Scheme 1). Analysis by HPLC and circular dichroism (CD) spectroscopy (*vide infra*) indicated that no detectable racemisation occurred during these reactions.

The CD spectra of enantiopure complexes **1b**, **1d**, and **1e** in solution all displayed bisignate curves with peaks near 515 nm and 468 nm (Fig. 1). These signals presumably originate from an intra-ligand $S_0 \rightarrow S_1$ electronic transition that is polarised along the long axis of the fully conjugated dipyrrinato chromophore.[9,14] Due to the spatial proximity of the three ligands in these complexes, exciton coupling of intra-ligand transitions is possible, resulting in the appearance of a characteristic split Cotton effect ('exciton couplet').[15] The sign of this exciton couplet is directly related to the relative disposition of the dipyrrin ligands and thus to the absolute stereochemical configuration of the metal centre. This correlation allowed us to assign the Λ configuration to complexes displaying a positive peak at higher wavelengths, and the Δ configuration to those displaying a negative peak in this region. Although exciton coupling theory reliably correlates the sign of the observed couplet and the relative stereochemistry of the interacting chromophores, our stereochemical assignments are also supported by X-ray crystallography (*vide infra*),‡ and they agree with a large body of literature describing [M(bipy)₃] and [M(phen)₃] complexes (bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline) in which the polarisation of intra-ligand transitions is analogous to that of the dipyrrin ligands in complexes **1**.[16] As expected, the CD spectrum of complex Δ-**1b** mirrors that of enantiomer Λ-**1b**.

The amplitudes of the CD spectra of complexes Λ-**1b**, **1d**, and **1e** (defined as $\Delta\varepsilon_1 - \Delta\varepsilon_2$, where $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are the heights of the high- and low-energy peaks, respectively) lie in the narrow range $1025–1100~M^{-1}~cm^{-1}$. The spectral amplitudes are presumably similar because the transitions responsible for the CD signal originate in the dipyrrinato groups, and there is little electronic communication with substituents located on the periphery. This is a useful observation, because it allows an estimate of the ee of any
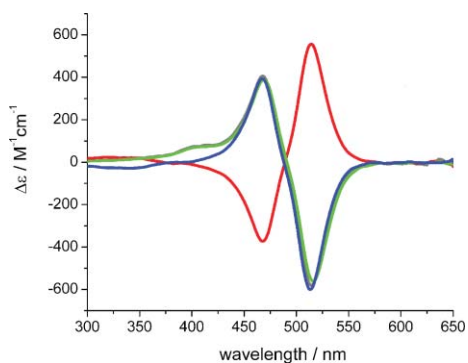
related tris(dipyrrinato)cobalt(III) complex to be made on the basis of CD spectroscopy alone, without the requirement for analysis by chiral HPLC.

Crystals of metallotecton Δ-**1b** could be grown by slowly evaporating a solution of the complex in ethyl acetate–toluene, and their structure was determined by X-ray diffraction (Fig. 2).‡ The complex was found to crystallise in the enantiomorphic space group *P*1, with two independent molecules in the unit cell. Both molecules proved to have the same absolute configuration (Δ), as anticipated by analysis of the CD spectra (*vide supra*).

The D_3-symmetric metallotecton **1b** is designed so that its three carboxyl groups extend outwards from the periphery and can freely hydrogen bond with neighbouring tectons, thereby generating a multidimensional network. In the observed structure, however, only two carboxyl groups engage directly in intertectonic hydrogen bonding, creating 1D zig-zag chains (Fig. 2b). This primary network motif is also found in the crystal structure of *rac*-**1b**.[17] The chains are then linked into a complex open 3D network by additional hydrogen bonds involving included molecules of H_2O. These additional hydrogen bonds link the third carboxyl group of each metallotecton (the one not engaged in forming the primary chains) to the oxygen atoms of two dimer-forming carboxyl groups belonging to two different chains (see the ESI for details†). Approximately 32% of the volume of the crystal is accessible to guests, as estimated by standard methods.[18] No significant continuous channels are present; instead, the available volume consists of discrete cavities occupied predominantly by toluene (three molecules per unit cell).

Supramolecular synthons involving diaminotriazine (DAT) groups are useful in crystal engineering because multiple hydrogen bonds are present. Networks held together by interactions of DAT groups have proven to be highly porous and robust,[19] thereby encouraging us to synthesise metallotecton Λ-**1e** (Scheme 1) and to determine its crystal structure. Single crystals of complex Λ-**1e** were grown by allowing MeOH to diffuse into a solution of the tecton in DMSO. The compound was found to crystallise in the space group *P*1. Two independent complexes, 3.5 molecules of H_2O, and 3.5 molecules of DMSO comprise the unit cell.

The resulting structure can be considered to be constructed from sheets in which each metallotecton is hydrogen bonded to three neighbours (Fig. 3). Each DAT group participates in four hydrogen bonds according to established motifs. A noteworthy
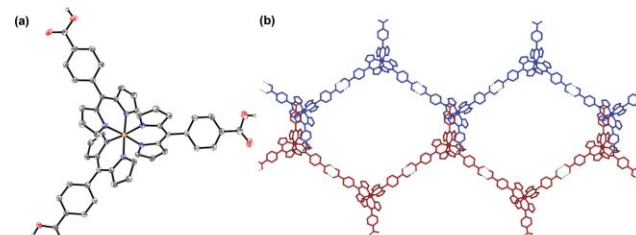

Fig. 1 CD spectra of solutions of metallotectons Δ-**1b** (grey), Λ-**1b** (red), Δ-**1d** (green), and Δ-**1e** (blue) in THF (10^{-5} M).

Fig. 2 (a) ORTEP view of the structure of one of the two crystallographically-independent molecules of metallotecton Δ-**1b**. Thermal ellipsoids are set at the 30% level. Atoms of Co appear in orange, N in blue, O in red, and C in grey. (b) Representation of 1D zig-zag chains of metallotecton Δ-**1b** linked by hydrogen bonds involving two of the three carboxyl groups of each tecton. Guest molecules and most hydrogen atoms have been omitted for clarity.
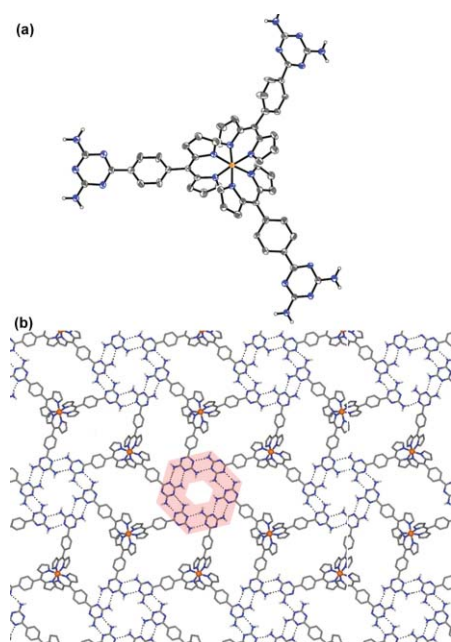
Fig. 3 (a) ORTEP view of the structure of metallotecton Λ-**1e**. Thermal ellipsoids are set at the 30% level. Atoms of Co appear in orange, N in blue, and C in grey. (b) The hydrogen-bonded network formed by compound Λ-**1e**, with the hexameric rosette of DAT groups highlighted in pink. Most H atoms and all guest molecules have been omitted for clarity.

feature of the structure is the formation of hexameric rosettes of DAT groups (Fig. 3b). Although each sheet consists of an open hydrogen-bonded network, adjacent layers are offset, and no significant channels penetrate the structure. Nevertheless, 32% of the volume is accessible to guests.[18]

Various supramolecular synthons involving DAT groups have been identified,[19] but we believe that metallotecton Λ-**1e** forms the first hexameric DAT rosette characterised by X-ray crystallography. This motif has been postulated to explain the aggregation of certain DAT-substituted compounds in liquid crystals,[20] in 2D assemblies on graphite surfaces,[21] and in reverse micelles.[22] The internal diameter of the rosettes formed by Λ-**1e** (average transannular N⋯N distance = 7.7 Å) is close to the value (7 Å) determined by analysis of STM images.[21] The crystal structure of compound Λ-**1e** gives firm support to these earlier propositions and underscores the importance of hexameric rosettes in the supramolecular chemistry of DAT groups.

We are now investigating the enantioselective inclusion of chiral guests in networks built from metallotecton Λ-**1e** and related dipyrrinato complexes, and we are exploring the utility of these compounds as ligands for the construction of chiral metal–organic frameworks.

Notes and references

‡ CCDC 643751–643752. For crystallographic data in CIF format see DOI: 10.1039/b705212j

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