

Two-Step Synthesis of Linear and Bent Dicarboxylic Acid Metalloligands with Lengths of up to Three Nanometers

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Supporting Information Placeholder

ABSTRACT: Nanometer-sized polycarboxylate ligands are interesting building blocks for metallasupramolecular chemistry, but access to these compounds is often limited by complicated synthetic pathways. Here, we describe a simple two-step protocol, which allows preparing linear and bent dicarboxylate ligands with lengths of up to three nanometers from commercially available compounds. The ligands are prepared by iron-templated polycondensation reactions involving arylboronic acids and nioxime. The final products contain two iron clathrochelate complexes, and two terminal carboxyphenylene groups. To demonstrate that the new ligands are suited for the construction of more complex molecular nanostructures, we have prepared a Cu-based metal-organic polyhedron, which represents the largest M_4L_4 cage described so far.

Introduction

The molecular basis of metallasupramolecular chemistry are interactions of metal complexes with polydentate ligands.¹ Two ligand classes have dominated the field: polypyridyl ligands, and ligands with two or more carboxylate groups. The latter are widely used for the synthesis of metal-organic frameworks (MOFs),² but they have also been employed to prepare molecularly defined macrocycles³ and cages (metal-organic polyhedra, MOPs).⁴ An advantage of polycarboxylates over polypyridyl ligands is the fact that carboxylate ligands can provide a charge compensation for the metal ions. Accordingly, it is possible to form charge-neutral assemblies and networks.

From a structural point of view, the key features of a polycarboxylate ligand are denticity (number of donor groups), geometry (orientation of the donor groups), flexibility, and size (distance between the donor groups). 'Size' matters, because it defines the spacing of the metal centers, and, accordingly, the potentially available void volume of MOFs, cages, and macrocycles. The synthesis of nanometer-sized polycarboxylates with sufficient solubility for solution-based reactions is still a challenging task. In this context, we have explored the utilization of inert clathrochelate⁵ complexes as scaffolds for the construction of polydentate metalloligands.^{6,7} We have focused on boronate ester-capped clathrochelates, because they are easily obtained in metal-

templated condensation reactions.⁵ Furthermore, the divergent side chains of these complexes prevent stacking interactions. As a consequence, the metalloligands tend to display good solubility in organic solvents.

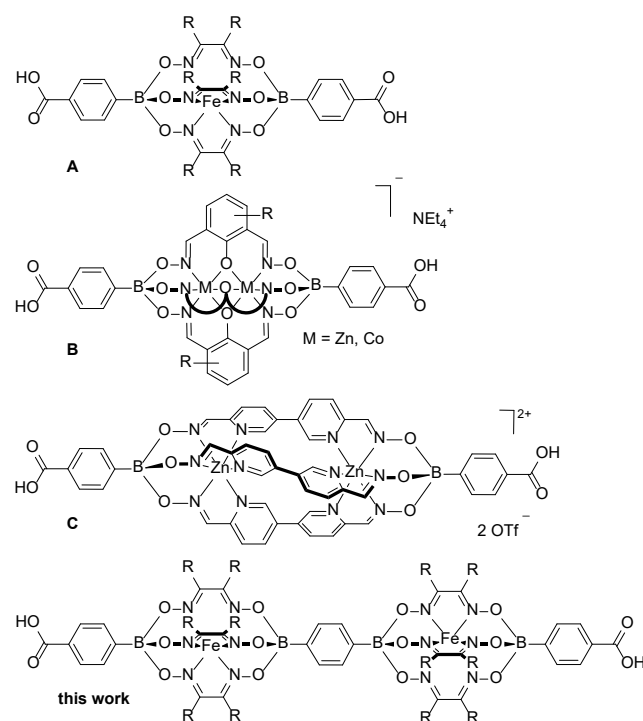


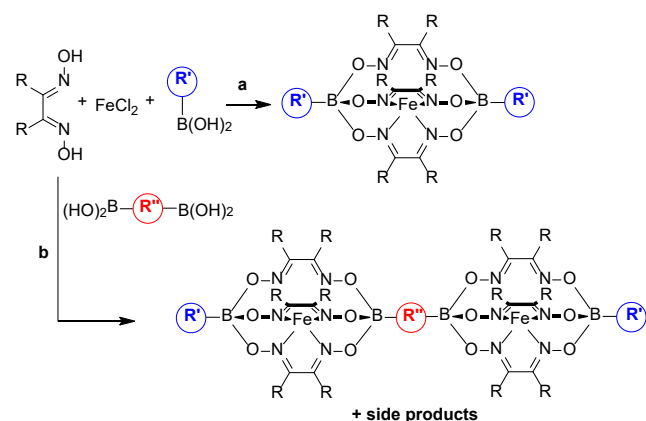
Figure 1 Examples of ditopic carboxylic acid ligands containing clathrochelate-type metal complexes.

Low spin Fe(II) complexes of type **A** (Figure 1) can be obtained by reaction of 4-carboxyphenylboronic acid with FeCl_2 and a dioxime ligand.^{8,9} By using a phenol-based dioxime, it is possible to synthesize dinuclear Zn(II) and Co(II) complexes of type **B**.⁸ Both, ligands **A** and **B**, are robust enough to be used for the synthesis of MOFs.⁸ Recently, we have reported the synthesis ligand **C**, which can be described as a capped helicate.¹⁰ The carboxylic acid groups in **C** are approximately 2.6 nm apart from each other ($\text{O}_2\text{C}\cdots\text{C}'\text{O}_2$ distance), which is substantially longer than what is found for metalloligands based on tetraphenylporphyrins (~ 1.9 nm).¹¹ However, the positive charge of **C** compromises its ability to

form charge-neutral assemblies. Below, we describe the synthesis of dicarboxylic acid ligands containing two Fe(II) clathrochelate complexes. The new ligands have donor-donor distances of up to three nanometers, and they are suited for applications in metallasupramolecular chemistry, as evidenced by the synthesis of an M_4L_4 -type MOP.

Results and Discussion

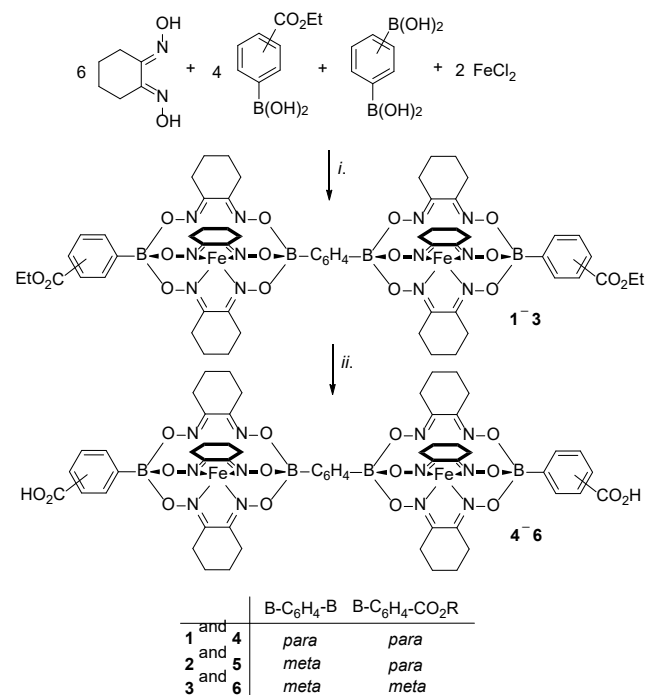
Iron clathrochelate complexes can be obtained by reaction of boronic acids with Fe(II) salts and dioxime ligands (Scheme 1a). When the reaction is performed with a mixture of a diboronic acid and a monoboronic acid, it is possible to obtain an extended dinuclear complex in a single step (Scheme 1b). We have previously used this approach to make large dipyridyl ligands.^{12,13} As expected, this multicomponent reaction is not selective, and mononuclear complexes are obtained along with higher oligomers. The formation of oligomers can be suppressed by using an excess of the monoboronic acid, but a chromatographic separation is in most cases needed to isolate the double clathrochelate complex in pure form. Size exclusion chromatography was found to be particularly useful for this purpose.^{12a}



Scheme 1. Synthesis on Single- and Double Clathrochelate Complexes.

We wanted to use the procedure outlined in Scheme 1b to make double clathrochelate complexes with terminal carboxylic acid groups. However, test reactions quickly revealed a problem: the products were only soluble in polar organic solvents, and a chromatographic separation of the product mixture was not accomplished. Therefore, we decided to use arylboronic acids featuring ester groups. Heating a mixture of nioxime (6 equiv), FeCl_2 (2 equiv), 3- or 4-ethoxycarbonylphenyl boronic acid (4 equiv, 2-fold excess), and 1,3- or 1,4-phenylenediboronic acid (1 equiv) in methanol under reflux for 12 h gave a mixture of complexes. The desired dinuclear complexes **1–3** were isolated in yields between 14 and 27% (Scheme 2). The esters were characterized by ^1H and ^{13}C NMR spectroscopy, and by high resolution mass spectrometry. In addition, the solid state structures of **1–3** were determined by single crystal X-ray diffraction (Figure 2). For the linear complex **1**, the terminal ester groups are 3 nm apart from each other ($\text{O}_2\text{C}\cdots\text{C}'\text{O}_2$ distance). Due to the presence of a *meta*-connected phenylene spacer, the complexes **2** and **3** display an overall bent geometry, with the ester groups being 2.5 nm (**2**) and 2.1 nm (**3**) apart from each other. In line with what is observed for other Fe clathrochelate

complexes,⁵ the geometry around the Fe centers can be described as distorted trigonal prismatic.



Scheme 2. Synthesis of the Double Clathrochelate Complexes 1–6. Conditions: (i) MeOH, Reflux, 12 h, 14–27% Yield; (ii) $\text{H}_2\text{O}/\text{THF}/\text{CH}_2\text{Cl}_2/\text{MeOH}$, NaOH (100 Equiv), 60 °C, 2–12 h, 62–85% Yield.

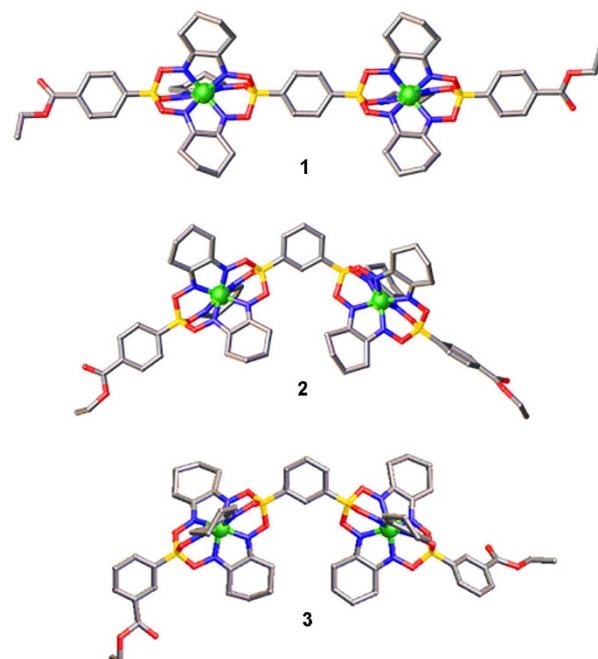


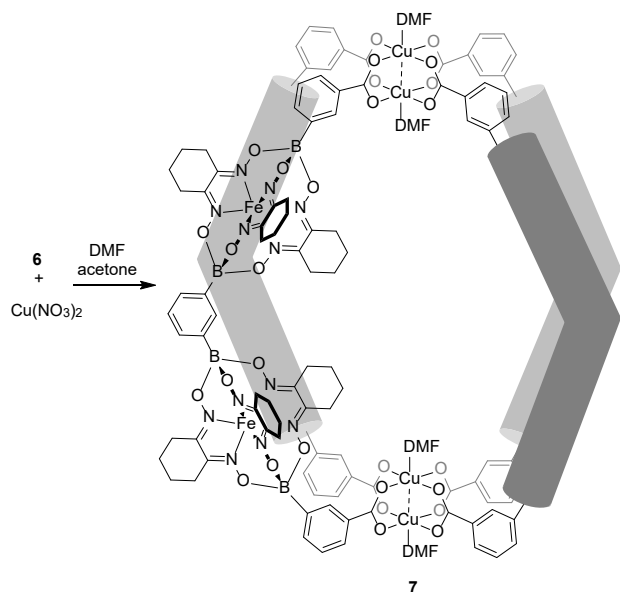
Figure 2. The molecular structures of **1, **2** and **3** in the crystal. Hydrogen atoms and solvent molecules (CH_2Cl_2) are not shown for clarity. Color coding: C: gray, B: yellow, O: red, N: blue, Fe: green.**

Saponification of **1–3** was achieved with NaOH at 60 °C using a solvent mixture of $\text{H}_2\text{O}/\text{THF}/\text{CH}_2\text{Cl}_2/\text{MeOH}$ (the

exact ratio depends on the compound, see the SI). Under these conditions, only minimal decomposition of the iron complexes was observed. The carboxylic acid ligands **4–6** can be dissolved in polar organic solvents such as DMF, DMAc and DMSO, but they are poorly soluble in MeOH or CH₂Cl₂.

In order to demonstrate that the new metalloligands are useful building blocks for the synthesis of more complex nanostructures, we have investigated the formation of an M₄L₄-type MOP. Assemblies of this general formula can be obtained by combination of bent dicarboxylate ligands with Cu(II), Mo(II), Cr(II) or Rh(II) metal precursors.¹⁴ In the resulting cages, the four ligands are connected by M₂(O₂CR)₄ paddle wheel-like complexes.

The reaction of metalloligand **6** with Cu(NO₃)₂(H₂O)₃ in DMF at room temperature resulted in the formation of a crystalline material (**7**). The very low solubility of the product hampered a solution-based characterization. However, we were able to obtain crystals of sufficient quality for an analysis by single crystal X-ray diffraction (XRD). The results showed that a Cu₄L₄-type cage had indeed formed (Scheme 3 and Figure 3).



Scheme 3. Synthesis of Coordination Cage 7.

As observed for other M₄L₄ cages, the ligands are connected via Cu₂(O₂C)₄ paddle wheel complexes. Each Cu is coordinated to one DMF molecule. The Cu...Cu distances within the two Cu₂(O₂C)₄ units of 2.618(1) Å are within the range found for other Cu(II) carboxylate complexes.¹⁶ In simple dinuclear Cu complexes such as Cu₂(OAc)₄(OH₂),¹⁷ the planes defined by the carboxylate groups cross at an angle of approximately 90°. For cage **7**, one can observe a strong deviation from the ideal square arrangement of the carboxylate ligands. This distortion is evident when the structure of **7** is viewed along the Cu...Cu axis (Figure 3c). As a consequence of the symmetry reduction at Cu, the eight Fe centers in **7** describe a rectangular- and not a square prismatic structure. One can observe pairs of clathrochelate complexes with closely interdigitated cyclohexyl side chains. The contacts between the aliphatic groups can contribute the stability of the structure via dispersion interactions and solvophobic effects.^{12a}

The overall 'height' of the cage, as defined by the maximum Cu...Cu distances, is 2.35 nm. This value is significantly larger than what is found other crystallographically characterized M₄L₄ cages, which show maximal M...M distances between 0.9 and 1.4 nm.¹⁴

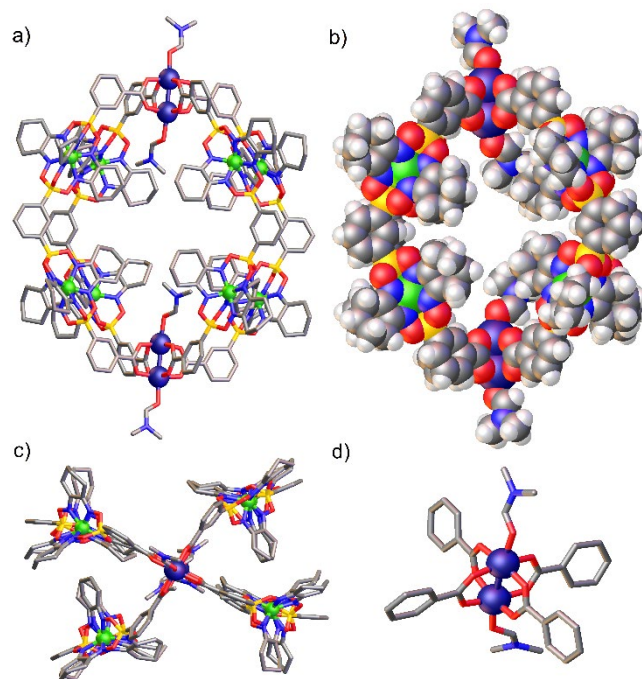


Figure 3. Different views of the molecular structure of **7** in the crystal (a–c), and close-up on one of the bridging Cu₂(O₂C)₄(DMF)₂ units (d). Hydrogen atoms are not shown for the stick representations a, c, and d. Color coding: C: gray, B: yellow, O: red, N: blue, Fe: green.

Charge-neutral MOPs can display permanent porosity in the solid state.⁴ Analysis of the void volume in crystalline **7** revealed a solvent accessible volume of >6000 Å³, which represents more than 50% of the unit cell. Most of the potential void volume is found in-between the cages, and not in the cage interior. In crystalline **7**, the accessible voids are filled with disordered solvent molecules, which have been removed by the solvent-masking program in Olex2 (for details, see SI). The large voids in crystalline **7** suggested that it might be possible to obtain a material with high porosity. However, the crystals were found to be very fragile, and rapid loss of crystallinity was observed when they were removed from the solvent. Nitrogen sorption experiments were performed after drying the solid for 8 h at 100°C under vacuum. A low porosity with an apparent BET surface area of 176 m²/g was deduced from the binding isotherm (see SI). Attempts to increase this value by solvent-exchange procedures were not successful.

Conclusions

We have developed a protocol, which allows synthesizing nanometer-sized dicarboxylate ligands in two steps from commercial starting materials. The first step of the procedure is an iron-templated condensation reaction between nioxime, a functionalized monoboronic acid, and a diboronic acid. This reaction is inherently unselective, and it gives a mixture of products. The utilization of ester-substituted monoboronic acids allowed separation of the product mixture by size exclusion chromatography. The desired carboxylate ligands

are then obtained by saponification, and we were able to find conditions, which result in minor decomposition of the iron complexes. In the present work, we describe three different metalloligands, a linear one and two bent ones, but we expect that the procedure is suited for accessing structurally related compounds when different boronic acids are employed. In order to demonstrate that these metalloligands are useful building blocks for metallasupramolecular assemblies, we have prepared a Cu₄L₄-type cage structure. This MOP represents the largest M₄L₄ cage described to date. While we have focused on a molecularly defined cage structure in the present work, we think that ligands such as 4–6 are also useful compounds for preparing MOFs and related materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>. Experimental details and Figures S1–S22.

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Notes

The authors declare no competing financial interests.

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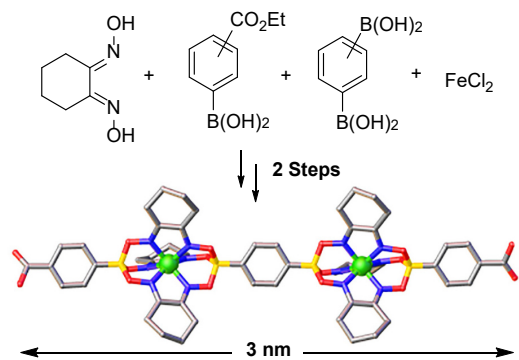
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Table of Contents



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