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Introduction

A metalloligand is a metal complex appended with functional groups capable of binding to other metal ions. Metalloligands have been used extensively in structural supramolecular chemistry. $1-3$ Compared to standard organic ligands, metalloligands have potential advantages. The internal metal ions can add novel functions such as redox-activity, color, magnetism, molecular recognition sites or catalytic activity. In addition, the metal ions can simplify the synthesis of the ligand if metal-templated reactions are employed. Metalloligands featuring two or more pyridyl groups have received particular interest. For example, metalloporphyrin ligands with terminal pyridyl groups have been used extensively for the construction of molecular and polymeric nanostructures.² Pyridyl-functionalized salen-type complexes have also found widespread applications, notably because the salen complexes can be used for catalytic reactions.³

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Surface functionalization of dinuclear clathrochelates via Pd-catalyzed cross-coupling reactions: facile synthesis of polypyridyl metalloligands†

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Dinuclear clathrochelate complexes are easily accessible by reaction of zinc(II) triflate or cobalt(II) nitrate with arylboronic acids and phenoldioximes. The utilization of brominated arylboronic acids and/or brominated phenoldioximes allows preparing clathrochelates with two, three, five or seven bromine atoms on the outside. These clathrochelates can undergo Pd-catalyzed cross-coupling reactions with 3- and 4-pyridylboronic acid to give new metalloligands featuring up to seven pyridyl groups. The pyridylcapped clathrochelates display characteristics which make them interesting building blocks for structural supramolecular chemistry: they are rigid, large (up to 2.7 nm), luminescent (for M = Zn), and anionic. The pentatopic pyridyl ligands display an unusual trigonal bipyramidal geometry. PAPER

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We have recently described the synthesis of metalloligands which feature two pyridyl groups attached to a dinuclear clathrochelate core containing either Zn^{2+} or Co^{2+} ions (Fig. 1).⁴ A special feature of these metalloligands is their negative charge, which can impart an increased stability to metallasupramolecular assemblies. Furthermore, they are very robust compounds, tolerating the rather harsh reaction conditions which are needed for the synthesis of metal–organic frameworks (MOFs). Capitalizing on the inert character of the clathrochelate, we now demonstrate that it is possible to postfunctionalize these complexes via Pd-catalyzed cross-coupling reactions. This synthetic strategy enabled us to prepare extended metalloligands containing two, three, five or seven pyridyl groups.

Fig. 1 Dinuclear clathrochelates with terminal 4-pyridyl groups.

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Results and discussion

Ditopic metalloligands

The dipyridyl ligands depicted in Fig. 1 were obtained by reaction of a Zn- or Co-salt with 4-pyridylboronic acid and a phenoldioxime.⁴ The synthesis of clathrochelates with other functional groups (e.g. carboxylic acids) in the periphery can be achieved by using different boronic acids and/or phenoldioximes.⁵ For mononuclear clathrochelates based on glyoximato ligands and $Fe(II)$ centers, it had been reported that metal-catalyzed reactions can be used for the post-functionalization of the clathrochelate skeleton.^{6,7} We were wondering if a similar strategy could be employed for the post-modification of dinuclear clathrochelates. To investigate this question, we have prepared the $Zn(\text{II})$ complex 1a and the Co(II) complex 1b having two bromine atoms in apical position following a standard protocol (Scheme 1).

The complexes 1a and 1b were then used as substrates for a Pd-catalyzed Suzuki–Miyaura cross-coupling reaction with 3- or 4-pyridylboronic acid using Buchwald's ligand SPhos.^{8,9} The reaction was found to give the desired coupling products 2a, 2b, and 3 in good to excellent yields (Scheme 1).

Subsequently, we have examined whether coupling reactions in meta position with respect to the boronate ester function are possible. We have therefore prepared clathrochelate 4 (Scheme 2) using 3-bromophenylboronic acid (yield: 67%). This complex was then subjected to the Buchwald-type coupling conditions used before. The desired dipyridyl ligand 5 could be isolated in 91% yield (Scheme 2).

The metalloligands 2a/b, 3, and 5 are well soluble in polar organic solvents such as DMSO, MeOH, acetonitrile or $CH₂Cl₂$. In line with the depicted structure, the NMR spectra of the diamagnetic Zn complexes 2a, 3, and 5 show one set of signals for the three lateral oximato ligands and one set of signals for the two terminal phenylpyridyl groups. The successful coupling of two pyridyl groups to the clathrochelates was also confirmed by high-resolution mass spectrometry. As observed for other Zn-based clathrochelates,⁴ solutions of 2a, 3, or 5 are luminescent, with an emission maximum of 445 nm (DMF, λ_{ex} = 330 nm). The excitation and the emission spectrum of a representative complex, clathrochelate 3, are shown in Fig. 2, and additional spectra are depicted in the ESI.†

The molecular structure of complex 2a in the crystal was determined by single crystal X-ray crystallography (Fig. 3). The two Zn^{2+} ions are coordinated in a trigonal prismatic fashion by three nitrogen (Zn–N_{av.} = 2.13 Å) and three oxygen atoms $(Zn-O_{av} = 2.12 \text{ Å})$. The oxygen atoms bridge the two metal ions resulting in a M…M distance of 2.971(1) Å. The terminal nitrogen atoms of the two pyridyl groups are 2.7 nm apart from each other. This metalloligand is thus substantially longer than the previously reported clathrochelate based on 4-pyridylboronic acid (1.8 nm; Fig. 1),⁴ and it is comparable in size to pyridyl-capped double clathrochelates introduced by our group $(2.7 \text{ nm})^6$ and to bis-(4'-ethynylpyridyl)-functionalized salen ligands (2.4 nm) .¹⁰

Scheme 1 Synthesis of the clathrochelates 1–3. Reagents and conditions: (i): 4-bromophenylboronic acid, $Zn(OTf)_2$ or $[Co(H_2O)_6](NO_3)_2$, MeOH, 70 °C, then NEt₄OH; (ii): 1a or 1b (1 eq.), 4-pyridylboronic acid (6 eq.), K₃PO₄ (3 eq.), Pd₂(dba)₃ (5 mol%), SPhos (10 mol%), n-BuOH/ toluene $(1:1)$, 120 °C, 12 h, then NEt₄OH; (iii): 1a $(1:1)$, 3-pyridylboronic acid (6 eq.), K_3PO_4 (3 eq.), $Pd_2(dba)_3$ (5 mol%), SPhos (10 mol%), n -BuOH/toluene (1 : 1), 120 °C, 12 h, then NEt₄OH.

Polytopic metalloligands

Next, we explored the reactivity of clathrochelates having bromo-substituents on the lateral oximato ligands. Reaction of 2,6-diformyl-4-bromophenol dioxime with zinc (n) triflate or $\cosh\left(\frac{\pi}{1}\right)$ nitrate and the respective boronic acid afforded the complexes 6–8 in good yields (Scheme 3). The clathrochelates 6 and 7 have three lateral bromo atoms, whereas complex 8 features a total of five arylbromide groups.

Scheme 2 Synthesis of the bent metalloligand 5. Reagents and con-
topic metalloligands $10a/b$ and 11 (Scheme 4). ditions: (i): 4 (1 eq.), 4-pyridylboronic acid (6 eq.), K_3PO_4 (3 eq.), Pd₂(dba)₃ (5 mol%), SPhos (10 mol%), n-BuOH/toluene (1:1), 120 °C, 12 h, then NEt_4OH .

Scheme 3 Synthesis of the polybrominated clathrochelates 6–8. Reagents and conditions: (i): 4-bromophenylboronic acid, Zn(OTf)_2 or $[Co(H₂O)₆](NO₃)₂$, MeOH, 70 °C, then NEt₄OH.

Subsequent Pd-catalyzed cross-coupling with 4-pyridylboronic acid afforded the tripyridyl ligand 9 as well as the penta-

Fig. 2 Excitation spectrum (blue curve, $\lambda_{\text{em}} = 445$ nm) and emission spectrum (red curve, λ_{ex} = 330 nm) of complex 3 in DMF (0.5 mM).

Fig. 3 Molecular structure of 2a in the crystal. Hydrogen atoms, the counterion (NEt_4^+), and solvent molecules have been omitted for clarity. Color coding: C: grey; O: red; N: blue; B: green; Zn: cyan.

10a: $M = Zn$, $Y = N$ (85%) **10b**: $M = Co, Y = N (82%)$ $NEt₄$ ⁺ O. Q Ω 11 (82%)

Scheme 4 Synthesis of the tri- and pentatopic metalloligands 9-11. Reagents and conditions: (i): 6 or 7a/b (1 eq.), 4-pyridylboronic acid (15 eq.), K₃PO₄ (7.5 eq.), Pd₂(dba)₃ (5 mol%), SPhos (10 mol%), n-BuOH/ toluene (1 : 1), 120 °C, 12 h, then NEt₄OH; (ii): 8 (1 eq.), 4-pyridylboronic acid (20 eq.), K_3PO_4 (10 eq.), $Pd_2(dba)_3$ (7.5 mol%), SPhos (15 mol%), n -BuOH/toluene (1 : 1), 120 °C, 12 h, then NEt₄OH.

The polypyridyl ligands 9–11 are well soluble in DMSO and moderately soluble in CH_2Cl_2 and acetonitrile. The solutionbased analysis by NMR spectroscopy and high resolution mass spectrometry confirmed the exhaustive replacement of the bromo atoms with 4-pyridyl groups. The luminescent properties of the Zn complexes 9, 10a, and 11 were in line with what was observed previously, with emission maxima at 445 nm (DMF, λ_{ex} = 330 nm; Fig. S33†).

Single crystal X-ray structural analyses of 10a and 11 confirmed the presence of five 4-pyridyl groups with divergent coordinate vectors (Fig. 4). The five peripheral nitrogen atoms are arranged in a distorted trigonal bipyramidal fashion. The distances between the two axial nitrogen atoms are 1.8 nm (10a) and 2.7 nm (11), and thus similar to what was found for the ditopic metalloligands described above. The average N⋯N distances for pairs of lateral pyridyl substituents are 1.7 nm (10a) and 1.7 nm (11) and the angles between the oximato ligands are 117.22°, 117.22°, and 125.57° for 10a, and 100.15°, 126.60° and 138.25° for 11. The deviations from the ideal 120° angle is likely due to packing effects in the crystal. The bond lengths and angles observed for the bimetallic core of the clathrochelates are within the expected range.

The good success of the five-fold coupling reactions with precursor 7a/b prompted us to push the synthetic concept even further. We thus synthesized clathrochelate 12 having seven bromine atoms. The complete surface functionalization of this complex was achieved under slightly more forcing coup-

Fig. 4 Molecular structures of the pentatopic metalloligands 10a (top) and 11 (bottom) in the crystal. Hydrogen atoms, counterions (NEt_4^+) , and solvent molecules have been omitted for clarity. Color coding: C: gray; O: red; N: blue; B: green; Zn: cyan.

Scheme 5 Synthesis of the heptatatopic metalloligand 13. Reagents and conditions: (i): 12 (1 eq.), 4-pyridylboronic acid (28 eq.), K_3PO_4 (14 eq.), $Pd_2(dba)_3$ (10 mol%), SPhos (20 mol%), n-BuOH/toluene (1:1), 120 °C, 12 h, then $NEt₄OH$.

ling conditions (10 mol% Pd; Scheme 5). The resulting heptapyridyl ligand 13 was characterized by NMR spectroscopy and high resolution mass spectrometry. Attempts to obtain single crystals of 13 were unfortunately not successful. In order to obtain an estimate of the dimensions of this metalloligand, we have performed an exploratory computational study of its geometry using Density Functional Theory $(DFT)^{11}$ with the PBE0 exchange–correlation functional. 12 The robustness of the method was first evaluated by comparing the XRD structure of clathrochelate 2a with the computed geometry of 2a, which

Fig. 5 Minimum-energy structure of the heptatatopic metalloligand 13 obtained by DFT/PBE0. Only the anionic clathrochelate was calculated. Hydrogen atoms have been omitted for clarity. Color coding: C: gray; O: red; N: blue; B: green; Zn: cyan.

resulted in a good match. We then calculated the minimumenergy structure of 13, and the result is shown in Fig. 5.

For clathrochelate 13, the computed average N⋯N distance for pairs of lateral pyridyl substituents is 1.7 nm, a value which is in line with the measured values for 10a and 11. The maximum N⋯N distance between opposite pyridyl groups of the terminal 3,5-(dipyridin-4-yl)phenyl moieties is 2.3 nm. These values give an idea about the size of this unusual heptatopic metalloligand.

Conclusions

We have shown that brominated clathrochelate complexes of Zn and Co can be used as substrates for Pd-catalyzed crosscoupling reactions. As nucleophilic reaction partner, we have employed 3- or 4-pyridylboronic acid. The poly-cross-coupling reactions are remarkably efficient and give the desired functionalized clathrochelates in high yields. In view of the characteristics of the new polypyridyl ligands (large, relatively rigid, anionic, and luminescent in case of $M = Zn$, we expect that they will be of interest as building blocks for supramolecular chemistry and materials science. The ditopic metalloligands 2, 3, and 5 could be used for the construction of molecularly defined nanostructures, as already demonstrated for shorter analogues.4,5,13 The polytopic metalloligands 9–11 and 13, on the other hand, appear to be more suited for the construction of polymeric structures such as metal–organic frameworks (MOFs). The penta- and heptatopic ligands 10, 11, and 13 are particularly interesting in this context, because MOFs based on ligands with five or seven donor groups have hardly been studied.^{14,15} Paper **Computer** in a good ranch. We then calculated the minimum

energy Article computed arrange in $\sqrt{2}$, α

For the present investigation, we have focused on the preparation of polypyridyl ligands. However, it appears likely that brominated clathrochelate complexes can be coupled in a similar fashion to boronic acids featuring other functional groups (e.g. cyano groups). We thus predict that brominated clathrochelates should become a versatile and easy-to-access scaffold for the synthesis of novel metalloligands with an unusual trigonal bipyramidal geometry.

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