Dinuclear clathrochelate complexes with pendent cyano groups as metalloligands†

Mathieu Marmier,a Giacomo Cecot,a Anna V. Vologzhanina,b José L. Bila,a Ivica Zivkovic,c Henrik M. Ronnow,c Balint Nafradi,c Euro Solari,a Philip Pattison,c,d Rosario Scopelliti,a and Kay Severina*

Dinuclear clathrochelate complexes with two, three, four, or five cyano groups in the ligand periphery were prepared following two distinct synthetic strategies: (a) zinc(II)- or cobalt(II)-templated polycondensation reactions of CN-functionalized arylboronic acids and phenoldioximes, or (b) postsynthetic cross-coupling reactions of polybrominated zinc(II) clathrochelates with 4-cyanophenylboronic acid. The new clathrochelate complexes were used as metalloligands for the construction of heterometallic Zn2+/Ag+ and Co2+/Ag+ coordination polymers (CPs), which were characterized by single crystal X-ray diffraction and FT-IR. A one-dimensional CP was observed for ditopic clathrochelates, whereas two- and three-dimensional CPs were generated from tetra- and pentatopic metalloligands. The three-dimensional network is unique as it displays an unprecedented network topology with the point symbol (8·102)(82·104)(82·10)(83·103). Furthermore, it is a self-catenated net with an extremely high topological density.

Introduction

Silver(I) ions tend to form labile complexes with a flexible coordination number and geometry.1 These features are attractive for the preparation of coordination polymers (CPs)2 because the reversible and malleable coordination chemistry facilitates crystallization, and thus characterization. A sizable fraction of the silver(I) CPs reported to date is based on polycyano ligands. Various ligands have been used in this context, including compounds with two,3 three,4 four,5 and more6 cyano groups. In addition to purely organic ligands, the utilization of metalloligands with cyano groups in the ligand periphery has been explored. Some selected examples are shown in Fig. 1.

The groups of Englert, Hosseini, Burrows and Mahon used homo- and heteroleptic metalloligands containing 3-cyanoacetylacetonato ligands for the construction of silver(I) CPs.7

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Fig. 1 Examples of neutral and anionic metalloligands with pendent cyano groups. The complexes were used to prepare heterometallic coordination polymers with silver(I) salts.7,8

Tritopic metalloligands were obtained with iron(III),7b aluminum(III),7c and chromium(III),7c whereas ditopic metalloligands were formed with copper(II)7b and palladium(II).7b
Carlucci and coworkers have used β-diketonate ligands with two benzonitrile groups to make hexadentate metalloligands. The complexes display an overall charge of zero or minus one, depending on the central metal ion. Very similar three-dimensional CPs were obtained with these metalloligands, despite the difference in overall charge. Notably, it was possible to perform anion exchange in single crystal to single crystal processes. Schulz and coworkers have prepared silver(I) CPs with a diamond-like topology using the tetrahedral [Al(OC₆H₄CN)₄]⁻¹ anion. Due to network interpenetration, large channels or pores were not observed.

We have recently started to explore the potential of dinuclear clathrochelate complexes as metalloligands. These complexes can be synthesized in metal-templated one-pot reactions from easily accessible starting materials. Their characteristics make them interesting building blocks for structural supramolecular chemistry: they are rigid, relatively large, luminescent (for M = Zn), and anionic. Furthermore, the metalloligands display an unusual trigonal bipyramidal geometry. So far, efforts have focused on clathrochelates with pendent pyridyl or carboxylic acid groups. Below, we show that clathrochelates can also be decorated with cyano groups. Following two distinct synthetic strategies, we were able to prepare clathrochelates containing two, three, four, or five cyano groups which are oriented in a divergent fashion. The utility of these new metalloligands is demonstrated by the synthesis of one-, two-, and three-dimensional coordination polymers, in which the clathrochelates are linked by Ag⁺ ions.

Results and discussion

Direct synthesis of CN-functionalized clathrochelates

Dinuclear clathrochelate complexes with boronate capping groups are generally prepared by polycondensation of a boronic acid with a phenolatoxime in the presence of a divalent metal ion (Mn⁺⁺, Zn⁺⁺, or Co⁺⁺). In order to introduce cyano groups in apical position, we have performed a similar condensation reaction using commercially available 4-cyanophenylboronic acid in combination with 2,6-diformyl-4-tert-butylphenol dioxime (L1). As metal salts, we have employed either [Co(H₂O)₆](NO₃)₂ or Zn(OTf)₂. The reactions proceeded in a clean fashion, and the desired clathrochelates 1 and 2 could be isolated in high yield following addition of tetraethylammonium hydroxide (Scheme 1). Both complexes were analyzed by Fourier-transform infrared spectroscopy (FT-IR) and high-resolution mass spectrometry. The diamagnetic zinc complex 1 was also analyzed by NMR spectroscopy (DMSO-d₆). Only one set of signals for the protons of the phenolatodioximato ligand were observed, corroborating the expected pseudo-C₃ symmetry of the complex. The FT-IR spectra showed a characteristic band at 2220 cm⁻¹, which can be assigned to the absorption frequency of the cyano groups. In line with earlier observations, complex 1 was found to be luminescent with an emission maximum at 445 nm (DMF, λₑₓ = 335 nm, Fig. S15†).

Previously, we had investigated the magnetism of dinuclear Co clathrochelates with pendent carboxylic acid groups using the Evans method. The data suggested that the Co(II) centers have a high spin configuration. For complex 2, we have now performed a more detailed analysis using a superconducting quantum interference device (SQUID) magnetometer. A plot of the magnetic susceptibility vs. temperature reveals an increase of susceptibility as temperature decreases and a broad maximum around 87 K below which a significant decrease of the susceptibility occurs (Fig. 2).

Given that the pair of cobalt ions are well separated from other magnetic ions, the inter-cluster interaction can be neglected and the Hamiltonian of the system can be written simply as $H = -J S_1 S_2$, where $S_1$ and $S_2$ are spins of two cobalt ions that form a pair and $J$ is the intra-cluster exchange interaction. The room temperature value of the effective moment per Co ion reaches 5.0$μ_B$, close to the theoretically maximum value for a high-spin cobalt(II) state with $L = 3$ orbital momentum included. The data has been analyzed using MagSaki software which takes into account the magnetic exchange

![Fig. 2](image-url)
coupling $J$, spin-orbit coupling $\lambda$, an orbital reduction factor $\kappa$ and the axial-splitting parameter $\Delta$. Very good agreement with measured data has been achieved with $J = -20(3) \text{ cm}^{-1}$, $\lambda = -110(10) \text{ cm}^{-1}$, $\kappa = 1(0.1)$ and $\Delta = 286(30)$ (see red line in Fig. 2, left). These parameters correspond to significant $g$-factor anisotropy, $g_x = 4.9(0.3)$ and $g_z = 3.0(0.3)$, which is in agreement with preliminary ESR measurements. These values are similar to those reported for other di-nuclear Co-based compounds with much larger intra-cluster magnetic interaction.\textsuperscript{14}

In order to prepare clathrochelates with cyano groups in lateral position, we have prepared the phenoldioxime ligand $L_2$. The synthesis of this ligand was accomplished by Pd-catalyzed cross-coupling of 4-cyanophenylboronic acid and 2,6-diformyl-4-bromophenol in presence of SPhos and Pd$_2$(dba)$_3$,\textsuperscript{15} followed by treatment of the crude dialdehyde with hydroxylamine hydrochloride (Scheme 2).

The tri- and pentatopic clathrochelates 3–5 were then obtained by using $L_2$ in combination of either 4-bromophenylboronic acid or 4-cyanophenylboronic following the standard protocol (Scheme 3). To the best of our knowledge, complexes 4 and 5 represent first examples of polycyano ligands with trigonal bipyramidal geometry. Zn-based clathrochelates 3 and 4 are luminescent, with emission maxima at 450 nm (DMF, $\lambda_{ex} = 335$ nm, Fig. S15†). Their emissions are thus slightly red-shifted compared to what was observed for 1. The analytical data for 3–5 are in line with the expected structures. The magnetic properties of 5 were expected to be similar to what was found for 2 and additional SQUID measurements were not performed.

**Synthesis of CN-functionalized clathrochelates by postsynthetic cross-coupling reactions**

Recently, we have shown that brominated clathrochelate complexes of Zn$^{2+}$ and Co$^{2+}$ are sufficiently stable to be used as substrates in Pd-catalyzed cross-coupling reactions, allowing the preparation of elongated polypyridyl ligands.\textsuperscript{9} We anticipated that a similar strategy could be used to prepare clathrochelate complexes with pendent benzonitrile groups. Indeed, the two-fold coupling of the previously described clathrochelate 6 featuring 3-bromophenylboronate ester caps\textsuperscript{30} with 4-cyanophenylboronic acid gave the desired complex 7 in 91% yield (Scheme 4). With regard to potential applications, it is worth noting that ditopic cyanoliogands with a bent shape have been used extensively for the preparation of silver(i)
Compared to the ligands used previously, clathrochelate 7 stands out because of its size and its negative charge. Attempts to prepare a linear dicyano ligand by cross-coupling of a clathrochelate with terminal 4-bromophenylboronate ester groups were unfortunately not successful. Even though we were able to detect the desired product by mass spectrometry, we were not able to achieve a complete reaction, and separation of the side products was found to be difficult. This result indicates that coupling reactions in para position to the boronate ester function are more problematic.

To further test the scope of the cross-coupling procedure, we prepared the tetrabrominated clathrochelate complex 8 using 3,5-dibromophenylboronic acid and dioxime L1. The subsequent four-fold coupling with 4-cyanophenylboronic acid in the presence of Pd2(dbA)3 and SPhos was remarkably clean, providing the tetratopic complex 9 in 89% yield (Scheme 5).

The elongated clathrochelates 7 and 9 are soluble in polar organic solvents such as DMSO, nitromethane and DMF, and the analytical data match the proposed structures. Both complexes are luminescent, with an emission maximum at 445 nm (DMF, λex = 335 nm, Fig. S16†).

Coordination polymers with silver(I)

After having established efficient protocols for the synthesis of CN-functionalized clathrochelate complexes, we started to explore their utilization as metalloligands in CPs. As outlined in the introduction, polycyano ligands are particularly suited for the preparation of silver(I) CPs, and we thus focused on reactions with Ag⁺ salts. For some clathrochelate complexes, we were able to obtain crystalline CPs upon reaction with silver salts, and the results are detailed below.

Single crystals of the CPs 10 and 11 were obtained by layering a solution of AgNO₃ in MeOH on top of a solution of 1 or 2 in nitromethane (Scheme 6). Crystallographic analyses revealed that both CPs are isostructural compounds having stoichiometry \([\text{AgL]}(\text{CH₃OH})\text{AgL}(\text{CH₃OH})\text{AgL}(\text{CH₃NO₂})\) for 10 and \([\text{AgL₂]}(\text{CH₃OH})\text{AgL}_2(\text{CH₃NO₂})\) for 11. The terminal cyano groups coordinate to the Ag⁺ ions in a slightly bent fashion (N–Ag–N = 154° and 155°) forming an infinite chain. The Ag⁺ ions display a trigonal pyramidal geometry, with one of the coordination sites being occupied by a methanol ligand. The fourth coordination site is occupied by the oxygen atom of an adjacent boronate ester group. It should be noted that coordination of a metal ion to the oxygen atom of clathrochelate complexes has not been observed before. As a result of this cross-linking, we observe an unusual double chain architecture (Fig. 3). A summary of the bond distances of the connecting silver complexes is given in Table 1.

The structures of 10 and 11 do not contain nitrate anions from the silver salt because the charge compensation is
achieved by the metalloligand itself. It should be noted that for previously reported silver(I) CPs, the anion derived from the silver salt was often found to influence the final structure.\textsuperscript{3,4,5,6}

We were also successful in preparing a CP using the tetra-topic metalloligand \textsuperscript{9}. Layering a solution of AgOTs in MeOH on top of a solution of \textsuperscript{9} in nitromethane led to the formation of transparent, plate-like crystals of coordination polymer \textsuperscript{12} (Scheme 7).

Single crystal X-ray analysis of \textsuperscript{12} revealed the formation of a two-dimensional network structure with the stoichiometry [Ag\textsubscript{2}(\textsuperscript{9})\textsubscript{2}](CH\textsubscript{3}OH)\textsubscript{1.5}(CH\textsubscript{3}NO\textsubscript{2})\textsubscript{3}. A graphical representation of the structure is depicted in Fig. 4. One can observe two distinct clathrochelate metalloligands in the structure. The first one is coordinated \textit{via} all of its cyano groups to silver ions Ag(1) and Ag(2), thereby forming an infinite double chain. The second clathrochelate is coordinated \textit{via} only one of the four cyano groups to silver ions Ag(2). The latter display a trigonal pyramidal geometry (Ag(2)–N\textsubscript{Av.} = 2.281 Å), with the fourth coordination site being occupied by the oxygen atom of a boronate ester group from an adjacent clathrochelate (Ag(2)–O = 2.587(6) Å). The Ag(1) ions display approximate trigonal planar geometry, with coordination of Ag(1) to two cyano groups (Ag(1)–N\textsubscript{Av.} = 2.173 Å) and one oxygen atom of a boronate ester (Ag(1)–O = 2.390(5) Å). The Ag–O–B linkages connect the double chains, resulting in an overall two-dimensional 3,6-coordinated network structure, where silver atoms act as three-connected nodes and clathrochelates as six-connected nodes (through four cyano and two boronate groups). The underlying net of this CP has the \textit{kgd} topology (kagome dual, given in terms of the RCSR notation;\textsuperscript{17} see ESI, Fig. S19) which is the most widespread topology for 3,6-coordinated two-dimensional CPs.\textsuperscript{18} As it was observed for CP \textsuperscript{10} and \textsuperscript{11}, the charge compensation is achieved by the metalloligands, and tosylate anions from the silver salt are not found in the structure.

Silver(I) CPs based on pentacyano ligands with a trigonal bipyramidal geometry are – to the best of our knowledge – not known. We were thus particularly interested to obtain CPs with the pentatopic metalloligands \textsuperscript{4} and \textsuperscript{5}. After several attempts, we were able to crystallize CP \textsuperscript{13} using metalloligand \textsuperscript{5} in combination with AgClO\textsubscript{4} in the presence of MeOH, DMF and 1,2-dichlorobenzene as solvents (Scheme 8). Single crystal X-ray analysis of \textsuperscript{13} showed that a three-dimensional network with the stoichiometry [Ag\textsubscript{3}(\textsuperscript{5})\textsubscript{2}(OMe)][C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2}][MeOH][sol.]\textsubscript{n} had formed (Fig. 5). The asymmetric unit of the crystal contains three silver ions and two clathrochelate complexes \textsuperscript{5}. Although the ratio of Ag to \textsuperscript{5} is equal to 3 : 2, the overall network is neutral due to presence of disordered methoxy groups which are coordinated to Ag(2) ions. Besides, the Ag(2)
ions act as linkers between two cobalt-containing metallo-
ligands (Ag(2)–Nav. = 2.119 Å). The Ag(1) and Ag(3) ions, on the
other hand, are coordinated in a trigonal planar fashion to
three cyano groups, with Ag(1)–N distances varying from
2.11(2) to 2.30(2) Å. Both metalloigands act as four-connected
nodes through both of the apical and two of the three lateral
cyano groups (one cyan group is ‘free’). The first crystallo-
graphically independent metalloilgand coordinates to one Ag(2)
and three Ag(1) ions, and the second one to one Ag(2) and
three Ag(3) ions. As a result, the Ag(2) ions links two inter-
penetrating CPs of the stoichiometry [Ag(3)] and the utp
topology (widespread among 3-coordinated CP nets)19 to form
a three-dimensional net.

A topological analysis of the resulting architecture by
means of the ToposPro package20 revealed that the net has a
point symbol (8·10^2)(8·10^3)(8·10^4)(8·10^5). To the best of our
knowledge, such a network topology has not been observed in
crystals before. The structure was deposited to the Topos TTD
collection under the abbreviation epf1.

An intriguing structural feature of 13 is that all eight- and
ten-membered circuits of the nodes are crossed by other rings,
resulting in self-catenation (Fig. S20 and S21†). Self-catenated
structures are single networks with regions in which chains
from the same net pass through the smallest topological
circuits in a fashion similar to that of interpenetrated systems.
The observation of self-catenation in 13 is unusual because
most of reported self-catenated nets are constructed from
flexible ligands.21 The catenation in 13 is very dense from a
topological point of view: the eight-membered rings are
crossed by at least 57 other rings. The topological density of
the net can be given as TD10 = 3127, which is the number of
nodes within the first 10 coordination spheres of a given node.
According to the RCSR database,27 this value represents the
highest topological density among all known 3,3,4,4-co-
ordinated nets, and is almost as high as TD10 = 3245 for a
recently published 3,4-coordinated mhq-z net.22 Despite the
high topological density, CP 13 displays a very large solvent-
accessible volume of 53% according to calculations with
Mercury.23 These voids are occupied by highly disordered
solvent molecules, some of which could not be located from
difference Fourier maps. The attempted desolvation of CP 13
resulted in rapid degradation of the material.

Conclusions

We have shown that dinuclear clathrochelate complexes with a
trigonal bipyramidal shape can be decorated with cyano
groups in apical and/or lateral position by using cyano-
functionalized starting materials for the clathrochelate syn-
thesis. Alternatively, we have been able to prepare elongated
clathrochelates with pendent benzonitrile groups by post-syn-
thetic modification of brominated clathrochelates in Pd-
catalyzed cross-coupling reactions. The functionalized clathro-
chelates can be used as metalloligands for the preparation of
heterometallic Co2+/Ag+ and Zn2+/Ag+ coordination polymers,
as evidenced by the synthesis of one-, two-, and three-dimen-
sional CPs in reactions with silver salts. Due to the negative
charge of the metalloilgands, the CPs are devoid of anions
derived from the silver salt. A structure-directing role of the
anion, as observed for many silver(i) CPs, is thereby avoided.
The three-dimensional CP 13 is of special interest because it
displays an unprecedented network topology and a very high
topological density.

Potential applications of the CN-functionalized clathro-
chelate complexes described above are not restricted to the
formation of polymeric networks. Polycyanoligands have also
been employed for the constructions of molecularly defined
nanostructures using coordination-based self-assembly,24 and
our new metalloligands should be useful building blocks in
this context as well.

Experimental section

Materials and general procedures

Clathrochelate 6 and 2,6-diformyl-4-tert-butylphenol dioxime
ligand (L1) were synthetized according to literature.10,11
1H and 13C NMR spectra were obtained on a Bruker Avance III
(1H: 400 MHz, 13C: 100 MHz). 1H and 13C chemical shifts are
reported in parts per million δ (ppm) referenced to the
internal solvent. All spectra were recorded at RT. Electrospray-
ionisation MS data were acquired on a Q-Tof Ultima mass
spectrometer (Waters) operated in the negative ionization
mode and data were processed using the MassLynx
4.1 software. APPI-FT-ICR experiments were performed on a hybrid linear ion trap Fourier transform ion cyclotron resonance mass spectrometer (LTQ FT-ICR MS, Thermo Scientific, Bremen, Germany) equipped with a 10 T superconducting magnet (Oxford Instruments Nanoscience, Abingdon, UK). Data analysis was carried out using XCalibur software (Thermo Scientific, Bremen, Germany). IR spectra were recorded on a Perkin Elmer Spectrum One Golden Gate FTIR spectrometer. Emission spectra were recorded with a Varian Cary Eclipse spectrophotometer. Magnetization and magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL 5 T superconducting quantum interference device (SQUID) magnetometer. The powder samples were contained in plastic capsules which were incorporated into two plastic straws as sample holder. The measurements were collected as a function of the applied field of 1 T and temperatures ranging from 5 to 350 K with Zero Field Cooled method (ZFC).

**Ligand L2.** Under inert atmosphere, 2,6-diformyl-4-bromo-phenol (600 mg, 2.62 mmol, 1.0 equiv.), 4-cyanophenylboronic acid (3.06 g, 20.83 mmol, 8.0 equiv.) and K3PO4 (2.23 g, 10.48 mmol, 4.0 equiv.) were suspended in degassed n-BuOH (250 ml). SPhos (54 mg, 0.13 mmol, 0.05 equiv.) and Pd(dba)3 (60 mg, 0.06 mmol, 0.025 equiv.) were added, and the mixture was stirred at 70 °C for 20 min. After a second addition of tetraethylammonium hydroxide (118 mg, 0.216 mmol, 77%) the solution was heated at 85 °C for 30 min. NH2OH·HCl (141 mg, 0.211 mmol, 25% in MeOH) was added and the yellow precipitate that formed was filtered, washed with n-BuOH (2 × 60 ml) and dried under vacuum. The yellow powder was then dissolved in H2O (200 ml) and the resulting solution was heated at 85 °C for 30 min. NH4OH-HCl (728 mg, 10.48 mmol, 4.0 equiv.) was added and the white suspension was heated at 85 °C. After cooling down to RT, the suspended product was isolated by filtration, washed with H2O (2 × 100 ml) and dried under vacuum to afford the dioxime L2 as an off-white powder (510 mg, 1.81 mmol, 69%).1H-NMR (400 MHz, DMSO-d6): δ = 11.64 (s, 2H), 11.04 (s, 1H), 8.44 (s, 2H), 7.93 (s, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H).13C-NMR (101 MHz, DMSO-d6): δ = 154.88, 146.79, 143.53, 132.93, 129.78, 127.28, 126.97, 119.78, 118.91, 109.65. HRMS-ESI: Calcd for C50H47B2Co2N8O9: 1043.2332; found: 1043.2307. IR: 2985, 2225, 1600, 1545, 1445, 1395, 1365, 1330, 1285, 1205, 1150, 980, 785, 775, 690, 635, 625, 565, 535 cm⁻1.

**Clathrochelate 2.** A mixture of 2,6-diformyl-4-tert-butylphenol dioxime (200 mg, 0.846 mmol, 3.0 equiv.), 4-cyanophenylboronic acid (83 mg, 0.564 mmol, 2.0 equiv.) and [Co(H2O)6][NO3]2 (164 mg, 0.564 mmol, 2.0 equiv.) in a mixture of MeOH (30 ml) and EtOH (30 ml) was heated to 70 °C until all solids had dissolved. Tetraethylammonium hydroxide (282 µl, 0.423 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 20 min. After a second addition of tetraethylammonium hydroxide (282 µl, 0.423 mmol, 25% in MeOH), the solution was cooled down to RT, and was concentrated to 5 ml. The orange precipitate was isolated by filtration, washed with EtOH (3 × 8 ml) and Et2O (2 × 50 ml) and dried under vacuum to afford 2 as an orange powder (254 mg, 0.216 mmol, 77%). HRMS-ESI: Calcd for C50H47B2Co2N8O9: 1043.2332; found: 1043.2307. IR: 2985, 2225, 1600, 1545, 1450, 1395, 1365, 1330, 1285, 1225, 1085, 1040, 1020, 995, 930, 875, 785, 775, 690, 635, 625, 565, 535 cm⁻1.

**Clathrochelate 3.** A mixture of dioxime L2 (100 mg, 0.355 mmol, 3.0 equiv.), 4-bromophenylboronic acid (47.6 mg, 0.237 mmol, 2.0 equiv.) and Zn(OTf)2 (86.2 mg, 0.237 mmol, 2.0 equiv.) in MeOH (40 ml) was heated to 70 °C until all solids had dissolved. Tetraethylammonium hydroxide (118 µl, 0.178 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 1 h. After a second addition of tetraethylammonium hydroxide (118 µl, 0.178 mmol, 25% in MeOH), the solution was cooled down to RT, and the solvent was removed under reduced pressure. The yellow precipitate was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (3 × 10 ml) and Et2O (2 × 50 ml) and dried under vacuum to afford 3 as a yellow powder (125 mg, 0.088 mmol, 74%).1H-NMR (400 MHz, DMSO-d6): δ = 8.51 (s, 6H), 7.91–7.85 (m, 12H), 7.82 (d, J = 8.3 Hz, 6H), 7.62 (d, J = 7.9 Hz, 4H), 7.43 (d, J = 7.8 Hz, 4H), 3.19 (q, J = 7.3 Hz, 8H), 1.15 (tt, J = 7.0, 2.9 Hz, 12H).13C-NMR (101 MHz, DMSO-d6): δ = 164.83, 154.07, 143.33, 134.05, 133.94, 132.79, 129.31, 126.03, 124.81, 119.81, 119.53, 119.05, 108.62, 51.37, 37.04. (C–B not detected). HRMS-ESI: Calcd for C57H38B2Br2N3O5Zn2: 1297.9440; found: 1297.9434. IR: 2985, 2225, 1600, 1545, 1445, 1340, 1305, 1200, 1180, 1080, 1040, 975, 930, 905, 840, 820, 795, 770, 735, 705, 680, 615, 545, 535 cm⁻1.

**Clathrochelate 4.** A mixture of dioxime L2 (100 mg, 0.355 mmol, 3.0 equiv.), 4-cyanophenylboronic acid (35 mg, 0.237 mmol, 2.0 equiv.) and Zn(OTf)2 (86.2 mg, 0.237 mmol, 2.0 equiv.) in MeOH (40 ml) was heated to 70 °C until all solids had dissolved. Tetraethylammonium hydroxide (118 µl, 0.178 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 1 h. After a second addition of tetraethylammonium hydroxide (118 µl, 0.178 mmol, 25% in MeOH),...
the solution was cooled down to RT, and the solvent was removed under reduced pressure. The yellow precipitate was suspended in EtOH (3 × 8 ml) and Et2O (2 × 50 ml) and dried under vacuum to afford 4 as a yellow powder (106 mg, 0.08 mmol, 68%).

1H-NMR (400 MHz, DMSO-d6): δ = 8.54 (s, 6H), 7.92–7.78 (m, 22H), 7.69 (d, J = 7.6 Hz, 4H), 3.19 (q, J = 7.2 Hz, 8H), 1.15 (t, J = 6.7 Hz, 12H).

13C-NMR (101 MHz, DMSO-d6): δ = 164.89, 154.38, 143.33, 134.14, 132.85, 132.56, 131.50, 129.74, 119.87, 119.51, 119.10, 108.90, 108.70, 51.41, 7.08 (C-B not detected).

HRMS-ESI: Calcd for C36H33B2N11O9Zn2: 1192.1139; found: 1192.1090. IR: 2985, 2220, 1600, 1555, 1545, 1480, 1445, 1390, 1305, 1245, 1205, 1180, 1075, 1035, 1020, 975, 930, 910, 830, 795, 775, 735, 690, 645, 615, 560, 545, 530 cm⁻¹.

**Clathrochelate 5.** A mixture of dioxime L2 (120 mg, 0.426 mmol, 3.0 equiv.), 4-cyanophenylboronic acid (42 mg, 0.284 mmol, 2.0 equiv.) and [Co(H2O)6](NO3)2 (82 mg, 0.284 mmol, 2.0 equiv.) in MeOH (40 ml) was heated to 70 °C until all solids had dissolved.

Tetraethylammonium hydroxide (142 μl, 0.213 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 1 h. After a second addition of tetraethylammonium hydroxide (142 μl, 0.213 mmol, 25% in MeOH), the solution was cooled down to RT, and the solvent was removed under reduced pressure. The orange precipitate was suspended in EtOH (10 ml), isolated by filtration, washed with EtOH (3 × 12 ml) and Et2O (2 × 50 ml) and dried under vacuum to afford 5 as an orange powder (150 mg, 0.114 mmol, 81%).

HRMS-ESI: Caled for C59H32B2N11O9Zn2: 1192.1139; found: 1192.1090. IR: 2985, 2220, 1600, 1555, 1545, 1480, 1445, 1390, 1305, 1245, 1205, 1180, 1075, 1035, 1020, 975, 930, 910, 830, 795, 775, 735, 690, 645, 615, 560, 545, 530 cm⁻¹.

**Clathrochelate 6.** A mixture of dioxime L2 (120 mg, 0.426 mmol, 3.0 equiv.), 4-cyanophenylboronic acid (91 mg, 0.62 mmol, 8 equiv.) and K2PO4 (66 mg, 0.31 mmol, 4.0 equiv.). Pd2(dba)3 (5.4 mg, 3.9 μmol, 0.05 equiv.) and SPhos (3.2 mg, 7.7 μmol, 0.1 equiv.) were then added, and the system was cycled two times with nitrogen. The sealed vial was then heated for 12 h at 90 °C. After cooling to RT, the reaction mixture was filtered through Celite, and washed with n-BuOH (10 ml) and degassed toluene (10 ml) were then added to a 25 ml pyrex vial containing 6 (100 mg, 0.62 mmol, 1.0 equiv.). 4-cyanophenylboronic acid (202 mg, 1.37 mmol, 20 equiv.) and K2PO4 (146 mg, 0.667 mmol, 10 equiv.). Pd2(dba)3 (6.4 μg, 6.9 μmol, 0.1 equiv.) and SPhos (5.7 mg, 13.8 μmol, 0.2 equiv.) were then added, and the system was scaled up two times with nitrogen. The sealed vial was then heated for 12 h at 90 °C. After cooling to RT, the reaction mixture was filtered through Celite, and washed with n-BuOH (5 ml), acetone (20 ml) and H2O (200 ml).

The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H2O (2 × 50 ml) and Et2O (100 ml), and dried under vacuum to afford 9 as a yellow powder (87 mg, 70 μmol, 89%).

1H-NMR (400 MHz, DMSO-d6): δ = 8.44 (s, 6H), 8.07 (s, 4H), 8.04 (d, J = 8.1 Hz, 8H), 7.97 (d, J = 8.1 Hz, 8H), 7.90 (s, 2H), 7.34 (s, 6H), 3.18 (q, J = 7.2 Hz, 8H), 1.22 (s, 27H), 1.14 (t, J = 7.0 Hz, 12H).

13C-NMR (101 MHz, DMSO-d6): δ = 162.48, 154.24, 154.83, 137.41, 137.02, 132.76, 132.27, 131.08, 128.05, 127.80, 119.03, 118.29, 109.62, 51.36, 33.41, 31.15, 7.04 (C-B not detected).

References


