Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2016, **45**, 15507

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 Severin*[a]

Received 12th July 2016,
Accepted 25th August 2016

DOI: 10.1039/c6dt02758j

www.rsc.org/dalton

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 Zn^{2+}/Ag^{+} and Co^{2+}/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 $(8{\cdot}10^2)(8^2{\cdot}10^4)(8^2{\cdot}10)(8^3{\cdot}10^3)$. 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 more[6] 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]

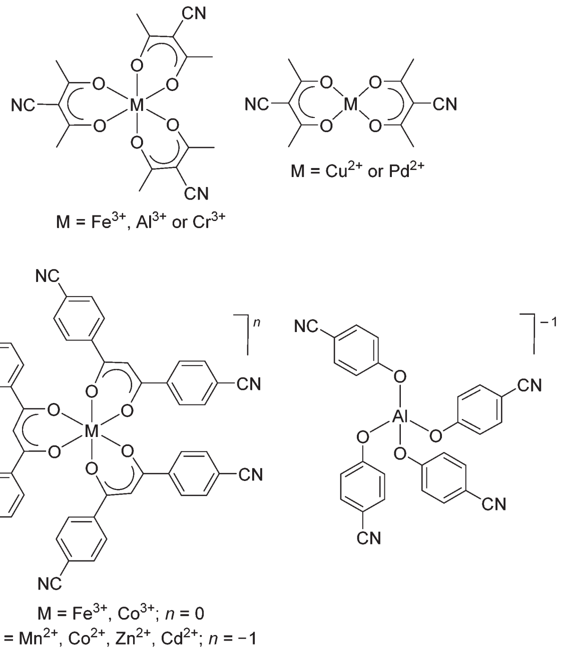


Fig. 1 Examples of neutral and anionic metalloligands with pendent cyanogroups. The complexes were used to prepare heterometallic coordination polymers with silver(I) salts.[7,8]

Tritopic metalloligands were obtained with iron(III),[7h] aluminum(III),[7c] and chromium(III),[7g] whereas ditopic metalloligands were formed with copper(II)[7h] and palladium(II).[7b]

---

[a] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland. E-mail: kay.severin@epfl.ch; Fax: (+41) 21-693-9305

[b] Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, 119991 Moscow, Russia

[c] Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

[d] Swiss-Norwegian Beam Lines at ESRF, 6 rue Jules Horowitz, 38043 Grenoble Cedex, France

† Electronic supplementary information (ESI) available. CCDC 1481126–1481129. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt02758j

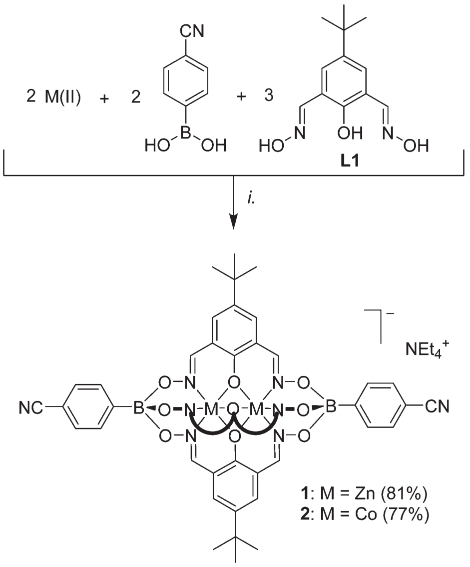
Carlucci and coworkers have used β-diketonate ligands with two benzonitrile groups to make hexadentate metalloligands. The complexes display an overall charge of zero or minus one, depending on the central metal ion. Very similar three-dimensional CPs were obtained with these metalloligands, despite 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 $[Al(OC_6H_4CN)_4]^{-1}$ anion.[8] 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.[9,10] 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[9] or carboxylic acid groups.[10] 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 clathrochelate ligands are linked by Ag^+ ions.

Results and discussion

Direct synthesis of CN-functionalized clathrochelates

Dinuclear clathrochelate complexes with boronate ester capping groups are generally prepared by polycondensation of a boronic acid with a phenoldioxime in the presence of a divalent metal ion (Mn^{2+}, Zn^{2+}, or Co^{2+}).[9–12] 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 $[Co(H_2O)_6](NO_3)_2$ 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-d_6). Only one set of signals for the protons of the phenolatodioximato ligand were observed, corroborating the expected pseudo-C_3 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,[9,10] complex **1** was found to be luminescent with an emission maximum at 445 nm (DMF, λ_{ex} = 335 nm, Fig. S15†).



Scheme 1 Synthesis of the ditopic clathrochelate complexes **1** and **2**. Reagents and conditions: (*i.*): $[Co(H_2O)_6](NO_3)_2$ or $Zn(OTf)_2$, EtOH/MeOH, 70 °C, then NEt_4OH.

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 $H = -2J\cdot S_1\cdot S_2$, 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 $5.0\mu_B$, 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[13] which takes into account the magnetic exchange

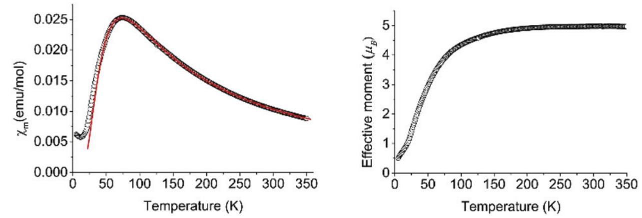
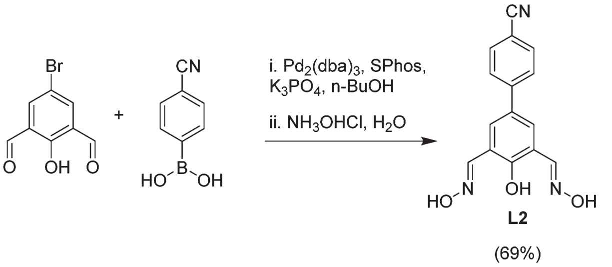


Fig. 2 The magnetic susceptibility and the effective magnetic moment of complex **2** as a function of temperature as determined by SQUID measurements.



Scheme 2 Synthesis of the dioxime ligand **L2**.

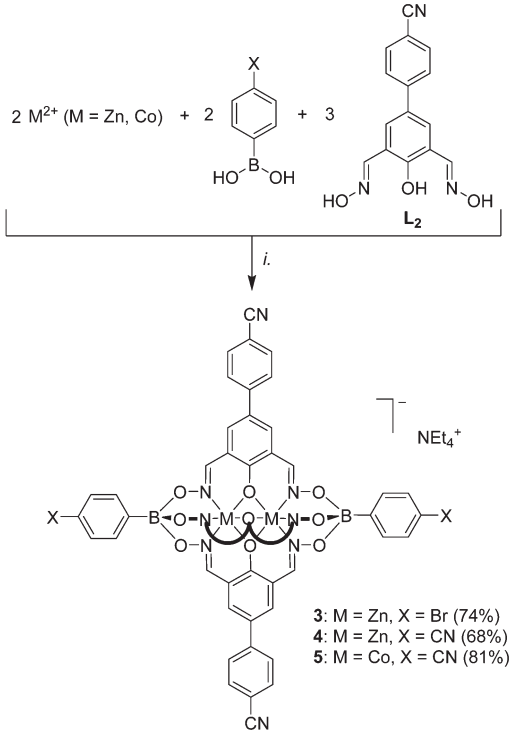
coupling *J*, spin–orbit coupling λ, an orbital reduction factor κ and the axial-splitting parameter Δ. Very good agreement with measured data has been achieved with $J = -20(3)\ \mathrm{cm}^{-1}$, $\lambda = -110(10)\ \mathrm{cm}^{-1}$, $\kappa = 1(0.1)$ and $\Delta = 286(30)$ (see red line in Fig. 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.[14]

In order to prepare clathrochelates with cyano groups in lateral position, we have prepared the phenoldioxime ligand **L2**. 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 $Pd_2(dba)_3$,[15] followed by treatment of the crude dialdehyde with hydroxylamine hydrochloride (Scheme 2).

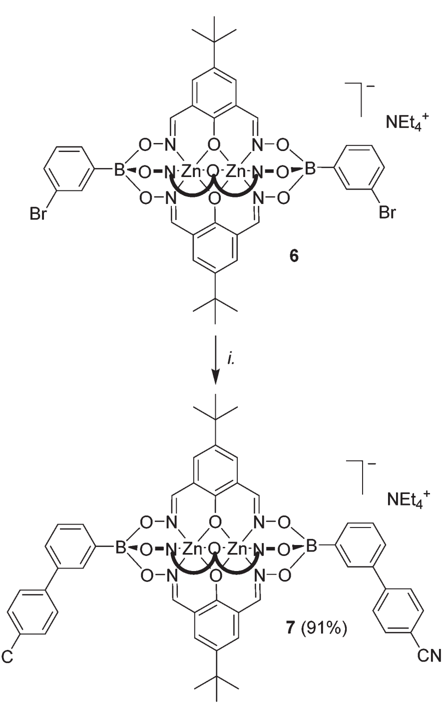
The tri- and pentatopic clathrochelates **3–5** were then obtained by using **L2** in combination of either 4-bromophenylboronic acid or 4-cyanophenylboronic following the standard protocol (Scheme 3). To the best of our knowledge, complexes **4** and **5** represent first examples of polycyano ligands with trigonal bipyramidal geometry. Zn-based clathrochelates **3** and **4** are luminescent, with emission maxima at 450 nm (DMF, λ_{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

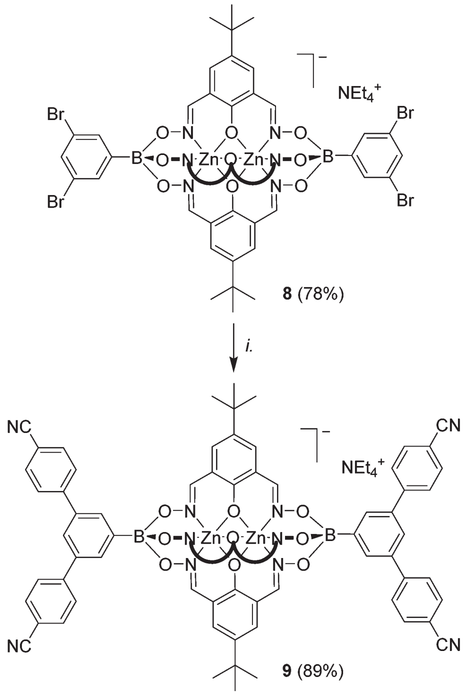
Recently, we have shown that brominated clathrochelate complexes of Zn^{2+} and Co^{2+} are sufficiently stable to be used as substrates in Pd-catalyzed cross-coupling reactions, allowing the preparation of elongated polypyridyl ligands.[9a] We anticipated that a similar strategy could be used to prepare clathrochelate complexes with pendent benzonitrile groups. Indeed, the two-fold coupling of the previously described clathrochelate **6** featuring 3-bromophenylboronate ester caps[9a] 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)



Scheme 3 Synthesis of the tri- and pentatopic clathrochelate complexes **3–5**. Reagents and conditions: (*i.*): 4-bromo- or 4-cyanophenylboronic acid, dioxime ligand **L2**, $Zn(OTf)_2$ or $[Co(H_2O)_6](NO_3)_2$, MeOH/EtOH, 70 °C, then NEt_4OH.



Scheme 4 Synthesis of the extended ditopic clathrochelate complex **7**. Reagents and conditions: (*i.*): **6** (1 eq.), 4-cyanophenylboronic acid (8 eq.), K_3PO_4 (4 eq.), $Pd_2(dba)_3$ (5 mol%), SPhos (10 mol%), *n*-BuOH/toluene (1 : 1), 90 °C, 14 h.



Scheme 5 Synthesis of the tetratopic clathrochelate complex **9**. Reagents and conditions: (*i*.): **8** (1 eq.), 4-cyanophenylboronic acid (20 eq.), K_3PO_4 (10 eq.), $Pd_2(dba)_3$ (5 mol%), SPhos (10 mol%), *n*-BuOH/toluene (1 : 1), 90 °C, 14 h.

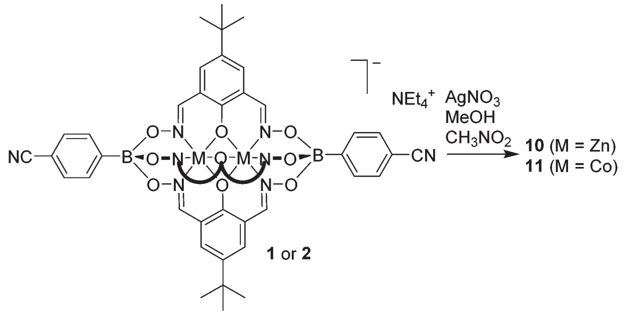
CPs.[3a–g] Compared to the ligands used previously, clathrochelate **7** stands out because of its size and its negative charge. Attempts to prepare a *linear* dicyano ligand by cross-coupling of a clathrochelate with terminal 4-bromophenylboronate ester groups were unfortunately not successful. Even 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 $Pd_2(dba)_3$ 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, λ_{ex} = 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.



Scheme 6 Synthesis of the heterometallic coordination polymers **10** and **11**.

Single crystals of the CPs **10** and **11** were obtained by layering a solution of $AgNO_3$ 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 $[Ag(\mathbf{1})(CH_3OH)](CH_3OH)_{1.5}(CH_3NO_2)$ for **10** and $[Ag(\mathbf{2})(CH_3OH)](CH_3OH)_{1.25}(CH_3NO_2)_{1.5}$ 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).[3d] 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

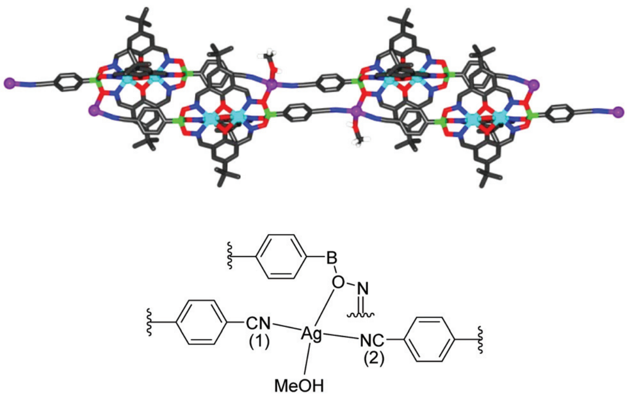
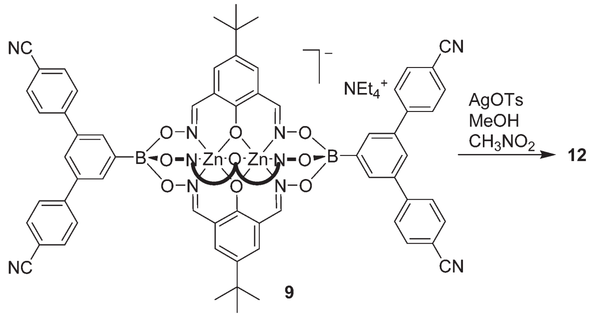


Fig. 3 Graphical representation of the double chain structure of coordination polymer **10** (top) and the first coordination sphere of the Ag^+ ions (bottom). Most hydrogen atoms and unbound solvent molecules have been omitted for clarity. Color coding: C: gray; hydrogen: white; O: red; N: blue; Ag: purple; B: green; Zn: cyan.

Table 1 Selected bond lengths for the coordination polymers **10** and **11**

Complex	Ag–N(1)	Ag–N(2)	Ag–O_{MeOH}	Ag–O_{Oxime}
10	2.158(6) Å	2.132(6) Å	2.627(4) Å	2.586(4) Å
11	2.171(3) Å	2.155(3) Å	2.526(5) Å	2.577(3) Å



Scheme 7 Synthesis of the heterometallic coordination polymer **12**.

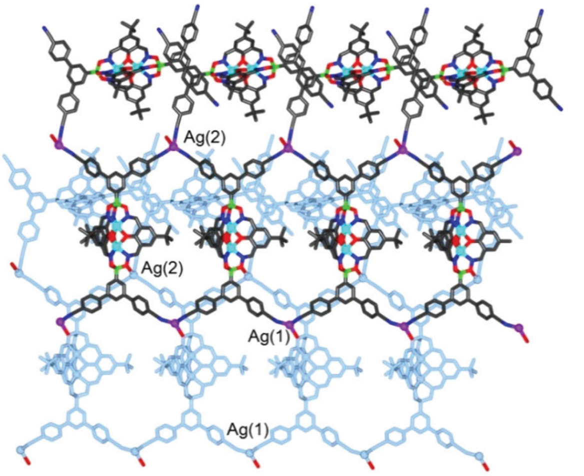


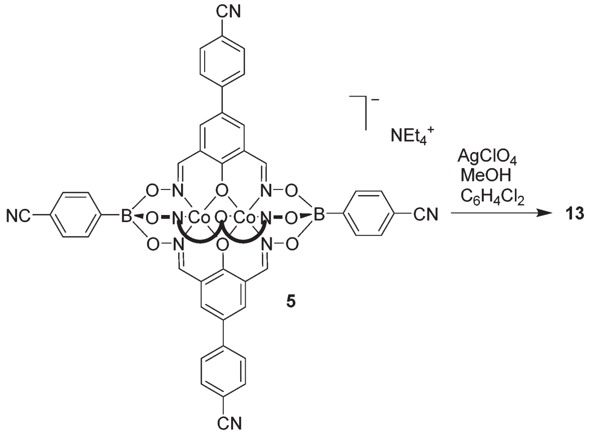
Fig. 4 Part of the structure of coordination polymer **12**. The shaded pale blue part of the structure is connected *via* Ag–O bonds. Hydrogen atoms and solvent molecules have been omitted for clarity. Color coding: C: gray; O: red; N: blue; Ag: purple; B: green; Zn: cyan.

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.[3d,4a,d,5b,g,16]

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

Single crystal X-ray analysis of **12** revealed the formation of a two-dimensional network structure with the stoichiometry $[Ag_2(\mathbf{9})_2](CH_3OH)_{1.5}(CH_3NO_2)_3$. 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 *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 *via* only one of the four cyano groups to silver ions Ag(2). The latter display a trigonal pyramidal geometry (Ag(2)–$N_{av.}$ = 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)–$N_{av.}$ = 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 **kgd** topology (kagome dual, given in terms of the RCSR notation;[17] see ESI, Fig. S19†) which is the most widespread topology for 3,6-coordinated two-dimensional CPs.[18] As it was observed for CP **10** and **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 **4** and **5**. After several attempts, we were able to crystallize CP **13** using metalloligand **5** in combination with $AgClO_4$ in the presence of MeOH, DMF and 1,2-dichlorobenzene as solvents (Scheme 8). Single crystal X-ray analysis of **13** showed that a three-dimensional network with the stoichiometry $[Ag_3(\mathbf{5})_2(OMe)](C_6H_4Cl_2)(MeOH)(sol.)_n$ had formed (Fig. 5). The asymmetric unit of the crystal contains three silver ions and two clathrochelate complexes **5**. Although the ratio of Ag to **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)



Scheme 8 Synthesis of coordination polymer **13** using pentatopic clathrochelate **5**.

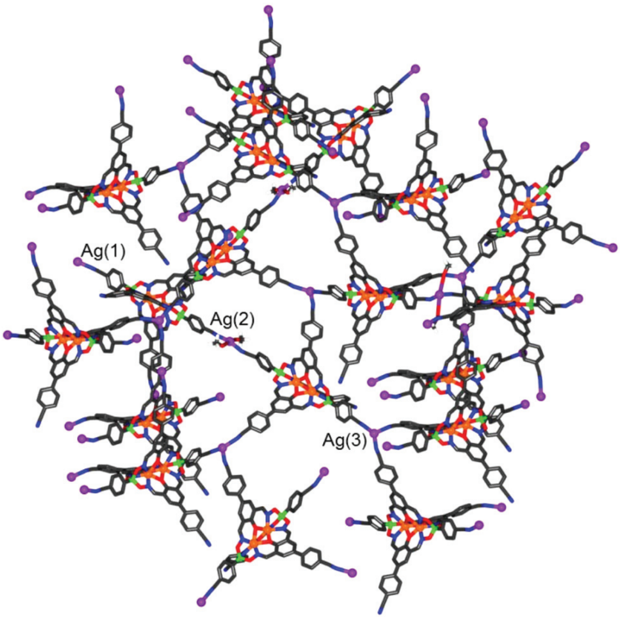


Fig. 5 Part of the structure of the three-dimensional coordination polymer **13**. Most hydrogen atoms and unbound solvent molecules have been omitted for clarity. Color coding: C: gray; H: white; O: red; N: blue; Ag: purple; B: green; Co: orange.

ions act as linkers between two cobalt-containing metalloligands (Ag(2)–N$_{av.}$ = 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 metalloligands act as four-connected nodes through both of the apical and two of the three lateral cyano groups (one cyano group is 'free'). The first crystallographically independent metalloligand 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 interpenetrating CPs of the stoichiometry [Ag(**5**)] 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 package[20] revealed that the net has a point symbol $(8{\cdot}10^2)(8^2{\cdot}10^4)(8^2{\cdot}10)(8^3{\cdot}10^3)$. 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 42 other rings and the ten-membered rings are crossed by at least 57 other rings. The topological density of the net can be given as TD$_{10}$ = 3127, which is the number of nodes within the first 10 coordination spheres of a given node. According to the RCSR database,[17] this value represents the highest topological density among all known 3,3,4,4-coordinated nets, and is almost as high as TD$_{10}$ = 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 synthesis. Alternatively, we have been able to prepare elongated clathrochelates with pendent benzonitrile groups by post-synthetic modification of brominated clathrochelates in Pd-catalyzed cross-coupling reactions. The functionalized clathrochelates can be used as metalloligands for the preparation of heterometallic Co^{2+}/Ag^{+} and Zn^{2+}/Ag^{+} coordination polymers, as evidenced by the synthesis of one-, two-, and three-dimensional CPs in reactions with silver salts. Due to the negative charge of the metalloligands, 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 clathrochelate 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] ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance III (^{1}H: 400 MHz, ^{13}C: 100 MHz). ^{1}H and ^{13}C 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 spectrometer. 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-bromophenol (600 mg, 2.62 mmol, 1.0 equiv.), 4-cyanophenylboronic acid (3.06 g, 20.83 mmol, 8.0 equiv.) and K_3PO_4 (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 $Pd_2(dba)_3$ (60 mg, 0.06 mmol, 0.025 equiv.) were added, and the mixture was stirred overnight at 85 °C under N_2 atmosphere. The reaction mixture was cooled down to RT, 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 H_2O (200 ml) and the resulting solution was heated at 85 °C for 30 min. $NH_2OH{\cdot}HCl$ (728 mg, 10.48 mmol, 4.0 equiv.) was added and the white suspension was heated 2 h at 85 °C. After cooling down to RT, the suspended product was isolated by filtration, washed with H_2O (2 × 100 ml) and dried under vacuum to afford the dioxime **L2** as an off-white powder (510 mg, 1.81 mmol, 69%). ^{1}H-NMR (400 MHz, DMSO-d_6): 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).^{13}C-NMR (101 MHz, DMSO-d_6): 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 $C_{15}H_{11}N_3O_3$: 282.0879; found: 282.0885. IR: 3250, 2225, 1735, 1630, 1605, 1455, 1280, 1200, 1180, 1030, 1000, 975, 940, 835, 700, 660, 600 cm^{-1}.

Clathrochelate 1. A mixture of 2,6-diformyl-4-*tert*-butylphenol dioxime (100 mg, 0.423 mmol, 3.0 equiv.), 4-cyanophenylboronic acid (41.5 mg, 0.283 mmol, 2.0 equiv.) and $Zn(OTf)_2$ (105.5 mg, 0.283 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 (141 µl, 0.211 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 20 min. After a second addition of tetraethylammonium hydroxide (141 µl, 0.211 mmol, 25% in MeOH), the solution was cooled down to RT and concentrated to 5 ml. The yellow precipitate was isolated by filtration, washed with EtOH (3 × 5 ml) and Et_2O (2 × 50 ml) and dried under vacuum to afford **1** as a yellow powder (135 mg, 0.114 mmol, 81%).^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.39 (s, 6H), 7.83 (d, J = 7.7 Hz, 4H), 7.67 (d, J = 7.8 Hz, 4H), 7.33 (s, 6H), 3.13 (q, J = 7.2 Hz, 8H), 1.21 (s, 27H), 1.15 (t, J = 7.1 Hz, 12H). ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 162.51, 154.40, 137.23, 132.64, 132.50, 130.17, 119.99, 118.27, 108.72, 51.456, 33.47, 31.21, 7.07 (C–B not detected). HRMS-ESI: Calcd for $C_{50}H_{47}B_2N_8O_9Zn_2$: 1057.2216; found: 1057.2269. IR: 2960, 2865, 2220, 1610, 1550, 1445, 1395, 1365, 1330, 1285, 1225, 1205, 1150, 1080, 1040, 1000, 930, 840, 785, 775, 690, 635, 625, 565, 525 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 $[Co(H_2O)_6](NO_3)_2$ (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 Et_2O (2 × 50 ml) and dried under vacuum to afford **2** as an orange powder (254 mg, 0.216 mmol, 77%). HRMS-ESI: Calcd for $C_{50}H_{47}B_2Co_2N_8O_9$: 1043.2332; found: 1043.2307. IR: 2960, 2220, 1740, 1610, 1550, 1450, 1395, 1365, 1330, 1285, 1225, 1205, 1085, 1040, 1020, 995, 930, 840, 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 Et_2O (2 × 50 ml) and dried under vacuum to afford **3** as a yellow powder (125 mg, 0.088 mmol, 74%). ^{1}H-NMR (400 MHz, DMSO-d_6): 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). ^{13}C-NMR (101 MHz, DMSO-d_6): 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, 7.04. (C–B not detected). HRMS-ESI: Calcd for $C_{57}H_{32}B_2Br_2N_9O_9Zn_2$: 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 (8 ml), isolated by filtration, washed with EtOH (3 × 8 ml) and Et_2O (2 × 50 ml) and dried under vacuum to afford **4** as a yellow powder (106 mg, 0.08 mmol, 68%). ^{1}H-NMR (400 MHz, DMSO-d_6): 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). ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 164.89, 154.38, 143.33, 134.14, 132.85, 132.56, 130.26, 126.10, 124.94, 119.87, 119.51, 119.10, 108.90, 108.70, 51.41, 7.08 (C–B not detected). HRMS-ESI: Calcd for $C_{59}H_{32}B_2N_{11}O_9Zn_2$: 1192.1139; found: 1192.1090. IR: 2985, 2220, 1600, 1555, 1545, 1480, 1445, 1390, 1335, 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 $[Co(H_2O)_6](NO_3)_2$ (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 Et_2O (2 × 50 ml) and dried under vacuum to afford **5** as an orange powder (150 mg, 0.114 mmol, 81%). HRMS-ESI: Calcd for $C_{59}H_{32}B_2Co_2N_{11}O_9$: 1178.1254; found: 1178.1234. IR: 3450, 2970, 2225, 1735, 1600, 1545, 1445, 1365, 1340, 1305, 1205, 1080, 1040, 1020, 985, 935, 910, 835, 800, 775, 735, 690, 615, 550 cm^{-1}.

Clathrochelate 7. Under inert atmosphere, degassed *n*-BuOH (10 ml) and degassed toluene (10 ml) were added to a 25 ml pyrex vial containing **6** (100 mg, 77 µmol, 1.0 equiv.), 4-cyanophenylboronic acid (91 mg, 0.62 mmol, 8 equiv.) and K_3PO_4 (66 mg, 0.31 mmol, 4.0 equiv.). $Pd_2(dba)_3$ (3.54 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 (5 ml), acetone (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 × 50 ml) and Et_2O (100 ml), and dried under vacuum to afford **7** as a yellow powder (85 mg, 70 µmol, 91%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.40 (s, 6H), 7.99 (s, 2H), 7.91 (dd, J = 8.4 Hz, 8H), 7.74 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.33 (s, 6H), 3.18 (q, J = 7.2 Hz, 8H), 1.22 (s, 27H), 1.14 (t, J = 7.2 Hz, 12H). ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 162.44, 154.04, 146.39, 136.98, 136.30, 132.75, 132.60, 132.19, 130.46, 127.45, 127.24, 124.84, 119.09, 118.31, 109.23, 51.35, 33.41, 31.16, 7.05 (C–B not detected). HRMS-ESI: Calcd for $C_{62}H_{55}B_2N_8O_9Zn_2$: 1209.2848; found: 1209.2838. IR: 2955, 2870, 2225, 1605, 1550, 1505, 1445, 1395, 1365, 1325, 1280, 1240, 1225, 1185, 1140, 1075, 1050, 1035, 995, 980, 950, 900, 840, 780, 720, 685, 635, 595, 555, 525 cm^{-1}.

Clathrochelate 8. A mixture of 2,6-diformyl-4-*tert*-butylphenol dioxime (400 mg, 1.69 mmol, 3.0 equiv.), 3,5-dibromophenylboronic acid (315 mg, 1.13 mmol, 2.0 equiv.) and $Zn(OTf)_2$ (410 mg, 1.13 mmol, 2.0 equiv.) in a mixture of MeOH (50 ml) and EtOH (50 ml) was heated to 70 °C until all solids had dissolved. Tetraethylammonium hydroxide (563 µl, 0.845 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 30 min. After a second addition of tetraethylammonium hydroxide (563 µl, 0.845 mmol, 25% in MeOH), the solution was cooled down to RT, and was concentrated to 5 ml. The yellow precipitate was isolated by filtration, washed with EtOH (2 × 10 ml) and Et_2O (2 × 50 ml) and dried under vacuum to afford **8** as a yellow powder (580 mg, 0.44 mmol, 78%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.41 (s, 6H), 7.73 (d, J = 1.7 Hz, 4H), 7.61 (s, 2H), 7.36 (s, 6H), 3.18 (q, J = 7.2 Hz, 8H), 1.21 (s, 27H), 1.14 (t, J = 7.2 Hz, 12H). ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 162.44, 154.47, 137.10, 133.32, 132.52, 130.66, 121.55, 118.17, 51.38, 33.41, 31.13, 7.03 (C–B not detected). HRMS-ESI: Calcd for $C_{48}H_{45}B_2N_6O_9Zn_2$: 1320.8707; found: 1320.8728. IR: 2955, 2865, 1610, 1585, 1550, 1540, 1445, 1390, 1365, 1330, 1280, 1235, 1225, 1190, 1100, 1080, 1045, 990, 960, 925, 880, 855, 840, 785, 775, 735, 720, 680, 640, 560, 525 cm^{-1}.

Clathrochelate 9. Under inert atmosphere, degassed *n*-BuOH (10 ml) and degassed toluene (10 ml) were added to a 25 ml pyrex vial containing **7** (100 mg, 69 µmol, 1.0 equiv.), 4-cyanophenylboronic acid (202 mg, 1.37 mmol, 20 equiv.) and K_3PO_4 (146 mg, 0.687 mmol, 10.0 equiv.). $Pd_2(dba)_3$ (6.4 mg, 6.9 µmol, 0.1 equiv.) and SPhos (5.7 mg, 13.8 µmol, 0.2 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 (5 ml), acetone (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 × 50 ml) and Et_2O (100 ml), and dried under vacuum to afford **9** as a yellow powder (87 mg, 70 µmol, 89%). ^{1}H-NMR (400 MHz, DMSO-d_6): 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). ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 162.48, 154.24, 145.83, 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). HRMS-ESI: Calcd for $C_{76}H_{61}B_2N_{10}O_9Zn_2$: 1411.3386; found: 1411.3365. IR: 2955, 2865, 2225, 1675, 1605, 1555, 1505, 1450, 1395, 1365, 1330, 1285, 1240, 1225, 1180, 1140, 1070, 1035, 995, 930, 890, 835, 785, 725, 680, 635, 605, 590, 565, 555 cm^{-1}.

CP 10. In a 5 mm-wide glass tube, a solution of $AgNO_3$ (10 mg) in MeOH (1.5 ml) was layered on top of a solution of **1** (10 mg) in nitromethane (1.5 ml) covered by a buffer layer of a 1 : 1 mixture of MeOH and nitromethane (2 ml). Transparent yellowish needles of **10** (7.4 mg) were obtained within four weeks. IR: 2960, 2865, 2245, 2165, 1615, 1550, 1445, 1395, 1365, 1330, 1280, 1220, 1200, 1080, 1035, 1000, 930, 875, 840, 815, 785, 775, 690, 635, 560, 540, 530 cm^{-1}.

CP 11. In a 5 mm-wide glass tube, a solution of $AgNO_3$ (10 mg) in MeOH (1.5 ml) was layered on top of a solution of **2** (10 mg) in nitromethane (1.5 ml) covered by a buffer layer of a 1 : 1 mixture of MeOH and nitromethane (2 ml). Orange needles of **11** (8.1 mg) were obtained within five weeks. IR: 2955, 2860, 2250, 2225, 2165, 1610, 1555, 1450, 1395, 1365, 1330, 1265, 1210, 1090, 1020, 970, 930, 840, 825, 785, 765, 695, 655, 635, 610, 570, 560 cm^{-1}.

CP 12. In a 5 mm-wide glass tube, a solution of AgOTs (10 mg) in MeOH (1.5 ml) was layered on top of a solution of **9** (10 mg) in nitromethane (1.5 ml) covered by a buffer layer of a 1 : 1 mixture of MeOH and nitromethane (2 ml). Transparent pale-yellow plates of **12** (4.1 mg) were obtained within eight weeks. IR: 2955, 2865, 2235, 1680, 1610, 1555, 1505, 1450, 1395, 1365, 1330, 1285, 1240, 1225, 1185, 1145, 1070, 1035, 995, 930, 890, 835, 785, 725, 680, 640, 605, 590, 570, 555 cm^{-1}.

CP 13. In a 5 mm-wide glass tube, a solution of $AgClO_4$ (10 mg) in MeOH (1.5 ml) was layered on top of a solution of **5** (10 mg) in 1,2-dichlorobenzene (1.5 ml) covered by a buffer layer of a 1 : 1 mixture of MeOH and 1,2-dichlorobenzene (2 ml). Orange plates of **13** (9.8 mg) were obtained within one week. IR: 3390, 2225, 1600, 1560, 1545, 1445, 1390, 1340, 1305, 1205, 1180, 1080, 1035, 1020, 980, 935, 910, 830, 800, 775, 750, 690, 655, 610, 550, 535 cm^{-1}.

Acknowledgements

The work was supported by the Swiss National Science Foundation and by the Ecole Polytechnique Fédérale de Lausanne (EPFL). We are grateful to the Swiss-Norwegian Beamline Consortium for providing access to synchrotron radiation.

References

1 (*a*) T. C. W. Mak and X.-L. Zhao, *Encyclopedia of Inorganic Chemistry*, 2006, John Wiley & Sons; (*b*) B. S. Fox, M. K. Beyer and V. E. Bondybey, *J. Am. Chem. Soc.*, 2002, **124**, 13613.

2 (*a*) C.-Y. Su, C.-L. Chen, J.-Y. Zhang and B.-S. Kang, in *Design and Construction of Coordination Polymers*, ed. M.-C. Hong and L. Chen, 2009, John Wiley & Sons, p. 111; (*b*) C.-L. Chen, B.-S. Kang and C.-Y. Su, *Aust. J. Chem.*, 2006, **59**, 3.

3 For examples see: (*a*) X.-M. Guo, L. Zhao, H.-Y. Zou, Y.-N. Yan, Y.-J. Qi and Q. Wang, *Inorg. Chem. Commun.*, 2015, **54**, 57; (*b*) S. P. Anthony, L. Wang, S. Varughese and S. M. Draper, *CrystEngComm*, 2013, **15**, 6602; (*c*) C. D. MacKinnon, S. L. M. Parent, R. C. Mawhinney, A. Assound and C. M. Robertson, *CrystEngComm*, 2009, **11**, 160; (*d*) Y.-B. Dong, H.-X. Xu, J.-P. Ma and R.-Q. Huang, *Inorg. Chem.*, 2006, **45**, 3325; (*e*) Y.-B. Dong, H.-Y. Wang, J.-P. Ma, D.-Z. Shen and R.-Q. Huang, *Inorg. Chem.*, 2005, **44**, 4679; (*f*) S. P. Anthony and T. P. Radhakrishnan, *Chem. Commun.*, 2004, 1058; (*g*) Y.-B. Dong, P. Wang and R.-Q. Huang, *Inorg. Chem.*, 2004, **43**, 4727; (*h*) J. Zhang, M. Nieuwenhuyzen, J. P. H. Charmant and S. L. James, *Chem. Commun.*, 2004, 2808; (*i*) Z. Xu, Y.-H. Kiang, S. Lee, E. B. Lobkovsky and N. Emmott, *J. Am. Chem. Soc.*, 2000, **122**, 8376; (*j*) K. A. Hirsch, S. R. Wilson and J. S. Moore, *Chem. – Eur. J.*, 1997, **3**, 765; (*k*) D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030.

4 For examples see: (*a*) J. Ni, K.-J. Wei, Y. Liu, X.-C. Huang and D. Li, *Cryst. Growth Des.*, 2010, **10**, 3964; (*b*) Y.-Q. Sun, C. Yang, Z. Xu, M. Zeller and A. D. Hunter, *Cryst. Growth Des.*, 2009, **9**, 1663; (*c*) S. Banfi, L. Carlucci, E. Caruso, G. Ciani and D. M. Prosperpio, *Cryst. Growth Des.*, 2004, **4**, 29; (*d*) F. C. Pigge, M. D. Burgard and N. P. Rath, *Cryst. Growth Des.*, 2003, **3**, 331; (*e*) Y.-H. Kiang, G. B. Gardner, S. Lee, Z. Xu and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1999, **121**, 8204; (*f*) W. Choe, Y.-H. Kiang, Z. Xu and S. Lee, *Chem. Mater.*, 1999, **11**, 1776; (*g*) G. B. Gardner, Y.-H. Kiang, S. Lee, A. Asgaonkar and D. Venkataraman, *J. Am. Chem. Soc.*, 1996, **118**, 6946; (*h*) D. Venkataraman, G. B. Gardner, S. Lee and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 11600; (*i*) G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature*, 1994, **374**, 792.

5 For examples see: (*a*) Z. Zhang, H. Zhao, M. M. Matsushita, K. Awaga and K. R. Dunbar, *J. Mater. Chem. C*, 2014, **2**, 399; (*b*) B. Blankschein, A. Schulz, A. Villinger and R. Wustrack, *ChemPlusChem*, 2014, **79**, 973; (*c*) C. S. Hawes, S. R. Batten and D. R. Turner, *CrystEngComm*, 2014, **16**, 3737; (*d*) A. V. Mossine, P. Thavornyutikarn and J. Atwood, *CrystEngComm*, 2013, **15**, 1673; (*e*) K. Akimoto, Y. Kondo, K. Endo, M. Yamada, Y. Aoyama and F. Hamada, *Tetrahedron Lett.*, 2008, **49**, 7361; (*f*) Y.-B. Dong, Y.-Y. Jiang, J.-P. Ma, F.-L. Liu, B. Tang, R.-Q. Huang and S. R. Batten, *J. Am. Chem. Soc.*, 2007, **129**, 4520; (*g*) K. S. Min and M. P. Suh, *J. Am. Chem. Soc.*, 2000, **122**, 6834; (*h*) C. Kleina, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 2000, 239–240; (*i*) I. Ino, J. Chu, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and Y. Kitamori, *Inorg. Chem.*, 2000, **39**, 4273; (*j*) G. Mislin, E. Graf, M. W. Hosseini, A. De Cian, N. Kyritsakas and J. Fischer, *Chem. Commun.*, 1998, 2545; (*k*) F.-Q. Liu and T. D. Tilley, *Inorg. Chem.*, 1997, **36**, 5090.

6 For examples see: (*a*) C. A. Hollis, S. R. Batten and C. J. Sumby, *Cryst. Growth Des.*, 2013, **13**, 2350; (*b*) C. A. Hollis, L. R. Hanton, J. C. Morris and C. J. Sumby, *Cryst. Growth Des.*, 2009, **9**, 2911.

7 (*a*) A. Wang, C. Merkens and U. Englert, *CrystEngComm*, 2015, **17**, 4293; (*b*) Q. Guo, C. Merkens, R. Si and U. Emglert, *CrystEngComm*, 2015, **17**, 4383; (*c*) C. Merkens, N. Becker, K. Lamberts and U. Englert, *Dalton Trans.*, 2012, **41**, 8594; (*d*) C. Merkens and U. Englert, *Dalton Trans.*, 2012, **41**, 4664; (*e*) B. Kilduff, D. Pogozhev, S. A. Baudron and M. W. Hosseini, *Inorg. Chem.*, 2010, **49**, 11231;

(*f*) D. Pogozhev, S. A. Baudron and M. W. Hosseini, *Inorg. Chem.*, 2010, **49**, 331; (*g*) M. Kondracka and U. Emglert, *Inorg. Chem.*, 2008, **47**, 10246; (*h*) A. D. Burrows, K. Cassar, M. F. Mahon and J. E. Warren, *Dalton Trans.*, 2007, 2499–2509.

8 M. Karsch, H. Lund, A. Schulz, A. Villinger and K. Voss, *Eur. J. Inorg. Chem.*, 2012, 5542–5553.

9 (*a*) M. Marmier, G. Cecot, B. F. E. Curchod, P. Pattison, E. Solari, R. Scopelliti and K. Severin, *Dalton Trans.*, 2016, **45**, 8422; (*b*) M. Pascu, M. Marmier, C. Schouwey, R. Scopelliti, J. J. Holstein, G. Bricogne and K. Severin, *Chem. – Eur. J.*, 2014, **20**, 5592.

10 M. Marmier, M. D. Wise, J. J. Holstein, P. Pattison, K. Schenk, E. Solari, R. Scopelliti and K. Severin, *Inorg. Chem.*, 2016, **55**, 4006.

11 S. Khanra, T. Weyhermüller, E. Bill and P. Chaudhuri, *Inorg. Chem.*, 2006, **45**, 5911.

12 J. Zhang, Z. Ma, H. Zhao, C. Ge, Y. Wang and X. Zhang, *Inorg. Chem. Commun.*, 2016, **65**, 63.

13 H. J. Sakiyama, *Chem. Software*, 2001, **7**, 171.

14 L. J. Daumann, P. Comba, J. A. Larrabee, G. Schenk, R. Stranger, G. Cavigliasso and L. R. Gahan, *Inorg. Chem.*, 2013, **52**, 2029.

15 T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 4685.

16 Selected examples: (*a*) K.-J. Wei, J. Ni, J. Gao, Y. Liu and Q.-L. Liu, *Eur. J. Inorg. Chem.*, 2007, 3868; (*b*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.

17 (*a*) M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782; (*b*) http://rcsr.anu.edu.au/.

18 T. G. Mitina and V. A. Blatov, *Cryst. Growth Des.*, 2013, **13**, 1655.

19 E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio, *CrystEngComm*, 2011, **13**, 3947.

20 V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.*, 2014, **14**, 3576.

21 For a self-penetrated net based on a rigid metalloligand see: L. Carlucci, G. Ciani, D. M. Proserpio and F. Porta, *Angew. Chem., Int. Ed.*, 2003, **115**, 331.

22 H. Ma, D. Sun, L. Zhang, R. Wang, V. A. Blatov, J. Guo and S. Dun, *Inorg. Chem.*, 2013, **52**, 10732.

23 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466.

24 For examples see: (*a*) B. Nohra, R. Réau and C. Lescop, *Eur. J. Inorg. Chem.*, 2014, 1788; (*b*) A. I. A. Perez, T. Biet, S. Graule, T. Agou, C. Lescop, N. R. Branda, J. Crassous and R. Réau, *Chem. – Eur. J.*, 2011, **17**, 1337; (*c*) Y. Yao, W. Shen, B. Nohra, C. Lescop and R. Réau, *Chem. – Eur. J.*, 2010, **16**, 7143; (*d*) B. Nohra, S. Graule, C. Lescop and R. Réau, *J. Am. Chem. Soc.*, 2006, **128**, 3520; (*e*) F. Fochi, P. Jacopozzi, E. Wegelius, K. Rissanen, P. Cozzini, E. Marastoni, E. Fisicaro, P. Manini, R. Fokkens and E. Dalcanale, *J. Am. Chem. Soc.*, 2001, **123**, 7539; (*f*) P. Jacopozzi and E. Dalcanale, *Angew. Chem., Int. Ed.*, 1997, **36**, 613.