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Discrete and Infinite Metallacyclic Coordination Architectures Based on a Conformationally Flexible Tripodal Aminotriazine-Derived Polypyridyl Ligand

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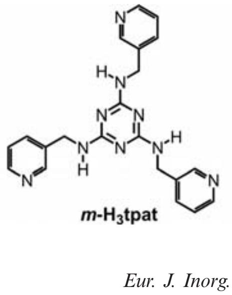
A novel tripodal semi-rigid ligand, 2,4,6-tris(3-picolylamino)-1,3,5-triazine (m-H_3tpat), consisting of a triazine central core and three pyridine donating functions attached to flexible –$NHCH_2$– arms has been designed and synthesized. The self-assembly reactions of m-H_3tpat with copper(II) chloride and cobalt(II) chloride yielded discrete Cu^{II} complex $[Cu_2Cl_4(m\text{-}H_3tpat)_2]\cdot 2H_2O\cdot 2EtOH$ (**1**$\cdot 2H_2O\cdot 2EtOH$) and polymeric Co^{II} complex $[Co(m\text{-}H_3tpat)_2(H_2O)_2]Cl_2$ (**2**), respectively. Complex **1** has a metallacyclophane structure with a metal-to-ligand ratio of 2:2. Each copper(II) ion adopts a pentacoordinate square-pyramidal geometry with a N_3Cl_2 coordination sphere. Complex **2** exhibits an extended chain structure based on $\{Co_2(m\text{-}H_3tpat)_2\}$ metallacyclic repeating units. Each cobalt(II) ion adopts a hexacoordinate octahedral geometry with a N_2O_4 coordination environment. Note that the m-H_3tpat ligand exists in a *cis*–*cis*–*cis* conformation in **1** and a *cis*–*trans*–*trans* conformation in **2**, with the central aminotriazine moiety appearing to be an asymmetric-configured all-amino tautomer in both conformers. The stabilities of the two coordination-directed structures may be enhanced by intramolecular π–π interactions between two pyridine rings from two different m-H_3tpat ligands within the metallacyclophane structure of **1** and by a set of complementary double hydrogen bonds (DA–AD arrays) between two aminotriazine moieties of two m-H_3tpat ligands within a metallacyclic unit for **2**.

Introduction

During the past two decades, tremendous effort has been devoted to the targeted construction of discrete and/or polymeric metallasupramolecular assemblies from tailored molecular components through metal–ligand direct coordination bonds and/or noncovalent interactions.[1–3] So far, a variety of organic *exo*-donating ligands have been used to achieve the target structures. Among the limitless choices, semi-rigid ligands provide efficient building blocks for the development of functional metallasupramolecular assemblies.[4–24] In general, a well-designed semi-rigid ligand has an inherent conformationally flexible yet restricted molecular structure that can self-adjust its conformation so as to adapt to a change in the self-assembled systems and to saturate the geometric requirements of different metal ions. In other words, with conformational flexibility and low symmetry, semi-rigid ligands can display many more coordination modes than rigid ligands, leading to the formation of metallasupramolecular assemblies with interesting topologies and properties.[4–25] This, unfortunately, also means that it is difficult to predict exactly the structure of the infinite coordination complexes when using semi-rigid ligands as molecular blocks.

On the other hand, aminotriazine derivatives are attractive due to their important hydrogen donor–acceptor abilities, which dominate potential complementary supramolecular recognitions, as well as their coordinative features.[20,26–29] The hydrogen bonds that form between the central triazine ring and the outer-ring –NH– groups have been intensively examined in crystal engineering as directional interactions that play an important role in constructing the resulting supramolecular structures.[20,30] Therefore we focused our attention on a novel aminotriazine-derived tripodal ligand, 2,4,6-tris(3-picolylamino)-1,3,5-triazine, abbreviated as m-H_3tpat, with highly flexible aminomethylene (–$NHCH_2$–) arms functionalized by 3-pyridyl donating groups. Herein we report on the synthesis and characterization of the m-H_3tpat ligand, a copper(II)-based dinuclear coordination metallacyclophane structure, and a cobalt(II)-based one-dimensional coordination chain array based on $\{M_2L_2\}$ metallacyclic repeating units.



m-H_3tpat

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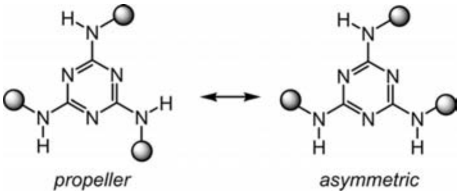
Results and Discussion

Synthesis, Characterization, and Structural Properties of *m*-H_3tpat

The designed tripodal pyridine-amine-triazine ligand, *m*-H_3tpat, was prepared in moderate yields (74%) by the reaction of cyanuric chloride with 3-picolylamine using triethylamine as the base in THF at 80 °C for 48 h. The molecular structure was characterized by NMR, mass spectrometry, and elemental analysis (Figures S1–S3).

As shown in Scheme 1, *m*-H_3tpat may adopt propeller and asymmetric conformers owing to restricted rotation about the amino–triazine bond.[31] In addition, with the flexible, freely rotating aminomethylene (–$NHCH_2$–) arms, it may also form *cis–cis–cis* (all three pyridyl donors lying above or below the basal aminotriazine plane) and *cis–trans–trans* conformations (two pyridyl donors lying above the basal aminotriazine plane and one pyridyl donor below). Moreover, the coordinative directions of the 3-pyridyl donating groups may also be taken into account. Therefore a variety of ligand conformations can be expected. Unfortunately, it appears to be difficult to produce a well-defined structure of the tripodal *m*-H_3tpat ligand by precisely controlling the experimental conditions because these conformers can interconvert.[31] This is consistent with the results of a ^{1}H NMR study performed at room temperature; broadened signals were observed, which indicates possible dynamic behavior between conformers in the solution state (Figure S1).[31]



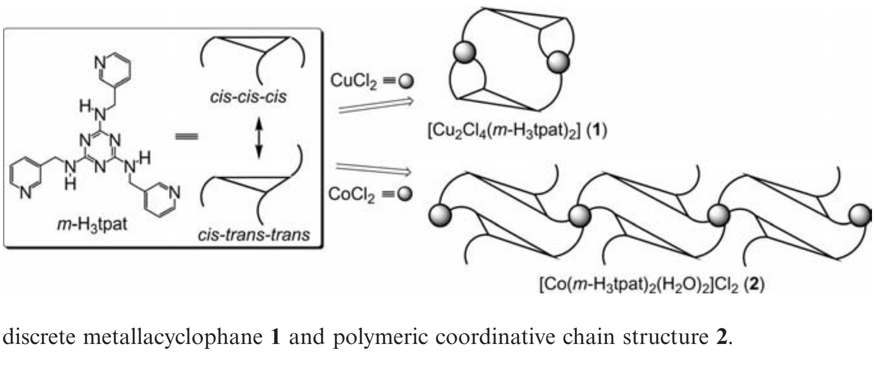
Scheme 1. Possible conformers of the *m*-H_3tpat ligand.

Synthesis and Crystal Structure of $[Cu_2Cl_4(m\text{-}H_3tpat)_2]\cdot 2H_2O\cdot 2EtOH$ ($1\cdot 2H_2O\cdot 2EtOH$)

Slow diffusion of an ethanol solution of *m*-H_3tpat into an aqueous solution of $CuCl_2$ with a mixture of EtOH and H_2O as buffer at room temperature yielded a blue crystalline product (Scheme 2), formulated as $[Cu_2Cl_4(m\text{-}H_3tpat)_2]\cdot 2H_2O\cdot 2EtOH$ (**1**$\cdot 2H_2O\cdot 2EtOH$) on the basis of a single-crystal X-ray diffraction analysis.

Compound **1** adopts a discrete coordination metallacyclophane structure with a metal-to-ligand ratio of 2:2 (Figure 1). Each copper(II) ion is pentacoordinated to three N-coordinating pyridyl groups belonging to two different *m*-H_3tpat ligands and two chloro ligands pointing away from the cavity of the cyclic structure. This N_3Cl_2 coordination sphere, which has a τ value of 0.17,[32] can be described as having a square-pyramidal geometry. The "axial" Cu1–Cl2 bond length is 2.4316(13) Å (Table 1), which contrasts with the shorter "equatorial" Cu1–Cl1 bond length of 2.3174(11) Å, reasonably attributed to the influence of Jahn–Teller distortion of the d^9-configured Cu^{II} ion. The *m*-H_3tpat ligand adopts a *cis–cis–cis* conformation in which the aminotriazine moiety appears to be an asymmetric-configured all-amino tautomer with all three pyridyl donating groups bridging two copper ions separated by 9.22 Å. The two *syn–syn* oriented pyridyl donors chelate to the same copper ion and the other one, which has *syn–anti* and *anti–anti* orientations relative to the former two, respectively, coordinates to the second. The three terminal pyridine rings are slightly off-perpendicular to each other with dihedral angles of around 68, 84, and 86°, and two of them are also slightly off-perpendicular to the central triazine ring with dihedral angles of 79 and 88° with the last adopting an off-parallel orientation (the dihedral angle is 21°). On the other hand, only two of the three pyridyl donating groups of the *m*-H_3tpat ligand form the walls of the cyclic structure, the third being inside the cavity and making contact with another pyridyl unit from the second *m*-H_3tpat ligand of the metallacyclophane through intramolecular π–π interactions. This π-stacking is offset with a centroid···centroid distance of 3.95 Å, a plane···plane distance of 3.35 Å, a horizontal displacement of 2.10 Å, and an angle of 32° between the ring normal and the centroid vector. However, it plays a role in stabilizing the whole metallacyclophane structure.

Each metallacyclophane interconnects with neighboring molecules through pertinent N_{amine}–H···Cl–Cu hydrogen bonds [N5···Cl1 3.261(4) Å; N5–H102···Cl1 159°; Table S1] between amine hydrogen atoms and the equatorial chloro [Cl(1)] ligands. The one-dimensional supramolecular polycyclic chain thus-obtained runs along the crystallographic *b* axis (Figure 2, a). Consequently, as the metallacyclophanes



Scheme 2. Synthesis of discrete metallacyclophane **1** and polymeric coordinative chain structure **2**.

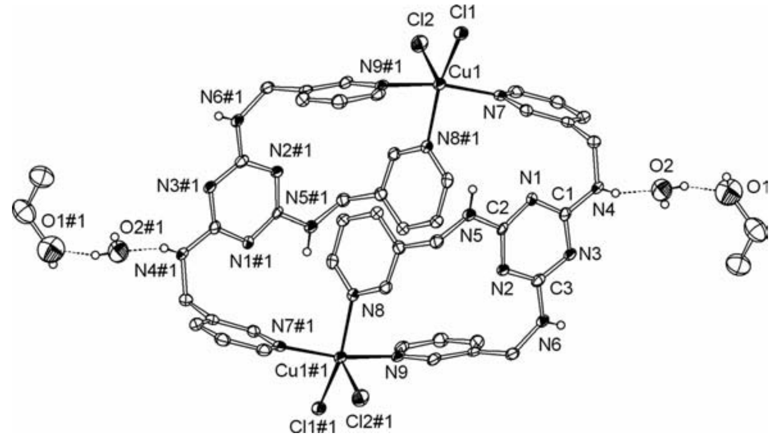


Figure 1. ORTEP drawing of the crystal structure of **1**·2H$_2$O·2EtOH showing the coordination environment around the metal ions and the coordination mode of *m*-H$_3$tpat with selected numbering scheme. Pertinent N$_{amine}$–H···O$_{water}$ and O$_{water}$–H···O$_{ethanol}$ hydrogen bonds are represented by dotted lines. The carbon-bonded hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Symmetry transformations used to generate equivalent atoms: #1: –*x* + 2, –*y* + 1, –*z*.

Table 1. Selected bond lengths [Å] and angles [°] for **1**·2H$_2$O·2EtOH and **2**.[a]

1·2H$_2$O·2EtOH		**2**	
Cu1–N7	2.000(4)	Co1–O1	2.0823(13)
Cu1–N9$^{\#1}$	2.014(4)	Co1–O1$^{\#1}$	2.0823(13)
Cu1–N8$^{\#1}$	2.109(3)	Co1–N9$^{\#2}$	2.1838(16)
Cu1–Cl1	2.3174(11)	Co1–N9$^{\#3}$	2.1838(16)
Cu1–Cl2	2.4316(13)	Co1–N7	2.2060(16)
		Co1–N7$^{\#1}$	2.2060(16)
N7–Cu1–N9$^{\#1}$	164.31(15)	O1$^{\#1}$–Co1–O1	180.0
N7–Cu1–N8$^{\#1}$	87.06(13)	O1$^{\#1}$–Co1–N9$^{\#2}$	92.50(6)
N9$^{\#1}$–Cu1–N8$^{\#1}$	86.10(13)	O1–Co1–N9$^{\#2}$	87.50(6)
N7–Cu1–Cl1	89.52(10)	O1$^{\#1}$–Co–N9$^{\#3}$	87.50(6)
N9$^{\#1}$–Cu1–Cl1	90.45(10)	O1–Co1–N9$^{\#3}$	92.50(6)
N8$^{\#1}$–Cu1–Cl1	153.97(11)	O1$^{\#1}$–Co1–N7$^{\#1}$	87.97(5)
N7–Cu1–Cl2	99.04(11)	O1–Co1–N7$^{\#1}$	92.03(5)
N9$^{\#1}$–Cu1–Cl2	96.12(11)	O1$^{\#1}$–Co1–N7	92.03(6)
N8$^{\#1}$–Cu1–Cl2	101.07(10)	O1–Co1–N7	87.97(5)
Cl1–Cu1–Cl2	104.95(4)	N9$^{\#2}$–Co1–N9$^{\#3}$	180.0
		N9$^{\#2}$–Co1–N7$^{\#1}$	86.05(6)
		N9$^{\#3}$–Co1–N7$^{\#1}$	93.95(6)
		N9$^{\#2}$–Co1–N7	93.95(6)
		N9$^{\#3}$–Co1–N7	86.05(6)
		N7$^{\#1}$–Co1–N7	180.0

[a] Symmetry codes for **1**, #1: –*x* + 2, –*y* + 1, –*z*; symmetry codes for **2**, #1: –*x*, –*y* + 1, –*z* + 2; #2: –*x*, –*y* + 2, –*z* + 1; #3: *x*, *y* – 1, *z* + 1.

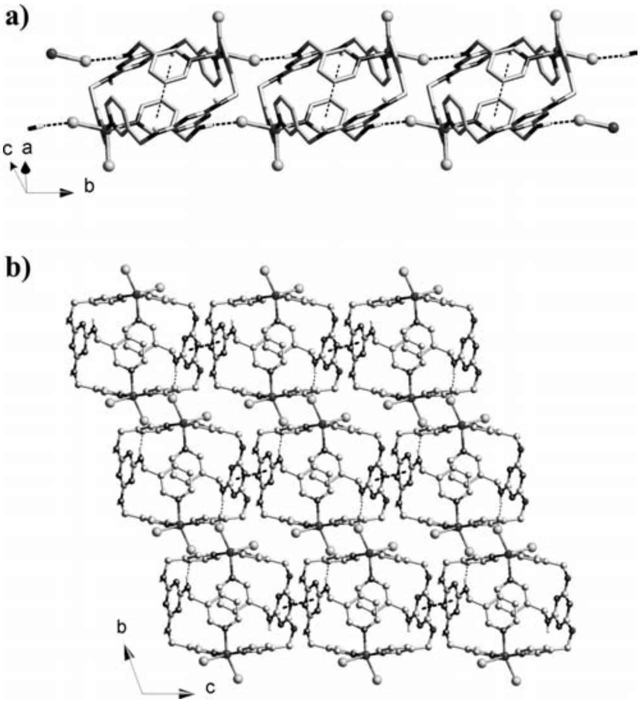


Figure 2. a) Hydrogen-bond (N$_{amine}$–H···Cl–Cu)-assisted supramolecular chain structure of **1** running along the crystallographic *b* axis. b) Supramolecular sheeted arrays in the *bc* plane, supported by weak intermolecular π–π interactions (dashed lines) and N$_{amine}$–H···Cl–Cu hydrogen bonds (dotted lines).

stack exactly atop of each other, small infinite open channels naturally form along the crystallographic *b* axis, in which lattice water and ethanol molecules reside forming numerous N–H···O$_{water}$, O$_{water}$–H···O$_{ethanol}$, O$_{water}$–H···N, and O$_{ethanol}$–H···Cl–Cu hydrogen bonds [D···A 2.788(7)–3.162(5) Å; D–H···A 146–170°; Figure S4]. Interestingly, two *m*-H$_3$tpat ligands, each owning a DAD-type aminotriazine moiety, and two lattice water molecules, which potentially serve pseudo-ADA-type hydrogen-bonding motifs, dominate the formation of two sets of inversion-center-related sequenced pseudo-complementary DAD–ADA triple hydrogen bonds (Figure S5). The supramolecular polycyclic chains pack through the formation of intermolecular π–π interactions between two triazine cores of two *m*-H$_3$tpat ligands of two neighboring metallacyclophanes, which show a centroid contact of 3.57 Å, a plane···plane distance of 3.21 Å, a horizontal displacement of 1.56 Å, and an angle of 26° between the ring normal and the centroid vector, giving rise to a sheeted supramolecular assembly in the *bc* plane (Figure 2, b). Similarly, another type of sheeted supramolecular assembly forms in the *ab* plane due to a second type of intermolecular π–π interactions between two parallel out-of-cavity pyridine rings of two close *m*-H$_3$tpat ligands from two neighboring metallacyclophanes in two

N_{amine}–H···Cl–Cu hydrogen-bond-assisted supramolecular chains (Figure S6). Here, the ring normal and the vector between the ring centroids form an angle of about 27° and the centroid contact, the plane···plane distance, and the horizontal displacement are 3.63, 3.25, and 1.62 Å, respectively. However, such an offset π-stacking interaction also has a contribution from a π–σ attraction, which increases with increasing offset.[33]

Synthesis and Crystal Structure of [Co(*m*-H_3tpat)$_2$(H_2O)$_2$]Cl_2 (2)

Slow diffusion of a methanol solution of *m*-H_3tpat into an aqueous solution of $CoCl_2$ with a mixture of MeOH and H_2O as buffer at room temperature yielded a pale-pink crystalline product characterized as [Co(*m*-H_3tpat)$_2$(H_2O)$_2$]Cl_2 (**2**; Scheme 2).

As shown in Figure 3, the asymmetric unit contains half of a cobalt ion lying on an exact crystallographic inversion center and one *m*-H_3tpat ligand, one coordinated aqua ligand, and one chloride counteranion in general positions. The hexacoordinate cobalt(II) ion is in an octahedral environment comprising of two crystallographically related pairs of *N*-coordinating pyridyl moieties belonging to four different *m*-H_3tpat ligands [Co–N 2.1838(16)–2.2060(16) Å; Table 1] and two *trans*-coordinating aqua ligands [Co–O 2.0823(13) Å]. The *m*-H_3tpat ligand exists in a *cis–trans–trans* conformation with an asymmetric-configured all-amino resonative aminotriazine moiety. Only two of the three pyridyl donating groups in the *m*-H_3tpat ligand, which have a relative *anti–anti* orientation, are involved in the binding of the two cobalt ions separated by 15.26 Å, therefore leaving the third one uncoordinated. Unlike in the case of **1**, the three terminal pyridine rings are neither perpendicular nor parallel to each other as the dihedral angles between them are around 53, 61, and 66°, respectively. However, they are all nearly perpendicular to the central triazine ring with slight deviations of ca. 1–15° (the three dihedral angles are ca. 75, 76, and 89°, respectively).

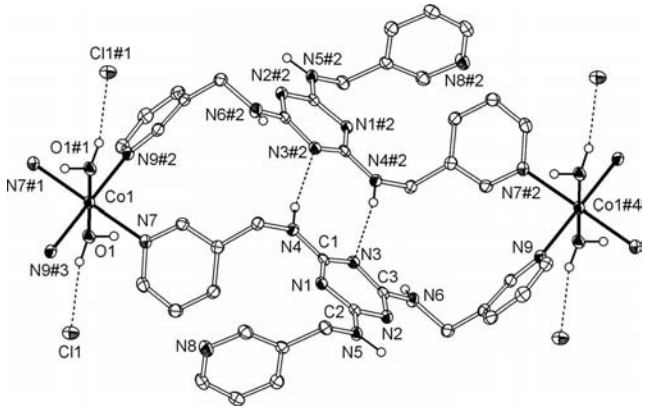


Figure 3. ORTEP drawing of the fundamental repeating unit of **2** showing the coordination environment around the metal ions and the coordination mode of the *m*-H_3tpat ligand with selected numbering scheme. Pertinent O_{aqua}–H···Cl and N_{amine}–H···$N_{triazine}$ hydrogen bonds are represented by dotted lines. Carbon-bonded hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Symmetry transformations used to generate equivalent atoms, #1: –*x*, –*y* + 1, –*z* + 2; #2: –*x*, –*y* + 2, –*z* + 1; #3: *x*, *y* – 1, *z* + 1; #4: *x*, *y* + 1, *z* – 1.

The coordination-directed motif of **2** suits an extended cationic chain structure with metallacyclic repeating units of {Co_2(*m*-H_3tpat)$_2$} running along the crystallographic *c* axis (Figure 4, a). Of particular interest, the two *m*-H_3tpat ligands from the same {Co_2(*m*-H_3tpat)$_2$} metallacycle form a set of complementary double N_{amine}–H···$N_{triazine}$ hydrogen bonds with N···N distances of 3.151(2) Å between the two aminotriazine moieties (see Table S1, Supporting Information), which undoubtedly increase the stability of the coordinative chain structure. Through chain-to-chain O_{aqua}–H···N_{py} hydrogen bonds [O···N 2.765(2) Å] between the coordinated aqua ligands and the uncoordinated pyridyl groups of the *m*-H_3tpat ligands, the coordinative chain can extend into a supramolecular sheeted structure further supported by N_{amine}–H···Cl hydrogen bonds (Figure 4, b). The chloride counteranions act as key hinges in organizing the overall three-dimensional supramolecular network through mainly O_{aqua}–H···Cl and N_{amine}–H···Cl hydrogen-bonding interactions [O/N···Cl 3.0618(14)–3.3727(17) Å] and also weaker C–H···Cl interactions [C···Cl 3.612(2)–3.646(2) Å; Figure S7]. However, no pertinent directed π–π interactions are observed. On the other hand, in view of the anion coordination,[34] it is worth noting that the chloride anion has a coordination number of five, which forms contacts with two N_{amine}–H, one O_{aqua}–H, one C_{py}–H, and one C_{alkyl}–H hydrogen atom (Figure S8).

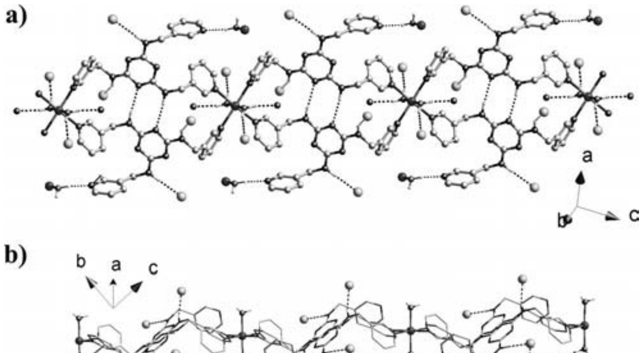


Figure 4. a) View of the coordinative chain structure in **2** illustrating the complementary double N_{amine}–H···$N_{triazine}$ hydrogen bonds formed between the aminotriazine moieties. Other types of hydrogen-bonding interactions around the chain are also shown. b) View of the O_{aqua}–H···N_{py} and N_{amine}–H···Cl hydrogen-bond-assisted two-dimensional supramolecular sheet structure in **2**.

Thermogravimetric Analysis

Thermogravimetric (TG) analyses of the tripodal semi-rigid ligand *m*-H_3tpat, the discrete metallacyclophane

1·$2H_2O$·2EtOH, and the polymeric coordinative chain structure **2** were performed under nitrogen to examine the thermal stabilities of these compounds (Figure S9). The TG analysis of *m*-H_3tpat exhibits high thermal stability as no weight loss took place before the structure began to decompose on approaching 320 °C. The TG curve of the partially desolvated material **1**·$2H_2O$·0.75EtOH illustrates that the lattice ethanol molecules were released between room temperature and 52 °C (found 3.0%, calcd. 3.0%), water molecules were lost between 170 and 200 °C (found 3.3%, calcd. 3.2%), and the metallacyclophane structure of **1** decomposed when the temperature was raised to 235 °C. For **2**, the TG trace is largely unchanged until the two ligating water molecules per formula started to leave at temperatures between 150 and 185 °C (found 4.5%, calcd. 3.7%) with the coordination network decomposing at around 320 °C.

Conclusion

We have successfully synthesized a conformationally flexible, tripodal, semi-rigid ligand, *m*-H_3tpat, which was treated with copper(II) chloride and cobalt(II) chloride to yield a discrete Cu^{II}-based metallacyclophane structure and a polymeric Co^{II}-based coordination chain structure with $\{Co_2(m\text{-}H_3tpat)_2\}$ metallacyclic repeating units, respectively. The *m*-H_3tpat ligand in both complexes shows different geometries with a *cis–cis–cis* conformation existing in **1** and a *cis–trans–trans* conformation in **2**. However, the aminotriazine moiety of the *m*-H_3tpat ligand in both conformations appears to be an asymmetric-configured all-amino tautomer.

Experimental Section

Materials and Instruments: Chemical reagents were purchased commercially and were used as received without further purification. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker AMX-300 Solution-NMR spectrometer. All chemical shifts are reported in δ units with reference to the residual protons of the deuteriated solvent. Coupling constants are given in Hz. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were recorded with a Bruker Daltonics flexAnalysis mass spectrometer. Thermogravimetric (TG) analyses were performed under nitrogen with a Perkin–Elmer Pyris 1 TG analyzer. Infrared (IR) spectra were recorded with a Perkin–Elmer RX1 FT-IR spectrometer. Elemental analyses (C,H,N) were performed with an Elementar Vario EL III analytical instrument.

2,4,6-Tris(3-picolylamino)-1,3,5-triazine (*m*-H_3tpat): A solution of cyanuric chloride (1.84 g, 10.0 mmol) in THF (50 mL) was slowly added to a solution of 3-(aminomethyl)pyridine (3.57 g, 33.0 mmol) in THF (50 mL) in an ice–water bath. Triethylamine (6.68 mL, 66.0 mmol) was then added at room temperature. The mixture was stirred at 80 °C and the reaction was monitored by TLC. The reaction was completed in approximately 48 h. After cooling to room temperature, the reaction solvent was removed under reduced pressure. The residue was extracted with an aqueous solution of potassium carbonate [aq. K_2CO_3, 4 equiv.] and dichloromethane (2 × 50 mL) followed by H_2O/CH_2Cl_2. The organic extracts were combined and dried with anhydrous $MgSO_4$. The crude product was purified by column chromatography (silica gel, $MeOH/CH_2Cl_2$ = 1:10 as eluent). If necessary, crystallization from $MeOH/H_2O$ was performed to obtain the pure product as a pale-yellow solid; yield 74% (2.96 g, 7.42 mmol). ^1H NMR ([D_6]-DMSO): δ = 8.46 (br. d, *J* = 22 Hz, 3 H), 8.39 (br. s, 3 H), 7.59 (br. dd, *J* = 41, 6 Hz, 3 H), 7.38–7.12 (br. m, 6 H), 4.38 (br. s, 6 H) ppm. $^{13}C\{^1H\}$ NMR ([D_6]DMSO): δ = 165.96, 148.97, 147.94, 136.25, 135.16, 123.49, 41.22 ppm. IR (KBr pellet): $\tilde{\nu}$ = 3424, 3250, 3112, 2945, 1629, 1539, 1509, 1449, 1407, 1359, 1317, 1216, 1162, 1102, 1072, 1030, 958, 922, 809, 785, 707, 618, 540, 432 cm^{-1}. MS (MALDI-TOF): *m/z* = 400.03 $[M]^+$. $C_{12}H_{13}N_3$ (199.25): calcd. C 63.14, H 5.30, N 31.50; found C 63.12, H 5.31, N 31.61.

$[Cu_2Cl_4(m\text{-}H_3tpat)_2]$·$2H_2O$·2EtOH (1·$2H_2O$·2EtOH): A solution of *m*-H_3tpat (19.9 mg, 5.0×10^{-2} mmol) in EtOH (5 mL) was carefully layered on top of a mixture of EtOH/H_2O (6 mL, 1:1 v/v, middle) and a solution of $CuCl_2$ (26.9 mg, 2.0×10^{-1} mmol) in H_2O (5 mL, bottom) at room temperature. The solution was allowed to stand for approximately 3 weeks, which resulted in the formation of blue-colored plate-shaped crystals; yield 72% (21.6 mg, 1.8×10^{-2} mmol). IR (KBr pellet): $\tilde{\nu}$ = 3783, 3435, 3328, 3071, 2969, 2933, 1563, 1526, 1437, 1413, 1359, 1329, 1162, 1114, 1060, 958, 934, 809, 707, 647, 527 cm^{-1}. $C_{42}H_{42}Cl_4Cu_2N_{18}$·$6H_2O$ (1175.90): calcd. C 42.90, H 4.63, N 21.44; found C 42.71, H 4.67, N 21.02.

$[Co(m\text{-}H_3tpat)_2(H_2O)_2]Cl_2$ (2): A solution of *m*-H_3tpat (19.8 mg, 5.0×10^{-2} mmol) in MeOH (5 mL) was carefully layered on top of a mixture of MeOH/H_2O (6 mL, 1:1 v/v, middle) and a solution of $CoCl_2$ (25.9 mg, 1.9×10^{-1} mmol) in H_2O (5 mL, bottom) at room temperature. The solution was allowed to stand for approximately 3 months, which led to the formation of pale-pink crystals; yield 80% (19.4 mg, 2.0×10^{-2} mmol). IR (KBr pellet): $\tilde{\nu}$ = 3741, 3262, 3112, 3041, 2939, 1610, 1563, 1532, 1503, 1431, 1341, 1192, 1150, 1114, 1054, 928, 809, 725, 635, 581, 516, 480, 420 cm^{-1}. $C_{42}H_{46}Cl_2CoN_{18}O_2$ (964.77): calcd. C 52.29, H 4.81, N 26.13; found C 51.56, H 4.84, N 25.86.

Crystal Structure Determination: Single-crystal X-ray diffraction analysis was performed by using a Bruker Smart CCD diffractometer equipped with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). Intensity data were collected at 296(2) K within the limits of $1.90° \leq \theta \leq 25.13°$ for **1**·$2H_2O$·2EtOH and $1.59° \leq \theta \leq 25.04°$ for **2**. Starting models for structure refinement were solved by direct methods using SIR92[35] and the structural data were refined by full-matrix least-squares methods on F^2 using the WINGX[36] and SHELX-97[37] program packages. Anisotropic thermal factors were assigned to non-hydrogen atoms. Carbon-bonded hydrogen atoms were generated geometrically and assigned isotropic thermal parameters. Oxygen- and nitrogen-bonded hydrogen atoms were structurally evident in difference Fourier maps and refined isotropically in the riding-model approximation with bond length and angle restraints. Experimental details of X-ray data collection and refinements are summarized in Table 2.

CCDC-797542 (for **1**·$2H_2O$·2EtOH) and -797543 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): NMR and MS spectra of *m*-H_3tpat (Figures S1–S3), additional structural diagrams for **1**·$2H_2O$·2EtOH (Figures S4–S6) and **2** (Figures S7 and S8), TG diagram (Figure S9), and hydrogen-bonding parameters for **1**·$2H_2O$·2EtOH and **2** (Table S1).

Table 2. Crystallographic data for **1**·2H$_2$O·2EtOH and **2**.

	1·2H$_2$O·2EtOH	**2**
Empirical formula	$C_{46}H_{58}Cl_4Cu_2N_{18}O_4$	$C_{42}H_{46}Cl_2CoN_{18}O_2$
M_w	1195.98	964.80
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.5935(6)	8.4202(2)
b [Å]	11.2647(5)	10.4541(3)
c [Å]	11.4417(6)	13.0111(3)
α [°]	110.344(2)	80.3150(10)
β [°]	92.304(3)	83.0550(10)
γ [°]	91.190(3)	72.5300(10)
V [Å^3]	1278.28(11)	1073.89(5)
Z	1	1
T [K]	296(2)	296(2)
λ [Å]	0.71073	0.71073
$\rho_{\mathrm{calcd.}}$ [g cm^{-3}]	1.554	1.492
μ [mm^{-1}]	1.105	0.586
$F(000)$	618	501
GOF	1.059	1.046
R_1[a] [$I > 2\sigma(I)$]	0.0522	0.0302
wR_2[b] [$I > 2\sigma(I)$]	0.1377	0.0770
R_1[a] (all data)	0.0712	0.0369
wR_2[b] (all data)	0.1511	0.0810
Largest diff. peak/hole [e Å^{-3}]	1.631/–0. 663	0.571/–0.270

[a] $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

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[1] a) J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213–1214; b) M. W. Hosseini, *Acc. Chem. Res.* **2005**, *38*, 313–323.

[2] a) D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1257–1283; b) J. J. Perry IV, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400–1417; c) G. R. Desiraju, *Acc. Chem. Res.* **2002**, *35*, 565–573.

[3] a) P. M. van Calcar, M. M. Olmstead, A. L. Balch, *Chem. Commun.* **1996**, 2597–2598; b) C.-K. Chan, K.-K. Cheung, C.-M. Che, *Chem. Commun.* **1996**, 227–228; c) P. J. Stang, B. Olenyuk, D. C. Muddiman, R. D. Smith, *Organometallics* **1997**, *16*, 3094–3096.

[4] a) L. Carlucci, G. Ciani, S. Maggini, D. M. Proserpio, *Cryst. Growth Des.* **2008**, *8*, 162–165; b) J.-D. Lin, J.-W. Cheng, S.-W. Du, *Cryst. Growth Des.* **2008**, *8*, 3345–3353; c) Z. Tian, J. Lin, Y. Su, L. Wen, Y. Liu, H. Zhu, Q.-J. Meng, *Cryst. Growth Des.* **2007**, *7*, 1863–1867; d) L. Wen, Y. Li, Z. Lu, J. Lin, C. Duan, Q. Meng, *Cryst. Growth Des.* **2006**, *6*, 530–537; e) W.-L. Meng, G.-X. Liu, T.-A. Okamura, H. Kawaguchi, Z.-H. Zhang, W.-Y. Sun, N. Ueyama, *Cryst. Growth Des.* **2006**, *6*, 2092–2102; f) L. Carlucci, G. Ciani, D. M. Proserpio, *Cryst. Growth Des.* **2005**, *5*, 37–39; g) L. Zhang, X.-Q. Lü, C.-L. Chen, H.-Y. Tan, H.-X. Zhang, B.-S. Kang, *Cryst. Growth Des.* **2005**, *5*, 283–287; h) J. Fan, W.-Y. Sun, T.-A. Okamura, Y.-Q. Zheng, B. Sui, W.-X. Tang, N. Ueyama, *Cryst. Growth Des.* **2004**, *4*, 579–584; i) B. Sui, J. Fan, T.-A. Okamura, W.-Y. Sun, N. Ueyama, *New J. Chem.* **2001**, *25*, 1379–1381.

[5] M. Arunachalam, P. Ghosh, *CrystEngComm* **2010**, *12*, 1621–1627.

[6] a) G.-C. Xu, Y.-J. Ding, T.-A. Okamura, Y.-Q. Huang, Z.-S. Bai, Q. Hua, G.-X. Liu, W.-Y. Sun, N. Ueyama, *Cryst. Growth Des.* **2009**, *9*, 395–403; b) G.-C. Xu, Y.-J. Ding, T.-A. Okamura, Y.-Q. Huang, G.-X. Liu, W.-Y. Sun, N. Ueyama, *CrystEngComm* **2008**, *10*, 1052–1062; c) J. Fan, M. H. Shu, T. Okamura, Y. Z. Li, W. Y. Sun, W. X. Tang, N. Ueyama, *New J. Chem.* **2003**, *27*, 1307–1309; d) H. K. Liu, W. Y. Sun, W. X. Tang, H. Y. Tan, H. X. Zhang, Y. X. Tong, X. L. Yu, B. S. Kang, *J. Chem. Soc., Dalton Trans.* **2002**, 3886–3891; e) H.-K. Liu, H.-Y. Tan, J.-W. Cai, Z.-Y. Zhou, A. S. C. Chan, S. Liao, W. Xiao, H.-X. Zhang, X.-L. Yu, B.-S. Kang, *Chem. Commun.* **2001**, 1008–1009; f) H. K. Liu, W. Y. Sun, D. J. Ma, K. B. Yu, W. X. Tang, *Chem. Commun.* **2000**, 591–592.

[7] a) X.-F. Wang, Y. Lv, T.-A. Okamura, H. Kawaguchi, G. Wu, W.-Y. Sun, N. Ueyama, *Cryst. Growth Des.* **2007**, *7*, 1125–1133; b) Z.-H. Zhang, Y. Song, T.-A. Okamura, Y. Hasegawa, W.-Y. Sun, N. Ueyama, *Inorg. Chem.* **2006**, *45*, 2896–2902; c) W. Zhao, Y. Song, T.-A. Okamura, J. Fan, W.-Y. Sun, N. Ueyama, *Inorg. Chem.* **2005**, *44*, 3330–3336; d) J. Fan, H. F. Zhu, T. Okamura, W. Y. Sun, W. X. Tang, N. Ueyama, *Inorg. Chem.* **2003**, *42*, 158–162; e) J. Fan, B. Sui, T. Okamura, W. Y. Sun, N. Ueyama, *J. Chem. Soc., Dalton Trans.* **2002**, 3868–3873; f) H.-K. Liu, X. Tong, *Chem. Commun.* **2002**, 1316–1317; g) J. Fan, W.-Y. Sun, T.-A. Okamura, J. Xie, W.-X. Tang, N. Ueyama, *New J. Chem.* **2002**, *26*, 199–201; h) W. Y. Sun, J. Fan, T. Okamura, J. Xie, K. B. Yu, N. Ueyama, *Chem. Eur. J.* **2001**, *7*, 2557–2562; i) H. K. Liu, W. Y. Sun, W. X. Tang, T. Yamamoto, N. Ueyama, *Inorg. Chem.* **1999**, *38*, 6313–6316.

[8] C. E. Willans, S. French, L. J. Barbour, J.-A. Gertenbach, P. C. Junk, G. O. Lloyd, J. W. Steed, *Dalton Trans.* **2009**, 6480–6482.

[9] a) S. Y. Wan, Y. Z. Li, T. Okamura, J. Fan, W. Y. Sun, N. Ueyama, *Eur. J. Inorg. Chem.* **2003**, 3783–3789; b) S.-Y. Wan, J. Fan, T.-A. Okamura, H.-F. Zhu, X.-M. Ouyang, W.-Y. Sun, N. Ueyama, *Chem. Commun.* **2002**, 2520–2521.

[10] a) C. Y. Su, Y. P. Cai, C. L. Chen, M. D. Smith, W. Kaim, H. C. zur Loye, *J. Am. Chem. Soc.* **2003**, *125*, 8595–8613; b) C. Y. Su, Y. P. Cai, C. L. Chen, F. Lissner, B. S. Kang, W. Kaim, *Angew. Chem.* **2002**, *114*, 3519–3523; *Angew. Chem. Int. Ed.* **2002**, *41*, 3371–3375.

[11] X.-L. Zhang, C.-P. Guo, Q.-Y. Yang, W. Wang, W.-S. Liu, B.-S. Kang, C.-Y. Su, *Chem. Commun.* **2007**, 4242–4244.

[12] A. K. Bar, R. Chakrabarty, P. S. Mukherjee, *Inorg. Chem.* **2009**, *48*, 10880–10882.

[13] C. M. Hartshorn, P. J. Steel, *Chem. Commun.* **1997**, 541–542.

[14] M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649–1650.

[15] a) G.-X. Liu, Y.-Q. Huang, Q. Chu, T.-A. Okamura, W.-Y. Sun, H. Liang, N. Ueyama, *Cryst. Growth Des.* **2008**, *8*, 3233–3245; b) H.-F. Zhu, J. Fan, T.-A. Okamura, Z.-H. Zhang, G.-X. Liu, K.-B. Yu, W.-Y. Sun, N. Ueyama, *Inorg. Chem.* **2006**, *45*, 3941–3948; c) Z.-H. Zhang, T.-A. Okamura, Y. Hasegawa, H. Kawaguchi, L.-Y. Kong, W.-Y. Sun, N. Ueyama, *Inorg. Chem.* **2005**, *44*, 6219–6227; d) H.-F. Zhu, Z.-H. Zhang, W.-Y. Sun, T.-A. Okamura, N. Ueyama, *Cryst. Growth Des.* **2005**, *5*, 177–182.

[16] a) H. Ohi, Y. Tachi, S. Itoh, *Inorg. Chem.* **2004**, *43*, 4561–4563; b) E. Leize, A. van Dorsselaer, R. Kramer, J.-M. Lehn, *J. Chem. Soc., Chem. Commun.* **1993**, 990–993.

[17] S. N. Wang, J. Bai, Y. Z. Li, Y. Pan, M. Scheer, X. Z. You, *CrystEngComm* **2007**, *9*, 228–235.

[18] G. Wu, X.-F. Wang, T.-A. Okamura, W.-Yi. Sun, N. Ueyama, *Inorg. Chem.* **2006**, *45*, 8523–8532.

[19] a) Q.-Y. Yang, S.-R. Zheng, R. Yang, M. Pan, R. Cao, C.-Y. Su, *CrystEngComm* **2009**, *11*, 680–685; b) D. J. Bray, L.-L. Liao, B. Antonioli, K. Gloe, L. F. Lindoy, J. C. McMurtrie, G. Wei, X.-Y. Zhang, *Dalton Trans.* **2005**, 2082–2083; c) M. Hong, Y. Zhao, W. Su, R. Cao, M. Fujita, Z. Zhou, A. S. C. Chan, *Angew. Chem.* **2000**, *112*, 2586–2588; *Angew. Chem. Int. Ed.* **2000**, *39*, 2468–2470.

[20] a) S. N. Wang, J. Bai, H. Xing, Y. Z. Li, Y. Song, Y. Pan, M. Scheer, X. Z. You, *Cryst. Growth Des.* **2007**, *7*, 747–754; b) S. N. Wang, H. Xing, J. Bai, Y. Z. Li, Y. Pan, M. Scheer, X. Z. You, *Chem. Commun.* **2007**, 2293–2295; c) S.-N. Wang, J. Bai, Y.-Z. Li, Y. Pan, M. Scheer, X.-Z. You, *CrystEngComm* **2007**, *9*, 1084–1095.

[21] A. K. Mishra, S. Verma, *Inorg. Chem.* **2010**, *49*, 3691–3693.

[22] a) B.-C. Tzeng, T.-H. Chiu, B.-S. Chen, G.-H. Lee, *Chem. Eur. J.* **2008**, *14*, 5237–5245; b) Y. Wang, T.-A. Okamura, W.-Y. Sun, N. Ueyama, *Cryst. Growth Des.* **2008**, *8*, 802–804; c) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 2607–2614; d) D. Moon, S. Kang, J. Park, K. Lee, R. P. John, H. Won, G. H. Seong, Y. S. Kim, G. H. Kim, H. Rhee, M. Soo Lah, *J. Am. Chem. Soc.* **2006**, *128*, 3530–3531; e) J. Fan, H.-F. Zhu, T.-A. Okamura, W.-Y. Sun, W.-X. Tang, N. Ueyama, *Chem. Eur. J.* **2003**, *9*, 4724–4731.

[23] a) M. J. Prakash, Y. Zou, S. Hong, M. Park, M.-P. N. Bui, G. H. Seong, M. S. Lah, *Inorg. Chem.* **2009**, *48*, 1281–1283; b) T. Min, B. Zheng, J. Bai, R. Sun, Y. Li, Z. Zhang, *CrystEngComm* **2010**, *12*, 70–72; c) R. Sun, Y. Z. Li, J. Bai, Y. Pan, *Cryst. Growth Des.* **2007**, *7*, 890–894; d) R. Sun, S. N. Wang, H. Xing, J. Bai, Y. Z. Li, Y. Pan, X. Z. You, *Inorg. Chem.* **2007**, *46*, 8451–8453.

[24] a) G.-C. Xu, Q. Hua, T.-A. Okamura, Z.-S. Bai, Y.-J. Ding, Y.-Q. Huang, G.-X. Liu, W.-Y. Sun, N. Ueyama, *CrystEngComm* **2009**, *11*, 261–270; b) J.-Y. Wu, Y.-F. Lin, C.-H. Chuang, T.-W. Tseng, Y.-S. Wen, K.-L. Lu, *Inorg. Chem.* **2008**, *47*, 10349–10356.

[25] B. Antonioli, B. Büchner, J. K. Clegg, K. Gloe, K. Gloe, L. Götzke, A. Heine, A. Jäger, K. A. Jolliffe, O. Kataeva, V. Kataev, R. Klingeler, T. Krause, L. F. Lindoy, A. Popa, W. Seichter, M. Wenzel, *Dalton Trans.* **2009**, 4795–4805.

[26] a) H.-F. Ji, X. Xu, *Langmuir* **2010**, *26*, 4620–4622; b) S. Yagai, S. Hamamura, H. Wang, V. Stepanenko, T. Seki, K. Unoike, Y. Kikkawa, T. Karatsu, A. Kitamura, F. Würthner, *Org. Biomol. Chem.* **2009**, *7*, 3926–3929; c) J. Hamblin, S. P. Argent, A. J. Blake, C. Wilson, N. R. Champness, *CrystEngComm* **2008**, *10*, 1782–1789; d) F. Silly, A. Q. Shaw, M. R. Castella, G. A. D. Briggs, *Chem. Commun.* **2008**, 1907–1909; e) C. Thalacker, A. Miura, S. de Feyter, F. C. de Schryver, F. Würthner, *Org. Biomol. Chem.* **2005**, *3*, 414–422.

[27] a) L. Zhang, J. Zhang, Z.-J. Li, J.-K. Cheng, P.-X. Yin, Y.-G. Yao, *Inorg. Chem.* **2007**, *46*, 5838–5840; b) C. Chen, C. W. Yeh, J. D. Chen, *Polyhedron* **2006**, *25*, 1307–1312; c) K. Sivashankar, A. Ranganathan, V. R. Pedireddi, C. N. R. Rao, *J. Mol. Struct.* **2001**, *559*, 41–48; d) D. M. L. Goodgame, I. Hussain, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **1999**, 2899–2900; e) R. Dorta, H. Stoeckli-Evans, U. Bodensieck, G. Süss-Fink, *J. Organomet. Chem.* **1998**, *553*, 307–315.

[28] a) P. Gamez, J. Reedijk, *Eur. J. Inorg. Chem.* **2006**, 29–42; b) H. Casellas, P. Gamez, J. Reedijk, I. Mutikainen, U. Turpeinen, N. Masciocchi, S. Galli, A. Sironi, *Inorg. Chem.* **2005**, *44*, 7918–7924; c) P. de Hoog, P. Gamez, M. Lüken, O. Roubeau, B. Krebs, J. Reedijk, *Inorg. Chim. Acta* **2004**, *357*, 213–218; d) P. de Hoog, P. Gamez, O. Roubeau, M. Lutz, W. L. Driessen, A. L. Spek, J. Reedijk, *New J. Chem.* **2003**, *27*, 18–21; e) P. Gamez, P. de Hoog, M. Lutz, W. L. Driessen, A. L. Spek, J. Reedijk, *Polyhedron* **2003**, *22*, 205–210; f) P. Gamez, P. de Hoog, M. Lutz, A. L. Spek, J. Reedijk, *Inorg. Chim. Acta* **2003**, *351*, 319–325; g) P. Gamez, P. de Hoog, O. Roubeau, M. Lutz, W. L. Driessen, A. L. Spek, J. Reedijk, *Chem. Commun.* **2002**, 1488–1489.

[29] a) C. Yuste, L. Cañadillas-Delgado, A. Labrador, F. S. Delgado, C. Ruiz-Pérez, F. Lloret, M. Julve, *Inorg. Chem.* **2009**, *48*, 6630–6640; b) L. A. Barrios, G. Aromí, A. Frontera, D. Quiñonero, P. M. Deyà, P. Gamez, O. Roubeau, E. J. Shotton, S. J. Teat, *Inorg. Chem.* **2008**, *47*, 5873–5881; c) S. Demeshko, S. Dechert, F. Meyer, *J. Am. Chem. Soc.* **2004**, *126*, 4508–4509; d) S. Demeshko, G. Leibeling, S. Dechert, F. Meyer, *Dalton Trans.* **2004**, 3782–3787.

[30] a) H. Walch, A.-K. Maier, W. M. Heckl, M. Lackinger, *J. Phys. Chem. C* **2009**, *113*, 1014–1019; b) P. A. Staniec, L. M. A. Perdigão, B. L. Rogers, N. R. Champness, P. H. Beton, *J. Phys. Chem. C* **2007**, *111*, 886–893; c) J. C. Swarbrick, B. L. Rogers, N. R. Champness, P. H. Beton, *J. Phys. Chem. B* **2006**, *110*, 6110–6114; d) S. Yagai, M. Higashi, T. Karatsu, A. Kitamura, *Chem. Mater.* **2005**, *17*, 4392–4398.

[31] a) A. Díaz-Ortiz, J. Elguero, C. Foces-Foces, A. de la Hoz, A. Moreno, S. Moreno, A. Sánchez-Migallón, G. Valiente, *Org. Biomol. Chem.* **2003**, *1*, 4451–4457; b) I. Ghiviriga, D. C. Oniciu, *Chem. Commun.* **2002**, 2718–2719.

[32] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

[33] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.

[34] a) S. O. Kang, R. A. Begum, K. Bowman-James, *Angew. Chem.* **2006**, *118*, 8048–8061; *Angew. Chem. Int. Ed.* **2006**, *45*, 7882–7894; b) K. Bowman-James, *Acc. Chem. Res.* **2005**, *38*, 671–678.

[35] *SIR92*, A program for crystal structure solution: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

[36] *WINGX*: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

[37] G. M. Sheldrick, *SHELX-97* (including *SHELXS* and *SHELXL*), University of Göttingen, Göttingen, Germany, **1997**.

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