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Meso-Helicates with Rigid Angular Tetradentate Ligand: Design, Molecular Structures, and Progress Towards Self-Assembly of Metal–Organic Nanotubes

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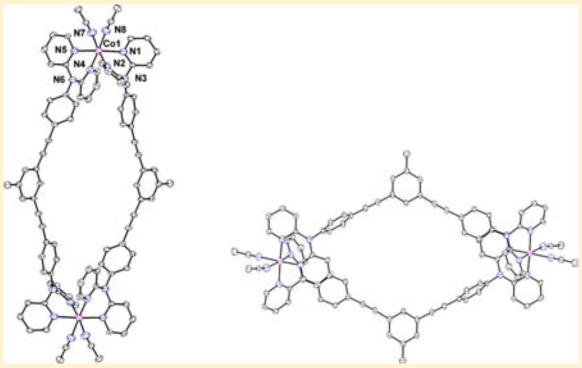
S *Supporting Information*

ABSTRACT: The self-assembly of two novel metallosupramolecular complexes of the general formulas $[L_2M_2(CH_3CN)_4][BF_4]_4$ (M = Co, **1a**; M = Ni, **1b**), where L stands for the tetradentate ligand 3,5-bis[4-(2,2′-dipyridylamino)phenylacetylenyl]toluene, is reported together with their molecular structures ascertained by single-crystal X-ray diffraction studies. Complexes **1a** and **1b** are isostructural and show the formation of dinuclear *meso*-helicates with the two octahedral metal centers displaying respectively Δ and Λ configurations. These *meso*-helicates display large nanocavities with metal---metal separation distance of >2 nm; furthermore, π–π-stacking occurs among individual units to form one-dimensional (1D) polymers which further autoassemble in another direction through π–π contacts among neighboring chains to generate a two-dimensional (2D) network with regular nanocavities. Our approach might be of interest to prepare metal–organic nanotubes via a bottom-up strategy depending on the assembling functional ligand and the geometry of molecular building block.



■ INTRODUCTION

Coordination-driven self-assembly has become an adequate tool to construct discrete nanoscopic metallosupramolecular species with predetermined shapes, geometries, and symmetries.[1−16] Directional metal–ligand bonds, a consequence of preferred coordination environments of the metal ions in combination with the appropriate rigid ligand, allow a certain control of the supramolecular architecture which is thermodynamically more stable than the starting components or any kinetically formed intermediates. Among the most aesthetically appealing metallosupramolecular architectures resulting from the self-assembly process are helicates.[17−24] Such compounds have been the focus of intense investigations. For instance Albrecht, Raymond, and co-workers demonstrated the influence of the ligand shape and the geometry of the metal ions as well as host–guest interaction are important factors that determine whether a helicate or a *meso*-helicate will be formed.[25−29]

In this paper we describe the design and synthesis of a novel rigid tetradentate ligand L displaying two dipyridylamino-phenylacetylenyl groups attached at the *meta*-positions of a central arene. Thus ligand 3,5-bis-[4-(2,2′-dipyridylamino)phenylacetylenyl]toluene (L) when combined with $MCl_2 \cdot 6H_2O$ (M = Co, Ni) provides two novel dinuclear *meso*-helicates where each metal center adopts opposite configuration whether Δ or Λ. The molecular structure of both *meso*-helicates were determined and showed that they display large cavities more than 2 nm, furthermore they show π–π stacking among individual units, which generate a one-dimensional (1D) chain of helicates. The latter undergoes further π–π interactions among individual chains providing a two-dimensional (2D) network with large cavities. This bottom-up approach holds promise for the preparation of metal–organic networks depending on the judicious choice of the geometry of the molecular building block and the assembling functional ligand. The magnetic properties of these compounds were also investigated. Overall these helicates with large cavities might show interesting applications for chemical transformation within confined cavities.

■ GENERAL EXPERIMENTAL PROCEDURES

All solvents used were reagent grade or better. Commercially available reagents were used as received. All experimental manipulations were carried out under argon using Schlenk techniques. IR spectra were recorded on a Bruker Tensor 27 equipped with a Harrick ATR. Elemental analyses were performed by microanalytical service of ICSN at Gif-sur-Yvette on a Perkin-Elmer 2400 apparatus. NMR experiments were carried out on a Bruker Avance 300 MHz spectrometer operating at 300 K with chemical shifts referenced to residual solvent peaks. Chemical shifts are reported on parts per million (ppm) and coupling constant (*J*) in hertz (Hz). Standard abreviations indicating multiplicity were used as follows: m = multiplet, t = triplet, d = doublet, s = singlet,

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b = broad. Magnetic measurements in direct current (dc) mode were performed on a Quantum Design MPMS SQUID on polycrystalline samples restrained in a plastic film. Data were corrected for the diamagnetism contributions of the samples using Pascal constants. The sample holder diamagnetism was measured and subtracted from the raw data.

Synthesis of 4-(2,2′-Dipyridylamino)-phenyl Iodide. 2,2′-Dipyridylamine (2,05 g, 12 mmol), 1,4-diiodobenzene (7,92 g, 24 mmol), cesium carbonate (1,20 g ; 14,40 mmol), *o*-phenanthroline (0,43 g, 2,40 mmol), and copper(I) iodide (0.17 g, 0,88 mmol) were placed in a 100 mL round-bottom flask. To the solid mixture 6 mL of dimethylformamide (DMF) was added, and the reaction flask was heated to 160 °C and stirred for 24 h. After the reaction mixture was cooled, water and dichloromethane were used to dissolve solids. The organic fractions were dried over anhydrous $MgSO_4$, and the product was isolated by using a chromatographic column of alumina neutral on hexane as eluent prior to removing the excess of reactant and then hexane/chloroform (1:1) as eluent to give the product as white crystals (3,9 g, 87% yield). IR (ATR): (ν, cm^{-1}) 1586, 1485, 1467, 1427, 1328, 1270, 1153, 1099, 1053, 1007, 990, 824, 769, 735, 714, 647, 615, 532, 509, 438, 412, 393, 326, 307, 236. ^1H NMR (300 MHz, $CDCl_3$) δ 8.33 (dd, J = 0.60, 6.00 Hz, 2H), 7.69 (d, J = 9.00 Hz, 2H), 7.59 (m, 2H), 7.01 (d, J = 9.00 Hz, 2H), 6.97 (m, 2H), 6.95 (d, J = 9.00 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 148.6, 144.8, 138.6, 137.7, 128.8, 118.6, 117.1, 89.5; Anal. Calcd for $C_{16}H_{12}IN_3$: C 51.49, H 3.24. Found: C 51.40, H 3.26.

Synthesis of 3,5-Bis[4-(2,2′-dipyridylamino)phenylacetylenyl]-toluene (L). Under an argon atmosphere CuI (0.011 g, 0.06 mmol) and $Pd(PPh_3)_2Cl_2$ (0.020 g, 0.03 mmol), followed by 3,5-diethynyltoluene (0.050 g, 0.28 mmol), were added to a solution of 4-(2,2′-Dipyridylamino)-phenyl iodide (0.116 g, 0.57 mmol) in 15 mL of a freshly distilled tetrahydrofuran (THF) and 15 mL of freshly distilled triethylamine. The resulting brown solution was stirred at room temperature for 24 h then diluted with ethylacetate (50 mL) and vigorously stirred with aqueous EDTA/NH_4OH (100 mL, 1M) for 1 h. The resulting organic phase was washed with saturated aqueous NH_4Cl (50 mL), water (50 mL), NaCl (50 mL), and dried with anhydrous $MgSO_4$. The solvent was removed under vacuum to give a reddish solid which was further purified by column chromatography of alumina neutral to give the tetradentate ligand L as a pale yellow solid (0.823 g, 72%). IR (ATR): (ν, cm^{-1}) 2206, 1582, 166, 1506, 1462, 1424, 1319, 1266, 1210, 1180, 1149, 1100, 1048, 1017, 990, 940, 860, 830, 770, 737, 700, 685, 657, 617, 601, 582, 537, 504, 460, 408, 379, 246. ^1H NMR (300 MHz, $CDCl_3$):δ 8.37 (dd, 4H), 7.61 (m, 4H), 7.58 (m, 4H), 7.51 (1H, s) 7.50 (d, 4H), 7.30 (s, 2H), 7.14 (d, 4H), 7.01 (d, 4H), 6.96 (m, 4H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 148.7, 145.1, 138.2, 137.7, 132.9, 132.0, 131.7, 126.3, 123.5, 119.7, 118.7, 117.5, 89.5, 88.8, 21.1. ES-MS (*m*/*z*): $[LH]^+$: 631.3; found: 631.4, $[LH_2]^{2+}$: 316.1; found: 316.3; Anal. Calcd for $C_{43}H_{30}N_6$: C 81.80, H 4.75. Found: C 80.90, H 4.99.

Synthesis of $[Co_2L_2(CH_3CN)_4]$ $[BF_4]_4$ (1a). To a solution of L (22,08 mg; 0,035 mmol) in 4 mL of THF, was added 4 mL of a solution of $Co(BF_4)_2 \cdot 6H_2O$ (7,95 mg; 0,0233 mmol) in 4 mL of EtOH under nitrogen atmosphere. The solution color becomes yellow and then a pale yellow suspension was formed. The reaction mixture was heated at 65 °C for 2 h then cooled at room temperature before removing the solvent under reduced pressure. The resulting crude was dissolved in 6 mL of acetonitrile and recrystallized from CH_3CN/ether through vapor diffusion affording yellow-orange crystals of **1a** (50.2 mg, 93%). IR (ATR): (ν, cm^{-1}) 1055 (B–F); ES-MS (*m*/*z*): $[Co_2L_2F_3]^+$: 1436.4; found: 1436,4 $[Co_2L_2F_2]^{2+}$: 708.7; found: 708.3; $[Co_2L_2(CH_3CN)_2]^{4+}$: 365.1; found: 365.3; $[Co_2L_2(CH_3CN)]^{4+}$: 354.9; found: 355.0; $[Co_2L_2]^{4+}$: 344.6; found: 344.8.

Synthesis of $[Ni_2L_2(CH_3CN)_4]$ $[BF_4]_4$ (1b). To a solution of L (22,08 mg; 0,035 mmol) in 4 mL of THF was added 4 mL of a solution of $Ni(BF_4)_2 \cdot 6H_2O$ (11,91 mg; 0,035 mmol) in 4 mL of EtOH under nitrogen atmosphere. The solution color becomes pale yellow and then evolved to a light blue suspension. The reaction mixture was heated at 65 °C for 2 h and then cooled at room temperature before removing the solvent under reduced pressure. The resulting crude was dissolved in 6 mL of acetonitrile and recrystallized from CH_3CN/ether through vapor diffusion affording violet crystals of **1b** (49 mg, 91%). IR (ATR): (ν, cm^{-1}) 1057 (B–F); ES-MS (*m*/*z*): $[Ni_2L_2F_3]^+$: 1434.4; found: 1434,3 $[Ni_2L_2F_2]^{2+}$: 708.2; found: 708.2; $[Ni_2L_2(CH_3CN)_4]^{4+}$: 385.1; found: 385.0.

X-ray Crystal Structure Determination of $[Co_2L_2(CH_3CN)_4]$ $[BF_4]_4$ (1a) and $[Ni_2L_2(CH_3CN)_4]$ $[BF_4]_4$ (1b). A single crystal of each compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII with graphite-monochromated Mo–Kα radiation (λ = 0.71073 Å). Data collection was performed with APEX2 suite (BRUKER). Unit-cell parameters refinement, integration, and data reduction were carried out with Bruker-SAINT program. SADABS (BRUKER) was used for multiscan absorption corrections.

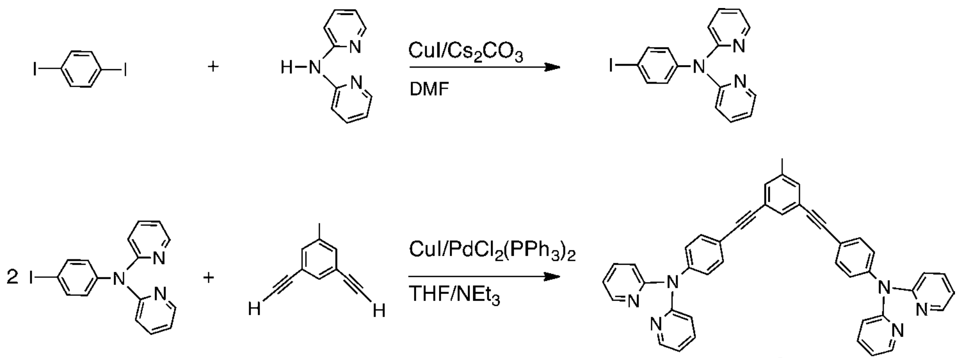
In the WinGX[50] suite of programs, the structures were solved with Sir92[51] or Superflip[52] and refined by full-matrix least-squares methods using SHELXL-97.[53] Almost all non-hydrogen atoms were refined anisotropically. A model of disorder was introduced for one of the $BF4^-$ anions and for a molecule of acetonitrile, the atoms of these moieties being the ones refined isotropically. H atoms were placed at calculated positions.

CCDC 945768, 945769 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.

■ RESULTS AND DISCUSSIONS

Preparation of 3,5-Bis[4-(2,2′-dipyridylamino)phenylacetylenyl]toluene (L) and Characterization. The bis(dipyridylaminophenylethynyl)toluene ligand L was synthesized in two steps: the first step involved the reaction of 1,4-diiodobenzene with dipyridylamine in DMF under reflux and in the presence of CuI to give after reaction workup 4-(2,2′-Dipyridylamino)-phenyl iodide as a white microcrystalline substance in 87% yield.[30] In a second step the latter was treated with 3,5-diethynyl-toluene

Scheme 1. Synthesis of L



L

following a Pd/Cu catalyzed Sonogashira coupling reaction to give the target tetradentate ligand 3,5-Bis[-(2,2′-dipyridylamino)-phenylacetylenyl]toluene after reaction workup. The novel ligand L was obtained as off-white microcrystalline solid in 72% yield (Scheme 1) and was fully characterized by NMR spectroscopy and infrared technique. Microanalytical data were also in accord with the proposed formula (see experimental section).

Coordination Chemistry of L and Formation of the *Meso*-Helicates 1a and 1b. The advantage of our ligand L resides in its rigidity, highly π-extended system, and the presence of two dipyridylamino groups available to strongly coordinate two metal centers to generate metallo-surpramolecular assemblies with large cavities. The presence of the specific functionalities promotes extensive $\pi-\pi$ interactions,[31−34] which might help to control the overall assembly in the hopes to obtain a metal−organic nanotube. It is surprising that metal−organic nanotubes remain largely unexplored[35−38] and in contrast to carbon based nanotubes and organic nanotubes which are well investigated.[39−42]

To this end we treated ligand L with 2 equiv of $CoBF_4 \cdot 6H_2O$ in EtOH/THF mixture for 2 h at 65 °C. Then the solvent was removed and the residue was recrystallized from CH_3CN/Et_2O to give yellow-orange crystals of **1a** in good yield. The electrospray (ES) mass spectrum was in accord with the proposed formula. The infrared spectrum revealed the presence of the alkyne $-C{\equiv}C-$ stretching bands at 2202−2214 cm^{-1} higher than that observed for the free ligand at 2206 cm^{-1}; furthermore a large band is visible centered at 1085 cm^{-1} attributed to the BF_4^- counterion.

To elucidate the molecular identity of **1a**, a suitable crystal for X-ray molecular structure study was carried out. Table 1 contains the crystal data for **1a**. Complex **1a** crystallizes in the triclinic space group $P\bar{1}$ and confirms the formation of a *meso*-helicate with the formula $[L_2Co_2(CH_3CN)_4][BF_4]_4$. A view of the cationic part of the complex and selected bond distances and angles are shown in Figure 1.

Table 1. Crystal Data for 1a and 1b

	1a	**1b**
CCDC reference	945768	945769
chemical formula	$C_{104}H_{87}B_4Co_2F_{16}N_{21}$	$C_{104}H_{87}B_4F_{16}N_{21}Ni_2$
formula weight	2096.05	2095.60
Z	1	1
T (K)	200(2)	200(2)
wavelength (Å)	0.71073	0.71073
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.2124(5)	12.2211(5)
b (Å)	12.2837(4)	12.3191(5)
c (Å)	20.3129(8)	20.3835(8)
α (deg)	80.283(2)	79.794(2)
β (deg)	82.214(2)	82.135(2)
γ (deg)	61.529(1)	61.101(1)
volume (Å^3)	2634.92(17)	2639.46(18)
density calculated (g cm^{-3})	1.321	1.318
crystal size (mm)	0.20 × 0.09 × 0.09	0.13 × 0.15 × 0.18
absorption coefficient (mm^{-1})	0.400	0.441
θ range	2.0−26.5	1.9−26.1
reflections collected/unique	36418/10893	32696/10395
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0683$ $wR_2 = 0.1950$	$R_1 = 0.0642$ $wR_2 = 0.1908$
final R indices [all data]	$R_1 = 0.1056$ $wR_2 = 0.2235$	$R_1 = 0.0882$ $wR_2 = 0.2099$
GOF on F^2	1.042	1.053
ΔFmin and ΔFmax (e Å^3)	1.651 and −0.645	0.89 and −050

The structure shows indeed that two rigid tetradentate ligands are chelating two cobalt centers; further each metal center is coordinated by two acetonitrile molecules which complement the distorted octahedral geometry of the cobalt with Co---N bond distances falling in the range of 2.080 Å to 2.160 Å in accord to those reported in the literature for cobalt complexes with 2, 2′-dipyridyl amino ligand.[43] The two metal centers have opposite configurations Δ and Λ respectively as expected for a *meso*-helicate. The two metal centers are far away by 2.179 nm, while the two facing central arenes are distal by 0.949 nm, to give a large nanocavity containing one molecule of acetonitrile. The BF_4 counterions are located outside the cavity. Further examination of the packing revealed important information; thus the metallo-supramolecular species undergoes a strong $\pi-\pi$ interaction (d = 3.32 Å) among individual units via the central arene to give a 1D chain of *meso*-helicates (Figure 2a). We also note that this 1D chain shows another $\pi-\pi$ contact ($d_{average}$ = 3.66 Å) with a neighbor chain which occurs between the alkyne unit $-C{\equiv}C-$ and the phenyl group of the phenyldiamine moiety to generate a 2D network containing large cavities (Figure 2c). In fact since the neighbor chains are offset by 7.44 Å, (distance between the two methyl groups of the central arene) it was not possible to form the desired metal−organic nanotubes.

We then examined the reaction of our tetradentate L with $Ni(BF_4)_2 \cdot 6H_2O$ to probe the effect of the metal ion on the formation of the metallosupramolecular assembly. The reaction was carried in a similar manner to the one described for the $Co(BF_4)_2 \cdot 6H_2O$. Upon recrystallization from CH_3CN/Et_2O violet crystals of **1b** were obtained. The spectroscopic data of **1b** was similar to that obtained for **1a**. After many attempts gratifyingly we were able to obtain crystals of **1b** convenient for X-ray structural determination.

The structure shows indeed the formation of a dinuclear *meso*-helicate of the formula $[L_2Ni_2(CH_3CN)_4][BF_4]_4$ (**1b**) and similar to the results obtained for **1a**. A view of the molecule of **1b** is shown in Figure 3. In this metallosupramolecular species two tetradentate ligands L hold the two Ni(II) metal centers. Furthermore two-coordinated acetonitriles are disposed in the equatorial positions and complement the distorted octahedral geometry around the metal center. The Ni---N bond distances range from 2.038 to 2.114 Å and are comparable to those reported for Ni(II) complexes displaying 2,2′-dipyridyl amine ligand.[44] As expected the two metals display opposite configuration Δ and Λ respectively. The two metal centers are separated by 2.174 nm while the two facing central arene units are at 0.950 nm and form a nanocavity which hosts one molecule of acetonitrile. These data are comparable to those obtained for **1a**. The four counterions are located outside the cavity. Examining the packing of **1b** showed similar results to that of **1a**, such as that these *meso*-helicates undergo two types of $\pi-\pi$ stacking to generate a 2D network containing large cavities.

Because of the rigid and π-conjugation nature of our tetradentate ligand L, we examined the magnetic properties of both compounds **1a**−**b** (vide infra).

Magnetic Properties of Complexes 1a, b. The magnetic behavior of **1a** and **1b** was investigated in the temperature range 2−300 K on polycrystalline samples in an applied field of 2500 Oe. The temperature dependences of $\chi_M T$ product vs T are shown in Figures 4 and 5 for **1a** and **1b**, respectively.

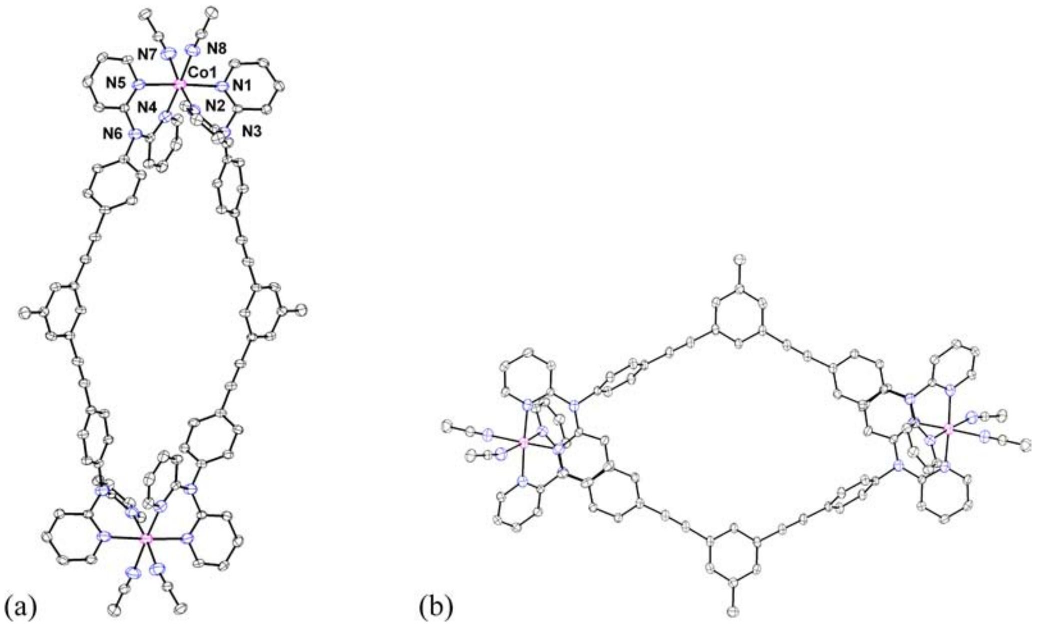


Figure 1. Views of the cationic part of *meso*-helicate **1a**. (a) Side view showing Δ and Λ configurations of the metal centers. (b) Top view showing the large cavity; anions and solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Co(1)−N(1) = 2.141(3), Co(1)−N(2) = 2.169(3), Co(1)−N(4) = 2.076(3), Co(1)−N(5) = 2.093(3), Co(1)−N(7) = 2.130(3), Co(1)−N(8) = 2.126(3), N(1)−Co(1)−N(2) = 85.74(12), N(4)−Co(1)−N(5) = 82.91(12), N(5)−Co(1)−N(7) = 90.15(13), N(8)−Co(1)−N1 = 87.54(13), N(8)−Co(1)−N(7) = 86.91(14), N(5)−Co(1)−N(8) = 94.87(12), N(7)−Co(1)−N1 = 92.53(13).

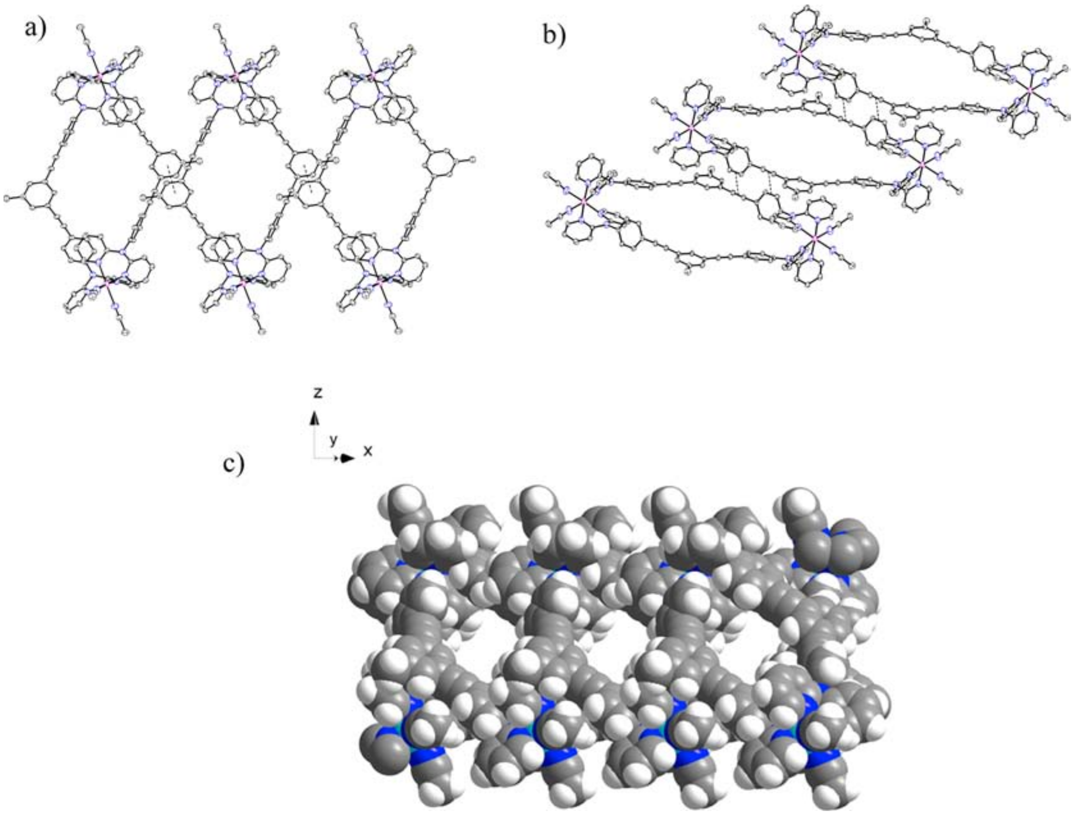


Figure 2. (a) 1D chain of *meso*-helicates **1a** formed by $\pi-\pi$ interaction between central arene. (b) $\pi-\pi$ stacking between neighbor chains showing the offset trend (only one *meso*-helicate of each chain is shown). (c) Overall generated 2D network with regular cavities.

For **1a** $\chi_M T$ is equal to 6.4 cm^3 mol^{-1} K at 300 K close to the typical value for two isolated Co^{II} ions. Upon cooling, the $\chi_M T$ product steadily decreases to reach a value of 3.7 cm^3 mol^{-1} K at 2 K. The $\chi_M T$ values and the shape of the curve do not show any evidence of exchange interaction between the two Co ions suggesting that the magnetic behavior can be modeled with

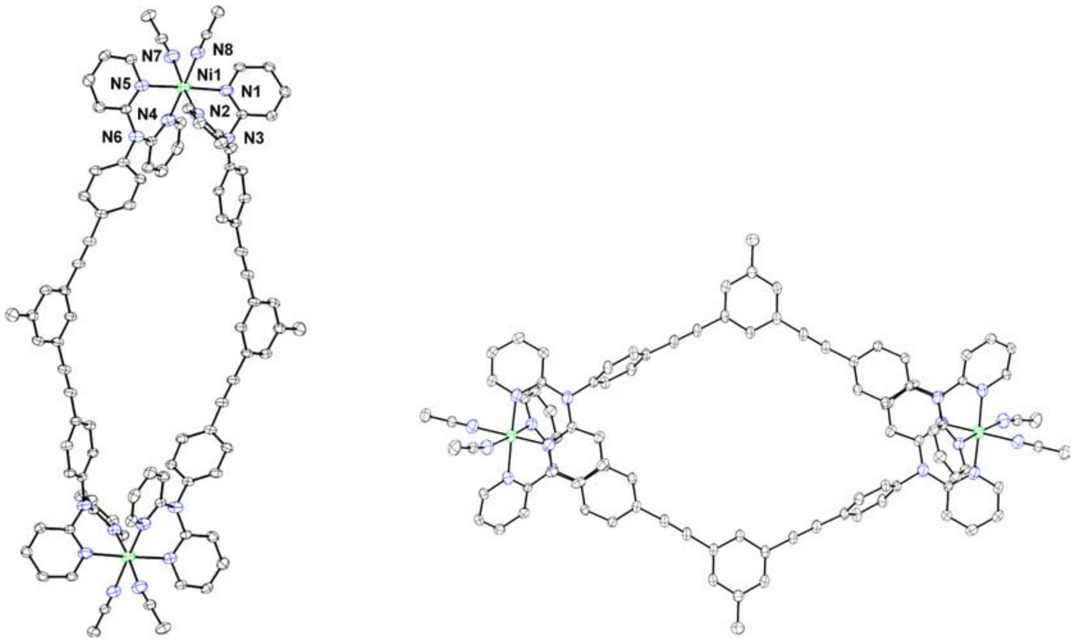


Figure 3. View of the cationic part of *meso*-helicate **1b** with atom numbering system. (a) Side view showing Δ and Λ configurations of the metal centers. (b) Top view showing large cavity; anions and solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−N(1) = 2.101(3), Ni(1)−N(2) = 2.114(3), Ni(1)−N(4) = 2.038(3), Ni(1)−N(5) = 2.053(3), Ni(1)−N(7) = 2.102(3), Ni(1)−N(8) = 2.090(3), N(1)−Ni(1)−N(2) = 86.40(11), N(4)−Ni(1)−N(5) = 84.48(11), N(5)−Ni(1)−N(7) = 89.06(12), N(8)−Ni(1)−N(1) = 87.13(11), N(8)−Ni(1)−N(7) = 87.72(12), N(5)−Ni(1)−N(8) = 94.48(11), N(7)−Ni(1)−N(1) = 92.45(12).

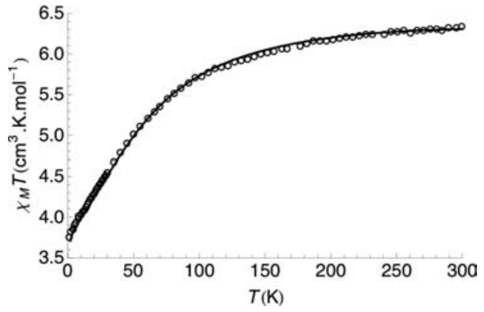


Figure 4. Experimental (open circle) and calculated (solid line) temperature dependence of $\chi_M T$ for **1a**.

two independent Co ions. The spin Hamiltonian for the Co ions is[45]

$$\mathbf{H}_{\mathrm{Co}} = -3\alpha\lambda/2\,\mathbf{L}\cdot\mathbf{S} + \Delta(\mathbf{L}_z^{\ 2} - 2/3) + \beta H(-3\alpha\mathbf{L}/2 + g_e\mathbf{S})$$

Where λ is spin−orbit coupling constant, and α is the orbital reduction factor arising from the covalent character of the metal−ligand bond. Δ is the energy gap between the singlet $^4A_2$ and doublet ^4E levels arising from the splitting of the $^4T_{1g}$ ground state under an axial distortion. The last term represents the Zeeman interaction. In this Hamiltonian the −3/2 coefficient is a scaling factor coming from the T ⇔ P isomorphism.[45] The least-squares fit of the experimental data using a full diagonalization of the Hamiltonian matrix led to α= 0.80, λ= −123. cm^{-1}, Δ=-652. cm^{-}.[45] Introduction of an exchange interaction term between the Co ions in the Hamiltonian does not lead to significative improvement of the quality of the fit showing that the interaction between the two Co ions is extremely weak.

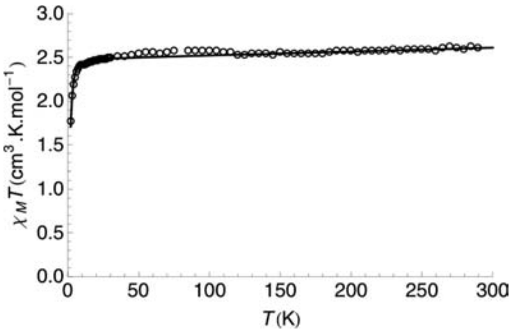


Figure 5. Experimental (open circle) and calculated (solid line) temperature dependence of $\chi_M T$ for **1b**.

For **1b** $\chi_M T$ value is constant and equal to 2.5 cm^3 mol^{-1} K in the 300−50 K temperature range. Below 50 K $\chi_M T$ product decreases to reach a value of 1.9 cm^3 mol^{-1} K at 2K. The Curie law observed above 50 K clearly shows that the interaction between the Ni ions is extremely weak. The decrease at low temperature could be due to zero field splitting (ZFS) on Ni ions or to exchange interaction between the Ni ions. Owing to the large distance between the two Ni ions the magnetic data has been modeled with only ZFS on Ni using the following spin Hamiltonian

$$\mathbf{H}_{\mathrm{Ni}} = g\beta H\mathbf{S} + D[\mathbf{S}_z^{\ 2} - S(S+1)/3]$$

The least-squares fit of the experimental data led to g = 2.22, D = 3.6 cm^{-1}.

As for the Co compound the magnetic data does not show any evidence of exchange interaction. In summary, both compounds magnetically behave as a monomer in spite of their binuclear structure, and there is no evidence of any coupling by a spin polarization mechanism through the *meta*-phenylene linkage.[46−49]

CONCLUDING REMARKS

In this paper, we reported the synthesis of a rigid angular tetradentate ligand L displaying a π-extended system with two dipyridylamino groups available to strongly coordinate two metal centers generating metallo-surpramolecular assemblies with large cavities. Indeed when L was treated with $MX_2\cdot 6H_2O$ salts (M = Co, Ni; X = BF_4), two *meso*-helicates $[L_2M_2(CH_3CN)_4]$-$[BF_4]_4$ (**1a**, **1b**) were formed. The X-ray molecular structure of either **1a** or **1b** confirmed the formation of a *meso*-helicate with a large cavity and metal−metal separation distances of >2 nm. These coordination assemblies undergo $\pi-\pi$ stacking in two different directions to generate 2D networks. The magnetic properties of these compounds were investigated and showed that magnetically the metal centers behave as monomers. Our future efforts will be devoted to study the coordination properties of this angular rigid ligand with other building blocks of different geometry in the hopes to prepare metal−organic nanotubes via a bottom-up strategy.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data of **1a** and **1b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Amouri, H.; Desmarets, C.; Moussa, J. *Chem. Rev.* **2012**, *112*, 2015.
(2) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810.
(3) Ward, M. D. *Chem. Commun.* **2009**, 4487.
(4) Fujita, M.; Ogura, K. *Coord. Chem. Rev.* **1996**, *148*, 249.
(5) Inokuma, Y.; Kawano, M.; Fujita, M. *Nat. Chem.* **2011**, 3, 349.
(6) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, 32, 975.
(7) Therrien, B. *J. Organomet. Chem.* **2011**, *696*, 637.
(8) Severin, K. *Chem. Commun.* **2006**, 3859.
(9) Han, Y.-F.; Jia, W.-G.; Yu, W.-B.; Jin, G.-X. *Chem. Soc. Rev.* **2009**, *38*, 3419.
(10) Bivaud, S.; Balandier, J.-Y.; Chas, M.; Allain, M.; Goeb, S.; Sallé, M. *J. Am. Chem. Soc.* **2012**, *134*, 11968.
(11) Dul, M.-C.; Pardo, E.; Lescouëzec, R.; Journaux, Y.; Ferrando-Soria, J.; Ruiz-GarcÌa, R.; Cano, J.; Julve, M.; Lloret, F.; Cangussu, D.; Pereira, C. L. M.; Stumpf, H. O.; Pasan, J.; Ruiz-Pèrez, C. *Coord. Chem. Rev.* **2010**, *254*, 2281.
(12) Amouri, H.; Rager, M. N.; Cagnol, F.; Vaisserman, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3636.
(13) Amouri, H.; Mimassi, L.; Rager, M. N.; Mann, B. E.; Guyard-Duhayon, C.; Raehm, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4543.
(14) Amouri, H.; Desmarets, C.; Bettoschi, A.; Rager, M. N.; Boubekeur, K.; Rabu, P.; Drillon, M. *Chem.—Eur. J.* **2007**, *13*, 5401.
(15) Desmarets, C.; Poli, F.; Le Goff, X. F.; Muller, K.; Amouri, H. *Dalton Trans.* **2009**, 10429.
(16) Desmarets, C.; Policar, C.; Chamoreau, L. M.; Amouri, H. *Eur. J. Inorg. Chem.* **2009**, 4396.
(17) Seeber, G.; Tiedemann, B. E. F.; Raymond, K. N. *Top. Curr. Chem.* **2006**, *265*, 147.
(18) Lehn, J. M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565.
(19) Lehn, J. M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995.
(20) Albrecht, M. *Chem. Rev.* **2001**, *101*, 3457.
(21) Provent, C.; Williams, A. F. *Perspect. Supramol. Chem.* **1999**, *5*, 135.
(22) Argent, S. P.; Adams, H.; Riis-Johannessen, T.; Jeffery, J. C.; Harding, L. P.; Mamula, O.; Ward, M. D. *Inorg. Chem.* **2006**, *45*, 3905.
(23) Bunzen, J.; Hovorka, R.; Lutzen, A. *J. Org. Chem.* **2009**, *74*, 5228.
(24) Fletcher, N. C.; Brown, R. T.; Doherty, A. P. *Inorg. Chem.* **2006**, *45*, 6132.
(25) Albrecht, M.; Burk, S.; Weis, P. *Synthesis* **2008**, 2963.
(26) Albrecht, M.; Issak, E.; Baumert, M.; Gossen, V.; Raabe, G.; Frohlich, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 2850.
(27) Albrecht, M. *Chem.—Eur. J.* **2000**, *6*, 3485.
(28) Albrecht, M.; Frohlich, R. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 797.
(29) Xu, J.; Parac, T. N.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2878.
(30) Kapnisti, M.; Hatzidimitriou, A. G. *Struct. Chem.* **2007**, *18*, 331.
(31) Tan, R.; Wang, Z.-B.; Li, Y.; Kozera, D. J.; Lu, Z.-H.; Song, D. *Inorg. Chem.* **2012**, *51*, 7039.
(32) Seward, C.; Pang, J.; Wang, S. *Eur. J. Inorg. Chem.* **2002**, 1390.
(33) Kang, Y.; Seward, C.; Song, D.; Wang, S. *Inorg. Chem.* **2003**, *42*, 2789.
(34) Branzea, D. G.; Fihey, A.; Cauchy, T.; El-Ghayoury, A.; Avarvari, N. *Inorg. Chem.* **2012**, *51*, 8545.
(35) Ostubo, K.; Wakabayashi, Y.; Ohara, J.; Yamamoto, S.; Matsuzaki, H.; Okamoto, H.; Nitta, K.; Uruga, T.; Kitagawa, H. *Nat. Mater.* **2011**, *10*, 291.
(36) Kilpin, K. J.; Gower, M. L.; Telfer, S. G.; Jameson, G. B.; Crowley, J. D. *Inorg. Chem.* **2011**, *50*, 1123.
(37) Sun, H.; Mei, H.; An, G.; Han, J.; Pan, Y. *CrystEngComm* **2011**, *13*, 734.
(38) Yamada, T.; Otsubo, K.; Makiurac, R.; Kitagawa, H. *Chem. Soc. Rev.* **2013**, *42*, 6655.
(39) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 988.
(40) Block, M. A. B.; Kaiser, C.; Khan, A.; Hecht, S. *Top. Curr. Chem.* **2005**, *245*, 89.
(41) Moralez, J. G.; Raez, J.; Yamazaki, T.; Motkuri, R. K.; Kovalenko, A.; Fenniri, H. *J. Am. Chem. Soc.* **2005**, *127*, 8307.
(42) Gong, B.; Shao, Z. *Acc. Chem. Res.* **2013** DOI: 10.1021/ar400030e and refs therein.
(43) Sarkar, B. N.; Bhar, K.; Kundu, S.; Fun, H.-K.; Ghosh, B. K. *J. Mol. Struct.* **2009**, *936*, 104.
(44) Wang, X.-T.; Wang, X.-H.; Wang, Z.-M.; Gao, S. *Inorg. Chem.* **2009**, *48*, 1301.
(45) Lines, M. E. *J. Chem. Phys.* **1971**, *55*, 2977.
(46) Weyland, T.; Costuas, K.; Mari, A.; Halet, J. F.; Lapinte, C. *Organometallics* **1998**, *17*, 5569.
(47) Fernandez, I.; Ruiz, R.; Faus, J.; Julve, M.; Lloret, F.; Cano, J.; Ottenwaelder, X.; Journaux, Y.; Munoz, M. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 3039.
(48) Glaser, T. *Coord. Chem. Rev.* **2013**, *257*, 140.
(49) Pascu, M.; Lloret, F.; Avarvari, N.; Julve, M.; Andruh, M. *Inorg. Chem.* **2004**, *43*, 5189.
(50) WinGX: Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(51) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(52) SUPERFLIP: Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786.
(53) SHELX: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.