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Synthesis and Structural Characterization of a Nonplanar Neutral [36]Metallacrown-12 Nickel Compound $[Ni(C_{13}H_9N_3O_2)(CH_3OH)]_{12}$

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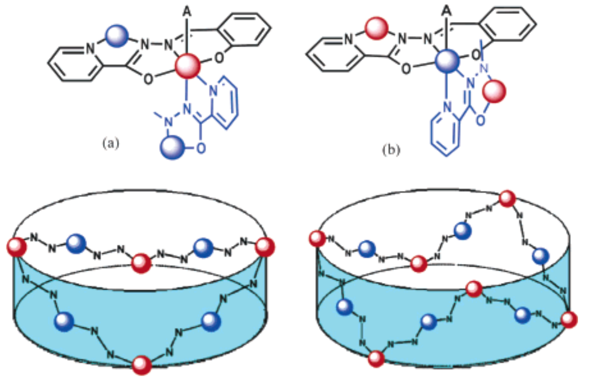
A nonplanar metallacrown $[Ni–N–N]_{12}$ was achieved using a pentadente ligand, salicylaldehyde 2-pyridinecarboxylhydrazone (H_2L) via a new modular self-assembly approach. The special bridging models of the ligand forced the macrocycle to form in a specific size with the wavelike conformation.

Metallacrowns have been one kind of important compounds in recent years due to their interesting molecular architectures, magnetic properties, and selective recognitions of cations and anions.[1−4] While metallacrowns have been prepared with ring sizes ranging from 9-metallacrown-3 (9-Mc-3)[5] to 36-metallacrown-12 (36-Mc-12),[6] the difficulties to achieve stable metallacrowns with high nuclearity are increasing. As the sizes of metallacrowns increased, controlling the M−M−M angle for a special polygon is beyond the precision of the coordination chemistry. Thus, new rational strategies to construct high nuclear metallacrowns are required. As the continuance of our research work in metallamacrocyclices,[7] we intend to modify the ring size and the physical properties of the metallamacrocycles. In this contribution, we outline our initial work on a nonplanar neutral [36]metallacrown-12 (36-Mc-12) nickel compound by using a potential pentadentate Schiff-base ligand (Scheme 1), salicylaldehyde 2-pyridinecarboxylhydrazone (H_2L).[8]

Scheme 1. Bridge Models of the Ligand; A Is the Auxiliary Ligand



The ligand has the potential to bridge the metal ions in two different ways: (a) the pyridine nitrogen atom occupies the trans position of the imino nitrogen atom with an M−M−M angle of about 90° and (b) the amide nitrogen atom occupies the trans position of the imino nitrogen atom with the M−M−M angle in the range of about 130−150°. Such a versatile bridging model provides the opportunity to connect the metal ions together alternatively, forming new metallacrown $[M−N−N]_n$, in which one kind of the metal atoms, M_1 (red ball), occupy the peaks and valleys of the ring and the other kind of the metal atoms, M_2 (blue ball), position in the middle. Theoretically, only the $[M−N−N]_n$ ring with $n = 8$, 12, or 16 might be stabilized because the numbers of the metal centers in the peaks and valleys of the cylindrical metallacrown should be equal and the numbers of M_2 are equal to those of M_1. Usually, the octanuclear or dodecanuclear species might be the only one product. Considering the nonplanar metallacrown 36-Mc-12 derived from $tpeshz^{3-}$ (N-*trans*-2-pentenoylsalicylhydrazide)[6] with

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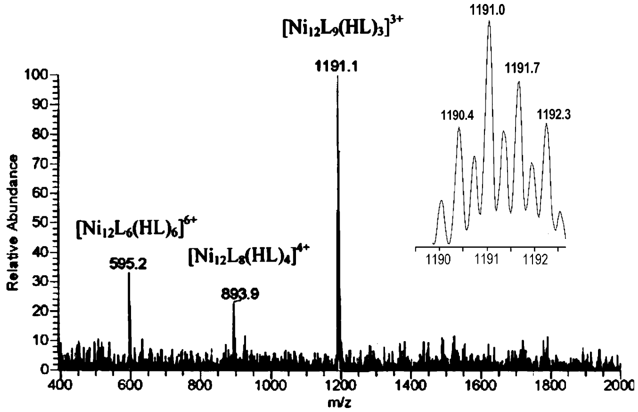

Figure 1. ESI-MS spectrum of complex **1** in CH_3OH/CH_2Cl_2 solution (in the presence of HOAc 1.0×10^{-4} M). The insert shows the isotope distribution pattern.

the largest metal numbers, it is expected that such a strategy offers a unique set of potential methods for the construction of high nuclear metallacrowns.

Reaction of H_2L with the related nickel salt gave the dodecanuclear neutral complex **1** ($Ni_{12}L_{12}(CH_3OH)_{12}$) in high yield via self-assembly.[9] The product was hard to dissolve in common organic solvents and only had a little solubility even in DMF and DMSO. Figure 1 showed ESI-MS (electrospray ionization mass) of complex **1**. The three main peaks at m/z = 1191.1, 595.2, and 893.9 seemed to be assigned to $[Ni_4L_3(HL)]^+$, $[Ni_3L_2(HL)]^+$, and $[Ni_2L(HL)]^+$, respectively. However, the isotopic distributions of the peaks suggested the presence of multiply charged species in the solution. Alternatively, the three peaks should be attributed to the species of $[Ni_{12}L_9(HL)_3]^{3+}$, $[Ni_{12}L_8(HL)_4]^{4+}$, and $[Ni_{12}L_6(HL)_6]^{6+}$, respectively, indicating that the dodecanuclear fragment was stable even in solution.

X-ray crystallographic study has unequivocally confirmed the existence of a neutral dodecanuclear species of the complex **1**.[10] Unlike most of the other metallacrown molecules,[5,11,12] the $[Ni-N-N]_{12}$ ring in the complex **1** is not planar. As an alternative, the metallacrown ring waves to form a molecular cylinder wound with $[Ni-N-N]_{12}$ lines

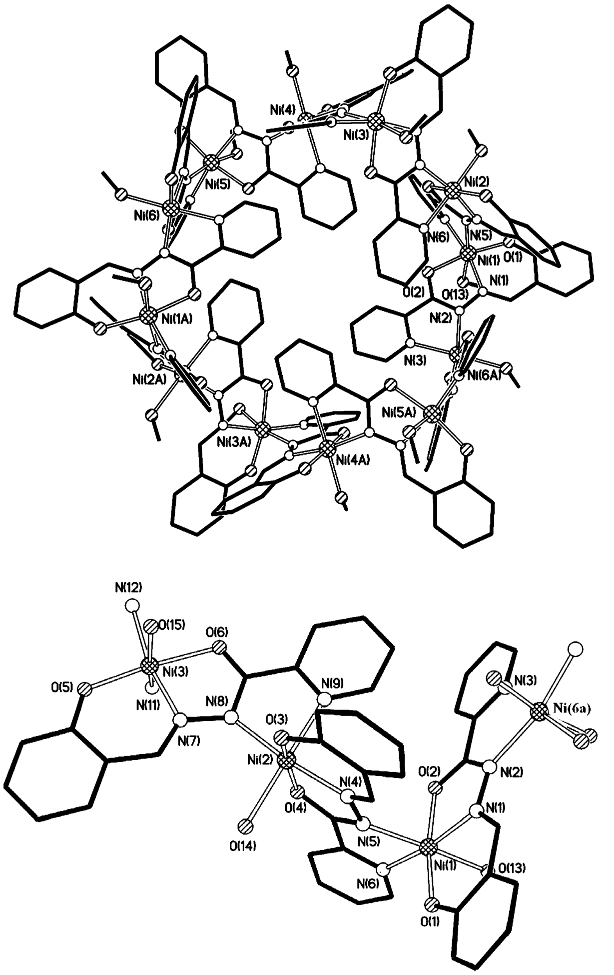

Figure 2. Perspective view of complex **1** showing the polygon structure azametallacrown; the solvent molecules and hydrogen atoms were omitted for clarity. Selected bond lengths [Å]: Ni(1)−O(1) 1.970(6), Ni(1)−N(1) 2.000(6), Ni(1)−N(6) 2.028(7), Ni(1)−O(2) 2.047(6), Ni(1)−N(5) 2.079(7), Ni(1)−O(13) 2.177(7), Ni(2)−N(4) 1.973(6), Ni(2)−O(3) 2.007(5), Ni(2)−O(4) 2.047(7), Ni(2)−N(8) 2.056(6), Ni(2)−N(9) 2.077(6), Ni(2)−O(14) 2.194(5), Ni(3)−O(5) 1.970(6), Ni(3)−N(7) 1.992(7), Ni(3)−N(12) 2.087(7), Ni(3)−O(6) 2.046(5), Ni(3)−N(11) 2.072(6), Ni(3)−O(15) 2.196(6), Ni(4)−O(7) 2.003(5), Ni(4)−N(10) 1.992(6), Ni(4)−N(15) 2.085(6), Ni(4)−O(8) 2.069(5), Ni(4)−N(14) 2.097(6), Ni(4)−O(16) 2.159(5), Ni(5)−O(9) 1.985(6), Ni(5)−N(13) 1.985(6), Ni(5)−N(18) 2.057(7), Ni(5)−O(10) 2.029(5), Ni(5)−N(17) 2.098(7), Ni(5)−O(17) 2.211(6), Ni(6)−O(11) 1.960(6), Ni(6)−N(16) 1.979(6), Ni(6)−N(2A) 2.080(6), Ni(6)−O(12) 2.041(6), Ni(6)−N(3A) 2.074(6), Ni(6)−O(18) 2.153(6), Symmetry code A: $-x, -y, 1 - z$.

(Figure 2). The shortest distance between the center of the metallacrown and the atoms in the ligands is ca. 3.14 Å, indicating the cavity at the center of the dodecanuclear complex is too small to include any guests. Each metal center has a distorted octahedral NiN_3O_3 environment with the neighboring Ni−Ni interatomic separation ranging from 4.87 to 4.96 Å. The deprotonated ligand L^{2-} acts as a multidentate ligand. While one phenolate oxygen atom, one carbonyl oxygen, and the imino nitrogen atom in the ligand bond to one nickel atom, the amide nitrogen atom and the pyridine nitrogen atom in the ligand chelate to the adjacent nickel atom. The average Ni−O distances are 1.98, 2.05, and 2.18 Å for the phenolate oxygen atom, the carbonyl oxygen atom, and the methanol oxygen atom, respectively. The average Ni−N distances are 1.99, 2.08, and 2.07 Å for the imino

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(9) Preparation of complex **1**: A solution of the H_2L ligand (0.025 g, 0.104 mmol) and Et_3N (0.011 g, 0.104 mmol) in methanol (4 mL) was layered onto a solution of CH_2Cl_2 (4 mL) containing $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.026 g, 0.104 mmol) at the bottom. The solutions were left for a few weeks at room temperature in darkness to give X-ray-quality crystals (yield, 83%). The crystals were sensitized in air. The powder used for the elemental analyses of C, H, and N was obtained by drying the crystals under vacuum. Anal. Calcd for $C_{168}H_{156}N_{36}O_{36}Ni_{12}$: C, 51.0; H, 4.0; N, 12.8; Found: C, 50.8; H, 4.1; N, 12.7. Uv−vis (DMF, λ_{max}/nm): 376 nm, (broad, log $\epsilon = 4.23$ with a shoulder at 269 nm).

(10) Crystal data for the complex 1 of $C_{185}H_{226}N_{36}O_{54}Ni_{12}$, Mr = 4522.32, monoclinic, space group $P2_1/n$ with $a = 20.095(2)$ Å, $b = 24.17(2)$ Å, $c = 24.02(2)$ Å, $\beta = 103.06(2)°$, $V = 11367(18)$ Å^3, $Z = 2$. $\rho_{cald} = 1.318$ Mg m^{-3}, $T = 293(2)$ K, $\mu = 1.048$ mm^{-1}. R1 = 0.0708, wR2 = 0.1560 for 7296 observed reflections with $I > 2\sigma(I)$, CCDC number 248693.

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nitrogen, the amide nitrogen, and the pyridine nitrogen atoms, respectively.

As expected, the coordination environments of the adjacent nickel atoms are different. For the nickel atoms labeled with odd numbers, such as Ni(1), the pyridine nitrogen atom N(6) occupies the trans position of the imino nitrogen atom N(1) from another ligand while the amide nitrogen atom N(5) occupies the trans position of the methanol oxygen atom O(13). The Ni(2)⋯Ni(1)⋯Ni(6A) angle is 91°, symmetry code A: $-x$, $-y$, $1 - z$. For the nickel atoms labeled with even numbers, such as Ni(2), the amide nitrogen atom N(8) occupies the trans position of the imino nitrogen atom N(4) from another ligand while the pyridine nitrogen atom N(9) occupies the trans position of the methanol oxygen atom O(14). The Ni(1)⋯Ni(2)⋯Ni(3) angle is 148°. Such an alternanting bridge model of the ligands leads to the slight difference in the interatomic Ni⋯Ni separations and significant difference in the Ni⋯Ni⋯Ni angles, with the Ni⋯Ni(odd)⋯Ni and Ni⋯Ni(even)⋯Ni angles being 91° and 146° on average, respectively.

Detailed structural analysis reveals that the adjacent nickel atoms with different coordination environments such as Ni(1) and Ni(2) possess the same chirality. The successive nickel centers are identified as possessing a ⋯ΛΛΔΔΛΛ⋯ chiral configuration. Consequently, the metal centers in the peaks and valleys of the ring exhibit different chiralities with the two faces of the cylindrical metallacrown having opposite chiralities. Such a chiral configuration is identical to that of the nonplanar metallacrown 36-Mc-12;[6] however, it is different from the complexes exhibiting a combination of the ⋯AAAA⋯ environment with the ⋯ΛΔΛΔ⋯ chiral configuration.[3a,12]

The magnetic properties of complex **1** have been investigated at a field of 5 KOe in the temperature range 2−300 K. As illustrated in Figure 3, the value of $\chi_m T$ at 300 K is 11.32 emu·K·mol^{-1}, which is slightly smaller than the sum value expected for 12 spin-only paramagnetic systems with $S = 1$ ($\chi_m T = 12.00$ emu·K·mol^{-1}), indicating the presence of the antiferromagnetic interaction between the Ni(II) ions. With decreasing temperature, the $\chi_m T$ value first decreases slightly, until reaching 7.92 emu·K·mol^{-1} at 80 K, and then decreases rapidly below this temperature, until reaching 0.06 emu·K·mol^{-1} at 2 K. The Curie−Weiss law fitting from 80 to 300 K gives a negative Weiss constant, θ, of −48.1 K.

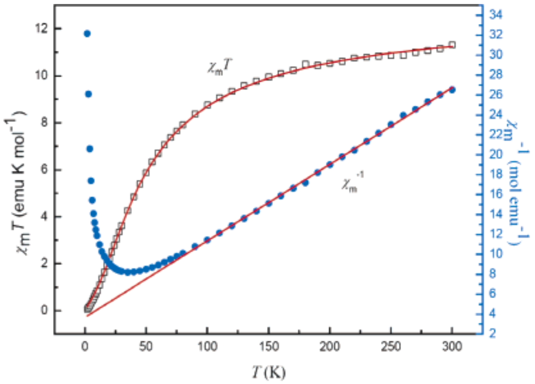

Figure 3. The ($\chi_m T$ (☐) and the χ_m^{-1} (●) data as a function T for compound **1**, and the solid lines (s) attached to χ_m^{-1} and ($\chi_m T$ depict fitting curves based on the Curie−Weiss law and on a simplified exchange fit, respectively.

There is no exact analytical expression to analyze the magnetic properties quantitatively due to the complexity of this system. To make the fitting easier, the $\chi_m T$ data are fitted by an analytical expression (eq 1),[13] derived from the numerical studies of Weng[14] for the susceptibility of an Heisenberg chain of antiferromagnetically coupled $S_i = 1$ ions:

$$\chi_m T = \frac{12Ng^2\mu_B^2}{k}\,\frac{2 + 0.0194x + 0.777x^2}{3 + 4.346x + 3.232x^2 + 5.834x^3} \qquad (1)$$

Where $x = |J/kT|$. Nonlinear least-squares fitting of the data in the temperature range 2−300 K gives $g = 2.07(1)$, $J/k = -27.5(2)$ K, and the agreement factor $F = \Sigma[(\chi_{obs} - \chi_{cald})^2/\chi_{obs}] = 6.17 \times 10^{-3}$.

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Supporting Information Available: CIF file of the title compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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