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Octanuclear Metallocyclic Ni_4Fc_4 Compound: Synthesis, Crystal Structure, and Electrochemical Sensing for Mg^{2+}

Mingxue Li, Ping Cai, Chunying Duan,* Feng Lu, Jin Xie, and Qingjin Meng*

*Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093, P. R. China*

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New, neutral octanuclearmacrocyclic compound Ni_4Fc_4 was achieved via self-assembly from $Ni(BF_4)_2$ and a ferrocene-containing bis-tridentate ligand. The compound exhibits a channeled structure with cavities inside and senses the Mg^{2+} electrochemically in the solid state.

Molecular squares and rectangles with metal corners and unsaturated ligand sides have become a representative class of "supramolecular" species.[1] In addition to the remarkable self-assembly formation reactions and the unusual structures, these systems have been receiving increasing attention due to their potential for the molecular recognition of substrates, for the interactions with light (antenna function), and for the intramolecular magnetic exchange coupling.[2,3] The desired functionality in metallosupramolecular squares may be introduced by employing functional ligands or properly functionalized metal corners with appropriate size and shape. Considerable efforts have been devoted to the design and preparation of metal corners, containing crown ether, calixarene, and ferrocene;[4] however, only few functional bridging ligands have been reported so far.[5]

On the other hand, molecular squares and rectangles have subsequently been used as building blocks for microporous materials,[6] and a number of cavity-containing supramolecular complexes have been reported as hosts for atomic or molecular guests;[7] however, only a small number of them could be additionally described as a binding signal transducer in the solid state.[8] As a continuance of our research work in the assemblies and properties of ferrocene-containing polynuclear complexes,[9] here we report the self-assembly of an octanuclear metallocyclic complex Ni_4Fc_4 by incorporating the redox-active unit, ferrocene, into a bis-carbazone ligand (Scheme 1), and study the potential application as an electrochemical sensor for Mg^{2+} both in solution and in the solid state.

Scheme 1

When 2-pyridinecarboxaldehyde was treated with 1,1′-ferrocenedicarboxylhydrazide in ethanol at reflux, an orange solid was formed. Elemental analysis supports the formation of the new bis-tridentate ligand, $(C_5H_4N)CH{=}N\ NHC(O)(C_5H_4)Fe(C_5H_4)C(O)NHN{=}CH(C_5H_4N)$, $\mathbf{H_2L}$. Interaction of

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* Authors to whom correspondence should be addressed. E-mail: duancy@nju.edu.cn (C.D.); mengqj@nju.edu.cn (Q.M.).

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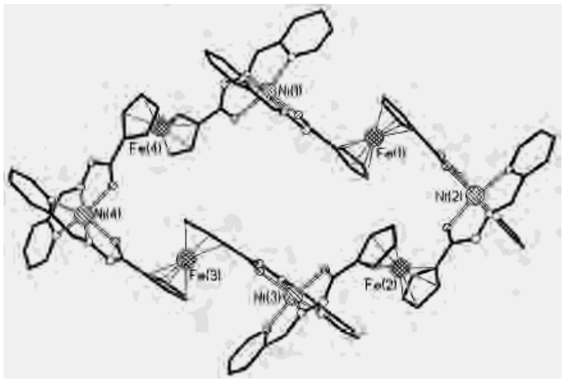

Figure 1. Molecular skeleton of the octanuclear metallocycle compound Ni_4Fc_4, with hydrogen atoms and the solvent molecules omitted for clarity.

H_2L with $Ni(BF_4)_2$ and NaOH (molar ratio = 1:1:2) in methanol at boiling temperature gave the ferrocene-containing macrocyclic compound $[Ni_4L_4]$ **1** via self-assembly (see Figure 1).[10] Macrocyclic compound **1** is a remarkably stable orange crystalline solid and is soluble in most organic solvents. The ESI-MS spectrum in ethanol solution exhibited a peak at *m*/*z* 537.1 with the isotropic distribution pattern separated by ca. 0.25 Da. The +4 charged species was assigned as the protoned macrocycle, $[Ni_4(HL)_4]^{4+}$, indicating that the ferrocene-containing macrocyclic Ni_4Fc_4 fragment is the most stable conformation in solution.

An X-ray crystallographic study[11] has unequivocally confirmed the existence of an octanuclear neutral ferrocene-containing molecular polygon in **1**. Two of the four ligands bridge the metal ions in *cis*-configuration with the Ni···Ni separation of ca. 10.0 Å, and the other two are in *trans*-configuration with Ni···Ni separation of ca. 10.6 Å. The unbridged Ni···Ni separations are 9.9 and 18.7 Å for short and long diagonal, respectively. Each nickel(II) is octahedrally coordinated by two N_2O tridentate moieties from two different ligands. These two ligands bind to the nickel(II) in a *mer*-configuration (with pairs of carbonyl O atoms and pyridine N atoms bearing a *cis*-relationship, whereas the imino N atoms are *trans* to each other). The C−N, C−O, and N−N bond distances in L^{2-} are intermediate between formal single and double bonds, pointing to extensive electron delocalization over the entire molecular skeleton.

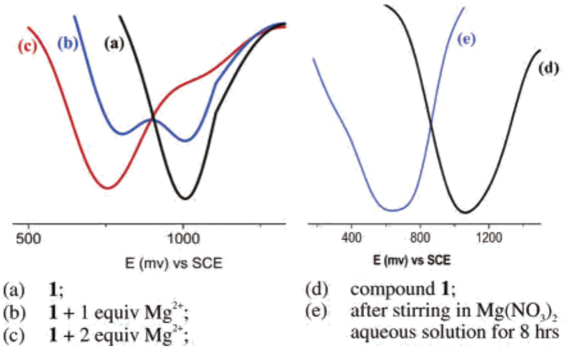

Figure 2. Differential pulse voltammetry for complex **1** in solution (left) and in the solid state (right).

The differential pulse voltammetry (Figure 2) of **1** showed a broad peak with half-wave potential ($E_{1/2}$) at 1.02 V, which was attributed to the single-electron Fe^{III}/Fe^{II} couple oxidation process. Compound **1** was not sensitive to $LiNO_3$, $NaNO_3$, KNO_3, and $Ba(NO_3)_2$ and poorly sensitive to $Ca(NO_3)_2$. However, stepwise addition of up to 2 equiv of $Mg(NO_3)_2$ to a solution of compound **1** resulted in a clear evolution of the voltammogram (Figure 2). The redox peak of the Fe^{III}/Fe^{II} couple shifted to 0.78 V, the presence of Mg^{2+} being thus heralded by an unexpected cathodic shift of −240 mV. Further addition of $Mg(NO_3)_2$ (until 5 equiv) had no significant effect, indicative of the formation of the stable 1:2 mole ratio [**1** $\subset$ $2Mg^{2+}$] interior. It is suggested that the Mg^{2+} was captured by the oxygen atoms coordinated to the long diagonal nickel atoms.

Generally, the addition of a metal cation into the sensor compounds will induce a classical anodic shift of the iron potential. In compound **1**, the opposite is observed. Few examples about the cathodic redox-potential shift have been reported upon cation addition and were assigned to the important electronic reorganization of molecules.[12] Theoretical calculations and experiments are underway to validate explanations of the intriguing electrochemical behavior involving the Mg^{2+} cation of compound **1**.

It is also interesting to find that the intermolecular $\pi-\pi$ interactions and C−H···π interactions between the ferrocene moieties and pyridine rings link the molecules together, featuring a two-dimensional channeled framework (Figure 3) with the water and methanol molecules in the channels. Since there are some pyridine rings extending within the channel, the channels align along the *c* axis form cavities

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(10) H_2L: The mixture of $[H_2NNHCO(C_5H_4)]_2Fe$ (1.51 g, 5 mmol) and 2-pyridinecarboxaldehyde (1.08 g, 10 mmol) was refluxed for 4 h. The orange solid formed was filtered and washed with ethanol. Yield: 90%. Calcd (%) for $C_{24}H_{20}N_6O_2Fe$: C 60.0, H 4.2, N 17.5. Found: C 59.9, H 4.3, N 17.2. ^1H NMR (500 MHz, DMSO): δ 8.67 (2H, s, CH═N), 8.52 (2H, s, NH), 8.34 (2H, s, C_5H_4N), 8.00 (2H, s, C_5H_4N), 7.73 (2H, s, C_5H_4N), 7.49 (2H, s, C_5H_4N), 5.09 (4H, s, C_5H_4), 4.7 (4H, s, C_5H_4), 2.56 (6H, s, CH_3). Ni_4Fc_4 **1**: H_2L (0.24 g, 0.5 mmol) was added to 30 mL of CH_3OH, followed by the addition of $NaOH/CH_3OH$ solution until it dissolves, and then $Ni(BF_4)_2$ (0.14 g, 0.5 mmol) dissolved in CH_3OH was added. When the resulting deep red solution was stirred for 2 h and was slowly evaporated to nearly dryness under reduced pressure, deep red solids were obtained. This crude product was recrystallized by dissolving it in CH_2Cl_2. Yield, 75%. Calcd (%) for $C_{96}H_{72}N_{24}O_8Fe_4Ni_4$: C 53.6, H, 3.4, N 15.64. Found: C 53.6, H, 3.2, N, 15.3. ES-MS, *m*/*z* (relative intensity): 537.1 $[(HL)_4Ni_4]^{4+}$.

(11) Crystals suitable for X-ray diffraction determination were grown by slow evaporation of its CH_3OH/CH_2Cl_2 solution at room temperature in the dark. Crystal data for **1**, $C_{100}H_{106}N_{24}O_{21}Fe_4Ni_4$, $M_r = 2438.33$, monoclinic, space group $P2_1/n$, $a = 18.367(2)$ Å, $b = 24.646(3)$ Å, $c = 25.691(3)$ Å, $\beta = 92.973(3)°$, $V = 11614(2)$ Å^3, $\rho_{cald} = 1.394$ Mg m^{-3}, $T = 293$ K, $Z = 4$, $\mu = 1.192$ mm^{-1}, R1 = 0.0767, wR2 = 0.1518 (all data, refined against $|F^2|$). Intensities of complex **1** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1. Anisotropic thermal parameters were refined for non-hydrogen atoms for complex **1**. Since the quality of the single crystal was not satisfactory, the observed unique reflection ratio was only 22% and there were also 643 restraints employed.

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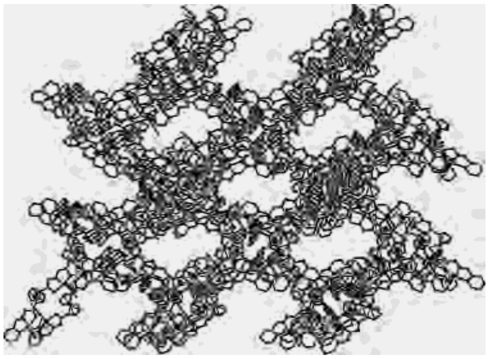

Figure 3. Crystal packing of compound **1** showing the channeled structure along the *c* axis, with hydrogen atoms and solvent molecules omitted for clarity.

with dimensions of a van deer Waals sphere about 4 × 8 × 11 Å^3. It is expected that, by carefully removing the solvent molecules from the cavities, solid-state species with empty cavities should be obtained. Such a solid has the potential to reabsorb small molecules or ionic species within its channels or cavities and provides the possibility for practical application.

According to the property of this complex in solution, Mg^{2+} might be absorbed within the channels and cavities and detected by the change of the electrochemical signal. To test such an expectation, the solid-state DPV is measured[13] for compound **1** and solid species **2**, obtained by stirring complex **1** in the aqueous solution of $Mg(NO_3)_2$ (1.0×10^{-4} M) for 8 h. While compound **1** exhibits a broad peak at about 1.04 V, solid **2** shows a broad peak at about 0.66 V, with a cathodic shift of −380 mV. There are several compounds reported in the literature which pertain to chemosensors that selectively detect Mg^{2+},[14] but there are relatively few electrochemical sensors for ionic species in the solid state.[15]

In summary, we report the synthesis, crystal structure, and electrochemical recognition for Mg^{2+} both in solution and in the solid state of a new, neutral ferrocene-containing octanuclear metallocycle Ni_4Fc_4. The ability to tune the cavity sizes of the molecular polygons, and the tendency of the polygons to form cavities in the solid state together with the electrochemical sensing for Mg^{2+} both in solution and in the solid state, will permit the corresponding material to be used in molecule sieving science wherein the exclusion limit can be altered by changing the dimensions of the polygon. A detailed study will be concentrated on the complete understanding of the unusual properties of this compound, the development of testing methods for the recognition ability, and the derivatives toward other ions.

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Supporting Information Available: Experimental procedure, ESI-MS spectra, and X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Solid-state voltammograms were measured by using a carbon-paste working electrode; a well-ground mixture of each bulk sample and carbon paste (graphite and mineral oil) was set in the channel of a glass tube and connected to a copper wire. A platinum wire counter electrode and an SCE reference electrode were used. Measurements were performed by using a three-electrode system in 0.1 mol·dm^{-3} Bu_4NClO_4 CH_2Cl_2 solutions at a scan rate of 20 mV s^{-1}, in the range 0−2.0 V.

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