Heptanuclear Nickel(II) Wheel with Eight Redox Active Ferrocenyl Groups

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The reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ with 3-ferrocenyl-5-(2-pyridyl)pyrazole (Hfcpp) and Et_3N in acetonitrile yielded a pentadecanuclear heterometallic complex of $[Ni_7(fcpp)_8(OH)_4](ClO_4)_2 \cdot 6CH_3CN$ (**1**). Complex **1** has a heptanuclear wheel core composed of seven Ni^{II} ions, and eight ferrocenyl groups are attached to the core through pyrazolyl groups. Magnetic susceptibility measurements for **1** revealed that overall antiferromagnetic interactions are operative within the heptanuclear core.

Research on multinuclear transition-metal complexes is a flourishing field, and they may exhibit interesting catalytic and physical properties due to synergy of assembled metal ions in molecules.[1–3] Pyrazole derivatives are well-known bridging ligands, and their multinuclear cyclic clusters such as $[\{cis\text{-}Cu(\mu\text{-}OH)(\mu\text{-}pz)\}_n]$ ($n = 6$, 8, 9, 12, and 14) (pz = pyrazolato anion),[4a] $[Au_3(\mu\text{-}3,5\text{-}Me_2\text{-}pz)_3]$,[4b] and $[Pt_3Br_2(\mu\text{-}pz)_6]$[4c] have been reported. Recently, Meyer et al. have reported pyrazolate-based dinuclear Ni^{II} complexes, which showed reversible two-step reduction processes and catalytic activity for olefin polymerization.[5] Ferrocenyl units are, on the other hands, frequently employed as redox-active sites in supramolecular assemblies,[6] which is due to their reversible redox properties as well as their synthetic versatilities. Clusters with ferrocenyl groups may exhibit synergistic functions due to multinuclear cores and redox active ferrocenyl groups.[7] We report here a novel heterometal complex of $[Ni_7(fcpp)_8(OH)_4](ClO_4)_2 \cdot 6CH_3CN$ (**1**) (Hfcpp = 3-ferrocenyl-5-(2-pyridyl)pyrazole, Chart 1).

A ligand, Hfcpp, was prepared by a cyclization reaction of 1-ferrocenyl-3-(2-pyridyl)-1,3-propanedione with hydrazine.[8] The reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ with Hfcpp and Et_3N in acetonitrile yielded a pentadecanuclear complex of **1** as red tablets.[9] **1** crystallized in monoclinic space group $P2_1/n$,[10] and the complex molecule locates on the inversion center (Figure 1). **1** has a heptanuclear wheel-like core structure consisting of three octahedral, two square-pyramidal, and two square-planer nickel ions. Peripheral Ni ions, linked to the central Ni ion (Ni4) via four μ_3-hydroxo and two pyrazolyl bridges, are doubly bridged to each other by μ_3-hydroxo and pyrazolyl groups. The central Ni ion (Ni4) has a six-coordinated NiN_2O_4 chromophore. The wheel core has eight ferrocenyl groups attached to pyrazolyl groups, and fifteen metal ions are assembled into a single molecule. Coordination geometry of Ni1 is square-planer with two pyrazolyl and one pyridyl nitrogen and one hydroxo oxygen atom. The nickel ions (Ni2) have a square-pyramidal coordination environment, where two hydroxo oxygen and two pyrazolyl nitrogen atoms occupy the equatorial positions and one pyridyl nitrogen atom coordinates from the apical position. The coordination structure of each Ni3 ion is regarded as an N_5O chromophore from three pyrazoyl and two pyridyl groups and μ_3-hydroxo groups. The bridging angles of μ_3-hydroxide are 97.1(4) and 99.7(3)° for Ni2–O1–Ni4 and Ni2–O2–Ni4, 113.9(4) and 116.6(3)° for Ni2–O2–Ni3 and Ni3–O2–Ni4, respectively. In the ferrocenyl moieties, the average coordination bond lengths (Fe–C) are 2.008–2.022 Å, characteristic of a low-spin iron(II) ion in ferrocene. In **1** pyridyl and cyclopentadienyl groups, coordinated to Ni1, Ni3, and Fe2 ions, respectively, are almost parallel to each other with close interatomic contacts of 3.216(10)–3.231(14) Å. Note that bulky diamagnetic ferrocenyl groups separate the wheel cores, and the shortest interatomic distance of paramagnetic Ni ions in neighboring molecules is 11.548(3) Å.

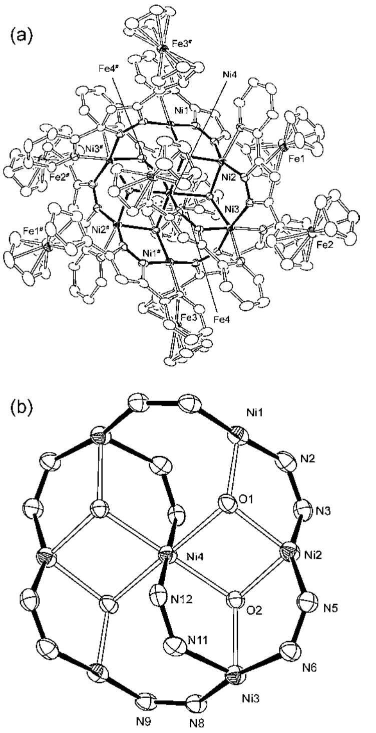

Figure 1. ORTEP views of **1**. (a) Complex cation and (b) core structure (A key to symmetry operation #: $-x$, $-y$, $-z$).

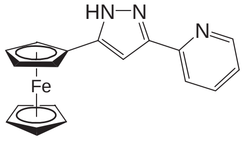

Chart 1.

Magnetic susceptibility measurements for **1** were performed in the temperature range of 1.8–300 K, and a $\chi_m T$ versus T plot is shown in Figure 2. Hence, two square-planar Ni ions in the complex molecule are diamagnetic, **1** has five paramagnetic Ni ions. A $\chi_m T$ value is 5.37 emu mol^{-1} K at 300 K, which corresponds to the value expected for the uncorrelated five Ni^{II} ions (5.00 emu mol^{-1} K with $g = 2$). The $\chi_m T$ values gradually

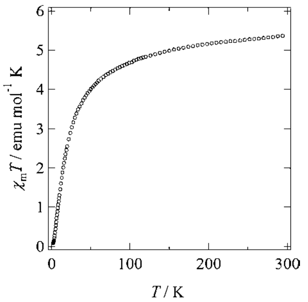

Figure 2. $\chi_m T$ vs. T plot of **1**.

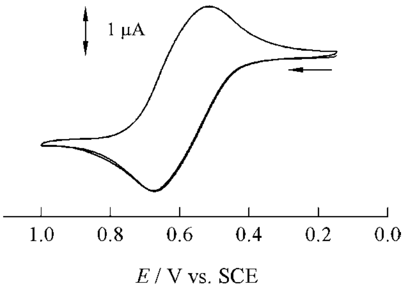

Figure 3. Cyclic voltammogram of **1** at a platinum electrode in 0.01 mol dm^{-3} [Bu_4N][PF_6]/acetone at a scan rate of 0.05 V s^{-1}.

decreased as the temperature was lowered, reaching the value of 0.08 emu mol^{-1} K at 1.8 K. This suggests substantial antiferromagnetic interactions operative among Ni ions, which was confirmed by the negative Weiss constant ($\theta = -22.50$ K) with Curie constant of 5.78 emu mol^{-1} K. Hydroxo and pyrazolate-bridged Ni^{II} complexes have been reported to show antiferromagnetic interactions with $J \approx -20$ K.[5a,11]

An electrochemical measurement on the ligand Hfcpp revealed the reversible one-step 1e$^-$ oxidation on the ferrocenyl group at $E^{0'} = 0.430$ V (versus SCE). In **1** a quasi-reversible oxidation wave was observed at $E^{0'} = 0.597$ V (Figure 3). Coulometry with applied potential at 0.9 V confirmed that the number of electrons per molecule upon oxidation is 8.1, suggesting that the redox wave was attributed to the one-step 8e$^-$ oxidation on eight ferrocenyl groups.

In summary, we synthesized a pentadecanuclear complex of **1**, which is composed of eight Fe^{II} ions and seven Ni^{II} ions. **1** showed antiferromagnetic interactions in the heptanuclear wheel core as well as quasi-reversible redox behavior in the eight ferrocenyl groups.

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8 Hfcpp was prepared by slight modification of reported procedure (W. R. Thiel, T. Priermeier, D. A. Fiedler, A. M. Bond, M. R. Mattner, *J. Organomet. Chem.* **1996**, *514*, 137). Synthesis of 1-ferrocenyl-3-(2-pyridyl)-1,3-propanedione: A solution of sodium ethoxide (1.09 g, 15.9 mmol), acetylferrocene (2.00 g, 8.77 mmol) and picolinic acid ethyl ester (2.89 g, 19.1 mmol) in 30 mL of toluene was refluxed for 2 h under nitrogen atmosphere. The solvent was removed under reduced pressure, and aqueous acetic acid was added to the residue. The resulting aqueous solution was extracted with diethyl ether and dried with sodium sulfate. The solvent was evaporated, and the recrystallization of crude products from methanol yielded a purple crystalline solid of 1-ferrocenyl-3-(2-pyridyl)-1,3-propanedione (Yield 2.35 g, 81%). Anal. Calcd (Found) for $C_{18}H_{15}NO_2Fe \cdot 0.1H_2O$: C, 64.54 (64.51); H 4.53 (4.63); N, 4.18 (4.16)%. ^{1}H NMR ($CDCl_3$): δ 4.22 (s, 5H, C_5H_5), 4.57 (s, 2H, C_5H_4), 4.96 (s, 2H, C_5H_4), 7.03 (s, 1H), 7.40 (dd, 1H), 7.85 (dd, 1H), 8.11 (d, 1H), 8.70 (d, 1H). Synthesis of Hfcpp: Hydrazine monohydrate (0.320 mL, 7.00 mmol) was added to a $CHCl_3$ solution of 1-ferrocenyl-3-(2-pyridyl)-1,3-propanedione (2.10 g, 6.30 mmol), and the mixture was refluxed for 2 h. The resulting mixture was evaporated and crude products were washed with acetonitrile. The obtained yellow solid was recrystallized from $CHCl_3$ to yield 1.66 g (5.03 mmol) of Hfcpp as a yellow crystalline solid. Yield 80%. Anal. Calcd (Found) for $C_{18}H_{15}N_3Fe$: C, 65.68 (65.47); H 4.59 (4.59); N, 12.77 (12.77)%. ^{1}H NMR ($CDCl_3$): δ 4.11 (s, 5H, C_5H_5), 4.32 (s, 2H, C_5H_4), 4.70 (s, 2H, C_5H_4), 6.81 (s, 1H), 7.22 (m, 1H), 7.76 (m, 2H), 8.62 (d, 1H).

9 Synthesis of **1**: An acetonitrile solution (30 mL) of $Ni(ClO_4)_2 \cdot 6H_2O$ (55 mg, 0.15 mmol) was added to a mixture of Hfcpp (50 mg, 0.15 mmol) and Et_3N (15 mg, 0.15 mmol). The resulting red solution was allowed to stand for a week at room temperature to give red plate crystals of **1** (Yield 6.9 mg, 13%). ESIMS observed *m/z* 1551.7 ([M – 2ClO_4]$^{2+}$). Anal. Calcd (Found) for $C_{144}H_{116}N_{24}Cl_2Fe_8Ni_7O_{12} \cdot 2CH_3CN \cdot 5H_2O$: C, 51.15 (50.98); H, 3.82 (3.62); N, 10.48 (10.55)%.

10 Crystallographic data for **1**: red plates ($0.4 \times 0.3 \times 0.2$ mm^3) $C_{156}H_{134}N_{30}Cl_2Fe_8Ni_7O_{12}$, $M_r = 3549.60$, Monoclinic, space group $P2_1/n$, $a = 16.287(3)$, $b = 26.451(5)$, $c = 17.158(3)$ Å, $\beta = 108.135(4)°$, $V = 7025(2)$ Å^3, $Z = 2$, $T = 200$ K. A total of 31424 were collected ($3° < \theta < 46°$) of which 10102 unique reflections ($R_{int} = 0.0717$) were measured. $R_1 = 0.0607$, $wR_2 = 0.1266$ ($I > 2\sigma(I)$).

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