

Cyanide Bridged Tetranuclear Complex with a Novel Terthiophene Based Ligand

Kiyotaka Mitsumoto^a, Hiroyuki Nishikawa^b and Hiroki Oshio^{a*}

^a*Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai 305-8577, Japan.*

^b*College of Science, Ibaraki University, 2-1-1 Bunkyo, Mito 310-8512, Japan.*

Keyword: multinuclear complex, heterometal complex, terthiophene, cyanide bridge

Abstract

A new terthiophene based ligand (L = 3-(2-pyridyl)-5-(2,2':5',2''-terthien-3'-yl)pyrazole) was synthesized. The reaction of Ni(BF₄)₂·6H₂O, L and nBu₄N[Fe(CN)₃tp*] (tp* = tris(3,5-dimethylpyrazol-1-yl)borohydride) with NaBPh₄ in MeOH/acetone yielded a cyanide bridged tetranuclear complex [Fe₂Ni₂(CN)₆(tp*)₂(L)₄](BPh₄)₂ (**1**). The electrochemical properties of both **1** and L

were investigated, and magnetic susceptibility measurements of **1** were conducted, revealing that ferromagnetic interactions were operative within the tetranuclear core.

1. Introduction

Multinuclear metal complexes with high spin ground states have attracted intense interest from the viewpoint of the construction of molecular-based superparamagnets, namely single molecule magnets (SMMs) [1]. Simultaneously, much research has been conducted into the synergy between high spin states and molecular conductivity [2]. Oligothiophenes are frequently used as building blocks for conductive polymers, solar cells and electrochromic supramolecular assemblies [3, 4], due to their readily accessible stable redox species, which can facilitate easy electropolymerization. Thus, a number of oligothiophene-functionalized complexes have been synthesized, however, most were mononuclear or organometallic compounds [3-5]. A system which combines a multinuclear complex with oligothiophene groups may be a good candidate to show multiple functionalities, such as magneto-resistance, conductive SMM behavior, and redox switching. Herein we report the syntheses and properties of a novel terthiophene ligand L and its heterometallic complex $[\text{Fe}_2\text{Ni}_2(\text{CN})_6(\text{tp}^*)_2(\text{L})_4](\text{BPh}_4)_2$ (**1**).

2. Experimental details

2.1. Materials

All solvents were reagent-grade, purchased commercially, and used without further purification unless otherwise noted. All chemicals were purchased from Aldrich, Kanto Chemical Co., or Wako and used as received. $n\text{Bu}_4\text{NPF}_6$, which was used as an electrolyte in the electrochemical measurements, was recrystallized from ethanol before use. Toluene was distilled from CaH_2 . 3'-acetyl-2,2':5',2''-terthiophene was prepared by the reported methods [6] and $n\text{Bu}_4\text{N}[\text{Fe}(\text{CN})_3\text{tp}^*]$ was prepared by slight modification of the reported procedure [7].

2.2. Synthesis of 1-(2-pyridyl)-3-(2,2':5',2''-terthien-3'-yl)1,3-propanedione (2)

A solution of sodium ethoxide (400 mg, 5.85 mmol), 3'-acetyl-2,2':5',2''-terthiophene (850 mg, 2.93 mmol) and ethyl 2-pyridinecarboxylate (883 mg, 5.86 mmol) in toluene (30 mL) was refluxed under nitrogen for 2h. The solvent was then removed under reduced pressure, and the

residue acidified with aqueous acetic acid. The resultant red precipitate was dissolved in diethylether and the solution was dried with sodium sulfate. The solvent was evaporated and the crude product recrystallized from ethanol to afford 690 mg (1.75 mmol) of **2** as an orange crystalline solid (yield 60%). Anal. Calcd. for $C_{20}H_{13}N_1O_2S_3 \cdot 0.1H_2O$: C 60.46, H 3.34 N 3.52. Found: C 60.30, H 3.33 N 3.35%. 1H NMR (270 MHz, $CDCl_3$): 7.59 (3H, *d*), 7.50 (3H, *d*), 7.40 (2H, *d*), 7.21 (2H, *d*), 7.03-7.10 (2H, *m*), 7.18 (1H, *s*), 7.23 (1H, *dd*), 7.28 (1H, *dd*), 7.38-7.42 (3H, *m*), 7.84 (1H, *dd*), 8.08 (1H, *d*), 8.53 (1H, *d*).

2.3. Synthesis of 3-(2-pyridyl)-5-(2,2':5',2''-terthien-3'-yl)pyrazole (L)

296 μ L of hydrazine monohydrate (300 mg, 6.00 mmol) was added to a solution of **2** (690 mg, 1.75 mmol) in 20 mL $CHCl_3$ and the mixture was refluxed for 2 h. The solvent was evaporated and the crude product was washed with acetonitrile. The yellow product was recrystallized from $CHCl_3$ to afford 540 mg (1.38 mmol) of ligand L as a pale yellow crystalline solid in 79% yield. Anal. Calcd for $C_{20}H_{13}N_3S_3 \cdot 0.1H_2O$: C 61.07, H 3.38 N 10.68. Found: C60.88, H 3.35 N 10.66%. 1H NMR (270 MHz, $CDCl_3$): 6.80 (1H, *s*), 7.01-7.07 (2H, *m*), 7.21-7.25 (5H, *m*), 7.35 (1H, *d*), 7.49 (1H, *s*), 7.72 (1H, *dd*), 8.63 (1H, *d*).

2.4. Synthesis of $[Fe_2Ni_2(CN)_6(tp^*)_2(L)_4](BPh_4)_2 \cdot 8H_2O \cdot 4MeOH \cdot 2((CH_3)_2CO)$ $(1 \cdot 8H_2O \cdot 4MeOH \cdot 2((CH_3)_2CO))$

Ni(BF₄)₂·6H₂O (5.4 mg, 0.016 mmol) and L (12 mg, 0.032 mmol) were combined in MeOH (2 mL), and stirred for 5 mins, before a second solution of *n*Bu₄N[Fe(CN)₃tp*] (11 mg, 0.016 mmol) and NaBPh₄ (5.5 mg, 0.016 mmol) in acetone (2 mL) was added and the reaction stirred for 10 min. Slow evaporation gave red plate crystals of $1 \cdot 8H_2O \cdot 4MeOH \cdot 2((CH_3)_2CO)$ (25 mg, 0.0069 mmol) in an 86% yield. Anal. Calcd for C₁₆₄H₁₃₆N₃₀B₄Fe₂Ni₂S₁₂·3H₂O: C 60.83, H 4.42 N 12.98. Found: C 60.95, H 4.47 N 12.83%.

2.5. X-ray crystallography

Crystal was mounted on glass capillaries, and data were collected at -173 °C (Bruker SMART APEX diffractometer coupled with a CCD area detector with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation). The structure was solved using direct methods and expanded using Fourier techniques in SHELXTL program. Empirical absorption corrections by SADABS (G.M. Sheldrick, 1994) were carried out. In the structure analyses, non-hydrogen atoms were refined with

anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms.

Crystallographic data for **1**:

$C_{164}H_{136}N_{30}B_4Fe_2Ni_2S_{12} \cdot 8H_2O \cdot 4MeOH \cdot 2(CH_3)_2CO$, $M_r = 3572.89$, Triclinic, space group $P\bar{1}$, $a = 13.993(3) \text{ \AA}$, $b = 16.128(3) \text{ \AA}$, $c = 20.793(4) \text{ \AA}$, $\alpha = 102.866(3)^\circ$, $\beta = 91.400(3)^\circ$, $\gamma = 101.284(3)^\circ$, $V = 4475(1) \text{ \AA}^3$, $Z = 1$, $T = 100 \text{ K}$. A total of 26399 were collected ($2.02^\circ < 2\theta < 54.4^\circ$) of which 18900 unique reflections ($R_{int} = 0.0520$) were measured. $R1 = 0.0804$, $wR2 = 0.1797$ ($I > 2\sigma(I)$). Disordered solvent molecules in the crystal voids have been removed from calculations by the SQUEEZE program. [8]

[Insert Scheme]

3. Results and discussions

3.1. Crystal structure

The complex cation of **1** is shown in Figure 1. In **1** cyanide ions bridge two Fe and two Ni ions to form a square structure. The coordination bond lengths, charge balance and magnetic susceptibility data suggest that the Fe1 and Ni1 ions are low spin (LS) Fe^{III} ion and Ni^{II} ion, respectively. The six coordination sites of Fe1 are occupied by three nitrogen atoms from the tridentate ligand tp*⁻ and the remaining facial positions are filled by three cyanide carbon atoms. Ni1 adopts a N₆ configuration with two cyanide nitrogen atoms and two bidentate ligands L. The square core has four terthiophene pendants attached to pyrazolyl groups. The vertex angles of the square (C1-Fe1-C2 and N1-Ni1-N2) are 85.9(2)-93.7(2)° and the Fe-C-N and Ni-N-C bonds have angles of 173.6(4)-175.5(5)°. The coordination bond lengths of the Fe1 ion are in the range of 1.976(5)-2.003(4) Å and 1.911(6)-1.930(7) Å for Fe-N_{tp*} and Fe-C_{CN}, respectively, while a slight axial elongation on the Ni1 site is observed with Ni-N_{py} = 2.107(5) and 2.1124(5) Å, and equatorial bond lengths in the range of 2.041(5)-2.083(5) Å.

[Insert Figure 1]

3.2. Magnetic properties

Magnetic susceptibility measurements for **1** were performed in the temperature range of 1.8-300 K, the $\chi_m T$ versus T plot of which is shown in Figure 2. The $\chi_m T$ value at 300 K is 3.79 emu mol⁻¹ K, which corresponds to the value expected for two uncorrelated LS Fe^{III} ($S = 1/2$ with $g = 2.7$ [7, 9, 10, 11]) and two Ni^{II} ions ($S = 1$ with $g = 2.2$ [10]). The $\chi_m T$ values gradually increased as the temperature was lowered, reaching a maximum value of 7.91 emu mol⁻¹ K at 5 K, before an abrupt decrease to 7.35 emu mol⁻¹ K at 1.8 K. The magnetic susceptibility data were analyzed by the reported method [10], and were fitted using the spin Hamiltonian $H = -2J_{\text{Fe-Ni}}\{(S_1 + S_2) \cdot (S_3 + S_4)\}$, where $J_{\text{Fe-Ni}}$ is the isotropic exchange interaction between Fe^{III} and Ni^{II} ions, S_i is the spin operator for each metal center ($S_i = 1$, Ni^{II}, with $i = 1-2$; $S_i = 1/2$, Fe^{III}, with $i = 3-4$), and no magnetic anisotropy was included. Least-squares calculations using the data above 5 K yielded $g = 2.28(2)$ and $J_{\text{Fe-Ni}} = 7.32(7)$ K, indicating ferromagnetic interactions were operative between Ni and Fe ions. Magnetization experiments conducted at 1.8 K gave an unsaturated value of 5.18 $N\beta$ at 5 kOe (Figure 2, inset), which is comparable to the values previously reported [Fe₂Ni₂] squares [9c, 10, 11], supposing an $S = 3$ spin ground state for **1**. Ac

magnetic susceptibility measurements were performed in the range of 1.8-4.0 K under a 3 G ac field oscillating at 1000 Hz. No out-of-phase signal was observed, indicating the absence of SMM properties.

[Insert Figure 2]

3.3. *Electrochemical properties*

The electrochemical properties of L and **1** were studied by cyclic voltammetry (CV). In a dichloromethane solution of L an observed quasi-reversible anodic wave centered at 0.71 V (versus SCE) was assigned to the oxidation of the terthienyl substituent (Figure 3(a)). Repeated scans within a range of 0 to 1.5 V resulted in electrochemical polymerization of L to form a green film (**poly-L**) which was deposited on the glassy carbon working electrode. The voltammetry of the **poly-L** film was measured in dichloromethane containing 0.1 M *n*Bu₄NPF₆ as a supporting electrolyte. Figure 3(b) shows the CV of the deposited **poly-L**. There is no decay of current, indicating the presence of an electroactive species on the working

electrode. In the CV of complex **1** (Figure 3(c)), the first scan from 0.2 to -0.5 V showed two reversible waves corresponding to the one electron reduction of both Fe^{III} ions at $E_{1/2} = 0.07$ and -0.12 V [11]. In addition, a quasi reversible redox process associated with the terthienyl groups was found in the range of 0.8-1.3 V when the potentials were scanned from -0.5 to 1.5 V. After the second scan, the reduction waves of the Fe^{III} centers could not be observed, suggesting decomposition of the complex. The electrochemical behavior of the deposited film (Figure 3(d)) was also indicative of instability in the formation of the polymer from the decomposition products of **1**.

[Insert Figure 3]

4. Conclusion

In summary, we synthesized a novel terthiophene based ligand L and its tetranuclear complex **1**. **1** showed intramolecular ferromagnetic interactions between Ni^{II} and Fe^{III} ions. L was deposited on the electrode as an electroactive

polymer.

5. Supplementary data

CCDC 804169 contains the supplementary crystallographic data for this paper.

These data can be obtained free of charge via

<http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)

1223-336-033; or e-mail: deposit@ccdc.ac.uk.

Acknowledgments

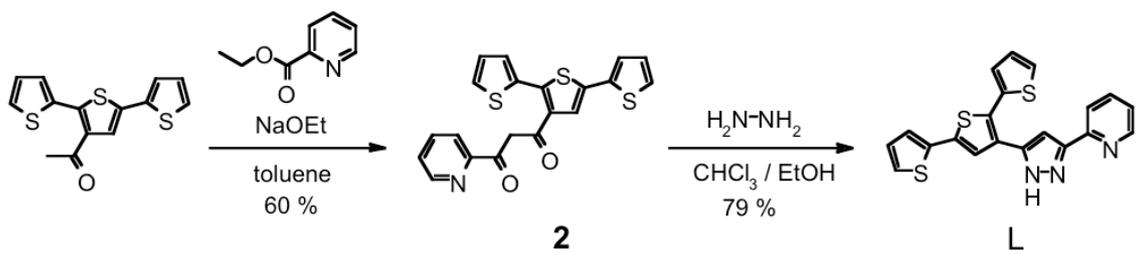
This work was supported by a Grant-in-Aid for Scientific Research and for Priority Area “Coordination Programming” (area 2107) from MEXT, Japan. K. M. thanks the JSPS Young Scientist Fellowship.

References

1. (a) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, **1993**, 365, 141-143. (b) R. Sessoli, H-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**,

- 115, 1804-1816. (c) D. Gatteschi and R. Sessoli, *Angew. Chem. Int. Ed.* **2003**, *42*, 268-297.
2. (a) H. Hiraga, H. Miyasaka, K. Nakata, T. Kajiwara, S. Takaishi, Y. Oshima, H. Nojiri and M. Yamashita, *Inorg. Chem.* **2007**, *46*, 9661-9671. (b) H. Hiraga, H. Miyasaka, R. Clérac, M. Fourmigué and M. Yamashita, *Inorg. Chem.* **2009**, *48*, 2887-2898. (c) L. Bogani, C. Danieli, E. Biavardi, N. Bendiab, A. L. Bara, E. Dalcanale, W. Wernsdorger and A. Cornia, *Angew. Chem. Int. Ed.* **2009**, *48*, 746-750.
3. Y. Saito, T. Azechi, T. Kitamura, Y. Hasegawa, Y. Wada and S. Yanagida, *Coord. Chem. Rev.* **2004**, *248*, 1469-1478.
4. K. Sugiyasu and M. Takeuchi, *Chem. Eur. J.* **2009**, *15*, 6350-6362.
- 5.(a) D. H. Kim, J. H. Kim, T. H. Kim, D. M. Kang, Y. H. Kim, Y. B. Shim and S. C. Shin, *Chem. Mater.* **2003**, *15*, 825-827. (b) G. C. Júnior, A. P. S. Silva and L. S. Guinesi, *Polyhedron* **2004**, *23*, 1953-1960. (c) B. Djukic and M. T. Lemaire, *Inorg. Chem.* **2009**, *48*, 10489-10491. (d) T. W. Hesterberg, X. Yang and B. J. Holliday, *Polyhedron* **2010**, *29*, 110-115.
6. T. Pollagi and M. B. Sinclair *Sandia National Laboratories [Technical Report]*, **1997**, *0158*, i-vi, 1-12.

7. $n\text{Bu}_4\text{N}[\text{Fe}(\text{CN})_3\text{tp}^*]$ was prepared using a modified procedure reported for $\text{Et}_4\text{N}[\text{Fe}(\text{CN})_3\text{tp}^*]\cdot\text{H}_2\text{O}$ (D. Li, S. Parkin, G. Wang, G. T. Yee and S. M. Holmes, *Inorg. Chem.* **2006**, *45*, 1951-1959.). Anal. Calcd. for $\text{C}_{34}\text{H}_{58}\text{N}_{10}\text{B}_1\text{Fe}_1$: C 60.62, H 8.67 N 20.80. Found: C 60.30, H 8.60 N 20.68%. IR (KBr, cm^{-1}) 2528 (s), 2120 (s).
8. (a) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13. (b) P. v. d. Sluis and A. L. Spek, SQUEEZE, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194-201.
9. (a) Y. Zhang, D. Li, R. Clérac, M. Kalisz, C. Mathonière and S. M. Holmes, *Angew. Chem. Int. Ed.* **2010**, *49*, 3752-3756. (b) K. Mitsumoto, M. Ui, M. Nihei, H. Nishikawa and H. Oshio, *CrystEngComm* **2010**, *12*, 2697-2699. (c) D. Li, S. Parkin, G. Wang, G. T. Yee, A. V. Prosvirin and S. M. Holmes, *Inorg. Chem.* **2005**, *44*, 4903-4905.
10. D. Li, R. Clérac, G. Wang, G. T. Yee and S. M. Holmes, *Eur. J. Inorg. Chem.* **2007**, 1341-1346.
11. C. -F. Wang, W. liu, Y. Song, X. -H. Zhou, J. -L. Zuo and X. -Z. You, *Eur. J. Inorg. Chem.* **2008**, 717-727.



Scheme.

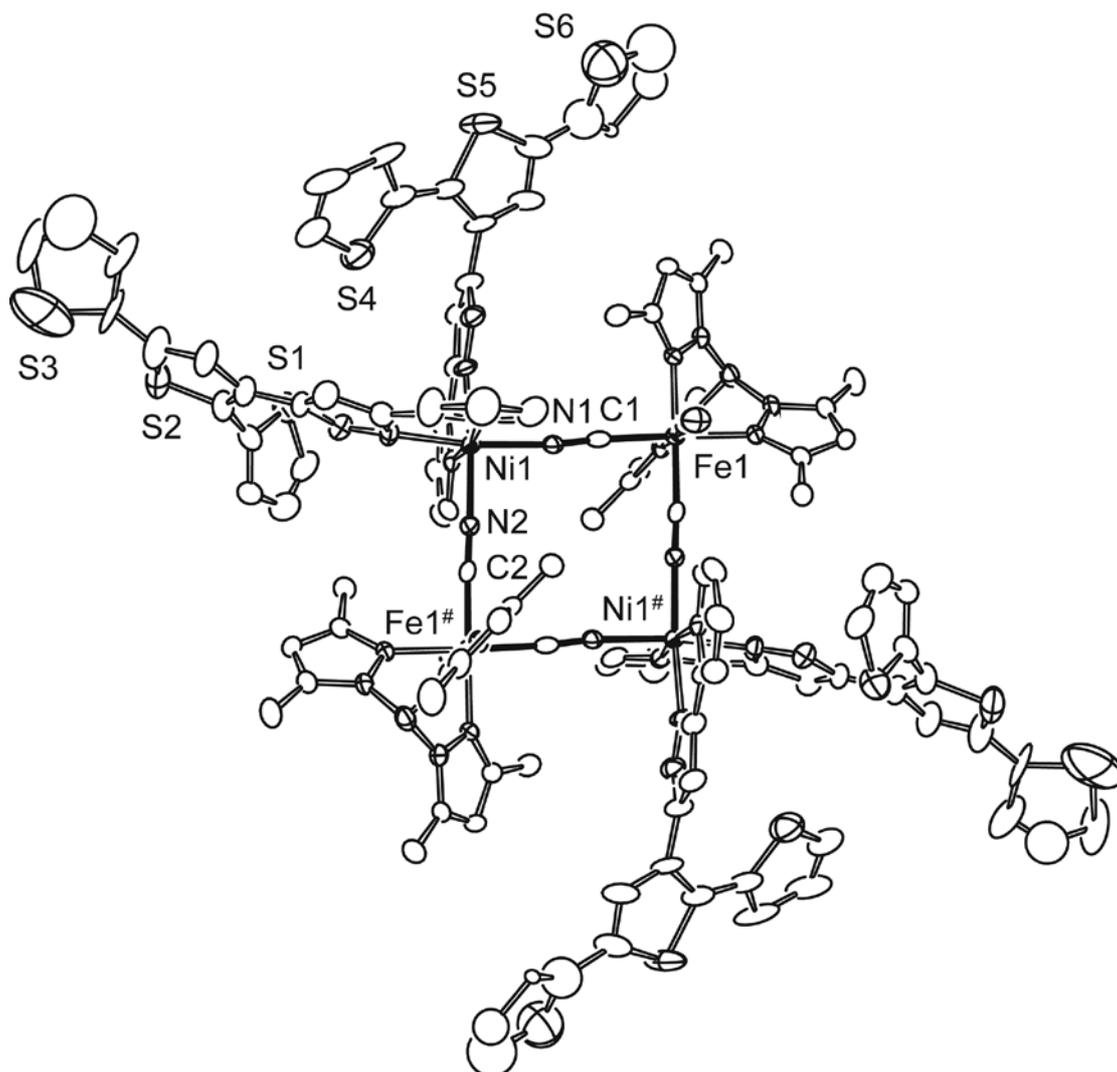


Figure 1. ORTEP view of the complex cation **1**. Symmetry operation used to generate equivalent (#) atom: $1-x, -y, -z$.

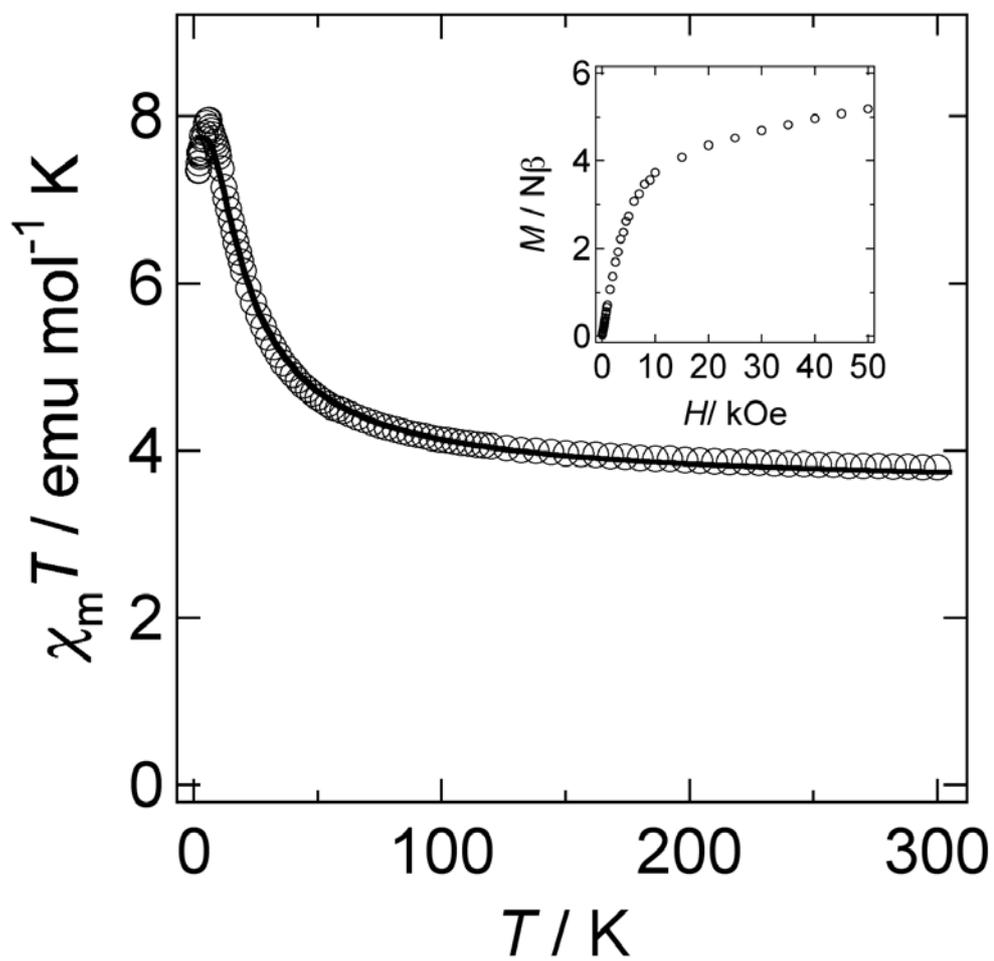


Figure 2. $\chi_m T$ versus T plot of **1**. The solid line represents a least square fit of the data. Inset: Magnetic field dependence of magnetization for **1** at 1.8 K.

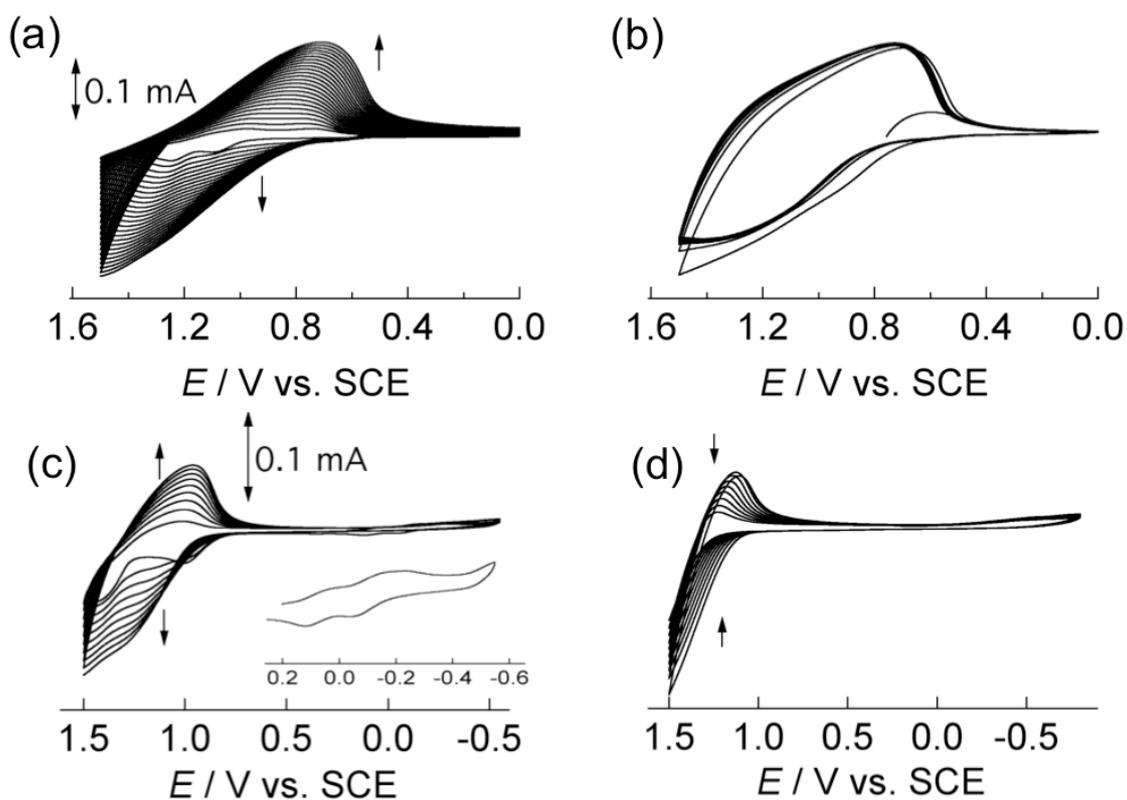


Figure 3. Electropolymerization of (a) **L** and (c) **1** in 0.01 M CH_2Cl_2 solution containing 0.1 M $n\text{Bu}_4\text{NPF}_6$. Cyclic voltammogram (CV) of deposited film formed by **L** (b) and by **1** (d) in CH_2Cl_2 solution, containing 0.1 M $n\text{Bu}_4\text{NPF}_6$. Inset of (c) shows first scan of CV data.

Contents

A heterometal tetranuclear Fe-Ni complex with terthiophene moieties was prepared. In this complex, cyanide ions bridge two Fe^{III} and two Ni^{II} ions to form square structure. Magnetic susceptibility measurements revealed ferromagnetic interactions between iron and nickel centers and the electrochemical properties were studied.

