

The First One-Dimensional Molecular Material Featuring Maleonitriledithiolate as a Subunit Exhibiting Metamagnetic-Like Behavior

Jingli Xie,^[a] Xiaoming Ren,^[a] Song Gao,^[b] Wenwei Zhang,^[a] Yizhi Li,^[a] Changsheng Lu,^[a] Chunlin Ni,^[a] Wenlong Liu,^[a] Qingjin Meng,^{*[a]} and Yuangen Yao^[c]

Keywords: Nickel / Maleonitriledithiolate / Crystal structure / Magnetic properties

An ion-pair complex $[\text{FBzPyNH}_2][\text{Ni}(\text{mnt})_2]$ $\{[\text{FBzPyNH}_2]^+ = [1-(4'\text{-fluorobenzyl})\text{-4-amino}]\text{pyridinium and } \text{mnt}^{2-} = \text{maleonitriledithiolate}\}$ has been obtained by I_2 oxidation of the corresponding dianion complex. It forms a well-segregated stacking column structure in the solid state, and

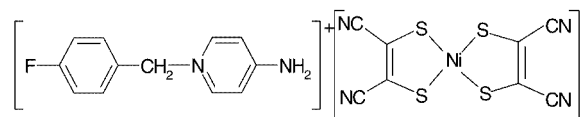
exhibits antiferromagnetic ordering below 2.5 K. It is the first complex in this series of complexes containing a maleonitriledithiolate dianion that exhibits metamagnetism.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Much effort has been devoted to the study of square-planar $\text{M}(\text{dithiolene})_2$ complexes in the areas of conducting and magnetic materials, dyes, non-linear optics and catalysis.^[1,2] Recently, we have employed a strategy of constructing one-dimensional molecule-based magnets based on ion-pair complexes containing $[\text{M}(\text{mnt})]^-$ ($\text{M} = \text{Ni}^{\text{III}}$, Pt^{III} ; $\text{mnt}^{2-} = \text{maleonitriledithiolate}$) anions with benzylpyridinium derivatives as counterions. Interestingly, varying the counterions led to a broader palette of complexes with markedly different magnetic-exchange properties, although they all have extremely similar molecular and stacking structures. Versatile magnetic properties such as ferromagnetic ordering at 2 K, unusual magnetic transitions from ferromagnetic coupling to diamagnetism or from paramagnetic to diamagnetic, or spin-Peierls-like transitions have been witnessed.^[3] In order to further understand the magnetic coupling mechanism in this series of complexes, we should explore the relationship between stacking structures and magnetic properties systematically. Within this framework, we report the synthesis and crystal structure of an ion-pair complex $[1-(4'\text{-fluorobenzyl})\text{-4-aminopyridinium}][\text{Ni}(\text{mnt})_2]$ (Scheme 1), which has well-segregated stacking

columns. A study of its magnetic properties shows antiferromagnetic ordering below 2.5 K and metamagnetic-like behavior.



Scheme 1. Molecular structure of **2**

Results and Discussion

$[\text{FBzPyNH}_2]_2[\text{Ni}(\text{mnt})_2]$ (**1**) was prepared by the direct combination of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Na_2mnt and $[1-(4'\text{-fluorobenzyl})\text{-4-amino}]\text{pyridinium chloride}$ in H_2O in a 1:2:2 molar ratio. The title complex **2** was prepared by I_2 oxidation of **1**,^[4] and well-shaped single crystals were obtained by allowing Et_2O to diffuse into an MeCN solution of **2** for about a week. Figure S1 depicts the molecular structure of **2**. The coordination geometry of Ni^{III} is square planar with four sulfur donor atoms; the $\text{Ni}-\text{S}$ bond lengths and $\text{S}-\text{Ni}-\text{S}$ bond angles are in agreement with reported values.^[3] The CN groups of the mnt^{2-} ligand are bent away from the plane defined by the Ni atom and four sulfur atoms. The deviation of the four terminal N atoms from the plane are 0.2926 Å, 0.3666 Å, 0.0802 Å and 0.1736 Å, respectively. In the $[\text{FBzPyNH}_2]^+$ cation, the dihedral angles between the $\text{C}(15)-\text{C}(14)-\text{N}(5)$ reference plane and the aryl rings are 80.5° for the phenyl ring and 106.6° for the pyridine ring; these values are in line with previous results.^[3] It should be noted that **2** possesses well-segregated stacking column along the c -axis (Figure 1a). Within an anion column, there exists a slipped nickel-over-sulfur con-

^[a] State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, 210093 Nanjing, P. R. China
Fax: (internat.) +86-25/331-4502
E-mail: njujlxie@yahoo.com

^[b] State Key Laboratory of Rare Earths Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871 P. R. China

^[c] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, 350002 Fuzhou, P. R. China

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

figuration of $[\text{Ni}(\text{mnt})_2]^-$ anions and the Ni...Ni distances between adjacent anions are identical (3.991 Å); the nearest S...S, S...Ni contacts are 3.797 Å and 3.663 Å, respectively. These distances are larger than the sum of the van der Waals radii of the corresponding atoms. The closest Ni...Ni separation between anion chains is 14.32 Å, which is significantly larger than the Ni...Ni separation within a chain. Therefore, each $[\text{Ni}(\text{mnt})_2]^-$ anion column can be considered as a one-dimensional (1-D) magnetic chain from the viewpoint of the crystal structure (Figure 1b). The $[\text{FBzPyNH}_2]^+$ cations orient themselves in the solid state. The pyridine rings of the neighboring cations are essentially parallel to each other with an identical center-center distance of 3.893 Å (Figure S2).

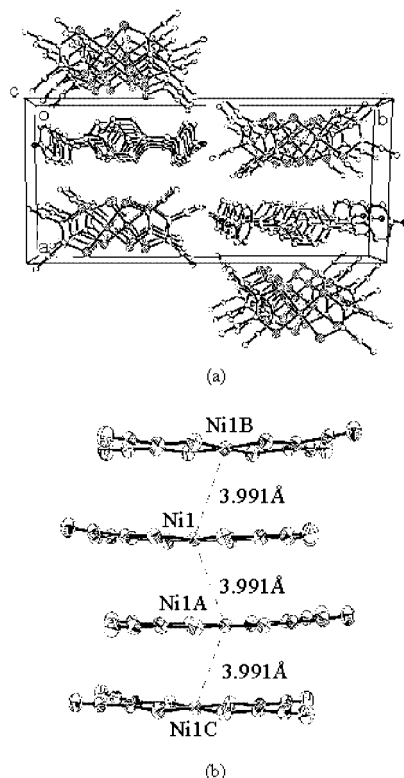


Figure 1. (a) Structure of anions and cations of **2** viewed along the *c*-axis; (b) side view of the 1-D anion chain of **2** (symmetry codes: A = *x*, 1.5 − *y*, 0.5 + *z*; B = *x*, 1.5 − *y*, −0.5 + *z*; C = *x*, *y*, *z* + 1)

The thermal variation of $\chi_m T$, measured at a field of 1 T, is shown in Figure 2. The observed $\chi_m T$ value at 308 K is 0.331 emu·K·mol^{−1}, slightly less than the theoretical value of 0.375 emu·K·mol^{−1} expected for a spin-only Ni^{III} ion with *S* = 1/2 and *g* = 2.0. Upon cooling down, the $\chi_m T$ values decrease smoothly and reaches a minimum of 0.223 emu·K·mol^{−1} at 24 K. This behaviour is characteristic of ferrimagnetic-like behavior. With a further decrease in temperature, the $\chi_m T$ values increase abruptly, reaching a maximum of 0.343 emu·K·mol^{−1} at 7.2 K, before decreasing again. The data above 24 K are best fit by the Bonner–Fisher model for a uniformly spaced chain of atoms with *S* = 1/2 spin.^[5] Equation (1) for $H = -2JS_1 \cdot S_2$ ^[6] with $z = J/k_B T$.

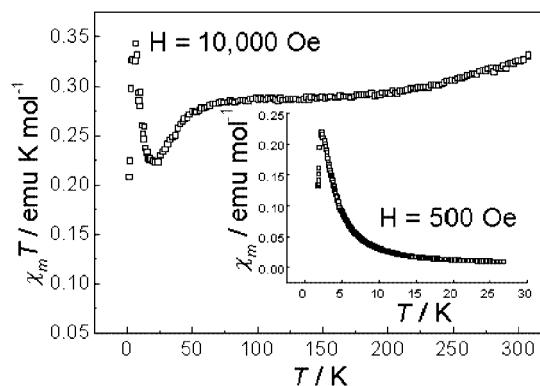


Figure 2. Temperature dependence of $\chi_m T$ for **2** measured at 10 KOe; inset: temperature dependence of χ_m for **2** measured at 500 Oe

$$\chi_m = \frac{Ng^2\mu_B^2}{k_B T} \frac{0.25 + 0.074975z + 0.075235z^2}{1.0 + 0.9931z + 0.172135z^2 + 0.757825z^3} \quad (1)$$

A fit of the data to Equation (1) gives $J = -6.8 \text{ cm}^{-1}$ and $g = 2.0$ (fixed), which suggests there exists weak anti-ferromagnetic coupling between adjacent *S* = 1/2 Ni^{III} spin carriers within the anion chain. The χ_m/T curve at 500 Oe field shows a sharp cusp at 2.5 K, suggesting a long-range antiferromagnetic (AF) ordering (inset of Figure 2). The *M* vs. *H* curve at 1.8 K exhibits a sigmoidal shape, indicating a metamagnetic-like behavior (Figure 3), which switches from an antiferromagnetic ground state to a ferrimagnetic-like state upon the application of a large enough field. At 1.8 K, the critical field is approximately 1000 Oe because the derivative d*M*/d*H* has an extremum (Figure S3). The saturation magnetization of **2** at 1.8 K (the higher applied magnetic field is 7 T) is 1310 emu·G·mol^{−1}, far from the theoretical saturation value of 5585 emu·G·mol^{−1}, which is usual in metamagnetic material if the temperature is not much lower than *T_N*.^[7,8] The AF transition is further manifested by the in-phase signal (χ') of zero-field ac magnetic susceptibility, which has a maximum at about 2.5 K (*T_N*). No out-of-phase signal (χ'') could be detected and their is no frequency dependence, thus excluding any ferromagnetic

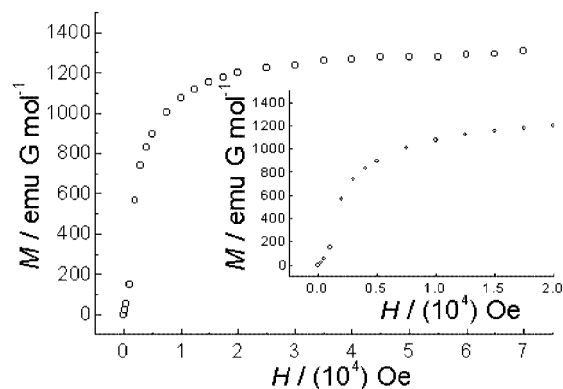


Figure 3. *M*-*H* curve of **2** measured at 1.8 K; inset: enlargement of the applied magnetic field range 0–20000 Oe

phase or spin-glass behavior (Figure S4). The FCM curves of **2** measured at lower fields (200 Oe and 1000 Oe) both show a maximum in χ_m at about 2.5 K (Figure S5), suggesting long-range magnetic ordering, whereas a higher field (5000 Oe) leads to the absence of the peak down to 2.0 K (inset of Figure S5).

Of all the commonly studied dithiolate systems, metamagnetism has been observed in some charge-transfer salts such as $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{edt})_2]$ (edt = ethylenedithiolate), $[\text{Mn}(\text{Cp}^*)_2][\text{M}(\text{tfd})_2]$ [$\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; tfd = bis(trifluoromethyl)ethylenedithiolate].^[7–9] For complexes containing the $[\text{Ni}(\text{mnt})_2]^-$ anion, previous studies have shown that the magnetic coupling between $[\text{Ni}(\text{mnt})_2]^-$ anions is very sensitive not only to intermolecular separation,^[2a] but also to the degree of overlap of neighboring $[\text{Ni}(\text{mnt})_2]^-$ anions.^[10–12] Several shorter contact distances, such as $\text{Ni}\cdots\text{Ni}$, $\text{Ni}\cdots\text{S}$, $\text{S}\cdots\text{S}$, $\text{S}\cdots\text{N}$, $\text{S}\cdots\text{C}$ and $\text{C}\cdots\text{N}$, play important roles in the superexchange pathway due to extensive electron delocalization in the $[\text{Ni}(\text{mnt})_2]^-$ unit.^[13] At very low temperature, superexchange and/or through-space intrachain antiferromagnetic couplings must be considered in order to yield a three-dimensional AF ordering state below 2.5 K.

In summary, a metamagnetic-like behavior is observed in the title complex, which, to the best of our knowledge, is the first example of metamagnetism in this series of complexes containing the maleonitriledithiolate dianion.

Experimental Section

All manipulations were carried out in air unless otherwise noted. Starting materials were purchased from Aldrich (4-fluorobenzyl chloride, 4-aminopyridine), and were used without further purification. $[1-(4'\text{-Fluorobenzyl})-4\text{-amino}]$ pyridinium chloride ($[\text{FBzPyNH}_2]\text{Cl}$) and disodium maleonitriledithiolate (Na_2mnt) were synthesized following the published procedures.^[4]

$[\text{FBzPyNH}_2]_2[\text{Ni}(\text{mnt})_2]$ (1**):** This compound was prepared by the direct combination of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Na_2mnt and $[\text{FBzPyNH}_2]\text{Cl}$ in H_2O in a 1:2:2 molar ratio. The red precipitate that formed was filtered off, washed with water and dried under vacuum. Yield: 93%. $\text{C}_{32}\text{H}_{24}\text{F}_2\text{N}_8\text{NiS}_4$ (745.5): calcd. C 51.55, H 3.24, N 15.03; found C 51.81, H 3.22, N 15.11. IR (KBr): $\nu(\text{NH}_2)$ 3420.3 cm^{-1} , 1657.4 vs; $\nu(\text{CN})$ 2196.4 vs; $\nu(\text{C}=\text{C})$ of mnt^{2-} 1485.3 s.

$[\text{FBzPyNH}_2]_2[\text{Ni}(\text{mnt})_2]$ (2**):** An MeCN solution (10 mL) of **1** (150 mg, 0.59 mmol) was slowly added to an MeCN solution (20 mL) of $[\text{FBzPyNH}_2]_2[\text{Ni}(\text{mnt})_2]$ (746 mg, 1.0 mmol), and stirred for 15 min. MeOH (90 mL) was then added, and the mixture allowed to stand overnight. The microcrystals formed were filtered off, washed with MeOH and dried in vacuo. Yield: 87%. $\text{C}_{20}\text{H}_{12}\text{FN}_6\text{NiS}_4$ (542.3): calcd. C 44.30, H 2.23, N 15.50; found C 44.52, H 2.22, N 15.42. IR: $\nu(\text{NH}_2)$ 3347.9 cm^{-1} , 1654.4 vs; $\nu(\text{CN})$ 2206.7 vs; $\nu(\text{C}=\text{C})$ of mnt^{2-} 1453.3 m. Good-shaped single crystals suitable for X-ray analysis were obtained by allowing Et_2O to diffuse into an MeCN solution of **2** for about a week.

X-ray Crystallography Study: $\text{C}_{20}\text{H}_{12}\text{FN}_6\text{NiS}_4$, $M_r = 542.31$, black, needle-shaped crystal, monoclinic, space group $P2_1/c$, $a = 12.0041(17)$ Å, $b = 26.095(4)$ Å, $c = 7.4809(11)$ Å, $\beta = 101.448(3)^\circ$,

$V = 2296.7(6)$ Å³, $Z = 4$, $D_c = 1.568$ g cm^{−3}, $\mu(\text{Mo-K}\alpha) = 1.237$ mm^{−1}, $\lambda = 0.71073$ Å, $-14 \leq h \leq 14$, $-31 \leq k \leq 22$, $-8 \leq l \leq 8$. A crystal of dimensions $0.20 \times 0.15 \times 0.10$ mm³ was selected for indexing and intensity data collection at 298 K. Data collection: SMART (Bruker, 1997). ω -Scans covering reciprocal space up to $\theta_{\text{max}} 24.99^\circ$ with 99.8% completeness, total of 11370 reflections (4031 unique) with $R_{\text{int}} = 0.1139$. Structure solution SHELXL-97, full-matrix least-squares based on F^2 using SHELXL-97, final $R = 0.058$, $wR = 0.154$, GOF = 1.006. Final residual density was in the range -0.497 to 0.923 e Å^{−3}.

CCDC-201344 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: ORTEP view, side view of cation chain, dM/dH vs. H plot, in-phase signal (χ') and FCM curve for **2** is available (see footnote on the first page of this article).

Acknowledgments

Financial support from the National Natural Science Foundation (No. 2017022, No. 29831010, No. 20125104), Jiangsu Science and Technology Department and The Center for Analysis and Determination of Nanjing University are gratefully acknowledged.

- [1] [1a] N. Robertson, L. Cronin, *Coord. Chem. Rev.* **2002**, 227, 93–127. [1b] P. Cassoux, L. Valade, H. Kobayashi, R. A. Clar, A. E. Underhill, *Coord. Chem. Rev.* **1991**, 110, 115–160.
- [2] [2a] A. T. Coomber, D. Beljonne, R. H. Friend, J. L. Brédas, A. Charlton, N. Robertson, A. E. Underhill, M. Kurmoo, P. Day, *Nature* **1996**, 380, 144–146. [2b] A. E. Pullen, C. Faulmann, K. I. Pokhodnya, P. Cassoux, M. Tokumoto, *Inorg. Chem.* **1998**, 37, 6714–6720. [2c] M. Uruichi, K. Yakushi, Y. Yamashita, J. Qin, *J. Mater. Chem.* **1998**, 8, 141–146. [2d] D. Arçon, A. Lappas, S. Margadonna, K. Prassides, E. Ribera, J. Veciana, C. Rovira, R. T. Henriques, M. Almeida, *Phys. Rev. B* **1999**, 60, 4191–4194.
- [3] [3a] J. L. Xie, X. M. Ren, Y. Song, Y. Zou, Q. J. Meng, *J. Chem. Soc., Dalton Trans.* **2002**, 2868–2872. [3b] J. L. Xie, X. M. Ren, Y. Song, W. J. Tong, C. S. Lu, Y. G. Yao, Q. J. Meng, *Inorg. Chem. Commun.* **2002**, 5, 395–398. [3c] J. L. Xie, X. M. Ren, Y. Song, W. W. Zhang, W. L. Liu, C. He, Q. J. Meng, *Chem. Commun.* **2002**, 2346–2347. [3d] X. M. Ren, Q. J. Meng, Y. Song, C. L. Lu, C. J. Hu, X. Y. Chen, Z. L. Xue, *Inorg. Chem.* **2002**, 5931–5933. [3e] J. L. Xie, X. M. Ren, C. He, Y. Song, Q. J. Meng, R. K. Kremer, Y. G. Yao, *Chem. Phys. Lett.* **2003**, 369, 41–48.
- [4] [4a] S. B. Bulgarevich, D. V. Bren, D. Y. Movshovic, P. Finocchiaro, S. Failla, *J. Mol. Struct.* **1994**, 317, 147–155. [4b] A. Davison, H. R. Holm, *Inorg. Synth.* **1967**, 10, 7–23.
- [5] J. C. Bonner, M. E. Fisher, *Phys. Rev.* **1964**, A135, 640–658.
- [6] W. E. Estes, D. P. Gavel, W. E. Hatfield, D. J. Hodgson, *Inorg. Chem.* **1978**, 17, 1415–1421.
- [7] V. Gama, D. Belo, S. Rabaça, I. C. Santos, H. Alves, J. C. Waerenborgh, M. T. Duarte, R. T. Henriques, *Eur. J. Inorg. Chem.* **2000**, 2101–2110.
- [8] W. E. Broderick, J. A. Thompson, B. M. Hoffman, *Inorg. Chem.* **1991**, 30, 2958–2960.
- [9] V. Gama, D. Belo, I. C. Santos, R. T. Henriques, *Mol. Cryst. Liq. Cryst.* **1997**, 306, 17–24.
- [10] J. Nishijo, E. Ogura, J. Yamaura, A. Miyazaki, T. Enoki, T.

- Takano, Y. Kuwatani, M. Iyoda, *Solid State Commun.* **2000**, *116*, 661–664.
- ^[11] S. Alvarez, R. Vicente, R. Hoffmann, *J. Am. Chem. Soc.* **1985**, *107*, 6253–6277.
- ^[12] N. Robertson, C. Bergemann, H. Becker, P. Agarwal, S. R. Julian, R. H. Friend, N. J. Hatton, A. E. Underhill, A. Kobayashi, *J. Mater. Chem.* **1999**, *9*, 1713–1717.
- ^[13] ^[13a] J. E. Huyett, S. B. Choudhury, D. M. Eichhorn, P. A. Bryngelson, M. J. Maroney, B. M. Hoffman, *Inorg. Chem.* **1998**, *37*, 1361–1367. ^[13b] B. L. Ramakrishna, *Inorg. Chim. Acta* **1986**, *114*, 31–34.

Received February 24, 2003