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Experimental and theoretical investigation of magnetic and photoconductive natures for a novel two-dimensional mixed-valence bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickel-ate molecular solid

Hao Yang,[†] Jian-Lan Liu,[†] Lan-Cheng Zhou[†] and Xiao-Ming Ren^{*,†,‡}

[†]State Key Laboratory of Materials-Oriented Chemical Engineering and College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China

[‡]State Key Laboratory & Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China

Phone: +86 25 58139476

Fax: +86 25 58139481

E-mail: xmren@njut.edu.cn

Details of broken-symmetry DFT approach

The broken-symmetry formalism, originally developed by Noodleman for SCF methods,¹ which involves a variational treatment within the restrictions of a single spin-unrestricted Slater determinant built upon using different orbitals for different spin. This approach has been later applied within the framework of DFT as a practical tool to investigate magnetic interactions on rather large systems (for example, dinuclear, polynuclear, 1-D, 2-D and 3-D spin systems)²⁻⁷ with reasonable accuracy due to partial consideration of electron correlation effects.^{8,9}

For three types of magnetic exchange pathways in **1**, the calculated energies for the high-spin state and the low-spin broken-symmetry (BS) state of the spin dimers associated with the spin exchange paths (i.e., structural units consisting of two adjacent magnetic anion sites) were combined to estimate the coupling constant J involved in the widespread used Heisenberg-Dirac-van Vleck Hamiltonian:¹⁰⁻¹²

$$\hat{H} = -2J\vec{S}_1\vec{S}_2 \quad (1)$$

Where \vec{S}_1 and \vec{S}_2 are the respective spin angular momentum operators, J is the magnetic coupling constant between two coupled magnetic centers. A positive sign of J indicates a ferromagnetic (FM) interaction, whereas the negative sign an AFM interaction. Assuming the so-called “weak bonding” regime, Noodleman et al.¹²⁻¹⁴ evaluated J values within broken symmetry framework by

$$J^{(1)} = \frac{E_{BS} - E_{HS}}{S_{\max}^2} \quad (2)$$

Where E_{BS} and E_{HS} denote the total energies in the low-spin broken symmetry (BS) state and the high-spin state, respectively, and S_{\max} corresponds to the total spin of the high-spin state. It has been suggested that the following expression might give more reasonable solutions in the strong overlap region:^{15, 16}

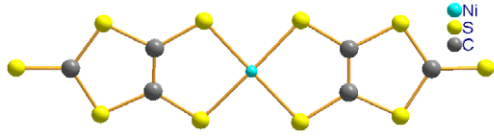
$$J^{(2)} = \frac{E_{BS} - E_{HS}}{S_{\max}(S_{\max} + 1)} \quad (3)$$

In the broken symmetry approach, the theoretical description of the high-spin state is not problematic because it corresponds to a “real” state. However, the low spin broken symmetry solution is not a state of the system and corresponds to a spin contaminated solution. The use of the spin projection techniques could eliminate such spin contamination, and Yamaguchi et al. claimed that magnetic coupling constant calculated by the approximate spin projection procedure reproduces the characteristic feature of J in the whole region,^{7, 17, 18} thus the magnetic coupling constants, J , obtained from Eq. (4) are used for the magnetic property analyses of **1**:

$$J^{(3)} = \frac{E_{BS} - E_{HS}}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}} \quad (4)$$

The $\langle S^2 \rangle_{HS}$ and $\langle S^2 \rangle_{BS}$ in Eq. (4) denote the total spin angular momentum of the high-spin state and the low-spin broken-symmetry state, respectively.

Table S1 Average bond lengths in [Ni(dmit)₂] moiety of **1**

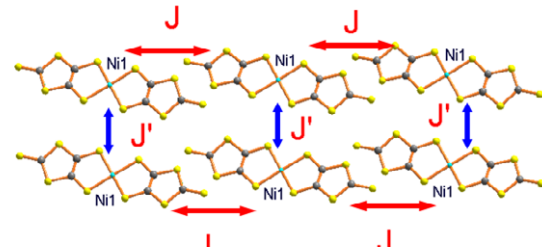


| | Ni-S (Å) | S-C (Å) | C=C (Å) | Ref. |
|--|-----------|-----------|-----------|-----------|
| [Ni(dmit) ₂] ²⁻ | 2.195(9) | 1.733(8) | 1.352(3) | 19 |
| [Ni(dmit) ₂] ¹⁻ | 2.166(10) | 1.715(10) | 1.360(6) | 20 |
| [Ni(dmit) ₂] ^{0.5-} | 2.163(3) | 1.701(4) | 1.382(7) | 21 |
| [Ni(dmit) ₂] ⁰ | 2.143(3) | 1.698(5) | 1.393(10) | 22 |
| Ni(1) moiety | 2.163(2) | 1.726(5) | 1.354(5) | This work |
| Ni(2) moiety | 2.148(8) | 1.721(4) | 1.373(1) | This work |

Table S2 The A_g vibrational modes and frequencies (cm⁻¹) for Ni(dmit)₂ⁿ⁻. The A_g(1) mode is apparently the C=C stretching mode, A_g(2) is assigned to the C=S stretching mode, and A_g(3) is referred to the C-S stretching mode, respectively, the data are taken from [23, 24].

| n | A _g (1) | A _g (2) | A _g (3) |
|-----------------|--------------------|--------------------|--------------------|
| 0 ²³ | 1329 | 1051 | 496 |
| 1 ²⁴ | 1343 | 1064 | 507 |
| This work | 1368, 1324 | 1068, 1054 | 514, 499 |

Table S3 Calculated Overlap integrals, transfer integrals and magnetic exchange constant for each spin dimer in the two-legged ladder chain of **1**



| | <i>S</i> | <i>t</i> | <i>J'</i> / <i>J</i> |
|-----------|------------|------------|------------------------|
| <i>J</i> | 0.00324807 | 0.03248070 | 39.3 |
| <i>J'</i> | 0.02036502 | 0.20365020 | |

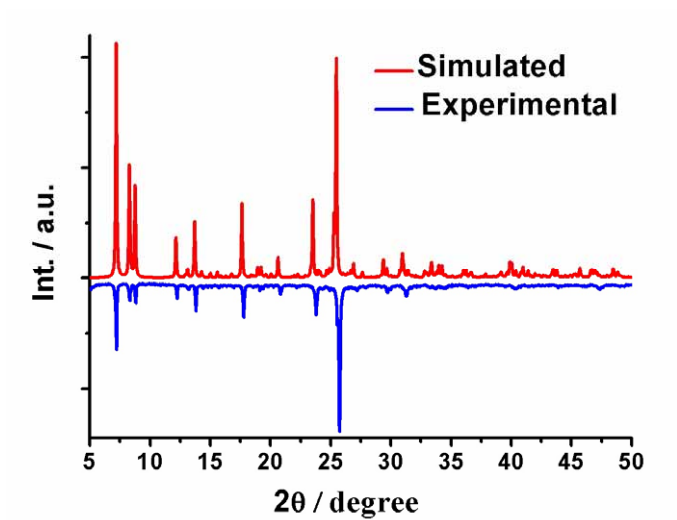


Figure S1 PXRD patterns of **1** at room temperature which confirmed **1** has high phase purity.

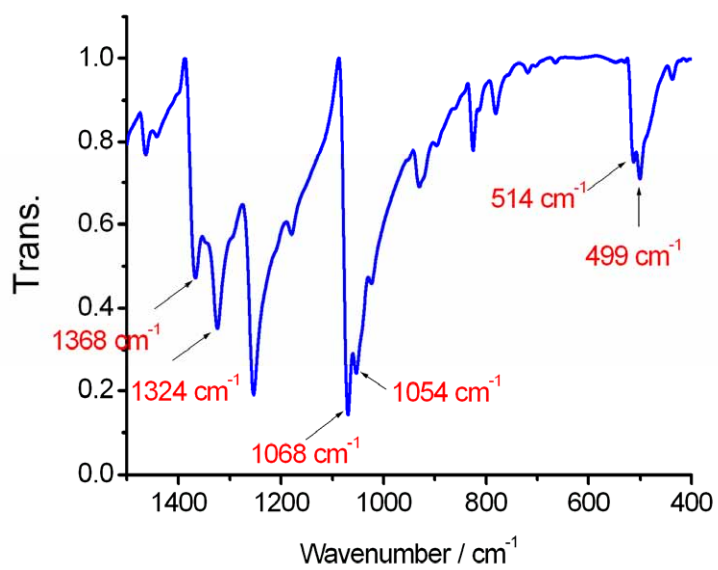


Figure S2 IR Spectrum of **1** shows the characteristic IR bands.

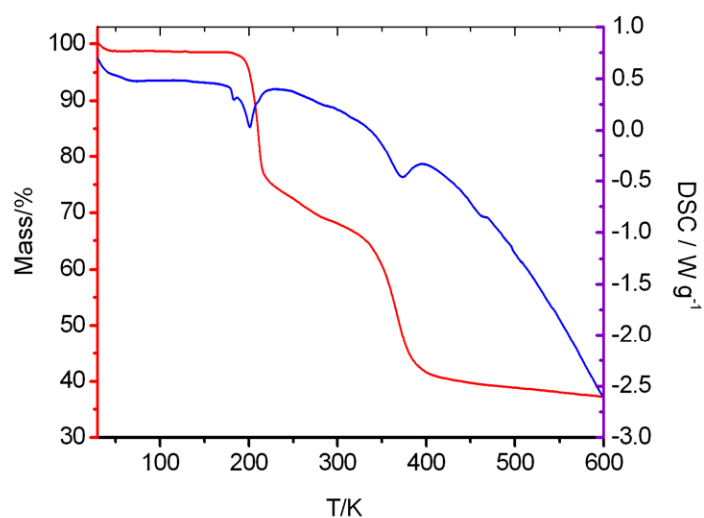


Figure S3 Thermogravimetric (red) and DSC (blue) curves of **1** indicated this compound is thermally stable up to 200 °C.

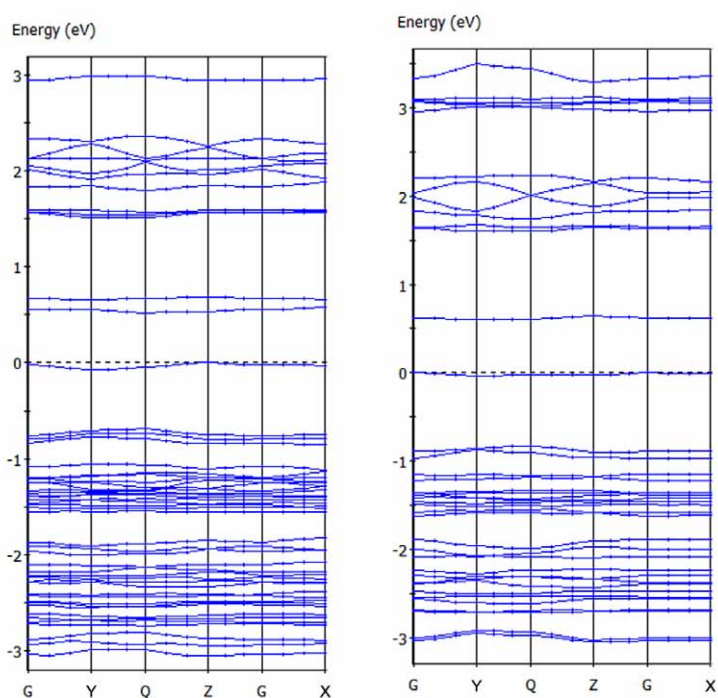


Figure S4 Dispersion relations of (a) the mixed valence layer and (b) the anion layer where the neutral $[\text{Ni}(\text{dmit})_2]$ species were removed in **1** (Fermi levels are shown by dashed lines, k-points: $G = (0, 0, 0)$, $X = (0.5, 0, 0)$, $Y = (0, 0.5, 0)$, $Z = (0, 0, 0.5)$ and $Q = (0, 0.5, 0.5)$).

References

1. L. Noodleman and J. G. Jr. Norman, *J. Chem. Phys.*, 1979, **70**, 4903.
2. E. Ruiz, *J. Comput. Chem.*, 2011, **32**, 1998; D. Venegas-Yazigi, D. Aravena, E. Spodine, E. Ruiz and S. Alvarez, *Coord. Chem. Rev.*, 2010, **254**, 2086; E. Vélez, A. Alberola and V. Polo, *J. Phys. Chem. A*, 2009, **113**, 14008; G. Manca, J. Cano and E. Ruiz, *Inorg. Chem.*, 2009, **48**, 3139; F. Yan and Z. D. Chen, *J. Phys. Chem. A*, 2000, **104**, 6295; E. Ruiz, P. Alemany, S. Alvarez and J. Cano, *J. Am. Chem. Soc.*, 1997, **119**, 1297.
3. R. Singh, A. Banerjee, E. Colacio and K. K. Rajak, *Inorg. Chem.*, 2009, **48**, 4753.
4. J. L. Manson, M. M. Conner, J. A. Schlueter, A. C. McConnell, H. I. Southerland, I. Malfant, T. Lancaster, S. J. Blundell, M. L. Brooks, F. L. Pratt, J. Singleton, R. D. McDonald, C. Lee and M.-H. Whangbo, *Chem. Mater.*, 2008, **20**, 7408.
5. J. L. Manson, J. A. Schlueter, K. A. Funk, H. I. Southerland, B. Twamley, T. Lancaster, S. J. Blundell, P. J. Baker, F. L. Pratt, J. Singleton, R. D. McDonald, P. A. Goddard, P. Sengupta, C. D. Batista, L. Ding, C. Lee, M.-H. Whangbo, I. Franke, S. Cox, C. Baines and D. Trial, *J. Am. Chem. Soc.*, 2009, **131**, 6733.
6. M. Mitsumi, Y. Yoshida, A. Kohyama, Y. Kitagawa, Y. Ozawa, M. Kobayashi, K. Toriumi, M. Tadokoro, N. Ikeda, M. Okumura and M. Kurmoo, *Inorg. Chem.*, 2009, **48**, 6680.
7. H. Nagao, M. Nishino, Y. Shigeta, T. Soda, Y. Kitagawa, T. Onishi, Y. Yoshioka and K. Yamaguchi, *Coord. Chem. Rev.*, 2000, **198**, 265.
8. I. Ciofini and C. A. Daul, *Coord. Chem. Rev.*, 2003, **238-239**, 187.
9. W. Heisenberg, *Z. Phys.*, 1928, **49**, 619.
10. P. A. M. Dirac, *The principles of quantum mechanics*, Clarendon Press, Oxford, U. K., 1947.
11. J. H. Van Vleck, *The theory of electric and magnetic susceptibilities*, Oxford University Press, Oxford, U. K., 1932.
12. A. P. Ginsberg, *J. Am. Chem. Soc.*, 1980, **102**, 111.
13. L. Noodleman, *J. Chem. Phys.*, 1981, **74**, 5737.

14. L. Noodleman and E. R. Davidson, *Chem. Phys.*, 1986, **109**, 131.
15. A. Bencini, F. Totti, C. A. Daul, K. Doclo, P. Fantucci and V. Barone, *Inorg. Chem.*, 1997, **36**, 5022.
16. E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Comput. Chem.*, 1999, **20**, 1391.
17. T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka and K. Yamaguchi, *Chem. Phys. Lett.*, 2000, **319**, 223.
18. Y. Takano, Y. Kitagawa, T. Onishi, Y. Yoshioka, K. Yamaguchi, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, 2002, **124**, 450.
19. H. K. Fun, K. Sivakumar, J. L. Zuo, T. M. Yao and X. Z. You, *Acta Crystallogr. Sect. C, Cryst. Struct. Commun.*, 1996, **52**, 312.
20. M. J. J. Mulder, H. Kooijman, A. L. Spek, J. G. Haasnoot and J. Reedijk, *J. Chem. Cryst.*, 2002, **32**, 347.
21. J. P. Cornelissen, R. L. Loux, J. Jansen, J. G. Haasnoot, J. Reedijk, E. Horn, A. L. Spek, B. Pomarede, J. P. Legros and D. Reefman, *J. Chem. Soc., Dalton Trans.*, 1992, 2911.
22. N. Kushch, C. Faulmann, P. Cassoux, L. Valade, I. Malfant, J. P. Legros, C. Bowlas, A. Errami, A. Kobayashi and H. Kobayashi, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, 1996, **284**, 247.
23. K. I. Pokhodnya, C. Faulmann, I. Malfant, R. Andreu-Solano, P. Cassoux, A. Mlayah, D. Smirnov and J. Leotin, *Synth. Met.*, 1999, **103**, 2016.
24. B. Cai, J. L. Liu, X. L. Sheng and X. M. Ren, *Inorg. Chem. Commun.*, 2011, **14**, 1971.