Chinese Chemical Letters Vol. 14, No. 10, pp 1089–1092, 2003 1089
http://www.imm.ac.cn/journal/ccl.html

Synthesis, Structure and Conductivity of (PyH)[Ni(dmit)$_2$]$_2$

Wen XU[1], Qi FANG[1,*], Gang XUE[1], Wen Tao YU[1], Hong Yu CHEN[1], Guo Qun LIU[1]
Wei XU[2], Cui Ying XU[2], De Qing ZHANG[2], Dao Ben ZHU[2]

[1]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100
[2]Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080

Abstract: A new molecular conductor (PyH)[Ni(dmit)$_2$]$_2$ (dmit = 4, 5-dimercapto-1, 3-dithiole-2-thione) has been prepared and its crystal structure has been determined. Crystallographic parameters for (PyH)[Ni(dmit)$_2$]$_2$: $C_{17}H_6NNi_2S_{20}$; triclinic system; *P*-1 space group; a = 5.9227 (4) , b =8.2279 (6) , c = 16.7535 (9) Å, α = 90.233 (5) °, β = 92.107 (6) °, γ = 104.654 (6) °; V = 789.25 (9) Å^3; Z = 1; D_c = 2.068 g/cm^3; F (000) = 491. The conductivity at one direction on (001) plane at room temperature was measured to be 0.13 $\Omega^{-1}\cdot$cm^{-1}. The resistivity-temperature curve in the temperature range of 90~290 K shows that this compound behaves as a semiconductor.

Keywords: Molecular conductor, synthesis, electrical conductivity, semiconductor, structure.

Molecular based electrical conductors, as a kind of new solid states, have been of interest for their prospective applications such as molecular conducting wires, bio-electrodes and nano-technologies. Z[M(dmit)$_2$]$_n$ type complexes, owing to their striking conducting properties and rich variety of structures, continue to receive significant attention. To date, a total of eight superconducting salts of this kind[1-7] have been obtained, in which the cations Z can be opened-shell radicals or closed-shell cations. Although the closed-shell cations have no contribution to the conductivity, their sizes and shapes play a predominant role in influencing the crystal structures and consequently influencing the electronic properties. So far, most of the closed-shell cations are tetraalkyl ammonium, additionally four planar aromatic cations were reported[8-10]. In order to explore new members of Z[M(dmit)$_2$]$_n$ family and get some insight into the structure-conductivity correlations, the title complex has been designed and synthesized, its structure and preliminary conducting property have also been reported in this paper.

Synthesis

Dmit(COPh)$_2$ (0.8128 g, 1.999 mmol) was treated with an excess of MeONa (9.0 mmol) in 20 mL MeOH under nitrogen at room temperature with stirring. To the resulting dark red solution, $NiCl_2\cdot 6H_2O$ (0.2360 g, 0.9929 mmol) in 20 mL MeOH, and a large excess of PyHBr (= pyridium bromide) (2.048 g, 12.80 mmol) in 20 mL MeOH were added. The precipitates were washed with MeOH and dried in a

* E-mail: Fangqi@icm.sdu.edu.cn

vacuum desiccator. This salt turned out to be $(PyH)[Ni(dmit)_2]$, instead of $(PyH)_2[Ni(dmit)_2]$. It was deduced from the peak (ν (C=C): 1339 cm^{-1}(s)) in the infrared spectroscopy. Oxidizing $(PyH)[Ni(dmit)_2]$ by I_2-NaI in acetone and evaporating the solvent in air produced large shining platelet title crystals. IR (KBr, cm^{-1}): ν (C=C) 1322(w), 1245(s), ν (S=C) 1041(s). Elemental analysis: Calcd. for $C_{17}H_6NNi_2S_{20}$: C, 20.77; H, 0.61; N, 1.42. Found C, 20.83; H, 0.47; N, 1.27.

Structural Analysis

All data were collected at room temperature on a Bruker P4 four-circle diffractometer with Mo Kα radiation. A platelet crystal of dimensions 0.38×0.36×0.015 mm^3 was used. Diffraction data (5333 unique reflections with h = -8→1, k = -11→11, l = -22→22) were collected by the ω-2θ scan technique in the θ range 2.43~29.00°. Reflections (4180) with $I > 2\sigma(I)$ were used in the structural analysis. The structure was resolved by direct methods and refined by using full-matrix least square methods. Anisotropic displacement parameters were refined for all non-H atoms. $(PyH)[Ni(dmit)_2]_2$ belongs to triclinic system, P-1 space group, a = 5.9227 (4) Å, b = 8.2279 (6) Å, c = 16.7535 (9) Å, α = 90.233 (5) °, β = 92.107 (6) °, γ = 104.654 (6) °; V = 789.25 (9) $Å^3$; Z = 1; D_c = 2.068 g/cm^3; F (000) = 491, R = 0.0435, wR = 0.1140.

As shown in **Figure 2**, $[Ni(dmit)_2]^{0.5-}$ units are stacked to form columns of dimerized pairs along the b-axis with the PyH^+ lying in between. The angle between the anionic plane and the cationic plane is 88.60°. $[Ni(dmit)_2]^{0.5-}$ and the PyH^+ counterion radicals are connected by N-H···S hydrogen bonds.

Figure 1 The molecular structure of $(PyH)[Ni(dmit)_2]_2$ (PyH^+ ring is disordered)

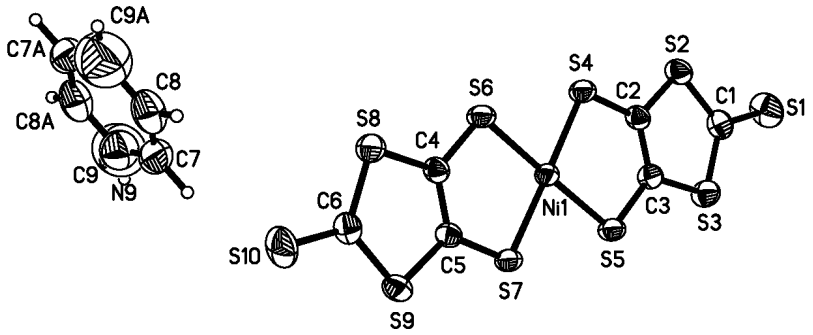


Figure 3 shows a two-dimensional network of short and intense S···S interactions within (001) plane. S···S distances shorter than 3.70 Å, the sum of van der Waals radii, are shown by dotted lines. Face-to-face S···S contacts of 3.5928 Å help to form a weakly dimerized structure along the column direction and many side-by-side S···S contacts (3.4747~3.6463 Å) with average distance of 3.598 Å link neighboring $[Ni(dmit)_2]^{0.5-}$ units forming a kind of two-dimensional cationic conducting structure.

Figure 2 View along the a-axis of (PyH)[Ni(dmit)$_2$]$_2$ crystal

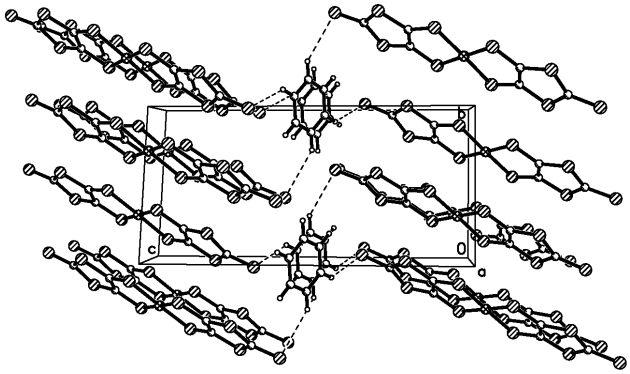
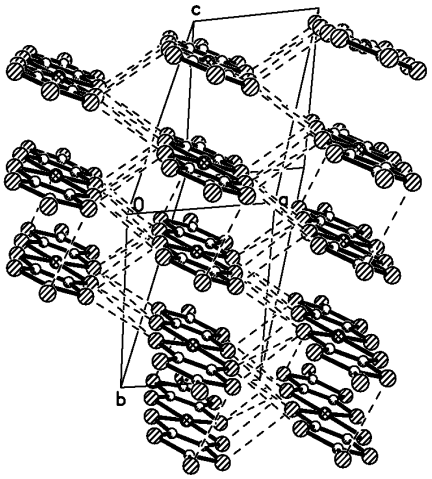


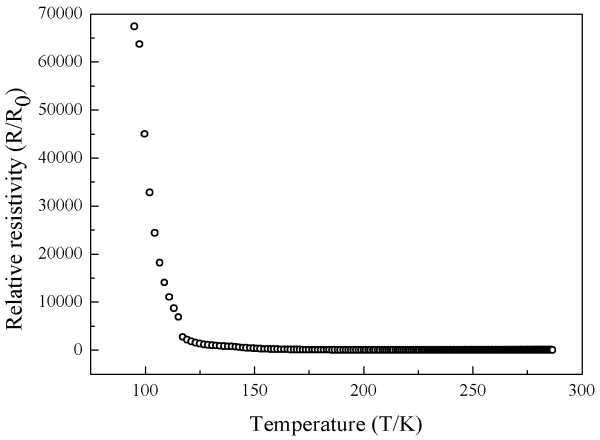
Figure 3 The two-dimensional network structure of the (001) plane (all cations are omitted for clarity)



Conductivity Measurement

Temperature dependent conductivity measurements were carried out along the longest axis of the platelet crystal by using the standard four-probe technique. The conductivity at one direction on (001) plane at room temperature was measured to be 0.13 $\Omega^{-1}\cdot cm^{-1}$. **Figure 4** shows that the title crystal behaves as a semiconductor in the temperature range of 90~290 K with quite narrow energy gap (Ea = 0.15 eV).

Figure 4 Resistivity-temperature curve of the title complex



Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20172034) and the Key Laboratory of Organic Solids, the Chinese Academic of Sciences.

References

1. A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, W. Sasaki, *Chem. Lett*., **1987**, 1819.
2. M. Bousseau, L. Valade, J. -P. Legros, P. Cassoux, M. Garbauskas, L. V. Interrante, *J. Am. Chem. Soc*., **1986**, *108* (8), 1908.
3. A. Kobayashi, H. Kobayashi, A. Miyamoto, R. Kato, R. A. Clark, A. E. Underhill, *Chem. Lett.*, **1991**, 2163.
4. H. Kobayashi, K. Bun, T. Naito, R. Kato, A. Kobayashi, *Chem. Lett*., **1992**, 1909.
5. L. Brossard, M. Ribault, L. Valade, P. Cassoux, *J. Phys. France*, **1989**, *50*, 1521.
6. H. Tajima, M. Inokuchi, A. Kobayashi, T. Ohta, R. Kato, H. Kobayashi, H. Kuroda, *Chem. Lett.*, **1993**, 1235.
7. R. Kato, Y. Kashimura, S. Aonuma, N. Hanasaki, H. Tajima, *Solid state Commun.*, **1998**, *105* (9), 561.
8. W. Xu, D. Q. Zhang, C. H. Yang, X. L. Jin, Y. F. Li, D. B. Zhu, *Synth. Met.*, **2001**, *122*, 409.
9. A. Miyazaki, A. Izuoka, T. Sugawara, *Bull. Chem. Soc. Jpn.*, **1992**, *65* (9), 2528.
10. Y. S. J. Veldhuizen, W. J. J. Smeets, N. Veldman, A. L. Spek, C. Faulmann, P. Auban-Senzier, D. Jerome, P. M. Paulus, J. G. Haasnoot, J. Reedijk, *Inorg. Chem.*, **1997**, *36* (22), 4930.

Received 21 October, 2002