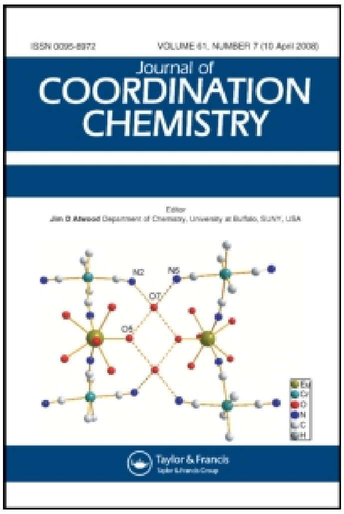


**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# 3D network structure and magnetic behaviour of a new Ni(III) maleonitriledithiolate complex with C-H • • • π and π • • • π interactions using 4-dimethylaminopyridinium cation

Chunlin Ni[ab]; Xiaoping Liu[a]; Lemin Yang[a]; Linliang Yu[a]
[a] Department of Applied Chemistry, College of Science, South China Agricultural University, Guangzhou, 510642 P.R. China [b] Laboratory of Inorganic Functional Materials, South China Agricultural University, Guangzhou, 510642 P.R. China

**To cite this Article** Ni, Chunlin , Liu, Xiaoping , Yang, Lemin and Yu, Linliang(2007) '3D network structure and magnetic behaviour of a new Ni(III) maleonitriledithiolate complex with C-H • • • π and π • • • π interactions using 4-dimethylaminopyridinium cation', Journal of Coordination Chemistry, 60: 11, 1203 — 1211

**To link to this Article: DOI:** 10.1080/00958970601026988

**URL:** http://dx.doi.org/10.1080/00958970601026988

*Journal of Coordination Chemistry*
Vol. 60, No. 11, 20 July 2007, 1203–1211

# 3D network structure and magnetic behaviour of a new Ni(III) maleonitriledithiolate complex with C–H ••• $\pi$ and $\pi$ ••• $\pi$ interactions using 4-dimethylaminopyridinium cation

CHUNLIN NI*†‡, XIAOPING LIU†, LEMIN YANG† and LINLIANG YU†

†Department of Applied Chemistry, College of Science, South China Agricultural University, Guangzhou, 510642 P.R. China
‡Laboratory of Inorganic Functional Materials, South China Agricultural University, Guangzhou, 510642 P.R. China

(*Received 16 March 2006; revised 27 May 2006; in final form 2 June 2006*)

A new ion-pair complex, $[\mathrm{DMAPH}][\mathrm{Ni(mnt)_2}]$ ($[\mathrm{DMAPH}]^+$ = 4-dimethylaminopyridinium and $\mathrm{mnt}^{2-}$ = maleonitriledithiolate), was prepared and characterized by elemental analysis, IR spectra, electrospray mass spectra and X-ray single-crystal diffraction. In the solid state, the $\mathrm{Ni(mnt)_2^-}$ anions and $[\mathrm{DMAPH}]^+$ cations are alternately stacked and form 1D column via $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions between the $\mathrm{Ni(mnt)_2^-}$ anion and neighboring $[\mathrm{DMAPH}]^+$ cations. The anion–anion C$\cdots$N interactions, and the anion–cation hydrogen bonds between adjacent columns further generate a 3D network structure. The variable temperature magnetic susceptibility measurement in the temperature range 1.8–300 K shows that the complex exhibits an antiferromagnetic behavior with a Neel temperature ($T_N$) of 7.0 K.

*Keywords*: Bis(maleonitriledithiolato)nickel(III); 4-Dimethylaminopyridinium; 3D network structure; Hydrogen bonding; Weak interaction; Magnetic properties

## 1. Introduction

An impressive amount of work has been devoted to introducing the principles of supramolecular chemistry into the area of materials science in which the non-covalent interactions such as hydrogen bonding and $\pi\cdots\pi$ stacking yield new materials exhibiting novel properties [1–3]. Molecular materials based on maleonitriledithiolate ($\mathrm{mnt}^{2-}$) transition metal complexes have attracted intense interest because they can be used as building blocks for magnetic molecular materials through weak M$\cdots$S (where M is Ni(III), Pd(III) or Pt(III) ion), S$\cdots$S and $\pi\cdots\pi$ stacking interactions [4–12]. Introduction of some inorganic or organic cations as counter ions of $\mathrm{M(mnt)_2^-}$ (where M is Ni(III), Pd(III) or Pt(III) ion) anion not only tunes the stacking pattern of the $\mathrm{M(mnt)_2^-}$ anions but also gives molecular materials with unusual magnetic

---

*Corresponding author. Email: niclchem@scau.edu.cn

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970601026988

properties [13–19]. Cation–cation or anion–cation hydrogen bonds result in the formation of 2D or 3D molecular magnets [20]. In order to study the effects of substituted groups of the 4-aminopyridinium cation on the stacking pattern and magnetic properties of $Ni(mnt)_2$ complexes, we report here the synthesis, crystal structure and magnetic property of a new ion-pair complex, $[DMAPH][Ni(mnt)_2]([DMAPH]^+$=4-dimethylaminopyridinium). Weak $\pi \cdots \pi$, $C \cdots N$, $C–H \cdots \pi$ interactions and extensive hydrogen bonds are found in the solid state, and give a 3D network structure and exchange pathways of the antiferromagnetic interaction with the Neel temperature ($T_N$) of 7.0 K of the title complex.

## 2. Experimental

Disodium maleonitriledithiolate ($Na_2mnt$) was prepared following published procedure [21]. The 4-dimethylaminopyridinium chloride ([DMAPH]Cl) was prepared by reaction between 4-dimethylaminopyridine and one equivalent of dilute hydrochloric acid. Elemental analyses of C, H, and N were run on a Model 240 Perkin Elmer CHN instrument. IR spectra were recorded on an IF66V FT-IR (400–4000 $cm^{-1}$ region) spectrophotometer in KBr pellets. The electrospray mass spectra [ESI-MS] were determined on a Finnigan LCQ mass spectrometer, (sample concentration ca 1.0 $mmol\,dm^{-3}$). Magnetic susceptibility data on crushed polycrystalline samples of **2** were collected over the temperature range of 1.8–300 K using a Quantum Design MPMS-5S super-conducting quantum interference device (SQUID) magnetometer, and the experimental data were corrected for diamagnetism of the constituent atoms estimated from Pascal's constants.

### 2.1. *Preparation of* $[DMAPH]_2[Ni(mnt)_2]$ *(1)*

This compound was prepared by the direct combination of 1 : 2 : 2 mol eq. of $NiCl_2 \cdot 6H_2O$, $Na_2mnt$ and [DMAPH]Cl in $H_2O$. A red precipitate was filtered off, washed by water, and dried under vacuum. Yield: 87% (Found: C, 45.06; H, 3.63; N, 19.01. Calcd for $C_{22}H_{22}N_8NiS_4$: C, 45.14; H, 3.79; N, 19.14%). IR (KBr, $cm^{-1}$): 3291(vs), 3135(m), 3107(m); 2957(w), 2921(m), 2217(m), 2189(s), 1649(s), 1570(s), 1463(vs), 1398(m), 1211(s), 1148(s), 997(s), 781(s), 513(m).

### 2.2. *Preparation of* $[DMAPH][Ni(mnt)_2]$ *(2)*

Dropwise addition of a MeCN solution (20 $cm^3$) of $I_2$ (200 mg, 0.79 mmol) to a stirred MeCN solution (50 $cm^3$) of $[DMAPH]_2[Ni(mnt)_2]$ (585 mg, 1 mmol) produced a black red solution. After the mixture was stirred for 5 h, 90 $cm^3$ MeOH was added, and the mixture was allowed to stand overnight. The 420 mg of black micro-crystals formed were filtered off, washed with MeOH and dried in vacuum. Yield: 90%. Anal. Calcd for $C_{15}H_{11}N_6NiS_4$: C, 38.98; H, 2.40; N, 18.18; Found: C, 38.88; H, 2.57; N, 18.09%.

Table 1. Crystal data and structure refinement for **2**.

| | |
|---|---|
| Chemical formula | $C_{15}H_{11}N_6NiS_4$ |
| Formula weight | 462.25 |
| Description | Black, block |
| Crystal size (mm$^3$) | $0.42 \times 0.31 \times 0.25$ |
| Temperature (K) | 293(2) |
| Crystal system | Monoclinic |
| Space group | $P2_1$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 8.681(3) |
| $b$ | 6.100(2) |
| $c$ | 17.682(6) |
| $\beta$ | 94.80(1) |
| Volume (Å$^3$) | 933.0(5) |
| $Z$ | 2 |
| $D_{\mathrm{Calcd}}$ (g cm$^{-3}$) | 1.645 |
| $F(000)$ | 470 |
| $\mu$ (mm$^{-1}$) | 1.499 |
| Absorption correction | Empirical |
| Min and max transition | 0.589, 0.687 |
| $\theta$ range (°) | 2.31–25.00 |
| Index ranges | $-10 \le h \le 10$, $-7 \le k \le 5$, $-20 \le l \le 21$ |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Reflections collected | 4566 |
| Independent reflections ($R_{\mathrm{int}}$) | 2463 ($R_{\mathrm{int}} = 0.065$) |
| Data, restraints, parameters | 2463, 0, 238 |
| Goodness of fit on $F^2$ | 1.039 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0527, 0.1368 |
| $R_1$, $wR_2$ (all data) | 0.0537, 0.1378 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0. 724 and −0.506 |

IR (KBr, cm$^{-1}$): 3291(vs), 3129(w), 3104(w), 2959(w), 2925(w), 2211(m), 1648(s), 1569(s), 1448(m), 1399(s), 1239(vs), 1213(s), 1159(s), 997(m), 779(s), 501(m).

### 2.3. *Crystal structure determination*

Black single crystals suitable for X-ray structure analysis were obtained by evaporating the MeCN and *i*-PrOH (v/v = 1 : 1) mixed solution of **2** about two weeks at room temperature. A suitable single crystal of **2** was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber, which was then mounted on a Bruker Smart APEX CCD area detector and used for data collection. Diffraction data were collected at 293(2) K using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) by $\omega-2\theta$ scan mode. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares, employing Bruker's SHELXTL [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions, assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic $U$ value of the attached atom, and allowed to ride on their respective parent atoms. Space group, lattice parameters, and other relevant information are listed in table 1.

## 3. Results and discussion

### 3.1. *Crystal structure of 2*

Complex **2** crystallizes in the monoclinic space group $P2_1$ with one pair of $[Ni(mnt)_2]^-$ and $[DMAPH]^+$ in an asymmetric unit. An ORTEP diagram of **2** together with the atom-numbering scheme is shown in figure 1. The dihedral angle between coordination plane of the anion defined by four sulfur atoms and the pyridine ring of the cation is 59.3°. In the $[DMAPH]^+$ moiety, the Cl(14) and C(15) atoms are slightly out of the pyridine ring plane, and the deviations from the plane are −0.0484 Å for C(14), 0.0102 Å for C(15). The Ni ion in the $Ni(mnt)_2^-$ moiety is coordinated by four sulfur atoms in a square-planar geometry. The Ni–S bond distances and the S–Ni–S bond angles (table 2) within the five-membered rings are similar to those observed in [4-aminopyridinium][$Ni(mnt)_2$] [20]. The anion containing Ni(1) is almost planar, and all deviations from four sulfur atoms are less than 0.03 Å. However, the CN groups for the anion are bent from the coordination plane defined by four sulfur atoms, and the deviations are −0.085 Å for the N(1) atom, 0.109 Å for the N(2) atom, −0.330 Å for the N(3) atom and −0.176 Å for the N(4), respectively.

The $Ni(mnt)_2^-$ anions and $[DMAPH]^+$ cations are alternately stacked and form a 1D column along the crystallographic *a*-axis (figure 2) in which two intermolecular

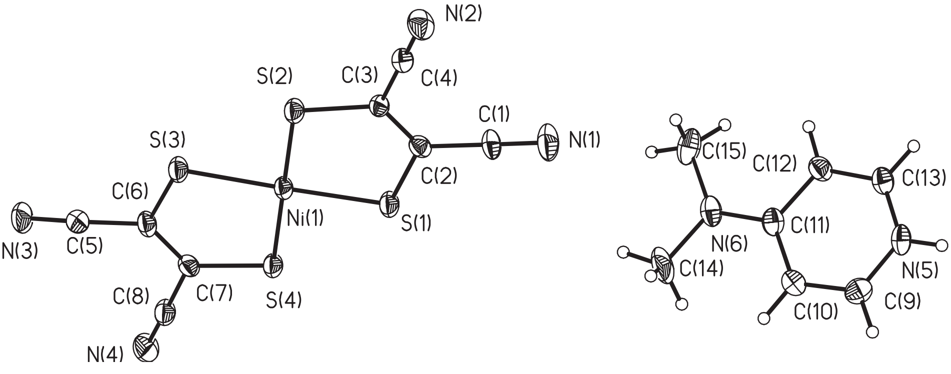
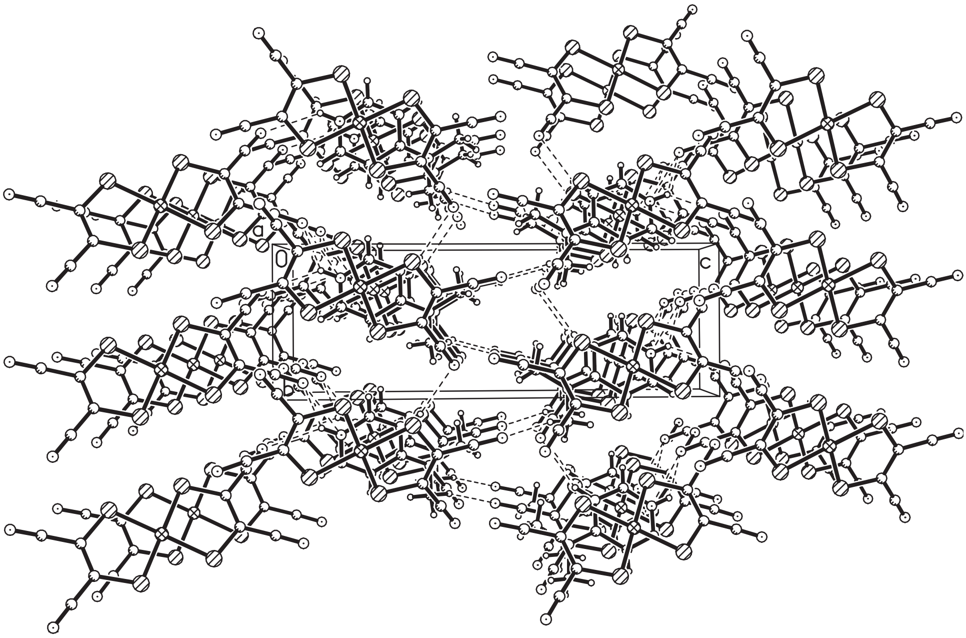


Figure 1. ORTEP plot (30% probability ellipsoids) showing the molecule structure of **2**.

Table 2. The relevant bond lengths (Å) and bond angles (°) for **2**.

| | |
|---|---|
| Ni(1)–S(1) | 2.143(2) |
| Ni(1)–S(2) | 2.144(2) |
| Ni(1)–S(3) | 2.140(2) |
| Ni(1)–S(4) | 2.146(2) |
| S(1)–C(2) | 1.712(6) |
| S(2)–C(3) | 1.719(6) |
| S(3)–C(6) | 1.713(7) |
| S(4)–C(7) | 1.716(6) |
| S(1)–Ni(1)–S(2) | 92.65 (6) |
| S(1)–Ni(1)–S(4) | 87.26 (7) |
| S(2)–Ni(1)–S(3) | 87.79 (7) |
| S(3)–Ni(1)–S(4) | 92.31 (6) |

interactions between the anion and neighboring cation are observed (figure 3). The one is the C–H $\cdots\pi$ interaction between C(15) and the center of the Ni(1)S(1)S(2)C(1)C(2) ring, with a distance of 3.662 Å (H $\cdots\pi$ 3.401 Å). The second is the $\pi\cdots\pi$ stacking interaction between the pyridine ring and the Ni(1)S(3)S(4)C(6)C(7) ring, with a distance of 3.646 Å between the S(4) atom and the centre of the pyridine ring. There are two types of significant interactions between anion-cation alternating columns: (i) the short C $\cdots$ N interactions of $Ni(mnt)_2^-$ anions, with the distances of the C atom and N atom from 3.353 to 3.769 Å (shown in figure 4); (ii) three non-classical hydrogen



Figuer 2. The packing diagram for **2** as viewed along the *a*-axis.

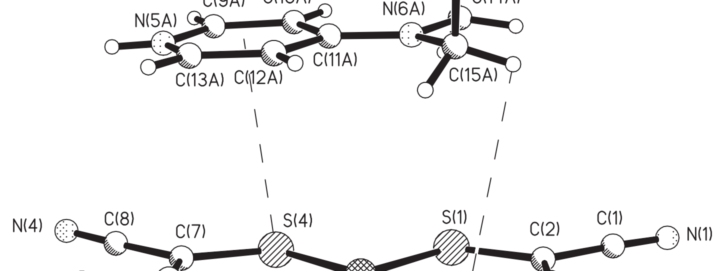


Figure 3. The $\pi\cdots\pi$, and C–H $\cdots\pi$ interactions between the $Ni(mnt)_2^-$ anion and neighboring $[DMAPH]^+$ cations in anion–cation alternating columns.

bonds observed between anion and cation, and the corresponding distances and angles of H-bonding contacts are summarized in table 3. These are at the distance for which significant Van der Waals interactions would be expected. These interactions are different from those found in [4-aminopyridinium][Ni(mnt)$_2$] [20]. The combination of these C $\cdots$ N short interactions and extensive hydrogen bonds in the solid state further generate a 3D network structure (figure 2), and provides exchange pathways of the antiferromagnetic interaction for **2**.

### 3.2. *IR spectra and electrospray mass spectra*

The infrared spectrum of complex **2** is very much consistent with the structural data presented above. $\nu$(N–H) bond of [DMAPH]$^+$ cation is exhibited at 3291 cm$^{-1}$. The bands at 3135, 3107 cm$^{-1}$ and 2957, 2921 cm$^{-1}$ are assigned to stretching vibrations of C–H in the aromatic ring and methyl groups of [DMAPH]$^+$. The very strong characteristic band due to $\nu$(C$\equiv$N) of nitrile is at 2211 cm$^{-1}$ [23]. The $\nu$(C=N) and $\nu$(C=C) bands for the pyridine ring are at 1648 and 1569 cm$^{-1}$. $\nu$(C=C) of mnt$^{2-}$

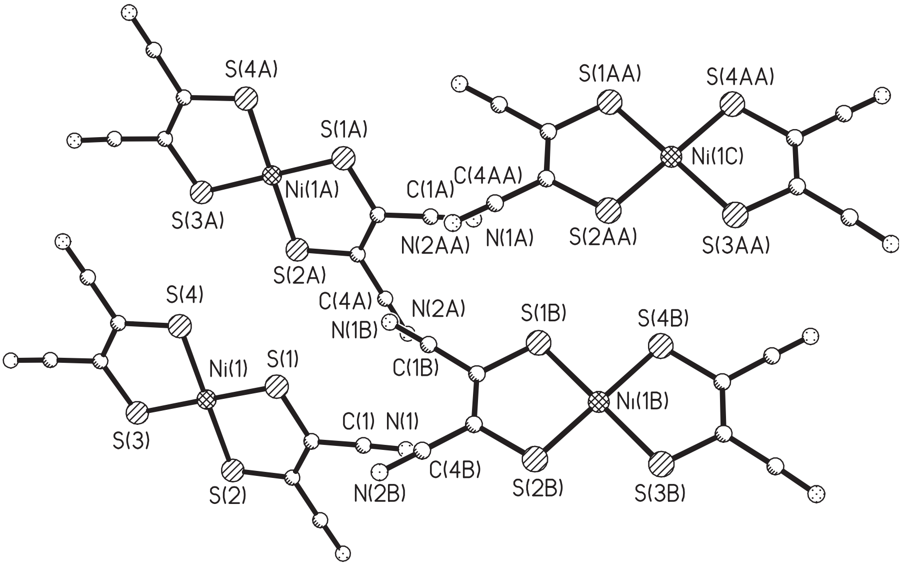


Figure 4. The short C $\cdots$ N interaction of anions between adjacent columns.

Table 3. Hydrogen bonds for **2** (Å and °).

| D–H $\cdots$ A | d(D–H) | d(H $\cdots$ A) | d(D $\cdots$ A) | ⟨(DHA) |
|---|---|---|---|---|
| N(5)–H(5) $\cdots$ N(3)#1 | 0.86 | 2.30 | 2.980(8) | 136.0 |
| N(5)–H(5) $\cdots$ N(4)#2 | 0.86 | 2.42 | 3.101(7) | 136.0 |
| C(10)–H(10) $\cdots$ N(2)#3 | 0.93 | 2.55 | 3.404(9) | 152.0 |

Symmetry transformations used to generate equivalent atoms, #1:$x+1$, $y-1$, $z-1$; #2:$x+1$, $y$, $z-1$; #3:$-x+2$, $y-3/2$, $-z+1$.

is at 1448(s) $\mathrm{cm^{-1}}$. The negative-ion ESI-MS spectra of **2** in MeCN shows that the mass spectrum is dominated by the 340.1 peak, which is assigned to $[\mathrm{Ni(mnt)_2+H}]^-$.

### 3.3. *Magnetic properties*

The temperature-dependent molar magnetic susceptibilities of **2** were measured in a magnetic field of 2000 Oe in the range of 1.8–300 K. As shown in figure 5, the magnetic susceptibility, $\chi_m$, increases as the temperature decreases and reaches a maximum of 0.0141 emu $\mathrm{mol^{-1}}$ around 10.0 K, then sharply goes down to 0.0114 emu $\mathrm{mol^{-1}}$ at 1.8 K. The $\chi_m T$ value at 300 K is 0.375 emu K $\mathrm{mol^{-1}}$, a value expected for Ni(III)($S = 1/2$) magnetically isolated. As the temperature is lowered, the $\chi_m T$ slightly decreases to 0.330 emu K $\mathrm{mol^{-1}}$ at 60 K, and then decreases rapidly below this temperature untill reaching 0.0206 emu K $\mathrm{mol^{-1}}$ at 1.8 K. The Neel temperature ($T_N$) of **2** may be estimated from the sharp peak of $d(\chi_m T)/dT$ *versus* $T$ shown in the inset of figure 5. The magnetic data can also be fit by the Curie–Weiss law and the best fitting curve for **2** is shown in figure 5. The parameters are $C = 0.48\ \mathrm{cm^3\,K\,mol^{-1}}$, $\theta = -20.20$ K, and the agreement factor $R = 2.88 \times 10^{-8}$ ($R$ is defined as $\Sigma\ ((\chi_m^{\mathrm{Calcd}} - \chi_m^{\mathrm{Obsd}})^2/(\chi_m^{\mathrm{Obsd}})^2)$. The negative value of Weiss temperature indicates antiferromagnetic exchange coupling between adjacent $S = 1/2$ $\mathrm{Ni^{III}}$ spin carriers exist in the anion chain of **2**.

For complexes containing $\mathrm{Ni(mnt)_2^-}$ anion, previous studies have shown that the magnetic coupling between $\mathrm{Ni(mnt)_2^-}$ anions is very sensitive not only to the overlap of neighboring $\mathrm{Ni(mnt)_2^-}$ anions but also intermolecular contacts, and small structural change can result in large changes in the properties of $\mathrm{Ni(mnt)_2^-}$ complexes [10, 11]. Theoretical studies using DFT have also revealed that the magnetic exchange nature depends highly on the interplane distance ($d$) and the rotation angle ($\theta$) [24]. Therefore, the magnetic behavior for **2** being different from [4-aminopyridium][$\mathrm{Ni(mnt)_2}$] [20] may be understood according to the differences in crystal structures and intermolecular interactions.

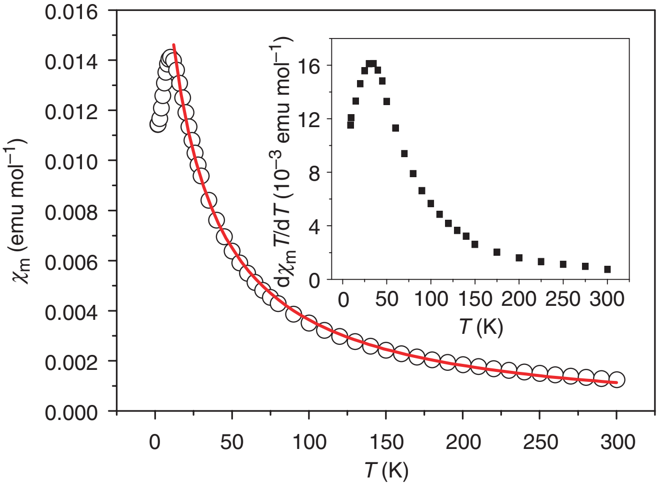


Figure 5. Plot of $\chi_m$ *vs.* $T$ in the range of 1.8–300 K for **2** (inset: plot of $d(\chi_m T)/dT$ *vs.* $T$ for **2**), the solid line is reproduced from the theoretic calculation and detailed fitting procedure described in the text.

In conclusion, an ion-pair complex, [DMAPH][Ni(mnt)$_2$], has been structurally characterized and its magnetic behavior investigated. The Ni(mnt)$_2^-$ anions and [DMAPH]$^+$ cations are alternately stacked and form a 1D column via $\pi \cdots \pi$, and C–H $\cdots \pi$ interactions between them. The anion and anion, anion and cation hydrogen bonds between adjacent columns give short C $\cdots$ N interactions. The combination of these interactions in the crystal generates a 3D network structure, and gives exchange pathways of the antiferromagnetic interaction with the Neel temperature ($T_N$) of 7.0 K of the title complex.

## Supplementary material

Supplementary data for the structure are available from Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk), on request quoting the deposition number CCDC-297318.

## Acknowledgments

This work was supported by the president's science foundation of South China Agricultural University (No. 2005K092). The Center of Analysis and Determination of South China Agricultural University are acknowledged.

## References

[1] S. Decurtins, R. Pellaux, G. Antorrena, F. Palacio. *Coord. Chem. Rev.*, **190–192**, 841 (1999).
[2] M.D. Hollingsworth. *Science*, **295**, 2410 (2002).
[3] W. Wernsdorfer, N. Allaga-Alcalde, D.H. Hendrickson, G. Christou. *Nature*, **416**, 406 (2002).
[4] N. Robertson, L. Cronin. *Coord. Chem. Rev.*, **227**, 93 (2002).
[5] A.T. Coomber, D. Beljonne, R.H. Friend, J.L. Brédas, A. Charlton, N. Robertson, A.E. Underhill, M. Kurmoo, P. Day. *Nature*, **380**, 144 (1996).
[6] X.M. Ren, Q.H. Okudera, R.K. Kremer, Y. Song, C. He, Q.J. Meng, P.H. Wu. *Inorg. Chem.*, **43**, 2569 (2004).
[7] M. Urichi, K. Yakushi, Y. Yamashita, J. Qin. *J. Mater. Chem.*, **8**, 141 (1998).
[8] A.E. Pullen, C. Faulmann, K.I. Pokhodnya, P. Cassoux, M. Tokumoto. *Inorg. Chem.*, **7**, 6714 (1998).
[9] N. Hideyasu, K. Mao, A. Minoru, K. Tadashi, M. Takehiko. *Inorg. Chem.*, **43**, 6075 (2004).
[10] J. Nishijo, E. Ogura, J. Yamaura, A. Miyazaki, T. Enoki, T. Takano, Y. Kuwatani, M. Iyoda. *Sol. State Commun.*, **116**, 661 (2000).
[11] N. Robertson, C. bergemann, H. Becher, P. Agarwal, S.R. Julian, R.H. Friend, N.J. Hatton, A.E. Underhill, A. Kobayashi. *J. Mater. Chem.*, **9**, 1713 (1999).
[12] X.M. Ren, Q.J. Meng, Y. Song, C.L. Lu, C.J. Hu, X.Y. Chen, Z.L. Xue. *Inorg. Chem.*, **41**, 5931 (2002).
[13] J.L. Xie, X.M. Ren, Y. Song, W.W. Zhang, W.L. Liu, C. He, Q.J. Meng. *Chem. Commun.*, 2346 (2002).
[14] J.L. Xie, X.M. Ren, Y. Song, Y. Zou, Q.J. Meng. *J. Chem. Soc., Dalton Trans.*, 2868 (2002).
[15] X.M. Ren, Q.J. Meng, Y. Song, C.S. Lu, C.J. Hu. *Inorg. Chem.*, **41**, 5658 (2002).
[16] J.L. Xie, X.M. Ren, S. Gao, W.W. Zhang, Y.Z. Li, C.S. Lu, C.L. Ni, W.L. Liu, Q.J. Meng, Y.G. Yao. *Eur. J. Inorg. Chem.*, 2393 (2003).
[17] C.L. Ni, D.B. Dang, Y. Song, S. Gao, Y.Z. Li, Z.P. Ni, Z.F. Tian, L.L. Wen, Q.J. Meng. *Chem. Phys. Lett.*, **396**, 353 (2004).
[18] C.L. Ni, D.B. Dang, Y.Z. Li, S. Gao, Z.P. Ni, Z.F. Tian, Q.J. Meng. *J. Sol. State Chem.*, **178**, 100 (2005).
[19] C.L. Ni, Y.Z. Li, D.B. Dang, Y. Song, Z.P. Ni, Q.J. Meng. *Inorg. Chim. Acta*, **358**, 2680 (2005).

[20] X.M. Ren, Y.C. Chen, C. He, S. Gao. *J. Chem. Soc., Dalton Trans.*, 3915 (2002).

[21] A. Davison, R.H. Holm. *Inorg. Synth.*, **10**, 8 (1967).

[22] SHELXTL, Version 5.10. *Structure Determination Software Programs*, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA (1997).

[23] X.M. Ren, C.S. Lu, Y.J. Liu, H.Z. Zhu, H.F. Li, C.J. Hu, Q.J. Meng. *Trans. Metal Chem.*, **26**, 136 (2001).

[24] Z.P. Ni, X.M. Ren, J. Ma, J.L. Xie, C.L. Ni, Z.D. Chen, Q.J. Mwng. *J. Am. Chem. Soc.*, **127**, 14330 (2005).