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Peculiar magnetic behavior in ion-pair complex [1-(4′-fluorobenzyl)pyridinium][Ni(mnt)$_2$] (mnt^{2-} = maleonitriledithiolate)†

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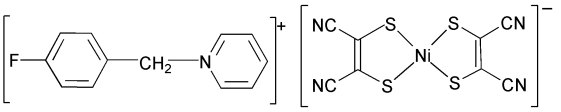
An ion-pair complex [FBzPy][Ni(mnt)$_2$], where [FBzPy]$^+$ = 1-(4′-fluorobenzyl)pyridinium and mnt^{2-} = maleonitriledithiolate, forms a discrete stacking column and shows a peculiar magnetic transition from paramagnetic to diamagnetic around 90 K.

Square-planar M(dithiolene)$_2$ complexes have attracted extensive interest in the areas of conducting and magnetic materials, dyes, non-linear optics, and catalysis.[1,2] In this series of complexes, previous works have shown that different counterions could induce versatile stacking modes in the solid state and, furthermore, have a great influence on molecular interactions and the resultant magnetic diversity.[3] Recently, we fabricated and structurally characterized a series of [BzPy]$^+$[M(mnt)$_2$]$^-$ (M = Ni or Pt) complexes, where [BzPy]$^+$ denotes a benzylpyridinium derivative, and found that there are markedly different magnetic exchange properties although these complexes have extremely similar molecular and stack structures.[4] Herein we report the synthesis and crystal structure of an ion-pair complex (Scheme 1), [1-(4′-fluorobenzyl)pyridinium][Ni(mnt)$_2$], with a discrete stacking column. Its magnetic properties show a peculiar magnetic transition from paramagnetic to diamagnetic around 90 K.

[FBzPy]$_2$[Ni(mnt)$_2$] (**1**) was prepared by the direct combination of 1:2:2 mol equiv. of NiCl$_2$·6H$_2$O, Na$_2$mnt and 1-(4′-fluorobenzyl)pyridinium chloride in H$_2$O. The title complex (**2**) was prepared by I$_2$ oxidation of **1**.[5] Fig. S1† depicts the molecular structure of **2**.‡ The coordination geometry of Ni(III) is square planar with four sulfur donor atoms, and Ni–S bond lengths and S–Ni–S bond angles are in agreement with those results reported.[4] In the [FBzPy]$^+$ cation, the dihedral angles between the C(15)–C(14)–N(5) reference plane and aryl rings, 103.4° for the benzene ring, 97.9° for the pyridine ring, are similar to previous results.[4] It should be noted that **2** possesses well-separated columns stacked along the ***c***-axis direction (Fig. 1a). Within an anion column, there exists a slipped nickel-over-sulfur configuration of the [Ni(mnt)$_2$]$^-$ anions and the Ni···Ni distances between adjacent anions are identical (3.964 Å), and the nearest S···S, S···Ni distances are 3.84 Å and 3.604 Å, respectively. The closest Ni···Ni separation between anion chains is 14.745 Å, and is significantly longer than the Ni···Ni separation within a chain. Therefore, the [Ni(mnt)$_2$]$^-$ anion column is considered as a one-dimensional (1-D) magnetic chain from the crystal structure viewpoint (Fig. 1b). The [FBzPy]$^+$ cations orient themselves in the solid state. The phenyl rings of the neighboring phenyls are parallel to each other with identical center–center distances of 3.912 Å (Fig. S2†).

The temperature dependence of χ_mT, measured under a field of 1 T, is shown in Fig. 2. The observed χ_mT value at 350 K is 0.308 emu K mol^{-1}, slightly less than the value of 0.375 expected for one spin-only Ni(III) ion with $S = 1/2$, $g = 2.0$. Upon cooling, χ_mT increases gradually and reaches a maximum of 0.465 emu K mol^{-1} at 93 K. At 93 K, the χ_mT value abruptly drops to nearly zero, and below 90 K this complex is



Scheme 1 Structure of **2**.

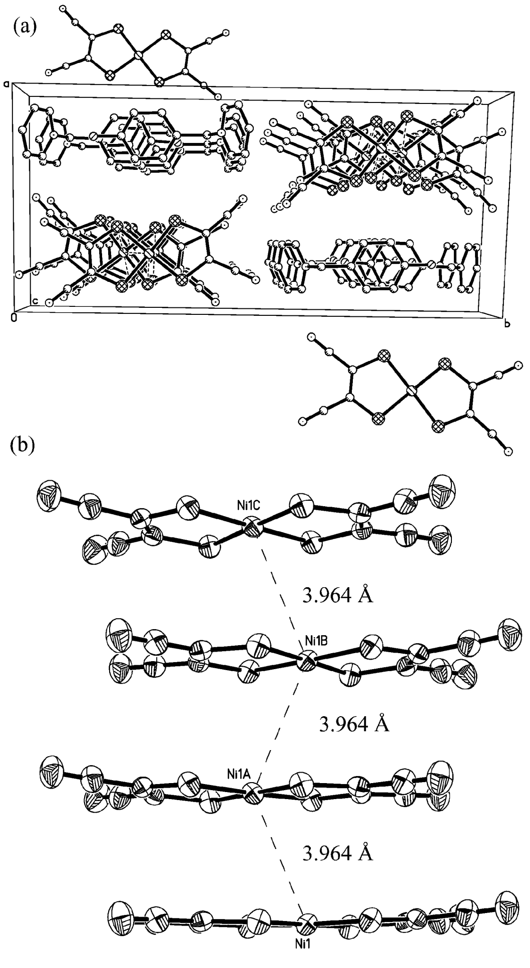


Fig. 1 (a) Structure of the anions and cations of **2** viewed along the *c*-axis. (b) Side view of the 1-D anion chain for **2** (symmetry codes: A = *x*, 0.5 − *y*, −0.5 + *z*; B = C = *x*, *y*, *z* − 1).

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† Electronic supplementary information (ESI) available: experimental details; crystal data, atomic coordinates, ORTEP view, side view of cation chain, χ_M *vs.* *T* plot for **2**. See http://www.rsc.org/suppdata/cc/b2/b205441h/

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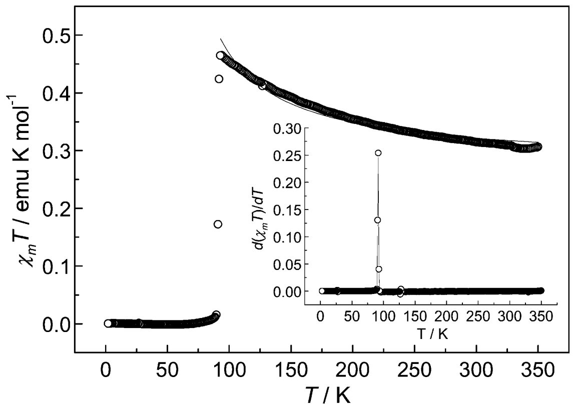

Fig. 2 Temperature dependence of $\chi_m T$ for **2** (inset: d($\chi_m T$)/dT *versus* T). The solid line represents the best fit in the high temperature range according to the Baker equation.

diamagnetic. When the temperature is increased from 2 K to 350 K, an identical curve was observed without hysteresis. Obviously, a phase transition takes place around 93 K. The transition temperature, 90 K, may be estimated from the d($\chi_m T$)/dT *vs.* T plot (inset of Fig. 2). In the temperature range 93–350 K, an estimation was made by fitting χ_m data to the Baker equation[6] (applicable for a chain of $s = 1/2$ spin) derived from a high-temperature series expansion. A fit of the data to the equation[6c] gives $g = 2.006$ (fixed), $J/k_B = 14.61$ K, TIP = -3.5×10^{-4} emu with a final agreement factor $R = 2.3 \times 10^{-4}$ [$R = \Sigma(\chi_m T^{obs} - \chi_m T^{calc})^2/\Sigma(\chi_m T^{obs})^2$]. The fitting results in the high temperature range are in agreement with those of similar Ni(III) complexes.[2c,7]

It is possible that there exist spin-Peierls-like dimeric lattic distortions[8–10] in the low-temperature phase for **2**. To measure the crystal structural data in the low-temperature phase are closely linked to explore the phase transition feature, however, this attempt up to now has been unsuccessful. As an accessorial measure, the variable-temperature X-ray diffraction (XRD) experiments of **2** were carried out and are displayed in Fig. 3, and the results show that there exist differences between the high- and low-temperature phase X-ray diffraction pattern, so the magnetic transition may accompany the structural phase transition, and the phenomenon is similar to cases where some heterocyclic thiazyl radicals undergo an abrupt magnetic/structural phase transition with thermal hysteresis, which are related to distortions of the π-stack arrangement.[10,11] Previous studies have shown that the magnetic coupling between $[Ni(mnt)_2]^-$ anions is very sensitive to not only the intermolecular separation,[2a] but also the manner of overlap between neighboring $[Ni(mnt)_2]^-$ anions.[7,12] Several shorter contact distances, such as Ni···Ni, Ni···S, S···S, S···N, S···C and C···N, play important roles in the superexchange pathway due to extensive electron delocalization in the $[Ni(mnt)_2]^-$ unit.[13] Therefore, changes of the contact distance between neighboring anions, which can arise from variation of the external pressure or temperature, may lead to the sign of the magnetic coupling constant (J) changing.

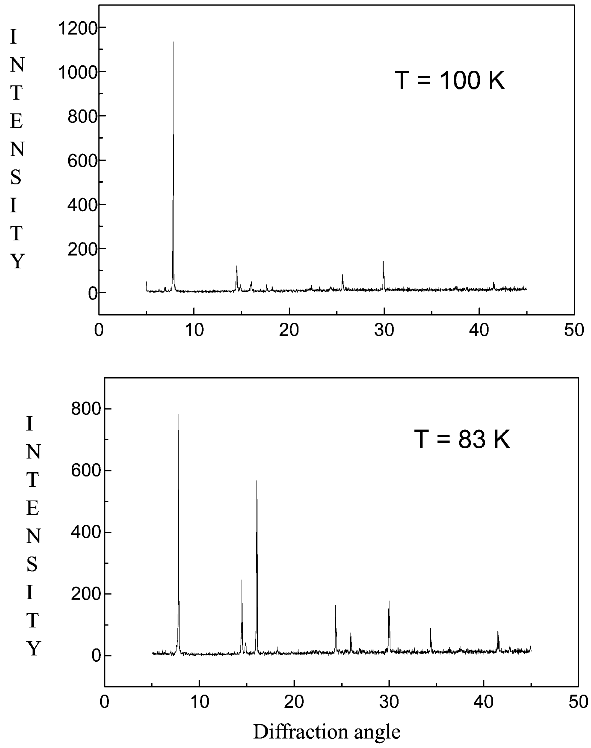

Fig. 3 XRD powder patterns for **2** at different temperatures.

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Notes and references

‡ *Crystal data*: $C_{20}H_{11}FN_5NiS_4$, $M = 527.29$, monoclinic, space group $P2_1/c$, $a = 12.1500(4)$, $b = 25.9523(6)$, $c = 7.3397(3)$ Å, $\beta = 101.74°$, $V = 2265.95(13)$ Å^3, $Z = 4$, $Dc = 1.546$ g cm^{-3}, μ(Mo-K$_\alpha$) = 1.251 mm^{-1}, $\lambda = 0.71073$ Å. A crystal of dimensions 0.15 × 0.10 × 0.10 mm was selected for indexing and intensity data collection at 298 K. ω-Scans covering reciprocal space up to θ_{max} 25.05° with 99.8% completeness, total of 7854 reflections (4013 unique) with $R_{int} = 0.0436$. Structure solution SHELX-97, full matrix least-squares based on F^2 using SHELXL-97, final $R = 0.062$, $wR = 0.154$. CCDC reference number 182194. See http://www.rsc.org/suppdata/cc/b2/b205441h/ for crystallographic data in CIF or other electronic format.

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$$\chi_m = \frac{Ng^2\beta^2}{4kT}\left[\frac{C}{D}\right]^{2/3}$$

$C = 1.0 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5$

$D = 1.0 + 2.7979916y + 7.0086780y^2 + 8.653644y^3 + 4.5743114y^4$

$y = J/2kT$.

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