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A paramagnetic lamellar polymer with a high semiconductivity

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The polymer $[Ni_2(C_4N_2H_3S)_4]_n$ with excellent electrical conductivity and ferromagnetic interaction between the nickel(II) centers has been prepared by the hydrothermal reaction of $Ni(O_2CMe)_2$ with pyrimidine-2-thiol in DMF–H_2O; X-ray diffraction shows that the polymer possesses a lamellar structure formed from the conjunction system of pyrimidine rings and Ni(II) centers.

The increasing interest in inorganic–organic hybrid framework assemblies has resulted in a great deal of research effort focused on the development of new functional materials ranging from zeolite-like coordination polymers[1] to multilayered perovskites,[2] which possess various potential applications, such as in electrical conductivity[3] and magnetism.[4,5] For instance, Shimizu *et al.* reported a layered 'inorgano–organic' solid where the inorganic component is composed of sulfonate-bridged silver(I) centers and the organic moiety is a phenyl group.[6a] Monfort *et al.* reported a metamagnetic two-dimensional molecular material prepared from nickel(II) and azide bridging ligand.[6b] In this field, studies have mainly been focused on inorganic–organic hybrid materials containing N-donor ligands, and relatively few efforts have been made to investigate transition metal organosulfur coordination polymers[7,8] although the coordination chemistry of organosulfur compounds has been intensively studied for more than twenty years.[9]

As a result of the tendency of thiolates to bridge metal centers to yield insoluble or sparingly soluble polymers, it is difficult to control the reactions of thiolates with metal ions and obtain single crystals of polymeric metal thiolates suitable for X-diffraction analysis. Our recent researches revealed the reaction of N-donor-containing thiols such as pyridine-2-thiol with silver ions led to soluble complex species, which can be converted into silver–thiolate or silver–thione polymers under appropriate conditions.[10] Considering that pyrimidine-2-thiol can adopt a variety of coordination modes in its coordination chemistry[11] it was deduced that coordination polymers with novel structures may be isolated through the reaction of M(II) transition metal ions with pyrimidine-2-thiol. We have succeeded in the isolation of coordination polymers by the hydrothermal reaction of bivalent transition metal ions and pyrimidine-2-thiol. Here, we demonstrate the formation of a nickel(II)–pyrimidine-2-thiolate polymer $[Ni_2(C_4H_3N_2S)_4]_n$ **1** ($C_4H_3N_2S$ = pyrimidine-2-thiolate), with lamellar structure. In contrast to other Ni(II) compounds and coordination polymers with lamellar structure,[6c] the interesting features of **1** are its paramagnetic and semiconducting properties.

At 90 °C, the hydrothermal reaction of $Ni(O_2CMe)_2$ with pyrimidine-2-thiol in DMF–H_2O (v : v = 1 : 2) for 48 h and crystallization by slow cooling of the reaction solution to room temperature led to the growth of a large amount of dark-brown, sheet-like crystals of **1**. The crystalline product **1** is very stable even at *ca.* 200 °C in air. Elemental analysis showed the formula of the product was $[Ni(C_4H_3N_2S)_2]$. X-Ray diffraction analysis conformed that **1** is a lamellar polymer built from the $[Ni_2(C_4H_3N_2S)_4]$ dimeric unit† as shown in Fig. 1. This unit develops along the *ab* plane into a honeycomb structure in which the shortest distance between metal centers is 3.774 Å. Therefore, the solid state polymer can be viewed as a two-dimensional lamellar structure composed of $[Ni_2(C_4H_3N_2S)_4]$ dimeric units, wherein the nickel(II) centers are linked by sulfur atoms of thiolate and the pyrimidine ring in the pyrimidine-2-thiolate ligands to form inorganic and organic layers, as shown in Figs. 2 and 3. Each pyrimidine-2-thiolate in **1** acts as a μ_3-bridge to link three nickel atoms through S and N atoms. There are two types of coordination modes for pyrimidine-2-thiolate: one in which pyrimidyl groups of pyrimidine-2-thiolate ligands protrude into the interlayer region [Scheme 1(a)]; and the other in which they act as bridges lying on the layer plane to link Ni(II) centers [Scheme 1(b)]. The interlayer distance is 8.119 Å. Each nickel atom is six-coordinated by three S atoms and three N atoms from three different pyrimidine-2-thiolate ligands in distorted octahedral fashion. The Ni–N bond lengths range between 2.055 and 2.142 Å, while the Ni–S bond lengths range from 2.438 to 2.593 Å. The average S–Ni–N, N–Ni–N and S–Ni–S angles are 85.14,

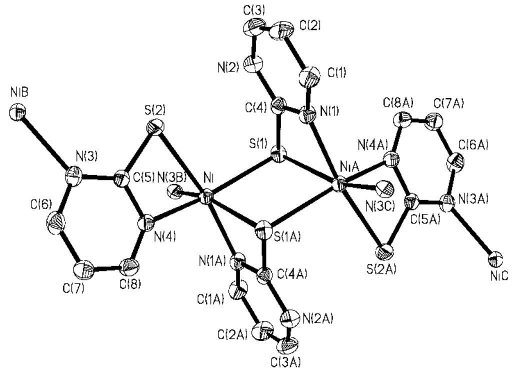


Fig. 1 Structure of the basic unit $[Ni_2(C_4H_3N_2S)_4]$. Selected bond lengths (Å) and angles (°): Ni–N(1A) 2.055(3), Ni–N(4) 2.074(3), Ni–N(3B) 2.142(3), Ni–S(1) 2.4378(10), Ni–S(2) 2.4522(10), Ni–S(1A) 2.5929(10); N(1A)–Ni–N(4) 98.09(12), N(1A)–Ni–N(3B) 93.72(11), N(4)–Ni–N(3B) 101.89(12), N(1A)–Ni–S(1) 91.61(9), N(4)–Ni–S(1) 159.62(8), N(3B)–Ni–S(1) 95.28(8), N(1A)–Ni–S(2) 166.20(9), N(4)–Ni–S(2) 68.52(8), N(3B)–Ni–S(2) 92.46(8), S(1)–Ni–S(2) 100.10(3), N(1A)–Ni–S(1A) 66.76(9), N(4)–Ni–S(1A) 84.59(8), N(3B)–Ni–S(1A) 160.25(8), S(1)–Ni–S(1A) 82.84(4), S(2)–Ni–S(1A) 107.24(3), Ni–S(1)–Ni(A) 97.16(4).

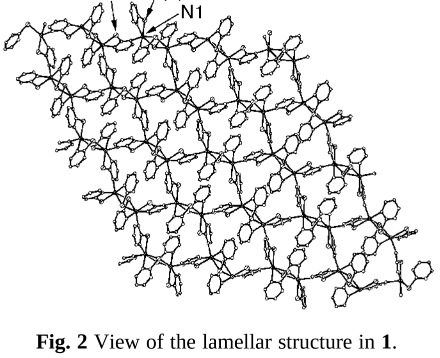


Fig. 2 View of the lamellar structure in **1**.

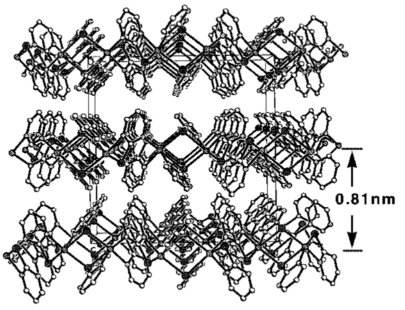
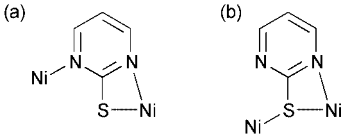


Fig. 3 Structure of **1** showing the interlayer network.



Scheme 1 Coordination modes of pyrimidine-2-thiolate in **1**.

97.90(1) and 96.72°, respectively. All nickel atoms of each layer are nearly coplanar with deviations being within 0.18 Å.

The cryomagnetic behavior of **1** has been studied. $\chi_{\mathrm{M}}T$ and χ_{M} *vs.* T plots of the temperature-dependent magnetic susceptibility data for **1** are shown in Fig. 4. At room temperature, $\chi_{\mathrm{M}}T$ is 2.60 cm^3 K mol^{-1} per dimer at 299.1 K and increases slightly to a maximum value of 2.78 cm^3 K mol^{-1} at 60 K. It decreases from 60 K and reaches 1.44 cm^3 K mol^{-1} at 7.9 K. The magnetic moments from 300 to 5 °C are slightly smaller than calculated values using the free-ion approximation for Ni(II) with high spin configuration. Least-square fitting using eqn. (1)‡ of all experimental data leads to J, J' and g values of 19.5 cm^{-1}, -7.3 cm^{-1} and 2.103 with the agreement factor $R = 2.0 \times 10^{-4}$. Fitting to this model demonstrates the existence of ferromagnetic interactions between the two nickel(II) centers of the dimer unit and antiferromagnetic interactions both between adjacent dimer units and between adjacent layers. The magnetic behavior for **1** is quite different from a nickel(II)–azide two-dimensional polymer, in which each nickel(II) center are high spin and normally show ferromagnetic interactions.[6b]

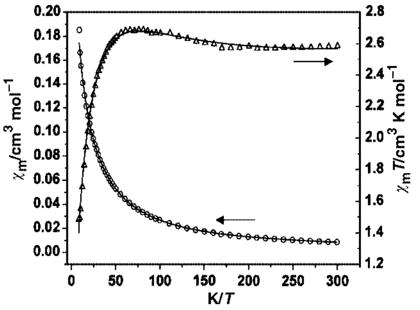


Fig. 4 Temperature–dependent magnetic susceptibility of **1**, (○)χ_{m}, (△)$\chi_{\mathrm{m}}T$ and (—) the best fit obtained.

According to the literature,[12] the evidence for interaction between metal cations in extended solid structures is provided not only by characteristic uniform structural features but also by their physical properties such as electrical conductivity. The semiconductivity of **1** was therefore studied. Determination of the conductivity of **1** (powder sample from ground crystals) indicates an electrical conductivity of 5.00×10^{-3} S cm^{-1} at 28 °C which increases with temperature (Fig. 5), indicating that **1** is a semiconductor. By examining its structure, the semiconducting property of **1** can be attributed to its characteristic structural feature of the interconnected array of nickel(II) with pyrimidine; the semiconducting property provides evidence for nickel and pyridine ring interactions.

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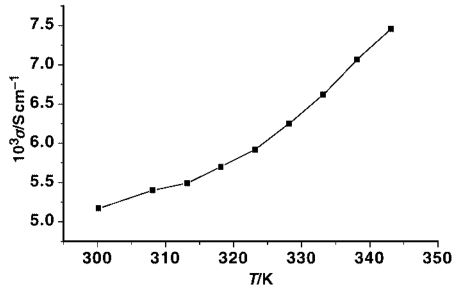

Fig. 5 Temperature dependent electrical conductivity of **1**.

Notes and references

† *Crystal data*: crystal dimensions 0.12 × 0.27 × 0.32 mm, $C_{16}H_{12}N_8S_4Ni_2$, $M_r = 562.00$, orthorhombic, space group *Pbca*, $a = 7.8860(6)$, $b = 15.5844(11)$, $c = 16.2399(12)$ Å, $V = 1995.9(3)$Å^3, $Z = 4$, R (wR) = 0.037 (0.095) for 1402 reflections with $F \geqslant 2.0\sigma(I)$. The intensity data were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation at room temperature. CCDC 159337. See http://www.rsc.org/suppdata/cc/b1/b101422f/ for crystallographic data in .cif or other electronic format.

‡ Magnetic model:

$$\chi_{\mathrm{m}}^{J+J'} = \frac{\chi_{\mathrm{m}}^{J}}{1-2J'\chi_{\mathrm{m}}^{J}/Ng^{2+}\beta^{2}} + \mathrm{TIP}$$

$$\chi_{\mathrm{M}}^{J} = \frac{2N\beta^{2}g^{2}}{kT}\left(\frac{\exp(J/2kT)+5\exp(3J/2kT)}{1+3\exp(J/2kT)+5\exp(3J/2kT)}\right)+\mathrm{TIP} \tag{1}$$

Here J is the coupling constant between the two centers of the dimer and J' is the coupling constant both between adjacent dimer units and between adjacent layers; TIP is the temperature-independent paramagnetism.

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