A One-dimensional Nickel(III) Chain Complex Showing Ferromagnetic Ordering: Crystal Structure and Magnetic Property

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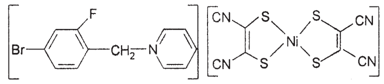
A ferromagnetic complex [BrFBzPy][Ni(mnt)$_2$], where [BrFBzPy]$^+$ = 1-(4′-bromo-2′-fluorobenzyl)pyridinium and mnt^{2-} = maleonitriledithiolate, has been prepared. The [Ni(mnt)$_2$]$^-$ anions and [BrFBzPy]$^+$ cations form a well-separated stacking column and [Ni(mnt)$_2$]$^-$ anions are uniformly spaced to give a one-dimensional (1-D) chain structure. Its magnetization studies shown it ferromagnetically ordered around 2 K.

Widespread attention has been paid on one-dimensional (1-D) compounds because they show novel physical properties such as Peierls transition, spin-Peierls transition, charge-density-wave states, spin-density-wave states, molecular bistabilities, etc.[1–4] 1-D transition metal complexes containing [M(mnt)$_2$]$^-$ (M = Ni(III), Pd(III) or Pt(III), mnt^{2-} = maleonitriledithiolate) ions have been studied extensively. In these complexes, the constituent planar molecules [M(mnt)$_2$]$^-$ form columnar stack structures, in which intermolecular d_{z^2} or π orbital interaction results in 1-D electronic nature.[5,6] We have developed a new class of complexes [RBzPy]$^+$[Ni(mnt)$_2$]$^-$ ([RBzPy]$^+$ = benzylpyridinium derivative).[7] Here we report the crystal structure and magnetic properties of a 1-D chain [BrFBzPy]$^+$[Ni(mnt)$_2$]$^-$ ([BrFBzPy]$^+$ = 1-(4′-bromo-2′-fluorobenzyl)pyridinium) complex, which is ferromagnetically ordered around 2 K.



Firstly, [BrFBzPy]$_2$[Ni(mnt)$_2$] was prepared by the direct combination of 1 : 2 : 2 mol ratio of NiCl$_2$·6H$_2$O, Na$_2$mnt and [BrFBzPy]Br in H$_2$O. Then, the title complex was prepared by oxidation of the [BrFBzPy]$_2$[Ni(mnt)$_2$] by I$_2$,[8] good shaped single crystals were obtained by dispersing Et$_2$O into MeCN solution of the complex about a week. Diffraction data were collected on a FR 590 CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. Magnetic data on powder-sample were collected over the temperature range of 1.8–300 K using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer (the molar diamagnetic contributions of the molecule is -3.04×10^{-4} emu·mol^{-1}).

The X-ray structure of title complex has been characterized[9] and the Ni(III) ion is co-ordinated to four sulfur atoms of two mnt^{2-} ligands, exhibiting square-planar coordination geometry. The CN groups of mnt^{2-} ligand are bent away from the coordinating plane defined by four sulfur atoms and the five-membered nickel-containing rings are slightly puckered, as have been found with other [M(mnt)$_2$]$^{n-}$ structures.[10] The average S–Ni–S bond angle within the five-membered ring is 92.6 °, and the average Ni–S bond distance is 2.14 Å, these values are in agreement with that of [Ni(mnt)$_2$]$^-$ complexes reported.[7]

The anion and cation possess the stacking structure with well-separated column along the direction of *c* axis (Figure 1a). When the Ni···Ni separation between anion chains is of the same magnitude as the distance of the Ni···Ni separation within a anion chain and interchain interaction becomes appreciable, 1-D character are damped.[11] The nearest S···S, S···Ni and Ni···Ni distances are of 3.73, 3.63 and 3.96 Å within the [Ni(mnt)$_2$]$^-$ anion chain, respectively. While the closest inter-chain Ni···Ni separation (11.89 Å) is significantly longer than intra-chain one (Figure 1b). Moreover, the magnetic interaction between two anion columns separated by a sizable diamagnetic cation column is generally weak. The cations also form a 1-D chain through the Br-π interactions between Br atoms and adjacent benzene rings similar to some complexes.[12] Therefore, this complex is a 1-D magnetic chain system.

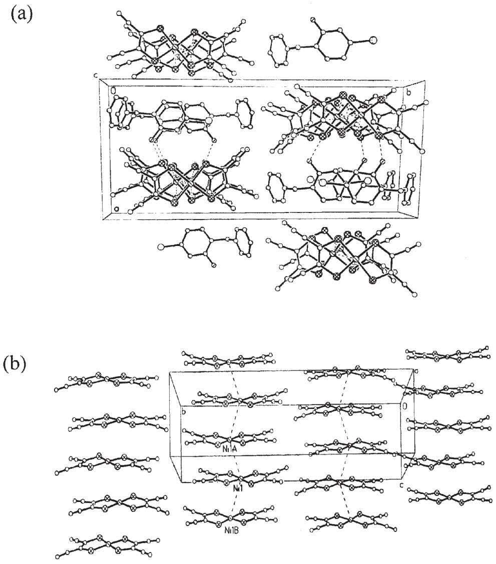


Figure 1. a) The packing diagram of a unit cell of [BrFBzPy]$^+$[Ni(mnt)$_2$]$^-$ viewed along the *c* axis. b) The side view of 1-D anion chain for [BrFBzPy]$^+$[Ni(mnt)$_2$]$^-$.

Figure 2a shows its magnetic properties, in which χ_m is the molar magnetic susceptibility. The value of $\chi_m T$ at 300 K is estimated at 0.412 emu·K·mol^{-1}, and slightly larger than that of spin-only of one s = 1/2 spin per formula unit. The $\chi_m T$ values increase with the temperature decreasing and reach a maximum at 3.7 K ($\chi_m T = 2.55$ emu·K·mol^{-1}). These results demonstrate the presence of ferromagnetic exchange interaction between the localized spins. When the temperature is below 3.7 K, the $\chi_m T$ values decrease and drop to 1.58 emu·K·mol^{-1} at 1.82 K. From these results, short-range ferromagnetic correlation is present in this 1-D chain system, and it may develop into a long range ordering state in low temperature.

From its ac susceptibility measurements, χ' show a maximum around 2 K indicating that the magnetic ordering may occur, and the nonzero χ'' was also observed below 2 K (inset of Figure 2a). Ferromagnetic ordering is demonstrated further by the field dependence of isothermal magnetization performed at 2 K, 5 K and 10 K, respectively (Figure 2b). The magnetization at 2 K increases very rapidly in low field, and reaches the saturation value of ca. 5400 emu·G·mol^{-1} at 50 kOe, which agree well with the theoretical saturation value of a $S = 1/2$, $g = 2$ system(Ni(III) is in low spin state). The rapid rise and approach to saturation in the M(H) data is typical for long range ferromagnetic coupling around 2 K. On the contrary, the magnetization at 5 K and 10 K increases slowly as magnetic field increases. Cycling the applied field between +5 kOe and −5 kOe at 2 K, an observable hysteresis loop characteristic of ferromagnetic behavior arises and it is so small that it seem to intersect at 0 Oe (inset of Figure 2b). Similar phenomenon has been reported by K. Hashimoto.[13]

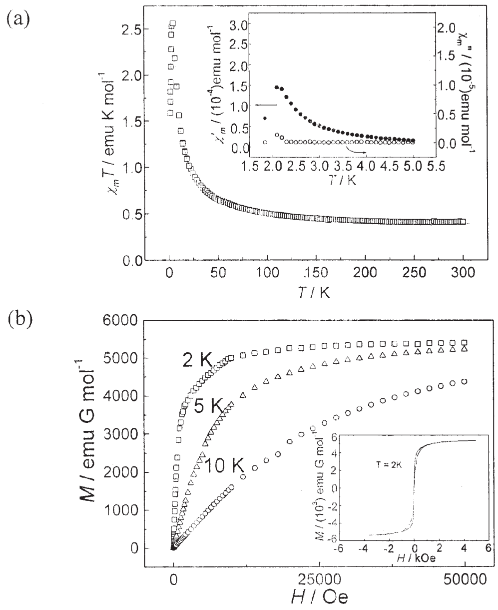


Figure 2. a) Plots of $\chi_m T$(□) of [BrFBzPy]$^+$[Ni(mnt)$_2$]$^-$ measured at 5 kOe field. The solid line represents the best fit. Inset: ac susceptibility obtained at zero external magnetic field. b) M-H plot at 2 K, 5 K and 10 K. Inset: Small hysteresis loop exhibited for [BrFBzPy]$^+$[Ni(mnt)$_2$]$^-$ at 2 K.

In the temperature range 5–300 K, the $\chi_m T$ data was fitted by the Baker equation[14] (expression 1) to give $g = 2.09$, $J = 42.2\,\mathrm{cm}^{-1}$, TIP $= 3.7 \times 10^{-4}$ emu·mol^{-1} with a final agreement factor $R = 3.7 \times 10^{-5}$ $[R = \sum(\chi_m T^{obs} - \chi_m T^{calc})^2 / \sum(\chi_m T^{obs})^2]$.

$$\chi_m = \frac{Ng^2\beta^2}{4kT}\left[\frac{C}{D}\right]^{2/3} \qquad (1)$$

$$y = J/2kT$$

Moreover, a two-dimensional model involving a "chain of chains"[15] was attempted to fit the data from 300 K to 3 K. In this model, at a given temperature, an effective total spin associated with each chain in the structure, S_{eff}, can be calculated as eq 2, where χ_{FC} is the susceptibility calculated for the ferromagnetic chain from eq 1. Below 5 K, the $\chi_{FC}T$

$$S_{\mathrm{eff}}(T) = -\frac{1}{2} + \frac{1}{2}\sqrt{1 + 8\chi_{FC}T} \qquad (2)$$

values are quite large ($\chi_{FC}T > 2.3$) so that the S_{eff} value derived from eq 2 is large enough ($S_{\mathrm{eff}} > 1.7$) to be treated as a classic spin.[15] So the classic spin model (eq 3) derived by Fisher[16] was used to treat the magnetic susceptibility (χ_{2D}) of this "chain of chains" model. From modified eq 3, the full fitting

$$\chi_m = \frac{Ng^2\beta^2}{3kT} S_{eff}(S_{eff} + 1)\frac{(1+u)}{(1-u)} \qquad (3)$$

$$u = \coth[J_{\mathrm{eff}}S_{\mathrm{eff}}(S_{\mathrm{eff}} + 1)/kT] - kT/S_{\mathrm{eff}}(S_{\mathrm{eff}} + 1)$$

parameters are as following: $g = 2.09$, $J = 42.2\,\mathrm{cm}^{-1}$, $g_{\mathrm{eff}} = 2.0$ (fixed), $J_{\mathrm{eff}} = -4.78\,\mathrm{cm}^{-1}$, $\mathrm{R} = 6.4 \times 10^{-5}$ (cf. Figure 2a). The sign of fitting results indicated that there exist ferromagnetically coupled interactions within [Ni(mnt)$_2$]$^-$ anion chain, and antiferromagnetically coupled interactions between [Ni(mnt)$_2$]$^-$ anion chains.

In conclusion, to our best knowledge, the uniformly spaced 1-D chain complex with ferromagnetism is rare for [Ni(mnt)$_2$]$^-$ anion. The origin of the ferromagnetic interactions is similar to previous reports on (EDO-TTFI$_2$)M(mnt)$_2$(M = Ni, Pt).[5] The orthogonality of the molecular orbitals suppresses the antiferromagnetic interaction between spin localized on the Ni(mnt)$_2$ molecules. Moreover, ferromagnetic interactions arise from the spin polarization effect (McConnell's theory[17]) between large positive spin densities on the Ni(III) ions and small negative spin densities on the S atom of adjacent [Ni(mnt)$_2$]$^-$ ions.

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9 Crystallographic data of [BrFBzPy][Ni(mnt)$_2$] are: C$_{20}$H$_{10}$BrFN$_5$NiS$_4$, monoclinic, $P2_1/c$, fw = 606.19, $a = 11.989(2)$, $b = 26.363(5)$, $c = 7.4860(15)$ Å, $\beta = 101.63(3)^\circ$, $V = 2317.5(8)$ Å^3, $Z = 4$, $d_{\mathrm{calc}} = 1.737\,\mathrm{g\,cm}^{-3}$, $T = 273$ K, $R = 0.079$ $[I > 2\sigma(I)]$, and 4022 independent reflections.
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