

4A02 Quasi-one-dimensional Molecular Magnets Based on $[M(\text{mnt})_2]^-$ ($M = \text{Ni}$ or Pt) Architectural Blocks: Structures and Magnetic Properties

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The solids with quasi-one-dimensional electronic feature have a wide range of ground states at low temperature, such as superconducting, SDW state, Peierls or spin-Peierls insulator, due to quasi-one-dimensional-electron gas instability, and attracted more research interest.¹⁻⁴ We have devoted to construct quasi-one-dimensional molecular solids based on $[M(\text{mnt})_2]^-$ ($M = \text{Ni}$, Pd and Pt ; $\text{mnt}^{2-} = \text{maleonitriledithiolate}$), and introduced 1-(4'-R-benzyl)pyridinium derivatives (R represents the substituent group) as the counter-cation to successfully induce completely segregated columnar stacks of cations and anions. The intermolecular interactions in an anionic column give rise to quasi-one-dimensional magnetic nature in those compounds, and a few indicate novel spin-Peierls-like phase transitions.

As for the structural feature in this series of compounds, the $[M(\text{mnt})_2]^-$ anions plane-to-plane stack into columns, and the adjacent anionic columns are completely separated by the cationic columns with diamagnetism which is shown in Fig. 1. The S...S, S...M and M...M interactions between neighboring anions, within an anionic column, are observed and illustrated as Fig. 2.

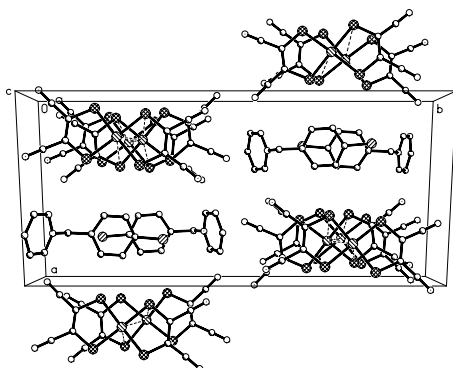


Fig. 1. Completely separated stacking columns.

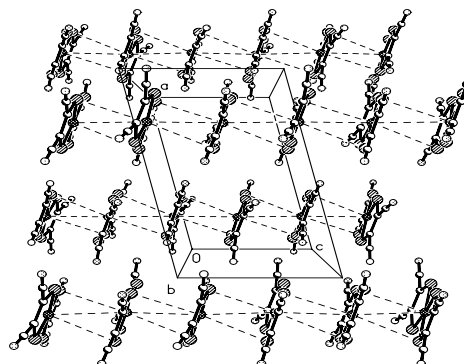


Fig. 2. The interactions of S...S, S...M and M...M.

The magnetic susceptibility measurements for these compounds revealed that the magnetic coupled interactions in these compounds are very sensitive to the intermolecular separations of M...S, S...S and M...M, and to the overlap patterns between the neighboring anions. Thereby their molecular and stacking structures in the series of compounds are similar to each other, however, the diverse magnetic behaviors were observed. For instance, a ferromagnetic one-dimensional chain shows long-range ferromagnetic ordering in the low temperature region (referred as Fig. 3), a ferromagnetic (FM) one-dimensional chain undergoes a phase transition from the paramagnetic to diamagnetic phase, and an antiferromagnetic (AFM) one-dimensional chain exhibits a phase transition from the

paramagnetic to the diamagnetic phase (which is illustrated in Fig. 4) and so on. Among these compounds with unusual phase transition, the magnetic phase transition associates with the dimerization of the anionic column and a sizable enthalpy change was also observed, in some compounds, around the phase transition temperature in DSC measurement, while no any structural and enthalpy change were detected in other compounds.

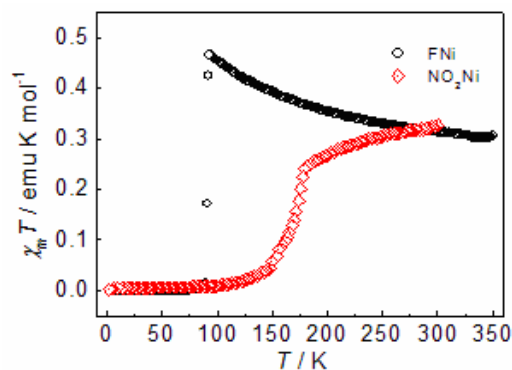
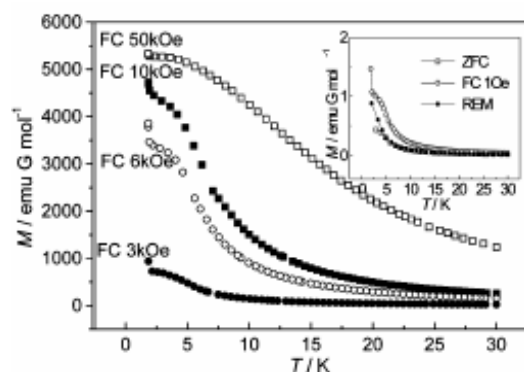


Fig. 3. Field- and zero-field-cooled magnetization.

Fig. 4. Magnetic phase transitions in FM and AFM chain.

In conclusion, a series of compounds with one-dimensional feature of the structure based on $[M(\text{mnt})_2]^-$ ionic architectural blocks ($M = \text{Ni}$ and Pt) were gained by introducing the counter-cation, 1-(4'-R-benzyl)pyridinium derivatives, with special molecular geometry. The crystal structural analyses and magnetic property investigations revealed that the behaviors of the magnetic exchange interactions between nearest spins in these compounds are strongly influenced by the intermolecular separations and overlap patterns of the $[M(\text{mnt})_2]^-$ ions. A few of compounds among them exhibit novel magnetic phase transition, namely, the magnetic susceptibility drops sharply from paramagnetic to diamagnetic as the temperature decreasing and it is phenomenally similar to spin-Peierls-transition. The phase transition natures were investigated by the temperature dependence of the lattice parameters and DSC measurements, the possible origins of the phase transition were discussed.

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