

Design of a One-Dimensional Stacked Spin Peierls System with Room-Temperature Switching from Quantum Mechanical Predictions

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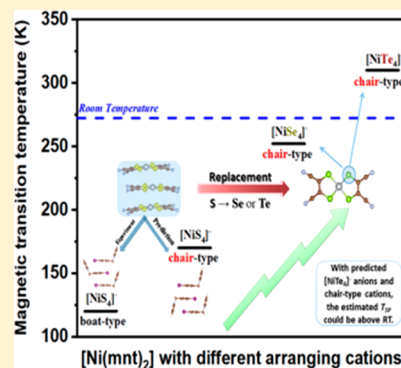
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Supporting Information

ABSTRACT: Planar bis-1,2-dithiolene complex anions of a transition metal (denoted as $[M(\text{dithiolato})_2]^-$ and $M = \text{Ni, Pd, or Pt}$ ion) favor forming columnar stacks of anions in the crystal that feature $S = 1/2$ spin-chains, and such a spin-chain compound often undergoes a spin-Peierls-type transition, making this a promising material for conducting and magnetic switching. However, current examples show the transition temperatures are far too low for most applications. We use quantum mechanics to predict that changing the cation arrangement from the boat-type to the chair-type packing configuration in a spin-Peierls-type $[\text{Ni}(\text{dithiolato})_2]^-$ complex will substantially stabilize the antiferromagnetic coupling, dramatically increasing the transition temperature. We estimate that the $[\text{Ni}(\text{mnt})_2]$ -based complexes (mnt = maleonitriledithiolate) with chair-type packing of cations will lead to critical temperatures of ~ 170 , ~ 252 , and ~ 310 K for S-, Se-, and Te-based mnt, respectively. We also suggest how to stabilize the chair-type configurations of these systems.



Bis-1,2-dithiolene transition-metal complexes show novel properties that are promisingly applied in the areas of conducting and magnetic materials, dyes, nonlinear optics, and catalysis.^{1–6} These applications arise from a combination of functional properties, specific geometries, and intermolecular interactions.^{7–9} The core is composed of a central metal, four sulfurs, and the C=C units in the metal-bis-1,2-dithiolenes anion (denoted as $[M(\text{dithiolato})_2]^-$ with $M = \text{Ni, Pd, or Pt}$ ion), and this leads to delocalization of the frontier orbitals over much or all of the molecule so that the negative charge is distributed over the anion skeleton. Moreover, the large sulfur atoms in the delocalized core can mediate intermolecular interactions between the $[M(\text{dithiolato})_2]^-$ anions.^{10–12} Thus, the planar $[M(\text{dithiolato})_2]^-$ anions favor forming columnar stacks in the crystal, and each anion stack features an $S = 1/2$ spin chain. In some cases, such a spin-chain compound often undergoes spin-Peierls-type transition,^{13–16} making these one-dimensional (1D) complex assemblies of planar $[M(\text{dithiolato})_2]^-$ ($M = \text{Ni, Pd, or Pt}$ ion) excellent candidates for various switching applications.

The positive counterions in cooperative electronic $[M(\text{dithiolato})_2]^-$ systems are important components, facilitating variation and control of the material properties. For the $[\text{Ni}(\text{mnt})_2]^-$ complexes (mnt = maleonitriledithiolate), the

valence state and the size and shape of the counterion (in some cases, the hydrogen bond donor ability of the counterion with the CN groups of mnt²⁻ ligands)^{17,18} control the packing manner of $[\text{Ni}(\text{mnt})_2]^-$ anions and hence the material's properties. Early studies of paramagnetic $[\text{Ni}(\text{mnt})_2]^-$ complexes involved mainly salts with large monovalent counterions, such as tetraalkylammonium, which usually led to dimerization of the $[\text{Ni}(\text{mnt})_2]^-$ components, resulting in a nonmagnetic ground state and low conductivity.^{19,20} Later work explored smaller alkali-metal counterions, which forced the metal complexes closer together, leading in some cases to equidistant stacks with greater potential for magnetically interesting or highly conducting salts.²¹ Planar monocationic counterions can promote the interactions between the metal complex and the planar monocation, leading to formation of a mixed stack.^{22,23} However, the role of cations in mediating the crystal packing structure has not been studied thoroughly.

In previous experimental studies, by introducing the Λ -shaped benzylpyridinium derivatives into $[M(\text{mnt})_2]^-$ spin systems, we harvested numerous 1D spin-Peierls-type $[M$ -

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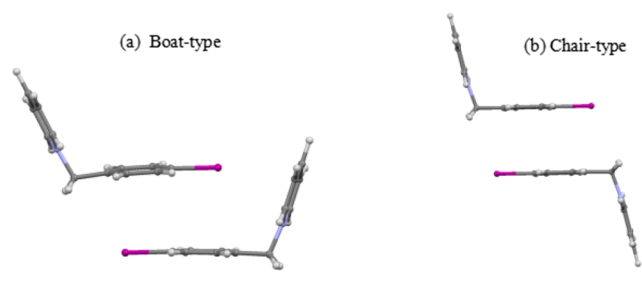
(mnt)₂)[−] complexes through systematic changing of substituents in the aromatic rings of the cations.^{24–28} In these monovalent cations, the Λ-shaped molecule conformation prevents the anion and the cation from the formation of the mixed stack. The flexible –CH₂– connected two aromatic rings by single bonds allows two aromatic rings in a cation to rotate easily, with a rotation energy barrier comparable to intermolecular stacking interactions. This permits the packing structure of [M(mnt)₂][−] anions to be tunable via control of the molecular conformation of the counteranion. Our experiments found that cations exist in two types of packing modes in 1D [M(mnt)₂][−] spin-Peierls-type complexes where

- the two adjacent cations in the [Ni(mnt)₂][−]-based complex always adopt the boat-type packing structure, leading to a switching transition below 120 K
- the two identical cations in the [Pt(mnt)₂][−]-based complex usually dimerize with the chair-type arranging mode, leading to a switching transition at higher temperature, but still below 200 K.

We speculated that changing the cation-arranging manner in the [Ni(mnt)₂][−]-based complex from boat- to chair-type might lead to a 1D spin-Peierls-type [M(mnt)₂][−] complex with transition temperature near room temperature. We validated this concept with quantum mechanics (QM)-based simulations as reported below.

In this Letter, we chose a typical 1D spin system of [1-(4'-iodobenzyl)pyridinium][Ni(mnt)₂] (abbr. as [IPyBz][Ni(mnt)₂]) to investigate the stability of different cationic packing modes (Scheme 1) in the room-temperature and low-temperature phases to predict new [Ni(mnt)₂]-based compounds with possible high magnetic transition points.

Scheme 1. Illustration of Two Distinct Packing Modes, for Cations in [M(mnt)₂]-Based Complexes (M = Ni, Pd, or Pt)



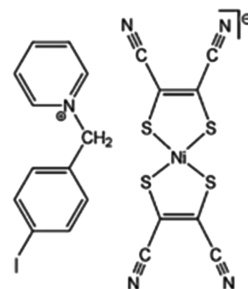
All calculations used the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) description of the exchange–correlation energy²⁹ of density functional theory. These calculations use the Grimme–Becke–Johnson D3 model to include London dispersion (van der Waals attraction) interactions.^{30,31} We carried out the calculations using VASP.^{32,33} The plane-wave basis set cutoff was set at 400 eV, and the convergence criteria were 1.0×10^{-6} eV for energy and 1.0×10^{-4} Å for force.

Dipole moment calculations for boat- and chair-type cations were performed with Jaguar.³⁴ These calculations used the hybrid B3LYP DFT functional^{35,36} including the Grimme D3^{30,31} correction with the 6-311G** basis set³⁷ for C, H, and N elements. We used the small core angular momentum corrected effective core potential or pseudopotential (LACVP³⁸) for Ni (so that 18 electrons are included explicitly) and the LAV 3p pseudopotential for iodine. The

energy cutoff was set to 1.0×10^{-6} hartree. The standard Poisson–Boltzmann continuum solvation model³⁹ was used to account for solvation.

The strategy was as follows: First, we constructed two model compounds where the boat-type arranging model was taken from the room-temperature crystal structure of [IPyBz][Ni(mnt)₂] compound⁴⁰ and the chair-type arranging model used the room-temperature [IPyBz][Pt(mnt)₂] structure⁴¹ but replaced the Pt by Ni (Scheme 2). Then we optimized fully

Scheme 2. Molecular Structure of Constructed Complex



the structures for the two models and compared the total energy of these two structures. Next, to evaluate the influence of spin configurations in these radical dithiolene complexes, we considered the spin coupling and reoptimized to further consider two cases: antiferromagnetic and ferromagnetic coupling for the low-temperature and room-temperature structures of [IPyBz][Ni(mnt)₂].

Figure 1 shows that both the anions and cations in the two model structures with segregated stacks parallel to the *a*-axis, in which the two adjacent cations adopt either

- the boat-type packing mode (left) or
- the chair-type (right) packing.

Boat-Type Cation Case. The Ni-based systems with boat-type cation arrangement exhibit antiferromagnetic (AFM) coupling at low temperature, leading to an experimental spin-Peierls transition point (*T*_{SP}) at ~120 K.

Indeed, for the low-temperature experimental structure of the boat-type cation, we calculated that the lowest energy within the anion chain is high spin or ferromagnetic (FM), but AFM coupling of adjacent chains is 0.43 eV more stable than FM coupling (see Table 1). These DFT calculations for the “AFM” state have *M*_s = 0, but they do not properly lead to a spin singlet because of the Slater determinant form of the wave function. Including the correction to a proper singlet state, the AFM coupled chains are stabilized by 0.86 eV, leading to the *T*_{SP} of 120 K.

However, for this boat-type cation case in the room-temperature configuration, we calculated that the coupling is too weak to stabilize the AFM phase, which is consistent with experiment.

Chair-Type Cation Case. There is no experimental structure for the Ni-based complex with a chair-type cation arrangement, but there is a room-temperature structure for the Pt-based complex. In order to predict the structure for the chair-type cation stacking case, we used QM to predict the minimized structure for both the Pt-based chair-type structure and the Ni-based chair-type structure with the results shown in Table 2. We see that there are only slight changes in the *a*, *b*, and *c* parameters. Thus, we assume that for the room-temperature Ni-chair case we can estimate the cell parameters by changing

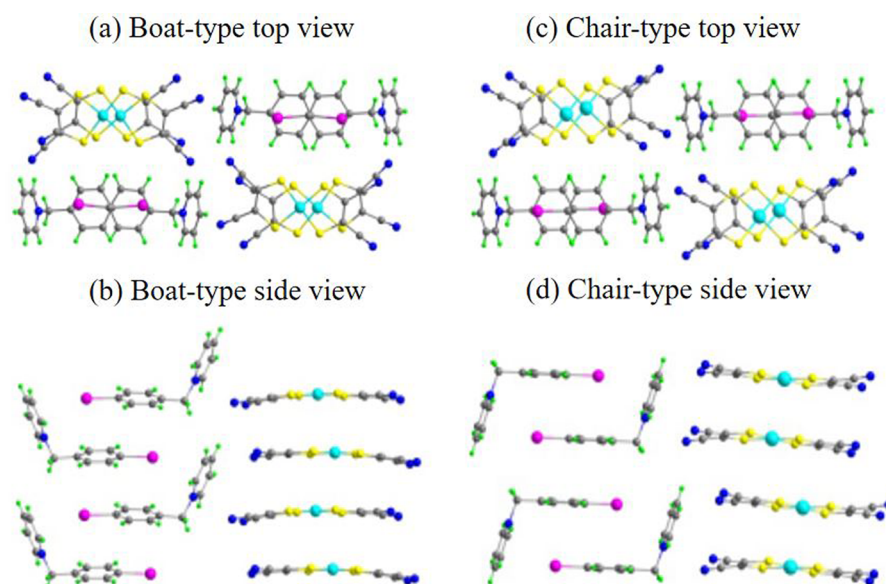


Figure 1. Segregated stacks of cations and anions of $[\text{IBzPy}][\text{Ni}(\text{mnt})_2]$ complex: (a) top-view and (b) side-view of boat-type packing; (c) top-view and (d) side-view of chair-type packing.

Table 1. Comparison of the Energy Differences of $[\text{IBzPy}][\text{Ni}(\text{mnt})_2]$ Compound within Different Spin Configurations^a

cation packing mode	phase type	spin state ^b	energy differences ^c (eV)
boat-type	RT	FM	0
		AFM	0.050
	LT	FM	0.226
		AFM	−0.205

^aAs reported previously,⁴⁰ $[\text{IBzPy}][\text{Ni}(\text{mnt})_2]$ undergoes a structural transition at ~ 120 K; therefore, we optimized the two experimental structures, i.e. room-temperature phase (RT, ~ 300 K) and low-temperature phase (LT, ~ 110 K), and calculated the energy differences for various spin configurations. ^bFM refers to ferromagnetic coupling, and AFM refers to antiferromagnetic coupling. The less stable FM state was obtained by fixing the spin at the maximum value during the QM calculation. ^cWe set the energy of FM state to 0 to provide relative energies for discussions.

the Pt-chair parameters by the same amount as for the QM, leading to the parameters in Table 2. As shown in Tables 2 and S3, the optimized unit cell parameters as well as the specific bond distances in these $[\text{M}(\text{mnt})_2]$ -based complexes are in excellent agreement with experimental values, showing the consistency between the calculation and experiment.

Using this predicted structure for the Ni-chair case, AFM coupling between chains is 1.21 eV more stable than the FM case. Comparing to the DFT energy splitting and the experimental transition energy for the boat-type cation case in $[\text{Ni}(\text{mnt})_2]$ case, we estimate that the predicted $[\text{Ni}(\text{mnt})_2]$

with chair-type cations can stabilize the AFM state below ~ 170 K (Table 3).

Table 3. Calculated QM Energy for the Predicted Structure of $[\text{IBzPy}][\text{Ni}(\text{mnt})_2]$ with the Chair-Type Cation Configuration for Both Spin Configurations^a

cation packing mode	spin state	energy difference ^b (eV)
chair-type	FM	0.280
	AFM	−0.323

^aThis shows that the chair-type cation stabilizes the AFM coupling substantially. ^bTo compare these relative energies directly, we set the energy of the $[\text{Ni}(\text{mnt})_2]$ with boat-type cations in the FM state (see Table 1) as the reference point.

Thus, we find that the energy stabilization of the AFM state relative to the FM state is much larger for the chair-type cation than for the boat-type, leading to much stronger magnetic stabilization for chair-type cations. In our DFT calculations, we found that the formation energy of chair-type crystal is 0.3 eV lower than that of boat-type, which indicates that the chair-type is more stable than the boat-type configuration. Geometry analyses show that the distances between the two adjacent $[\text{Ni}(\text{mnt})_2]$ monomers of the chair-type configuration is 3.42 Å, much closer than that of the boat-type configuration (3.61 Å). The distance between the anions and cations are also closer. These considerations suggest a more effective dimerization, which provide extra stability. Next, we discuss below how to stabilize the boat-type stacking for experimental tests of these predictions.

Table 2. Comparison of Calculated and Experimental Values of Unit Cell Parameters for Pt-Based and Ni-Based Structures with Chair-Type Cation Configurations

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)
Pt-chair case (experimental)	7.604	12.302	14.251	111.39	90.640	103.39
Pt-chair case (optimized)	7.515	12.234	14.109	111.65	90.575	103.47
Ni-chair case (optimized)	7.337	11.965	14.021	110.69	91.609	102.90
Ni-chair case (predicted)	7.423	12.031	14.162	110.41	91.383	102.62

In order to achieve much higher AFM coupling, we tested two more cases for chair-type cations in which the two Sulfur atoms in the mnt^{2-} ligand are replaced by selenium or tellurium. As shown in Table S4, compared to the predicted $[\text{Ni}(\text{mnt})_2]^-$ (i.e., $[\text{NiS}_4]^-$) structure, the cell parameters for the Se/Te replaced case are changed just a little (within 1%); it is understandable that, for this kind of molecular crystals, bond distance is the minor contribution to the cell, while the nonbond interaction is dominant in determining the cell parameters. Table 4 shows the predictions. Given the

Table 4. Calculated Energy Differences and Estimated Spin-Transition Temperature for Various Chalcogenides Replacing the S of the $[\text{Ni}(\text{mnt})_2]^-$ Spin System

anion species	cation stacking type	ΔE (AFM-FM) (eV)	J value	estimated T_{SP}
$[\text{Ni}(\text{mnt})_2]^-$ ($[\text{NiS}_4]^-$)	boat-type	0.43	0.86	120 K ^a
$[\text{Ni}(\text{mnt})_2]^-$ ($[\text{NiS}_4]^-$)	chair-type	0.61	1.22	~170 K
$[\text{NiSe}_4]^-$	chair-type	0.90	1.80	~252 K
$[\text{NiTe}_4]^-$	chair-type	1.11	2.22	~310 K

^aExperimental value.

calculated AFM stabilizations over FM of 1.22, 1.80, and 2.22 eV for S, Se, and Te, respectively, we estimate that the spin-Peierls transition points will be 170, 252, and 310 K for S, Se, and Te, respectively. Thus, we predict that the NiTe_4^- anion with the chair-type cation will have a spin-Peierls transition point above room temperature.

Synthesizing the Ni-Chair AFM Structure. The experiments led to the boat-type not the chair-type cationic stacking. To understand why, we calculated the energy difference between the boat-type and chair-type cations for the acetonitrile solvent used in the experiments. We find that the large dipole moment of 2.4 D (Table 5) stabilizes the boat-type conformation in

Table 5. Calculated Dipole Moments and Energy Differences for Boat-Type and Chair-Type Cationic Configurations for Various Solvents

condition	dipole moment (debye)		energy difference ^a (ΔE , eV)
	boat-type	chair-type	
vacuum	2.061	0.019	0.188
cyclohexane	3.300	0.276	0.121
ethanol	3.093	0.061	0.123
THF	2.828	0.216	0.123
acetonitrile	2.389	0.036	-0.119

^aThe energy difference refers to $\Delta E = E_{\text{boat}} - E_{\text{chair}}$ using the DFT electronic energy.

Acetonitrile. However, for less hydrophilic solvents such as THF or ethanol, we predict that the less polar chair-type cation form is stable. Thus, to synthesize the Ni-chair form, we suggest using a more hydrophobic solvent in the synthesis (see the Supporting Information and Table S2). We have tested the possibility of harvesting the crystals from the THF solvent; however, our materials suffered from poor solubility. We failed to grow 1D spin-Peierls-type complex with chair-type cations. Therefore, to get a stable chair-type stacking $[\text{Ni}(\text{mnt})_2]^-$ -based complex, we must consider both a less polar solvent but must also ensure sufficient solubility. Such studies are in progress.

We used PBE-D3 DFT calculations to predict the structures and interactions for $[\text{Ni}(\text{mnt})_2]^-$ -based model compounds with either boat-type or chair-type cations. We find that the boat-type cation leads to weak AFM coupling, 0.86 eV, leading to a low spin-Peierls transition temperature (experimentally 120 K). However, for the chair-type cation, we predict much stronger pairing, 1.21 eV, which we estimate will lead to a $T_{\text{SP}} \approx 170$ K. Using the same chair-type cation configuration but replacing S with Se or Te, we predict that the spin-Peierls transition temperature will increase to ~252 K for Se and ~310 K for Te. Thus, the Te-based $[\text{Ni}(\text{mnt})_2]^-$ with Te and chair-type cation should lead to switching slightly above room temperature, which is suitable for switching applications.

We use DFT to show that using less polar solvents such as ethanol or THF should stabilize the synthesis of $[\text{Ni}(\text{mnt})_2]^-$ structures with the chair-type cations.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcclett.9b02219.

Computation methods for calculating spin coupling parameters and spin Peierls transition temperature, optimized structural parameters and bond distances for $[\text{Ni}(\text{mnt})_2]$ and $[\text{Pt}(\text{mnt})_2]$, and dipole moment and dielectric constant for selected solvents (PDF)

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Notes

The authors declare no competing financial interest.

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