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

Hao Yang,^{a, b, c} Tao Cheng,^{b, c, *} William A. Goddard III,^{b, c, *} Xiao-Ming Ren^{a, d, *}

^a *State Key Laboratory of Materials-Oriented Chemical Engineering and College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 210009, People's Republic of China*

^b *Materials and Process Simulation Center,*

California Institute of Technology, Pasadena, California 91125, United States

^c *Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Joint International Research Laboratory of Carbon-Based Functional Materials and Devices, Soochow University, Suzhou 215123, People's Republic of China*

^d *College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, People's Republic of China*

E-mail: wag@caltech.edu (W.A.G.) xmren@njtech.edu.cn (X.M.R.) tcheng@suda.edu.cn (T.C.)

Abstract: Planar bis-1,2-dithiolene complex anions of transition metal (denoted as $[M(\text{dithiolato})_2]^-$ and $M = \text{Ni, Pd or Pt}$ ion) favor to form columnar stacks of anions in the crystal that feature as $S = 1/2$ 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 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 manner 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 with chair-type packing manner of cations will lead to critical temperatures of ~ 170 K, ~ 252 K, and ~ 310 K for S, Se, and Te based mnt, respectively. We also suggest how to stabilize the chair-type configurations for these systems.

TOC Graphic

Bis-1, 2-dithiolene transition metal complexes show novel properties that are promisingly applied in the areas of conducting and magnetic materials, dyes, non-linear 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 $[M(\text{dithiolato})_2]^-$ and $M = \text{Ni, Pd or Pt}$ 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 to form columnar stacks in the crystal, and each anion stack features as a $S = 1/2$ 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) to be excellent candidates for various switching applications.

The positive counter-ions 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, the valence state, the size and the shape of the counter-ion (in some cases, the hydrogen bond donor ability of the counter cation with the CN groups of mnt^{2-} ligands)^{17, 18} control the packing manner of $[\text{Ni}(\text{mnt})_2]^-$ anions and hence the materials properties. Early studies of paramagnetic $[\text{Ni}(\text{mnt})_2]^-$ complexes involved mainly salts with large mono-valent counter-ions, 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 counter-ions, 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 mono-counter-cations can promote the interactions between the metal-complex and the planar mono-cation, leading to formation of a mixed stack.^{22, 23} However, the role of cations in mediating crystal packing structure has not been studied thoroughly.

In previous experimental studies, by introducing the Λ -shaped benzyropyridinium derivatives into $[M(\text{mnt})_2]^-$ spin systems, we harvested numerous 1D spin-Peierls-type $[M(\text{mnt})_2]^-$ complexes through systematic changing of substituents in the aromatic rings of the cations.²⁴⁻²⁸ In these mono-valent cations, the Λ -shaped molecule conformation prevents the anion and the cation from the formation of the mixed stack. The flexible $-\text{CH}_2-$ 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 $[M(\text{mnt})_2]^-$ anions to be tunable *via* control of the molecular conformation of counter cation. Our experiments found that cations exist in two types of packing modes in 1D $[M(\text{mnt})_2]^-$ spin-Peierls type complexes, where

- the two adjacent cations in $[\text{Ni}(\text{mnt})_2]^-$ -based complex always adopt the boat-type packing structure, leading to a switching transition below 120 K
- the two identical cations in $[\text{Pt}(\text{mnt})_2]^-$ -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 $[\text{Ni}(\text{mnt})_2]^-$ -based complex from boat- to chair-type might lead to a 1D spin-Peierls-type $[\text{M}(\text{mnt})_2]^-$ complex with transition temperature near room temperature. We validated this concept with QM based simulations as reported below.

In this paper, we chose a typical 1D spin system of $[1-(4'\text{-Iodobenzyl})\text{pyridinium}][\text{Ni}(\text{mnt})_2]$ (abbr. as $[\text{IPyBz}][\text{Ni}(\text{mnt})_2]$) to investigate the stability of different cationic packing modes in the room-temperature and low-temperature phases to predict new of $[\text{Ni}(\text{mnt})_2]^-$ -based compounds with possible high magnetic transition points.

Scheme 1. Illustration of two distinct packing modes, for cations in $[\text{M}(\text{mnt})_2]^-$ -based complexes (M refers to Ni, Pd, or Pt.) a) boat-type, b) chair-type alignment.

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 cut-off was set at 400 eV and the convergence criteria were 1.0×10^{-6} eV for energy and $1.0 \times 10^{-4}/\text{\AA}$ 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 LAV3p 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: firstly, we constructed two model compounds where the boat-type arranging model was taken from the room-temperature crystal structure of $[\text{IPyBz}][\text{Ni}(\text{mnt})_2]$ compound⁴⁰ and the chair-type arranging model used the room-temperature $[\text{IPyBz}][\text{Pt}(\text{mnt})_2]$ structure⁴¹ but replaced the Pt by Ni. Then we optimized fully 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 re-optimized to further consider two cases: antiferromagnetic and ferromagnetic coupling for the low-temperature and room temperature structures of [IPyBz][Ni(mnt)₂].

Scheme 2. Molecular structure of constructed complex.

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 (top) or
- the chair-type (bottom) packing.

Figure 1. The segregated stacks of cations and anions of [IBzPy][Ni(mnt)₂] complex, a) top-view, b) side-view of boat-type packing, c) top-view, d) side-view of chair-type packing.

The boat-type cation case

The Ni based systems with boat-type cations arrangement exhibit antiferromagnetic (AF) 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 AF coupling of adjacent chains is 0.43 eV more stable than FM coupling (see Table 1). These DFT calculations for the “AF” state have $M_s = 0$, but they do not properly lead to a spin singlet because of the Slater determinant form of the wavefunction. Including the correction to a proper singlet state, the AF coupled chains is 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 AF phase, which is consistent with experiment.

Table 1. Comparison of the energy differences of [IBzPy][Ni(mnt)₂] compound within different spin configurations.

Cation packing mode	Phase type	Spin state ^a	Energy differences ^b / eV
Boat-type	RT	FM	0
		AFM	0.050
	LT	FM	0.226
		AFM	-0.205

Notes: As reported previously,⁴⁰ [IBzPy][Ni(mnt)₂] undergoes a structural transition at ~120 K, so 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.

^aFM 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.

^bWe set the energy of FM state to 0 to provide relative energies for discussions.

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

Table 2. Comparison of calculated and experimental values of unit cell parameters for Pt-based and Ni-based structures with chair-type cation configurations.

	a/Å	b/Å	c/Å	$\alpha/^{\circ}$	$\beta/^{\circ}$	$\gamma/^{\circ}$
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

Table 3. Calculated QM energy for the predicted structure of [IBzPy][Ni(mnt)₂] with the chair-type cation configuration for both spin configurations. This shows that the chair-type cation stabilizes the AFM coupling substantially.

Cation packing mode	Spin state	Energy difference ^a / eV
Chair-type	FM	0.280
	AFM	-0.323

Note: ^aTo compare these relative energies directly, we set the energy of the [Ni(mnt)₂] with boat-type cations in the FM state (see Table 1) as the reference point.

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 [Ni(mnt)₂] case, we estimate that the predicted [Ni(mnt)₂] with chair-type cations can stabilize the AFM state below ~170K.

Thus, we find that **the energy stabilization of 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 chair-type is more stable than boat-type. Geometry analysis show that the distances between the two adjacent [Ni(mnt)₂] monomers of chair-type is 3.42 Å, much closer than that of boat-type (3.61 Å). The distance between the anions and cations are also closer. These considerations suggests a more effective dimerization, which provide extra stability. Then, We discuss below how to stabilize the boat-type stacking for experimental tests of these predictions.

In order to achieve much higher AFM, we tested two more cases for chair-type cations in which the two Sulfur atoms in the mnt²⁻ ligand are replaced by Selenium or tellurium. As shown in Table S4, compared to predicted [Ni(mnt)₂] (*i.e.* [NiS₄]) strucutre, the cell parameters for Se/Te replaced case are just changed a little (within 1 %), it is understandable that, for this kind of molecule crystals, bond distance is the minor contribution to the cell, while the non-bond interaction is dominant in determining the cell parameters. Table 4 shows the predictions. Based on the 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 310K 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.**

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*
$[\text{Ni}(\text{mnt})_2]^-$ ($[\text{NiS}_4]^-$)	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

*Experimental value.

Synthesizing the Ni-chair AF 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 Debye (Table 5) stabilizes the boat-type conformation in 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 SI&Table S2). We have tested the possibility of harvesting the crystals of the from THF solvent, however, our materials suffered from poor solubility, so that we failed to grow 1D spin-Peierls-type complex with chair-type cations. So, to get 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.

Table 5. Calculated dipole moments (Debye) and energy differences (eV) for boat-type and chair-type cationic configurations for various solvents.

Condition	Dipole moments (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.

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 $T_{SP} \sim 170$ K. Using same chair-type cation configuration but replacing S with Se or Te, which 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.

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Supporting Information Available: 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 $[\text{Pt}(\text{mnt})_2]$, dipole moment and dielectric constant for selected solvents.

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