

Introducing selenium in single component molecular conductors based on nickel bis(dithiolene) complexes

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Supplementary Information

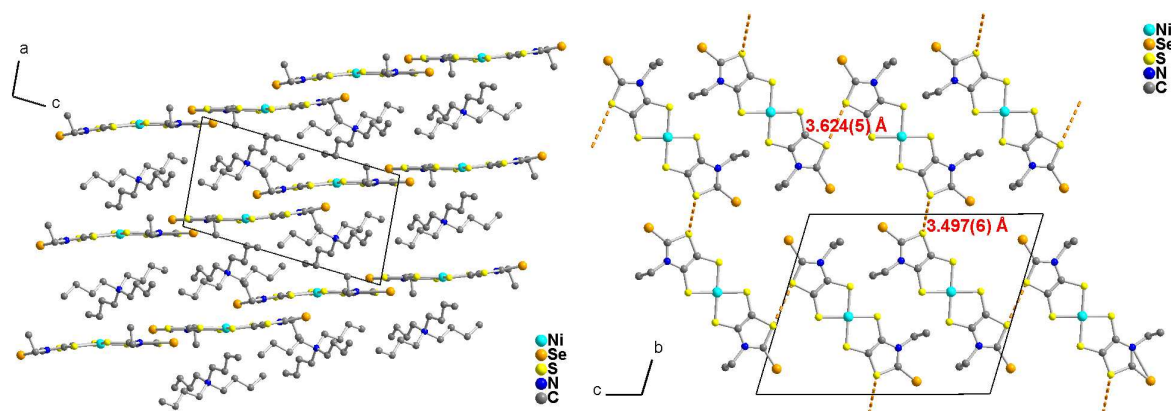


Figure S1. Layered solid state organization of $[\text{NBu}_4][\text{Ni}(\text{Et-thiazSedt})_2]$. H atoms were omitted for clarity.

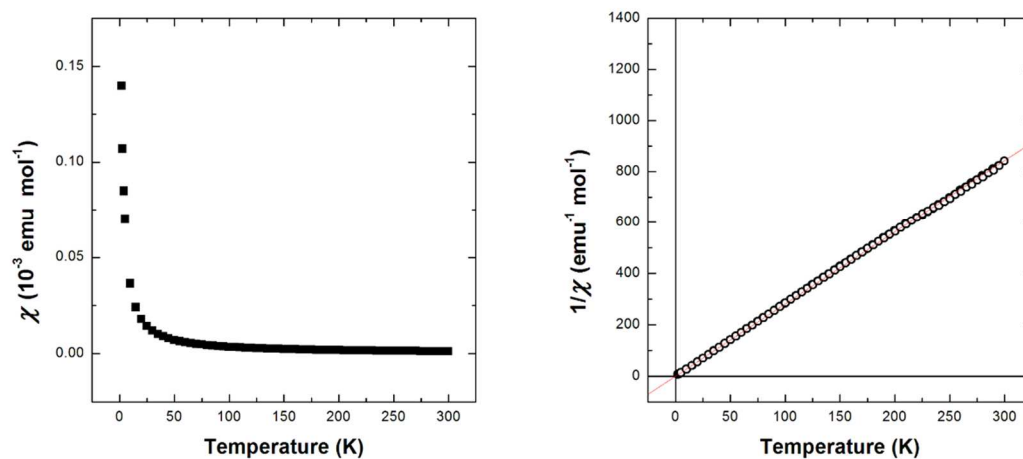


Figure S2 Temperature dependence of the magnetic susceptibility (left) and $1/\chi$ vs. T with Curie-Weiss fit (red line) (right) for $[\text{NBu}_4][\text{Ni}(\text{Et-thiazSedt})_2]$.

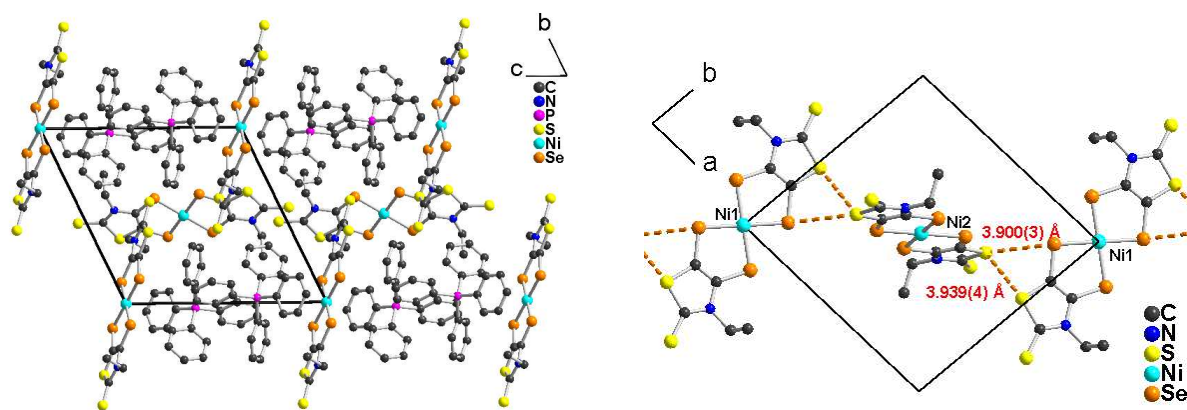


Figure S3. Left: Projection along the a axis of two unit cells of $[\text{PPh}_4][\text{Ni}(\text{Et-thiazds})_2]$ showing the limited intermolecular interactions between radical anion species. Right: Detail of the shortest (but long) chalcogen...chalcogen contacts. H atoms were omitted for clarity.

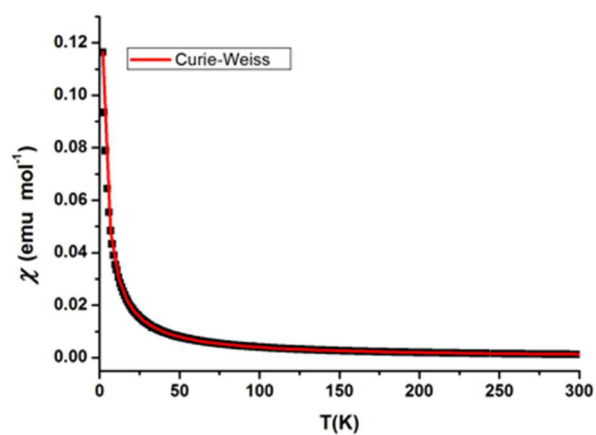


Figure S4. Left: Temperature dependence of the magnetic susceptibility of $[\text{Ph}_4\text{P}][\text{Ni}(\text{Et-thiazds})_2]$ with (in red) fit to Curie-Weiss law (See text).

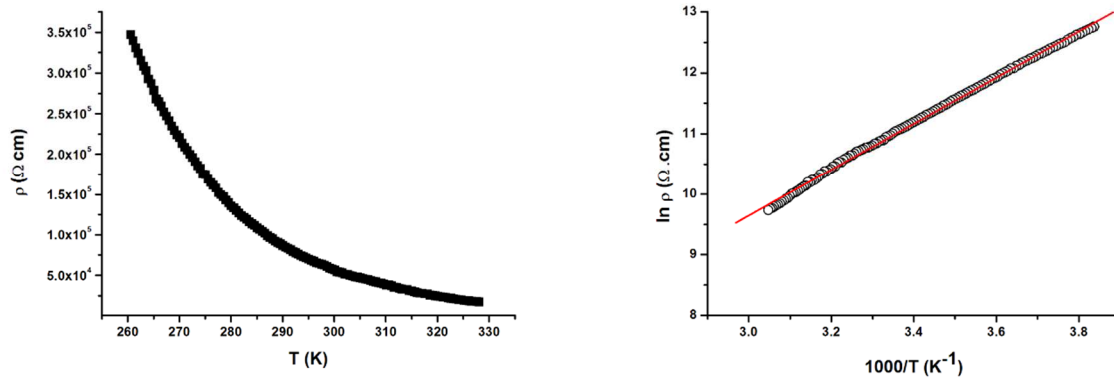


Figure S5. Temperature dependence of the resistivity of [Ni(Et-thiazSedt)₂]. Due to the small size of the crystals, the transport measurement was performed on two points.

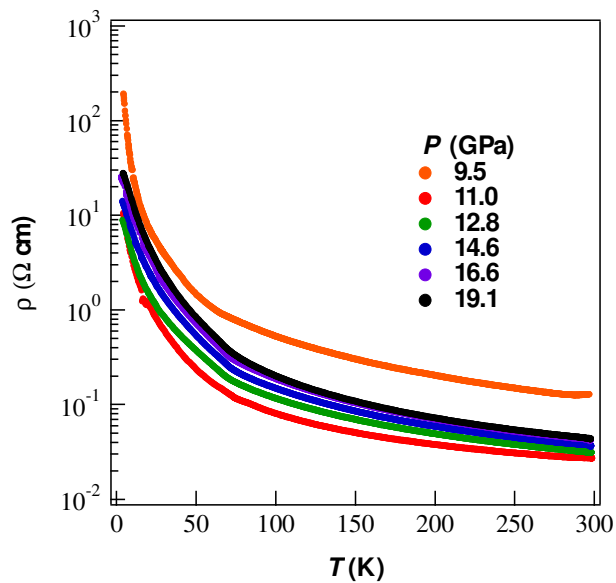


Figure S6. Temperature dependence of the resistivity of [Ni(Et-thiazds)₂] as a function of pressure determined on sample 3 between 9.5 and 19.1 GPa.

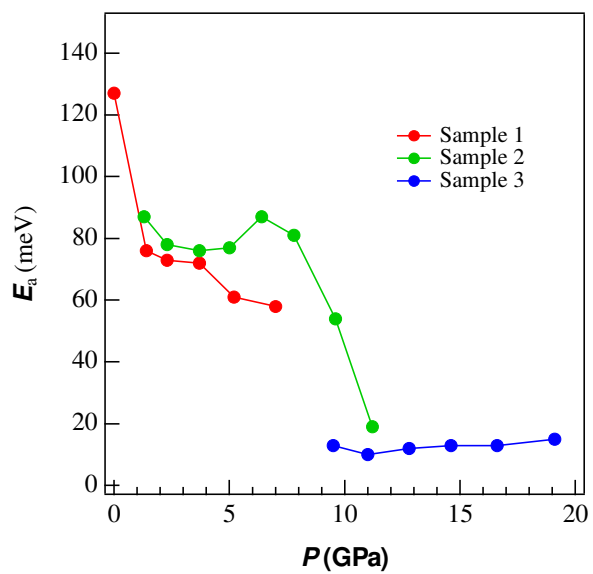


Figure S7 Evolution of the activation energy of the resistivity for the three samples

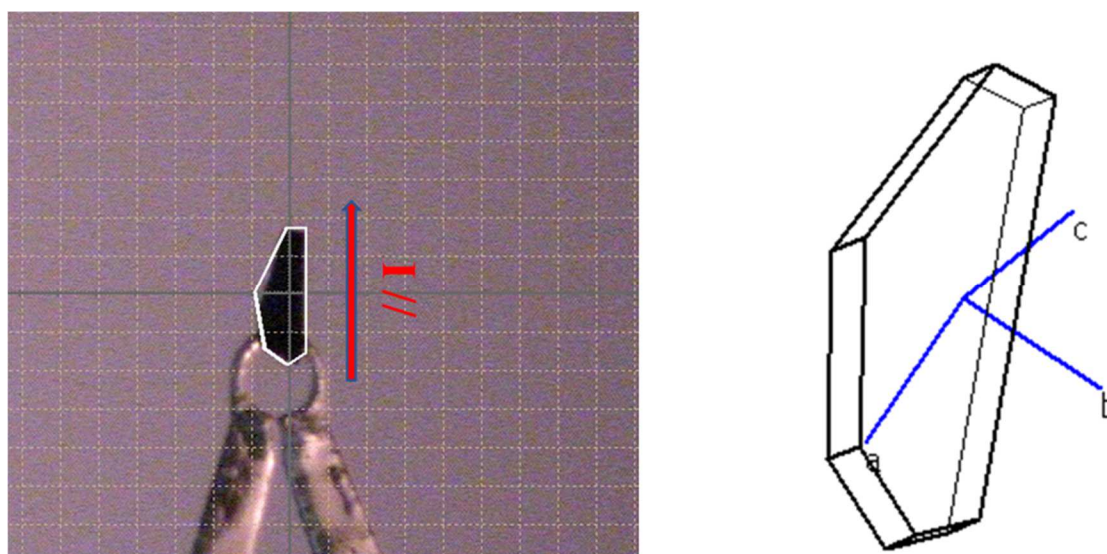


Figure S8. Orientation of the crystal of $[\text{Ni}(\text{Et-thiazds})_2]$ for transport measurements

Table S1. Exponents, contraction coefficients, and atomic parameters used in band structure calculations

STO Ni 4s. 4p. 3d.

-9.170000 1.825000 1.00000

-5.150000 1.125000 1.00000

-13.490000 5.750000 0.568300 2.000000 0.629200

STO S 3s. 3p.

-20.000000 2.662000 0.556400 1.688000 0.487300

-13.300000 2.338000 0.521200 1.333000 0.544300

STO Se 4s. 4p.

-20.500000 3.138700 0.616250 1.889960 0.512890

-13.200000 2.715040 0.550890 1.511400 0.572150

STO C 2s. 2p.

-21.400000 1.625000 1.00000

-11.400000 1.625000 1.00000

STO H 1s.

-13.600000 1.300000 1.00000

STO N 2s. 2p.

-26.000000 1.950000 1.00000

-13.400000 1.950000 1.00000

Computational details

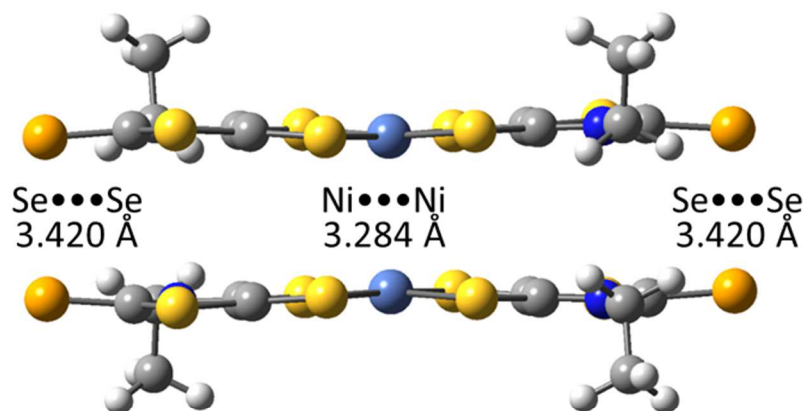
Full geometry optimization was performed with Density Functional Theory¹ using the hybrid Becke-3 parameter exchange functional² and the Lee-Yang-Parr nonlocal correlation functional³ (B3LYP) implemented in the Gaussian 09 (revision D.01) program suite and using the LANL2DZ basis set.⁴ Gaussview 5.0 was used to generate the figures.

Optimized cartesian coordinates for [Ni(Et-thiazSedt)₂] and its dimer, and the sulfur analogue [Ni(Et-thiazdt)₂] are provided separately as a single XYZ text file in a format for convenient visualization.

- [1] (a) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.*, **1964**, *136*, B864. (b) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989.
- [2] (a) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, **1988**, *38*, 3098. (b) Becke, A. D. A new mixing of Hartree-Fock and local density-functional theories. *J. Chem. Phys.*, **1993**, *98*, 1372. (c) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, **1993**, *98*, 5648.
- [3] Lee, C.; Yang, W., Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, **1988**, *37*, 785.
- [4] (a) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *J. Chem. Phys.*, **1985**, *82*, 284. (b) Hay P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.*, **1985**, *82*, 299.

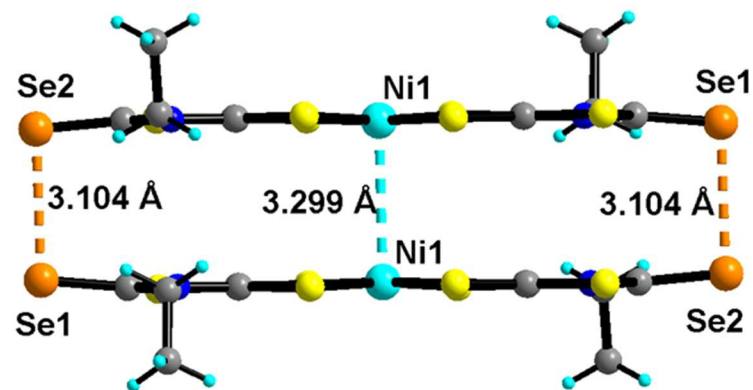
Structure of the Ni(Et-thiazSedt)₂ dimer

Calculated (DFT B3LYP/LanL2DZ)



Short H•••H contacts (from left to right)
2.84450 2.68815 2.68722 2.84481 Å

X-ray crystal structure



Short H•••H contacts (from left to right)
2.743(5) 2.716(5) 2.716(5) 2.743(5) Å

Figure S9. Details of the structure of the [Ni(Et-thiazSedt)₂] dimer calculated (left) and experimentally determined (right)

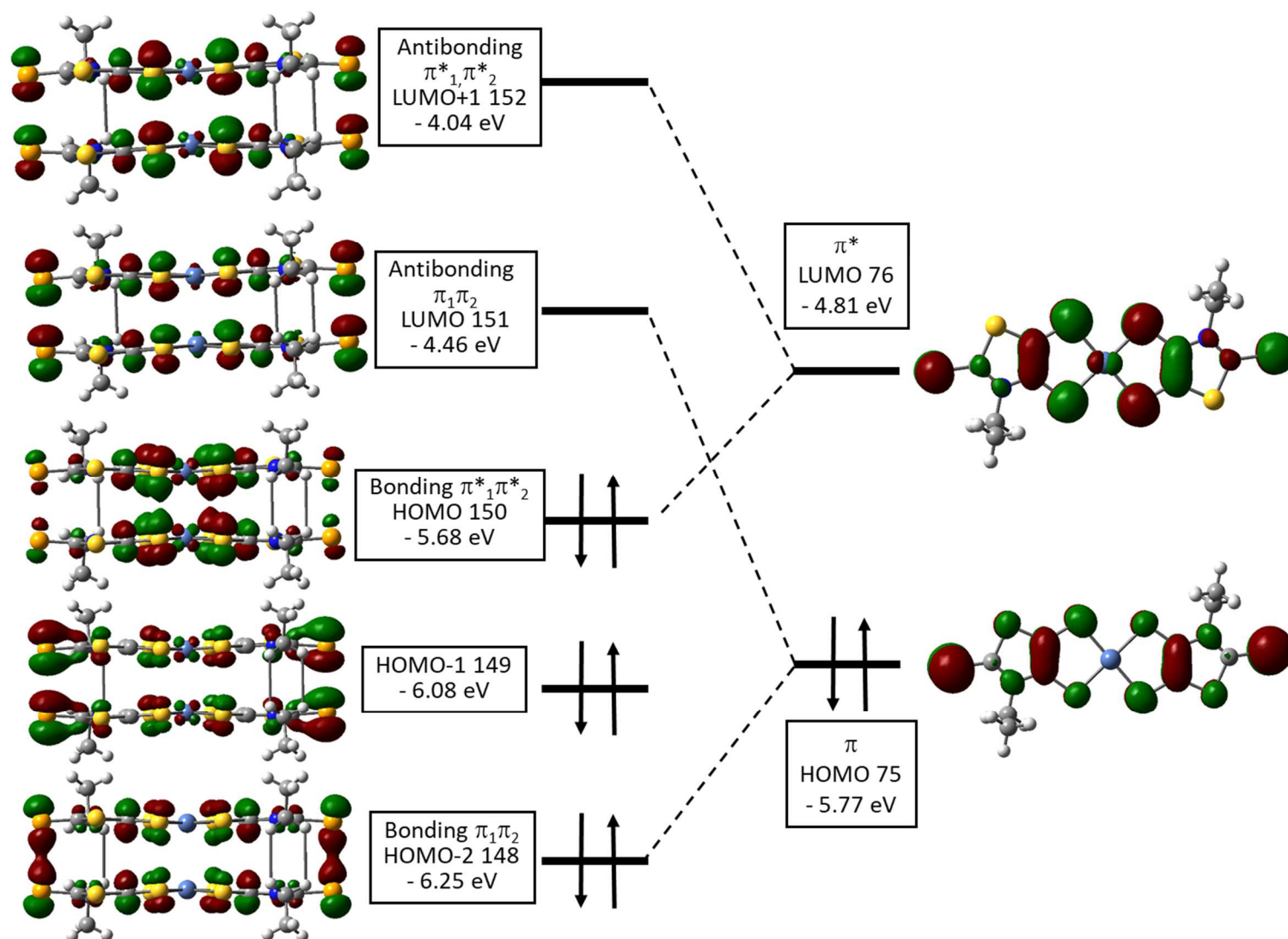


Figure S10 Sketch of the frontier molecular orbitals for the $[\text{Ni}(\text{Et}(\text{thiazSedt})_2)]$ dimer (left) and the monomer (right) drawn with a cutoff of 0.03 $[\text{e}/\text{bohr}^3]^{1/2}$.