

Supporting Information for:

Electronic Structure of Ni_2E_2 complexes (E = S, Se, Te) and a Global Analysis of M_2E_2 Compounds: A Case for Quantized E_2^{n-} Oxidation Levels with $n = 2, 3$, or 4

Shu A. Yao,^a Vlad Martin-Diaconescu,^b Ivan Infante,^c Kyle M. Lancaster,^d Andreas W.

Götz,^e Serena DeBeer,^{b,d} and John F. Berry^{a,*}

- a. Department of Chemistry, University of Wisconsin – Madison, 1101 University Ave. Madison, WI 53706, USA
- b. Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, D-45470, Mülheim/Ruhr, Germany
- c. Kimika Fakultatea, Euskal Herriko Unibertsitatea, and Donostia International Physics Center (DIPC), P. K. 1072, 20080 Donostia, Euskadi (Spain)
- d. Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853 (USA)
- e. San Diego Supercomputer Center, University of California San Diego, La Jolla, CA 92093 (USA)

Email: berry@chem.wisc.edu

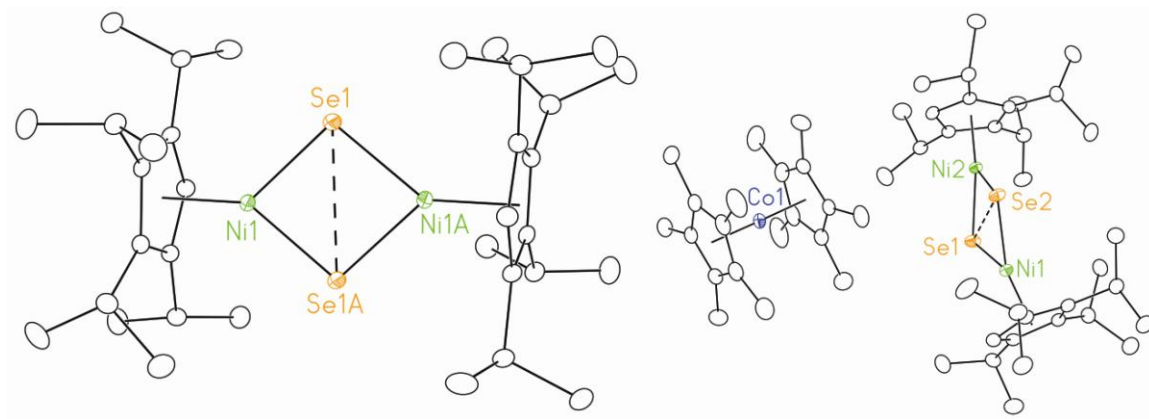


Figure S1. Crystal structures of **2** (Cp'NiSe)₂ and **2red** [Cp*₂Co]⁺[(Cp'NiSe)₂]⁻.¹ All molecules are drawn with displacement ellipsoids at 30 % probability level and all hydrogen atoms have been omitted for clarity.

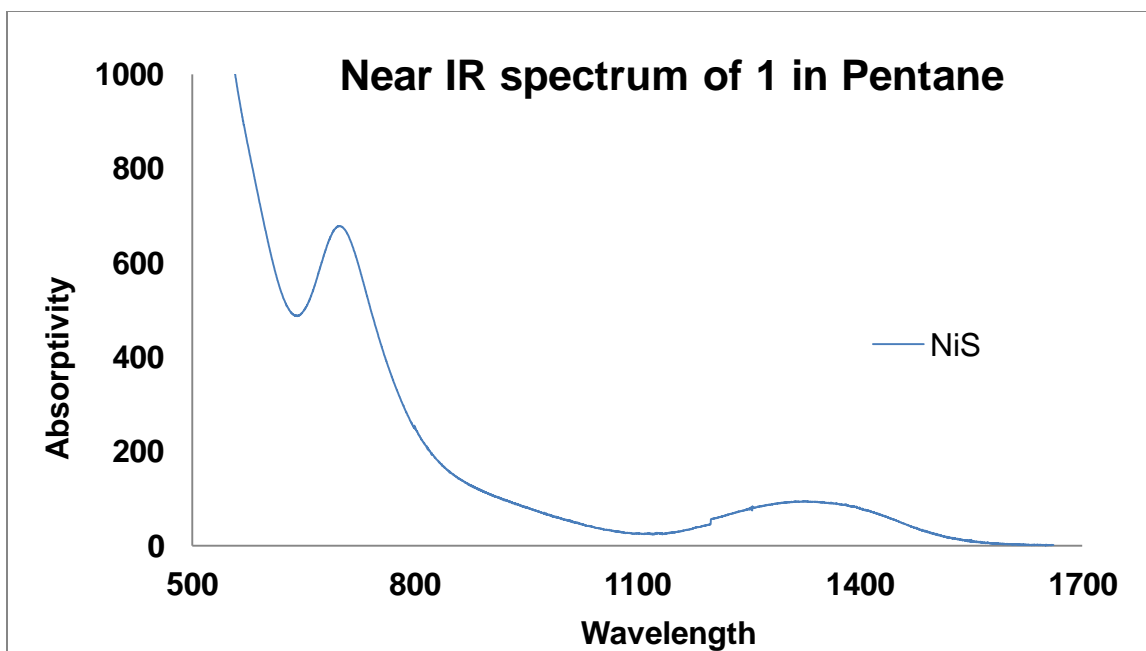


Figure S2. Near IR spectrum of Compound **1** in pentane solution.

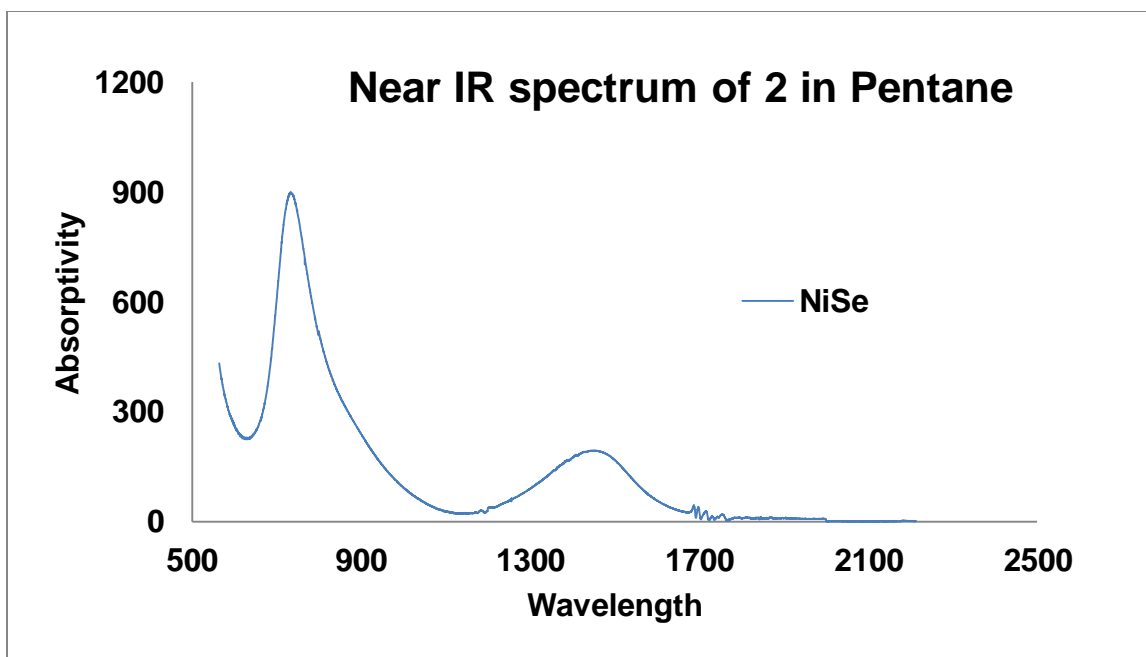


Figure S3. Near IR spectrum of compound **2** in pentane solution.

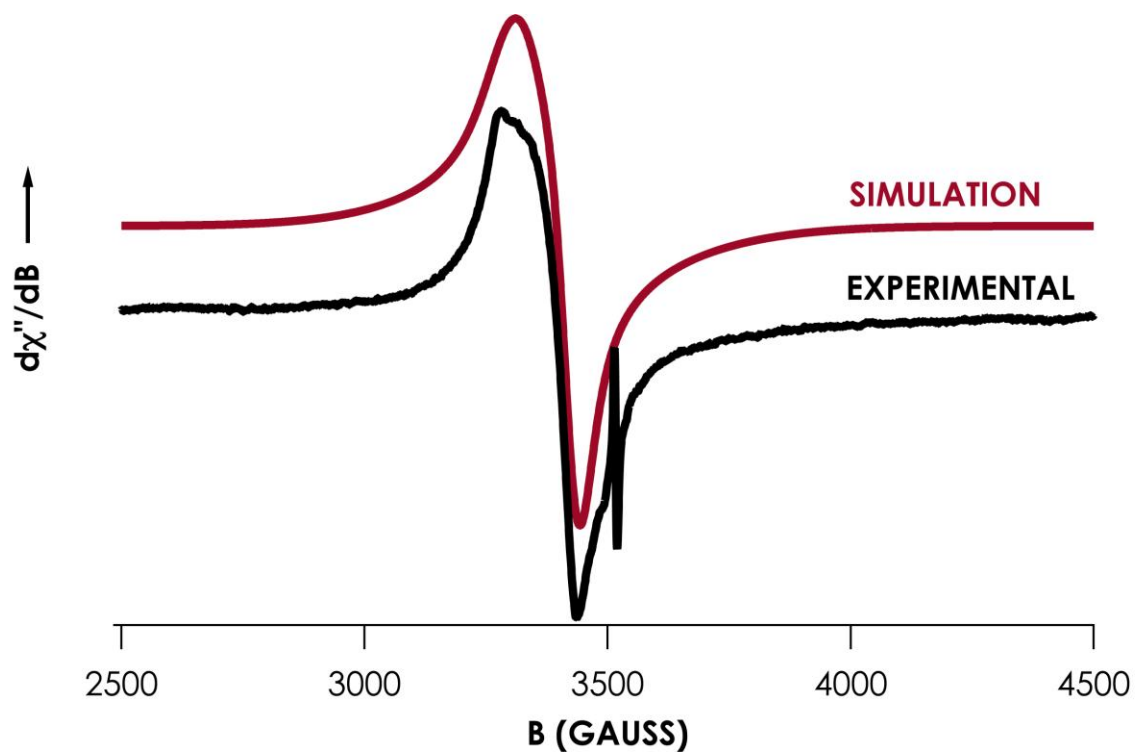


Figure S4. X-band EPR spectrum of solid **1red** $[(\text{Cp}^*\text{Ni})_2\text{S}_2]^- \text{Cp}^*_2\text{Co}^+$, experimental (black) and simulation (red). Simulated parameters: $g_1 = 2.067$, $g_2 = 2.059$, $g_3 = 2.112$; $g(\text{strain})_1 = 0.417$, $g(\text{strain})_2 = 0.029$, $g(\text{strain})_3 = 0.070$.

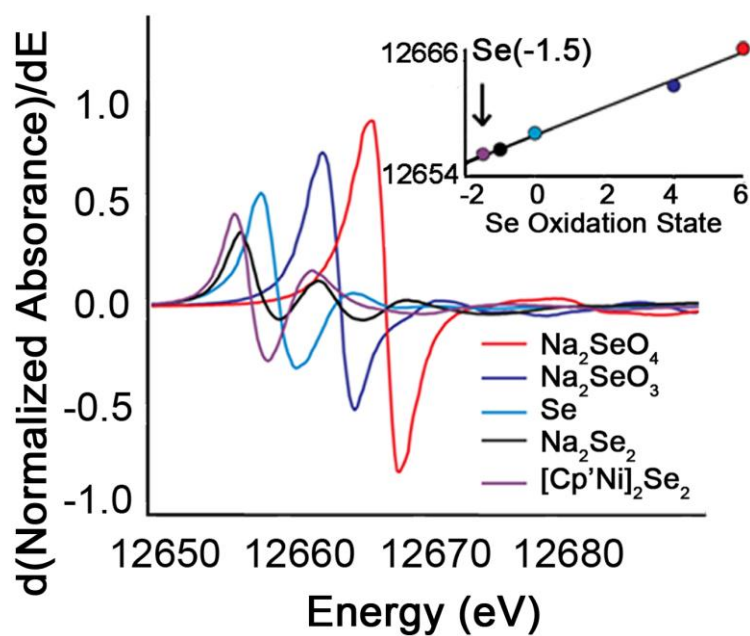


Figure S5. The XAS Spectroscopic analysis of **2**: The Se K-edge of **2** (purple) overlaid with spectra of Se^{VI} (red), Se^{IV} (blue), Se^0 (cyan) and Se^{-1} (blank) standards; inserts the plot of oxidation stated versus the energy, this spectra has been previously communicated by Yao et al.¹

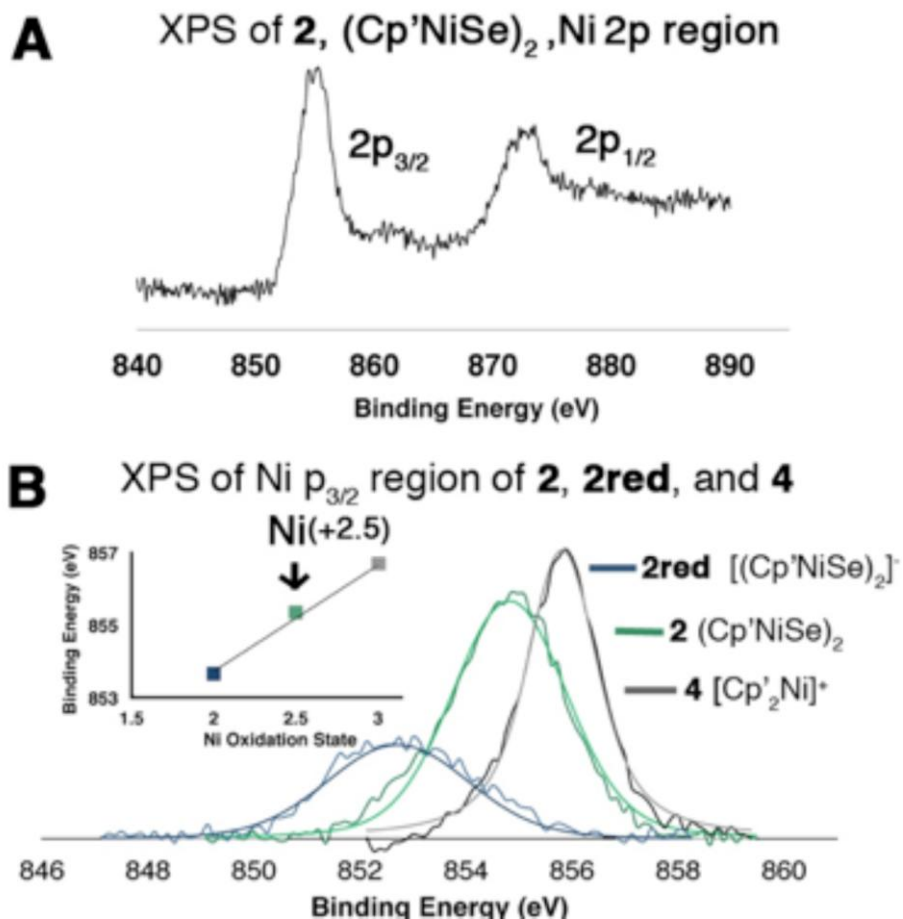


Figure S6. XPS analysis of **2**: A. The Ni(2p) region of the X-ray photoelectron spectrum (XPS) of **2**. B. The XPS Ni(2p_{3/2}) region of **2** (green), **2red** (grey), and **4** (blue); insert: plot of binding energy against Ni oxidation state.

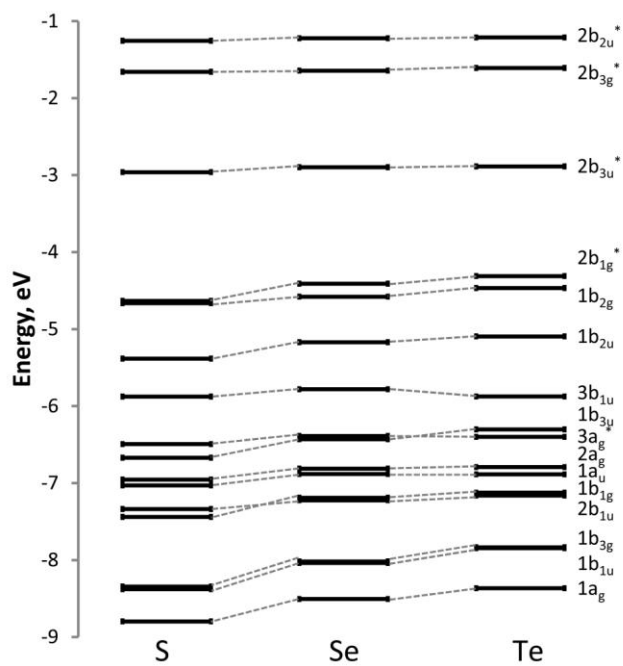


Figure S7. Orbital energies of the $\text{Cp}'_2\text{Ni}_2\text{E}_2$ complexes with $\text{E} = \text{S}, \text{Se}, \text{Te}$ derived from B3LYP calculations.

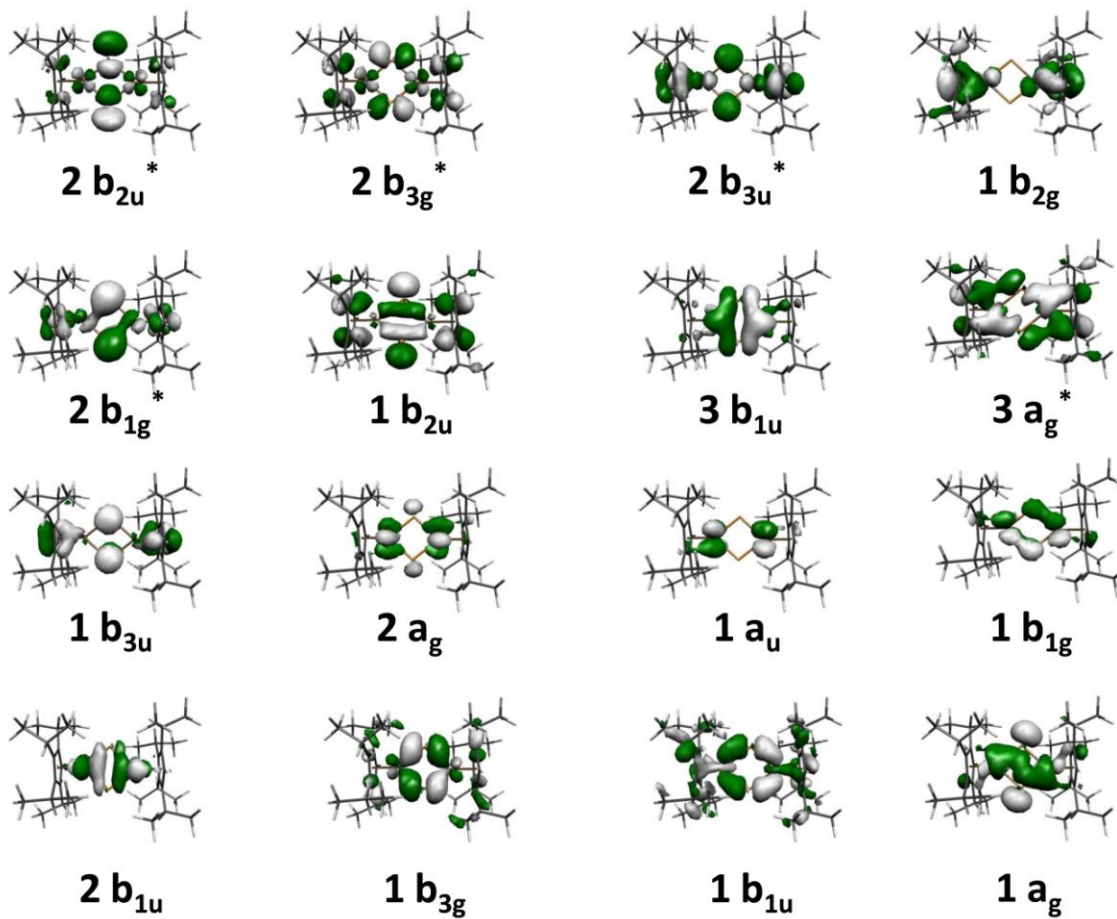


Figure S8. DFT (B3LYP) orbitals for $\text{Cp}'_2\text{Ni}_2\text{S}_2$, with no truncation of the Cp' ligand.

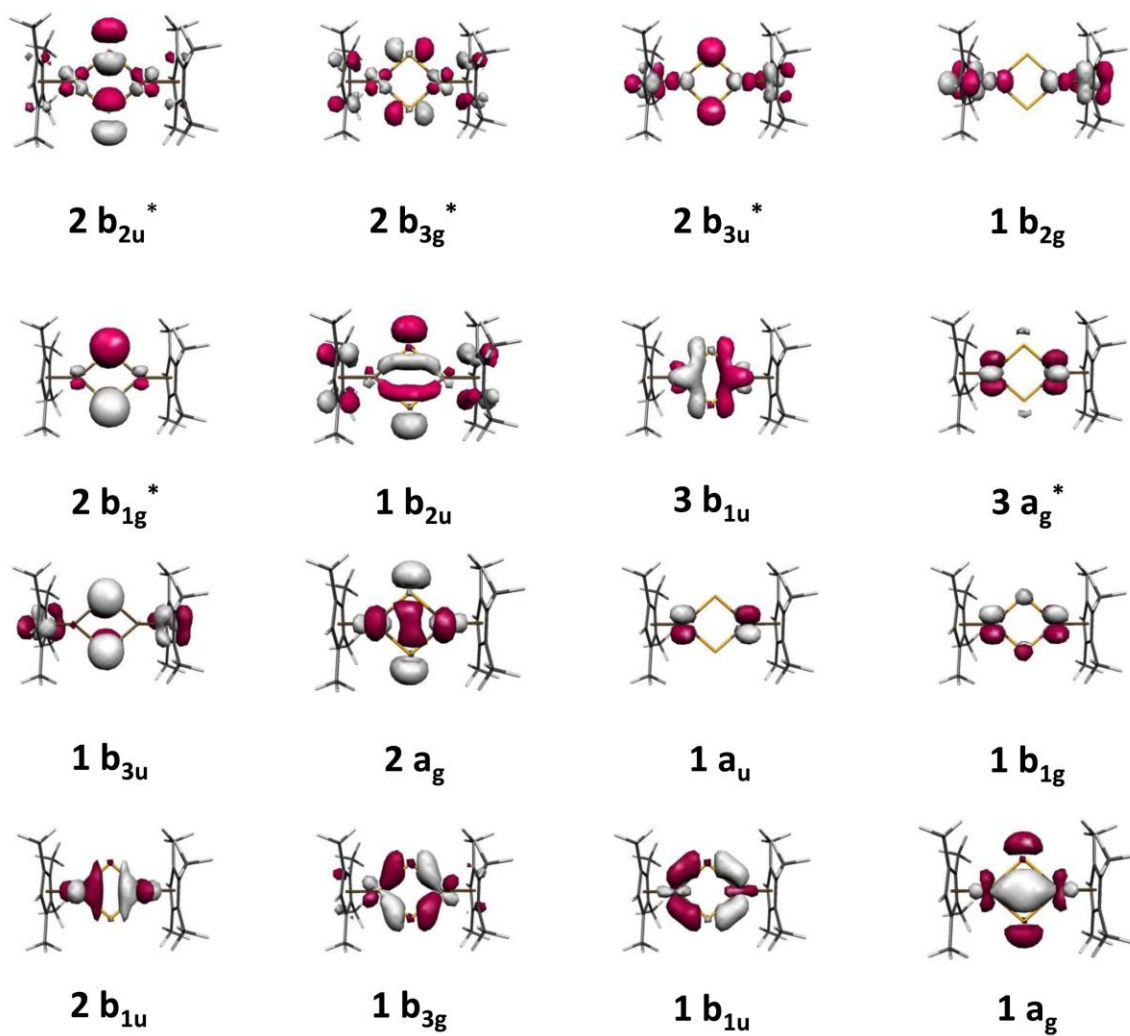


Figure S9. DFT (B3LYP) orbitals for $\text{Cp}''_2\text{Ni}_2\text{Se}_2$.

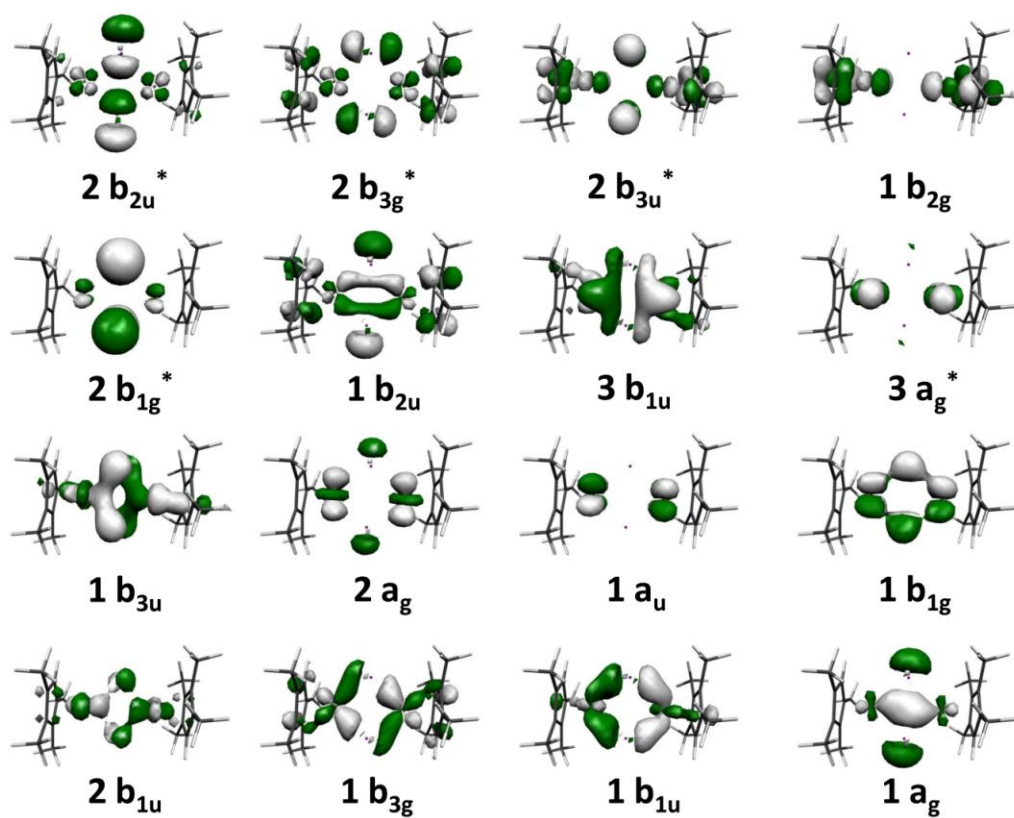


Figure S10. DFT (B3LYP) orbitals for $\text{Cp}''_2\text{Ni}_2\text{Te}_2$.

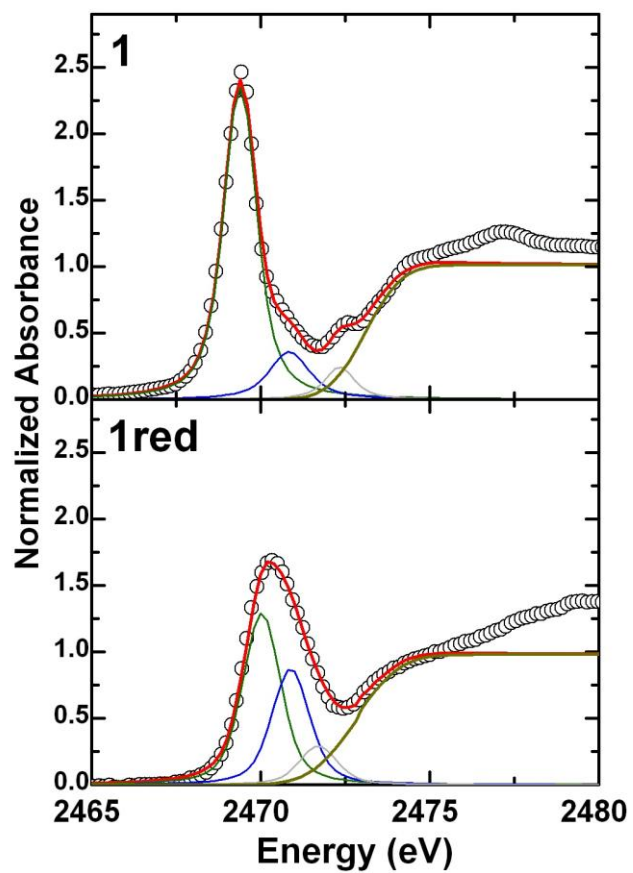


Figure S11. S K-edge fits of **1** and **1red** to determine edge energies. Color scheme: data (circles), total fit (red), edge jump (yellow).

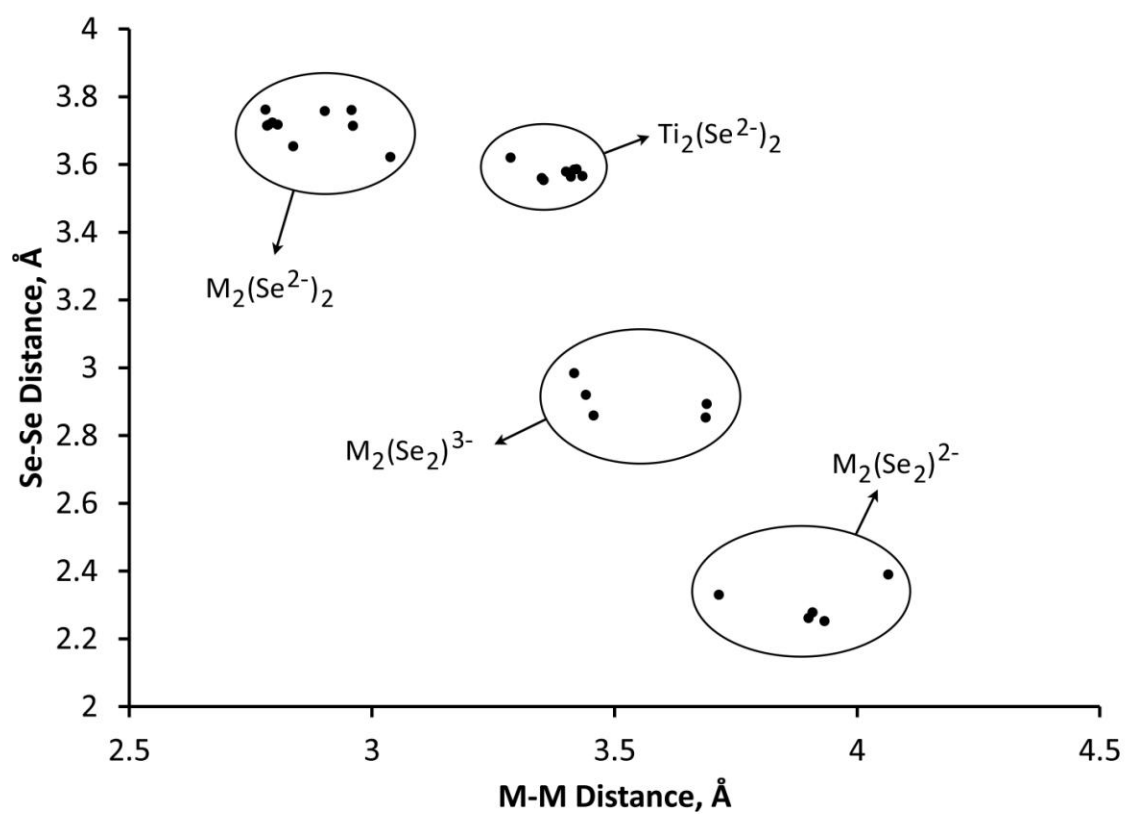


Figure S12. Plot of M–M vs Se–Se distance for all M_2Se_2 compounds from the CCDC that contain first-row transition metals with no metal-metal bonds and no bridging ligands other than the Se atoms.

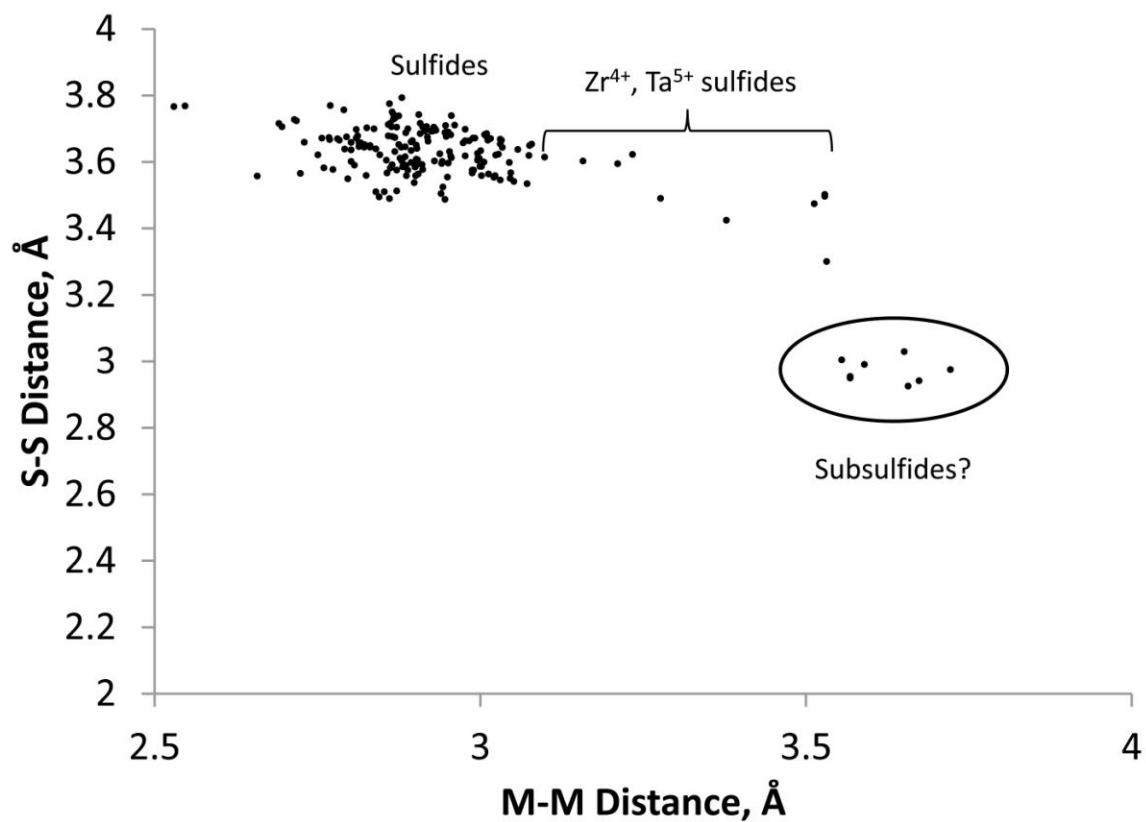


Figure S13. Plot of data from the Cambridge Structural Database for all compounds with a planar M_2S_2 core having second and third row M atoms. The plot excludes compounds with bridging ligands other than the S atoms.

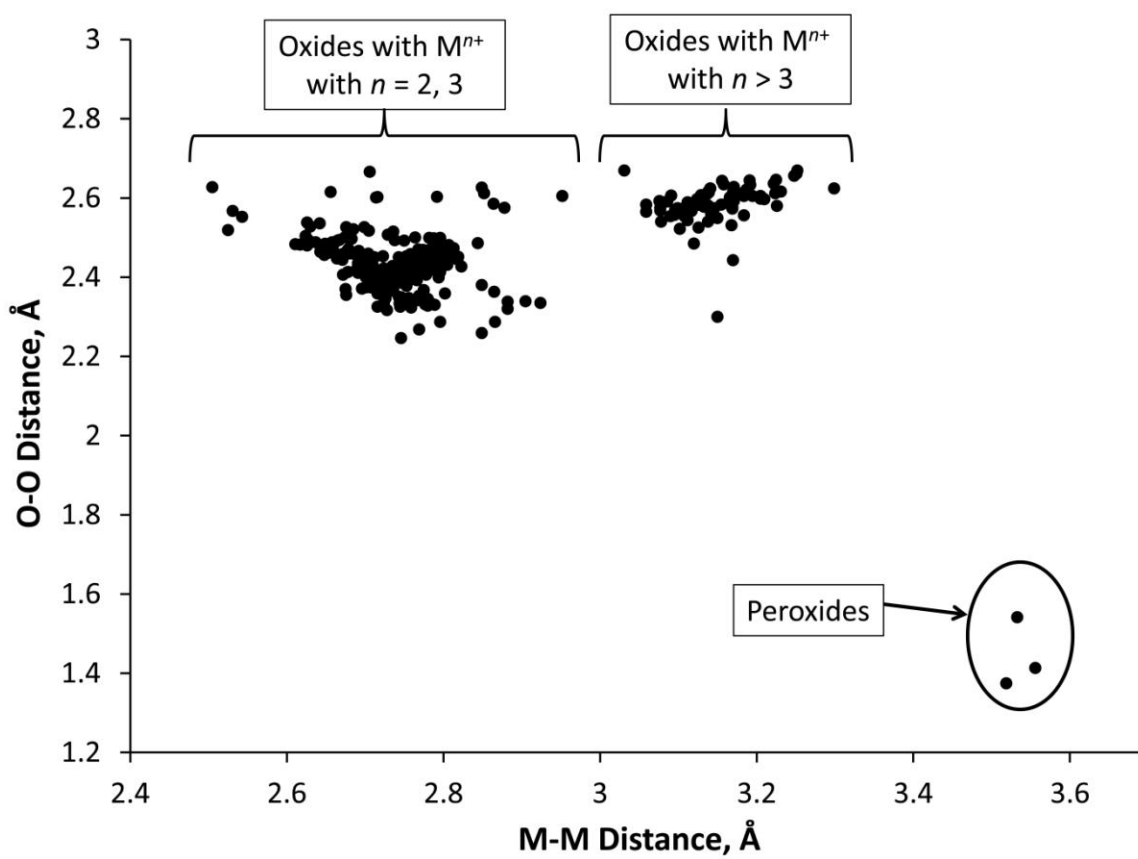


Figure S14. Plot of M–M vs O–O distance for all M_2O_2 compounds from the CCDC that contain first-row transition metals with no bridging ligands besides the O atoms.

References.

- (1) Yao, S. A.; Lancaster, K. M.; Gotz, A. W.; DeBeer, S.; Berry, J. F. *Chem. Eur. J.* **2012**, *18*, 9179.