

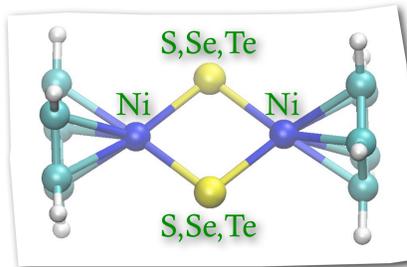
Can half-sigma bond exist in organometallic bridging complexes ?

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Introduction

A group of unusual dinickel dicyclopentadiene chalcogens bridging complexes, $(Cp'NiE)_2$ ($E=S, Se, \text{ and } Te$; $Cp' = 1,2,3,4$ tetraisopropylcyclopentadienyl) contain extraordinary $E\cdots E$ bond distances of 2.84 Å for $E=S$, 2.92 Å for $E=Se$, and 3.05 Å for Te that lie between the sums of the non-bonding Van der Waals radii and covalent radii. We investigated the electronic structure of these complexes using computational tools like the CASSCF/CASPT2 method, and experimental measurements using X-ray absorption spectroscopy, resonance Raman and EPR spectroscopy [1,2]. The experiments seem to suggest the existence of an unprecedented E_2^{3-} species in these complexes, paving the way to the presence of a half-sigma bond between the chalcogen atoms. Both experiment and theory agree well in the determination of several geometrical and spectroscopic parameters.



In the CASSCF/CASPT2 approach, the ideal active space for $Cp_2Ni_2S_2$ would be composed of all the valence orbitals of the $\{Ni_2S_2\}^{2+}$ ring including linear combinations of the five Ni 3d and 4s orbitals as well as the combinations of 3p orbitals on the sulfur atoms. This means that the active space would contain a total of 26 electrons, i.e. 9 valence electrons from each Ni^+ atom and 4 valence electrons from each set of sulfur 3p orbitals. In total we would have a CAS of (26e/18o). From a simple DFT/B3LYP calculation, we noticed that the $3d_{z^2}-3d_{z^2}$ bonding/antibonding pair is fully occupied with electrons and lies low in energy such that these two orbitals and four electrons can be removed. A similar procedure can be done with the four filled (eight electrons) non-bonding orbitals of delta symmetry derived from the $3d_{x^2-y^2}$ orbitals. Based on these considerations we reach a space of (14e/12o). We have calculated six excited states for each irreducible representation, i.e. a total of 24 transition energies for the singlet and 24 transition energies for the triplet. Calculations were carried out with the MOLCAS 7.6 package [3]. DFT/PBE/TZ2P runs were performed to obtain the geometrical structures with the ADF2010 package[4].

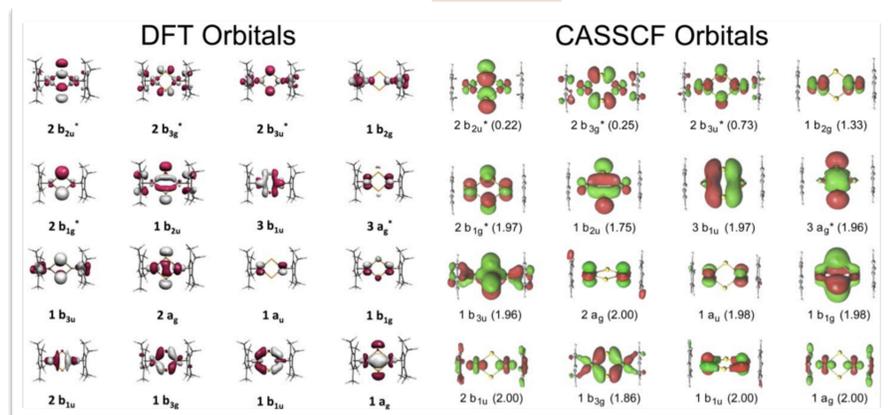
Methodology

Results and Discussion

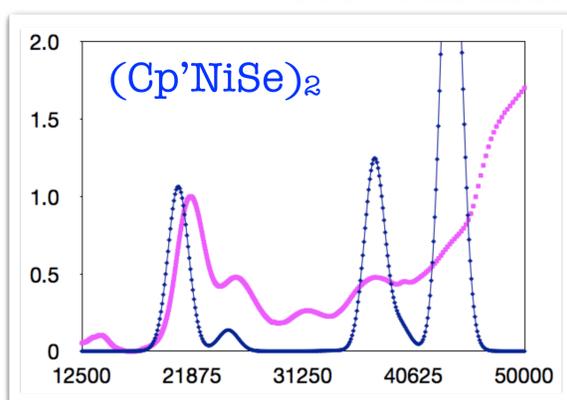
Structure

	E-E (Å)	Ni-Ni (Å)	Ni-E (Å)	Ni-Cp' (Å)	E-Ni-E (°)	Ni-E-Ni (°)
$(Cp'NiS)_2$ Exp	2.806(1)	3.225(1)	2.141(1) 2.133(1)	1.725(2)	82.04(2)	97.96(2)
$(Cp'NiS)_2$ DFT	2.873	3.232	2.161 2.163	1.740	83.3	96.7
$(Cp'NiSe)_2$ Exp	2.916(3)	3.438(3)	2.251(2) 2.257(2)	1.728(2)	80.60(1)	99.40(1)
$(Cp'NiSe)_2$ DFT	3.012	3.424	2.280 2.280	1.739	82.7	97.3
$(Cp'NiTe)_2$ Exp	3.091	3.771	2.434 2.430	1.735		
$(Cp'NiTe)_2$ DFT	3.140	3.602	2.396 2.382	1.680		

MO's



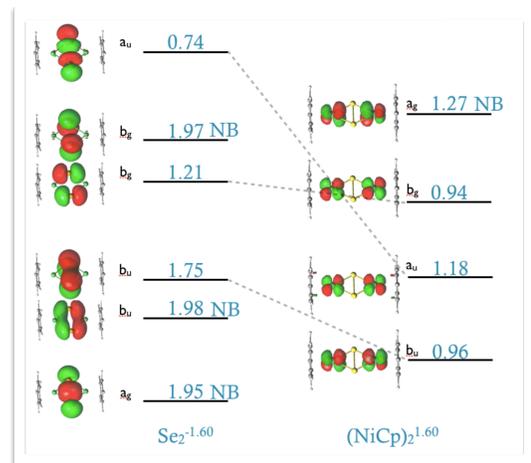
UV-Vis Spectra



$(Cp'NiSe)_2$ MS-CASPT2
 $(Cp'NiSe)_2$ Experiment
Energies are in cm^{-1}

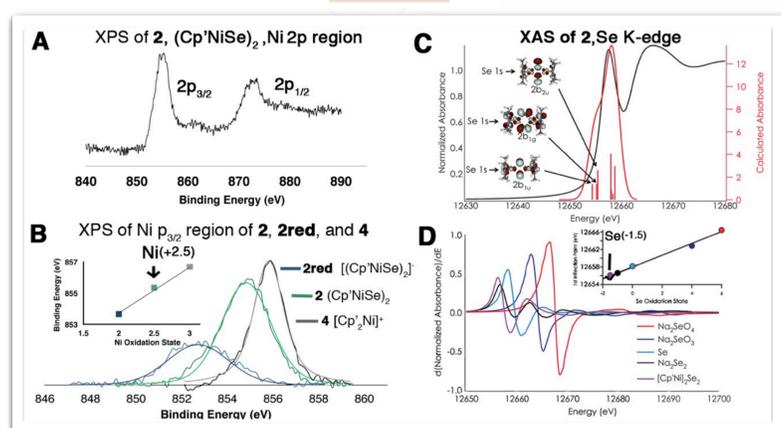
- ◆ Superb agreement theory vs experiment
- ◆ Similar agreements are found for the $(Cp'NiS)_2$ and $(Cp'NiTe)_2$ spectra
- ◆ Ligand to metal charge transfer (LMCT) transitions are predominant: $E_2 \pi^* \rightarrow NiE\pi^*$

LNO's



- ◆ Localized Natural Orbitals (LNO's) pinpoint to a Se_2^{2-} group, different from the one proposed in the experiment: Se_2^{3-}
- ◆ The bond order of Se_2^{2-} is 0.88, larger than 0.5 in Se_2^{3-}
- ◆ Antiferromagnetic coupled Ni atoms.
- ◆ NiSe bond order of 0.36

XAS



Conclusions

In conclusion, we provide strong experimental and computational evidence for the Se_2 moiety as a ligand to transition metals. The computational DFT results indicate that this stabilization is through a strong covalent interaction involving the Se_2 half-filled σ^* antibonding orbital and the Ni_2 3d orbitals, resulting in a covalent and delocalized Ni_2Se_2 ring. The new one-electron paradigm will facilitate better understanding of the crucial role of one-electron redox processes involving the chalcogens in both Nature and in modern chemical systems. These insights will ultimately inspire the design of novel compounds and materials.

References

1. Yao, Lancaster, Gotz, DeBeer, Berry, manuscript in preparation
2. Yao, Lancaster, Gotz, Infante, DeBeer, Berry, manuscript in preparation
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Acknowledgments

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