Binding of Divalent Metal Ions with Deprotonated Peptides: Do Gas-Phase Anions Parallel the Condensed Phase?

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Supplementary Material.

Contents:

I. Structures and Energies of Complexes

Energies (kJ/mol) are relative to the lowest-energy complex of the given metal and isomer. Values in parentheses are free energies (harmonic vibrations, free rotors) at 300 K.

Peptide / conformer	Ni^{2+}	Cu^{2+}
AAH		
Im2[NNON]a	0 (0)	0 (0)
Im2[NNON]b	2 (2)	3 (4)
Im2[NNNR]	26 (29)	13 (12)
Im2[NNON(R)]		56 (52)
Im1CS1[NOOR]		159 (153)
AHA		
Im2[NNON]a	0 (0)	0 (1)
Im2[NNON]b	5 (5)	2 (0)
Im2[NNON(R)]	56 (46)	73 (69)
Im1CS1[NOOR]	74 (70)	83 (83)
HAA		
Im2[NNON]a	0 (0)	0 (0)
Im2[NNON]b	2 (2)	31 (28)
Im2[NNOR]	59 (59)	36 (39)
Im1CS1[NOOR]	109 (102)	60 (68)
Im2[NNON(R)]	114 (98)	*

* Rearranges to Im2[NNON]b

Fig. S1. Computed structures for complexes of Cu^{2+} and Ni^{2+} with AlaAlaHis with an overall –1 charge (ligand triply deprotonated). Relative energies are given in kJ/mol with free energies in brackets.

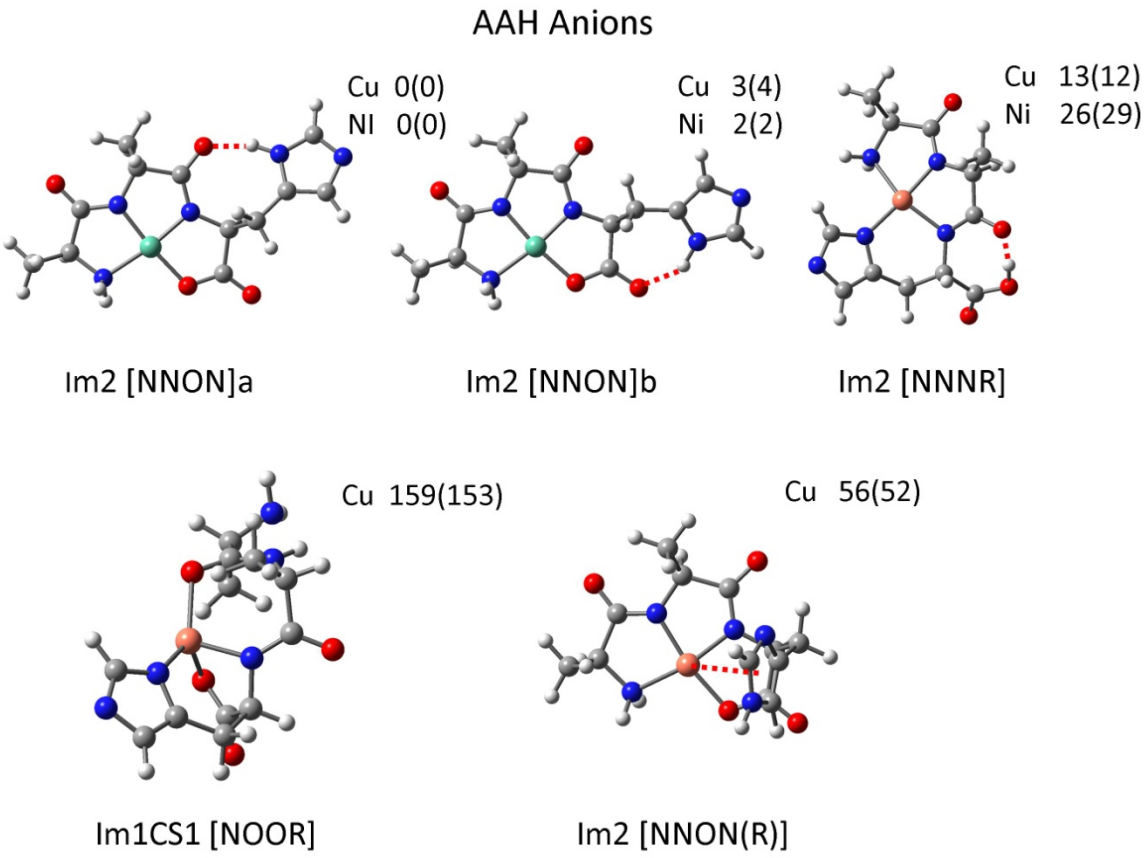


Fig. S2. Computed structures for complexes of Cu^{2+} and Ni^{2+} with AlaHisAla with an overall –1 charge (ligand triply deprotonated). Relative energies are given in kJ/mol with free energies in brackets.

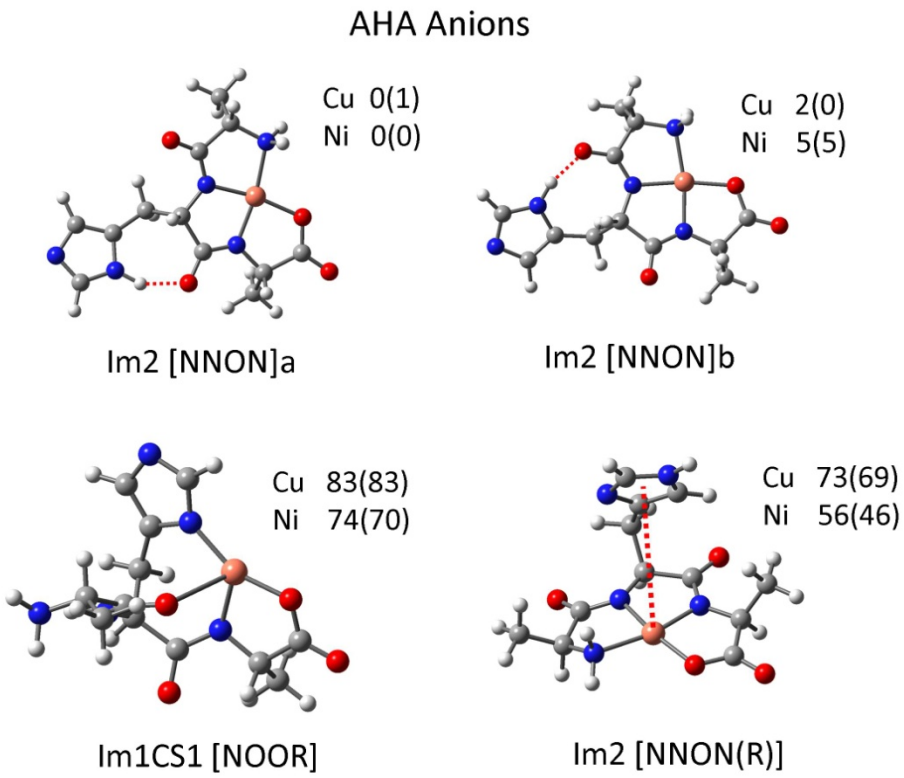
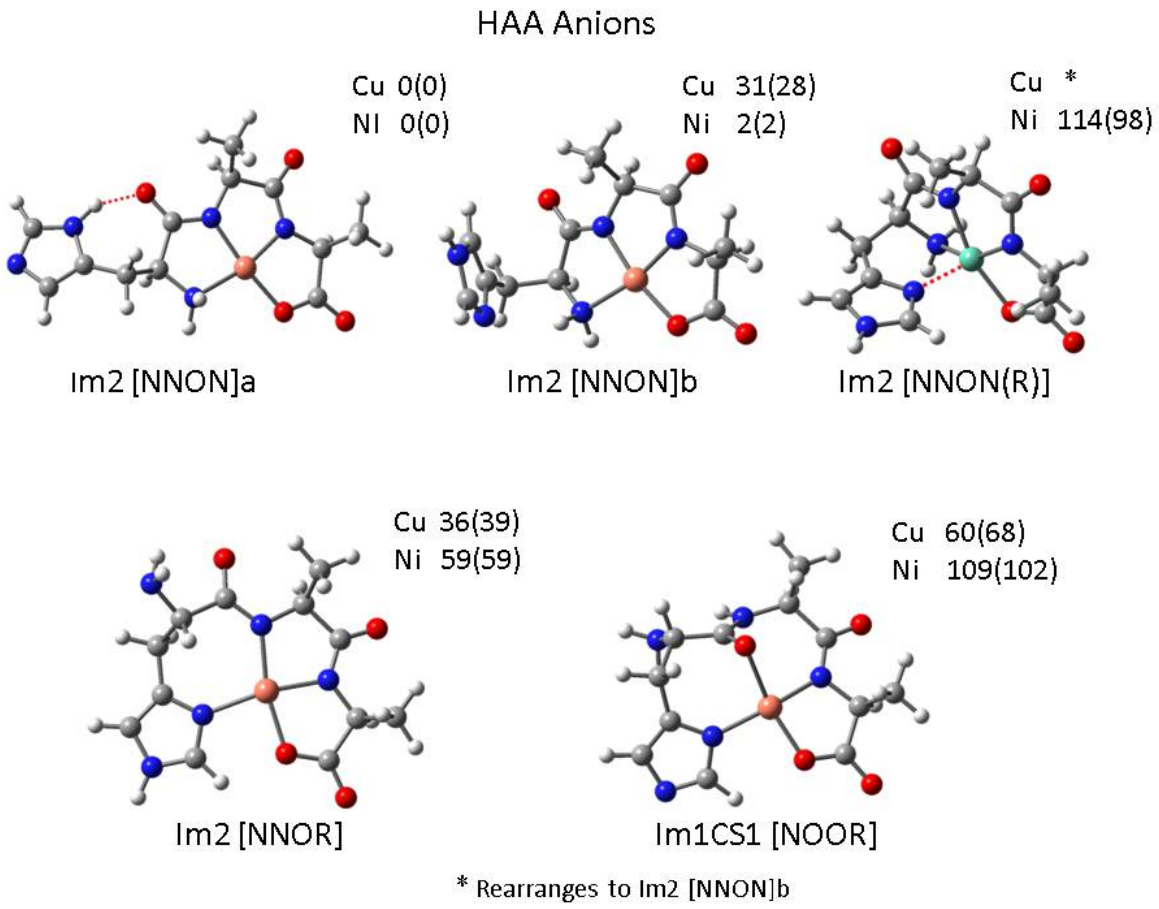


Fig. S3. Computed structures for complexes of Cu^{2+} and Ni^{2+} with HisAlaAla with an overall –1 charge (ligand triply deprotonated). Relative energies are given in kJ/mol with free energies in brackets.



II. Computed spectra and fits to experiment

Fig. S4: IRMPD spectrum of the CuAAH anion compared to computed spectra for different coordination motifs and different conformations of them. The green modeled spectrum in the top panel is a 1:1 average of the two lowest-energy Im2[NNON] structures, with 25% of the spectrum of Im2[NNNR] added. Computed energies in kJ mol^{-1} are given.

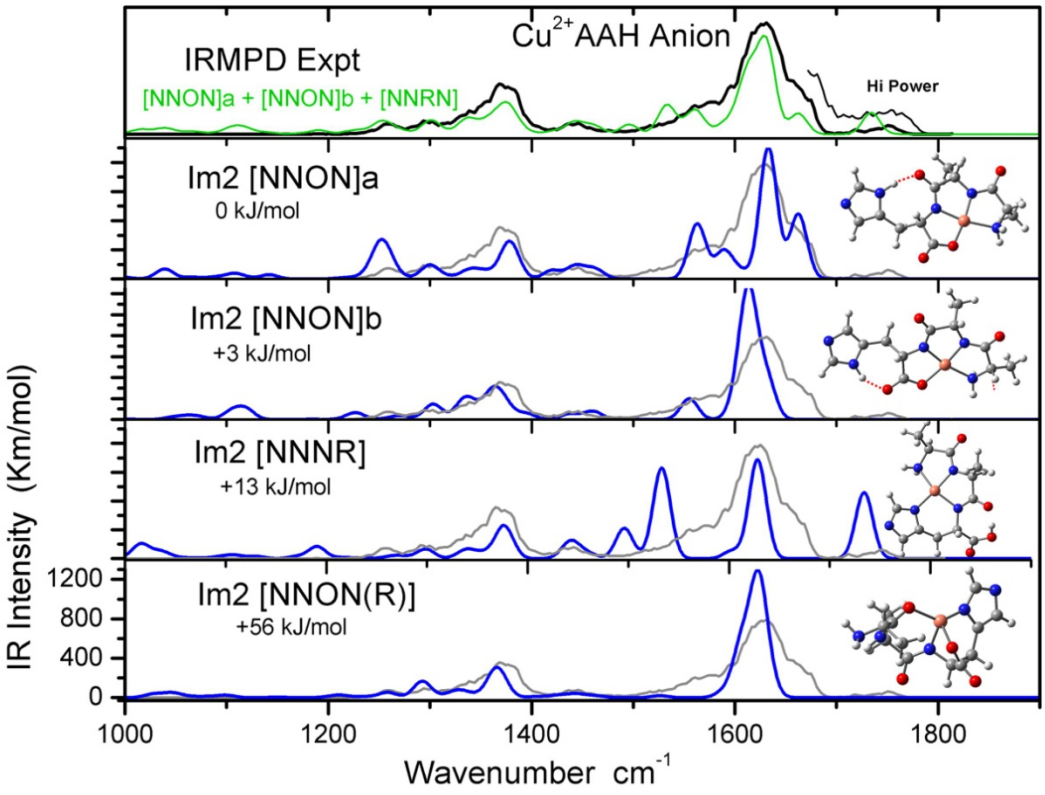


Fig. S5: IRMPD spectrum of the NiAAH anion compared to computed spectra for different coordination motifs and different conformations of them. The green modeled spectrum in the top panel is a 1:1 average of the two lowest-energy Im2[NNON] structures, with 25% of the spectrum of Im2[NNNR] added. Computed energies in kJ mol^{-1} are given.

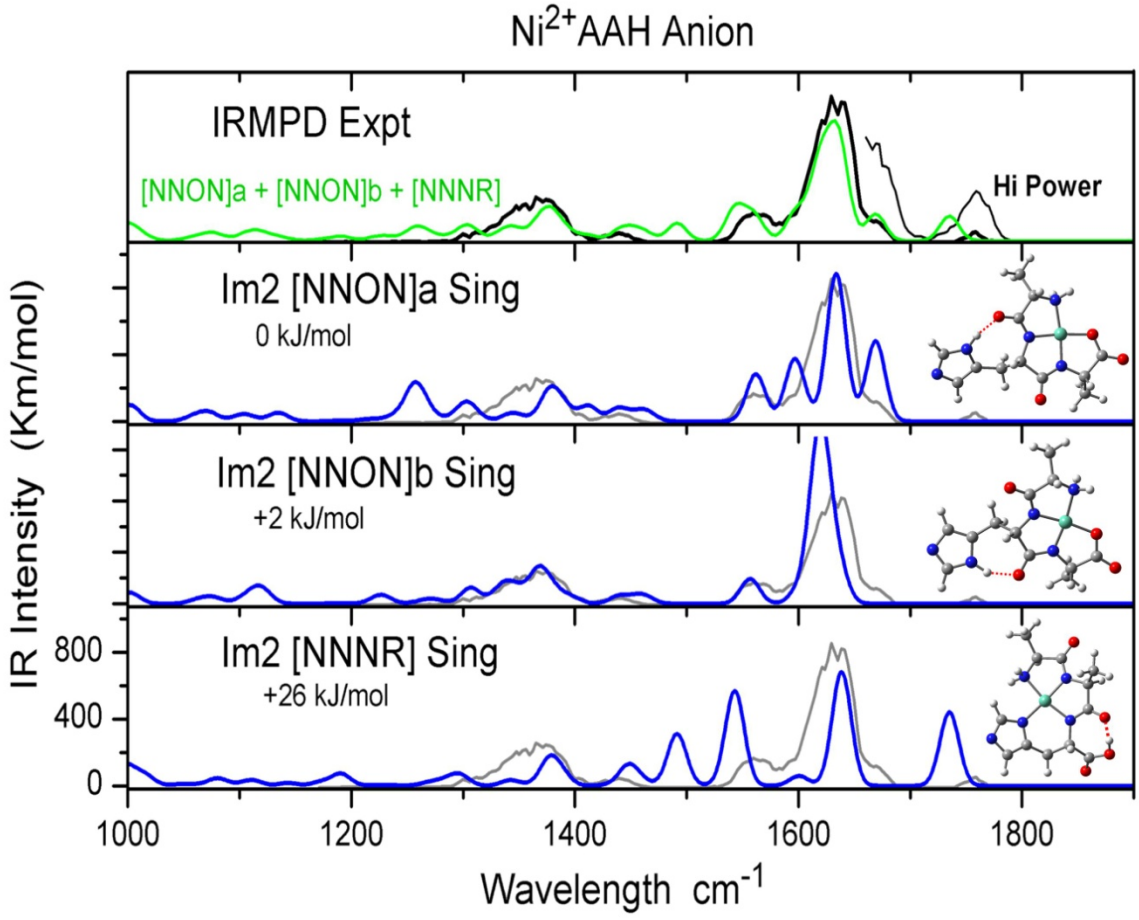


Fig. S6: IRMPD spectrum of the CuAHA anion compared to computed spectra for different coordination motifs and different conformations of them. The green modeled spectrum in the top panel is a 1:1 average of the two lowest-energy Im2[NNON] structures. Computed energies in kJ mol^{-1} are given.

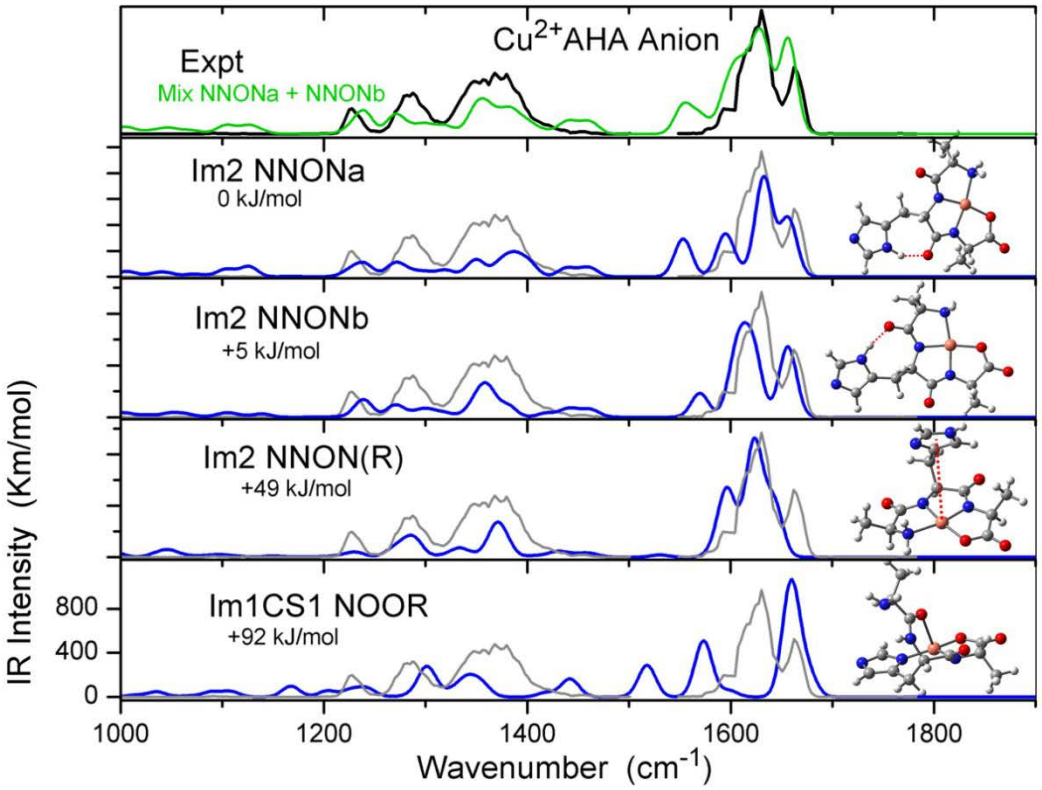


Fig. S7: IRMPD spectrum of the NiAHA anion compared to computed spectra for different coordination motifs and different conformations of them. The green modeled spectrum in the top panel is a 1:1 average of the two lowest-energy Im2[NNON] structures. Computed energies in kJ mol^{-1} are given.

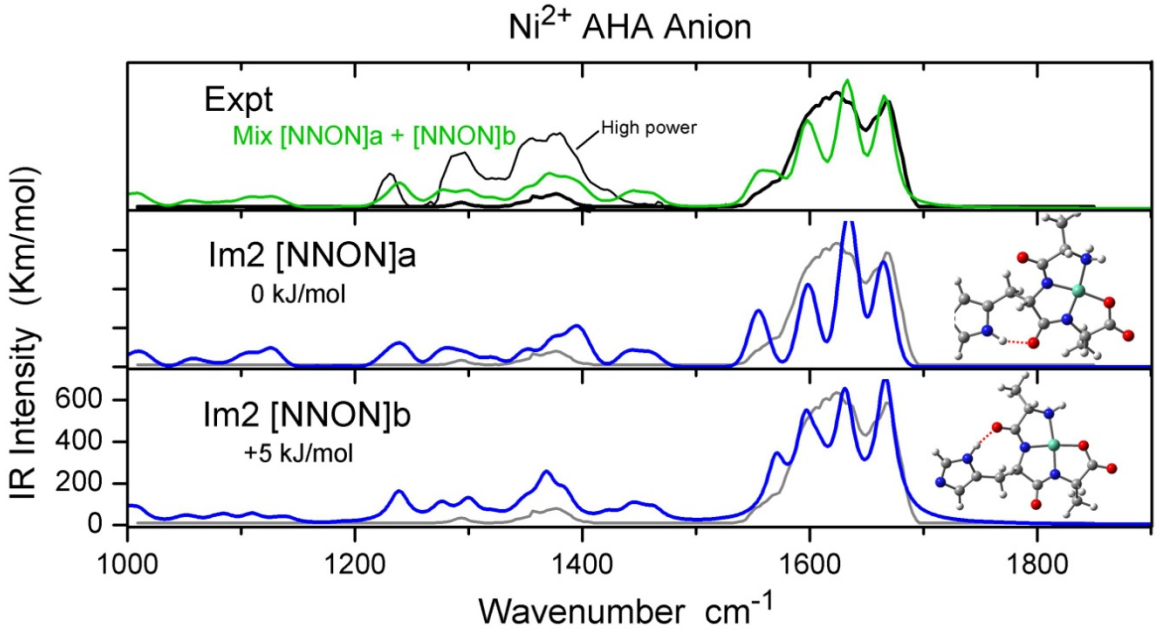


Fig. S8: IRMPD spectrum of the CuHAA anion compared to computed spectra for different coordination motifs and different conformations of them. Computed energies in kJ mol^{-1} are given.

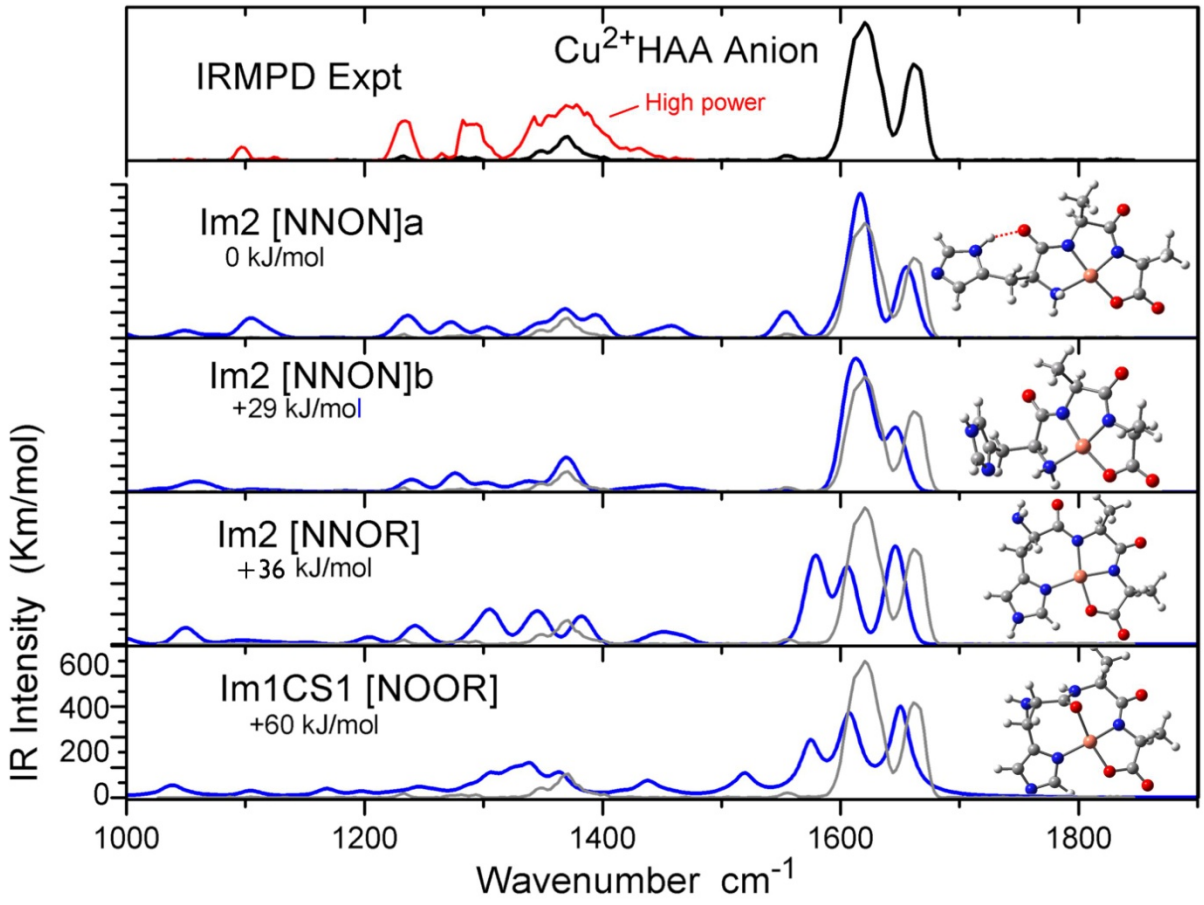
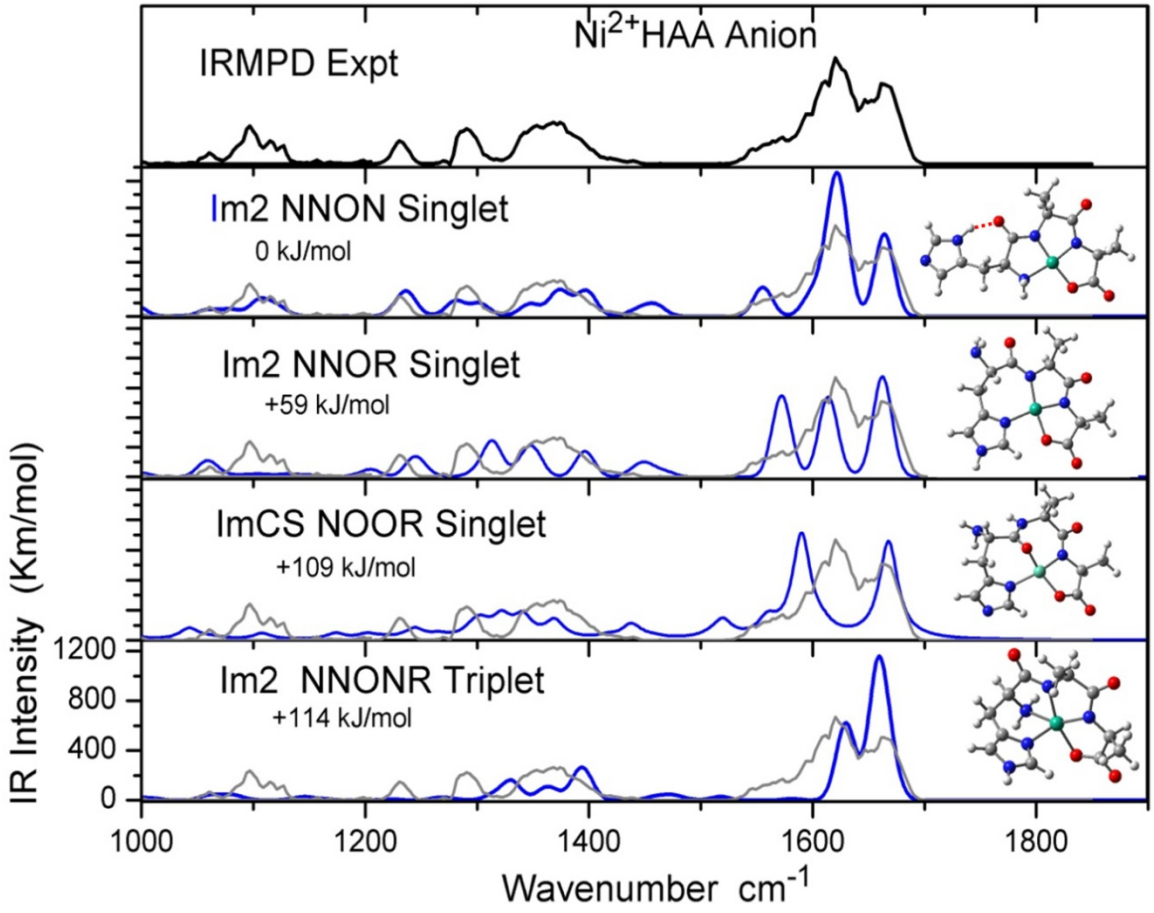


Fig. S9: IRMPD spectrum of the NiHAA anion compared to computed spectra for different coordination motifs and different conformations of them. Computed energies in kJ mol^{-1} are given.



III. Complete Citation for Reference 43.

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.