

Electronic Supplementary Information:

Complexes of Ni(II) and Cu(II) with Small Peptides: Deciding Whether to Deprotonate

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1. Complete Citation for Ref. 83.

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.

2. Comparative structure plots and vibrational assignments for Ni(II) and Cu(II) complexes. Enlarged drawings of all the Ni(II) structures.

Coordinates for all the optimized structures mentioned in the paper are available on request from the first author.

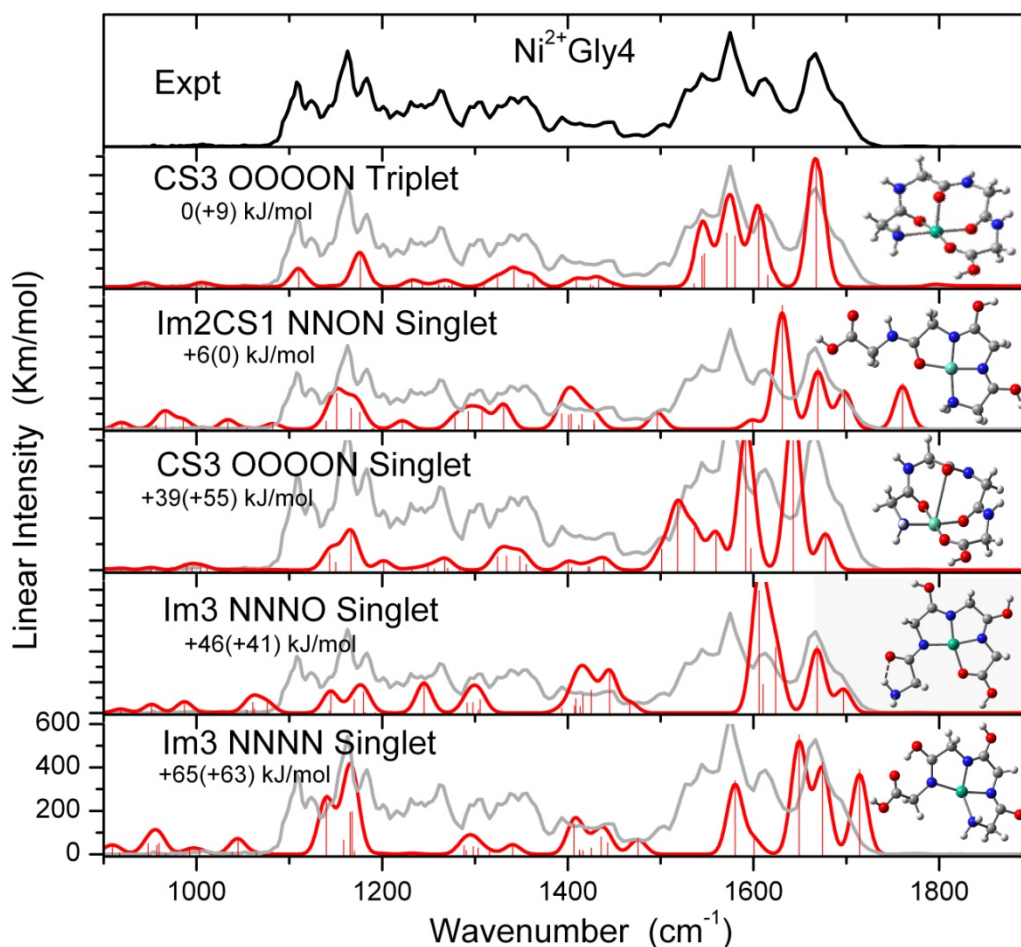
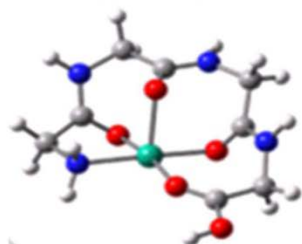
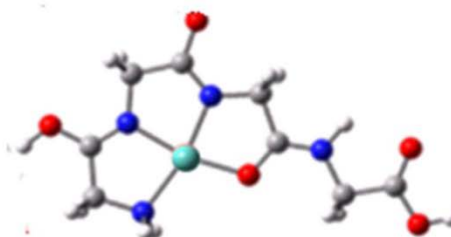


Fig. S1. Computed (red) spectra of conformations of the $\text{Ni}^{2+}\text{Gly}_4$ complex, compared with the IRMPD spectrum (black). Ni^{2+} ion is green. Peaks having diagnostic value for the CS3 ground state are as follows: 1100 (NH_2 bend); 1160 (carboxyl OH bend); 1330 (CH, NH bends); 1530 (amide NH bend); 1560-1620 (amide stretches); 1660 (carboxyl CO stretch).

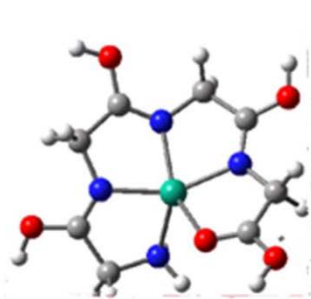
Fig. S1b. Ni²⁺Gly₄ Enlarged Structures



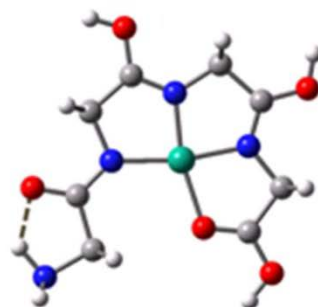
CS [OOOON] Triplet



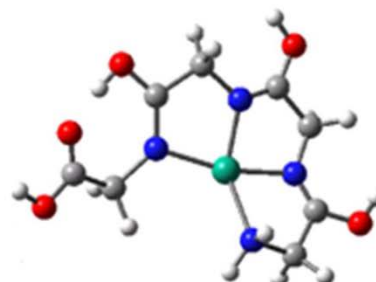
Im2CS1 [NNON] Singlet



Im3 [NNNON] Singlet



Im3 [NNNO] Singlet



Im3 [NNNN] Singlet

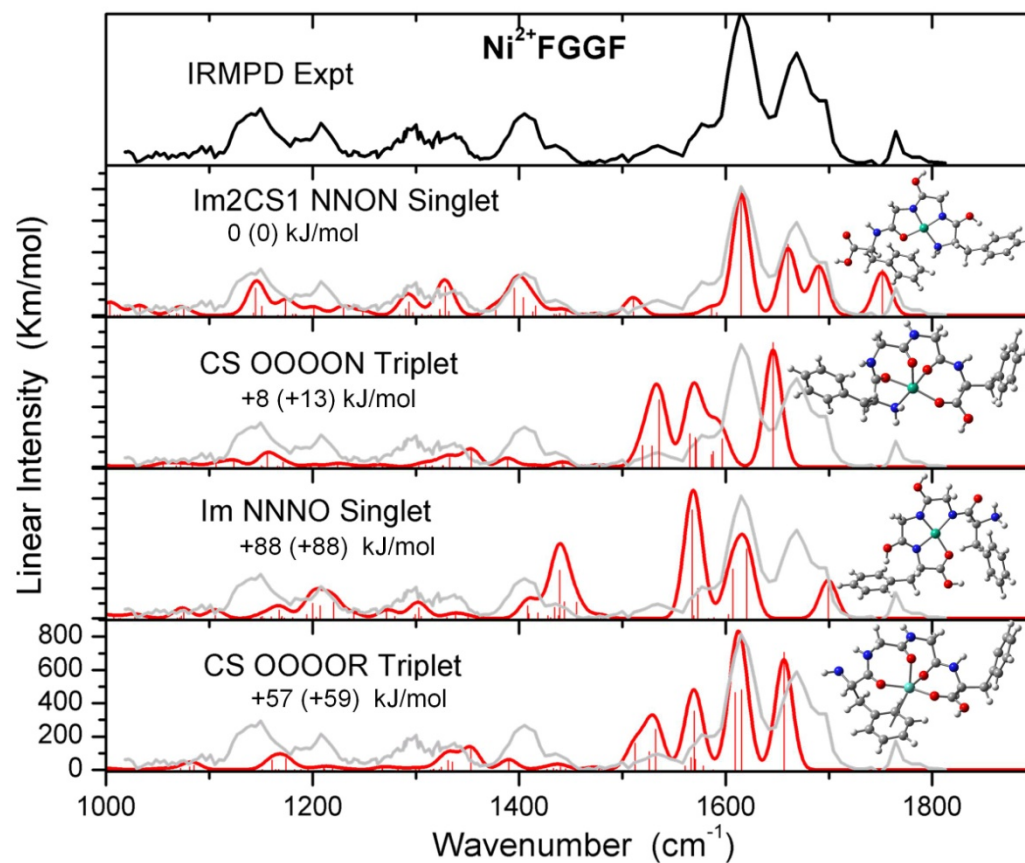
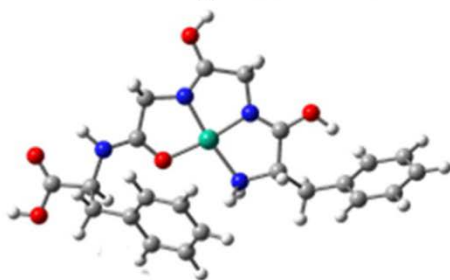
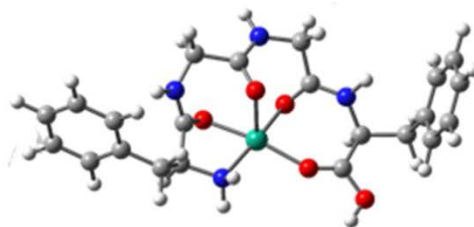


Fig. S2. Computed (red) spectra of conformations of the $\text{Ni}^{2+}\text{FGGF}$ complex, compared with the IRMPD spectrum (black). Peaks having diagnostic value for the Im2CS1 ground state: 1300 (CH bend); 1400 (Iminol antisymmetric CCO stretch); 1760 (carboxyl CO stretch).

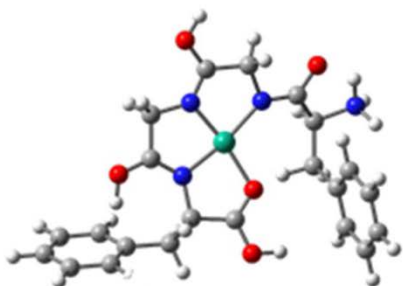
Fig. S2b. Ni²⁺FGGF Enlarged Structures



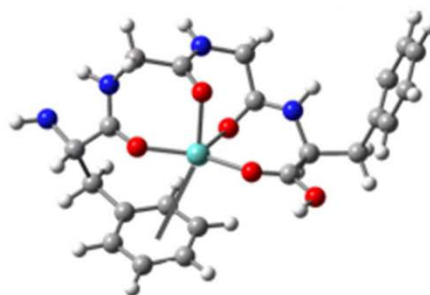
Im2CS1 [NNON] Singlet



CS [OOOON] Triplet



Im3 [NNNO] Singlet



CS [OOOOR] Triplet

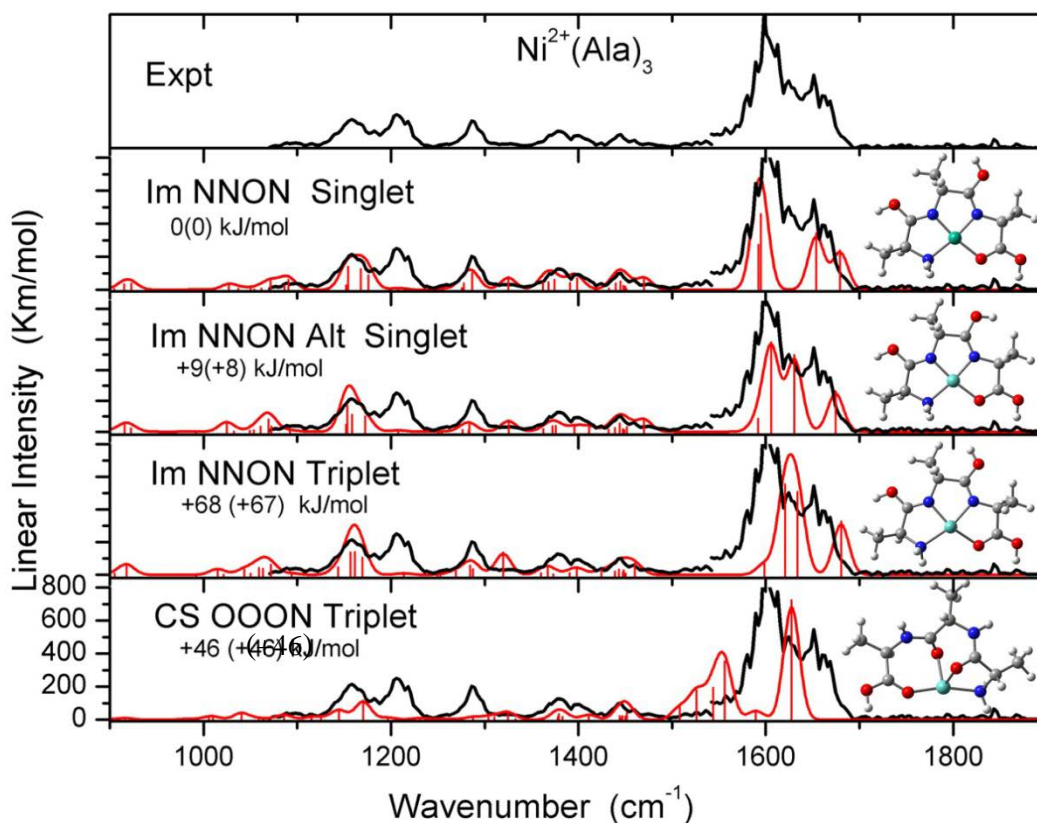
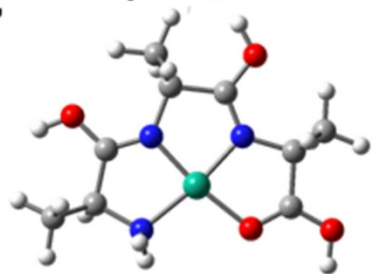
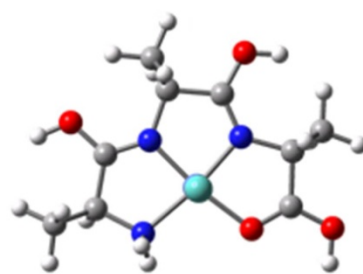


Fig. S3. Computed (red) spectra of conformations of the $\text{Ni}^{2+}\text{Ala}_3$ complex, compared with the IRMPD spectrum. Note: The computed spectra of the two low-lying Im [NNON] isomers are shown separately. The best fit to the observed spectrum is actually achieved with a mixed population containing similar fractions of each of these, and this best-fit spectrum is the one displayed (red) as the computed Iminol spectrum in Fig. 4 and Fig. S4. Peaks having diagnostic value for the two low-lying Im NNON conformations: 1170 (carboxyl OH bend); 1295 (CH bends); 1400 (CH bends); 1440 methyl CH bends); 1600-1650 (mixed NH_2 bend and carboxyl antisymmetric OCO stretch); 1650-1680 (iminol CN stretch).

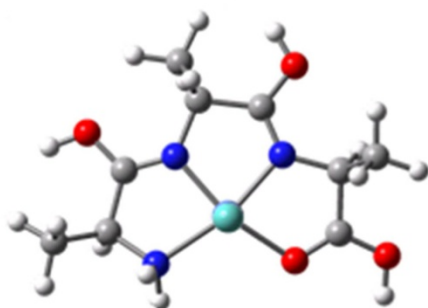
Fig. S3b. Ni²⁺Ala₃ Enlarged Structures



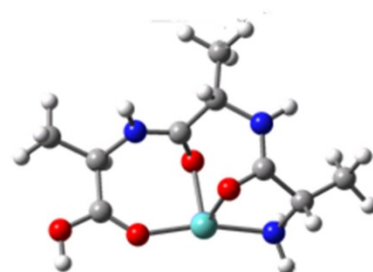
Im [NNON] Singlet



Im [NNON] Alt Singlet



Im [NNON] Triplet



CS [OOON] Triplet

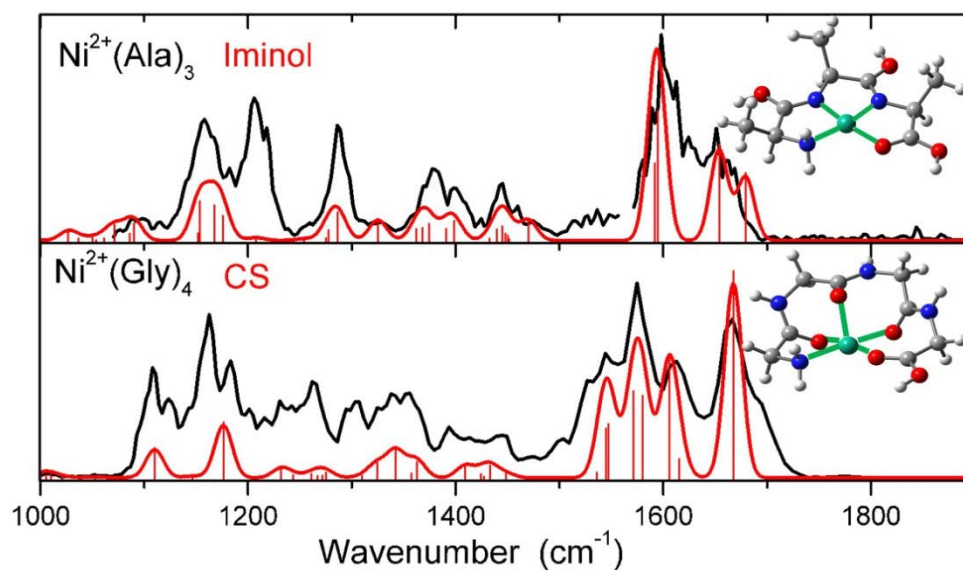


Fig. S4. Comparison of the spectra and structures of the two simple-chain peptide complexes, showing the switch from Im to CS upon lengthening the chain from 3 to 4 residues. Key to this interpretation (in addition to the very good agreement with the calculations) is the region 1500 to 1550 cm^{-1} , which has a strong (and predicted) Amide II feature with the tetrapeptide, but not with the tripeptide. The low and high frequency segments of the $\text{Ni}_2^+\text{Ala}_3$ spectrum are separate runs, with somewhat uncertain relative intensities. This computed spectrum is for the Im NNON structure. See Fig. 4 for the fit to a mixed-population simulation of the two low-lying isomeric structures that are shown in Fig. S3.

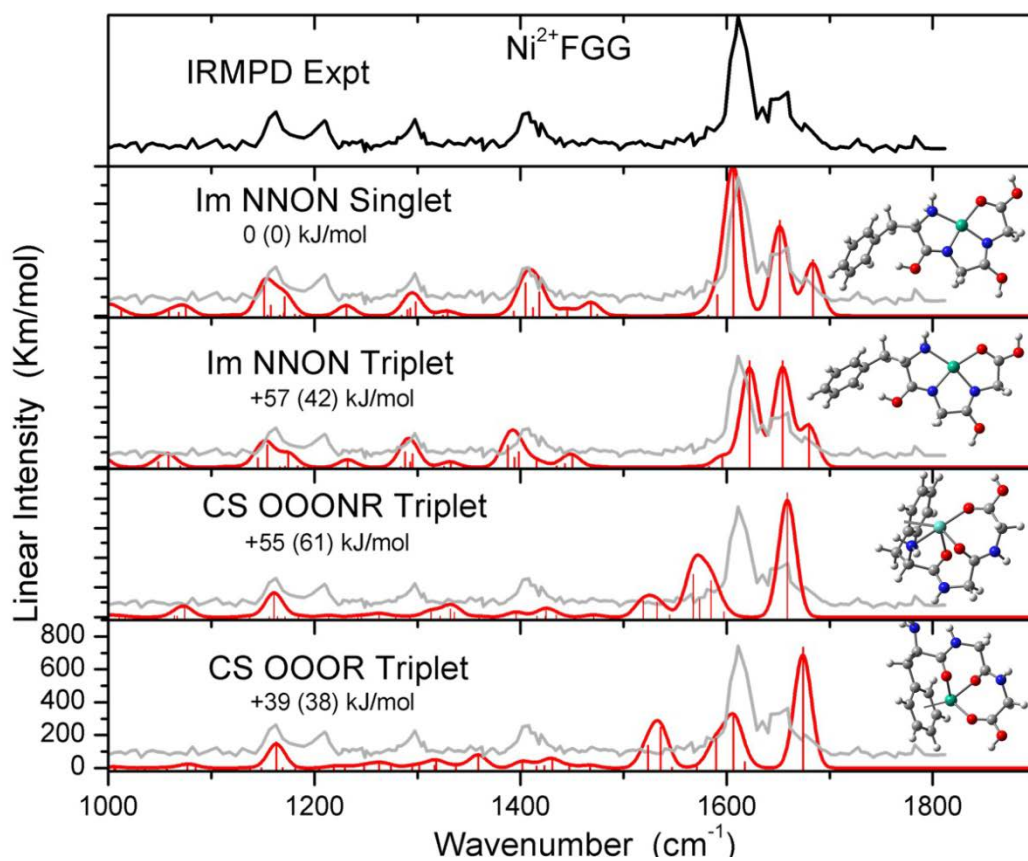
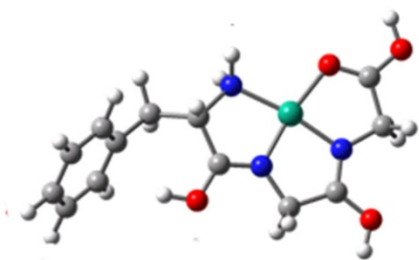
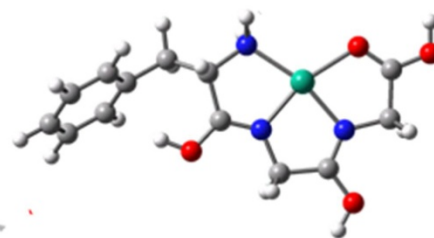


Fig. S5. Computed (red) spectra of conformations of the Ni^{2+}FGG complex, compared with the IRMPD spectrum (black). Peaks for the iminol structure having diagnostic value for the Im NNON ground state: 1300 (CH bends); 1410 (CH bends and iminol CO stretch).

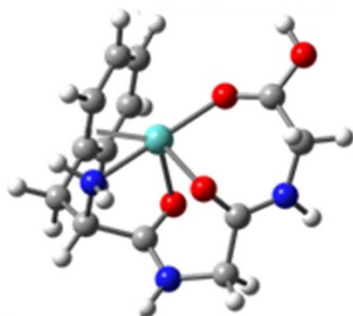
Fig. S5b. Ni²⁺FGG Enlarged Structures



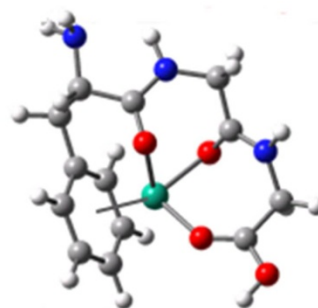
Im [NNON] Singlet



Im [NNON] Triplet



CS [OONR] Triplet



CS [OOOR] Triplet

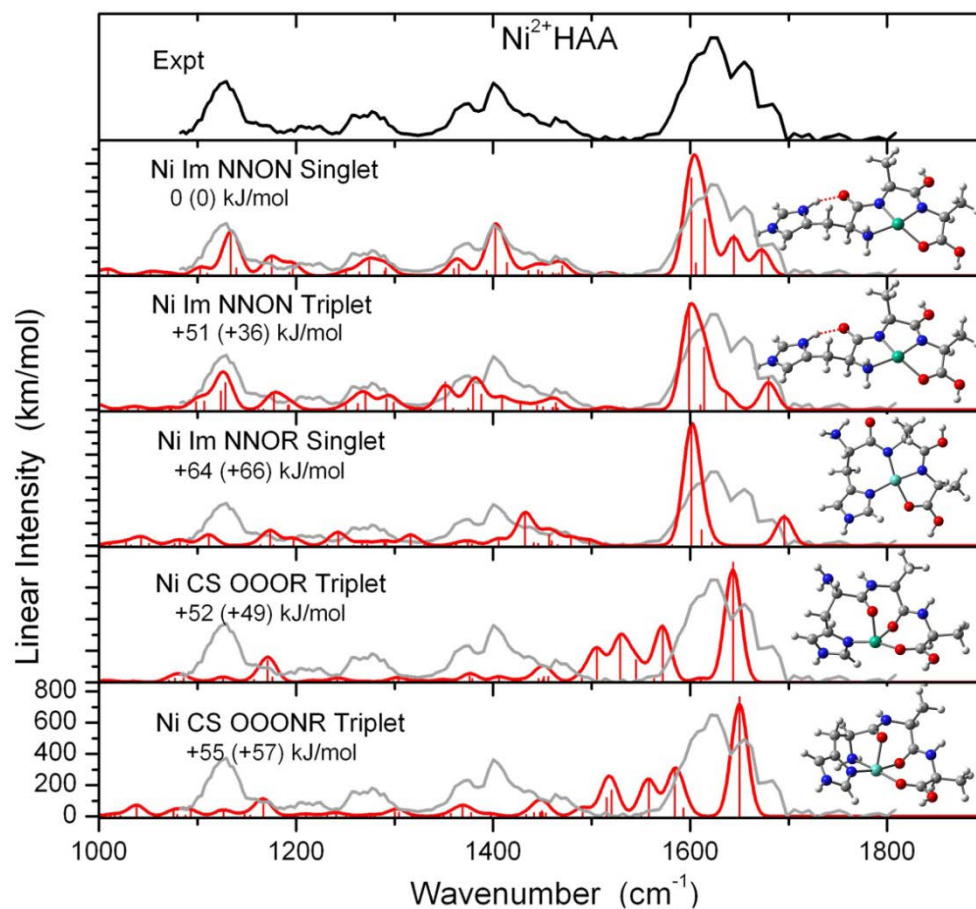
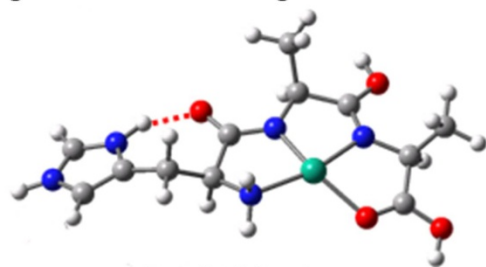
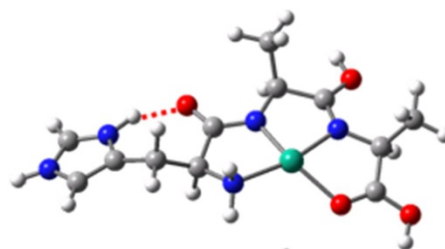


Fig. S6. Computed (red) spectra of conformations of the Ni^{2+}HAA complex, compared with the IRMPD spectrum (black). Peaks having diagnostic value for the Im NNON ground state: 1130 (imidazole); 1380 (methyl CH bends); 1400 (amidate CN stretch); 1600 (NH_2); 1610 (carboxyl antisymmetric OCO stretch).

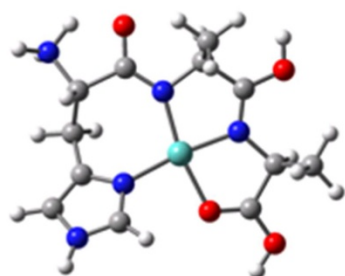
Fig. S6b Ni²⁺HAA Enlarged Structures



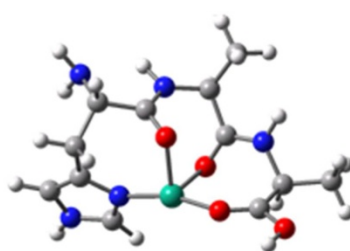
Im [NNON] Singlet



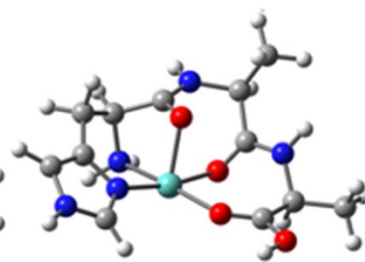
Im [NNON] Triplet



Im [NNOR] Singlet



CS [OOR] Triplet



CS [OOONR] Triplet

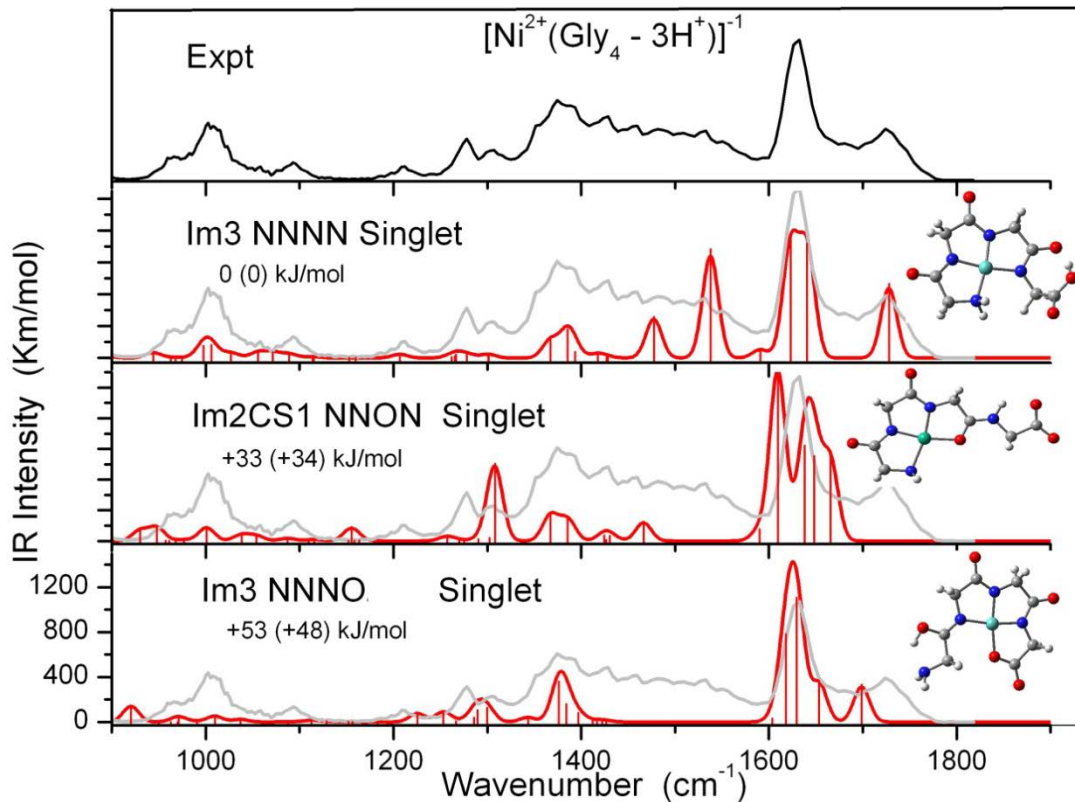
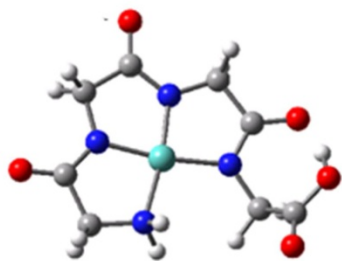
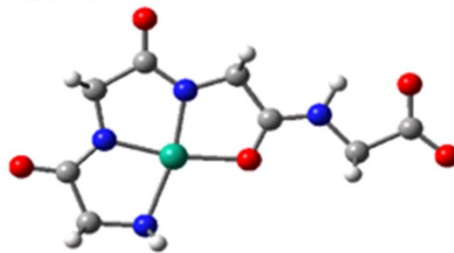


Fig. S7. Computed (red) spectra of conformations of the $[\text{Ni}^{2+}(\text{Gly}_4 - 3\text{H}^+)]^{-1}$ complex, compared with the IRMPD spectrum (black). Peaks observed for the Im3 NNNN ground state: 1390 (amidate CN stretch); 1490 (carboxyl OH bend, broadened); 1530 (H-bonded amidate antisymmetric OCN stretch, broadened); 1620-1630 (amidate OCN antisymmetric stretch); 1730 (carboxyl OCO antisymmetric stretch). The strong peak at 1305 diagnostic for the Im2CS1 conformation is the carboxylate antisymmetric OCC stretch.

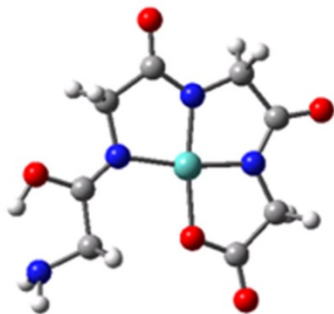
Fig. S7b. $\text{Ni}^{2+}(\text{Gly}_4 - 3\text{H}^+)$ Enlarged Structures



Im3 [NNNN] Singlet



Im2CS1 [NNON] Singlet



Im3 [NNNO] Singlet

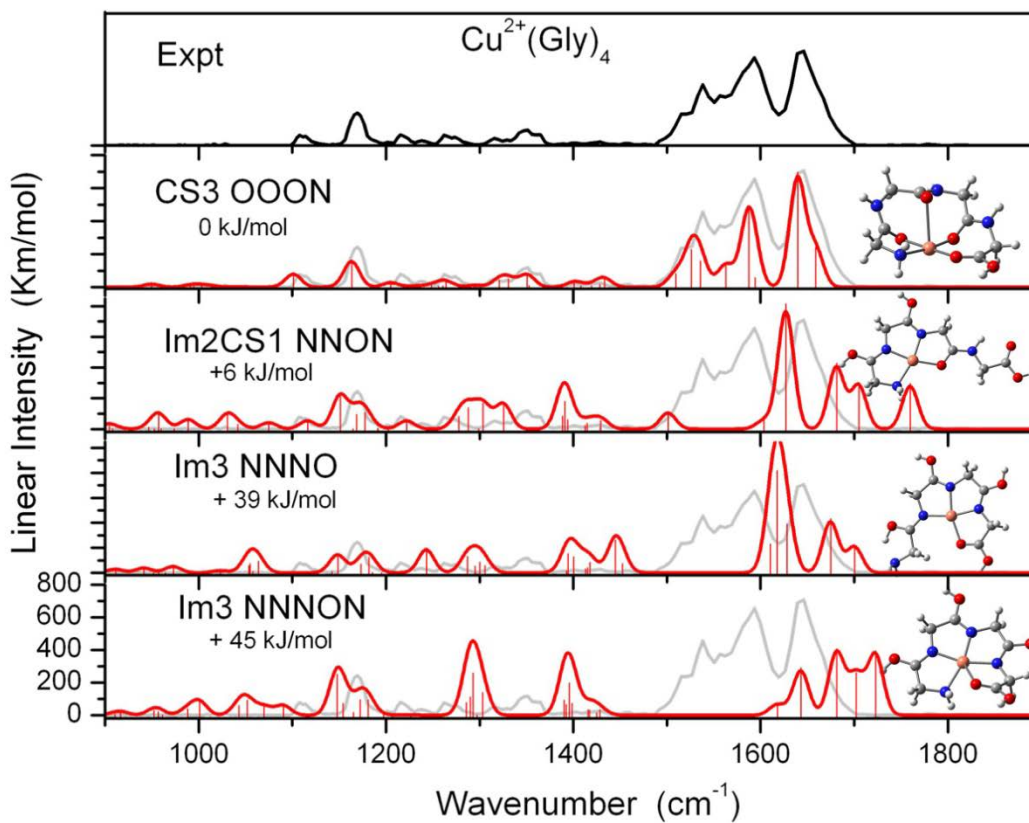


Fig. S8. Computed (red) spectra of conformations of the complex, compared with the IRMPD spectrum (black). The Cu^{2+} ion is pink. Vibrational assignments are similar to $\text{Ni}^{2+}\text{Gly}_4$ above.

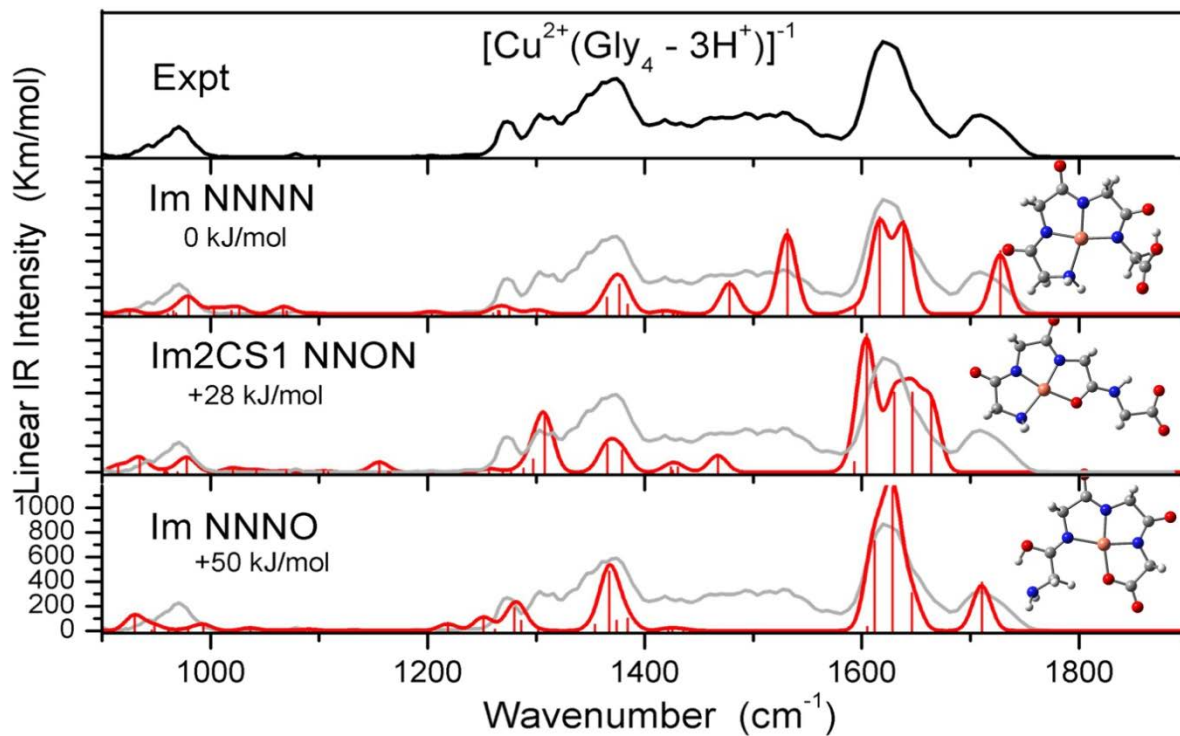


Fig. S9. Computed (red) spectra of conformations of the $[\text{Cu}^{2+}(\text{Gly}_4 - 3\text{H}^+)]^{-1}$ complex, compared with the IRMPD spectrum (black). Vibrational assignments are similar to $[\text{Ni}^{2+}(\text{Gly}_4 - 3\text{H}^+)]^{-1}$ above.

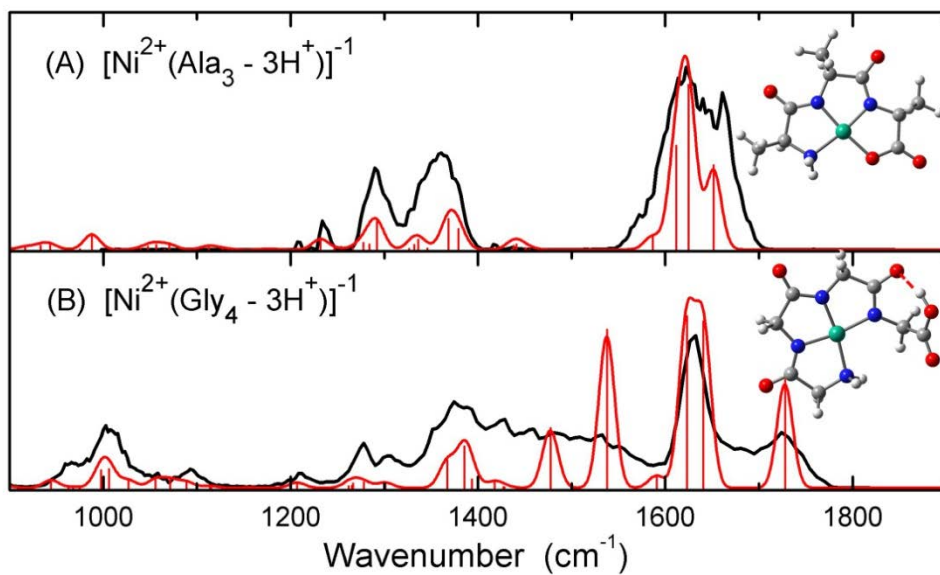


Fig. S10. Here we reproduce Fig. 6 from the main text, in order to note the vibrational assignments for the Iminol ground state of Im $[\text{Ni}^{2+}(\text{Ala}_3 - 3\text{H}^+)]^{-1}$, as follows: 1295 (CH stretches); 1330 (CH stretches); 1370-80 (many mixed displacements); 1610-20 (amidate CO stretch); 1650 (carboxylate antisymmetric OCO stretch).