Quantum chemical calculations of giant metal complexes: structural optimization of macrocyclic supramolecules by the GRRM method

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A 728 atoms-formed, as well as 624 atoms-formed macrocyclic metal complexes, were found to self-assemble through octahedral coordination of 14 Ni atoms and 12 Ni atoms with flexible tripeptide ligands, respectively. Derived from the monodentate, the bidentate, and the tridentate binding between the -NH_2 and -CO moieties, the octahedral coordination enables the giant metal complexes to have magical macrocyclic structured. [1] Herein, macrocyclic supramolecules are investigated by quantum chemical calculation, the structural optimization of supramolecule with a large number of atoms is achieved by the Global Reaction Route Mapping (GRRM) method [2] under one of the semiempirical molecular orbital methods, PM7. The aim of our research is to demonstrate the formation process of giant metal complexes by quantum chemical calculations and to achieve a theoretical understanding of supramolecule properties.

Previous studies have yielded nice results including a model calculation of the macrocyclic metal complex that the isomerization pathways had been effectively explored using the GRRM method and structural optimizations considering different combinations of charges and spins. Recently, the geometrical features and the octahedral coordination of supramolecules were improved by separate consideration of the Coulomb potential energy in corresponding directions through the Artificial Force Induced Reaction (AFIR) method.[3] Further research has confirmed that the dissociated structures from earlier results can be successfully repaired when appropriate energy induced in monodentate coordination. Hence, coordination bond with monodentate binding has a critical role in the formation of supramolecules. On this basis, our research makes it possible to optimize supramolecules with a large number of atoms, providing a theoretical premise to understand supramolecule properties.

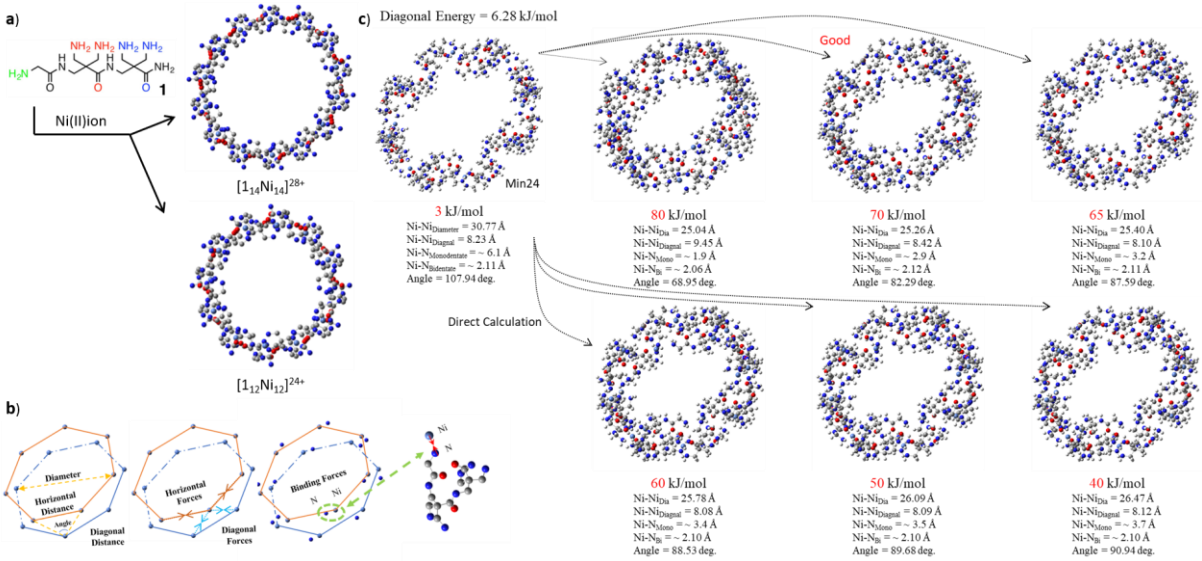

Fig 1. **a**) structure of tripeptide **1** possessing three coordination sites and structure of Ni (II) complexes; **b**) geometrical features used to judge the results and the directions of Coulomb forces induced by AFIR method; **c**) partial repair results from a dissociated structure to demonstrate the importance of coordination bond with monodentate binding. (More details will be shown in the poster.)

References

[1] R. Miyake, A. Ando, M. Ueno, T. Muraoka. *J. Am. Chem. Soc.,* 2019, **141**, 8675-8679. [2] S. Maeda, K. Ohno, K. Morokuma. Phys. Chem. Chem. Phys., 2013,15, 3683-3701. [3] S. Maeda, Y. Harabuchi, Y. Sumiya, M. Takagi, K. Suzuki, M. Hatanaka, Y. Osada, T. Taketsugu, K. Morokuma, K. Ohno, GRRM17, see http://iqce.jp/GRRM/index_e.shtml.