Controlling heteromeric arrangements is desirable when creating compounds that provide novel functionality based on electronic communications between metal centers. Biological molecules could provide suitable platforms for directing these arrangements because their structures can adopt appropriate metal binding sites for targeted arrangements. In addition, their structural flexibility also causes metal arrangements to be stimulus responsive using their structural varieties. Despite this potential, biological compounds are inefficient at providing through-bond interactions for metal centers with coordinatively unsaturated sites, which would signal for their further coordination and are required to produce an active site for functions such as molecular recognition, catalysis, and adsorption.

Due to unconjugated parts in their backbone, interactions between metal centers were formed by either direct connection or connection through bridging ligands that fill the coordinatively unsaturated sites. For same reason, metal arrangements by biological molecules have been reported to be linear in many cases. However, cyclic metal interactions are more efficient than linear arrays at producing uniformly conjugated electronic state from multiple metal centers and providing cooperativity between each metal center. Therefore, developing such cyclic metal arrangements using biological molecules could offer a new method for designing sophisticated functions based on electronic interactions at metal centers.

We envisioned that peptides could provide square-planar coordination sites that connect metal centers through their amide groups by designing metal binding sites on both the side chains and main chain (Fig. 1a). Herein, we report the efficient formation of cyclic heteromeric arrangements through peptide amide groups that link the electron orbitals of CuII and NiII metal centers, as well as their coordinating sites. This complex exhibited the desired heteromeric interactions, and we observed efficient antiferromagnetic spin coupling ($J/k_B = 25$ K) in the cyclic connections of the square-planar CuII centers ($S = 1/2$) and the octahedral NiII centers ($S = 1$). In order to clarify the element-specific electronic and structural properties, we employed extended x-ray absorption fine structure analysis (XAFS/EXAFS) in Ni and Cu K-edges.

We successfully produced cyclic CuII-NiII complex [(1-3H+)Cu4Ni4]$^{4+}$ (1-Cu4Ni4) and all Ni case (1-Ni8). For the XAFS measurements, the powder samples were diluted with BN powders and were formed to pellets for the measurements in the transmission mode at KEK-PF BL-12C. The sample was cooled using a conventional He cryostat. Transmitted X-rays were detected by the ionization chamber filled by Ar gas.

An air-dried crystalline sample was characterized by XAFS, which revealed a square-planar CuII center and the ratio of CuII/NiII ions to be ca. 1 (Fig. 1b). X-ray absorption near edge structure (XANES) displayed an intense, pre-edge peak at 8986 eV for 1-Cu4Ni4, which is characteristic of CuII ions with square planar (or pyramidal) symmetry. A similar peak was not observed for NiII ions with a D$_{4h}$ point group symmetry (8336 eV), but it was seen in the 1-Ni8 spectrum. The spectra of 1-Cu4Ni4 taken at 300 K and 10 K were almost identical, suggesting that the basic cyclic heteromeric arrangement present in the original sample remained intact in the dried sample and does not drastically change with temperature.

Fig. 1, (a) Schematic view of the formation of the cyclic CuII–NiII arrangement using a flexible peptide ligand. (b) XAFS of 1-Cu4Ni4 at room temperature in the Ni K-edge range and Cu K-edge, each with comparisons to those of metal foil and 1-Ni8.

References


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