

Synthesis and Characterization of Ruthenium Metal-Organic Frameworks with a Pyrazine Ligand

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1 Introduction

Since their introduction in the early 1990s, metal-organic frameworks (MOFs) have grown into a major area of research, with applications ranging from gas storage and molecular separation to catalysis. Despite this versatility, only a relatively narrow set of transition metal ions is typically employed, most often first-row transition metals as well as a few heavier elements such as zirconium and cadmium, which are known to consistently form stable and highly crystalline frameworks [1].

By contrast, noble metal ions such as ruthenium, osmium, iridium, and platinum remain underexplored in MOF construction. Their limited use is largely due to slow ligand exchange kinetics, which impede efficient error correction during assembly and often lead to poorly ordered or amorphous products. Nevertheless, incorporating such metals into well-defined frameworks would offer exciting opportunities, potentially introducing new structural motifs and electronic properties. Developing effective synthetic strategies to overcome these challenges therefore represents an important step toward expanding the scope of MOF chemistry into previously inaccessible areas.

In this study, Ru-based MOFs were synthesized using pyrazine linkers under both solvothermal and solvent-free conditions. XAFS were used to analyze the local structure of all MOFs and revealed 2D square-grid frameworks.[2]

2 Experiment

X-ray absorption spectra (XAS) were measured at NW-10A (Ru K-edge) station at the Photon Factory in KEK, Japan. The powders were ground together with boron nitride and then pressed into pellets (diameter = 7 mm, thickness = 0.5 mm). The edge position was calibrated using Ru pellets. The data was analyzed using Athena software.

3 Results and Discussion

X-ray absorption spectroscopy is a useful tool for determining the local coordination environment of metal centers because it is independent of the sample's crystallinity. In particular, extended X-ray absorption fine structure (EXAFS) analysis provides distances to the nearest atoms of the coordinating ligands, which can be used to reconstruct the coordination sphere of Ru. All Ru-MOF samples were analyzed using this technique. Furthermore, the *trans*-[Ru(pz)₄Cl₂] complex was measured, as it shares the same coordination environment as the MOF structure and thus serves as a model compound. The refined structures of the Ru-pz frameworks (Fig. 1a)

show a high degree of similarity to each other and to the model complexes, particularly in the low-*k* range. The Fourier transform (FT) of the data reveals the radial distances between the Ru center and surrounding atoms (Fig. 1b). Two major peaks, located around 2.0 and 2.4 Å, are attributed to contributions from Ru-N and Ru-Cl, respectively. Additionally, a smaller peak, located around 6.60 Å, was detected in the MOF data but is absent in the model complexes. Therefore, this peak is attributed to the single scattering (SS) contribution from neighboring Ru atoms bridged by pyrazine within the 2D layer. This result proves the local coordination of Ru and the formation of the framework.

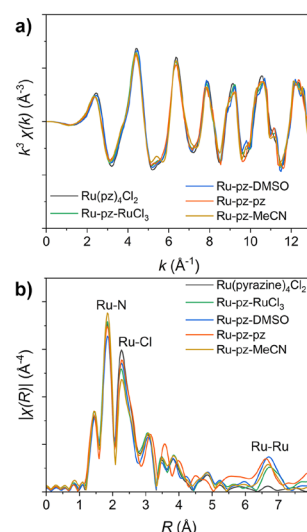


Fig. 1: a) k^3 -weighted EXAFS spectra and b) Fourier transformed k^3 -weighted EXAFS spectra of *trans*-[Ru(pz)₄Cl₂] complex and Ru-pz MOFs.

Acknowledgement

We are grateful to the staff of the Photon Factory for their assistance with data collection.

References

- [1] T. Henry *Chem. Rev.* **50**, 69-126 (1952).
- [2] W. Zhang et al. *Chem. Mater.* **37**, 415-428 (2025).

Research Achievements

1. W. Zhang et al. *Chem. Mater.* **37**, 415-428 (2025).

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