

HETEROMETALLIC PENTANUCLEAR COMPLEXES CONSTRUCTED FROM A RUTHENIUM(II) PRECURSOR COMPLEX

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1,2,3-Triazoles are known for their unique coordination to transition metals, e.g. heteronuclear complexes [1] and metal-organic frameworks (MOFs). Herein, we report a ruthenium precursor complex, in which six 5,6-dimethylbenzo[1,2,3]triazole (Me_2btaH) ligands are coordinated to a single Ru(II) metal ion. In contrast to many other monodentately coordinated triazolato complexes the Me_2btaH ligands are bound exclusively via their central (N2) nitrogen atoms, thus providing a topologically ideal template for adding further metal ions to the precursor. The resulting pentanuclear complexes represent novel members of the family of so-called Kuratowski complexes, which are also found as structural building units of MOFs (e.g. MFU-4l(arge) [2], and most recently CFA-19 [3]). Our research shows that the availability of a stable 4d-TM precursor opens a synthetically facile route towards a vast variety of heterometallic complexes. Thus, $\text{Ru}^{\text{II}}(\text{Me}_2\text{btaH})_4(\text{Me}_2\text{bta})_2$ was reacted with different 3d TM ions (Zn^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+}) leading to the corresponding Kuratowski complexes. In addition, ligand exchange reactions of the halogenide ligand, employing scorpionate (Tp^*) ligands, have been carried out successfully. The magnetic properties of the $[\text{RuCu}_4]$ derivatives were studied in detail by SQUID and ESR measurements, revealing a predominantly antiferromagnetic exchange of the outer $[\text{Cu}_4]$ tetrahedron. Furthermore, the coordination change of the peripheral metal centers increases the solubility of the complexes immensely and enables further characterization. The electrochemical characteristics were examined for those complexes by cyclic voltammetry showing multiple redox steps. Hence, current studies target multiple electron transfer in the heterometallic complexes by the addition of electron-deficient triazole ligands.

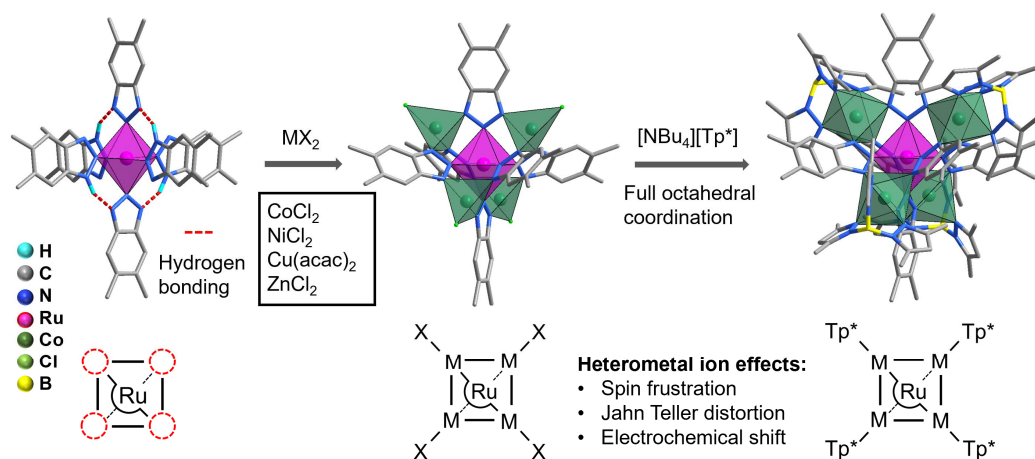


Figure 1: $\text{Ru}^{\text{II}}(\text{Me}_2\text{btaH})_4(\text{Me}_2\text{bta})_2$ reacting to the corresponding pentanuclear Kuratowski complex and subsequent ligand exchange of the terminal ligand.

[1] Biswas, S.; Volkmer, D. *et al. Inorg. Chem.* **2010**, 49 (16), 7424–7434.

[2] Denysenko, D. Volkmer, D. *et al. Angew. Chem. Int. Ed.* **2014**, 53, 5832–5836.

[3] Röß-Ohlenroth, R; Volkmer D. *et al. Inorg. Chem.* **2022**, 61 (41), 16380–16389.