

Temperature-dependent Wiggling of a Cu(II) Ion in Hydrogen-bonded Networks of a Zr–Mo Cluster

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Coordination compounds with a degenerate energy state are known to distort spontaneously to remove its degeneracy owing to Jahn–Teller effect. A typical example of Jahn–Teller distortion in first-row transition metal ion is a hexacoordinated Cu(II) complex, which often exhibits a tetragonal elongation.¹ On the other hand, a trigonal distortion is difficult for Cu(II) complexes because the degeneracy will not be removed in this symmetry. We recently reported a Ti–Mo cluster, $[\text{Ti}\{\text{MoO}_3(\text{tacn})\}_6]^{4+}$ (tacn = 1,4,7-triazacyclononane).² This cluster spontaneously takes trigonal symmetry by intramolecular hydrogen-bonds and can propagate the symmetry over the crystal by intermolecular hydrogen-bonds. In this study, we focused on putting the simplest hexacoordinated Cu(II) complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in trigonal coordination environment by incorporating in hydrogen-bonded networks of $[\text{Zr}\{\text{MoO}_3(\text{tacn})\}_6]^{4+}$ (**ZrMO6**⁴⁺), which is analogous to the Ti–Mo cluster, and ClO_4^- .

A double salt of $[\text{Cu}(\text{H}_2\text{O})_6]\text{ZrMO6}(\text{ClO}_4)_6$ was prepared by a reaction of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $[\text{MoO}_3(\text{tacn})]$ and $\text{Cu}(\text{ClO}_4)_2$. At 100 K, single-crystal X-ray analysis revealed that $[\text{Cu}(\text{H}_2\text{O})_6]\text{ZrMO6}(\text{ClO}_4)_6$ was crystallized in a trigonal system, and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ was successfully located at the crystallographic trigonal axis. At room temperature, on the other hand, the Cu(II) ions exhibited a positional disorder to form an aggregated compound with the Zr–Mo cluster (Figure 1). This positional disorder was observed even when the same crystal was employed for the measurements at both temperatures. This indicates that a Cu(II) ion is moving back and forth between two positions even in the crystal at high temperature. This temperature-dependent wiggling of the Cu(II) ion is further supported by variable temperature EPR measurements. This unique solid-state dynamic disorder for Cu(II) ion is presumably due to the frustrated secondary coordination sphere which enforces $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cation in trigonal symmetry.

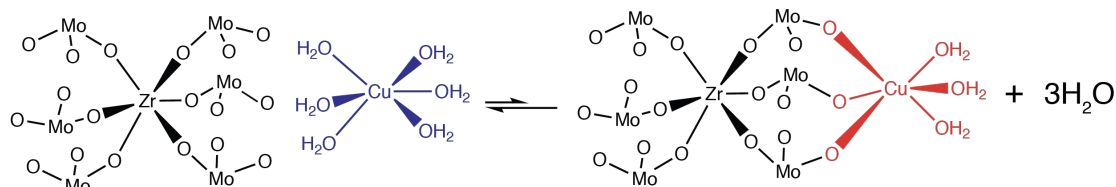


Figure 1. Schematic view of temperature-dependent wiggling of Cu(II) ion in the crystal.

1) M. A. Halcrow, *Chem. Soc. Rev.* **2013**, 42, 1748. 2) Sugiarto et al., *Inorg. Chim. Acta* **2020**, 509, 119691.