

Fluctuating coordination geometry of copper(II) ion in trigonal hydrogen-bonded networks of Zr–Mo cluster

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Octahedral mononuclear copper(II) complexes are known to undergo tetragonal distortion because of the Jahn–Teller effect to remove the ground state degeneracy.¹ By contrast, trigonally distorted examples are rare as the trigonal symmetry affords no benefit toward distortion. On the other hand, we recently reported a D_3 -symmetric Ti–Mo cluster $[\text{Ti}^{\text{IV}}\{\text{Mo}^{\text{VI}}(\text{tacn})\text{O}_3\}_6]^{4+}$ ($\text{tacn} = 1,4,7\text{-triazacyclononane}$).² Since this cluster possesses N–H groups as hydrogen-bonding donors, the trigonal symmetry of the cluster can be propagated over the crystal by constructing hydrogen-bonded networks with counter anions. Such hydrogen-bonded networks can act as template to induce trigonal symmetry on the complex incorporated in the networks. To achieve trigonal symmetry in mononuclear Cu^{II} complex, we focused on incorporating the simplest hexacoordinated Cu^{II} complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ into hydrogen-bonded networks of an analogous Zr–Mo cluster $[\text{Zr}^{\text{IV}}\{\text{Mo}^{\text{VI}}(\text{tacn})\text{O}_3\}_6]^{4+}$ with perchlorate or perrhenate anion.

Double salts of $[\text{Cu}(\text{H}_2\text{O})_6][\text{Zr}\{\text{Mo}(\text{tacn})\text{O}_3\}_6](\text{ClO}_4)_6$ and $[\text{Cu}(\text{H}_2\text{O})_6][\text{Zr}\{\text{Mo}(\text{tacn})\text{O}_3\}_6](\text{ReO}_4)_6$ were crystallized from aqueous solutions of ZrOCl_2 , $[\text{Mo}(\text{tacn})\text{O}_3]$ and $\text{Cu}(\text{ClO}_4)_2$ or $\text{Cu}(\text{ReO}_4)_2$. Both salts were crystallized in the trigonal system. Although the crystal structures at 100 K are nearly isostructural, the positions of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cation were slightly different. In the perchlorate salt, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ was successfully located at the crystallographic trigonal axis with a nearly ideal octahedral geometry. On the other hand, the Cu^{II} ion was located beside the trigonal axis and the coordination geometry was not trigonal. The EPR spectra on the perchlorate at various temperatures exhibited a reversible change indicating variation in the coordination geometry at above 100 K, although the spectra were unchanged in the perrhenate salt. The crystallographic analysis of the perchlorate salt at room temperature revealed that $[\text{Zr}\{\text{Mo}(\text{tacn})\text{O}_3\}_6]^{4+}$ acted as a tridentate ligand to coordinate to the Cu fragment with dissociation of some H_2O ligands. Thus, the frustrated trigonal coordination geometry of the Cu center induced this unique solid-state reaction of Cu^{II} ion.

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