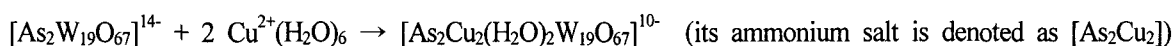


Identification of Pseudo-C₃ Axis in (NH₄)₁₀[As₂W₁₉O₆₇Cu₂(H₂O)₂] · nH₂O Single Crystal by Using EPR Spectroscopy

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The anion [As₂W₁₉O₆₇]¹⁴⁻, consisting of two AsW₉O₃₃ subunits and linked by one WO octahedron, provides two coordination sites for Cu²⁺ ion ;



The two AsW₉O₃₃ units are linked by Cu₂W belt, mixed-bridge, lying in a mirror plane. This anion has a twofold symmetry axis perpendicular to the mirror plane. Its single crystal EPR spectra were measured at room temperature with the magnetic field in three mutually perpendicular planes. The spectrum exhibited quite different from that expected for simple single crystal of binuclear complexes due to the random occupation among Cu₂W belt sites. All the single crystal spectrum of [As₂Cu₂] is actually a composite of single crystal spectra in three different orientations. The spectral patterns clearly show the evidence of an equal random occupation of two copper(II) ions around triangular Cu₂W belt sites. This random occupation of two copper(II) ions in triangular Cu₂W belt induces the loss of twofold symmetry axis, producing pseudo-threefold axis. Single crystal EPR spectra could be properly interpreted by considering this in mind. Detailed analysis of angular dependent spectra around pseudo-C₃ axis clearly demonstrates the statistically equal and random occupation of Cu(II) pair among triangular Cu₂W sites with clear periodicity at every 60° rotation. Another notable feature found in the single spectra is the low-field ΔM=1 transition which is well resolved into a seven line hyperfine pattern with the apparent intensities of 1:2:3:4:3:2:1. This pattern arises from coupling of the nuclei of the two copper(II) ions (I=3/2) in the molecule. This can only be found for the exchange coupled Cu(II), I=3/2, pair system with appreciable coupling, |J| ≥ 3hν (by our experience), allowing transitions within triplet state only. The EPR spectra clearly show the nature of exchange interaction between pair of Cu(II) ions