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# Identification of Pseudo-$C_3$ Axis in $(NH_4)_{10}[As_2W_{19}O_{67}Cu_2(H_2O)_2]$ · $nH_2O$ Single Crystal by Using EPR Spectroscopy

**Young-Hwan Cho**

*Korea Atomic Energy Research Institute, P.O. Box 105 Yusong, Taejon 305-600, Korea*

*e-mail: yhcho@kaeri.re.kr*

The anion $[As_2W_{19}O_{67}]^{14-}$, consisting of two $AsW_9O_{33}$ subunits and linked by one WO octahedron, provides two coordination sites for $Cu^{2+}$ ion ;

$[As_2W_{19}O_{67}]^{14-} + 2\ Cu^{2+}(H_2O)_6 \rightarrow [As_2Cu_2(H_2O)_2W_{19}O_{67}]^{10-}$ (its ammonium salt is denoted as $[As_2Cu_2]$)

The two $AsW_9O_{33}$ 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 $[As_2Cu_2]$ 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 $Cu_2W$ belt sites. This random occupation of two copper(II) ions in triangular $Cu_2W$ 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-$C_3$ 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 $\Delta M$=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, $|J| \geq 3h\nu$(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