



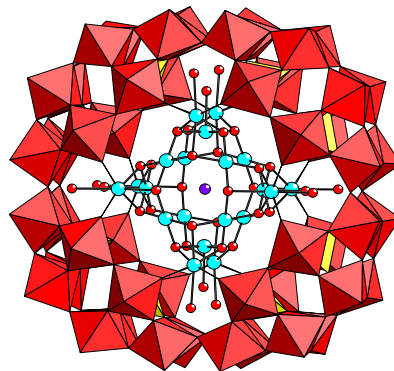
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Magnetic Clusters in Polyoxometalates

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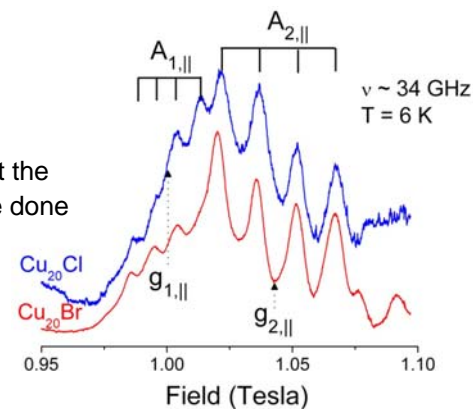
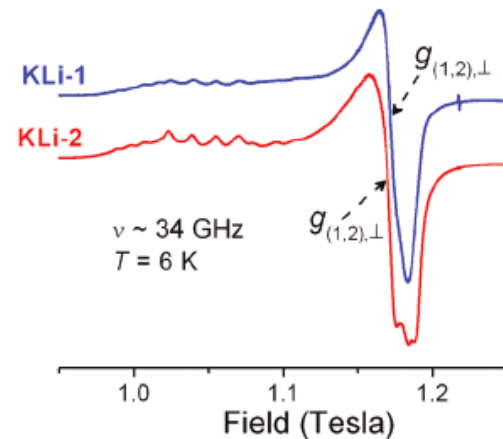
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The wheel shaped tungstophosphates, $[Cu_{20}X(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$ ($X = Cl, Br, I$), containing twenty Cu^{2+} ions cluster were synthesized and characterized^{1,2}, for the first time, to evaluate the role of the different halide guests by a multitude of techniques. $Cu_{20}-Cl$ has recently been evaluated as a potential candidate for vesicle formation, surface science and oxidation catalysis.^{3,4}

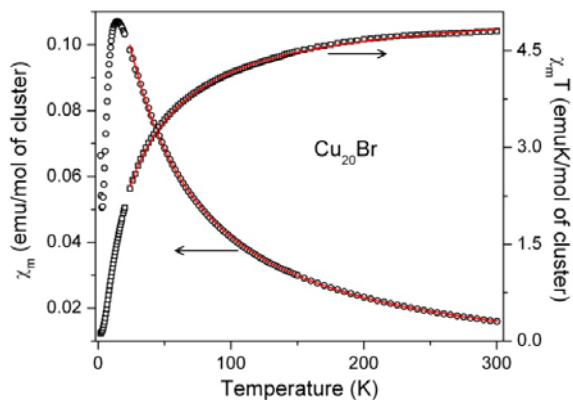


Molecular structure of Cu_{20} tungstophosphate. Color code is: WO_6 , PO_4 , Cu , O and X .

Magnetic susceptibility and magnetization data over 1.8 – 300 K show that the Cu^{2+} ions in $Cu_{20}-Cl$ and $Cu_{20}-Br$ are coupled antiferromagnetically, leading to a diamagnetic ground state. The effective exchange coupling constant J_{eff} was estimated as ~ 3 K for both compounds, suggesting that the halide ion does not effect the spin-spin interactions in these systems. EPR measurements were done over 5 - 295 K at 9.5, 34.5 and 220 GHz frequencies. The observed (weak) signals were characteristic of randomly distributed Cu^{2+} ions only, with g values and hyperfine constants typical⁵ of the unpaired electron in a $3d_{x^2-y^2}$ orbital of Cu^{2+} . No signals attributable to the copper-hydroxo cluster were detected, supporting the conclusions from the magnetization measurements.



EPR spectra of $Cu_{20}-Cl$ and $Cu_{20}-Br$ at 34 GHz and 6 K. Bottom panel shows the hyperfine structure.



Magnetic susceptibility of $Cu_{20}-Br$ as a function of temperature. Solid line is a fit to spin Hamiltonian shown in Eq. 1.

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2. Mal, S. S.; Kortz, U. *Angew. Chem., Int. Ed.* **2005**, *44*, 3777.
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