Magnetic properties of the wheel-shaped Tungstophosphate Cu_{20}

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Introduction

Recently, a new large wheel-shaped tangstophosphate $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$ ($Cu_{20}P_8W_{48}$), in short Cu_{20} was synthesized.[a b] The solid solution like structure of Cu_{20} allows studies in host-guest chemistry, ion exchange, gas storage, catalysis, and medicine.
In this work we study the magnetic properties of the wheel-shaped Cu_{20}. The model we adopt for describing the magnetic molecules of Cu_{20}-Tungstophosphate is the Heisenberg spin Hamiltonian together with a Zeeman term of an applied magnetic field along the z-axis given by

$$\underset{\sim}{H} = \sum_{i \neq j}^{N} J_{ij} \vec{s}_i \cdot \vec{s}_j + g\mu_B B \sum_{u}^{N} \underset{\sim}{s}_z(u),$$

where the individual spin operators are those for intrinsic spin $S = 1/2$ and they are given in units of $\hbar$, and g is the spectroscopic splitting factor.

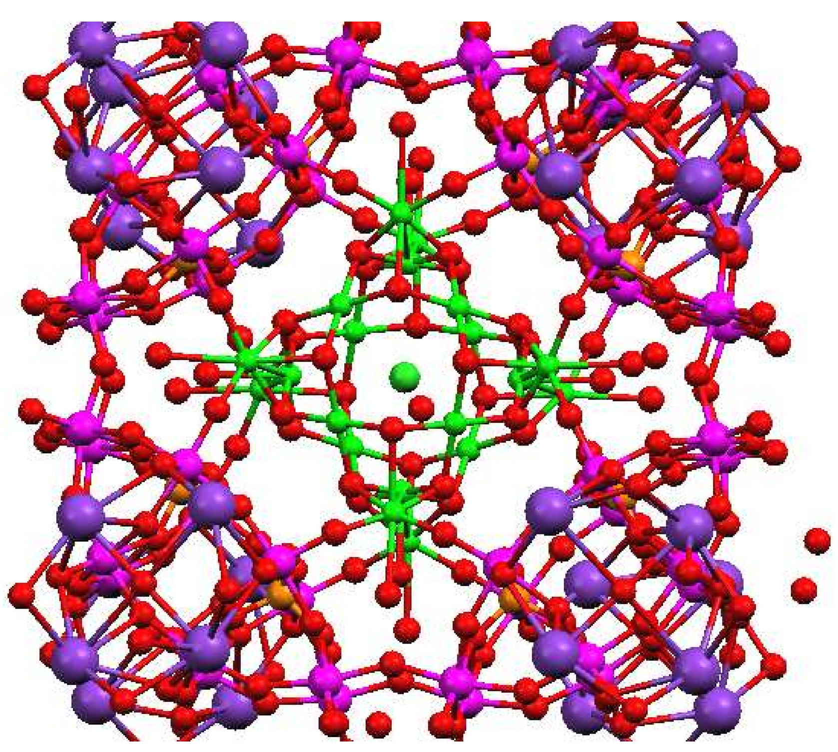

Figure 1 Structure of $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$. The 20 Cu ions of spin $1/2$ are represented by large green spheres.

Due to the very large size of the molecule and consequently also of the related Hilbert space, we approximate the spin system by a smaller one. Then, using numerically exact diagonalization of the Heisenberg model, we calculate the energy spectrum for various possible couplings, and compare our findings to the available low-field susceptibility data as well as to high-field magnetization measurements.

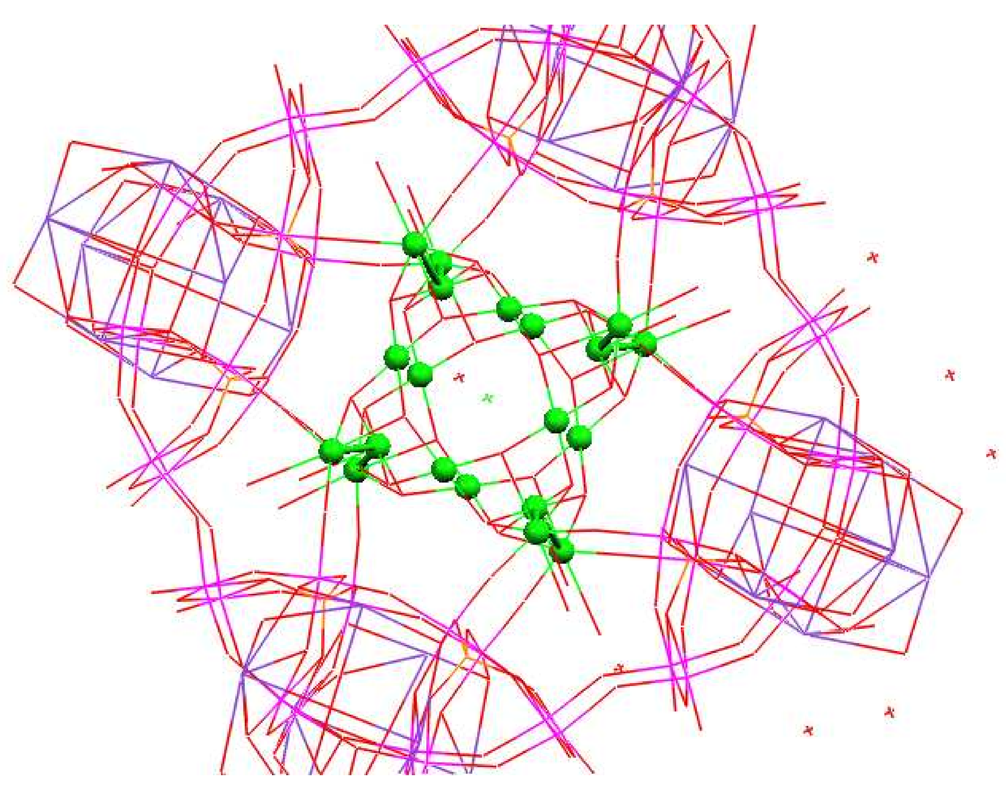

Figure 2 Structure of $\{Cu_{20}\}$. The 20 Cu ions of spin $1/2$ are represented by large green spheres.

Figure 2 shows the structure of Cu_{20}, where the 20 Cu ions of spin 1/2 are represented by large green spheres, which are connected by oxygen bridges.

[a] Jabbour, D.; Keita, B.; Nadjo, L.; Kortz, U.; Mal. S.S.Electrochem. Comm. 2005, 7, 841-847.
[b] Sib Sankar Mal and Ulrich Kortz, Angrew. Chem. Int. Ed. **44**, 2-5 (2005).

Approximation with single spin 1/2 impurity

The low-temperature low-field susceptibility is Curie-like, which suggests a non-negligible impurity contribution. Eventually, we have approximated the system with a single spin $1/2$ impurity plus one singlet-triplet gap of 15K. Figure 3 shows an excellent agreement between theory and experiment for magnetic field dependence of the magnetization.

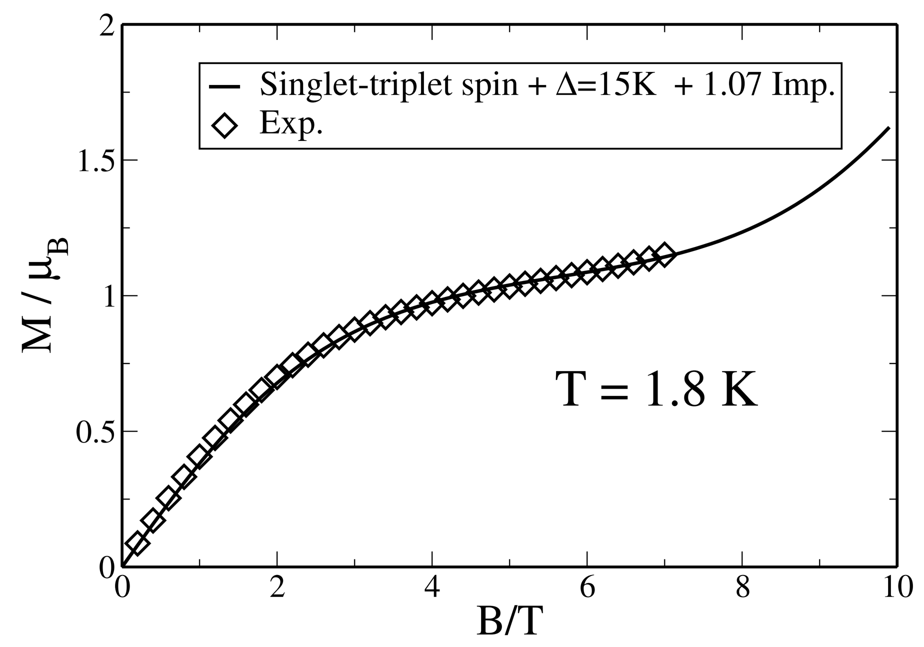

Figure 3 Magnetization vs magnetic field.

Approximations with 4 spins 3/2 and 8 spins Cu 1/2

The distance between the 3 Cu ions in the triads is only 2.81 Å. We assume that they interact strongly and can be treated as one effective spin.

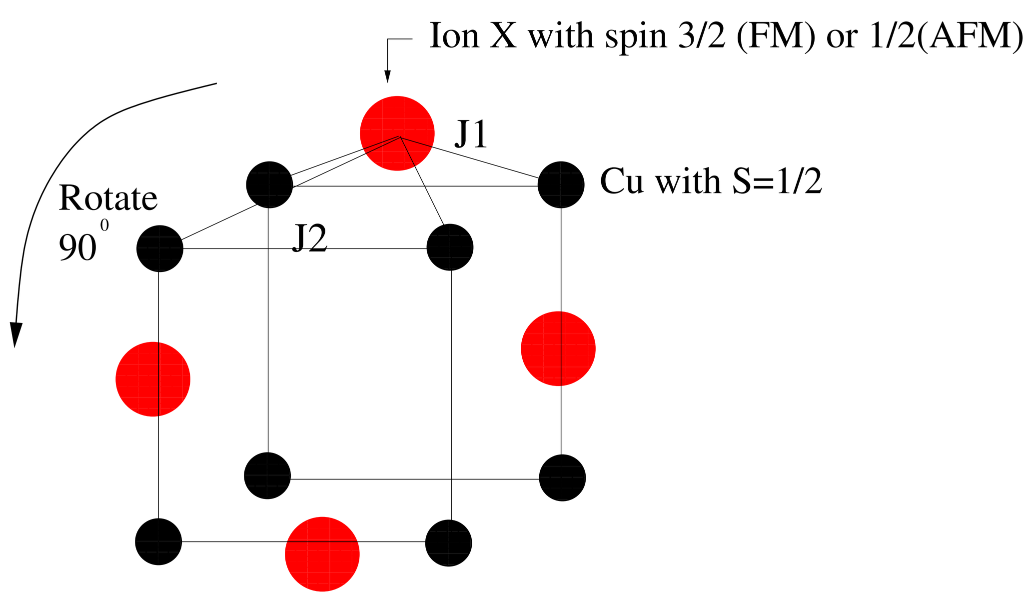

Figure 4 Schematic representation of symmetry operation (rotation of the X ion by π/4) and the exchange coupling used in our calculation for molecular magnetic $\{Cu_{20}\}$.

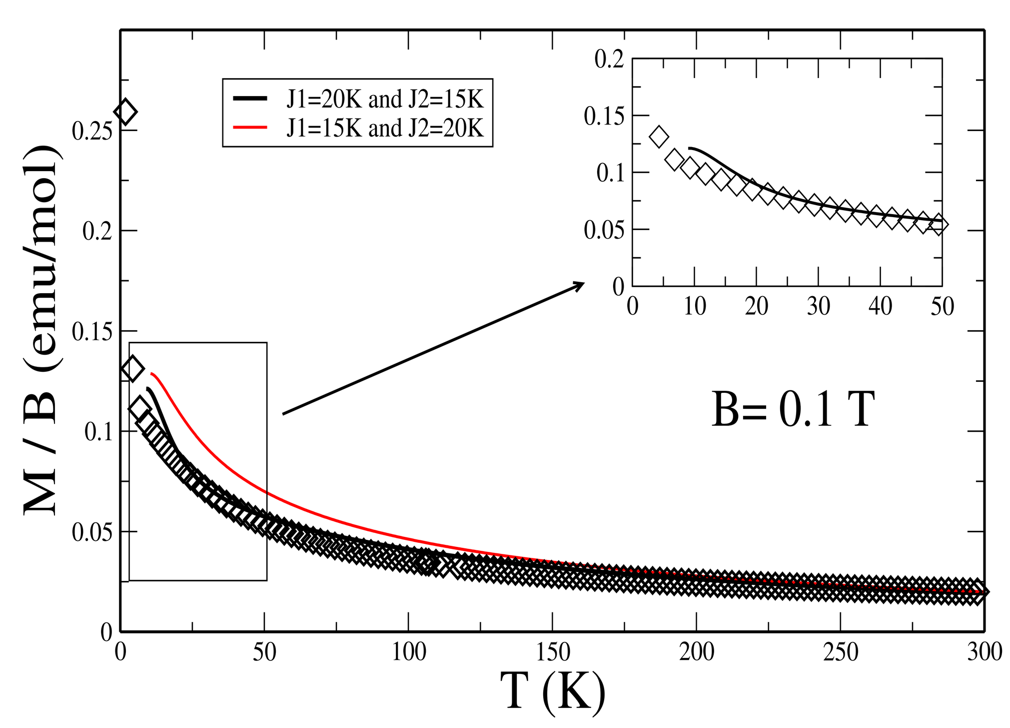

Figure 5 Variation of $\mathcal{M}/B$ as a function of temperature T for $\{Ni_{12}\}$: The experimental data are given by black squares. The theoretical fit are depicted by a solid curve for AFM interactions: $J_1 = 20$ K and $J_2 = 15$ K black solid curve, for $J_1 = 15$ K and $J_2 = 20$ K red solid curve; $B = 0.1$ T and $g = 2$.

We assume that the three spins couple ferromagneti-cally, which we can approximate with one spin S 3/2. From this, we can easily model the system wi 4 spins 3/2 and eight central "cage" Cu ions, as show in Figure 4. The operator $\underset{\sim}{H}$ corresponding to this a proximation is defined on a Hilbert space of dimensi 4^4 x 2^8 = 65536. Using the numerical exact diagonaliz tion method, we have been able to estimate the nume ical values of the two exchange constants which pr vide a reasonable temperature-dependent susceptibili in good agreement with the experimental results, Fi ure 5.

Symmetry of Cu_{20} with 20 spins 1/2

The operator $\underset{\sim}{H}$ is defined on the Hilbert space of d mension 2^{20} =1048576.

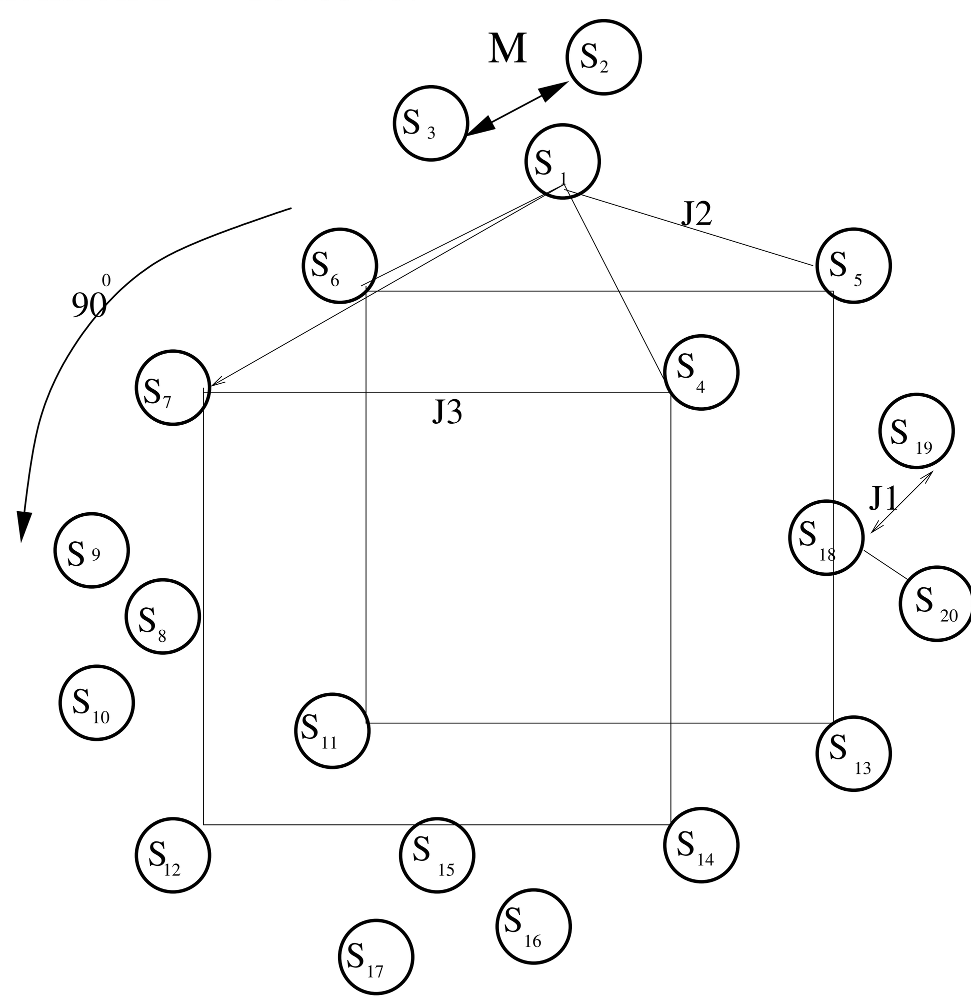

Figure 6 Schematic representation of symmetry oper tion and the exchange coupling used in our calculati for e molecular magnetic $\{Cu_{20}\}$ with 20 spins 1/ Op.1: rotation of the triads by π/4 and Op.2: mirr symmetry inside (Work ongoing).

According to the symmetries existing in the molecul we can use only two symmetry operations represent in Figure 6: mirror symmetry in the triads and rot tional symmetry of the triads by π /4. Fortunately, w may finally decompose the complete Hilbert space in the mutually orthogonal subspaces, where all energ eigenvalues and eigenvectors can be computed, usi complex*16 numbers with 9 GB RAM needed.

Summary

In this work we have investigated the magnetic pro erties of $Cu_{20}P_8W_{48}$. Due to the very large size the molecule, we have approximated the spin syste by a smaller one. First with single spin $1/2$ impuri plus one singlet-triplet system with a gap of 15 K. T second, we have approximated with 4 spins $3/2+8$ sp $1/2$ where we found that the best fit is FM interactio in triads which are AFM to the eight central "cag Cu and AFM inside of the cage. This work will continued.