

MAGNETIC PROPERTIES OF ASYMMETRIC Co(II) DIMER AT LOW TEMPERATURES

Nenad Dj. LAZAROV,^{a*} Vojislav SPASOJEVIĆ,^a Vladimir M. MATIĆ,^a Vladan KUSIGERSKI^a
and Maurice GUILLOT^b

^aLaboratory for Theoretical and Condensed Matter Physics, The Vinca Institute, P.O. Box 522, 11001 Belgrade, Serbia

^bService National des Champs Intenses, CNRS, B.P. 166X, 38042 Grenoble Cedex, France

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Magnetic properties of the dinuclear cobalt complex $[\text{Co}_2(\text{ox})\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ have been studied from the magnetization data obtained in the high magnetic field-low temperature experiments ($B \leq 20$ T, $2.2 \text{ K} \leq T \leq 29$ K). An excellent agreement between experimental and calculated data for all experimental temperatures was achieved within the framework of the isolated Ising Co(II) pairs in the ground state, where each cobalt ion from the pair was situated in a differently distorted octahedral environment (“asymmetric dimer”). The obtained values for g -factors (g_a and g_b), and for the intracuster exchange integral $J/k_B = (-16.0 \pm 0.5)$ K confirm both the previous results on the crystal structure of the complex under consideration and the assumption on the strong antiferromagnetic coupling between cobalt ions realized by the superexchange interaction over the asymmetric oxalato bridge.

INTRODUCTION

Magnetic properties of transition metal complexes with polynuclear metal cores embedded in the diamagnetic ligand matrix (often referred to as “cluster complexes”) have attracted a lot attention during the last few decades from both experimental and theoretical viewpoints.¹⁻³ The main reason is their convenience for the studies of magnetic clusters properties due to a relative magnetic isolation between them so that cluster eigenvalue problem in most cases can be solved either exactly or approximately.

Among other experimental techniques, measurement of magnetization in high magnetic fields at low temperatures (sometimes called “magnetization-steps spectroscopy”) proved to be a valuable tool for investigation of magnetic clusters.^{4,5} The characteristic “step-like” behavior of the $M(H)$ curves originates from the change of the cluster ground state due to an energy level crossing under the applied magnetic field. From the analysis of the position and shape of magnetization steps much information on intrinsic system properties can be gained, such as crystal

field parameters, Landé g -value, population of the clusters, and exchange constant J .

In this work we present results of the high magnetic fields study on the magnetic properties of the dinuclear cobalt complex $[\text{Co}_2(\text{ox})\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, where ox^{2-} denotes oxalato anion, and $\text{tpmc} = \text{N}, \text{N}', \text{N}'', \text{N}'''$ -(tetrakis 2-pyridilmethyl)-1,4,8,11-tetraaza-cyclotetradecan. The crystal structure analysis revealed the unusual asymmetric oxalato bridging between the Co(II) cations,⁶ and our scope was to investigate the ground state magnetic properties of such asymmetric cobalt dimer. It should be emphasized that each cobalt ion from the dimer is situated in a differently distorted octahedral environment due to the asymmetry of the oxalato bridge.

EXPERIMENTAL PART

The synthesis of the dinuclear cobalt(II) complex $[\text{Co}_2(\text{ox})\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ was done from an aqueous suspension of tpmc , $\text{K}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Details on the synthesis and crystal structure investigation are published elsewhere.⁶ Here we shall point only to the details of the crystal structure that presents basis for the analysis of the magnetic properties.

* Corresponding author: p1lazarov@panet.co.yu or
lazarov@vin.bg.ac.yu

The unit cell consists of four dinuclear $[\text{Co}_2(\text{ox})\text{tpmc}] (\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ molecules, and each of them contains one of the two slightly different monomeric unit, A and B. In the first approximation we shall not distinguish between them, *i.e.* they will be considered crystallographically identical. Each Co(II) ion from the dimer is placed in a distorted octahedra made of four N atoms and two O atoms, Fig. 1. Oxalato group bridges two cobalt ions (denoted by Co1 and Co2), where O2 oxygen atom is common for both of them. The essential fact is the asymmetry of the oxalato bridge, meaning that bond lengths $\text{Co1-O2}=2.17 \text{ \AA}$ and $\text{Co2-O2}=2.29 \text{ \AA}$ are not equal. This also means that octahedras around cobalt ions are differently distorted. This is the first known example of unsymmetrical

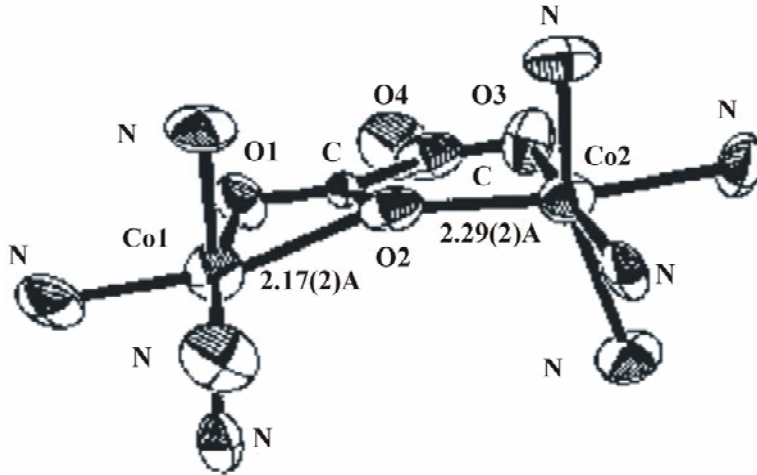


Fig. 1 – Monomeric unit with two Co(II) ions and distorted octahedral surrounding around each of them. The asymmetry of the oxalato bridge should be noticed.

THEORETICAL MODEL

Low-temperature magnetic properties of Co(II) ion originate from its 28-fold degenerate ^4F ground state which is difficult to describe theoretically. However, the combined effects of spin-orbit coupling and distortion of the octahedral ligand environment reduces the ground state to a spin-doublet (Kramers doublet) and two excited (one 4-fold and one 6-fold) energy levels.^{1-3,7-9} The ground doublet has an effective (*i.e.* pseudospin) value of $S=1/2$, while the first excited (quartet) level is separated by the energy gap of $\sim 10^2 \text{ K}^{1-3}$

$$H = -2JS_a^z S_b^z - \mu_B H_z (g_a S_a^z + g_b S_b^z), \quad (1)$$

where J denotes intracluster exchanged integral, μ_B stands for Bohr magneton, H_z is the z-axis component of the applied magnetic field, while the ligand field influence is ascribed to Landé

oxalato coordination through the three oxygen atoms.⁶ The existence of the oxalato bridge gives rise to the superexchange coupling between magnetic Co(II) ions, and the absence of chemical bonding between cobalt ions from distinct molecules provides interdimer magnetic isolation.

Measurements of the magnetization at several low temperatures in the $2.2 \text{ K} \leq T \leq 29 \text{ K}$ range have been done by the extraction technique magnetometer in the fields up to 20 T at the Grenoble High Magnetic Field Laboratory (GHMFL, France).

and consequently it can be neglected in the low temperature region.^{7,8} Another simplification arises from the well-known anisotropy of Co(II) ion that is prominent especially at low temperatures.^{1-3,7,8} As a result, the exchange coupling energy can be approximated by the pure Ising model rather than the Heisenberg one.

From the above quoted reasons, as well as taking into account the fact that each Co(II) ion from the dimer is located in the differently distorted octahedral ligand field, the Hamiltonian of the asymmetric dimer can be written as:

g -factors, g_a and g_b . Since the value of spins are $S_a = S_b = \pm 1/2$, one can easily see that four possible eigenvalues are:

$$E_1(S_a = 1/2, S_b = 1/2) = -J/2 - \mu_B H_z g_+, \quad (2a)$$

$$E_2(S_a = 1/2, S_b = -1/2) = J/2 - \mu_B H_z g_-, \quad (2b)$$

$$E_3(S_a = -1/2, S_b = 1/2) = J/2 + \mu_B H_z g_-, \quad (2c)$$

$$E_4(S_a = -1/2, S_b = -1/2) = -J/2 + \mu_B H_z g_+, \quad (2d)$$

where $g_{\pm} = (g_a \pm g_b)/2$.

The partition function Z for cobalt dimer can be readily found to be:

$$Z = \sum_{i=1}^4 e^{-\beta E(i)} = 2 \exp(-\beta J/2) \cosh(\beta g_- \mu_B H_z) + 2 \exp(\beta J/2) \cosh(\beta g_+ \mu_B H_z), \quad (3)$$

where $\beta = 1/k_B T$, and k_B denotes the Boltzmann constant.

The expression for magnetization of the asymmetric dimer can be readily obtained by finding

the first derivative of the free energy $F = -k_B T \ln(Z)$ with respect to magnetic field:

$$\frac{m(H_z)}{\mu_B} = -\frac{1}{\mu_B} \frac{\partial F}{\partial H_z} = \frac{2 \exp(-\beta J/2) g_- \sinh(\beta g_- \mu_B H_z) + 2 \exp(\beta J/2) g_+ \sinh(\beta g_+ \mu_B H_z)}{Z}. \quad (4)$$

RESULTS AND DISCUSSION

The obtained experimental $M(H)$ data for the complex under consideration recorded at four different temperatures are shown in Fig. 2a-d as magnetization per cobalt dimer versus magnetic field.

Obtained magnetization dependencies for temperatures $T \leq 11.9$ K exhibit a single wide step that is typical for antiferromagnetically coupled pair of magnetic ions.^{4,5} In contrast to this, at $T = 29$ K magnetization vs. field dependence is linear up to the highest field values pointing to the paramagnetic behavior. These results are in compliance with the low-field magnetic susceptibility χ measurements on this complex which showed a maximum in the $\chi(T)$ curve at $T_{\max} = 26$ K thus indicating magnetic decoupling of the cobalt ions in the dimer at temperatures higher than T_{\max} .⁸

Results of the $M(H)$ calculation obtained by a least-square fitting of the eq. (4) to the experimental data are also presented in Fig. 2. In this procedure g_a and g_b values, as well as exchange integral J , were treated as fitting parameters. As it can be seen from Fig. 2a) and 2b)

this approach gives non-negligible discrepancy between experimental and calculated values for $T = 2.2$ K and 4.2 K, while excellent agreement has been achieved for higher temperatures of 11.9 K and 29 K, Fig. 2c) and 2d) respectively. It can be concluded that low temperature data are more sensitive to $M(H)$ contributions which are neglected in the proposed model. Presumably the most important among these contributions are those that concern the influence of the ligand environment on the magnetic pair, especially the posted approximation on identity of molecules with different monomeric units, A and B, as already outlined in the Experimental section. Namely, slight crystallographic difference between these molecules can cause different ligand fields to act on cobalt dimers. The common manner of taking this into account is by replacing the actual experimental temperature T with the "effective temperature" T_{eff} .^{5,10} The $M(H)$ curves calculated by this approach are depicted by full lines in Figs. 2a) and 2b), where a high agreement between calculated and experimental data can be seen. Values of fitted parameters obtained in the above described calculations are summarized in Table 1 for all experimental temperatures.

Table 1

The values of magnetic parameters for cobalt dimer in dinuclear complex $[\text{Co}_2(\text{ox})\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ obtained by fitting equation (4) to the experimental data

$T_{\text{exp}}(\text{K})$	$T_{\text{eff}}(\text{K})$	g_a	g_b	$J/k_B(\text{K})$
29	29	4.4±0.1	4.4±0.1	-15.4±0.5
11.9	11.9	4.59±0.03	3.58±0.03	-16.8±0.5
4.2	5.1±0.1	4.5±0.1	3.3±0.1	-16.0±0.5
2.2	3.5±0.1	4.43±0.03	3.12±0.03	-15.3±0.5

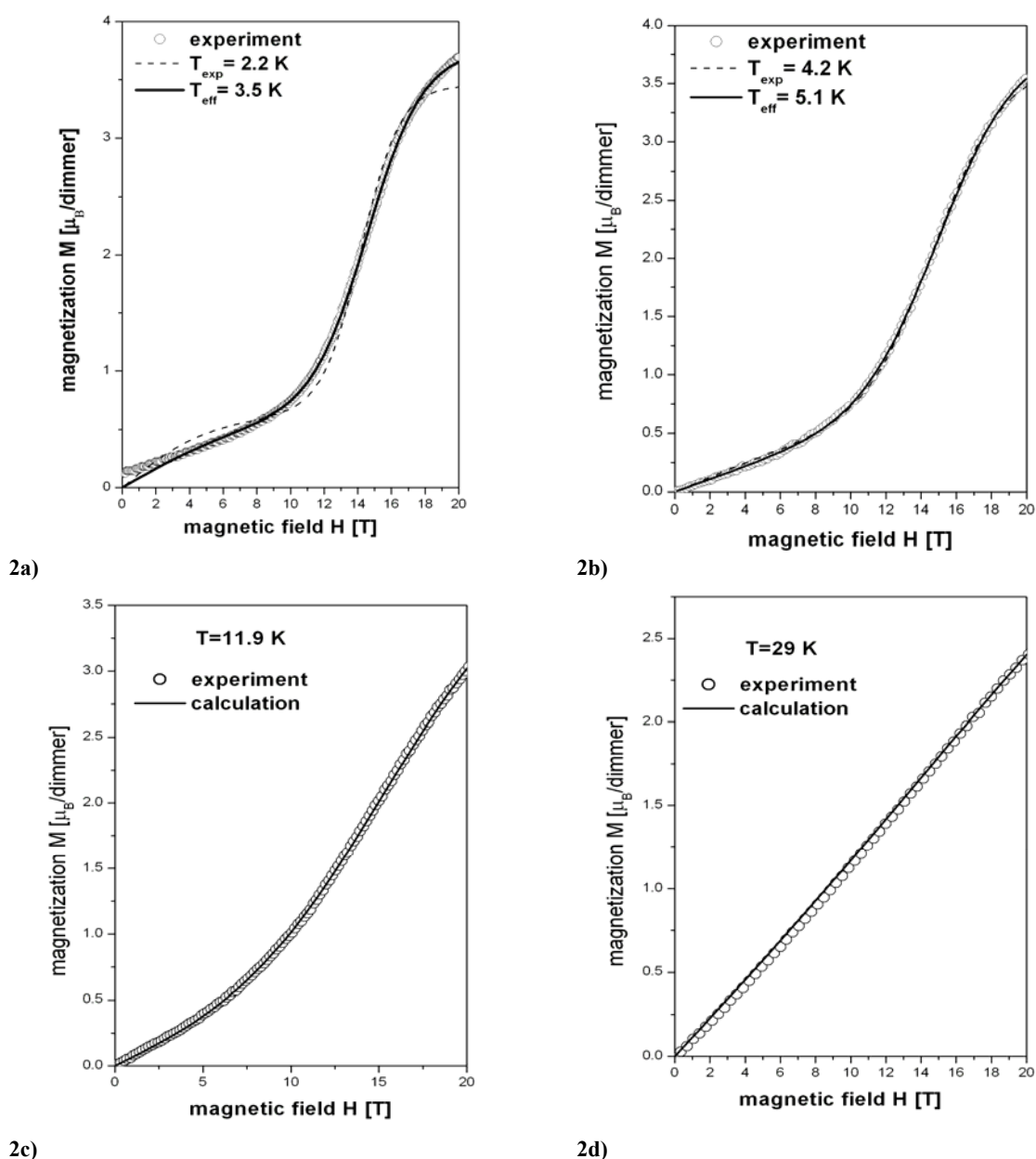


Fig. 2a-d – Experimental and calculated $M(H)$ dependences per cobalt dimer in dinuclear complex $[\text{Co}_2(\text{ox})\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ for different values of temperature.

CONCLUSIONS

Magnetic properties of the dinuclear Co(II) complex were studied by the magnetization-step spectroscopy. The experimental $M(H)$ data were analysed by the "asymmetric dimer" model where each Ising-type Co(II) ion from the dimer is placed in the differently distorted octahedral ligand field. By fitting the eq. (4) to the experimental data the values of magnetic parameters listed in Table 1 are obtained. On the basis of this parameters and model assumptions several conclusions on both magnetic and structural properties can be drawn:

- (i) Co(II) ions are in the ground (Kramers) state with the $S=1/2$ pseudospin due to the influence of the distorted octahedral ligand field;
- (ii) Different values of g_a and g_b are a result of differently distorted octahedras around each cobalt ion from the dimer;
- (iii) The difference between experimental and effective temperatures in the low temperature region points to the existence of two crystallographically different monomeric units;
- (iv) Cobalt ions in the dimer are antiferromagnetically coupled over the asymmetric oxalato bridge with the exchange integral $J \approx -16\text{K}$.

It should be emphasized that the above conclusions (i)-(iii) are in line with the previously published crystal structure results on the complex under consideration.⁶

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