

Magnetic susceptibility calculation of the dinuclear cobalt complex $[\text{Co}(\text{ox})\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$

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Abstract: Magnetic properties of the dinuclear cobalt complex originate from the magnetically isolated "asymmetric dimers" where each Co(II) ion within the dimer is situated in the differently distorted octahedral ligand field. Calculated values of magnetic susceptibility, obtained by use of the anisotropic Heisenberg-asymmetric dimer model, are found to be in excellent agreement with experimental $\chi(T)$ data over a wide range of temperature (4–295K). Values of fitted parameters, the exchange integral J and both g -factors of the dimer, are in a very good agreement with the literature data.

The aim of this paper is magnetic susceptibility calculation applied to the recently synthesized dinuclear cobalt complex $[\text{Co}_2(\text{ox})\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ [4], where (ox)⁻ denotes oxalato anion, and tpmc=N,N',N'',N'''-tetrakis(2-pyridylmethyl)-1,4,8,11 tetraazacyclotetradecane.

Structure of the complex

The unit cell of the crystal 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 units, A and B. However, since these monomeric units are almost crystallographically identical we do not distinguish between them. Each of the two Co(II) ions in the molecule is placed in a distorted hexa-coordinated octahedral geometry made of four N atoms and two O atoms. The conformation of ligators around both Co(II) ions is depicted in Fig. 1. and it can be seen that the oxalato group bridges two cobalt ions (Co1 and Co2), where O2 oxygen atom is common for both of them. Such bonding gives rise to the superexchange coupling between magnetic Co1 and Co2 ions. Since no chemical bonding exists between cobalt ions from distinct molecules we can consider each Co(II) pair as magnetically isolated. The most interesting 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 ("asymmetric dimer"). It is the first example of unsymmetrical oxalato coordination through the three oxygen atoms.

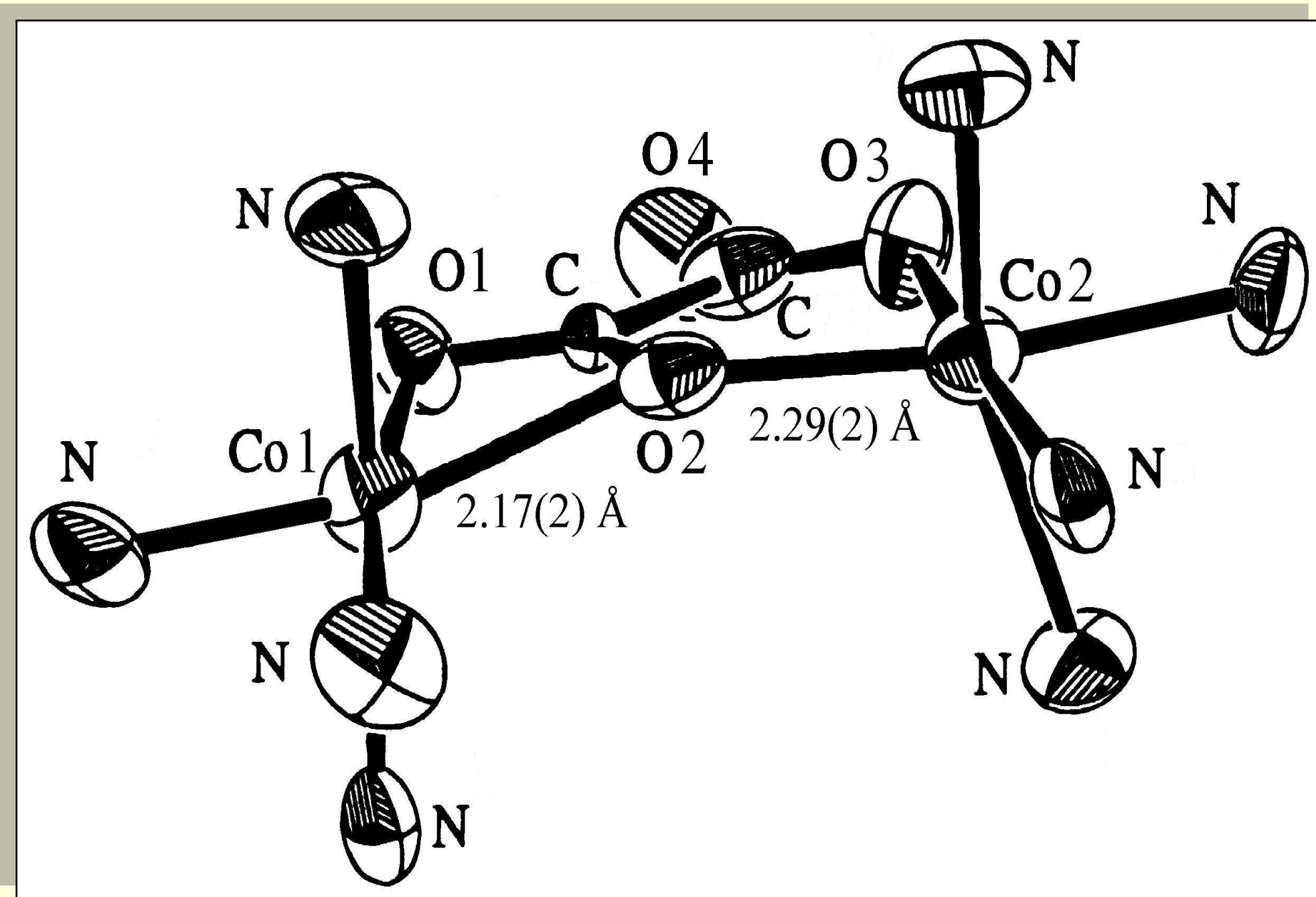


Fig. 1. The conformation of ligators around two Co(II) ions in the monomeric unit. Each cobalt ion from the dimer is placed in a differently distorted octahedral environment due to the asymmetric oxalato bridge.

Known facts about Co²⁺ ion in octahedral crystal field:

The combined effects of spin-orbit coupling and local distortion of the octahedral ligand environment reduces the 28-fold degenerate ⁴F ground state of Co²⁺ ion to a ground Kramers doublet and two excited (one 4-fold and one 6-fold) levels. The ground doublet has pseudospin value of $S=1/2$ while the first excited level with $S=3/2$ is separated by the energy gap of the 10^2 K order of magnitude. The Co²⁺ ion in a distorted octahedral crystal field is generally known for its pronounced anisotropic properties.

Theoretical models and assumptions:

Ising model- for low temperatures, where only Kramers doublet is populated ($k_B T \leq 10^2 \text{ K}$).

Modified anisotropic Heisenberg model- in the temperature range of the experiment, with the terms describing (1) exchange interaction, (2) Zeeman splitting in the applied field H , and (3) zero-field splitting with the parameter D . In this model exchange interaction J is treated as anisotropic one with $J_x=J_y=0$ and $J_z=J$, spin operator \hat{S}_z for each ion in the dimer has eigenvalues $m_i=\{-3/2, -1/2, 1/2, -3/2\}$. Since an each ion from the pair is located in a differently distorted octahedral ligand field, we assumed different Landé factors g_1 and g_2 ("asymmetric dimer"). Thus, the Hamiltonian, its eigenvalues and partition function of the dimer have the following forms:

$$H = -2J \hat{S}_{1z} \hat{S}_{2z} + \frac{1}{2} \mu_B H_z (g_1 \hat{S}_{1z} + g_2 \hat{S}_{2z}) + D(\hat{S}_{1z}^2 + \hat{S}_{2z}^2)$$

$$E(m_1, m_2) = -2J m_1 m_2 + \frac{1}{2} \mu_B H_z (g_1 m_1 + g_2 m_2) + D(m_1^2 + m_2^2)$$

$$Z(H_z) = \sum_{m_1=-3/2}^{3/2} \sum_{m_2=-3/2}^{3/2} \exp\left(-\frac{E(m_1, m_2)}{k_B T}\right)$$

The magnetic susceptibility of the asymmetric dimer can be found from the usual relation $\chi = -k_B T \partial^2 [\ln(Z)] / \partial H_z^2$, and for $H_z \rightarrow 0$ it follows:

$$\chi(T) = \frac{N \mu_B^2}{8 k_B T Z_{(H_z=0)}} \times \left[9 g_+^2 a_1^{-9/2} + G_- a_4^{-1/2} + G_+ a_3^{-1/2} + g_-^2 a_2^{-1/2} + 9 g_-^2 a_2^{-9/2} + g_+^2 a_1^{-1/2} \right]$$

where

$$Z_{(H_z=0)} = 2 \left[a_1^{-9/2} + 2 a_4^{-1/2} + 2 a_3^{-1/2} + a_2^{-1/2} + a_2^{-9/2} + a_1^{-1/2} \right]$$

$$a_{1,2} = \exp\left(\frac{D \pm J}{k_B T}\right) \quad a_{3,4} = \exp\left(\frac{5D \pm 3J}{k_B T}\right)$$

$$g_{\pm} = (g_1 \pm g_2) \quad \text{and} \quad G_{\pm} = (10g_1^2 \pm 12g_1g_2 + 10g_2^2).$$

Results: The magnetic susceptibility of the complex was measured by the Faraday method over the 4-295 K and the obtained data are shown in the Fig. 2. The theoretical $\chi(T)$ dependence has been fitted to the experimental data and the following best-fit parameters were obtained: $J/k_B = (-12.9 \pm 0.5) \text{ K}$, $g_1 = 3.42 \pm 0.04$, $g_2 = 4.02 \pm 0.04$, $D/k_B = (6.6 \pm 0.1) \text{ K}$. The obtained $\chi(T)$ curve is depicted in Fig. 2 where also best fit curves for both $D=0$ and $g_1=g_2$ models are shown. It can be seen that in last two cases departure from the experimental data is significant for $T < 50 \text{ K}$ showing the importance of anisotropy and crystal field contributions at low temperatures.

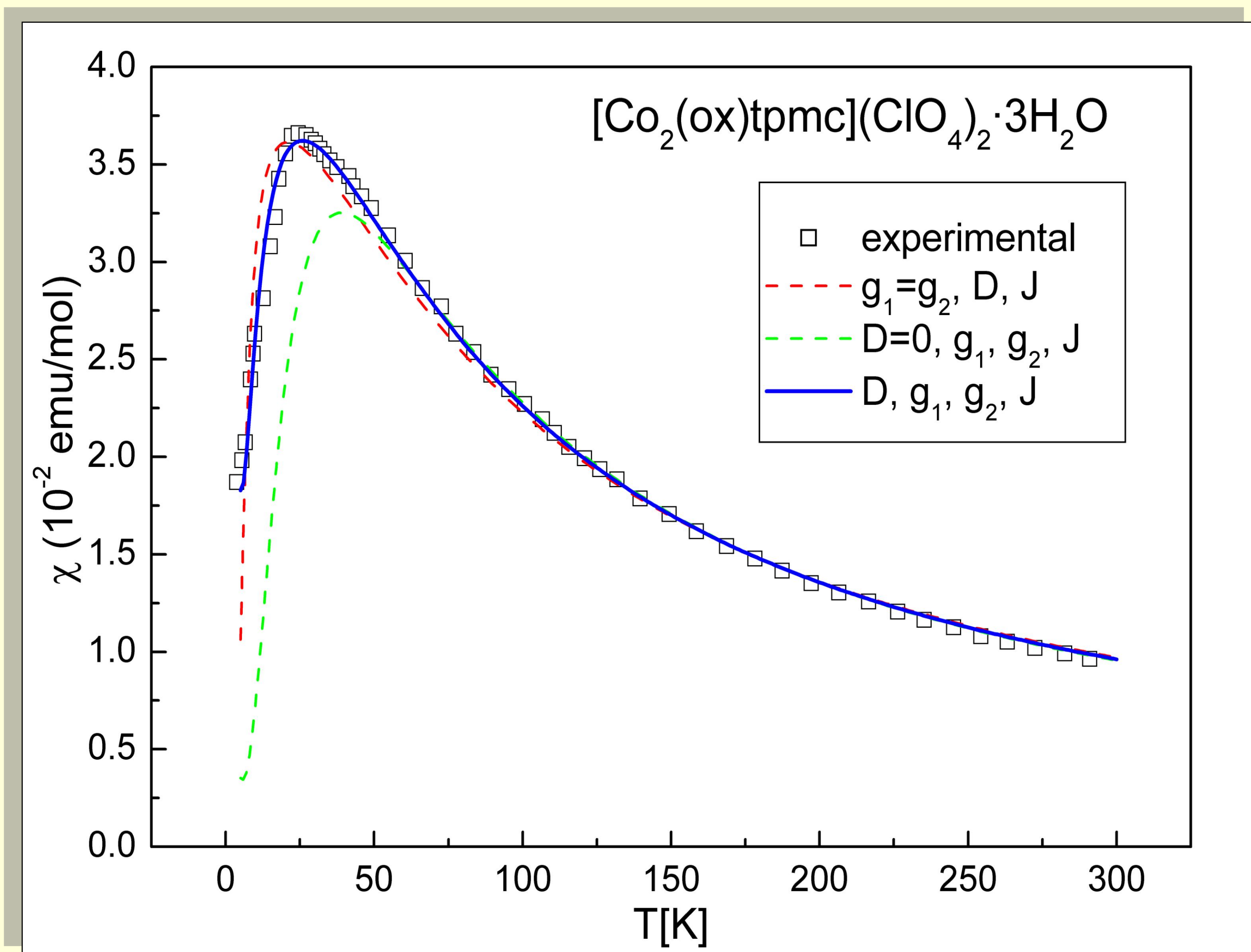


Fig. 2. Experimental and calculated temperature dependence of magnetic susceptibility.

Conclusion: (i) Co(II) ions are situated in a distorted octahedral ligand field; (ii) considerable difference between g_1 and g_2 values confirms the X-ray diffraction results on the unsymmetrically bonded Co²⁺ ions in the dimer; (iii) a relatively large negative value of the exchange constant $J/k_B \approx -13 \text{ K}$ shows the presence of the strong antiferromagnetic interaction between Co(II) ions in the dimer. This implies that unsymmetrical oxalato coordination over oxygen atoms can provide intense superexchange coupling.