Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Magnetooptical Study of (4-(2-dibutylaminoethanolato-N,O,O,O,) Chlorido Copper (II)) a Cubane Complex with Dominant Ferromagnetic Interactions

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Study of the effects of the antisymmetric and anisotropic contributions to the exchange interaction on the low temperature magnetic behavior of the ferromagnetically coupled Cu4 complex

High temperature magnetic properties (χT vs. T at T > 50 K) can be simulated with the use of the isotropic exchange only. It results in the value of the isotropic exchange interaction (J_{ex} = 30 cm^{-1}) and the value of the orbital reduction factor (κ = 0.7). The last one is used for the calculation of the principal values of the local **g**-tensors (see paper). Although the anisotropy of the local *g*-factors is significant, the anisotropy of the *g*-factor for the whole complex is less pronounced due to the different mutual orientation of the principal axes of the local **g**-tensors for different Cu ions. As a result, the simulation of the magnetic behavior of the whole complex in the whole temperature region can be done using some isotropic averaged *g*-factor. This averaged *g*-factor is calculated from the principal values of the local **g**-tensors and is g_{av}= 2.106. Now the effect of the antisymmetric and anisotropic contributions to the exchange interaction on the low temperature magnetic behavior of the ferromagnetically coupled Cu4 complex can be studied.

Antisymmetric contributions to the exchange interaction

With the account of the antisymmetric part of the exchange interaction the exchange Hamiltonian for the complex under study looks as

$$\begin{aligned} H_{ex} = &-2J_{ex}\left(\boldsymbol{S}_1\boldsymbol{S}_3 + \boldsymbol{S}_1\boldsymbol{S}_4 + \boldsymbol{S}_2\boldsymbol{S}_3 + \boldsymbol{S}_2\boldsymbol{S}_4\right) \\ &+ \boldsymbol{G}_{13}\left[\boldsymbol{S}_1 \times \boldsymbol{S}_3\right] + \boldsymbol{G}_{14}\left[\boldsymbol{S}_1 \times \boldsymbol{S}_4\right] + \boldsymbol{G}_{23}\left[\boldsymbol{S}_2 \times \boldsymbol{S}_3\right] + \boldsymbol{G}_{24}\left[\boldsymbol{S}_2 \times \boldsymbol{S}_4\right], \end{aligned} \tag{S1}$$

where the first part is the isotropic exchange interaction and the second one is the antisymmetric exchange interaction.

It is assumed that the absolute values of all $\boldsymbol{G}_{ij}$ vectors are equal. Unfortunately, the symmetry of all exchange coupled Cu pairs is very low, so it is not possible to predict the direction of $\boldsymbol{G}_{ij}$ vectors. However, since the g-factors of the Cu ions are assumed to be isotropic, for calculation of the powder averaged magnetic behavior in the presented model it is significant not absolute direction of $\boldsymbol{G}_{ij}$ vectors but their mutual orientation. All calculations are performed in the molecular frame of reference. The Z-axis of this molecular frame of reference is chosen to coincide with the S_4 symmetry axis of the complex. The X-axis of the molecular frame of reference is chosen in such a way that $\boldsymbol{G}_{13}$ is in the molecular XZ plane. So, in the molecular frame $G_{13}^Z = G\cos\alpha$, $G_{13}^X = G\sin\alpha$ and $G_{13}^Y = 0$ with α being the angle between Z axis and $\boldsymbol{G}_{13}$ vector. Due to the symmetry of the studied complex for other $\boldsymbol{G}_{ij}$ vectors one finds: $G_{14}^Z = G\cos\alpha$, $G_{14}^X = 0$ and $G_{14}^Y = G\sin\alpha$; $G_{23}^Z = G\cos\alpha$, $G_{23}^X = 0$ and $G_{23}^Y = -G\sin\alpha$; $G_{24}^Z = G\cos\alpha$, $G_{24}^X = -G\sin\alpha$ and $G_{24}^Y = 0$.

The magnetic behavior is simulated at different values of the angle α. In this simulation the values of the isotropic exchange parameter and the averaged *g*-factor are those obtained from the analysis of the high temperature magnetic behavior, namely, J_{ex} = 30 cm^{-1} and g_{av}= 2.106. According to the estimation of T. Moriya (Phys. Rev. 120, 1960, 91), $G \sim (\Delta g / g) J_{ex}$, where G and J_{ex} are vector, and scalar quantities determining the antisymmetric and isotropic exchange interactions, respectively, Δg is the deviation of the g-factor from the pure spin one g_0=2. It means that for transition metals without first order orbital angular momentum the antisymmetric exchange interaction ranges from 1 to 10% of the isotropic one. Since this estimation gives only order of magnitude of G, in the subsequent sample calculations the value G = 6 cm^{-1} is used that is equal to the upper limit of 10% from the magnitude of the isotropic exchange predicted for transition metals. It was found that the largest effect on the low temperature magnetic behavior of the studied Cu4 complex is at α=90°, however, this effect is very small. Figure S1 demonstrates magnetic behavior with and without antisymmetric exchange interaction. It is seen that the difference is really negligible.

During the study of the effects of antisymmetric exchange on the behavior of the exchange coupled dimeric complex composed of spins 1/2 it was found that the splitting of the triplet level due to the AS exchange is about $\Delta \sim G^2/8J_{ex}$ (see, for example, Tsukerblat et al, in Molecular Magnetism: From Molecular Assemblies to the Devices, p.85). In our calculations for J_{ex} = 30 cm^{-1} and G = 6 cm^{-1} the splitting of the ferromagnetic ground state is about 0.2 cm^{-1} that is comparable for the results obtained for dimers. It is clear that so small splitting is not able to produce noticeable effect on the low temperature magnetic behavior since even at very low temperature all sublevels of the S=2 ferromagnetic ground state are thermally populated.

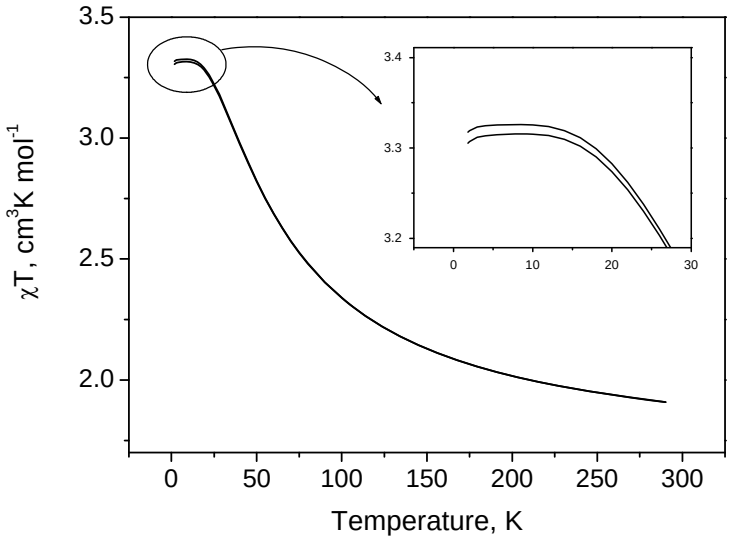

Fig.S1. Temperature dependence of χT product calculated at J_{ex} = 30 cm^{-1}, g_{av}= 2.106 and G = 6 cm^{-1} (α=90°).

At the next stage of the study the magnetic behavior was calculated at some unrealistically large value of the antisymmetric exchange interaction G = 15 cm^{-1}. For this value of the G-parameter the largest effect on the low temperature magnetic behavior is achieved at α=0°. The result is shown in Fig.S2.

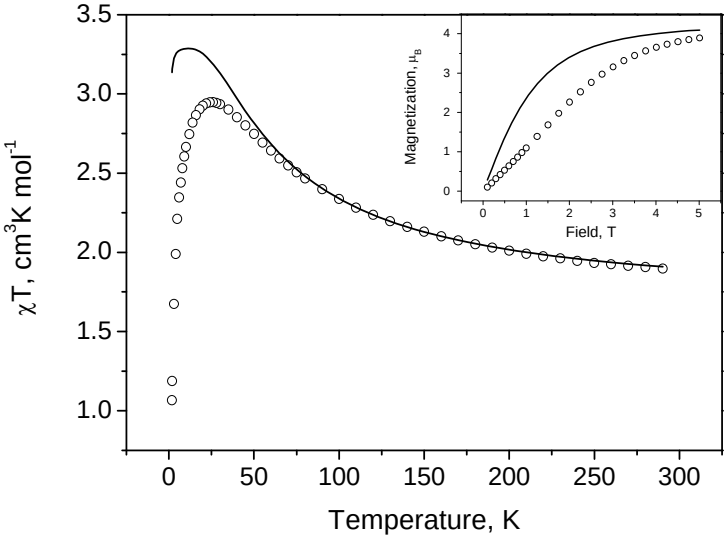

Fig.S2. Magnetic behavior of $(C_{10}H_{22}NOCuCl)_4$ compound calculated at J_{ex} = 30 cm^{-1}, g_{av}= 2.106 and G = 15 cm^{-1} (α=0°).

It is seen that even at this unrealistically large value of the *G* parameter the magnetic behavior of the complex is not reproduced and some intercluster interaction is required. This interaction was added to the Hamiltonian eq.(S1). The account of the antisymmetric exchange interaction with the reasonable values of the exchange parameter ($G < 6$ cm^{-1}) has only small effect on the magnetic behavior. The strength of the intercluster interaction necessary to simulate the magnetic behavior of the studied compound with and without antisymmetric exchange is almost the same.

Finally, the case of extremely strong (unrealistic) antisymmetric exchange interaction was regarded. Fig. S3 presents magnetic behavior simulated for $G = 15$ cm^{-1}. It is seen that even for this unrealistic antisymmetric exchange parameter the obtained value of the interacluster interaction is large enough ($zJ' = -0.7$ cm^{-1}) and comparable with the case of no antisymmetric exchange ($zJ' = -0.8$ cm^{-1}).

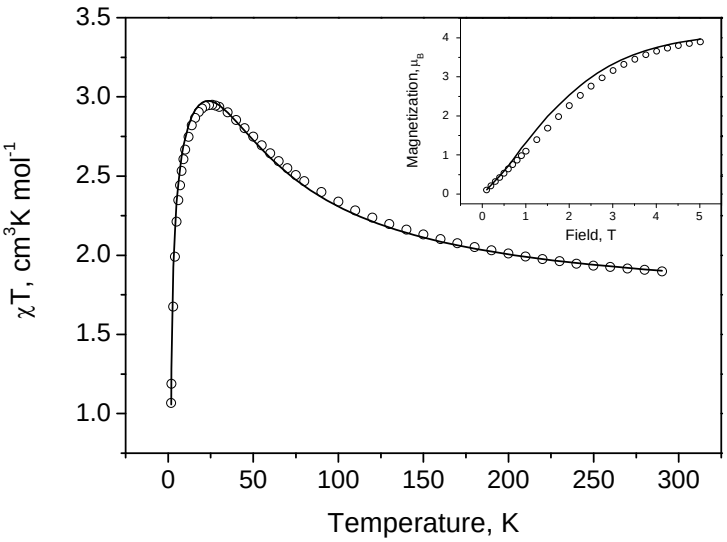

Fig.S3. Magnetic behavior of $(C_{10}H_{22}NOCuCl)_4$ compound calculated at $J_{ex} = 30$ cm^{-1}, $g_{av} = 2.106$ and $G = 15$ cm^{-1} (α=0°) and $zJ' = -0.7$ cm^{-1}.

Anisotropic contributions to the exchange interaction

With the account of the anisotropy of the exchange interaction the exchange Hamiltonian for the complex under study looks as

$$\begin{aligned} H_{ex} = &-2J_{ex}\left(\boldsymbol{S}_1\boldsymbol{S}_3 + \boldsymbol{S}_1\boldsymbol{S}_4 + \boldsymbol{S}_2\boldsymbol{S}_3 + \boldsymbol{S}_2\boldsymbol{S}_4\right) \\ &+ \boldsymbol{S}_1\boldsymbol{D}_{13}\boldsymbol{S}_3 + \boldsymbol{S}_1\boldsymbol{D}_{14}\boldsymbol{S}_4 + \boldsymbol{S}_2\boldsymbol{D}_{23}\boldsymbol{S}_3 + \boldsymbol{S}_2\boldsymbol{D}_{24}\boldsymbol{S}_4 \end{aligned} . \qquad \text{(S2)}$$

Let us assume that for each Cu-Cu pair the anisotropy of the exchange interaction is axial. It means that in the local frame of reference for this pair the $\boldsymbol{D}_{ij}$-tensor is

$$\boldsymbol{D}_{loc} = \begin{pmatrix} -\frac{1}{2}D & 0 & 0 \\ 0 & -\frac{1}{2}D & 0 \\ 0 & 0 & D \end{pmatrix}. \qquad \text{(S3)}$$

Similar to the case of antisymmetric exchange, all calculations are performed in the molecular frame of reference. The Z-axis of this molecular frame of reference is chosen to coincide with the S_4 symmetry axis of the complex. The X-axis of the molecular frame of reference is chosen in such a way that the local z_{13}-axis of the pair Cu_1-Cu_3 is in the molecular XZ plane. As a consequence, in the molecular frame the local z_{13}-axis is along the direction (α, 0). The quantities in the parentheses are the polar and azimuthal angles, respectively, and α is the angle between Z and z_{13} axes. Due to the symmetry of the studied complex one finds that the local z_{24}-axis of the Cu_2-Cu_4 pair in the molecular frame of reference is along the (α, 180°) direction, the local z_{14}-axis of the Cu_1-Cu_4 pair is along the (180°-α, 270°) direction and the local z_{23}-axis of the Cu_2-Cu_3 pair is along the (180°-α, 90°) direction. To obtain $\boldsymbol{D}_{ij}$-tensors in the molecular frame of reference one needs to perform the corresponding unitary transformation: for Cu_1-Cu_3 pair the rotation around the molecular Y-axis on the angle -α, for Cu_2-Cu_4 pair the rotation around the molecular Y-axis on the angle α, for Cu_1-Cu_4 pair the rotation around the molecular X-axis on the angle α, for Cu_2-Cu_3 pair the rotation around the molecular X-axis on the angle -α. The $\boldsymbol{D}_{ij}$-tensors in the molecular frame of reference can be found with the use of eqs.(S4)-(S7).

$$\boldsymbol{D}_{13} = \boldsymbol{A}_Y^{-1}(-\alpha)\boldsymbol{D}_{loc}\boldsymbol{A}_Y(-\alpha), \tag{S4}$$

$$\boldsymbol{D}_{24} = \boldsymbol{A}_Y^{-1}(\alpha)\boldsymbol{D}_{loc}\boldsymbol{A}_Y(\alpha), \tag{S5}$$

$$\boldsymbol{D}_{14} = \boldsymbol{A}_X^{-1}(\alpha)\boldsymbol{D}_{loc}\boldsymbol{A}_X(\alpha), \tag{S6}$$

$$\boldsymbol{D}_{23} = \boldsymbol{A}_X^{-1}(-\alpha)\boldsymbol{D}_{loc}\boldsymbol{A}_X(-\alpha). \tag{S7}$$

The corresponding rotation matrices are:

$$\boldsymbol{A}_X(a) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos a & -\sin a \\ 0 & \sin a & \cos a \end{pmatrix}, \tag{S8}$$

$$\boldsymbol{A}_Y(a) = \begin{pmatrix} \cos a & 0 & \sin a \\ 0 & 1 & 0 \\ -\sin a & 0 & \cos a \end{pmatrix}. \tag{S9}$$

The magnetic behavior is simulated at different values of the angle α. It was found that the largest effect on this magnetic behavior is at α=0. Under these conditions the local anisotropy axes are parallel and the anisotropies of the interaction in the different pairs do not cancel each other resulting in the anisotropy of the properties of the whole complex.

According to the estimations of T. Moriya (Phys. Rev. 120, 1960, 91), $D \sim (\Delta g / g)^2 J_{ex}$. It means that for transition metals without first order orbital angular momentum this anisotropy is not bigger

than 1% from the exchange interaction. In the subsequent sample calculations $|D| = 1$ cm^{-1} was used. In this case the exchange anisotropy calculated as $|J_x-J_z|/J_z$ is about 2.5%. The results of calculation for the most favorable case of parallel local anisotropy axes (α=0°) and the neglect of intercluster interaction are shown in Fig.S4.

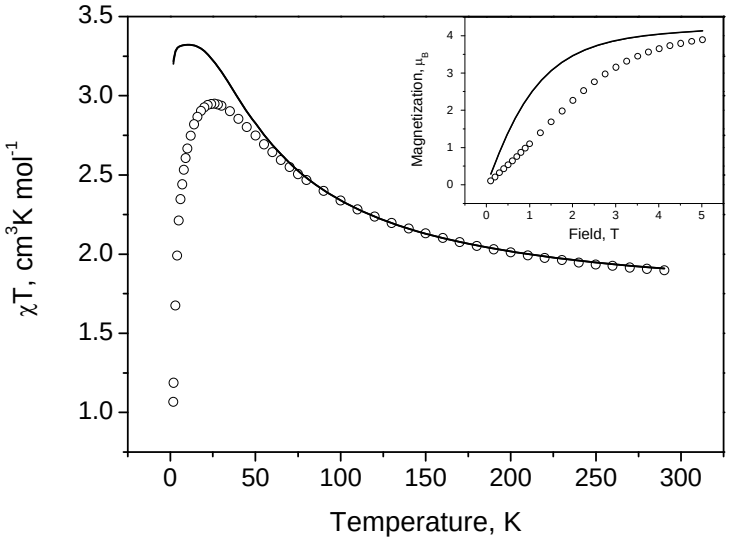

Fig.S4. Magnetic behavior of $(C_{10}H_{22}NOCuCl)_4$ compound calculated at J_{ex} = 30 cm^{-1}, g_{av}= 2.106 and $D = \pm 1$ cm^{-1} (α=0°, no intercluster interaction).

It is seen that although the effect of the anisotropy of the exchange interaction is much stronger that the effect of the antisymmetric exchange (see Fig.S1), it is not enough to explain the magnetic behavior of the complex under study.

Figure S5 demonstrates the joint effect of the anisotropic exchange and the intercluster interaction. It is seen that for negative values of the *D*-parameter the effect of the anisotropy of the exchange interaction is stronger and, as a consequence, the smaller value of the intercluster interaction is required for the explanation of the experimental magnetic data. However, the values of the intercluster interaction are still comparable with the value for the case of the neglect of the anisotropy of the exchange (zJ' = -0.8 cm^{-1}). In the real compound the effect of the reduction of the strength of the intercluster interaction due to the anisotropy of the exchange interaction will be even less pronounced since the local anisotropy axes are not parallel and the parameter of the anisotropy *D* according to the estimations of T. Moriya should be smaller than the value used in the sample calculations presented above.

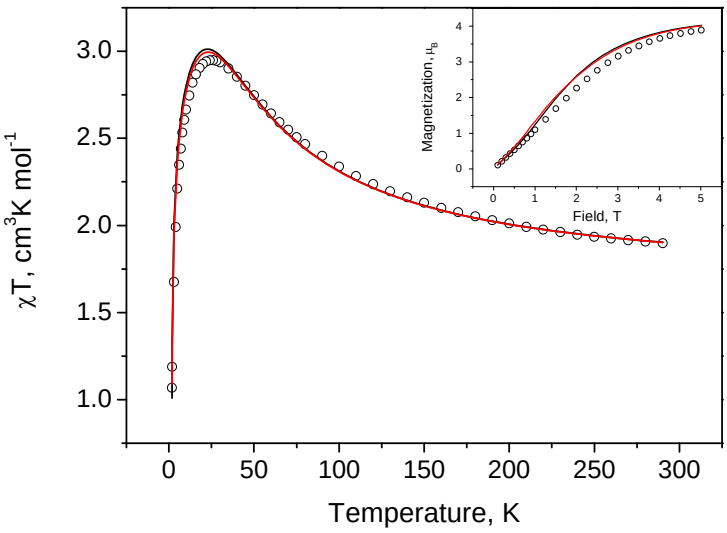

Fig.S5. Magnetic behavior of $(C_{10}H_{22}NOCuCl)_4$ compound calculated at J_{ex} = 30 cm^{-1}, g_{av}= 2.106 and (i) D = -1 cm^{-1}, zJ' = -0.65 cm^{-1} (black lines), (ii) D = 1 cm^{-1}, zJ' = -0.7 cm^{-1} (red lines).

Summarizing, the introducing in the consideration of the anisotropy of the exchange interaction (as well as the antisymmetric exchange one) with the reasonable values of the corresponding parameter does not change significantly the situation with the intercluster interaction. The strength of this intercluster interaction is almost the same with and without anisotropic exchange coupling.