Supporting Information for

The role of π-π stacking in stablizing *a,a-trans*-cyclohexane-1,4-dicarboxylate in a 2D Co(II) network

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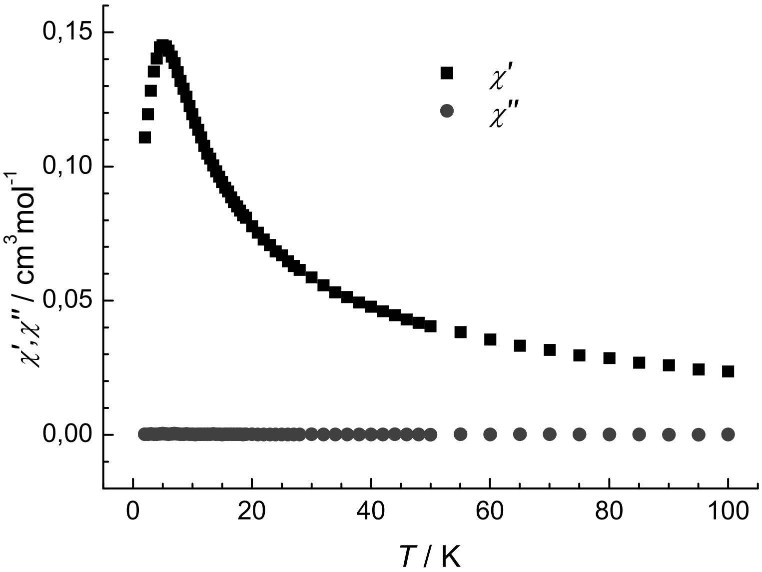

Fig. S1 Temperature-dependent ac magnetic susceptibility at f = 1000 Hz of **1** (B_0 = 0 T).

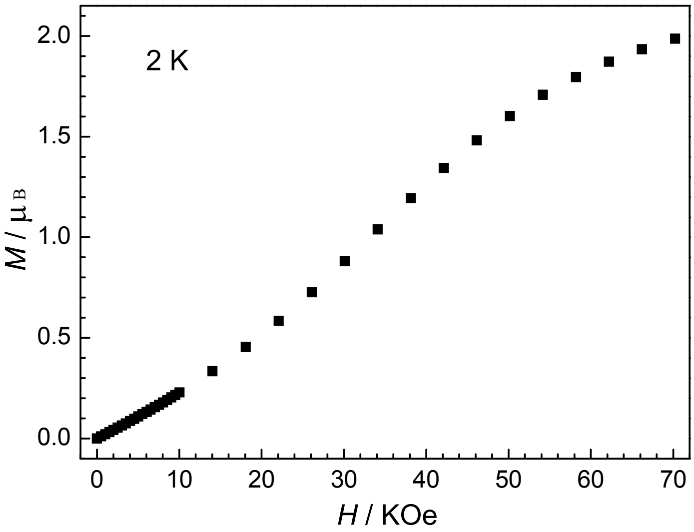

Fig. S2. Magnetization (M) *vs*. field (H) plot of **1** at 2.0 K.

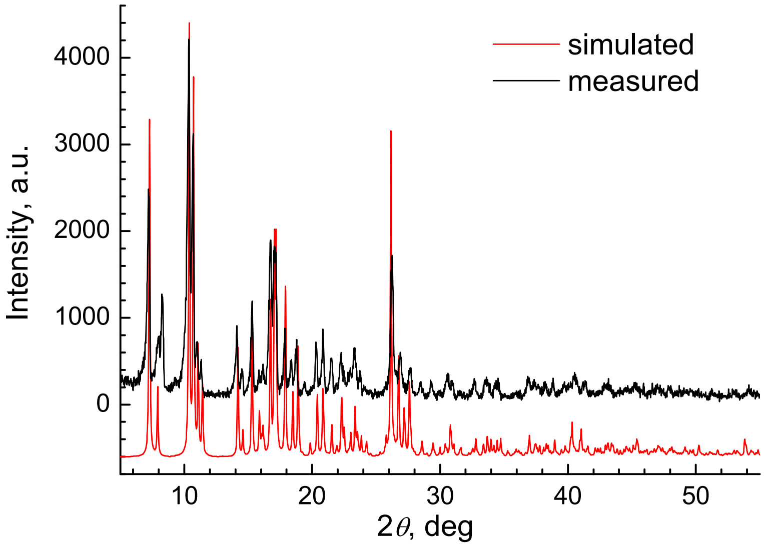

Fig. S3. Measured and calculated X-ray powder diffraction (XRD) pattern of **1.**

Introduction of the program CONDON and the magnetochemical fitting process

The free-ion ground term of Co(II) is ^4F and the first excited state ^4P follows more than 10^4 cm^{-1} higher. In a weak ligand field with octahedral symmetry [1], the ^4F term splits into $^4T_1$, $^4T_2$ and $^4A_2$ terms, in this situation the ^4P is not split and changes into the $^4T_1$ term. As the ground term of the high-spin Co(II) is $^4T_1$ under pure octahedral symmetry, the contribution of the orbital momentum cannot be ignored [2]. The orbital momentum complicates the magnetochemical interpretation, a difficulty that has prevented from analyzing the magnetic susceptibility of cobalt(II) complexes. In 1963 Lines reported a calculation method for a $^4T_1$ ground state magnetism in an axially distorted field, considering the axial-splitting and the spin-orbit coupling [3]. Lines described a statistical approximation for the analysis of the spin-spin coupling in dinuclear Co(II) complexes, but is was limited to the case of pure O_h symmetry [4]. In this study, we have synthesized new dinuclear cobalt complexes and their magnetic data have been analyzed with the program CONDON. The benefit of the program is the use of complete basis set (full d manifolds) and the consideration of the applied field dependence of magnetic quantities. CONDON analyzes the magnetic susceptibility of transition metal and lanthanide systems. For the d metal compounds under investigation the program serves to evaluate all necessary single ion effects: interelectronic repulsion (H_{ee}), spin-orbit coupling (H_{so}), ligand-field effect (H_{lf}) and the applied field (H_{mag}) [5].

Theory. We consider a magnetically isolated $3d^N$ metal ion surrounded by ligands imposing a distinct point symmetry upon the magnetic center. In a static magnetic field in direction the Hamiltonian of the metal ion is then represented by

$$\hat{H} = \underbrace{\sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + V(r_i)\right]}_{\hat{H}^{(0)}} + \underbrace{\sum_{i>j}^{N}\frac{e^2}{r_{ij}}}_{\hat{H}_{\mathrm{ee}}} + \underbrace{\sum_{i=1}^{N}\zeta(r_i)\,\kappa\;\hat{\boldsymbol{l}}_i\cdot\;\hat{\boldsymbol{s}}_i}_{\hat{H}_{\mathrm{so}}} + \underbrace{\sum_{i=1}^{N}\sum_{k=0}^{\infty}\left\{B_0^kC_0^k(i)+\sum_{q=2}^{k}\left[B_q^k\left(C_{-q}^k(i)+(-1)^qC_q^k(i)\right)\right]\right\}}_{\hat{H}_{\mathrm{LF}}} + \underbrace{\sum_{i=1}^{N}\mu_B(\kappa\;\hat{\boldsymbol{l}}_i+2\;\hat{\boldsymbol{s}}_i)\cdot\;\boldsymbol{B}}_{\hat{H}_{\mathrm{mag}}} \tag{1}$$

While $H^{(0)}$ represents the energy in the central field approximation, H_{ee} and H_{so} account for interelectronic repulsion and spin-orbit coupling (modified by the orbital reduction factor κ), respectively. The former is taken into account by the Racah parameters B, C, the latter by the one-electron spin-orbit coupling parameter ζ. The sets of interelectronic repulsion parameters as well as ζ, and κ are used as constant. H_{lf} describes the electrostatic effect of the ligands in the framework of ligand field theory on the basis of the global parameters B_q^k. The summation i is carried out over the number N of d electrons. The spherical tensors C_q^k are directly related to the spherical harmonics $C_q^k = \sqrt{4\pi/(2k+1)}\,Y_q^k$ and the real ligand field parameters B_q^k (Wybourne notation [6,7], are given by $\mathrm{A}_q^k\langle r^k\rangle$ where A_q^k is a numerical constant describing the charge distribution in the environment of the metal ion and $\langle r^k\rangle$ is the expectation value of $\langle r^k\rangle$ for the wave function. For d electrons the terms in the expansion with $k \leq 4$ are nonzero, where all the terms with k-odd vanish since we consider solely configurations containing equivalent electrons. The values of k and q are limited by the point symmetry of the metal ion site. If the spherically symmetric term $B_0^0C_0^0$ which does not lead to any splitting, is ignored, in cubic or tetragonal systems only spherical tensors with $k \leq 4$ are relevant. The ligand field operator with reference to the fourfold rotation axis for the angular part of the wave function reads

$$H_{\mathrm{lf}}^{\mathrm{tet}} = B_0^2\sum_{i=1}^{N}C_0^2(i) + B_0^4\sum_{i=1}^{N}C_0^4(i) + B_4^4\sum_{i=1}^{N}\left(C_4^4(i)+C_{-4}^4(i)\right) \tag{2}$$

In cubic systems the lf parameter B_0^2 is zero and a fixed relation between $B_4^4 = \sqrt{5/14}\,B_0^4$ exist, so that only the coefficient B_0^4 is essential. Exchange interactions between the magnetic centers are considered in the Heisenberg-model

$$H_{\mathrm{ex}} = -2J_{\mathrm{ex}}\,\hat{S}_1\cdot\hat{S}_2 \tag{3}$$

In the course of magnetochemical analysis is J_{ex} the exchange integral between the adjacent centers. Negative and positive J_{ex} indicates an antiferromagnetic and ferromagnetic interaction, respectively, between the magnetic centers. For magnetochemical analyses of Co(II) (d^7) we used the complete basis set of microstate consisting of 120 functions. The effective magnetic moment of the cobalt complex at 290.0 K is 4.76 μ_B per Co(II) ion, which is lager than the spin-only value 3.87 μ_B

but close to the value expected when the spin momentum and the orbital momentum exist independently [$\mu_{\mathrm{LS}} = [L(L+1) + 4S(S+1)]^{1/2} = 5.20\ \mu_B$]. For octahedral Co(II) high-spin complexes ($S = 3/2$), in magnetically dilute systems, we expected μ_{eff} values in the range 4–5 [8], as a result of spin and first-order orbital contributions. Furthermore, the μ_{eff}-values exhibit temperature dependence. This indicates a contribution of spin and first-order orbital momentum typical for the $^4T_1$ ground state. The most difficult point in the magnetochemical analysis of the compound is the description of the exchange coupling between the magnetic centers in consideration of the ligand field effect.

For modeling the magnetic behavior of the ligand-field effect, spin-orbit coupling and exchange coupling have to be taken into account. The values for spin-orbit coupling constant ζ were taken as 426 cm^{-1}. The Racah parameters (interelectronic repulsion) are chosen as $B = 780$ and $C = 3680$ cm^{-1} determined from optical spectra [9–11]. These parameters are kept constant during the calculation.

Fitting procedures. Fig. 2 shows the results of the magnetic measurement in the temperature range 2–300 K using molar susceptibility and effective Bohr magneton μ_{eff} *vs.* T plots. The molar susceptibility curve shows a rounded maximum at 5.0 K (155.8×10^{-3} cm^3 mol^{-1}), whereas μ_{eff} exhibits a continuous decrease upon cooling to give $\mu_{\mathrm{eff}} = 4.76$ at room temperature. This is a reasonable value for a high-spin cobalt(II)-ion in a tetragonal distorted environment with strong orbital contributions. The extrapolated value of μ_{eff} vanishes as T approaches zero. Such behavior is characteristic of an antiferromagnetic interaction.

The parameterization of the ligand field acting on a d-electron system require three lf-parameter B_0^2, B_0^4 and B_4^4 for a tetragonally distorted octahedron. The exchange interaction has to been taken into account by the Heisenberg-model (intradimer) and the molecular field model (interdimer). The complete Hamiltonian used was therefore

$$\hat{H} = H_{\mathrm{ee}} + H_{\mathrm{lf}} + H_{\mathrm{so}} + H_{\mathrm{ex}} + H_{\mathrm{mag}} \tag{4}$$

The parameters J_{ex} and B_q^k were determined by minimizing the least-squares fit. The best fit for calculated and experimental χ_{m} values was found for $J_{\mathrm{ex}} = -0.91$ cm^{-1}, $\lambda_{\mathrm{mf}} = -1.46$ mol cm^{-3}, $B_0^2 = 11353$ cm^{-1}, $B_0^4 = 41350$ cm^{-1}, $B_4^4 = 13783$ cm^{-1} and $SQ = 0.63$ %. *SQ*1[1] represents the fit quality. As expected, negative spin-spin-coupling parameters J_{ex} and λ_{mf} are essential for a good fit. The blue line in Fig. 2 corresponds to the calculated line, and this show a good agreement between the experimental and theoretical χ_{m} data. The black line demonstrates only the influence of the ligand field effect without any antiferromagnetic intradimer exchange interactions. The red line exhibits the ligand field effect and the intradimer exchange and illustrates the need to account for weak interdimer exchange interaction between neighboring dinuclear units.

References:

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[1] *SQ* is defined as $SQ = \sqrt{FQ} \times 100\,\%$ where $FQ = \sum_{i=1}^{n} ([\chi_{obs}(i) - \chi_{cal}(i)] / \chi_{obs}(i))^2$.

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