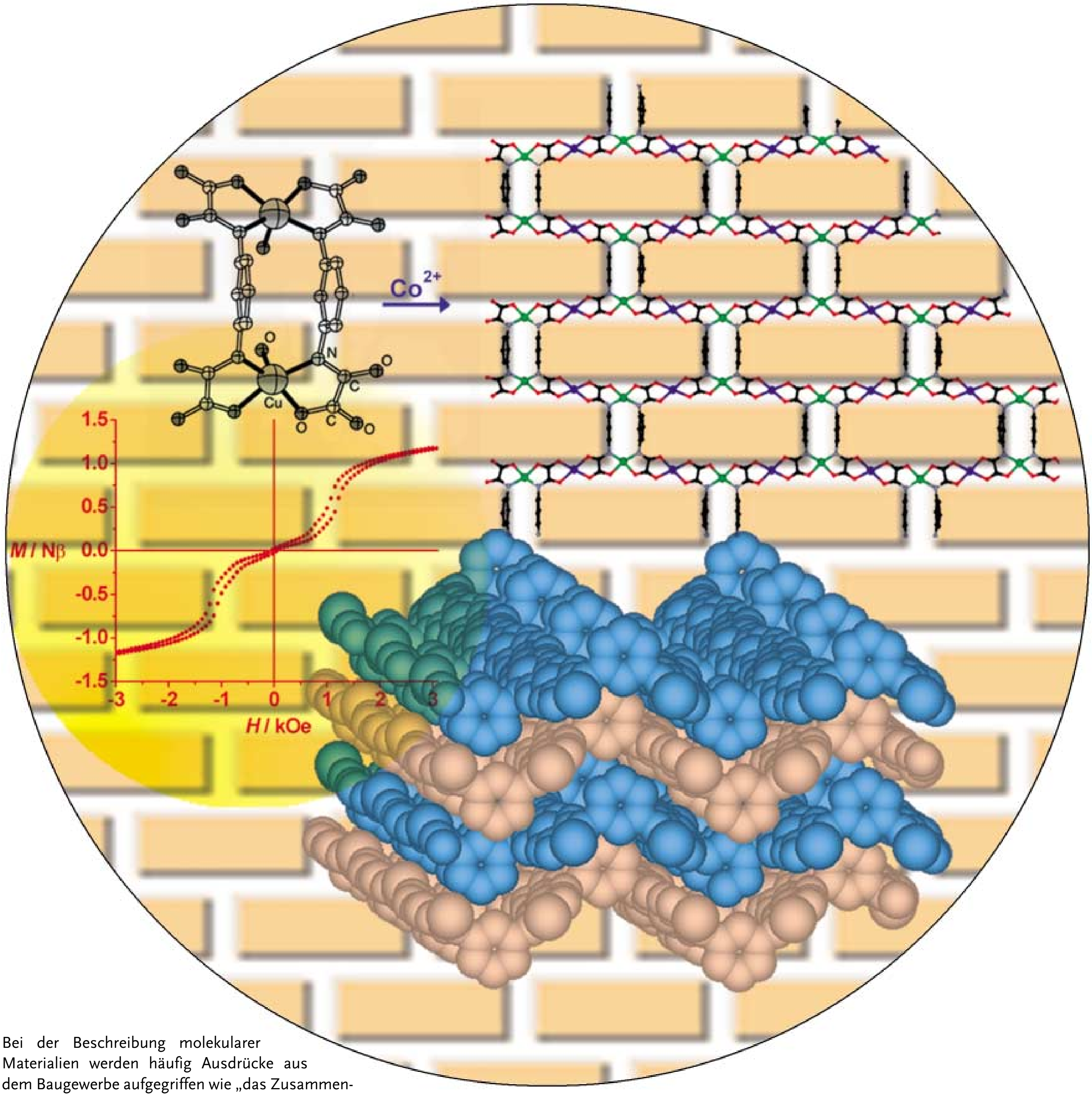
Zuschriften



Bei der Beschreibung molekularer Materialien werden häufig Ausdrücke aus dem Baugewerbe aufgegriffen wie „das Zusammenfügen von Bausteinen“, molekulare „Architekturen“ oder molekulares „Engineering“. H. O. Stumpf, Y. Journaux und Mitarbeiter beschreiben in der folgenden Zuschrift eine Cu^{II}/Co^{II}-Verbindung, die in ihrem Bau exakt der abgebildeten Mauer entspricht. Durch eine spezielle Strategie gelingt die gezielte Synthese dieses Komplexes mit interessanten magnetischen Eigenschaften.

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Molecular Magnets

A $Cu^{II}Co^{II}$ Metallacyclophane-Based Metamagnet with a Corrugated Brick-Wall Sheet Architecture**

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The design and synthesis of polynuclear metal complexes and extended networks with predictable magnetic properties have been an intellectual challenge for inorganic chemists interested in the field of molecular magnetism over the last two decades.[1] In particular, the design of molecule-based magnets[2] have focused the interest of many research groups around the world. Along this line the synthetic approach we exploit consists of designing heterobimetallic coordination polymers of varying dimensionality (1D–3D) that show ferrimagnetic behavior and of assembling these polymers within the crystal lattice in a ferromagnetic fashion.[3] It is well known that a pure 1D system cannot present magnetic ordering at $T \neq 0$.[4] Only interchain interactions can lead to ordering with spontaneous magnetization. In two dimensions long-range ordering occurs only in the Ising limit.[5] This thermodynamic behavior is the major drawback of our approach due to the weak control of the interchain interaction.

Recently, we designed a new building block, namely the ferromagnetically-coupled binuclear $[Cu_2(mpba)_2]^{4-}$ entity (mpb*a* = *m*-phenylenebis(oxamato)).[6] The $\{Cu_2(mpba)_2\}^{4-}$ unit is a metallamacrocycle of the [3,3]*meta*cyclophane type, with a π-stacked arrangement of the aromatic rings connected by two N–Cu–N linkages. When coordinated to divalent metal ions through the oxamato groups, this building block is able to link the ferrimagnetic chains, thus ensuring a ferromagnetic interaction between them.

In the work presented herein, we have used $\{Cu_2(mpba)_2\}^{4-}$ units and Co^{II} centers to obtain the first extended network with this building block, a bimetallic complex whose formula is $[Co_2Cu_2(mpba)_2(H_2O)_6]\cdot 6\,H_2O$ (**1**). Single crystals of **1** were obtained by slow diffusion in aqueous solution by using an H tube. Its structure consists of brick wall 2D networks assembled by chains linked with cyclophane moieties (Figure 1).[7] The end result is a corrugated structure.

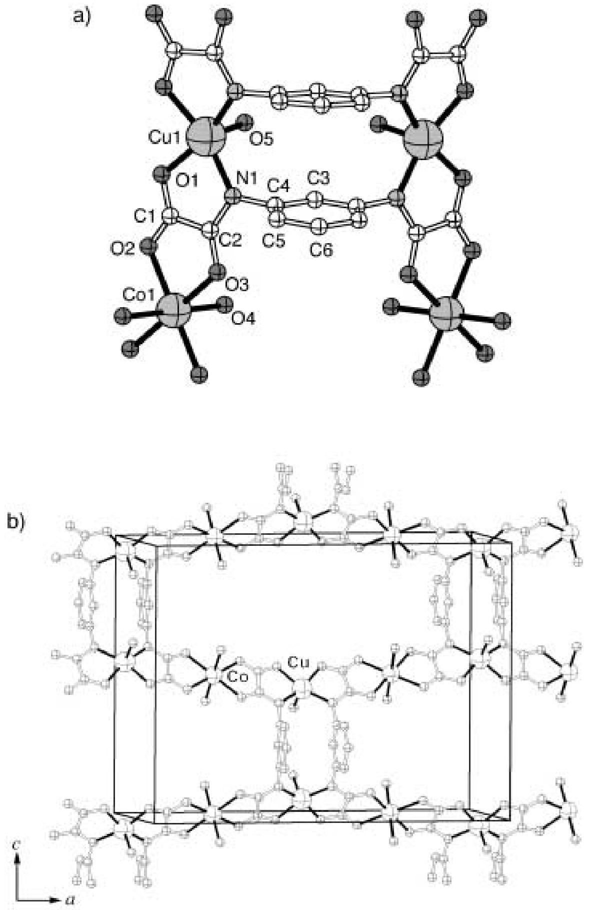

Figure 1. View of the structure of **1**. a) Detail of a Cu_2Co_2 unit emphasizing the atom labels and b) a simplified view of the content of the unit cell showing a layer.

Each brick is formed by four Co^{II} ions and six Cu^{II} ions (see Figure 1b). The Cu–Cu distance across the cyclophane moiety is 6.398 Å while the distance Cu–Cu in the middle of the brick is longer (10.683 Å). The length of each brick is equal to the *a* axis of the unit cell, namely 21.108 Å. The copper atoms are in a square pyramidal environment and the Co^{II} ions form a bis-chelate in a distorted octahedral geometry with two water molecules in *trans* positions. The aromatic rings almost face each other (dihedral mean angle of 8.1°; mean separation of 3.5 Å).

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Figure 2 shows the corrugated layers stacking along the crystallographic *b* axis. Each sheet packs above each other, corner to corner, in a perfect stack. The aromatic rings change the catenation direction in a zigzag fashion with an angle of 121.5°, nearly the expected for the *meta* substitution pattern of the benzene rings. The shortest metal–metal interlayer separations involve ions of the same nature: Cu−Cu = 5.111 and 5.133 Å; Co−Co = 4.848 Å. The distances between Cu−Co of different layers are 7.210 and 7.217 Å. Hydrogen bondings are also present between the layers. The shortest intermolecular contacts are between an oxygen atom (O4) of water molecule coordinated to the Co^{II} ion and an oxygen atom (O3) belonging to the oxamato group of an adjacent layer with a distance of 2.795 Å.

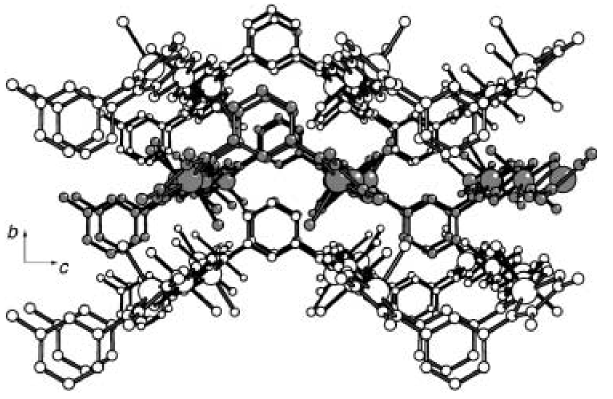

Figure 2. Perspective view of the stacking of corrugated sheets. The solvent molecules have been omitted for the sake of clarity.

The magnetic properties of **1** have been investigated in the 2–300 K temperature range by using a polycrystalline powder. The temperature dependence of the dc magnetic susceptibility is shown in Figure 3a in the form of the $\chi_{M}T$ versus T plot, χ_{M} being the molar magnetic susceptibility. At room temperature $\chi_{M}T$ is equal to 5.4 emu K mol^{-1}. This value is slightly below those expected for isolated Co^{II} and Cu^{II} ions in similar compounds which falls in the 5.5–7.5 emu K mol^{-1} range.[8] This indicates that strong AF (antiferromagnetic) coupling between Cu^{II} and Co^{II} ions, as found for similar oxamato ligands ($J_{\mathrm{Cu\text{–}Co}} \approx -30\ \mathrm{cm}^{-1)}$,[2] are operative at room temperature. $\chi_{M}T$ decreases further owing to this AF interaction passing through a minimum at 76 K ($\chi_{M}T = 4.0$ emu K mol^{-1}) and then increases owing to ferrimagnetic correlation within the chain. In addition, the presence of ferromagnetic coupling between the Cu^{II} ions ($J_{\mathrm{Cu\text{–}Cu}} \approx +17\ \mathrm{cm}^{-1}$)[6] enhances further the value of $\chi_{M}T$. Short-range 2D ferrimagnetic order is thus expected to be established.

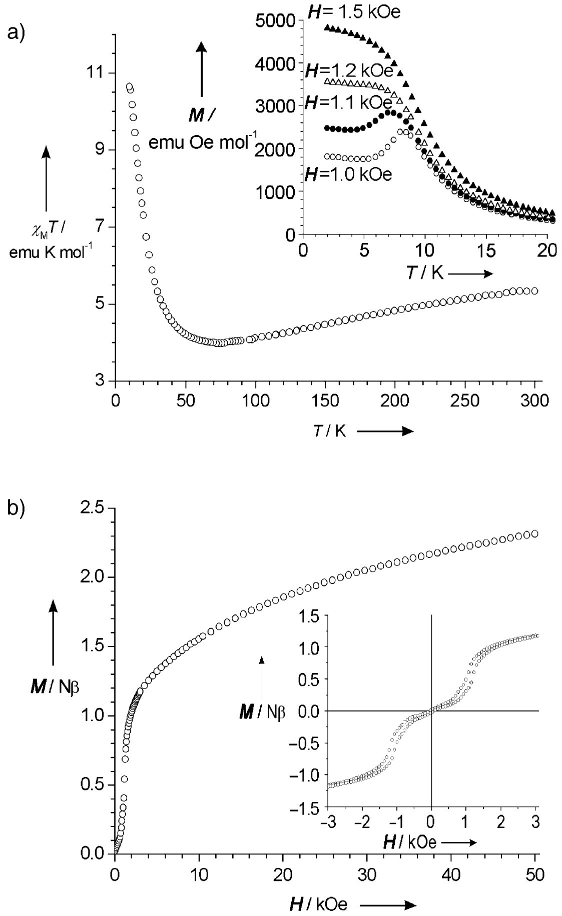

Figure 3. a) $\chi_{M}T$ versus T for the field strength $H = 5$ kOe. Inset: Magnetization (***M***) versus T at 1.0, 1.1, 1.2 and 1.5 kOe ; b) First Magnetization at 2 K. Inset: Hysteresis loop at 2 K.

The temperature dependence of the magnetization at various fields is shown in the inset of Figure 3a. For applied fields below 1.2 kOe, the field-cooled (FC) curves present a maximum at 8.5 K indicating that some interlayer antiferromagnetic interactions are operative. However, a magnetic field of 1.2 kOe is sufficient to overcome these weak interactions and the compound presents a field-induced transition from an antiferromagnetic to a ferromagnetic-like state.

The field dependence of the magnetization was also measured in the 2–10 K temperature range. In Figure 3b we show the 2 K isotherm in which it is clear that even with 50 kOe the saturation is not reached ($\boldsymbol{M} = 2.3\,N\beta$). At this temperature, only the doublet ground state of Co^{II} ions in the octahedral geometry is populated. An effective spin $S = 1/2$ and $g_{\parallel}$values between 6 and 8 is normally used (g is the g factor).[9] In this limit the expected saturation magnetization (per $\{Cu_2Co_2\}$ unit) is $2(g_{Co}S_{Co} - g_{Cu}S_{Cu}) = 4N\beta$. High-field measurements and single-crystal measurements should be carried out to explain this point.

The low-field magnetization presents a small butterfly-shaped hysteresis (inset of Figure 3b) with a metamagnetic-like transition around 1200 Oe, in agreement with the FC results (inset of Figure 3a). This value may be accounted by considering the weak interactions between neighboring planes (dipolar and through hydrogen bonds). We attribute this behavior to the reversal of ferrimagnetic sheets from antiparallel to parallel configuration. This reversal involves an increase of approximately 1 Bohr magneton/$\{Cu_2Co_2\}$ units.

The ac magnetic susceptibility presented in Figure 4 shows a frequency-independent peak of the real component at 9.5 K due to AF interactions discussed above and a frequency-dependent shoulder around 5 K. The imaginary component presents a maximum with a frequency dependence characterized by $\Delta\log(f)/\Delta T = 4.3$, which is reminiscent of spin-glass dynamics.[10]

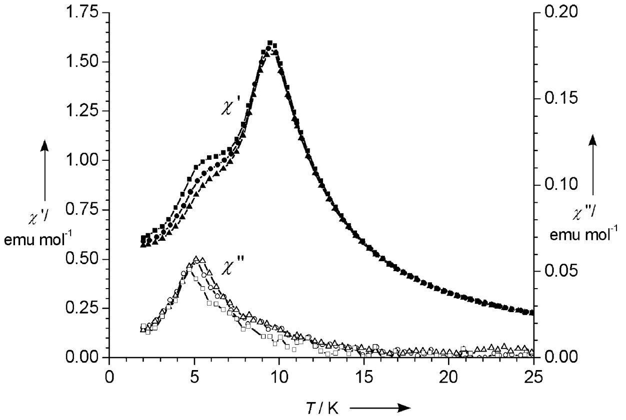

Figure 4. Temperature dependence of the in-phase, χ', and out-of-phase, χ'', ac magnetic susceptibilities for **1**, measured at 100 Hz (■), 1 kHz (●) and 5 kHz (▲) for χ', and 100 Hz (□), 1 kHz(○) and 5 kHz (△) for χ''. The solid lines joining the experimental points are to guide the eyes.

The origin of the observed small hysteresis, related to this slow relaxation is an interesting open problem observed in several molecule-based magnets[11] and should be further investigated. In our case the glassy behavior may be attributed to interacting magnetically correlated planar regions, which become progressively blocked as the temperature is lowered.

In conclusion, we have synthesized and characterized a new compound with a planar corrugated structure. Among the oxamato-ligand compounds, it is rare to obtain good single crystals with 2D architectures. In addition, this system presents a beautiful low-field metamagnetic-like transition and magnetic glassy behavior and finally to the best of our knowledge, **1** is the first example of brick-wall sheet structure to be reported on this field.

Experimental Section

Synthesis: The precursor $Na_4[Cu_2(mpba)_2]\cdot 10H_2O$ was synthesized as already described.[6] Green crystals of **1** were obtained by slow diffusion in an H tube: $Na_4[Cu_2(mpba)_2]\cdot 10H_2O$ (48.1 mg, 0.056 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (16.2 mg, 0.056 mmol) are placed in each side of the tube, then water was added slowly; after two months, at room temperature, the product was separated by filtration. Yield: 13 mg (25%). Elemental analyses calcd (%) for $C_{20}H_{32}Co_2Cu_2N_4O_{24}$ (957): C 25.09, H 3.34, N 5.85, Cu 13.27; Co 12.31; found C 24.30, H 3.25, N 5.59, Cu 12.70, Co 11.77. The presence of 12 molecules of H_2O was confirmed by thermogravimetric analysis.

Crystal data for $[Co_2Cu_2(mpba)_2(H_2O)_6]\cdot 6H_2O$ (**1**): $C_{20}H_{32}Co_2Cu_2N_4O_{24}$, $M_r = 957.44$, orthorhombic, space group *Cmcm*, $a = 21.108(5)$, $b = 9.697(5)$, $c = 16.102(5)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 3296.2$ Å^3, $T = 150.0$ K, $Z = 8$, $\rho_{calcd} = 1.930\ \text{g cm}^{-3}$, μ ($Mo_{K\alpha}$) = 0.71069 nm, 6181 unique reflections, and 1441 observed with $I > 2\sigma(I)$. Crystal size: $0.22 \times 0.10 \times 0.03$ mm^3. The structure was solved by direct methods by using SHELXS 97, and refined by the full-matrix least squares method on F^2 by using SHELXL 97.[12] The hydrogen atoms from the organic ligand were located from a difference synthesis and refined with an overall isotropic thermal parameter, while those from the water molecules were not found or calculated. Refinement of 127 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0414$ and $R_w = 0.0807$, with $S = 0.892$. CCDC-216906 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Magnetic measurements: The magnetic measurements have been studied in commercial Quantum Design PPMS system and Quantum Design SQUID MPMS instruments. The diamagnetism of the sample and sample holder were taken into account.

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