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Synthesis, Magnetic Properties, and STM Spectroscopy of Cobalt(II) Cubanes $[Co^{II}_4(Cl)_4(HL)_4]$**

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Dedicated to Professor Alfred X. Trautwein on the occasion of his 70th birthday

Abstract: Reaction of cobalt(II) chloride hexahydrate with N-substituted diethanolamines H_2L^{2-4} (**3**) in the presence of LiH in anhydrous THF leads under anaerobic conditions to the formation of three isostructural tetranuclear cobalt(II) complexes $[Co^{II}_4(Cl)_4(HL^{2-4})_4]$ (**4**) with a $[Co_4(\mu_3\text{-}O)_4]^{4+}$ cubane core. According to X-ray structural analyses, the complexes **4a**,**c** crystallize in the tetragonal space group $I4_1/a$, whereas for complex **4b** the tetragonal space group $P\bar{4}$ was found. In the solid state the orientation of the cubane cores and the formation of a 3D framework were controlled by the ligand substituents of the cobalt(II) cubanes **4**. This also allowed detailed magnetic investigations on single crystals. The analysis of the SQUID magnetic susceptibility data for **4a** gave intramolecular ferromagnetic couplings of the cobalt(II) ions ($J_1 \approx 20.4$ K, $J_2 \approx 7.6$ K), resulting in an $S=6$ ground-state multiplet. The anisotropy was found to be of the easy-axis type ($D = -1.55$ K) with a resulting anisotropy barrier of $\Delta \approx 55.8$ K. Two-dimensional electron-gas (2DEG) Hall magnetization measurements revealed that complex **4a** is a single-molecule magnet and shows hysteretic magnetization characteristics with typical temperature and sweep-rate dependencies below a blocking temperature of about 4.4 K. The hysteresis loops collapse at zero field owing to fast quantum tunneling of the magnetization (QTM). The structural and electronic properties of cobalt(II) cubane **4a**, deposited on a highly oriented pyrolytic graphite (HOPG) surface, were investigated by means of STM and current imaging tunneling spectroscopy (CITS) at RT and standard atmospheric pressure. In CITS measurements the rather large contrast found at the expected locations of the metal centers of the molecules indicated the presence of a strongly localized LUMO.

Keywords: cobalt · magnetic properties · N,O ligands · pi interactions · single-molecule magnets

Introduction

Research on molecular magnetism has been one of the most active areas in molecular inorganic chemistry since $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2HOAc$ $\{Mn_{12}\}$ was found to function as a molecular nanomagnet in 1993.[2] Single-molecule magnets (SMMs),[3] built up from paramagnetic transition metals and appropriate ligand systems, have attracted enormous attention due to their characteristic quantum behavior and possible technical application to data storage and quantum computation.[4] Essentially all SMMs exhibit slow magnetic relaxation when T approaches 0 K. This relaxation is caused by quantum tunneling of magnetization (QTM)[5] and one of the major goals is the design of future SMMs to control QTM for the desired applications.

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[**] Chelate Complexes, Part 41; for Part 40 see reference [1].

Polynuclear transition-metal complexes based on N-substituted diethanolamines[6,7] have attracted considerable attention recently owing to their diverse electrochemical and magnetic properties. In this context, we reported on the synthesis of neutral iron(III)-coronand $[Fe^{III}_6Cl_6(L^1)_6]$[8] and ferric star $[Fe^{III}\{Fe^{III}(L^1)_2\}_3]$ (**1**)[3l,9] (Figure 1) with iron(III)

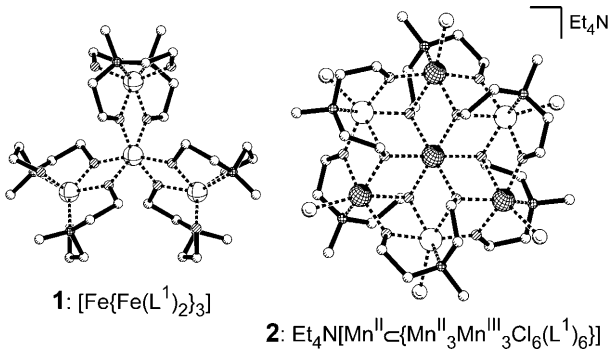
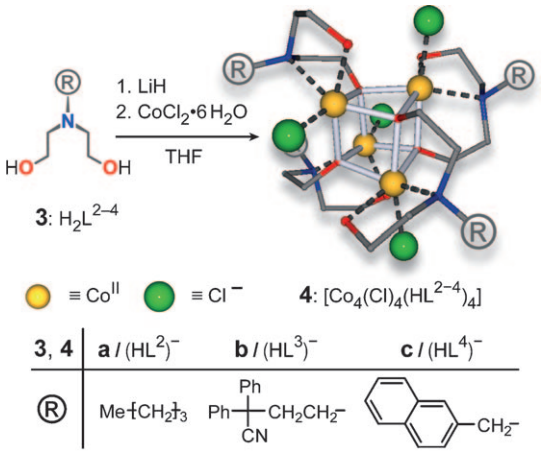


Figure 1. Molecular structure of ferric star **1** and mixed-valent manganese wheel **2** synthesized with *N*-methyldiethanolamine H_2L^1. H atoms are omitted for clarity. C: shaded; N: net; O: diagonal; Cl: segment; Fe^{3+}: cross; Mn^{2+}: globe; Mn^{3+}: void.

chloride and *N*-methyldiethanolamine H_2L^1 in THF, depending on the hydride and metal/ligand stoichiometry used. Furthermore, when bis(tetraethylammonium) tetrachloromanganate(II) was used as the metal source in the presence of H_2L^1 together with cesium carbonate, the metal-centered, heptanuclear, mixed-valent, six-membered manganese wheel $Et_4N[Mn^{II}\subset\{Mn^{II}_3Mn^{III}_3Cl_6(L^1)_6\}]$ (**2**) was isolated under aerobic conditions (Figure 1).[6d] Reports on diethanolamine-based cobalt complexes in the literature are scarce[10] and this prompted us to study another cobalt metal source in combination with this type of ligand, on which we report here.

Results and Discussion

Synthesis: As part of our effort to expand the coordination chemistry of N-substituted diethanolamine ligands, we report on the synthesis through self-assembly,[11] the structural characterization, and the magnetic behavior of novel cobalt(II) cubanes. Diethanolamines H_2L^{2-4} (**3**) were deprotonated with LiH as the base under anaerobic conditions in anhydrous THF for 1 h. The resulting white suspension was treated with cobalt(II) chloride hexahydrate (2 equiv) and was stirred for a further three days (Scheme 1). After extraction of the smeary crude reaction product with chlorinated hydrocarbons, filtration and evaporation to dryness afforded a purple solid. On the basis of elemental analysis, mass spectrometry, and IR spectroscopy, compounds **4** were identified as tetranuclear cobalt(II) complexes $[Co^{II}_4(Cl)_4(HL^{2-4})_4]$ with metal/ligand/chloride ratio (M/HL/Cl) = 1:1:1.



Scheme 1. Synthesis of tetranuclear cobalt(II) cubanes **4** from N-substituted diethanolamines H_2L^{2-4} (**3**) and $CoCl_2{\cdot}6H_2O$ in the presence of lithium hydride.

X-ray crystallography: To differentiate the cubane-like structure[12] of **4** from other possible tetranuclear metal arrangements[13] or even higher polynuclear cobalt(II) aggregates,[14] purple cuboids of **4**, obtained from suitable solvent systems, were unambiguously characterized by X-ray structure analysis (Table 1).[15,16] According to these analyses all three Co^{II} cubanes are in principle isostructural with slight differences in bond lengths, angles, and the orientation of their *N*-alkyl substituents. For that reason, only the structure of **4a** (Figure 2) is discussed in detail. Complex **4a** crystallizes in the tetragonal space group $I4_1/a$ with four molecules in the unit cell. It has a cubane $[Co_4(\mu_3\text{-}O)_4]^{4+}$ core with Co^{II} and oxygen atoms occupying alternate vertices. Thus, the molecule consists of two interpenetrating tetrahedra, one of four Co^{II} atoms and one of four μ_3-oxygen donors originating from the tritopic, tridentate diethanolateamine ligands. In addition to these three μ_3-oxygen donors, each Co^{II} ion is coordinated to one nitrogen atom, one ethanolamine OH group and a single chloride ion to complete a distorted octahedral coordination environment and charge compensation (Figure 2, bottom).

There are two types of Co–O bonds for each metal ion: one bond is rather elongated to 2.244 Å (Co–OH), whereas the other two bonds are shorter (Co–μ_3-O = 2.065 and 2.121 Å). The cube deviates from the ideal geometry and possesses a molecular C_2 axis, running through the center of the plane that is capped by the ligands (Figures 2 and 3). The internal cube angles (O-Co-O) at the metal vertices have an average value of 79.8°, whereas the comparable angles at the alkoxide corners (Co-O-Co) are much larger (mean value 98.8°). The Co···Co cube-face diagonals in complex **4a** (3.384, 3.107, and 3.113 Å), reflecting the different alkoxide-type Co–O bond lengths, are longer than the three other face diagonal vectors (μ_3-O–μ_3-O = 2.760, 2.760, and 2.594 Å). The bond lengths around the Co^{II} ions are typical of those found in octahedrally distorted high-spin cobalt(II) complexes with O/N/Cl ligation.[12e]

Table 1. Crystal data, data collection, and structure refinement details for the X-ray structure determinations for complexes **4**.

	4a	**4b**	**4c**
formula	$C_{32}H_{72}Cl_4Co_4N_4O_8$	$C_{80}H_{92}Cl_4Co_4N_8O_8 \cdot 2CHCl_3$	$C_{60}H_{72}Cl_4Co_4N_4O_8 \cdot 2.301CH_2Cl_2 \cdot 0.355Et_2O$
M_r [gmol^{-1}]	1018.46	1909.87	1576.45
crystal size [mm^3]	$0.30\times0.25\times0.25$	$0.32\times0.28\times0.23$	$0.31\times0.28\times0.24$
crystal system	tetragonal	tetragonal	tetragonal
space group	$I4_1/a$	$P\bar{4}$	$I4_1/a$
a [Å]	18.5102(5)	14.789(2)	15.442(2)
c [Å]	13.0739(3)	21.088(3)	58.625(3)
V [Å^3]	4479.5(2)	4612.3(11)	13979(3)
Z	4	2	8
ρ_{calcd} [Mg m^{-3}]	1.510	1.375	1.498
T [K]	173(2)	100(2)	100(2)
μ ($Mo_{K\alpha}$) [mm^{-1}]	1.741	1.051	1.317
F(000)	2112	1968	6492
θ range [°]	2.91–27.47	3.37–27.10	3.35–28.01
index ranges	$-23\le h\le23$	$-18\le h\le18$	$-20\le h\le18$
	$-16\le k\le16$	$-18\le k\le18$	$-20\le k\le20$
	$-14\le l\le16$	$-26\le l\le27$	$-77\le l\le71$
reflns collected	4174	65486	42384
independent reflns	2550	10132	8425
reflns observed [$I>2\sigma(I)$]	2272	7751	5451
max/min transmission	0.670/0.623	0.790/0.703	0.730/0.651
[R_{int}]	0.0132	0.0777	0.0478
data/parameters	2550/118	10132/554	8425/508
GoF on F^2	1.038	1.065	1.024
Flack parameter[a]	–	−0.005(15)	–
final R_1 [$I>2\sigma(I)$]	0.0268	0.0476	0.0428
wR_2 (all data)	0.0737	0.1179	0.1106
largest residuals [e Å^{-3}]	0.584/−0.681	1.071/−0.504	0.691/−0.556

[a] See Ref. [31].

The packing of the cobalt(II) cubanes **4** in the solid state is influenced by the nature of the sidearm in the ligands. In **4a**,**b**, the more-or-less aliphatic substituents of $(HL^{2,3})^-$ interdigitate and Co^{II} cubanes function as building bricks, thus creating 1D strands[6e] along the c axis of the unit cell with $\{Co^{II}_4\}$ cubane separations $d=13.07$ and 21.09 Å, respectively. This effect is more pronounced in the crystal structure of **4a** (Figure 3), because the aliphatic N substituents of $(HL^2)^-$ $(\mathbf{3a})^-$ do not contain any branches. Despite the presence of the terminal phenyl rings in $(HL^3)^-$ $(\mathbf{3b})^-$, no π–π interaction could be detected.

The striking feature in the crystal structure of cobalt(II) cubane **4c** is the formation of a 3D framework, caused by strong π–π interactions of 2-naphthyl groups in the sidearm of ligand $(HL^4)^-$ $(\mathbf{3c})^-$ (Figure 4). The $\{Co^{II}_4\}$ cubanes are aligned along the c axis (Figure 4) and the extension to a 3D network is propagated by tight intermolecular π–π interactions of all four naphthyl substituents in **4c** along the a and b axes (Figure 4). Nearly

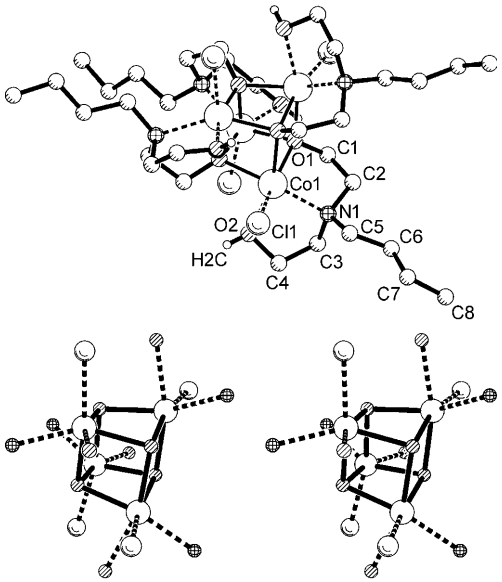


Figure 2. Top: PLUTON presentation of the molecular structure of complex **4a** with the numbering of the heavy atoms. Hydrogen atoms (except for OH) are omitted for clarity. Bottom: Stereo view (PLUTON presentation) of the central $[Co_4(\mu_3\text{-}O)_4(OH)_4(N)_4(Cl)_4]$ cubane core of **4a** highlighting the distorted octahedral coordination sphere at each Co^{II} ion. The $[Co_4(\mu_3\text{-}O)_4]$ fragment is indicated by solid lines. Carbon atoms of the alkyl chain and hydrogen atoms are omitted for clarity. Co: void; Cl: segment; O: diagonal; N: net.

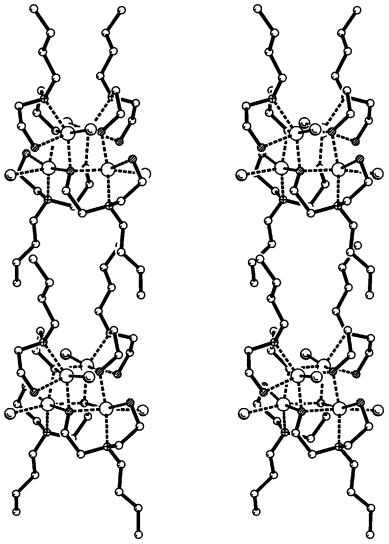


Figure 3. Stereo view (PLUTON presentation) of the crystal structure of **4a**, highlighting the structural motif interdigitation of the *n*-butyl N substituents of $(HL^2)^-$, giving rise to 1D strands and alignment of cobalt(II) cubanes along the c axis. Hydrogen atoms are omitted for clarity. Co: void; Cl: segment; O: diagonal; N: net; C: shaded.

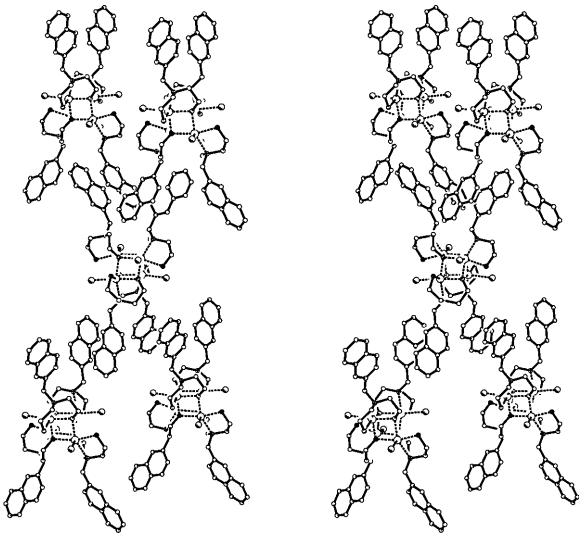


Figure 4. Stereo view (PLUTON presentation) of the crystal structure of **4c**, highlighting the four face-to-face π–π interactions of 2-naphthyl N substituents in each Co^{II} cubane (view along the *a*,*b* plane diagonal of the unit cell). Highly disordered solvate molecules and hydrogen atoms are omitted for clarity. Co: void; Cl: segment; O: diagonal; N: net; C: shaded.

perfectly parallel 2-naphthyl substituents show an intermolecular separation of $d=3.50$ Å with a slight lateral shift (centroid–centroid distance $d=3.87$ Å, typical distances for such face-to-face π–π interactions between the arene planes).[17]

Magnetic investigations: Naturally, SMMs have a negative magnetoanisotropy ($D<0$ K), which provides the ground spin state either S or $-S$. It is known that metal ions with d^n electrons ($n>5$) typically have $D>0$ K, which makes them less attractive candidates for building an SMM. Nevertheless, it could be possible to build a SMM with negative molecular magnetoanisotropy $D<0$ K even out of metal ions that have single-ion zero-field interactions with positive D. Among numerous SMMs investigated during recent decades, far fewer molecules with more than five d electrons have been reported for cobalt ions.[18] It has been shown that $[Co^{II}_4(hmp)_4(MeOH)_4Cl_4]$ possesses an $S=6$ ground spin state and has a negative magnetoanisotropy with $D=-4$ K.[18b] There was evidence of hysteretic behavior of magnetization for this complex, although the opening of rather irregular hysteresis loops (in other words, the coercive field) was found to be very small. The blocking temperature observed was as low as about 1.2 K; above this temperature the hysteretic magnetization behavior vanished completely. In this paper we show, on the basis of our magnetic investigations of this system, that cubane complexes $[Co^{II}_4(Cl)_4(HL^2)_4]$ (**4a**),[19] demonstrate even more prominent SMM-like properties.

The magnetic properties of **4a** were investigated by using a commercial MPMS SQUID system as well as a home-made micro-Hall-bar magnetometer.[20] We used the SQUID magnetometer for susceptibility measurements of a powder sample of **4a** at magnetic fields of 0.2, 0.5, 1, and 5 T in the 1.8–300 K range (Figure 5). The $\chi_{mol}T$ value of 12 K cm^3 mol^{-1} is compatible with four Co^{II} ions with spins $S=\frac{3}{2}$. This is also supported by the magnetization versus field measurements of the powder sample of **4a** (Figure 6).

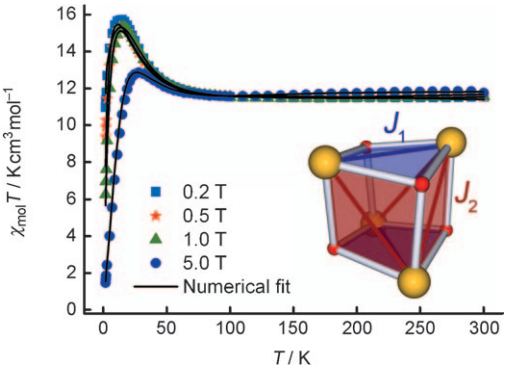


Figure 5. Molar susceptibility of **4a** versus temperature at different magnetic-field values. Inset: 3D coupling scheme with $J_1\approx20.4$ K (blue: top and bottom faces), $J_2\approx7.6$ K (red: side faces), and single anisotropy value $D'\approx59$ K.

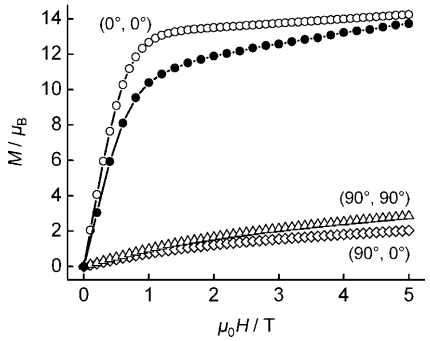


Figure 6. Magnetization versus applied magnetic field of **4a** measured at 1.8 K. The open symbols show data collected from the single-crystal measurements (○ = along the easy axis, and △,◇ = along the hard plane) and ● represents the powder sample data. The origin of the weak increase in the (0°,0°) measurement after 1 T is due to imperfect parallel alignment relative to the easy axis.

To investigate the magnetic anisotropy of **4a** further, we measured the angular resolved magnetization at the lowest possible temperature (1.8 K) of a single crystal of **4a** that had been placed in the MPMS SQUID magnetometer equipped with a rotator. The results of the measurements along the three principal axes are summarized in Figure 6. Magnetization along the easy axis, at angle (0°,0°), clearly demonstrates ferromagnetic-like behavior. It already becomes saturated at a magnetic field of around 1 T (Figure 6, ○). Magnetization within the hard plane, for example, along the orthogonal axes (90°,90°) and (90°,0°), shows a typical paramagnetic response (Figure 6, △ and ◇, respectively). The hard-plane magnetization does not reach saturation even at 5 T, at which it is approximately seven times

lower than that along the easy axis. This suggests a very strong easy-axis type of magnetic anisotropy for the system **4a**, which is a typical feature of SMMs.

In theory, only three ground-spin-state formations are possible for the molecule consisting of four Co^{II} ions with spins $S=\frac{3}{2}$: pure ferromagnetic coupling ($\uparrow\uparrow\uparrow\uparrow$) would give $S=6$, uncompensated antiferromagnetic coupling ($\uparrow\uparrow\uparrow\downarrow$) would give $S=3$, and compensated antiferromagnetic coupling ($\uparrow\uparrow\downarrow\downarrow$) can build $S=0$. It is known that a strong spin–orbit coupling exists for cobalt(II) ions.[21] To take these effects into account an effective Hamiltonian in the form of Equation (1)[18b,22] was used to fit the susceptibility data.

$$\mathscr{H}_{\mathrm{int}} = -J_1(S_1S_2 + S_3S_4) - J_2(S_1S_4 + S_2S_4 + S_2S_3 + S_3S_1) + D'(S_{1x}^2 + S_{2y}^2 + S_{3x}^2 + S_{4y}^2) \quad (1)$$

An additional single-ion anisotropy term was taken into account in addition to the Heisenberg term with the coupling scheme shown in the inset of Figure 5. The solid lines in Figure 5 show the best fit. For the exchange coupling constants we obtained $J_1 \approx 20.4$ K, $J_2 \approx 7.6$ K with $g \approx 2.2$, and D' ≈ 59 K for the axial single-ion zero-field splitting parameter. This leads to the conclusion that the ground-state spin of the system is $S=6$.

For further confirmation of the SMM properties of **4a**, we measured the single-crystal magnetization on a home-made micro-Hall-bar magnetometer, which consisted of several $10\times10\ \mu m^2$ Hall bars on top of which a micrometer-sized single crystal of **4a** was placed with the easy axis approximately parallel to the applied magnetic field. The measurements were performed at several temperatures in the 0.3–4.5 K range, and the magnetic-field sweeps were at rates of 25–400 $mT\,s^{-1}$. As can be seen from the results in Figure 7 for a sweep rate 50 $mT\,s^{-1}$, hysteresis loops (one of the typical features of an SMM) were evident for the complex **4a**.[23] The hysteresis disappeared only at 4.4 K (the blocking temperature), at which no opening of the curve was apparent. Note that the blocking temperature of the first Co^{II} cubane-based SMM was only around 1.2 K.[18b]

Figure 8 shows an ac susceptibility measurement on **4a**; the absence of the M versus H hysteresis loop opening at $H=0$ for this complex is caused by the presence of a relatively fast zero-field relaxation. Therefore, to minimize this effect, we measured the ac susceptibility under an applied dc field of 0.5 T, at which the opening of the hysteresis measured by the single-crystal Hall-bar magnetometer is maximal (Figure 7, center). The shape and the temperature–frequency dependence of the ac signal indicate the SMM nature of **4a**. Indeed, the out-of-phase signal χ'' shows a prominent peak, which shifts to lower temperatures on decreasing the ac driving frequency (Figure 8, bottom). This plot demonstrates that the out-of-phase signal for low frequencies does not go to zero at low temperatures but stays at a constant value. This can be considered as an indication for a high blocking temperature. The so-called Argand plot, that is, the dependence of χ'' as a function of χ', of the dispersion data (Figure 8, bottom, inset) gives an almost perfect semicircle. This is clear evidence for a relaxation process with a single-relaxation time τ_0.[24]

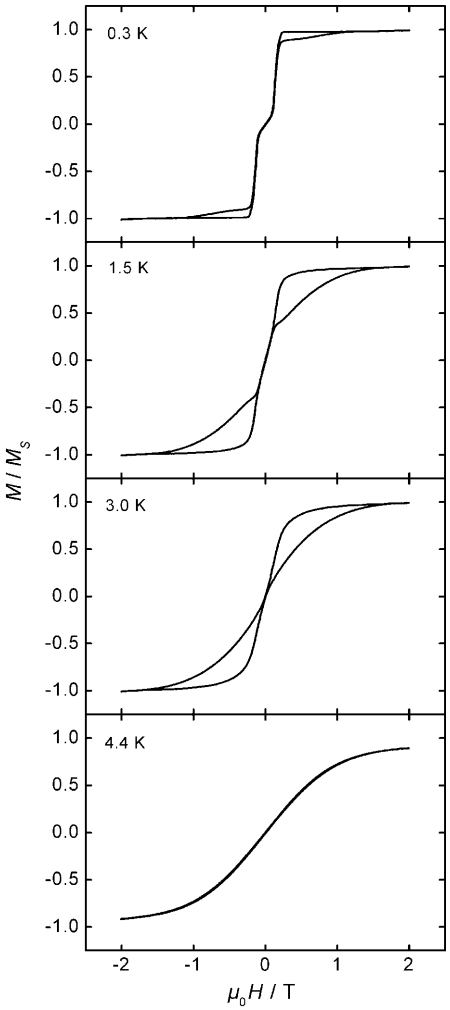


Figure 7. Magnetization of **4a**, normalized to the saturation magnetization M_s, versus H measured at different temperatures. Magnetic bistability is evident up to 4.4 K. Measurement sweep rate = 50 $mT\,s^{-1}$.

Therefore, from the Arrhenius plot in Figure 9 we estimated the relaxation time τ_0 to be $\approx 10^{-8}$ s and the anisotropy barrier Δ to be ≈ 55.8 K. The barrier height of **4a** is comparable with that of $\{Mn_{12}\}$ (approximately 62 K), whereas the pre-exponential factor τ_0 ($\approx 10^{-7}$ s) is faster by an order of magnitude.[24] The barrier height suggests that the uniaxial anisotropy parameter D is at least approximately -1.55 K ($\approx$32.3 GHz). We believe that the relaxation mechanism at 0.5 T is due to the direct process.[21]

Tunneling microscopy and spectroscopy: For many potential applications of molecular magnets, surface deposition and access to individual molecules are essential.[25] For our investigations we deposited a very low concentration of **4a** in a dichloromethane solution on a highly oriented pyrolytic graphite (HOPG) surface and investigated single molecules by STM using constant-current topography measurements

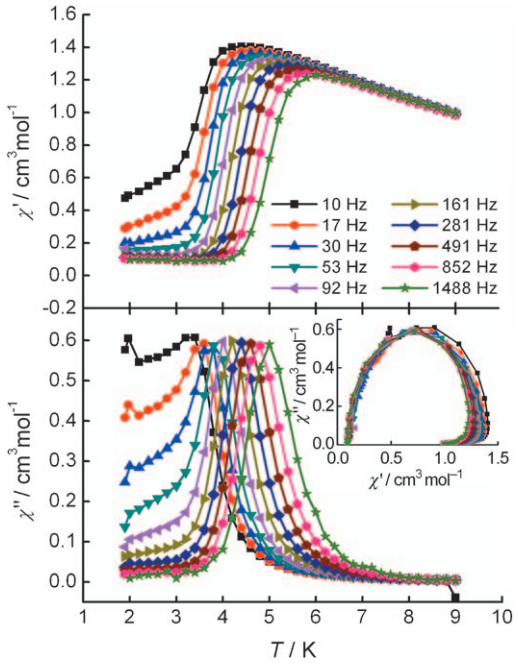


Figure 8. Frequency dependence of the in-phase χ' (top) and out-of-phase χ'' (bottom) ac susceptibility of **4a** from 1.8 to 9 K at 0.2 K intervals under a dc magnetic field of 0.5 T in the frequency interval 10–1488 Hz. The ac driving amplitude is 2.56 Oe. Bottom inset: The Argand plot for **4a**.

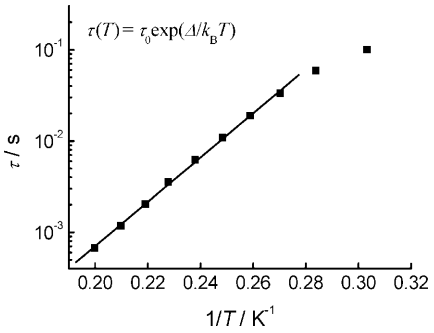


Figure 9. Magnetization relaxation time τ_0 versus T^{-1} for **4a** (dc field 0.5 T). The solid line corresponds to the Arrhenius law. $\tau_0 \approx 10^{-8}$ s, $\Delta \approx 55.8$ K.

and current-imaging tunneling spectroscopy (CITS). CITS records a full I versus V curve (tunneling spectrum) for every sample point, thus providing information about the density of states close to the Fermi energy. As already demonstrated,[26] direct addressing of metal centers in complex molecules is possible with this technique.

Sticking of the molecules to the graphite surface was rather poor. Molecules not directly attached to defects were often found to detach at high bias voltages or after repeated scanning. The blurry topographic image (Figure 10a) that was recorded during CITS measurements can be attributed to the very long and thin ligands that could not be resolved. The square of four bright spots nearly in the center of the current map at +800 mV bias in Figure 10b can be identified with the metal ions of the cubane motif. The measured distances of about 2 Å between the metal centers match the edge length of the cubane very well and, therefore, also the projected distance between the metal ions. Because the tunneling current is proportional to the integrated local density of states, a strong contrast, at positive bias voltages applied to the sample, indicates the presence of a LUMO strongly localized at the positions of the metal centers. The positions of the upper and lower metal centers could not be unambiguously ascertained.

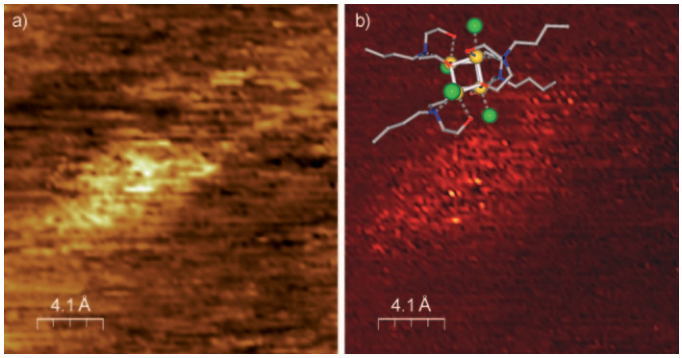


Figure 10. a) Topography recorded during CITS measurement; b) current image at +800 mV sample bias of the same measurement at RT and standard atmospheric pressure. Inset: true-to-scale representation of cubane **4a**, with one Co^{II} ion (gold) at the front face hidden by chloride (green). The setpoint for the tunneling current was 30 pA. During spectroscopy, the bias did not exceed ±800 mV for stability reasons.

We have, therefore, demonstrated that it is feasible to perform spectroscopy on a single molecule; however, poor sticking and the shape of the ligands limit the quality of the results. Investigation of cubanes **4b**,**c** with aromatic substituents in the ligand chain did not improve the situation.

Conclusion

Starting from differently N-substituted diethanolamines H_2L^{2-4} (**3**), we present here the synthesis of three tetranuclear cobalt(II) cubanes $[Co^{II}_4(Cl)_4(HL^{2-4})_4]$ (**4**) through self-organization. The structures of complexes **4** were solved by a combination of IR spectroscopy, mass spectrometry, elemental analysis, and single-crystal X-ray analysis. By selecting different ligand substitutions (branches, alkyl or aryl groups), we could control the orientation and alignment of **4** in the crystal structure (interdigitation and π–π interactions) and, moreover, this allowed detailed magnetic studies on single crystals. In the case of **4a**, the pure ferromagnetic couplings ($J_1 \approx 20.4$ K, $J_2 \approx 7.6$ K) of these cobalt(II) centers result in an $S = 6$ ground-state multiplet. Owing to an anisotropy of the easy-axis type, magnetization reversal at low temperatures is hindered by an anisotropy barrier $\Delta \approx 55.8$ K ($D = -1.55$ K) that is of the same order of magnitude as that of $\{Mn_{12}\}$. The cobalt(II) cubane **4a** is a single-molecule magnet and shows hysteretic magnetization characteristics below a blocking temperature of about 4.4 K;

however, unlike other SMMs, **4a** suffers from fast tunneling at $\mu_0 H = 0$ T. Furthermore, by tunneling-microscopic and spectroscopic measurements on HOPG at room temperature and standard atmospheric pressure, we were able to visualize the square topology of the cobalt centers in **4a** (2D projection), which is in good agreement with the dimensions determined by X-ray crystallography.

Experimental Section

General techniques: Unless stated otherwise, all manipulations were carried out under a dry dinitrogen atmosphere and the solvents used were purified and dried according to standard procedures. All the reagents (high-grade-purity materials), metal salts, and H_2L^2 (**3a**) employed were commercially available and used as supplied (Fluka, Aldrich, and Acros Organics). Compounds $H_2L^{3,4}$ (**3b**,**c**) were prepared as described earlier.[6f] Melting points were determined on a Wagner–Munz apparatus and are not corrected. IR spectra of the films or powder films were recorded on an ASI React IR-1000 spectrometer. FAB-MS spectra were recorded on a Micromass ZABSpec (Cs^+) spectrometer with *m*-nitrobenzyl alcohol as matrix. Elemental analyses were performed on a Carlo Erba EA1110 CHN instrument and on a Heraeus CHN-Mikroautomat.

Single-crystal X-ray structure analyses: Details of crystal data, data collection, and refinement are given in Table 1. X-ray data for **4a** were collected on a Nonius KappaCCD area detector, with $Mo_{K\alpha}$ radiation ($\lambda =$ 0.71073 Å). The structures were solved by direct methods with SHELXS-97[27] and refined with full-matrix least-squares against F^2 with the SHELXL-97 program system.[27] Lorentz, polarization, and absorption corrections[28] were applied. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were fixed in ideal positions (riding model) and were included without refinement and with fixed isotropic *U*.

Data for **4b**,**c** were collected on a Bruker-Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The structures were solved by direct methods, and full-matrix least-squares refinements were carried out on F^2 by using SHELXTL NT 6.12.[29] A semiempirical absorption correction based on multiple scans (SADABS)[30] was performed. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically positioned with their isotropic displacement parameters being tied to the equivalent isotropic displacement parameter of the corresponding carrier atom by a factor of either 1.2 U_{eq} or 1.5 U_{eq}. Disorder was found in structures **4b** and **4c**. Some restraints (for **4b**: DFIX, SADI, and ISOR; for **4c**: DFIX, SADI, and SIMU) were applied in the treatment of this disorder. In **4b**, two solvate molecules per formula unit could be located that were disordered on three sites; no hydrogen atoms were included for these disordered solvate molecules in the structure model. In **4c**, the co-crystallizing solvate molecules were all disordered and located on twofold crystallographic sites. In one case, a dichloromethane solvate molecule shares its crystallographic site with a diethyl ether molecule; no hydrogen atoms were included for these disordered solvate molecules in the structure model.

STM experiments: All measurements were carried out by using a home-built STM head and control system under ambient conditions. Before adding the solution onto the substrate surface, we ensured that the tunneling tip had a sufficiently high resolution by observing the atomic lattice of the HOPG surface. Different settings for the tunneling current and the bias voltage were used, ranging from 5 to 50 pA and ± 50 to ± 200 mV, respectively. The concentration of the solutions of **4** was 10^{-9} M. All images were recorded in constant-current mode and CITS was measured with the interrupted feedback technique. Different tips and samples were used to check for reproducibility and to ensure that no image artifacts were introduced by the tips or samples. The images were flattened to compensate for tilting of the substrate and scan-line distortions, and a Gaussian-filtered transform was employed to remove scanning noise in the STM images. The data were visualized and treated with WSxM Software.[32] The scan frequency was varied between 2 and 5 Hz. The resolution was 256×256 points for topography measurements and 128×128 points for CITS. We used Pt/Ir (90:10) tips mechanically cut from wires with a diameter of 0.25 mm.

General method for the synthesis of cobalt(II) cubanes: N-substituted diethanolamine ligands H_2L^{2-4} (**3**; 4 mmol) were added to a suspension of LiH (0.08 g, 10 mmol) in anhydrous THF (50 mL). The reaction mixture was stirred at 20 °C for 1 h, then $CoCl_2 \cdot 6H_2O$ (1.9 g, 8 mmol) was added in small portions. A purple precipitate was formed and the resulting slurry was stirred at 20 °C for three days. After the solvent had been removed under reduced pressure, the crude remaining precipitate was extracted with chloroform or dichloromethane. After filtration the solvent was again removed under reduced pressure to give **4** as purple solids.

*$[Co_4(Cl)_4(HL^2)_4]$ (**4a**)*: H_2L^2 (**3a**, 0.64 g); yield: 0.39 g (38%); purple cuboids from chloroform by vapor diffusion of diethyl ether (20 °C); m.p. > 236 °C (decomp); IR: $\tilde{\nu} = 3204$, 2949, 2876, 1073, 1011, 907, 730 cm^{-1}; MS: *m/z* (%): 1041 (18) $\{[Co_4Cl_4(HL^2)_4]+Na\}^+$, 1018 (3) $[Co_4Cl_4(HL^2)_4]^+$, 983 (6) $[Co_4Cl_3(HL^2)_4]^+$, 952 (19), 857 (10) $[Co_4Cl_3(HL^2)_4]^+$, 820 (56) $[Co_4Cl_3(HL^2)_3]^+$, 783 (20) $[Co_4Cl_2(HL^2)_3]^+$, 748 (100) $[Co_4Cl(HL^2)_3]^+$, 659 (44) $[Co_4Cl_3(HL^2)_2]^+$, 624 (65) $[Co_4Cl_2(HL^2)_2]^+$, 566 (26) $[Co_3Cl_2(HL^2)_2]^+$, 530 (97) $[Co_3Cl(HL^2)_2]^+$; elemental analysis calcd (%) for $C_{32}H_{72}Cl_4Co_4N_4O_8$ (1018.49): C 37.74, H 7.13, N 5.50; found: C 37.60, H 7.11, N 5.36.

*$[Co_4(Cl)_4(HL^3)_4]$ (**4b**)*: H_2L^3 (**3b**, 1.30 g); yield: 0.92 g (24%); purple tetrahedral prisms from chloroform by vapor diffusion of *n*-pentane (20 °C); m.p. > 200 °C (decomp); IR: $\tilde{\nu} = 3460$, 3022, 2876, 1462, 1088 cm^{-1}; MS: *m/z* (%): 1671 (5) $[CoCl(HL^3)_4]^+$, 1636 (30) $[Co_4Cl_3(HL^3)_4]^+$, 1312 (100) $[Co_4Cl_3(HL^3)_3]^+$, 1276 (85) $[Co_4Cl_2(HL^3)_3]^+$, 987 (20) $[Co_4Cl_3(HL^3)_2]^+$; elemental analysis calcd (%) for $C_{80}H_{92}Cl_4Co_4N_8O_8$ (1671.22): C 57.50, H 5.55, N 6.70; found: C 57.78, H 5.41, N 6.90.

*$[Co_4(Cl)_4(HL^4)_4]$ (**4c**)*: H_2L^4 (**3c**, 0.98 g); yield: 0.54 g (36%); purple irregular crystals from dichloromethane by vapor diffusion of diethyl ether (20 °C); m.p. > 220 °C (decomp); IR: $\tilde{\nu} = 3040$, 2988, 2896, 2842, 1086 cm^{-1}; MS: *m/z* (%): 1131 (40) $[Co_2Cl(HL^4)_4)]^+$, 1072 (20) $[Co_4Cl_3(HL^4)_3]^+$, 1000 (80) $[Co_4Cl(HL^4)_3]^+$, 698 (100) $[Co_3Cl(HL^4)_2]^+$; elemental analysis calcd (%) for $C_{60}H_{72}Cl_4Co_4N_4O_8$ (1354.79): C 53.19, H 5.36, N 4.14; found: C 53.26, H 5.28, N 4.22.

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