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Synthesis, structure and magnetism of a linear Cu–Cl–Cu entity found in $[(\mathrm{Cu}(tach\mathrm{H})(tach))_2(\mu\text{-Cl})]^{5+}$

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Abstract

Coordination of *cis*,*trans*-1,3,5-triaminocyclohexane (*tach*) to copper(II) at pH 11 in the presence of chloride ions results in the formation of a μ_2-chloro-linked dimer of Cu(*tach*)$_2$ units, which was characterized by single-crystal X-ray analysis, UV/Vis and IR spectroscopy, elemental analysis and magnetic measurements. Within the Cu(*tach*)$_2$ halves, the structurally rigid, chelating *tach* ligands are oriented *syn* to each other and each ligand binds to the copper center via two amino groups, forming a near-square planar coordination environment. Under the present reaction conditions, half of the *tach* ligands are protonated at the pendant, non-coordinated amino group. The Cu(*tach*)$_2$ halves are joined in a D_{2h}-symmetric fashion. This complex is of special interest as only few Cu$^{\mathrm{II}}$ dimers based on a single linear Cu–Cl–Cu motif are known. For the first time a magnetochemical analysis of such a species is provided that characterizes the weak antiferromagnetic intramolecular interactions between the two $s = 1/2$ Cu$^{\mathrm{II}}$ centers.

Keywords: Copper(II); Coordination compounds; Dinuclear complexes; Molecular magnetism

1. Introduction

One of the objectives of magnetochemistry is to establish structure–property correlations. To a simple degree this involves the association between an exchange constant between two coupled spin centers and the geometry of the superexchange pathway, i.e., the constituents that mediate the intramolecular magnetic exchange [1]. Although the exchange energy depends on the degree of mixing and overlap between the magnetic orbitals of the involved spin centers and the frontier orbitals of the exchange pathway [2–4], various attempts have been made to directly correlate bond lengths and angles with the exchange constants established for simple dinuclear complexes. In this context, many dimeric bis-halide or bis-oxo-bridged copper(II) complexes have been isolated and characterized in the past and models linking the Cu–Cu exchange constants with the Cu–X–Cu bond angles and Cu–X bond lengths have been established [5]. However, dimeric copper(II) complexes involving single monoatomic bridging ligands as exchange pathways have remained rare [6–10] and therefore are of special interest. We found that bulky, structurally rigid ligand systems are key in achieving such geometries, as their shapes allow both directing and limiting of the

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Table 1
Selected bond length (Å) and angles (°) for **1**

C(1)–N(1)	1.501(6)
C(5)–N(3)	1.501(6)
C(9)–N(5)	1.504(7)
C(11)–N(6)	1.478(7)
N(1)–Cu(1)	2.043(4)
N(2)–Cu(1)	2.058(5)
N(4)–Cu(1)	2.047(5)
N(5)–Cu(1)	2.047(4)
Cl(1)–Cu(1)	2.6458(7)
Cu(1)#1–Cl(1)–Cu(1)	180.00(1)
N(1)–Cu(1)–N(4)	88.39(18)
N(1)–Cu(1)–N(5)	174.93(17)
N(4)–Cu(1)–N(5)	92.19(18)
N(1)–Cu(1)–N(2)	91.92(17)
N(4)–Cu(1)–N(2)	179.45(18)
N(5)–Cu(1)–N(2)	87.54(17)
N(1)–Cu(1)–Cl(1)	91.03(12)
N(4)–Cu(1)–Cl(1)	88.53(13)
N(5)–Cu(1)–Cl(1)	94.03(13)
N(2)–Cu(1)–Cl(1)	91.02(12)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y+1$, $-z+2$.

M–X–M link by steric repulsion. One such ligand system we are focusing on is *cis*,*trans*-1,3,5-triaminocyclohexane (*tach*), a multifunctional synthon, that upon protonation can be used to engineer supramolecular solid-state structures. For instance we have recently reported a trinuclear cluster based upon *tach*, {(CuCl$_2$-(*tach*H))$_3$Cl}, which incorporates both coordinative and hydrogen bonds; this is because the *tach* ligand can accommodate multiple coordination modes, and its amino groups can act as both hydrogen bond donors and acceptors [11]. Under more basic conditions, the amino groups are not fully protonated and different types of discrete molecular species are formed. We herein report the reaction of *tach* and CuCl$_2$ which produces a dimeric complex of $s = 1/2$ Cu^{II} centers that features a single, linear Cu–Cl–Cu linking group (see Table 1).

2. Experimental

2.1. Materials, measurements, and calculations

cis,*trans*-1,3,5-Triaminocyclohexane (*tach*) was synthesized according to [12]; all other reagents were of analytical grade, purchased commercially and used as obtained. IR spectra were recorded on a Jasco FTIR-410 spectrometer using a *Golden Gate* single reflection diamond ATR setting for solid material. UV/VIS spectra were recorded on a Shimadzu UV-3101PC UV–VIS–NIR Scanning Spectrophotometer. Extended Hückel calculations were performed using the YAEHMOP 3.03 package [13]. The program's default parameters were employed.

2.2. Preparation of [(μ$_2$-chloro)-di-{syn-bis(cis,trans-1,3,5-triaminocyclohexane-κ^2-N,N′)-copper(II)}]-trichloride dihydrochloride (1)

A methanolic solution (15 ml) of copper(II) chloride anhydrous (58 mg, 0.43 mmol) was added to a solution of *tach* (110 mg, 0.85 mmol) in methanol (25 ml) giving an instant color change from colorless to dark blue. Reducing the volume to 2 ml and crystallization by diffusion of ether yielded dark blue crystals of **1** suitable for single crystal X-ray analysis. Amorphous material was obtained by addition of ether (10 ml) and filtration. Yield: 14 mg (0.02 mmol, 10% based on Cu) crystals, 54 mg (0.08 mmol, 37%) amorphous solid. M.p. 195 °C (dec.). The identity of **1** was confirmed by IR, UV/Vis spectroscopy and elemental analysis. IR spectrum (in cm^{-1}; s = strong, m = medium): 3217(s), 3116(s), 2920(m), 1609(s), 1558(s), 1458(s), 1346(s), 1165(s), 1119(m), 918(s). UV/Vis (MeOH) $\lambda(\varepsilon)$/nm (M^{-1} cm^{-1}): 247 (3235), 301 (1822, shoulder), 328 (1070, minimum), 355 (1518), 352 (442), 571 (106). MS (ES-TOF+) *m/z* (%) 491 (100, [Cu$_2$(*tach*)$_2$Cl$_3$]$^+$), 419 (5, [Cu$_2$(*tach*)$_2$Cl − 2H]$^+$), 356 (8, [Cu(*tach*)$_2$Cl]$^+$), 290 (32, [Cu$_2$(*tach*)Cl − 2H]$^+$), 227 (33, [Cu(*tach*)Cl]$^+$). Elemental analysis for $C_{24}H_{60}Cl_4Cu_2N_{12} \cdot 2HCl \cdot H_2O$ (M = 948.72 g mol^{-1}), found (expected) %: C, 33.36 (32.88); H, 8.09 (7.36); N, 18.88 (19.17).

2.3. Single-crystal X-ray structure

Crystallographic data was collected on a Rigaku R-axis image plate area detector (graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å) at 293 K on a needle-shaped single crystal with dimensions $0.3 \times 0.15 \times 0.03$ mm^3. The crystal system was found to be monoclinic, space group $P2_1/n$, $a = 8.726(2)$, $b = 18.500(4)$, $c = 13.341(3)$ Å, $\beta = 96.731(2)°$, $V = 2138.8(9)$ Å^3, $Z = 2$, $\rho_c = 1.473$ g cm^{-3}. A total of 9933 reflections were collected.

2.4. Magnetic measurements

Susceptibility data of a polycrystalline sample of **1** were recorded using a Quantum Design MPMS-5 SQUID magnetometer over the temperature range 2–290 K for various magnetic fields (0.1–5.0 T). All susceptibility data were corrected for diamagnetic and temperature-independent paramagnetic contributions ($\chi_{dia/TIP}(\mathbf{1}) = -410 \times 10^{-6}$ emu mol^{-1}). Magnetization measurements at 2.0 and 25 K indicated the presence of a small percentage (1.5%) of an $s = 1/2$ species, which was attributed to disassociated Cu(*tach*)$_2$ dimer halves. Corresponding $s = 1/2$-Brillouin function fits to the experimental field-dependence of the magnetization confirmed an isotropic *g* factor of 2.15. Intermolecular dipole–dipole interactions are negligible due to the large spacing between the dimeric units with closest Cu–Cu distances between neighboring $\{Cu_2Cl\}$ cations of 7.4 Å.

3. Results and discussion

3.1. Synthesis

The *tach* ligand system allows several coordination modes due to its two *cis* and one *trans* positioned amino groups that are connected to the rigid cyclohexane framework [11]. For a stoichiometric *tach*:metal cation ratio of 2:1, the preferred coordination is represented by a chelating binding mode in which the two *cis*-positioned amino groups assume an axial orientation with regard to the cyclohexane framework in its chair conformation, while the third amino group remains uncoordinated in an equatorial position. This coordination mode is targeted in the reaction of the *tach* base with copper(II) chloride in a water/methanol solution at unadjusted pH (11.0), which results in the formation of the partially protonated dinuclear copper(II) complex $[(Cu(tachH)(tach))_2(\mu\text{-}Cl)]^{5+} = \{Cu_2Cl\}^{5+}$ which was isolated as its chloride salt $[(Cu(tachH)(tach))_2(\mu\text{-}Cl)]Cl_5 \cdot H_2O$ (**1**).

3.2. Crystal structure

The single-crystal X-ray structure reveals D_{2h}-symmetric dinuclear Cu^{2+} complexes, consisting of two symmetry-equivalent halves. Two *tach* ligands coordinate to each copper center in a *syn* fashion via *bis*-bidentate coordination of two $–NH_2$ groups per *tach* molecule, with slightly elongated N–C bonds (1.501–1.511 Å) compared to the non-coordinated N–C bonds (1.478–1.500 Å). The cyclohexane ring planes of the two coordinated *tach* ligands are separated by 5.58(6) Å. This coordination mode results in a near-square-planar coordination environment around the copper(II) center (N1–N2 and N4–N5: 2.95 Å, N1–N4 and N2–N5: 2.85 Å) and the Cu position only slightly deviates from the coordination plane. Cu–N bond lengths range from 2.047 to 2.058 Å. Two of the resulting C_{2v}-symmetric $Cu(tach)_2$ units are then linked by a linear μ_2-bridging chloro ligand that completes the square pyramidal coordination geometry around the copper(II) centers (Fig. 1). On average, half of the non-coordinated, equatorially oriented amino residues of the *tach* ligands are protonated as shown by elemental analysis and single crystal X-ray diffraction, and **1** may be classified as a di-hydrochloride salt. As discussed above, the linear μ_2-chloro bridging motif between two copper(II) centers is rare and with a copper(II)-chloro distance of 2.646(2) Å, falls in the range observed for the few reported $Cu^{II}–Cl–Cu^{II}$-type complexes [6–10]. In the crystal lattice of **1**, the $\{Cu_2Cl\}$ units are stacked along the crystallographic *c* axis in a fishbone arrangement (Fig. 2), while being hexagonally arranged around the *a* axis (Fig. 3).

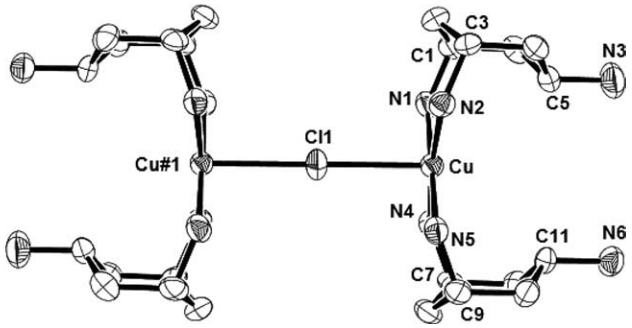

Fig. 1. Thermal ellipsoid (50%) ORTEP-3 representation of the $\{Cu_2Cl\}^{5+}$ cation in **1**, seen along one of the C_2 axes.

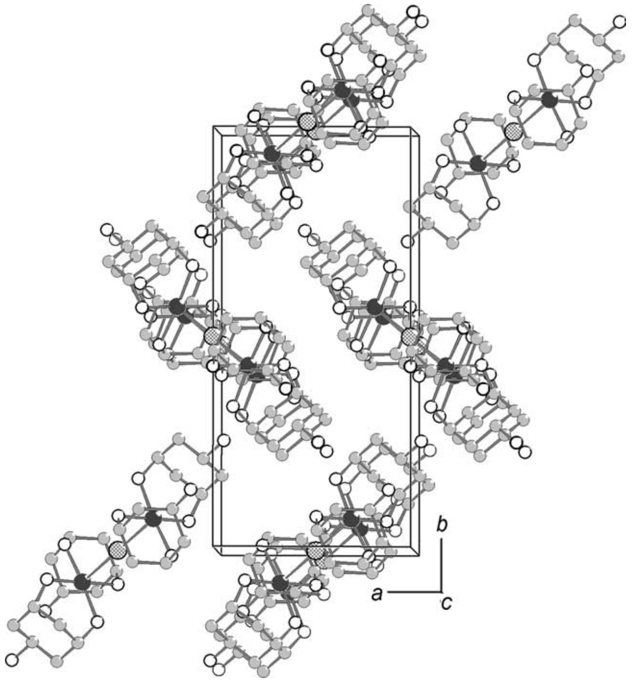

Fig. 2. Schematic representation of the $\{Cu_2Cl\}^{5+}$ dimers' packing in the crystal lattice of **1**, seen approximately along the crystallographic *c* axis and showing the dimensions of one unit cell (Cu: dark grey, Cl: hatched, C: grey, N: white spheres; counter ions and solvent molecules are omitted).

3.3. Magnetic properties

The measured magnetic susceptibility indicates weak antiferromagnetic coupling between the two $s = 1/2$ Cu^{II} centers and follows the Curie–Weiss law with a Weiss temperature of −0.17 K. The situation of a discrete dimer of $s = 1/2$ centers can be modeled using a simple Heisenberg Hamiltonian $\boldsymbol{H} = -J\mathbf{S}_A\mathbf{S}_B$, the eigenstates of which result in the Bleaney–Bowers equation. Here,

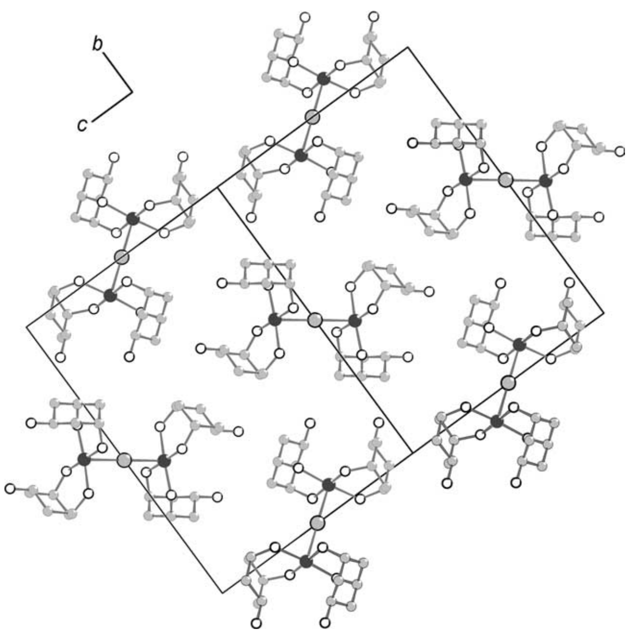

Fig. 3. Crystal packing of **1** along the crystallographic *a* axis. The $\{Cu_2Cl\}^{5+}$ cations are arranged hexagonally around the *a* axis (same codes as in Fig. 2).

a least-squares fit of the experimentally derived susceptibility data was performed using a modified Bleaney–Bowers equation

$$\chi = \frac{2N_A g^2 \mu_B^2}{kT(3 + e^{-J/kT})}(1 - \alpha) + \frac{N_A g^2 \mu_B^2}{2kT}\alpha,$$

where α represents the fraction of an $s = 1/2$ impurity, i.e., dissociated dimer halves. This yielded $J/k = -1.24$ K ($J = -0.86\ \text{cm}^{-1}$), an isotropic *g* value of $g_{iso} = 2.15$ (cmp. Section 2.4), and a paramagnetic impurity fraction of $\alpha = 1.5\%$ (Fig. 4). The least-squares fit yielded a correlation factor of 0.994. The relatively high percentage of uncoupled, paramagnetic dimer halves reflects the weak bonding via the Cu-μ-Cl–Cu bridge. The low value of the magnetic exchange can be explained by the axial Jahn–Teller distortion of the Cu^{II} coordination environment, with the nitrogen positions of the coordinating *tach* amino groups providing a strong crystal field and forming an equatorial basal plane to which the Cu–Cl bond vector is oriented perpendicular, defining the pyramidal apex. This causes the two unpaired electrons to reside in molecular orbitals of dominantly Cu(3d) $d_{x^2-y^2}$ character, interacting with the nitrogen ligands, while the (unoccupied) d_{z^2} atomic orbitals of the Cu centers that strongly interact with the Cl(2p) orbitals are only weakly mixed into the magnetic molecular orbitals, thereby limiting the magnetic exchange between the Cu centers. This ligand-field argument is also directly substantiated by simple Extended Hückel-MO calculations that verify the dominating atomic orbital contributions to the magnetically relevant frontier molecular orbitals (Fig. 5).

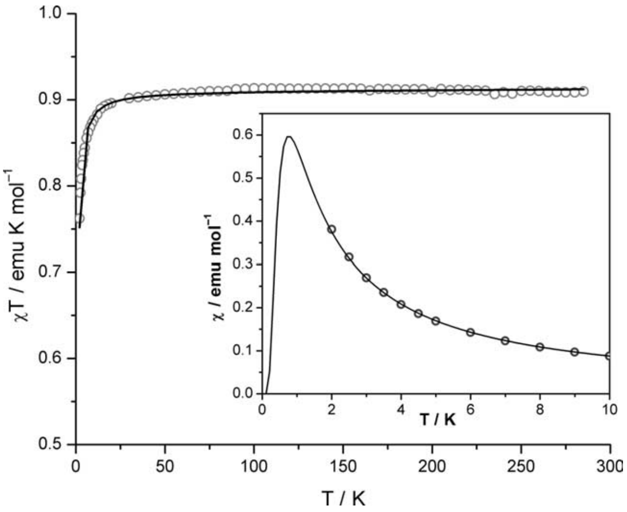

Fig. 4. Temperature dependence of χT for **1** at 0.1 T (experimental data: grey circles, data calculated from least-squares fit: solid line). Inset: the magnetic susceptibility at low temperatures displaying a maximum at 0.8 K (the experimental data was corrected for the determined paramagnetic impurity contribution, the simulated curve is correspondingly calculated for $\alpha = 0$, i.e., representing the pure dimer contribution).

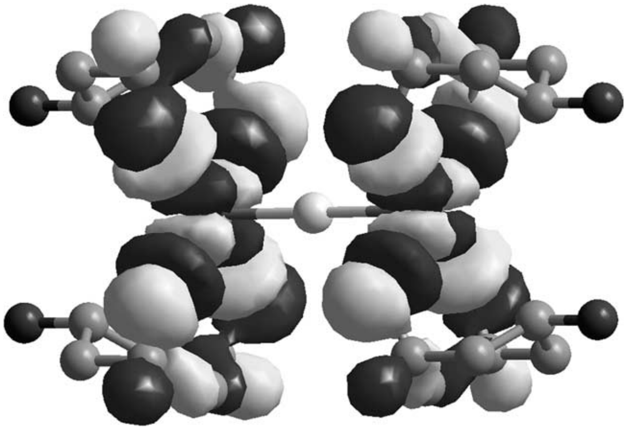

Fig. 5. An overlay representation of one of the two degenerated highest occupied molecular orbitals in the $\{Cu_2Cl\}^{5+}$ cations (omitting all H positions for clarity), illustrating the dominant $d_{x^2-y^2}$ character of these magnetic molecular orbitals.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 268-196. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.05.008.

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