A chiral C_3-symmetric hexanuclear triangular-prismatic copper(II) cluster derived from a highly modular dipeptidic *N*,*N'*-terephthaloyl-bis(*S*-aminocarboxylato) ligand

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Experimental

NMR spectra were collected on a Bruker Avance DPX200 with calibration against the solvent signal (DMSO-d_6 ^{1}H NMR 2.52 ppm, ^{13}C NMR 39.5 ppm). IR spectra were measured on a Bruker Optik IFS25 as KBr pellets (1 mg sample/100 mg KBr) from 4000 to 400 cm^{-1}. UV/VIS spectra were measured on a Jasco V-570 UV/VIS/NIR-Spectrophotometer. The optical rotation was measured with a Perkin Elmer 241 Polarimeter. The susceptibility measurements were carried out with a MPMS 7 from Quantum Design applying a magnetic field of 1T. All samples of dried **1** were prepared and handled under argon atmosphere prior to the magnetic measurements.

N,*N'*-terephthaloyl-bis(L-phenylalanine), TBPheH$_2$:

A solution of L-phenylalanine (3.47 g, 21.0 mmol) and sodium hydroxide (2.00 g, 50.0 mmol) in water (20 ml) was cooled in a ice bath. A solution of terephthaloyl chloride (2.03 g, 10.0 mmol) in absolute toluene was added so that the temperature remained below 10 °C. After complete addition the mixture was stirred overnight at room temperature. Then, the aqueous phase was separated and acidified with concentrated hydrochloric acid. The precipitate was separated by filtration, washed with deionized water and recrystallized from dilute acetic acid to give colorless crystals (yield 3.89 g, 79 %). $C_{26}H_{24}N_2O_6 \cdot 2H_2O$ (492.51): calc. C 62.89, H 5.68, N 5.64; found C 62.63, H 5.64, N 5.62 %. M.p.: > 200 °C. IR: ν_{max}/cm^{-1}: 3444m, 3295m, 3155m, 3061m, 2944m, 2577m, 1968w, 1741s, 1618s, 1551s, 1496m, 1455, 1443m, 1358m, 1325m, 1271m, 1249m, 1225m, 1186m, 1028m, 983w, 911w, 872m, 847m, 741m, 695m, 609m, 496w, 437w. ^{1}H NMR: δ(DMSO-d_6): 12.4 (br.s, 2H, -CO_2H), 8.72 (d, 2H, -NH, ^3J = 8.1 Hz), 7.83 (s, 4H, $H_{\text{-C6H4-}}$), 7.36 – 7.16 (m, 10H, H_{phenyl}), 4.64 (m, 2H, -CH-, ^3J = 8.1 Hz), 3.28 – 3.01 (m, 4H, -CH_2-). ^{13}C NMR: δ(DMSO-d_6): 173.2 (-CO_2H), 166.0 (C=O), 138.4 (ipso-C_{phenyl}), 136.7 (ipso-$C_{\text{-C6H4-}}$), 129.3 (m-C_{phenyl}), 128.5 (o-C_{phenyl}), 127.6 ($C_{\text{-C6H4-}}$), 126.7 (p-C), 54.5 (-CH-), 36.7 (-CH_2-). UV/VIS: λ_{max} [nm] (ε [l·mol^{-1}·cm^{-1}]) (in MeOH, $c = 2.4 \cdot 10^{-3}$ mol/l): 266 (3840). $[\alpha]^{23}_{D}$(methanol): –70 ° (c = 10 mg/ml).

$[Cu_2(\mu_4\text{-TBPhe-}\kappa O{:}\kappa O'{:}\kappa O''{:}\kappa O''')_2(EtOH)(H_2O)]_3 \cdot \sim 28(H_2O/0.33EtOH)$ (1)

A solution of copper(II) acetate (20.0 mg, 0.05 mmol, 399.3 g/mol) and TBPheH_2 (49.3 mg, 0.1 mmol) in ethanol (20 ml) was stored at room temperature. The solvent was allowed to evaporate slowly. After several days green needle crystals formed which were suitable for single crystal X-ray analysis (yield 46.7 mg, 82 % based on TBPheH_2). Compound **1** is soluble in methanol and dimethyl sulfoxide. $C_{162}H_{156}Cu_6N_{12}O_{42}$ (3324.35) + 10H_2O (3504.50): calcd. C 55.52, H 5.06, N 4.79; +15H_2O (3594.57): calcd. C 54.13, H 5.22, N 4.68; found C 55.35, H 5.23, N 4.67 %. IR: ν_{max}/cm^{-1}: 3321m, 3063w, 3029w, 1703m, 1636s, 1541m, 1497m, 1416m, 1364m, 1288m, 1230w, 1161w, 1092w, 1031w, 864w, 735w, 701m, 669w, 622w, 572w, 500w. UV/VIS: λ_{max} [nm] (ε [l·mol^{-1}·cm^{-1}]) (in MeOH, $c = 4 \cdot 10^{-4}$ mol/l): 266 (5100, shoulder), 298 (5710), 707 (1270). $[\alpha]^{23}_{D}$(methanol): +63 ° (c = 1 mg/ml).

Structure determination and refinement

Data collection: Bruker AXS or APEXII with CCD area-detectors, temperature –70 °C, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, ω-scans. Data collection and cell refinement with SMART[1], data reduction with SAINT,[1] experimental absorption correction with SADABS.[2] *Structure analysis and refinement*: The structure was solved by direct methods (SHELXS-97); refinement by full-matrix least squares on F^2 using the SHELXL-97 program suite.[3] All non-hydrogen positions were found and refined with anisotropic temperature factors. On average, about one third of the aqua ligand on Cu2 may be replaced by an ethanol ligand, since a carbon atom can be refined with ~33% occupancy in the vicinity of 1.5 Å to the Cu-coordinated oxygen atom. Atom C55 was found within C-O bonding distance to O14, hence was refined isotropically as a methylene carbon atom of a C_2H_5OH ligand; the CH_3 group was within the O atoms of the disordered crystal water.

The benzyl group C30-C35 which is tangentially oriented away from the triangle is more disordered or mobile than the others, as evidenced by high temperature factors and large thermal ellipsoids of its carbon atoms.

The noted intracrystal homochirality from the tangential orientation of the benzyl group C30-C35 and the canting of the terephthaloyl aryl groups in the trigonal prism may be a crystallographic space-group induced artefact. Domains of the hexanuclear clusters may exist in the other diastereomer and thereby contribute to crystal imperfections. Two of the crystals were found to diffract to 2θ-angles not higher than ~40° which is an indication of crystal imperfections.

The electron density in the interior of the trigonal prism cannot be clearly localized, that is, the solvent of crystallization is highly disordered. It cannot be distinguished between water or ethanol molecules. The residual electron density within one cluster corresponds to about 28 oxygen atoms or the equivalent of C and O atoms of ethanol (at the most about 9 EtOH molecules). The occupancies of all 27 crystal water O atoms were refined simultaneously until the very last refinement cycles. Occupancies refined to between 0.06317 and 0.67544 with an average of 0.34568 for the 27 O atoms in the asymmetric unit. For $Z = 3$ this gives 0.34568 x 27 x 3 = 28 crystal water O atoms per formula unit or the equivalent of C_2H_5OH atoms. Thus, this electron density is disordered (even at –70 °C) over more than 80 positions within the space surrounded by the triangular prism and represents another source of crystal imperfection.

The 27 identified O atom positions in the asymmetric unit were refined isotropically with "anti-bumping" restraints, BUMP in SHELXL. If the sum of occupancies of the two atoms is less than 1.1, no restraint is generated. The short Inter D···A contacts (< 2.5 Å) between crystal water O atoms which are still listed by CheckCif have to viewed as a *time-averaged* disordered water structure. This disorder is also a manifestation of high mobility and dynamic behavior among the crystal solvent molecules. At a given moment only two out of three of the O atoms will really be present on average at their position because of the averaged 0.34568 occupancy. Hence, if one half to two thirds of the refined O atoms are removed, such that the remaining O···O contacts are larger then 2.7-2.8 Å, these remaining O atom positions would then represent a real picture of the hydrogen-bonded crystal water phase at this moment.

Hydrogen atoms were placed at calculated positions with an appropriate riding model (AFIX 43 for aromatic CH and amide NH, 13 for CH, 23 for CH_2, 83 for ethanol OH, 3 for OH_2 and

137 for CH_3) and an isotropic temperature factor of Ueq(H) = 1.2 Uiso(CH, NH, CH_2) or 1.5 Uiso(CH_3, OH_2); further details in Table 1. Graphics were drawn DIAMOND.[4]

Table 1 Crystal data and structure refinement for **1**

Compound	**1**
Empirical formula	$C_{163}H_{156}Cu_6N_{12}O_{70}$ [e,f)]
M/g mol^{-1}	3784.24 [f)]
Crystal size/mm	0.26 × 0.07 × 0.06
θ range/°	1.77 – 25.70
h; k; l range	–48, 47; –43, 48; ± 12
Crystal system	trigonal
Space group	$R3$
a/Å	39.7978(3)
b/Å	39.7978(3)
c/Å	10.1735(2)
α/°	90.00
β/°	90.00
γ/°	120.00
V/Å^3	13954.7(3)
Z	3
D_{calc}/g cm^{-3}	1.351
F (000)	5856 [f)]
μ/mm^{-1}	0.765
Max/min transmission	0.9527/0.8237
Reflections collected	46114
Independent reflections	11811 [R_{int} = 0.1351]
Obs. reflect. [$I > 2\sigma(I)$]	7411
Parameters refined	766
Max./min. $\Delta\rho$ [a)] /e Å^{-3}	0.382/–0.368
R_1/wR_2 [$I > 2\sigma(I)$] [b)]	0.0579/0.0952
R_1/wR_2 (all reflect.) [b)]	0.1179/0.1140
Goodness-of-fit on F^2 [c)]	0.980
Flack parameter 5	0.011(12)
Weight. scheme w; a/b [d)]	0.0352/0.0000

[a)] Largest difference peak and hole. – [b)] $R_1 = [\Sigma(\| F_o | - | F_c \|)/\Sigma\ | F_o |]$; $wR_2 = [\Sigma\ [w(F_o^2 - F_c^2)^2]\ /\Sigma[w(F_o^{\ 2})^2]]^{1/2}$. – [c)] Goodness-of-fit = $[\Sigma\ [w(F_o^2 - F_c^2)^2]\ /(n - p)]^{1/2}$. – [d)] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2$ or $0) + 2F_c^2)/3$. – [e)] Hydrogen atoms on crystal water or crystal ethanol were neither found nor calculated. – [f)] About 56 H atoms not included.

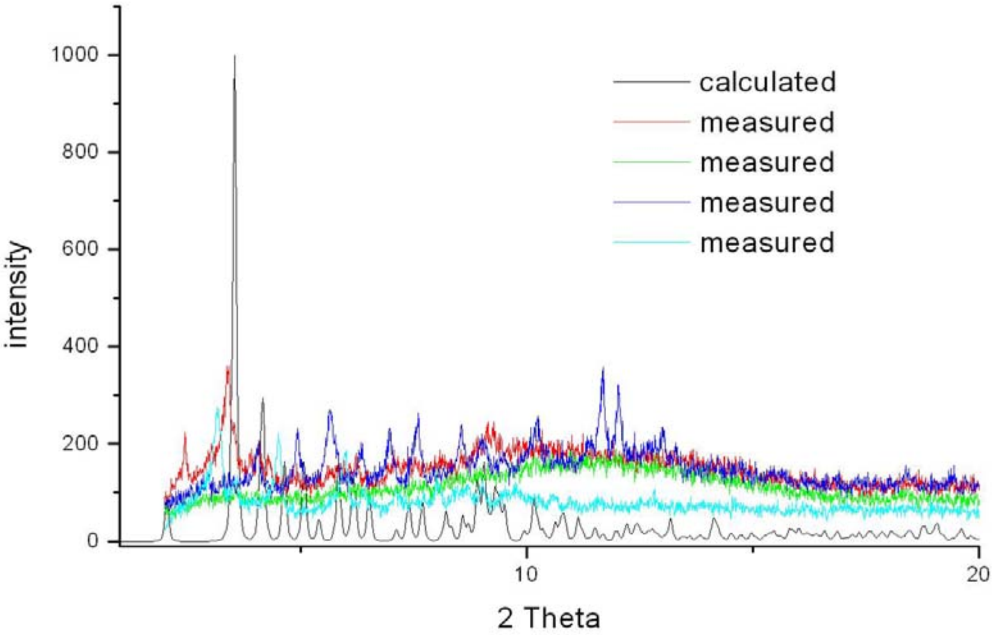

Fig. 1 X-ray powder diffractograms. Black curve is simulated from single-crystal X-ray data of [Cu_2(μ_4-TBPhe-κ*O*:κ*O′*:κ*O″*:κ*O‴*)$_2$(EtOH)(H_2O)]$_3$ · ~28(H_2O/0.33EtOH) (**1**). Other curves are measured on various samples of **1** after air-drying. X-ray powder diffractograms were collected on a Stoe STADI P with Debye-Scherrer geometry, Mo-Kα radiation (λ = 0.7093 Å), a Ge(111) monochromator and the samples in glass capillaries on a rotating probe head.

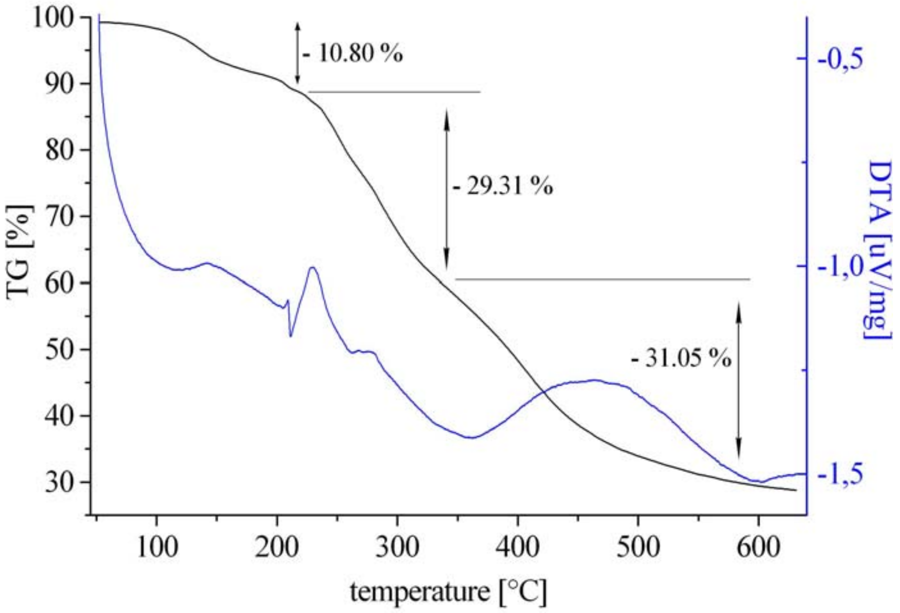

Fig. 2 Thermogravimetric analysis of [Cu_2(μ_4-TBPhe-κ*O*:κ*O′*:κ*O″*:κ*O‴*)$_2$(EtOH)(H_2O)]$_3$ · ~28(H_2O/0.33EtOH) (**1**) under nitrogen after a vacuum cycle. Thermogravimetric analyses were carried out on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen (heating rate: 10 K min^{-1}, flow-rate: 75 ml/min) after a vacuum cycle.

Table 1 Hydrogen bonding interactions between the amine and carbonyl functions in $[Cu_2(\mu_4\text{-TBPhe-}\kappa O{:}\kappa O'{:}\kappa O''{:}\kappa O''')_2(EtOH)(H_2O)]_3 \cdot {\sim}28(H_2O/0.33EtOH)$ (**1**) [a]

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
intra-hexanuclear cluster				
N1–H1···O10^{3}	0.87	2.14	2.970(2)	158
N3–H3···O4^{2}	0.87	2.21	3.016(2)	155
inter-hexanuclear cluster				
N2–H2A···O9$^{3'}$	0.87	2.13	2.980(2)	166
N4–H4B···O3$^{2'}$	0.87	2.20	2.994(2)	152

[a] D = Donor, A = acceptor. For found and refined atoms the standard deviations are given. Symmetry relation: 2 = *–y*, 1+*x–y*, *z*; 2' = *–y*, 1+*x–y*, –1+*z*, 3 = –1–*x*+*y*, –*x*, *z*; 3' = –1–*x*+*y*, –*x*, 1+*z*

Table 2 Analysis of C–H···Cg Interactions (H···Cg < 3.0 Å, Cg = Centroid)

C–H···Cg(J) [symm. rel.]	H···Cg [Å]	C–H···Cg [°]	C···Cg [Å]
C6–H6···Cg(6) [*a*] [3456]	2.89	144	3.695(2)
C34–H34···Cg(4) [*b*] [6454]	2.75	140	3.518

[a] Cg(6) = ring(C46-47-48-49-50-51), symmetry relation [3456] = 1–X+Y, –X, 1+Z
[b] Cg(4) = ring (C30-C31-32-33-34-35), symmetry relation [6454] = 2/3–X+Y, 2/3–X, –1/3+Z

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