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A Homochiral 2D Copper(II) Coordination Framework

John Fielden,[a] Kyle Quasdorf,[a] Arkady Ellern,[b] and Paul Kögerler*[a,c]

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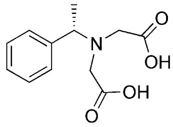
Reaction of copper(II) salts with (*S*)-phenylethylaminodiacetate [(*S*)-peadaa] results in the 2D coordination network (*S*)-$[Cu(peadaa)]_n$ (space group $P2_1$), which displays an unusual Cu···Cu connectivity mode. Solid-state circular dichroism (CD) indicates a strong interaction between the ligand chiral centre and the metal centres, whereas magnetic measurements show both antiferromagnetic coupling and strong ligand field effects.

Introduction

Chiral coordination compounds are interesting both for their fundamental properties and potential applications in optical, electro-optical and magneto-optical communication and data processing technologies.[1–5] In addition to their well-known ferroelectric[4] and nonlinear optical properties,[5] such systems can show unusual magneto-optical cross effects such as magnetochiral dichroism.[6] This has led to an increasing interest in chiral magnetic materials with asymmetry being introduced by enantiomerically pure organic ligands including nitroxides,[1] amines,[2,7,8] amino acids,[3,5] carboxylates[9] and hydroxamates.[10] In the solid state, a common orientation of ligand chiral centres should enhance the optical activity of such materials. Consequently, we are interested in coordination networks based on reasonably rigid, chiral ligands capable of directing the assembly of extended framework structures.

With this in mind, we synthesised the novel, chiral amino bis(carboxylate) ligand (*S*)-phenylethylamino-*N*,*N*-diacetic acid [(*S*)-peadaa, Scheme 1]. Coordination to a metal centre through the N,O,O-tris-chelating unit locks the rotation of the carboxylate arms, and the rigid (*S*)-[M(peadaa)] unit presents two orthogonal carboxylate chelating groups to allow connection into a network. Furthermore, the rigidity and steric demand of the ligand phenyl group is likely to help impose the chirality of the ligand over the entire structure. Herein, we present preliminary studies of the coordination chemistry of this ligand with Cu^{II}, resulting in the synthesis of a thermally stable, homochiral 4^4 copper(II) network. This structure shows a unique pattern of long and short Cu···Cu connections, and through its CD spectrum, the peadaa ligand demonstrates its ability to transfer chirality to coordinated metal centres.



Scheme 1. The (*S*)-peadaa ligand in its protonated form, (*S*)-H_2peadaa.

Results and Discussion

Synthesis of the proligand (*S*)-$Na_{0.4}H_{1.6}$peadaa (**1**) can be achieved in high yields (90%) by reaction of the parent amine (*S*)-phenylethylamine with iodoacetic acid and NaOH in water. The coordination network (*S*)-$[Cu(peadaa)]_n$ (**2**) was accessed as a microcrystalline material in 29% yield by aqueous reaction of copper(II) nitrate with an equimolar amount of **1** and 0.5 equivalents of KOH under hydrothermal conditions. Small single crystals suitable for X-ray diffraction were obtained in a lower yield (20%) by reaction under analogous conditions without base.[11] The synthesis of **2** was achieved in comparable yields through the reaction with copper(II) perchlorate at room temperature, indicating that a preferred coordination mode exists in **2**. In addition to single-crystal X-ray diffraction, compound **2** was characterised by XRPD, elemental analysis, TGA, FTIR, solid state UV and CD and magnetic measurements.

The copper centre in **2** adopts a highly distorted octahedral geometry, with an (*S*)-peadaa ligand binding in a *mer* fashion to the equatorial coordination sites with its single N and two carboxylate O donors (Figure 1). The other three coordination sites allow interlinking of the (*S*)-[Cu(peadaa)] monomers into the network: the remaining equatorial position and one axial site are chelated by a carboxylate group from one adjacent monomer, whereas the second axial site

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[a] Ames Laboratory, Iowa State University,
Ames, IA 50011, USA
[b] Department of Chemistry, Iowa State University,
Ames, IA 50011, USA
[c] Institut für Anorganische Chemie, RWTH Aachen University,
52074 Aachen, Germany
E-mail: paul.koegerler@ac.rwth-aachen.de

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is occupied by the *exo* oxygen atom from another. Copper bond lengths indicate considerable Jahn–Teller distortion; the Cu–O distances in the equatorial plane average 1.965(3) Å, the equatorial Cu–N distance is 2.053(3) Å, and the two elongated, markedly different axial Cu–O distances are 2.208(3) and 2.686(3) Å. Bond angles also deviate substantially from 90°, varying between 53.72(8) and 111.73(12)°. The noncentrosymmetry of the metal environment is also indicated by the considerable displacement (ca. 0.4 Å) of the Cu centre from the centroid described by the six donor atoms.

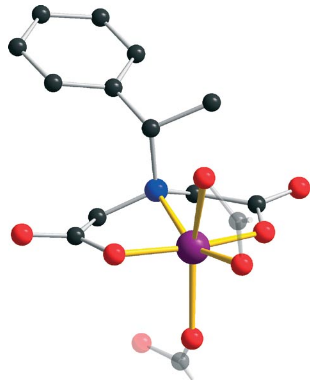


Figure 1. Section of (*S*)-[Cu(peadaa)] (**2**) highlighting the copper coordination mode. Besides tris-coordination of a peadaa group, two additional carboxylate groups (semitransparent) bind to Cu (violet). C, black; O, red; N, blue; H, omitted.

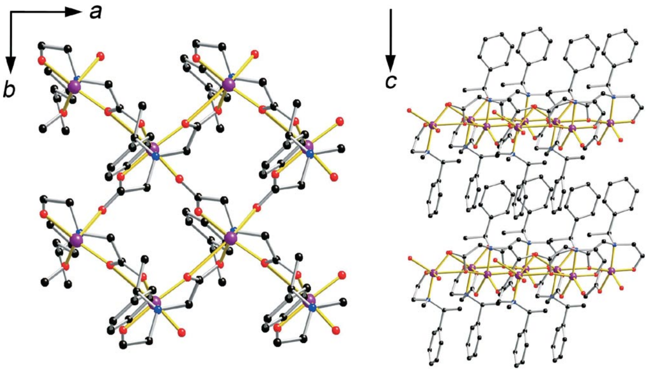
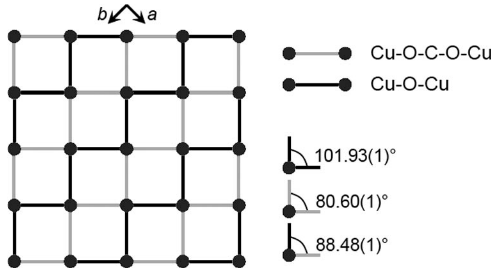


Figure 2. The (*S*)-[Cu(peadaa)]$_n$ network (**2**). View along the crystallographic *c* axis (left); view along the crystallographic *ab* plane showing the interpenetrating phenyl groups (right). Colour scheme as in Figure 1.



Scheme 2. Representation of the 2D network in **2** showing long [grey, 5.521(1) Å] and short [black, 4.597(1) Å] Cu···Cu connectivity modes.

Assembly of the monomers into a network results in rhombic 4^4 (*S*)-[Cu(peadaa)]$_n$ layers propagating along the *ab* plane, with the structure displaying only two different orientations for the ligand chiral centre (Figure 2). Each Cu_4 rhombus has two long and two short sides described by Cu···Cu distances of 4.597(1) and 5.521(1) Å and angles of 80.60(1), 88.48(1) and 101.93(1)° (Scheme 2). As a result, each Cu centre shares two short and two long connections with its nearest neighbours: these are composed of two short Cu–μ_2-O–Cu bridges and two long Cu–O–C–O–Cu bridges. The resulting linear chains of alternating long and short Cu···Cu connections intersect the *a* and *b* axes at the origin. Consequently, the network in **2** can be broken into 1D zigzag chains of Cu–μ_2-O–Cu linkages, which run parallel to the *b* axis. These chains are interconnected by the longer Cu–O–C–O–Cu bridges. To the best of our knowledge, this particular connectivity is unprecedented in transition-metal carboxylate chemistry.[12]

The layers themselves are perfectly stacked along the *c* axis and appear to assemble through C–H···π interactions (Figure 2, right), with carbon-to-ring centroid distances of ca. 3.670 and 3.767 Å. This combination of strong copper carboxylate coordination bonds with the dense interlayer packing explains the insolubility of **2** in all common solvents. Thermogravimetric measurements show no significant mass loss up to 270 °C, confirming the absence of included solvent indicated by the calculated accessible void space of zero.[13] There follows a rapid mass loss between 270 and 330 °C, corresponding to thermal decomposition of **2**. This thermal stability, along with the apparent lack of temperature or anion dependence in its formation, is an indicator that network structure **2** represents a thermodynamic stability maximum.

Because of the insolubility of **2**, UV/Vis and circular dichroism (CD) measurements were recorded on the solid material as KBr discs. The UV/Vis spectrum of **2** (see Supporting Information) shows one very broad absorption at 823 nm and a stronger peak at 258 nm (which may partly be associated with absorption by the disc). CD measurements indicate a positive Cotton effect at ≈310 nm when corrected for the KBr disc, with a weaker, negative signal at ≈250 nm also being observed (Figure 3). Unfortunately, the lower energy absorption observed in the UV/Vis spectrum was beyond the measurement range of the CD spectrophotometer. Note that ligand **1** shows no Cotton effects at either of these wavelengths, indicating that these CD absorptions are associated with the Cu^{II} centre, and also establishing the ability of the (*S*)-peadaa ligand to transfer chirality to the metal environment.

Discrete Cu_4 carboxylate squares have been seen to show global ferri-,[14] ferro-[15] and antiferromagnetic behaviour,[16] often with both competing ferro- and antiferromagnetic couplings present in the same molecule.[17] Magnetic susceptibility measurements (Figure 4) show relatively weak antiferromagnetic coupling between the $s = 1/2$ Cu^{2+} centres in **2**. This is in line with other Cu^{II} systems showing

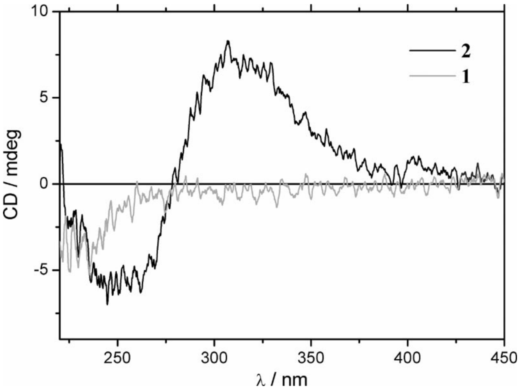


Figure 3. Solid-state (KBr) CD spectra of the uncomplexed ligand (*S*)-$Na_{0.4}H_{1.6}$peadaa (**1**) and coordination network (*S*)-[Cu(peadaa)]$_n$ (**2**).

similar carboxylate/oxo bridging modes, which tend to exhibit weak ferro- or antiferromagnetic coupling.[18] The observed monotonous decrease in $\chi_{\text{mol}}T$ with decreasing temperature, with a clear drop below 25 K, is not only due to antiferromagnetic exchange coupling but also an effect of orbital momentum contributions. Thus, we simulated[19] both local Cu^{II} site (ligand field, spin-orbit coupling) effects and Cu–Cu coupling by using the molecular field model approximation $\chi^{-1} = \chi^{-1}(\zeta,B_q^{\,k}) - \lambda_{\text{MF}}$, where χ_{m} designates the single-ion susceptibility and λ_{MF} the molecular field parameter (positive and negative values of λ indicate dominant ferromagnetic and antiferromagnetic interactions, respectively),[20] ζ represents the spin-orbit coupling energy and $B_q^{\,k}$ are the ligand-field parameters in Wybourne notation.[21] The λ_{MF} and $D_q^{\,k}$ values, for a Jahn–Teller-distorted tetragonal ligand field, were determined by least-squares fitting, with the best fit (SQ = 0.9%) yielding $\lambda_{\text{MF}} = -0.754\times10^6\ \text{mol cm}^{-3}$ and $B_0^{\,2} = 2900\ \text{cm}^{-1}$, $B_0^{\,4} = -4866\ \text{cm}^{-1}$, $B_4^{\,4} = 4324\ \text{cm}^{-1}$, which are in good agreement with published standard data for tetragonal $Cu^{II}L_6$ environments ($D_q = 100\ \text{cm}^{-1}$, $D_t = 500\ \text{cm}^{-1}$, $\kappa = -1$).[22] Note that the effects of solely the tetragonal ligand field on the Cu^{II} centres, minus the Cu–Cu exchange interactions, are shown in Figure 4 as the dark-grey line.

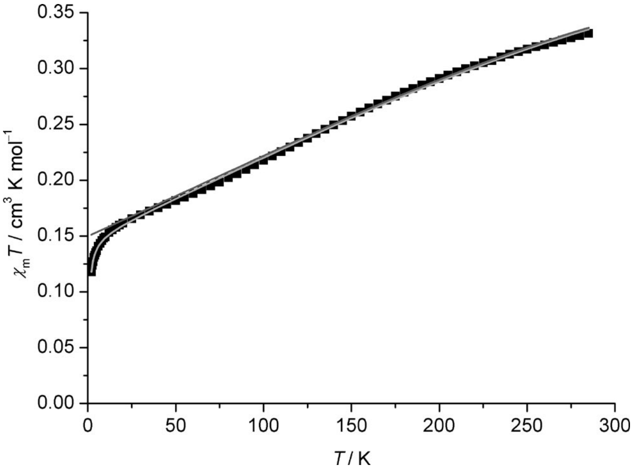


Figure 4. Temperature dependence of $\chi_{\text{mol}}T$ for (*S*)-[Cu(peadaa)]$_n$ (**2**) at 0.1 Tesla (black squares). Light-grey line: best fit resulting for a model expression of ligand field and exchange coupling effects; dark-grey line: simulated single-ion behaviour for isolated Jahn–Teller distorted tetragonal CuL_6 environments (see text).

Conclusions

In summary, reaction of the dicarboxylate ligand (*S*)-peadaa with copper(II) demonstrates the ability of this chiral ligand system to direct formation of coordination networks. The resulting 4^4 copper(II) coordination framework is thermally stable and also shows a highly unusual Cu···Cu connectivity that mediates moderate antiferromagnetic coupling. The network forms in a range of reaction conditions (temperature, anion and pH), suggesting it represents a structural archetype that can be achieved for a range of other transition-metal ions. Furthermore, CD spectroscopy indicates that peadaa strongly transfers chirality to coordinated metal centres, making it a promising, readily accessible building block for multiproperty chiral coordination compounds.

Experimental Section

(*S*)-$Na_{0.4}H_{1.6}$peadaa (1): (*S*)-(–)-1-Phenylethylamine (1.05 g, 8.40 mmol) was added to a stirred, ice-cooled solution of iodoacetic acid (6.564 g, 17.6 mmol) in water (10 mL), resulting in a cloudy white suspension. A solution of sodium hydroxide (1.410 g, 35.3 mmol) in water (10 mL) was added dropwise, and after stirring for ca. 1 h, the mixture was warmed to room temperature before heating to 50 °C for 5 d. The resulting solution (pH ≈ 9.3) was then acidified to pH ≈ 5.5 by using 2.0 M aqueous HCl, and the water was removed in vacuo. Ethanol (50 mL) was added, and the mixture was stirred and sonicated and then filtered to remove NaCl. The ethanol was then evaporated in vacuo, and the dissolution/filtration/evaporation cycle repeated until addition of ethanol resulted in a completely clear solution. At this point, the solvent was evaporated one last time, yielding **1** as an off-white crystalline solid (2.126 g, 7.60 mmol, 90% yield based on the formula **1**·0.4EtOH·$0.2H_2O$·0.2NaCl). This material, although pure enough for further reaction, contained trace amounts of unreacted iodoacetic acid. ^1H NMR (400 MHz, [D_6]DMSO): δ = 7.35–7.19 (m, 5 H, 5Ar*H*), 3.98 (q, 1 H, PhC*H*MeN), 3.28 (m, 4 H, 2NCH_2), 1.27 (d, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 175.32 (acid, C), 144.14 (Ar, C), 128.21 (Ar, CH), 126.98 (Ar, CH), 126.78 (Ar, CH), 60.15 (CH), 57.37 (CH_2), 19.50 (CH_3) ppm. MS (APCI+): *m*/*z* = 238.3 [M + H]$^+$. FTIR (KBr disc): $\tilde{\nu}$ = 3418 (s), 3026 (m), 2968 (m), 1605 (vs), 1351 (w), 1329 (m), 1213 (m), 1157 (w), 1122 (w), 1090 (w), 1064 (w), 1029 (w), 980 (w), 926 (w), 909 (m), 885 (w), 850 (w), 780 (m) cm^{-1}. A small, iodoacetic acid free sample was prepared for elemental analysis by esterification of **1** in dry methanol (under an atmosphere of dry N_2) and 98% H_2SO_4, followed by chromatographic purification of the resulting methyl ester and base hydrolysis to recover **1**. $C_{12.8}H_{17.4}NO_{4.6}Na_{0.6}Cl_{0.2}$ (**1**·0.4EtOH·$0.2H_2O$·0.2NaCl, 279.76): calcd. C 54.95, H 6.27, N 5.01, Na 5.2, Cl 2.54; found C 55.18, H 6.72, N 4.91, Na 4.93, Cl 2.21.

(*S*)-[Cu(peadaa)]$_n$ (2): A solution of (*S*)-$Na_{0.4}H_{1.6}$peadaa (**1**; 0.071 g, 0.25 mmol) and KOH (0.0072 g, 0.13 mmol) in water (3 mL) was mixed with $Cu(NO_3)_2$·$2.5H_2O$ (0.060 g, 0.26 mmol) in water (3 mL), resulting in a cloudy blue-green suspension. This was filtered, transferred to a 23-mL PTFE Parr acid digestion bomb liner and purged with bubbling argon for 5–10 min, before sealing the bomb and heating to 110 °C for 72 h. After slow cooling, **2** was recovered as a bright-blue microcrystalline solid (0.021 g, 0.07 mmol, 29%). Small single crystals suitable for X-ray diffraction were prepared by using the same method without adding base (0.015 g, 0.05 mmol, 20%). FTIR (KBr disc): $\tilde{\nu}$ = 3442 (w), 3024 (vw), 2981 (w), 2962 (w) 2938 (w), 1650 (s), 1600 (vs), 1573 (s), 1492 (w), 1450 (w), 1435 (w), 1421 (s) 1398 (w), 1380 (w), 1362 (w), 1335 (m), 1295 (m), 1267 (m), 1218 (w), 1198 (m), 1148 (m), 1124 (w), 1103 (m), 1080 (m), 1045 (w), 1015 (m), 972 (w), 944 (w), 917 (m), 813 (m), 790 (w), 755 (m), 739 (s), 710 (m), 652 (m), 634 (m), 614 (w), 576 (w), 536 (m), 508 (w), 488 (w), 454 (w), 417 (m) cm^{-1}. $C_{12}H_{13}NO_4Cu$ (298.77): calcd. C 48.24, H 4.39, N 4.81; found C 48.10, H 4.32, N 4.98.

Supporting Information (see footnote on the first page of this article): Full experimental section, crystallographic data, thermogravimetric data, UV/Vis and IR spectra.

Acknowledgments

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[11] Crystal data for $[Cu(peadaa)]_n$ (**2**): monoclinic, $P2_1$, 298.77 $g\,mol^{-1}$, a = 7.090(2) Å, b = 7.142(2) Å, c = 11.224(2) Å, β = 90.145(3)°, V = 568.4(2) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.746 $g\,cm^{-3}$, $\mu(Mo\text{-}K_\alpha)$ = 1.927 mm^{-1}, 5092 reflections measured, 2583 [R_{int} = 0.0503] unique, which were used in all calculations. GooF on F^2 = 1.002, final R_1 = 0.0387 and wR_2 = 0.0848 (all data). Flack absolute structure parameter x = 0.039(18). Data were measured at 193(2) K with a Bruker CCD-1000 diffractometer [$\lambda(Mo\text{-}K_\alpha)$ = 0.71073 Å] with a graphite monochromator. CCDC-704969 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] A search of the CSD (v7.29, November 07+1 update) for carboxylate-bridged TM tetramers found 701 structures. Only two were 4^4 nets, and neither showed the pattern of long and short M···M connections observed in **2**.

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