

Supporting Information for

Copper(II) Carboxylate Tetramers Formed from an Enantiopure Ligand Containing a π -Stacking Supramolecular Synthone: Single-Crystal to Single-Crystal Enantioselective Ligand Exchange

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(S)-4-amino-2-(1,8-naphthalimido)-4-oxobutanoic acid (HL_{asn})

To a stirred solution of L-asparagine (2.91 g, 22 mmol) in water (25 mL) was added solid potassium hydroxide (1.12 g, 20 mmol). This solution was allowed to stir for 20 minutes, and 1,8-naphthalic anhydride (3.96 g, 20 mmol) and ethanol (75 mL) were added. The solution was heated at reflux for 6-8 hours, during which time the cream-colored suspension of 1,8-naphthalic anhydride dissolved. The heat was removed, and a solution of 1 M aqueous HCl (20 mL, 20 mmol) was added. The stirring was stopped, and the reaction mixture was allowed to stand undisturbed overnight. The solid product that formed was filtered and washed with 4 x 50 mL portions of water followed by 50 mL ice-cold anhydrous ethanol. The solid was dried under vacuum overnight to afford analytically pure ligand, yield: 4.83 g (75%). Due to the extremely low solubility of this compound in organic solvents, the NMR spectrum was measured as the potassium salt of the ligand. ¹H NMR (CD₃OD) δ 7.02 (d, J = 7.3 Hz, 2 H, 2-*nphth*), 6.80 (d, J = 8.5 Hz, 2 H, 4-*nphth*), 6.26 (t, J = 7.3 Hz, 2 H, 3-*nphth*), 4.44 (dd, J = 5.5, 8.8 Hz, 1 H, α -CH), 1.84, 1.45 (m, 2 H, β -CH₂). Anal. Calcd for C₁₆H₁₂N₂O₅: C, 61.54; H, 3.87; N, 8.97. Found: C, 61.29; H, 3.82; N, 8.79.

[Cu₄(L_{asn})₈(py)(MeOH)] (1)

To a powdered sample of HL_{asn} (1.25 g, 4.0 mmol) suspended in water (40 mL) containing a few drops of pyridine was added a solution of 1 M KOH in methanol (4 mL, 4.0 mmol). This solution was stirred until the suspension had completely cleared (ca. 5 minutes). To this solution was added a solution of copper(II) acetate (400 mg, 1.0 mmol) in water (40 mL). A purple precipitate formed immediately. This solution was stirred for two hours and the purple precipitate was isolated by filtration, and washed twice each with water, absolute ethanol, and diethyl ether. After drying under vacuum, this powder was dissolved in approximately 400 mL 1:9 MeOH:CH₂Cl₂. An equal volume of hexane was added, and the solvents were removed via rotary evaporation to give the title compound (1.26 g, 88%) as a green powder. Single crystals were grown by layering diethyl ether on top of a 1:9 MeOH:CH₂Cl₂ solution of this solid (ca. 5 mg/mL), and allowing the solutions to rest undisturbed in a quiet location. Crystals suitable for X-ray analysis were obtained after 4-7 days. Anal. (crystals dried to constant weight) Calcd for C₁₃₄H₉₇N₁₇O₄₁Cu₄: C, 56.36; H, 3.42; N, 8.34. Found: C, 56.53; H, 3.58; N, 8.12.

Vapor-Phase Single-Crystal to Single-Crystal Ligand Exchange

For the vapor-phase single-crystal to single-crystal ligand exchange, the crystallization solvent from a test tube containing freshly grown crystals of $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(\text{MeOH})]$ on the walls was carefully removed from the bottom of the test tube, and the crystals were washed with a small amount of 10:9:1 diethyl ether/dichloromethane/methanol mixture. The crystals were briefly allowed to air-dry (~30-60 sec), and a small test tube lined with filter paper containing ~1 mL of the desired ligand ((*S*)-ethyl lactate (*S*-EtLac) or racemic ethyl lactate) was carefully placed inside the test tube. The system was sealed with a rubber septum and allowed to sit undisturbed for approximately 48 hours. Single crystals were selected from the tube for X-ray crystallographic analysis and shown to be $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(\text{S-EtLac})]$. Anal. (crystals dried to constant weight) Calcd for $\text{C}_{138}\text{H}_{103}\text{N}_{17}\text{O}_{43}\text{Cu}_4$: C, 56.35; H, 3.53; N, 8.09. Found: C, 56.12; H, 3.43; N, 8.09.

X-Ray Crystallographic Data Collection and Refinement

All X-ray intensity data were measured at 150(2) K using a Bruker SMART APEX diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). Crystals were transferred rapidly from the crystallization or vapor exchange apparatus to the cold stream of the diffractometer to avoid decomposition. Highly redundant datasets were collected for each crystal by a combination of omega and phi scans. Raw area detector data frame processing was performed with the SAINT+ and SADABS programs.¹ Final unit cell parameters were determined by least-squares refinement of large sets of reflections from each data set. Direct methods structure solutions, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.² All X-ray crystallographic data can be found in the accompanying CIFs.

Blue-green rectangular bar-shaped crystals of $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(\text{MeOH})]$ (**1**) adopt the orthorhombic space group $P2_12_12_1$ as determined by the pattern of systematic absences in the intensity data. The crystallographically identifiable contents of the asymmetric unit consist of one $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(\text{MeOH})]$ molecule, one diethyl ether molecule, two methanol molecules and three dichloromethane molecules. The eight independent ligands of the copper complex were numbered identically except for label suffixes "A" through "H". Solvent species in some regions of the asymmetric unit could not be resolved due to disorder. These were treated as diffusely scattering volumes, and their contributions to the structure factors were removed with the SQUEEZE program implemented in PLATON.³ These disordered volumes amount to a total of 3973.1 \AA^3 (23.2% of the unit cell volume) and account for $1006 e^-$ per unit cell. Based on trial disorder modeling attempts, the disordered species are likely a mixture of ether, methanol and dichloromethane. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions and included as riding atoms. Reasonable positions for the methanol hydrogens were located in difference maps; subsequently they were treated as riding atoms. The final absolute structure (Flack) parameter is 0.044(6), indicating the correct absolute structure and the absence of racemic twinning.

Blue rectangular bars of $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(S\text{-EtLac})]$ (**2**) also adopt the space group $P2_12_12_1$ as determined uniquely by the pattern of systematic absences in the intensity data. The crystallographically identifiable contents of the asymmetric unit consist of one $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(S\text{-EtLac})]$ molecule and three non-coordinated *S*-ethyl lactate molecules. The $\{\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})\}$ part of the copper complex is similar to that found in the MeOH adduct **1**, and in fact atomic coordinates from **1** were used as a starting model for refinement of **2**. The atom numbering scheme is the same used for compound **1**. Aside from the *S*-ethyl lactate coordinated to Cu3, the copper complex in **2** differs from that in **1** in the following respects: (a) There is disorder of the $-\text{CHCH}_2\text{C}(\text{O})\text{NH}_2$ substituent of ligand "A" that bridges the two dicopper units (atoms C13, C14, C15, N2, O3). The second component of this group has the atom label suffix "Z". This substituent occupies two orientations with equal populations. (b) The pyridine molecule (atoms N3, C21-C25) coordinated to Cu1 is also disordered over two equally populated, closely spaced positions (atom label suffixes I and J). These groups were refined as rigid hexagons with a common isotropic displacement parameter. After identification of the primary $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(S\text{-EtLac})]$ molecule and the three non-coordinated ethyl lactate molecules, a large region of essentially featureless electron density remained in the vicinity of naphthalimide rings "B" and "C". This electron density was assumed to be heavily disordered guest species, probably including more ethyl lactate molecules. No reliable disorder model could be achieved despite many trials, and therefore the program SQUEEZE³ was used to remove this electron density from subsequent structure factor calculations. The guest region occupies a volume of 3232.5 Å³, or 19% of the total unit cell volume. Only the four copper atoms were refined anisotropically; all other non-hydrogen atoms were refined isotropically. A full anisotropic refinement was not warranted because of the diminished data quality caused by weak diffraction and disorder. Four naphthalimide ring systems (A, B, C, F) and two non-coordinated ethyl lactate molecules (O56, O66) were each assigned common isotropic displacement parameters. A total of 1351 geometric restraints were employed in the refinement. These were mostly used to maintain reasonable naphthalimide geometry, by restraining all naphthalimide rings to be similar to ring "G", which was deemed to be the most well-behaved. Geometric restraints were also used for the disordered $-\text{CHCH}_2\text{C}(\text{O})\text{NH}_2$ substituent of ligand "A" and for the three non-coordinated *S*-ethyl lactate molecules, which were restrained to be similar to the coordinated *S*-ethyl lactate. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. The hydroxyl protons of the four *S*-ethyl lactate molecules could not be located and were not calculated. The final absolute structure (Flack) parameter refined to 0.05(2), reliably indicating the correct chiral sense of the crystal and the absence of racemic twinning.

Blue rectangular bars of $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(S\text{-EtLac})]$ (**3**) created by exchange with racemic ethyl lactate vapor also adopt the space group $P2_12_12_1$ as determined uniquely by the pattern of systematic absences in the intensity data. Structural features of the copper complex are similar to those in compound **2**. Only the $[\text{Cu}_4(\text{L}_{\text{asn}})_8(\text{py})(S\text{-EtLac})]$ complex could be crystallographically identified; all interstitial species are too severely disordered to impose a physically reasonable disorder model. There is again two-fold disorder of the $-\text{CHCH}_2\text{C}(\text{O})\text{NH}_2$ substituent of ligand "A" (atoms C13, C14, C15, N2, O3). The second

component of this group has the atom label suffix "Z". The pyridine molecule (atoms N3, C21-C25) coordinated to Cu1 is also disordered over two equally populated, closely spaced positions (atom label suffixes I and J). These groups were refined as rigid hexagons with a common isotropic displacement parameter. The guest region occupies a volume of 5914.7 Å³, or 34% of the total unit cell volume. All diffusely scattering species in these regions were removed from the structure factor calculations with SQUEEZE.³ Four naphthalimide ring systems (A, B, C, F), some atoms of rings G and E, and the *S*-ethyl lactate molecule were each assigned common isotropic displacement parameters. Only the four copper atoms were refined anisotropically; all other non-hydrogen atoms were refined isotropically. A full anisotropic refinement was not warranted because of the diminished data quality caused by weak diffraction and disorder. A total of 1041 geometric restraints were employed in the refinement. These were mostly used to maintain reasonable naphthalimide geometry, by restraining all naphthalimide rings to be similar to ring "G", which was deemed to be the most well-behaved. Geometric restraints were also used for the disordered -CHCH₂C(O)NH₂ substituent of ligand "A" and for the *S*-ethyl lactate molecule (neighboring C-C and C-O distances only; no restraints affecting the chiral sense of the molecule were used). Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. The hydroxyl proton of the *S*-ethyl lactate molecule could not be located and was not calculated. The final absolute structure (Flack) parameter refined to 0.06(3), reliably indicating the correct chiral sense of the crystal and the absence of racemic twinning.

- (1) SMART Version 5.630, SAINT+ Version 6.45, and SADABS Version 2.05.
Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.
- (2) Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.
- (3) Squeeze: Sluis, P. v.d.; Spek, A. L. Acta Crystallogr., Sect A 1990, 46, 194-201.
PLATON: (a) Spek, A. L. Acta Crystallogr., Sect A 1990, 46, C34. (b) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. 1998.