

Chiral Coordination Polymers with Amino Acids: $\infty[\text{Cu}_2(\mu\text{-L-tryptophanato})_2(\mu\text{-4,4'-bipyridine})(\text{H}_2\text{O})_2](\text{NO}_3)_2$

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Received February 20th, 2007.

Abstract. The two-dimensional mixed-ligand network catena- $[(\mu\text{-4,4'-bipyridine})\text{-bis}(\mu\text{-L-tryptophanato-}\kappa^3\text{N,O,O'})\text{-diaqua-dicopper(II) dinitrate}]$ is constructed through the bridging action of both the tridentate amino carboxylate and the bidentate 4,4'-bipyridine ligand. The enantiomeric L-tryptophanato ligand acts as an *N,O* chelate towards one copper atom and bridges through the

second carboxylate oxygen atom to the adjacent copper ion. Stacking of the corrugated nets creates channels which are occupied by the hydrogen-bonded and very weakly Cu-coordinating nitrate ions.

Keywords: Copper; Chiral coordination polymers; Amino acids

Introduction

Metal-organic networks or coordination polymers currently attract much attention because of the potential properties in adsorption, catalysis, luminescence, magnetism etc. [1, 2]. There is ongoing work in the formation of chiral coordination polymers, which as chiral microporous materials could be used in enantiomer separation or chiral synthesis [1, 3–5]. The synthesis of molecular chiral metal complexes is of continued interest [6, 7]. Increasing research can be noted in the coordination and supramolecular chemistry of (inexpensive) enantiomeric ligands, like *S*-1,1'-bi-2-naphthol (*S*-BINOL) [8] and derivatives [9], (*R*)-(aryl)ethylamines [10], amino acids [11, 12] and others [13] for the formation of extended (one- to three-dimensional) structures. L-amino acids are easily accessible from the chiral pool and upon deprotonation chelate metal atoms through their amino nitrogen and carboxylate oxygen atom. The construction of extended coordination networks with L-amino carboxylate groups is possible through additional bridging ligands, such as 4,4'-bipyridine [4, 5]. Herein we report the synthesis and crystal structure of a two-dimensional coordination polymer built from copper nitrate, L-tryptophanato and 4,4'-bipyridine. The possibility of a nitrate against halide anion exchange was investigated [1].

Results and Discussion

Crystals of $[\text{Cu}_2(\text{L-tryptophanato})_2(4,4'\text{-bipyridine})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (**1**) could be grown from the molar ratio of

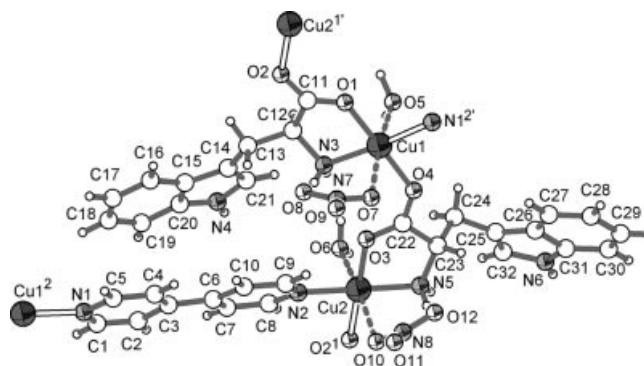


Fig. 1 The asymmetric unit in $\infty[\text{Cu}_2(\text{L-tryptophanato})_2(4,4'\text{-bipyridine})(\text{H}_2\text{O})_2](\text{NO}_3)_2$. Selected distances/Å and angles/°:

Cu1–N1^{2'} 2.005(3), Cu1–N3 1.982(4), Cu1–O1 1.971(3), Cu1–O4 1.968(3), Cu1–O5 2.353(4), Cu1–O7 2.633(5), Cu2–N2 2.006(3), Cu2–N5 1.978(4), Cu2–O2¹ 1.977(3), Cu2–O3 1.970(3), Cu2–O6 2.312(4), Cu2–O10 2.639(5), O4–Cu1–O1 176.6(2), O4–Cu1–N3 97.3(1), O1–Cu1–N3 83.1(1), O4–Cu1–N1^{2'} 88.5(1), O1–Cu1–N1^{2'} 91.0(1), N3–Cu1–N1^{2'} 173.8(2), O4–Cu1–O5 89.3(2), O1–Cu1–O5 94.1(2), N3–Cu1–O5 94.4(2), N1^{2'}–Cu1–O5 87.6(2), O3–Cu2–O2¹ 179.2(1), O3–Cu2–N5 83.6(1), O2¹–Cu2–N5 97.1(1), O3–Cu2–N2 90.0(1), O2¹–Cu2–N2 89.4(1), N5–Cu2–N2 169.8(2), O3–Cu2–O6 92.5(2), O2¹–Cu2–O6 87.1(1), N5–Cu2–O6 97.8(2), N2–Cu2–O6 90.3(2), symmetry operation 1 = 1+x, y, z; 1' = –1+x, y, z; 2 = 0.5–x, 2–y, 0.5+z; 2' = 0.5–x, 2–y, –0.5+z

L-tryptophane, $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ and 4,4'-bipyridine in a mixture of distilled water, methanol and ethanol. The single-crystal structure shows the copper(II) atom in a square-planar coordination by the nitrogen and oxygen atom of a chelating tryptophanato ligand, a nitrogen atom of a bridging 4,4'-bipyridine and the oxygen atom of a bridging tryptophanato carboxylate group. An aqua ligand and an oxygen atom from a terminal nitrate anion coordinate along the Jahn-Teller elongated axial positions (Fig.1). Each tryptophanato ligand bridges with its carboxylate group between two copper(II) ions.

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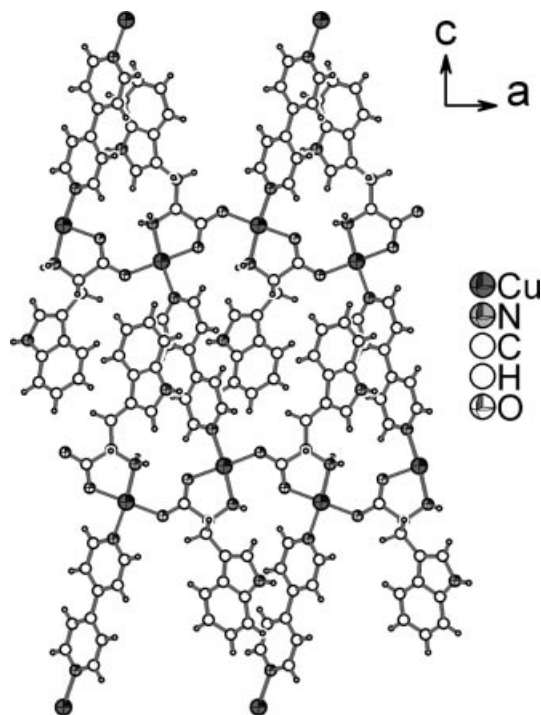


Fig. 2 2D layer in **1**

The two-dimensional network can be subdivided into 1D chains of copper ions with bridging tryptophanato ligands through their carboxylate groups along the *a*-axis. These chains are interconnected with the 4,4'-bipyridine ligands along the *c*-axis (Fig. 2). Modest-to-strong π -stacking [14] is operating between the tryptophane indole moiety and bipyridine (Fig. 1 and 2) with centroid-centroid contacts of 3.76–3.79 Å and interplanar separations of 3.36–3.69 Å between the slightly tilted rings (dihedral angles 10.6 and 13.6°).

Stacking of the corrugated 2D nets along the *b*-direction leaves channels colinear to the *a*-axis which are occupied by the nitrate anions together with the aqua ligands. Hydrogen bonding is operating from the amino groups and the aqua ligands to the nitrate anions (not detailed here).

A thermogravimetric analysis of **1** under nitrogen shows a weight loss between 90 to 220 °C of 5.0 % which can be attributed to the loss of the aqua ligands (calc. 4.2 %). From 220 °C on loss of the bipyridine ligand and decomposition of the amino carboxylate occurs.

We have tried to exchange the nitrate anions in **1** against fluoride or chloride. A dried solid sample of **1** was added to an alcoholic solution with an excess of $(\text{Et}_4\text{N})^+\text{X}^-$ ($\text{X} = \text{F}, \text{Cl}$). The solid **1** changed color from turquoise to more bluish. An infrared analysis of the solid revealed a decrease in the intensity of the N–O stretching vibration for NO_3^- at 1385 cm^{-1} and the appearance of a new band at 1626 cm^{-1} . The possibility of a fluorine–nitrate exchange was also checked by ^{19}F NMR spectroscopy. Addition of a solid sample of **1** to a methanol- d_4 solution of $(\text{Et}_4\text{N})\text{F}$ (molar ratio **1** to $\text{F}^- = 1:5$) led to a disappearance of the ^{19}F

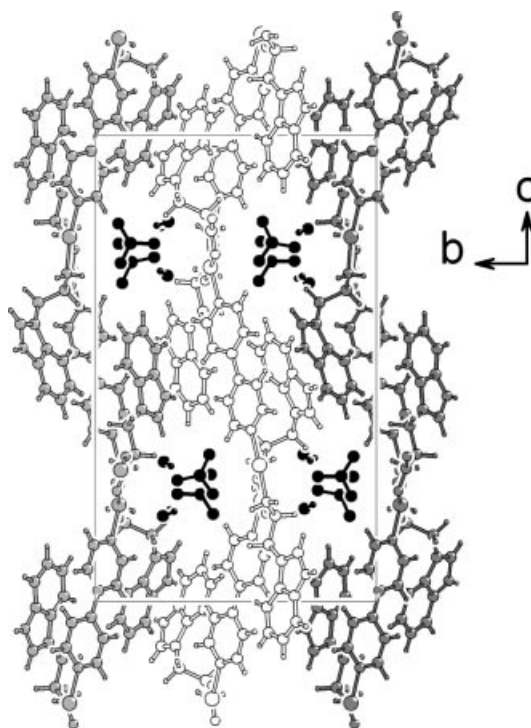


Fig. 3 Stacking of three corrugated layers along *b* with highlighted nitrate anions and aqua ligands (in black) in **1**. Layers are differentiated by white, light and dark gray.

resonance at -157.1 ppm (relative to the internal standard of decafluorobiphenyl with resonances at -140.7 , -153.6 and -164.1 ppm). Further increase in the excess of $(\text{Et}_4\text{N})\text{F}$ eventually returned a broadened signal for the F^- -resonance at -157.1 ppm . While this behavior was initially seen as evidence for an anion exchange, a careful analysis of the solubility of **1** in methanol instead revealed a paramagnetic effect of Cu^{II} on the F^- -NMR signals. Polarographic copper analysis of the supernatant solution for a solid sample of **1** in methanol gave a Cu^{2+} concentration of $0.35\text{ mg}/100\text{ ml}$, corresponding to a solubility of **1** of $2.3\text{ mg}/100\text{ ml}$ methanol. Repeating the ^{19}F NMR study with this copper(II) concentration set by copper(II) nitrate showed the same effect on the F^- -NMR signal from $(\text{Et}_4\text{N})\text{F}$. Hence, the disappearance and broadening at higher excess of the F^- -resonance is due to the paramagnetic influence of Cu^{2+} in a dynamic equilibrium between F^- and copper-fluorine species like $[\text{CuF}_3]^-$, $[\text{CuF}_4]^{2-}$ or $[\text{CuF}_6]^{4-}$ in solution [15].

Experimental Section

Elemental analyses were obtained on a VarioEL from Elementar-analysensysteme GmbH. IR spectra (2–4 mg compound/300 mg KBr pellet) were measured on a Bruker Optik IFS25. NMR spectra were collected on a Bruker ARX 200 (200 MHz for ^1H , 188 MHz for ^{19}F) with calibration against the residual protonated solvent signal (DMSO- d_6 2.52 ppm, MeOH- d_4 3.31 ppm). Thermogravimetric analysis was carried out on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen (heating rate 10 K min^{-1}). Polarographic analysis was done on a 797 VA Computrace

from Metrohm Ionenanalytik equipped with a multi mode Hg electrode. The measurement was carried out under nitrogen atmosphere with the static Hg drop electrode in the differential pulse mode (SMDE).

catena-[(μ -4,4'-bipyridine)-bis(μ -L-tryptophanato- κ^3 N,O,O')-diaqua-di-copper(II) dinitrate], $[\text{Cu}_2(\mu\text{-L-tryptophanato})_2(\mu\text{-4,4'-bipyridine})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (1**). A solution of 4,4'-bipyridine (15.6 mg, 0.1 mmol) in ethanol (3 ml) was given to a mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ (24.2 mg, 0.1 mmol) and L-tryptophane (20.4 mg, 0.1 mmol) in methanol (3 ml) and distilled water (1 ml). The solvent was allowed to evaporate slowly at room temperature. After two days turquoise crystals formed which were suitable for X-ray single crystal analysis.**

Yield 35.0 mg, 82 % based on L-tryptophane. Calc for $\text{C}_{32}\text{H}_{34}\text{Cu}_2\text{N}_8\text{O}_{12}$ (849.75) C 45.23, H 4.03, N 13.19. Found C 44.75, H 4.13, N 12.95 %.

IR/ cm^{-1} : 3397s, 1621m, 1609s, 1587s, 1539m, 1490m, 1456m, 1431s, 1417s, 1389s, 1359s, 1334s, 1219m, 1115m, 1098m, 1070m, 1040m, 1010m, 932w, 831m, 812m, 755m, 724m, 674m, 665m, 646m, 611m, 590m, 514m, 428m.

¹H-NMR: ($\text{DMSO-d}_6 + \text{KCN}$ to transform Cu^{2+} to diamagnetic $[\text{Cu}(\text{CN})_4]^{3-}$) 10.80 (s, 2H, $\text{H}_{\text{LTPP}}\text{-NH}$), 8.74 (dd, 4 H_{bipy} , $\text{H}_2/\text{H}_6/\text{H}_2'/\text{H}_6'$, $^3J_{2,3} = ^3J_{5,6} = ^3J_{2',3'} = ^3J_{5',6'} = 4.6$ Hz, $^4J_{2,5} = ^4J_{3,6} = ^4J_{2',5'} = ^4J_{3',6'} = 1.6$ Hz), 7.83 (dd, 4 H_{bipy} , $\text{H}_3/\text{H}_5/\text{H}_3'/\text{H}_5'$, $^3J_{2,3} = ^3J_{5,6} = ^3J_{2',3'} = ^3J_{5',6'} = 4.5$ Hz, $^4J_{2,5} = ^4J_{3,6} = ^4J_{2',5'} = ^4J_{3',6'} = 1.7$ Hz), 7.56 (d, 2 H_{LTPP} , H_7 , $^3J_{6,7} = 7.2$ Hz), 7.34 (d, 2 H_{LTPP} , H_4 , $^3J_{4,5} = 7.6$ Hz), 7.18 (s, 2 H_{LTPP} , H_2), 7.01 (m, 4 H_{LTPP} , H_5/H_6), 3.76 (br. s, 4H, $-\text{OH}_2$), 3.50 (dd, 4 H_{LTPP} , $-\text{NH}_2$, $^3J_{\text{CH}_2\text{-NH}_2} = 9.0$ Hz, $^4J_{\text{CH}_2\text{-NH}_2} = 3.8$ Hz), 3.24 (dd, 4 H_{LTPP} , $-\text{CH}_2$, $^3J_{\text{CH}_2\text{-CH}_2} = 14.6$ Hz, $^4J_{\text{CH}_2\text{-NH}_2} = 3.8$ Hz), 2.86 (dd, 4 H_{LTPP} , $-\text{CH}$, $^3J_{\text{CH}_2\text{-CH}_2} = 14.6$ Hz, $^3J_{\text{CH}_2\text{-NH}_2} = 9.0$ Hz).

Reactivity of **1** with $(\text{Et}_4\text{N})^+ \text{X}^-$

(a) A solid sample of **1** (17.0 mg, 0.02 mmol) was placed in solution of $(\text{Et}_4\text{N})\text{X}$ (with $\text{X} = \text{F}$ 29.4 mg, 0.2 mmol or $\text{X} = \text{Cl}$ 33.1 mg, 0.2 mmol) in alcohol (methanol or ethanol, 10 ml). After three days the solid was separated by filtration, washed with alcohol and investigated by IR spectroscopy.

(b) **1** (34.0 mg, 0.04 mmol), $(\text{Et}_4\text{N})\text{F}$ (12.0–120 mg, 0.08–0.8 mmol) and decafluorobiphenyl (10.0 mg, 0.03 mmol, as fluorine standard) were combined in MeOH-d_4 (0.6 ml) for ^{19}F NMR measurements.

Polarographic Analysis

A solid sample of **1** (34.0 mg, 0.04 mmol) was placed in methanol (20 ml) and kept for 20 hours at room temperature. The solution was filtered and the filtrate evaporated. The filtrate residue was dissolved in distilled water (5 ml) and was digested by UV-irradiation with hydrogen peroxide (35 %, 0.05 ml) for 30 min to destroy organic matrix components. The solution was brought to 100 ml with acetate buffer (1 ml, 1.5 mol/l) and distilled water. Quantitative analysis was based on two standard additions with an appropriate $\text{Cu}(\text{NO}_3)_2$ standard.

Structure determination

Data Collection: Bruker AXS with CCD area-detector, temperature 243(2) K, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), graphite monochromator, ω -scans, Data collection and cell refinement with SMART [16], data reduction with SAINT [16], experimental absorption correction with SADABS [17]. *Structure Analysis and*

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

Empirical formula	$\text{C}_{32}\text{H}_{34}\text{Cu}_2\text{N}_8\text{O}_{12}$
$M/g \text{ mol}^{-1}$	849.75
Crystal size/mm	0.40 x 0.13 x 0.07
θ range/ $^\circ$	0.99–26.60
$h; k; l$ range	$\pm 12; \pm 18; -29, 30$
Crystal system	orthorhombic
Space group	$P2_12_12_1$
$a/\text{\AA}$	9.8373(12)
$b/\text{\AA}$	14.6653(19)
$c/\text{\AA}$	24.263(3)
$V/\text{\AA}^3$	3500.4(8)
Z	4
$D_{\text{calc}}/g \text{ cm}^{-3}$	1.612
$F(000)$	1744
μ/mm^{-1}	1.291
Max/min transmission	0.9162/0.6263
Reflections collected	29381
Independent reflections	7321 ($R_{\text{int}} = 0.0572$)
Obs. reflect. [$I > 2\sigma(I)$]	5238
Parameters refined	517
Max./min. $\Delta\rho$ a / $e \text{ \AA}^{-3}$	0.708/−0.648
R_1/wR_2 [$I > 2\sigma(I)$] b	0.0400/0.0861
R_1/wR_2 (all data) b	0.0783/0.1037
Goodness-of-fit on F^2 c	1.031
Flack parameter [20]	−0.017(16)
Weight. scheme $w; a/b$ d	0.0430/2.8210

a) Largest difference peak and hole. b) $R_1 = [\sum(|F_o| - |F_c|)]/\sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]]^{1/2}$. c) Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$. d) $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3$.

Refinement: The structure was solved by direct methods (SHELXS-97) [18]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [18]. All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms on the aromatic rings and the carbon atoms of the methanol or ethanol molecule were placed at calculated positions with an appropriate riding model (AFIX 43 for CH, AFIX 23 for CH_2 and AFIX 33 or 133 for CH_3) and an isotropic temperature factor of $\text{Ueq}(\text{H}) = 1.2 \text{ Ueq}(\text{CH}, \text{CH}_2)$ and $1.5 \text{ Ueq}(\text{CH}_3)$. Details of the X-ray structure determinations and refinements are provided in Table 1. Graphics were drawn with DIAMOND [19]. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as spheres of arbitrary radii. CCDC reference number 639132. See http://www.ccdc.cam.ac.uk/data_request/cif for crystallographic data in CIF format.

Acknowledgements. The work was supported by DFG grant Ja466/14-1.

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