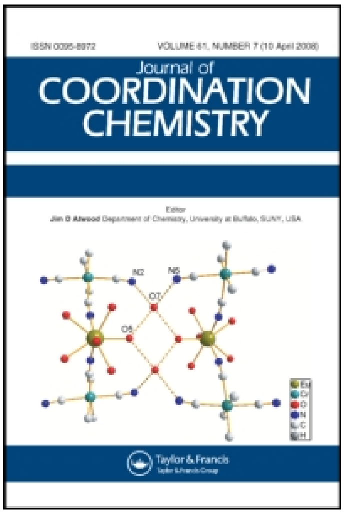

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Meng, Xianghua , Shi, Ji-Cheng , Tong, Qingsong , Liu, Pei and Jia, Li(2008) 'Synthesis, characterization and crystal structure of a chiral polymeric Cu(II) complex bridged by tartrate', Journal of Coordination Chemistry, 61: 22, 3549 — 3555

To link to this Article: DOI: 10.1080/00958970802074571
URL: http://dx.doi.org/10.1080/00958970802074571

Journal of Coordination Chemistry
Vol. 61, No. 22, 20 November 2008, 3549–3555

Synthesis, characterization and crystal structure of a chiral polymeric Cu(II) complex bridged by tartrate

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(*Received 17 December 2007; in final form 22 January 2008*)

A chiral metal-organic coordination polymer, [Cu(Tar)(2,2′-bipy) · 5H_2O] (**1**) (Tar = L-tartrate dianion, 2,2′-bipy = 2,2′-bipyridine), has been synthesized by hydrothermal reaction of $Cu(OAc)_2$, Na_2T (H_2T = 2,3-*O*-isopropylidene-L-tartaric acid) and 2,2′-bipyridine, and characterized by IR, UV–vis spectra, elemental analyses, TG-DTA, and single crystal X-ray diffraction. In the hydrothermal reaction, the protection group isopropylidene for tartaric acid was hydrolyzed. The crystal structure of the coordination polymer **1** shows that each tartrate chelates two Cu(II) ions at opposite ends using one carboxylate oxygen and one hydroxyl oxygen and each Cu(II) ion is chelated by two halves of tartrate dianions, forming coordination polymer chains. Distorted octahedral geometry around copper is completed by a chelating 2,2′-bipyridine molecule. The 2,2′-bipyridine groups in two of parallel 1-D chains are interwoven, constituting ladder-shaped double chains. Strong offset π–π stacking interactions with a face-to-face distance of 3.33 Å for pyridine rings are observed. All the lattice water molecules hydrogen-bond to each other or to the carbonyl oxygen of tartrate, forming a 3-D supramolecular structure.

Keywords: L-Tartaric acid; 2,2′-Bipyridine; Copper; Hydrothermal synthesis; Water chain; X-ray crystal structure

1. Introduction

Construction of chiral coordination polymers from organic molecules and metal ions has attracted considerable attention due to their intriguing structures and potential utility in asymmetric catalysis [1–3], chiral separation [4, 5], and nonlinear optical materials [6–8]. The L-tartaric acid derivatives have been found to be useful in asymmetric epoxidation [9, 10]. We are interested in using the carboxylate oxygens of L-tartaric acids to coordinate to transition metal ions forming chiral metal-organic frameworks, and later introducing other metal ions as catalysis centers which would be coordinated by the oxygen atoms of the remaining hydroxyl groups. Herein, we report the synthesis and characterization of a new chiral metal-organic coordination polymer [Cu(Tar)(2,2′-bipy) · 5H_2O] (**1**) (Tar = L-tartrate dianion, 2,2′-bipy = 2,2′-bipyridine).

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802074571

2. Experimental

2.1. *General procedure*

The starting materials were purchased and used without further purification. The value of pH was determined by pHs-25. Infrared spectra were recorded with a NICOLET-5700 FT–IR spectrophotometer as KBr pellets in the range 4000–400 $\mathrm{cm^{-1}}$. Elemental analyses (C, H and N) were determined on an Elementar Vario EL III elemental analyzer. TG-DTA thermal analysis was performed on a TGA-SDTA 851 instrument in flowing N_2 at a heating rate of $5\,\mathrm{K\,min^{-1}}$ from 30 to 500°C. UV–Vis spectra were recorded on a Lambda 900 spectrometer.

2.2. *Synthesis of tartaric acid derivative*

2,3-*O*-Isopropylidene-L-tartrate acid disodium salt (Na_2T) was prepared from L-tartaric acid by three steps according to literature methods [11, 12]. IR ($\mathrm{cm^{-1}}$): 2989m, 2939m ($\nu_{as}CH_3$), 1616s ($\nu_{as}C=O$), 1408s ($\nu_{s}C=O$), 1316m, 1265s, 1212m, 1163m, 1078s, 973w, 874s, 822m, 784m, 745s.

2.3. *Synthesis of [Cu(Tar)(2,2′-bipy)·5H$_2$O] (1)*

A mixture of $Cu(CH_3COO)_2$ (0.090 g, 0.50 mmol), Na_2T (0.117 g, 0.50 mmol), 2,2′-bipyridine (0.080 g, 0.50 mmol) was dissolved in distilled water (4 mL)/ CH_3COOH (4 mL) and the pH of the mixture was adjusted to 7.5 with 0.1 mol/L HCl. The resulting solution was sealed in a 20 mL Teflon-lined autoclave and heated under autogenous pressure at 80°C for 50 h. The pH of the final reaction mixture was 6.5. Upon cooling to room temperature, blue prism crystals were filtered and dried at room temperature. Yield 76% (based on Cu). Anal. Calcd for $C_{14}H_{22}CuN_2O_{11}$: C, 36.72; H, 4.84; N, 6.12. Found: C, 36.52; H, 5.24; N, 5.92. IR ($\mathrm{cm^{-1}}$): 3425s ($\nu_{as}O-H$), 3109w, 2892w, 1621s ($\nu_{as}C=O$), 1601s, 1472w, 1446m, 1383s ($\nu_{s}C=O$), 1363s, 1307w, 1135m, 1065w, 1031w, 833w, 778m, 726m. A suitable crystal was selected for single-crystal X-ray diffraction.

2.4. *X-ray structure analyses*

A single crystal was carefully selected under a microscope and then glued to the tip of a glass fiber. Intensity data were collected on a Mercury CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 273 K. All absorption corrections were performed using the CrystalClear programs [13]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms bonded to C atoms were positioned geometrically and refined using a riding model [C–H 0.93 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$]. The H atoms bonded to O atoms were located from difference maps and refined isotropically. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data and structure refinement for **1**.

Formula	$C_{14}H_{22}CuN_2O_{11}$
Formula weight (g mol^{-1})	457.88
T (K)	173
Crystal size (mm^3)	0.5000 × 0.1500 × 0.1000
Crystal color	Blue
Crystal system	Orthorhombic
Space group	$P2(1)2(1)2(1)$
Unit Cell dimensions (Å, °)	
a	6.685(2)
b	14.344(6)
c	18.95(3)
α	90
β	90
γ	90
V(Å^3)	1817(3)
Z	4
D_{Calcd} (mg cm^{-3})	1.674
μ (mm^{-1})	1.266
F(000)	948
Data/restraints/parameters	3144/2/257
Relections collected	11756
Unique relections	3144
Goodness of fit	1.002
$R_1[I>2\sigma(I)]$	0.0393
$\omega R_2[I>2\sigma(I)]$	0.0771
R_1 (all data)	0.0472
ωR_2 (all data)	0.0808
Residuals (e · Å^{-3})	0.502, −0.348

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Cu(1)–O(1)	1.959(3)	O(1)–Cu(1)–O(6)#1	97.34(14)
Cu(1)–O(6)#1	1.968(4)	O(1)–Cu(1)–N(2)	92.85(14)
Cu(1)–N(2)	1.998(5)	O(6)#1–Cu(1)–N(2)	161.59(15)
Cu(1)–N(1)	2.006(3)	O(1)–Cu(1)–N(1)	162.90(16)
Cu(1)–O(3)	2.358(3)	O(6)#1–Cu(1)–N(1)	93.42(13)
Cu(1)–O(4)#1	2.426(3)	N(2)–Cu(1)–N(1)	80.61(13)
N(2)–C(10)	1.344(5)	O(1)–Cu(1)–O(3)	75.45(11)
N(2)–C(6)	1.355(5)	O(6)#1–Cu(1)–O(3)	88.25(14)
C(5)–N(1)	1.347(5)	N(2)–Cu(1)–O(3)	109.20(15)
C(1)–N(1)	1.334(5)	N(1)–Cu(1)–O(3)	91.69(14)
C(11)–O(1)	1.268(5)	O(1)–Cu(1)–O(4)#1	85.43(11)
C(12)–O(3)	1.421(5)	O(6)#1–Cu(1)–O(4)#1	74.47(12)
C(13)–O(4)	1.425(6)	N(2)–Cu(1)–O(4)#1	91.19(13)
C(14)–O(6)	1.277(5)	N(1)–Cu(1)–O(4)#1	110.34(14)
O(4)–H(4B)	0.8400	O(3)–Cu(1)–O(4)#1	152.41(10)
O(3)–H(3B)	0.843(10)		

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

3. Results and discussions

3.1. *Synthesis*

To apply the hydroxyl groups of tartaric acid to coordinate other metal atoms, Na_2T, in which the hydroxyl groups are protected with isopropylidene to exclude them coordinating skeleton metal ions, was synthesized according to literature methods [10, 11]. NaT_2 reacting with $Cu(CH_3COO)_2$ and 2,2′-bipyridine in a Teflon-lined stainless steel reactor at 80°C for 50 h afforded light-blue crystals of **1** with formula $C_{14}H_{22}CuN_2O_{11}$ suggested by combustion analysis. The peak at 2989 cm^{-1} in the IR spectrum attributed to C–H stretching of CH_3 in Na_2T disappeared in that of **1**, indicating hydrolysis of H_2T to lose isopropylidene during the reaction. Although at beginning the pH of the reaction mixture was adjusted to 7.5, the final value of the reaction was 6.5 implying the reasonableness of hydrolysis. The separation (Δ) 238 cm^{-1} between $\nu_{asym}(COO^-)$ at 1621 cm^{-1} and $\nu_{sym}(COO^-)$ at 1383 cm^{-1} indicates that carboxylate is monodentate [15]. Strong absorptions centered around 3400 cm^{-1} with shoulders at 3200 cm^{-1} indicated several types of hydrogen-bonding interactions in **1**. Bands at 1601, 1472 and 1446 cm^{-1} indicated the presence of 2,2′-bipyridine. The diffuse-reflectance spectrum of **1** was recorded in the range of 200–1400 nm. Three absorption peaks at 292, 321 and 800 nm were observed. The intense absorption at 292 nm ascribed to intraligand π–π^* transition indicated the presence of 2,2′-bipyridine, and the LMCT absorption at 321 nm suggested coordination of 2,2′-bipyridine to Cu. The absorption at 800 nm is assigned to d–d transition of Cu [16, 17].

3.2. *Description of the structure*

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in orthorhombic space group *P*2(1)2(1)2(1). As shown in figure 1(a), each tartrate chelates two Cu(II) ions at opposite ends using one carboxylate oxygen and one hydroxyl oxygen and each Cu(II) is chelated by two halves of tartrate dianions, forming coordination polymer chains [figure 1(b)]. The distorted octahedral geometry around the copper is completed by a chelating 2,2′-bipyridine. Equatorial positions of Cu(II) ion are occupied by two nitrogens and two carboxylate oxygens (O6 and O1A), and the axial positions are taken by the oxygens (O4 and O3A) of hydroxyl groups. The equatorial distances of Cu–O (Cu–O1 = 1.959(3) Å and Cu–O6A 1.968(4) Å) and Cu–N (Cu–N1 = 2.006(3) Å and Cu–N2 = 1.998(5) Å) are within normal regions [18]. The longer Cu–O distances (Cu–O3 = 2.358(3) Å and Cu–O4A = 2.426(3) Å) at axial position partly result from the weak coordination of neutral hydroxyl oxygens to Cu(II) [19].

Figure 1(b) displays the pyridine groups of parallel 1-D chains are interwoven with those of another chain to constitute a ladder-shaped double chain structure. Strong offset π–π stacking interactions are clearly indicated by the face-to-face distance of 3.33 Å for pyridine rings.

Water clusters $(H_2O)_n$ are studied to understand the "anomalous" behavior of bulk water for probing its possible roles in the stabilization and function of biomolecules and designing new materials [20]. As shown in figure 2, there are five crystallographically unique lattice H_2O molecules in an asymmetric unit. The average $O \cdots O$ distances of 2.8315 Å between these oxygen atoms indicate that they interact through hydrogen bonding. OW3, OW2, OW3A, OW1, and OW2A form a cyclic pentamer, and a 1-D water chain forms by sharing edges. The water chain is anchored to polymer chains through hydrogen-bonding of OW5 and OW4 to O2. A similar water chain has been observed in a recently synthesized analogue [21]. As illustrated in figure 3, for **1** four polymeric chains and four water chains interact to form a 1-D channel with

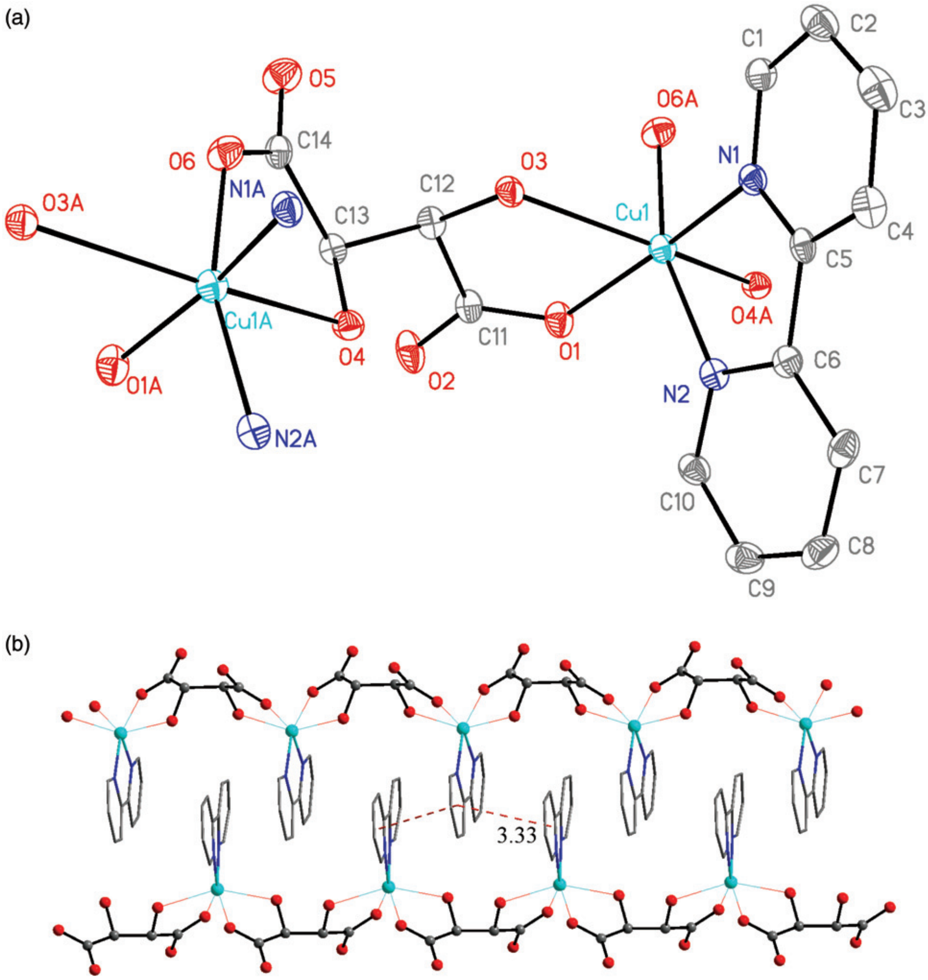

Figure 1. Along *a* axis (a) view of the repeat unit in the coordination polymer and (b) ladder-shaped double chains.

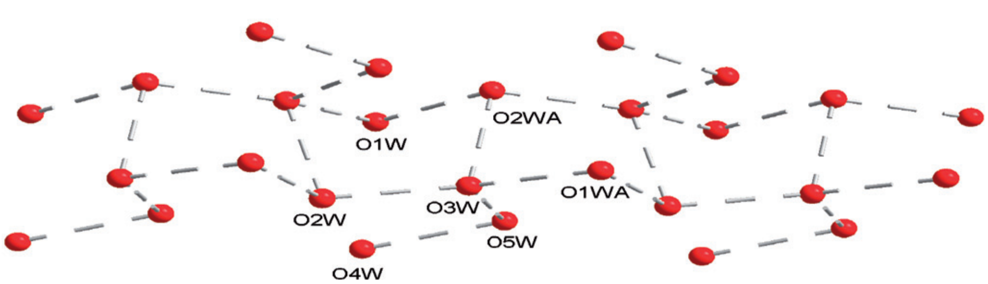

Figure 2. Water chain formed by the lattice water molecules. The lengths of O···O distance (Å): O1w–O2wA 2.8662(56), O1wA–O3w 2.8393(56), O2w–O3w 2.8059(53), O2wA–O3w 2.7864(46), O3w–O5w 2.8025(56), O4w–O5w 2.8841(56), O4w–O2 2.8359(49).

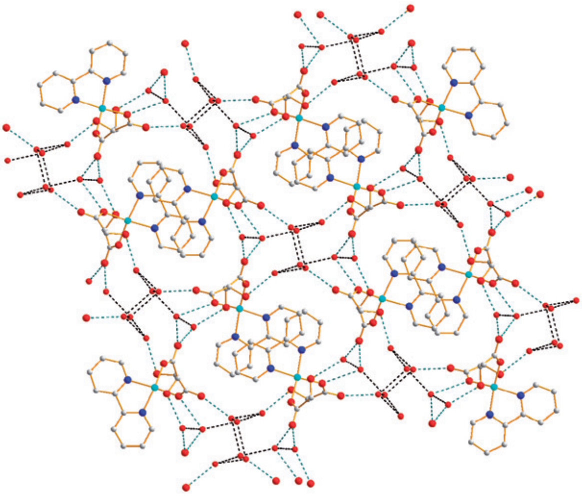

Figure 3. Packing view along the crystallographic *bc* plane for the supramolecular system. Online: carbon, white; nitrogen, blue; oxygen, red; copper, light blue; water molecule, light gray.

approximate dimension 14.21 × 7.23 Å, which accommodates the 2,2′-bipyridine molecules.

3.3. *Thermogravimetric analysis*

The thermal stability of **1** was tested by TG-DTA thermal analysis (TGA) under a nitrogen atmosphere with a heating rate of $5\,\mathrm{K\,min^{-1}}$. Thermal gravimetric analysis of polycrystalline **1** revealed two steps of weight losses. The first stage with weight loss of 18.27% occurred in the temperature range from 40 to 88°C from loss of water (calculated 19.77%). Nearly no weight loss occurred between 90 to 190°C, reflecting the stability of the polymeric chains. The second stage of weight loss of 64.95% occurred above 200°C, in agreement with the removal of L-tartaric frame and 2,2′-bipyridine (ca 62.86%). Complete decomposition of **1** was achieved at 350°C. The residue with a weight of 17.86% corresponded to CuO (17.37%).

4. Conclusion

A chiral Cu(II) coordination polymer has been synthesized and characterized. The protecting group isopropylidene was hydrolyzed in the hydrothermal reaction. Each tartrate chelates two Cu(II) ions at opposite ends using one carboxylate oxygen and one hydroxyl oxygen and each Cu(II) ion is chelated by two halves of tartrate dianions, forming coordination polymer chains. All the lattice water molecules are hydrogen bonded to each other or to the carbonyl oxygen of tartrate, constituting a 3-D supramolecular structure.

Supplementary material

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (No: CCDC-665871). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (20473089), the Natural Science Foundation of Fujian Province (2007J0306), and Fujian Normal University.

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