

三维 1, 4-二-(4-羧基吡啶基)丁烷合铜(II)、 银(I)配合物的合成及晶体结构表征

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利用 1, 4-二-(4-羧基吡啶基)丁烷(**L**)合成了铜(II)、银(I)的配合物 $\{[\text{CuL}(\text{H}_2\text{O})_3] \cdot 2(\text{H}_2\text{O}) \cdot 2(\text{NO}_3)\}_n$ (**1**)、 $\{[\text{AgL}] \cdot (\text{H}_2\text{O}) \cdot (\text{NO}_3)\}_n$ (**2**)。X射线晶体结构表征结果表明:**1**属于 $P2_1/n$ 空间群, 晶胞参数为 $a = 1.72410(3)$, $b = 0.66320(1)$, $c = 2.11380(4)$ nm, $\beta = 103.05(3)^\circ$, $Z = 4$ 。**2**属于 $P\bar{1}$ 空间群, 晶胞参数为 $a = 0.7766(2)$, $b = 0.9370(2)$, $c = 1.3357(3)$ nm, $\alpha = 98.99(3)$, $\beta = 99.49(3)$, $\gamma = 109.05(3)^\circ$, $Z = 2$ 。**1**和**2**的金属原子被**L**联接成一维结构。**1**中的配位链通过配位的水分子与晶格水分子及硝酸根离子间形成的氢键扩展为三维结构。**2**中未配位的羧基氧原子与吡啶环上的 α -氢原子形成 $\text{C}-\text{H}\cdots\text{O}$ 氢键从而将配位链扩展为阶梯状二维结构, 而层与层之间通过 $\pi-\pi$ 堆积结合在一起形成三维结构。

关键词: 1, 4-二-(4-羧基吡啶基)丁烷 晶体结构 氢键 $\pi-\pi$ 堆积
分类号: O614

Three-Dimensional Hydrogen Bonded Coordination Polymer of Cu (II) and C – H...O Joined $\pi-\pi$ Stacked Polymer of Ag (I) with 1, 4-Bis(4-Carboxypyridinium)butane: Synthesis and Characterization

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Reaction of a newly synthesized double betaine 1, 4-bis(4-carboxypyridinium) butane **L** with $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and AgNO_3 leads to the formation of coordination polymers $\{[\text{CuL}(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O} \cdot 2\text{NO}_3\}_n$ **1** and $\{[\text{AgL}] \cdot \text{H}_2\text{O} \cdot \text{NO}_3\}_n$ **2**, respectively. X-ray structure analysis indicates that **1** crystallizes in space groups $P2_1/n$ with $a = 1.7241(3)$, $b = 0.6632(1)$, $c = 2.1138(4)$ nm, $\beta = 103.05(3)^\circ$ and $Z = 4$; **2** in space group $P\bar{1}$ with $a = 0.7766(2)$, $b = 0.9370(2)$, $c = 1.3357(3)$ nm, $\alpha = 98.99(3)$, $\beta = 99.49(3)$, $\gamma = 109.05(3)^\circ$ and $Z = 2$. In both **1** and **2**, the metal atoms are bridged by monodentate **L** to form coordination chains. For **1**, the chains are linked by aqua ligands, lattice water molecules and nitrate anions through hydrogen bonds to form a

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three-dimensional structure. For **2**, the chains are joined by the C – H...O hydrogen bonds between the pendent oxygen atoms of **L** and the hydrogen atoms on the pyridyl rings forming stepped layers, which are further extended to three-dimensional structure by π - π stacking.

Keywords: 1, 4-bis(4-carboxypyridinium)butane crystal structure hydrogen bonding π - π stacking

0 Introduction

Owing to their potential electronic, magnetic, optical, catalytic properties and their fascinating molecular structures, the construction of coordination supramolecules with various topologies has been subjected to extensive investigations in recent years^[1]. The most widely used organic building blocks in these studies were 4, 4'-bipyridyl and its derivations such as trans-1, 2-bis(4-pyridyl) ethane, 4, 4'-azopyridine etc.^[2], and compounds bearing multi-carboxylate groups such as terephthalate^[3] and 1, 3, 5-benzenetricarboxylate^[4] etc. In addition, interactions such as hydrogen bonding and π - π stacking^[5] also play an important role in constructing structures with special topologies.

Bearing a positive charged quaternary ammonium moiety and a naked carboxylate group, betaine (prototype $\text{Me}_3\text{N}^+\text{CH}_2\text{CO}_2^-$) derivatives are neutral ligands that exhibit not only the versatile coordination fashions of carboxylic acids^[6] but also some special ligation properties toward metal ions^[7]. It is expected that, when ligating to metal ions, multiple betaine may behave like multidentate N-heterocycle compounds and furthermore, the oxygen atoms of the carboxylate groups can also form hydrogen bonds with aqua ligands or lattice water molecules thus enable them to construct complicated high dimensional structures.

In present research, a new double betaine ligand 1, 4-bis(4-carboxypyridinium) butane (**L**) has been prepared and allowed to react with $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and AgNO_3 . Two novel compounds, namely $\{[\text{CuL}(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O} \cdot 2\text{NO}_3\}_n$ **1** and $\{[\text{AgL}] \cdot \text{H}_2\text{O} \cdot \text{NO}_3\}_n$ **2**, were obtained. Single crystal X-ray analysis of **1** and **2** shows that both compounds are coordination chains which are held together by various non-bonding interactions to form complicated three-dimensional structures.

1 Experimental

All chemicals were commercially available and used as received. The IR spectra were recorded from KBr pallet in the range of $4000 \sim 400\text{cm}^{-1}$ on a Bio-Bad Exalibur FTS 3000 spectrometer.

1.1 Synthesis of 1, 4-bis(4-carboxypyridinium)butane (**L**)

To the solution of 1, 4-dibromobutane(0.1mol) in acetone(100cm^3), ethyl isonicotatate(0.22 mol, excess 10%) was added. The mixture was refluxed for 7 days and the resulted precipitate was filtered, rinsed with acetone for several times and air-dried. The product was dissolved in 15% HCl (100cm^3) and refluxed for 5 hours, then the solvent was removed under reduced pressure. The residue was redissolved in minimum amount of water and treated with 1, 2-epoxypropane until the $\text{pH}=7$. After the solvent was removed under reduced pressure, the colorless crystalline 1, 4-bis(4-carboxypyridinium) butane was obtained from the recrystallization of the residue in $\text{H}_2\text{O}/\text{EtOH}$

(yield: 70%)^[8]. IR: 1659cm⁻¹[carboxylate ν_{asym}], 1364cm⁻¹[carboxylate ν_{sym}].

1.2 Synthesis of {[CuL(H₂O)₃] · 2H₂O · 2NO₃}_n (1) and {[AgL] · H₂O · NO₃}_n (2)

The synthesis process of **1** and **2** were similar: the mixture of L and the corresponding metal salt in H₂O (*c. a.* 8cm³) was heated at about 60°C for *c. a.* 15min and filtered. The crystals of **1** and **2** available to X-ray analysis were obtained after standing of the filtration at ambient temperature for several days (**2** crystallized in darkness). For **1**, L(1mmol) and Cu(NO₃)₂ · 4H₂O (1mmol), blue block-like crystals, yield 91%, IR: 1625cm⁻¹[carboxylate ν_{asym}], 1366cm⁻¹[carboxylate ν_{sym}], 1381cm⁻¹[nitrate anion $\nu_{\text{str}}(\text{N-O})$]; for **2**, L(0.5mmol) and AgNO₃(0.5mmol), colorless block-like crystals, yield 83%, IR: 1630cm⁻¹[carboxylate ν_{asym}], 1363cm⁻¹[carboxylate ν_{sym}], 1385cm⁻¹[nitrate anion $\nu_{\text{str}}(\text{N-O})$].

1.3 Crystallographic Data Collection and Structure Determination

The diffraction data for both **1** (blue block-like crystal, 0.25 × 0.20 × 0.08mm³) and **2** (colorless block-like crystal, 0.20 × 0.20 × 0.15mm³) were collected at 298(2) K on a Bruker SMART-CCD diffractometer (graphite-monochromated Mo K α radiation: λ = 0.071073nm). Both structures were solved by direct method, and the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 using the SHELXTL program package^[9]. All hydrogen atoms other than those of some water molecules of **1** and **2** were located on the difference Fourier map and allowed to ride on their respective parent atoms. These hydrogen atoms were included in the structure factor calculations, but their positions were not varied.

Crystallographic data for **1** and **2** were listed in Table 1. Final atomic coordinates and equivalent isotropic thermal parameters along with their estimated standard deviation, a listing of observed and calculated structure factors, anisotropic thermal parameters and H-atom coordinates are available from the corresponding author.

2 Results and Discussion

2.1 Crystal Structure of {[CuL(H₂O)₃] · 2H₂O · 2NO₃}_n (1)

As depicted in Fig. 1, the compound is a one-dimensional coordination polymer: Cu(II) atoms, which are in MO₆ [Cu-O: 0.1936(3) ~ 0.2438(7) nm] and MO₄ [Cu-O: 0.1940(4) ~ 0.1955(5) nm] coordination spheres, are bridged by monodentate L forming a zig-zag chain. The neighboring chains are linked by hydrogen bonds between the adjacent aqua ligands and lattice water molecules [O2WA...O4WA = 0.2722nm, O4WA...O2WH = 0.2794nm, O4WA...O1WB = 0.2861nm] thus forming a hydrogen-bonded layer (Fig. 2, 4). The layers are mutually parallel, and stack as ABAB fashion (B-type layers are formed by rotating 180° of A-type layers) with the CuO₄ moieties on one type layers locating in the centers of four neighboring CuO₆ moieties on adjacent layers of other type. As a result, the layers extend to a three-dimensional structure (topologic sketch Fig. 3) through hydrogen bonds between the aqua ligands on CuO₄, CuO₆ moieties, lattice water molecules and the nitrate anions (Fig. 4, Table 3). It is worthy to note that O4WA forms four hydrogen bonds with neighboring aqua ligands and nitrate anion, either as hydrogen bonding donor and hydrogen bonding acceptor.

Table 1 Crystal Data and Structure Refinement for 1 and 2

formula	C ₁₆ H ₂₆ CuN ₄ O ₁₅ (1)	C ₁₆ H ₁₈ AgN ₃ O ₈ (2)
<i>M</i>	577.95	488.20
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
crystal size/mm ³	0.25 × 0.20 × 0.08	0.20 × 0.20 × 0.15
<i>a</i> /nm	1.7241(3)	0.7766(2)
<i>b</i> /nm	0.6632(1)	0.9370(2)
<i>c</i> /nm	2.1138(4)	1.3357(3)
α /(°)	90	98.99(3)
β /(°)	103.05(3)	99.49(3)
γ /(°)	90	109.05(3)
<i>V</i> /nm ³	2.3545(8)	0.8829(3)
<i>Z</i>	4	2
<i>D_c</i> /(Mg · m ⁻³)	1.630	1.836
<i>F</i> (000)	1196	492
μ /mm ⁻¹	1.010	1.195
theta range/(°)	1.38 to 25.02	1.59 to 26.40
reflections collected	9182	4212
independent reflections	4147[<i>R</i> (int) = 0.0861]	3590[<i>R</i> (int) = 0.0191]
goodness-of-fit on <i>F</i> ²	0.999	1.041
<i>R</i>	0.0612	0.0451
<i>R_w</i>	0.1409	0.1137
largest diff. peak and hole	0.537 and -0.572	0.992 and -0.763

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega F_o^2]^{1/2}$$

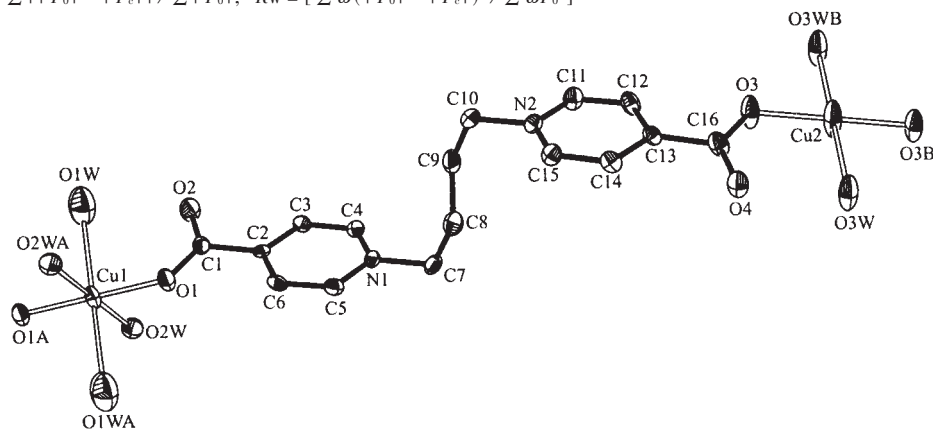


Fig. 1 Coordination structure and atom numbering in 1

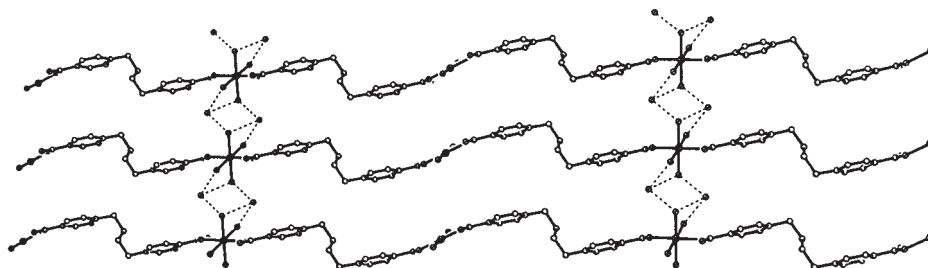


Fig. 2 Perspective view of the crystal graph of compound 1 and its Polymerization through aqua ligands to extend to two-dimensional networks

Table 2 Bond Lengths(nm) and Angles(°) for 1, 2

1					
Cu1-O1	0.1936(3)	Cu1-O2W	0.2024(5)	Cu1-O1W	0.2438(7)
O3-Cu2	0.1940(4)	Cu2-O3W	0.1955(5)		
O1A-Cu1-O1	180.0(4)	O1-Cu1-O2W	88.4(2)	O2WA-Cu1-O2W	180.0(4)
O1-Cu1-O1W	92.9(2)	O1W-Cu1-O1WA	180.0(4)	O3-Cu2-O3B	180.0(3)
O3-Cu2-O3W	94.6(2)	O3W-Cu2-O3WB	180.0(2)		
2					
Ag1-O1	0.2207(3)	Ag1-O3	0.2239(3)	Ag1-O7	0.2688(4)
O1-Ag1-O3	170.84(11)	O1-Ag1-O7	87.2(10)	O3-Ag1-O7	101.8(11)

Symmetrical code: **1**: A: $1-x, -y, -z$; B: $3-x, -y, 1-z$

Table 3 Bond Lengths(nm) and Angles(°) for H-bonding in 1, 2

1					
O4WA...O10C	0.2771	O4WA...O1WB	0.2861	O4WA...O2WH	0.2794
O4WA...O2WA	0.2722	O9C...O3WC	0.2693	O4WE...O2WH	0.2722
O4WE...O2WA	0.2794				
O2WA...O4WA...O2WH	82.3	O2WH...O4WA...O1WB	63.4	O1WB...O4WA...O10C	153.2
O10C...O4WA...O2WA	126.2				
2					
O1A...H12C	0.2540	O4A...H11C	0.2231		
O1A...H12C - C12C	153.6	O4A...H11C - C11C	157.9		

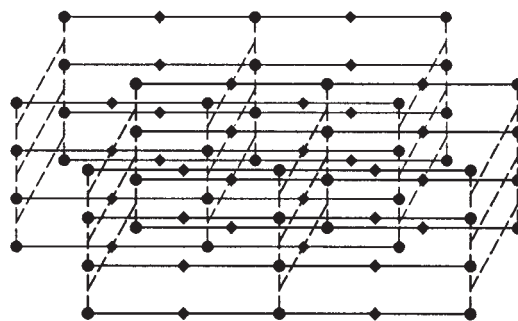
Symmetrical code: **1**: A: x, y, z ; B: $x, 1+y, z$; C: $1-x, -y, z$; D: $-x, -1-y, 1-z$;E: $-x, -y, 1-z$ **2**: A: x, y, z ; C: $1+x, y, z$

Another interesting feature of **1** is that the distances [0.2438(7)nm] between the axial aqua ligands and Cu1 atom are much longer than those between the equatorial oxygen atoms and Cu1 atom [average 0.1980(4)nm], which indicates a significant Jahn-Teller effect. Furthermore, for Cu2 the Jahn-Teller effect is so strong that the axial aqua ligands only weakly interact with the Cu2 atom [Cu2A ... O5WA: 0.2647nm (Fig. 4)].

2.2 Crystal Structure of 2

As shown in Fig. 5 each Ag(I) atom is linked by L in a nearly linear MO₂ [Ag-O: 0.2207(3) ~ 0.2239(3)nm; O1-Ag1-O3: 170°] coordination sphere forming a zig-zag chain. In addition, the Ag(I) atom is also secondly coordinated by the nitrate anions [Ag1-O7: 0.2688nm], which is evidenced by the fact that O1-Ag1-O3 angle is 170°, significantly deviates from linearity.

The chains are further extended to a two-dimensional stepped network through C-H...O hydrogen bonds formed between the pendent oxygen atoms of the carboxylate groups(O4A) and the α -H atoms (H11C etc.), which are activated by the positively charged nitrogen atoms, on pyridyl

Fig. 3 Sketch of the topologic structure of **1**

● represents CuO₆ moiety and ◆ CuO₄ moiety;
dashed line indicates hydrogen bond and solid line
coordination bond

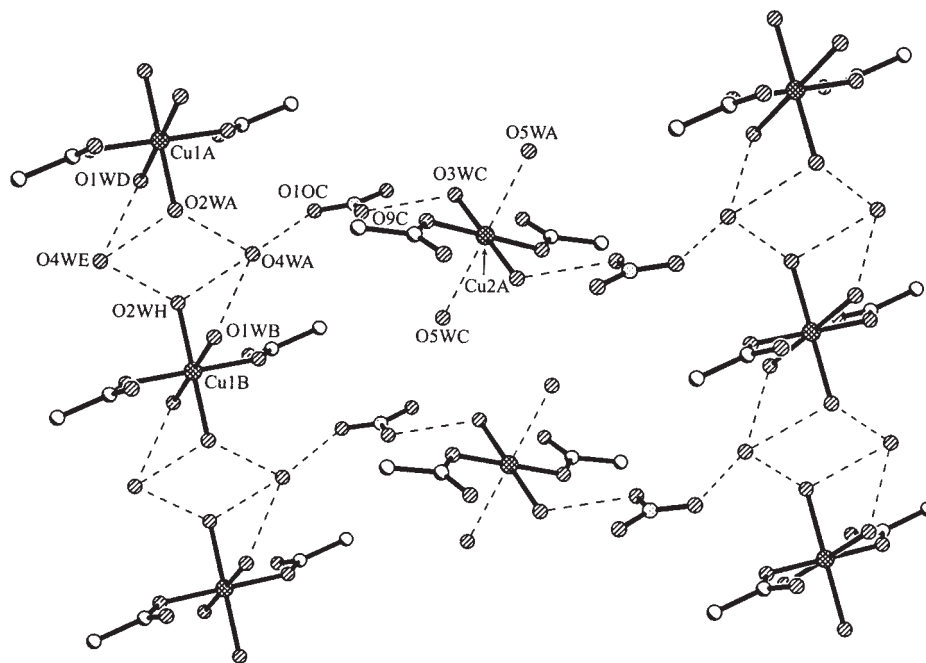


Fig. 4 Perspective view of the crystal structure of compound **1** and the hydrogen bonds to extend to three-dimensional structure

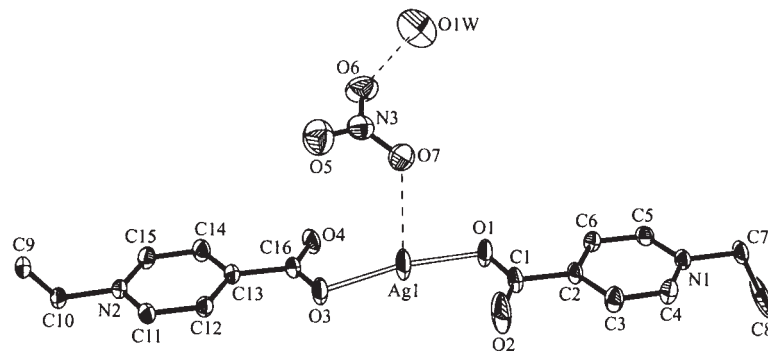


Fig. 5 Coordination structure and atom numbering in complex **2**

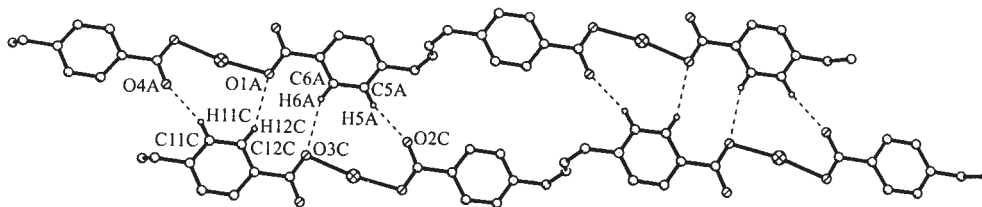
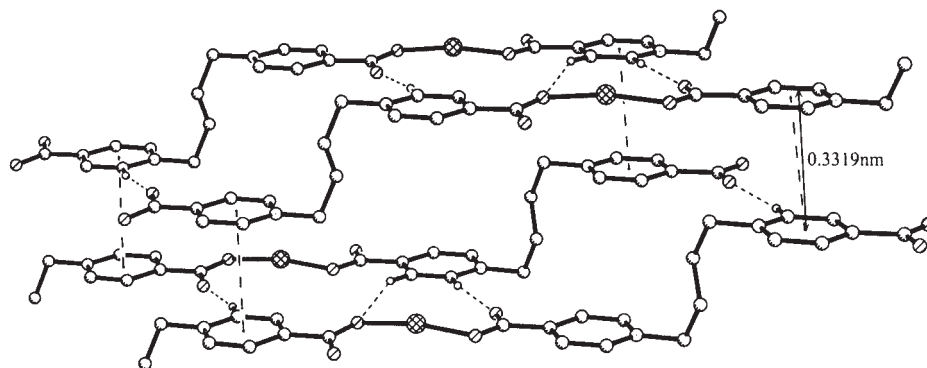


Fig. 6 Two-dimensional stepped layer extended by hydrogen bonding rings of adjacent chains (Fig. 6). The H11C...O4A distance of 0.2231 nm and C11C – H11C...O4A

Fig. 7 View of the stacking forms of the sheets in complex **2**

The nitrate anions are omitted for clarity

angle of 157.9° are comparable with those of the short $C-H\cdots O=C$ hydrogen bonds reviewed by Thomas Steiner etc.^[10]. In addition, some weaker $C-H\cdots O$ hydrogen bonds also exist, which are formed between ligating oxygen atom (O1A etc.) of the carboxylate groups and the β -H atoms (H12C etc.) on pyridyl ring of adjacent chains with the $H12C\cdots O1A$ distance of 0.2540nm and $C12C-H12C\cdots O1A$ angle of 153.6° . Furthermore, as expected, the crystal structure of **2** is consisted of π - π stacking as shown in Fig. 7. The distance of neighboring paralleled pyridyl rings is 0.3319nm with an offset about 0.2252nm. The distance is comparable with that of graphite [0.3354nm in highly crystalline graphite; 0.3440nm in poorly crystalline carbons]^[11], indicating a strong edge-to-face offset π - π stacking interaction^[5, 12].

3 Conclusion

Two novel linear metal coordination polymers with three-dimensional structures have been prepared and structurally characterized. The results show that 1,4-bis(4-carboxypyridinium) butane usually acts as a monodentate ligand, which means the existence of pendent carboxylate oxygen atoms in the resulting coordination compounds. In addition, the positively charged nitrogen atom makes the α -H atoms of the pyridyl ring more acidic. The structure characteristic enables it to form π - π stacking and various kinds of hydrogen bonds thus helping it to assemble higher dimensional networks. Furthermore, the flexibility of the butenylene moiety of the ligand also facilitates the construction of various topological structures.

Reference

- [1] (a) Li Song-Lin, Mak T. C. W. *Inorg. Chim. Acta*, **1997**, **258**, 11;
(b) Swiegers G. F., Malefetse T. J. *Chem. Rev.*, **2000**, **100**, 3483;
(c) Batten S. R., Robson R. *Angew. Chem. Int. Ed.*, **1998**, **37**, 1461.
- [2] (a) Noro S. I., Kondo M., Ishii T., Kitagawa S., Matsuzaka H. *J. Chem. Soc., Dalton Trans.*, **1999**, 1569;
(b) Munno G. D., Armentano D., Poerio T., Julve M., Real J. A. *J. Chem. Soc., Dalton Trans.*, **1999**, 1813;
(c) Carlucci L., Ciani G., Moret M., Proserpio D. M., Rizzato S. *Angew. Chem. Int. Ed.*, **2000**, **39**, 1506.

- (d) Fujita M., Kwon Y. J., Washizu S., Ogura K. *J. Am. Chem. Soc.*, **1994**, **116**, 1151.
- [3] (a) LI Hai-Lian, Eddaoudi M., Groy T. L., Yaghi O. M. *J. Am. Chem. Soc.*, **1998**, **120**, 8571;
(b) Hong C. S., Do Y. *Inorg. Chem.*, **1998**, **37**, 4470;
(c) Fun H. K., Raj S. S. S., XIONG Ren-Gen, ZUO Jing-Lin, YU Zhi, YOU Xiao-Zeng *J. Chem. Soc., Dalton Trans.*, **1999**, 1915.
- [4] (a) Yaghi O. M., LI Hai-Lian, Davis C., Richardson D., Groy T. L. *Acc. Chem. Res.*, **1998**, **31**, 474;
(b) Yaghi O. M., Jernigan R., LI Hai-Lian, Davis C. E., Groy T. L. *J. Chem. Soc., Dalton Trans.*, **1997**, 2383;
(c) Yaghi O. M., LI Hai-Lian, Groy T. L. *J. Am. Chem. Soc.*, **1996**, **118**, 9096;
(d) Yaghi O. M., Davis C., LI Guang-Ming, LI Hai-Lian *J. Am. Chem. Soc.*, **1997**, **119**, 2681.
- [5] (a) Janiak C. *J. Chem. Soc., Dalton Trans.*, **2000**, 3885;
(b) Hunter C. A. *Chem. Soc. Rev.*, **1994**, 101.
- [6] Oldham C. *In Comprehensive Coordination Chemistry*, Wilkinson G., Gillard R. D., McCleverty, J. A., Eds., Pergamon Press: Oxford, **1987**, Vol. 3, ch. 15.
- [7] (a) LI Song-Lin, Mak T. C. W. *Struct. Chem.*, **1997**, **8**, 49;
(b) LI Song-Lin, Mak T. C. W. *J. Chem. Soc., Dalton Trans.*, **1995**, 1519.
- [8] Starks C. M., Liotta C. L. *Phase Transfer Catalysis: Principles and Techniques*, Academic Press: New York, **1978**.
- [9] Sheldrick G. M., *SHELXTL Version 5*, Siemens Industrial Automation Inc., Madison, WI, **1995**.
- [10] Steiner T., Kanters J. A., Kroon J. *Chem. Commun.*, **1996**, 1277.
- [11] Wells A. F. *Structural Inorganic Chemistry. Fourth Edition*, Clarendon Press: Oxford, **1975**, p734.
- [12] Hartshorn C. M., Steel P. J. *J. Chem. Soc., Dalton Trans.*, **1998**, 3927.