

单一手性烯烃铜(I)配位聚合物

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A Homochiral Olefin-copper(I) Coordination Polymer

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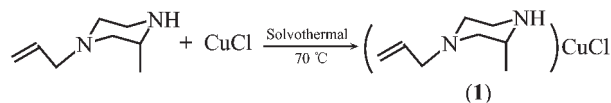
Abstract: The solvothermal reaction of CuCl with *R*-(−)-1-allyl-3-methylpiperazine at 70 °C gives one-dimensional chain Cu-coordination polymer through olefin moiety binding to Cu atoms formulated as $[\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_2)\text{Cl}]$. It is interesting to note that through Cu_2Cl_2 dimer unit **1** results in a supramolecular 3-dimensional coordination polymer. Powdered sample measurement of **1** reveals that **1** is second-harmonic generation (SHG) active compound. Crystal parameters for **1**, space group $P2_12_12_1$, $a=0.763\ 1(9)$ nm, $b=0.891\ 0(10)$ nm, $c=1.494\ 6(17)$ nm, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$, $V=1.016(2)$ nm³, $Z=2$, $M=478.44$, $D_c=1.564$ Mg·m^{−3}. CCDC: 650193.

Key words: olefin-copper(I); solvothermal; coordination polymer; crystal structure

0 Introduction

Olefin moiety coordination to copper(I) has found a wide spread applications such as olefin derivatives separation, bioinorganic chemistry, and purification CO for petroleum industry. On the other hand, the formation of olefin-copper(I) coordination polymer stabilizes the bond of olefin-Cu(I) so that many olefin-Cu(I) coordination polymers have been produced recently in my group while they have found many practical utilizations like SHG materials, ferroelectricity and fluorescent materials^[1~7]. Homochiral olefin copper coordination polymers reported in literatures show that there are only two cases based on natural product cinchona with olefin moiety, as we are aware^[5,6]. The synthesized homochiral

ligand with olefin moiety reacting with Cu(I) to form the olefin-Cu(I) coordination polymers is very rare and remains largely unexplored. As a continuation of our olefin copper(I) coordination chemistry program, we have performed the following reaction as shown in Scheme 1. The produced olefin copper(I) coordination polymer (**1**) ($\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_2)\text{Cl}$, copper chloride mono[*R*-(−)-1-allyl-3-methylpiperazine] displays a one-dimensional infinite chain structural feature with a 3-dimensional supramolecular structure through a pseudo-dimer Cu_2Cl_2 unit. Herein we report its synthesis and crystal



Scheme 1

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structure and preliminary SHG measurement.

1 Experimental

1.1 Materials and physical measurements

All starting materials were of A.R. grade, obtained from commercial suppliers and used without further purification. The FTIR spectra were recorded as solid in KBr matrix in the range 4 000~400 cm^{-1} on VECTOR-22 FTIR spectrometer.

1.2 Preparation of the Ligand (*R*-(-)-1-allyl-3-methylpiperazine)

The *R*-(-)-3-methylpiperazine (0.6 mol) was reacted with allyl bromide (0.2 mol) at 65 $^{\circ}\text{C}$ in the solvent of methylbenzene to give the product (*R*-(-)-1-allyl-3-methylpiperazine). Yield: ca. 70.5% based on *R*-(-)-3-methylpiperazine. b.p.191 $^{\circ}\text{C}$.

IR (KBr, cm^{-1}): 3 422.53(s), 2 936.00(s), 2 804.19(s), 1 642.48(m), 1 457.30(m), 1 376.08(w), 1 326.07(w), 1 140.19(s), 1 054.40(w), 996.76(w), 919.15(m), 821.54(w), 573.47(w).

MS(m/e): ($\text{M}+1$)⁺ 141.20 (isotopic peak 142.23)

1.3 Preparation of the $[\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_2)\text{Cl}]$ (**1**)

Solvothermal treatment of CuCl (1 mmol), *R*-(-)-1-allyl-3-methylpiperazine (1 mmol) and methanol (2 mL) over 1 day at 70 $^{\circ}\text{C}$ yield a pale yellow prismatic crystalline product. The yield of **1** was about 43%.

IR (KBr, cm^{-1}): 3 453.25(w), 3 148.38(s), 2 934.64(s), 2 815.37(s), 2 759.46(m), 1 526.80(w), 1 448.45(s), 1 385.32 (w), 1 333.27 (w), 1 305.40 (w), 1 253.18(m), 1 167.83 (m), 1 135.49 (s), 1 096.11 (m), 1 012.08(s), 983.11(s), 954.41(w), 900.22(w), 850.80(m), 800.15(m), 442.31(w).

2 Results and discussion

Under solvothermal reaction conditions (Scheme 1), the produced olefin copper coordination polymer, **1** has a tri-coordinated linear central Cu atom as shown in Fig.1 while the ligand [*R*-(-)-1-allyl-3-methylpiperazine] acts as bidentate linker to bridge two Cu atoms through N atom and olefin moiety to result in the formation of one-dimensional Cu coordination polymer (Fig.2). It is interesting to note that the terminal Cl atom also takes part in to another Cu atom through weak

dimer Cu_2Cl_2 unit to result in the pseudo-three-dimensional coordination polymer, as depicted in Fig.3.

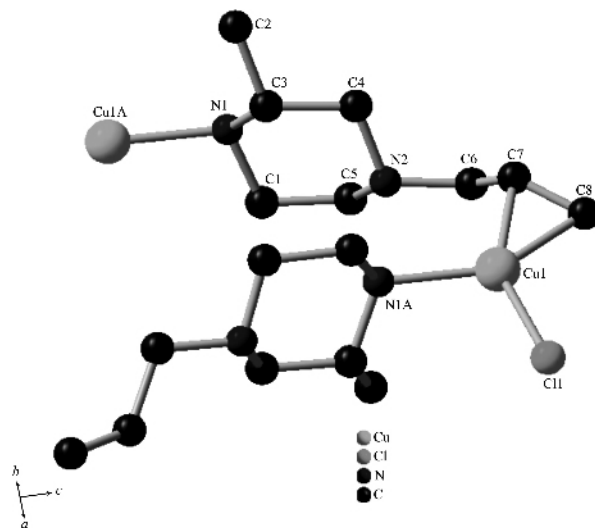


Fig.1 Asymmetric unit of $\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_2)\text{Cl}$ (**1**) showing that the local coordination environment around Cu atom can be best described as linearly trigonal mode composed of N atom, olefin moiety and a terminal Cl atom

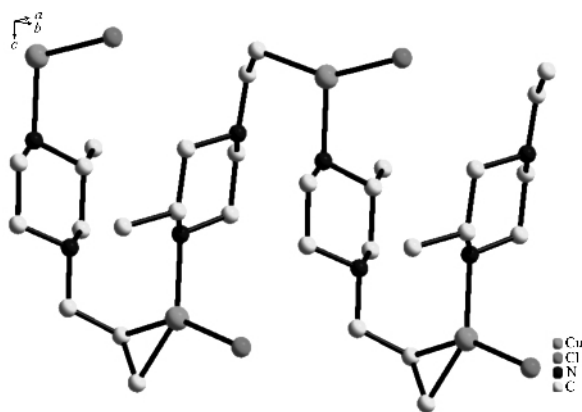


Fig.2 One-dimensional infinite chain representation of $\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_2)\text{Cl}$

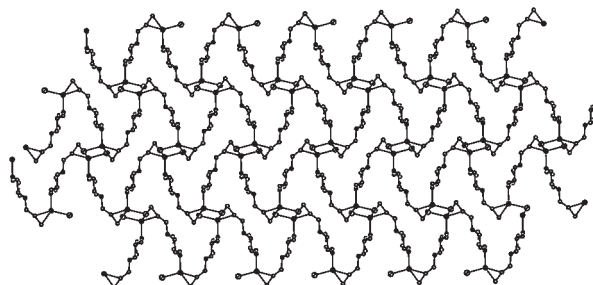


Fig.3 A pseudo-three-dimensional representation of $\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_2)\text{Cl}$ through weak coordination Cl to another Cu atom to resulting to the formation of a weak Cu_2Cl_2 dimer unit

To confirm its space group, the powdered sample measurement of SHG shows that **1** is active nonlinear optical materials about as the same as that of KDP.

CCDC: 650193.

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