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1D polymeric copper(I) complex $[Cu_2(\mu\text{-}(2,6\text{-Cl-ba})_2en)(\mu\text{-}I)_2]_n$ with exceptionally short Cu–Cu distance: Synthesis, characterization, thermal study and crystal structure

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ABSTRACT

A new 1D polymeric three coordinated copper(I) complex, $[Cu_2(\mu\text{-}(2,6\text{-Cl-ba})_2en)(\mu\text{-}I)_2]_n$, with the bidentate Schiff base ligand N,N′-bis(2,6-dichlorobenzylidene)ethane-1,2-diamine containing a flexible spacer (=NCH_2–CH_2–N=) was synthesized and characterized by elemental analyses, UV-Vis, FT-IR and ^{1}H NMR spectroscopy and thermal analysis. Its molecular structure was determined by single-crystal X-ray diffraction and shows the $(2,6\text{-Cl-ba})_2en$ acts as a bis-monodentate bridging ligand forming the dinuclear $[Cu_2(\mu\text{-}(2,6\text{-Cl-ba})_2en)]$ groups. Such dinuclear groups are bridged by two iodine anions $[(\mu\text{-}I)_2]$ to form a 1D polymeric copper(I) complex. The copper(I) ions are coordinated in a distorted trigonal planar geometry by two I atoms and one nitrogen atom of Schiff base ligand $(2,6\text{-Cl-ba})_2en$.

1. Introduction

Copper(I) containing d^{10} electronic configuration is one of the best ions, for the preparation of one, two and three-dimensional coordination polymers with suitable bridging ligands [1–4]. Copper(I) polymers have received much attention because of their various applications and properties [1,2]. The symmetric bidentate Schiff base ligands, prepared from the reaction of diamine and aldehyde or ketone have been known to be versatile ligands which may coordinate to d^{10} metal ions in many different ways such as chelating or bridging ligands [5–8]. Recently, in our laboratory, we prepared and characterized 1D polymeric copper(I) complexes containing bridging Schiff base ligands and also bridging halide or pseudohalides [9–12]. Herein, we report the synthesis, crystal structure, spectral and thermal studies of a new 1D polymeric copper(I) complex $[Cu_2(\mu\text{-}(2,6\text{-Cl-ba})_2en)(\mu\text{-}I)_2]_n$ (Scheme 1).

2. Experimental

2.1. Material and method

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN–O-Rapid analyzer, and results agreed with calculated values. Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on a FT-IR Perkin–Elmer spectrophotometer. The ^{1}H NMR spectrum was recorded on a BRUKER DRX-400 AVANCE spectrometer at 400 MHz for the Schiff base ligand. All chemical shifts are reported in δ units downfield from TMS. The TG/DTA were performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in nitrogen atmosphere with a heating rate of 20 °C/min in the temperature span of 50–800 °C. The Schiff base ligand $(2,6\text{-Cl-ba})_2en$ was prepared using the reported procedure [13].

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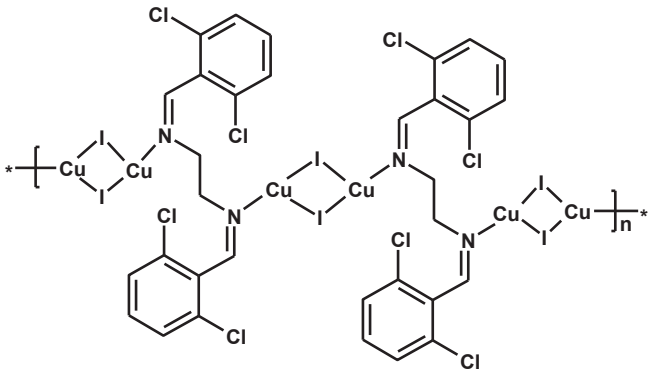

Scheme 1. Chemical structure of 1D polymeric copper(I) complex $[Cu_2(\mu\text{-}(2,6\text{-Cl-ba})_2en)(\mu\text{-I})_2]_n$.

2.2. X-ray structure determination

A single crystal of the dimensions 0.46 mm × 0.41 mm × 0.10 mm was chosen for X-ray diffraction study. Crystallographic measurements were done at 120 K with a four circle CCD diffractometer Gemini of Oxford diffraction, using Mo-*Kα* radiation from a classical sealed tube monochromated by graphite and collimated by fibre-optics Enhance collimator. As a detector we used the CCD detector Atlas S2. The sample was split and exhibiting partial overlaps of diffraction spots, and data were processed considering these overlaps in the hklf5 data format. Crystal structures were easily solved by charge flipping with program SUPERFLIP [14] and refined with the Jana2006 program package [15] by full-matrix least-squares technique on F^2. The molecular structure plots were prepared by Diamond 4.0 [16]. All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, H atoms bonded to C were kept in ideal positions with C—H = 0.96 Å and with U_{iso}(H) set to 1.2U_{eq}(C). No hydrogen atoms were found on nitrogen. All non-hydrogen atoms were refined using harmonic refinement. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

2.3. Preparation of [Cu((2,6-Cl-ba)$_2$en)(μ-I)]$_n$

To a solution of CuI (19 mg, 0.1 mmol) in CH_3CN (5 mL) was added, with continuous stirring, a solution of (2,6-Cl-ba)$_2$en (37 mg, 0.1 mmol) in the minimum amount of CH_3CN. The mixture was stirred at room temperature for about 10 min to give a clear yellow-orange solution. Yellow-orange single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature for several days. Anal. Calcd. for $C_{16}H_{12}Cl_4Cu_2I_2N_2$: C, 25.43.; H, 1.59.; N, 3.71%. Found; C, 25.49.; H, 1.63.; N, 3.75%. FT-IR (KBr, cm^{-1}): 1597 (-C═N-). ^{1}H NMR (DMSO-d_6, ppm): 4.01 (s, 4H, C—C**H**$_2$—C**H**$_2$—C), 7.38–7.51 (m, 6H, Ar—**H**), 8.58 (s, 2H, -C**H**═N-).

Table 1
Crystallographic data and structural refinement details of [Cu((2,6-Cl-ba)$_2$en)(μ-I)]$_n$.

Formula weight	$C_{16}H_{12}Cl_4Cu_2I_2N_2$
Formula weight	755
Crystal system, Space group	Monoclinic, *P*2/*c*
a, Å	8.2683(7)
b, Å	7.5983(6)
c, Å	17.1938(13)
β, deg	94.384(6)
V, Å^3	1077.04(15)
Z	2
μ, mm^{-1}	5.34
S	1.51
Measured reflections	23113
Measured independent	6419
Parameters	119
Reflections with I > 3σ(I)	4883
$R(F^2 > 2\sigma(F^2))$	0.038
wR (F^2)	0.102
$\Delta\rho_{max,\ min}$	0.55, −0.53

3. Results and discussion

3.1. Synthesis and characterization

The 1D polymeric copper(I) complex $[Cu((2,6\text{-Cl-ba})_2en)(\mu\text{-I})]_n$ was prepared using the synthetic details given in the experimental section. The FT-IR and ^{1}H NMR spectra were found to be in agreement with its expected chemistry. The band corresponding to the azomethine group of the ligand (C═N) appears at 1597 cm^{-1}. This band is shifted to a lower frequency relative to the free ligand (1608 cm^{-1}) due to the coordination of the imine nitrogen to the metal ions [9–12]. The ^{1}H NMR spectra show that the Schiff base ligand (2,6-Cl-ba)$_2$en has a symmetric structure. Aliphatic protons (—CH_2—CH_2-) appear as a singlet signal at 4.008 ppm, while the aromatic protons appear as multiplet signal at 7.38–7.51 ppm. The iminic protons of (-CH═N-) appear at 8.58 ppm as a singlet signal.

3.2. Thermal study

Thermal stability of the title compound $[Cu((2,6\text{-Cl-ba})_2en)(\mu\text{-I})]_n$ was examined under Ar atmosphere. The TG curve (Fig. 1) shows there is no detectable change up to ≈220 °C, while during further heating the title compound undergoes thermal decomposition in two stages, loosing ≈44% of its weight between 220 and 375 °C and ≈39% of its weight between 505 and 780 °C. The final product is 2Cu (16.8%).

3.3. Crystal structure of [Cu((2,6-Cl-ba)$_2$en)(μ-I)]$_n$

X-ray diffraction for $[Cu((2,6\text{-Cl-ba})_2en)(\mu\text{-I})]_n$ reveals that the asymmetric unit contains one Cu, one I and one half Schiff base ligand (2,6-Cl-ba)$_2$en. The second half of the ligand is generated by the screw axis and translation x+1, y, -z+1/2. As shown in Fig. 2, the Schiff base ligand acts as a bis-monodentate bridging ligand while the iodine ions act as a single bridging ligand (*μ*-I), linking the [Cu(μ-(2,6-Cl-ba)$_2$en)] fragments into a 1D polymeric copper(I) complex $[Cu((2,6\text{-Cl-ba})_2en)(\mu\text{-I})]_n$ (Fig. 2). As shown in Fig. 2, the coordination geometry of the copper(I) atom can be described as a triangle, formed by two iodine ions and one nitrogen atom from the bis-monodentate Schiff base bridging ligand (2,6-Cl-ba)$_2$en. The angles around the copper(I) center deviate from 109.5° {∠ $I1^i$-Cu1-I1 = 121.286(18)°, ∠ I1—Cu1—N1 = 124.91(8)°, ∠ $I1^i$-Cu1-N1 = 113.52(8)° and ∠ Cu1—I1—$Cu1^i$ = 58.343(15)°} (symmetry code: (i) -*x*, *y*, -*z*+0.5), indicating distortion of the trigonal planar geometry. The Cu1—N1 and Cu1—$I1^i$ and Cu1—I1 distances, being 1.981(3), 2.5840(6) and 2.5415(6) Å, respectively, are similar to these bonds in the other 1D polymeric copper(I) complexes [9–12]. The Cu···Cu distance in the Cu-(*μ*-I)$_2$-Cu^i fragment is 2.4986(7) Å, while the Cu···Cu distance in the Cu-(*μ*-(2,6-Cl-ba)$_2$)-Cu fragment is 5.89(11) Å. The obtained Cu—Cu distance is very short compared with similar compounds [9–12]. A CSD search, The Cambridge Structural Database [17,18], using the latest update from May 2016, and restricted to single crystal data sets with R ≤ 0.1, without disorder and with two bands on iodine, has shown that out of 611 hits only 18 compounds have the Cu—Cu distance below 2.51 Å.