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$[Cu_2(\mu\text{-}(3,4,5\text{-meo-ba})_2bn)(\mu\text{-}I)_2]_n$, a new 1D polymeric copper(I) chain

Synthesis, crystal structure, spectral and thermal studies

Aliakbar Dehno Khalaji · Smail Triki ·
Debasis Das

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Abstract New 1D-chain copper(I) complex $[Cu_2(\mu\text{-}(3,4,5\text{-MeO-ba})_2bn)(\mu\text{-}I)_2]_n$ (**1**), where $(3,4,5\text{-MeO-ba})_2bn$ = *N,N′*-bis(3,4-dimethoxybenzylidene)-butane-1,4-diamine, involving a new bidentate Schiff-base containing a flexible spacer (=N–C–C–C–C–N=) has been synthesized and characterized by elemental analyses (CHN) and FT-IR spectroscopy. The crystal structure of **1** was determined from single-crystal X-ray diffraction analyses and shows the $(3,4,5\text{-MeO-ba})_2en$ acts as a bridging ligand with the nitrogen atoms of the two imine functions and leading to the dinuclear $[Cu_2((\mu\text{-}(3,4,5\text{-MeO-ba})_2en)]$ groups. Such dinuclear $[Cu_2((\mu\text{-}(3,4,5\text{-MeO-ba})_2en)]$ groups are bridged by two iodine anions $[(\mu\text{-}I)_2]$ to form a neutral 1D-chain copper(I) iodide coordination polymer. The coordination polyhedron about the copper(I) center in **1** is best described as a distorted trigonal planar. Thermogravimetric analyses reveal the thermal stability and decomposition pattern of **1**.

Keywords Schiff-base · 1D-chain · Flexible spacer · Copper(I) iodide coordination polymer

Introduction

Copper(I) complexes with bridging halides and pseudohalides have attracted considerable attentions as an important part of coordination chemistry in recent years, not only due to their structural novelty [1–4] but also for their potential application in catalysis [5, 6] and photophysical properties [7–9]. The azomethine compounds known in the literature as Schiff-bases, having imine groups (–C=N–), are extensively studied as a bidentate chelating ligand in copper(I) complexes [10–13]. The structure of copper(I) complexes formed by the reaction of CuX and Schiff-base ligand depends on the nature of the solvent, Schiff-base ligand, and X (where X = halide and pseudohalide) [1–4, 7–16]. Recent studies have focused on the copper(I) halides systems for their ability to form 1D [14], 2D [15], and 3D [16] complexes. However, synthesis, characterization, and thermal decomposition of the transition metal complexes with Schiff-base ligands have been extensively studied in recent years [17–25].

This study is a part of our ongoing effort to synthesize and characterize an extensive series of new 1D copper(I) coordination polymers with Schiff-base ligand [10–13]. Herein, we report the synthesis, crystal structure, spectral and thermal studies of a new 1D-chain copper(I) complex $[Cu_2(\mu\text{-}(3,4,5\text{-MeO-ba})_2bn)(\mu\text{-}I)_2]_n$ (**1**) (Fig. 1).

Experimental

Physical techniques and materials

All reagents and solvents for synthesis and spectroscopic studies were commercially available and used as received without further purification. The infrared spectrum was

A. D. Khalaji (✉)
Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran
e-mail: alidkhalaji@yahoo.com

S. Triki
UMR CNRS 6521, Université de Bretagne Occidentale, BP 809, 29285 Brest Cedex, France

D. Das
Department of Chemistry, The University of Burdwan, Burdwan, West Bengal, India

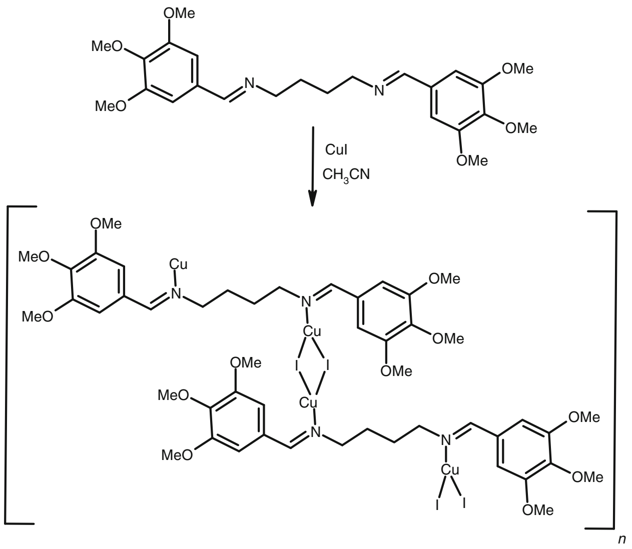


Fig. 1 Chemical structures of the Schiff-base ligand (3,4,5-MeO-ba)$_2$bn, and its 1D-chain copper(I) complex [Cu$_2$(μ-(3,4,5-MeO-ba)$_2$bn)(μ-I)$_2$]$_n$ (**1**)

recorded on a Perkin Elmer FT-IR spectrophotometer (4000–400 cm^{-1}) as a KBr pellet. Elemental analyses were carried out using a Heraeus CHN–O-Rapid analyzer. Thermogravimetric analyses were done on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in nitrogen atmosphere with a heating rate of 20 °C/min from 35 to 700 °C.

Preparation of (3,4,5-MeO-ba)$_2$bn

This ligand was prepared following a literature procedure similar to the synthesis of (3,4-MeO-ba)$_2$bn [26] using 0.02 mol of 3,4,5-trimethoxybenzaldehyde. Yield: 89%. Anal. calc. for $C_{24}H_{32}N_2O_6$: C, 64.85; H, 7.26; N, 6.30%. Found: C, 64.91; H, 7.20; N, 6.33%. IR (KBr pellet, cm^{-1}): 3010–3088 (m, C–H aromatic), 2839–2989 (m, C–H aliphatic), 2821 (–HC=N), 1644 (s, C=N), 1435–1585 (m, C=C aromatic).

Preparation of [Cu$_2$((μ-(3,4,5-MeO-ba)$_2$bn)(μ-I)$_2$]$_n$ (**1**)

A solution of (3,4,5-MeO-ba)$_2$bn (0.076 g, 0.2 mmol) in 20 mL acetonitrile was heated for 25 min at 50 °C and then stirred for about 25 min. To this stirring solution, a solution of copper(I) iodide (0.2 mmol) in 20 mL acetonitrile was added dropwise with constant stirring. The mixture was heated under stirring condition for about 15 min and allowed to cool overnight at 273 K. The resulting yellow crystals were collected by filtration, washed with Et$_2$O and dried at room temperature. Yield: 78%. Anal. calc. for $C_{24}H_{33}Cu_2I_2N_2O_6$: C, 34.93; H, 3.90; N, 3.39%. Found: C, 35.01; H, 3.95; N, 3.32%. IR (KBr pellet, cm^{-1}): 2997–3025 (m, C–H aromatic), 2857–2959 (m, C–H aliphatic), 2835 (–HC=N), 1630 (s, C=N), 1462–1583 (m, C=C aromatic).

Crystal structure determination and refinement of **1**

A bright yellow single crystal of **1** with approximate dimensions 0.18 × 0.12 × 0.09 mm^3 was placed at the top of a glass fiber with silicone grease and mounted on an Xcalibur 2 CCD Diffractometer (Oxford Diffraction) fitted with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected at 170 K. The structure was solved by direct methods and successive Fourier difference syntheses, and was refined on F^2 by weighted anisotropic full-matrix least-square methods using the SHELXL97 program [27]. All non-hydrogen atoms were refined anisotropically while the hydrogen atoms were calculated and, therefore, included as isotropic fixed contributors to F_c. Data collection and data reduction were done with the CRYSALIS-CCD and CRYSALIS-RED programs [28]. All other calculations were performed with standard procedures (WINGX) [29]. Crystal data, structure refinement, and collection parameters for **1** are listed in Table 1.

Table 1 Crystal data and structural refinement parameters for **1**

Empirical formula[a]	$C_{24}H_{32}Cu_2I_2N_2O_6$
Molecular weight	825.40
Space group	$P2_1/n$
a (Å)	7.5214(7)
b (Å)	22.7515(8)
c (Å)	8.6470(5)
β (°)	99.59(1)
V (Å^3)	1459.0(2)
Z[a]	2
ρ_{calc} (g cm^{-3})	1.879
μ (mm^{-1})	3.612
F(000)	804
Reflections measured	14846
2θ range (°)	5.78–63.24
Reflections unique/R_{int}	4594/0.0198
Reflections with $I > 2\sigma(I)$	3515
N_v	191
$R1$[b]/$wR2$[c]	0.0284/0.0624
GooF[d]	1.134
$\Delta\rho_{max/min}$ (eÅ^{-3})	+0.839/−0.365

[a] The empirical formula corresponds to two asymmetric units

[b] $R1 = \sum|F_o - F_c|/F_o$

[c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

[d] $\mathrm{GooF} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{var})\}^{1/2}$

Results and discussion

Synthesis and FT-IR spectra

The flexible Schiff-base ligand (3,4,5-MeO-ba)$_2$bn used in this study was prepared under mild condition and is stable in air at room temperature. The reaction of this ligand with the stoichiometric amount of CuI resulted 1D-chain copper(I) coordination polymer **1** in 78% yield. Complex **1** is stable in acetonitrile solution under air for about 1 day and in chloroform or methanol solution under air for about 3 h. But crystals of this complex are stable in air at room temperature for about 50–70 days. The FT-IR spectrum of the free ligand exhibits the characteristic band of the azomethine group of the ligand (C=N), which appears at 1644 cm^{-1}. This band is shifted to lower frequency, 1630 cm^{-1}, relative to the free ligand in the FT-IR spectra of the complex due to the coordination of the imine nitrogen to the central copper ion. The new bands in the spectra of the title complex **1** in the frequency range 459–524 cm^{-1} can be assigned to the stretching frequencies υCu–N and υCu–I [20]. The solubility of the title complex **1**, in common organic solvents, is very low; therefore, the solution properties (i.e., ^{1}H-NMR, CV, and UV–Vis spectra) of this complex were not studied [12].

Crystal structure description of 1

Single-crystal X-ray analysis has revealed that complex $[Cu_2((\mu\text{-}(3,4,5\text{-MeO-ba})_2bn)(\mu\text{-}I)_2]_n$ (**1**) is a neutral and crystallizes in monoclinic space group $P2_1/n$. As shown in Fig. 2, the coordination geometry of the copper(I) atom can be described as distorted trigonal planar, and it is coordinated by two iodine ions and one nitrogen atom from Schiff-base ligand. The angles of the trigonal structure deviate from 120° (Table 2). The organic Schiff-base ligand acts as a bis-monodentate bridge ligand through its two iminic nitrogens leading to the $[Cu_2(\mu\text{-}(3,4,5\text{-MeO-ba})_2bn)]$ dinuclear fragment (Fig. 3). The two iodine ions, acting as a doubly bridging ligand $(\mu\text{-}I)_2$, linked $[Cu_2(\mu\text{-}(3,4,5\text{-MeO-ba})_2bn)]$ dinuclear fragment together and formed 1D-chain copper(I) coordination polymer $[Cu_2((\mu\text{-}(3,4,5\text{-MeO-ba})_2bn)(\mu\text{-}I)_2]_n$ (**1**) (Fig. 3). The Cu–N1 distance in this

Table 2 Selected bond length (Å) and bond angles (°) for compound **1**

Bond length (Å)	
Cu–I	2.5491(4)
Cu–I$^{(b)}$	2.5647(4)
Cu–N1	1.9730(18)
C1–N1	1.272(3)
C8–N1	1.478(3)
C9–C9$^{(a)}$	1.517(4)
Cu–Cu$^{(b)}$	2.5584(6)
Bond angles (°)	
Cu–I–Cu$^{(b)}$	60.036(13)
N1–Cu–I	122.81(5)
N1–Cu–Cu$^{(b)}$	172.52(6)
I–Cu–Cu$^{(b)}$	60.285(14)
N1–Cu–I$^{(b)}$	116.77(5)
I–Cu–I$^{(b)}$	119.964(13)
C9$^{(a)}$–C9–C8	112.5(2)
N1–C1–C2	125.5(2)
Cu$^{(b)}$–Cu–I$^{(b)}$	59.678(13)
C1–N1–C8	116.76(19)
C1–N1–Cu	129.85(16)
C8–N1–Cu	113.17(15)
N1–C8–C9	110.72(19)

Code of equivalent position: (a) $-x+1,-y,-z+1$; (b) $-x+1,-y,-z+2$

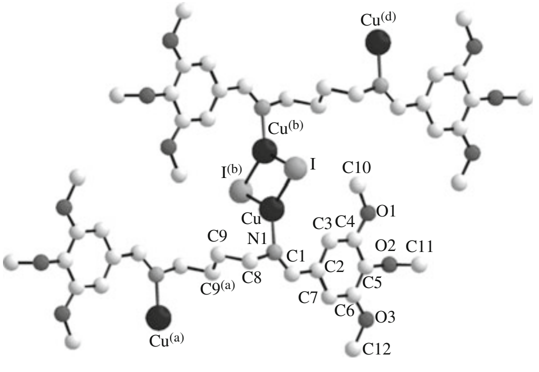


Fig. 2 Projection view of **2** showing the symmetric units, the atom labeling scheme, the molecular structure of the flexible Schiff-base ligand and the Cu environment. Code of equivalent position: **a** $-x+1,-y,-z+1$; **b** $-x+1,-y,-z+2$

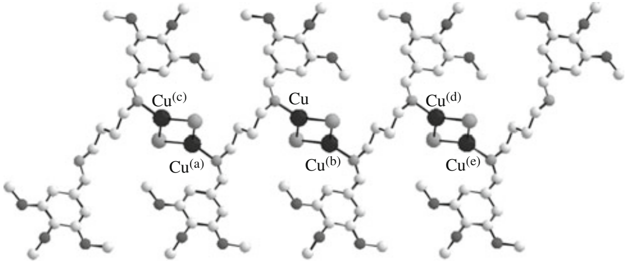


Fig. 3 The fragment of 1D chain of complex **2** running along the [001] direction. Code of equivalent position: (a) $-x+1,-y,-z+1$; (b) $-x+1,-y,-z+2$

complex (Table 2), being 1.9733(19) Å, is similar to this bond in other copper(I) complexes [10–13]. The Cu–I distances of 2.5491(4) and 2.5648(3) Å are slightly shorter than those of 2.6650(5) and 2.7393(5) Å in the 1D-chain copper(I) complex $[Cu_2(\mu\text{-}I)_2(PPh_3)_2(4,4'\text{-bpy})]_n$ [8]. The Cu···Cu distance in the Cu–(μ-I)$_2$–Cu fragment of **1** is 2.5583(6) Å, which is shorter than other similar Cu–(μ-I)$_2$–Cu complexes [12].

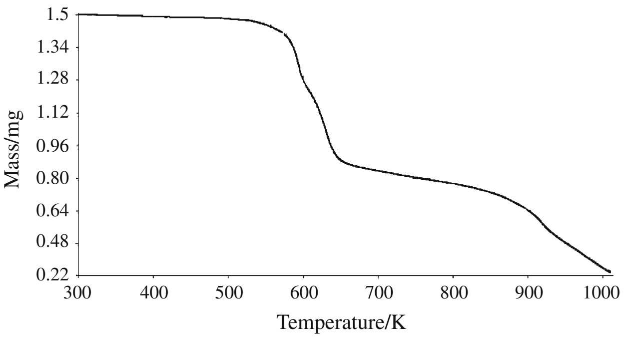


Fig. 4 The TG curve of **1**

Table 3 Thermal analysis data of **1**

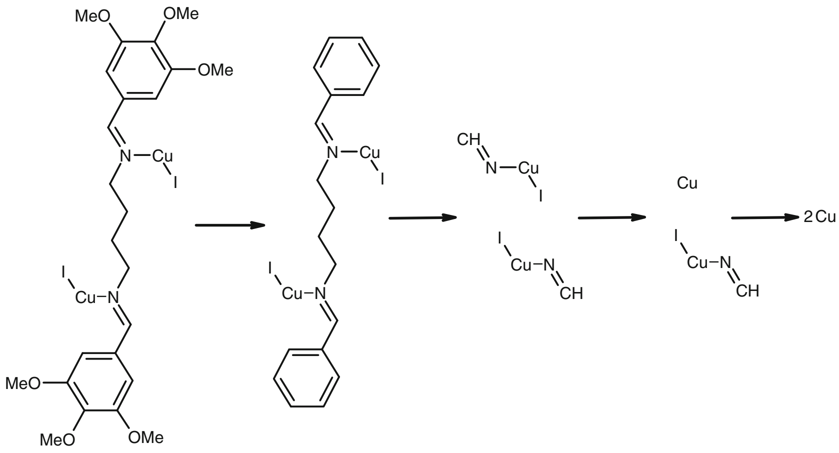
Temperature range/K	Mass loss/%		Products	Residue
	Exp.	Calcd.		
493–585	21.50	22.53	6 CH_3O–	$C_{18}H_{14}Cu_2I_2N_2$
585–634	22.31	24.07	2 Ph– –CH_2–CH_2–CH_2–CH_2–	2 CuCHNI
634–908	17.04	18.41	1 I 1 HC=N	Cu + CuCHNI
908–1010	17.68	18.41	1 I 1 HC=N	2 Cu

Thermal behavior of 1

Thermogravimetric analyses of complex under N_2 were examined. The TG curve, at a 20 K min^{-1} heating rate, of the complex is represented in Fig. 4. The decomposition temperatures along with observed mass losses (in percent) are compared with the theoretically calculated values for the complex and presented in Table 3. A probable decomposition pathway of the complex **1** is proposed in Fig. 5.

There is no detectable change in TG curve up to 490 K for **1**, then the title compound **1** is almost stable up to 490 K and during further heating undergoes decomposition in forth stages. In the first stage, complex **1** shows a weight loss of 21.50% (≈177.47 g) in the temperature range 490–585 K, corresponding to the loss of six methoxy groups (≈186 g, 22.53%). In the second stage, complex **1** shows a weight loss of 22.31% (≈184.15 g) in the temperature range 585–634 K, corresponding to loss of two phenyl rings and –CH_2–CH_2–CH_2–CH_2– groups (≈204 g, 24.07%). Complex **1** shows a weight loss of 17.04% (≈140.65 g) in the temperature range 634–908 K, in the third stage, corresponding to the loss of one iodide atom and one HC=N group (≈152 g, 18.41%). In the last stage, complex **1** shows a weight loss of 17.68% (≈145.93 g) in the temperature range 908–1010 K, corresponding to the loss of one iodide atom and one HC=N group (≈152 g, 18.41%). The final decomposition product is Cu (Fig. 5) (supported by the absence of any stretching frequencies of the ligand of the final residue).

Fig. 5 A part of the probable decomposition diagram of the complex **1** on TG analysis



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