Macedonian Journal of Chemistry and Chemical Engineering, Vol. **38**, No. 2, pp. 207–214 (2019)

MJCCA9 – 780

ISSN 1857-5552
e-ISSN 1857-5625
DOI: 10.20450/mjcce.2019.1800
Original scientific paper

Received: May 20, 2019
Accepted: August 25, 2019

CRYSTAL STRUCTURES OF THE BIS-BIDENTATE N_2S_2 SCHIFF BASE LIGAND AND ITS COPPER(I) COORDINATION POLYMER

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A new flexible bis-bidentate N_2S_2 Schiff base ligand (2,4-Cl-ba)$_2$dapte = *N,N′*-bis-(2,4-dichlorobenzaldehyde)-1,2-di(*o*-iminophenylthio)ethane and its copper(I) coordination polymer [Cu_2(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$, were synthesized and characterized by CHN elemental analysis, FT-IR and UV-Vis spectroscopy and single-crystal X-ray diffraction. The molecule of (2,4-Cl-ba)$_2$dapte adopts a *trans* conformation of the 1,2-di(*o*-iminophenylthio)ethane unit. The (2,4-Cl-ba)$_2$dapte acts as a bis-bidentate ligand with two iminic nitrogen and two sulfur atoms, coordinating to copper(I) ions in an anti-form leading to the dinuclear Cu_2(μ-(2,4-Cl-ba)$_2$dapte) groups. These groups are then bridged by two iodide anions to form a copper(I) coordination polymer [Cu_2(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$. The coordination geometry around the copper(I) ions is a distorted tetrahedron. Finally, a nano-sized form of the copper(I) coordination polymer [Cu_2(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$ was prepared by an ultrasonic bath assisted process and characterized by elemental analysis, FT-IR and SEM.

Keywords: bis-bidentate ligand; copper(I) coordination polymer; single-crystal;
distorted tetrahedral coordination; nano-sized material; crystal structure

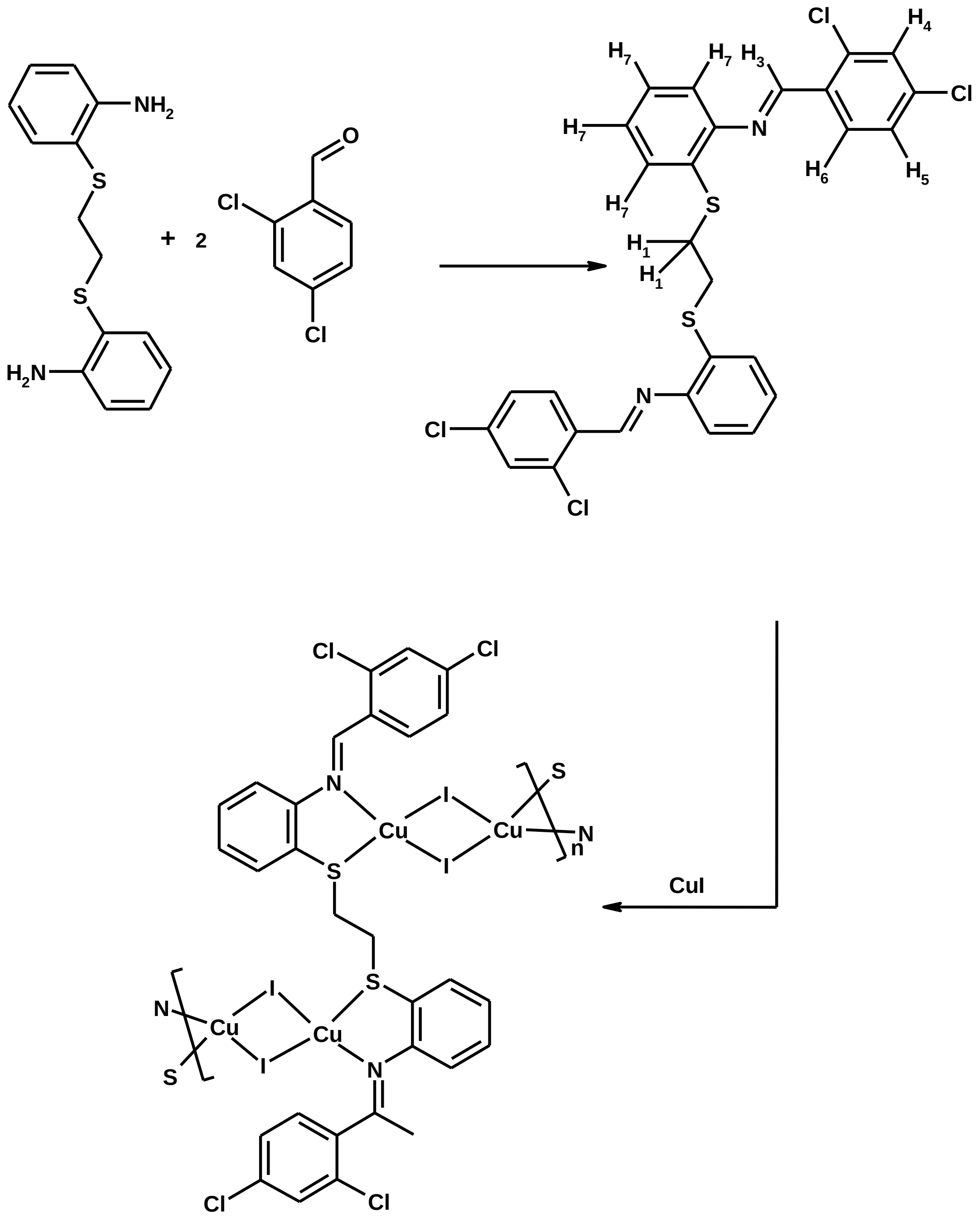
КРИСТАЛНИ СТУРКТУРИ НА БИС-БИДЕНТАТЕН N_2S_2 ЛИГАНД ОД ШИФОВА БАЗА И НЕГОВИОТ БАКАР(I) КООРДИНАЦИСКИ ПОЛИМЕР

Со елементна CHN-анализа, FT-IR и UV-Vis спектроскопија, како и рендгенска дифракција со монокристали беше синтетизиран и карактеризиран еден нов бид-бидентаген лиганд на N_2S_2 на Шифова база (2,4-Cl-ba)$_2$dapte = *N,N′*-bis-(2,4-дихлоробензалдехид)-1,2-ди(*о*-иминофенилтио)етан и неговиот координациски полимер на бакар(I) [Cu_2(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$. Молекулата на (2,4-Cl-ba)$_2$dapte зазема *транс*-конмформација на делот на 1,2-ди(*о*-иминофенилтио)етан, (2,4-Cl-ba)$_2$dapte делува како бис-бидентатен лиганд со два имински азотни атома и два сулфурни атоми, што се координираат со јоните на бакар(I) во антиконформација, што доведува до бинуклеарни групи на Cu_2(μ-(2,4-Cl-ba)$_2$dapte). Овие групи потоа се премостени со два јодини анјони при што образуваат бакар(I) координациски полимер [Cu_2(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$. Координациската геометрија околу бакар(I) јоните претставува деформиран тетраедар. Покрај тоа, во процес потпомогнат со ултразвучна бања, беше подготвен координациски полимер на бакар(I) [Cu_2(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$ со нано димензии, а беше карактеризиран со елементна анализа, FT-IR и SEM.

Клучни зборови: бис=бидентатен лиганд; бакар(I) координациски полмиер; монокристал; координација на деформиран тетраедар; материјал со нано димензии; кристална структура

1. INTRODUCTION

The chemistry of complexes with Schiff bases containing various donor atoms has attracted much attention in recent years [1–8]. There has been interest in designing polynuclear complexes [9–12]. Among them, copper(I) complexes containing bis-bidentate Schiff base ligands have been of considerable interest in recent years, not only for their structures, but also for properties such as emission [13–18]. Recently, our group reported the structural characterization of multinuclear Schiff base complexes [19, 20]. However, to the best of our knowledge, there are only rare reports on the coordination polymers of copper(I) complexes containing bis-bidentate ligand N_2S_2 [21, 22]. As part of our ongoing study of the copper(I) coordination polymer by bis-bidentate N_2S_2 ligand [23], we present here the synthesis, characterization, thermal properties and crystal structures of a new flexible bis-bidentate Schiff base ligand (2,4-Cl-ba)$_2$dapte and its copper(I) coordination polymer [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$ (Scheme 1).



Scheme 1

2. EXPERIMENTAL

2.1. *Materials and methods*

All materials were commercially available and used as received without further purification. Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on an FT-IR Perkin–Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and the results agreed with the calculated values. UV-Vis spectra were recorded on a PerkinElmer Lambda 25 spectrometer. ^{1}H NMR spectra were recorded on a BRUKER DRX-400 AVANCE spectrometer at 400 MHz. All chemical shifts are reported in δ units downfield from tetramethylsilane (TMS). The scanning electron microscopy (SEM) image of the complex was obtained from a Philips XL-30ESEM.

2.2. *Structure analysis*

Suitable single crystals of (2,4-Cl-ba)$_2$dapte and its copper(I) coordination polymer [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$ were chosen for an X-ray diffraction study. The data of (2,4-Cl-ba)$_2$dapte were collected on SuperNova Rigaku OD four-circles diffractometer using a mirror monochromated Cu-*K*α (λ = 1.54184 Å) radiation from a micro-focused sealed X-ray tube and AtlasS2 CCD detector, while the data of [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$ were collected on Gemini Rigaku OD four-circles diffractometer using graphite monochromated Mo-*Kα* (λ = 0.71073 Å) radiation from sealed X-ray tube and AtlasS2 CCD detector. Crystal structures were solved by charge flipping with program SUPERFLIP [24] and refined with the Jana2006 program [25] by full-matrix least-squares technique on F^2. The molecular structure plots were prepared by Diamond 3.0 [26]. The hydrogen atoms were discernible in different Fourier maps and could be refined to a reasonable geometry, but they were kept in ideal positions during the refinement, according to common practice, with a C–H distance of 0.96 Å and their isotropic atomic displacement parameters were set to 1.2U_{eq} of their parent atoms. The bridging iodine atom in the complex was found to be disordered over two distinct positions with refined occupancy 0.962(3) and 0.038(3). Crystal data, data collection, structure solution, and refinement details are summarized in Table 1.

Table 1

Experimental details

	(2,4-Cl-ba)$_2$dapte	[Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$
Chemical formula	$C_{28}H_{20}Cl_4N_2S_2$	$C_{14}H_{10}Cl_2CuINS$
M	590.4	485.7
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P–1
T (K)	100(1)	120(1)
a (Å)	21.7248(19)	9.1061 (6)
b (Å)	7.0996(7)	9.5551 (8)
c (Å)	16.5830(10)	10.6260 (6)
α (°)	90	69.574 (6)
β (°)	90.535(6)	71.013 (6)
γ (°)	90	68.762 (7)
V (Å^3)	2557.6(4)	786.36 (10)
Z	4	2
μ (mm^{-1})	5.91	3.83
R_{int}	0.071	0.030
No of measured, independent	8985, 4991	5643, 3602
No observed [$I > 3\sigma(I)$]	3234	2320
$R[F^2 > 2\sigma(F^2)]$	0.093	0.041
$wR(F^2)$	0.247	0.109
No. of reflections	4991	3602
No. of parameters	325	185
$\Delta\rho_{max}$ (e Å^{-3})	1.11	1.29
$\Delta\rho_{min}$ (e Å^{-3})	–1.05	–0.89

2.3. *Preparation of (2,4-Cl-ba)$_2$dapte*

The bis-bidentate Schiff base ligand (2,4-Cl-ba)$_2$dapte was prepared in high yield following the literature using 2,4-dichlorobenzaldehyde instead of thiophenecarbaldehyde [14]. To a solution of dapte (0.01 mol, 2.76 g) in CH_3OH (5 ml), a solution of 2,4-dichlorobenzaldehyde (0.02 mol, 3.5 g) in the minimum amount of CH_3OH was added with continuous stirring. The mixture was stirred at room temperature for about 0.5 h to give a yellow solution. Yellow single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature for several days. Yield: 85 %. Anal. Calc. for $C_{28}H_{20}Cl_4N_2S_2$: C, 57.89; H, 3.39; N, 4.74; Found: C, 57.96; H, 3.44; N, 4.79 %. FT-IR data (KBr, cm^{-1}): 3046, 2911 (C–H aromatic and aliphatic), 1589 (C=N), 1558, 1443 (C=C). UV-Vis [DMSO, λ_{max} (nm)]: 272 (π-π*), 368 (n-π*). ^{1}H NMR (DMSO-d_6, δ ppm): 8.69 (s, 2H$_3$), 8.09 (d, J = 8.51, 2H$_6$), 7.77 (s, 2H$_4$), 7.57 (dd, 2H$_5$), 7.17–7.27 (m, 8H$_7$), 3.163 (s, 4H$_1$).

2.4. *Preparation of [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$*

The coper(I) coordination polymer [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$ was prepared in high yield following the literature using (2,4-Cl-ba)$_2$dapte instead of (thio)$_2$dapte [14]. To a solution of CuI (0.1 mmol, 19 mg) in CH_3CN (5 mL), a solution of (2,4-Cl-ba)$_2$dapte (0.1 mmol, 59 mg) in the minimum amount of CH_3CN was added with continuous stirring. 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. Yield: 83%. Anal. Calc. for $C_{14}H_{10}Cl_2CuINS$: C, 34.59; H, 2.06; N, 2.89%; Found: C, 34.54; H, 2.03; N, 2.93%. FT-IR data (KBr, cm^{-1}): 3046, 2914 (C–H aromatic and aliphatic), 1556 (C=N), 1533, 1445 (C=C). UV-Vis [DMSO, λ_{max} (nm)]: 282 (π-π*), 370 (n-π*). ^{1}H NMR (DMSO-d_6, δ ppm): 8.72 (s, 2H$_3$), 8.17 (d, J = 8.75, 2H$_6$), 7.72 (s, 2H$_4$), 7.50 (dd, 2H$_5$), 7.24–7.40 (m, 8H$_7$), 3.14 (s, 4H$_1$).

Nanoparticles: To a solution of (2,4-Cl-ba)$_2$dapte (0.01 mmol, 59 mg) in CH_3CN (5 ml) positioned in an ultrasonic bath, a solution of CuI (0.1 mmol, 19 mg) in CH_3CN (5 ml) was added and exposed to ultrasound for 20 min. The obtained yellow-orange precipitate was filtered off and washed with Et_2O. Anal. Calcd. for $C_{14}H_{10}Cl_2CuINS$: C, 34.59; H, 2.06; N, 2.89%; Found: C, 34.43.; H, 2.09.; N, 2.81%. FT-IR data (KBr, cm^{-1}): 3043, 2910 (C–H aromatic and aliphatic), 1559 (C=N), 1529, 1447 (C=C).

3. RESULTS AND DISCUSSION

3.1. *Spectroscopic characterization*

The FT-IR spectrum of bis-bidentate Schiff base ligand (2,4-Cl-ba)$_2$dapte exhibits the characteristic band of an imine group (C=N) that appears at 1589 cm^{-1}. This band is shifted to a lower frequency in the complex (1556 cm^{-1}) due to the coordination of (2,4-Cl-ba)$_2$dapte to copper(I) ion from the nitrogen imine atom [22, 23].

The ^{1}H NMR spectra of (2,4-Cl-ba)$_2$dapte and its copper(I) coordination polymer [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$ predict that the molecule of the ligand possesses an inversion center in a free form as well as in the complex. The corresponding ^{1}H NMR peak assignments are given in the experimental section for (2,4-Cl-ba)$_2$dapte and [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$. IR and ^{1}H NMR spectra are provided in the *supporting information*. The two iminic hydrogen atoms appear as a singlet at 8.69 ppm in free ligand and at 8.72 ppm in the complex. The downfield shift of this proton in the complex relative to free ligand can be attributed the coordination of (2,4-Cl-ba)$_2$dapte to copper(I) ion from nitrogen imine atom [22, 23]. In the UV-Vis spectra there are π-π* and n-π* transitions which manifest at 272 and 368 nm for (2,4-Cl-ba)$_2$dapte, and at 282 and 370 nm for [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$.

3.2. *Crystal structure of (2,4-Cl-ba)$_2$dapte*

The molecular structure of (2,4-Cl-ba)$_2$dapte is shown in Figure 1 and the selected bond lengths and angles are given in Table 2. The ligand has a *trans* conformation with regard to the central –CH$_2$–CH$_2$– group. Also, the phenyl rings around the C=N are in *trans* position. The Ph–S–CH$_2$–CH$_2$–S–Ph segment is almost planar, while the Ph–N=CH–Ph segment features considerable rotation of the aromatic rings (dihedral angles 18.0(4)° and 22.7(4)°).

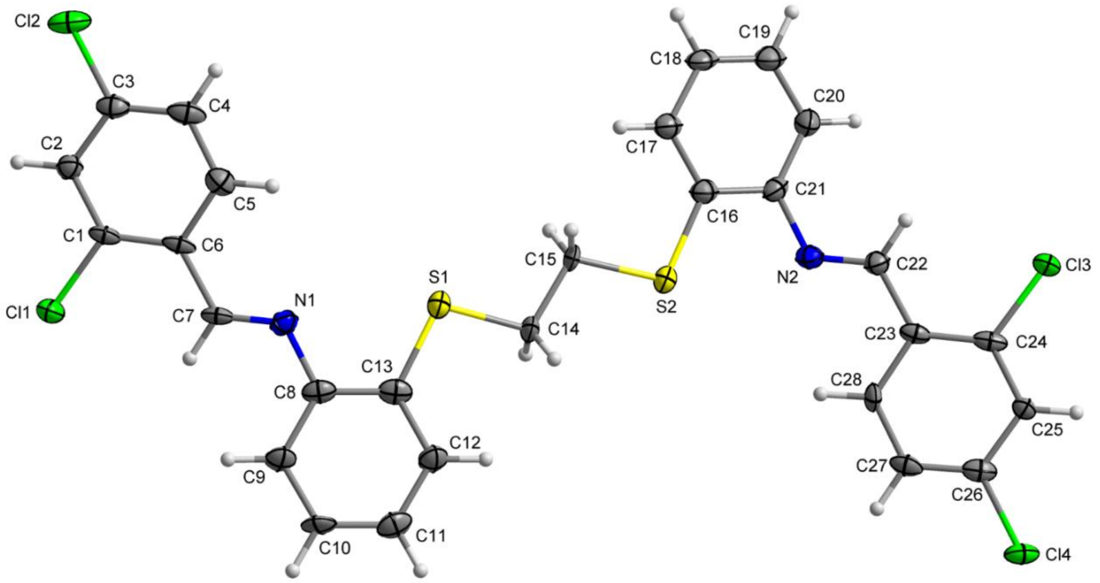


Fig. 1. The molecular structure of (2,4-Cl-ba)$_2$dapte, showing 50% probability displacement ellipsoids for non-H atoms

Table 2

Selected bond distances (Å) and angles (°) of (2,4-Cl-ba)$_2$dapte

Cl1–C1	1.749(7)	Cl3–C24	1.746(7)
Cl2–C3	1.730(8)	Cl4–C26	1.729(8)
S1–C13	1.771(7)	S2–C16	1.778(8)
S1–C14	1.810(7)	S2–C15	1.807(7)
N1–C7	1.240(10)	N2–C22	1.247(10)
N1–C8	1.407(10)	N2–C21	1.407(10)
C13–S1–C14	101.9(4)	C15–S2–C16	102.2(4)
C7–N1–C8	121.1(6)	C21–N2–C22	120.2(6)
C6–C7–N1	122.5(6)	C23–C22–N2	122.2(7)
N1–C8–C13	117.4(6)	N2–C21–C16	116.5(7)
C8–C13–S1	116.7(6)	C21–C16–S2	116.6(6)
S1–C14–C15	106.7(5)	S2–C15–C14	108.6(5)

3.3. *Crystal structure of [$Cu_2(\mu\text{-}I)_2(\mu\text{-}(2,4\text{-}Cl\text{-}ba)_2\,dapte)]_n$*

The molecular structure of [$Cu_2(\mu$-I)$_2(\mu$-(2,4-Cl-ba)$_2$dapte)]$_n$ is shown in Fig. 2, and the selected bond lengths and angles are given in Table 3. The complex is centrosymmetric with the asymmetric unit formed by one disordered iodide, one copper(I) cation and one half of Schiff base (2,4-Cl-ba)$_2$dapte ligand. In this complex, the ligand (2,4-Cl-ba)$_2$dapte acts as a bis-bidentate chelating ligand and coordinated to the copper(I) cation through iminic nitrogen and sulfur atoms. Two (μ-I) bridges connect two Cu(I) cations and form a 1D copper(I) coordination polymer [$Cu_2(\mu$-I)$_2(\mu$-(2,4-Cl-ba)$_2$dapte)]$_n$. The bridging iodine is disordered over two distinct positions with unequal occupancy 0.962(3) and 0.038(3). The Cu···Cu distance observed is 2.7585(11) Å and is larger than the corresponding distance seen in similar 1D copper(I) coordination polymers [22, 23]. The Cu(I) cation adopts distorted tetrahedral geometry with bond lengths ranging from 2.131(4) Å to 2.76(3) Å and bond angles ranging from 86.56(12)° to 127.58(16)°, when coordination to iodide with high occupancy is considered. The bond distance of Cu1-S1 = 2.3097(16) Å is larger than the bond distance of Cu1-N1 = 2.131(4) Å. Compared with the free ligand, the conformation of the coordinated ligand is changed. Significantly, the two phenyl rings in the Ph-S-CH_2-CH_2-S-Ph segment are parallel to each other. Moreover, rotation of the aromatic rings in the Ph-N=CH-Ph segment occurred (dihedral angle 51.4(3)°).

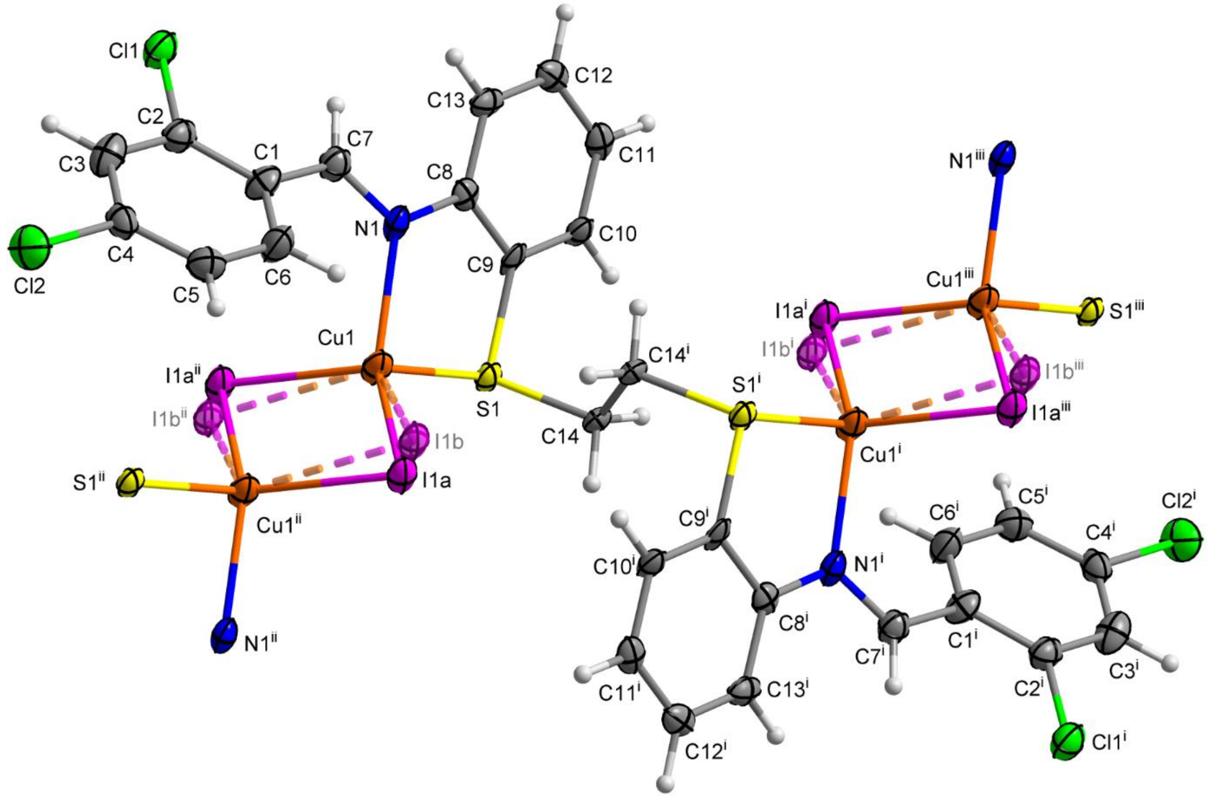


Fig. 2. The molecular structure of $[\mathrm{Cu_2}(\mu\text{-I})_2(\mu\text{-(2,4-Cl-ba)}_2\text{dapte})]_n$, showing 50 % probability displacement ellipsoids for non-H atoms. Weakly occupied iodide is depicted as semi-transparent with dashed bonds. The symmetry codes: (*i*) 1 – *x*, –*y*, –*z*; (*ii*) –*x*, –*y*, –*z*; (*iii*) 1 + *x*, *y*, *z*.

Table 3

Selected bond distances and angles of $[\mathrm{Cu_2}(\mu\text{-I})_2(\mu\text{-(2,4-Cl-ba)}_2\text{dapte})]_n$

Cu1–I1a	2.5747(14)	Cl1–C1	1.747(7)
Cu1–I1a	2.6544(18)	Cl2–C3	1.741(6)
Cu1–I1b	2.76(3)	S1–C13	1.779(5)
Cu1–I1b^{i}	3.13(4)	S1–C14	1.828(8)
Cu1–S1	2.3097(16)	N1–C7	1.293(8)
Cu1–N1	2.131(4)	N1–C8	1.437(7)
I1a–Cu1–I1a^{i}	116.34(4)	Cu1–I1b–Cu1^{i}	55.4(7)
I1a–Cu1–S1	114.54(6)	Cu1–S1–C13	98.17(18)
I1a–Cu1–N1	127.58(16)	Cu1–S1–C14	113.69(17)
I1a^{i}–Cu1–S1	105.67(7)	C13–S1–C14	100.6(3)
I1a^{i}–Cu1–N1	101.04(19)	Cu1–N1–C7	124.4(4)
S1–Cu1–N1	86.56(12)	Cu1–N1–C8	114.5(3)
Cu1–I1a–Cu1^{i}	63.66(4)	C7–N1–C8	116.5(4)

Symmetry code: (*i*) –*x*, –*y*, –*z*

3.4. *Nano-sized form of* $[\mathrm{Cu_2}(\mu\text{-I})_2(\mu\text{-(2,4-Cl-ba)}_2\text{ dapte})]_n$

A nano-sized form of the copper(I) complex $[\mathrm{Cu_2}(\mu\text{-I})_2(\mu\text{-(2,4-Cl-ba)}_2\text{dapte})]_n$ was prepared using an ultrasonic bath-assisted reaction in an acetonitrile solution. The resulting product was characterized by SEM (Fig. 3). The SEM images show that the particles have practically uniform shapes and sizes.

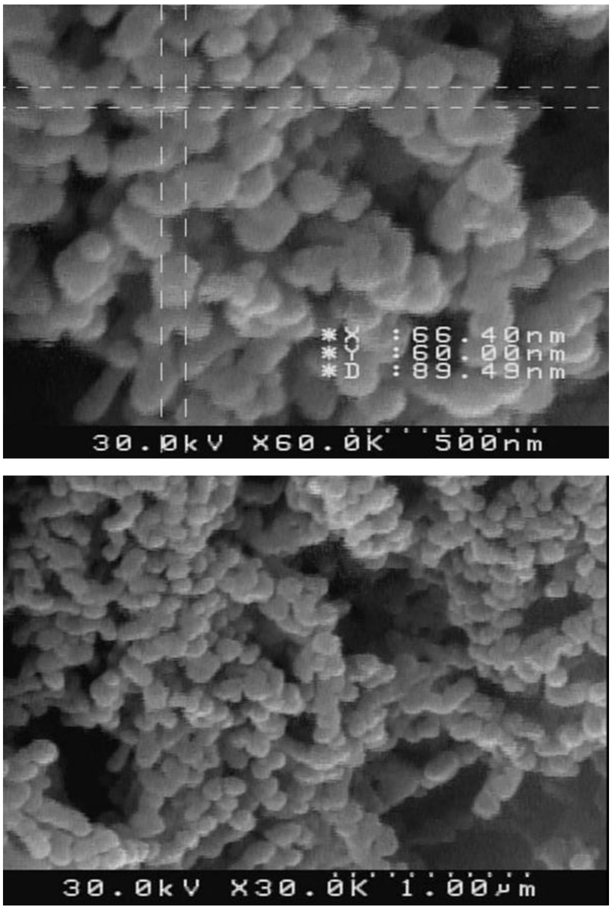


Fig. 3. SEM images of copper(I) complex prepared *via* ultrasonic bath assisted at two different scales

4. CONCLUSIONS

New flexible bis-bidentate N_2S_2 Schiff base ligand (2,4-Cl-ba)$_2$dapte and its copper(I) coordination polymer [$Cu_2(\mu\text{-}I)_2(\mu$-(2,4-Cl-ba)$_2$dapte)]$_n$, were synthesized and characterized. The Schiff base ligands (2,4-Cl-ba)$_2$dapte acts as a bis-bidentate ligand, coordinating to copper(I) ions to form a copper(I) coordination polymer [$Cu_2(\mu\text{-}I)_2(\mu$-(2,4-Cl-ba)$_2$dapte)]$_n$. Finally, a nano-sized form of the copper(I) coordination polymer [$Cu_2(\mu\text{-}I)_2(\mu$-(2,4-Cl-ba)$_2$dapte)]$_n$ was prepared by an ultrasonic bath-assisted process and characterized.

Acknowledgements. We are grateful to Payame Noor University and Golestan University for the financial support of this work. Structural analysis was supported by Project 18-10438S of the Czech Science Foundation using instruments of the ASTRA lab established within the Operation program Prague Competitiveness, project CZ.2.16/3.1.00/2451.

Supplementary data. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Center, CCDC Nos. 1939093 (ligand) and 1939094 (complex). A copy of the data can be obtained free of charge from deposit@ccdc.cam.ac.uk.

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