

1D Copper(I) Coordination Polymer $[\text{Cu}_2(\mu\text{-L})(\mu\text{-I})_2]_n$: Synthesis, Crystal Structure, Spectral and Thermal Study

Vahid Mirdarvatan^a, Bahram Bahramian^a, Aliakbar Dehno Khalaji^{b,*}, Seyyed Javad Peyghoun^c, Michal Dusek^d and Vaclav Eigner^d

^aDepartment of Chemistry, Shahrood University of Technology, Shahrood, Iran

^bDepartment of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran

^cDepartment of Chemistry, Payame Noor University, Mashhad, Iran

^dInstitute of Physics of the Czech Academy of Sciences, Na Slovance 2, 182 21 Prague, Czech Republic

(Received 14 October 2020, Accepted 20 December 2020)

A new 1D copper(I) coordination polymer $[\text{Cu}_2(\mu\text{-L})(\mu\text{-I})_2]_n$ (1), where L is *N,N*-bis(4-nitrobenzylidene)butane-1,4-diamine, was synthesized and characterized by CHN, FT-IR, ¹H NMR, and single-crystal X-ray analyses. Based on X-ray results, this new compound crystallizes in a monoclinic system with space group $P2_1/c$. The asymmetric unit consists of one copper and one iodine atoms and half of the Schiff base ligand (L). The flexible Schiff base compound is coordinated to copper(I) ion as a bis-monodentate ligand. The coordination geometry around the copper(I) ions is distorted trigonal planar. The thermal behavior of 1 was studied using thermogravimetry analysis. Moreover, the nanoparticles of 1 were prepared via the ultrasonic-assisted method and characterized by XRD and SEM analyses.

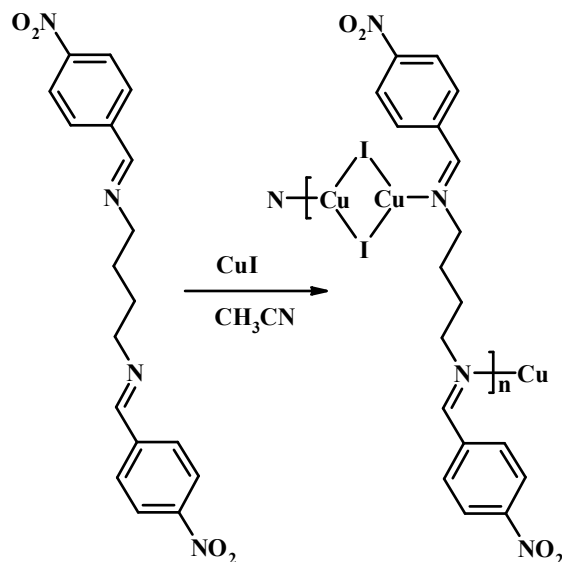
Keywords: 1D copper(I) coordination polymer, Thermogravimetry, Crystal structure, Nanoparticles, Ultrasonic bath

INTRODUCTION

Copper, one of the most abundant transition metals in the earth's crust, has played a key role in biological, technological, and industrial processes [1]. The coordination chemistry of copper consists of a wide variety of different ligands, with monovalent (+1) and divalent (+2) metal oxidation states. The Cu(I) with d^{10} electron configuration is known as a soft acid. Much attention has been devoted to the synthesis of copper(I) complexes that are involved in different catalytic reactions [2-7]. Moreover, these compounds exhibit interesting photochemical, photophysical, and optical properties [8-13]. In particular, the copper(I) complexes containing nitrogen, phosphorus, and sulfur organic ligands are of interest as an important class of thermally activated delayed fluorescence (TADF) materials in organic light-emitting diodes (OLEDs) or light-emitting electrochemical cells (LEECs) [14-18].

The coordination geometry of the transition metal complexes is influenced by the competition between the rigid and flexible ligands. Thus, the careful selection of the ligand topology can facilitate the structural prediction of the crystal [19]. The rigid ligands allow controlling the coordination chemistry occurring at the metal center [20,21], while the flexible ligands have been used to form mono, di, and polynuclear metal complexes [22,23]. In recent years, new coordination polymers based on copper(I) metal have been the subject of intense interest due to their low toxicity, low cost, and wide availability [24-27]. Several flexible nitrogen donor ligands with the general formula $\text{L}(\text{CH}_2)_n\text{-L}$ have been reported in the literature [28]. The symmetric NN-bidentate Schiff base ligands containing various spacers are among the most studied compounds due to their ease of preparation and their stability under several oxidative and reductive conditions [29]. Usually, both nitrogen atoms of these ligands prefer to form chelate complexes. However, a greater value of *n* increases the conformational flexibility of the ligand led to a

*Corresponding author. E-mail: ad.khalaji@gu.ac.ir



Scheme 1. The preparation procedure of 1

bridge between metal ions. Moreover, the bridging co-ligands such as I^- and NCS^- ions participate extensively in the formation of the Cu(I) coordination polymers [30-32].

In our previous works, we reported various copper(I) coordination polymers containing $[Cu^I(\mu-I)_2Cu^I]$ cores [33-38]. Herein, we present a new 1D copper(I) coordination polymer $[Cu_2(\mu-L)(\mu-I)_2]_n$ (1) prepared from the reaction of a neutral symmetric NN-bidentate Schiff base ligand with CuI (Scheme 1). As another objective of this research, we have prepared the nanoparticles of 1 using the ultrasonic-assisted method.

EXPERIMENTAL

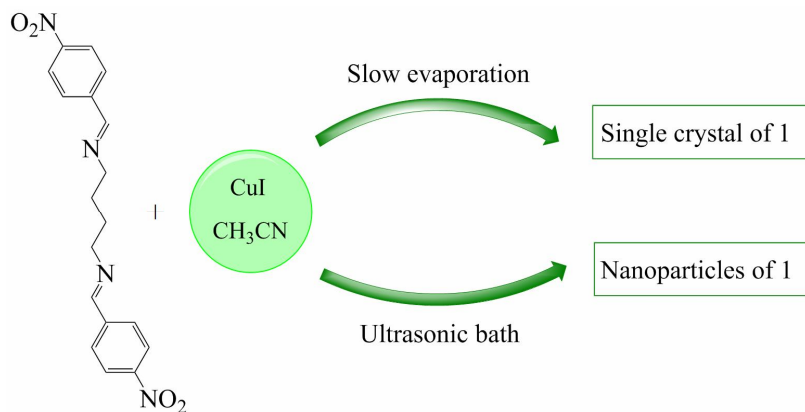
Materials and Methods

The required chemicals and solvents were commercially available and used as received without further purifications. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. Fourier transform infrared (FT-IR) spectra were recorded on a KBr disk on an FT-IR Perkin-Elmer spectrophotometer. The 1H NMR spectrum was recorded on a BRUKER DRX-400 AVANCE spectrometer at 400 MHz for the Schiff base ligand (L). All chemical shifts are reported in δ units downfield from TMS. The TG/DTA was performed on a

Perkin-Elmer TG/DTA lab system 1 (Technology by SII) in a nitrogen atmosphere with a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ in the temperature span of $50\text{-}800\text{ }^\circ\text{C}$. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-K α radiation with nickel beta filter in the range $2\theta = 10^\circ\text{-}80^\circ$. The scanning electron microscopy (SEM) images were obtained from a Philips XL-30ESEM.

Preparation of $[Cu_2(\mu-L)(\mu-I)_2]_n$ (1)

The flexible Schiff-base ligand (L) was prepared from the condensation of 4-nitro-benzaldehyde with 1,4-butanediamine in methanol in molar ratio 2:1 as described in Ref. [39,40]. For the preparation of 1, a solution of L (0.1 mmol) in the minimum amount of CH_3CN was slowly added to a solution of CuI (0.1 mmol) in CH_3CN (5 mL) under the stirring condition to give a clear yellow-orange solution after 10 min. The resulting solution was filtered off and left for several days at ambient temperature to form suitable single crystals for X-ray crystallography. Anal. Calc. for $C_9H_9Cu_2I_2N_2O_2$: C, 29.40; H, 2.47; N, 7.62%. Found; C, 29.58; H, 2.32; N, 7.82%. FT-IR (KBr, cm^{-1}): 3091, 2915, 2880, 2828 (C-H), 1615 (C=N), 1574, 1514, 1488 (C=C). 1H NMR (DMSO- d_6 , ppm): $\delta = 1.69$ (4H, C- CH_2 - CH_2 -C), 3.67 (4H, CH_2 -C-C- CH_2), 7.98 (4H, Ar-H),



Scheme 2. Schematic diagram for the preparation of single crystal and nanoparticles of 1

8.28 (4H, Ar-H), 8.50 (2H, CH=N).

Preparation of $[\text{Cu}_2(\mu\text{-L})(\mu\text{-I})_2]_n$ (1) Nanoparticles

For the preparation of nanoparticles of 1, a solution of CuI (0.1 mmol) in CH_3CN (5 mL) was placed in an ultrasonic bath with a power output of 40 KHz. Then, a solution of L (0.1 mmol) in CH_3CN (10 mL) was added dropwise to the above solution. After filtration, the prepared nanoparticles of 1 were washed with acetonitrile and then dried at room temperature (Scheme 2).

X-ray Structure Determination

A single crystal of the dimension $0.26 \text{ mm} \times 0.17 \text{ mm} \times 0.13 \text{ mm}$ was chosen for X-ray diffraction study. Both experiments were done at 95 K on a four-circle diffractometer SuperNova of Rigaku Oxford Diffraction using Cu-K α ($\lambda = 1.54184 \text{ \AA}$) microfocus mirror-collimated source and a CCD detector Atlas S2. The reason for measuring a strongly absorbing sample of the complex with the copper source was the very small size of the crystals. Crystal structures were easily solved by charge flipping with program SUPERFLIP [41] and refined with the Jana2006 program package [42] by full-matrix least-squares technique on F^2 . The structure plots were prepared by Diamond 4.0. 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 \AA and with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. No hydrogen atoms were found on nitrogen. All non-hydrogen atoms were refined

using harmonic refinement. The bridging iodine atom was found to be disordered between a major and minor occupied position with an occupancy ratio of 0.898(6):0.102(6). Crystallographic data, details of the data collection, structure solution and refinements are listed in Table 1.

RESULTS AND DISCUSSION

Synthesis and Characterization

The 1D chain copper(I) coordination polymer was prepared by the reaction of L ligand with CuI in CH_3CN . The crystals of 1 are stable in air at room temperature for about 50-70 days. The FT-IR spectrum of the free ligand (L) shows a characteristic band at 1638 cm^{-1} corresponding to the azomethine (C=N) group [33-35]. The FT-IR spectrum of 1 indicates about a 23 cm^{-1} shift of the C=N stretching to the lower frequency. This observation confirms that the L ligand is coordinated to Cu(I) ion. The bands that appeared in the region $2828\text{-}3091 \text{ cm}^{-1}$ in the FT-IR spectrum of 1 are assigned to the aromatic and aliphatic C-H stretching vibrations. Also, the FT-IR spectrum of 1 indicates some bands in the region $1488\text{-}1514 \text{ cm}^{-1}$, attributed to the aromatic C=C stretching vibration.

The ^1H NMR spectrum of 1 in $\text{DMSO-}d_6$ is shown in Fig. S1. The signals at 1.69 and 3.67 ppm correspond to the aliphatic protons. The signals at 7.98 and 8.28 ppm are related to the aromatic protons. The single signal at 8.50 ppm is assigned to the iminic protons. Therefore, all the protons in the spectrum conform to the proposed structure [39].

Table 1. Crystallographic Data and Structure Refinement Details of 1

Chemical formula, Formula weight	C ₉ H ₉ Cu ₁ I ₁ N ₂ O ₂ , 367.6
Crystal system, Space group	Monoclinic, <i>P2₁/c</i>
<i>a</i> (Å)	5.2742 (2)
<i>b</i> (Å)	20.9770 (7)
<i>c</i> (Å)	10.2107 (3)
β (°)	100.766 (3)
Volume (Å ³)	1109.80 (7)
Z, S	4, 1.45
μ (mm ⁻¹), <i>R</i> _{int}	24.49, 0.054
Measured reflections, independent	9834, 1978
Parameters	140
Reflections with <i>I</i> > 3 σ (<i>I</i>)	1855
<i>R</i> (<i>F</i> ² > 3 σ (<i>F</i> ²)), <i>wR</i> (<i>F</i> ²)	0.033, 0.090
<i>T</i> _{min} , <i>T</i> _{max}	0.019, 0.399
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.65, -0.86

Thermal Study of 1

The thermal behavior of 1 was studied under a nitrogen atmosphere. The thermogravimetric curve of the title compound is represented in Fig. 1. The TG results reveal that there is no detectable change up to about 190 °C. Therefore, the Cu(I) coordination polymer is stable up to 190 °C, while further heating causes its thermal decomposition in two steps. In the first step, the title compound shows a weight loss of 45.95% in the temperature range of 190-435 °C. In the second step, the compound exhibits a weight loss of 36.77% between 435 and 700 °C. The final product is 2Cu (17.28%).

Crystal Structure of 1

X-ray analysis shows that the [Cu₂(μ -L)(μ -I)₂]_n (1) complex crystallizes in a monoclinic system with space group *P2₁/c*. An ORTEP diagram of 1 is shown in Fig. 2, and the selected bond lengths and angles are given in Table 2. Based on X-ray analysis, the asymmetric unit

contains one copper and one iodine atom, and half of the Schiff base ligand (L). The second half of L is formed by an inversion center located between the two copper(I) centers.

As shown in Fig. 2, the coordination sphere around both Cu(I) ions can be described as distorted trigonal planar consisting of two iodine and one nitrogen atom of the Schiff base ligand (L). X-ray results exhibit that the symmetric Schiff base compound (L) acts as a bis-monodentate ligand to form [Cu₂(μ -L)] units. These units are connected *via* iodine bridges (μ -I), forming a 1D network [Cu₂(μ -L)(μ -I)₂]_n (Fig. 3). The Cu-N2(_{imine}) distance is 1.977(4) Å, similar to the corresponding values for other reported Cu(I) Schiff base complexes. The Cu-I distance of 2.5830(10) and 2.612(9) Å are consistent with other Cu(I) coordination polymers containing [Cu^I(μ -I)₂Cu^I] cores [31, 36,43,44]. The distance between Cu(I) centers in the Cu-(μ -I)₂-Cu fragment (2.5647(9) Å) is lower than that of Cu-(μ -L)-Cu fragment (7.9853(9) Å). The bridging bond angles between Cu(I) ions are: N2-Cu-I = 117.72(10),

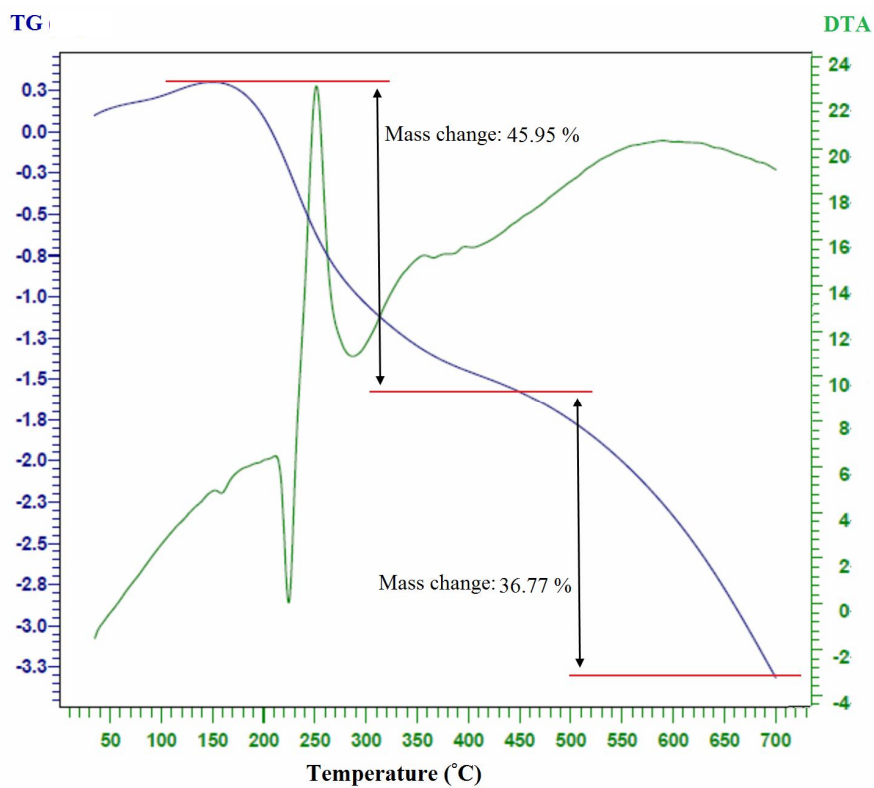


Fig. 1. TG/DTA curves of 1.

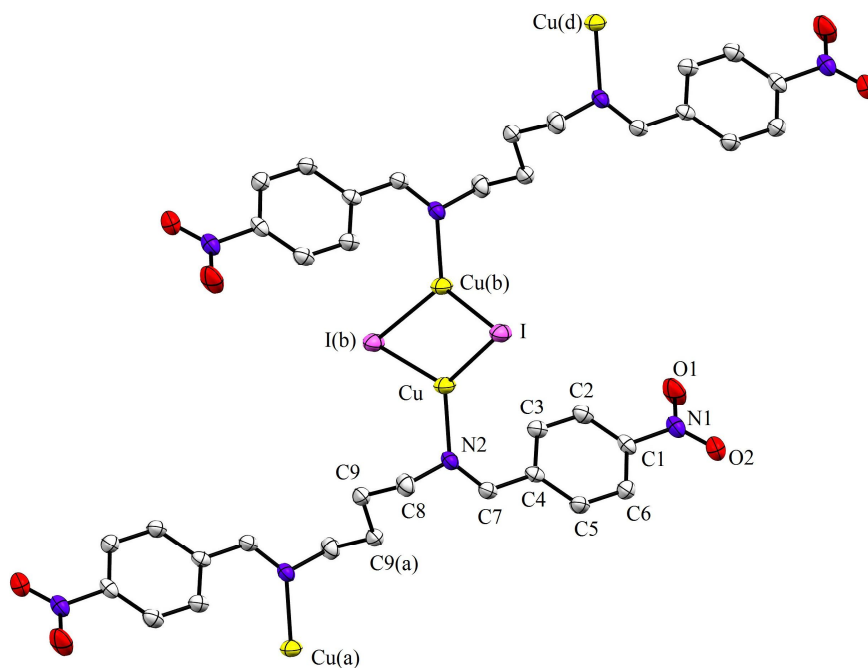
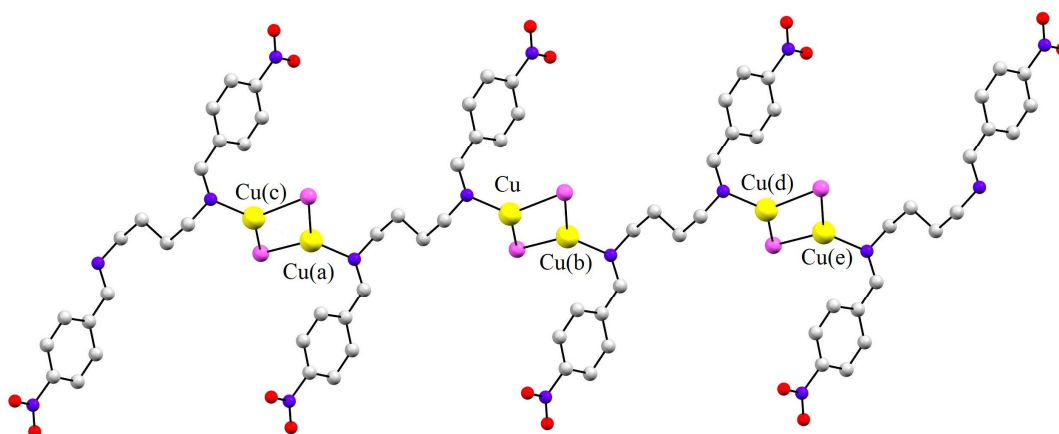


Fig. 2. ORTEP diagram of 1 showing the asymmetric unit and atom labeling scheme. The displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for 1

Bond lengths	(Å)	Bond angles	(°)	Bond angles	(°)
Cu-I	2.5830(10)	Cu-I-Cu(b)	59.93(3)	N1-C1-C6	119.2(4)
Cu-I(b)	2.612(9)	N2-Cu-I	117.72(10)	C7-N2-C8	116.0(4)
Cu-N2	1.977(4)	N2-Cu-Cu(b)	177.12(10)	C7-N2-Cu	128.9(3)
N2-C8	1.483(6)	I-Cu-Cu(b)	59.42(3)	N2-C8-C9	111.3(4)
Cu-Cu(b)	2.5646(10)	N2-Cu-I(b)	124.63(15)	N2-C7-C4	124.6(4)
N1-C1	1.465(6)	I-Cu-I(b)	121.23(18)	Cu-I(b)-Cu(b)	59.93(19)
N2-C7	1.275(5)				
C9-C9(a)	1.535(6)				

**Fig. 3.** A perspective view of 1D chain of 1 running along the [001] direction.

$N2-Cu-I(b) = 124.63(15)$, $I-Cu-I(b) = 121.23(18)^\circ$. These deviations confirm a distorted trigonal planar geometry for the Cu(I) centers. As a result, although the substituent on the benzene ring of the Schiff-base ligand is changed compared to our previous reports [33,36], the final product has a similar structure.

Nanoparticles of 1

Nanoparticles of 1 were prepared by the ultrasonic-assisted method in acetonitrile solution. Figure 4 shows the XRD pattern of the prepared nanoparticles. The sharp peaks in the XRD pattern confirm the high crystallinity of the

nanoparticles. The XRD pattern of the nanoparticles is consistent with the simulated XRD pattern. The morphology of the nanoparticles was studied using scanning electron microscopy (SEM) analysis (Fig. 5). The SEM images show that the particles don't have uniform shapes and sizes. There are some particles with crystal sizes below 100 nm.

CONCLUSIONS

A flexible Schiff base ligand (L) was reacted with CuI to generate a new 1D copper(I) coordination polymer containing iodine bridges. The new compound was

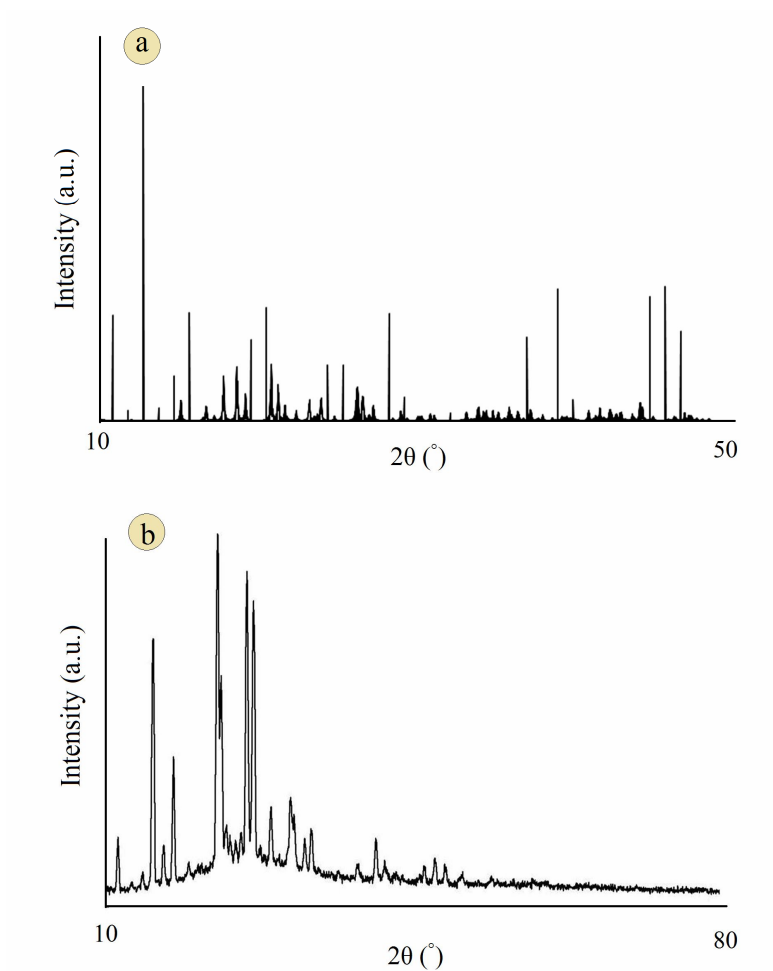


Fig. 4. XRD patterns of (a) simulated, and (b) nanoparticles of 1.

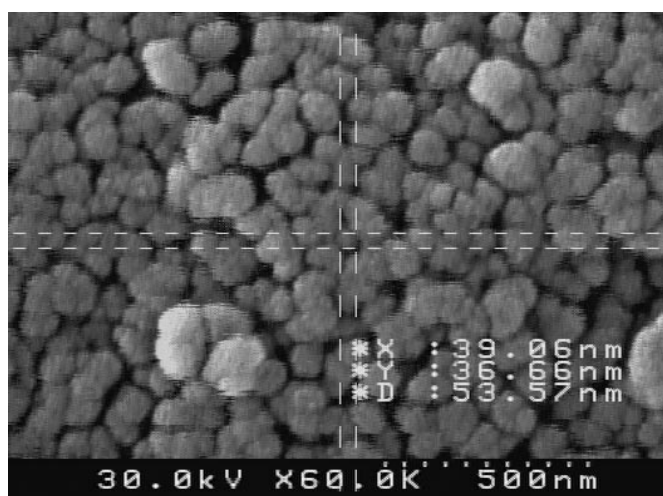


Fig. 5. SEM image of the nanoparticles of 1.

characterized using FT-IR, ¹H NMR, and single-crystal X-ray analyses. X-ray structure analysis confirms the distorted trigonal planar geometry around the copper(I) ions. In the crystal structure, the Schiff base compound (L) is coordinated to copper(I) ions as a bis-monodentate ligand. The result of the TG analysis shows that the new compound is stable up to about 190 °C. The XRD pattern and SEM images confirm the preparation of the nanoparticles of 1.

ACKNOWLEDGMENTS

We are grateful to the Shahrood University of Technology (SUT), Golestan University (GU), and Payame Noor University for financial support of this work. The crystallography was supported by the project 14-03276S of the Czech Science Foundation using instruments of the ASTRA lab established within the Operation program Prague Competitiveness - project CZ.2.16/3.1.00/24510.

SUPPLEMENTARY DATA

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 1488879. Copy of the data can be obtained free of charge on deposit@ccdc.cam.ac.uk.

REFERENCES

- [1] S. Meghdadi, M. Amirnasr, E. Yavari, K. Mereiter, M. Bagheri, *Compt. Rend. Chim.* 20 (2017) 730.
- [2] N. Navon, H. Cohen, P. Paoletti, B. Valtancoli, A. Bencini, D. Meyerstein, *Ind. Eng. Chem. Res.* 39 (2000) 3536.
- [3] J.C. Castillo, N.F. Bravo, L.V. Tamayo, P.D. Mestizo, J. Hurtado, M. Macias, J. Porttila, *ACS Omega* 5 (2020) 30148.
- [4] D. Khalili, R. Evazi, A. Neshat, J. Aboonajmi, F. Osanlou, *Inorg. Chim. Acta* 506 (2020) 119470.
- [5] K. Ramakrishna C. Sivasankar, *J. Org. Chem.* 81 (2016) 6609.
- [6] L. Meng, K.Y. Ngai, X. Chang, Z. Lin, J. Wang, *Org. Lett.* 22 (2020) 1155.
- [7] R. Yuan Z. Lin, *ACS Catal.* 4 (2014) 4466.
- [8] A. N. Gupta, V. Singh, V. Kumar, L.B. Prasad, M.G. B. Drew, N. Singh, *Polyhedron* 79 (2014) 324.
- [9] X. Liu, Y. Shan, J. Xu, X. Zhang, S. Shang, X.L. Li, *Polyhedron* 164 (2019) 152.
- [10] J. Xiang, S.-C. Cheng, X.-X. Jin, Q.-Q. Su, X. Zhou, W.-K. Chu, C.-F. Leung, C.-C. Ko, *Dalt. Trans.* 48 (2019) 741.
- [11] A.P. Borges, Z.A. Carneiro, F.S. Ptado, J.R. Souza, L.H. Furlan, Silva, C.G. Oliveira, V.M. Deflon, S. Albuquerque, N.B. Leite, A.E.H. Machado, A.O.T. Patrocinio, P.I.S. Maia, *Polyhedron* 155 (2018) 170.
- [12] S. Chen, J. Gao, J. Chang, Y. Li, C. Huangfu, H. Meng, Y. Wang, G. Xia, L. Feng, *ACS Appl. Mater. Interfaces* 11 (2019) 17513.
- [13] C. Li, W. Li, A.F. Henwood, D. Hall, D.B. Cordes, A.M.Z. Slawin, V. Lemaure, T. Olivier, I.F.W. Samuel, E. Zysman-Colman, *Inorg. Chem.* 59 (2020) 14772.
- [14] A. Schinabeck, M.J. Leidl, H. Yersin, *J. Phys. Chem. Lett.* 9 (2018) 2848.
- [15] M.J. Leidl, F.R. Kuchle, H.A. Mayer, L. Wesemann, H. Yersin, *J. Phys. Chem. A* 117 (2013) 11823.
- [16] D.M. Zink, D. Volz, T. Baumann, M. Mydlak, H. Flugge, J. Friedrichs, M. Nieger, S. Brase, *Chem. Mater.* 25 (2013) 4471.
- [17] H. Ohara, A. Kobayashi, M. Kato, *Dalt. Trans.* 43 (2014) 17317.
- [18] A.V. Artem'Ev, M.P. Davydova, A.S. Berezin, M.R. Ryzhikov, D.G. Samsonenko, *Inorg. Chem.* 59 (2020) 10699.
- [19] M. Morshedi, M. Amirnasr, A.M.Z. Slawin, J.D. Woollins, A.D. Khalaji, *Polyhedron* 28 (2009) 167.
- [20] S.M. Kuang, D.G. Cuttall, D.R. McMillin, P.E. Fanwick, R.A. Walton, *Inorg. Chem.* 41 (2002) 3313.
- [21] C.C. Chou, C.C. Su, A. Yeh, *Inorg. Chem.* 44 (2005) 6122.
- [22] H.V.R. Dias, H.V.K. Diyabalanage, M.A. Rawashdeh-Omary, M.A. Franzman, M.A. Omary, *J. Am. Chem. Soc.* 125 (2003) 12072.
- [23] H. Wang, M.X. Li, M. Shao, X. He, *Polyhedron* 26 (2007) 5171.
- [24] E. Baladi, V. Nobakht, A. Tarassoli, D.M. Proserpio, L. Carlucci, *Cryst. Growth Des.* 18 (2018) 7207.
- [25] J. Troyano, E. Zapata, J. Perles, P. Amo-Ochoa, V. Fernandez-Moreira, J.I. Martinez, F. Zamora, S.

- Delgado, *Inorg. Chem.* 58 (2019) 3290.
- [26] A. Kobayashi, M. Fujii, Y. Shigeta, M. Yoshida, M. Kato, *Inorg. Chem.* 58 (2019) 4456.
- [27] A. Tarassoli, V. Nobakht, E. Baladi, L. Carlucci, D. M. Proserpio, *Cryst. Eng. Comm.* 19 (2017) 6116.
- [28] A. Beheshti, W. Clegg, V. Nobakht, R.W. Harrington, *Polyhedron* 81 (2014) 256.
- [29] A.D. Khalaji, S.J. Peyghoun, A. Akbari, N. Feizi, M. Dusek, V. Eigner, *Polyhedron* 119 (2016) 429.
- [30] Y. Li, Z.X. Zhang, T. Li, K.C. Li, *Russ. J. Coord. Chem.* 36 (2010) 48.
- [31] M. Morshedi, M. Amirnasr, S. Triki, A.D. Khalaji, *Inorg. Chim. Acta* 362 (2009) 1637.
- [32] A. Beheshti, V. Nobakht, L. Carlucci, D.M. Proserpio, C. Abrahams, *J. Mol. Struct.* 1037 (2013) 236.
- [33] A.D. Khalaji, S. Triki, D. Das, *J. Therm. Anal. Calorim.* 103 (2011) 779.
- [34] A.D. Khalaji, J. Rohlicek, P. Machek, D. Das, *J. Clust. Sci.* 25 (2014) 1425.
- [35] A.D. Khalaji, S.J. Peyghoun, A. Akbari, N. Feizi, M. Dusek, V. Eigner, *J. Mol. Struct.* 1127 (2017) 511.
- [36] A.D. Khalaji, S.J. Peyghoun, M. Dusek, V. Eigner, *J. Struct. Chem.* 60 (2019) 1983.
- [37] A.D. Khalaji, S.J. Peyghoun, M. Dusek, M. Kocerakova, V. Eigner, A. Akbari, N. Feizi, *Maced. J. Chem. Chem. Eng.* 38 (2019) 207.
- [38] A.D. Khalaji, K. Jafari, B. Bahramian, K. Fejfarova, M. Dusek, *Monats. Chem.* 144 (2013) 1621.
- [39] H. Naeimi, F.A.M. Malayeri, Z. Rashid, K. Rabiei, *Polycycl. Arom. Compd.* 35 (2015) 457.
- [40] C. Glidewell, J.N. Low, J.M.S. Skakle, J.L. Wardell, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* 62 (2006) 2.
- [41] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* 40 (2007) 786.
- [42] V. Petricek, M. Dušek, L. Palatinus, *Z. Krist.* 229 (2014) 345.
- [43] A.D. Khalaji, M. Amirnasr, J.C. Daran, *Acta Crystallogr. Sect. E Struct. Rep.* 62 (2006) 2200.
- [44] K. Marjani, M. Mousavi, E. Ahmadi, D.L. Hughes, *Inorg. Chim. Acta* 376 (2011) 408.