CRYSTAL STRUCTURES OF THE BIS-BIDENTATE N₂S₂ SCHIFF BASE LIGAND AND ITS COPPER(1) COORDINATION POLYMER

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A new flexible bis-bidentate N₂S₂ Schiff base ligand (2,4-Cl-ba)₂dapte = N,N'-bis-(2,4-dichlorobenzaldehyde)-1,2-di(o-iminophenylthio)ethane and its copper(I) coordination polymer [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]₀, 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)₂dapte adopts a trans conformation of the 1,2-di(o-iminophenylthio)ethane unit. The (2,4-Cl-ba)₂dapte 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 Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte) groups. These groups are then bridged by two iodide anions to form a copper(I) coordination polymer [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]₀. The coordination geometry around the copper(I) ions is a distorted tetrahedron. Finally, a nano-sized form of the copper(I) coordination polymer [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]₀ 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 СТРУКТУРИ НА БИС-БИДЕНТАТЕН N₂S₂ ЛИГАНД ОД ШИФОВА БАЗА И НЕГОВИОТ БАКАР(I) КООРДИНАЦИСКИ ПОЛИМЕР

Со елементна CHN-анализа, FT-IR и UV-Vis спектроскопија, како и реидгенска дифракција со монокристал беше синтетизиран и карактеризиран еден нов бис-бидентатен лиганд на N₂S₂ на Шифова база (2,4-Cl-ba)₂dapte = N,N'-bis-(2,4-дихлоробензаледехид)-1,2-ди(o-иминофенилтио)етан и неговиот координациски полимер на бакар(I) [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]₀. Молекулата на (2,4-Cl-ba)₂dapte зазема транс-конформација на делот на 1,2-ди(o-иминофенилтио)етан, (2,4-Cl-ba)₂dapte делува како бис-бидентатен лиганд со два имински азотни атоми и два сулфурни атоми, што се координираат со јоните на бакар(I) во антиконформација, што доведува до бинуклеарни групи на Cu₂(μ-(2,4-Cl-ba)₂dapte). Овие групи потоа се преместени со два јодни аниони при што образуваат бакар(I) координациски полимер [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]₀. Координациската геометрија околу бакар(I) јоните претставува деформиран тетраедар. Покрај тоа, во процес потпомогнат со ультразвучна бања, беше подготвен координациски полимер на бакар(I) [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]₀ со нано димензии, а беше карактеризиран со елементна анализа, FT-IR и SEM.

Ключни зборови: бис-бидентатен лиганд; бакар(I) координациски полимер; 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)_2dapte and its copper(I) coordination polymer [Cu_2(μ-I)_2(μ-(2,4-Cl-ba)_2dapte)]_n (Scheme 1).

![Scheme 1](image)
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. All chemical shifts are recorded on a BRUKER Lambda 25 spectrometer. H NMR spectra were recorded as a KBr disk on an FTIR 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. All chemical shifts are recorded on a BRUKER Lambda 25 spectrometer. H NMR spectra were recorded as a KBr disk on an FTIR Perkin Elmer spectrophotometer. 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2.2. Structure analysis

Suitable single crystals of (2,4-Cl-ba)$_2$dapte and its copper(I) coordination polymer [Cu$_2$(μ-1)$_2$(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-Kα ($\lambda = 1.54184$ 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 ($\lambda = 0.71073$ 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 1.2$U_{eq}$ 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.

| Experimental details | (2,4-Cl-ba)$_2$dapte | [Cu$_2$(μ-I)$_2$(μ-(2,4-Cl-ba)$_2$dapte)]$_n$ |
|----------------------|----------------------|---------------------------------------------|
| Chemical formula     | C$_{24}$H$_{20}$Cl$_2$N$_2$S$_2$ | C$_{24}$H$_{20}$Cl$_2$I$_2$CuNS |
| 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                                         |
| Δρ$_{max}$ (e Å$^{-3}$) | 1.11               | 1.29                                        |
| Δρ$_{min}$ (e Å$^{-3}$) | -1.05              | -0.89                                       |

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2.3. Preparation of (2,4-Cl-ba)₂dapte

The bis-bidentate Schiff base ligand (2,4-Cl-ba)₂dapte 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 CH₂OH (5 ml), a solution of 2,4-dichlorobenzaldehyde (0.02 mol, 3.5 g) in the minimum amount of CH₂OH was added with continuous stiring. 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 C₂₄H₂₈Cl₄N₂S₂: 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, 4.79; H, 3.39; N, 4.74).

Yield following the literature using (2,4-Cl-ba)₂dapte [14]. To a solution of CuI (0.01 mmol, 2.76 g) in CH₂CN (5 mL), a solution of (2,4-Cl-ba)₂dapte (0.1 mmol, 59 mg) in the minimum amount of CH₂CN was added with continuous stiring. 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 C₁₆H₁₀Cl₂CuINS: 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, 2911 (C–H aromatic and aliphatic), 1556 (C=N, 3.43); 1445 (C=C). UV-Vis spectra [DMSO, λmax (nm)]: 282 (π-π*), 370 (n-π*). ¹H NMR (DMSO-d₆, δ ppm): 8.72 (s, 2H₃), 7.50 (dd, 2H₃), 7.24–7.40 (m, 8H₂), 3.14 (s, 4H₁).

2.4. Preparation of [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]ₙ

The copper(I) coordination polymer [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]ₙ was prepared in high yield following the literature using (2,4-Cl-ba)₂dapte instead of (thio)dapte [14]. To a solution of CuI (0.01 mmol, 19 mg) in CH₂CN (5 mL), a solution of (2,4-Cl-ba)₂dapte (0.01 mmol, 59 mg) in the minimum amount of CH₂CN was added with continuous stiring. 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 C₁₆H₁₀Cl₂CuINS: 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, 2911 (C–H aromatic and aliphatic), 1556 (C=N, 3.43); 1445 (C=C). UV-Vis spectra [DMSO, λmax (nm)]: 282 (π-π*), 370 (n-π*). ¹H NMR (DMSO-d₆, δ ppm): 8.72 (s, 2H₃), 7.50 (dd, 2H₃), 7.24–7.40 (m, 8H₂), 3.14 (s, 4H₁).

Nanoparticles: To a solution of (2,4-Cl-ba)₂dapte (0.01 mmol, 59 mg) in CH₂CN (5 mL) positioned in an ultrasonic bath, a solution of CuI (0.1 mmol, 19 mg) in CH₂CN (5 mL) was added and exposed to ultrasound for 20 min. The obtained yellow-orange precipitate was filtered off and washed with Et₂O. Anal. Calc. for C₁₆H₁₀Cl₂CuINS: 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)₂dapte 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)₂dapte to copper(I) ion from the nitrogen imine atom [22, 23].

The ¹H NMR spectra of (2,4-Cl-ba)₂dapte and its copper(I) coordination polymer [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]ₙ predict that the molecule of the ligand possesses an inversion center in a free form as well as in the complex. The corresponding ¹H NMR peak assignments are given in the experimental section for (2,4-Cl-ba)₂dapte and [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]ₙ.

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

The molecular structure of (2,4-Cl-ba)₂dapte 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 –CH₂–CH₂– group. Also, the phenyl rings around the C=N are in trans position. The Ph–S–CH₂–CH₂–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)°).
3.3. Crystal structure of [Cu₂(μ-I)_2(μ-(2,4-Cl-ba)_2 dapte)]ₙ

The molecular structure of [Cu₂(μ-I)_2(μ-(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 [Cu₂(μ-I)_2(μ-(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-CH₂-CH₂-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 [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]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 [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]ₙ

| Bond/Angle | Cu1−I1a | Cu1−I1b | Cu1−S1 | Cu1−N1 | Cu1−Cu1′ | Cu1−Cu1′′ |
|------------|---------|---------|--------|--------|----------|-----------|
| Cu1−I1a    | 2.5747(14) | 2.6544(18) | 2.76(3) | 3.13(4) | 2.3097(16) | 2.131(4) |
| Cu1−I1b    | 2.5747(14) | 2.6544(18) | 2.76(3) | 3.13(4) | 2.3097(16) | 2.131(4) |
| Cu1−S1     | 2.3097(16) | 2.3097(16) | 2.131(4) | 2.3097(16) | 2.3097(16) | 2.131(4) |
| Cu1−N1     | 2.131(4) | 2.131(4) | 2.3097(16) | 2.131(4) | 2.3097(16) | 2.131(4) |
| Cu1′−Cu1′   | 1.747(7) | 1.74(5) | 1.79(5) | 1.74(5) | 1.747(7) | 1.74(5) |
| Cu1′−Cu1′′  | 1.437(7) | 1.437(7) | 1.437(7) | 1.437(7) | 1.437(7) | 1.437(7) |

Symmetry code: (i) −x, −y, −z

3.4. Nano-sized form of [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]ₙ

A nano-sized form of the copper(I) complex [Cu₂(μ-I)₂(μ-(2,4-Cl-ba)₂dapte)]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.
New flexible bis-bidentate N₂S₂ Schiff base ligand (2,4-Cl-ba)₂dapte and its copper(I) coordination polymer \([\text{Cu}_2(\mu-\text{Cl})(\mu-(2,4-\text{Cl-ba})_2\text{dapte})]_n\), were synthesized and characterized. The Schiff base ligands (2,4-Cl-ba)₂dapte acts as a bis-bidentate ligand, coordinating to copper(I) ions to form a copper(I) coordination polymer \([\text{Cu}_2(\mu-\text{Cl})(\mu-(2,4-\text{Cl-ba})_2\text{dapte})]_n\). Finally, a nano-sized form of the copper(I) coordination polymer \([\text{Cu}_2(\mu-\text{Cl})(\mu-(2,4-\text{Cl-ba})_2\text{dapte})]_n\) was prepared by an ultrasonic bath-assisted process and characterized.

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**Supplementary data.** Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data 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.

**REFERENCES**

[1] C. Hopa, I. Cokay, Designing a heterotrinuclear Cu³⁻–Ni²⁺–Cu³⁺ complex from a mononuclear Cu²⁺ Schiff base precursor with dicyanamide as a coligand: synthesis, crystal structure, thermal and photoluminescence properties, *Acta Crystallogr.* **C72**, 601–606 (2016). DOI: 10.1107/S205322961600944X

[2] E. Gungor, A new stepped tetranuclear copper(II) complex: synthesis, crystal structure and photoluminescence properties, *Acta Crystallogr.* **C73**, 393–398 (2017). DOI: 10.1107/S2053229617004946

[3] P. Pandey, A. Verma, K. Brotoor, J. P. Sutter, S. S. Sunkari, Template directed synthesis of half condensed Schiff base complexes of Cu(I) and Co(III): Structural and magnetic studies, *Polyhedron* **164**, 80–89 (2019). DOI: 10.1016/j.poly.2019.02.037

[4] R. Eggekenze, Y. Gultne, R. Butcher, Catalysis of alkene epoxidation by manganese(II) and (III) complexes of both Schiff base and reduced Schiff base ligands utilizing environmentally benign H₂O₂, *Polyhedron* **144**, 198–209 (2018). DOI: 10.1016/j.poly.2018.01.008

[5] A. N. Gusev, V. F. Shul'gin, E. V. Braga, I. Nemec, W. Linert, Synthesis and photophysical properties of Zn(II) Schiff base complexes possessing strong solvent-dependent solid-state fluorescence, *Polyhedron* **155**, 202–208 (2018). DOI: 10.1016/j.poly.2018.08.019

[6] M. Shabbir, Z. Akhter, H. Ismail, B. Mirza, Synthetic bioactive novel ether based Schiff bases and their copper(II) complexes, *J. Mol. Struct.* **1146**, 57–61 (2017). DOI: 10.1016/j.molstruc.2017.05.

[7] M. Shabbir, Z. Akhter, I. Ahmad, S. Ahmed, M. Bolte, H. Ismail, B. Mirza, Ferrocene-based Schiff bases copper (II) complexes: Synthesis, characterization, biological and electrochemical analysis, *Inorg. Chem. Acta* **463**, 102–111 (2017). DOI: 10.1016/j.ica.2017.04.034

[8] D. Y. Huang, H. M. Haoa, P. F. Yaoa, X. H. Qina, F. P. Huang, Q. Yua, H. D. Biana, CuX (X=Cl,Br,I) inorganic networks separated and stabilized by a mercaptotetrazole ligand, *Polyhedron* **97**, 260–267 (2015). DOI: 10.1016/j.poly.2015.05.030

[9] C. Hopa, I. Cokay, Synthesis, structural characterization and thermal properties of a new copper(II) one-dimensional coordination polymer based on bridging N,N'-bis(2-hydroxybenzylidene)-2,2-dimethylpropane-1,3-diamine and dicyanamide ligands, *Acta Crystallogr.* **C72**, 149–154 (2016). DOI: 10.1107/S205322961600978

[10] S. Solihah Khaidir, A. Mohd Tajuddin, K. Ramsamy, B.M.Yamin, Synthesis, characterization and anticancer activity of mono- and dinuclear Ni(II) and Co(II) complexes of a Schiff base derived from o-vanillin, *Polyhedron* **161**, 84–92 (2019). DOI: 10.1016/j.poly.2018.12.055

[11] A. Hazari, C. Diaz, A. Ghosh, H-bond assisted coordination bond formation in the 1D chains based on azido and phenoxido bridged tetranuclear Cu(II) complexes with reduced Schiff base ligands, *Polyhedron* **142**, 16–24 (2018). DOI: 10.1016/j.poly.2017.12.022

[12] Y. Jiang Manna, L. Daliang, L. Xi-Ming, S. Xiaohong Chang, Mixed μ-azido-Schiff-base cyclometallated

**Fig. 3.** SEM images of copper(I) complex prepared via ultrasonic bath assisted at two different scales
Pd(II) complexes as a template for novel palladacycles bearing bridging carbodiimido, tetrazolato ligands, and tetrazole-thiolato linkers, *J. Organomet. Chem.* **871**, 103–110 (2018). DOI: 10.1016/j.jorganchem.2018.06.009

[13] A. A. Khandar, R. J. Butcher, M. Abedi, S. A. Hosseinizadeh, M. Akkurt, M. N. Tahir, Synthesis, characterization and crystal structures of dinuclear macrocyclic Schiff base copper(I) complexes bearing different bridging polyhedral metal complexes, *Polyhedron* **29**, 3178–3182 (2010). DOI: 10.1016/j.poly.2010.08.031

[14] J. Keegan, P. E. Kruger, M. Nieuwenhuyzen, N. Martin, Molecular Box versus Helicate: Selective synthesis of macrocyclic [Cu2L2]2+ and helical [Cu2L3]4+ species, *Cryst. Growth Des.* **2**, 329–332 (2002). DOI: 10.1021/cg0255341

[15] A. D. Khalaji, M. Amirnasr, R. Welter, Synthesis and X-ray crystal structure of the dinuclear copper(I) complex [Cu1(Me-Pk2)2En(PPh3)4][ClO4]2·2CHCl3, *Russ. J. Coord. Chem.* **36**, 835–837 (2010). DOI: 10.1134/S1070328410110084

[16] P. K. Pal, S. Chowdhury, P. Purkayastha, D. A. Tocher, D. Datta, A novel double-stranded dinuclear copper(I) helicate having a photoluminescent Cu3S2 chromophore, *Inorg. Chem. Commun.* **3**, 585–589 (2000). DOI: 10.1016/S1387-7003(00)00147-7

[17] X. H. Zhou, T. Wu, D. Li, Structural variations and spectroscopic properties of copper(I) complexes with bis(Schiff base) ligands, *Inorg. Chim. Acta* **359**, 1442–1448 (2006). DOI: 10.1016/j.ica.2005.10.031

[18] L. J. Childs, J. Malina, B. E. Rolfsnes, M. Pascu, M. J. Prieto, M. J. Broome, P. M. Rodger, E. Sletten, V. Moreno, A. Rodger, M. J. Hannon, A DNA-Binding Copper(I) Metallocsupramolecular Cylinder that Acts as an Artificial Nuclease, *Chem. Eur. J.* **12**, 4919–4927 (2006). DOI: 10.1002/chem.200600606

[19] A. D. Khalaji, S. J. Peyghoun, A. Akbari, N. Feizi, M. Dusek, V. Eigner, 1D polymeric copper(I) complex [Cu2(μ-(2,6-CI-ba)en)(μ-l-1)En]2+ with exceptionally short Cu-Cu distance: Synthesis, characterization, thermal study and crystal structure, *J. Mol. Struct.* **1127**, 511–514 (2017). DOI: 10.1016/j.molstruc.2016.07.097

[20] M. Ghorbani, A. D. Khalaji, N. Feizi, A. Akbari, V. Eigner, M. Dusek μ2-Oxido bridged dinuclear vanadium(V) complex: Synthesis and characterization, *J. Mol. Struct.* **1130**, 442–446 (2017). DOI: 10.1016/j.molstruc.2016.10.024

[21] M. Morshed, M. Amirnasr, A. M. Z. Slawin, J. D. Woolfins, A. D. Khalaji, Synthesis and coordination chemistry of new tetradentate N,S donor Schiff-base ligand ca2-dapte: Mononuclear and dinuclear copper(I) complexes [Cu(ca2dapte)ClO4] and [Cu(PPh3)(X)],[ca2dapte] (X = I and Br), *Polyhedron* **28**, 167–171 (2009). DOI: 10.1016/j.poly.2008.10.018

[22] M. Amirnasr, M. Rasouli, K. Mereiter, Copper(I) complexes of new N,S donor Schiff-base ligands derived from 1,2-bis-(2-amino-phenylsulfanyl)ethane, *Inorg. Chim. Acta* **404**, 230–235 (2013). DOI: 10.1016/j.ica.2013.04.007

[23] M. Morshed, M. Amirnasr, S. Triki, A. D. Khalaji, New (NS): Schiff base with a flexible spacer: Synthesis and structural characterization of its first coordination polymer [Cu2(μ-I)(μ-(thio)dapte)],[1], *Inorg. Chim. Acta* **362**, 1637–1640 (2009). DOI: 10.1016/j.ica.2008.07.002

[24] L. Palatinus, G. Chapuis, *SUPERFLIP* – a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, *J. Appl. Crystallogr.* **40**, 786–790 (2007). DOI: 10.1107/S0021889807029238

[25] V. Petricek, M. Dusek, L. Palatinus, Crystallographic Computing System JANA2006; General features, *Z. Kristallogr.* **229**, 345–352 (2014). DOI: 10.1515/zkri-2014-1737

[26] Diamond Crystal and Molecular Structure Visualization, Crystal Impact – Brandenburg, K., Putzm H. & Rathausgasse, G. R. 30, D-53111 Bonn.