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Transition Metal-Mediated Hydrolysis of the Imine Bond in 2-Azomethine Benzothiazoles

Valentina Rep Kaulić,[1] Natalija Pantalon Juraj,[2,*] Berislav Perić,[2] Zoran Štefanić,[3] Srećko I. Kirin,[2] Silvana Raić-Malić[1]

[1] Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia
[2] Laboratory for Solid-State and Complex Compounds Chemistry, Division of Materials Chemistry, Ruđer Bošković Institute, Zagreb, Croatia
[3] Laboratory for Chemical and Biological Crystallography, Division of Physical Chemistry, Ruđer Bošković Institute, Zagreb, Croatia
* Corresponding author's e-mail address: Natalija.Pantalon.Juraj@irb.hr

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THIS PAPER IS DEDICATED TO PROF. BRANKO KAITNER ON THE OCCASION OF HIS 80TH BIRTHDAY

Abstract: An ultrasound-assisted synthesis has been used for the preparation of novel benzothiazole Schiff bases (**1–3**) as ligands for Zn(II) and Cu(II) metal complexes. In this class of Schiff base ligands, the isolated complexes **1a** and **2a** appear to be the only ones that have structures which include both the Schiff base ligand and the hydrolysis product 2-aminobenzothiazole in the same complex molecule. The aldehydes formed by Schiff base hydrolysis formed a rare example of a *trans*-isomer in pentacoordinated 2,4-disubstituted benzaldehyde complexes.

Keywords: ultrasound-assisted synthesis, Schiff base, hydrolytic cleavage, metal complexes.

INTRODUCTION

SCHIFF BASES, a class of compounds prepared by condensation of amines with carbonyl compounds, are often used as ligands in biologically active metal complexes due to their simple synthesis and presence of the imine C=N group as a known pharmacophore.[1] Besides conventional synthesis in solution, Kaitner et. al. described mechanochemical synthesis of Schiff bases,[2] showing interesting effects on the formation of polymorphs and solvates.[3,4] Among heterocycles with an azomethine functionalized framework that are recognized for their pharmacological potential,[5] 2,4-dihydroxy benzaldehyde derived Schiff bases were developed as small molecule Hsp90 inhibitors with significant antiproliferative effect.[6]

The continuous interest towards transition metal complexes containing Schiff bases has developed new effective therapeutic agents in antimicrobial and anticancer chemotherapy.[7–10] Overall, metal complexes of Schiff bases have shown enhanced biological properties as compared to free ligands. Thus, palladium(II) complexes of benzothiazole bearing a bidentate Schiff base showed a strong cytotoxic effect.[11] Due to their flexi-dentate property, i.e. coordination of the ligand without using all the donor atoms, Schiff bases were found to serve as efficient chelating frameworks, which are expected to coordinate with the nitrogen atom of the azomethine group.[7] However, coordination of the imine nitrogen in metal complexes can cause weakening of the N=C double bond, making it more susceptible to hydrolytic cleavage.[12,13] Hydrolysis of Schiff base ligands is described in literature for various Schiff base complexes with Ru(II),[12] Cu(II),[13] Fe(III),[14] and Hg(II).[15] Although the unwanted hydrolysis reactions often lead to lower reaction yields[16] or the need for dry reaction conditions, in some cases the hydrolysis has been used to an advantage, such as metal ion sensing. For example, differences in the fluorescent response of the Schiff base and the hydrolysis products enabled detection of Hg(II) and Fe(III),[17] Al(III) and Zn(II),[18] Cu(II),[19,20] and Au(III) ions.[21] Hydroxybenzaldehyde derived Schiff bases with an appended cholesterol moiety studied as stimuli responsive gelators utilized the possibility of imine bond cleavage in the sensing of metal ions by sol-gel methodology,[15] while dynamic

covalent chemistry of the readily cleavable imine bond was utilized in the specific capture of sialylated glycans which have an important role as cancer biomarkers.[22]

To further explore the prominence of Schiff bases, herein we describe the synthesis of *N*-heterocyclic Schiff bases with a hydroxyl-substituted phenyl moiety and their structures of Zn(II) and Cu(II) complexes formed during transition metal-mediated hydrolysis of the imine bond. The hydrolysis of the ligands in Zn(II) complexes is observed by NMR spectroscopy, while the solid state structures of Zn(II) and Cu(II) complexes were determined by single crystal X-ray diffraction.

RESULTS AND DISCUSSION

Ligands

Ligands **1–3** were synthesized by the condensation reaction of 2-aminobenzothiazole and corresponding 2,4-disubstituted benzaldehydes (Scheme 1) in ethanol by the application of ultrasound, as a green, energy efficient process.[23,24] The reactions were carried out for 5 hours and ligands were obtained by simple filtration of the reaction mixture in moderate yields.

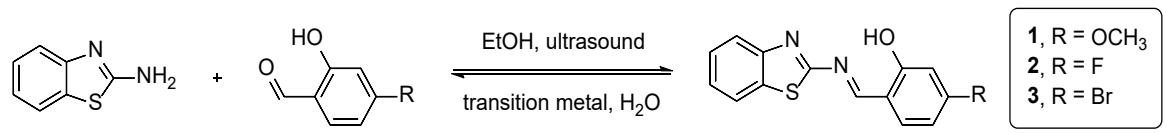
During the preparation of metal complexes, due to the low solubility of ligand **3** in polar solvents, the free ligand crystallized from acetonitrile in the form of orange prismatic crystals. Ligand **3** crystallizes in the $P2_1/c$ space group with 4 molecules in the unit cell. The ligand exhibits an intramolecular hydrogen bond between the hydroxy group and imine nitrogen (Figure 1).

Schiff bases with a hydroxyl group in the *ortho* position are of particular interest for many applications due to the possibility of prototropic tautomerism, which features proton transfer between the hydroxyl group and imino nitrogen.[26–30] The keto-amine form is most likely to be observed in polar solvents due to the stabilizing effect of solvation.[31] In the ^{1}H NMR spectra of the ligands in polar solvents DMSO-d_6 and acetone-d_6, we observed only one peak for the imino proton, indicating presence of only the phenol-imine form. However, due to the possibility of tautomer exchange faster than the NMR timescale, existence of the keto-amine form cannot be excluded.

In the solid state, the tautomeric form of **3** can be determined by the comparison of selected bond lengths with characteristic values for each tautomeric form.[32,33] The data presented in Table 1 show that **3** is in the form of the enol-imino tautomer.

Zn(II) and Cu(II) complexes

Metal complexes were prepared by mixing solutions of the ligands with $Zn(NO_3)_2$ or $Cu(NO_3)_2$. ^{1}H NMR spectra of Zn(II) complexes revealed hydrolysis of the Schiff base ligands. Lowering of the imine peak intensity accompanied by appearance of the amine and carbonyl peaks and complete hydrolysis after one day were observed for both ligands **1** and **2** (Figure 2). On the other hand, the hydrolysis of ligands in acetone-d_6 solution without added Zn(II) was significantly slower, showing only a small amount of the hydrolysis products for **1** and a somewhat larger amount for **2** after five days (Figure 2). Complexes of ligand **3** were not studied further due to its lower solubility in polar solvents.



Scheme 1. Synthesis and hydrolysis of Schiff base ligands.

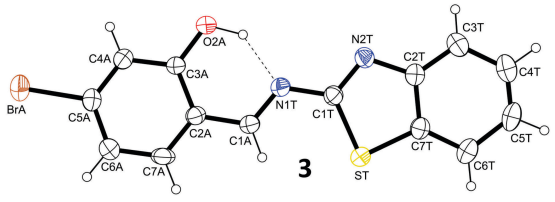


Figure 1. Molecular structure of **3** with thermal ellipsoids drawn at the 30% probability level and atom labeling.[25] The O2A-H2A···N1T intramolecular hydrogen bond is shown as a dashed line.

Table 1. Selected bond lengths in **3** and their characteristic values for the enol-imino and keto-amino tautomers.

		Characteristic bond lengths in Schiff base tautomers derived from *o*-hydroxyaryl aldehydes as described in Ref. [32]	
Bond length / Å	**3**	enol-imino	keto-amino
C3A-O2A	1.331(5)	1.35(1)	1.29(2)
C3A-C2A	1.418(5)	1.41(2)	1.43(1)
C2A-C1A	1.438(5)	1.45(2)	1.41(2)
C1A-N1T	1.269(5)	1.28(2)	1.30(1)

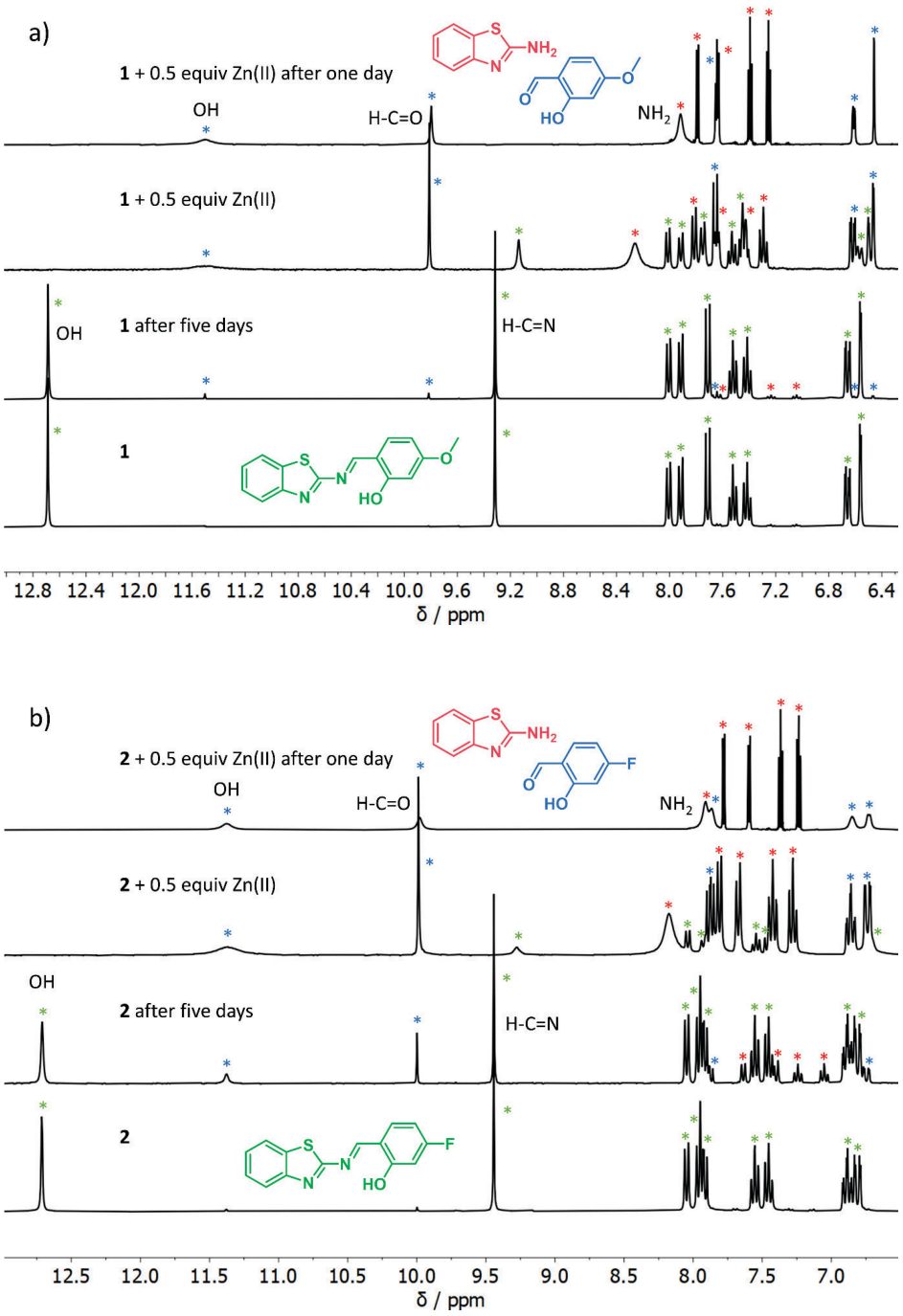


Figure 2. ^{1}H NMR (acetone-d_6) spectra showing hydrolysis of ligands **1** (a) and **2** (b).

Although hydrolysis of the ligands is apparent, the question remained of how the moieties present in solution coordinated the metal ions. Interestingly, two crystal structures were obtained having both the Schiff base ligand and the hydrolysis product 2-aminobenzothiazole in the same complex molecule. The two similar structures **1a** and **2a** were obtained from syntheses using ligand **1** with $Zn(NO_3)_2$, or ligand **2** with $Cu(NO_3)_2$, respectively (Figure 3). In both structures, the deprotonated hydroxy group and imine nitrogen coordinate the metal forming a six-membered chelate ring. The hydrolysis product amino-benzothiazole coordinates *via* the thiazole nitrogen. The amino group on the benzothiazole moiety participates in hydrogen bonding interactions towards the imine nitrogen

of the coordinated Schiff base ligand (Figure 3), and towards the nitrate anion of the neighboring complex molecule (Figure S6).

Complexes **1a** and **2a** differ in the coordination geometry and the nitrate anion coordination mode. Monodentate coordination of the nitrate anion lead to tetrahedral geometry of the Zn(II) complex **1a**. On the other hand, the nitrate anion in the pentacoordinated Cu(II) complex **2a** is coordinated bidentately. The program FindGeo[34] shows an irregular geometry for **2a** (Table 2). According to Addison's structural parameter τ used to describe the geometry of pentacoordinated complexes,[35] the τ of 0.16 for **2a**, classifies the geometry closer to square pyramidal than trigonal bipyramidal.

Table 2. The geometry of complexes classified using the program FindGeo.[34]

Complex	Geometry	RMSD (Å)
1a	Tetrahedron (regular)	0.405
2a	Irregular (n/a)	–
2b	Square plane (regular)	0.089
2c	Square pyramid (regular)	0.190

A Cambridge Structural Database search (CSD version 5.43, March 2022) of metal complexes containing similar Schiff base ligands consisting of a 2-aminobenzimidazole or 2-aminobenzothiazole and benzaldehyde fragment gave 12 results. None of the literature structures contained both the ligand and a fragment of the hydrolyzed ligand as we observed in structures **1a** and **2a**. While transition metal-mediated hydrolysis of Schiff base ligands is well known, interestingly, our structures appear to be the only crystal structures containing both the ligand and the amine product of the ligand hydrolysis in this type of Schiff base ligands.

In the synthesis using ligand **2** and $Cu(NO_3)_2$, three types of crystals were obtained: dark red rhombic **2a**, dark green prismatic **2b**, and light green needle-like **2c**. Both crystal structures determined from the analysis of the green crystals contain two 2-hydroxy-4-fluoro benzaldehyde fragments coordinated as *trans*-isomers in the equatorial plane of Cu(II) (Figure 4). Complex **2b** has square planar geometry, while the geometry of **2c** is square pyramidal due to coordination of a water molecule in the apical position.

2b and **2c** are both *trans*-isomers. CSD searches of metal complexes containing two 2-hydroxybenzaldehyde

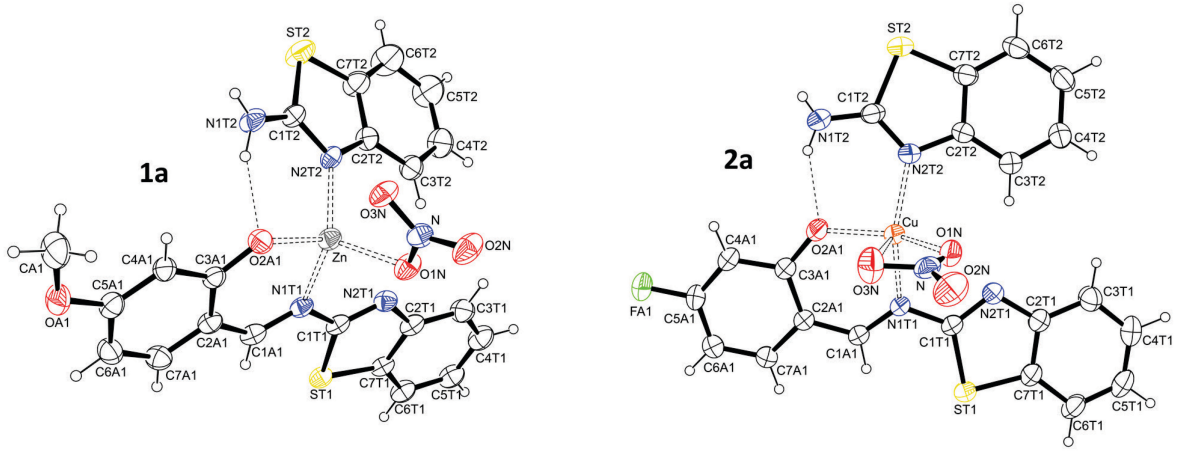


Figure 3. Molecular structures of **1a** and **2a** with thermal ellipsoids drawn at the 30 % probability level and atom labeling.[25] Intramolecular hydrogen bonds N1T2-H2T2···O2A1 are shown as dashed lines.

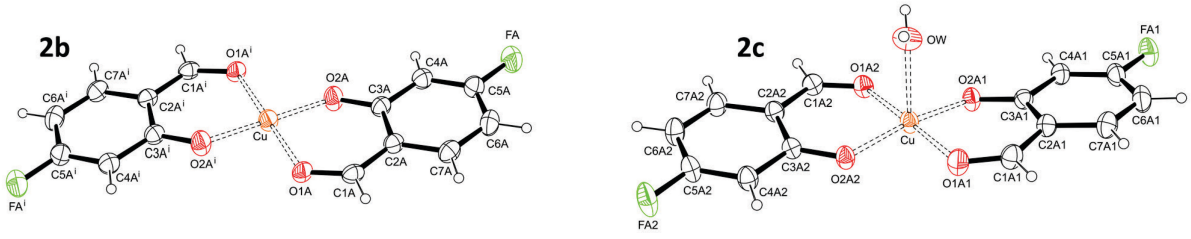


Figure 4. Molecular structure of **2b** [Symmetry code: (i) −*x*+1, −*y*+2, −*z*+1] and **2c** with thermal ellipsoids drawn at the 30 % probability level and atom labeling.[25]

Table 3. Results of Cambridge Structural Database searches (CSD version 5.43, March 2022) of metal complexes containing two 2-hydroxybenzaldehyde ligands.

Coordination number	*cis*-isomers	*trans*-isomers	total no. of complexes
4	0	17	17
5	6	0	6
6	20	30	83[(a)]
7–9	–	–	93

[(a)] the remaining 33 complexes are not classified as *cis*- or *trans*-isomers

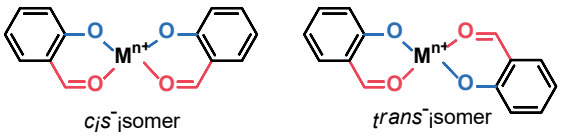


Figure 5. *Cis-isomer*, *trans*-isomer of square planar bis-2-hydroxybenzaldehyde complexes.

ligands showed dependence of the stereochemistry (Figure 5) on the coordination number of the metal ion (Table 3). Seventeen tetracoordinated complexes all have square planar geometry and are all *trans*-isomers, while six pentacoordinated complexes are all *cis*-isomers with square pyramidal geometry. In five of the six pentacoordinated complexes, the apical position of the square pyramid is occupied by a water molecule as observed in **2c.** Interestingly, complex **2c** is the first example of a pentacoordinated complex of two 2-hydroxybenzaldehyde ligands that is a *trans*-isomer.

A large number of structures (83) was found for the coordination number six. Here the coordination is also dependent on the additional ligand(s). If the additional ligand is bidentate, occupying *cis*-positions of the octahedron, the two benzaldehydes cannot coordinate in the equatorial plane. If the additional ligands are monodentate, in most cases the benzaldehydes are coordinated in the equatorial plane and both *cis*- and *trans*-isomers are found for such complexes. In some cases, the monodentate ligands occupy *cis*-positions, for example if the monodentate ligands are chloride anions. Structures were also found with large metal ions that have coordination numbers higher than six. However, their geometries are not suitable for the classification of *cis*- or *trans*-isomers.

CONCLUSIONS

A facile sonochemical synthesis of benzothiazole Schiff bases **1–3** was carried out. The first examples of structures simultaneously featuring a Schiff base ligand and amine product of Schiff base hydrolysis, as well as a rare example of a *trans*-isomer of two benzaldehyde moieties coordinated in the equatorial plane of a pentacoordinated Cu(II) complex give insight into the coordination of fragments formed upon transition metal-catalyzed hydrolysis of the imine bond in Schiff base ligands, a feature often utilized in sensors for metal ion detection.

EXPERIMENTAL PART

General remarks

For monitoring the progress of a reaction and for comparison purpose, thin layer chromatography (TLC) was performed on precoated Merck silica gel 60F-254 plates (Merck. Kenilworth. NJ. USA) using an appropriate solvent system, and the spots were detected under ultraviolet (UV) light (254 nm). Melting points (uncorrected) were determined with a Kofler Mikroheitztisch apparatus (Reichert, Wien). The ultrasound-assisted reactions were carried out in a Bandelin Bath Cleaner (Sonorex DL 1028 H, Berlin, Germany) with a nominal power of 1000 W and frequency of 35 kHz.

NMR spectra were obtained on a Bruker Avance 300 or 600 spectrometer, operating at 300.13 or 600.13 MHz for ^{1}H and 75.47 or 150.90 MHz for ^{13}C. Chemical shifts, δ (ppm), indicate a downfield shift from the residual solvent signal.[36] For NMR measurements, metal complexes were prepared *in situ*, by dissolving the ligand and zinc(II) nitrate in deuterated acetone. IR(ATR) spectra were recorded on a PerkinElmer UATR Two instrument.

SYNTHESIS

Synthesis of ligands 1–3

2-Aminobenzothiazole (1.00 mmol), aromatic aldehyde (1.00 mmol), and ethanol were taken in a round bottom flask (10 mL). The reaction mixture was irradiated in the water bath of an ultrasonic cleaner at 60 °C for 5 hours. The progress of the reaction was monitored by TLC. The precipitate formed in reaction mixture was separated by filtration, washed with ethanol, and dried to obtain ligands **1–3**.

(*E*)-2-((4-Methoxy-4-hydroxybenzylidene)amino)benzothiazole (1) Using the above described method compound **1** was obtained as a yellow powder (71.0 mg); mp = 145–147 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.11 (OH, s, 1H), 9.32 (NCH, s, 1H), 8.06 (dd, J = 8.0, 0.7 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.41 (td, J = 7.8, 1.2 Hz, 1H), 6.65 (dd, J = 8.8, 2.4 Hz, 1H), 6.58 (d, J = 2.4 Hz, 1H), 3.85 (OCH_3, s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 170.20, 165.71 (NCH), 165.67, 163.23, 151.22, 133.91, 133.63, 126.59, 125.01, 122.27, 112.95, 108.17, 100.79, 55.72 (OCH_3). Anal.calcd. for $C_{15}H_{12}N_2O_2S$ (M_r =

284.33): C 63.36, H 4.25, N 9.85; found: C 63.22, H 4.25, N 9.82. IR (ATR) $\tilde{\nu}$/cm^{-1}: 3053, 2930, 1631, 1590, 1557, 1511, 1434, 1391, 1346, 1283, 1230, 1152, 1113, 1022, 965, 807, 760, 728, 665, 564.

(*E*)-2-((4-Fluoro-2-hydroxybenzylidene)amino)benzothiazole (2) Using the above described method compound **2** was obtained as a yellow powder (148.5 mg); mp = 180–182 °C. ^{1}H NMR (600 MHz, DMSO) δ 12.03 (OH, s, 1H), 9.41 (NCH, s, 1H), 8.08 (d, J = 7.9 Hz, 1H), 8.03 (dd, J = 8.6, 7.0 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.46 – 7.42 (m, 1H), 6.89 (td, J = 8.6, 2.5 Hz, 1H), 6.86 (dd, J = 10.8, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 170.24, 166.41 (d, J_{CF} = 253.4 Hz), 164.73 (NCH), 162.57 (d, J_{CF} = 13.3 Hz), 151.15, 133.92, 133.54 (d, J_{CF} = 11.8 Hz), 126.68, 125.24, 122.53, 122.36, 116.86, 107.85 (d, J_{CF} = 22.7 Hz), 103.70 (d, J_{CF} = 24.1 Hz). Anal.calcd. for $C_{14}H_9FN_2OS$ (M_r = 272.30): C 61.75, H 3.33, N 10.22; found: C 61.46, H 3.33, N 10.22. IR (ATR) $\tilde{\nu}$/cm^{-1}: 3045, 2992, 1615, 1580, 1513, 1434, 1483, 1400, 1359, 1277, 1181, 1111, 980, 756, 678, 510.

(*E*)-2-((4-Bromo-2-hydroxybenzylidene)amino)benzothiazole (3) Using the above described method compound **3** was obtained as a yellow powder (86.3 mg); mp = 225–227 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.76 (OH, s, 1H), 9.41 (NCH, s, 1H), 8.08 (dd, J = 8.0, 0.7 Hz, 1H), 7.96 (dd, J = 8.0, 0.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.44 (td, J = 7.7, 1.2 Hz, 1H), 7.26 (d, J = 1.8 Hz, 1H), 7.22 (dd, J = 8.4, 1.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 170.45, 164.19 (NCH), 160.86, 151.18, 134.02, 131.76, 128.71, 126.72, 125.31, 123.04, 122.61, 122.38, 119.64, 119.28. Anal.calcd. for $C_{14}H_9BrN_2OS$ (M_r = 333.20): C 50.47, H 2.72, N 8.41; found: C 50.28, H 2.72, N 8.36. IR (ATR) $\tilde{\nu}$/cm^{-1}: 3056, 2996, 1602, 1558, 1494, 1433, 1360, 1259, 1183, 1061, 911, 827, 801, 759, 730, 690, 592. An acetonitrile solution of **3** was heated until the compound was fully dissolved. The solution was left to cool to room temperature and orange prismatic crystals suitable for X-ray diffraction were obtained after 1 hour.

Synthesis of Zn(II) and Cu(II) complexes

Zn(II) complex 1a. Ligand **1** (2.4 mg, 0.008 mmol) and $Zn(NO_3)_2 \times 4H_2O$ (1.1 mg, 0.004 mmol) were dissolved in acetone, heated, mixed and placed in a tank for diffusion of diethyl-ether. Orange prismatic crystals suitable for X-ray diffraction were obtained after 1 week.

Cu(II) complexes 2a, 2b, and 2c. Ligand **2** (6.4 mg, 0.024 mmol) dissolved in chloroform and $Cu(NO_3)_2 \times 3H_2O$ (2.8 mg, 0.012 mmol) dissolved in methanol were mixed and left for slow evaporation at room temperature. After 3 days, a mixture of dark red rhombic (**2a**), dark green prismatic (**2b**), and light green needle-like (**2c**) crystals suitable for X-ray diffraction was obtained.

Crystallography

X-ray intensity data were collected at room temperature on an Oxford diffraction diffractometer using monochromatic Cu-Kα radiation (λ = 1.54184 Å). The data were processed by the CrysalisPro1 program[37] (unit cell determination and data reduction). The structures were solved by the program SXELXT[38] and refined according to the least-squares procedure (F^2 on all data) by the program SHELXL-2018.[39] Basic experimental data are given in Table S1. All non-hydrogen atoms are refined in an anisotropic model of displacement parameters (ADP). For a better description, rigid body restraints were added for atoms in the aminobenzothiazole group in **3** and for atoms in the nitrate anion in **2a**. Positions of hydrogen atoms on carbon atoms were treated in riding rigid body model, i.e. their positions were calculated according to the positions of carbon atoms. C-H distances and isotropic displacement parameters for aromatic H-atoms were constrained to 0.93 Å and to U_{iso}(H) = 1.2 × U_{iso}(C), respectively. Similar parameters for methyl H-atoms in **1a** were constrained to 0.96 Å and to U_{iso}(H) = 1.5 × U_{iso}(C), respectively. The torsion angle of the methyl group in **1a** was refined. Positions and isotropic displacement parameters for H-atoms bonded to oxygen or nitrogen atoms were refined. The CCDC refcodes 2191029-2191033 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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Supplementary Information. Supporting information to the paper is attached to the electronic version of the article at: https://doi.org/10.5562/cca3907.

REFERENCES

[1] M. N. Uddin, S. S. Ahmed, S. M. R. Alam, *J. Coord. Chem.* **2020**, *73*, 3109–3149. https://doi.org/10.1080/00958972.2020.1854745

[2] D. Cinčić, I. Brekalo, B. Kaitner, *Chem. Commun.* **2012**, 48, 11683–11685. https://doi.org/10.1039/c2cc36357g

[3] D. Cinčić, I. Brekalo, B. Kaitner, *Cryst. Growth Des.* **2012**, 12, 44–48. https://doi.org/10.1021/cg2013705

[4] V. Stilinović, D. Cinčić, M. Zbačnik, B. Kaitner, *Croat. Chem. Acta* **2012**, 85, 485–493. https://doi.org/10.5562/cca2111

[5] M. A. Malik, O. A. Dar, P. Gull, M. Y. Wani, A. A. Hashmi, *Med. Chem. Comunn.* **2018**, 9, 409–436. https://doi.org/10.1039/C7MD00526A

[6] S. Dutta Gupta, B. Revathi, G. I. Mazaira, M. D. Galigniana, C. V. S. Subrahmanyam, N. L. Gowrishankar, N. M. Raghavendra, *Bioorg. Chem.* **2015**, 59, 97–105. https://doi.org/10.1016/j.bioorg.2015.02.003

[7] J. M. Mir, S. A. Majid, A. H. Shalla, *Rev. Inorg. Chem.* **2021**, 41, 199–211. https://doi.org/10.1515/revic-2020-0020

[8] C. Vidya Rani, M. P. Kesavan, G. G. Vinoth Kumar, M. J. D. Jeyaraj, J. Rajesh, G. Rajagopal, *Appl. Organomet. Chem.* **2018**, 32, e4538. https://doi.org/10.1002/aoc.4538

[9] M. Sönmez, L. Abdulkadir, M. Şekerci, *Synth. React. Inorg. Met. Chem.* **2003**, 33, 1747–1761. https://doi.org/10.1081/SIM-120026545

[10] S. Shukla, R. S. Srivastava, S. K. Shrivastava, A. Sodhi, P. Kumar, *Med. Chem. Res.* **2013**, 22, 1604–1617. https://doi.org/10.1007/s00044-012-0150-7

[11] S. Dayan, M. Tercan, F. A. Özdemir, G. Aykutoğlu, N. Özdemir, Z. Şerbetçi, M. Dinçer, O. Dayan, *Polyhedron* **2021**, 199, 115106. https://doi.org/10.1016/j.poly.2021.115106

[12] D. Sukanya, M. R. Evans, M. Zeller, K. Natarajan, *Polyhedron* **2007**, 26, 4314–4320. https://doi.org/10.1016/j.poly.2007.05.055

[13] G. L. Eichhorn, I. M. Trachtenberg, *J. Am. Chem. Soc.* **1954**, 76, 5183–5185. https://doi.org/10.1021/ja01649a074

[14] M. Bera, U. Mukhopadhyay, D. Ray, *Inorg. Chim. Acta* **2005**, 358, 437–443. https://doi.org/10.1016/j.ica.2004.07.034

[15] A. Panja, K. Ghosh, *New J. Chem.* **2019**, 43, 5139–5149. https://doi.org/10.1039/C8NJ05056B

[16] J. S. Rebouças, E. L. S. Cheu, C. J. Ware, B. R. James, K. A. Skov, *Inorg. Chem.* **2008**, 47, 7894–7907. https://doi.org/10.1021/ic800616q

[17] C. Li, L. Xiao, Q. Zhang, X. Cheng, *Spectrochim. Acta A* **2020**, 243, 118763. https://doi.org/10.1016/j.saa.2020.118763

[18] N. Phukan, J. B. Baruah, *Inorg. Chem. Commun.* **2013**, 37, 89–92. https://doi.org/10.1016/j.inoche.2013.09.051

[19] Y.-L. Liu, L. Yang, P. Li, S.-J. Li, L. Li, X.-X. Pang, F. Ye, Y. Fu, *Spectrochim. Acta A* **2020**, 227, 117540. https://doi.org/10.1016/j.saa.2019.117540

[20] Y. Wang, P.-D. Mao, W.-N. Wu, X.-J. Mao, X.-L. Zhao, Z.-Q. Xu, Y.-C. Fan, Z.-H. Xu, *Sensors Actuators B Chem.* **2017**, 251, 813–820. https://doi.org/10.1016/j.snb.2017.05.134

[21] S. Mondal, S. K. Manna, S. Pathak, A. Ghosh, P. Datta, D. Mandal, S. Mukhopadhyay, *New J. Chem.* **2020**, 44, 7954–7961. https://doi.org/10.1039/D0NJ01273D

[22] Y. Xiong, X. Li, M. Li, H. Qin, C. Chen, D. Wang, X. Wang, X. Zheng, Y. Liu, X. Liang, G. Qing, *J. Am. Chem. Soc.* **2020**, 142, 7627–7637. https://doi.org/10.1021/jacs.0c01970

[23] E. Ruiz, H. Rodríguez, J. Coro, V. Niebla, A. Rodríguez, R. Martínez-Alvarez, H. N. de Armas, M. Suárez, N. Martín, *Ultrason. Sonochem.* **2012**, 19, 221–226. https://doi.org/10.1016/j.ultsonch.2011.07.003

[24] V. Tiwari, A. Parvez, J. Meshram, *Ultrason. Sonochem.* **2011**, 18, 911–916. https://doi.org/10.1016/j.ultsonch.2010.12.003

[25] L. Farrugia, *J. Appl. Crystallogr.* **2012**, 45, 849–854. https://doi.org/10.1107/S0021889812029111

[26] D. Ortegón-Reyna, C. Garcías-Morales, I. Padilla-Martínez, E. García-Báez, A. Aríza-Castolo, A. Peraza-Campos, F. Martínez-Martínez, *Molecules* **2013**, 19, 459–481. https://doi.org/10.3390/molecules19010459

[27] A. Filarowski, *J. Phys. Org. Chem.* **2005**, 18, 686–698. https://doi.org/10.1002/poc.940

[28] A. Filarowski, A. Kochel, M. Kluba, F. S. Kamounah, *J. Phys. Org. Chem.* **2008**, 21, 939–944. https://doi.org/10.1002/poc.1403

[29] K. Pyta, P. Przybylski, W. Schilf, B. Kołodziej, A. Szady-Chełmieniecka, E. Grech, B. Brzezinski, *J. Mol. Struct.* **2010**, 967, 140–146. https://doi.org/10.1016/j.molstruc.2010.01.002

[30] G. Kaştaş, Ç. A. Kaştaş, *J. Mol. Struct.* **2019**, 1184, 427–434. https://doi.org/10.1016/j.molstruc.2019.02.058

[31] G. Kaştaş, Ç. A. Kaştaş, B. K. Kırca, C. C. Ersanlı, *J. Mol. Struct.* **2020**, 1200, 127109. https://doi.org/10.1016/j.molstruc.2019.127109

[32] A. Blagus, D. Cinčić, T. Friščić, B. Kaitner, V. Stilinović, *Maced. J. Chem. Chem. Eng.* **2010**, 29, 117. https://doi.org/10.20450/mjcce.2010.159

[33] M. Gavranić, B. Kaitner, E. Meštrović, *J. Chem. Crystallogr.* **1996**, 26, 23–28. https://doi.org/10.1007/BF02018692

[34] C. Andreini, G. Cavallaro, S. Lorenzini, *Bioinformatics* **2012**, 28, 1658–1660. https://doi.org/10.1093/bioinformatics/bts246

[35] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalt. Trans.* **1984**, 1349–1356. https://doi.org/10.1039/DT9840001349

[36] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, 29, 2176–2179. https://doi.org/10.1021/om100106e

[37] Rigaku OD, **2018**, CrysAlisPro, Version 1.171.39.46.
[38] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, A71, 3–8. https://doi.org/10.1107/S2053273314026370
[39] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, C71, 3–8. https://doi.org/10.1107/S2053229614024218