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Novel 3d-metal complexes with 1,2-diamino-3-(2-benzothiazolyl)-4(5H)-ketopyrrole: Synthesis, spectroscopic and structural investigations

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ABSTRACT

A series of new 3d-metal complexes have been prepared by the reaction of $M(CH_3COO)_2$ (M = Zn(II), Co(II), Ni(II)) and 1,2-diamino-3-(2-benzothiazolyl)-4(5H)-ketopyrrole (**HL**) in a methanol (**3**) or a methanol/dmf (**1, 2**) medium. All the complexes have been studied by elemental analyses, electronic and IR spectroscopies. The zinc(II) complex **1** and the ligand **HL** have been investigated using the method of ^{1}H NMR-spectroscopy at various temperatures. The disappearance of the signal from one proton of the amino group H(5) in the spectrum of complex **1** confirmed the existence of the ligand in the deprotonated form. According to the data of the ^{1}H NMR-spectroscopy, the ligand **HL** is coordinated to zinc(II) through the nitrogen atom of the deprotonated amino group and the nitrogen atom of the benzothiazole substituent. These data are in agreement with X-ray structural studies for the ligand **HL** and the zinc(II) complex **1**.

1. Introduction

Biologically active ligands and their metal ion complexes have received increasing attention owing to the role which such systems play in many biological processes. Many organic compounds which are used in medicine do not have a purely organic mode of action; some are activated or biotransformed by metal ions. Many drugs have been known to exhibit increased anticancer activity when administered as metal complexes [1–4].

In light of the increase in biological activity of chemicals due to their coordination to metal ions and keeping in mind the high anticancer activity of 2-amino-4(5H)-ketopyrroles [5], their use as ligands towards transition metal ions is interesting and promising. It should be noted that 2-amino-4(5H)-ketopyrroles (as well as 2-amino-4(5H)-ketothiophens) potentially have a wide spectrum of binding possibilities, but to date examples of coordination compounds with such ligands are scarce [6,7]. So, in order to test and extend the scope of the coordination abilities of 2-amino-4(5H)-ketopyrroles, the residue with an additional amino group, 1,2-diamino-3-(2-benzothiazolyl)-4(5H)-ketopyrrole, has been used as a ligand towards 3d-metal ions. In this paper we describe the synthesis and spectroscopic characterization of new Zn(II), Co(II) and Ni(II) complexes with 1,2-diamino-3-(2-benzothiazolyl)-4(5H)-ketopyrrole, as well as X-ray structural investigations of the aforementioned ligand **HL** and its zinc(II) complex **1**.

2. Experimental

2.1. Materials and instruments

Elemental analyses were performed by atomic absorption spectroscopy (for metals) and with a Perkin–Elmer 2400 CHN Analyzer (for C, H, N). Infrared spectra were recorded as KBr pellets on a *BX* (*Perkin–Elmer*) spectrometer in the 4000–400 cm^{-1} region using conventional techniques. Electronic spectra of the compounds in dmf solution were recorded on a LOMO MDR-23 spectrophotometer in the 400–800 cm^{-1} region at room temperature. ^{1}H NMR spectra in DMSO-d^6 solution were recorded on a Varian 400 spectrometer (with Me_4Si as an internal standard).

2.2. Crystal structure determination

Crystallographic data and parameters of data collection, structure solution and refinement are listed in Table 1. Intensities of reflections were measured on an automatic Xcalibur-3 diffractometer (graphite monochromated Mo Kα radiation, CCD-detector, ω scanning). All structures were solved by direct methods using the SHELX97 package [8]. Positions of hydrogen atoms were located from electron density difference maps and refined isotropically.

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Table 1
Crystal data and structure refinement for **HL** and **1**.

Compound	HL	1
Empirical formula	$C_{11}H_{10}N_4OS$	$C_{22}H_{18}N_8O_2S_2Zn$, C_3H_7NO, H_2O
Molecular weight	246.29	647.05
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	9.54570(10)	10.9481(4)
b (Å)	11.8099(2)	11.3100(3)
c (Å)	10.0749(2)	12.3978(2)
α (°)		94.085(2)
β (°)	98.762(2)	108.668(2)
γ (°)		104.372(3)
T (K)	293	293
V (Å^3)	1122.53(3)	1389.73(7)
Z	4	2
$F(0\,0\,0)$	512	668
D_{calc} (g/cm^3)	1.457	1.546
μ(Mo Kα) (mm^{-1})	0.276	1.084
$2\theta_{max}$ (°)	60	60
Measured reflections	17 137	29 061
Independent reflections	3153	7978
R_{int}	0.020	0.028
Reflections with $F > 4\sigma(F)$	2413	5401
Number of parameters	194	478
wR_2	0.098	0.073
R_1 ($F > 4\sigma(F)$)	0.033	0.030
S	1.07	0.91

Full-matrix least-squares refinement against F^2 was performed for non-hydrogen atoms within anisotropic approximation.

2.3. Preparations

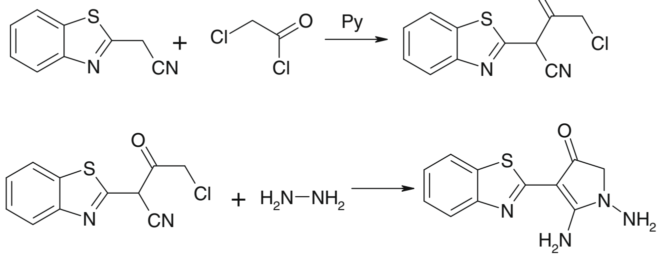
The ligand **HL** was prepared in two steps according to Scheme 1, by reaction of 2-cyanomethyl-1,3-benzothiazole with chloracetyl chloride, followed by the interaction of the obtained 2-benzothiazolyl-3-keto-4-chlorobutyronitrile with hydrazine.

2.3.1. Preparation of 2-benzothiazolyl-3-keto-4-chlorobutyronitrile

To a solution of 0.01 mol of pyridine and 5 mol of 2-cyanomethyl-1,3-benzothiazole in absolute dioxane (20 mL) at 25 °C was added slowly 0.006 mol of chloracetyl chloride. After refluxing for 2 h, the dark brown solution was cooled to room temperature, and 2-benzothiazolyl-3-keto-4-chlorobutyronitrile was precipitated. This precipitate was filtrated, washed with water and cold ethanol, and then dried in air. Yield: 1.01 g (80%). M.p. = 157 °C. *Anal.* Calc. for $C_{11}H_7ClN_2OS$: C, 52.70; H, 2.81; N, 11.17. Found: C, 52.61; H, 2.89; N, 11.23%. The compound is soluble in ethanol, dmf and dmso.

2.3.2. Preparation of 1,2-diamino-3-(2-benzothiazolyl)-4(5H)-ketopyrrole (*HL*)

About 0.0025 mol of the above 2-benzothiazolyl-3-keto-4-chlorobutyronitrile was dissolved in 20 mL of an ethanol solution of 0.0075 mol of hydrazine. The reaction mixture was refluxed for 4 h. Control for the reaction completion was achieved by monitoring of disappearance of the starting chlorobutyronitrile by TLC. The resulting pale yellow crystals were filtrated, washed with cold ethanol and dried in the air. Yield: 0.52 g (85%). M.p. = 237 °C. *Anal.* Calc. for $C_{11}H_{10}N_4OS$: C, 53.64; H, 4.09; N, 22.75. Found: C, 53.58; H, 4.13; N, 22.67%. ^{1}H NMR (200 MHz in DMSO-d^6, δ, ppm): 7.83 (1H, d, benzothiazole), 7.70 (1H, d, benzothiazole), 7.33 (1H, t, benzothiazole), 7.19 (1H, t, benzothiazole), 8.32 (1H, s, amine), 7.97 (1H, s, amine), 4.88 (2H, s, amine), 3.87 (2H, s, methylene). The compound is soluble in ethanol, dmf and dmso.



Scheme 1. Synthetic scheme for the ligand **HL**.

2.3.3. Preparation of [ZnL$_2$]·H$_2$O·dmf (**1**)

To a solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.15 mmol) in 5 mL of methanol was added 10 mL of a dmf solution of HL (0.3 mmol). The resulting solution was allowed to stand at room temperature. Pale yellow crystals of **1** suitable for X-ray crystallography were formed after 5 days. The crystals were filtered off, washed with methanol and dried in the air. Yield: 64 mg (77%). *Anal.* Calc. for $C_{25}H_{27}N_9O_4S_2Zn$: C, 46.41; H, 4.21; N, 19.48; Zn, 10.10. Found: C, 46.55; H, 4.15; N, 19.57; Zn, 10.13%. IR (KBr pellet, ν, cm^{-1}): 1590 (C=O), 1520 (C=N), 3450 and 3330 (N–H). The compound is soluble in dmso and dmf.

2.3.4. Preparation of [CoL$_2$]·H$_2$O (**2**)

This complex was obtained in a similar manner to **1**, except with the use of $Co(CH_3COO)_2 \cdot 2H_2O$ instead of $Zn(CH_3COO)_2 \cdot 2H_2O$. Yield: 54 mg (65%). *Anal.* Calc. for $C_{21}H_{20}N_8O_3S_2Co$: C, 46.56; H, 3.55; N, 19.74; Co, 10.38. Found: C, 46.42; H, 3.64; N, 19.61; Co, 10.21%. IR (KBr pellet, ν, cm^{-1}): 1580 (C=O), 1525 (C=N), 3315 and 3455 (N–H). The compound is soluble in dmso and dmf.

2.3.5. Preparation of [NiL$_2$] (**3**)

This complex was obtained in a similar manner to **1**, except with the use of $Ni(CH_3COO)_2 \cdot 2H_2O$ instead of $Zn(CH_3COO)_2 \cdot 2H_2O$ in methanol medium. Yield: 49 mg (59%). *Anal.* Calc. for $C_{21}H_{20}N_8O_2S_2Ni$: C, 48.11; H, 3.30; N, 20.40; Ni, 10.69. Found: C, 47.94; H, 3.13; N, 19.91; Ni, 10.61%. IR (KBr pellet, ν, cm^{-1}): 1590 (C=O), 1535 (C=N), 3320 and 3450 (N–H). The compound is soluble in dmso and dmf.

3. Results and discussion

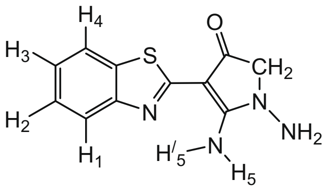
3.1. Synthesis and spectroscopic characterization

The reaction between 1,2-diamino-3-(2-benzothiazolyl)-4(5H)-ketopyrrole (**HL**) in dmf and the appropriate metal salt $M(CH_3COO)_2$ (M = Zn(II), Co(II) and Ni(II)) in methanol affords the coordination compounds [ZnL$_2$]·H$_2$O·dmf (**1**), [CoL$_2$] H$_2$O (**2**) and [NiL$_2$] (**3**). Noticeably, 2-amino-4(5H)-ketopyrroles are structural analogues of cytosine, which is coordinated by metal ions in deprotonated form in the presence of a strong base. In contrast to this, 2-amino-4(5H)-ketopyrroles are coordinated by metal ions in the deprotonated form even with the use of metal carboxylates:

$$M(CH_3COO)_2 + 2\mathbf{HL} = [ML_2] + 2CH_3COOH$$

The IR-spectrum of the ligand **HL** in the 3600–3000 cm^{-1} region shows stretching vibrations of the amino group ν(N-H) at 3350 cm^{-1} (asymmetrical) and 3245 cm^{-1} (symmetrical). In contrast to **HL**, the spectra of complexes **1–3** show two sets of bands due to $\nu(NH_2)$ and ν(NH) vibrations. The broad band around 3460–3445 cm^{-1} may be attributed to the stretching vibrations of a non-coordinated NH$_2$ group, while the sharp band appearing in the range 3330–3310 cm^{-1} could be assigned to the vibration of the N–H bond of a deprotonated amino group. The presence of the last band in the spectra of **1–3** could be a result of simultaneous deprotonation of the NH_2 group of the ligand and its coordination to the metal ion, which is confirmed by the data of ^{1}H NMR-spectroscopy and X-ray analysis for **1**.

The spectrum of **HL** reveals a very broad and intense band in the range 1610–1560 cm^{-1} with several shoulders, assigned to a superposition of stretching vibrations of C=O, C=N and C=C bonds. In the spectra of complexes **1–3** the band for the C=O stretching vibration is observed at 1590–1580 cm^{-1} and the C=N stretching vibration at 1535–1520 cm^{-1}. The shift of the ν(C=N) band to an area of lower frequencies is used as a criterion of ligand coordination to 3d-metal ions through the nitrogen of the benzothiazole substituent and the deprotonated amino group of pyrrole. Since all the complexes synthesized and discussed here demonstrate very similar IR spectra, an assumption about the analogous coordination modes of **2** and **3** to **1**, the structure of which has been determined by X-ray analysis, has been made.



Scheme 2. The hydrogen atoms numbering scheme of the ligand **HL**.

The ^{1}H NMR spectrum of the ligand **HL** shows four signals from non-equivalent aromatic protons attributed to the benzothiazole substituent. The ligand **HL** contains two different amino groups. The protons of the first one are observed in the spectrum as a sharp singlet (two equivalent protons H(6) at δ = 4.85 ppm), while the protons of the second one show up as two separate singlets (H(5) at δ = 7.95 ppm and H(5′) at δ = 8.33 ppm). The non-equivalence of the protons of the second amino group is caused by the participation of H(5′) in the intramolecular hydrogen bonding with nitrogen atom of the benzothiazole substituent. A comparison of the ^{1}H NMR spectra of **1** and **HL** reveals the shift of the aromatic ring protons of **1** to the high-field region, with the lowest shift value for H(4). This fact could be explained by the remoteness of H(4) from the metal centre (see Scheme 2) in contrast to the other aromatic ring protons H(1)–H(3), which are most sensitive to the coordination by zinc(II). The existence of the ligand in the deprotonated form is confirmed by the disappearance of the signal from one proton of the amino group H(5′) in the ^{1}H NMR spectrum of the complex **1**. Additionally, the signal of the proton H(5) (singlet at δ = 6.38 ppm) is shifted to higher field in comparison with the free ligand, which proves the coordination of the ligand by zinc(II) ion through the nitrogen atom of the deprotonated amino group (see Fig. 1). The protons of the CH_2 group of pyrrole ring of **HL** are equivalent on the NMR-time scale at 20 °C and are observed at δ = 3.87 ppm as a singlet. In contrast to this, the corresponding peak in complex **1** is shown as an AB quartet at δ = 3.95 ppm, $^2J_{H-H}$ = 17 Hz. This splitting of the protons of the CH_2 group is caused by the slower interconversion process for the pyrrole ring of the complex as compared to the free ligand. On increasing the

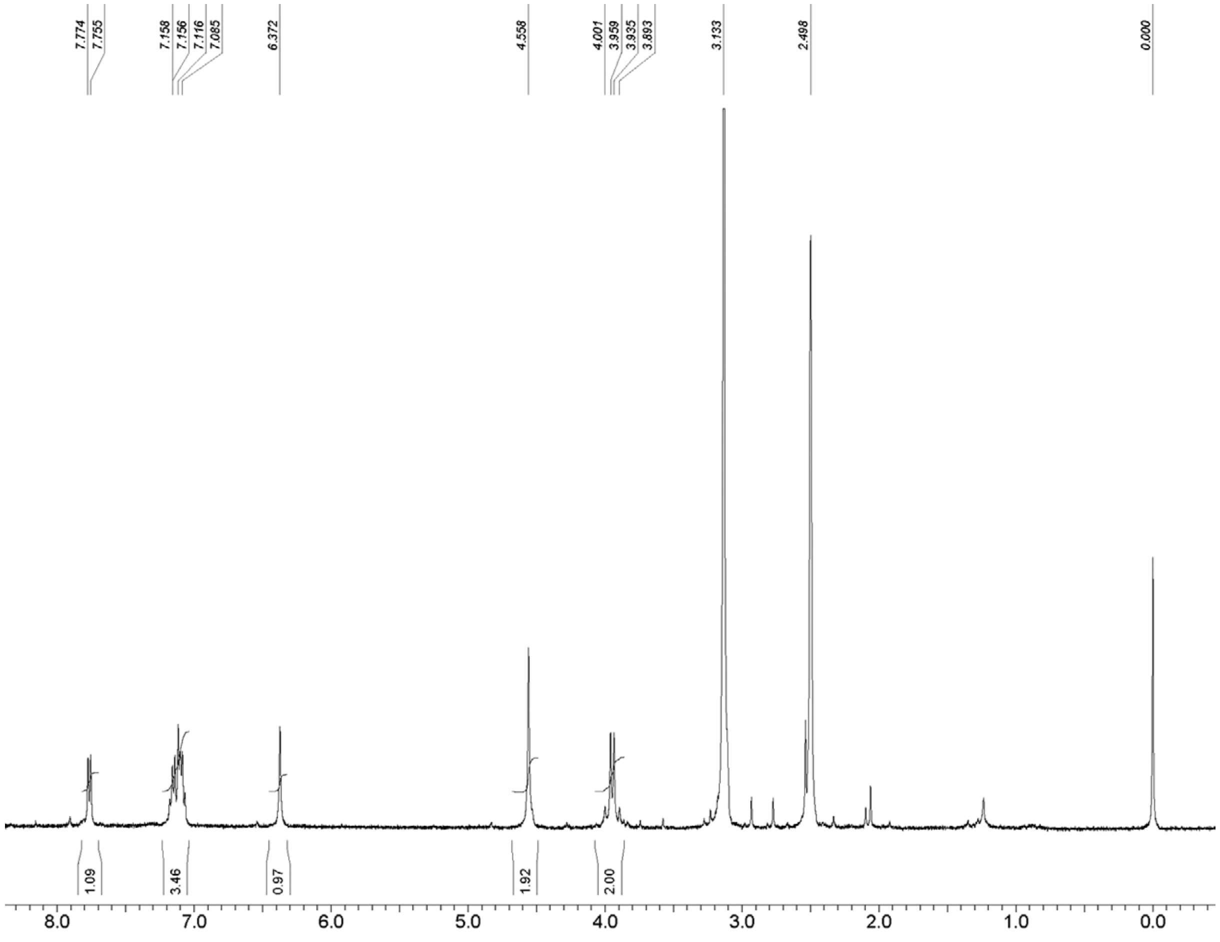


Fig. 1. ^{1}H NMR spectrum of $[ZnL_2]\cdot dmf\cdot H_2O$ (**1**) in DMSO-d^6 solution at 20 °C.

temperature up to 70 °C, the signal from two inequivalent methylene protons broadens and then coalesces. At temperatures higher than 70 °C, this broadened signal is transformed into a singlet with a narrow line width, which is the averaged signal from the CH_2 groups of the two conformers (see Fig. 2).

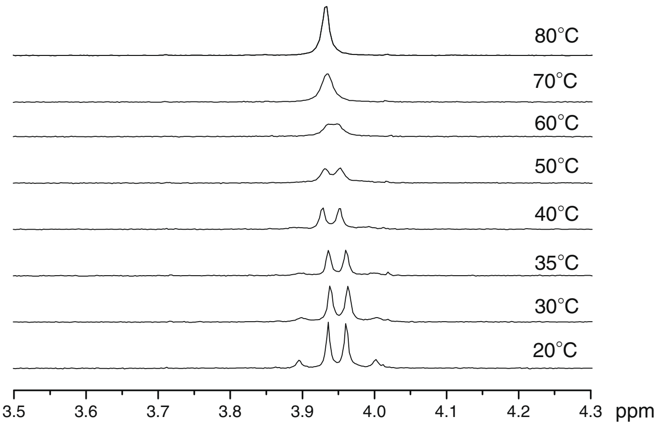


Fig. 2. Fragments of selected ^1H NMR spectra of $[ZnL_2]\cdot dmf\cdot H_2O$ (**1**) in the region of the methylene protons at different temperatures. Solution of the complex in DMSO-d^6.

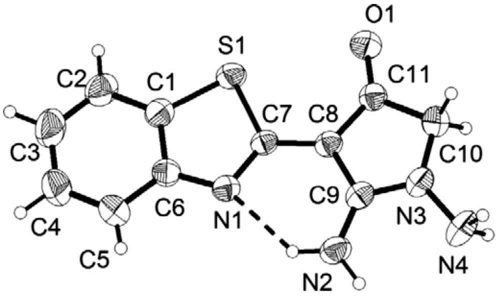


Fig. 3. Molecular structure of the compound **HL** with the atom numbering scheme. Atom displacement ellipsoids are shown at the 50% probability level.

The electronic spectra of **2** and **3** were recorded in dmf solution. The spectrum of **2** shows only one band without any clear splitting in the visible region. The absorption features are most likely d–d transitions in origin, typical for Co(II) octahedral species. The band at 20 500 cm^{-1} could be tentatively attributed to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition [9]. The spectrum of **3** is typical for a square–planar nickel(II) complex, and displays an intense absorption at 22 000 cm^{-1}, assigned to a metal-to-ligand charge transfer (MLCT) band.

*3.2. Crystal structures of the ligand **HL** and complex **1***

X-ray structural investigations have been carried out for **HL** and **1**, where compound **1** represents the complex of zinc(II) with the deprotonated form of the ligand **HL**. The molecular structures of **HL** and **1**, together with their labelling schemes, are shown in Figs. 3 and 4, respectively. Selected bond lengths and angles are summarized in Table 2.

In the structure of the free ligand **HL**, the pyrrole and benzothiazole fragments are co-planar (the angle between the planes is 1.5°). Such a conformation of the molecule is stabilized by an intramolecular N(2)–H(2B)···N(1) hydrogen bond (Table 3) and a S(1)···O(1) interaction (the S···O distance is 2.998(3) Å, the van der Waals radii sum is 3.11 Å [10] and the C(1)–S(1)···O(1) angle is 164.10(4)°), which can be considered as a σ-hole bonding [11], i.e. an attractive interaction between the electron deficient sulfur atom and electron excessive carbonyl oxygen. The geometry at the N(3) atom of the pyrrole ring is best described as being slightly pyramidal (the sum of bond angles centred at N(3) atom is 358.2°). The deviation of the N(3) atom from the mean square plane of other atoms of the pyrrole ring is 0.064 Å, reflecting a flattened envelope conformation of the heterocycle. The amino group $N(2)H_2$ has an almost planar orientation with respect to the pyrrole ring (the torsion angle H(2A)–N(2)–C(9)–C(8) is 175.36(12)°). The second amino group, $N(4)H_2$, has an orthogonal orientation relative to the heterocycle (the torsion angle H(4A)–N(4)–N(3)–C(9) is 110.48(12)°), which is usual for hydrazine fragments.

The molecules of **HL** in the crystal phase form dimers because of a stacking interaction of the aromatic fragments of the molecules (the distance between their mean planes is 3.40 Å) and intermolec-

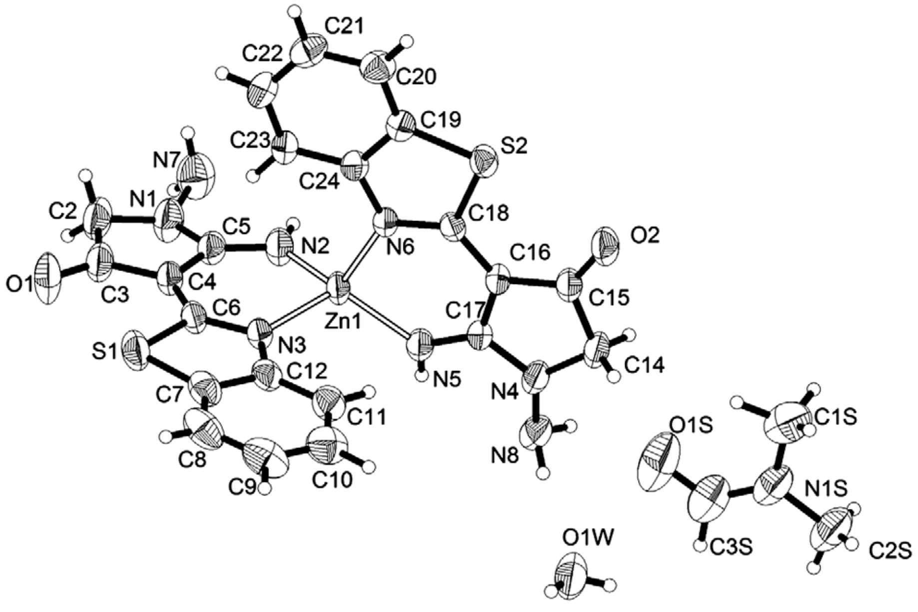


Fig. 4. Molecular structure of the compound $[ZnL_2]\cdot dmf\cdot H_2O$ (**1**) with the atom numbering scheme. Atom displacement ellipsoids are shown at the 50% probability level.

Table 2
Selected bond distances (Å) and angles (°) for the compounds **HL** and **1**.

HL					
S(1)–C(1)	1.736(1)	C(1)–S(1)–C(7)	88.94(5)	C(11)–C(8)–C(7)	127.4(1)
S(1)–C(7)	1.756(1)	C(7)–N(1)–C(6)	110.48(9)	C(9)–C(8)–C(7)	124.7(1)
O(1)–C(11)	1.236(2)	C(9)–N(3)–N(4)	120.9(1)	N(2)–C(9)–N(3)	123.0(1)
N(1)–C(7)	1.315(1)	C(9)–N(3)–C(10)	111.3(1)	N(2)–C(9)–C(8)	126.4(1)
N(1)–C(6)	1.384(2)	N(4)–N(3)–C(10)	126.0(1)	N(3)–C(9)–C(8)	110.6(1)
N(2)–C(9)	1.321(2)	C(2)–C(1)–S(1)	128.9(1)	N(3)–C(10)–C(11)	102.8(1)
N(3)–C(9)	1.334(1)	C(6)–C(1)–S(1)	109.7(1)	O(1)–C(11)–C(8)	129.1(1)
N(3)–N(4)	1.396(1)	N(1)–C(6)–C(5)	124.9(1)	O(1)–C(11)–C(10)	123.7(1)
N(3)–C(10)	1.452(2)	N(1)–C(6)–C(1)	115.5(1)	C(8)–C(11)–C(10)	107.2(1)
C(7)–C(8)	1.422(2)	N(1)–C(7)–C(8)	124.1(1)	C(8)–C(7)–S(1)	120.5(1)
C(8)–C(11)	1.413(2)	N(1)–C(7)–S(1)	115.4(1)	C(11)–C(8)–C(9)	107.9(1)
C(8)–C(9)	1.420(1)				
C(10)–C(11)	1.524(2)				
1					
Zn(1)–N(2)	1.9442(16)	N(2)–Zn(1)–N(5)	125.0(1)	N(1)–C(5)–C(4)	108.2(1)
Zn(1)–N(5)	1.9458(13)	N(2)–Zn(1)–N(3)	96.3(1)	N(3)–C(6)–C(4)	125.8(1)
Zn(1)–N(3)	2.0393(12)	N(5)–Zn(1)–N(3)	116.9(1)	O(2)–C(15)–C(16)	129.0(1)
Zn(1)–N(6)	2.0425(11)	N(2)–Zn(1)–N(6)	117.1(1)	O(2)–C(15)–C(14)	123.8(1)
O(1)–C(3)	1.234(2)	N(5)–Zn(1)–N(6)	96.0(1)	C(16)–C(15)–C(14)	107.2(1)
O(2)–C(15)	1.2391(18)	N(3)–Zn(1)–N(6)	105.2(1)	C(18)–C(16)–C(15)	125.3(1)
N(1)–N(7)	1.402(2)	C(6)–N(3)–C(12)	112.2(1)	C(18)–C(16)–C(17)	125.8(1)
N(2)–C(5)	1.303(2)	C(6)–N(3)–Zn(1)	120.7(1)	C(15)–C(16)–C(17)	108.9(1)
N(3)–C(6)	1.3264(19)	C(12)–N(3)–Zn(1)	126.4(1)	N(5)–C(17)–N(4)	125.1(1)
N(3)–C(12)	1.390(2)	C(17)–N(5)–Zn(1)	123.6(1)	N(5)–C(17)–C(16)	126.9(1)
N(4)–C(14)	1.443(2)	C(18)–N(6)–C(24)	112.0(1)	N(4)–C(17)–C(16)	107.9(1)
N(5)–C(17)	1.3013(19)	C(18)–N(6)–Zn(1)	121.5(1)	N(6)–C(18)–C(16)	125.9(1)
N(6)–C(18)	1.3253(18)	C(24)–N(6)–Zn(1)	126.3(1)	N(6)–C(18)–S(2)	114.1(1)
N(6)–C(24)	1.3927(17)	N(1)–C(2)–C(3)	103.0(2)	C(16)–C(18)–S(2)	120.0(1)
C(2)–C(3)	1.512(3)	O(1)–C(3)–C(4)	129(2)	C(6)–C(4)–C(5)	126.3(1)
C(3)–C(4)	1.415(2)	O(1)–C(3)–C(2)	123.6(2)	C(3)–C(4)–C(5)	108.5(2)
C(4)–C(6)	1.400(2)	C(4)–C(3)–C(2)	107.4(2)	N(2)–C(5)–N(1)	125.3(2)
C(4)–C(5)	1.443(2)	C(6)–C(4)–C(3)	125.2(2)	N(2)–C(5)–C(4)	126.5(2)
C(14)–C(15)	1.519(2)				
C(15)–C(16)	1.412(2)				
C(16)–C(18)	1.4113(19)				
C(16)–C(17)	1.437(2)				

Table 3
Hydrogen bonding distances (Å) and angles (°) for the compounds **HL** and **1**.

H-bond (number)	Symmetry	H···A	D–H···A
HL			
N(2)–H(2B)···N(1)	x, y, z	2.13(2)	135.1(13)
N(2)–H(2A)···O(1)	$-x+1, y+1/2, -z+1/2$	2.15(2)	166.8(14)
N(4)–H(4A)···O(1)	$x, -y+1/2, z-1/2$	2.20(2)	155.1(16)
N(4)–H(4B)···C(1)π	$1-x, 1-y, 1-z$	2.86(2)	127(1)
C(10)–H(10B)···C(5)π	$1-x, 1-y, 1-z$	2.81(2)	147(1)
C(2)–H(2C)···N(1)π	$x, 1/2-y, 1/2-z$	2.74(2)	174(1)
1			
O(1 W)–H(102)···O(1)	$-x, -y+1, -z$	2.07(3)	165(3)
O(1 W)–H(106)···O(2)	$-x+1, -y+2, -z+1$	2.08(4)	177(4)
N(8)–H(8A)···O(1 W)	x, y, z	2.13(2)	166(2)
N(8)–H(8B)···O(1S)	x, y, z	2.13(2)	152(2)
N(7)–H(7A)···N(8)	$-x+1, -y+1, -z$	2.52(3)	170(2)
N(7)–H(7B)···O(1 W)	$x, y, z-1$	2.32(2)	145(2)

ular N–H···π and C–H···π hydrogen bonds (Table 3). Neighboring dimers of compound **HL** interact with each other by intermolecular N–H???O, C–H···π hydrogen bonds and S···π interactions. In the last case, the distance between the S(1) and C(9′) atoms (3.424(2) Å) is considerably shorter than the van der Waals radii sum (3.55 Å), and the value of the C(7)–S(1)···C(9′) angle (154.59(4)°) meets the requirements for σ-hole bonding. These interactions finally form a two-dimensional supramolecular network of **HL** parallel to the (1 0 1) crystallographic plane (Fig. 5).

The asymmetric part of the unit cell of the crystal structure of **1** contains one molecule of complex formed by zinc(II) and two anionic ligands $\mathbf{L}^-$, one molecule of dmf and one molecule of water. The zinc(II) is tetrahedrally coordinated by two nitrogen atoms of the deprotonated amino groups (N(2) and N(5) in **1** corresponding to N(2) in **HL**) and two nitrogen atoms of the benzothiazole fragment (N(3) and N(6) in **1** corresponding to N(1) in **HL**) of two deprotonated residues of 1,2-diamino-3-(2-benzothiazol-yl)-4(5H)-ketopyrrole. The dihedral angle between the N(2)–Zn(1)–N(3) and N(5)–Zn(1)–N(6) planes is 86.8°. The angles around the central atom are distorted from an ideal tetrahedral configuration (Table 2). The deprotonation of the ligand and its coordination to Zn(II) leads to some changes in the geometrical parameters of $\mathbf{L}^-$ as compared to structure of **HL**. This includes an increase of the distance between the N(1) and N(2) atoms (2.866(3) Å in **HL** and 2.963(4), 2.968(3) Å in **1**) and a strengthening of the S···O intramolecular attractive interaction (the distances are 2.891(3) and 2.896(3) Å in **1** and 2.998(3) Å in **HL**). There is also a shortening of the C(4)–C(6), C(16)–C(18), N(2)–C(5) and N(5)–C(17) bonds and elongation of the N(3)–C(6), N(6)–C(18), C(4)–C(5) and C(16)–C(17) bonds in the ligand of compound **1** as compared to **HL**.

The lengths of the $\text{Zn–N}_{(\text{amino})}$ and $\text{Zn–N}_{(\text{benzothiazole})}$ bonds are 1.944(2), 1.946(1) and 2.039(1), 2.043(1) Å, respectively. It should be noted that the lengths of the $\text{Zn–N}_{(\text{amino})}$ bonds correspond to the formation of partly covalent bonds. Both six-membered metallocycles, Zn(1)–N(2)–C(5)–C(4)–C(6)–N(3) and Zn(1)–N(6)–C(18)–C(16)–C(17)–N(5), adopt a twist-boat conformation (puckering parameters [12] are $S = 0.16$, $\theta = 59.3$, $\psi = 19.9$ and $S = 0.09$, $\theta = 89.3$, $\psi = 25.9$, respectively).

The N(1) and N(4) atoms of the pyrrole ring have a pyramidal configuration (the sum of the bond angles centred at the N(1) and N(4) atoms are 355.6° and 358.4°, respectively). Deviations of the N(1) and N(4) atoms from the mean plane of the remaining atoms of the pyrrole rings are 0.14 and 0.08 Å, respectively, reflect-

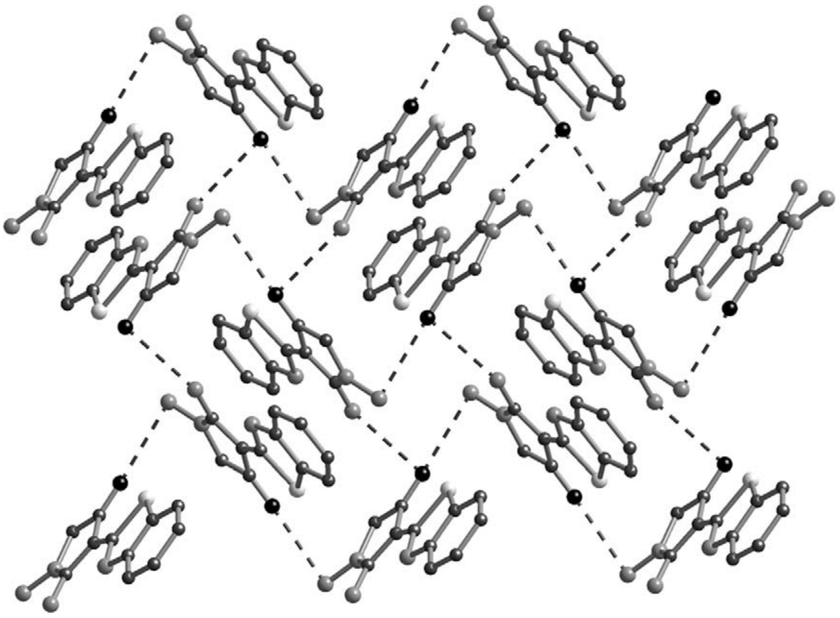


Fig. 5. Two-dimensional supramolecular network of the compound **HL** along the (1 0 1) crystallographic direction.

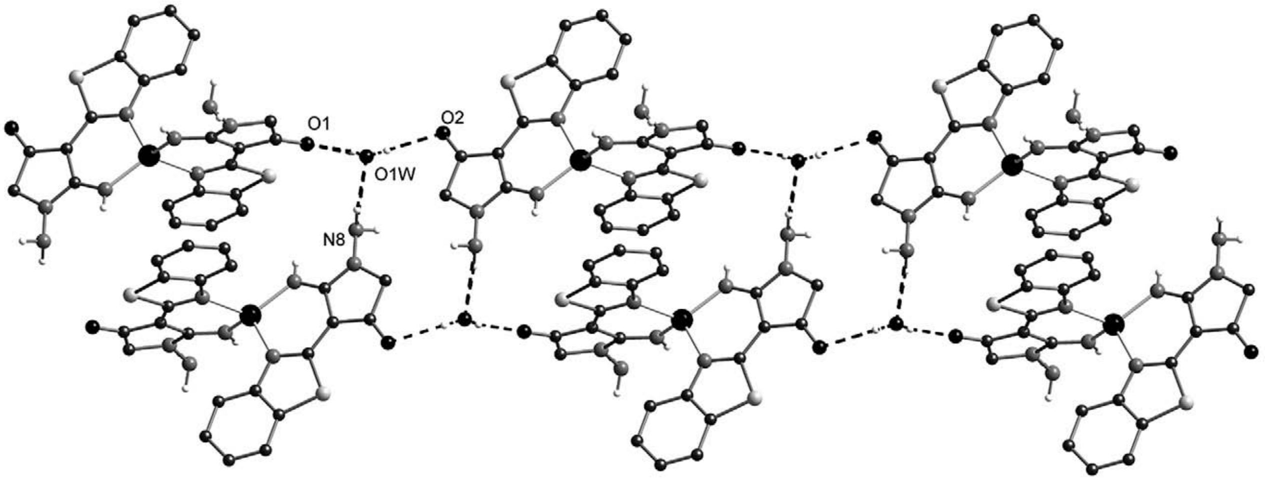


Fig. 6. Fragment of the infinite chain of the compound [ZnL$_2$]·dmf·H$_2$O (**1**).

ing a flattened envelope conformation of the heterocycles. The amino groups N(7)H$_2$ and N(8)H$_2$ have an orthogonal orientation relative to the heterocycles (the H(7A)–N(7)–N(1)–C(5) and H(8A)–N(8)–N(4)–C(17) torsion angles are 137.71(2)° and −122.11(1)°, respectively), which is usual for hydrazine fragments and is similar to the conformation of **HL**.

In the crystals of compound **1**, solvate dmf molecules are H-bonded to N(8)H$_2$ groups of neighboring ligands of **1**. The role of the solvate water molecules in the crystal architecture of **1** is more significant. The latter are joined by O–H···O hydrogen bonds with the oxygen atoms of carbonyl groups of two neighboring complexes units. These interactions connect [ZnL$_2$] complexes together into infinite chains (Fig. 6). Neighboring chains are linked together into a 2d sheet through hydrogen bonds between the oxygen atoms of water molecules and the hydrogen atoms of N(8)H$_2$ groups (Fig. 7). An additional attraction between the neighboring sheets is provided by stacking of aromatic fragments of the ligands (the distance between parallel fragments is 3.40 Å) and S···π σ-hole interactions (the S(2)···C(9′) distance is 3.45(1) Å and the C(18)–S(2)···C(9′) angle is 144.10(1)°). These interactions result in the formation of a three-dimensional supramolecular network in the crystal structure of complex **1**.

4. Conclusions

The presented work describes the first example of the usage of 1,2-diamino-3-(2-benzothiazolyl)-4(5H)-ketopyrrole as a ligand towards 3d-metal ions. To explore the coordination abilities of **HL**, we have used acetate salts of 3d-metals, yielding three novel mononuclear coordination compounds of zinc(II), cobalt(II) and nickel(II). The coordination of **HL** by the metal ion in the deprotonated form is proposed, based on spectroscopic investigations, mainly the ^{1}H NMR spectrum of the zinc(II) complex **1**. Analogous IR spectra of the other obtained complexes (**2** and **3**) to **1**, characterized by ^{1}H NMR-spectroscopy and X-ray analysis, suggests the coordination of **HL** in the deprotonated form in the same mode in these compounds.

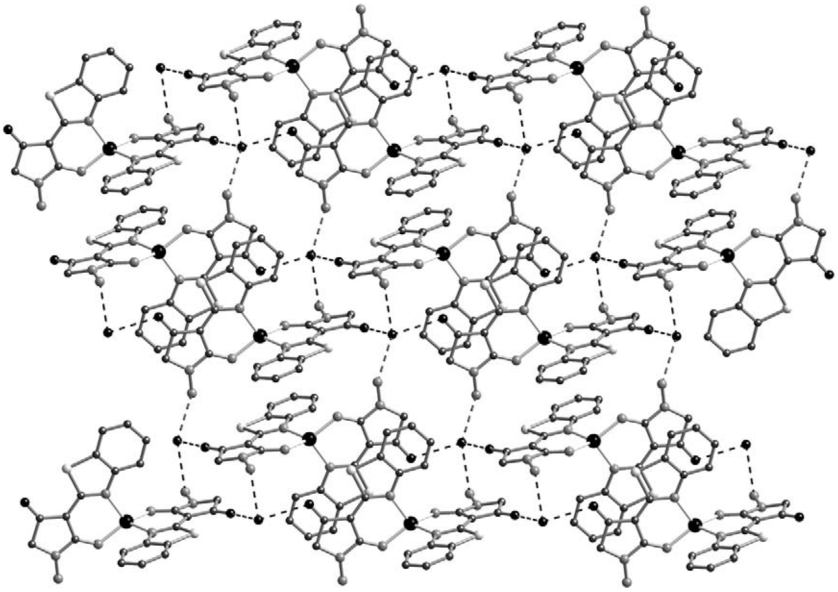


Fig. 7. Fragment of the supramolecular sheet of the compound [ZnL_2]·dmf·H_2O (**1**).

Supplementary data

CCDC 736005 and 736004 contain the supplementary crystallographic data for **HL** and **1**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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