Inorganica Chimica Acta 382 (2012) 127–138

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, structural and spectral characterization of Zn(II) complexes, derived from thiourea and thiosemicarbazide

S.I. Orysyk [a,*], V.V. Bon [a], O.O. Obolentseva [a], Yu. L. Zborovskii [b], V.V. Orysyk [b], V.I. Pekhnyo [a], V.I. Staninets [b], V.M. Vovk [b]

[a] *V.I. Vernadskii Institute of General and Inorganic Chemistry NAS of Ukraine, Palladin Av. 32/34, 03680 Kyiv, Ukraine*

[b] *Institute of Organic Chemistry NAS of Ukraine, Murmanska Str. 5, 02660 Kyiv, Ukraine*

ARTICLE INFO

Article history:
Received 9 April 2011
Received in revised form 18 August 2011
Accepted 6 October 2011
Available online 20 October 2011

Keywords:
Thiourea derivatives
Carbothioamide
Zn(II) complexes
NMR spectroscopy
X-ray diffraction study

ABSTRACT

Novel mono- and binuclear complexes of Zn(II) with thiourea derivatives (H_2L) (*N*-2-propenyl-*N*′-2-pyridinylthiourea) and thiosemicarbazide, H_3L (2-[(2-hydroxyphenyl)methylene]hydrazine-*N*-(2-propenyl)carbothioamide, (2-[(2-hydroxyphenyl)methylene]hydrazine-*N*-phenylcarbothioamide) have been synthesized. The possibility of mono- or tridentate coordination to the central metal ion of these ligands both in neutral and in monodeprotonated thionic tautomeric form with the stoichiometric ratios Zn:L = 1:1 and 1:2 has been shown. The synthesized complexes $Zn(CH_3COO)_2(H_2L)_2$ (**I**), $Zn_2(CH_3COO)_2(H_2L)_2{\cdot}Zn_2(CH_3COO)(H_2O)(H_2L)_2$ (**II**), $Zn(H_2L)_2$ (**III**), $Zn_2(CH_3COO)_2(H_2L)_2$ (**IV**) have been studied by IR, UV–Vis, ^1H, ^{13}C NMR spectroscopy and single crystal X-ray diffraction (**I, II, IV**). It has been established that in compound (**I**) the central Zn atom forms a strongly distorted tetrahedral ZnS_2O_2 coordination, while in (**II**) and (**IV**) it forms a square-pyramidal $ZnSNO_3$ environment. In the case of complex (**II**) the asymmetric unit contains two molecules of binuclear complex compounds, which are slightly differ by coordination in vertex direction of Zn polyhedron. The square-pyramidal geometry of Zn(II) ions from the first molecule completed by two acetate anions, which is similar to compound (**IV**). In the second molecule, the Zn(II) coordination polyhedrons are completed by one acetate anion and one water molecule.

1. Introduction

Zinc is a biologically essential element [1]. Zn(II) ions as a cofactor are part of over 300 enzymes (carbonic anhydrases, zinc proteinases, histone deacetylases, alkaline phosphatases, alcohol dehydrogenases, aminopeptidases, etc.), which involved in metabolic processes of living organisms: viruses, bacteria, plants and animals [1–8]. Many of the above mentioned enzymes can also participate in processes giving rise to pathological states. For example, zinc-containing proteinases, which are produced by viruses, split the host's protein into small fragments, from which new copies of viruses are then created [9,10]. Zinc proteinases are included in the life cycle of different kind of bacteria sometimes also pathogenic ones [8]. The activity of zinc proteinases and histone deacetylases increases greatly when cancer diseases or a number of other diseases arise [3,5–7,11–14]. Therefore, the efforts of many laboratories are directed at search for effective inhibitors of zinc-containing enzymes, which are of interest as potential pharmaceuticals. The compounds that are able to bind into stable complexes Zn(II) ions, located in the active site of enzymes can serve as such inhibitors [3–7,11,14,15]. It is logical to assume that the functional derivatives of thiocarbamic acid, in particular thiourea and thiosemicarbazone, which are known in literature as sensitive reagents for the extraction–photometric determination of Zn(II) [16], will possess such an activity. Moreover, complexes of thiosemicarbazones with a number of transition metal ions show a high bioactivity and are of interest as potential anticancer, antiviral, antibacterial and anti-inflammatory drugs [17–21].

In the synthetic aspect, thiourea and thiosemicarbazide derivatives are of interest as effective complexing agents for transition metal ions. In particular, it has been shown that *N*-2-propenyl-*N*′-2-pyridinylthiourea forms stable complexes with Bi(III) ions [22], while 2-[(2-hydroxyphenyl)methylene]hydrazincarbothioamide derivatives form ones with Zn(II) ions [23–25].

Thiourea and its derivatives are part of the complexes as polydentate ligands since their molecule contains several nucleophilic electron-donor centers, the geometry of whose arrangement and the electronic configuration of complexing metal determine the possibility of forming various structure complexes [26–30]. Like other ambidentate ligand systems, they are characterized by competitive coordination; which defines the scientific interest in study

---

* Corresponding author.
E-mail address: orysyk@ionc.kiev.ua (S.I. Orysyk).

0020-1693/$ - see front matter
doi:10.1016/j.ica.2011.10.027

their interaction with metal ions, in particular with Zn(II), which is able to form both a tetrahedral and an octahedral coordination unit.

In the present work, the ability of a number of chelating thiourea derivatives: *N*-2-propenyl-*N*′-2-pyridinylthiourea (A), 2-[(2-hydroxyphenyl)methylene]hydrazine-*N*-(2-propenyl)carbothioami de(B) and 2-[(2-hydroxyphenyl)methylene]hydrazine-*N*-phenylcarboth ioami de (C) (Scheme 1) for complex formation with zinc ions has been shown. The procedures for the synthesis of coordination compounds in the crystalline form has been developed, their spectral characteristics, composition and structure have been studied.

2. Materials and methods

2.1. Material sources

Chemically pure $Zn(CH_3COO)_2 \cdot 2H_2O$ was used as a source of zinc salts for the synthesis of complexes **I, II, IV**, and chemically pure $Zn(NO_3)_2 \cdot 6H_2O$ was used for synthesize the product **III**.

2.2. Physical measurements

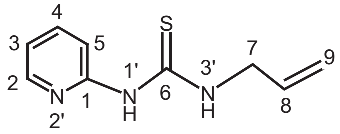
The UV–Vis spectra of compounds in 10^{-4} M DMF solutions were recorded on Specord M 40 spectrophotometer in the range of 50 000–11 000 cm^{-1} ($l_{quartz\ cells} = 0.1$ cm). The IR spectra were obtained on Specord M 80 spectrophotometer in the range 4000–200 cm^{-1} using pellets with KBr. The ^1H and ^{13}C NMR spectra were measured on Bruker Advance DRX-500 spectrometer (500.13 and 125.75 MHz, respectively), in DMSO-d_6 solution using TMS as internal standard.

2.3. X-ray crystallography

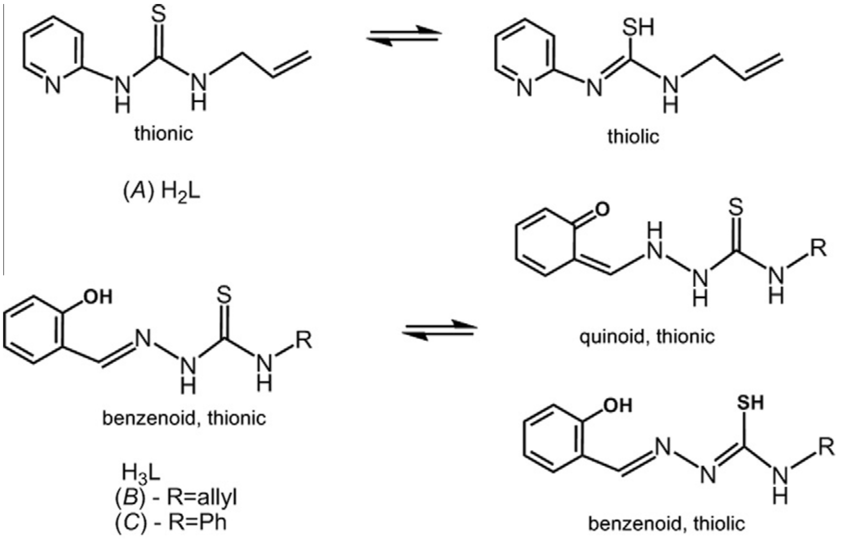
The unit cell parameters and three-dimensional set of reflection intensities for single crystals of **I, II** and **IV** were measured on a Bruker Smart Apex II diffractometer (Mo K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at room temperature. The experimental data from X-ray structural experiment are listed in Table 1. The structures were solved by direct methods and refined by the full-matrix least-squares on F^2 in anisotropic approximation for non hydrogen atoms using the SHELXTL program package [31]. The hydrogen atoms bonded to nitrogen and oxygen atoms were located objectively from a difference map of electron density and refined using the distance restraints d(O–H) = 0.82 ± 0.04 Å, $U_{iso}(H) = 1.5\ U_{eq}(O)$ and d(N–H) = 0.87 ± 0.04 Å, $U_{iso}(H) = 1.2\ U_{eq}(N)$. The H atoms bonded to C atoms were placed in turn in geometrically idealized positions in accordance with hybridization of the accompanying atom and refined using a riding model with $U_{iso}(H) = 1.5\ U_{eq}(C)$ in the case of CH_3 group and $U_{iso}(H) = 1.2\ U_{eq}(C)$ in all other cases. When refining the structure of **I**, disorder of the allyl groups C^7–C^9 and C^{16}–C^{18} over two positions was established. As a result, the mentioned groups were refined with occupancies of 0.348/0.652 and 0.563/0.437, respectively. During refining the structure **II**, a highly disordered lattice water molecule was observed, all positions of which could not be refined. Therefore, SQUEEZE/PLATON routine was employed to correct reflection intensities with subtraction of the electron density of the disordered molecule [32]. Besides, disorder of the allyl fragment C^{13}–C^{15} over two positions with occupancies of 0.374/0.626 was established in the course of refinement. CCDC 817648–817650 contain the complete set of data on the compounds **I, II** and **IV** and can be request free of charge from Cambridge Crystallographic Data, 12 Union Road, Cambridge, CB2 1EZ, UK (http://www.ccdc.cam.ac.uk/products/csd/request/).

3. Experimental

3.1. *N-2-Propenyl-N′-2-pyridinylthiourea, H_2L (**A**)*



It has been synthesized by the method reported in [33], m.p. 100–101 °C. Yield: 88%; *Anal.* Calc. for $C_9H_{11}N_3S$: C, 55.93; H, 5.74; N, 21.74; S, 16.59. Found: C, 55.61; H, 5.59; N, 21.42; S, 16.29%. UV–Vis date, ν, cm^{-1} (DMF): 40 560 (1710); 37 400 (1930) and 34 050 (1960). IR data, ν, cm^{-1}: 3243, ν(NH); 3117,



Scheme 1. Tautomeric forms of the ligands.

Table 1
Crystal data and structure refinement for **I**, **II** and **IV**.

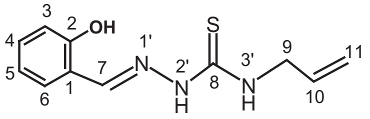
Complexes	**I**	**II**	**IV**
Molecular formula	$C_{22}H_{28}N_6O_4S_2Zn$	$C_{52}H_{62}N_{12}O_{13}S_4Zn_4$	$C_{32}H_{30}N_6O_6S_2Zn_2$
Crystal size (mm)	0.35 × 0.25 × 0.15	0.20 × 0.15 × 0.03	0.35 × 0.25 × 0.05
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.0669 (12)	8.1414 (12)	14.751 (10)
b (Å)	16.2275 (16)	28.470 (4)	29.57 (2)
c (Å)	16.6857 (17)	27.907 (4)	7.820 (4)
β (°)	92.818 (5)	95.858 (2)	100.51 (4)
V (Å^3)	2722.5 (5)	6434.7 (16)	3354 (4)
Z	4	4	4
D_{calc} (g cm^{-3})	1.391	1.500	1.564
μ (mm^{-1})	1.0 93	1.670	1.608
F(000)	1184	2984	1616
θ Range (°)	$1.75 \leqslant \theta \leqslant 26.48$	$1.02 \leqslant \theta \leqslant 26.34$	$1.56 \leqslant \theta \leqslant 26.63$
Range of indices	$-9 \leqslant h \leqslant 2$ $-19 \leqslant k \leqslant 20$ $-20 \leqslant l \leqslant 20$	$-10 \leqslant h \leqslant 10$ $-35 \leqslant k \leqslant 28$ $-34 \leqslant l \leqslant 34$	$-18 \leqslant h \leqslant 18$ $-36 \leqslant k \leqslant 36$ $-9 \leqslant l \leqslant 9$
Total/independent reflections	19269/5591 [R(int) = 0.0249]	43211/13045 [R(int) = 0.0731]	29441/6802 [R(int) = 0.0978]
Number of reflections with $I > 4\sigma(I)$	4261	6997	3680
Number of parameters to be refined	348	809	447
GOOF (F^2)	1.054	0.931	1.005
R_1, wR_2 ($I \geqslant 4\sigma(I)$)	0.0371, 0.0955	0.0556, 0.1074	0.0538, 0.1092
R_1, wR_2 (all reflections)	0.0570, 0.1098	0.1254, 0.1271	0.1267, 0.1370
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.564/−0.234	0.687/−0.379	0.553/−0.444

ν(=CH); 3057, ν(CH$_{Py}$); 2960, asymmetric vibrations ν(CH$_2$)$_{allyl}$; 2859, ν(C–H); 1600, 1556, 1536 in-plane deformation vibrations δ(NH–CS–NH); 1478, 1450, 1422, pyridine ring vibrations ν(PyH); 1330, 1302, 1275, 1260; 1242; 1194; 1143 ν(NH–CS–NH); 1103; 998, 953, 935; 915, 897 in-plane deformation vibrations δ(CH); 849; 811; 760; 707, 687 out-of-plane deformation vibrations δ(CH); 626; 538, 525, 512 deformation vibrations δ(CH$_{allyl}$). ^{1}H NMR data, δ, ppm (DMSO-d_6): 4.31 (m, 2H, C^{7}H$_2$); 5.16–5.26 (dd, J = 10.5, 17.0 Hz, 2H, =C^{9}H$_2$); 5.93–6.06 (m, 1H, =C^{8}H); 7.04 (t, J = 6.0 Hz, 1H, C^{3}H$_{Py}$); 7.18 (d, J = 8.5 Hz, 1H, C^{5}H$_{Py}$); 7.78 (t, J = 8.5 Hz, 1H, C^{4}H$_{Py}$);8.23 (d, J = 5.0 Hz, 1H, C^{2}H$_{Py}$); 10.65 (s, 1H, N$^{3'}$H); 11.80 (s, 1H, N$^{1'}$H). ^{13}C NMR data, δ, ppm (DMSO-d_6): 46.68 C$^{(7)}$; 112.71 C$^{(5)}$; 115.75 C$^{(9)}$; 117.58 C$^{(3)}$; 134.19 C$^{(8)}$; 138.78 C$^{(4)}$; 145.12 C$^{(2)}$; 153.75 C$^{(1)}$; 179.77 C$^{(6)}$.

3.2. Bis[(N-2-propenyl-N′-2-pyridinylthiourea-κ-S)(acetate -κ-O)]zinc(II), Zn(CH$_3$COO)$_2$(H$_2$L)$_2$ (*I*)

Twenty milliliter of ethanolic solution of Zn(CH$_3$COO)$_2$·2H$_2$O (0.2194 g, 0.1 mmol) acidified with 3 ml of concentrate acetic acid was mixed with 20 ml of hot ethanolic solution of ligand (**A**) (0.3866 g, 0.2 mmol). The mixture was stirred for 25 min at 65 °C until evaporation of more than half of its volume. The resulting colorless solution was corked and left for crystallization for 3 weeks. I result, the needle-shaped transparent crystals of the complex **I** formed. m.p. 124–125 °C. Yield 0.39 g (65%). *Anal.* Calc. for $C_{22}H_{28}N_6O_4S_2Zn$: C, 46.32; H, 4.91; N, 14.74; S, 11.23. Found: C, 46.35; H, 4.95; N, 14.79; S, 11.25%. UV–Vis date, ν, cm^{-1} (DMF): 40330 (2830); 36645 (1452) and 33635 (1555). IR data, ν, cm^{-1}: 3239 (shoulder), 3185, ν(NH); 3071, ν(=CH); 3011, ν(CH$_{Py}$); 2977 asymmetric vibrations, ν (CH$_2$)$_{allyl}$; 2935, ν(CH$_3^{Ac}$); 2859, 2783, ν(CH); 1630, ν(C=O$_{Ac}$); 1577,1544 d, in-plane deformation vibrations δ(NH–CS–NH); 1478, 1437, 1400 pyridine ring vibrations ν(PyH); 1330; low intensity 968, 943, 917; 898, 878 in-plane deformation vibrations δ(CH); 839; intense 773, 722, 660, out of-plane deformation vibrations δ(CH); 629, 616, 550, 514 deformation vibrations δ(CH$_{allyl}$); 284, ν(Zn–S). 1H NMR data, δ, ppm (DMSO-d_6): 1.83 (s, 3H, CH$_3$CO); 4.31 (m, 2H, C^{7}H$_2$); 5.15–5.26 (dd, 2H, J = 10.5, 17.0 Hz, =C^{9}H$_2$); 5.93–6.06 (m, 1H=C^{8}H); 7.04 (t, 1H, J = 6.0 Hz, C^{3}H$_{Py}$); 7.19 (d, 1H, J = 8.5 Hz, C^{5}H$_{Py}$); 7.78 (t, 1H, J = 8.5 Hz, C^{4}H$_{Py}$); 8.23 (d, 1H, J = 5.0 Hz, C^{2}H$_{Py}$); 10.66 (s, 1H, N$^{3'}$H); 11.79 (s, 1H, N$^{1'}$H). ^{13}C NMR data, δ, ppm (DMSO-d_6): 22.47 C$^{(Ac)}$; 46.72 C$^{(7)}$; 112.42 C$^{(5)}$; 115.78 C$^{(9)}$; 117.63 C$^{(3)}$; 133.78 C$^{(8)}$; 138.65 C$^{(4)}$; 145.37 C$^{(2)}$; 153.81 C$^{(1)}$; 176.63 C$^{(C=O)}$; 179.75 C$^{(6)}$.

3.3. 2-[(2-Hydroxyphenyl)methylene]hydrazine-N-(2-propenyl)-carbothioamide, H$_3$L (*B*)



It has been synthesized by the method reported in [34]. m.p. 153–154 °C. Yield 79%. *Anal.* Calc. for $C_{11}H_{13}N_3SO$: C, 56.17; H, 5.53; N, 17.87; S, 13.62. Found: C, 56.20; H, 5.60; N, 17.81; S, 13.66%. UV–Vis date, ν, cm^{-1} (DMF): 34200 shoulder (670); 32650 (710); 30055 (695). IR data, ν, cm^{-1}: 3291, ν(NH); 3168, ν(OH); 3099, ν(=CH); 2943, asymmetric vibrations ν(CH$_2$)$_{allyl}$; 3005, ν(CH); 1624, d, ν(C=N); 1604, 1550, 1528, in-plane deformation vibrations δ(NH–CS–NH); 1489, 1472, 1438, 1414, phenolic ring vibrations ν(PhH); 1357, 1330, ν(CS); 1294, 1228 ν(C–O$_{Ph}$); 1154, 1127, 1090, ν(NH–CS–NH); 1042, 1010, ν(N–N); 978, 948 d, 936, 905, in-plane deformation vibrations δ(CH); 800, 738, 650, out-of-plane deformation vibrations δ(CH); broadened 619, 577, 548, 525, 481, 464, deformation vibrations δ(CH$_{allyl}$). ^{1}H NMR data, δ, ppm (DMSO-d_6): 4.23 (m, 2H, C^{9}H$_2$); 5.09–5.18 (dd, 2H, J = 10.0, 17.0 Hz, C^{11}H$_2$); 5.90–5.95 (m, 1H, =C^{10}H); 6.84 (t, 1H, J = 7.5 Hz, C^{5}H$_{Ar}$); 6.89 (d, 1H, J = 8.5 Hz, C^{3}H$_{Ar}$); 7.23 (t, 1H, J = 8.0 Hz, C^{4}H$_{Ar}$); 7.96 (d, 1H, J = 7.5 Hz, C^{6}H$_{Ar}$); 8.40 (s, 1H, =C^{7}H); 8.60 (t, 1H, J = 5.5 Hz, N$^{3'}$H); 9.90 (s, 1H, OH); 11.46 (s, 1H, $N^{2'}H$). ^{13}C NMR data, δ, ppm (DMSO-d_6): 45.71 $C^{(9)}$; 115.40 $C^{(11)}$; 115.95$C^{(3)}$; 118.92 $C^{(5)}$; 120.35 $C^{(1)}$; 126.43 $C^{(6)}$; 130.77 $C^{(4)}$; 134.73 $C^{(10)}$; 139.12 $C^{(7)}$; 156.32 $C^{(2)}$; 177.00 $C^{(8)}$.

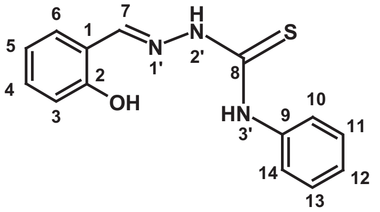
3.4. Bis{μ^2-O[(E)-2-[(2-hydroxyphenyl)methylene]hydrazine-N-(2-propenyl)carbothioamide–κ^3-O,N,S][acetate–κ-O]zinc(II)}, $Zn_2(CH_3COO)_2(H_2L)_2{\cdot}Zn_2(CH_3COO)(H_2O)(H_2L)_2$ (***II***)

Twenty milliliter of ethanolic solution of Zn $(CH_3COO)_2{\cdot}2H_2O$ (0.47 g, 0.1 mmol) (acidified with 3 ml of concentrate acetic acid) was mixed with 20 ml of hot ethanol solution of ligand (**B**) (0.44 g, 0.1 mmol). The mixture was refluxed for 45 min. The color of reaction mixture solution changed to yellow immediately after adding the first drops of ligand solution. The mixture was left for crystallization in dark place. After 4 days, needle-shaped light green-yellow crystals grown. Decomposition temperature 265–270 °C. Yield 0.86 g (95%). *Anal.* Calc. for $C_{52}H_{62}N_{12}O_{13}S_4Zn_4$: C, 42.94; H, 4.27; N, 11.56; S, 8.81. Found: C, 42.92; H, 4.29; N, 11.75; S, 8.88%. UV–Vis date, ν, cm^{-1} (DMF): 32 190 shoulder (290); 31 000 (275); 26 650 (342). IR data, ν, cm^{-1}: 3242, ν(NH); 3076, ν(=CH); 3017, ν(CH); 2975, asymmetric vibrations $\nu(CH_2)_{allyl}$; 2917, $\nu(CH_3{}^{Ac})$; 1631, $\nu(C{=}O^{Ac})$; 1608, 1592, 1550, ν(C=N) and in-plane deformation vibrations δ(NH–CS–NH); 1474, 1438, 1409, phenolic ring vibrations ν(PhH); 1345, 1321, ν(CS); 1279, 1257, 1205, $\nu(C\text{–}O_{Ph})$; 1152, 1125, 1088, ν(NH–CS–NH); 1039 d, 1017, ν(N–N); 993, 973, 944, 905, in-plane deformation vibrations δ(CH); 800, 743, 653, out-of-plane deformation vibrations δ(CH); 613, 575, 557, 464, deformation vibrations $\delta(CH_{allyl})$; 438, ν(Zn–N); 285 ν(Zn–S). 1H NMR data, δ, ppm (DMSO-d_6): ^1H NMR, δ, ppm (DMSO-d_6): 1.91 (s, 3H, CH_3CO); 3.91 (m, 2H, C^9H_2); 5.01–5.15 (dd, 2H, J = 10.0, 17.5 Hz, $=C^{11}H_2$); 5.86–5.92 (m, 1H, $=C^{10}H$); 6.65 (m, 1H, C^5H_{Ar}); 6.78 (m, 1H, C^3H_{Ar}); 6.89 (m, 1H, C^4H_{Ar}); 7.10 (m, 1H, $N^{3'}H$); 7.25 (m, 1H, C^6H_{Ar}); 8.38 (s, 1H, $=C^7H$); 11.80 (s, 1H, $N^{2'}H$). ^{13}C NMR data, δ, ppm (DMSO-d_6): 21.19 $C^{(Ac)}$; 44.25$C^{(9)}$; 114.71 $C^{(11)}$; 116.06 $C^{(3)}$; 120.74$C^{(1)}$; 121.06 $C^{(5)}$; 130.28 $C^{(6)}$; 132.95 $C^{(4)}$; 136.29 $C^{(10)}$; 152.23 $C^{(7)}$; 163.15 $C^{(2)}$; 172.42 $C^{(8)}$; 173.29 $C^{(C{=}O)}$.

3.5. Bis[μ^2-O(E)-2-[(2-hydroxyphenyl)methylene]hydrazine-N-(2-propenyl)carbothioamide–κ^3-O,N,S][acetate–κ-O][aqua-κ-O]zinc(II)acetate, $Zn(H_2L)_2$ (***III***)

The synthesis was carried out analogously to complex **II** using molar ratio M:L = 1:2 and $Zn(NO_3)_2{\cdot}6H_2O$ as initial Zn salt. Decomposition temperature >260 °C. Yield 73%. *Anal.* Calc. for $C_{22}H_{24}N_6O_2S_2Zn$: C, 49.44; H, 4.49; N, 15.73; S, 11.99. Found: C, 49.48; H, 4.52; N, 15.68; S, 12.02%. UV–Vis date, ν, cm^{-1} (DMF): 32 360, shoulder (165); 30 900 (157); 26 650 (170). IR data, ν, cm^{-1}: 3230, ν(NH); 3063, ν(=CH); 3015 ν(CH); 2985, asymmetric vibrations $\nu(CH_2)_{allyl}$; 1604, 1594, d, 1568, 1547, ν(C=N) and in-plane deformation vibrations δ(NH–CS–NH); 1470, 1438, 1412, phenolic ring vibrations ν(PhH); 1348, 1312 ν(CS); 1275, 1254, 1203, $\nu(C\text{–}O_{Ph})$; 1157, 1125, 1095, ν(NH–CS–NH); 1042, 1019, ν(N–N); 993, 972, 940, 901, in-plane deformation vibrations δ(CH); 840, 801, 749, 655, out-of-plane deformation vibrations δ(CH); 613, 575, 557, 464, deformation vibrations $\delta(CH_{allyl})$; 438, ν(Zn–N); 285 ν(Zn–S). 1H NMR data, δ, ppm (DMSO-d_6): 3.90 (m, 2H, C^9H_2); 5.01–5.15 (dd, 2H, J = 10.0, 17.5 Hz, $=C^{11}H_2$); 5.86–5.92 (m, 1H, $=C^{10}H$); 6.64 (m, 1H, C^5H_{Ar}); 6.78 (m, 1H, C^3H_{Ar}); 6.89 (m, 1H, C^4H_{Ar}); 7.11 (m, 1H, $N^{3'}H$); 7.25 (m, 1H, C^6H_{Ar}); 8.39 (s, 1H, $=C^7H$); 11.80 (s, 1H, $N^{2'}H$). ^{13}C NMR data, δ, ppm (DMSO-d_6): ^{13}C NMR, δ, ppm (DMSO-d_6): 44.25$C^{(9)}$; 114.70 $C^{(11)}$; 117.06 $C^{(3)}$; 120.68$C^{(1)}$; 121.09 $C^{(5)}$; 130.20 $C^{(6)}$; 132.86 $C^{(4)}$; 136.33 $C^{(10)}$; 152.16 $C^{(7)}$; 163.00$C^{(2)}$; 172.39 $C^{(8)}$.

3.6. 2-[(2-Hydroxyphenyl)methylene]hydrazine-N-phenyl)carbothioamide, H_3L (***C***)



It was obtained by the modified method [35] the interaction of 4-phenylthiosemicarbazide with 2-hydroxybenzaldehyde in refluxing ethanol. m.p. 186–187 °C (with decomposition). Yield 77%. *Anal.* Calc. for $C_{14}H_{13}N_3OS$: C, 61.97; H, 4.83; N, 15.49; S, 11.82. Found: C, 61.85; H, 4.78; N, 15.35; S, 11.38%. UV–Vis date, ν, cm^{-1} (DMF): 33 450, shoulder (490); 32 470 (510); 29 360 (670). IR data, ν, cm^{-1}: 3340, w, ν(NH); 3156 ν(OH); 3056, 2999 $\nu(CH_{Ar})$; 2856 ν(C–H); 1623, 1602, 1595, d, 1539, 1515 ν(C=N) and in-plane deformation vibrations δ(NH–CS–NH); 1472, 1447, 1403, phenolic ring vibrations ν(PhH); 1342, 1320, d, ν(CS); 1279, d, 1267, 1218 $\nu(C\text{–}O_{Ph})$; 1159, 1088, ν(NH–CS–NH); 1044, d, 1013 ν(N–N); 960, 930, d, 914 in-plane deformation vibrations δ(CH); 880, 781, 744 d, 731, 681, 648, out-of-plane deformation vibrations δ(CH); 601, 567, out-of-plane deformation vibrations of aromatic ring $\delta(CH_{Ar})$. ^1H NMR data, δ, ppm (DMSO-d_6): 6.86 (t, 1H, J = 7.5 Hz, C^5H_{Ar}); 6.90 (d, 1H, J = 8.5 Hz, C^3H_{Ar}); 7.21 (t, 1H, J = 7.0 Hz, $C^{12}H_{Ar}$); 7.25 (t, 1H, J = 8.0 Hz, C^4H_{Ar}); 7.38 (t, 2H, J = 8.0 Hz, $C^{11,13}H_{Ar}$); 7.61 (d, 2H, J = 8.5 Hz, $C^{10,14}H_{Ar}$); 8.10 (d, 1H, J = 7.0 Hz, C^6H_{Ar}); 8.52 (s, 1H, $=C^7H$); 9.98 (s, 1H, OH); 10.06 (s, 1H, $N^{3'}H$); 11.78 (s, 1H, $N^{2'}H$). ^{13}C NMR,δ, ppm (DMSO-d_6): 116.05$C^{(3)}$; 119.14 $C^{(5)}$; 120.20 $C^{(1)}$; 125.05 $C^{(12)}$; 125.49 $C^{(10,14)}$; 127.12 $C^{(6)}$; 128.00 $C^{(11,13)}$; 131.20 $C^{(4)}$; 139.10 $C^{(9)}$; 140.15 $C^{(7)}$; 156.54 $C^{(2)}$; 175.70 $C^{(8)}$.

3.7. Bis{μ^2-O[(E)-2-(2-[(hydroxyphenyl)methylene]hydrazine-N-phenylcarbothioamide–κ^3-O,N,S][acetate–κ-O]zinc(II)}, $Zn_2(CH_3COO)_2(H_2L)_2$ (IV)

The synthesis was carried out analogously to complex **II** using molar ratio Zn:H_2L = 1:1. Decomposition temperature >260 °C. Yield 89%. *Anal.* Calc. for $C_{32}H_{30}N_6O_6S_2Zn_2$: C 48.63; H 3.80; N 10.64; S 8.11. Found: C 48.73; H 3.75; N 10.75; S 8.15%. UV–Vis date, ν, cm^{-1} (DMF): 33 760, shoulder (417); 31 840 (423); 25 960 (550). IR data, ν, cm^{-1}: 3217, w, ν(NH); 3014 $\nu(CH_{Ar})$; 2918 $\nu(CH_3{}^{Ac})$; 2818; 1632 $(C{=}O_{Ac})$; 1598, 1549, 1493 ν(C=N) and in-plane deformation vibrations δ(NH–CS–NH); 1475, 1434, 1412, 1384, phenolic ring vibrations ν(PhH); 1326, 1301 ν(CS); 1202 $\nu(C\text{–}O_{Ph})$; 1159, 1118 ν(NH–CS–NH); 1044, d, 1025 ν(N–N); 942, 907, 914 in-plane deformation vibrations δ(CN); 852, 790, 740, 697, d, 682, 645, out-of-plane deformation vibrations δ(CH); 564, out-of-plane deformation vibrations of aromatic ring $\delta(CH_{Ar})$; 418 ν(Zn–N); 301 ν(Zn–S). 1H NMR data, δ, ppm (DMSO-d_6): 1.92 (s, 3H, CH_3CO); 6.70 (m, 1H, C^5H_{Ar}); 6.88 (t, 1H, J = 7.0 Hz, C^4H_{Ar}); 6.97 (m, 1H, C^3H_{Ar}); 7.22 (m, 3H, $C^{11,12,13}H_{Ar}$); 7.36 (m, 1H, C^6H_{Ar}); 7.82 (d, 2H, J = 8.0 Hz, $C^{10,14}H_{Ar}$); 8.61 (s, 1H, $=C^7H$); 8.92 (s, 1H, $N^{3'}H$); 11.97 (s, 1H, $N^{2'}H$). ^{13}C NMR, δ, ppm (DMSO-d_6): 21.11$C^{(Ac)}$; 119.52$C^{(10,14)}$; 120.26 $C^{(1)}$; 120.79 $C^{(3)}$; 121.15$C^{(5)}$; 128.09 $C^{(11,13)}$; 131.08 $C^{(6,12)}$; 133.45 $C^{(4)}$; 141.51 $C^{(9)}$; 155.21 $C^{(7)}$; 168.40 $C^{(2)}$; 171.99 $C^{(8)}$; 173.31 $C^{(C{=}O)}$.

4. Results and discussion

4.1. Spectroscopic characterization

The ligands **A–C** are characterized by the presence of thione–thiol (H_2L) and/or benzoid–quinoid (H_3L) tautomerism (Scheme 1), which allows them to act both as monobasic, dibasic and as polybasic acid with ensuring of N-, S- and/or O-, N-, S-donor interaction. In this case, the composition and structure of the complexes formed depend on reaction conditions: pH, heating temperature and time, ratio and concentration of the initial substances.

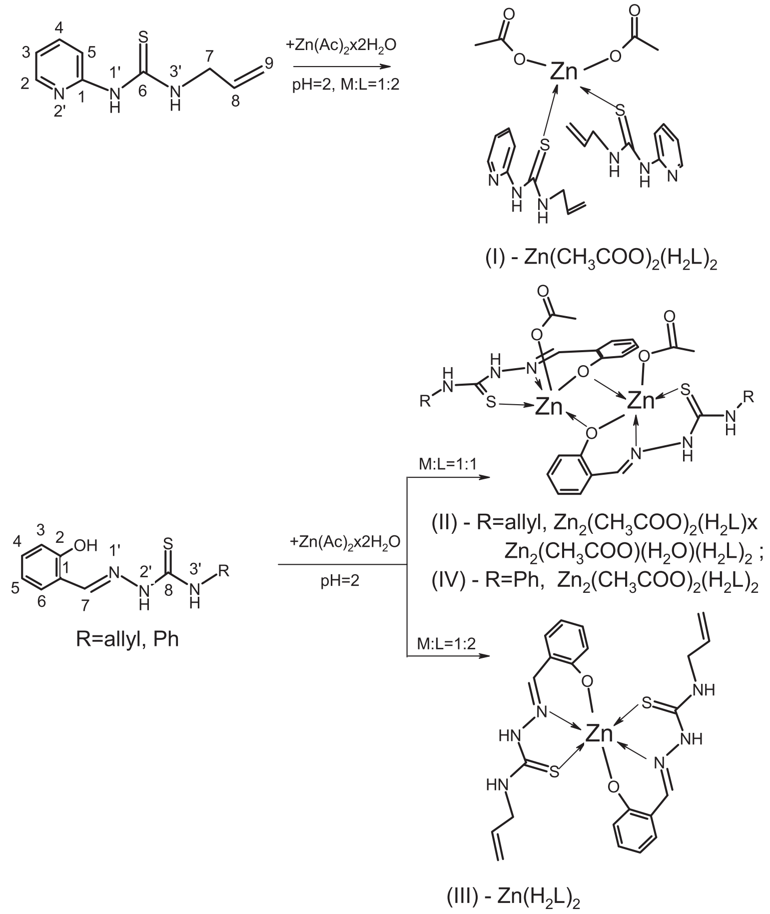
It has been found that reaction of thiourea derivatives **A** and thiosemicarbazides **B**, **C** with Zn(II) ions in the acid media, where ligands exist in thionic form and behave as monobasic acids with coordination to the central metal ion in mono- or tridentate manner, led to formation of complexes **I–IV** (Scheme 2). The location of coordination bonds and the structure of the complexes were determined by comparing of IR, UV–Vis and ^1H, ^{13}C NMR spectra of the ligands **A–C** and corresponding complexes **I–IV**.

4.1.1. IR spectra

The high-frequency region of infrared spectra of thiourea (**A**) and thiosemicarbazones (**B**, **C**) characterized by the presence of absorption bands at 3243, 3291, 3340 cm^{-1}, related to stretching vibrations ν(NH) of thioureide group. The frequency of the second peak is lower by 58 cm^{-1} in comparison with the original ligand, which may be due to the coordination of thiourea (**A**) to the metal ion vis sulfur atom of the thioureide group and/or, as shown by X-ray diffraction study, most likely due to formation of the hydrogen bonds $N^{(3)}–H^{(3N)}\ldots N^{(2)}$ and $N^{(1)}–H^{(1N)}\ldots O^{(2)}(C{=}O_{Ac})$ (Table 3, Fig. 4). In the IR spectra of thiosemicarbazones **B** and **C**, the broadened bands of stretching vibrations of ν(OH) from phenyl rings at 3168 and 3156 cm^{-1} are found. It may indicates the presence of the intramolecular hydrogen bond between OH and C=N groups, the existence of which has been confirmed by X-ray diffraction (Tables 5 and 7).

IR-spectra of the complexes **II–IV** contain no ν(OH) absorption band due to the deprotonation of hydroxyl group, while the vibration frequency ν(NH) is lower by 58, 49 or 123 cm^{-1} in comparison with the spectra of uncoordinated ligands, which may be due to the coordination to the metal ion *via* thioureide group and/or formation of an intramolecular hydrogen bond. In according with the results of X-ray diffraction study of the complexes **I–IV**, the decreasing of ν(NH) frequencies can be explain by formation of the hydrogen bonds $N^{(6)}H\ldots N^{(5)}$, $N^{(3)}H\ldots N^{(2)}$ и $N^{(4)}H\ldots O^{(4)}$, $N^{(1)}H\ldots O^{(2)}$ in the complex **I**, $N^{(9)}H\ldots O^{(4)}$, $N^{(11)}H\ldots O^{(3)}$, $N^{(3)}H\ldots O^{(13)}$, $N^{(5)}H\ldots O^{(12)}$ in the complex **II**, $N^{(1)}H\ldots O^{(5)}$, $N^{(3)}H\ldots O^{(3)}$, $N^{(4)}H\ldots O^{(4)}$, $N^{(6)}H\ldots O^{(6)}$ in the complex **IV**. Besides, the IR spectra of the complexes contain a set of low-intensity absorption bands of stretching vibrations ν(=CH), $\nu(CH)_{Py}$, $\nu(CHz)_{allyl}$ and symmetrical vibrations ν(C–H) of acetic acid molecules. The absence of absorption bands of stretching vibrations ν(S–H) in the range 2550–2590 cm^{-1} indicates coordination of the ligands **A**–**C** in thionic tautomeric form.

It should be noted that coordination of acetic acid molecules to the metal ion complicates the interpretation of the IR spectra of the complexes **I**, **II** and **IV** in the frequency range 1630–1500 cm^{-1} since the vibrations of carbonyl group (C=O), partially overlapped



Scheme 2. Scheme of synthesis of the complex compounds.

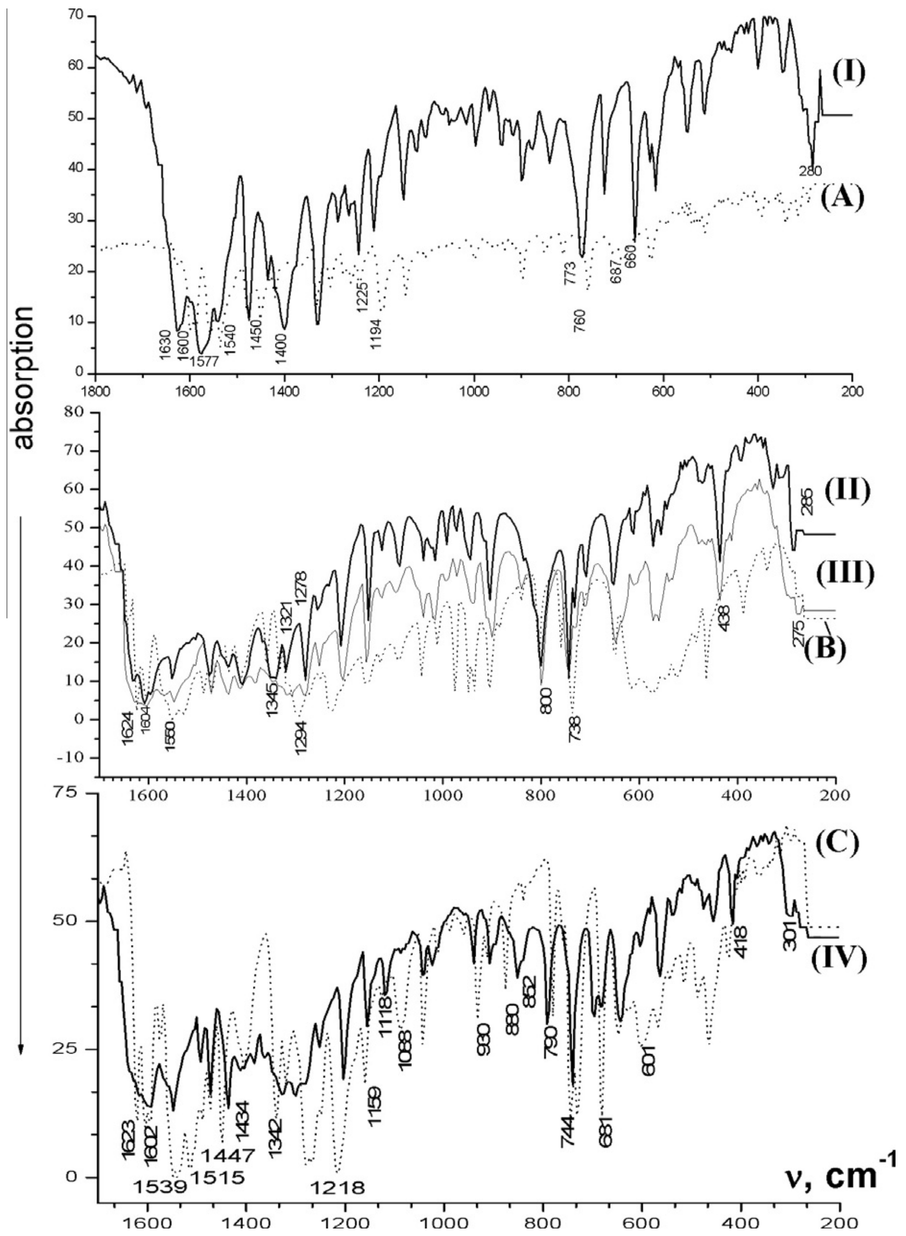


Fig. 1. IR spectra of the thiourea (**A**), thiosemicarbazones (**B**, **C**) and there complexes **I–IV**.

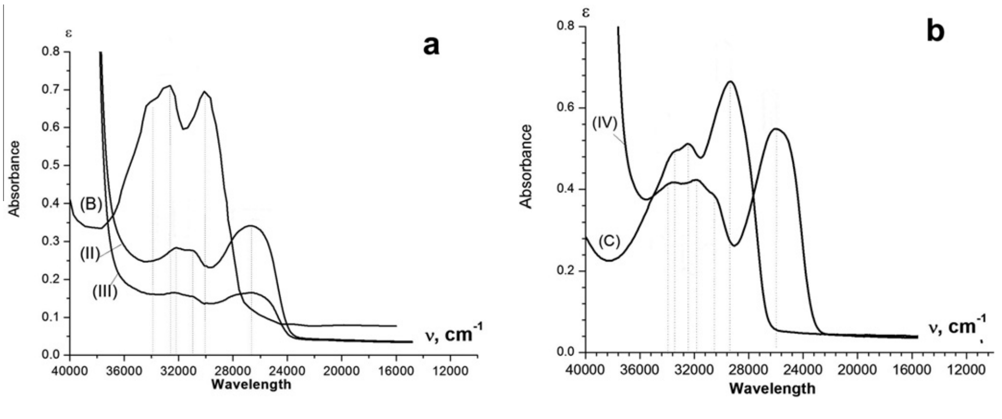


Fig. 2. UV–Vis spectrum of the thiosemicarbazones (**B**, **C**) and the complexes **II–IV**.

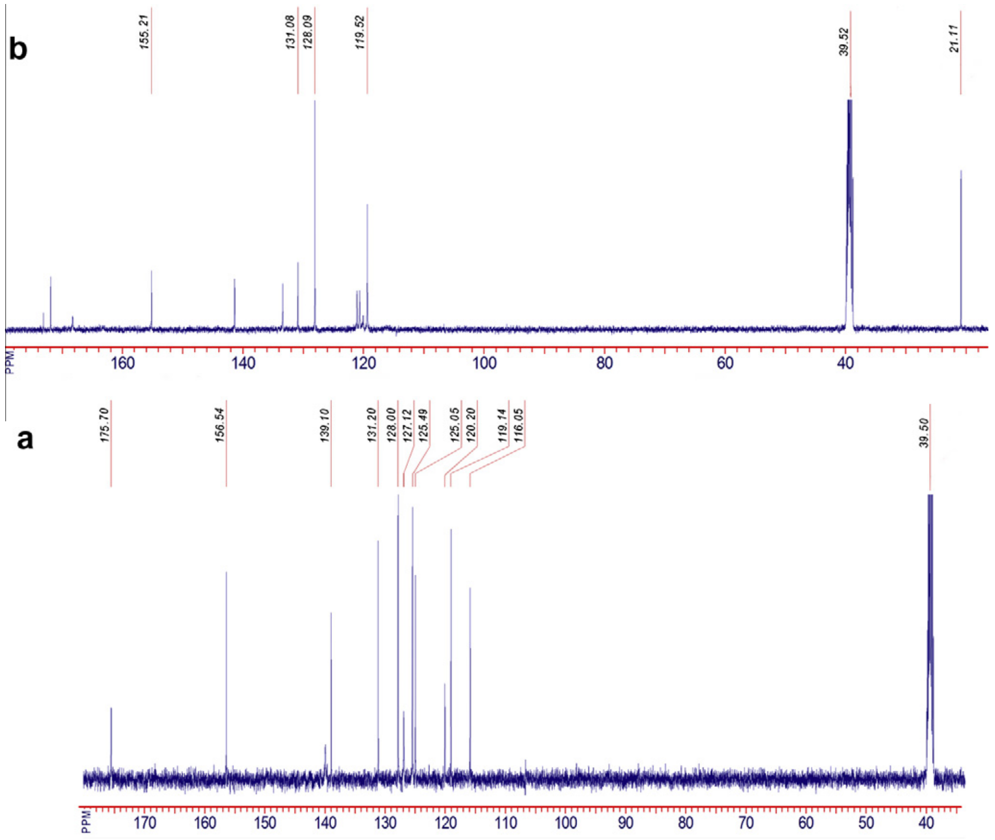


Fig. 3. NMR ^{13}C spectrum of the ligand C (a) and complex **IV** (b).

Table 2
Bond lengths and valence angles of the complex **I**.

Parameter	Value (Å, °)	Parameter	Value (Å, °)
$Zn^{(1)}$–$O^{(3)}$	1.9437(19)	$O^{(3)}$–$Zn^{(1)}$–$O^{(1)}$	96.63(8)
$Zn^{(1)}$–$O^{(1)}$	1.9516(18)	$O^{(3)}$–Zn(1)–$S^{(2)}$	117.81(7)
$Zn^{(1)}$–$S^{(2)}$	2.3451(8)	$O^{(1)}$–$Zn^{(1)}$–$S^{(2)}$	105.80(6)
$Zn^{(1)}$–$S^{(1)}$	2.3588(8)	$O^{(3)}$–$Zn^{(1)}$–$S^{(1)}$	104.55(8)
$S^{(1)}$–$C^{(1)}$	1.719(3)	$O^{(1)}$–$Zn^{(1)}$–$S^{(1)}$	117.91(6)
$S^{(2)}$–$C^{(10)}$	1.725(3)	$S^{(2)}$–$Zn^{(1)}$–$S^{(1)}$	113.51(3)
$N^{(1)}$–$C^{(1)}$	1.343(3)	$N^{(3)}$–$C^{(1)}$–$N^{(1)}$	119.6(2)
$N^{(3)}$–$C^{(1)}$	1.313(3)	$N^{(3)}$–$C^{(1)}$–$S^{(1)}$	121.7(2)
$N^{(4)}$–$C^{(10)}$	1.343(3)	$N^{(1)}$–$C^{(1)}$–$S^{(1)}$	118.67(19)
$N^{(6)}$–$C^{(10)}$	1.310(3)	$N^{(6)}$–$C^{(10)}$–$N^{(4)}$	120.2(2)
$N^{(6)}$–$C^{(10)}$–$S^{(2)}$	121.3(2)	$N^{(4)}$–$C^{(10)}$–$S^{(2)}$	118.5(2)

with vibrations of δ(NH–CS–NH) and ν(C=N) groups. By analyzing the positions of mentioned absorption bands in the spectra of complexes with uncoordinated ligands one can identify the absorption bands of stretching vibrations ν($C{=}O_{Ac}$) of the carbonyl group of coordinated acetic acid molecules at 1630–1632 cm^{-1}. The lower vibration frequency ν$(C{=}O)_{Ac}$ indicates the formation of the intramolecular hydrogen bond C=O…HN, which was confirmed later by X-ray diffraction (Fig. 4).

In the IR spectrum of the complex **I**, some frequencies corresponding to stretching vibrations of pyridine ring are lowered by 13–22 cm^{-1} due to the participation of pyridine nitrogen atom in the formation of six-membered pseudoheterocycles through the hydrogen bonds $N^{(3)}$–$H^{(3N)}$…$N^{(2)}$ and $N^{(6)}$–$H^{(6N)}$…$N^{(5)}$ (Fig. 4).

The identification of the ν(C=S) absorption bands involves certain difficulties because of its partially overlapping with absorption bands from another groups in the low-frequency region. The absorption bands of other molecule fragments, e.g. out-of-plane deformation vibrations δ(–CH=CH$_2$) of allyl fragment and δ(CH) of pyridine ring at 897–687 cm^{-1} appear in the same region as well. However, the absorption bands in the range 1143–1194 cm^{-1} also correspond to the stretching vibration ν(C=S) of the thioureide group (–N–CS–N–) [29,30,36]. The value of these frequencies in the spectra of the complexes increased by 17 cm^{-1} (Fig. 1), indicating participation of the sulfur atom in coordination to the central metal ion.

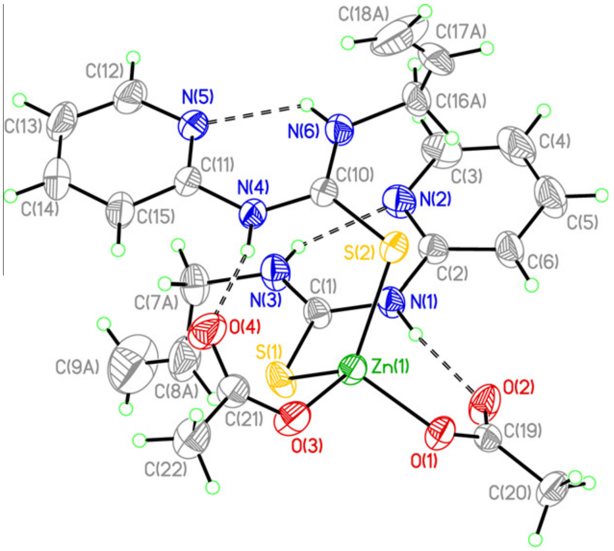


Fig. 4. General view of the complex **I** molecule. The thermal ellipsoids are shown with 30% probability. The dashed lines denote intramolecular hydrogen bonds.

The low-frequency region of the IR spectrum of the complex **I** contains intense absorption bands of the stretching vibrations

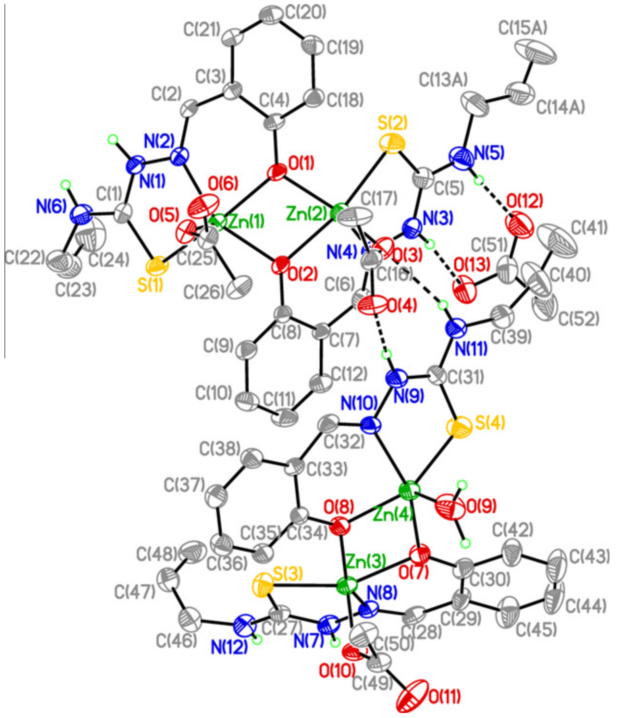


Fig. 5. Asymmetric unit of the complex **II**. The thermal ellipsoids for all nonhydrogen atoms are shown with 30% probability. The hydrogen atoms bonded to carbon atoms were omitted for clarity.

Table 3
Geometric parameters of the hydrogen bonds in the crystal structure of complex **I**.

D–H…A	d(D–H)	d(H…A)	d(D…A)	<(DHA)
$N^{(1)}–H^{(1N)}…O^{(2)}$	0.83(3)	1.93(3)	2.757(3)	171(3)
$N^{(3)}–H^{(3N)}…N^{(2)}$	0.77(3)	2.01(3)	2.666(3)	143(3)
$N^{(4)}–H^{(4N)}…O^{(4)}$	0.83(3)	1.94(3)	2.747(3)	165(3)
$N^{(6)}–H^{(6N)}…N^{(5)}$	0.80(3)	2.09(3)	2.685(3)	132(3)

ν(Zn–O$_{Ac}$) and ν(Zn–S) at 550 and 284 cm^{-1}, which confirms the coordination of ligand to metal.

The valuable changes are observed in the range 1350–1200 cm^{-1} (Fig. 1), there the vibrations bands ν(CS) and ν(C–O$_{Ph}$) are located. In the spectra of the complexes **II–IV**, the stretching vibration frequency of mentioned bonds is lowered by 12–23 cm^{-1}, which indicates their coordination to the metal ion. In contrast to **I**, besides stretching vibrations ν(Zn–S) at 285/301 cm^{-1}, the low-frequency region of the IR spectra of **II–IV** are characterized by appearance of stretching vibrations ν(Zn–N) at 438/418 cm^{-1}. The bond vibrations ν(Zn–O) in the IR spectra of **II–IV** cannot be identified because of overlapping with δ(CH)$_{allyl}$ in the case of compounds **II** and **III** or with out-of-plane deformation vibrations δ(CH)$_{Ar}$ of aromatic ring in the case of **IV**.

Thus, comparison of the characteristic absorption bands of the IR spectra of complexes and uncoordinated thiosemicarbazones (**B**, **C**) allows one to conclude that in the complexes **II–IV**, the ligand molecules are bonded to the central metal atom in a tridentate manner *via* oxygen atoms of the deprotonated OH group of benzene ring, azomethine nitrogen atom (C=N) and sulfur of thioureide group with the formation of five- and six-membered metallocycles.

4.1.2. UV–Vis spectra

The UV–Vis spectrum of thiourea (**A**) includes three absorption bands at 40 560, 37 400 and 34 050 cm^{-1} of the intraligand charge-transfer transitions $\pi \rightarrow \pi^*_{Py}$ and $n \rightarrow \pi^*$, (C=N$_{Py}$)/(C=S). When the complex is formed, a 685–365 cm^{-1} shift of these bands to the low-frequency region is observed, which confirm the coordination of the ligand A to the central metal ion.

The UV–Vis spectra of the thiosemicarbazones **B** and **C** are of the same type and consist of absorption bands at 34 200–33 450, 32 650–32 470 and 30 055–29 360 cm^{-1}, corresponding to the intraligand $n \rightarrow \pi^*$ transitions of the azomethine fragment (C=N) and (C=S) of thioureide group (Fig. 2). The first band has a shoulder-like form. When the complexes are formed, a valuable shift of these bands to the low-frequency region is observed, which indicates participation of the above functional groups in coordination to the central metal ion. It should be noted that the broad absorption bands at 28 000, 26 650 cm^{-1} (**II**, **III**) and 25 960–25 100 cm^{-1} (**IV**) correspond to charge transfers from ligand to metal [S → Zn], which is associated with the participation of the ligand (C=S) group in coordination to the central metal ion with the formation of a chelate metallocycle. In contrast to the complexes **II–IV**, there is no charge transfer band [S→Zn] in the spectrum of complex **I**, which is, most likely, due to the monodentate coordination of thiourea (A) in a non-chelate manner.

4.1.3. ^{1}H and ^{13}C NMR spectra

The comparative analysis of ^{1}H NMR spectra of the complex **I** and uncoordinated thiourea (**A**) showed the slight shift of all protons signals, mainly to the strong field direction by $\Delta\delta$ = −0.01 ppm (with the exception of =C^{9}H$_2$, $\Delta\delta$ = +0.02 and N$^{1'}$H, $\Delta\delta$ = +0.01), in the spectrum **I**. In the ^{13}C NMR spectrum of the complex **I**, the signals of carbon atoms shift slightly in comparison with spectrum of uncoordinated thiourea both to the upfield and downfield ($\Delta\delta$ = −0.02 (C^6), −0.13 (C^4), −0.41 (C^8), −0.29 ppm (C^5); $\Delta\delta$ = +0.06 (C^1), 0.25 (C^2), +0.05 (C^3), +0.03 (C^9), +0.04 ppm (C^7)). This indicates the presence of N–H…N$_{Py}$ hydrogen bonds both in thiourea and in the complex **I**. In this case, the coordination of ligand only via the sulfur atom of thioureide group does not affect the chemical shift of signals in ^{1}H and ^{13}C NMR spectra. The presence of coordinated acetate anions in the compound **I** is confirmed by appearance of intense singlet signal in the upfield at 1.83 ppm (^{1}H NMR) and signals of carbon atoms at 176.63 ppm (C=O) and 22.47 ppm (CH$_3$) (^{13}C NMR).

In the complex compounds **II** and **III**, all proton signals (with the exception of N$^{(2')}$H, $\Delta\delta$ = +0.34 ppm) shift to the upfield, which is typical for five- and six-membered chelate metallocycles. The protons signals from benzene rings in the positions 6, 4 and 5 ($\Delta\delta$ = −0.71, −0.34, −0.19 ppm), as well as NH of thioureide group (N$^{(3')}$H, $\Delta\delta$ = −1.49; N$^{(2')}$ H, $\Delta\delta$ = +0.34 ppm) are most sensitive to complex formation. In the ^{13}C NMR spectra of the complexes **II** and **III**, the strongest shift to the upfield corresponds to signals of carbon atoms (C^8, $\Delta\delta$ = −4.61; C^2, $\Delta\delta$ = −3.91 (−4.16); C^7, $\Delta\delta$ = −2.83), which are directly bonded to sulfur, oxygen and nitrogen, involved in the formation of the bonds Zn←S, Zn–O and Zn←N. The downfield shift observed for the signals of carbon atoms C^4 ($\Delta\delta$ = +2.18 (+2.09)) and C^6 ($\Delta\delta$ = +3.85 (+3.77)), located in the *ortho*- and *para*- positions referring to thiosemicarbazone substituent.

In the ^{1}H NMR spectrum of complex **IV**, the most sensitive for complex formation are protons signals of benzene ring at the positions 6, 4 and 5 ($\Delta\delta$ = −0.75, −0.32, −0.16 ppm) as well as NH of thioureide group (N$^{(3')}$H, $\Delta\delta$ = −1.14; N$^{(2')}$H, $\Delta\delta$ = +0.19 ppm). The signals of benzene ring protons in the positions 10 and 14 ($\Delta\delta$ = +0.218 ppm) are shifted to the downfield significantly. In contrast, another pair of protons at the positions 11 and 13 are shifted to the upfield ($\Delta\delta$ = −0.15 ppm). Signals, corresponding to protons at carbon atoms 3, 7 and 12 are shifted slightly by $\Delta\delta$ = +0.05, +0.09 and −0.03 ppm, respectively.

In the ^{13}C NMR spectrum of the complex **IV** (Fig. 3), most signals of carbon atoms are shifted to the downfield (with the exception of C^8, $\Delta\delta$ = −3.71; C^{10} and C^{14}, $\Delta\delta$ = −5.97). In this case, a considerable shift to the downfield is observed for the signals of the atoms C^{2} ($\Delta\delta$ = +11.86) and C^{7} ($\Delta\delta$ = +15.06), which is typical for the formation of a covalent (Zn–O) and a donor-acceptor (Zn←N) bond [37].

4.2. X-ray diffraction study

4.2.1. Structure of complex I

The complex **I** crystallize in the monoclinic crystal system (space group $P2_1/c$) with one molecule per asymmetric unit. The central Zn$^{(1)}$ atom forms a strongly distorted tetrahedral $\mathrm{ZnS_2O_2}$ environment with a valence angle range 96.63(8)–117.91(6)°. The Zn–S and Zn–O bond lengths correlate well with the previously published for the complexes with similar coordination of ligands [38–40]. Both molecules of organic ligand coordinate in monodentant manner *via* the sulfur atom of thioureide fragment. The lengths of the C–S and C–N bonds do not allow determining the tautomeric form of the ligand unambiguously (Table 2). However, the sum of the adjacent valence angles around the atoms C$^{(1)}$ (359.97(20)°) and C$^{(10)}$ (360.0(2)°) indicates their sp^{2} hybridization, which together with the presence of objectively identified hydrogen atoms on the nitrogen atoms of thiourea fragment makes it possible to formally determine the form of coordinated ligands to be thionic one. The pyridine and thiourea fragments are coplanar, which is accounted for the presence of strong intramolecular hydrogen bonds N$^{(6)}$–H$^{(6N)}$…N$^{(5)}$ and N$^{(3)}$–H$^{(3N)}$…N$^{(2)}$, producing six-membered pseudoheterocycles (Fig. 4, Table 2). The mean deviation from planes S$^{(1)}$/C$^{(1)}$/N$^{(3)}$/N$^{(1)}$/C$^{(2)}$/N$^{(2)}$/C$^{(3)}$/C$^{(4)}$/C$^{(5)}$/C$^{(6)}$ and S$^{(2)}$/C$^{(10)}$/N$^{(6)}$/N$^{(4)}$/C$^{(11)}$/N$^{(5)}$/C$^{(12)}$/C$^{(13)}$/C$^{(14)}$/C$^{(15)}$ is 0.0364 and 0.0720 Å, respectively. The solid angle between the above planes is 5.00(10)°, which indicates coplanarity of the mentioned fragments.

Two acetic acid molecules are monodentate-coordinated to the central zinc ion. In this case, the uncoordinated oxygen atom of each of the carboxyl groups participates in the formation of the strong intramolecular hydrogen bonds N$^{(1)}$–H$^{(1N)}$…O$^{(2)}$ and N$^{(4)}$–H$^{(4N)}$…O$^{(4)}$ (Fig. 4, Table 3). The molecules of the complex **I** interact to each other in the crystal structure mainly by weak Van der Waals interactions.

As had been shown earlier [36], in contrast to Zn(II) ion, the ligand **A** coordinates to Pd(II) under similar conditions in a bidentate manner with the formation of a six-membered metalla rings. It is probable that utilizing another synthesis conditions (heating time, initial zinc salts) can lead to formation of the complex with bidentate coordination of **A** as well.

4.2.2. Structure of complex *II*

The asymmetric unit of the compound **II** contains two molecules of binuclear complex compounds with the ratio metal:ligand = 1:1, in which the base of the distorted square-pyramidal coordination environment of zinc ion is formed in all cases by the thioureide sulfur atom, imine nitrogen atom and two μ^{2}-bridging phenyl oxygen atoms (Fig. 5). The vertices of the coordination polyhedra of the zinc ions Zn$^{(1)}$, Zn$^{(2)}$ and Zn$^{(3)}$ are occupied by monodentate-coordinated acetic acid molecules. In the case of Zn$^{(4)}$ atom, the vertex of square pyramid is completed by the coordination of water molecule. The lengths of the Zn–S, Zn–N and Zn–O bonds in the molecule of the complex correspond to published data for such compounds (Table 4) [25,41].

The S–Zn–N valence angles deviate from the ideal values and are in range 82.19(13)–83.34(12)°, which is caused by the steric influence of five-membered metallocycles (Table 4). The values of μO–Zn–μO angles are in turn 76.62(12)–78.09(13)°, which is due to the mutual repulsion of zinc ions. The Zn$^{(1)}$–Zn$^{(2)}$ and Zn$^{(3)}$–Zn$^{(4)}$ distances in molecules are 3.1813(9) and 3.1569(9) Å, which are much smaller than the sum of Van der Waals radii (~4.5 Å). The values of the valence angles between the atom from the vertex and the atoms from the base of the square-pyramidal environment of zinc atoms are 98.03(18)–115.41(13)°, indicating a considerable tetrahedral distortion of the coordination polyhedron.

Table 4
Geometric parameters of the complex **II**.

Parameter	Value (Å, °)	Parameter	Value (Å, °)
Zn$^{(1)}$–Zn$^{(2)}$	3.1813(9)	O$^{(5)}$–Zn$^{(1)}$–O$^{(2)}$	115.41(13)
Zn$^{(3)}$–Zn$^{(4)}$	3.1566(9)	O$^{(5)}$–Zn$^{(1)}$–O$^{(1)}$	100.05(14)
Zn$^{(1)}$–O$^{(5)}$	1.991(3)	O$^{(2)}$–Zn$^{(1)}$–O$^{(1)}$	76.88(12)
Zn$^{(1)}$–O$^{(2)}$	2.000(3)	O$^{(5)}$–Zn$^{(1)}$–N$^{(2)}$	102.80(13)
Zn$^{(1)}$–O$^{(1)}$	2.069(3)	O$^{(2)}$–Zn$^{(1)}$–N$^{(2)}$	139.65(13)
Zn$^{(1)}$–N$^{(2)}$	2.102(4)	O$^{(1)}$–Zn$^{(1)}$–N$^{(2)}$	84.45(14)
Zn$^{(1)}$–S$^{(1)}$	2.4012(16)	O$^{(5)}$–Zn$^{(1)}$–S$^{(1)}$	104.11(11)
Zn$^{(2)}$–O$^{(3)}$	1.990(3)	O$^{(2)}$–Zn$^{(1)}$–S$^{(1)}$	99.44(10)
Zn$^{(2)}$–O$^{(1)}$	2.030(3)	O$^{(1)}$–Zn$^{(1)}$–S$^{(1)}$	154.57(10)
Zn$^{(2)}$–O$^{(2)}$	2.051(3)	N$^{(2)}$–Zn$^{(1)}$–S$^{(1)}$	82.59(12)
Zn$^{(2)}$–N$^{(4)}$	2.097(4)	O$^{(3)}$–Zn$^{(2)}$–O$^{(1)}$	117.25(14)
Zn$^{(2)}$–S$^{(2)}$	2.3669(15)	O$^{(3)}$–Zn$^{(2)}$–O$^{(2)}$	98.37(14)
Zn$^{(3)}$–O$^{(10)}$	1.995(3)	O$^{(1)}$–Zn$^{(2)}$–O$^{(2)}$	76.62(12)
Zn$^{(3)}$–O$^{(8)}$	2.035(3)	O$^{(3)}$–Zn$^{(2)}$–N$^{(4)}$	95.81(14)
Zn$^{(3)}$–O$^{(7)}$	2.045(3)	O$^{(1)}$–Zn$^{(2)}$–N$^{(4)}$	143.70(15)
Zn$^{(3)}$–N$^{(8)}$	2.124(4)	O$^{(2)}$–Zn$^{(2)}$–N$^{(4)}$	84.52(14)
Zn$^{(3)}$–S$^{(3)}$	2.3741(16)	O$^{(3)}$–Zn$^{(2)}$–S$^{(2)}$	105.91(12)
Zn$^{(4)}$–O$^{(9)}$	2.014(5)	O$^{(1)}$–Zn$^{(2)}$–S$^{(2)}$	100.25(10)
Zn$^{(4)}$–O$^{(8)}$	2.024(3)	O$^{(2)}$–Zn$^{(2)}$–S$^{(2)}$	153.78(10)
Zn$^{(4)}$–O$^{(7)}$	2.025(3)	N$^{(4)}$–Zn$^{(2)}$–S$^{(2)}$	83.34(12)
Zn$^{(4)}$–N$^{(10)}$	2.079(4)	O$^{(10)}$–Zn$^{(3)}$–O$^{(8)}$	108.17(13)
Zn$^{(4)}$–S$^{(4)}$	2.3780(16)	O$^{(10)}$–Zn$^{(3)}$–O$^{(7)}$	103.83(15)
S$^{(1)}$–C$^{(1)}$	1.695(5)	O$^{(8)}$–Zn$^{(3)}$–O$^{(7)}$	77.40(13)
S$^{(2)}$–C$^{(5)}$	1.692(5)	O$^{(10)}$–Zn$^{(3)}$–N$^{(8)}$	101.68(13)
S$^{(3)}$–C$^{(27)}$	1.707(5)	O$^{(8)}$–Zn$^{(3)}$–N$^{(8)}$	147.33(13)
S$^{(4)}$–C$^{(31)}$	1.696(5)	O$^{(7)}$–Zn$^{(3)}$–N$^{(8)}$	82.92(15)
O$^{(10)}$–Zn$^{(3)}$–S$^{(3)}$	108.08(12)	O$^{(8)}$–Zn$^{(3)}$–S$^{(3)}$	100.48(10)
O$^{(7)}$–Zn$^{(3)}$–S$^{(3)}$	146.88(11)	N$^{(8)}$–Zn$^{(3)}$–S$^{(3)}$	82.19(13)
O$^{(9)}$–Zn$^{(4)}$–O$^{(8)}$	107.19(17)	O$^{(9)}$–Zn$^{(4)}$–O$^{(7)}$	103.39(17)
O$^{(8)}$–Zn$^{(4)}$–O$^{(7)}$	78.09(13)	O$^{(9)}$–Zn$^{(4)}$–N$^{(10)}$	98.03(18)
O$^{(8)}$–Zn$^{(4)}$–N$^{(10)}$	84.88(14)	O$^{(7)}$–Zn$^{(4)}$–N$^{(10)}$	155.75(16)
O$^{(9)}$–Zn$^{(4)}$–S$^{(4)}$	105.53(14)	O$^{(8)}$–Zn$^{(4)}$–S$^{(4)}$	146.26(11)
O$^{(7)}$–Zn$^{(4)}$–S$^{(4)}$	102.11(10)	N$^{(10)}$–Zn$^{(4)}$–S$^{(4)}$	82.67(12)

Table 5
Geometric parameters of the hydrogen bonds for the complex **II**.

D–H…A	d(D–H)	d(H…A)	d(D…A)	<(DHA)
N$^{(1)}$–H$^{(1N)}$…O$^{(10)}$#1	0.89(3)	1.99(3)	2.843(5)	160(4)
N$^{(3)}$–H$^{(3N)}$…O$^{(13)}$	0.88(3)	1.88(3)	2.748(5)	169(4)
N$^{(5)}$–H$^{(5N)}$…O$^{(12)}$	0.87(3)	1.90(3)	2.762(6)	177(6)
N$^{(6)}$–H$^{(6N)}$…O$^{(11)}$#1	0.90(3)	1.90(3)	2.800(6)	173(5)
N$^{(7)}$–H$^{(7N)}$…O$^{(5)}$#2	0.85(3)	1.97(3)	2.790(5)	162(4)
N$^{(9)}$–H$^{(9N)}$…O$^{(4)}$	0.86(3)	1.81(3)	2.664(5)	172(5)
N$^{(11)}$–H$^{(11N)}$…O$^{(3)}$	0.83(3)	2.23(4)	3.013(5)	157(5)
N$^{(12)}$–H$^{(12N)}$…O$^{(6)}$#2	0.85(3)	2.00(3)	2.843(5)	170(5)
O$^{(9)}$–H$^{(92O)}$…O$^{(13)}$#3	0.79(4)	1.82(4)	2.571(5)	160(7)

Symmetry elements used for the generation of symmetrically dependent atoms: #1 − x + 1, y + ½, −z + ½; #2 − x + 1, y − ½, −z + ½; #3 x − 1, y, z.

In both molecules of the complex from the asymmetric unit, the molecules of organic ligand are coordinated in the tridentate manner in thionic form with conjugation of five- and six-membered chelate metallocycles. The thionic form of coordinated ligand molecules is confirmed by the values of C–S bond length (1.692(5)–1.707(5) Å) on the one hand and by the presence of objectively identified hydrogen atoms on the nitrogen atoms of thiourea group on the other hand. The five-membered metallocycles Zn$^{(1)}$/S$^{(1)}$/C$^{(1)}$/N$^{(1)}$/N$^{(2)}$, Zn$^{(2)}$/S$^{(2)}$/C$^{(5)}$/N$^{(3)}$/N$^{(4)}$, Zn$^{(3)}$/S$^{(3)}$/C$^{(27)}$/N$^{(7)}$/N$^{(8)}$ and Zn$^{(4)}$/S$^{(4)}$/C$^{(31)}$/N$^{(9)}$/N$^{(10)}$ are planar with a mean deviation from planes of 0.0488, 0.0625, 0.0747 and 0.0975 Å, respectively. The six-membered metallocycles Zn$^{(1)}$/O$^{(1)}$/C$^{(4)}$/C$^{(3)}$/C$^{(2)}$/N$^{(2)}$, Zn$^{(2)}$/O$^{(2)}$/C$^{(8)}$/C$^{(7)}$/C$^{(6)}$/N$^{(4)}$, Zn$^{(3)}$/O$^{(7)}$/C$^{(30)}$/C$^{(29)}$/C$^{(28)}$/N$^{(8)}$ and Zn$^{(4)}$/O$^{(8)}$/C$^{(34)}$/C$^{(33)}$/C$^{(32)}$/N$^{(10)}$ have an envelope conformation with dihedral angles of

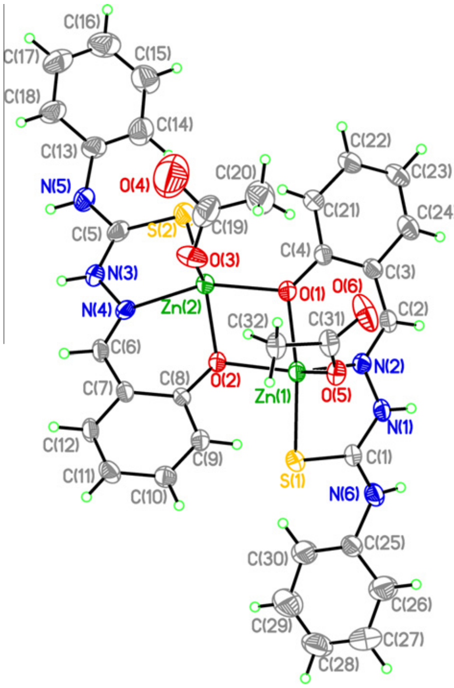


Fig. 6. General view of the complex **IV** molecule. The thermal ellipsoids are shown with 30% probability.

Table 6
Geometric parameters of the molecule of **IV**.

Parameter	Value (Å, °)	Parameter	Value (Å, °)
Zn$^{(1)}$–Zn$^{(2)}$	3.174(2)	O$^{(2)}$–Zn$^{(1)}$–N$^{(2)}$	147.88(15)
Zn$^{(1)}$–O$^{(5)}$	2.006(4)	O$^{(1)}$–Zn$^{(1)}$–N$^{(2)}$	84.09(15)
Zn$^{(1)}$–O$^{(2)}$	2.034(3)	O$^{(5)}$–Zn$^{(1)}$–S$^{(1)}$	108.16(12)
Zn$^{(1)}$–O$^{(1)}$	2.053(4)	O$^{(2)}$–Zn$^{(1)}$–S$^{(1)}$	98.87(11)
Zn$^{(1)}$–N$^{(2)}$	2.115(4)	O$^{(1)}$–Zn$^{(1)}$–S$^{(1)}$	148.79(12)
Zn$^{(1)}$–S$^{(1)}$	2.398(2)	N$^{(2)}$–Zn$^{(1)}$–S$^{(1)}$	82.70(12)
Zn$^{(2)}$–O$^{(3)}$	2.000(5)	O$^{(3)}$–Zn$^{(2)}$–O$^{(2)}$	100.05(17)
Zn$^{(2)}$–O$^{(2)}$	2.008(4)	O$^{(3)}$–Zn$^{(2)}$–O$^{(1)}$	108.10(17)
Zn$^{(2)}$–O$^{(1)}$	2.085(3)	O$^{(2)}$–Zn$^{(2)}$–O$^{(1)}$	78.07(13)
Zn$^{(2)}$–N$^{(4)}$	2.164(4)	O$^{(3)}$–Zn$^{(2)}$–N$^{(4)}$	99.97(17)
Zn$^{(2)}$–S$^{(2)}$	2.333(2)	O$^{(2)}$–Zn$^{(2)}$–N$^{(4)}$	83.95(14)
S$^{(1)}$–C$^{(1)}$	1.716(5)	O$^{(1)}$–Zn$^{(2)}$–N$^{(4)}$	148.79(15)
S$^{(2)}$–C$^{(5)}$	1.735(6)	O$^{(3)}$–Zn$^{(2)}$–S$^{(2)}$	107.32(15)
O$^{(5)}$–Zn$^{(1)}$–O$^{(2)}$	109.78(14)	O$^{(2)}$–Zn$^{(2)}$–S$^{(2)}$	151.12(12)
O$^{(5)}$–Zn$^{(1)}$–O$^{(1)}$	101.90(15)	O$^{(1)}$–Zn$^{(2)}$–S$^{(2)}$	101.46(11)
O$^{(2)}$–Zn$^{(1)}$–O$^{(1)}$	78.23(13)	N$^{(4)}$–Zn$^{(2)}$–S$^{(2)}$	82.44(12)
O$^{(5)}$–Zn$^{(1)}$–N$^{(2)}$	99.93(15)		

20.1(2)°, 22.2(2)°, 20.8(2)° and 20.2(2)°, respectively. Besides, the molecules of complexes contain several almost planar fragments: S$^{(1)}$/C$^{(1)}$/N$^{(1)}$/N$^{(2)}$/C$^{(2)}$/C$^{(3)}$/C$^{(4)}$/O$^{(1)}$/C$^{(18)}$/C$^{(19)}$/C$^{(20)}$/C$^{(21)}$ (plane A, mean deviation from plane: 0.0552 Å), S$^{(2)}$/C$^{(5)}$/N$^{(3)}$/N$^{(4)}$/C$^{(6)}$/C$^{(7)}$/C$^{(8)}$/O$^{(2)}$/C$^{(9)}$/C$^{(10)}$/C$^{(11)}$/C$^{(12)}$ (plane B, mean deviation from plane: 0.0590 Å), S$^{(3)}$/C$^{(27)}$/N$^{(7)}$/N$^{(8)}$/C$^{(28)}$/C$^{(29)}$/C$^{(30)}$/O$^{(7)}$/C$^{(42)}$/C$^{(43)}$/C$^{(44)}$/C$^{(45)}$ (plane C, mean deviation from plane: 0.0471 Å), S$^{(4)}$/C$^{(31)}$/N$^{(9)}$/N$^{(10)}$/C$^{(32)}$/C$^{(33)}$)/C$^{(34)}$/O$^{(8)}$/C$^{(35)}$/C$^{(36)}$/C$^{(37)}$/C$^{(38)}$ (plane D, mean deviation from plane: 0.0330 Å). The dihedral angles between the planes A/B and C/D are 64.95(10)° and 46.12(12)°, respectively, which may be due to the different mode of intermolecular interactions of fragments.

The asymmetric unit of the compound **II** contains an acetate anion, which compensates the charge of one of the molecules and is strongly bonded to one of the molecules of complexes by N–H…O hydrogen bonds, forming a six-membered ring (Fig. 5, Table 5). In the crystal structure, the molecules of the complex are bonded to a network by strong; mainly N–H…O hydrogen bonds (Table 5).

4.2.3. Structure of complex **IV**

In contrast to the compound **II**, crystal structure of the independent **IV** contains one molecule of binuclear zinc complex. The zinc atoms Zn$^{(1)}$ and Zn$^{(2)}$, as in the case of the compound **II**, form a distorted square-pyramidal coordination environment of ZnO_3NS, whose base contains a thioureide sulfur atom, and imine nitrogen atom and two μ^2-bridging phenyl oxygen atoms. The monodentate-coordinated acetic acid molecules are in both cases (Zn$^{(1)}$ and Zn$^{(2)}$) at the vertices of the pyramid (Fig. 6). It has to be mentioned that similar binuclear Zn complex with 2,4-dihydroxybenzaldehyde 4-phenyl thiosemicarbazone was synthesized by Tan et al. [25] using zinc chloride as a starting metal salt. The main structural difference between complex **IV** and mentioned compound is coordination environment of Zn in vertical direction. In the case of complex, reported by Tan et al. vertical positions in the square-pyramidal coordination environment of Zn occupied by chlorine anions, which cause a slight influence on molecular structure. The dihedral angles between pyramidal bases increasing from 43.3° in the case of **IV** to 49.8° for earlier reported compound. This effect can be explained by repulsion effect between two chlorine anions.

The atoms Zn$^{(1)}$ and Zn$^{(2)}$ are at distances of 0.5668(6) and 0.5288(6) Å from the planes of the bases of their coordination polyhedra O$^{(1)}$/O$^{(2)}$/N$^{(2)}$/S$^{(1)}$ and O$^{(1)}$/O$^{(2)}$/N$^{(4)}$/S$^{(2)}$. The solid angle between the above planes is 43.22(14)°. The distance Zn$^{(1)}$–Zn$^{(2)}$ = 3.174(2) Å as well as other linear and angular characteristics of the coordination environment of zinc ions are in agreement with the analogous parameters of the compound **II** (Table 6). The molecules of the ligands are coordinated, as in the case of the compound **II**, in a tridentate cyclic manner with the formation of conjugate five- and six-membered metallocycles. Formally, the molecules of the ligands are coordinated in a thionic tautomeric form, as evidenced by the presence of objectively identified hydrogen atoms on the nitrogen atoms bonded to the (CS) group. At the same time, the C$^{(1)}$–S$^{(1)}$ and C$^{(5)}$–S$^{(2)}$ bonds are somewhat slightly longer than those in the complex **II** (Tables 4 and 6), indicating a delocalization of electron density between the C–S and C–N bonds. The five-membered metallocycles Zn$^{(1)}$/N$^{(2)}$/N$^{(1)}$/C$^{(1)}$/S$^{(1)}$ and Zn$^{(2)}$/N$^{(4)}$/N$^{(3)}$/C$^{(5)}$/S$^{(2)}$ are planar with a mean deviation from planes of 0.0654 and 0.0494 Å, respectively.

The six-membered metallocycles Zn$^{(1)}$/O$^{(1)}$/C$^{(4)}$/C$^{(3)}$/C$^{(2)}$/N$^{(2)}$ and Zn$^{(2)}$/O$^{(2)}$/C$^{(8)}$/C$^{(7)}$/C$^{(6)}$/N$^{(4)}$ have an envelope conformation with dihedral angles of 17.9(2)° and 26.8(2)°, respectively. The dihedral angle between the planes containing the atoms S$^{(1)}$/C$^{(1)}$/N$^{(1)}$/N$^{(2)}$/C$^{(2)}$/C$^{(3)}$/C$^{(4)}$/O$^{(1)}$/C$^{(21)}$/C$^{(22)}$/C$^{(23)}$/C$^{(24)}$ and S$^{(2)}$/C$^{(5)}$/N$^{(3)}$/N$^{(4)}$/C$^{(6)}$/C$^{(7)}$/C$^{(8)}$/O$^{(2)}$/C$^{(9)}$/C$^{(10)}$/C$^{(11)}$/C$^{(12)}$ is 48.06(12)°, which corresponds to the conformation of one of the molecules of the compound **II**. The molecules of the complex in the crystal structure of **IV** form a branched network of N–H…O hydrogen bonds, which stabilize the structure (Fig. 7, Table 7).

The formation of zinc complexes such as **II** and **IV** is fairly typical for the ligands containing a “rigid” donor center (in these cases oxygen atoms of phenoxyl group and acetic acid hydroxyl). As is known, the appearance of “rigid” oxygen donor atoms in the coordination sphere of the central ion makes it coordinatively unsaturated, which may result in the formation of heteroligand and polynuclear complexes, in which the central ion has the coordination number 5 or 6, as occurred in this particular case.

5. Conclusions

Thus, we have reported the synthesis and structure investigation of novel Zn(II) complexes with different coordination mode of thiourea and thiosemicarbazide derivatives. It has been shown that in above synthesis conditions two molecules of ligand (**A**)

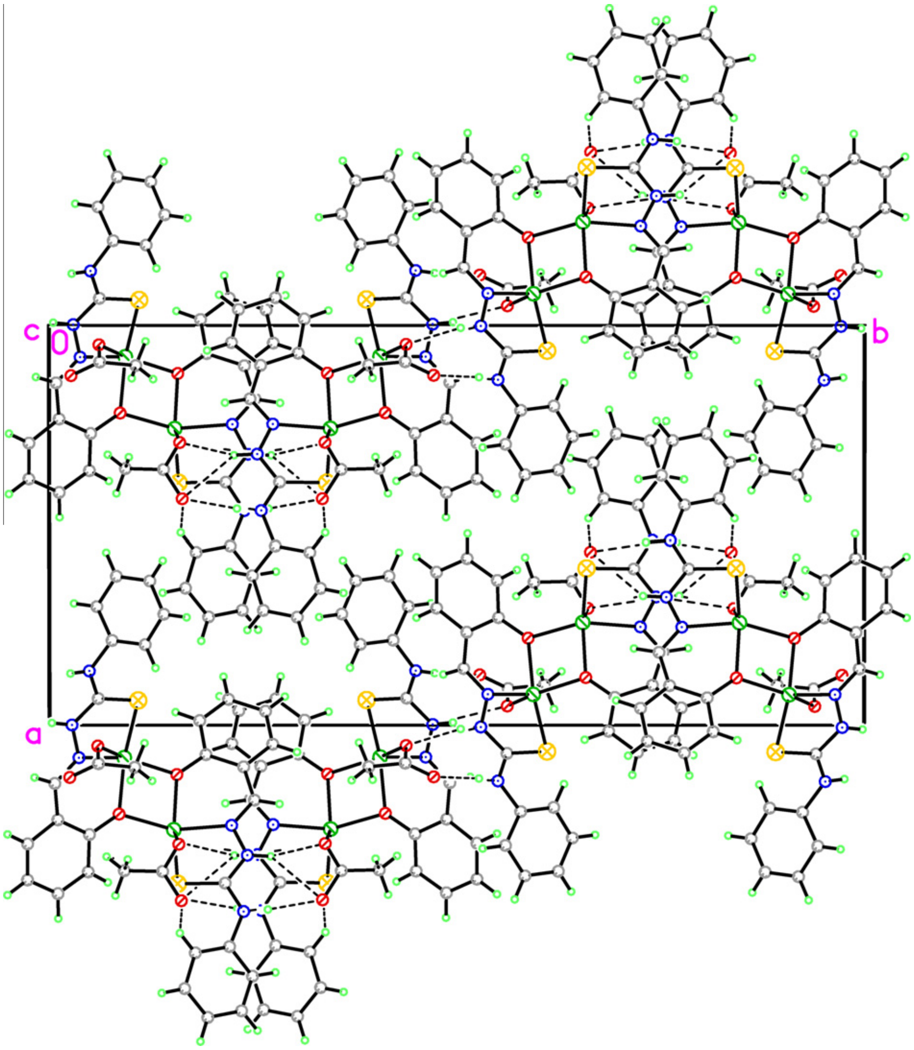


Fig. 7. Packings of the compound **IV**. Projection along the *z* axis. The hydrogen bonds are denoted by dashed lines.

Table 7
Geometric parameters of the hydrogen bonds for the complex **IV**.

D–H…A	*d*(D–H)	*d*(H…A)	*d*(D…A)	<(DHA)
$N^{(1)}$–$H^{(1N)}$…$O^{(5)}$#1	0.79(5)	2.10(5)	2.873(6)	165(6)
$N^{(3)}$–$H^{(3N)}$…$O^{(3)}$#2	0.84(5)	2.17(5)	2.950(7)	153(5)
$N^{(3)}$–$H^{(3N)}$…$O^{(4)}$#2	0.84(5)	2.47(6)	3.174(10)	142(5)
$N^{(5)}$–$H^{(5N)}$…$O^{(4)}$#2	0.88(6)	2.08(6)	2.956(9)	169(6)
$N^{(6)}$–$H^{(6N)}$…$O^{(6)}$#1	0.82(3)	1.92(3)	2.743(6)	175(6)

Symmetry elements used for the generation of symmetrically dependent atoms: #1 −*x*, −*y*, −*z* + 1, #2 *x*, −*y* + ½, *z* − ½.

coordinates to the zinc ion in monodentate manner *via* the sulfur atom of thioureide group. The zinc ion forms distorted tetrahedral coordination geometry, consist of two sulfur atoms of thioureide group and two oxygen atoms of acetate ions (Fig. 4). It has been shown that the heating of reaction mixture and oxygen affinity of zinc ions did not allow the potentially bidentate ligand **A** to be coordinated additionally by the nitrogen atom of pyridine ring.

In contrast to thiourea **A**, the thiosemicarbazones **B** and **C** behave as monobasic acids with coordination to the metal ion in a tridentate manner *via* the oxygen atom of the deprotonated phenoxyl group, thioureide sulfur and azomethine nitrogen. We have synthesized two types of complexes (**II**, **IV**). At the component ratio M:L = 1:1, binuclear zinc complexes (**II** and **IV**) have been obtained, in which two metal ions are bonded by the bridging oxygen of phenoxyl group (Figs. 5 and 6).

X-ray diffraction study of **II** and **IV** showed that the central zinc atom forms a square pyramid coordination geometry, whose vertices are formed by three oxygen atoms, azomethine group nitrogen and thioureide sulfur. The two oxygen atoms belonging to the deprotonated phenoxyl group, as well as nitrogen and sulfur make up the base of the pyramid, and acetic acid oxygen is at the vertex of the formed pyramid.

At the component ratio M:L = 1:1, we have obtained a mononuclear zinc complex **III**, in which two ligand molecules form a distorted octahedron, whose base consists of thioureide sulfur atoms and deprotonated phenoxyl group oxygen, and at the vertices are azomethine group nitrogen atoms (Scheme 2).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.10.027.

References

[1] E. Kimura, T. Koike, Adv. Inorg. Chem. 44 (1997) 229.
[2] E. Kimura, Pure Appl. Chem. 65 (1993) 355.

[3] C.A. Kontogiorgis, P. Papaioannou, D.J. Hadjipavlou-Litina, Curr. Med. Chem. 12 (2005) 339.
[4] A. Scozzafava, C.J. Supuran, J. Med. Chem. 43 (2000) 3677.
[5] M.T. Rubino, M. Agamennone, C. Campestre, G. Fracchiolla, et al., Chem. Med. Chem. 4 (2009) 352.
[6] Y.-H. Chiu, G.J. Gabriel, J.W. Canary, Inorg. Chem. 44 (2005) 40.
[7] T.A. Miller, D.J. Witter, S.J. Belvedere, J. Med. Chem. 46 (2003) 5097.
[8] C.C. Häse, R.A. Finkelstein, Microbiol. Mol. Biol. Rev. 57 (1993) 823.
[9] A.K. Patick, K.E. Potts, Clin. Microbiol. Rev. 11 (1998) 614.
[10] S.V. Ghuge, M.C. Zarkar, S.R. Deshmukh, S.K. Choubey, J. Adv. Bioinf. Appl. Res. 1 (2010) 17.
[11] K. Takahashi, M. Ikura, H. Habashita, M. Nishizaki, et al., Bioorg. Med. Chem. 13 (2005) 4527.
[12] N. Borkakoti, Biochem. Soc. Trans. 32 (2004) 17.
[13] J.D. Durrant, C.A.F. de Oliveira, J.A. Mc Cammon, J. Mol. Recognit. 23 (2010) 173.
[14] T. Suzuki, A. Matsuura, A. Kouketsu, H. Nakagawa, N. Miyata, Bioorg. Med. Chem. Lett. 15 (2005) 331.
[15] J. Zhang, X. Li, H. Zhu, Q. Wang, et al., Drug Discoveries Ther. 4 (2010) 5.
[16] S. Sarma, J.R. Kumar, K.J. Reddy, T. Thrivenib, A.V. Reddy, J. Braz. Chem. Soc. 17 (2006) 463.
[17] W. Hernández, J. Paz, A. Vaisberg, E. Spodine, R. Richter, L. Beyer Bioinorganic Chemistry and Applications, 2008, ID 690952. doi:10.1155/2008/690952; <http://www.hindawi.com/journals/bca/2008/690952.abs.html>.
[18] S. Bjelogrlić, T. Todorović, A. Bacchi, M. Zec, et al., J. Inorg. Biochem. 104 (2010) 673.
[19] K. Alomar, A. Landreau, M. Kempf, M.A. Khan, et al., J. Inorg. Biochem. 104 (2010) 397.
[20] T.P. Stanojkovic, D. Kovala-Demertzi, A. Primikyri, I. Garcia-Santos, et al., J. Inorg. Biochem. 104 (2010) 467.
[21] F.R. Pavan, P.I.S. Maia, S.R.A. Leite, V.M. Deflon, et al., Eur. J. Med. Chem. 45 (2010) 1898.
[22] L.P. Battaglia, A.B. Corradi, J. Chem. Soc., Dalton Trans. N1 (1981) 23.
[23] E.B. Seena, M.R.P. Kurup, Spectrochim. Acta, Part A. 69 (2008) 726.
[24] Z.-P. Deng, S. Gao, S.W. Ng, Acta Crystallogr., Sect. E 63 (2007) m1650.
[25] K.W. Tan, C.H. Ng, M.J. Maah, S.W. Ng, Acta Crystallogr., Sect. E 65 (2009) m549.
[26] M.A. Ali, A.H. Mirza, W.B. Ejau, P.V. Bernhardt, Polyhedron 25 (2006) 3337.
[27] A. Sreekanth, S. Sivakumar, M.R.P. Kurup, J. Mol. Struct. 655 (2003) 47.
[28] N. Bharti, S. Sharma, F.N. Azam, A. Azam, Bioorg. Med. Chem. 11 (2003) 2923.
[29] P. Novak, K. Pičuljan, T. Hrenar, T. Biljan, Z. Meic, J. Mol. Struct. 919 (2009) 66.
[30] A. Garoufis, S.K. Hadjikakou, N. Hadjiliadis, Coord. Chem. Rev. 253 (2009) 1384.
[31] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[32] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
[33] Yu. L. Zborovskii, V.V. Orysyk, V.I. Staninets, E.B. Rusanov, A.N. Chernega, Zh. Org. Khim. 43 (2007) 1036–1040;
Russ. J. Org. Chem. 43 (2007) 1030–1034.
[34] H. Hempel, Chemishe Berichte, vol. 27, Berlin, 1894, p. 625.
[35] I. Đilović, M. Rubčić, V. Vrdoljak, S.K. Pavelić, M. Kralj, I. Piantanidab, M. Cindrić, Bioorg. Med. Chem. 16 (2008) 5189.
[36] S. Orysyk, V. Bon, V. Pekhnyo, Acta Crystallogr., Sect. E E65 (2009) m1059.
[37] G.S. Borodkin, I.G. Borodkina, A.I. Uraev, I.S. Vasilchenko, I.D. Sadekov, A.D. Garnovskii, Russ. J. Chem. (Russ. J. Chem. Mendeleev Soc.) 58 (2004) 117.
[38] A. Beheshti, W. Clegg, S.H. Dale, R. Hyvadi, Inorg. Chim. Acta 360 (2007) 2967.
[39] T.S. Lobana, R. Sharma, R. Sharma, R. Sultana, R.J. Butcher, Z. Anorg. Allg. Chem. 634 (2008) 718.
[40] I.A. Razak, A. Usman, H.-K. Fun, B.M. Yamin, G.W. Keat, Acta Crystallogr., Sect. C 58 (2002) m31.
[41] K.N. Zelenin, L.A. Khorseeva, M.T. Toshev, V.V. Alekseev, Kh. B. Dustov, Zh. Obshch. Khim. (Russ. J. Gen. Chem.) 60 (1990) 2549.