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Nickel(II) Complexes with Pentane-2,4-dione Bis(4-allylthiosemicarbazone)

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Abstract—Reaction of pentane-2,4-dione with *N*-(prop-2-en-1-yl)hydrazinecarbothioamide at a 1 : 2 molar ratio in ethanol resulted in the formation of a pyrazole derivative. The latter reacted with nickel perchlorate at a 1 : 1 molar ratio to form the nickel complex with pentane-2,4-dione bis(4-allylthiosemicarbazone). The same type of nickel complex was obtained as a result of *N*-(prop-2-en-1-yl)hydrazinecarbothioamide reaction with pentane-2,4-dione and nickel nitrate at a 2 : 1 : 1 molar ratio. Antimicrobial, antifungal, antioxidant, and anticancer activities of the obtained compounds were studied.

Keywords: Ni(II) coordination compounds, acetylacetone bis(4-allylthiosemicarbazone), anticancer activity

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Thiosemicarbazones are an important class of organic compounds. Possessing a wide range of donor atoms, they form a variety of coordination compounds with transitional metals. Both, thiosemicarbazones and coordination compounds with thiosemicarbazones as ligands, often exhibit various types of biological activity: antimicrobial, antifungal, anti-cancer, etc. [1–5]. Coordination of thiosemicarbazones to a metal often changes their biological activity and increases selectivity of their action. Coordination compounds of acetylacetone bis(thiosemicarbazones) were proposed as pharmaceutical radio drugs [6]. The biological activity of such substances is well consistent with their structure [7]. In this regard, the synthesis and study of new coordination compounds of acetylacetone bis(thiosemicarbazones) are relevant.

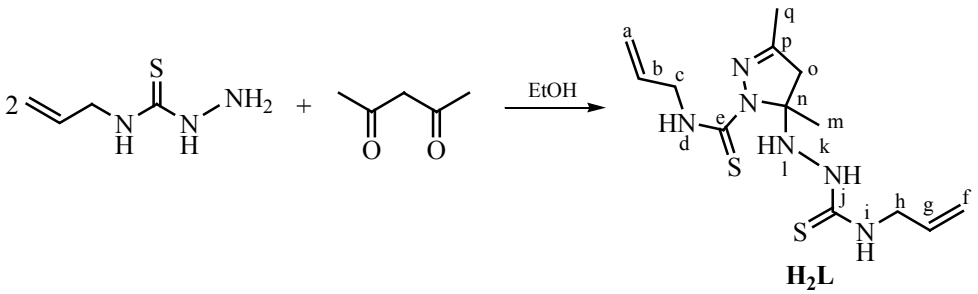
We have synthesized nickel coordination compounds with pentane-2,4-dione bis(4-allylthiosemicarbazone) (**H_2L**), determined their composition and structure, and studied their physical-chemical and biological properties.

In the reaction of *N*-(prop-2-en-1-yl)hydrazinecarbothioamide (4-allylthiosemicarbazide) with pentane-2,4-dione at a 2 : 1 molar ratio in ethanol a pyrazole derivative **H_2L** is formed instead of the expected bis(thiosemicarbazone). Its structure was determined with the help of the ^1H and ^{13}C NMR spectroscopy.

As a result of the recrystallization of the **H_2L** compound from ethanol single crystals were obtained and their structure was determined by the X-ray structural analysis (Fig. 1, Tables 1 and 2). The five-membered cycle A ($N^1N^2C^5C^6C^8$) in the compound molecule accepts the *envelope* conformation. The deviation of the C^8 atom from the root-mean-square plane is 0.106 Å, whereas deviations of the other atoms are within the limits of 0.029–0.092 Å. The dihedral angles between cycle A and fragments B ($S^1N^2N^3C^1$) and C ($S^{1A}N^{2A}N^{3A}C^{1A}$) are 9.5° and 83.4°, respectively, and the angle between the root-mean-square planes B and C is 86.11°, the torsion angles $N^3C^2C^3C^4$ and $C^1N^3C^2C^3$ are 0.01° and 91.02°.

In the structure of the **H_2L** compound centrosymmetric dimers are formed due to the N^3–H···S^{1A} and N^{2A}–H···N^1 hydrogen bonds. The intramolecular hydrogen bonds stabilize the molecule conformation. In the crystal Van der Waal's interaction arises between the dimers (Table 3, Fig. 2).

Scheme 1.



The reaction of a hot (50–55°C) ethanol solution of 4-allylthiosemicarbazide with pentane-2,4-dione and nickel(II) nitrate hexahydrate at a 2 : 1 : 1 molar ratio results in finely crystalline compound **1** with the composition $Ni(HL)NO_3$. Nickel(II) perchlorate hexahydrate reacts in similar conditions with an $\mathbf{H_2L}$ ethane solution at a 1 : 1 molar ratio to form complex **2**, for which the composition of $Ni(HL)ClO_4$ was found on the basis of elemental analysis data. Resulting coordination compounds **1** and **2** are insoluble in diethyl ether, slightly soluble in water, better, in alcohols, and readily soluble in DMF and DMSO. The determination of molar electrical conductivity showed that complexes **1** and **2** are binary electrolytes, 1 : 1.

Regardless of whether the synthesis is carried out on a matrix or $\mathbf{H_2L}$ is used as the source compound, the same-type nickel coordination compounds with bis(4-allylthiosemicarbazone)pentane-2,4-dione are formed. Thus, the reaction of 3,5-dimethyl-*N*-(prop-2-en-1-yl)-5-[2-(prop-2-en-1-ylcarbamothioyl)hydrazinyl-4,5-dihydro-1*H*-pyrazole-1-carbothioamide $\mathbf{H_2L}$ with nickel ions results in the disclosure of the pyrazole cycle and the formation of bis(4-allylthiosemicarbazone)pentane-2,4-dione, which is coordinated to the nickel ion.

Recrystallization of coordination compounds **1** and **2** from ethanol resulted in single crystals, the structure of which was determined by the X-ray structural analysis (Figs. 3, 4). In the outer sphere of crystalline coordination compounds **1** and **2** there are nitrate and perchlorate ions, respectively. The coordination of nickel atoms in the both compounds is square planar. Two sulfur atoms and two nitrogen atoms are in *trans*-positions, a slightly distorted coordination square is planar within the limits of 0.037 and 0.024 Å, respectively. The average Ni–S and Ni–N distances in complex **2** are 2.156, 1.861 Å, and in complex **1**, 2.141 and 1.855 Å. Complexes **1** and **2** form two five-membered and one six-membered metal cycles with dihedral angles between six-membered and five-membered cycles not exceeding 5.8°.

Because of the fact that outer-sphere ions in complexes **1** and **2** are different, packings of these compounds in the crystal appeared to be different. The nitrate group binds complex cations of compound **1** in endless chains along the direction [101] in the crystal through the N^2–H···O^{2N} and N^3–H···O^{1N} hydrogen bonds (Table 3, Fig. 5). According to the criterion proposed in the work [8], (CgI···CgJ < 6.0 Å, β < 60.0°, where β is the angle between the CgICgJ vector and the normal to the CgI

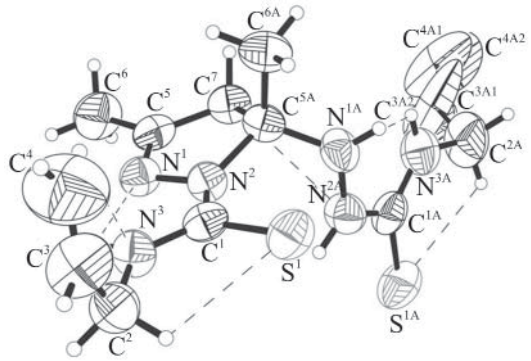


Fig. 1. General view of the $\mathbf{H_2L}$ compound molecule in the crystal.

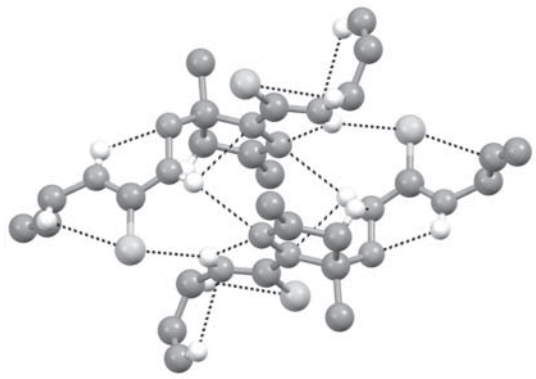


Fig. 2. Formation of dimers by $\mathbf{H_2L}$ compound molecules.

Table 1. Experimental data and crystallographic characteristics of the structure of **H_2L**, **1**, and **2** compounds

Parameter	**H_2L**	**1**	**2**
Formula	$C_{13}H_{20}N_6S_2$	$C_{13}H_{15}N_7NiO_3S_2$	$C_{13}H_{14}ClN_6NiO_4S_2$
M	324.47	440.15	476.58
Crystal system	Monoclinic	Monoclinic	Rhombic
Space group	$P2_1/c$	$C2/c$	*Pbca*
Z	4	4	8
a , Å	10.7721(8)	9.6056(8)	8.0073(4)
b, Å	11.3680(4)	21.761(2)	15.9123(7)
c, Å	16.3665(12)	9.1956(7)	31.4854(14)
α, deg	90	90	90
β, deg	119.565(5)	92.289(7)	90
γ, deg	90	90	90
V, Å ^{3}	1743.24(19)	1920.6(3)	4011.7(3)
d_{calc} , g/cm^3	1.236	1.522	1.578
λ, Å	0.71073	0.71073	0.71073
m	0.308	1.255	1.340
T, K	293(2)	293(2)	293(2)
Sample size, mm	0.35×0.22×0.09	0.25×0.135×0.02	0.60×0.325×0.15
Limits of *h*, *k*, *l*	$-12 \le h \le 12$ $-12 \le k \le 13$ $-19 \le l \le 13$	$-11 \le h \le 6$ $-16 \le k \le 25$ $-10 \le l \le 10$	$-9 \le h \le 5$ $-12 \le k \le 18$ $-37 \le l \le 35$
Number of reflections: measured/indendent	7103/3062	3152/1687	9160/3548
R_1/wR_2 by N_1	0.0628/0.1337	0.0535/0.0831	0.0535/0.1359
R_1/wR_2 by N_2	0.1215/0.1596	0.1420/0.0969	0.0714/0.1460
S	0.996	0.791	1.051
$\Delta_{(max)}/\Delta r$	0.343/–0.307	0.305/–0.248	0.504/–0.422

cycle surface), in structure **1** between chains there is a π–π stacking interaction between the $Ni^1S^{1a}C^{1a}N^{2a}N^{1a}$ and $Ni^1N^1C^5C^6C^{5a}N^{1a}$ cycles. The Cg1···Cg2 (–*x*, –*y*, 1–*z*) distance between the centroids of these fragments is 3.86 Å, and the value of β is 53.4°. Along with the specified π–π interaction, in this compound there is the interaction Y–X···Cg (π-ring) (X···Cg < 4.0 Å, γ < 30.0°, γ is the angle between the XCg vector and the normal to the Cg cycle). For the N^{1N}–$O^{2N}\cdots$Cg ($Ni^1S^1C^1N^2N^1$) (–*x*, *y*, 1/2–*z*) interaction the $O^{2N}\cdots$Cg distance is 3.46 Å and the value of γ is 14.3°.

In the complex **2** crystal structure the perchlorate-ion binds molecules into layers due to the hydrogen bonds N^3–H···O^2 and C^{2A}–H···O^1 directed along the axis A. These layers are combined with each other by the hydrogen bonds N^{3A}–H···O^{31} (Table 3, Fig. 6). As in complex **1** between the cycles $Ni^1N^1C^5C^6C^{5A}N^{1A}$ and $Ni^1S^1C^1N^2N^1$ there is a π–π stacking interaction. The distance Cg1···Cg2 (–1/2+*x*, *y*, 1/2–*z*) between the centroids of these fragments is 3.67 Å and the β value is 10.7°.

In vitro study of antimicrobial and antifungal activity of the **H_2L** compound and complex **1** in relation to a series

Table 2. Some interatomic distances and valence angles in molecules of compounds $\mathbf{H_2L}$, **1**, and **2**

Bond	*d*, Å			Angle	ω, deg		
	$\mathbf{H_2L}$	**1**	**2**		$\mathbf{H_2L}$	**1**	**2**
$Ni^1–N^1$		1.855(4)	1.871(3)	$N^1Ni^1N^{1A}$		94.9(3)	93.93(16)
$Ni^1–N^{1A}$		1.855(4)	1.861(4)	$N^1Ni^1S^{1A}$		175.71(15)	176.93(11)
$Ni^1–S^{1A}$		2.1412(17)	2.1537(13)	$N^{1A}Ni^1S^{1A}$		88.84(13)	88.42(12)
$Ni^1–S^1$		2.1412(17)	2.1573(13)	$N^1Ni^1S^1$		88.84(13)	89.22(12)
$S^1–C^1$	1.685(4)	1.689(5)	1.703(5)	$N^{1A}Ni^1S^1$		175.72(15)	175.95(13)
$N^1–C^5$	1.281(4)	1.309(6)	1.326(5)	$S^{1A}Ni^1S^1$		87.53(9)	88.51(5)
$N^1–N^2$	1.409(4)	1.397(5)	1.398(5)	$C^1S^1Ni^1$		98.3(2)	97.04(17)
$N^2–C^1$	1.359(4)	1.328(6)	1.316(6)	$C^5N^1Ni^1$		127.4(3)	127.9(3)
$N^2–C^8$	1.507(4)			$N^2N^1Ni^1$		116.0(3)	115.4(3)
$N^3–C^1$	1.334(5)	1.326(6)	1.333(6)	$C^1N^3C^2$	125.2(3)	124.9(5)	123.9(4)
$N^3–C^2$	1.453(4)	1.424(7)	1.457(6)	$C^1N^2N^1$	118.5(3)	119.6(4)	119.8(4)
$C^2–C^3$	1.464(6)		1.457(9)	$C^5N^1N^2$	107.8(3)	116.6(4)	116.6(4)
$C^3–C^4$	1.183(6)			$N^3C^1N^2$	115.3(3)	120.1(5)	118.9(4)
$C^5–C^6$	1.487(5)	1.391(5)	1.381(7)	$N^3C^1S^1$	122.7(3)	122.7(5)	122.7(4)
$C^5–C^7$	1.495(5)	1.495(6)	1.517(6)	$N^2C^1S^1$	121.9(3)	117.2(4)	118.5(4)
$C^8–C^6$	1.523(4)			$N^1C^5C^6$	114.4(3)	121.3(5)	121.3(4)
$C^8–C^9$	1.530(4)			$N^1C^5C^7$	120.9(4)	120.7(5)	120.3(4)
				$C^6C^5C^7$	124.7(3)	118.1(5)	118.4(4)

of standard strains of *Staphylococcus aureus* and *Enterococcus faecalis* gram-positive bacteria, *Escherichia coli* and *Salmonella abony* gram-negative coliform bacilli, and the representative of yeast-like fungi *Candida albicans* showed that the uncoordinated compound $\mathbf{H_2L}$ has the values of minimal suppressive (MSC) and minimal bactericidal (MBC) concentrations of 1000 μg/mL, whereas MSC and MBC values of complex **1** are in the range of 250–500 μg/mL. Consequently, the coordination of the ligand to the nickel atom leads to a 2–4-fold increase in the antimicrobial and antifungal activity.

The study of antioxidant activity was carried out by the $ABTS^{\bullet+}$ method [9]. The experimental values of concentrations of 50% inhibiting (IC_{50}) are presented in Table 4. Compound $\mathbf{H_2L}$ and nickel complex **1** show antioxidant activity, complex **1** being more active not only

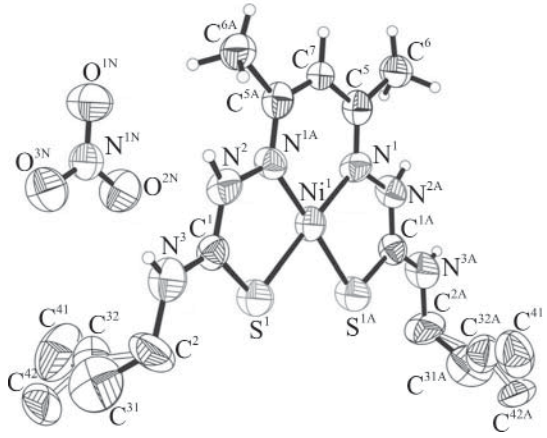


Fig. 3. General view of the complex **1** molecule in the crystal.

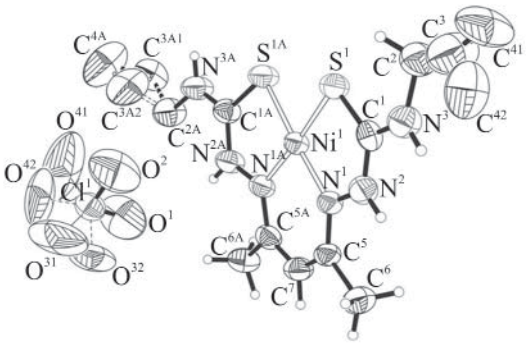


Fig. 4. General view of the complex **2** molecule in the crystal.

Table 3. Geometric parameters of hydrogen bonds in molecules of compound $\mathbf{H_2L}$, **1**, and **2**

D–H···A bond	*d*, Å			DHA angle, deg	A coordinates atom
	D–H	H···A	D···A		
			H_2L		
N^{3A}–H^{3AA}···N^{1A}	0.86	2.21	2.6158	109	*x*, *y*, *z*
N^{2A}–H^{2A}···N^{1}	0.86	2.52	3.3344	159	1–*x*, 1–*y*, 1–*z*
N^{3}–H^{3}···N^{1}	0.86	2.18	2.6012	110	*x*, *y*, *z*
N^{3}–H^{3}···S^{1A}	0.86	2.69	3.4277	144	1–*x*, 1–*y*, 1–*z*
C^{2}–H^{2C}···S^{1}	0.97	2.68	3.0895	106	*x*, *y*, *z*
C^{2A}–H^{2AB}···S^{1A}	0.97	2.71	3.1074	105	*x*, *y*, *z*
C^{4}–H^{4A}···N^{3}	0.93	2.56	2.8713	100	*x*, *y*, *z*
C^{6}–H^{6A}···N^{2A}	0.97	2.54	2.9281	104	*x*, *y*, *z*
			1		
N^{2}–H^{2}···O^{2N}	0.81	2.33	3.0895	156	*x*, –*y*, 1/2+*z*
N^{3}–H^{3}···O^{1N}	0.75	2.06	2.7808	161126	1–*x*, –*y*, 1–*z*
			2		
N^{2}–H^{2}···O^{2}	0.86	2.13	2.8937	147	1–*x*, 1/2+*y*, 1/2–*z*
N^{3}–H^{3}···O^{2}	0.86	2.10	2.8702	149	1–*x*, 1/2+*y*, 1/2–*z*
N^{3A}–H^{3A}···O^{31}	0.86	2.11	2.8967	153	*x*, *y*, *z*
C^{2A}–H^{2AA}···O^{1}	0.97	2.60	3.4193	143	3/2–*x*, 1/2+*y*, *z*

in comparison with the uncoordinated $\mathbf{H_2L}$ compound, but also with trolox, which used as a standard antioxidant in medical practice as a free radical inhibitor.

Study of the anti-proliferative activity of $\mathbf{H_2L}$ and **1** compounds in relation to HeLa cervical cancer cells, BxPC-3 pancreas, RD rhabdomyosarcoma, and also normal MDCK cells of the dog kidney showed that the $\mathbf{H_2L}$ compound inhibits the growth and reproduction of none of these cells in the concentration interval of 0.1–100 μmol/L, whereas complex **1** selectively inhibits the growth and reproduction of RD cancer cells by 43–58% at concentrations of 0.1–100 μmol/L and does not have a negative effect on normal MDCK cells. The calculated IC_{50} value for complex **1** in relation to RD cancer cells was 6.72 μmol/L. The results on the antiproliferative activity point to the prospect of further search for selective anti-cancer substances among coordination compounds of metals with pentane-2,4-dione bis(thiosemicarbazones).

EXPERIMENTAL

The X-ray analysis was carried out on an Oxford Diffraction diffractometer [10]. The structures were solved by direct methods and refined by the least squares method in anisotropic approximation for non-hydrogen atoms using the SHELX-97 programs [11]. Hydrogen atoms were included in the refinement in geometrically calculated positions, and their U_H temperature factors were taken to be 1.2 times greater than those of carbon and oxygen atoms bound with them. Refinement of the position of perchlorate ions in complex **2** was carried out taking into account their disordering. The basic parameters of the experiment, the solution and refinement of the structures are presented in Table. 1, and some interatomic distances, valence angles, and hydrogen bonds are given in Tables 2 and 3. The coordinates of the basic atoms in the studied structures are deposited in the Cambridge database (CCDC 1919221-1919223). Geometric calculations and drawings are fulfilled using the Mercury program

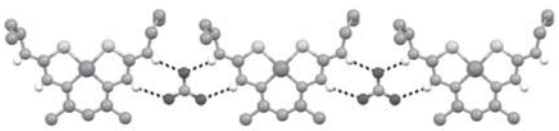


Fig. 5. Fragment of complex **1** crystal packing.

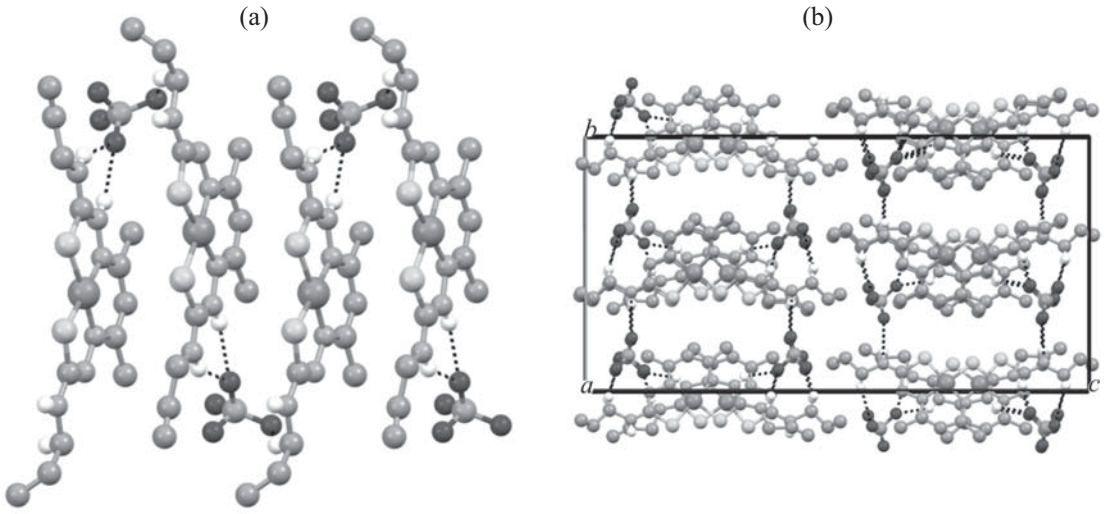


Fig. 6. (a) Formation of a layer and (b) fragment of molecular packaging in the complex **2** crystal.

[12], and only those hydrogen atoms that participate in hydrogen bonds are left to illustrate the packaging of the structures.

Resistance of solutions of complexes **1** and **2** in DMF (20°C, $c = 0.001$ M) was measured with a P-38 rheochord bridge. The NMR spectra were recorded on a Bruker DRX-400 spectrometer in DMSO-d_6.

Antimicrobial, antifungal, anti-cancer, and antioxidant activities were studied using the standard procedures [13, 14].

3,5-Dimethyl-*N*-(prop-2-en-1-yl)-5-[2-(prop-2-en-1-ylcarbamothioyl)hydrazinyl-4,5-dihydro-1*H*-pyrazole-1-carbothioamide (H_2L). A hot solution (55–60°C) of 10 mmol of pentane-2,4-dione in 15 mL of ethanol was mixed with a solution of 20 mmol of *N*-(prop-2-en-1-yl)hydrazinecarbothioamide in 35 mL of ethanol. When the reaction mixture was cooled, a light yellow precipitate was formed, which was filtered off on a glass filter, washed with a small amount of alcohol, and dried in air. Yield 78%. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.39 t (1H, NH$^{d/i}$, J = 6.0 Hz), 8.25 t (1H, NH$^{d/i}$, J = 5.9 Hz), 7.98 br. s (1H, NH$^{k/l}$), 6.40 br. s (1H, NH$^{k/l}$), 5.87 m (2H, CH^{b+g}), 5.10 m (4H, CH$_2^{a+f}$), 4.12 m (4H, CH$_2^{c+h}$), 2.91 d (1H, CH$_2^{o1}$, J = 18.6 Hz), 2.82 d (1H, CH$_2^{o2}$, J = 18.6 Hz), 1.99 s (3H, CH$_3^q$), 1.77 s (3H, CH$_3^m$). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 182.34 (C^j=S), 174.16 (C^e=S), 154.77 (C^p=N), 135.11 (C^b, C^g), 115.68 (C^f), 115.39 (C^a), 84.57 (C^n), 47.09 (C^c), 45.67 (C^o), 45.21 (C^h), 23.55 (C^m), 15.95 (C^q).

Table 4. Antioxidant activity of H_2L and 1 compounds in relation to cation radicals ABTS$^{\bullet+}$

Compound	IC_{50}, μmol/L
H_2L	42
1	25
Trolox	33

2,2'-Pentane-2.4-diylidenebis[*N*-(prop-2-en-1-yl)-hydrazinecarbothioamido]nickel(II) nitrate (1). A solution of 20 mmol of *N*-(prop-2-en-1-yl)hydrazinecarbothioamide in 20 mL of ethanol and a solution of 10 mmol of nickel(II) nitrate hexahydrate in 20 mL of ethanol were added to a solution of 10 mmol of pentane-2,4-dione in 25 mL of ethanol with heating (50–55°C) and continuous mixing. The reaction mixture was heated for 50–60 min. After cooling to room temperature, the precipitate was filtered off, washed with small amounts of alcohol and ether, and dried in air up to a constant weight. Yield 72%, æ 88 Ω^{-1} cm^2 mol^{-1} (294 K, DMF). Found, %: Ni 13.07; N 22.06; S 14.43. $C_{13}H_{21}N_7NiO_3S_2$. Calculated, %: Ni 13.15; N 21.98; S 14.37.

2,2'-Pentane-2.4-diylidenebis[*N*-(prop-2-en-1-yl)-hydrazinecarbothioamido]nickel(II) perchlorate (2). A solution of 10 mmol of nickel(II) perchlorate hexahydrate in 20 mL of ethanol was added to a solution of 10 mmol of **H_2L** compounds in 50 mL of ethanol with heating (50–55°C) and continuous mixing. The reaction mixture was heated for 50–60 min. After cooling to room temperature, the precipitate was filtered off, washed with small amounts of alcohol and ether, and dried in air up to a constant weight. Yield 72%, æ 81 Ω^{-1} cm^2 mol^{-1}

(294 K, DMF). Found, %: Ni 12.21; N 17.24; S 13.13. $C_{13}H_{21}ClN_6NiO_4S_2$. Calculated, %: Ni 12.14; N 17.38; S 13.26.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Yu, Y., Kalinowski, D.S., Kovacevic, Z., Siafakas, A.R., Jansson, P.J., Stefani, C., and Richardson, D.R., *J. Med. Chem*., 2009, vol. 52, no. 17, p. 5271. https://doi.org/10.1021/jm900552r
2. Beraldo, H. and Gambino, D., *Mini Rev. Med. Chem*., 2004, vol. 4, no. 1, p. 31. https://doi.org/10.2174/1389557043487484
3. Prisakar', V.I., Tsapkov, V.I., Buracheeva, S.A., Byrke, M.S., and Gulya, A.P., *Pharm. Chem. J*., 2005, vol. 39, no. 6, p. 313. https://doi.org/10.1007/s11094-005-0142-8
4. Pahontu, E., Fala, V., Gulea, A., Poirier, D., Tapcov, V., and Rosu, T., *Molecules*, 2013, vol. 18, no. 8, p. 8812. https://doi.org/10.3390/molecules18088812
5. Kalinowski, D.S., Quach, P., and Richardson, D.R., *Future Med. Chem*., 2009, vol. 1, no. 6, p. 1143. https://doi.org/10.4155/fmc.09.80
6. Cowley, A.R., Dilworth, J.R., Donnelly, P.S., Gee, A.D., and Heslop, J.M., *Dalton Trans*., 2004, no. 16, p. 2404. https://doi.org/10.1039/B406429A
7. Pelosi, G., *Open Crystallogr. J*., 2010, vol. 3, p. 16. https://doi.org/10.2174/1874846501003010016
8. Spek, A.L., *J. Appl. Cryst*., 2003, vol. 36, p. 7. https://doi.org/10.1107/S0021889802022112
9. Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M., and Rice-Evans, C., *Free Radical Biol. Med*., 1999, vol. 26, nos. 9–10, p. 1231. https://doi.org/10.1016/s0891-5849(98)00315-3
10. CrysAlisPro, Version 1.171.33.52 (release 06-11-2009 CrysAlis171.NET). Oxford Diffraction Ltd.
11. Sheldrich, G.M., *Acta Crystallogr. (A)*, 2008, vol. 64, p. 112. https://doi.org/10.1107/S0108767307043930
12. Macrae, C.F., Edgington, P.R., McCabe, P., Pidcock, E., Shields, G.P., Taylor, R., and Van De Streek, J., *J. Appl. Crystallogr*., 2006, vol. 39, no. 3, p. 453. https://doi.org/10.1107/s002188980600731x
13. Gulea, A., Poirier, D., Roy, J., Stavila, V., Bulimestru, I., Tapcov, V., and Popovschi, L., *J. Enzyme Inhib. Med. Chem*., 2008, vol. 23, no. 6, p. 806. https://doi.org/10.1080/14756360701743002
14. Pahontu, E., Usataia, I., Graur, V., Chumakov, Yu., Petrenko, P., Gudumac, V., and Gulea, A., *Appl. Organomet. Chem*., 2018, vol. 32, no. 12, p. e4544. https://doi.org/10.1002/aoc.4544