The Cycle Destruction during Complex Formation of 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole with Ni (II) ions

[1]Perizad. A. Fatullayeva, Ajdar A. Medjidov, Idayat. M. Mamedov, Pavel V. Dorovatovskiy,
[3] Jan. V. Zubavichus,[4]Victor. N. Khrustalev, [5]Rayyat Huseyn Ismayilov
[1]Institute of Catalysis and Inorganic Chemistry, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan.
[2]National Research Center "Kurchatov Institute", Moscow, Russian Federation.
[3]Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation.
[4]Peoples' Friendship University of Russia, Moscow, Russian Federation.
[5]"OilGasScientificResearchProject" Institute, SOCAR, Baku, Azerbaijan.
Rayyet.ismayilov@socar.az*

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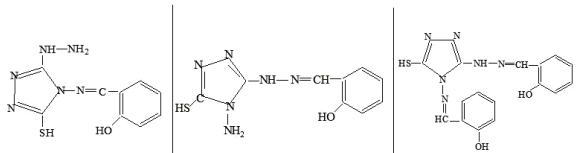
Summary: Using single crystal X-ray diffraction method, it was shown that the interaction of 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole with Ni (II) acetate yields a complex of nickel with salicylidene-thiosemicarbazone instead of the expected complex with the corresponding Schiff base. A possible mechanism of hydrolysis of the thiotriazole ring is proposed. The N- (salicylidene) thiosemicarbazone is a tridentate and almost flat structure ligand coordinates to the nickel (II) cation through thiosemicarbazone sulphur, phenolic oxygen, and azomethine nitrogen atoms. The nickel (II) ion in the complex is four-coordinated in distorted square-planar geometry. The intermolecular hydrogen bonds N─H···N, as well as hydrogen bonds N─H···O, O─H···O and O─H···S through the solvate water molecules, give rise to the 3-D network of the complex $[Ni(TSC)((NH_2)_2CS)]\bullet H_2O$.

Keywords: Schiff base; Nickel complex; Thiosemicarbazone ligand; Hydrogen bonds.

Introduction

Schiff bases of 5- substituted-3-hydrazino -4-amino--1,2,4-triazole possess bactericidal and fungicidal activity [1,2], and exhibit biological activity [1,3]. It is also known for the application of 4-salicylidene-amino-3-hydrazino-5-mercapto-1,2,4-triazole, as a steel corrosion inhibitor [4]. The presence of two active NH_2 groups in 4-amino-3-hydrazino-5-mercapto -1,2,4-triazole capable of forming an azomethine bond with aldehydes (in particular salicylic aldehyde) promotes the formation of three types of Schiff bases I, II and III:



I II III

In previously published papers, three types of structures are proposed. Thus, the formation of a Schiff base through 4-amino groups was assumed by Kaya, *et al.* [5]. The same structure was proposed in [6]. On the contrary, the formation of Schiff bases through a hydrazine nitrogen atom was assumed by Zhou, *et al.* [3,7]. The synthesis with a ratio of initial reagents thiatriazole: salicylic aldehyde 1: 2 gives a double Schiff base on both amino groups [2]. It should be noted that so far there is no X-ray structural data on these ligands and their complexes with metals.

Here we report for the first time the synthesis of a Ni (II) complex with Schiff's base, obtained from salicylic aldehyde and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole. Unexpectedly, an interaction of obtained Schiff base with nickel acetate instead of the expected complex with this Schiff base forms a complex of nickel with N- (salicyliden) thiosemicarbazone (TSC).

Experimental

Materials and measurements

All reagents and solvents were supplied by Sigma-Aldrich and were used as received unless otherwise noted. 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole and 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole (Schiff base) were synthesized according to the literature methods [4,8].

Absorption spectra were recorded on an UV-VİS Evolution 60S spectrophotometer. IR spectra were performed with a Thermo Scientific Nicolet iS10 FTIR Spectrometer in the range of 400-4000 cm^{-1}. For elemental analysis used FlashEA 1112 Series CHNS-O Analyzer.

***To whom all correspondence should be addressed.**

Preparation of nickel complex [Ni(TSC)((NH$_2$)$_2$CS)]•H$_2$O

To 0.50 g (2 mmol) of the ligand dissolved in 30 ml of ethanol. Then Ni (CH$_3$COO)$_2$•4H$_2$O 0.249 g (1 mmol) in methanol (20 ml) was added to the solution and the mixture was heated to 50^{o}C for 15 minutes. The solution was filtered to remove insoluble impurities and left to crystallize. After a few days, dark brown single crystals suitable for X-ray diffraction were obtained, which washed on the filter with water and dried under the vacuum (yield: 72%). IR (ν/cm^{-1}): 3510 m (OH), 3420 s (NH), 3400 s (NH), 3280 s (NH), 3160 s (NH), 1545 s (C = N), 1525 s, 1412 m, 1209 w, 1150 w, 1083 w, 1030 w, 948 w, 909 w, 818 w, 756 m, 727 m, 485 w. T_{mp} = 195^{o}C. Elemental analysis (%) $C_9H_{13}NiN_5O_2S_2$: calc. C 31.24, H 3.79, N 16.96; found: C 31.33, H 3.85, N 16.87.

Crystal structure determinations

Cell parameters and the intensities of a reflection for [Ni(TSC)(NH$_2$)$_2$CS)]•H$_2$O were measured at the "Belok" station of the Synchrotron Centre in Kurchatov Institute equipped with a high resolution Rayonix SX165 CCD detector (T = 100 K, λ = 0.9626 Å, φ- scanning with a step 1.0^o). The iMOSFLM program included in the CCP4 software package using for the experimental data processing [9]. For the data obtained, X-ray absorption was taken into account applying for the Scala program [10]. The detailed crystal data and refinement parameters are listed in Table-1. The structure was solved using direct methods and refined by the full-matrix least squares on F^2 values. The non-hydrogen atoms were refined anisotropically. There is water molecules present in the crystal lattice. Hydrogen atoms of amino groups and solvate water molecules were objectively identified in Fourier-difference syntheses and included in the refinement with fixed isotropic displacement parameters (U iso (H) = 1.2U eq (N) and 1.5U eq (O)). The positions of the remaining hydrogen atoms are calculated geometrically and included in the refinement with fixed positional parameters (the rider model) and isotropic displacement parameters (U iso(H) = 1.2U eq (C)). All calculations were carried out with the SHELXTL program package [11]. CCDC 1874684 contains the supplementary crystallographic data for complex [Ni(TSC)(NH$_2$)$_2$CS)]•H$_2$O. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 1. Crystal structure data for [Ni(TSC)(NH$_2$)$_2$CS)]•H$_2$O.

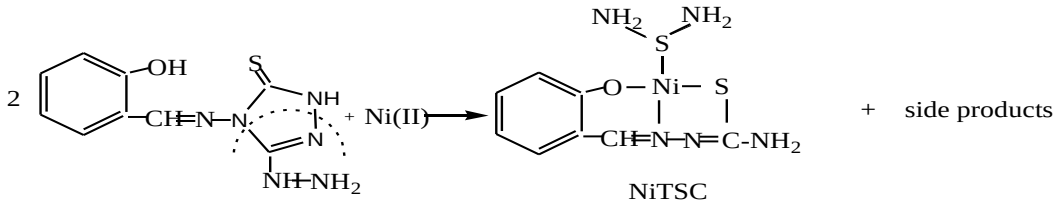
Compound	[Ni(TSC)(NH$_2$)$_2$CS)]•H$_2$O
Empirical formula	$C_9H_{13}N_5O_2S_2Ni$
Formula weight	346.05
Crystal sizes, mm	0.03×0.20×0.30
Crystal system	Monoclinic
Space group	P21/c
a , Å	16.280(3)
b, Å	5.8675(12)
c, Å	14.010(3)
β,^{o}	97.61(3)
V, Å^3	1326.5(5)
Z	4
d_c, g·cm^3	1.733
F(000)	712
μ, мм$^{-1}$	4.073
$2\theta_{max}$, ^{o}	76.90
the number of the measured reflections	12353
number of independent reflections (R_{int})	2802 (0.089)
the number of reflections with $I> 2\sigma(I)$	2265
the number of refined parameters	173
R1; wR2 (for reflections with $I> 2\sigma(I)$)	0.079; 0.187
R1; wR2 (all measured reflections)	0.092; 0.205
GOF on F^2	0.808
Extinction coefficient	0.006(1)
$T_{min;}T_{max}$	0.320; 0.860

Results and Discussion

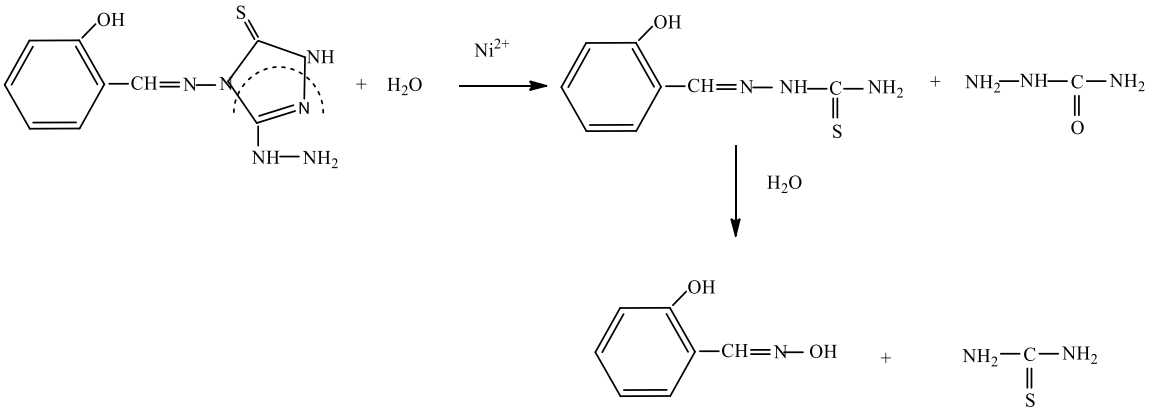
The single X-ray structure investigation revealed, that the interaction of the 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole with nickel acetate instead of the expected complex with this Schiff base forms a complex of nickel with N-(salicylidene) thiosemicarbazone (TSC) (Scheme-1). The formation of thiosemicarbazone ligand is possible when decomposition of the triazole ring is happened according to the following scheme:

The ability of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole to hydrolyse with cycle destruction was noted in [8]. In our case, the fast cleavage of the thiatriazole ring can be caused by the presence of nickel ions, which have a catalytic *impact* on the decomposition process. It is most likely that the hydrolysis reaction occurs in coordinated ligands. The formation of the thiocarbamide molecule, which is present in the final complex, could be due to the hydrolysis of thiosemicarbazone (Scheme-2).

The scheme-2 of hydrolysis of an initial ligand can be represented as follows:



Scheme-1: The decomposition of the triazole ring and formation of the nickel complex.



Scheme-2: The hydrolysis of 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole ligand.

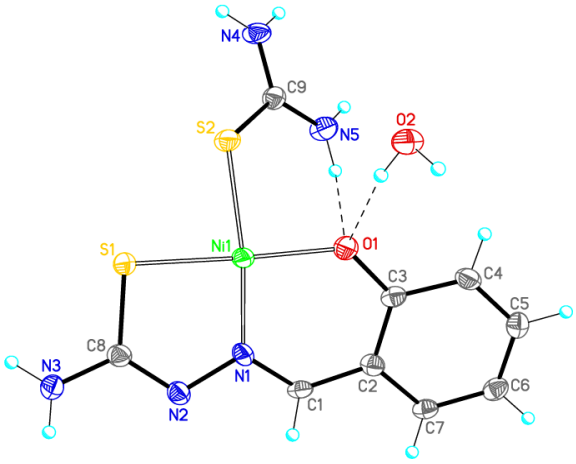


Fig. 1: Molecular structure of complex $[Ni(TSC)(NH_2)_2CS)]•H_2O$.

The structure of the complex $[Ni(TSC)((NH_2)_2CS)]•H_2O$ was studied by X-ray crystallography and shown in Fig. 1. The N-(salicylidene) thiosemicarbazone ligand has an almost flat structure (rms deviations of atoms from the middle plane is 0.061 Å) and is tridentate, coordinating to the nickel (II) cation with sulfur (S1), oxygen (O1) and nitrogen N1 of hydrazine fragment with the formation of two chelate five- and six-membered cycles. The distances C(1) – N(1) and C(8) – N(2) have the characteristic values for the double bond C = N (1.312 (4) and 1.327 (4) Å), and the distance C(8) – S(1) (1.763 (3) Å) has the characteristic value for the ordinary bond C – S. Consequently, the N- (salicylidene) thiosemicarbazone ligand in the complex $[Ni(TSC)((NH_2)_2CS)]•H_2O$ is dianionic, and its structure corresponds to the thiolate tautomeric form

The coordination environment of the Ni (II) cation complements to a distorted plane-square (the values of the valence angles lie in the range 85.47 (4) - 96.44 (10)°) the molecule of thiocarbamide, bonding with the metal atom through the sulfur atom. The conformational position of the thiocarbamide molecule relative to the organic ligand (the torsion angle of O1─Ni1←S(2) – C(9) is equal 56.0(2)°) and determined by the strong intramolecular hydrogen bonding N–H ··· O (Table-2, Fig. 1), which closes the six-membered cycle. As might be expected, the lengths of Ni1─S1 (2.1581 (9) Å) and Ni1 ← S2 (2.2516 (9) Å) bonds differ significantly because of their covalent and coordination type. It is important to note that the distances Ni1─O1 (1.890 (2) Å) and Ni─N1 (1.894 (2) Å) are almost similar. The intermolecular hydrogen bonds N─H ··· N, as well as hydrogen bonds N─H ··· O, O─H ··· O and O─H ··· S through the solvate water molecules connect the molecules into a three-dimensional framework in a crystal (Table-2).

The infrared spectra contain absorption bands at 3200, 3320 and 3400 cm^{-1}, which were assigned to the stretching vibrations of the N─H bonds of the initial Schiff basis of thiotriazole. The absorption band of the phenolic hydroxyl group is not visible on the spectrum due to the strong hydrogen bond with the C = N group. The absorption band of S─H is also absent, which indicates that the thiotriazole sulfur in the ligand is in thione form. The strong absorption band at 1620 cm^{-1} represents the vibration of the azomethine group. The IR spectra of the nickel complex in the region of valence vibrations of N─H contain four absorption bands of 3160, 3280, 3400 and 3420 cm^{-1}, referring to the stretching vibrations of νN-H in the thiosemicarbazonate fragment (the first two bands ν_{sym} and ν_{ass}) and to the valence N ─H vibrations in the coordinated thiocarbamide molecule. Moreover, the azomethine band of the free ligand at 1620 cm^{-1} underwent a shift towards the lower frequency region at 1545 cm^{-1} due to complexation of the ligand with the nickel ion. A narrow band at 3510 cm^{-1} can be attributed to the crystalline water molecule.

Table 2. Hydrogen bonds in $[Ni(TSC)(NH_2)_2CS)]\cdot H_2O$ complex [Å and °].

D─H···A	d(D─H)	d(H···A)	d(D···A)	<(DHA)
N3─H3A···N2[a]	0.88	2.32	3.083(4)	145.7
N4─H4A···O2[b]	0.88	2.32	3.141(3)	155.3
N4─H4B···O2[c]	0.88	2.28	3.158(3)	177.0
N5─H5A···O2[b]	0.88	2.53	3.301(3)	146.5
N5─H5B···O1	0.88	2.12	2.870(3)	142.8
O2─H2A···O1	0.91	2.03	2.926(3)	168.1
O2─H2B···S[d]	0.91	2.67	3.504(2)	152.4

Symmetric operations for the generation of equivalent atoms:

[a] – x +1, – y +2, – z +2; [b] – x, y – 1/2, – z +3/2; [c] – x, y+ 1/2, – z +3/2; [d] x, – y +3/2, z – ½.

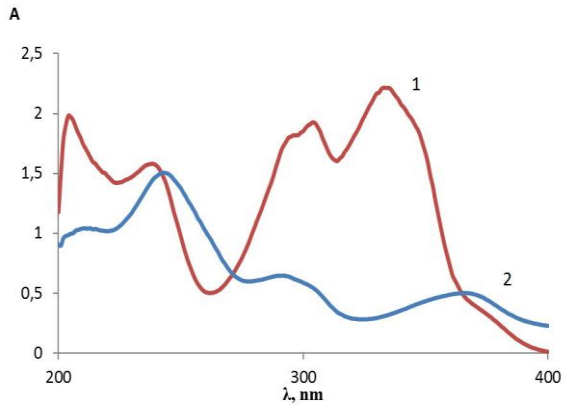


Fig. 2: Electronic absorption spectra of ethanolic solutions: 1- salicyliden-3-hydrazino- 4-amino-5- mercapto -1,2,4-triazole, 2- nickel complex (TSC) $Ni((NH_2)_2CS) \cdot H_2O$.

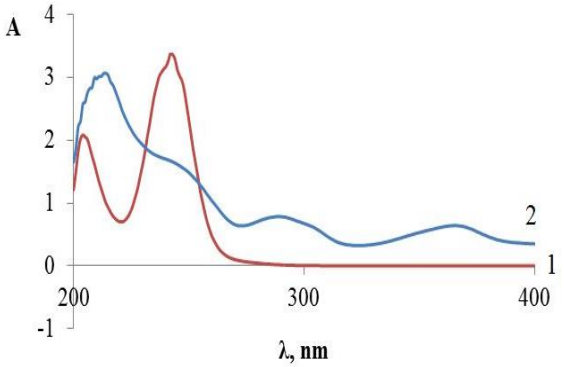


Fig. 3: Electronic absorbtion spectra of ethanolic solutions: 1- thiosemicarbazide, 2- mixture of nickel acetate, salicylic aldehyde and thiosemicarbazide.

The electronic absorption spectrum (Fig. 2) of the initial ligand contains the following absorption bands: 210, 240, 300, and 330 nm. The band at 240 nm should be attributed to the absorption of the chromophore group C═S since thiocarbamide absorbs precisely at this wavelength (Fig. 3). We note the almost complete similarity of the electronic spectra of thiocarbamide and thiosemicarbazone. The remaining bands belong to the π-π* and n-π* transitions in the salicylaldiminate and triazole fragments. The UV spectra of the complex $[Ni(TSC)((NH_2)_2CS)]\cdot H_2O$ (Fig. 2) also has absorption at 240 nm, which is associated with the presence of coordinated thiocarbamide in the complex.

The disintegration of the initial ligand and the formation of the salicylicidenesemi-carbazonate complex $[Ni(TSC)((NH_2)_2CS)]\cdot H_2O$ occurs very quickly. The UV spectrum of the complex formed by mixing equimolar solutions of nickel acetate and the original ligand 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole for 5 min completely coincides with the spectrum of the complex $[Ni(TSC)((NH_2)_2CS)]\cdot H_2O$. The UV spectrum of the mixture of solutions of thiosemicarbazide, salicylic aldehyde and nickel acetate and spectrum of the complex $[Ni(TSC)(NH_2)_2CS)]\cdot H_2O$ are similar except that the absorption band at 240 nanometers has a low-intensity (Fig. 3). This is due to the absence of urea as part of the complex formed, which absorbs at this wavelength and is present in the $[Ni(TSC)((NH_2)_2CS)]\cdot H_2O$ complex (Fig. 2).

Conclusions

It was shown that the interaction of nickel (II) acetate with 4-salicylideneamino-3-hydrazino-5-

mercapto-1,2,4-triazole results in the opening of the triazole ring with the formation of (salicylidene) thiosemicarbazonate nickel complex. This, in turn, serves as evidence that, in the original Schiff base, salicylic aldehyde forms an azomethine bond with the amino group located on the nitrogen atom of the triazole ring. Extensive hydrogen bonds give rise to the 3-D network of the complex. X-ray diffraction study revealed that in the resulting complex the geometry about the Ni(II) ion can be described as distorted square planar and N- (salicylidene) thiosemicarbazone coordinates the Ni(II) cation as a tridentate dianion ligand.

Acknowledgments

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