

Synthesis and study of coordinating agents for the synthesis of new coordination compounds

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Abstract. Two compounds were obtained from the condensation reaction of semicarbazide (hydrazinecarboxamide) and semithiocarbohydrazide (hydrazinecarbothioamide) compounds with a 3-pyridinecarboxaldehyde carbonyl compound: (E)-1-(pyridin-3-ylmethylene)thiourea (L-1) and (E)-1-(pyridin-3-ylmethylene)urea (L-1) (L-2). The structure and composition of these compounds were determined using theoretical calculations with the GAMESS software package and IR spectroscopy. The new organic molecules L-1 and L-2 have the potential to be used as mono- or bidentate coordinating agents in the construction of coordination compounds with various useful properties.

Keywords: bridging ligand, coordinating compound, synthesis, condensation, hydrazinecarboxamides, hydrazinecarbothioamides, carbonyl compound, IR spectrum, spectrophotometry, GAUSSIAN, theoretical calculations.

Sinteza și studiul unor agenți de coordinare pentru sinteza noilor compuși coordinațivi

Rezumat. În baza reacției de condensare dintre compușii semicarbazida (hidrazinecarboxamide) și semitiocarbhidrazida (hidrazinecarbothioamide) cu un compus carbonilic 3-piridincarboxaldehidă au fost obținuți doi compuși: (E)-1-(pyridin-3-ylmethylene)thiourea (L-1) și (E)-1-(pyridin-3-ylmethylene)urea (L-2). Structura și compoziția acestor compuși a fost descifrată în baza calculelor teoretice folosind pachetul de programe GAMESS, cât și prin intermediul spectroscopiei IR. Moleculele organice noi L-1 și L-2 prezintă perspective de utilizare în calitate de agenți de coordinare mono- sau bidentati cu scopul asamblării compușilor coordinațivi cu diverse proprietăți utile.

Cuvinte cheie: ligand punte, compus coordinațiv, sinteză, condensare, hidrazinecarboxamidă, hidrazinecarbothioamidă, compus carbonilic, spectru IR, spectrofotometrie, GAUSSIAN, calcule teoretice.

1. INTRODUCTION

One of the branches of modern chemistry that offers the possibility of obtaining numerous coordination compounds with predetermined properties is coordination compound chemistry. The methods for obtaining coordinating compounds can be varied by changing

the metal atoms, the nature of ligands, the sets of atoms that can participate in coordination, the nature of the chemical bonds, the intermolecular interactions and the diversity of the structures that these compounds can form among other things. The structure of the coordinating compound can be influenced by using different ligands and the modification or choice of optimal synthesis conditions will condition the arrangement of structural units in space and the properties of obtained products.

At the moment, an important direction in Materials Science is the synthesis of new chemical compounds with useful properties for various fields of industry. Synthetic precursors (different ligands) are later used in the synthesis of vitally important coordinating compounds.

A neutral ion or molecule is traditionally defined as a ligand that is directly attached around a central ion or atom. Thus, we can admit that ligands are coordinating atoms or groups of atoms that contain one or more coordinating atoms (donors, ligates, ligators, or binders) that are directly attached to a nuclear or central atom. Multidentate (polydentate) ligands are groups that contain more than one potential coordinating atom. If a ligand is attached to a central atom via two or more coordinating atoms, it is referred to as a chelate ligand; if it is attached to more than one coordination center, it is referred to as a bridging group or a link group [1].

Obtaining useful compounds is focused on various methods of chemical synthesis of new complexes with composition, structure and manifested useful properties. Later, these compounds are subjected to qualitative composition and structure determination using modern physical methods of analysis, theoretical study of the energy state of molecular systems, analysis of some of them as stimulators of biosynthesis processes of enzymatic preparations, gas traps and so on.

Quantum-chemical calculations, which allow to calculate the energy of these systems, predict the direction of some reactions (e.g. condensation reactions), the mechanisms of substitution and so on; are a useful mechanism for understanding some phenomena and processes that occur in simple and complex molecular systems. These methods can be used to decipher and model the structure of the investigated compounds by comparing the results to theoretical data. Different research methods are employed. Some of them are based on the use of several programs, one being GAMESS, which contains various calculation methods, beginning with those of molecular dynamics and mechanics, semi-empirical methods, *ab initio* methods based on the Hartree-Fock theory, or methods based on density functional theory and can be used to calculate a wide range of molecular properties [2]. Furthermore, powerful instrumental methods such as IR spectroscopy and

nuclear magnetic resonance (NMR) can be used to decipher the composition and structure of the synthesized ligands.

Infrared spectroscopy (IR spectroscopy) is a spectroscopic technique that studies the interaction of infrared radiation with matter. Infrared spectroscopy employs a variety of techniques, the majority of which are based on absorption spectroscopy. Its applications include the identification and study of specific compounds in solid, liquid, or gas samples.

A molecule must be IR active, i.e. have a specific vibration in order to absorb in the IR range. Molecular vibration is associated with changes in the dipole moment, so the molecule does not have to be a permanent dipole to occur [3].

Compound identification using infrared spectra is so safe and convenient that it has largely replaced older methods based on melting point, refractive index and so on. Its main advantage is the certainty of the conclusion even for partially impure materials; one disadvantage is the space required to unfold all of the details of a spectrum.

Nuclear magnetic resonance (NMR) is a physical phenomenon based on the quantum mechanical properties of atomic nuclei. It should be noted that due to NMR experiments are performed on atom nuclei rather than electrons, the information provided refers to the spatial positioning of these nuclei in the studied chemical compound, which is based on an intrinsic property known as spin. NMR is a property of atomic nuclei with nuclear spins (e.g. ^1H , ^{13}C , ^{17}O , ^{19}F , ^{31}P , ^{129}Xe ...) in a magnetic field. When exposed to electromagnetic (radiofrequency) radiation, most commonly in the form of pulses, atomic nuclei can absorb the energy and then release it during relaxation.

Depending on the magnetic field and other molecular factors, the energy delivered during this resonance phenomenon corresponds to a very precise frequency. As a result of this phenomenon, the quantum magnetic properties of nuclei in gas, liquid, or solid phases can be noticed. As a result, only atoms with magnetic nuclei exhibit the resonance phenomenon [4].

When investigating a newly synthesized structure in organic chemistry, NMR spectrometry represents the method with the greatest potential for structural elucidation. NMR spectrometry is an investigative technique that requires minimal sample preparation in advance and provides the ability to obtain quantitative and qualitative structural information for any molecule characterized by atoms with a nuclear kinetic moment.

2. METHODOLOGY OF THE EXPERIMENT

The ligands **(E)-1-(pyridin-3-ylmethylene)thiourea (L-1)** and **(E)-1-(pyridin-3 -ylmethylene)urea (L-2)** were obtained as a result of the condensation reaction between

the compounds semicarbazide (hydrazinecarboxamides) or semithiocarbohydrazide (hydrazinecarbothioamides) with a carbonyl compound – 3-pyridinecarboxaldehyde (Figure 1).

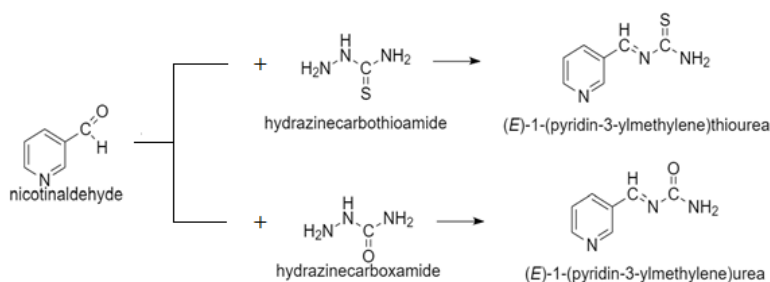


Figure 1. Scheme for obtaining the ligands L-1 and L-2

Following the condensation reaction between the compounds 3-pyridinecarboxaldehyde (nicotinaldehyde) and hydrazinecarbothioamide, the bridging ligand **(E)-1-(pyridin-3-ylmethylene)thiourea (L-1)** was obtained (semithiocarbazide). The semithiocarbazide (2.88 g, 31 mmol) was dissolved (CH₃CN) in 40 mL of H₂O and 10 mL of acetonitrile.

At a temperature of about 35°C, it was magnetically stirred for 45 minutes before adding 3.15 mL of 3-pyridinecarboxaldehyde dropwise. The precipitated pale yellowish product was filtered, washed in 50 mL of C₂H₅OH, and dried at room temperature. The dry precipitate was weighed and found to have a 50% yield.

The second bridging ligand **(E)-1-(pyridin-3-ylmethylene)urea (L-2)** was also obtained as a result of the condensation reaction between 3-pyridinecarboxaldehyde (nicotinaldehyde) and semicarbazide. Semicarbazide (1 g, 7.5 mmol) was dissolved in 50 mL H₂O under magnetic stirring, adding 1.3 mL 3-pyridinecarboxaldehyde dropwise, then the temperature of the solution was raised to about 50°C, stirring for 2 hours. After stirring, the solution was left for crystallization for 72 hours.

The obtained precipitate was filtered, washed in 50 mL of C₂H₅OH and was left to dry at room temperature for 48 hours. The white precipitate was weighed, giving a yield of 44%.

3. RESULTS AND DISCUSSIONS

High-performance instrumental methods such as IR spectroscopy, which is the most suitable method for identifying functional groups in the structure of organic compound molecules, were used to decipher the composition and structure of the synthesized ligands. Infrared radiation (IR) is a region of the electromagnetic spectrum that includes the visible and microwave regions and has wavelengths of the order of 10⁻⁵ m.

Wavelengths in the 2.5-25 μm range are used to record IR spectra in order to determine the structure of organic compounds (most often the wave numbers cover the range 400-4000 cm^{-1}). An IR spectrum contains absorption bands caused by vibrations that occur simultaneously with the participation of all atoms in the molecular structure (normal vibrations) of the analyzed organic compound. The position of an absorption band formed by vibrational excitation of a particular functional group in the spectrum is well defined, varying within narrow limits with the environment of functional group within the molecule. An absorption band characteristic of the same functional group is found at almost the same wavenumber value in the IR spectrum of any molecule (characteristic group vibrations). This fact enables the identification of a molecule's component structural elements by assigning characteristic absorption bands in the IR spectrum [5].

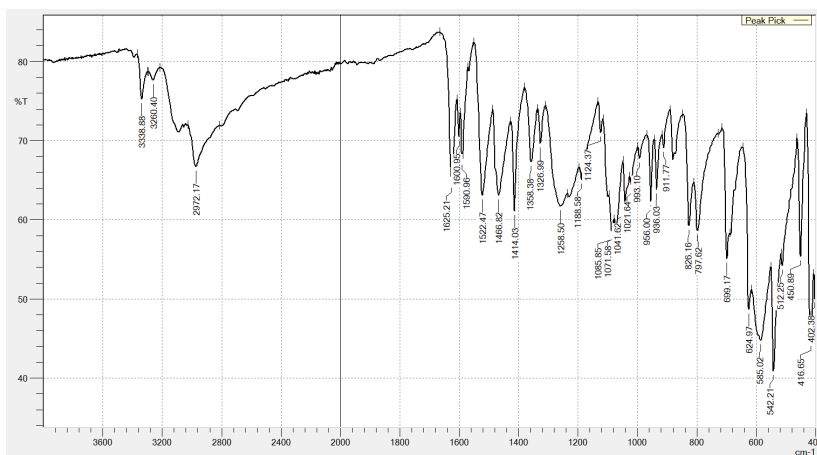


Figure 2. IR spectrum of the L-1 ligand

The IR spectrum (Figure 2) shows the presence of functional groups characteristic of compound L-1, as assigned in Table 1.

At the same time, theoretical calculations for the L-1 and L-2 ligands were done, obtaining the most energetically stable geometric structure. The calculations were carried out using the GAUSSIAN set of modern programs, the DFT theory and the standard 6-31G basis set. The theoretical vibrations of the functional groups shown in Figure 3 and Figure 6, as well as the theoretical wavelengths shown in Table 2 and Table 4, were obtained.

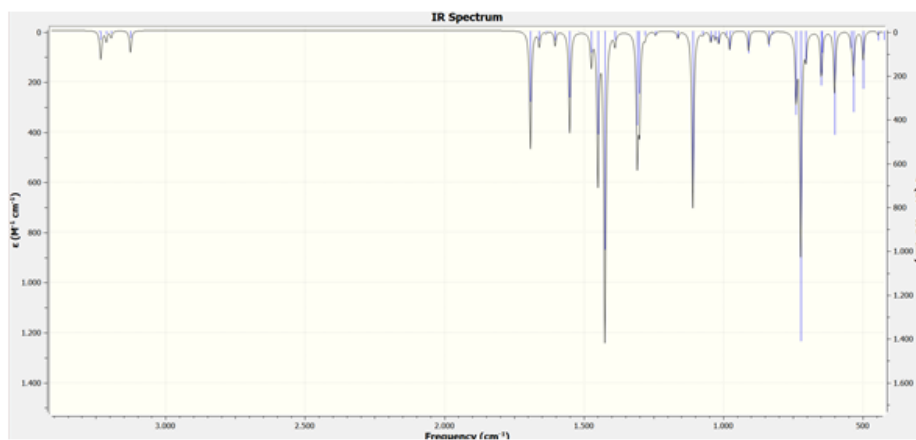
The presence of various electron-donating atoms in the L-1 compound, such as the nitrogen atom of the pyridine ring, the nitrogen atom of the amine group, the sulfur atom, and so on, allows to formulate the hypotheses regarding the compound's potential use as a monodentate and bidentate (bridging) coordinating agent.

Table 1. Functional groups and wavelengths characteristic of ligand L-1

Functional groups	Practical wavelength
C=S	1258.5 cm^{-1}
N-C-N	1071.58 cm^{-1} ; 1085.85 cm^{-1}
C-H:C=C:C=N	797.62 cm^{-1} ; 826.16 cm^{-1}
The ring vibrations	1590.96 cm^{-1} , 1600.95 cm^{-1}
C-H	2972.17 cm^{-1}
NH2	3260.40 cm^{-1} ; 3338.88 cm^{-1}

Table 2. Functional groups and theoretical wavelengths assigned to the ligand L-1

Functional groups	Theoretical wavelength
C=S	1300.78 cm^{-1}
N-C-N	1044.82 cm^{-1} ; 1074.33 cm^{-1}
C-H:C=C:C=N	704.11 cm^{-1} ; 738.70 cm^{-1} ; 909.64 cm^{-1}
The ring vibrations	1603.35 cm^{-1} ; 1635.35 cm^{-1}
C-H	3125.93 cm^{-1}
NH2	3591.06 cm^{-1} ; 3731.09 cm^{-1}

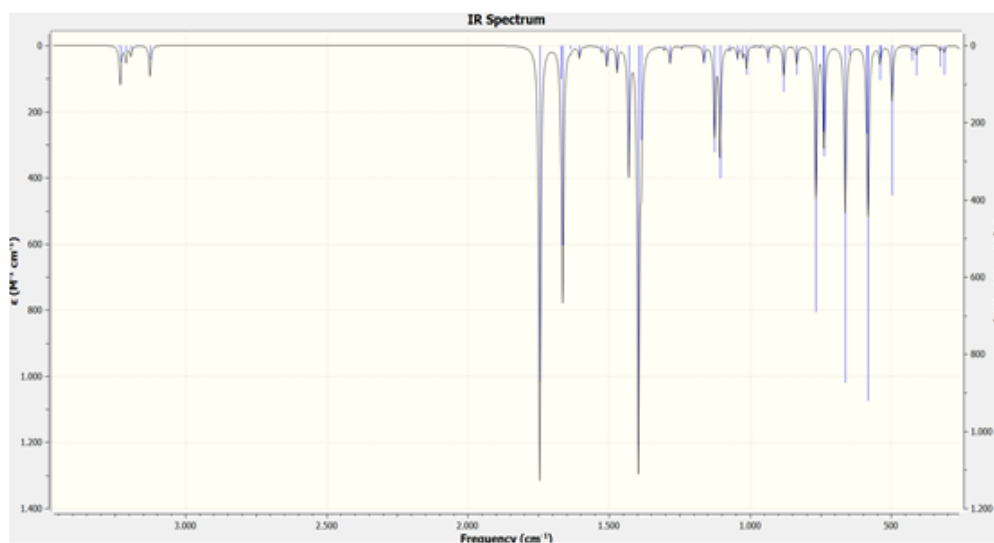
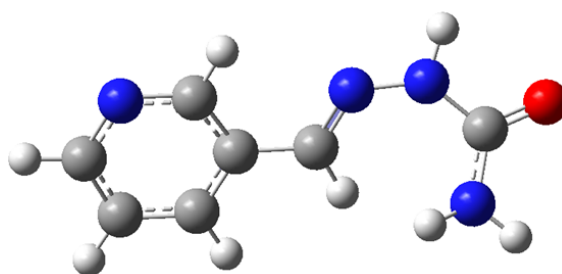
**Figure 3.** Theoretical spectrum of the L-1 ligand

The L-1 bridging ligand molecule is illustrated in Figure 4 and the L-2 ligand molecule is illustrated in Figure 7.

The presence of functional groups characteristic of compound L-2, as assigned in Table 3, can be seen in the IR spectrum (Figure 5).

Table 4. Functional groups and theoretical wavelengths assigned to the ligand L-2

Functional groups	Theoretical wavelength
C=O	1745.19 cm^{-1}
N-C-N	1073.52 cm^{-1} ; 1125.56 cm^{-1}
C-H:C=C:C=N	737.38 cm^{-1} ; 880.92 cm^{-1}
The ring vibrations	1604.81 cm^{-1} ; 1635.79 cm^{-1}
C-H	3125.67 cm^{-1}
NH2	3613.34 cm^{-1} ; 3748.41 cm^{-1}

**Figure 6.** Theoretical spectrum of the L-2 ligand**Figure 7.** The L-2 ligand molecule

Compound L-2, like L-1, has a set of electron-donating atoms capable of forming coordinate bonds, the only difference being the sulfur atom replaced by an oxygen atom.

SYNTHESIS AND STUDY OF COORDINATING AGENTS FOR THE SYNTHESIS OF NEW COORDINATION COMPOUNDS

Analysis methods such as IR spectroscopy and a set of modern GAUSSIAN programs were used to determine the composition and structure of the obtained compounds.

4. CONCLUSIONS

The primary findings of this study are the development of methods for the synthesis of two ligands based on the condensation reaction of compounds as semicarbazide (hydrazinecarboxamides) and semithiocarbohydrazide (hydrazinecarbothioamides) with the carbonyl compound 3-pyridinecarboxaldehyde. Two compounds were obtained: (E)-1-(pyridin-3-ylmethylene)thiourea (L-1) and (E)-1-(pyridin-3-ylmethylene)urea (L-2). The structure and composition of these compounds were determined using theoretical calculations with the GAMESS software package, as well as by means of IR spectroscopy.

The ligands will then be described using nuclear magnetic resonance (NMR) to specify their composition and structure before being used in the synthesis of coordination compounds of transition metals (Zn, Cd, Fe, etc.) with useful properties for agriculture and industry.

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