

MONITORING THE REACTIVITY OF THE COORDINATED THIOSEMICARBAZONES USING PHYSICAL METHODS

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The presentation is dedicated to the investigation of the reactivity of the ligands. The thiosemicarbazide $R_1R_2N(1)-N(2)R_3-C(3)(=S)-N(4)R_4R_5$ is a relevant species allowing to study the influence of the coordination on the properties of the ligands. The last years we have investigated the impact of coordination on each atom from this fragment (N(1), N(2), C(3), S, and N(4)), changing the nature of the metal ions, origin of the carbonyl partner, the place, size and nature of the substituents R. As a result we have concluded that the coordination manifests a direct and indirect influence on the reactivity of the each constituting atom. The noncoordinated thiosemicarbazide is able to form the thiosemicarbazones after the condensation via the hydrazine N(1) atom, when $R_1=R_2=H$. This property is the most important and gives rise to an impressive number of potential ligands and coordination compounds having different composition, structure and properties. The condensation via nitrogen atom N(4) was observed for the noncoordinated thiosemicarbazide ($R_4=R_5=H$), when it reacts with α -diketones and produces heterocyclic compounds. The third reaction known for the free thiosemicarbazide was the thioalkylation. The investigation of the behavior of the coordinated thiosemicarbazide fragments, has demonstrated a real increase of the reactivity of each atom, and a series of new transformations were described.

- When $R_1=Ph$, $R_2=H$, the coordination to the nickel(II), cobalt(III), iron(II) and palladium via N(1) provokes the one-electron oxidation of the ligand, formation of the anion-radicals, stabilized as ligands.
- The coordination as chelate ligand via N(1)S donor atoms gives rise to the activation of the protolytic properties and deprotonation of the fragment.
- Thioalkylation changes the coordination mode of the fragment from N(1)S to N(1)N(4) and promote the activation of the marginal group N(4) R_4R_5 when $R_4=R_5=H$
- After coordination the thioalkyl groups can be removed by Raney nickel or substituted by alkoxy groups in the presence of sodium alcoholates.
- The oxidative dimerisation via $-S-S-$ bridges in the presence of the manganese ensures the and formation of new ligands incorporated in the complexes of different nuclearity.
- For the marginal group N(4) R_4R_5 when $R_4=R_5=H$ a series of transformations promoted by coordination was described:
 - Addition of a carbonyl molecule, formation of the hemiaminals stabilized as ligands;
 - Formation of the esters after addition;
 - Deprotonation of the N(4) and hemiaminal hydroxil.
 - Condensation of the N(4) R_4R_5 when $R_4=R_5=H$, formation of the symmetric and asymmetric ligands
 - Oxidative amidation of the carbonyls using the coordinated N(4)H₂ group.
 - Formation of the nitozoamides promoted by palladium(II).

The changes of the thiosemicarbazide fragment's reactivity were monitored using a large number of physical methods (X ray analysis, electrochemistry, spectral methods, mass-spectrometry, magnetochemistry, etc), which give a wide information and unequivocal demonstrations.