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# QUANTUM-CHEMICAL STUDY OF GLICLAZIDE MOLEKULE IN VARIOUS SOLVENTS

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## ABSTRACT

For years now, results obtained through quantum chemistry methods have made it possible to assess the geometry and electronic structure of organic molecules. In coordination chemistry, the theoretical evaluation of a complex molecule's potential as a ligand is highly important both for studying the mechanism of complex formation and for selecting optimal conditions for synthesizing coordination compounds. To study the ability of the gliclazide molecule to form coordination bonds with a central atom (complex-forming metal), we calculated and analyzed its energetic, electronic, and structural properties using the semi-empirical Quantum-Chemical AM1 method.

**KEYWORDS:** Coordination compounds, Ligands, donor atom, complexation, diabetes.

## INTRODUCTION

Gliclazide is an antidiabetic agent from the sulfonylurea group. Its hypoglycemic effect is associated with enhanced insulin secretion during pancreatic beta-cell activity. Gliclazide increases insulin release and improves its pharmacodynamics. (Fig. 1, Fig.2)

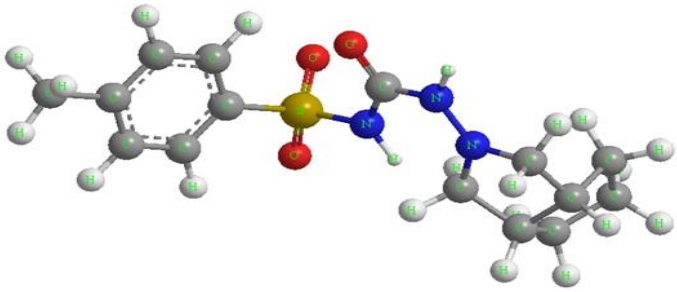

***Fig. 1: Gliclazide molecule.***

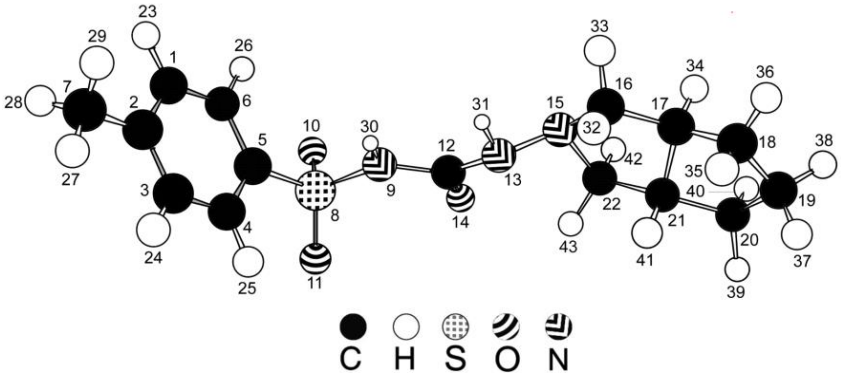


***Fig. 2: Numbering of atoms in the gliclazide molecule.***

Calculations were carried out for the isolated molecule in the gas phase as well as in various solvents. The solvents selected—water, dimethyl sulfoxide (DMSO), methanol, ethanol, acetone, chloroform, and hexane—differ in their dielectric constants (Table 1).

***Table 1: Heat of formation (ΔH) and dipole moment (μ) of the gliclazide molecule in gas and various solvents.***

| Heat of formation, kJ/mol | Dipole moment, Debye |
|---|---|
| **Gas** | |
| -159.127 | 8.211 |
| **Water** | |
| -311.048 | 15.797 |
| **Dimethylsulfoxide** | |
| -307.136 | 15.662 |
| **Methanol** | |
| -302.862 | 15.482 |
| **Ethanol** | |
| -312.642 | 14.933 |
| **Acetone** | |
| -309.827 | 14.819 |
| **Chloroform** | |
| -257.374 | 12.471 |
| **Hexane** | |
| -208.102 | 10.694 |

The heat of formation values of the gliclazide molecule are all negative, reaching a maximum in the gas phase (-159.127 kJ/mol), which suggests that solvents significantly increase the molecule's stability. The dipole moment is lowest in the gas phase (8.211 Debye) and increases in all solvents (ranging from 10.694 to 15.797 Debye), which can be explained by the induction of a dipole moment.

The analysis of total atomic populations (electron density) and their effective charges revealed a significant electron density deficit on the sulfur atom **S(8)** (charge q = +2.874), which immediately excludes this atom from participating in complex formation.

Relatively high values of electron density (0.343 to 0.530) and negative charge (-0.343 to -0.530) are observed on the oxygen atoms **O(14).** The bond length between atoms **C(12)-O(14)** ranges from 1.248 to 1.267 Å, which suggests that this oxygen atom is in an sp hybrid state and forms a double bond with carbon **C(12).** Analysis of the valence orbitals of the **O(14)** atom indicates that one non-hybridized py orbital is involved in π-bond formation, while a high electron density on the pz orbital suggests the presence of a lone electron pair—thus excluding **O(14)** from complex formation (Tabl.2).

Carbon atoms show an electron density deficit, except for atom **C(5),** which has a relatively high negative charge ranging from -0.853 to -0.884, compared to other carbon atoms. The bond lengths **C(4)-C(5)** and **C(5)-C(6)** are approximately 1.400 Å, and the **C(4)-C(5)-S(8)** bond angle ranges from 114.268° to 121.153°, indicating that **C(5)** is in an $sp^2$ hybrid state. However, analysis of orbital population reveals that the electron pair is localized on the pz orbital, excluding its participation in complexation.

A different picture is observed for the nitrogen atom N(9). Its electron density ranges from 5.842 to 5.858 with a charge of q = -0.842 to -0.858. The bond length **N(9)-C(12**) is 1.408–1.413 Å, and the bond angle S(8)-N(9)-H(30) is 119.947–122.281°, suggesting that the nitrogen atom is in an $sp^2$ hybrid state. However, orbital population analysis shows that the electron pair of **N(9)** is concentrated on the pz orbital. Since π orbitals correspond to this state, the orbital overlap area between donor and acceptor atoms is effectively zero. Therefore, despite its high negative charge, **N(9)** cannot provide an electron pair to form a σ donor-acceptor bond, excluding it from participation in complex formation.

Although nitrogen atom N(15) has relatively high electron density (5.117–5.858), it has a low negative charge (-0.312 to -0.231). The bond angle **N(13)-N(15)-C(16)** is 110.856–111.641°, and bond lengths **N(15)-C(16)** and **N(15)-C(22)** are 1.512–1.517 Å, indicating $sp^3$ hybridization. All four hybrid orbitals are involved in single σ-bonds with neighboring atoms, meaning **N(15)** also lacks the ability to form a donor-acceptor bond.

***Table 2: Dielectric permittivity of solvents (ε), charge on atoms (q) and distribution of electrons on atomic orbitals (s, p) in the gliclazide molecule.***

| № | Solvent | atom | Charge on an atom | Electron density per atom | n | Distribution of electrons over orbitals | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | ns | $np_x$ | $np_y$ | $np_z$ |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 1 | Gas | C(5) | -0.853 | 4.853 | 2 | 1.318 | 1.077 | 1.221 | 1.237 |
| | | S(8) | 2.874 | 3.126 | 3 | 0.985 | 0.729 | 0.712 | 0.700 |
| | | N(9) | -0.858 | 5.858 | 2 | 1.577 | 1.673 | 1.314 | 1.295 |
| | | O(10) | -0.913 | 6.913 | 2 | 1.932 | 1.427 | 1.845 | 1.709 |
| | | O(11) | -0.914 | 6.914 | 2 | 1.932 | 1.709 | 1.572 | 1.701 |
| | | C(12) | 0.385 | 3.615 | 2 | 1.219 | 0.753 | 0.794 | 0.848 |
| | | N(13) | -0.234 | 5.234 | 2 | 1.599 | 1.355 | 1.264 | 1.015 |
| | | O(14) | -0.343 | 6.343 | 2 | 1.919 | 1.452 | 1.417 | 1.556 |
| | | N(15) | -0.154 | 5.154 | 2 | 1.681 | 1.246 | 1.189 | 1.038 |
| | | H(31) | 0.185 | 0.815 | 1 | 0.815 | | | |
| 2 | $H_2O$, Water 78.5 | C(5) | -0.878 | 4.878 | 2 | 1.300 | 1.068 | 1.197 | 1.312 |
| | | S(8) | 2.986 | 2.986 | 3 | 0.940 | 0.675 | 0.692 | 0.708 |
| | | N(9) | -0.844 | 5.844 | 2 | 1.555 | 1.254 | 1.195 | 1.841 |
| | | O(10) | -1.056 | 7.056 | 2 | 1.930 | 1.810 | 1.754 | 1.562 |
| | | O(11) | -1.057 | 7.057 | 2 | 1.930 | 1.806 | 1.707 | 1.614 |
| | | C(12) | 0.488 | 3.512 | 2 | 1.834 | 0.799 | 0.815 | 0.715 |
| | | N(13) | -0.310 | 5.310 | 2 | 1.478 | 1.006 | 1.097 | 1.730 |
| | | O(14) | -0.530 | 6.530 | 2 | 1.919 | 1.745 | 1.240 | 1.626 |
| | | N(15) | -0.117 | 5.117 | 2 | 1.692 | 1.005 | 1.075 | 1.346 |
| | | H(31) | 0.286 | 0.714 | 1 | 0.714 | | | |
| 3 | $C_2H_6SO$, DMSO 49.0 | C(5) | -0.879 | 4.879 | 2 | 1.300 | 1.068 | 1.198 | 1.312 |
| | | S(8) | 2.983 | 3.017 | 3 | 0.941 | 0.676 | 0.692 | 0.709 |
| | | N(9) | -0.845 | 5.845 | 2 | 1.555 | 1.254 | 1.194 | 1.842 |
| | | O(10) | -1.053 | 7.053 | 2 | 1.930 | 1.809 | 1.753 | 1.561 |
| | | O(11) | -1.054 | 7.054 | 2 | 1.930 | 1.805 | 1.707 | 1.611 |
| | | C(12) | 0.487 | 3.513 | 2 | 1.184 | 0.799 | 0.815 | 0.715 |
| | | N(13) | -0.311 | 5.311 | 2 | 1.477 | 1.006 | 1.097 | 1.731 |
| | | O(14) | -0.527 | 6.527 | 2 | 1.919 | 1.746 | 1.239 | 1.624 |
| | | N(15) | -0.117 | 5.117 | 2 | 1.692 | 1.005 | 1.075 | 1.346 |
| | | H(31) | 0.285 | 0.715 | 1 | 0.715 | | | |
| 4 | $CH_3OH$, Methanol 32.6 | C(5) | -0.877 | 4.877 | 2 | 1.300 | 1.068 | 1.198 | 1.310 |
| | | S(8) | 2.981 | 3.019 | 3 | 0.942 | 0.676 | 0.692 | 0.709 |
| | | N(9) | -0.845 | 5.845 | 2 | 1.555 | 1.254 | 1.193 | 1.843 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | O(10) | -1.050 | 7.050 | 2 | 1.930 | 1.808 | 1.751 | 1.560 |
| | | O(11) | -1.051 | 7.051 | 2 | 1.930 | 1.805 | 1.708 | 1.608 |
| | | C(12) | 0.486 | 3.514 | 2 | 1.184 | 0.799 | 0.816 | 0.716 |
| | | N(13) | -0.312 | 5.312 | 2 | 1.477 | 1.006 | 1.096 | 1.733 |
| | | O(14) | -0.523 | 6.523 | 2 | 1.919 | 1.746 | 1.236 | 1.621 |
| | | N(15) | -0.115 | 5.115 | 2 | 1.692 | 1.003 | 1.075 | 1.345 |
| | | H(31) | 0.284 | 0.716 | 1 | 0.716 | | | |
| 5 | $C_2H_5OH$, Ethanol 24.3 | C(5) | -0.884 | 4.884 | 2 | 1.300 | 1.072 | 1.197 | 1.315 |
| | | S(8) | 2.975 | 3.025 | 3 | 0.944 | 0.679 | 0.695 | 0.708 |
| | | N(9) | -0.841 | 5.841 | 2 | 1.557 | 1.258 | 1.305 | 1.721 |
| | | O(10) | -1.041 | 7.041 | 2 | 1.930 | 1.844 | 1.806 | 1.461 |
| | | O(11) | -1.047 | 7.047 | 2 | 1.930 | 1.769 | 1.634 | 1.714 |
| | | C(12) | 0.468 | 3.532 | 2 | 1.203 | 0.806 | 0.796 | 0.726 |
| | | N(13) | -0.262 | 5.262 | 2 | 1.552 | 1.005 | 1.179 | 1.526 |
| | | O(14) | -0.485 | 6.485 | 2 | 1.917 | 1.801 | 1.261 | 1.506 |
| | | N(15) | -0.165 | 5.165 | 2 | 1.671 | 1.031 | 1.128 | 1.335 |
| | | H(31) | 0.242 | 0.758 | 1 | 0.758 | | | |
| 6 | $(CH_3)_2CO$, Acetone 20.7 | C(5) | -0.884 | 4.884 | 2 | 1.300 | 1.072 | 1.198 | 1.314 |
| | | S(8) | 2.974 | 3.026 | 3 | 0.944 | 0.679 | 0.695 | 0.709 |
| | | N(9) | -0.842 | 5.842 | 2 | 1.557 | 1.257 | 1.309 | 1.718 |
| | | O(10) | -1.039 | 7.039 | 2 | 1.930 | 1.842 | 1.806 | 1.460 |
| | | O(11) | -1.045 | 7.045 | 2 | 1.930 | 1.770 | 1.633 | 1.712 |
| | | C(12) | 0.468 | 3.532 | 2 | 1.203 | 0.806 | 0.796 | 0.727 |
| | | N(13) | -0.263 | 5.263 | 2 | 1.550 | 1.004 | 1.183 | 1.525 |
| | | O(14) | -0.482 | 6.482 | 2 | 1.917 | 1.802 | 1.260 | 1.504 |
| | | N(15) | -0.164 | 5.164 | 2 | 1.671 | 1.032 | 1.128 | 1.332 |
| | | H(31) | 0.242 | 0.758 | 1 | 0.758 | | | |
| 7 | $CHCl_3$, Chloroform 4.7 | C(5) | -0.871 | 4.871 | 2 | 1.306 | 1.074 | 1.204 | 1.287 |
| | | S(8) | 2.945 | 3.055 | 3 | 0.956 | 0.687 | 0.698 | 0.714 |
| | | N(9) | -0.852 | 5.852 | 2 | 1.563 | 1.278 | 1.359 | 1.653 |
| | | O(10) | -0.994 | 6.994 | 2 | 1.930 | 1.851 | 1.826 | 1.387 |
| | | O(11) | -1.006 | 7.006 | 2 | 1.930 | 1.724 | 1.594 | 1.757 |
| | | C(12) | 0.448 | 3.552 | 2 | 1.205 | 0.789 | 0.792 | 0.766 |
| | | N(13) | -0.266 | 5.266 | 2 | 1.555 | 1.028 | 1.301 | 1.381 |
| | | O(14) | -0.427 | 6.427 | 2 | 1.917 | 1.826 | 1.258 | 1.425 |
| | | N(15) | -0.148 | 5.148 | 2 | 1.669 | 0.973 | 1.072 | 1.435 |
| | | H(31) | 0.218 | 0.782 | 1 | 0.782 | | | |
| 8 | $C_6H_{12}$, Hexane 1.9 | C(5) | -0.868 | 4.868 | 2 | 1.313 | 1.081 | 1.212 | 1.262 |
| | | S(8) | 2.916 | 3.084 | 3 | 0.968 | 0.715 | 0.706 | 0.695 |
| | | N(9) | -0.863 | 5.863 | 2 | 1.573 | 1.412 | 1.548 | 1.730 |
| | | O(10) | -0.944 | 6.944 | 2 | 1.931 | 1.608 | 1.863 | 1.543 |
| | | O(11) | -0.963 | 6.963 | 2 | 1.931 | 1.669 | 1.528 | 1.835 |
| | | C(12) | 0.423 | 3.577 | 2 | 1.209 | 0.756 | 0.766 | 0.846 |
| | | N(13) | -0.261 | 5.261 | 2 | 1.559 | 1.223 | 1.432 | 1.047 |
| | | O(14) | -0.365 | 6.365 | 2 | 1.918 | 1.600 | 1.367 | 1.481 |
| | | N(15) | -0.141 | 5.141 | 2 | 1.662 | 1.048 | 1.048 | 1.383 |
| | | H(31) | 0.193 | 0.807 | 1 | 0.807 | | | |

A different situation is found with nitrogen atom **N(13).** It has a relatively high negative charge (-0.234 to -0.312), a bond angle **C(12)-N(13)-N(15)** of 116.630–121.549°, and bond lengths **C(12)-N(13)** (1.443–1.386 Å) and **N(13)-N(15)** (1.376–1.396 Å), indicating $sp^2$ hybridization. Orbital analysis shows a deficiency of electrons in the Pz orbital, with lone pairs concentrated in $sp^2$ hybrid orbitals. The hydrogen atom H(31) bonded to N(13) shows a large electron density deficit and a low charge (q = +0.185 to +0.286), suggesting that under certain conditions it may act as an acidic proton. Therefore, through substitution of this hydrogen, **N(13)** can form a coordination bond with the central atom.

Oxygen atoms **O(10)** and **O(11)** possess high negative charges, with their electron densities ranging from 6.056 to 7.914. The bond lengths between **S(8)-O(10)** and **S(8)-O(11)** range from 1.398 to 1.425 Å, indicating that both oxygen atoms are in $sp^2$ hybridization states.

However, orbital population analysis shows that the lone pair on **O(11)** is concentrated on the Pz orbital, whichsimilar to **N(9)** likely excludes it from participating in complex formation.

In contrast, oxygen atom **O(10)** presents a different scenario. Orbital population data shows an electron deficiency on the pz orbital, while lone pairs are concentrated in the $sp^2$ hybrid orbitals. Therefore, **O(10)** has the ability to participate in coordination bond formation.

***Table 3: Bond length (Rij) and bond order (Pij) in the gliclazide molecule.***

| № | Interatomic bond | | solvent | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Gas | $H_2O$, | $C_2H_6SO$, | $CH_3OH$, | $C_2H_5OH$, | $(CH_3)_2CO$, | $CHCl_3$, | $C_6H_{12}$, |
| 1 | C(4)–C(5) | Leng, Å | 1.400 | 1.413 | 1.412 | 1.412 | 1.411 | 1.411 | 1.408 | 1.401 |
| | | Bond order | 1.369 | 1.316 | 1.317 | 1.318 | 1.320 | 1.321 | 1.340 | 1.365 |
| 2 | C(5)–C(6) | Leng, Å | 1.401 | 1.401 | 1.402 | 1.401 | 1.403 | 1.403 | 1.402 | 1.404 |
| | | Bond order | 1.362 | 1.357 | 1.356 | 1.357 | 1.350 | 1.351 | 1.355 | 1.348 |
| 3 | S(8)–N(9) | Leng, Å | 1.662 | 1.620 | 1.621 | 1.622 | 1.627 | 1.627 | 1.638 | 1.653 |
| | | Bond order | 0.556 | 0.658 | 0.657 | 0.654 | 0.645 | 0.644 | 0.614 | 0.578 |
| 4 | S(8)–O(10) | Leng, Å | 1.398 | 1.425 | 1.425 | 1.424 | 1.422 | 1.422 | 1.411 | 1.401 |
| | | Bond order | 1.274 | 1.142 | 1.145 | 1.148 | 1.157 | 1.159 | 1.202 | 1.250 |
| 5 | S(8)–O(11) | Leng, Å | 1.398 | 1.425 | 1.425 | 1.424 | 1.424 | 1.424 | 1.415 | 1.406 |
| | | Bond order | 1.273 | 1.142 | 1.144 | 1.147 | 1.150 | 1.152 | 1.190 | 1.230 |
| 6 | N(9)–C(12) | Leng, Å | 1.411 | 1.413 | 1.413 | 1.413 | 1.408 | 1.408 | 1.410 | 1.412 |
| | | Bond | 0.985 | 0.993 | 0.992 | 0.992 | 1.010 | 1.009 | 0.998 | 0.986 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | order | | | | | | | | |
| *7* | C(12)–N (13) | Leng, Å | 1.443 | 1.386 | 1.386 | 1.386 | 1.419 | 1.419 | 1.425 | 1.436 |
| | | Bond order | 1.008 | 1.170 | 1.168 | 1.165 | 1.075 | 1.075 | 1.044 | 1.012 |
| *8* | C(12)–O (14) | Leng, Å | 1.248 | 1.267 | 1.266 | 1.265 | 1.260 | 1.259 | 1.253 | 1.248 |
| | | Bond order | 1.755 | 1.560 | 1.564 | 1.568 | 1.634 | 1.635 | 1.688 | 1.743 |
| *9* | N(13)–N (15) | Leng, Å | 1.396 | 1.384 | 1.383 | 1.383 | 1.380 | 1.379 | 1.377 | 1.376 |
| | | Bond order | 0.959 | 0.942 | 0.943 | 0.943 | 0.966 | 0.966 | 0.970 | 0.976 |
| *10* | N(15)–C (16) | Leng, Å | 1.513 | 1.515 | 1.515 | 1.515 | 1.515 | 1.515 | 1.515 | 1.512 |
| | | Bond order | 0.955 | 0.954 | 0.954 | 0.954 | 0.942 | 0.942 | 0.944 | 0.944 |
| *11* | N(15)–C (22) | Length, Å | 1.507 | 1.517 | 1.517 | 1.517 | 1.511 | 1.511 | 1.510 | 1.509 |
| | | Bond order | 0.954 | 0.948 | 0.948 | 0.948 | 0.942 | 0.942 | 0.943 | 0.946 |

***Table 4: Values of bond angles between atoms in the gliclazide molecule.***

| № | Valence angle | Solvent | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Gas | $H_2O$, | $C_2H_6SO$, | $CH_3OH$, | $C_2H_5OH$, | $(CH_3)_2CO$, | $CHCl_3$, | $C_6H_{12}$, |
| 1 | C(4)–C(5)–S(8) | 120.805 | 114.268 | 114.219 | 114.162 | 115.175 | 115.120 | 115.856 | 121.153 |
| 2 | C(5)–S(8)–N(9) | 97.970 | 106.096 | 106.018 | 105.925 | 105.267 | 105.235 | 103.333 | 99.035 |
| 3 | C(5)–S(8)–O(10) | 108.599 | 109.264 | 109.213 | 109.176 | 109.459 | 109.376 | 108.982 | 109.121 |
| 4 | C(5)–S(8)–O(11) | 108.643 | 109.573 | 109.514 | 109.470 | 110.146 | 110.177 | 109.666 | 109.380 |
| 5 | S(8)–N(9)–C(12) | 123.741 | 121.896 | 121.910 | 121.923 | 123.618 | 123.722 | 124.227 | 125.153 |
| 6 | N(9)–C(12)–N(13) | 118.698 | 119.324 | 119.300 | 119.269 | 118.700 | 118.653 | 117.990 | 117.208 |
| 7 | N(9)–C(12)–O(14) | 117.784 | 116.516 | 116.550 | 116.594 | 117.075 | 117.083 | 117.620 | 118.179 |
| 8 | C(12)–N(13)–N(15) | 116.630 | 121.549 | 121.536 | 121.536 | 118.283 | 118.280 | 118.797 | 116.910 |
| 9 | N(13)–N(15)–C(16) | 111.288 | 111.363 | 111.360 | 111.357 | 110.972 | 110.964 | 110.856 | 111.641 |
| 10 | N(13)–N(15)–C(22) | 114.426 | 113.158 | 113.183 | 113.188 | 115.857 | 115.917 | 116.208 | 116.085 |
| 11 | S(8)–N(9)–H(30) | 119.947 | 122.281 | 122.281 | 122.277 | 120.725 | 120.683 | 120.024 | 119.028 |
| 12 | C(12)–N(13)–H(31) | 111.389 | 119.375 | 119.375 | 119.388 | 113.623 | 113.787 | 112.580 | 113.619 |

## RESULT AND CONCLUSION

Based on the analysis above, the gliclazide molecule is capable of exhibiting properties of a bidentate ligand. According to Chugaev's rule for chelate ring formation, it can form a coordination bond with a central atom via substitution of the hydrogen atom bonded to nitrogen **N(13)** and through the oxygen atom O(10), thereby forming a six-membered metallacycle.

Based on the assumptions discussed, a hypothetical model of a neutral cobalt chloride complex was developed using the MM2 quantum-chemical method. In this model, the

coordination number of the cobalt atom is six, and the coordination bond with the ligand molecule is formed through the nitrogen atom of the imino group and one of the oxygen atoms from the sulfo group.

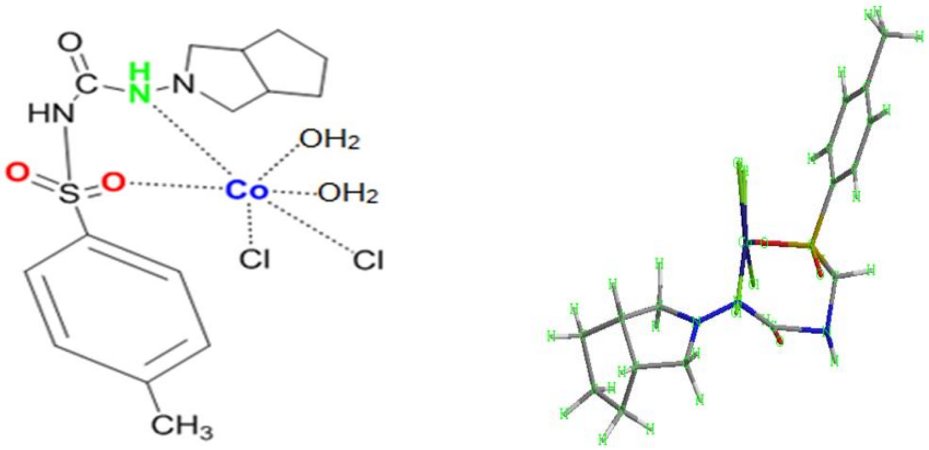


***Figure 3: Model of a cobalt chloride complex compound.***

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