CRYSTAL AND IN SILICO INVESTIGATION OF A MULTIFUNCTIONAL N,O,S-DONOR LIGAND: STRUCTURAL PREORGANIZATION, HYDROGEN BONDING AND ELECTROSTATIC FEATURES

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Abstract. The coordination potential of organic ligands is largely dictated by their intrinsic structural and electronic characteristics in the free state. In this work, a multifunctional ligand containing nitrogen, oxygen, and sulfur donor atoms was investigated exclusively in its uncoordinated form using crystal-structure-based and in silico approaches. Detailed analysis of donor–donor distances reveals a favorable N–O separation of 2.875 Å, indicating effective preorganization for chelation, while significantly larger N–S (3.880 Å) and O–S (4.488 Å) distances suggest restricted accessibility of the sulfur donor in the free ligand conformation. Intramolecular hydrogen bonding interactions were identified and shown to play a key role in stabilizing the observed geometry. Molecular electrostatic potential (MEP) mapping further highlights electron-rich regions localized primarily on the nitrogen and oxygen atoms, supporting their dominant donor character. The combined structural and electronic analyses provide a comprehensive ligand-only perspective and establish a reliable foundation for understanding the coordination aptitude of multifunctional ligands prior to metal binding.

Keywords: multifunctional ligand; donor geometry; hydrogen bonding; molecular electrostatic potential; crystal structure

Аннотация. Координационный потенциал органических лигандов в значительной степени определяется их внутренними структурными и электронными характеристиками в свободном состоянии. В данной работе многофункциональный лиганд, содержащий донорные атомы азота, кислорода и серы, исследовался исключительно в некоординированной форме с использованием подходов, основанных на кристаллической структуре и компьютерном моделировании. Детальный анализ расстояний между донорами показывает благоприятное расстояние N–O, равное 2,875 Å, что указывает на эффективную предварительную организацию для хелатирования, в то время как значительно большие расстояния N–S (3,880 Å) и O–S (4,488 Å) предполагают ограниченную доступность донора серы в свободной конформации лиганда. Были идентифицированы внутримолекулярные водородные связи, которые, как было показано, играют ключевую роль в стабилизации наблюдаемой геометрии. Картирование молекулярного электростатического потенциала (МЭП) дополнительно

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выделяет богатые электронами области, локализованные преимущественно на атомах азота и кислорода, что подтверждает их доминирующий донорный характер. Совместный структурный и электронный анализ обеспечивает всесторонний взгляд только на лиганд и закладывает надежную основу для понимания координационных способностей многофункциональных лигандов до связывания с металлом.

Ключевые слова: многофункциональный лиганд; геометрия донора; водородная связь; молекулярный электростатический потенциал; кристаллическая структура

Annotatsiya. Organik ligandlarning koordinatsiya potensiali asosan ularning erkin holatdagi ichki strukturaviy va elektron xususiyatlari bilan belgilanadi. Ushbu ishda azot, kislorod va oltingugurt donor atomlarini o'z ichiga olgan ko'p funksiyali ligand faqat kristall strukturaga asoslangan va in silico yondashuvlar yordamida muvofiqlashtirilmagan shaklda o'rganildi. Donor-donor masofalarining batafsil tahlili 2,875 Å ning qulay N-O ajralishini ko'rsatadi, bu esa xelatlanish uchun samarali oldindan tashkil etilganligini ko'rsatadi, N-S (3,880 Å) va O-S (4,488 Å) masofalarining sezilarli darajada kattaroqligi esa erkin ligand konformatsiyasida oltingugurt donorining cheklangan kirish imkoniyatini ko'rsatadi. Molekulyar ichidagi vodorod bog'lanish o'zaro ta'siri aniqlandi va kuzatilgan geometriyani barqarorlashtirishda muhim rol o'ynashi ko'rsatildi. Molekulyar elektrostatik potensial (MEP) xaritalash asosan azot va kislorod atomlarida joylashgan elektronga boy mintaqalarni ko’rsatadi va ularning dominant donorlik xususiyatini qo'llab-quvvatlaydi. Birlashtirilgan strukturaviy va elektron tahlillar faqat ligandga oid keng qamrovli nuqtai nazarni taqdim etadi va metall bog'lanishdan oldin ko'p funksiyali ligandlarning koordinatsiya qobiliyatini tushunish uchun ishonchli poydevor yaratadi.

Kalit so'zlar: ko'p funksiyali ligand; donor geometriyasi; vodorod bog'lanishi; molekulyar elektrostatik potensial; kristall tuzilishi

1. Introduction

Multidentate ligands containing heteroatoms such as nitrogen, oxygen, and sulfur have attracted sustained interest in coordination chemistry due to their versatility and tunable donor properties. The ability of such ligands to stabilize metal centers is not only governed by the identity of the donor atoms but also by their spatial arrangement, conformational flexibility, and electronic characteristics in the free state [1–3]. Consequently, understanding ligand behavior prior to metal coordination has become an essential step in the rational design of coordination compounds.

Crystallographic investigations offer direct insight into ligand geometry and intramolecular interactions, allowing donor atom disposition to be assessed with

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high accuracy. Complementary computational tools, particularly molecular electrostatic potential (MEP) analysis, enable visualization of electron density distribution and provide valuable information on donor strength and reactivity trends [4–6]. In addition, intramolecular hydrogen bonding can significantly influence ligand conformation by locking molecules into energetically favorable geometries, thereby modulating donor accessibility [7,8].

While numerous studies focus on metal complexes derived from multifunctional ligands, ligand-only investigations remain comparatively underexplored despite their importance. Such studies allow intrinsic structural and electronic features to be isolated from metal-induced effects. In this context, the present work is deliberately restricted to the free ligand in its crystalline form. Previously reported analyses such as crystal packing and Hirshfeld surface studies are not reproduced; instead, the emphasis is placed on donor atom arrangement, intramolecular hydrogen bonding, and MEP analysis[9].

The aim of this study is to provide a comprehensive ligand-only evaluation that links crystallographic geometry with electronic features relevant to coordination behavior. By correlating donor–donor distances, hydrogen bonding interactions, and electrostatic potential distribution, this work establishes a coherent framework for understanding the coordination aptitude of multifunctional ligands prior to metal binding[10].

2. Materials and Methods

2.1 Crystal structure and geometric analysis

The crystallographic information file (CIF) of the ligand was used as the primary source of structural data. The molecular geometry was visualized using standard crystallographic software, and hydrogen atoms were included according to crystallographic conventions. Potential donor atoms were identified based on chemical functionality and lone pair availability.

Donor–donor distances between nitrogen, oxygen, and sulfur atoms were measured directly from the crystallographic coordinates. In addition, the relevant donor–donor angle was determined to assess the overall donor framework geometry. These parameters were used to evaluate the degree of preorganization and potential chelation behavior of the ligand.

2.2 Intramolecular hydrogen bonding analysis

Intramolecular hydrogen bonds were identified based on donor–acceptor (D···A) distances observed in the crystal structure. Hydrogen bonding interactions were considered significant when the D···A distances fell within commonly accepted ranges for stabilizing intramolecular interactions. The role of these hydrogen bonds in shaping ligand conformation and donor accessibility was analyzed qualitatively and quantitatively.

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2.3 Molecular electrostatic potential analysis

MEP calculations were performed on the isolated ligand geometry using a semi-empirical quantum chemical method. The electrostatic potential was mapped onto the molecular surface to visualize regions of negative (electron-rich) and positive (electron-poor) potential. Particular attention was given to the correlation between electron-rich regions and the location of potential donor atoms.

3. Results and Discussion

3.1 Donor atom arrangement and geometry

The ligand under investigation contains three chemically distinct donor atoms: nitrogen, oxygen, and sulfur. Analysis of the crystallographic geometry reveals a non-uniform spatial distribution of these donor sites, which has important implications for coordination behavior.

The nitrogen and oxygen donor atoms are positioned in close proximity, with a measured N–O donor–donor distance of **2.875 Å** (Figure 2). This value lies well within the range typically associated with effective chelation and indicates a high degree of preorganization for simultaneous donor interaction. Such short separations are characteristic of ligands capable of stabilizing metal centers through bidentate coordination and are frequently reported for mixed N,O-donor systems [1,2].



Figure 1. Molecular structure of the ligand showing the labeling and spatial arrangement of the potential donor atoms (O, N, and S).

In contrast, the sulfur atom is spatially displaced relative to the nitrogen and oxygen donors. The measured **N–S distance of 3.880 Å** (Figure 3) exceeds the optimal range for cooperative chelation, suggesting limited accessibility of sulfur as a donor in the free ligand conformation. This trend is even more pronounced for the **O–S separation of 4.488 Å** (Figure 4), which effectively precludes simultaneous involvement of oxygen and sulfur in chelation without substantial conformational rearrangement.

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Figure 2 and 3. Donor–donor distance between N and O atoms (2.875 Å) illustrating favorable bidentate chelation geometry and spatial separation between N and S donor atoms (3.880 Å) indicating limited sulfur accessibility in the free ligand conformation.

Angular analysis provides further insight into the donor framework. The donor–donor angle of approximately **81.8°** reflects a relatively compact geometry that favors chelation between closely spaced donors while imposing geometric constraints on more distant donor atoms. Such angular features are commonly observed in multifunctional ligands where only a subset of donor atoms is optimally positioned in the free state [3].

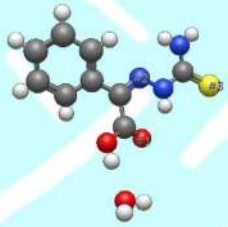


Figure 4. Intramolecular hydrogen bonding interactions in the free ligand, contributing to conformational stabilization.

Overall, the donor geometry indicates a dominant N,O-based donor framework, with sulfur acting as a secondary or latent donor. This asymmetry is not unusual and often arises from a balance between steric effects and intramolecular interactions that stabilize specific conformations in the solid state.

3.2 Influence of intramolecular hydrogen bonding

Intramolecular hydrogen bonding was clearly identified in the crystal structure of the ligand (Figure 5). The observed donor–acceptor distance of approximately **2.61 Å** is indicative of a strong stabilizing hydrogen bond, which plays a central role in defining the observed molecular conformation.Such hydrogen bonding interactions are well known to restrict conformational flexibility by locking ligands into energetically favorable geometries [7,8]. In the present case, intramolecular hydrogen bonding contributes to the stabilization of a conformation in which the nitrogen and oxygen donors are optimally aligned, while the sulfur atom remains spatially displaced. This provides a rational explanation for the extended N–S and O–S distances observed in the donor geometry analysis.

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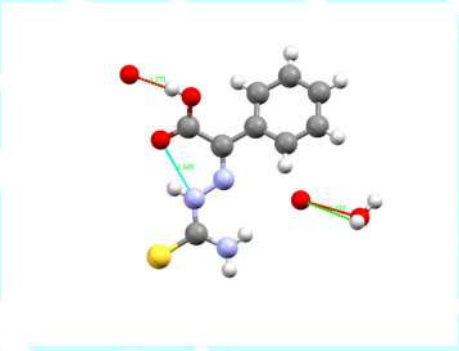


Figure 5. Intramolecular hydrogen bonding interactions in the free ligand, contributing to conformational stabilization.

Importantly, the presence of intramolecular hydrogen bonding does not negate the coordination potential of the ligand. Rather, it reflects the preferred conformation in the absence of external interactions. From a ligand-only perspective, these hydrogen bonds serve as an internal structural element that modulates donor accessibility and contributes to the overall stability of the free ligand.

3.3 Molecular electrostatic potential analysis

The MEP surface of the ligand (Figure 6) provides valuable insight into the electronic features underlying the observed donor geometry. Pronounced regions of negative electrostatic potential are localized primarily around the nitrogen and oxygen atoms, indicating high electron density and strong donor capability.In contrast, the sulfur atom exhibits comparatively weaker negative potential, consistent with its reduced accessibility inferred from geometric analysis. This electronic asymmetry reinforces the conclusion that nitrogen and oxygen constitute the primary donor sites in the free ligand, while sulfur plays a secondary role.



Figure 6. Molecular electrostatic potential (MEP) surface of the ligand, highlighting electron-rich regions around donor atoms.

The strong agreement between geometric parameters, hydrogen bonding effects, and MEP distribution highlights the complementary nature of structural and electronic analyses. Together, these results provide a coherent picture of the ligand's intrinsic coordination aptitude.

3.4 Integrated structural and electronic interpretation

By integrating donor geometry, intramolecular hydrogen bonding, and MEP analysis, a comprehensive ligand-only understanding emerges. The ligand is

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preorganized for N,O-based coordination through favorable donor–donor distances and angular parameters, while intramolecular hydrogen bonding stabilizes this arrangement in the solid state. The electronic structure, as revealed by MEP mapping, further supports the dominant donor role of nitrogen and oxygen.Such preorganization is a key factor in determining ligand behavior and is widely recognized as an important design principle in coordination chemistry [1,3]. The present findings demonstrate that meaningful insights into coordination potential can be obtained without invoking metal complexes, provided that structural and electronic features are analyzed in a systematic manner.

4. Conclusion

A detailed ligand-only investigation was carried out using crystallographic and in silico methods. Donor–donor distance and angular analyses reveal a well-defined N,O donor framework, while larger separations involving sulfur indicate its limited accessibility in the free ligand conformation. Intramolecular hydrogen bonding plays a crucial role in stabilizing this geometry, and MEP analysis confirms the dominant donor character of nitrogen and oxygen atoms. The combined results provide a robust structural and electronic basis for understanding the intrinsic coordination aptitude of the ligand and offer valuable guidance for future coordination chemistry studies.

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