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Teaching Geometries of Coordination Compounds Using Computational Chemistry: Examples of Two Kinds of Four-coordinate Complexes

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Abstract: *In this article, two examples have been designed to be used for teaching geometries of coordination compounds by using computational chemistry, including molecular dynamics and quantum chemistry calculations. Specifically, we describe three kinds of software packages, molclus, GFN2-xTB and ORCA, and show how they can be used to predict the geometries of $[Zn(NH_3)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$. All assignments are aimed at helping students gain practice with computational chemistry software while at the same time understanding the differences between tetrahedral and square planar configurations.*

Keywords: *Coordination Compounds; Computational Chemistry; Geometries*

1. Introduction

For an undergraduate student, he has learned that four-coordinate complexes have two common geometries: tetrahedral and square planar. For example, $[Zn(NH_3)_4]^{2+}$ adopts the former one while $[Cu(NH_3)_4]^{2+}$ the latter. The difference is usually analyzed on the bases of valence bond method from the viewpoint of hybrid orbitals. Sp^3 hybrid Zn^{2+} controlling the tetrahedral configuration while dsp^2 hybrid Cu^{2+} controlling the square planar geometry. Although hybridization is a useful way to explain an observed complex geometry, there is no implication that it is an actual process. What's more, orbital mixing method can never predict the formation of a particular structure.

Here, we try to use another method to explain the formation and stability of $[Zn(NH_3)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$. This method is based on a series of simple and efficient software packages, including molclus [1], GFN2-xTB [2] and ORCA 4.2.1 [3].

2. Computational Steps and Discussion

2.1. Molecular Dynamics Simulations with GFN2-Xtb

In the first step, the input structure is constructed by Gaussview [4] and then be saved as mol2 format, which should be further transformed into xyz format by VMD program [5] since mol2 input format is not supported by xTB. It should be noted that the geometry of input structure can be tetrahedral or square planar, which will create almost the same MD results. 2000 initial configurations were randomly generated by performing MD simulations with GFN2-xTB at 300K for 100 ps in 1 fs interval (0.05 ps interval for trajectory printout) (Fig. 1).

Another point: multiple wall potentials should be created by adding instructions in the input file like:

```
$wall
    potential=logfermi
    sphere: auto, all
```

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$end

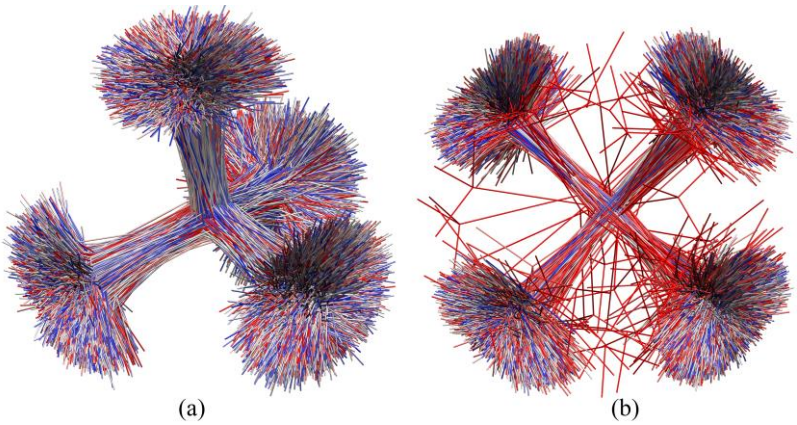

Figure 1: Overlap of 2000 complex configurations after 100 ps MD. (a) $[Zn(NH_3)_4]^{2+}$; (b) $[Cu(NH_3)_4]^{2+}$. Every configuration is denoted with different color.

It can be seen from fig.1 that both complexes created tetrahedral and square planar configurations, as well as various transition configurations. But the vast majority configurations of $[Zn(NH_3)_4]^{2+}$ is more close to tetrahedral structure, while the majority configurations of $[Cu(NH_3)_4]^{2+}$ is more close to square planar structure. This means that these two complexes have different conformation probabilities, indicating their different stable geometries.

2.2. Preliminary Optimizations with GFN2-xTB

GFN2-xTB is a more recently developed semiempircal quantum-mechanical (SQM) tight-binding method developed specifically for non-covalent interactions. Compared with other methods in the GFNn-xTB family[6], GFN2-xTB proved to be more robust, efficient and accurate for structure optimization and thermochemistry of transition-metal complexes [7]. In terms of the overall error, the GFN2-xTB method is significantly better than the other SQM methods. So, in this second step, the extensive geometrical optimizations were carried out for these 2000 complex configurations with GFN2-xTB to determine the order of the low-lying isomers through their total energies.

If GFN2-xTB were called through Molclus program, all 2000 optimized configurations and corresponding energies will be written into isomers.xyz file in the current directory. Then the “isostat” module in Molclus can be used to undertake clustering analysis on this file. Isostat take both energy differences and distance matrix among configurations / conformers as the clustering criterions. By default, 0.25 kcal/mol will be used as the energy threshold and 0.1 Angstrom be used as the geometry threshold for distinguishing different clusters. Of course, we can choose any threshold values as we like.

Clustering analysis results of $[Zn(NH_3)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ are listed in Tables 1 and 2, respectively. The corresponding four geometries are overlapped together into Fig. 2.

Table 1 Clustering analysis results of $[Zn(NH_3)_4]^{2+}$.

Count	energy difference with respect to the lowest one (kcal/mol)	minimal geometry difference with respect to all other clusters (Angstrom)
155	0.00	0.10
1840	0.00	0.10
4	0.03	0.11
1	0.37	0.37

Table 2 Clustering analysis results of $[Cu(NH_3)_4]^{2+}$.

Count	energy difference with respect to the lowest one (kcal/mol)	minimal geometry difference with respect to all other clusters (Angstrom)
1965	0.00	0.22
22	0.30	0.30
9	0.56	0.22
4	6.80	0.40

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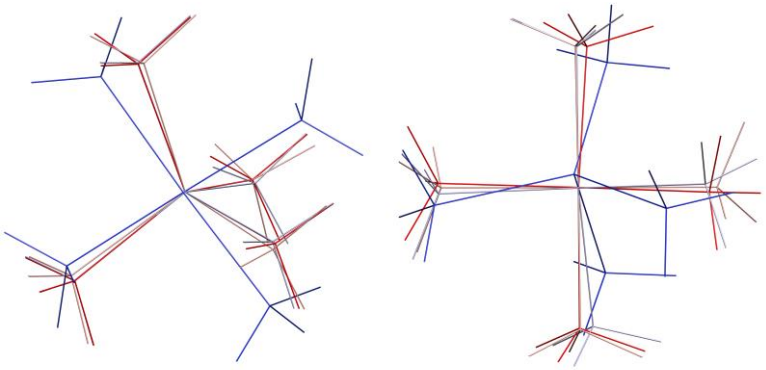

Figure 2 Overlap of 4 complex configurations after extensive geometrical optimization and structural screening. (a) $[Zn(NH_3)_4]^{2+}$; (b) $[Cu(NH_3)_4]^{2+}$. Every configuration is denoted with different color.

For $[Zn(NH_3)_4]^{2+}$, three lowest energy structures (including 155 + 1840 + 4 = 1999 counts) adopt tetrahedral configurations (red, cyan and coffee structures in Fig. 2a), and the highest structure (including only one counts) adopts square planar conformation (blue structure in Fig. 2a). The energy difference between tetrahedral and square planar configurations is much larger than that among different tetrahedral configurations.

For $[Cu(NH_3)_4]^{2+}$, three lowest energy structures (including 1965 + 22 + 9 = 1996 counts) adopt square planar configurations (red, cyan and coffee structures in Fig. 2b), and the highest structure (including only 4 counts) adopts tetrahedral conformation (blue structure in Fig. 2b). The energy difference between tetrahedral and square planar configurations is much larger than that among different square planar configurations.

Obviously, $[Zn(NH_3)_4]^{2+}$ will adopt tetrahedral configuration and $[Cu(NH_3)_4]^{2+}$ will adopt square planar configuration on the point of electronic energy. That's the results on the basis of preliminary SQM optimizations with GFN2-xTB.

2.3. High-level Optimizations with ORCA

Two sets of four conformers screened in the preliminary optimizations with GFN2-xTB were re-optimized by using ORCA program package (Version 4.2.1) at an advanced level of theory DLPNO-CCSD(T)/cc-pVTZ with normalPNO and RIJCOSX. Unexpectedly, all four conformers of $[Zn(NH_3)_4]^{2+}$ were optimized into the same tetrahedral configuration; and all four conformers of $[Cu(NH_3)_4]^{2+}$ were optimized into the same square planar configuration (Fig. 3).

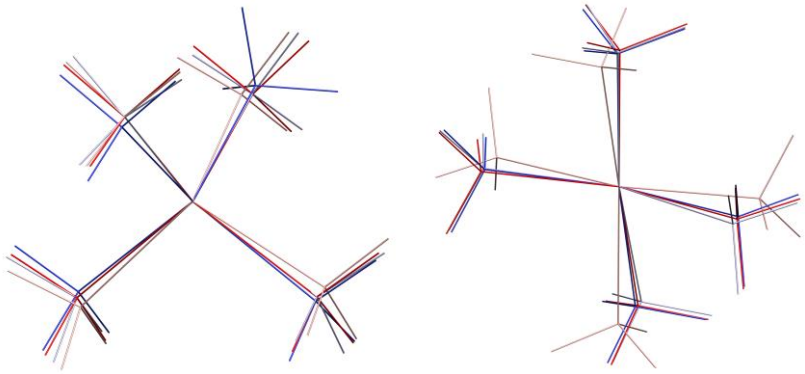

Figure 3 Overlap of 4 complex configurations after high-level optimizations with ORCA. (a) $[Zn(NH_3)_4]^{2+}$; (b) $[Cu(NH_3)_4]^{2+}$. Every configuration is denoted with different color.

The results of high level optimizations indicate that tetrahedral configuration may be the global minimum structure of $[Zn(NH_3)_4]^{2+}$; and square planar configuration may be the global minimum structure of $[Cu(NH_3)_4]^{2+}$. This is in good agreement with the experimental results and with the narrations in our textbooks.

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3. Conclusion

This article has described our teaching method about two typical conformations of four-coordinate complexes. We have tried to choose the most simple, efficient and free software packages that are fundamental to the quantum chemistry for the aim of explaining the global minimum structure of complexes. When combined with other branches of chemistry, inorganic chemistry can be clearly recognized as a basis for discovery-based learning. We will continue to find new ways and new teaching modules to develop the structural information and its associated software tools as a major resource in chemical education.

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