Generation of two-dimensional spectrochemical series in tetrahedral complexes

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Abstract. The physical properties of metal complexes that exist in many places are due to the ligand field splitting and electronic configuration of the d-orbital of the central transition metal, so changing the ligand field splitting of the d-orbital allows to control the physical properties. The arrangement of metals and ligands in order of the ligand field splitting is called a spectrochemical series. There is already a spectrochemical series only in the case of octahedral hexa-coordination complexes, but no equivalent index is shown for any other symmetry such as tetrahedral tetra-coordination complexes. In this study, we have investigated the creation of spectrochemical series in tetrahedral tetra-coordinated metal complexes. As a result, it is possible to accurately grasp the ligand field splitting of a tetrahedral tetra-coordinated metal complex, and to more effectively apply energy for expressing a spin crossover phenomenon in which the magnetism reversibly changes.

1. Introduction
A metal complex is a generic name for compounds in which a ligand present as an anion or neutral molecule is coordinated to a centrally located metal ion (which may be neutral or anionic), and is used for photosynthesis and production of plants or haemoglobin in the body is essential to our lives. The metal complex is located between the inorganic compound and the organic compound because it has the element diversity / functionality of the inorganic compound, the excellent molecular property of the organic compound, and the designability. And the physical properties of the metal complex originate from the ligand field splitting and the electron configuration of the d-orbital of the central transition metal. That is, its physical properties can be freely controlled by changing the ligand field splitting of the d-orbital. The electronic structure of the d-orbital varies depending on the coordination number and symmetry of the complex, but in the case of d^3 to d^6 tetrahedral tetra-coordinated complex, a plurality of spins such as a high spin state and a low spin state exists. The reversibility of the spin state interchanges the magnetism of the metal complex. This phenomenon is called spin crossover (SCO).

Spectrochemical series and Tanabe-Sugano diagrams (TSD) are indicators of ligand field splitting and electron configuration. The spectrochemical series is a sequence in which the ligand and the metal ion are arranged in the order of the magnitude of the energy difference of the d-d transition of the metal complex. Although it only holds in the case of the combination of a specific metal and ligand of an octahedral hexa-coordination complex, it is well shown that the ligand field splitting of a metal
complex depends on the kind of ligand. The spectrochemical series of octahedral hexa-coordination complexes are shown below.

(Metal): \( \text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Fe}^{3+} < \text{Co}^{3+} < \text{Ru}^{2+} < \text{Ru}^{3+} < \text{Ir}^{3+} < \text{Pt}^{4+} \)

(Ligand): I \(<\) Br \(<\) S\(^2\)- \(<\) SCN\(^-\) \(<\) NO\(_3\) \(<\) F \(<\) OH\(^-\) \(<\) ox\(^2\)- \(<\) H\(_2\)O \(<\) NCS\(^-\) \(<\) CH\(_3\)CN \(<\) NH\(_3\) \(<\) en \(<\) bpy \(<\) phen \(<\) NO\(_2\) \(<\) PPh\(_3\) \(<\) CN \(<\) CO

On the other hand, the Tanabe-Sugano diagram shows the relationship between ligand field splitting and multiplet energy of the d-orbitals, and is known as an indicator of the spin crossover. From these two indexes, it is considered that controlling of ligand field splitting and spin crossover of the metal complex, that is, controlling of magnetism is possible. However, in the tetra-coordinated complex, neither index equivalent to octahedral hexa-coordinated has been shown yet. In this study, we aimed to create the spectrochemical series and the Tanabe-Sugano diagram of tetrahedral complex, to understand the ligand field splitting correctly and to apply energy for expressing the spin crossover phenomenon more effectively. In this DV-X\(\alpha\) conference, we will report on the spectrochemical series of tetrahedral metal complexes.

2. Research procedure

In this research, first create a metal complex model to be calculated, then calculate the ligand field splitting of the 3d orbital of the central metal ion by the DV-X\(\alpha\) method, then make a two-dimensional spectrochemical series to predict ligand field splitting at a glance. However, the number of reported coordination data of the tetrahedral metal complexes is small, so the number of models that can be created is small simply by examining the metal-ligand bond distance from the Cambridge Structural Database (CSD) and applying the average to the metal complex model to be calculated. Therefore, for complexes that cannot be modelled from CSD, modelling is carried out using two methods: Method of distort a planar four-coordinated complex into a tetrahedral shape and Method of finding regularity of bond distance by comparing each complex. I will explain it in detail.

2.1 (Method to distort planar four-coordinated complex into tetrahedral form)

We searched for a planar four-coordination model in CSD, and created a regular tetrahedral complex model using distortion parameter \( \tau_4 \) (Fig. 1) which can express the degree of distortion of four-coordination complex with the bond angle without changing the bond distance.

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\tau_4 = \frac{360^\circ - \gamma - \delta}{141^\circ}
\]

Figure.1 Distortion parameters \( \tau_4 \).

2.2 (Model creation by comparison)

There are two ways to make a model by finding the regularity of bond distance by comparison. Comparison between tetrahedral complex and comparison with octahedral hexa-coordinates. First, we will show an example of model creation by comparison with a tetrahedron complex in Table 1. I will find the bond distance of Pd\(^{4+}\)-I comparing with the same d\(^6\) metal complex. The product average of the bonding distance was 1.0795 when the ligand changes from bromine to iodine in each metal complex. In order to obtain the bonding distance of Pd\(^{4+}\)-I, 2.3550 was multiplied by 1.0795.
Table 1. Bonding distance in each complex

| M        | L    | Bonding distance |
|----------|------|------------------|
| Pd⁴⁺     | Br   | 2.3550           |
| Co³⁺     | I    | 2.3184           |
| Rh³⁺     | Br   | 2.4206           |
| Pt⁴⁺     | I    | 2.3761           |
| Ru²⁺     | Br   | 2.4609           |
| Ir³⁺     | I    | 2.3969           |

Subsequently, we will show an example of model creation by comparison with an octahedral six-coordinate complex in Table 2. We will find the bond distance of Rh³⁺ - CO comparing with the same d⁶ metal complex. The product average of the bonding distance was 0.9745 when the structure changes to tetrahedral complex from octahedral six-coordinate complex whose ligand is a carbonyl group. In order to obtain the binding distance of Rh³⁺ - CO, 1.88925 was multiplied by 0.9745 to obtain the binding distance.

Table 2. Bonding distance in each complex.

| L    | M Coordination | Fe²⁺ Coordination | Ru²⁺ Coordination | Rh³⁺ Coordination |
|------|----------------|-------------------|-------------------|-------------------|
| CO   | 1.777          | 1.825             | 1.816             | 1.862             |

Average = 0.9745

3. Result

A tetrahedral complex model created from a combination of 12 metals and 13 ligands is shown in Table 3.

Table 3. Combination of 12 kinds of metal with 13 kind of ligand in CSD.

| Γ      | Br | S²⁻ | SCN⁻ | Cl⁻ | NO₃⁻ | F⁻ | OH⁻ | H₂O | NCS⁻ | NO₂⁻ | CN⁻ | CO |
|--------|----|-----|------|-----|------|----|-----|-----|------|------|-----|----|
| Mn²⁺   | 1  | 1   | ×    | ×   | ×    | ×  | ×   | ×   | 1    | ×    | ×   | ×  |
| Ni²⁺   | 1  | 1   | ×   | ×   | ×    | ×  | ×   | ×   | 3    | 1    | 3   | 1  |
| Co³⁺   | 1  | 1   | ×   | ×   | ×    | ×  | ×   | ×   | 3    | 1    | ×   | 3  |
| Fe²⁺   | 1  | 1   | ×   | ×   | ×    | ×  | 2   | ×   | ×   | ×    | 1   | 3  |
| Fe³⁺   | 1  | 1   | ×   | ×   | ×    | ×  | ×   | ×   | 4    | ×    | ×   | ×  |
| Co⁴⁺   | 4  | 4   | ×   | ×   | ×    | ×  | 2   | ×   | ×   | ×    | 4   | ×  |
| Rh³⁺   | 4  | 4   | ×   | ×   | ×    | ×  | 2   | ×   | ×   | ×    | 4   | 4  |
| Ru²⁺   | 4  | 4   | ×   | ×   | ×    | ×  | 4   | ×   | ×   | ×    | 4   | ×  |
| Ru³⁺   | 2  | 4   | ×   | ×   | ×    | ×  | 4   | ×   | ×   | ×    | 4   | ×  |
| Pd⁴⁺   | 2  | 4   | ×   | ×   | ×    | ×  | 2   | ×   | ×   | ×    | ×   | ×  |
| Ir³⁺   | 4  | 4   | ×   | ×   | ×    | ×  | 4   | ×   | ×   | ×    | 4   | 4  |
| Pt⁴⁺   | 4  | 4   | ×   | ×   | ×    | ×  | 4   | ×   | ×   | 3    | 4   | ×  |

1: Model created as it is from CSD  2: Model created by comparison between tetrahedral complex  3: Model created by distorting a plane tetra-coordinate into a tetrahedron  4: Model created by comparison with octahedral hexa-coordinates

The two-dimensional spectrochemical series created this work is shown in Figure 2. It was found that the color changed continuously from red (small) to black (large) as the numbers of the metal series and the ligand series increased. It was also found that the spectrochemical series of the conventional octahedral hexa-coordination complex tends to hold for tetrahedral complexes. By using this figure, we think it is possible to predict the magnitude of ligand field splitting to a certain extent even for combinations of metals and ligands that have not been calculated in this work.
4. Conclusion
In tetrahedral metal complexes, one electron calculation by DV-Xα molecular orbital method was performed to calculate ligand field splitting. As a result, for the combination of 12 kinds of metals and 13 kinds of ligands, the ligand field splitting of the tetrahedral structure complex was created as a two-dimensional spectrochemical series. At that time, it has been found that the spectrochemical series of tetrahedral structure complex also holds to some extent in the conventional octahedral hexacoordinated complex. Therefore, we think that the system design by two-dimensional visualization of spectrochemical series has made it easier to discuss the design of functional materials. In the future, it is thought that new complexes will continue to be synthesized through research activities that are constantly advancing. Therefore, by registering new metal complexes in CSD, it is possible to add combinations of metals and ligands that could not be modeled in this study. As future research, we will work on the creation of the Tanabe-Sugano diagram for each metal complex created in this work. Thereby, the tendency of spin crossover in each metal complex can be shown.

Reference
[1] Shino Tsuboi (2007) “An electronic study of ligand field splitting and physical properties of metal complexes”. Kagawa University master’s thesis.