



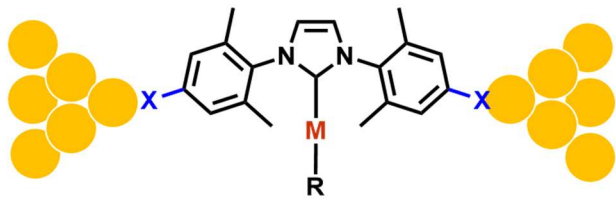
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| Title        | Study on Electronic Properties of N-Heterocyclic Carbene Metal Complexes at the Single Molecule Level                                                 |
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## Abstract of Thesis

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| Name ( Yosephin Dewiani Rahmayanti )                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                         |
| Title                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Study on Electronic Properties of <i>N</i> -Heterocyclic Carbene Metal Complexes at the Single Molecule Level<br>( <i>N</i> -複素環カルベン金属錯体の単分子電子物性に関する研究) |
| <p>Abstract of Thesis</p> <p>This thesis describes the electronic properties of <i>N</i>-heterocyclic carbene (NHC) metal complexes, consisting of two chapters.</p> <p>The first chapter is devoted to summarizing the background of molecular electronics and NHC, and describing the research objectives. Molecular electronics is a research field in which single molecules or small groups of molecules are designed to perform electronic functions.<sup>1</sup> Initiated by Aviram's proposal of molecular rectifier,<sup>2</sup> a device that allows the current to flow in one direction only, single molecular electronic systems with various functions such as switching, transistor, and wire have been rapidly developed.<sup>3</sup> Metal-containing single molecule devices are particularly attractive because of multiple redox states and spin states of metals. Several ligands have been reported to be used for metal-containing single molecules, e.g. bis-(terpyridine), porphyrin, and phenanthroline. The ligands mentioned above are nitrogen-based multidentate ligands where there is no empty site on the metal, so they are less reactive and have less structural variation. The weakly binding of nitrogen-based ligands to metals makes it difficult to form stable metal complexes only in monodentate coordination. To design stable new metal complexes with monodentate ligands, it is considered to select a structural design that can bind firmly to the metal and still have a vacant site in the metal.</p> <p><i>N</i>-heterocyclic carbenes (NHCs) have been recognized as privileged ligands that can bind firmly to metals due to their strong sigma donor properties. NHC metal complexes are commonly used for organometallic catalysts and some organic light-emitting diodes.<sup>4-5</sup> Several applications of NHC metal complexes in the field of nanoscience, such as nanoparticles, self-assembled monolayers, and single molecule electronics, have been reported.<sup>6</sup> Based on the NHC's strong binding properties to metals and its stability in monodentate fashion, the author designed a new metal-containing single molecule using NHC ligands. It is expected that the NHC single molecule could form a stable molecular junction, and the metal on the NHC could tune the molecular orbital in the molecule. This metal-containing single molecule design was accomplished by synthesizing a series of NHC metal complexes with two anchoring groups in the NHC core and metal in the center, and constructing metal-molecule-metal complex junctions, and measuring the conductance of single molecules (Figure 1). With the anchoring group attached to the para position of aryl, it is expected that the current passes through the backbone of the NHC molecule. The metal in the NHC can adjust the molecular orbitals of the junction, hence tune the conductance.</p>  <p>Figure 1. Design of <i>N</i>-heterocyclic carbene metal complexes (X= anchoring groups, M= metals, R = Cl or carbazolidene).</p> <p>The second chapter is devoted to the synthesis and conductance properties of single-molecule NHC metal complexes. The author synthesized two NHC copper complexes with different anchoring groups, namely alkyne and methyl sulfide, to compare the junction stability during measurement. The author also synthesized three different NHC complexes with different metals (Cu, Ag, and Au) to elucidate the metal effect on the single molecule conductance. Lastly, the author synthesized three NHC copper complexes, NHC copper</p> |                                                                                                                                                         |

chloride with one and two ethynyl anchors, and NHC copper carbazolidine complexes to investigate the junction conformation. The single-molecule conductance properties of these series of NHC metal complexes were measured by using scanning tunneling microscopy–break junction (STM-BJ) methods.

The stability of metal-molecule-metal junctions was investigated by comparing NHC copper chloride complexes with methyl-sulfide and alkyne as anchoring groups (Figure 2a). NHC copper chloride with alkyne anchoring group gave a higher conductance value around  $5 \times 10^{-5} G_0$  than the corresponding methyl sulfide complex did (around  $1.5 \times 10^{-5} G_0$ , Figure 2b). Meanwhile, the 2D histograms showed longer plateau for methyl sulfide anchor than alkyne anchor (Figure 2 c, d). The longer plateau suggests a stronger binding for methyl sulfide anchor to the gold electrode and a higher stability of the single molecule junction.

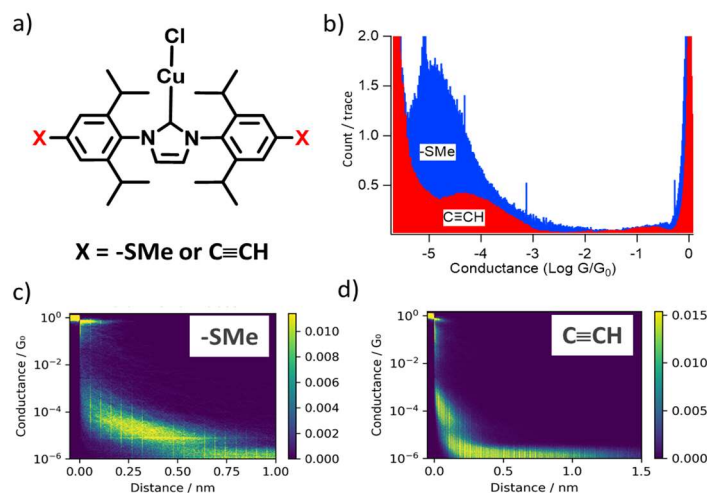


Figure 2. a) The structure of NHC copper chloride with alkyne and methyl sulfide as anchoring groups. b) Logarithmically binned one-dimensional (1D) conductance histograms. c–d) Two-dimensional (2D) conductance histograms of NHC copper chloride with two different anchoring groups.

For the single molecule junctions of NHC metal complexes, there are two possible type of conformation as shown in Figure 3a. To distinguish them, measurement of two NHC complexes with one or two ethynyl anchors was conducted. The results show the similar conductance with the value of  $5.25 \times 10^{-5} G_0$  and  $5.00 \times 10^{-5} G_0$  for one and two ethynyl anchors, respectively. These results suggest that the molecular junction is formed in type A conformation, wherein the metal on the NHC core binds to the electrode.

To make type B junction conformation, it is important to prevent the contact between the gold electrode and the metal atom on the NHCs. Therefore, the synthesis of NHC-metal complex is carried out by replacing chloride atom with bulky carbazole. From the 1D histogram in Figure 5, the conductance of the NHC copper carbazole is different from that of the NHC copper chloride ( $6 \times 10^{-6} G_0$  vs  $1.5 \times 10^{-5} G_0$ ), implying the formation of type B junction. These results indicated that by limiting the NHC metal center's contact to the electrodes, the junction conformation can be controlled. The conductance value of the conformation B is smaller than the conformation A, possibly due to the torsion angle between the imidazole ring and the aryl rings in the NHC.

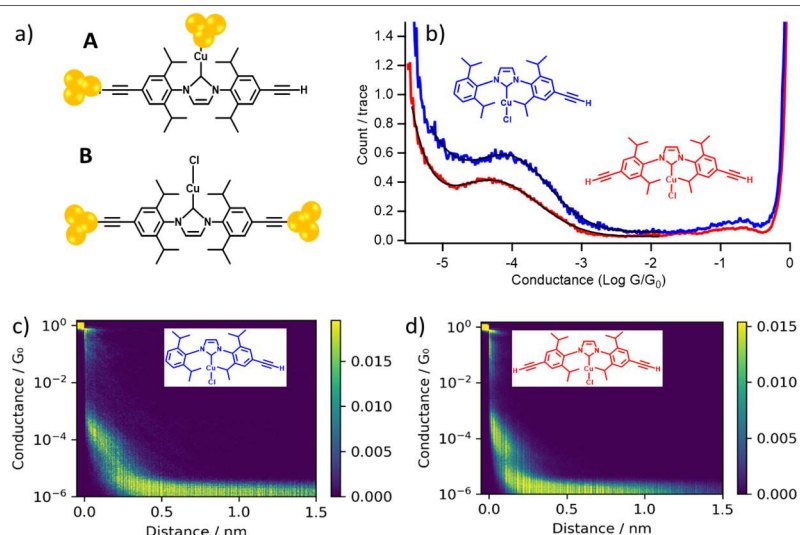


Figure 3. a) Two molecular junction conformations of NHC metal complexes. 1D (b) and 2D (c and d) conductance histograms of NHC metal complexes with one and two ethynyl anchors.

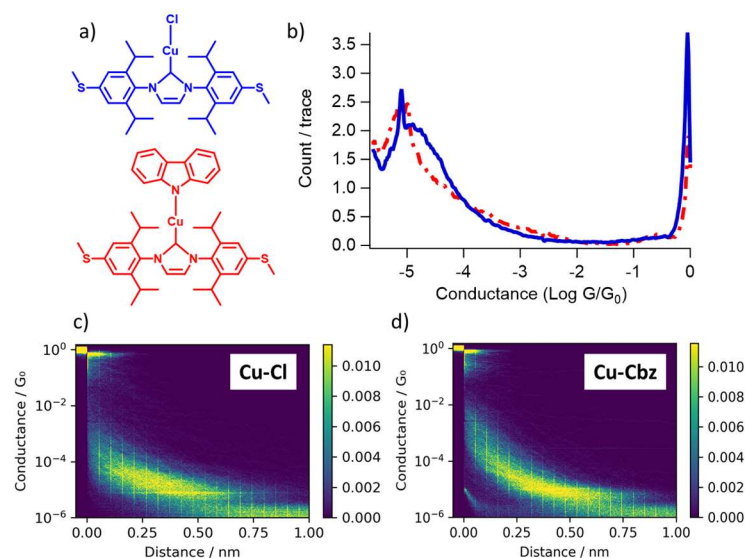


Figure 4. a) Structure of NHC copper chloride and NHC copper carbazole. b) 1D conductance histogram of NHC copper chloride (blue solid line) and NHC copper carbazole (red dashed line). 2D conductance histogram of c) NHC copper chloride and d) NHC copper carbazole complex.

The author also investigated the metal effect on the single-molecule conductance value of NHC complexes using methyl sulfide anchoring group. The NHC metal chloride complexes exhibited different conductance, with a value of  $3.5 \times 10^{-5} G_0$  for Au,  $1.9 \times 10^{-5} G_0$  for Cu, and  $1.4 \times 10^{-5} G_0$  for Ag ( $Au > Cu > Ag$ , Figure 5). Theoretical calculation suggested that the conductance value is also affected by the binding site of the metals, and the comparison with experimental results implied the binding geometries are different for metals (Table 1). Interestingly, 2D histograms (Figure 5 b–d) indicate that the plateau length also depends on the metals with the order  $Au > Ag > Cu$ . These results imply that the binding strength to the electrode depends on the metals and their binding geometries.

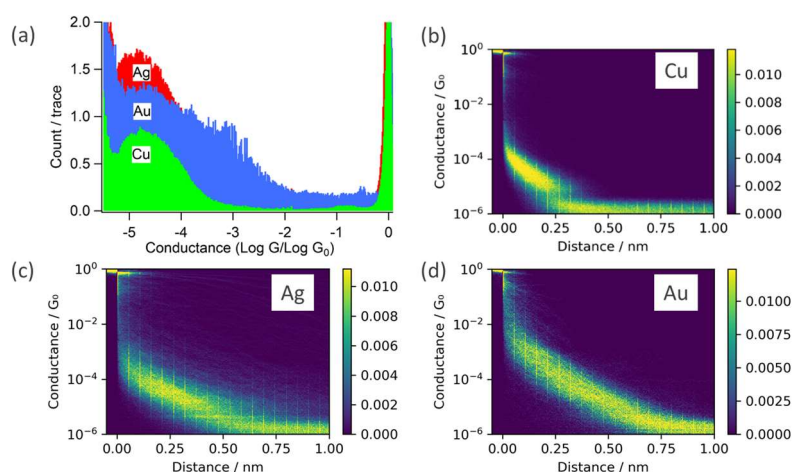


Figure 5. 1D (a) and 2D (b–d) conductance histograms of NHC metal complexes with three different metal centers (Cu, Ag, and Au) with methyl sulfide as anchoring group.

Table 1. Comparison of NHCs conductance from experimental results and theoretical calculations

| Metal              | Experimental result ( $G_0$ ) | Theoretical calculation ( $G_0$ ) |
|--------------------|-------------------------------|-----------------------------------|
| <b>Au (hollow)</b> | $3.5 \times 10^{-5}$          | $9.88 \times 10^{-4}$             |
| <b>Cu (hollow)</b> | $1.9 \times 10^{-5}$          | $7.16 \times 10^{-4}$             |
| <b>Ag (bridge)</b> | $1.4 \times 10^{-5}$          | $1.84 \times 10^{-4}$             |

In conclusion, the findings from this research are; (1) *N*-heterocyclic carbene can be used for ligand in metal-containing molecular wire since it strongly binds to metal during single-molecule conductance measurement; (2) The metal attached on the NHC ligand can act as anchoring group; (3) The conductance of NHC metal complexes depends on the metals and binding geometry of metals to the electrode; and (4) The molecular junction conformation can be changed by placing bulky group on metals. These results pave a way for the exploration of metal-containing molecular junction of NHC with novel functionalities such as switching, transistor and insulator by choosing such appropriate metals. The functional group attached to the metal in NHC also could be changed, thus presumably will bring out interesting properties. Since the NHC could form a stable metal complex in the monodentate fashion thus there is still a vacant site for metal interactions.

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論文審査の結果の要旨及び担当者

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**論文審査の結果の要旨**

単一分子電気伝導は、10 年くらい前に実験的な研究が可能となり、それまでに確立されていた集合体の電気伝導現象とは全く異なる現象が次々と発見されている物性科学の新規領域である。多くの研究は、比較的簡単な構造を持つ分子で行われてきているが、金属錯体など複雑な構造の分子が予想されなかった興味深い現象を表すことが見出されており、有機合成と物性科学の境界領域として興味を持たれている。

本申請者は、N-ヘテロ環状カルベン (NHCs) 金属錯体の単分子電気特性の研究を行った。NHCs は、世界初の安定カルベンとして見出され、カルベン部分で種々の金属に配位できる興味深い分子である。通常の配位子であると金属の空軌道を全て埋める形で配位するが、NHCs はその立体的な特性から金属の空軌道を残すところに特徴がある。そのため、空いている金属の空軌道に他の分子や原子が一時的に入り込んで、触媒機能やセンサー機能を示すことが知られている。

両末端にチオメチル基を電極へのアンカー部として持つ分子を合成し、Au, Ag, Cu の錯体を作り、走査トンネル顕微鏡－架橋破断法 (STM-BJ) を用いて単分子接合を作り、各錯体の単分子電導度を次のように求めた： $3.5 \times 10^{-5} G_0$  for Au,  $1.9 \times 10^{-5} G_0$  for Cu, and  $1.4 \times 10^{-5} G_0$  for Ag (Au > Cu > Ag)。各種のモデル分子の合成と単分子計測、理論計算などから、この単分子接合は当初想定していたチオメチル基二つをアンカーとして持つ単分子接合ではなく、片方が錯体中の金属部分で、他方がチオメチル基で金電極につながっている非対称な単分子接合であることが分かった。

金表面に有機分子が結合する場合に、一つの原子だけがかかわる atop、二つの原子が結合する bridge、3つの原子が結合する hollow の 3 種類の様式が有り、それぞれで電導度が異なることが知られている。これらの結合様式でつながった分子接合の単分子電導度を理論計算で求めたところ、錯体金属が Au と Cu は hollow で、Ag は bridge で結合していると考ええると、実験で求められた電導度の順をよく説明できた。

当初の予定であったチオメチル基で対称に分子架橋を作ることは成功しなかったが、NHCs 金属錯体中の金属が良いアンカーとなることを見出したともいえる。また、錯体の金属が異なると金表面への吸着の様式が変わることも興味深い。複雑な現象を緻密な合成、計測、解析で、明らかにした仕事であり、博士論文にふさわしいと判断した。