

Highlight Review**Secondary Thioamides as Multidentate Ligands for Functional Metal Complexes**Ken Okamoto,¹ Junpei Kuwabara,² and Takaki Kanbara*²¹National Institute for Materials Science (NIMS), 1-1 Sengen, Tsukuba, Ibaraki 305-0047²Tsukuba Research Center for Interdisciplinary Materials Science (TIMS),
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Abstract

This highlight review describes recent progress in thioamide-based transition-metal complexes, including their preparation methods and functionalities. In particular, pincer organometallics with secondary thioamide ligands are unique tools that can be used for applications in various areas such as chemical-sensor materials, tunable redox-potential complexes, polymer hybrid-luminescence materials, building blocks for multinuclear complexes, and catalysts for cross-coupling reactions.

Introduction

Among previous studies in coordination chemistry, multidentate sulfur-containing ligands have not been investigated as much as other heteroatom-containing ligands, namely nitrogen-, phosphorous-, and oxygen-based ligands. The commercially available multidentate-sulfur ligands are very limited.^{1–3} This is partly due to the instability of thiocarbonyl compounds and their difficult synthesis, which makes use of malodorous reagents such as phosphorus pentasulfide, Lawesson's reagent, and alkyl- and aryl thiols. Recent investigations on thioamides ($R-C(=S)-NR'R''$) proposed an alternative simple one-step synthetic procedure for multidentate thioamide-based ligands from commercial sulfur sources.^{4–10} In addition, thioamides possess a higher stability compared to that of other thiocarbonyls such as thionoesters, thioketones, and thioaldehydes. Thus, thioamides are increasingly being used as organosulfur ligands in the field of coordination chemistry and organometallic chemistry.

Since our first report of a thioamide-based $S^{\wedge}C^{\wedge}S$ pincer complex,¹¹ a decade has already passed. In these years, several studies have shown the advantages of using multidentate thioamide-based transition-metal complexes in a diverse range of fields, namely photochemistry, structural chemistry, catalyst development, polymer-based materials science, electrochemistry, and supramolecular chemistry. Our initial synthetic methods were established by 2006.^{4,12,13} Since then, our research has focused on the investigation of the external stimuli-responsive behavior of secondary thioamide (*sec*-TA)-based $S^{\wedge}X^{\wedge}S$ ($X = C$ or N) pincer complexes. Figure 1 shows the basic physical properties of simple *sec*-TA and secondary amide (*sec*-A); among these, the most relevant are: a) suitable hydrogen-bond donor properties,¹⁴ b) high acidity,^{15,16} and c) deprotonation-driven structural-changeability. Thioamides are better hydrogen-bond donors than the corresponding *sec*-A compounds (Figure 1a). This is due to the higher acidity of *sec*-TA compared to that of the corresponding amides (Figure 1b). The structure of *sec*-TA can be converted by the addition of inorganic and organic bases (Figure 1c). As a result of a deprotonation reaction, the thioamide is converted to a bridging ligand.

In this highlight review, we offer an overview of recent progress in various TA-based transition-metal complexes with a central focus on *sec*-TA-based $S^{\wedge}X^{\wedge}S$ ($X = C$ or N) pincer complexes. The discussion is divided into the following six sections: preparation of $S^{\wedge}X^{\wedge}S$ pincer complexes, their responses to external stimuli (photochemical, electrochemical, or chemical stimuli), structural features of thioamides as bridging ligands, catalytic activity, and brief summary and scope.

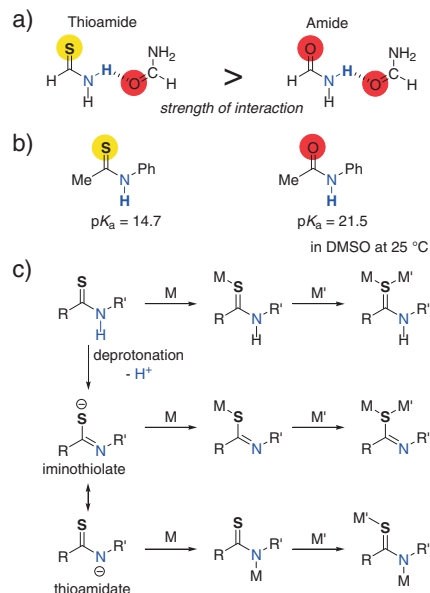


Figure 1. Basic physical properties of thioamides and corresponding amides; a) hydrogen-bonding strength of thioamide is about 2 kcal mol^{-1} more favorable than that of amide and b) acidity. c) The neutral and anionic forms of a secondary thioamide unit and possible coordination modes as a building block of multinuclear metal complex ($M = \text{metal ion}$).

Preparation of Thioamide-based $S^{\wedge}X^{\wedge}S$ Pincer Complexes and Features of *sec*-TA Ligands

A number of reviews have already described the structural features of pincer ligands,^{17,18} catalytic properties of pincer complexes,¹⁹ and development of chemical sensors²⁰ with the use of pincer complexes. Early examples of pincer ligands were defined as monoanionic, tridentate, and meridionally metal-coordinating agents. Technically, the classic pincer-named complexes have two metallacycles on the structure (Figure 2a).

However, from the early stage of “Pincer Chemistry,” in the mid-70’s, a large variety of pincer-named complexes has been reported; for instance, dianionic $C^{\wedge}N^{\wedge}C$ pincer complexes,²¹ nonmeridional (facial) pincer complex,^{22,23} and heteroaromatic-centered pincer complexes;^{13,22,23} these are not included in the classical definition of pincer. Hence, for the sake of clarity, here we will use the term “pincer” in a wider sense as shown in Figure 2b.

In general, three methods are used for the preparation of classical pincer complexes (Figure 3a):¹⁸ i) oxidative addition using zero-valent metal precursors, ii) transmetalation via lithiated pincer ligands, and iii) direct cyclometalation assisted by the chelation reaction. The research group of van Koten systematically investigated the characteristics of all preparation methods (Figure 3b).^{24–26} Among these three methods, the cyclometalation route is the most favorable, because it does not require any air-sensitive chemical and strictly inert atmosphere. In addition, cyclometalation enables the rapid construction of pincer complexes via the C–H activation (or N–H activation) process. Fortunately, all TA-based $S^{\wedge}C^{\wedge}S$ pincer complexes can be prepared by route iii). This is probably

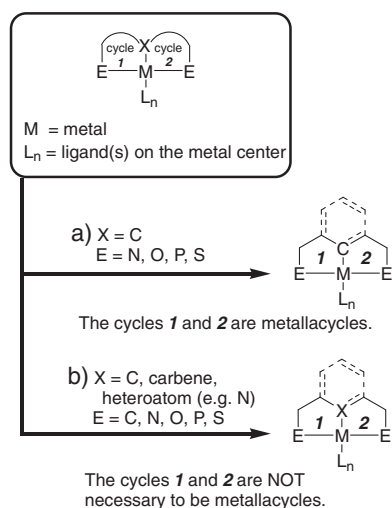


Figure 2. General skeleton of pincer complexes; a) in limited (classical) sense and b) in wider sense.

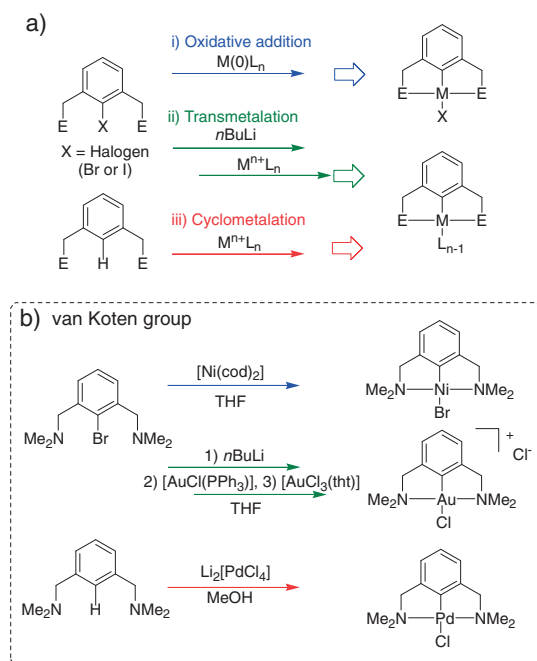


Figure 3. a) General preparation routes of pincer complex and b) examples of the synthetic routes reported by the van Koten group (tht: tetrahydrothiophene).

due to the strong coordination ability of the two sulfur atoms to transition metals. Obviously, pyridyl-centered S[^]N[^]S pincer ligands follow a chelation reaction of multisite coordination without the above-mentioned cyclometalation.

The pioneering studies of Nonoyama described the preparation of a wide variety of TA-based cyclometalated transition-metal complexes (e.g., Pd, Pt, Rh, and Ru).^{27–33} In addition, S[^]C[^]S pincer palladium complexes were also reported.^{29,33} These studies prompted us to synthesize and conduct studies on various TA-based S[^]X[^]S pincer complexes; these are listed in Table 1.

Table 1. Our reports of various TA-based pincer complexes

Year	Coordination mode	Centered unit	Metal	Ref
2004	S [^] C [^] S	phenyl	Pt	11
2005	S [^] C [^] S	phenyl	Pd	12
2006	S [^] N [^] S	pyrrolyl	Ni, Pd, Pt	13
2010	S [^] C [^] S	azulenyl	Pd, Pt	34
	S [^] C [^] S	phenyl	Ni	35
	S [^] C [^] S	phenyl	Ru	36
2011	S [^] N [^] S	pyrrolyl	Ru	
	S [^] N [^] S	pyrrolyl	Cu	37
2014	S [^] N [^] S	pyridyl	Ru	38

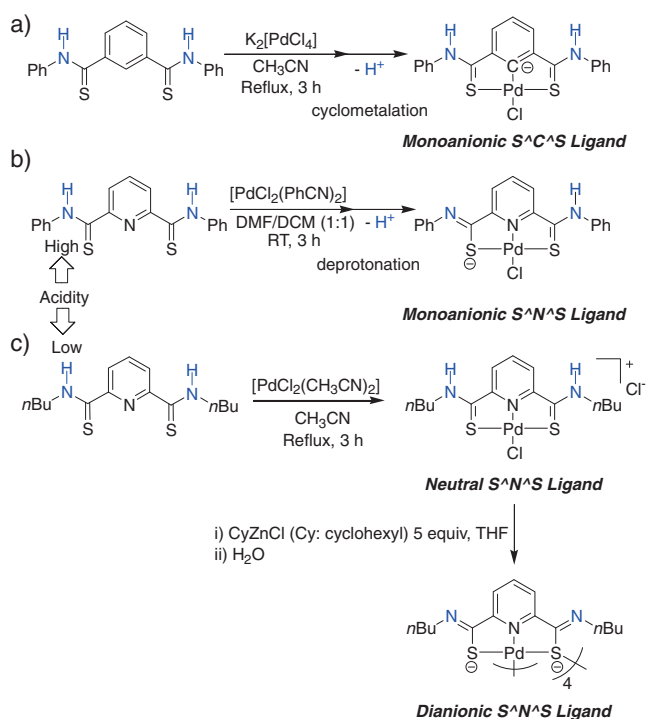


Figure 4. Complexation behavior of a) S[^]C[^]S ligand, b) *N*-phenyl S[^]N[^]S ligand, and c) *N*-alkyl S[^]N[^]S ligand with each Pd(II) sources.

One of the most interesting features of the synthesis of the *sec*-TA-based pincer complex is that the cyclometalation of the ligands with a transition-metal source affords a uniform S[^]X[^]S (X = C or N) coordination mode. At the beginning of our synthetic studies, our concern was that the high acidity of the N–H on the secondary thioamide (R–C(=S)–NHR) might afford different coordination modes and mixtures such as N[^]C[^]S or non-cyclometalated complexes. However, the ¹H NMR and single-crystal X-ray analyses showed that only the S[^]C[^]S coordination mode occurred (Figure 4a).^{39,40} Although the electronegativity of nitrogen is higher than that of sulfur, the metal–S bonds are stabilized by backdonation from the metal center to the empty, relatively low-energy d-orbitals of the sulfur atom in the TA moieties.⁴¹

Another important feature (Figure 4) is the ability of the *sec*-TA-based pincer ligands to form a multivalent structure upon deprotonation of the *sec*-TA moiety. As shown in Figure 4a, the phenyl-centered S[^]C[^]S ligand has a monoanionic-coordination mode. Alternatively, pyridyl-centered S[^]N[^]S ligands may give monoanionic-coordination modes or neutral-coordination modes, depending on the *N*-end substituents (Figures 4b and 4c top for *N*-phenyl and *N*-butyl, respectively). In general, acetanilide (Me-C(=O)-NHPh) has a higher acidity than the corresponding *N*-methyl *sec*-A (Me-C(=O)-NHMe), because the resonance structure of the amide unit is affected by the π -conjugation effect of the anilide group.^{16,42} Therefore, the monoanionic S[^]N[^]S coordination of pyridyl-centered *N*-phenyl TA can be related to the high acidity of the *sec*-TA moiety. In addition, further treatment of the cationic *N*-butyl TA-based S[^]N[^]S Pd(II) complex with an organometallic base can afford a dianionic ligand structure (Figure 4c, bottom).⁴³ This charge versatility is a unique property of *sec*-TA-based pincer ligands.

For this reason, both centered aromatics and *N*-end substituents should be carefully considered in accordance with a selected metal center and the intended use. Based on this perspective, the coordination mode of the *sec*-TA-containing unsymmetrical S[^]X[^]E ligand (X = C or N, and E = heteroatom including sulfur), the so-called hybrid-type pincer ligand, is also expected to yield regioselective S[^]X[^]E coordination structures. For instance, Odinets et al. demonstrated the preparation of unsymmetrical S[^]C[^]S' pincer Pd(II) and Pt(II) complexes, having *sec*-TA- and phosphine sulfide moieties, by a similar preparation method in Figure 4a.^{44,45} Complexation of multidentate secondary amide analogues (R-C(=O)-NHR) to transition metals is somewhat different from that of the *sec*-TA ligand.^{46,47}

External Stimuli/Medium-responsive Photochemical Properties of the *sec*-TA-based Pincer Complex

As already reviewed by K.J. and T.K.,⁴⁸ TA-based S[^]C[^]S pincer complexes with Pd(II) and Pt(II) show photoluminescence and electroluminescence properties. In addition, our research group investigated anion- and neutral-molecular receptors using *sec*-TA-based macrocyclic molecules.^{49,50} These studies showed that anion and molecular recognition can be achieved by exploiting the hydrogen bonding between the *sec*-TA-based molecule and a hydrogen-bond acceptor such as the anion or amides. Jurczak's research group also studied the anion-recognition properties of *sec*-TAs compared to those of their amide analogues.^{51,52} Pincer chemistry is seemingly unrelated to anion-receptor chemistry, which is a branch of supramolecular chemistry; however, the combination of transition-metal complexes and hydrogen-bond interactions has received much attention in recent years.^{53,54}

Hydrogen bonding is capable of stabilizing specific conformations of molecules and inducing new transition states. As a result, these interactions enable the control of proton-, electron-, and energy-transfer events. In order to provide a deeper understanding of the features of TA-based S[^]C[^]S pincer complexes, studies have been conducted on the external stimuli-responsive photochemical behavior of *sec*-TA-based S[^]X[^]S (X = C or N) pincer complexes. We focused on three types of surrounding fluid mediums (pure solution, a solution

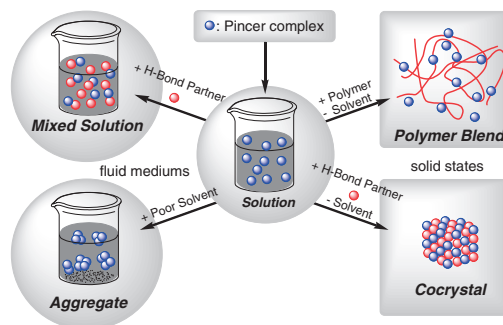


Figure 5. External stimuli and surrounding media for *sec*-TA-based S[^]C[^]S complex.

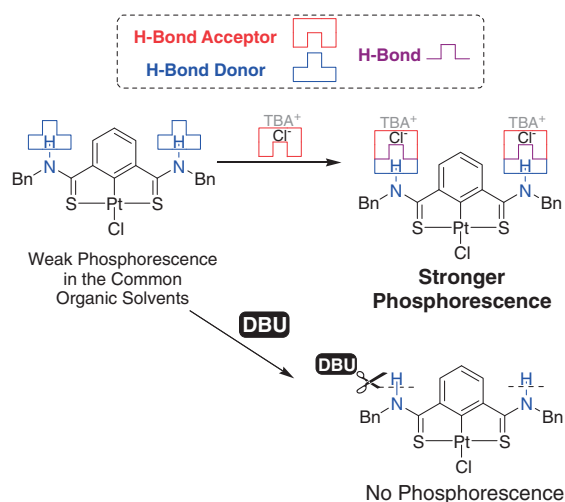


Figure 6. Tunable photochemical properties of *sec*-TA-based S[^]C[^]S Pt complex in the solution states (fluid mediums in Figure 5).

with hydrogen-bond acceptor, and an aggregation state in poor solvent) along with two solid states (polymer-blend thin film and cocrystal) as shown in Figure 5.

The basic optical properties and the reactivity of *sec*-TA-based S[^]C[^]S Pt complexes have been examined.⁵⁵ The presence of the coordinated *sec*-TA linkage in the ligand was found to function as a reactive site upon the addition of bases and anions and to result in the modulation of the absorption and emission properties of the Pt complexes (Figure 6). These results indicate that the *sec*-TA linkage can serve as a sort of switch between the emission-on and -off states by the addition of external stimuli. Furthermore, the efficient emission was caused by the suppression of the molecular motion resulting from the hydrogen-bond interaction between the N-H moiety in the *sec*-TA group and the hydrogen-bond acceptor (e.g., the chloride anion of the tetrabutylammonium salt).

In order to immobilize such emissive complexes by hydrogen bonding, the *sec*-TA-based S[^]C[^]S Pd complex was blended into a poly(vinylpyrrolidone) (PVP) matrix (Figure 7, left).⁵⁶ The well-dispersed Pd complex blended in the PVP film showed strong phosphorescence at room temperature, with the phosphorescence intensity of the complex in the polymer being much stronger than that in the solution and powder states. The efficient

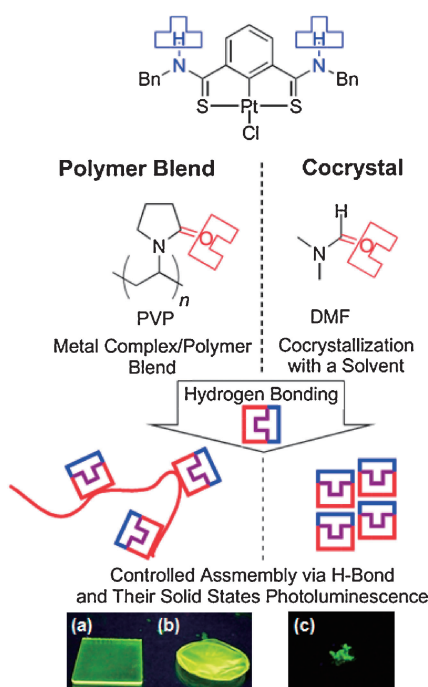


Figure 7. Schematic Image for photochemical properties of *sec*-TA-based S^CS Pd complex in the solid states, and photographs of the Pd complex in PVP films (a) on a glass plate (2 × 2 cm) by spin-coating and (b) free-standing film peeled from a polyethylene (PE) dish, and (c) cocrystal powder of the Pd complex with DMF molecule under UV light at the wavelength of 254 nm.

emission is presumably caused by the suppression of the molecular motion resulting from the intermolecular interaction of the Pd complex and host polymer. Moreover, the resulting hybrid film showed reversible luminescence switching upon exposure to volatile organic compounds because the intermolecular interaction is disturbed by the absorption of volatile organic molecules.

As shown in Figure 7, the PVP repeating unit is similar to *N,N*-dimethylformamide (DMF). Therefore, crystal-engineering studies using the same Pd pincer complex have been reported.^{57,58} The conformation of the Pd complex in the crystal depends on the hydrogen bonding of the cocrystallized solvent molecules. The molecular arrangement affects the intensity of the photoluminescence from the crystals. For instance, a relatively strong emission was observed from a crystal with a densely packed arrangement of the complex, in contrast to the aforementioned solutions and dried powders of the Pd complex at room temperature, which did not exhibit such a strong emission.

Since 2001, aggregation-induced emission (AIE) has been widely recognized as a type of luminescence in the solid state, and many efforts have been recently made to understand this photophysical behavior.⁵⁹ AIE-active materials are chromophores that exhibit quenching in solution, in contrast to their solid (or aggregated) state, which shows luminescence. Briefly, in the nonaggregation state, the light emission is turned “off,” while its aggregated state turns “on” the light emission. This “on–off” light-emission behavior is fundamental for sensing applications. Our latest research on this topic deals with the AIE-

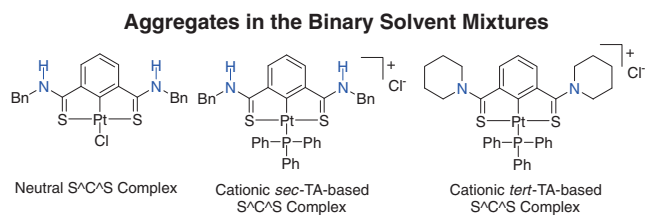


Figure 8. The structures of AIE active complexes.

active phosphorescent cationic pincer Pt(II) complexes bearing a *sec*-TA ligand.^{60,61} The AIE activity was evaluated in three different types of S^CS Pt complexes, namely neutral *sec*-TA-based S^CS Pt, cationic *sec*-TA-based S^CS Pt, and cationic tertiary-TA-based complexes (Figure 8). Only the cationic *sec*-TA-based S^CS Pt complex formed aggregates in various solvent systems, and the aggregates showed AIE behavior.

The hitherto known photoluminescent metal complexes have been mainly evaluated in solution or solid states. The relationship between the hydrogen-bonding ability of *sec*-TA-based S^CS complexes and their photoluminescent properties may provide new insight for the investigation of pincer complexes.

Deprotonation of *sec*-TA Ligands for the Control of Electrochemical Response, Optical Response, and Structural Transformation

Several recent studies about proton-coupled electron transfer (PCET)-active pincer complexes showed remarkable progress in small-molecule activation.^{62–66} Thus, the proper design of a pincer ligand may provide tunable chemical and physical properties, not only for the activation of small molecules, but also for the electrochemical and optical properties of redox-active and/or photoresponsive pincer complexes.

To gain a deeper insight into the electron-transfer events (e.g., PCET⁶³ and nonlinear optical properties) as well as into the activation of a coordination site by controlling the deprotonation/protonation of *sec*-TA-based pincer complexes, we will describe in this section different metal complexes such as redox-active metal complexes and five- or six-coordinate complexes.

First, the effect of centered-aromatic units on the redox potential of Ni(II)/Ni(III) (Figure 9a) has been investigated.³⁵ Cyclic voltammetry shows that the S^CS ligand has a stronger electron-donating ability than the S^NS ligand. Second, the modulation of the redox potential in S^CS Ni complexes was systematically investigated by the addition of external chemical stimuli (e.g., organic bases), because the deprotonation of the thioamide group is expected to change the electron density of the Ni center by forming thioamidate and iminothiolate as resonance structures (Figure 1c).⁶⁷ Indeed, the deprotonation of the thioamide moiety led to a negative shift of the Ni(II)/Ni(III) redox potential by approximately 500 mV (Figure 9b).

The modulation of the electronic properties of the *sec*-TA-based S^XS (X = C or N) Ru pincer complex (Figure 10) has also been examined.³⁶ Both complexes showed a two-step deprotonation reaction upon treatment with 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU); this resulted in a shift of the

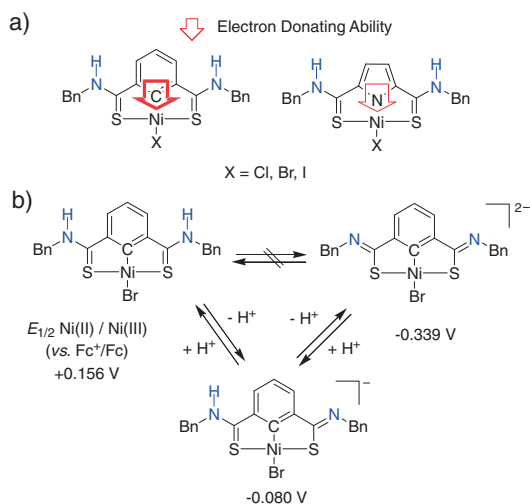


Figure 9. a) Comparison of electron-donating ability of *sec*-TA-based S^CS and S^NS ligands, b) effect of deprotonation to the redox potential of *sec*-TA-based S^CS Ni complex.

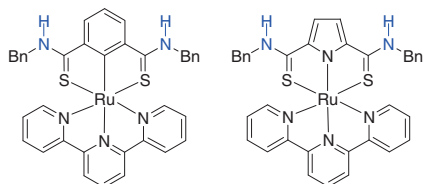


Figure 10. The structures of *sec*-TA-based S^CS and S^NS Ru complexes.

centered-metal redox couples to a lower potential (for S^CS by 720 mV and for S^NS by 550 mV, respectively); these results are consistent with those obtained from the Ni pincer complexes. The Pourbaix diagram revealed that the *sec*-TA-based S^CS Ru complex undergoes a one-proton/one-electron transfer process in the pH range of 5.83–10.35, and a two-proton/one-electron process at a pH above 10.35, indicating that the deprotonation/protonation of the complexes is related to the PCET process.

Switchable nonlinear-optical (NLO) metallochromophores have received much attention owing to their novel application in electrooptical technologies.^{68,69} In 2012, Qiu, Liu, et al. investigated the second-order NLO properties of a series of two-dimensional S^CS pincer Ru(II) complexes by density functional theory (DFT) calculations.⁷⁰ At the time of writing, although the calculated NO₂ group-ended Ru complex has not been synthesized yet, these authors concluded that the studied Ru complexes may be the promising candidates for good 2D-NLO switchable materials at the external stimulus of a proton-manipulation (deprotonation/protonation) reaction (Figure 11).

The activation of a coordination site is important for designing transition-metal catalysts and controlling molecular self-assembly. Our group reported the preparation of *sec*-TA-based S^NS Ru(II) complexes and their transformation via the deprotonation/protonation of the *sec*-TA ligands.³⁸ The stepwise deprotonation of *sec*-TAs affords neutral, mononuclear, and dinuclear complexes (Figure 12), and the dimerization process is affected by the *N*-end substituents, e.g., phenyl and benzyl groups.

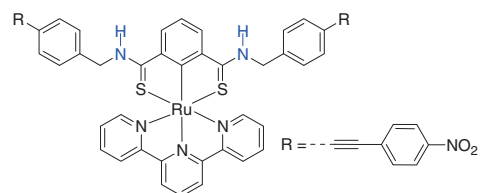


Figure 11. The suggested 2D switchable NLO active *sec*-TA-based S^CS Ru complex by deprotonation reaction.

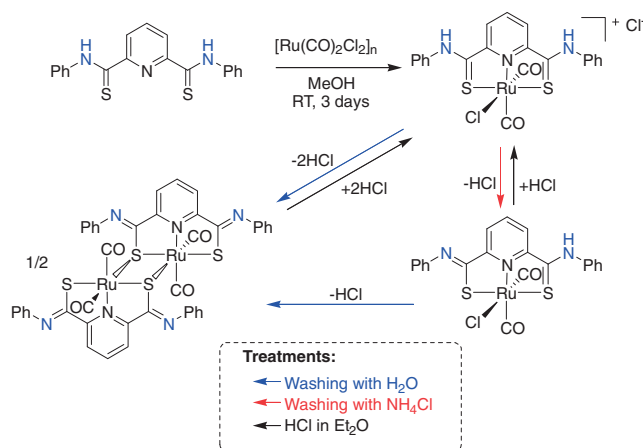


Figure 12. Preparation of *sec*-TA-based S^CS Ru complex and deprotonation/protonation reactions. The colored arrows show the treatment to Ru complex.

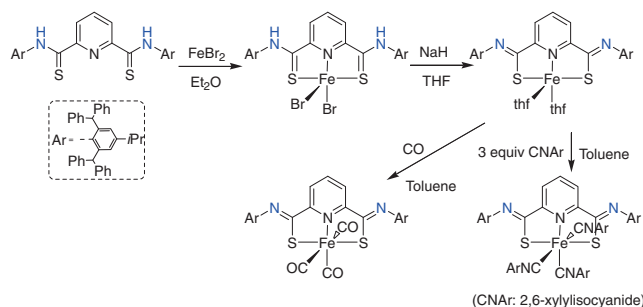


Figure 13. Synthesis and activation of coordination sites of *sec*-TA-based S^CS Fe complexes.

A similar concept using *sec*-TA-based S^NS Fe(II) complexes was reported by Masuda's research group (Figure 13).⁷¹ Deprotonation of the *sec*-TA ligand invokes the activation of coordination sites, and the resulting THF-coordinated complex can be converted into new structures with several small molecules such as CO and CN-Ar.

***sec*-TA-based Pincer Ligand as a Bridging Ligand for Multinuclear-complex Preparation**

The aforementioned deprotonation of *sec*-TA-based pincer complexes was based on single molecules, except for those involving *sec*-TA-based S^NS Ru(II) complexes. However, the

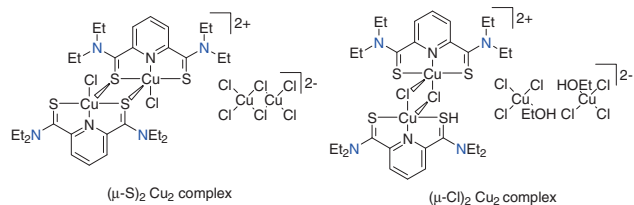


Figure 14. The structures of *sec*-TA-based S[^]N[^]S Cu complexes.

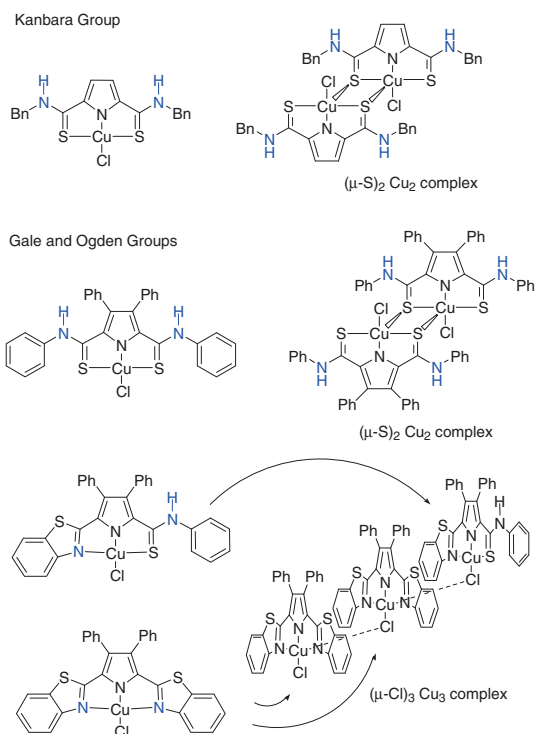


Figure 15. The structures of demeric and trimeric Cu complexes.

development of multistep-redox systems and multispin control, such as Fe–S clusters and molecular magnets, are also important for bioinorganic chemistry and materials science.

In 2004, Kapoor et al. reported the structure and magnetic properties of two S- or Cl-bridged Cu complexes (Figure 14).⁷² Magnetic susceptibility measurements showed that both complexes have an overall antiferromagnetic behavior. From 2010 to 2011, our group³⁷ and Gale and Ogden's groups⁷³ independently obtained the assembled structure of *sec*-TA-based Cu complexes (Figure 15). Since these 2,5-pyrrolyl-centered S[^]N[^]S Cu pincer complexes are neutral, the assemblies of the complexes, such as doubly layered assemblies via hydrogen bonding and triple-decker structures via bridging Cl ligands, are unique.

The deprotonated *sec*-TA-based S[^]X[^]S ligand with other transition metals, such as Ru(II),³⁸ Pd(II),⁴³ and Pt(II),³⁷ also give multinuclear complexes (Figure 16). The formation of the Ru and Pt complexes was elucidated by NMR, FT-IR, and MALDI-TOF mass spectrometry. The molecular structures of these multinuclear complexes were confirmed by single-crystal X-ray analysis. In the case of the Pt complex, a mixture of

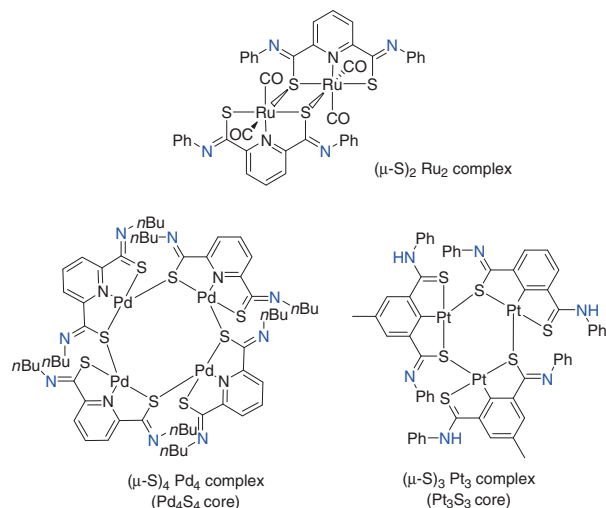


Figure 16. The structures of dimeric Ru complex, tetrameric Pd complex, and trimeric Pt complex.

oligomeric complexes in a protic solvent (e.g., EtOH/DMSO mixed solvent) is obtained. The mass spectrum indicates the existence of monomers, dimers, trimers, tetramers, and pentamers in the solution. Although Lei and Yang did not discuss the details of the formation process and the structural features of the Pd₄S₄ core complex, they identified the structure of the tetranuclear complex and showed the catalytic activity of the Pd complex for the Negishi coupling reaction.⁴³

In spite of the abundance of sulfur cluster studies, the utilization of *sec*-TA-based S[^]X[^]S ligands for cluster chemistry is limited. However, the hydrogen bonding of thioamide and the bridging-ligand behavior of iminothiolate may pave the way to the design of two- or three-dimensional molecular assemblies and their multistep redox systems, and to the control of their magnetic properties.

Catalytic Activity

To best of our knowledge, the number of reactions catalyzed with thioamide-based transition-metal complexes is still small compared to those catalyzed with phosphine-based transition-metal catalysts. Table 2 summarizes the structures of the Pd catalysts and the name of cross-coupling reactions.

In a recent perspective paper, Singh et al. overviewed the progress in organosulfur ligands;⁷⁸ he stated: “Since 2000, palladium(II) complexes of organosulphur and related ligands have emerged as viable alternatives to palladium–phosphine/carbene complexes as they have sufficient thermal stability, air and moisture insensitivity. Moreover synthesis of complexes of such ligands is easy.” Therefore, since thioamide is one of those organosulfur compounds (ligands) and can be prepared using a very simple method, the multidentate *sec*-TA-based ligand will be used more and more for cross coupling. For instance, Ramesh et al. have recently reported the synthesis and catalytic activity of TA-based Ru complexes (Figure 17);⁷⁹ the synthesized S[^]N Ru complexes worked as highly efficient catalysts for the synthesis of secondary or tertiary amides by the coupling of amines and alcohols with low-catalyst loading, obtaining a maximum yield of 97%.

Table 2. Various TA-based complexes and their catalytic activities

Structure of Catalyst	Cross-coupling Reaction	Remarks	Ref
	Mizoroki–Heck	presence of oxygen, high TON in short reaction time	74
	Suzuki–Miyaura	natural product	75, 77
	Negishi	high TON	43, 76
	Suzuki–Miyaura	electrically-deactivated aromatics	77

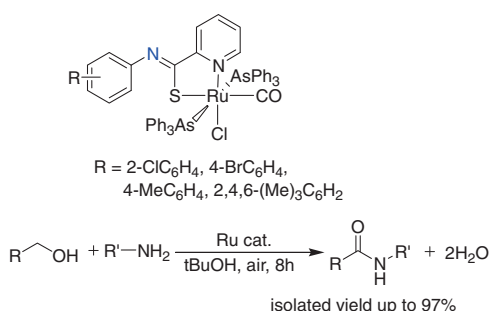


Figure 17. The structures of S^N TA-based Ru complexes and direct amides synthesis from alcohols and amines.

Summary and Scope

This review presents the recent developments in *sec*-TA-based transition-metal complexes as well as in the ligand design concepts for chemical tuning such as the control of photo-physical and redox properties and constructing multinuclear complexes. *sec*-TA serves not only as an organosulfur ligand, but also as a unique pincer ligand, owing to the hydrogen-bond donor ability, reactivity (deprotonation), and transformability of the structure.

Our primary goal is on “how to utilize and control the unique properties of the *sec*-TA-based transition-metal complexes” for developing future materials. Future research efforts on multidentate *sec*-TA would contribute to the development of further tunable photoluminescent complexes, controlled multi-nuclear-molecular assemblies, and catalysts for various applications in the field of materials chemistry.

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