



Reversible and stable redox behavior of a Pt(II) bis(dithiobenzoate)-type complex attributed to rotaxane-based stabilization

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ABSTRACT

A three-dimensionally insulated Pt(II) bis(dithiobenzoate) complex with a [1]rotaxane structure was synthesized using permethylated cyclodextrins. We have confirmed macrocyclic insulation is necessary to yield the Pt(II) bis(dithiobenzoate) complex with high selectivity. Furthermore, the formed Pt(II) complex showed highly stable and reversible two-step redox behavior in cyclic voltammetry due to the three-dimensional insulation.

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Redox properties are one of the most basic parameters used to understand the nature of a molecule because they directly reflect the energy levels of frontier orbitals. The study of redox properties provides information about chemical reactivity and physical properties of the molecule. Redox-active molecules have received much attention not only in basic science but also in applications such as molecular switching devices because the physical properties can be controlled by changing the number of electrons [1]. Among such molecules, transition metal complexes are the most promising because their redox states can be changed reversibly and variously. In particular, transition metal complexes bearing π -conjugated organosulfur chelating ligands have been extensively investigated, as represented by metal dithiolene complexes [2]. The sulfur atom is softer than the oxygen atom, which gives rise to a better electronic coupling and covalent nature between metals and organic ligands. Based on the covalency, these complexes form hybrid molecular orbitals between metal d-orbitals and ligand π -orbitals. This results in complexes with superior properties from both the metal and ligands. It has been reported that electric conductivity, magnetic properties, and optical properties can be modified by changing the redox state [3]. Accordingly, it is important to discover the redox potential of the complex and improve the stability of the oxidized or reduced species in order to utilize the metal complex as a practical molecular switching device.

Metal bis(dithiobenzoate) complexes are one of the known π -conjugated organosulfur chelate complexes [4]. These complexes have linearly elongated conjugated systems through the four-membered chelate structures including metal–sulfur bonds, which is attributed to the abovementioned d– π hybridized molecular orbitals. It is noteworthy that the d– π conjugated system can be extended by introducing other π -conjugated functional groups on dithiobenzoate ligands. Therefore, by expanding and modifying the conjugated system of the ligands, bis(dithiobenzoate) complexes are expected to exhibit fascinating properties, particularly optical and redox properties. However, the reports on metal bis(dithiobenzoate) complexes are limited, while other π -conjugated organosulfur chelate complexes have been widely explored. This is mainly due to the instability of the complexes; it has been reported that these complexes easily decompose in solution [4c,g]. Thus, the electrochemical properties of metal bis(dithiobenzoate) complexes are still obscure because they are generally unstable so the physical properties of metal bis(dithiobenzoate) complexes are still unexplored despite their potential to exhibit unique properties.

To stabilize such unstable complexes, macrocyclic insulation is one of the most effective methods [5]. Kano et al. reported that an O₂ adduct of iron-porphyrin, which is unstable in H₂O, can be stably isolated even in H₂O by using omnidirectional protection using a cyclodextrin-based rotaxane structure [5a,b]. In addition, we have previously reported on the Ni(II) bis(dithiobenzoate) complex, which is a three-dimensionally insulated complex with a [1]rotaxane structure using permethylated α -cyclodextrins

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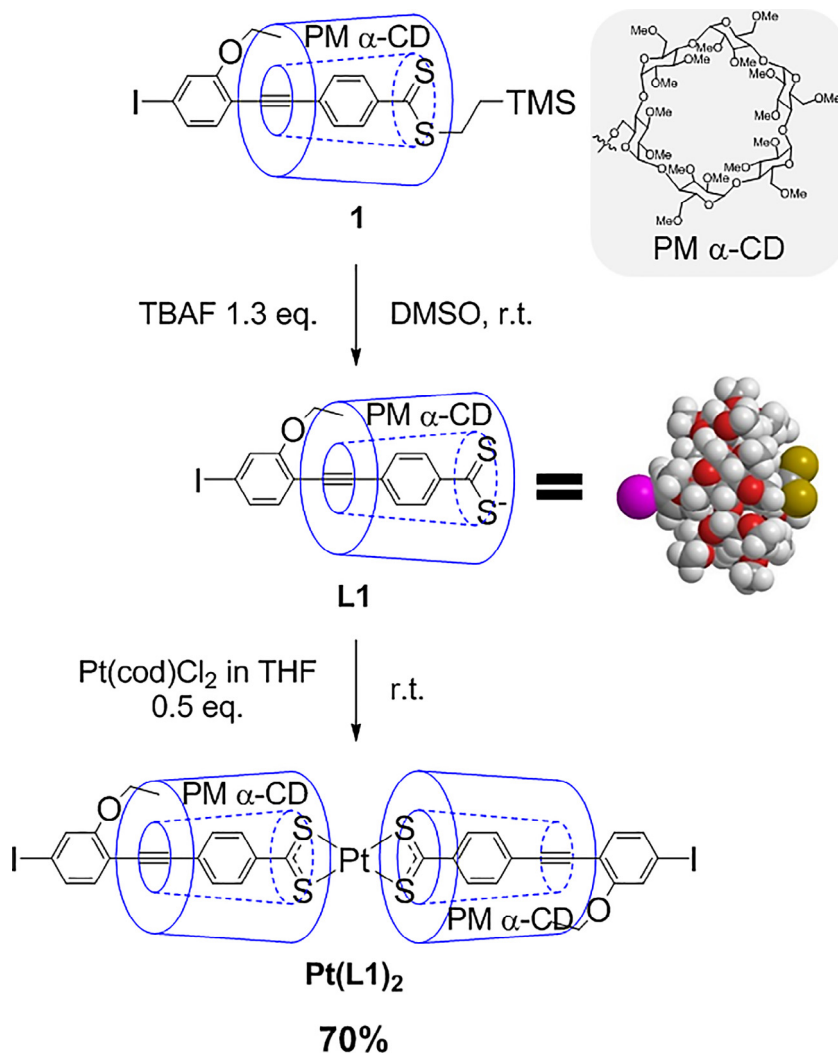
(PM α -CD) [6a]. As a result of macrocyclic insulation, the reduced species of the complex were kinetically stabilized and we were able to observe reversible redox behavior of a metal bis(dithiobenzoate) complex for the first time. In this study, we have attempted to introduce Pt(II) to improve the stability of redox behavior of the metal bis(dithiobenzoate) complex. Pt(II), which is a substitution-inactive metal, is expected to bind to the dithiobenzoate ligand more stably than Ni(II).

The synthetic scheme of the Pt(II) bis(dithiobenzoate) complex (**Pt(L1)₂**) is shown in Scheme 1. An insulated dithiobenzoate ligand precursor **1** was synthesized according to our previous report [6a]. The ethyl(trimethylsilyl) group was cleaved by the reaction with tetrabutylammonium fluoride (TBAF) to generate an insulated dithiobenzoate ligand **L1** *in situ*. After dichloro(1,5-cyclooctadiene) platinum(II) ($\text{Pt}(\text{cod})\text{Cl}_2$) was added to the reaction mixture, the resulting complex was purified by extraction and preparative size-exclusion chromatography (SEC) to yield 70% **Pt(L1)₂** as a bright orange solid. **Pt(L1)₂** was characterized by ¹H NMR, ¹³C NMR, ¹H NOESY NMR, and MALDI TOF-MS. Strong nuclear Overhauser enhancements (NOEs) between the aromatic proton of the axial oligo(phenylene ethynylene) and inner protons of PM α -CDs were observed in the ¹H NOESY NMR spectrum (Fig. 1a), which indicates the rotaxane structure was maintained during the reaction [6]. **Pt(L1)₂** showed an absorption band at 515 nm, which was characterized by UV–vis absorption spectroscopy in

chloroform (Fig. 1b). This strong absorption in the visible region supports the formation of a metal–dithiobenzoate complex [4c]. This absorption band is supposed to correspond to a charge transfer transition, as proposed in the case of the platinum(II) bis(dithiobenzoate) complex (absorption band near 430 nm) [4c]. The bathochromic shift of the band is considered to reflect the π -expansion.

In order to investigate insulation effects, we tried to synthesize the non-insulated reference complex **Pt(L1')₂** via two synthetic routes (Scheme 2): Path A is the same procedure used in synthesizing **Pt(L1)₂**, using a non-insulated ligand **L1'** instead of **L1**, and Path B uses the intramolecular de-slipping methodology by heating **Pt(L1)₂** in a hydrophobic solvent [6a,e]. However, we could not obtain the desired **Pt(L1')₂** via both Path A and B and only an undesirable by-product was yielded. Two pairs of signals originating from **L1'** were observed in the ¹H NMR experiment of this by-product (Fig. S3). Although we could not determine the exact molecular structure, it is assumed that one of the ligands underwent a structural change near the metal–dithiobenzoate moiety [4g,7]. These results demonstrate that the macrocyclic insulation effectively inhibits the formation of the by-product and plays an important role on selective synthesis of Pt(II) bis(dithiobenzoate) complex.

Finally, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to investigate the redox properties of **Pt**



Scheme 1. Synthetic route to **Pt(L1)₂** and CPK model [6a] of **L1** calculated by HF/LANL2DZ.

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