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Metalladithiolenes

Cyclization of TEMPO Radicals Bound to Metalladithiolene Induced by SOMO–HOMO Energy-Level Conversion**

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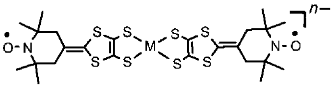
In recent decades, it has been demonstrated that the appropriate control of the electronic structure of a metalladithiolene moiety in several planar metalladithiolenes is a promising way to realize desired physical[1a–c] and/or chemical[1d,e] properties. We have recently developed a new metalladithiolene containing a 2,2,6,6-tetramethyl-1-piperidinyl *N*-oxide (TEMPO) radical moiety, (tempodt)Pt, and have revealed that this complex has a quite unique electronic structure, in which the energy level of the singly occupied molecular orbital (SOMO; resulting from the TEMPO radical) is lower than that of the highest occupied molecular orbital (HOMO; centered on the π-conjugated dithiolene moiety).[2] One-electron ($1e^-$) oxidation of the complex led to the generation of a π radical on the HOMO.

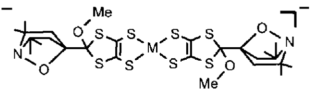
Next, we focused on the application of this unique electronic structure to the development of new chemical phenomena, by employing planar metalladithiolenes, $[M(\text{dithiolene})_2]^{n-}$ ($M = Au^{3+}$, Ni^{2+}; $n = 0, -1, -2$). These complexes are well known to have interesting electronic structures in which their HOMOs (SOMOs) delocalize over π-conjugated dithiolene ligands, and they are easily oxidized to produce ligand-based π-radical species.[3] From this perspective, we designed novel planar metalladithiolenes $[M(\text{tempodt})_2]^{n-}$ **1** (**1a**: $M = Au^{3+}$, $n = 1$; **1b**: $M = Ni^{2+}$, $n = 2$).

These compounds are composed of a planar π-conjugated dithiolene moiety and two TEMPO radical moieties. Because of a strong donating ability of this type of π-conjugated dithiolene skeleton, a SOMO–HOMO converted electronic structure similar to (tempodt)Pt was expected for compound **1**. It was also expected that a π radical would be produced on the π-conjugated skeleton upon $1e^-$ oxidation, and that the resulting multispin species would show peculiar chemical reactivity and/or physical properties. Herein, a particular intramolecular cyclization by radical coupling through **1** according to this scenario is reported.



1

1a: M = Au^{3+}, *n* = 1
1b: M = Ni^{2+}, *n* = 2



2

2a: M = Au^{3+}
2b: M = Ni^{2+}

The complexes **1a**, **2a**, and **2b** were newly synthesized by reaction of tempodtR$_2$ with $NaAuCl_4$ or $NiCl_2$ in the presence of Bu_4NOH in THF/MeOH (see the Supporting Information). In the case of $M = Au^{3+}$, **1a** and the reduced side products were initially formed as purple precipitates, followed by precipitation of the green solid **2a**, whereas compound **2b** formed as a dark green precipitate when $M = Ni^{2+}$. Note that a $[Ni(\text{dithiolene})_2]^{2-}$ dianion species generated in situ is spontaneously oxidized to afford the $[Ni(\text{dithiolene})_2]^-$ ion. This difference in behavior was attributed to differences in donating ability: the Ni^{2+}-containing π-conjugated skeleton was much more easily oxidized than the Au^{3+}-containing one (Supporting Information, Figure S1).

The molecular structure of **1a**, analyzed by single-crystal XRD, is shown in Figure 1a.[4] The Au atom was located at the inversion center, and the conjugated dithiolene skeleton appeared to be fairly planar. The N–O bond length in the TEMPO moiety was 1.307(19) Å, close to the lengths in the other TEMPO derivatives. An EPR spectrum of **1a** in CH_2Cl_2 showed a triplet signal with $g = 2.006$ and $A_N = 1.52$ mT (A_N: hyperfine coupling constant for N atom), which are typical values for TEMPO, thus suggesting little exchange interaction between the two TEMPO moieties in **1a** (Figure 3a). The calculated molecular orbitals (MOs) are shown in Figure 2.

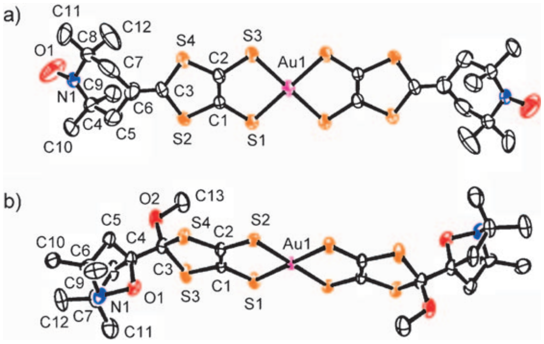


Figure 1. ORTEP plots of **1a** and **2a** with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

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TEMPO = 2,2,6,6-tetramethyl-1-piperidinyl *N*-oxide; SOMO = singly occupied molecular orbital; HOMO = highest occupied molecular orbital.

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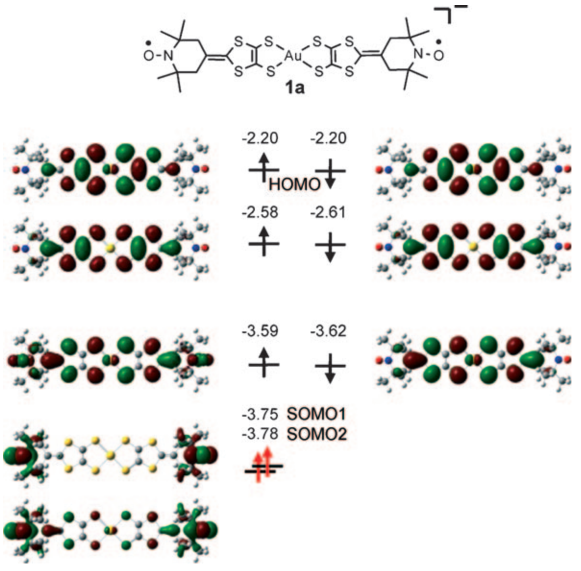


Figure 2. MO diagram of **1a** calculated by the DFT method. Energies are presented in eV.

Electrons are delocalized over the π-conjugated dithiolene moiety on the HOMO, and the energy levels of the SOMOs resulting from TEMPO moieties are lower than that of the HOMO, as expected.

A single crystal of **2a** was obtained by recrystallization from CH_2Cl_2/Et_2O, and that of **2b** was precipitated from DMF/Et_2O. The crystal structures of **2a** and **2b** were successfully determined by single-crystal XRD analysis as Bu_4N^+ salts,[4] even though both crystals were unstable and decomposed within 15 s upon exposure to air. The instability of the crystals was thought to originate from the evaporation of solvent molecules from the crystal lattice.

In **2a**, two halves of the monoanions and one Bu_4N^+ ion were crystallographically independent, and each Au atom was located at the inversion center (Supporting Information, Figure S2). One of the molecular structures of **2a** is depicted in Figure 1b. The conjugated dithiolene skeleton was almost flat, with the exception of carbon atom C3, to which an OMe group was attached. The terminal moieties formed an interesting cyclized molecular structure, in which the piperidine skeleton formed a boat conformation, and oxygen atom O1 and carbon atom C4 formed a single bond. It was obvious that the TEMPO radicals no longer appeared, and that the expected C3=C4 double bond was oxidized to yield a C3−C4 single bond with the sp^3 bonding environment.

In **2b**, two halves of the monoanions and one Bu_4N^+ ion were crystallographically independent, and each Au atom was located at the inversion center (Supporting Information, Figure S3). The molecular structure of **2b** was nearly identical to that of **2a**, in which the TEMPO radical moiety formed a cyclized structure and an OMe group was attached to the C3 atom.

In contrast to the similarity of their molecular structures, the spin states of **2a** and **2b** were quite different. Compound **2b** had an unpaired electron and showed a paramagnetic $S = 1/2$ spin state, which was evidenced by EPR spectroscopy (Figure 3b), whereas **2a** was in a diamagnetic singlet state.

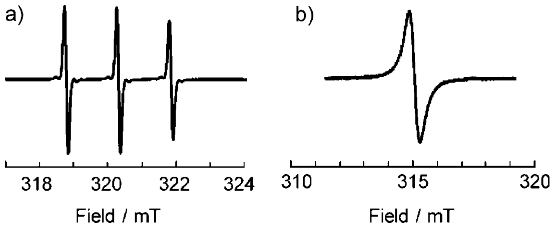


Figure 3. EPR spectra of CH_2Cl_2 solutions of a) **1a** ($g = 2.006$, $A_N = 1.52$ mT) and b) **2b** ($g = 2.041$) at room temperature.

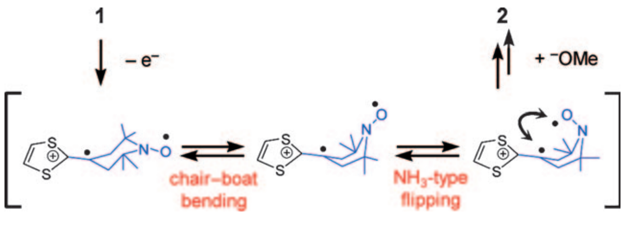
Delocalization of the unpaired electron onto the π-conjugated skeleton in **2b** was revealed not only by the EPR spectrum but also by comparison of the bond lengths of **2a** and **2b** in combination with their DFT calculations (Supporting Information, Figures S4 and S5). The bond lengths of the anions and their differences were in accord with the electron density distribution of their HOMO (SOMO) calculated by DFT methods, in which the bonding C−C bonds were elongated and the antibonding C−S bonds were shortened under $1e^-$ oxidation (Supporting Information, Table S1).

We next considered the formation mechanism of **2** to focus on the chemical reactivity of 1,4-bis(methylene)cyclohexane (**3**), and its "rigid" derivatives **4** and **5**. Since the molecular/electronic structure of **1** around the TEMPO moiety was similar to that of **3** (TEMPO had an unpaired electron on the antibonding π orbital on the N−O bond), it was helpful to compare the reactivities of **1** and **3**–**5** to elucidate the formation mechanism of **2**.

1 **3** **4** **5**

It has been reported that $1e^-$-oxidized **3** did not afford any cyclized molecular structure,[5] while intramolecular bond formation preferentially proceeded upon reaction with Br_2 for **4**[6] and with acid for **5**,[7] which resulted in cyclized molecular structures similar to that of **2** (Supporting Information, Figure S6). The difference in the reactivity between these compounds stems mainly from the proximity of the reaction centers (two double bonds). These considerations are relevant to the formation of **2** in light of the electronic structure of **1** and the flexibility of the TEMPO moiety.

Scheme 1 shows the suggested mechanism for the formation of **2**. In the case of **1**, the electron was removed from



Scheme 1. Proposed reaction mechanism for the formation of **2**.

the π-conjugated dithiolene skeleton (= HOMO, shown in Figure 2 and the Supporting Information, Figure S7) under 1e$^-$ oxidation. The resulting π-radical species could be described by several resonance structures (Supporting Information, Figure S8), but the structure shown in Scheme 1 was the most stable one because of the quasi-aromatization of the dithiolene rings. Consequently, the generated π radical reacted with the TEMPO radical, which resulted in a cyclized structure through C–O bond formation.

In contrast to **3**, compound **1** was flexible around the TEMPO moiety as a result of the NH_3-type flipping of the $[C(CH_3)_2]_2N-O$ moiety coupled with the chair–boat bending of the piperidine skeleton, which realized the near location of the two π radicals (reaction centers). To our knowledge, this is the first example of TEMPO radicals that achieved this type of cyclization through C–O bond formation. It is reasonable that **2b** was formed smoothly in the reaction mixture, whereas **2a** was obtained as a side product: the generation of the π radical, which was the first and critical step for the cyclization reaction, occurred more easily when M = Ni than when M = Au, as indicated by the oxidation potential of their related complexes (Supporting Information, Figure S1).

In conclusion, a new class of cyclization reactions of TEMPO was achieved by intramolecular radical coupling. This phenomenon is based on the SOMO–HOMO converted unique electronic structure (properly designed energy levels and electron density distributions in the MOs) of the complexes and on the conformational flexibility of the TEMPO skeleton. We are currently investigating the reversible cyclization–ring opening of **2a** and **2b** by external stimuli, such as heat.

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