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# Photocatalytic Splitting of $CS_2$ to $S_8$ and a Carbon−Sulfur Polymer Catalyzed by a Bimetallic Ruthenium(II) Compound with a Tertiary Amine Binding Site: Toward Photocatalytic Splitting of $CO_2$?

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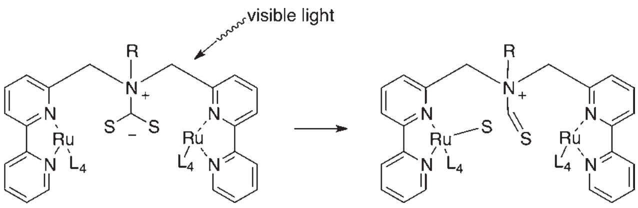
Supporting Information

**ABSTRACT:** The catalytic photocleavage of $CS_2$ to $S_8$ and a $(C_xS_y)_n$ polymer with visible light using a dinuclear ruthenium(II) compound with a bipyridine units for photoactivity and a vicinal tertiary amine binding site for $CS_2$ activation was studied. The catalyst was characterized by X-ray diffraction, $^1$H NMR, and $^{13}$C NMR, ESI-MS and elemental analysis. $CS_2$ photocleavage was significant (240 turnovers, 20 h) to yield isolable $S_8$ and a $(C_xS_y)_n$ polymer. A mononuclear catalyst or one without an amine binding site showed significantly less activity. XPS of the $(C_xS_y)_n$ polymer showed a carbon/sulfur ratio ∼1.5−1.6 indicating that in part both C−S bonds of $CS_2$ had been cleaved. Catalyst was also included within the polymer. The absence of peaks in the $^1$H NMR verified the $(C_xS_y)_n$ nature of the polymer, while $^{13}$C NMR and IR indicated that the polymer had multiple types of C−S and C−C bonds.

Reduction of $CO_2$ is a hot research topic in efforts to reduce its environmental impact and recycle fossil fuels. Besides higher temperature heterogeneous catalytic methods[1] and application of electrochemical cells,[2] five main low-temperature and/or photocatalytic approaches can be identified: (1) thermal reduction of $CO_2$ with $H_2$ often under basic conditions via the formation of bicarbonate to yield formic acid or formate salts;[3] (2) photocatalytic reduction of $CO_2$ to CO using tertiary amines as sacrificial reducing agents and proton donors in a "half-cell" approach;[4] (3) the use of $H_2$ in a photocatalytic reverse water−gas shift reaction;[5] (4) photoreduction with $H_2O$ as the reducing agent;[6] (5) catalytic and noncatalytic reactions of $CO_2$ with stoichiometric acceptors.[7] These methods all have disadvantages such as the use of nonrenewable reducing agents such as amines and $H_2$, the apparent need for UV light for the one-electron reduction of $CO_2$ with $H_2O$, or the need for stoichiometric oxygen-acceptor reagents.

The photocatalytic cleavage of $CO_2$ to yield CO and $O_2$ under ambient conditions with solar energy would be beneficial because CO formed could be stored and then combusted when needed. Alternatively, CO could be reacted with $H_2O$ using water−gas shift technology to yield $H_2$; the latter could then be reacted with additional CO to yield methanol as a liquid fuel. As a *prelude* to the photocatalytic splitting of $CO_2$, here we describe our research on the photocatalytic splitting of isostructural $CS_2$ to the corresponding $(C_xS_y)_n$ polymer and molecular sulfur, $S_8$, with emphasis on catalytic design principles needed to effect such a photocatalytic splitting reaction. Such a photocleavage of $CS_2$ has not been reported.

**Scheme 1. Catalytic Design for Photocleavage of $CS_2$**



Carbon disulfide is a linear molecule with relatively strong C═S double bonds. On the one hand, the electrophilic carbon atom easily reacts with good nucleophiles such as amines; for example, the reaction with ammonia and primary and secondary amines yields dithiocarbamates. On the other hand, the formation of CS and elemental sulfur from $CS_2$ is significantly endoergic ($\Delta G_r$ = +27.12 kcal/mol); thus, such a splitting reaction seemingly should be carried out under photocatalytic conditions. The catalytic module that was designed for the photocatalytic splitting pathway of $CS_2$ (Scheme 1) consists of (a) a binuclear metal complex that can lead to $CS_2$ insertion and activation,[8] (b) a nucleophilic binding site for $CS_2$ complexation, such as a tertiary amine, that will lead to the formation of a trigonal zwitterionic $R_3N^+CS_2^-$ unstable transient species that will, however, have lengthened (weaker) C−S bonds.[9] A position vicinal to the binuclear center will combine the advantages of the amine binding site and the binuclearity for C−S bond activation. (c) The catalyst ideally will be photoactive; that is, it should be able to absorb visible light; ruthenium bipyridine based compounds appear to be excellent candidates, and (d) metal sulfide species formed in the carbon−sulfide bond splitting step should be in a position to recombine to yield molecular sulfur after a series of $CS_2$ binding and C−S bond splitting reactions. Therefore, the catalysts that were prepared were based on ditopic 1,2-bis(2,2′-bipyridyl-6-yl) ligands to form dinuclear ruthenium(II) complexes with tertiary amine containing a bridge. For verification of the catalyst design, both an acetylene-bridged compound to

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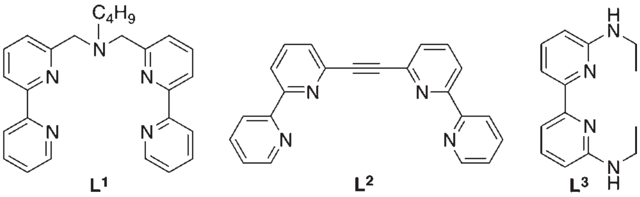
**Scheme 2. Designed and Control Ligands**



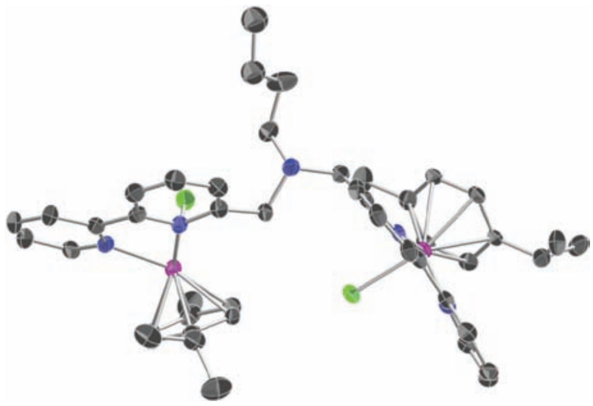


**Figure 1.** ORTEP representation (50% probability) of $[Ru_2\mathbf{L}^1(p\text{-cymene})_2Cl_2](BF_4)_2 \cdot 1.5CH_3CN$. Anions, solvates, and hydrogen atoms are not shown for clarity. Color code: C, black; N, blue; Ru, magenta; Cl, green.

demonstrate the importance of a tertiary amine binding site for $CS_2$ and a mononuclear complex to show the advantage of activation of both C−S bonds were prepared (Scheme 2).

The ligand *N*,*N*-bis([2,2′-bipyridin-6-yl]methyl)butan-1-amine ($\mathbf{L}^1$) was prepared by the reaction of 2 equiv of 6-(chloromethyl)-2,2′-bipyridine[11] with *n*-butylamine. The first control ligand, 1,2-bis(2,2′-bipyridyl-6-yl)ethyne ($\mathbf{L}^2$), was prepared as recently described through consecutive Suzuki and Sonogashira coupling reactions of 6-bromo-2,2-bipyridine with sodium acetylide,[10] and the second control ligand, $N^6$,$N^{6\prime}$-diethyl[2,2′-bipyridinyl]-6,6′-diamine ($\mathbf{L}^3$), was prepared by the palladium-catalyzed coupling of 6,6′-dibromo-2,2′-bipyridine with ethylbenzylamine, followed by debenzylation with concentrated $H_2SO_4$. These ligands were then reacted with a ruthenium(II) precursor, $[(p\text{-cymene})RuCl_2]_2$, to yield the desired orange dinuclear ruthenium(II) complexes $[Ru_2\mathbf{L}^1(p\text{-cymene})_2Cl_2]^{2+}$ (**1**), $[Ru_2\mathbf{L}^2(p\text{-cymene})_2Cl_2]^{2+}$ (**2**), and $[Ru\mathbf{L}^3(p\text{-cymene})Cl]$ (**3**). Structures derived from X-ray diffraction measurements are shown in Figure 1 and in the Supporting Information (SI). The structures have the expected coordination spheres around the ruthenium(II) centers with typical Ru−N, Ru−C, and Ru−Cl bond lengths (see the SI for full data). The lability of the *p*-cymene and chloride ligands was also evaluated. Thus, the chloride ligand could be replaced by a solvent such as acetonitrile by the addition of $AgBF_4$, and heating or irradiation with light from a tungsten lamp led to the replacement of the *p*-cymene ligand by a solvent. Representative structures (Figures S2 and S3 in the SI) show that after these treatments the binuclear ruthenium(II) nature of these compounds is retained. Notably, the relative positions of the proposed ruthenium(II) active sites can vary because of free rotation around the bridging unit between the bipyridine groups.

**Table 1. Photocleavage of $CS_2$ to $S_8$ and $(C_xS_y)_n$** $^a$

| catalyst | solvent | yield $S_8$, mol % | TON |
|---|---|---|---|
| $[Ru_2\mathbf{L}^1(p\text{-cymene})_2Cl_2]^{2+}$ | $THF/H_2O$ | 12.3 | 242 |
| $[Ru_2\mathbf{L}^1(p\text{-cymene})_2Cl_2]^{2+a}$ | $THF/H_2O$ | 0 | 0 |
| $[Ru_2\mathbf{L}^1(p\text{-cymene})_2Cl_2]^{2+b}$ | $THF/H_2O$ | 4.7 | 92 |
| $[Ru_2\mathbf{L}^2(p\text{-cymene})_2Cl_2]^{2+}$ | $THF/H_2O$ | 3.9 | 77 |
| $[Ru_2\mathbf{L}^3(p\text{-cymene})_2Cl_2]^{2+}$ | $THF/H_2O$ | 2.4 | 48 |
| $[(p\text{-cymene})RuCl_2]_2$ | $THF/H_2O$ | <0.5 | ~10 |
| none | $THF/H_2O$ | 0 | 0 |

$^a$ Reaction conditions: 5 mg of catalyst, 0.5 mL of $CS_2$, 1 mL of solvent, 20 h, 70 °C, light from a 60-W tungsten lamp: (a) no light; (b) 22 °C.

Carbon disulfide was photocleaved in $H_2O$/tetrahydrofuran (THF), which dissolves both the catalysts and $CS_2$ (Table 1). There was no reaction in other solvents that dissolved both components such as acetonitrile and dimethyl sulfoxide (DMSO). In a typical procedure, a 15-mL pressure tube was loaded with 5 mg (4.2 $\mu$mol, 0.05 mol %) of **1**, 1 mL of 1:1 $H_2O$/THF, and 0.5 mL (8.28 mmol) of $CS_2$. The pressure tube was purged with argon, in order to remove all traces of oxygen, and then hermetically sealed and stirred vigorously. An ordinary 60-W light bulb was used as a photon source in all reactions. Typically, reactions were carried out at 70 °C. After 3−4 h, a dark insoluble material started to form; reactions were continued for 20 h. In the workup procedure, $H_2O$ and toluene were added to the reaction mixture to form three different phases. The lower, aqueous phase contained the catalyst, which was partially decomposed as seen by $^1H$ NMR. Also, a small amount of $H_2$ was detected, indicating some catalyst decompostion (see also below). The upper, organic phase was analyzed by gas chromatography−mass spectrometry (GC−MS), and besides $CS_2$, elemental sulfur ($S_8$) in isolable quantities after evaporation was found (30 mg, 12.3% yield, 242 turnovers). $S_8$ was identified by GC−MS and by comparison to a reference standard. At the interface between the aqueous and organic phases, there were dark, opaque, and very thin films (Figure S4 in the SI), which strongly suggested a polymeric nature of the product. Control experiments with **2** and **3** as catalysts under identical conditions yielded $S_8$ (10.5 mg, 3.9% yield, 81 turnovers and 6.4 mg, 2.4%, 48 turnovers, respectively) in significantly smaller amounts, supporting the design concept that an amine binding site and dinuclear catalyst would significantly increase the activity for $CS_2$ cleavage. There was no reaction in the absence of catalyst or light, and only traces of $S_8$ were formed using $[(p\text{-cymene})RuCl_2]_2$ as a catalyst. Reactions at 22 °C were less effective.

There is not much published research on $(C_xS_y)_n$ polymers. Initially, $CS_2$ was polymerized at very high pressures of up to 40 000 bar and ~180 °C.[12] Later on, photopolymerization at 313 nm of $CS_2$ in the gas phase[13] and plasma-polymerized $CS_2$ were described.[14] The polymers all have a 1:2 carbon/sulfur atom ratio except for the plasma-polymerized $CS_2$, where various ratios, C < S, were obtained depending on the polymerization conditions. Here, elemental analysis of the $(C_xS_y)_n$ polymer was not quantitative because only ~61% of the total mass could be accounted for, presumably because of incomplete pyrolysis of the material. Elemental analysis did, however, reveal significant amounts of nitrogen and hydrogen, indicating that the catalyst had been at least partially encapsulated within the polymer. XPS measurements were, therefore, carried out that also showed catalyst encapsulation and a carbon/sulfur ratio of 1.5−1.6 after correction for catalyst inclusion. This is the first $(C_xS_y)_n$ polymer

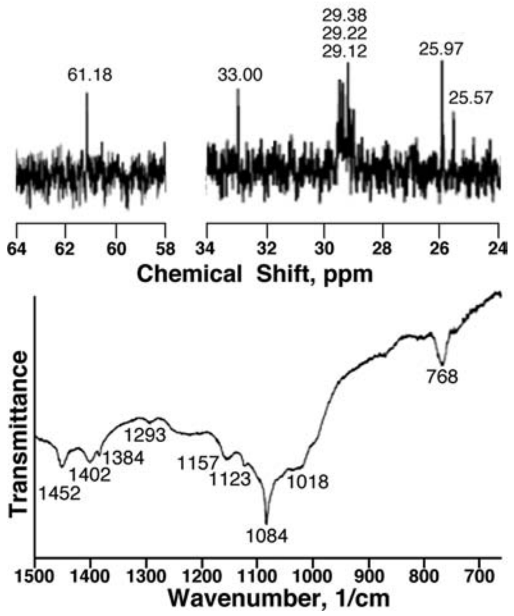


**Figure 2.** $^{13}$C NMR (top) and IR (bottom) spectra of the $(C_xS_y)_n$ polymer.

where $x > y$ and indicates that, in part, *both* C−S bonds of $CS_2$ had been cleaved in the photocatalytic process.

The $(C_xS_y)_n$ polymers are only soluble in apolar solvents such as DMSO. $^1$H NMR in DMSO-$d_6$ again showed residue of catalyst but no other hydrogen-atom-containing compound. The $^{13}$C NMR spectrum (Figure 2, top) showed seven peaks associated with the $(C_xS_y)_n$ polymer at 25.57, 25.97, 29.02, 29.22, 29.78, and 33.00 ppm for C−S single bonds and 61.18 ppm for C═S double bonds. Clearly, the $^{13}$C NMR spectrum is indicative of various different types of C−S bond connectivity. The IR spectrum (Figure 2, bottom) likewise showed several distinctive peaks at 1452, 1084, and 1018 cm$^{-1}$ attributable to the various possible C−S bonds.[13d,14] Multiple matrix-assisted laser desorption ionization time-of-flight MS measurements were of low quality but showed mostly molecular weights between 350 and 580 amu.

The photocatalytic splitting of $CO_2$ was also attempted using $[Ru_2\mathbf{L}^1(p\text{-cymene})_2Cl_2]^{2+}$ as the catalyst in THF/$H_2O$ in various ratios as the solvent. Although on one or two occasions we observed the formation of CO, the experiments were not sufficiently repeatable. More typically, the formation of molecular hydrogen was observed, which we associate with catalyst decomposition because it is well-known that photoirradiation of tertiary amines leads to decomposition via the formation of cation radicals.[4] Therefore, although we have successfully designed an efficient catalyst for the photocleavage of $CS_2$ with visible light to its components, molecular sulfur, and a $(C_xS_y)_n$ polymer, similar photocleavage of $CO_2$ to CO and $O_2$ will require a more robust catalyst design.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** X-ray crystallographic data in CIF format, full experimental details, and additional structures, spectra, and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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