Oxygenation of a Ruthenium(II) Thiolate to a Ruthenium(II) Sulfinate Proceeds via Ruthenium(III)

Craig A. Grapperhaus,* Selma Poturovic, and Mark S. Mashuta

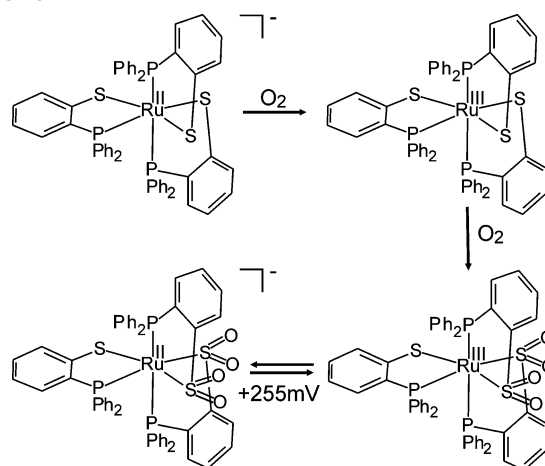*Department of Chemistry, University of Louisville, Louisville, Kentucky 40292*

Exposure of acetonitrile/methanol solutions of [PPN][Ru(DPPBT)$_3$] [PPN = bis(triphenylphosphoranylidene); DPPBT = 2-diphenylphosphinobenzene thiolate] to oxygen initiates metal-centered oxidation, yielding the ruthenium(III) thiolate Ru(DPPBT)$_3$. Ru-(DPPBT)$_3$ further reacts with oxygen, at sulfur, to give the ruthenium(III) sulfinate complex [Ru(DPPBT-O$_2$)$_2$(DPPBT)], which is reduced under ambient conditions to [PPN][Ru(DPPBT-O$_2$)$_2$-(DPPBT)]. Ruthenium(II) sulfinate is the only product isolated from acetonitrile/methanol. Yellow crystals of [PPN][Ru(DPPBT-O$_2$)$_2$-(DPPBT)] were obtained. Ruthenium(III) sulfinate was isolated as green prism-shaped crystals upon oxygenation of [PPN][Ru-(DPPBT)$_3$] in chlorobenzene/hexane. Electrochemical oxidation of ruthenium(II) sulfinate yields the ruthenium(III) derivative, which is rapidly reduced back to ruthenium(II) upon the addition of hydroxide.

The sulfur-centered reactivity of transition-metal thiolates with dioxygen to yield sulfur oxygenates is well documented, with initial efforts focused largely on cobalt(III) and nickel(II).[1–4] Interest in the oxygen reactivity of iron thiolates was prompted by crystallographic studies of nitrile hydratase (NHase) by Endo and co-workers.[4–9] They reported that the active site of NHase contains iron(III) coordinated by three cysteine-derived sulfur donors with a mixed thiolato (RS$^-$), sulfenato (RSO$^-$), and sulfinato (RSO$_2^-$) donor set. To date,

Scheme 1

only one synthetic complex, Ru(DPPBT)(DPPBT-O(H))-(DPPBT-O$_2$) (DPPBT = 2-diphenylphosphinobenzene thiolate), that reproduces this asymmetric sulfur-donor environment has been structurally characterized.[10] The parent complex, [HNEt$_3$][Ru(DPPBT)$_3$], displays an air sensitivity that is solvent-dependent, with metal-centered oxidation favored in dichloromethane and ligand-centered oxidation in mixed solvents. During our own electrochemical studies of the parent thiolate as the bis(triphenylphosphoranylidene)(PPN) salt,[11,12] [PPN][Ru(DPPBT)$_3$], we also observed sulfur-centered oxygenation. We now report the reaction of ruthenium(II) thiolate to a ruthenium(II) sulfinate via Ru(III) intermediate species, as shown in Scheme 1.

In the current work, oxygen was purged through a 0.66 mM acetonitrile/methanol solution of [PPN][Ru(DPPBT)$_3$] for 15 min, which was then stirred under an O$_2$ atmosphere for 48 h. The reaction was monitored by UV–visible spectroscopy (Figure 1). Within the first hour, the light-orange solution (—) changed to red-brown (- - -) as the weak absorption band at 435 nm associated with [PPN][Ru-(DPPBT)$_3$] was replaced by stronger bands at 540, 797, and

* To whom correspondence should be addressed. E-mail: grapperhaus@louisville.edu. Phone: (502) 852-5932. Fax: (502) 852-8149.

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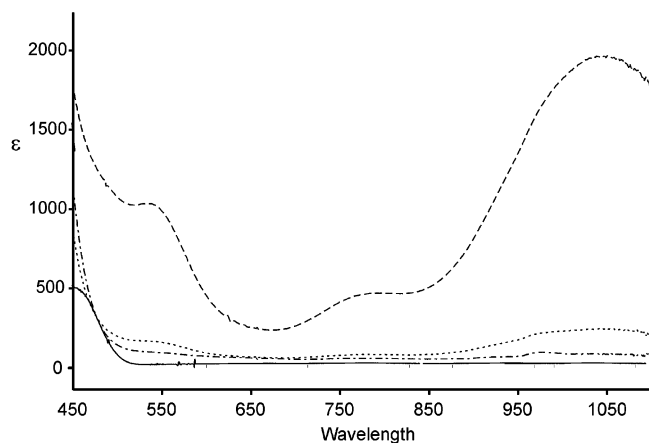(10) Dilworth, J. R.; Zheng, Y. F.; Lu, S. F.; Wu, Q. J. *Transition Met. Chem.* **1992**, *17*, 364–368.
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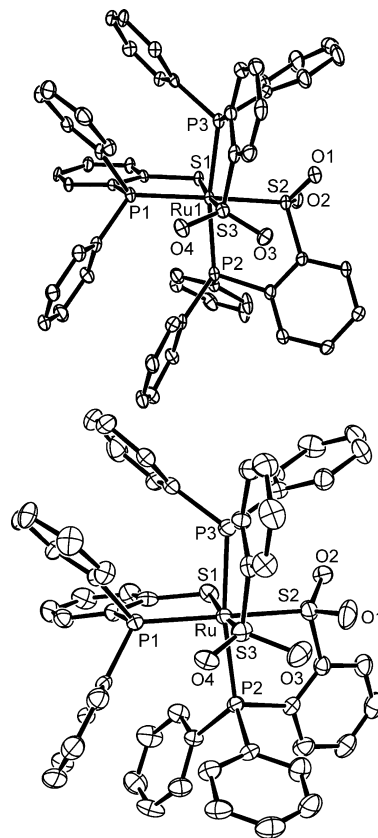(12) Grapperhaus, C. A.; Poturovic, S.; Mashuta, M. S. *Inorg. Chem.* **2002**, *41*, 4309–4311.

Figure 1. UV−visible spectrum of aliquots from the reaction of [PPN]-[Ru(DPPBT)₃] with oxygen after 0 min (—), 15 min (- - -), 15 h (···), and 39 h (-··-).

1041 nm. These bands are indicative of the previously reported Ru(III) derivative, Ru(DPPBT)₃, demonstrating that the initial oxygen reactivity is metal-based. A voltammogram recorded after 2 h shows no new redox events. After ∼15 h, the solution became light yellow as Ru(DPPBT)₃ was consumed (···). The reaction was complete within 39 h (-··-). Following workup, the *Ru(II) complex* [PPN][Ru-(DPPBT-O₂)₂(DPPBT)] was obtained as a yellow solid. Chromatographic analysis of the crude product [performed on a silica plate with THF/hexanes (1:1)] revealed a single complex. The ESI-MS displays a parent peak at $m/z = 1045$ with an isotopic envelope consistent with ruthenium, three DPPBT ligands, and four oxygen atoms (Figure S1 in the Supporting Information). While it is not possible to assign the location of the oxygen atoms from the mass spectrum, the infrared spectrum displays intense peaks at 1017 and 1115 cm^{-1} consistent with sulfinato (RSO₂$^-$) donors (Figure S2 in the Supporting Information).[3]

X-ray-quality crystals of [PPN][Ru(DPPBT-O₂)₂(DPPBT)] were obtained from dichloromethane/hexanes at room temperature.[13−20] An ORTEP representation of the metal-containing anion is provided in Figure 2 (top). Ruthenium

(13) Crystal data for [PPN][Ru(DPPBT-O₂)₂(DPPBT)]: yellow plate, triclinic, $P\bar{1}$, $a = 13.528(2)$ Å, $b = 15.278(3)$ Å, $c = 19.181(3)$ Å, $\alpha = 98.811(3)°$, $\beta = 96.488(3)°$, $\gamma = 92.197(3)°$, $V = 3886.2(11)$ Å^3, $D_{calcd} = 1.353$ g cm^{-3}, $Z = 2$. Final refinement on F^2 converged at R1 = 0.0970 and wR2 = 0.1465 with a GOF of 1.069. Crystal data for [Ru(DPPBT-O₂)₂(DPPBT)]: green prism, monoclinic, $C2/c$, $a = 18.374(3)$ Å, $b = 12.436(2)$ Å, $c = 40.497(6)$ Å, $\beta = 99.995(3)°$, $V = 9113(2)$ Å^3, $D_{calcd} = 1.522$ g cm^{-3}, $Z = 8$. Final refinement on F^2 converged at R1 = 0.0961 and wR2 = 0.1285 with a GOF of 1.07. See the Supporting Information for further experimental crystallographic details.
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Figure 2. ORTEP[20] view of the anionic complex of [PPN][Ru(DPPBT-O₂)₂(DPPBT)] (top) and [Ru(DPPBT-O₂)₂(DPPBT)] (bottom) showing 40% probability displacement ellipsoids. H atoms, the PPN cation, and the solvent are not shown.

sits in a pseudo-octahedral P₃S₃ donor environment with meridional coordination of phosphorus and sulfur. One sulfur, S1, is a thiolato donor, while two cis sulfurs, S2 and S3, are sulfinato donors. The Ru−P bond distances range from 2.3608(16) to 2.3901(16) Å, which is similar to those in related complexes.[10,12,21] The Ru−S$_{thiolato}$ bond distance of 2.4056(16) Å is slightly longer than the Ru−S$_{sulfinato}$ bond distances of 2.3463(15) and 2.2849(16) Å to S2 and S3, respectively. A decrease in Ru−S bond distances (Table 1) was previously observed upon alkylation of [PPN][Ru-(DPPBT)₃] and is consistent with similar observations with nickel complexes.[3,22]

The cyclic voltammogram of [PPN][Ru(DPPBT-O₂)₂-(DPPBT)] (Figure S3 in the Supporting Information) displays a reversible oxidation event at +255 mV vs Ag/Ag$^+$. This is shifted by +600 mV with respect to the parent complex, consistent with the modification of two thiolato donors to sulfinates.[3] The peak separation remains constant ($\Delta E = 73-88$ mV) over a range of scan rates from 50 to 1000 mV/s, indicating a reversible event. Bulk oxidation in acetonitrile, with in situ UV−visible monitoring, at an applied potential of +550 mV confirms a one-electron process, yielding the Ru(III) derivative, [Ru(DPPBT-O₂)₂(DPPBT)], as a green product with absorption bands at 369 and 651 nm. The EPR

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Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for [PPN][Ru(DPPBT-O$_2$)$_2$(DPPBT)] and [Ru(DPPBT-O$_2$)$_2$(DPPBT)]

	[PPN][Ru(DPPBT-O$_2$)$_2$(DPPBT)]	[Ru(DPPBT-O$_2$)$_2$(DPPBT)]
Ru−S1	2.4056(16)	2.4099(15)
Ru−S2	2.3463(15)	2.3553(15)
Ru−S3	2.2849(16)	2.2989(16)
Ru−P1	2.3683(15)	2.3498(15)
Ru−P2	2.3901(16)	2.4066(15)
Ru−P3	2.3608(16)	2.3565(16)
S2−O1	1.449(4)	1.537(4)
S3−O3	1.464(4)	1.564(4)
S1−Ru−S3	174.33(5)	174.17(6)
P1−Ru−S2	175.24(6)	168.55(6)
P3−Ru−P2	169.13(5)	170.63(5)
P1−Ru−S3	95.94(6)	96.11(5)
Ru−S3−O4	114.90(18)	122.2(3)
Ru−S2−O1	116.11(19)	112.2(2)
O4−S3−O3	111.4(2)	108.3(4)
O1−S2−O2	112.2(3)	111.5(4)

of [Ru(DPPBT-O$_2$)$_2$(DPPBT)] reveals a rhombic signal with $g_1 = 2.07$, $g_2 = 2.04$, and $g_3 = 2.03$. X-ray quality crystals of [Ru(DPPBT-O$_2$)$_2$(DPPBT)] were obtained from serendipitous exposure of chlorobenzene/hexane solutions of [PPN][Ru(DPPBT)$_3$] to trace levels of oxygen.

X-ray crystallographic analysis of green prism-shaped crystals of [Ru(DPPBT-O$_2$)$_2$(DPPBT)] reveals a coordination environment that is nearly superimposable with its Ru(II) analogue.[13−20] An ORTEP representation is shown in Figure 2 (bottom). The Ru−P bond distances of 2.3498(15)− 2.4066(15) Å differ only slightly, ±0.0185 Å, when compared to those of the Ru(II) derivative. Similarly, the Ru−S$_{thiolato}$ and Ru−S$_{sulfinato}$ bond distances are 2.4099(15), 2.3553(17), and 2.2989(16) Å to S1, S2, and S3, respectively.

As noted above and highlighted in Scheme 1, the sulfur oxygenation of [PPN][Ru(DPPBT)$_3$] yields [PPN][Ru(DPPBT-O$_2$)$_2$(DPPBT)] via the Ru(III) complex [Ru(DPPBT)$_3$]. An intriguing question is, how can exposure of ruthenium(III) thiolate to oxygen induce reduction to [PPN][Ru-(DPPBT-O$_2$)$_2$(DPPBT)]? As evidenced by the cyclic voltammogram, sulfur oxygenation decreases the donor ability of the sulfur donors, which stabilizes the reduced oxidation state. In this case, the Ru(III)/Ru(II) potential shifts from −345 to +255 mV. Thus, once isolated, [PPN][Ru(DPPBT-O$_2$)$_2$(DPPBT)] is stable in air. While voltammetry indicates that the Ru(II) oxidation state is thermodynamically preferred following sulfur oxygenation, it does not identify the reducing agent.

Bulk oxidation of [PPN][Ru(DPPBT-O$_2$)$_2$(DPPBT)] to [Ru(DPPBT-O$_2$)$_2$(DPPBT)] was conducted under a nitrogen atmosphere in freshly distilled acetonitrile. Following oxidation, the solution was allowed to stand under nitrogen for 1 h with no significant change in the UV−visible spectrum. The introduction of 10% water initiated a slow, but consis-tent, reduction to [PPN][Ru(DPPBT-O$_2$)$_2$(DPPBT)] that was 10% complete after 3 h. Previously, Sawyer et al. reported that hydroxide is an effective one-electron reducing agent in polar, nonaqueous solvents.[23,24] In acetonitrile, the $E_{1/2}$ for the oxidation of hydroxide is reported as +0.59 V vs NHE.[23,24] To probe whether hydroxide may be the reducing agent in our study, 1.3 equiv of tetrabutylammonium hydroxide was added to a solution of electrochemically generated [Ru(DPPBT-O$_2$)$_2$(DPPBT)]. Monitoring of the UV−visible spectrum reveals a rapid and complete reduction to the Ru(II) derivative. A voltammogram recorded after hydroxide-induced reduction reveals no significant changes, indicating that the ruthenium complex remains intact. The source of hydroxide in the bulk oxygenation reactions may result from the autoionization of trace water or by the reaction of superoxide, generated during the metal-centered oxidation, with water. Notably, crystals of ruthenium(III) sulfinate were obtained in dry chlorobenzene/hexane, which lack a reducing hydroxide. Although hydroxide is a competent reducing agent under our conditions, it must be noted that thiolate (from complex degradation) cannot be completely excluded as the reductant.

In conclusion, oxygen exposure of ruthenium(II) thiolate initially results in metal-centered oxidation to Ru(III). Further oxygen exposure results in ligand-centered oxygenation, followed by reduction of Ru(III) to Ru(II). It is hypothesized that hydroxide serves as the reducing agent in acetonitrile. It has previously been suggested that an inner-sphere metal−oxygen interaction may facilitate oxygenation of metal-coordinated thiolates.[3] The role of the metal in tuning the thiolate nucleophilicity has also received recent attention.[22,25] The results of the current study indicate that it is also possible that metal-centered oxidation precedes ligand-centered events, with subsequent reduction upon shifts in metal redox potentials that are induced by sulfur modification. Detailed investigations are underway.

Supporting Information Available: Experimental procedures, mass spectrum, infrared spectrum, and cyclic voltammogram in PDF format. X-ray structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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