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A bis-bipyridine osmium(II) complex with an N,S-chelating 2-aminoethanesulfinate: photoinduced conversion of an amine to an imine donor group by air oxidation[†]

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Treatment of $[Os(bpy)_2Cl_2]$ (bpy = 2,2'-bipyridine) with 2-aminoethanethiolate was accompanied by air oxidation to give $[Os(2-aminoethanesulfinato-N,S)(bpy)_2]^+$ ([1]⁺), which was further oxidized by air to be converted into [Os(2-iminoethane $sulfinato-N,S)(bpy)_2]^+$ ([2]⁺) under photoirradiation. Complex [2]⁺ was reverted back to [1]⁺ by treatment with BH₄⁻.

2-Aminoethanethiolate (aet) containing both soft S and hard N donors is a well-known chelating ligand available for the formation of a wide variety of coordination compounds.¹ The thiolato group of aet bound to a metal center possesses a relatively high nucleophilicity that enables chemical modifications, such as S-metalation and S-alkylation.^{2,3} Moreover, it has been recognized that the oxidation reactions of aet complexes afford sulfenato and sulfinato derivatives that show unique spectroscopic and electrochemical properties.⁴ Recently, we have reported that the reaction of [Ru(bpy)₂Cl₂] with aet in air leads to the isolation of a sulfinato complex, $[Ru(aesi)(bpy)_2]^+$ (aesi = 2-aminoethanesulfinate), in which aesi chelates to a Ru^{II} center through amine-N and sulfinato-S donors, rather than an expected thiolato complex, [Ru(aet)(bpy)₂]^{+,5} This result is indicative of a higher reactivity of an aliphatic thiolato group bound to a Ru^{II} center toward dioxygen. Osmium, which is an alternative member of group 8 elements, has been known to form coordination compounds analogous to ruthenium compounds.⁶ However, osmium compounds often exhibit characteristic redox and photophysical properties that are not observed for the corresponding ruthenium compounds.^{6b-e} In this context, it is interesting to investigate the reaction of [Os(bpy)₂Cl₂] with aet under similar conditions employed for [Ru(bpy)2Cl2]. Herein, we report that this reaction produces an aminosulfinato-type osmium(II) complex, [Os(aesi)(bpy)₂]⁺, analogous to [Ru(aesi)(bpy)₂]⁺, accompanied by air oxidation. Remarkably, [Os(aesi)(bpy)₂]⁺ was found



Scheme 1 Synthetic routes of $[1]^+$ and $[2]^+$.

to be further oxidized by air under photoirradiation, forming an iminosulfinato-type complex, $[Os(iesi)(bpy)_2]^+$ (iesi = 2-iminoethanesulfinate), with retention of the coordination environment about an Os^{II} center (Scheme 1).

The reaction of $[Os(bpy)_2Cl_2]^7$ with 1 molar equiv. of Haet/ NaOH (1:1) in aqueous ethanol under a nitrogen atmosphere, followed by exposure to air, gave a dark brown solution. From this reaction solution, a dark green complex ([1] PF_6) was isolated after the purification by means of a cation-exchange column chromatography (SP-Sephadex C-25).[†] The ¹H NMR spectrum of [1]PF₆ in D₂O exhibits two methylene proton signals at δ 3.04 and 2.80 and aromatic proton signals in the region of δ 10.04–7.12 (Fig. 1a). In addition, a broad signal is observed at δ 5.43, which is characteristic of an amine group bound to a metal center.8 In the IR spectrum, [1]PF6 gives two intense bands at 1114 cm⁻¹ and 1006 cm⁻¹ assignable to ν_{asym} s=0 and $\nu_{\text{sym S}=0}$ for an S-bonded sulfinato group (Fig. S1, ESI[†]).^{4a,5,9} From these spectral features, together with the elemental analysis, $[1]^+$ is assigned to a bis(bipyridine)osmium(II) complex with an N,S-chelating aesi ligand, $[Os(aesi)(bpy)_2]^+$.

The structure of $[1]^+$ was determined by single-crystal X-ray analysis for $[1]ClO_4$ ·NaClO₄ that was obtained by the slow diffusion of diethyl ether into an ethanol solution containing $[1]PF_6$ and NaClO₄. As shown in Fig. 2, $[1]^+$ has an expected



Fig. 1 ¹H NMR spectra of (a) [1]PF₆ and (b) [2]PF₆ in D_2O .

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Fig. 2 Perspective views of the complex cations $[1]^+$ (left) and $[2]^+$ (right) with the atomic labeling scheme.

mononuclear structure in $[Os(aesi)(bpy)_2]^+$, in which an Os^{II} atom is surrounded by an aesi and two bpy ligands in an approximately octahedral geometry.[‡] The aesi ligand coordinates to an Os^{II} center through amine-N and sulfinato-S atoms to form a five membered chelate ring. This is the first example of a crystallographically characterized osmium species with an S-bonded sulfinato group.¹⁰ The overall structure in $[1]^+$ is very similar to that in the corresponding ruthenium(II) complex, $[Ru(aesi)(bpy)_2]^+$, and the bond distances around an Os^{II} center in $[1]^+$ (Os–S = 2.248(2) Å, Os–N_{aesi} = 2.160(6) Å, av. Os–N_{bpy} = 2.078(6) Å), as well as the S–O distances (av. 1.477(6) Å) are comparable well with those in $[Ru(aesi)(bpy)_2]^+$ (av. Ru–S = 2.246(1) Å, Ru–N_{aesi} = 2.144(4) Å, Ru–N_{bpy} = 2.083(4) Å, S–O = 1.481(4) Å).⁵ In crystal [1]ClO₄· NaClO₄, the sulfinato group binds to two Na⁺ ions using two O atoms (O···Na = 2.236(6) Å, 2.356(6) Å), constructing a unique dimeric structure (Fig. S2, ESI[†]).

The electronic absorption spectrum of [1]PF₆ in water shows an intense visible band at 414 nm, which is assigned as arising from a singlet metal-to-ligand(bpy) charge-transfer (¹MLCT) transition and a more intense band at 285 nm due to an intraligand π – π * transition of bpy (Fig. 3).^{6a,d} This absorption spectral feature is very similar to that of [Ru(aesi)(bpy)₂]⁺ in water, which gives ¹MLCT and π – π * bands at 413 nm and 284 nm, respectively (Fig. S3, ESI†). However, [1]PF₆ exhibits an additional weak band at 547 nm, which is assigned as arising from a ³MLCT transition that is partially allowed as a result of the heavy-atom effect. A similar ³MLCT band has been characteristically found in the absorption spectra of [Os(bpy)₃]²⁺ and its related complexes.^{6a,d} To check the stability of [1]⁺ in solution, a D₂O solution of

To check the stability of [1] $^{+}$ in solution, a D₂O solution of [1]PF₆ was allowed to stand under ambient light in air for a



Fig. 3 Electronic absorption spectra of [1]PF $_6$ (---) and [2]PF $_6$ (----) in H₂O.

month. Notably, this solution showed new proton signals, in addition to the original signals for $[1]^+$, in the ¹H NMR spectrum, while the spectrum remained almost unchanged upon storing in the dark. Then, the ¹H NMR spectral change for $[1]PF_6$ was monitored at 0 °C in D₂O under the irradiation of a high pressure Hg lamp in air. As a result, the original proton signals for $[1]^+$ decreased with time and almost disappeared within 1.5 days, followed by the appearance and growth of a set of new signals that are identical with those appeared under ambient light (Fig. S4, ESI†). This spectral change implies that $[1]^+$ is photosensitive to be almost quantitatively converted into another bis(bipyridine)osmium(II) species $([2]^+)$ in solution.

Compound [2]PF₆ was successfully isolated in a satisfactory yield from an irradiated aqueous solution of [1]PF₆.† While the absorption spectral feature of [2]⁺ in water resembles that of [1]⁺ over the whole region, its ¹MLCT and ³MLCT bands are slightly blue-shifted compared with those of [1]⁺ (Fig. 3). In the ¹H NMR spectrum in D₂O, [2]PF₆ exhibits characteristic signals at δ 12.20 assignable to an imine proton,^{11,12} with the lack of amine proton signals found in [1]⁺ (Fig. 1b). From these results, together with the elemental analysis, it is assumed that [2]⁺ contains 2-iminoethanesulfinate (iesi) as a chelating ligand, in place of aesi in [1]⁺.

This assumption was confirmed by X-ray analysis of $[2]PF_6$ · NH₄PF₆, which was obtained by slow diffusion of diethyl ether into an ethanol solution containing $[2]PF_6$ and NH₄PF₆. As shown in Fig. 2, $[2]^+$ has an octahedral structure in $[Os(iesi)(bpy)_2]^+$, in which iesi chelates to an Os^{II} center through imine-N and sulfinato-S groups.‡ The N–C bond distance (1.291(5) Å) of iesi in $[2]^+$ is shorter and its N1–C2–C1 angle $(120.7(4)^\circ)$ is larger than the corresponding distance (1.503(11) Å) and angle $(113.8(6)^\circ)$ of aesi in $[1]^+$, compatible with the formation of an imine group. The Os–N_{iesi} bond in $[2]^+$ (2.069(3) Å) is appreciably shorter than the Os–N_{aesi} bond in $[1]^+$ (2.160(6) Å), which is a general trend observed for aliphatic imine and amine complexes.¹³ As expected, the Os–S bond distance in $[2]^+$ (2.230(1) Å) is similar to that in $[1]^+$ (2.248(2) Å).

When the same irradiation experiment was carried out for $[1]^+$ under a nitrogen atmosphere, no significant change of its ¹H NMR spectrum was observed. This suggests that the conversion of $[1]^+$ to $[2]^+$ is a result of air oxidation, which is induced by photoirradiation. Prompted by this result, we also investigated the possibility of the conversion of $[1]^+$ to $[2]^+$ by chemical oxidation. Notably, the ¹H NMR spectrum of [1] PF_6 turned to be identical with that of $[2]^+$ by adding excess AgClO₄ in the dark within 1 h (Fig. S6, ESI[†]), indicative of the facile conversion of $[1]^+$ to $[2]^+$ by Ag^I oxidation. While a similar amine-to-imine conversion by chemical oxidation has been reported for several Ru^{II} complexes, Ce^{IV}, which is a strong oxidant, has commonly been employed for the reaction, rather than a milder oxidant Ag^{I,12,14} The reversible conversion from $[2]^+$ to $[1]^+$ was also achieved by treatment of $[2]^+$ with BH₄⁻; the ¹H NMR spectrum of a D_2O solution containing [2]PF₆ and excess BH_4^- in the dark turned to be identical with that of $[1]^+$ within 1.5 h (Fig. S7, ESI[†]). Here, it should be noted that similar treatment of $[Ru(aesi)(bpy)_2]^+$ with AgClO₄ did not cause any spectral change, and furthermore, the photoirradiation of an aqueous solution of $[Ru(aesi)(bpy)_2]^+$ led to its decomposition into several unidentified species.



Fig. 4 Cyclic voltammograms of [1]PF₆ (left) and [2]PF₆ (right) in $H_2O/NaNO_3$ (0.1 M) at 25 °C with a scan rate of 100 mV s⁻¹.

As shown in Fig. 4, the cyclic voltammogram (CV) of $[1]PF_6$ in water under a nitrogen atmosphere is characterized by two irreversible oxidation waves at $E_{\rm pa}$ = +0.55 and +0.70 V (vs. Ag/AgCl). On the other hand, the CV of [2]PF₆ displays only one irreversible oxidation wave at $E_{pa} = +0.70$ V, the potential of which is the same as the second oxidation wave for $[1]^+$ (Fig. 4). The spectroelectrochemical experiments were carried out for $[1]PF_6$ using an optically transparent thin-layer electrode cell. When the potential was increased from 0 V, the absorption spectrum of [1]PF₆ gradually changed with several isosbestic points, and the absorption spectrum recorded at +0.45 V was almost the same as that of [2]⁺ (Fig. S8, ESI[†]). From these results, it is considered that the first oxidation at $E_{\rm pa} = +0.55$ V observed for [1]⁺ is due to the amine-to-imine conversion. On the other hand, the CV of $[Ru(aesi)(bpy)_2]^+$ in water under the same conditions showed only one irreversible oxidation wave at $E_{pa} = +1.00$ V (Fig. S9, ESI[†]), which is 0.45 V more positive than the first oxidation wave for $[1]^+$.¹⁵ Thus, the facile conversion of $[1]^+$ to $[2]^+$ by the photoinduced air oxidation or by the Ag^I oxidation is ascribed to the relatively low oxidation potential of $[1]^+$.

In summary, we showed that 2-aminoethanethiolate (aet) is easily air oxidized to 2-aminoethanesulfinate (aesi) on binding with an $[Os^{II}(bpy)_2]^{2+}$ core to form $[Os(aesi-N,S)(bpy)_2]^+$ ([1]⁺). Remarkably, the aesi in [1]⁺ was found to be further air oxidized to 2-iminoethanesulfinate (iesi) on irradiating light to form $[Os(iesi-N,S)(bpy)_2]^+$ ([2]⁺).^{16,17} Although a similar amine-toimine conversion by air oxidation has been recognized in several coordination systems,^{14b} the photoinduced conversion found in this work is unprecedented.¹⁸ Note that [1]⁺ is also readily converted to [2]⁺ with use of Ag⁺, and furthermore, [2]⁺ is reverted back to [1]⁺ with use of BH₄⁻ in aqueous media. Thus, the present system represents a clean, reversible amine-toimine conversion, which is most likely due to the presence of a redoxactive Os^{II} center whose + III state is more accessible than that of Ru^{II}, together with the presence of an inert sulfinato donor.

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[‡] Crystal data for [1]ClO₄·NaClO₄: C₂₂H₂₂Cl₂N₅NaO₁₀OsS, M = 832.60, monoclinic, space group C2/c, a = 9.5421(3), b = 16.8001(7), c = 34.0526(10) Å, $\beta = 96.6130(10)^\circ$, V = 5422.6(3) Å³, Z = 8, T = 200 K, 26 730 reflections collected, 6220 independent reflections, 5150 observed reflections $(I > 2\sigma(I))$, R_1 $(I > 2\sigma(I)) = 0.046$, w R_2 (all data) = 0.125. H atoms of amine and imine groups were found in difference Fourier maps and were refined with $[U_{iso} = 1.2U_{eq}(N)]$.

Crystal data for [2]PF₆·NH₄PF₆: C₂₂H₂₄F₁₂N₆O₂OsP₂S, M = 916.67, monoclinic, space group $P2_1/c$, a = 15.9170(3), b = 9.4043(2), c = 20.2031(5) Å, $\beta = 100.5150(10)^\circ$, V = 2973.38(11) Å³, Z = 4, T = 200 K, 28 325 reflections collected, 6779 independent reflections, 6065 observed reflections ($I > 2\sigma(I)$), R_1 ($I > 2\sigma(I)$) = 0.026, w R_2 (all data) = 0.064. H atoms of amine and imine groups were found in difference Fourier maps and were refined with [$U_{iso} = 1.2U_{eq}(N)$].

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