Unprecedented Sequential Deprotonation of Ruthenium–Aqua Framework Affording Ruthenium–Oxo–Dithiolene Complex

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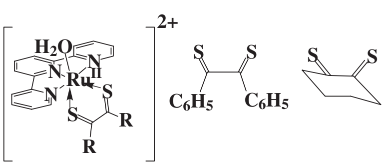
A new type of aqua ruthenium–terpyridine complexes with dithiolenes ($S_2C_2Ph_2$, $S_2C_6H_8$) were synthesized. The pK_a values were 3.8 and 7.0 for $S_2C_2Ph_2$ complex and 6.5 for $S_2C_6H_8$ one. The $S_2C_2Ph_2$ complex gives the corresponding oxo one by the sequential deprotonation, whereas the $S_2C_6H_8$ complex is just converted to the hydroxo one.

Much attention has been paid to reactivity of metal–oxo complexes depending on their oxidation states from the viewpoints of fundamental, industrial, and biochemical interest,[1] because metal–oxo complexes work as oxidants to various hydrocarbons by electron transfer,[2] proton-coupled electron transfer,[3] hydrogen and/or hydride abstraction,[4] and oxygen atom transfer.[5] One of most documented metal–oxo complexes is ruthenium–monooxo–polypyridyl compounds derived from its aqua precursor such as $[Ru(H_2O)(bpy)(tpy)]^{2+}$,[6,7] $[Ru(H_2O)(bpy)_2py]^{2+}$,[8] $[Ru(H_2O)(acac)(tpy)]^{+}$,[9] which have been developed by Meyer's group. Since these aqua complexes dissociate proton above pH 8 and the resultant Ru(II)–hydroxo complexes do not show deprotonation, formation of the oxo species needs oxidation of the aqua or hydroxo complexes. The aqua/oxo conversion on metals without using any oxidants, therefore, may provides more versatile methods for preparation of ruthenium–oxo complexes. Recently, we have demonstrated that dioxolene ligands of ruthenium–aqua–terpyridine complexes such as $[Ru(H_2O)(Bu_2SQ)(tpy)](ClO_4)_2$ and $[Ru(H_2O)(4ClSQ)(tpy)](ClO_4)_2$ assist deprotonation of the aqua ligands in CH_2Cl_2 and stabilize oxyl and hydroxyl radicals through intramolecular electron transfer from the resultant O^{2-} and OH^- to Ru–dioxolene moieties upon stepwise deprotonation, respectively.[10] We also have reported that ruthenium–dithiolene complexes as well as ruthenium–dioxolene complexes are featured by charge distribution between metal and the ligands.[11] Here, we introduce new members of ruthenium–aqua–polypyridyl system, $[Ru(H_2O)(S_2C_2Ph_2)(tpy)](CF_3SO_3)_2$ ($[\mathbf{1}](CF_3SO_3)_2$) and $[Ru(H_2O)(S_2C_6H_8)(tpy)](CF_3SO_3)_2$ ($[\mathbf{2}](CF_3SO_3)_2$), since $[\mathbf{1}]^{2+}$ undergoes sequential deprotonation to form its neutral oxo form $[RuO(S_2C_2Ph_2)(tpy)]^0$ without any oxidants in aqueous media.



Complexes $[\mathbf{1}](CF_3SO_3)_2$[12] and $[\mathbf{2}](CF_3SO_3)_2$[12] were obtained by hydrolysis of $[Ru(CF_3SO_3)(S_2C_2Ph_2)(tpy)]CF_3SO_3$[11] and $[Ru(CF_3SO_3)(S_2C_6H_8)(tpy)]CF_3SO_3$,[13] respectively. These formulas were confirmed by ESIMS spectral and elemental analytical data. The similar ^{1}H NMR signal patterns with those of other octahedral ruthenium(II)–aqua–terpyridine complexes of $[Ru(H_2O)(XX)(tpy)]^{n+}$ (XX = bidentate ligands)[7,9,14,15] support the octahedral structures of $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$.

Figure 1 depicts pH titration curves of the complexes $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ in H_2O to evaluate the acidity of the coordinate aqua ligands. Interestingly, $[\mathbf{1}]^{2+}$ shows two successive deprotonation (Figure 1a), while $[\mathbf{2}]^{2+}$ dissociates only one proton (Figure 1b). Each pK_a value simulated is 3.8 and 7.0 for $[\mathbf{1}]^{2+}$, and 6.5 for $[\mathbf{2}]^{2+}$ (Table 1), respectively, and these values are consistent to those caluclated from electronic spectral changes about both complexes at various pH.

All Ru(II) and Ru(III) aqua complexes reported so far dissociate only one proton under normal conditions, pK_a values obtained in some ruthenium aqua complexes are listed in Table 1. Complex $[\mathbf{1}]^{2+}$, therefore, is the first example that dissociates two protons only by pH gradient without any oxidants to forms the oxo complex. The acidity of ruthenium–aqua complexes is

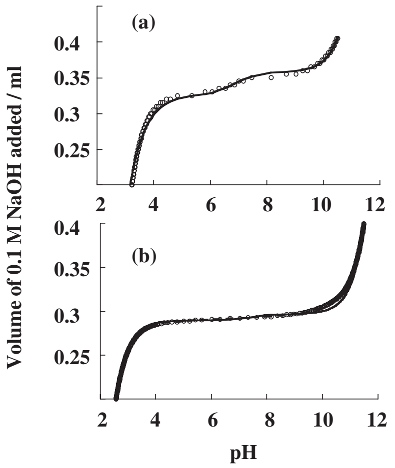


Figure 1. Titration curves of 0.22 mM of $[\mathbf{1}]^{2+}$ (a) and 0.25 mM of $[\mathbf{2}]^{2+}$ (b) in 0.01 M CF_3SO_3H. Circles and lines indicate observed and simulated ones, respectively.

Table 1. pK_a values of various monoaqua–ruthenium complexes

Complex	pK_{a1}	pK_{a2}	Ref
$[Ru(H_2O)(S_2C_2Ph_2)(tpy)]^{2+}$	3.8	7.0	[a]
$[Ru(H_2O)(S_2C_6H_8)(tpy)]^{2+}$	6.5	—	[a]
$[Ru(H_2O)(bpy)(tpy)]^{2+}$	9.7	—	7
cis-$[Ru(H_2O)(pic)(tpy)]^{+}$	10.0	—	14
$[Ru(H_2O)(tmen)(tpy)]^{2+}$	10.2	—	15
$[Ru(H_2O)(acac)(tpy)]^{+}$	11.2	—	9

[a] This work.

noticeably enhanced by oxidation of the complexes, indeed, the pK_a values of 9.7 and 10.0 in $[\mathrm{Ru^{II}(H_2O)(bpy)(tpy)}]^{2+}$ and *cis*-$[\mathrm{Ru^{II}(H_2O)(pic)(tpy)}]^{+}$, respectively, decrease to 1.7 and 3.7 in their one electron oxidized ones.[14,16] In contrast to ruthenium–polypyridyl complexes, ruthenium–dithiolenes ones are featured in terms of the charge distribution between the metal and the ligands, and the extent is largely dependent on the substituents on dithiolenes. The actual electronic configuration of the present Ru–dithiolene complexes would be expressed by a resonance hybrid among Ru(II)–dithiolene(0), Ru(III)–dithiolene(−), and Ru(IV)–dithiolene(2−) (Eq 1).

$$\begin{aligned}\mathrm{Ru(II)(dithiolene^{0})} &\leftrightarrow \mathrm{Ru(III)(dithiolene^{-})}\\ &\leftrightarrow \mathrm{Ru(IV)(dithiolene^{2-})}\end{aligned}\tag{1}$$

Taking into account that Ru(III)–hydroxo complexes reported so far do not dissociate their hydroxo proton in H_2O, the unusual double deprotonation of the aqua ligand of $[\mathbf{1}]^{2+}$ may be explained by the contribution of the Ru(IV)–dithiolene(2−) framework of Eq 1. Appearance of a strong absorption band of $[\mathbf{1}]^{2+}$ ($\lambda_{\max} = 570\,\mathrm{nm}$, $\varepsilon = 13500\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) at pH = 1.2 and disappearance of the band above pH 8.0 also support the shift of the resonance of Eq 1 to the right in the deprotonation form of $[\mathbf{1}]^{2+}$,[17] since $[\mathrm{Ru^{IV}O(bpy)(tpy)}]^{2+}$ and its analogues Ru(IV)–oxo complexes have no strong absorption band in the visible region.[7] Diamagnetic $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ showed fine-structure ESR spectra attributed to triplet species in the presence of an equimolar amount of base (^{t}BuOK) in CH_2Cl_2 at 4 K.[10] Their spin multiplicities were unequivocally identified by electron spin transient nutation spectroscopy.[18] Although the ESR spectral patterns of both complexes were similar, the signal intensity of the latter was about 1/10 smaller than that of the former.[19] This observation also implies that the degree of the shift of the resonance of Eq 1 to the right in the deprotonation form of $[\mathbf{1}]^{2+}$ is larger than that of $[\mathbf{2}]^{2+}$. The strong acidity of the aqua ligand of $[\mathbf{1}]^{2+}$, therefore, may result from the contribution of the Ru(IV)–dithiolene(2−) core that is stabilized by the electron-withdrawing Ph group contained in $S_2C_2Ph_2$, while the contribution is less important in the deprotonation of $[\mathbf{2}]^{2+}$ that contains the electron-releasing alkyl group. Thus, the noninnocent $S_2C_2Ph_2$ plays a key role in the unusual enhancement of the acidity of the aqua ligand in $[\mathbf{1}]^{2+}$.

The present study demonstrates that an aqua complex is converted to the oxo one without any oxidants by introduction of noninnocent dithiolene ligands into ruthenium–polypyridyl systems.

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6 Ligand abbreviation. bpy = 2,2′-bipyridyl, tpy = 2,2′:6′,2″-terpyridine, acac = acetylacetonato, Bu_2SQ = 3,5-di-*tert*-butyl-1,2-benzosemiquinone, 4ClSQ = 4-chloro-1,2-benzosemiquinone, $S_2C_2Ph_2$ = 1,2-diphenyl-ethane-1,2-dithione, $S_2C_6H_8$ = cyclohexane-1,2-dithione, pic = picolinate, tmen = *N*,*N*′-tetra-methyl-ethylenediamine.

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12 Characterization data of $[\mathbf{1}](CF_3SO_3)_2\cdot 2H_2O$. Anal. Calcd for $C_{31}H_{27}F_6N_3O_9RuS_4$ (MW: 928.86): C 40.09, H 2.93, N 4.52. Found: C 39.84, H 2.91, N 4.32%. ^{1}H NMR (acetone-d_6): δ 9.02 (2H, d), 8.77 (3H, m), 8.22 (2H, t), 7.77 (2H, d), 7.64 (2H, q) and 7.2–7.6 (10H, m). ESIMS (acetone): m/z 288.5 ($[M - H_2O]^{2+}$), 317.5 ($\{[M - H_2O]^{+} + \text{acetone}\}^{2+}$). Characterization data of $[\mathbf{2}](CF_3SO_3)_2$. Anal. Calcd for $C_{23}H_{21}F_6N_3O_3RuS_4$ (MW: 794.74): C 34.76, H 2.66, N 5.29. Found: C 34.99, H 2.85, N 5.32%. ^{1}H NMR (acetone-d_6): δ 9.01 (2H, d), 8.77 (3H, m), 8.25 (2H, t), 7.77 (2H, d), 7.50 (2H, q) and 7.44 (2H, d), 3.61 (2H, br), 3.32 (2H, br), 1.96 (2H, br), 1.78 (2H, br). ESIMS (acetone): m/z 628.0 ($\{[M - H_2O] + CF_3SO_3\}^{+}$).

13 Characterization data of $[\mathrm{Ru(CF_3SO_3)(S_2C_6H_8)(tpy)}]\mathrm{CF_3SO_3}$. Anal. Calcd for $C_{23}H_{19}F_6N_3O_6RuS_4$ (MW: 776.72): C 35.57, H 2.47, N 5.41. Found: C 35.65, H 2.42, N 5.41%.

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17 UV–vis of $[\mathrm{Ru(H_2O)(S_2C_2Ph_2)(tpy)}]^{2+}$: $\lambda_{\max}$/nm (pH 1.2) (ε/dm^3 mol^{-1} cm^{-1}), 282 (37000), 329 (32000), 380 (8100), 570 (13500). UV–vis of $[\mathrm{RuO(S_2C_2Ph_2)(tpy)}]$: $\lambda_{\max}$/nm (pH 8) (ε/dm^3 mol^{-1} cm^{-1}): 272 (23500), 310 (21500), 380 (4600).

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19 At the present stage, we could not discuss detailed electronic structures of deprotonated forms of $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$, because of possibility of a formation of hydroxyl radical caused by intramolecular electron transfer from OH^- to ruthenium–dithiolene moieties as found in ruthenium–dioxolene complexes.[10]

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