Oxorhenium(V) Complex of Amidophenolate: Structure and Redox Characteristics

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A new mono-oxo rhenium(V) complex with a chelating ligand amidophenolate was synthesized and structurally characterized. Significance of the protonation at the amido nitrogen was demonstrated by the large positive shift of the redox potential of Re(IV/III) in the presence of weak proton donors in acetonitrile.

2-Aminophenol (ampH$_3$) is a unique ligand that possesses characteristics of both catechol and amines. It can be deprotonated to give 2-aminophenolate (ampH$_2$), 2-amidophenolate (ampH) and 2-imidophenolate (amp). The dianion, ampH, is isoelectronic to catecholate dianion (cat). In contrast to the rich chemistry of redox active catecholate complexes which involve quinone - semiquinone - catecholate dianion series,[1] coordination chemistry of the anions of 2-aminophenol has not been the subject of extensive study. Only two structurally characterized complexes of 2-aminophenolate are available, i.e. *cis*-[MoO$_2$(ampH$_2$)$_2$] [2] and *cis*-[SnCl$_2$(ampH$_2$)$_2$].[3] The only structurally characterized 2-amidophenolate complex is Pt(ampH)(PPh$_3$)$_2$.[4] Other hitherto reported complexes of ampH and substituted amidophenolate anion include Pt(ampH)(PMe$_3$)$_2$ and Tc(DBcat)$_2$(DBampH) (DBcat = 3,5-di-*tert*-butyl-1,2-catecholate, DBampH = 3,5-di-*tert*-butyl-2-amidophenolate).[4,5] No detailed study on the redox properties, in particular proton-coupled one, of the complexes of these ligands, has been reported. No example is available for the pair of complexes having cat and isoelectronic ampH. We recently reported an oxorhenium(V) complex having cat and η^3-tpa (tpa = tris(2-pyridylmethyl)amine), [ReO(cat)(η^3-tpa)]$^+$,[6] which possesses a free 2-pyridylmethyl arm. We now have prepared the ampH analog of oxorhenium(V)-tpa, and studied its redox characteristics.

ReOCl$_3$(PPh$_3$)$_2$ (0.30 g, 0.36 mmol) was added to a solution of 2-aminophenol (0.04 g, 0.36 mmol) and tpa (0.11 g, 0.36 mmol) in CH$_3$OH (50 ml). The suspension was stirred for several days, during which time it gradually changed to a clear brown solution. Brown microcrystalline powder was formed after the addition of NH$_4$PF$_6$ (0.16 g, 1 mmol) in CH$_3$OH (5 ml) to the solution. Recrystallization from acetonitrile-ethanol gave brown crystals of [ReO(ampH)(tpa)]PF$_6$ ([**1**](PF$_6$)) which contained single crystals suitable for X-ray analysis.[7,8]

Figure 1 shows the structure of the complex cation in [1](PF$_6$). As expected from the same space group and similar cell constants of [**1**](PF$_6$) to the previously reported [ReO(cat)(tpa)]PF$_6$ ([**2**](PF$_6$)), the overall structural feature of these two complexes are very similar to each other. Rhenium(V) center of **1** takes a distorted octahedral environment with three facially coordinated atoms from tpa (two pyridyl nitrogens and one tertiary amine nitrogen), and two coordinated atoms of the chelating ligand. The terminal oxo ligand is trans to the tertiary amine nitrogen. The two donor atoms of ampH were designated as E(2) and E(3), since it is difficult to assign them unambiguously to the oxygen and the nitrogen atoms. The average distance of E(2)-C(8) and E(3)-C(7) is 1.39(1)Å, which is comparable to that in the chelating dianion of [Pt(ampH)(PPh$_3$)$_2$] (1.36Å)[4] and the cat ligand of [**2**](PF$_6$).[6] The distances of NH$_2$-C and O(phenolate)-C bonds of the ampH$_2$ complexes are 1.447(6) and 1.371(6)Å for *cis*-[MoO$_2$(ampH$_2$)$_2$]),[2] and 1.456(16) and 1.374(14)Å for *cis*-[SnCl$_2$(ampH$_2$)$_2$]).[3] The E(2)-C(8) and E(3)-C(7) distances in **1** are clearly shorter than the NH$_2$-C bond distances, suggesting that the deprotonated amino group is coordinated.

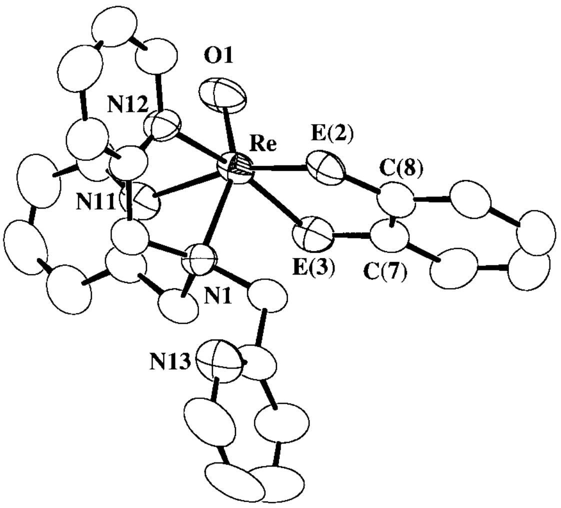


Figure 1. ORTEP drawing of the cation **1** with 50% probability thermal ellipsoid. Selected bond distances (Å) and angles (°) : Re-O(1), 1.686(6); Re-E(2), 1.934(7); Re-E(3), 1.977(6); E(2)-C(8), 1.400(11); E(3)-C(7), 1.387(11); O(1)-Re-E(2), 107.9(3); O(1)-Re-E(3), 106.3(3); E(2)-Re-E(3), 81.2(3); Re-E(2)-C(8), 115.1(6); Re-E(3)-C(7), 112.9(5).

The deprotonation at the coordinated nitrogen must be achieved primarily by the coordination to the high-valent rhenium(V) center. The basicity of the coordinated nitrogen of ampH would increase with lowering the oxidation state of the metal center. Thus it is possible that the reduction of the rhenium center would be coupled with the protonation at the ampH nitrogen and/or oxo ligand. Proton-coupled redox behavior of the oxide bridged diruthenium complex, [Ru$_2$(O)(CH$_3$COO)$_2$-(bpy)$_2$(Meim)$_2$]$^{2+}$ (Meim = 1-methylimidazole) (**3**), has been investigated in acetonitrile by adding proton-donors with different pK_a values (this procedure corresponds to change pH in aqueous solution).[9] This approach has been applied to investigate the proton-coupled redox behavior of the present complex **1**. Cyclic voltammogram of **1** (Fig. 2, upper) in aprotic solvent acetonitrile shows a reversible wave of the Re(V)/(IV) process at -1.37 V vs Ag/AgCl and an irreversible Re(IV)/(III) peak at -1.88 V. These potentials should represent processes which have no relation to

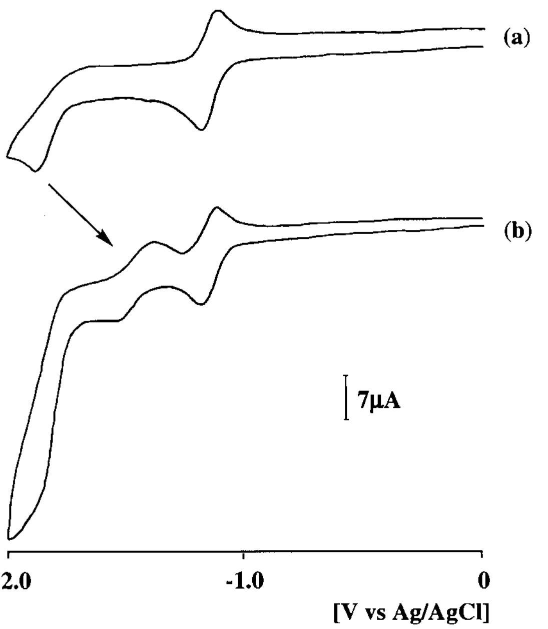
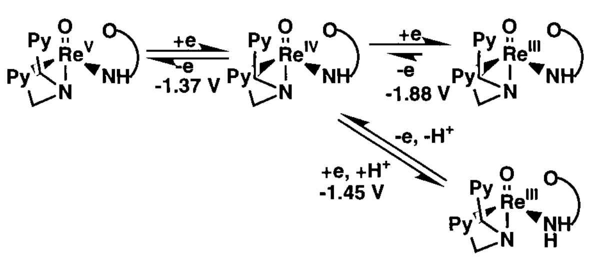


Figure 2. Cyclic voltammograms of 1 in acetonitrile (0.1 mol dm^{-3} Bu_4NPF_6) solution. (a) Without proton source, (b) on addition of 1 equiv. of imidazole.

protons, and are similar to the corresponding values of **2** and $[ReO(eg)(tpa)]^+$ (eg = ethyleneglycolate(2-)). Unfortunately addition of a strong acid, *p*-toluenesulfonic acid, caused some decomposition of the complex. On addition of an equimolar amount of a weak proton donor imidazole (pK_a = 14.4 in water) to the acetonitrile solution of **1**, however, a new quasi-reversible wave appeared at $E_{1/2}$ = -1.45 V with the original Re(IV)/(III) region obscured by the influence of the increased back-ground current (Fig. 2, lower). Addition of β-naphtol also caused significant positive shift of the Re(IV)/(III) wave to -1.45V, although the process is observed as irreversible one (strong background current at -1.9 V was not observed in this case).[10] The CV of the acetonitrile solutions of the cat and eg complexes in the presence of these proton donor did not show any new wave (the original Re(IV/III) region was again obscured by a back-ground current in the case of imidazole). Since the new wave was observed only in the solution of **1** and the redox potential of the Re(V)/(IV) process was unchanged, it is concluded that the new wave is actually a consequence of significant positive shift of the Re(IV)/(III) wave associated with protonation. The positive shift is possible when the basicity of the coordinated nitrogen center at the Re(III) state exceeds that of imidazole and β-naphtol. Protonation site must be the coordinated nitrogen, since similar observation was not made for the cat and eg complexes. Similar significant positive shift was observed for **3** in acetonitrile in the presence of imidazole. It is difficult at this stage to obtain quantitative data such as acidity constant of the coordinated nitrogen (and also that of oxo ligand) at different oxidation states of the rhenium center, but the present study clearly indicates the versatility of $ampH_n$ ligands in conjunction with the change in metal oxidation state, since the protonation-deprotonation can take place without the cleavage of metal-N bond.

Scheme 1.



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7 Yield: 0.15g (55%). Characterization data of [**1**](PF_6). Anal. Calcd for $C_{24}H_{23}N_5F_6O_2PRe$ (MW 762.7): C, 38.25; H, 3.21; N, 9.29. Found: C, 38.23; H, 3.61; N, 9.09. IR (KBr pellet, cm^{-1}) ν(Re=O) 962, ν(Re-O) 665, ν(C-O) 1242. UV-vis (CH_3CN) λmax = 490 (ε = 1060) nm. FAB MS (CH_3CN): *m/z* 600 (M^+).

8 Crystal data: Intensity data of [**1**](PF_6) was collected with a graphite-monochromated Mo Kα radiation (λ = 0.71059Å) on a MacScience MXC18 diffractometer at 293K corrected for Lorentz polarization effect and absorption (psi-scans). Crystal data for [**1**](PF_6) ($C_{24}H_{23}O_2PF_6N_5Re$): Triclinic, space group $P\bar{1}$(no. 2), a = 10.558(2), b = 10.610(2), c = 13.255(2)Å, α = 104.01(1), β = 101.27(1), γ = 90.69(1)°, V = 1409.9(4)Å^3, Z = 2, ρ_{calcd} = 1.75 g cm^{-3}. R = 0.042 and R_w = 0.056 against 5630 observed reflections [$I > 2\sigma(I_o)$].

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