Novel Intramolecular Rearrangement of Hepta-Coordinate Rhenium(V) Complex with Catecholato and Terpyridine Ligands

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Novel hepta-coordinate rhenium(V) complex with two 3,6-di-*tert*-butyl-catecholate and one terpyridine ligands was synthesized and structurally characterized. Temperature dependent ^{1}H NMR spectra reveal dynamic behavior of the complex resulting from the site exchange of an equatrial position between two catecholate ligands.

Rhenium complexes with dioxolene ligand have been synthesized in the past decade and those complexes are interested in the viewpoint of the charge distribution between metal and the ligand.[2] Recently, we have synthesized a series of ruthenium terpyridine (tpy) dioxolene complexes with the intention of introducing three redox sites (Ru, tpy and dioxolene) to develop a new type of electrocatalysts, which work in a wide potential range.[3] Dioxolene ligands linked to Re are likely to take the most reduced form, catecholate dianion (2-), because the energy of the third element, rhenium, is relatively higher than that of p-orbital of the dioxolene ligands. Rhenium-dioxolene complexes, therefore, are expected to have strong reducing ability compared with the corresponding Ru-dioxolene complexes. We have tried to prepare a rhenium-tpy-dioxolene complex and isolated an unexpected hepta-coordinate rhenium complex from the reaction of $ReCl_3(tpy)$ with 3,6-di-*tert*-butyl-catechol (diBucatH$_2$). In this communication, we wish to report the synthesis , the crystal structure and properties of $[Re(tpy)(diBucat)_2]^+$.

$ReCl_3(tpy)$ (0.10 mmol) was added to a methanol solution (20 ml) containing 3,6-di-tert-butyl-catechol (0.2 mmol) and triethylamine (0.4 mmol) under N_2 atmosphere. The suspension was refluxed with stirring for 5 h to give a clear blue-black solution. Exposure of the solution to air at room temperature resulted in a color change from black to purple. Then, NH_4PF_6 (1.0 mmol) in CH_3OH (5 ml) was added to the solution. Slow evaporation of the solution afforded purple microcrystalline powder. Recrystallization from acetonitrile-ethanol gave purple crystals of $[Re(tpy)(diBucat)_2]PF_6{\cdot}CH_3CN$ ([**1**]$PF_6{\cdot}CH_3CN$) which contained single crystals suitable for X-ray analysis.[4, 5]

Figure 1 shows the crystal structure of the cation of [**1**]$PF_6{\cdot}CH_3CN$. Rhenium center was ligated by three nitrogen of terpyridine and four oxygen atoms of two dioxolene ligands to form a hepta-coordinate environment. Two dioxolene ligands are not equivalent: namely, O(1) and O(2) of the first one are located in the equatorial and axial positions, respectively, and O(3) and O(4) of the second one are located above the equatorial plane of terpyridine. The structure of [**1**]$^+$ can be regarded as a capped trigonal prism. N(1), N(2) and O(4) atoms, and O(2), N(3) and O(3) atoms make triangles, respectively. The two triangles are almost parallel to each other. A plane consists of N(1), O(2), O(3) and O(4) is capped by the O(1) atom. The rhenium atom is located above 1.02 Å from the mean plane consists of three nitrogen of terpyridine and O(2) atoms. The average of C-O bond lengths (1.35 (1) Å) is in the range of that of catecholate dianion, cat (2-). Indeed, the IR spectrum of [**1**]$PF_6{\cdot}CH_3CN$ displays a strong band at 1192 cm^{-1} assignable to ν(C-O) band of cathecolate ligands. The electronic structure of [**1**]$^+$, therefore, is formulated as $[Re^V(tpy)(diBucat)_2]^+$. A few hepta-coordinated Re(V) complexes such as $[Re^VO(quarty)(OCH_3)_2]^+$ [**2**],[6] $[Re^VN(quarty)(PPh_3)Cl]^+$ [**3**],[6] and $[Re^VO(tpen)]^{3+}$ [**4**][7] have been reported. It is worthy to note that these Re(V) complexes with an oxo or nitride ligand as a strong electron-donating group take a distorted pentagonal bipyramid structure. Thus, [**1**]$^+$ is the first hepta-coordinate Re(V) complex with a capped trigonal prism structure.

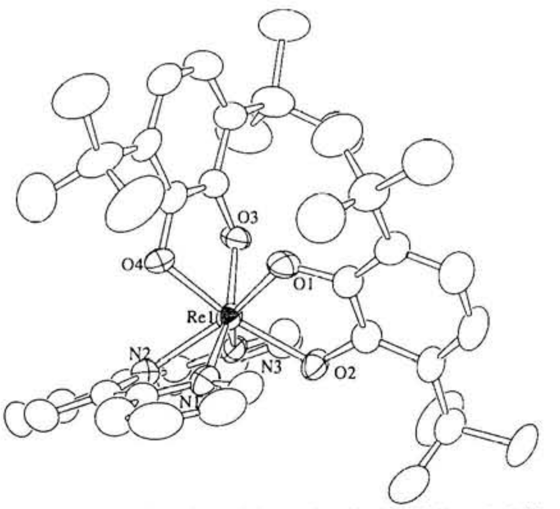

Figure 1. ORTEP drawing of the cation **1** with 50% probability thermal ellipsoid. Selected bond distances (Å) and angles (°) : Re-O(1), 1.955(7); Re-O(2), 2.000(7); Re-O(3), 1.974(7); Re-O(4), 1.980(7); Re-N(1), 2.17(1); Re-N(2), 2.086(9); Re-N(3), 2.114(9); O(1)-C(16), 1.37(1); O(2)-C(17), 1.36(1); O(3)-C(31), 1.36(1); O(4)-C(30), 1.32(1); O(1)-Re-O(3), 84.0(3); O(1)-Re-O(4), 81.3(3); O(1)-Re-N(1); 87.6(4); O(1)-Re-N(2), 151.6(4); O(1)-Re-N(3), 137.2(3); O(2)-Re-O(3),108.6(3); O(2)-Re-O(4), 156.3(3); O(2)-Re-N(1), 86.4(3); O(2)-Re-N(2), 117.3(3); O(2)-Re-N(3), 78.0(3); O(3)-Re-N(1), 160.6(3); O(3)-Re-N(2), 111.3(3); O(3)-Re-N(3), 71.8(3); O(4)-Re-N(1), 82.4(3); O(4)-Re-N(2), 78.2(3); O(4)-Re-N(3), 125.4(3).

The complex [**1**]$^+$ displays two reversible reduction process at $E_{1/2}$ = -0.56 and -1.54 V, and one reversible and one irreversible oxidation processes at $E_{1/2}$ = +0.52 and E_{pa} = +0.93 V (vs. $[Fe(C_5H_5)_2]^{+/0}$) in cyclic voltammetry in the range of -2.0 to +1.0 V in CH_3CN containing $(n\text{-}C_4H_9)_4NBF_4$ (0.1 M). The two reduction processes are assigned to the Re^V/Re^{IV} and Re^{IV}/Re^{III} redox couples (metal-centered redox reactions), respectively, on the basis of the electronic configuration of $[Re^V(tpy)(diBucat)_2]^+$. The redox potential of the Re^V/Re^{IV} couple of [**1**]$^+$ is about 0.8 V more positive than that of Re(V)-catecholate complexes, $[ReO(diBucat)(tpa)]^+$ [8] and

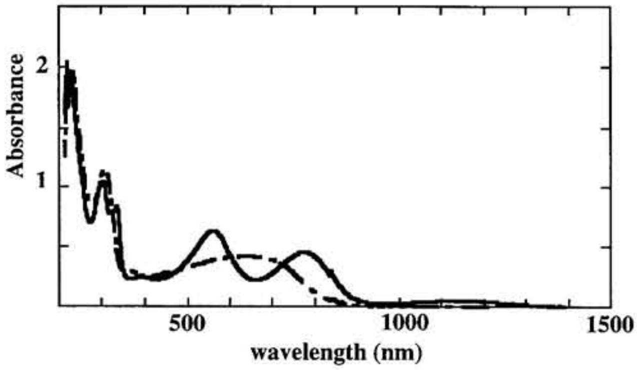

Figure 2. Electronic spectra of $[\mathbf{1}]^+$ (solid line) and $[\mathbf{1}]$ (dashed line) in CH_3CN.

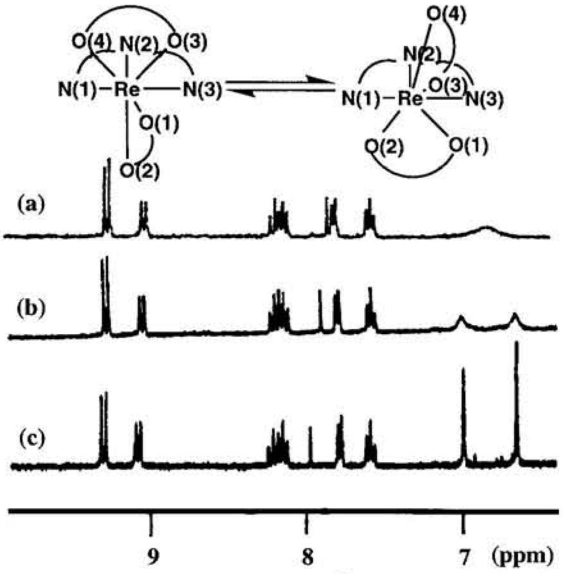

Figure 3. Temperature dependent ^1H NMR spectra of the complex $[\mathbf{1}]^+$ in CD_2Cl_2; (a) 50 ℃, (b) 30 ℃, (c) -20 ℃.

$[ReO(cat)(tacn)]^+$[9] (-1.39 and -1.38 V, respectively), but is close to that of $[ReO(cat)(tpy)]^+$[10] [**5**].

The electronic absorption spectra of $[\mathbf{1}]^+$ in CH_3CN shows two strong absorption bands at 550 (ε : 11000 $M^{-1}cm^{-1}$) and 766 nm (ε : 8500 $M^{-1}cm^{-1}$) in the visible region (Figure 2). The facts that $Re^VO(quarty)(OCH_3)_2]^+$ has two intense absorption bands at 524 (ε : 2910 $M^{-1}cm^{-1}$) and 654 nm (ε : 1480 $M^{-1}cm^{-1}$), while $[ReO(cat)(L)]^+$ (L = tpa, tacn) and $[ReO(L')(diBucat)_2]$ (L' = $OPPh_3$, CH_3OH)[11] display only a weak d-d transition band in the visible region, indicate the bands of $[\mathbf{1}]^+$ are associated with MLCT bands from Re to tpy. (1 M = 1 mol dm^{-3}) These two bands disappear upon one-electron reduction of $[\mathbf{1}]^+$ under the controlled potential electrolysis at -0.90 V, and the resultant $[Re^{IV}(tpy)(diBucat)_2]$ displays a new band at 628 nm (Figure 2). The electronic absorption spectra between Re(V) and Re(IV) reversibly changed under N_2.[12]

One-electron oxidation of $[\mathbf{1}]^+$ under the electrolysis at +0.75 V also resulted in a disappearance of the 550 and 766 nm bands, and a new strong band appeared at 688 nm in the initial stage. Prolonged electrolysis, however, caused an irreversible oxidation of $[\mathbf{1}]^{2+}$ possibly due to the occurrence of two-electron oxidation (Ep = +0.93 V). Thus, it is not clear in the present study whether the electronic configuration of $[\mathbf{1}]^{2+}$ is expressed by $[Re^{VI}(tpy)(diBucat)_2]^{2+}$ or $[Re^V(tpy)(diBucat)(diBuseq)]^{2+}$.

The ^1H NMR spectra of $[\mathbf{1}]^+$ in CD_2Cl_2 reveal fluctuation of the catecholate ligands. Aromatic protons of two diBucat ligands emerge as two sharp singlet signals (δ = 6.98 and 6.67 ppm) at -20 °C. Despite the non-equivalence of 4,5-protons of diBucat containing O(1) and O(2), the appearance of the singlet signal is probably caused by an incidental agreement of the chemical shifts of the two protons.[13] The two singlets broaden with increasing temperatures, and coalesced to one broad signals at 50 °C (Figure 3). On the other hand, no fluctuation was observed in the proton signals of tpy in the temperature range. Such chracteristic behavior of the proton signals of the diBucat and tpy ligands of $[\mathbf{1}]^+$ is explained by the exchange of O(3) and O(1) in the equatorial position between two diBucat ligands.[14] This is the first example of dynamic behavior between two mono-capped trigonal prism structures of hepta-coordinate metal complexes. Detailed thermodynamic behavior and parameters will be discussed in elsewhere.

References and Notes

1 Abbreviations of ligands: tpy, 2,2':6',2"-terpyridine; quarty = 2,2':6',2":6",2'"-quaterpyridine; tpen, *N,N,N',N'* - tetrakis(2-pyridylmethyl)ethylenediamine; tpa, tris(2-pyridylmethyl)amine; tacn, triazacyclononane; diBuseq, 3,6-di-*tert*-butyl-semiquinone.

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4 Yield: 0.15g (55%). Characterization data of $[\mathbf{1}]PF_6.CH_3CN$. Anal. Found: C, 51.39; H, 5.25; N, 5.41 %. Calcd for $C_{45}H_{54}O_4PF_6N_4Re$ (MW 1005.1): C, 51.67; H, 5.20; N, 5.36 %. ESI MS (CH_3CN): *m/z* 860.1 (M^+).

5 Crystal data: Intensity data of $[\mathbf{1}]PF_6{\cdot}CH_3CN$ was collected with a graphite-monochromated Mo Kα radiation (λ = 0.71059Å) on a Rigaku AFC5S diffractometer at 293 K and corrected for Lorentz polarization effect and absorption (psi-scans). Crystal data for $[\mathbf{1}]PF_6{\cdot}CH_3CN$ ($C_{45}H_{54}O_4PF_6N_4Re$): Triclinic, space group $P\bar{1}$(no. 2), a = 11.824(2), b = 20.544(4), c = 10.881(2)Å, α = 103.62(1), β = 103.20(1), γ = 98.20(2)°, V = 2446.4(8)$Å^3$, Z = 2, ρ_{calcd} = 1.42 g cm^{-3}. The structure was solved by direct methods and all the non-hydrogen atoms were refined anisotropically. Hydrogen atom were located by caluclation and only thermal parameters were refined isotropically. The refinement calculations were converted at R = 0.049 and R_W = 0.063 against 7141 observed reflections [$I > 3.5\sigma(I_O)$]. Detailed X-ray date are available on request to the authors.

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12 With regard to Uv-vis data of Re(IV), only [**4**] is available (511 (1640), 836 nm (556 $M^{-1}cm^{-1}$).

13 The methyl protons of four butyl group also appeared at two singlet signals incidentally.

14 If the coalescence is due to the rotation of the diBucat containing O(3) and O(4), the singlet signal of 4,5-protons on diBucat containing O(1) and O(2) should be unchanged.