Localization in *trans,trans*-$[(tpy)(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2(tpy)]^+$ (tpy = 2,2′:6′,2″-Terpyridine)

Konstantinos D. Demadis, Thomas J. Meyer,* and Peter S. White

Department of Chemistry, Venable and Kenan Laboratories CB# 3290, University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27599-3290

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In the mixed-valence chemistry of $d\pi^5-d\pi^6$ ligand-bridged complexes based on Fe, Ru, and Os there are localized and delocalized examples in closely related coordination environments *e.g.* $[(NH_3)_5Ru^{III}(4,4'\text{-bpy})Ru^{II}(NH_3)_5]^{5+}$ [1] (4,4′-bpy is 4,4′-bipyridine) and $[(NH_3)_5Os^{II.5}(N_2)Os^{II.5}(NH_3)_5]^{5+}$.[2] There is also growing evidence for a class of molecules that exist at the localized-to-delocalized transition for which an appropriate description of electronic structure and coupling to the surrounding molecular vibrations and solvent is complicated. Examples are $[(NH_3)_5Ru^{III}(pz)Ru^{II}(NH_3)_5]^{5+}$ [3] and *cis*-$[(bpy)_2ClOs^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$ (pz is pyrazine, bpy is bipyridine).[4] In previous examples, with N_2 as bridge, $[(NH_3)_5M(N_2)M(NH_3)_5]^{5+}$ (M = Ru, Os),[2] $[(CH_3CN)(NH_3)_4Os(N_2)Os(NH_3)_4(CH_3CN)]^{5+}$,[5] and $[Cl(NH_3)_4Os(N_2)Os(NH_3)_4Cl]^{3+}$,[6] evidence for strong electronic coupling and the oxidation state description $M^{II.5}-M^{II.5}$ has been found. For example, in $[(NH_3)_5Ru(N_2)Ru(NH_3)_5]^{5+}$, $[Cl(NH_3)_4Os(N_2)Os(NH_3)_4Cl]^{3+}$, and $[(CH_3CN)(NH_3)_4Os(N_2)Os(NH_3)_4(CH_3CN)]^{5+}$, there is no $\nu(N{\equiv}N)$ stretch in the infrared. In the structure of the latter, as determined by X-ray crystallography, there are equivalent coordination environments at the two Os's. We report here that oxidation states are localized in *trans,trans*-$[(tpy)(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2(tpy)]^+$ (tpy = 2,2′:6′,2″-terpyridine) and that the ion is at the localized to delocalized transition.

Following the work of Che[5] and Taube,[7] we have prepared *trans,trans*-$(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)$ (**2**) in 70% yield by 1-electron reduction and coupling of *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ (**1**)[8] by using HS^- or Et_3N in MeCN or CH_2Cl_2,[9]

$$\underset{\mathbf{1}}{2[Os^{VI}(tpy)(Cl)_2(N)]^+} + 2e^- \rightarrow \underset{\mathbf{2}}{(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)} \quad (1)$$

2 can also be prepared by electrochemical reduction at −0.36 V *vs* SSCE ($n = 1$) with 0.1 M in $[N(n\text{-}Bu)_4](PF_6)$ in CH_3CN. Subsequent oxidation by ferrocenium or I_2 gave the mixed-valence form (**3**) which was isolated in 60−70% yield and characterized as the BF_4^- salt.[10]

$$trans,trans\text{-}\underset{\mathbf{2}}{(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)} + Fc^+ \rightarrow trans,trans\text{-}\underset{\mathbf{3}}{[(tpy)(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2(tpy)]^+} + Fc \quad (2)$$

In cyclic voltammograms of **2** in DMF, reversible $Os^{III}-Os^{II}/Os^{II}-Os^{II}$ and $Os^{III}-Os^{III}/Os^{III}-Os^{II}$ couples appear at +0.21 and +0.77 V *vs* SSCE ($\Delta E_{1/2} = 560$ mV). For **2** a very weak $\nu(N{\equiv}N)$ stretch appears at 2035 cm^{-1} in KBr ($\nu(^{15}N{\equiv}^{15}N)$ at 1972 cm^{-1}). An intense $\nu(N{\equiv}N)$ stretch for **3** appears at 2007 cm^{-1} in KBr ($\nu(^{15}N{\equiv}^{15}N)$ at 1942 cm^{-1}). In CD_3CN $\nu(N{\equiv}N)$ appears at 2012 cm^{-1} ($\epsilon = 1220\ M^{-1}\ cm^{-1}$).

The appearence of the intense $\nu(N{\equiv}N)$ stretch in **3** points to a redox asymmetry across the μ-N_2 bridge. This is supported by the X-ray structure in Figure 1.[11] Important features in the structure include the nearly staggered tpy ligands with a dihedral angle of ~74° and the bent N_2 bridge with Os(1)−N(1)−N(2) and Os(2)−N(2)−N(1) angles of 171.5(9) and 172.1(9)°, respectively. The Os(1)···Os(2) distance is 4.9726(7) Å. The N(1)−N(2) bond length is 1.132(13) Å, slightly longer than that of free N_2 (1.0976(2) Å).[12] The Os−N(bridge) bond lengths are not equivalent (Os(1)−N(1) 1.968(9) Å and Os(2)−N(2) 1.909(10) Å). Furthermore, there are two distinct sets of Os−Cl bond lengths. There are "short" bond lengths, Os(1)−Cl(1) 2.352(3) Å and Os(1)−Cl(2) 2.371(3) Å, consistent with $Os^{III}-Cl$[13] and "long" bond lengths, Os(2)−Cl(3) 2.401(3) Å and Os(2)−Cl(4) 2.402(3) Å, consistent with $Os^{II}-Cl$.[14] The BF_4^- counterion is located 6.22 Å from Os(1) and 6.74 Å from Os(2). The structural evidence supports localized Os^{III} (Os(1)) and Os^{II} (Os(2)) on the basis of the Os−Cl bond lengths and

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(9) Anal. Calc for $Os_2Cl_4N_8C_{30}H_{22}\cdot 2DMF$ (**2**, MW 1162.9): C, 37.15; H, 3.10; N, 12.04. Found: C, 37.24; H, 3.04; N, 13.90. UV−vis (DMF) [λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)]: 272 (48 800), 332 (46 600), 364 (16 400), 394 (13 000), 444 (10 800), 592 (16 000), 660 (14 500), 885 (9100). Infrared (cm^{-1}, KBr disks): $\nu(N{\equiv}N)$ 2035 (vw); $\nu(^{15}N{\equiv}^{15}N)$ 1972 (vw); ν(tpy) 1448 (vs), 1435 (vs), 1383 (vs).

(10) Anal. Calc for $Os_2Cl_4F_4BN_8C_{30}H_{22}$ (**3**, MW 1103.0): C, 32.64; H, 2.00; N, 10.15. Found: C, 32.55; H, 2.63; N, 9.96. UV−vis (MeCN) [λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)]: 234 (62 800), 270 (47 900), 282 (35 100), 322 (43 300), 480 (10 200), 506 (11 200), 678 (3800), 840 (3600). Infrared (cm^{-1}, KBr disks): $\nu(N{\equiv}N)$ 2007 (vs); $\nu(^{15}N{\equiv}^{15}N)$ 1942 (vs); ν(tpy) 1451 (vs), 1439 (s), 1391 (vs).

(11) Crystals of *trans,trans*-$[(tpy)(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2(tpy)](BF_4)\cdot DMF\cdot H_2O$ (**3**) were grown by vapor diffusion of Et_2O into a 10:1 MeCN−DMF solution of the salt. They are triclinic, space group $P\bar{1}$, with a = 8.6350(1) Å, b = 14.1004(2) Å, c = 16.0212(1) Å, α = 103.328(1)°, β = 93.209(1)°, γ = 96.412(1)°, V = 1879.53(4) $Å^3$, Z = 2, fw = 1192.66, d_{calc} = 2.107 g/cm^3, and μ = 7.10 mm^{-1}. Intensity data were collected at −150 °C on a Siemens CCD SMART diffractometer with Mo Kα radiation and a graphite monochromator using the $\theta-2\theta$ scan technique. A total of 6652 unique reflections were measured, with 4126 having $I > 2.5\sigma(I)$ used in the structure refinement by full-matrix least-squares techniques (497 parameters). Final R_f = 0.048, R_w = 0.039, and GoF = 1.28 (for all reflections, R_f = 0.106, R_w = 0.053). NRCVAX was used as the software package. Full details can be found in the Supporting Information.

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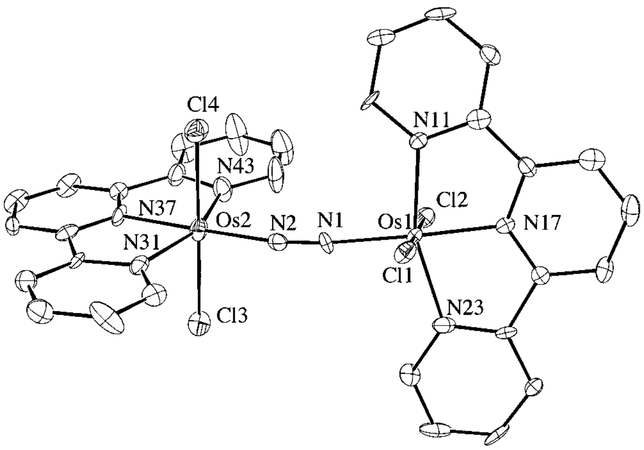

Figure 1. ORTEP diagram (30% probability ellipsoids) of the cation in *trans,trans*-$[(tpy)(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2(tpy)](BF_4)\cdot DMF\cdot H_2O$ (**3**). Important bond lengths (Å) and angles (deg): N(1)−N(2) 1.132(13), Os(1)···Os(2) 4.9726(7), Os(1)−N(1) 1.968(9), Os(1)−Cl(1) 2.352(3), Os(1)−Cl(2) 2.371(3), Os(1)−N(11) 2.084(9), Os(1)−N(17) 1.996(9), Os(1)−N(23) 2.084(10), Os(2)−N(2) 1.909(10), Os(2)−Cl(3) 2.401(3), Os(2)−Cl(4) 2.402(3), Os(2)−N(31) 2.064(9), Os(2)−N(37) 2.006(9), Os(2)−N(43) 2.087(10); Os(1)−N(1)−N(2) 171.5(9), Os(2)−N(2)−N(1) 172.1(9), Cl(1)−Os(1)−Cl(2) 177.6(1), Cl(3)−Os(2)−Cl(4) 179.0(1), N(11)−Os(1)−N(23) 159.4(4), N(31)−Os(2)−N(43) 157.9(4).

counterion placement in the lattice. The $Os^{II}{}_2$−N(bridge) bond length is shorter than $Os^{III}{}_1$−N(bridge) because of Os^{II}−N back-bonding.[15]

The redox asymmetry in the solid state is maintained in solution as shown by the appearence of ν(N≡N) at 2012 cm^{-1}. The near-infrared (NIR) spectrum of **3** in CD_3CN is dominated by intense bands at 3150 nm (3175 cm^{-1}; $\epsilon = 6400$ M^{-1} cm^{-1}; $\Delta\bar{\nu}_{1/2} = 500$ cm^{-1}; 3050 cm^{-1} in KBr) and 2119 nm (4720 cm^{-1}; $\epsilon = 2600$ M^{-1} cm^{-1}; $\Delta\bar{\nu}_{1/2} = \sim 400$ cm^{-1}; 4630 cm^{-1} in KBr). Additional features appear at 1905 nm (5250 cm^{-1}; $\epsilon = 1200$ M^{-1} cm^{-1}), 1512 nm (6610 cm^{-1}; $\epsilon = 230$ M^{-1} cm^{-1}), and ~1000 nm (~10000 cm^{-1}). On the basis of a previous analysis[16] three intervalence transfer (IT) bands and two interconfigurational $d\pi \rightarrow d\pi$ bands are expected for a localized structure. In *trans*-$[Os^{III}(tpy)(Cl)_2(CH_3CN)]^+$ $d\pi \rightarrow d\pi$ bands appear at 2457 nm (4070 cm^{-1}; $\epsilon = 65$ M^{-1} cm^{-1}) and 1486 nm (6730 cm^{-1}; $\epsilon = 123$ M^{-1} cm^{-1}) in CD_3CN.[17] We tentatively assign the intense bands to IT(1) and IT(2) and the remaining features to a combination of $d\pi \rightarrow d\pi$ and IT(3). On the basis of the analysis of Hush,[18ab] the resonance energy arising from donor−acceptor orbital mixing is given by

$$H_{DA} = ((4.2 \times 10^{-4})\epsilon_{max}\Delta\bar{\nu}_{1/2}E_{op}/d^2)^{1/2}$$

(ϵ_{max} is the molar extinction coefficient at the maximum in M^{-1} cm^{-1}, $\Delta\bar{\nu}_{1/2}$ is the bandwidth at half-height in cm^{-1}, E_{op} is the absorption maximum in cm^{-1}, and d is the metal−metal distance in Å.[18c] H_{DA} is 414 cm^{-1} for IT(1) and 289 cm^{-1} for IT(2). The NIR band energies are the same within experimental error in CD_3NO_2, CD_3CN, and $(CD_3)_2SO$. By comparison, the lowest-lying Os^{II} → tpy metal-to-ligand charge transfer band is somewhat solvent dependent with $\lambda_{max} = 850$ nm (CD_3NO_2), 840 nm (CD_3CN), and 850 nm ($(CD_3)_2SO$).

The available evidence places **3** at the transition between the limiting localized and delocalized descriptions for class II and class III in the Robin−Day scheme.[19] On the basis of the magnitude of $\Delta E_{1/2}$ (=560 mV), there appears to be medium to strong electronic coupling. There are trapped oxidation states from the structural data and a residual intramolecular barrier to electron transfer arising from low energy Os−Cl, Os−N vibrations. Given the narrow IT bands and the absence of a solvent dependence, intramolecular $Os^{II} \rightarrow Os^{III}$ electron transfer is apparently more rapid than the solvent reorientation time of ~1 ps and the solvent does not contribute to the barrier.[20] With $E(IT_1) \sim 2H_{DA}(1) + \lambda_i$, $\lambda_i \sim 2350$ cm^{-1}. λ_i is the intramolecular reorganizational energy. On the basis of this analysis, the classical energy of activation for the lowest energy electron transfer pathway corresponding to IT(1)[4b,16] is $E_a \sim \lambda_i/4 \sim 590$ cm^{-1}.

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Supporting Information Available: Text giving experimental procedures for the preparation and characterization of the compounds, IR and NIR spectra, details of the crystallographic analysis of *trans,trans*-$[(tpy)(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2(tpy)](BF_4)\cdot DMF\cdot H_2O$ (**3**), a fully labeled ORTEP diagram as well as a packing diagrams, and tables of atomic coordinates, isotropic thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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