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What a Difference Ancillary Thienyl Makes: Unexpected Additional Stabilization of the Diruthenium(III,II) but Not the Diosmium(III,II) Mixed-Valent State in Tetrazine Ligand-Bridged Complexes

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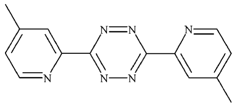
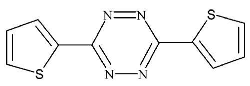
The $Ru_2^{III,II}$ mixed-valent state is strongly stabilized in $[(bpy)_2Ru(\mu\text{-bttz})Ru(bpy)_2]^{5+}$ (**3**$^{5+}$), bttz = 3,6-bis(2-thienyl)-1,2,4,5-tetrazine, as evident from lowered oxidation potentials and isolability, a strongly increased comproportionation constant $K_c = 10^{16.6}$, and a high-energy intervalence charge transfer band at 10100 cm^{-1}. Curiously, no such effects were observed for the diosmium(III,II) analogue, whereas the related systems $[(bpy)_2M(\mu\text{-bmptz})M(bpy)_2]^{5+}$, bmptz = 3,6-bis(4-methyl-2-pyridyl)-1,2,4,5-tetrazine, exhibit conventional behavior, i.e., a slightly higher K_c value of the $Os_2^{III,II}$ analogue. EPR signals were observed at 4 K for **3**$^{5+}$ but not for the other mixed-valent species, and high-frequency (285 GHz) EPR was employed to study the diruthenium(II) radical complexes **2**$^{3+}$ and **3**$^{3+}$.

1,2,4,5-Tetrazines and especially the 3,6-bis(2-pyridyl) derivative bptz have become increasingly popular as bridging ligands with unusual electronic properties and the capacity for forming coordination oligomers and polymers.[1] One noted aspect[1−3] has been the capability of strongly π-accepting tetrazine bridges to stabilize mixed-valent intermediates.[4] Whereas $[(H_3N)_4Ru(\mu\text{-bptz})Ru(NH_3)_4]^{5+}$ was established[2a] with a comproportionation constant $K_c = 10^{15.0}$, the related $[(bpy)_2Ru(\mu\text{-bptz})Ru(bpy)_2]^{5+}$ (**1**$^{5+}$) with the competing π acceptor ligands bpy = 2,2′-bipyridine still showed $K_c = 10^{8.5}$.[2] Dinuclear complexes of bptz with $[RuCl([9]aneS_3)]^{2+/+}$, $[9]aneS_3$ = 1,4,7-trithiacyclononane,[3] or $[Ru(acac)_2]^{+/0}$ [2c] yielded K_c values of $10^{8.1}$ and 10^{13}, respectively.

Within attempts to modify bptz we now used 3,6-bis(4-methyl-2-pyridyl)-1,2,4,5-tetrazine (bmptz) and 3,6-bis(2-thienyl)-1,2,4,5-tetrazine (bttz)[5] as bridging ligands in complexes **2**$^{n+}$ and **3**$^{n+}$ with $[Ru(bpy)_2]^{3+/2+}$ and in complexes **4**$^{n+}$ and **5**$^{n+}$ with $[Os(bpy)_2]^{3+/2+}$, respectively. Electrochemical and spectroscopic data (UV−vis−NIR, EPR) are summarized in Table 1.



bmptz



bttz

The complexes were originally obtained in the $Ru_2^{II,II}$ and $Os_2^{II,II}$ forms which are distinguished by the typical low-energy metal-to-(tetrazine)ligand charge transfer (MLCT) transitions. The donor character of 2-thienyl vs 2-pyridyl or 2-(4-methylpyridyl) is evident from a hypsochromic shift of the MLCT bands for **3**$^{4+}$ vs those of **2**$^{4+}$ (Table 1) or **1**$^{4+}$.[2d] The osmium(II) species **4**$^{4+}$ and **5**$^{4+}$ exhibit less variation

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Table 1. Electrochemical and Spectroscopic Data for Redox Systems

	2^{n+} (Ru$_2$/bmptz)	3^{n+} (Ru$_2$/bttz)	4^{n+} (Os$_2$/bmptz)	5^{n+} (Os$_2$/bttz)
		Redox Potentials[a]		
$E_{1/2}(6+/5+)$	1.63	1.42	1.18	0.53
$E_{1/2}(5+/4+)$	1.10	0.44	0.51	0.07
$E_{1/2}(4+/3+)$	−0.45	−1.26	−0.65	−1.11
$E_{1/2}(3+/2+)$	−1.36	−2.22	−1.62	−1.89
$E_{1/2}(2+/0)$	−1.96	−2.54	−1.97	−2.24
$K_c(5+)$[b]	$10^{9.0}$	$10^{16.6}$	$10^{11.4}$	$10^{7.8}$
		Absorption Maxima[c]		
$\lambda_{MLCT}(4+)$ [ϵ]	700 [13100]	500 [7400], 580sh	1005 [7500], 670 [18000]	1148 [7800], 720 [15500]
λ (4+) [ϵ]	410 [7300], 280 [64000]	345 [38400], 290 [57700]	485 [1400], 451 [20000], 285 [5500]	520 [13000], 433sh, 290 [57000]
$\lambda_{IVCT}(5+)$ [ϵ; $\Delta\nu_{1/2}$]	1490 [2700; 1100]	990 [1650; 2000]	1655 [1750; 1350]	1375 [1950; 1150]
λ (5+) [ϵ]	620 [12000]	583 [4650], 432 [14000], 353 [30300]	1265 [8500], 955 [12000], 705 [10500], 455 [13000]	984 [1800], 605 [16000], 495 [14500], 335sh, 285 [56500]
		EPR		
g_1, g_2, g_3 (5+)[d]	*e*	2.479, 2.313, 1.807	*e*	*e*
$g_{\parallel}, g_{\perp}$ (3+)	2.0130, 1.9869[f]	1.9929, 2.0053[f]	2.0126, 2.0057[d]	2.0238, 2.0051, 1.9565[d]
g_{iso}	1.9985[g]	2.0042[h]	n.o.[i]	n.o.

[a] From cyclic voltammetry at 0.1 V/s in acetonitrile/0.1 mol dm^{-3} Bu$_4$NPF$_6$. Potentials in V vs ferrocenium/ferrocene. [b] $K_c = 10^{\Delta E(5+)/59\text{mV}}$. [c] From OTTLE spectroelectrochemistry in acetonitrile/0.1 mol dm^{-3} Bu$_4$NPF$_6$. Wavelengths in nm, molar extinction coefficients in dm^3 mol^{-1} cm^{-1}, bandwidths at half-height in cm^{-1}. [d] In frozen acetonitrile solution at 4 K (X band, 9.5 GHz). [e] No signal observed down to 4 K. [f] In frozen CH$_3$CN at 4 K (285 GHz). [g] In acetonitrile at 298 K, tetrazine ^{14}N hfs of ca. 0.55 mT. [h] In acetonitrile at 298 K, tetrazine ^{14}N hfs of ca. 0.51 mT. [i] Not observed.

with slightly lower absorption energies for the bttz complex $\mathbf{5}^{4+}$ (Table 1). The spectra of the osmium analogues are more complicated[6] because singlet−triplet transitions are enhanced by spin−orbit coupling. The redox potentials, two metal-centered one-electron oxidations and series of ligand-centered reduction processes, are shifted to more negative values in systems $\mathbf{3}^{n+}$ vs $\mathbf{2}^{n+}$ and $\mathbf{5}^{n+}$ vs $\mathbf{4}^{n+}$ (Figure 1, Table 1). Expectedly,[6] the oxidation of the Os^{II} complexes occurs at lower potentials. As a result, the oxidation potential is lowest for complex ion $\mathbf{5}^{4+}$. The effect of the methyl groups in $\mathbf{2}^{5+}$ vs $\mathbf{1}^{5+}$[2d,e] is marginal.

The most striking result is the unexpectedly strong stabilization of the Ru$_2^{III,II}$ state of $\mathbf{3}^{5+}$ ($K_c = 10^{16.6}$) in comparison to $\mathbf{1}^{5+}$ or $\mathbf{2}^{5+}$ ($K_c = 10^{8.5}$ or $10^{9.0}$, respectively). This stability contributes to the facile isolation of (**3**)(PF$_6$)$_5$ through oxidation with NO$^+$. Spectroscopic analysis of this isolated mixed-valent material as well as spectroelectrochemical investigation of the precursor (**3**)(PF$_6$)$_4$ (Figure 2) exhibits the weak ($\epsilon = 1650$ M^{-1} cm^{-1}) intervalence charge transfer (IVCT) band at 990 nm (10100 cm^{-1}), a high energy in comparison to the ca. 6700 cm^{-1} (ca. 1500 nm) for $\mathbf{2}^{5+}$ (Table 1) or $\mathbf{1}^{5+}$.[2e] Application of the Hush formula[7] $\Delta\nu_{1/2}(\text{calc}) = (2310\nu_{IVCT})^{1/2}$ for not completely delocalized mixed-valent systems (class II systems according to the Robin/Day classification[8]) yields 4830 cm^{-1}, a much larger number than the observed value of 2000 cm^{-1}. In agreement with the unusually large comproportionation constant the $\mathbf{3}^{5+}$ ion is thus formulated as a fully delocalized class III species with averaged oxidation states. Accordingly, the interaction parameter H_{AB} is estimated at $\nu_{IVCT}/2 = 5050$ cm^{-1}, a comparatively high value.[9,10]

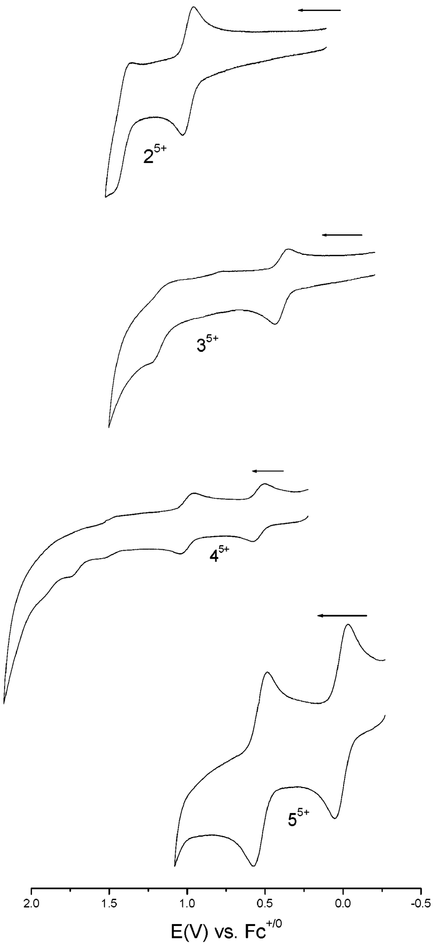

Figure 1. Cyclic voltammograms of complexes (**2**)(PF$_6$)$_4$−(**5**)(PF$_6$)$_4$ in acetonitrile/0.1 M Bu$_4$NPF$_6$ at a scan rate of 100 mV/s.

The application of Hush's formula to the diosmium analogue $\mathbf{5}^{5+}$ yields $\Delta\nu_{1/2}(\text{calc}) = 4100$ cm^{-1}, again much larger than the observed value of 1150 cm^{-1} and thus indicative of a class III system.

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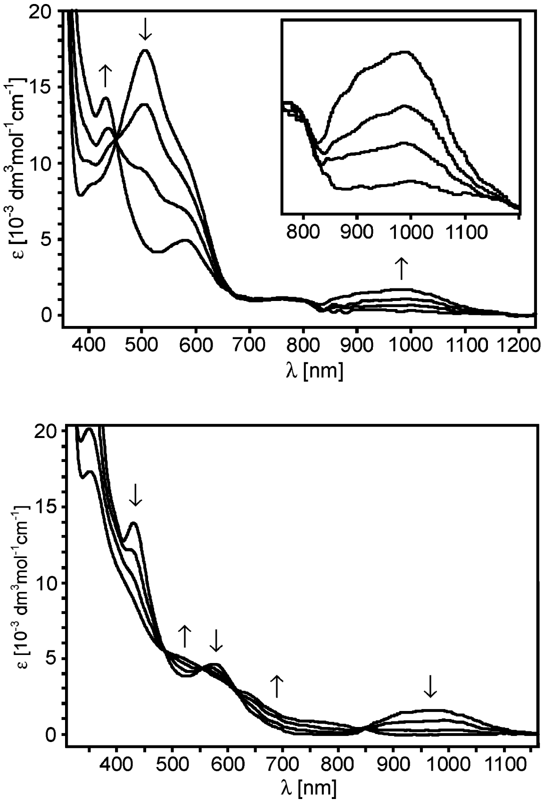

Figure 2. UV−vis−NIR spectroelectrochemistry of the conversion $\mathbf{3}^{4+} \rightarrow \mathbf{3}^{5+}$ and $\mathbf{3}^{5+} \rightarrow \mathbf{3}^{6+}$ (from top to bottom) in acetonitrile/0.1 M Bu_4NPF_6.

In contrast to the diruthenium complexes the diosmium analogues exhibit a reversed pattern of electrochemical stability. The K_c value of the bmptz complex $\mathbf{4}^{5+}$ is higher than that of the diruthenium species $\mathbf{2}^{5+}$ (Table 1), in agreement with previous experience with π acceptor bridged $M_2^{III,II}$ compounds (M = Ru, Os).[4,6,11] However, at $10^{7.8}$ the K_c of the diosmium complex $\mathbf{5}^{5+}$ with the bttz ligand bridge is much smaller than the exceptional value of $10^{16.6}$ of the diruthenium species $\mathbf{3}^{5+}$, reflecting a π donor contribution[10] attributed to the thienyl rings. This unexpected situation is further illustrated by the result that the K_c of the bttz complex ($\mathbf{5}^{5+}$) is smaller in the diosmium complex series $\mathbf{4}^{5+}$/$\mathbf{5}^{5+}$ whereas it is much larger for the bttz diruthenium(III,II) complex $\mathbf{3}^{5+}$ as compared to the bmptz system $\mathbf{2}^{5+}$ (Table 1).

The strong metal−metal coupling in $\mathbf{3}^{5+}$ is also evident from EPR studies. Whereas $\mathbf{1}^{5+}$, $\mathbf{2}^{5+}$, $\mathbf{4}^{5+}$, and $\mathbf{5}^{5+}$ are EPR silent even at 4 K due to rapid relaxation resulting from close-lying paramagnetic states, complex $\mathbf{3}^{5+}$ exhibits a typical Ru^{III} EPR spectrum (Table 1).

One-electron *reduction* of the (4+) complexes leads to tetrazine-centered radical anion complexes with tetrazine-^{14}N EPR hyperfine splitting in fluid solution. Predominant ligand contribution to the singly occupied MOs is also evident from isotropic g values close to g(electron) = 2.0023 (Table 1) and from the results of high-frequency (285 GHz) EPR spectroscopy of $\mathbf{2}^{3+}$ and $\mathbf{3}^{3+}$ in frozen CH_3CN (Table 1).[12] The g anisotropies g_1-g_3 of the diruthenium(II) radical complexes $\mathbf{2}^{3+}$ and $\mathbf{3}^{3+}$ are comparable, but the axial splitting patterns are different, confirming again the difference between the electronic structures of systems $\mathbf{2}^{n+}$ and $\mathbf{3}^{n+}$.

We attribute the exceptional stabilization of the $Ru_2^{III,II}$ mixed-valent state in $\mathbf{3}^{5+}$ after a seemingly minor modification to the special σ and π donor effect of the thienyl substituents at the tetrazine bridge. In contrast, triple thioether coordination in $[([9]aneS_3)ClRu(\mu\text{-bptz})RuCl([9]aneS_3))]^{3+}$ did not greatly affect the K_c and ν_{IVCT} values[3] in comparison to $\mathbf{1}^{5+}$ or the slightly modified $\mathbf{2}^{5+}$. In a not necessarily[4] parallel manner the electronic metal−metal interaction also increases significantly on going from $\mathbf{1}^{5+}$ or $\mathbf{2}^{5+}$ to $\mathbf{3}^{5+}$. The synergism of donor and acceptor functions in enhancing metal−metal interaction was reported recently;[10] these results demonstrate that the metal−metal interaction in mixed-valent species is still difficult to estimate and that exploratory chemistry in this area can lead to materials of surprising stability.

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Supporting Information Available: Synthetic procedures, analysis, and NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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