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Article

Probing Mixed Valence in a New tppz-Bridged Diruthenium(III,II) Complex $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}^{3+}$ (tppz = 2,3,5,6-Tetrakis(2-pyridyl)pyrazine, bik = 2,2′-Bis(1-methylimidazolyl)ketone): EPR Silence, Intervalence Absorption, and ν_{CO} Line Broadening

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The complex dication of the diruthenium(II) compound $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}(\mathrm{ClO_4})_2$ can be oxidized and reduced in two one-electron steps each. In $\mathrm{CH_3CN}$/0.1 M $\mathrm{Bu_4NPF_6}$, the odd-electron intermediates$\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}^{n+}$, $n = 1$ and 3, have comproportionation constants of 7×10^8 and 1×10^5, respectively. Both exhibit near-infrared absorptions, in the case of $n = 3$ the 1640 nm band ($\epsilon = 1200$ M^{-1} cm^{-1}, $\Delta\nu_{1/2} = 1560$ cm^{-1}) is attributed to an intervalence charge-transfer transition. While the mixed-valent intermediate ($n = 3$) is EPR silent even at 4 K, the $n = 1$ form shows $g(\parallel)$ 2.005 and $g(\perp)$ 1.994 at that temperature, signifying a diruthenium(II) complex of the tppz$^{\bullet-}$ radical anion. The variation of energy and intensity of ν_{CO} and of the ring vibration band around 1590 cm^{-1} has been monitored not only for $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}^{n+}$, $n = 0$–4, but also for the mononuclear $\{(\mathrm{tppz})\mathrm{Ru(bik)Cl}\}^{n+}$, $n = 0$–2. In the dinuclear complex the carbonyl stretching bands of the spectator ligand bik are shifted by about 15 cm^{-1} on each one-electron-transfer step, increasing with the positive charge. The mixed-valent $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}^{3+}$ shows a perceptibly broader ν_{CO} band, suggesting incomplete valence averaging (partial localization).

Introduction

The 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) bridging ligand has been popular in mixed-valence research[1−4] because of (1) its relation to unsubstituted pyrazine of Creutz−Taube ion (**1a**) fame,[1b,5] (2) its potential bis(tridentate) ("bis-terpy-type") coordination[1a,2d,6] (promising enhanced stability), and (3) its low-lying π^* acceptor orbital.[2,3]

In general, pyrazines have long been recognized[7a] as potentially noninnocent, active components of special coordination compounds[6,7] and other unusual chemical entities,[7a] allowing for accommodation of extra charge and spin.

Diruthenium complexes of μ-tppz with partially mixed halide, amine, polypyridyl, azo, and azole ligation have been

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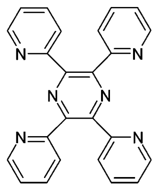
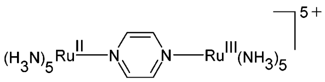
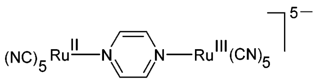


tppz



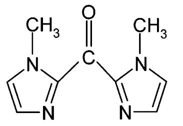
1a



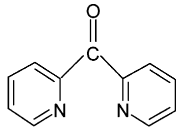
1b

reported.[1−3] One special feature of complexes with tppz is the inability of the potentially conjugated ligand π-system to adopt a coplanar conformation because of steric repulsion between the hydrogen substituents in the 3-position of the pyridyl groups.[1a,2d,6] Twisting of the pyridyl rings to allow bismeridional−tridentate binding has been observed, e.g., for copper[6a,b] and ruthenium complexes.[1a,2d]

In this work we describe results obtained for the $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}^{n+}$ (**2**$^{n+}$) redox system ($n = 0, 1, 2, 3, 4$), where bik is the established[8] 2,2′-bis(1-methylimidazolyl)ketone chelate ligand which contains both electron-rich N-donor heterocycles (for stabilizing higher metal oxidation states) and an electron-accepting carbonyl function, usable as an indicator of complex symmetry via the strong, well-separated ν_{CO} band. The latter approach has been employed by us recently[2a] for $\{(\mu\text{-tppz})[\mathrm{Ru(dpk)Cl}]_2\}^{n+}$ (**4**$^{n+}$) where dpk is the better π-accepting 2,2′-dipyridylketone. Since the electron-transfer mechanism rather than the hole-transfer alternative is believed to be operating for valence exchange in diruthenium(III,II) complexes bridged by π-accepting pyrazine-type ligands,[9] the competition between tppz and dpk for the π-electron donor capacity of ruthenium(II) is expected to affect the electronic coupling. Such competition between bridging and ancillary ligands has been studied also in the diruthenium−pyrazine series,[1b] including the cyanide analogue **1b** of the Creutz−Taube ion.[10] Conversely, the use of bik in the new $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}^{n+}$ was expected to provide altered electronic interaction and stability as well as further insight into the mixed-valent intermediate ($n = 3$) and into additional oxidation states, including the other odd-electron form with $n = 1$. For comparison and referencing, we also studied the mononuclear analogue $\{(\mathrm{tppz})\mathrm{Ru(bik)Cl}\}^{n+}$ (**3**$^{n+}$), $n = 0-2$.



bik



dpk

Monitoring the carbonyl band during stepwise oxidation or reduction provides information on the symmetry of the system on the vibrational time scale of <1 ps.[11] While most studies using this approach have involved metal carbonyl functions,[11−13] the use of ancillary ligands is also possible, provided that sufficient redox-induced shift is observed. Mixed-valent complexes such as $\{(\mu\text{-tppz})[\mathrm{RuL}_3]_2\}^{n+}$ have often been investigated[1] with the emphasis on establishing the extent of valence delocalization (or valence averaging), associated with a certain classification according to Robin and Day.[14] However, detailed analyses have shown a medium-dependent continuum of valence exchange rates which has given rise to designations of some systems as "borderline" or class II or III.[1b,c]

Additionally, the electrochemical potential splitting of the two separated redox processes involving the mixed-valent intermediate as translated into the comproportionation constant $K_c = 10^{\Delta E/0.059}$ has often been taken as another piece of evidence for weak or strong metal−metal coupling.[15] However, many examples have demonstrated meanwhile[16] that the electrochemical metal−metal interaction gives a different kind of information, depending on quite a number of factors,[17] and may thus bear little relation to the results obtained for the actual rate of valence exchange or from spectroscopic measurements. Spectroscopic data may thus substantiate strong metal−ligand−metal interaction despite rather moderate K_c values (or vice versa), depending on the coordination situation which determines orbital overlap and metal−metal distance.[16] For instance, in contrast to bis-

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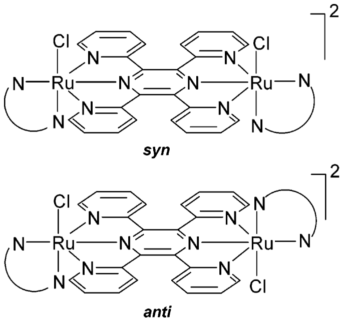

Figure 1. Syn and anti isomers of dinuclear complexes $\{(\mu\text{-tppz})[\mathrm{Ru(N{-}N)Cl}]_2\}^{n+}$.

(bidentate)-bridged systems[18] the bis(tridentate)-bridged complexes such as those with $\mu,\eta^3;\eta^3$-tppz exhibit well-detectable narrow intervalence charge-transfer (IVCT) absorptions, while the K_c values remain relatively modest.[1−3,19]

Another method to study mixed-valent intermediates is electron paramagnetic resonance (EPR) which can provide information via hyperfine coupling,[20] via the g factor and its anisotropy,[21] or via the relaxation as apparent from the EPR line width.[10,21b]

The following contains a report on the synthesis, electrochemical, and spectroelectrochemical (UV−vis−NIR−IR, EPR) studies of the redox systems $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}^{n+}$ ($\mathbf{2}^{n+}$), $n = 0-4$, and $\{\mathrm{(tppz)Ru(bik)Cl}\}^{n+}$ ($\mathbf{3}^{n+}$), $n = 0-2$.

Results and Discussion

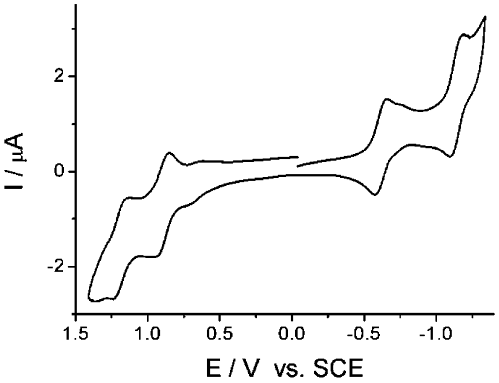

Figure 2. Cyclic voltammogram of $\mathbf{2}^{2+}$ in $\mathrm{CH_3CN}$/0.1 M $\mathrm{Bu_4NPF_6}$.

Table 1. Electrochemical Data[a]

complex	E^0_{298}/V (ΔE_p/mV)			
	ox 1	ox 2	red 1	red 2
$\mathbf{2}^{2+}$	0.89 (66)	1.19 (68)	−0.62 (60)	−1.14 (66)
$\mathbf{3}^{+}$	0.85 (60)		−1.13 (60)	−1.40[b]

[a] From cyclic voltammetry in $\mathrm{CH_3CN}$/0.1 M $\mathrm{Bu_4NPF_6}$ vs SCE. ΔE_p: peak potential difference. [b] Cathodic peak potential; the reduction step is coupled to an irreversible chemical reaction.

Preparation and Characterization. The mononuclear and diruthenium(II) complexes $\{\mathrm{(tppz)Ru(bik)Cl}\}(\mathrm{ClO_4})$ and $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}(\mathrm{ClO_4})_2$ were obtained by reacting $[\mathrm{Cl_3Ru^{III}}(\mu\text{-tppz})\mathrm{Ru^{III}Cl_3}]$ and bik in refluxing ethanol under dinitrogen atmosphere in the presence of excess LiCl. Mass spectroscopy, elemental analysis, and conductivity measurements confirmed their composition (see the Experimental Section). Similar as related complex ions $\{(\mu\text{-tppz})[\mathrm{Ru(N{-}N)Cl}]_2\}^{2+}$, N−N = bpy[1a] or pap = 2-phenylazopyridine,[2d] the dinuclear dication may exist as syn or anti (cis or trans) isomers with respect to the position of the chloride ligands relative to the approximate[1a,2d] Ru(tppz)Ru plane (Figure 1). The presence of only one ν(C═O) band in [**2**]$(\mathrm{ClO_4})_2$ in corroboration with a single Ru−Cl vibration band at 302 $\mathrm{cm^{-1}}$ signifies a single isomer, identified as the anti compound, with respect to the position of the two chloride groups. The ^{1}H NMR spectrum of $\mathbf{3}^+$ in $\mathrm{(CD_3)_2SO}$ shows the partial overlapping expected for 20 protons in the aromatic region and an $\mathrm{NCH_3}$ signal at 3.89 ppm (see the Experimental Section). The appearance of 24 severely overlapping proton signals in the aromatic region and of 4 $\mathrm{NCH_3}$ signals from $\mathbf{2}^{2+}$ (see the Experimental Section) suggests a lack of symmetry due to the nonplanarity of tppz and of the bik ligands and/or the presence of a mixture of two diastereoisomeric forms in solution.

Electrochemistry. While the dinuclear $\{(\mu\text{-tppz})[\mathrm{Ru(bik)Cl}]_2\}(\mathrm{ClO_4})_2$ can be oxidized and reduced in two reversible one-electron steps each (Figure 2), the mononuclear analogue $\{\mathrm{(tppz)Ru(bik)Cl}\}(\mathrm{ClO_4})$ shows just one reversible oxidation and reduction. A second reduction in cyclic voltammetry appears without an anodic counter peak and is coupled to an irreversible chemical change as supported also by spectroelectrochemistry (Table 1). Expectedly, the potentials for the dinuclear compound are shifted to lower values after replacement of 2,2′-dipyridylketone (dpk)[2a] in $\mathbf{4}^{n+}$ by the less π-accepting bik in $\mathbf{2}^{n+}$, the effect being significant for the (metal-centered) oxidation steps and only slight for the (tppz-based) reduction processes (cf. the following). The comproportionation constants K_c for the mixed-valent intermediates $\mathbf{4}^{3+}$ and $\mathbf{2}^{3+}$ are virtually unchanged, amounting to a typically[2a] modest[16] 1×10^5 for the one-electron oxidized $\mathbf{2}^{3+}$.

The K_c value for the one-electron reduced $\mathbf{2}^+$, a radical complex (see below), is higher at 7×10^8, a value found similarly for other complexes of $\mathrm{tppz}^{\bullet-}$.[2a] In comparison to the mononuclear $\mathbf{3}^+$ the dinuclear $\mathbf{2}^{2+}$ is oxidized and reduced at higher potentials (Table 1), reflecting the increased positive charge.

EPR Spectroscopy. The paramagnetic forms (one-electron reduced or oxidized in situ in $\mathrm{CH_3CN}$/0.1 M $\mathrm{Bu_4NPF_6}$) have been studied by X-band EPR (9.5 GHz) at various temperatures. Remarkably low temperatures were necessary to study not only the oxidized but also the reduced species. The $\mathbf{2}^+$

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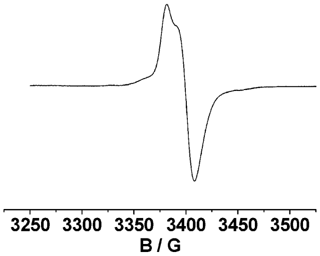

Figure 3. EPR spectrum of electrogenerated $\mathbf{2}^{+}$ in CH_3CN/0.1 M Bu_4NPF_6 at 4 K.

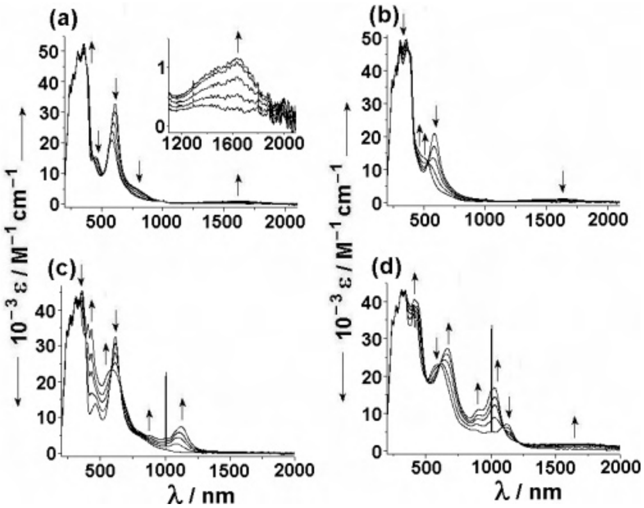

Figure 4. UV−vis−NIR spectroelectrochemical responses of system $\mathbf{2}^{n+}$ in CH_3CN/0.1 M Bu_4NPF_6: (a) $\mathbf{2}^{2+} \rightarrow \mathbf{2}^{3+}$ (inset shows the expanded spectra between 1200 and 2000 nm), (b) $\mathbf{2}^{3+} \rightarrow \mathbf{2}^{4+}$, (c) $\mathbf{2}^{2+} \rightarrow \mathbf{2}^{+}$, and (d) $\mathbf{2}^{+} \rightarrow \mathbf{2}$.

Table 2. UV−Vis−NIR Data of $\mathbf{2}^{n}$ [$n = 0, 1, 2, 3, 4$] and $\mathbf{3}^{n}$ [$n = 0, 1, 2$] from Spectroelectrochemistry[a]

complex	λ_{max} (nm) (ϵ ($M^{-1}\ cm^{-1}$))
2	1750 (1900), 1030 (16900), 905 (11100), 665 (27200), 438,[b] 409 (40600), 342 (42800), 312 (41900), 270 (38900), 241 (35000)
$\mathbf{2}^{+}$	1120 (7400), 875,[b] 805,[b] 590 (23200), 430 (34800), 402 (36100), 341 (43300), 311 (43800), 268 (38600), 242 (34400)
$\mathbf{2}^{2+}$	795,[b] 612 (32500), 453 (15500), 357 (52300), 307 (49700), 270 (42600), 243 (38900)
$\mathbf{2}^{3+}$	1637 (1200; 1565 cm^{-1}),[c] 585 (21200), 388,[b] 355 (49300), 308 (48800), 271 (41300), 242 (37300)
$\mathbf{2}^{4+}$	525 (13200), 450,[b] 390,[b] 365 (46500), 307 (45900), 269 (39900), 241 (35400)
3	925 (1800), 840 (2200), 627 (5000), 539 (5300), 428 (8000), 395,[b] 335(26500), 309 (28300), 237 (18300)
$\mathbf{3}^{+}$	740,[b] 534 (6200), 395,[b] 340 (25500), 310 (27400), 272sh, 240 (17500)
$\mathbf{3}^{2+}$	525 (1900), 425,[b] 348 (25000), 310 (25400), 270,[b] 240[b]

[a] Measurements in CH_3CN/0.1 M Bu_4NPF_6 (OTTLE spectroelectrochemistry). [b] Shoulder. [c] Bandwidth at half-height ($\Delta\nu_{1/2}$ in cm^{-1}).

ion, for instance, did not exhibit a signal at 110 K in frozen solution but only at 4 K (Figure 3), although the data ($g(\parallel)$, 2.005; $g(\perp)$, 1.994; g_{av}, 1.998) clearly indicate (tppz) ligand-centered spin, i.e., a radical anion complex[22] of coordinated low-spin ruthenium(II), typically having $g_{av} < 2$.[22b] Such rapid EPR relaxation effects for radical complexes of diruthenium(II) have been noted before, e.g., for $\{(\mu\text{-bptz})[Ru(NH_3)_4]_2\}^{3+}$, bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine.[18a] They may be caused by the presence of one or more states lying very close to the radical ground state.

Reduction of the mononuclear complex ion $\mathbf{3}^{+}$ to $\{(tppz^{\bullet-})Ru^{II}(bik)Cl\}$ yields $g(\parallel) = 2.019$ and $g(\perp) = 1.995$ at 110 K. Oxidation of the mononuclear precursor to $\mathbf{3}^{2+}$ yields a low-spin d^5 system $\{(tppz)Ru^{III}(bik)Cl\}^{2+}$ with rather pronounced g factor anisotropy at $g_1 = 2.564$, $g_2 = 2.406$, $g_3 = 1.645$, $\Delta g = 0.919$, $g_{av} = 2.24$. This large Δg is likely to be caused by the distortion imposed by the ligand;[1a,2d,6] the initially mentioned inability of tppz to adopt a coplanar conformation is reflected also in the coordination geometry of bonded metal ions.

The further increased strain in the monooxidized dinuclear complex may contribute to the absence of detectable EPR response for mixed-valent $\mathbf{2}^{3+}$, even at 4 K. The related $\mathbf{4}^{3+}$ showed a relatively weak signal at 4 K.[2a] EPR silence is not uncommon for d^5/d^6 mixed-valent compounds; it has been observed, e.g., for the pentacyano-substituted analogue **1b** of the Creutz−Taube ion,[10] for diosmium(III,II) species[9a] as well as for diiron(III,II) complexes.[23] In addition to the effect from large spin−orbit coupling through the heavier transition metal the presence of close-lying excited states with nonzero angular momentum can be made responsible for EPR silence.

The absence of detectable EPR response thus confirms the diruthenium(III,II) character of $\mathbf{2}^{3+}$, as supported by electronic spectroscopic (see below). In this context it may be noted that the molecular rectangle $[Rh_4(\mu\text{-}O_2CMe)_2(\mu\text{-}tppz)_2(MeOH)_4]^{4+}$ was reported with an EPR signal at $g = 2.003$, compatible with a radical formulation $(Rh_2^{II,II})_2(tppz^{\bullet-})_2$ instead of a mixed-valent description $(Rh_2^{II,I})_2(tppz)_2$.[4] As stated in ref 4, the Rh−Rh distance of 2.6060(11) Å does not allow a clear assignment to either $Rh_2^{I,II}$ or $Rh_2^{II,II}$ oxidation states.

UV−Vis−NIR Spectroelectrochemistry. Absorption spectra were obtained for all states $\mathbf{2}^{n+}$, $n = 0-4$, and $\mathbf{3}^{n+}$, $n = 0-2$, using an optically transparent thin-layer electrode (OTTLE) cell and CH_3CN/0.1 M Bu_4NPF_6 solutions (Figure 4, Table 2).[24]

The mononuclear system $\mathbf{3}^{n+}$ shows the behavior expected from the EPR results: The metal-to-ligand charge-transfer (MLCT) band in the visible (534 nm) for the allowed transition $d(Ru^{II}) \rightarrow \pi^*(tppz)^{1-3}$ disappears on oxidation, while reduction leads to a decrease and shift of that band in addition to the intraligand features of $tppz^{\bullet-}$ radical anion which extend into the near-infrared (NIR) region (Table 2). Continuing the reduction at more negative potentials (second peak) causes instability of the complex; the product formed cannot be reoxidized back to the original compound.

The dinuclear redox system $\mathbf{2}^{n+}$ also starts with the an intense MLCT band at 612 nm for the isolated ($n = 2$) species; the additional long-wavelength shoulder may be due to forbidden MLCT transitions, and additional absorptions at higher energies can be assigned as MLCT transitions to unoccupied π^* orbitals lying higher than the tppz-based LUMO. One-electron oxidation produces a weak ($\epsilon = 1200$

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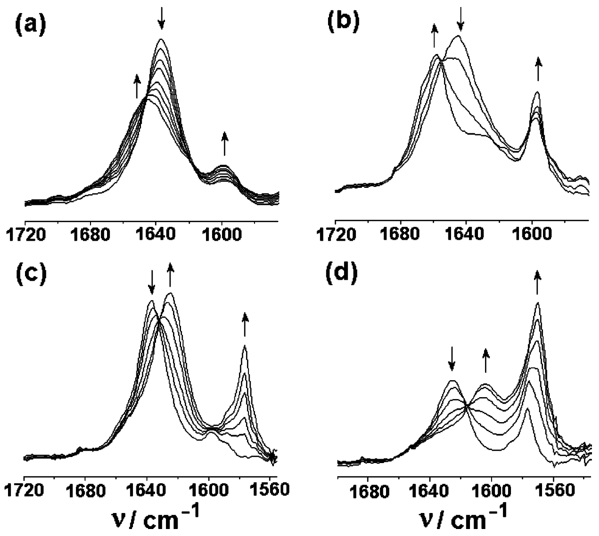

Figure 5. IR spectroelectrochemical responses of system $\mathbf{2}^{n+}$ in CH$_3$CN/0.1 M Bu$_4$NPF$_6$: (a) $\mathbf{2}^{2+} \rightarrow \mathbf{2}^{3+}$, (b) $\mathbf{2}^{3+} \rightarrow \mathbf{2}^{4+}$, (c) $\mathbf{2}^{2+} \rightarrow \mathbf{2}^{+}$, and (d) $\mathbf{2}^{+} \rightarrow \mathbf{2}$.

M^{-1} cm^{-1}) but clearly detectable (Figure 4a) slightly unsymmetrical band in the NIR at $\lambda_{\max} = 1640$ nm, which disappears after the second oxidation. It is attributed to an intervalence charge-transfer (IVCT) transition and has similarly been observed for $\mathbf{4}^{3+}$ and other such oxidized species.[2a,d]

Although the IVCT band for $\mathbf{2}^{3+}$ appears to be broader than for $\mathbf{4}^{3+}$, the experimental bandwidth at half-height, $\Delta\nu_{1/2}$, of 1560 cm^{-1} is still much smaller than the value of 3754 cm^{-1} calculated from the Hush approximation, $\Delta\nu_{1/2} = (2310E_{\mathrm{op}})^{1/2}$ ($\Delta\nu_{1/2}$ = bandwidth at half-height and E_{op} = energy of the IVCT band) for a valence-trapped situation (class II).[25] This result already indicates a high degree of valence delocalization in $\mathbf{2}^{3+}$ albeit not as complete as for $\mathbf{4}^{3+}$.

The MLCT band is diminished and slightly high-energy shifted through one-electron oxidation to $\mathbf{2}^{3+}$; it disappears on the second oxidation to the all-ruthenium(III) complex ion $\mathbf{2}^{4+}$. The tppz-centered reduction is typically accompanied[2] by the appearance of intraligand (IL) bands in the near-infrared, including a very characteristic narrow band around 1100 nm for $\mathbf{2}^{+}$ and one weak broad ($\lambda_{\max} = 1750$ nm) and one enhanced narrow band system ($\lambda_{\max} = 1030$, 905 nm) for **2** (Figure 4, Table 2). The band at 590 nm for $\mathbf{2}^{+}$ may contain a ligand-to-metal charge-transfer (LMCT) absorption $\pi(\mathrm{bik}) \rightarrow \mathrm{d(Ru^{II})}$ which is also invoked for the 665 nm band of **2**.

IR Spectroelectrochemistry. Vibrational spectra were obtained from OTTLE spectroelectrochemistry in CH$_3$CN/0.1 M Bu$_4$NPF$_6$ in the infrared region 1560−1720 cm^{-1} for all eight redox states in the series $\mathbf{2}^{n+}$, $n = 0-4$, and $\mathbf{3}^{n+}$, $n = 0-2$ (Figure 5, Table 3).

Not only the ν_{CO} band of the terminal spectator ligands bik but also the ring vibration band around 1590 cm^{-1} is of interest. The former is expected to provide independent information about the equivalence of the two {Ru(bik)Cl} moieties on one-electron oxidation, whereas the latter absorptions may include symmetrical bridge modes.[12a,b] In pyrazine-bridged mixed-valent complexes of iron,[26] ruthenium,[1b,10] and osmium[27] the intensity of such bands has been used to assess the valence (de)localization. However, Londergan and Kubiak have clearly shown that higher band intensity, often greater than in related asymmetric non-mixed-valent complexes, may be caused by vibronic enhancement instead of electronic asymmetry.[12b] The practice of using such bands to assign near-delocalized mixed-valent complexes to class II has thus been called into question.[12a]

Table 3. Carbonyl (bik) and Ring (tppz) Vibration Band Energies (cm^{-1}) from IR Spectroelectrochemistry[a]

complex	$\nu_{\mathrm{CO(bik)}}$ ($\Delta\nu_{1/2}$)	$\nu_{\mathrm{ring(tppz)}}$
2	1604[b]	1570 vs
$\mathbf{2}^{+}$	1625 (26)	1576 s
$\mathbf{2}^{2+}$	1637 (26)	1598 w
$\mathbf{2}^{3+}$	1646 (39)	1597 m
$\mathbf{2}^{4+}$	1660 (27)	1597 s
3	1640	1572 m
$\mathbf{3}^{+}$	1639 (25)	1589 w
$\mathbf{3}^{2+}$	1670 (23)	1600 w

[a] In CH$_3$CN/0.1 M Bu$_4$NPF$_6$. [b] Partial overlap between ν_{CO} and ν_{ring}.

In the present series of $\mathbf{2}^{n+}$ the energy of the tppz ring vibration band clearly reflects the location of the electron-transfer process; there is little change on metal-centered oxidation but a low-energy shift on tppz-centered reduction (Table 3). More unexpected is the pronounced variation of the intensity of that band, being low for the "native" $\mathbf{2}^{2+}$ but growing strongly and continuously for both oxidation and reduction (Figure 5, Table 3). Both effects rule out a simple connection between the intensity of that band and mixed valency,[12a,b] either through asymmetry or vibronic coupling. As compared to the single ring pyrazine bridge the tppz ligand with its five six-membered rings can be expected to display a more complicated vibrational pattern which apparently does not lend itself to ready correlations with existing concepts. This result also demonstrates how imperative it can be (i) to study all three states relevant to a mixed-valency situation and (ii) to consider the ligand-based electron-transfer processes as well. Remarkably, the (unsymmetrical) mononuclear system $\mathbf{3}^{n+}$ shows relatively weak ring vibrational bands in the 1590 cm^{-1} region. At this point we cannot give explanations for the strong intensity variations on both reduction and oxidation of the dinuclear system $\mathbf{2}^{n+}$.

The energy of the carbonyl stretching band of the spectator/reporter ligand bik reflects foremost the charge, decreasing by a ca. 15 cm^{-1} increment on each one-electron reduction step for $\mathbf{2}^{n+}$ (Table 3). The mononuclear compound $\mathbf{3}^{2+}$ shows a rather high shift on oxidation $\mathrm{Ru^{II}} \rightarrow \mathrm{Ru^{III}}$ because no Ru$^{2.5}$ mixed-valent intermediate has to be encountered for metal-coordinated bik. The intensity of ν_{CO} (bik) for $\mathbf{2}^{n+}$ is rather invariant in contrast to that of the tppz

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ring vibration band (Figure 5). There is one remarkable feature, however: the bandwidth at half-height, $\Delta\nu_{1/2}$, is rather constant at 25 cm^{-1} except for the mixed-valent form $\mathbf{2}^{3+}$ (39 cm^{-1}). This small but detectable broadening accompanied by a distinctive decrease of the band maximum (Figure 5a) indicates a partially incomplete averaging of the metal valence under the experimental conditions; it was not observed for the dpk analogue $\mathbf{4}^{3+}$.[2a] Nevertheless, the appearance of only one, albeit slightly broadened, ν_{CO} (bik) band for the mixed-valent intermediate $\mathbf{2}^{3+}$ between the values of the homovalent neighboring redox states indicates an essentially valence-averaged, i.e., (μ-tppz)$Ru_2^{2.5}$ situation.

Conclusion. Within the much studied[1−3] class of tppz-bridged diruthenium complexes, the redox system $\mathbf{2}^{n+}$ ($n = 0-4$) presented here is distinguished through the amount of information available from spectroelectrochemistry. The redox potentials and the derived comproportionation constants K_c for intermediates are not very different from those of analogues,[2a] and the IVCT band of the mixed-valent $\mathbf{2}^{3+}$ shows similar features as those of previously reported[1,2] examples $\{(\mu\text{-tppz})[Ru(N-N)Cl]_2\}^{3+}$, (symmetrical band at 1640 nm maximum, $\epsilon = 1200$ M^{-1} cm^{-1}, $\Delta\nu_{1/2} = 1560$ cm^{-1} smaller than calculated value from the Hush approximation). However, the EPR results are more unusual: the $(tppz^{\bullet-})Ru_2^{II,II}$ radical complex $\mathbf{2}^{+}$ shows a signal around $g = 2$ for ligand-centered spin only at 4 K, and the mixed-valent $\mathbf{2}^{3+}$ is even EPR silent at this temperature, suggesting rapid relaxation.

The most revealing kind of information comes from IR spectroelectrochemistry of the complete series $\mathbf{2}^{n+}$ ($n = 0-4$) and from studies of the mononuclear analogue. The tppz ring vibrations around 1590 cm^{-1} reflect nicely the charge location, but their intensity variation cannot be simply explained through symmetry or vibronic coupling effects. The ν_{CO} band from bik, on the other hand, shows little intensity change but a charge-dependent shift; its distinctly visible broadening for *only* the mixed-valent state $\mathbf{2}^{3+}$ is a clear indication of a not yet completely averaged metal valence situation. In comparison with the related system $\mathbf{4}^{3+}$,[2a] the mixed-valent $\mathbf{2}^{3+}$ appears to show slightly decreased metal−metal interaction as evident from the lower IVCT band intensity, from the EPR silence,[10] and from the onset of ν_{CO} band splitting. The recently reported use of the (tppz)/Ru combination in electroactive polymers[7b] is a further incentive to continue these studies and to extend the range of vibrationally active reporter ligands[11,12] for analyzing (de)-localization in mixed valency.

Experimental Section

Instrumentation. Infrared spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. ^1H NMR spectra were recorded for $(CD_3)_2SO$ solutions using a 300 MHz Varian FT spectrometer. The EPR measurements were made in a two-electrode capillary tube[22b] with an X-band Bruker EMX system. UV−vis−NIR and IR spectroelectrochemical studies were performed in CH_3CN/0.1 M Bu_4NPF_6 at 298 K using an OTTLE cell mounted in the sample compartments of a J&M Tidas spectrophotometer or a Nicolet 6700 FTIR instrument, respectively.[24] Cyclic voltammetric and coulometric measurements were carried out using a PAR model 273A electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. Tetrabutylammonium hexafluorophosphate was the supporting electrolyte, and the solution concentration was ca. 10^{-3} M; the scan rate used was 50 mV s^{-1}. Under these conditions the ferrocene(0/+) couple was located at +0.40 V. A platinum gauze working electrode was used in the coulometric experiments. All electrochemical experiments were carried out under dinitrogen or argon atmosphere. The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Electrospray mass spectra were recorded on a Micromass Q-ToF mass spectrometer. Solution electrical conductivity was checked using a Systronic conductivity bridge 305.

Syntheses. The precursor complex $[Cl_3Ru^{III}(\mu\text{-tppz})Ru^{III}Cl_3]$ was prepared following the reported procedure.[1a] Bis(1-methyl-2-imidazolyl)ketone was synthesized according to the reported procedure.[8a] Other chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies HPLC grade solvents were used.

CAUTION! *Perchlorate salts of metal complexes are generally explosive. Care should be taken while handling such complexes.*

Synthesis of $[\{(bik)ClRu^{II}\}_2(\mu\text{-tppz})](ClO_4)_2$, $[\mathbf{2}](ClO_4)_2$, and $[(bik)ClRu^{II}(tppz)](ClO_4)$, $[\mathbf{3}](ClO_4)$. The precursor complex $[Cl_3Ru^{III}(\mu\text{-tppz})Ru^{III}Cl_3]$ (100 mg, 0.12 mmol) and the free ligand L = bik (50 mg, 0.26 mmol) were dissolved in ethanol (15 mL) and refluxed for 3 h under dinitrogen atmosphere in the presence of excess LiCl (50 mg, 1.2 mmol). The initial light green solution gradually changed to greenish blue. A saturated aqueous solution of $NaClO_4$ was then added to the concentrated acetonitrile solution of the product. The solid precipitate thus obtained was filtered and washed thoroughly by cold ethanol followed by ice-cold water. The dried product was then purified by using a neutral alumina column. The violet mononuclear complex $[\mathbf{3}](ClO_4)$ and greenish-blue dinuclear complex $[\mathbf{2}](ClO_4)_2$ were eluted by 4:1 $CH_2Cl_2-CH_3CN$ and 2:3 $CH_2Cl_2-CH_3CN$ mixtures, respectively. Evaporation of solvent under reduced pressure yielded the pure compounds $[\mathbf{3}](ClO_4)$ and $[\mathbf{2}](ClO_4)_2$, respectively.

$[\mathbf{2}](ClO_4)_2$. Yield: 54 mg (35%). Anal. Calcd (Found) for $C_{42}H_{36}Cl_4N_{14}O_{10}Ru_2$: C, 40.66 (40.31); H, 2.92 (2.98); N, 15.80 (15.98). Molar conductivity $[\Lambda_M/\Omega^{-1}$ cm^2 $M^{-1}]$ in acetonitrile at 298 K: 245. The positive ion electrospray mass spectrum of $[\mathbf{2}](ClO_4)_2$ in acetonitrile exhibited molecular ion peak *m*/*z* at 1142.88 corresponding to $\{[\mathbf{2}](ClO_4)\}^+$ (calculated molecular mass, 1141.34). ^1H NMR [$(CD_3)_2SO$, δ(*J*/Hz)]: 8.76 (d, 8.1, 4H), 8.58 (s, 1H), 8.51 (s, 1H), 8.30 (m, 8H), 8.01 (m, 4H), 7.67 (multiplet, 4H), 7.57 (s, 1H), 7.46 (s, 1H), 4.46 (s, 3H, NCH_3), 4.44 (s, 3H, NCH_3), 4.05 (s, 3H, NCH_3), 3.96 (s, 3H, NCH_3). IR (KBr disk): $\nu(ClO_4^-)$/cm^{-1}, 1099/623. IR (Nujol mull): ν(Ru−Cl)/cm^{-1}, 302.

$[\mathbf{3}](ClO_4)$. Yield: 15 mg (15%). Anal. Calcd (Found) for $C_{33}H_{26}Cl_2N_{10}O_5Ru$: C, 48.66 (48.22); H, 3.22 (3.13); N, 17.19 (17.44). Molar conductivity $[\Lambda_M/\Omega^{-1}$ cm^2 $M^{-1}]$ in acetonitrile at 298 K: 120. The positive ion electrospray mass spectrum of $[\mathbf{3}](ClO_4)$ in acetonitrile exhibited molecular ion signals centered at *m*/*z* value of 715.08 corresponding to $\{\mathbf{3}\}^+$ (calculated molecular mass, 715.16). ^1H NMR [$(CD_3)_2SO$, δ(*J*/Hz)]: 8.74 (d, 4.8, 1H), 8.32 (d, 4.5, 1H), 8.24 (m, 3H), 8.04 (d, 7.5, 1H), 7.98 (d, 6.3, 1H), 7.94 (t, 6.6/6.9, 1H), 7.72 (m, 4H), 7.51 (m, 4H), 7.37 (t, 7.2/6.0, 1H), 7.22 (d, 8.2, 1H), 7.12 (broad, 2H), 3.89 (6H, NCH_3). IR (KBr disk): $\nu(ClO_4^-)$/cm^{-1}, 1078/623.

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