

## Spectroelectrochemical Characterization of the Two-Step Redox System $\{(\mu\text{-pz})[\text{Os}(\text{CN})_5]_2\}^{n-}$ ( $n = 4, 5, 6$ ; pz = Pyrazine). Similarities and Differences in Relation to the Creutz–Taube System

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The pyrazine-bridged osmium(II) complex  $\{(\mu\text{-C}_4\text{H}_4\text{N}_2)[\text{Os}(\text{CN})_5]_2\}^{6-}$  has been synthesized as the hexapotassium salt and was converted to the hexakis(tetrabutylammonium) compound by ion exchange. Its stepwise oxidation to the  $\text{Os}_2^{\text{III}}\text{Os}^{\text{II}}$  and  $\text{Os}_2^{\text{III}}\text{Os}^{\text{III}}$  states was monitored spectroelectrochemically in acetonitrile/0.1 M  $\text{Bu}_4\text{NPF}_6$  in the UV–vis–NIR and IR regions and by EPR. The  $\text{Os}^{\text{II}}$  species exhibits long-wavelength solvatochromic MLCT bands at 14 800 and 18 480  $\text{cm}^{-1}$ . The pentaanionic mixed-valent ion has a comproportionation constant  $K_c$  of  $10^{5.8}$  and is distinguished by several electronic absorptions in the IR region. The bands at 1972, 2480, 4000, 5000, 7170, and 11 900  $\text{cm}^{-1}$  are similar but appreciably lower in energy than those reported for the analogous complex  $\{(\mu\text{-C}_4\text{H}_4\text{N}_2)[\text{Os}(\text{NH}_3)_5]_2\}^{5+}$ . In addition to CN vibrational stretching features shifted on electron transfer there is an additional sharp band *only* for the 5– ion at 1582  $\text{cm}^{-1}$  which is attributed to a pyrazine ring vibration. The intensity of this band suggests an unsymmetrical situation and thus valence localization on the vibrational time scale. The EPR signals at  $g_{\perp} = 2.0563$  and  $g_{\parallel} = 1.761$  point toward excited states lying close to the doublet ground state and to significant metal/cyanide interaction. Compared to the Creutz–Taube ion  $\{(\mu\text{-C}_4\text{H}_4\text{N}_2)[\text{Ru}(\text{NH}_3)_5]_2\}^{5+}$  and its osmium homologue, the 5– ion described here exhibits a lower degree of metal–metal coupling.

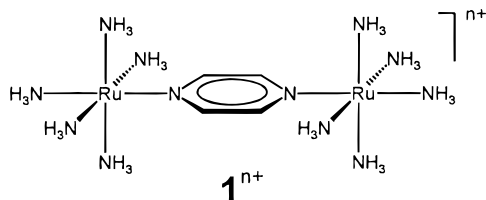
There is continued interest in understanding the electronic structures of symmetrical molecule-bridged mixed-valent dinuclear complexes<sup>1</sup> of which the Creutz–Taube ion  $\mathbf{1}^{5+}$  resembles the prototype.<sup>1,2</sup> Efforts to vary the metal (within group 8<sup>1,3</sup> or beyond<sup>1,3,4</sup>), the bridging ligand (size,<sup>1,5</sup> acceptor vs donor characteristics,<sup>6</sup> metal–metal distance,<sup>7</sup> metal–ligand interface properties<sup>8a</sup> and substitution pattern,<sup>8b,c</sup> coordination mode such as hapticity<sup>6ab,9</sup> or nuclearity<sup>10</sup>), the ancillary ligands

(donor or acceptor,<sup>11</sup> classical or organic<sup>4b–d,9b</sup>), and the overall charge and thus the suitable medium<sup>1b,3,12</sup> have been presented by various groups to probe the electronic structures and better

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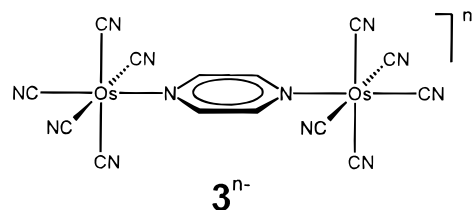
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understand the sometimes controversial<sup>13–16</sup> nature of  $1^{5+}$ . Different experimental<sup>13,14</sup> and theoretical approaches<sup>15,16</sup> have added to this material, yet there are still unexplored systems to be imagined which are closely connected to the parent system  $1^{5+}$  and its diosmium homologue  $2^{5+}$ .<sup>3a</sup>



Herein we describe one such new two-step redox system  $\{(\mu\text{-pz})[\text{Os}(\text{CN})_5]_2\}^{n-}$  ( $3^{n-}$ ,  $n = 4, 5, 6$ ; pz = pyrazine) with a stable  $d^5/d^6$  mixed-valent intermediate. Whereas the small symmetrical pyrazine  $\pi$  system remains unchanged as bridging  $\pi$ -acceptor ligand, the difference in comparison to  $1^{5+}$  and  $2^{5+}$  involves mainly the ancillary ligands and, consequently, the overall charge. As it is now accepted<sup>13,14</sup> that  $1^{5+}$  and certainly  $2^{5+}$  are delocalized systems with average metal oxidation states of +2.5, we can now explore the effect of the replacement of all ten neutral and exclusively  $\sigma$ -donating ammine coligands by negatively charged and  $\pi$ -bonding cyanide groups. Introduction of  $\pi$ -bonding ligands (which may compete with the bridging ligand for  $\pi$  back-donation from the metal) as ancillary ligands was shown to result in decreased metal–metal interaction;<sup>11</sup> often, however, the species studied had mixed-ligand patterns in contrast to the highly symmetrical systems  $1^{5+}$  or  $2^{5+}$ .

In the following we describe the synthesis and (spectro)-electrochemistry of the system  $3^{n-}$ , ( $n = 4, 5, 6$ ) in acetonitrile, including particularly UV–vis–NIR, IR, and EPR data. Pentacyanoosmium complexes have been well documented now in their interaction with N-heterocyclic acceptor ligands<sup>17,18</sup> so that direct comparisons can be made with the various states of  $3^{n-}$ . In addition to the kind of electrochemical and spectroscopic data available for the related series  $2^{4+/5+/6+}$ ,<sup>3a</sup> we can use here information from cyanide stretching frequencies and from EPR features observed in aprotic frozen solution.



## Experimental Section

**Synthesis of Potassium Decacyano( $\mu$ -pyrazine)diosmate(II) Pentahydrate,  $\text{K}_6[(\text{CN})_5\text{Os}^{\text{II}}(\text{pz})\text{Os}^{\text{II}}(\text{CN})_5] \cdot 5\text{H}_2\text{O}$ . Method A.** To 53 mg (0.114 mmol) of  $\text{K}_2[\text{Os}^{\text{II}}(\text{CN})_5(\text{N}_2\text{H}_5)] \cdot 2\text{H}_2\text{O}$ <sup>17</sup> dissolved in 5 mL of water was added 1 equiv (57 mg, 0.114 mmol) of potassium pentacyano(pyrazine)osmate(II) trihydrate,  $\text{K}_3[\text{Os}^{\text{II}}(\text{CN})_5(\text{pz})] \cdot 3\text{H}_2\text{O}$ ,<sup>17</sup> under an argon atmosphere. The solution, which was kept at 60 °C for 3 h turned dark red, was passed through a  $\text{K}^+$ -loaded Dowex 50 W X 2 cation-exchange column and was subsequently purified by elution on a Sephadex G10 column (ca.  $3 \times 150$  cm). The dinuclear product came off the column as an orange-red zone followed by a yellow fraction; the latter was characterized as the mononuclear compound. The orange-red solution was collected and reduced to 0.5 mL; after addition of 50 mL acetone the product precipitated as a red powder, yielding 80 mg (0.077 mmol; 67%).

**Method B.** To a solution of 230 mg (0.492 mmol) of  $\text{K}_2[\text{Os}^{\text{II}}(\text{CN})_5(\text{N}_2\text{H}_5)] \cdot 2\text{H}_2\text{O}$  in 10 mL of  $\text{H}_2\text{O}$  was added 0.5 equiv of pyrazine (19.7 mg, 0.246 mmol) under an argon atmosphere. The solution was kept at 70 °C for 5 h and subsequently worked up as described in method A, yielding 153 mg (0.147 mmol) of the red dinuclear complex (59%) and small amounts of the chromatographically separated mononuclear compound. Anal. Calc for  $\text{K}_6[(\text{CN})_5\text{Os}^{\text{II}}(\text{pz})\text{Os}^{\text{II}}(\text{CN})_5] \cdot 5\text{H}_2\text{O}$ : C, 16.09; H, 1.35; N, 16.08. Found: C, 15.51; H, 0.84; N, 16.16. <sup>1</sup>H-NMR ( $\text{D}_2\text{O}$ ):  $\delta = 8.78$  ppm (pz-H). <sup>13</sup>C-NMR ( $\text{D}_2\text{O}$ ):  $\delta = 138.0$  ((CN)<sub>ax</sub>), 148.1 ((CN)<sub>eq</sub>), 153.5 ppm (pz-C;  $J_{\text{CH}} = 185$  Hz). IR (KBr):  $\nu = 3300$  (br;  $\text{H}_2\text{O}$ ), 2120 (s), 2058 (vs)  $\text{cm}^{-1}$ . Hydrate water could be only partially removed under vacuum.

For reasons of better solubility in aprotic solvents the tetrabutylammonium salt of  $[(\text{CN})_5\text{Os}^{\text{II}}(\text{pz})\text{Os}^{\text{II}}(\text{CN})_5]^{6-}$  was prepared by converting the potassium salt (0.1 M) on a Dowex 50 W X 2 cation exchange column. The column was loaded with  $\text{Bu}_4\text{NOH}$  after cleaning with hydrochloric acid. Evaporation of the resulting red solution had to take place at temperatures below 30 °C, otherwise an uncharacterized dark side product began to form. The noncrystalline blue tetrabutylammonium salt thus obtained was dried for several hours under vacuum and proved to be extremely hygroscopic; therefore, elemental analysis could not be performed. The dried material was used for spectroelectrochemical measurements in acetonitrile and solvatochromism experiments; extinction coefficients are estimated to have a  $\pm 15\%$  error margin because of the very hygroscopic nature of the material.

**Instrumentation.** EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were taken on a Bruker AC 250 spectrometer; infrared spectra were obtained using Perkin-Elmer 684 and 283 instruments and a Paragon 1000 PC FTIR spectrometer. UV/vis/NIR absorption spectra were recorded on

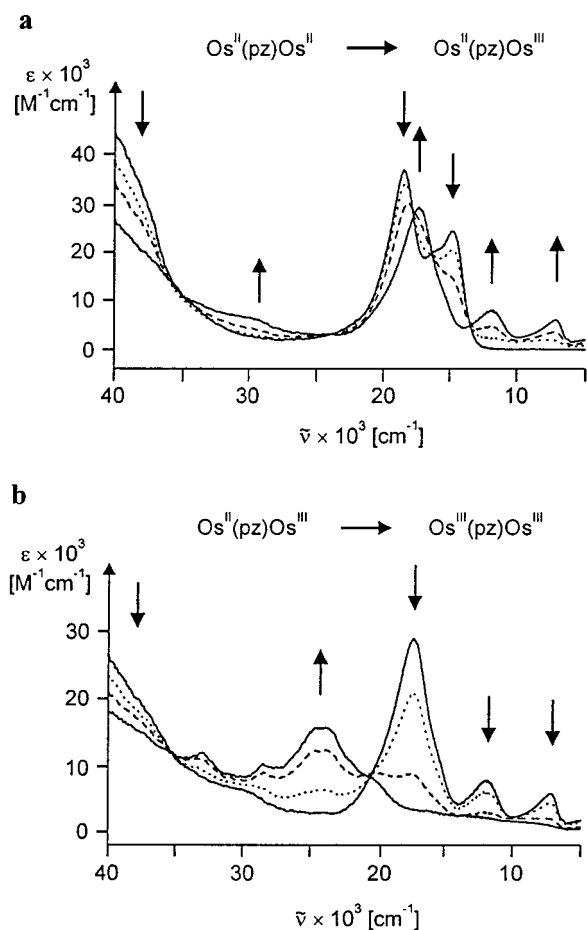
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**Table 1.** Redox Potentials of Complexes<sup>a</sup>

compound	$E_{1/2(\text{ox}1)}$	$E_{1/2(\text{ox}2)}$	$E_{1/2(\text{red}1)}$
$3^{6-}$ <sup>b</sup>	-0.85	-0.51	-2.61 <sup>d</sup>
$[(\text{pz})\text{Os}(\text{CN})_5]^{3-}$ <sup>b</sup>	-0.68	n.o.	n.o.
$[(\text{mpz})\text{Os}(\text{CN})_5]^{2-}$ <sup>c</sup>	-0.17	n.o.	-1.55

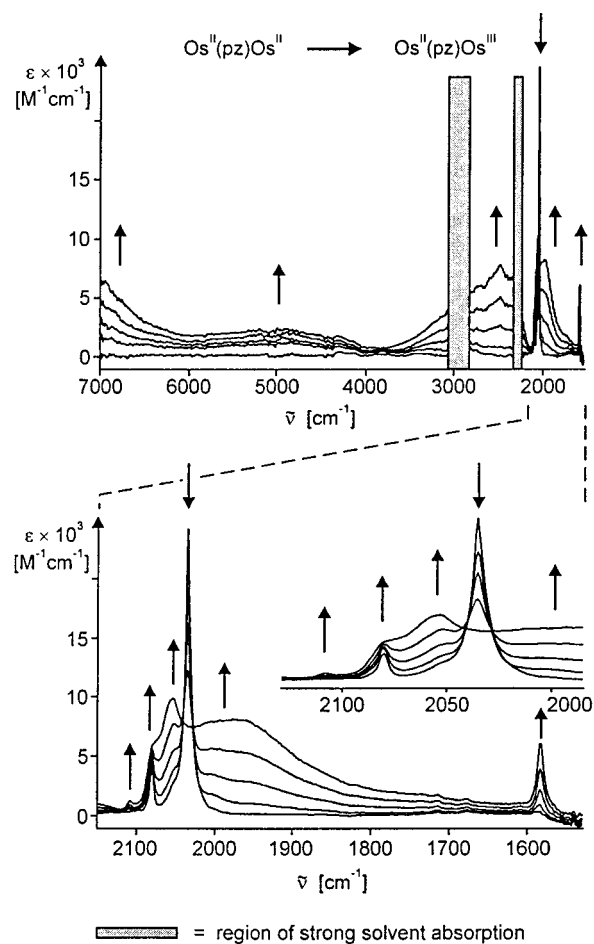
<sup>a</sup> Measurements in  $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$ ; scan rate 200 mV/s. Potentials in V versus ferrocene/ferrocenium as internal standard.  
<sup>b</sup> Tetrabutylammonium compound. <sup>c</sup> Potassium salt with [2.2.2]cryptand, from ref 18. <sup>d</sup> Irreversible; cathodic peak potential.

**Figure 1.** UV-vis-NIR spectroelectrochemistry of the transitions  $3^{6-} \rightarrow 3^{5-}$  (a, top) and  $3^{5-} \rightarrow 3^{4-}$  (b, bottom) in acetonitrile/0.1 M  $\text{Bu}_4\text{NPF}_6$ .

a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out in acetonitrile/0.1 M  $\text{Bu}_4\text{NPF}_6$  using a three-electrode configuration (glassy carbon electrode, Pt counter electrode,  $\text{Ag}/\text{AgCl}$  reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal standard.<sup>19</sup> Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell<sup>20</sup> for UV/vis spectra and a two-electrode capillary for EPR studies.<sup>21</sup>

## Results

The diosmium(II) complex hexaanion  $3^{6-}$  was synthesized as the hexapotassium salt. Even during the workup procedure some amount of the mixed-valent  $\text{Os}^{\text{III}}/\text{Os}^{\text{II}}$  material was formed as evident from spectroscopy. For studies in aprotic media we converted the hexapotassium salt to the less crystalline but more

**Figure 2.** NIR-IR spectroelectrochemistry of the transition  $3^{6-} \rightarrow 3^{5-}$  in acetonitrile/0.1 M  $\text{Bu}_4\text{NPF}_6$ .

soluble hexakis(tetrabutylammonium) species, using ion-exchange techniques. The dinuclear identity of the compounds is apparent from microanalysis and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy; small amounts of the mononuclear derivative  $[(\text{pz})\text{Os}(\text{CN})_5]^{3-}$ <sup>17</sup> were obtained as side product.

In acetonitrile/0.1 M  $\text{Bu}_4\text{NPF}_6$  the  $3^{6-}$  ion can be oxidized stepwise at -0.85 and -0.51 V in electrochemically reversible fashion. There is also an irreversible reduction at more negative potentials. Electrochemical data for  $3^{6-}$  and of related species<sup>18</sup> are listed in Table 1.

Following these results, the stepwise oxidation to the  $3^{5-}$  and  $3^{4-}$  states could be monitored spectroelectrochemically in the UV-vis-NIR and IR regions (Figures 1-3; Tables 2 and 3) and by EPR.

The  $\text{Os}^{\text{II}}_2$  species  $3^{6-}$  exhibits two intense, solvatochromic<sup>17,18</sup> long-wavelength MLCT bands in the visible region (Figure 1a; Tables 2 and 4). The positions of the band maxima of both transitions correlate with the acceptor number ( $\text{AN}^{22,23}$ ); the linear correlations are  $\nu = 16820 \text{ cm}^{-1} + 102 \text{ cm}^{-1} \times \text{AN}$  ( $r = 0.950$ ) and  $\nu = 12780 \text{ cm}^{-1} + 125 \text{ cm}^{-1} \times \text{AN}$  ( $r = 0.956$ ).

On one-electron oxidation there is one MLCT band remaining in the vis region (Figure 1a); however, there are now several smaller electronic absorption bands emerging in the near-infrared (NIR) and infrared regions, viz., at 11900, 7170, 4960, 3950, 2480, and  $1972 \text{ cm}^{-1}$  (Figures 1a and 2). On further oxidation

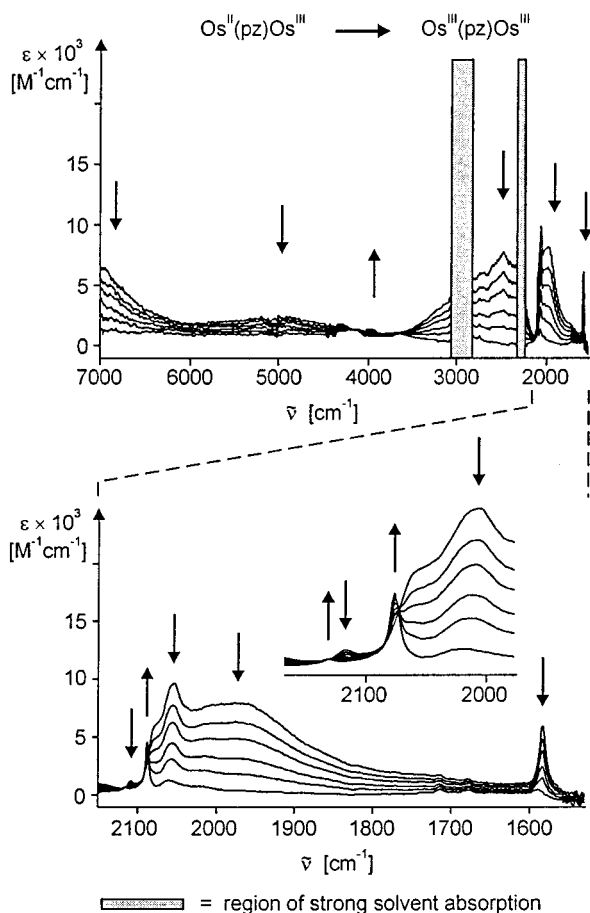
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**Figure 3.** NIR-IR spectroelectrochemistry of the transition  $3^{5-} \rightarrow 3^{4-}$  in acetonitrile/0.1 M  $\text{Bu}_4\text{NPF}_6$ .

**Table 2.** Absorption Band Maxima of Electronic Transitions<sup>a</sup>

$\nu_{\text{max}} (\epsilon), \Delta\nu_{1/2}$		
$3^{5-}$	$3^{6-}$	$3^{4-}$
39000 (sh)	29700 (6.7)	32930 (12.2)
18680 (36.6), 3500	17430 (29.0), 3300	28620 (10.4)
16150 (sh)	11900 (7.9), 2050	24300 (15.9), 4700
15100 (29.3), 2600	7170 (6.6), 1450	20450 (sh)
	4960 (1.7), 950	16000 (3.1)
	3950 (0.7)	12500 (sh)
	2480 (8.1), 960	8500 (sh)
	1972 (7.0), 220	3900 (0.5)

<sup>a</sup> From spectroelectrochemistry; in acetonitrile solution/0.1 M  $\text{Bu}_4\text{NPF}_6$ ; wavenumbers  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ , molar extinction coefficients  $\epsilon \times 10^3$  in  $\text{M}^{-1} \text{cm}^{-1}$  ( $\pm 15\%$ ) in parentheses, band widths at half-height  $\Delta\nu_{1/2}$  in  $\text{cm}^{-1}$  in italics.

**Table 3.** Absorption Maxima of Vibrational Bands<sup>a</sup>

$\nu_{\text{max}} (\epsilon)$		
$3^{5-}$	$3^{6-}$	$3^{4-}$
2080 (3.4)	2108 (1.0)	2115 (0.4)
2052 (2.3)	2080 (sh)	2088 (4.3)
2035 (23.2)	2054 (8.6)	2060 (1.0)
	1582 (5.5)	

<sup>a</sup> From spectroelectrochemistry; in acetonitrile solution/0.1 M  $\text{Bu}_4\text{NPF}_6$ ; wavenumbers  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ , molar extinction coefficients  $\epsilon \times 10^3$  in  $\text{M}^{-1} \text{cm}^{-1}$  ( $\pm 15\%$ ) in parentheses.

to the  $\text{Os}^{\text{III}}_2$  state  $3^{4-}$  most of these prominent electronic absorption bands in the NIR disappear and a broad absorption appears, centered at  $24\,300 \text{ cm}^{-1}$  with shoulders at lower and higher energies (Figures 1b and 3).

**Table 4.** Solvent Dependence of MLCT Absorption Bands of  $3^{6-}$  <sup>a</sup>

solvent	acceptor no. <sup>b</sup> AN	$\lambda_{1\text{max}} (10^3 \nu_{1\text{max}})$	$\lambda_{2\text{max}} (10^3 \nu_{2\text{max}})$
THF	8.0	548 (18.3)	690 (14.5)
acetonitrile	18.9	534 (18.7)	662 (15.1)
DMSO	19.3	532 (18.8)	658 (15.2)
$\text{CH}_2\text{Cl}_2$	20.4	540 (18.5)	673 (14.9)
$t\text{BuOH}$	27.1	512 (19.5)	620 (16.1)
EtOH	37.1	500 (20.0)	596 (16.8)
$n\text{PrOH}$	37.3	502 (19.9)	602 (16.6)
formamide	39.8	467 (21.4)	542 (18.5)
MeOH	41.3	475 (21.1)	552 (18.1)
$\text{H}_2\text{O}$	54.8	436 (22.9)	496 (20.8)

<sup>a</sup> Wavelengths  $\lambda_{\text{max}}$  in nm, wavenumbers  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ . <sup>b</sup> From ref 23.

Of the high-energy vibrational bands the cyanide stretching features appear clearly with two narrow absorptions at  $2035$  and  $2080 \text{ cm}^{-1}$  for  $3^{6-}$  and at  $2088$  and  $2115 \text{ cm}^{-1}$  for  $3^{4-}$  (Figures 2 and 3). For the mixed-valent intermediate the broad, intense electronic absorption band at  $1970 \text{ cm}^{-1}$  seems to obscure CN stretching features; narrow bands can be identified at  $2080$  and  $2108 \text{ cm}^{-1}$ , while a broad absorption at  $2054 \text{ cm}^{-1}$  may also be tentatively assigned to a vibrational transition.

Most notably, however, there appears an additional sharp band *only* for the  $5-$  ion in the midinfrared region at  $1582 \text{ cm}^{-1}$  (Figures 2 and 3); i.e., in the aromatic ring vibrational region.<sup>3a,24</sup>

The paramagnetic mixed-valent state  $3^{5-}$  is EPR-silent at room temperature but shows broad EPR signals in frozen solution at  $3.5 \text{ K}$  with  $g_{\perp} = 2.0563$  and  $g_{\parallel} = 1.761$  (axial symmetry). No metal ( $^{189}\text{Os}$ :  $I = 3/2$ , 16.1% natural abundance)<sup>25</sup> or other hyperfine coupling was observed. The  $\text{Os}^{\text{III}}_2$  state  $3^{4-}$  is EPR-silent even at  $3.5 \text{ K}$ .

## Discussion

The use of tetrabutylammonium counterions has allowed us to study the redox system  $3^{6-/5-/4-}$  by spectroelectrochemistry in aprotic polar acetonitrile. As a first measure of “metal-metal coupling” we note that the pentaanionic intermediate exhibits a redox potential difference of  $\Delta E = 0.34 \text{ V}$  which translates to a comproportionation constant of  $K_c = 10^{5.8}$ .

$$K_c = 10^{\Delta E/0.059 \text{ V}} = [\text{Os}^{\text{III,II}}]_2 / [\text{Os}^{\text{III}}_2][\text{Os}^{\text{II}}_2] \quad (1)$$

This number for the  $\text{Os}^{\text{III}}\text{Os}^{\text{II}}$  mixed-valent intermediate is slightly lower than the value of  $10^{7.3}$  determined for  $1^{5+}$  in acetonitrile<sup>24</sup> and in  $0.1 \text{ M HCl}$  ( $10^{6.8}$ )<sup>3a</sup> and significantly smaller than  $10^{13.0}$  as reported for  $2^{5+}$  in hydrochloric acid.<sup>3a</sup> Following these first results we may anticipate that metal-metal interaction is indeed smaller for  $3^{5-}$  as compared to  $2^{5+}$ . On the other hand, a value of  $K_c = 50$ , typical of a class II mixed-valence compound,<sup>1b</sup> was estimated for  $\{(\mu\text{-pz})[\text{Fe}(\text{CN})_5]_2\}^{5-}$ ,  $4^{5-}$ , in aqueous solution.<sup>3b</sup>

In comparison to the potential of the mononuclear  $[(\text{pz})\text{Os}(\text{CN})_5]^{3-/2-}$  system (Table 1) the two redox potentials for  $3^{6-/5-/4-}$  lie fairly symmetrical at lower and higher values. This was also observed for systems **1** and **2**.<sup>3a</sup> The complex  $[(\text{mpz})\text{Os}(\text{CN})_5]^{2-/1-}$  ( $\text{mpz}^+ = N\text{-methylpyrazinium}$ ) has an anodically shifted osmium(II/III) potential (Table 1) because of the positive charge and more pronounced  $\pi$ -acceptor character of the cationic  $\text{mpz}^+$  ligand.<sup>18</sup>

The use of acetonitrile has also allowed us to determine a cathodic peak potential for the irreversible reduction of the

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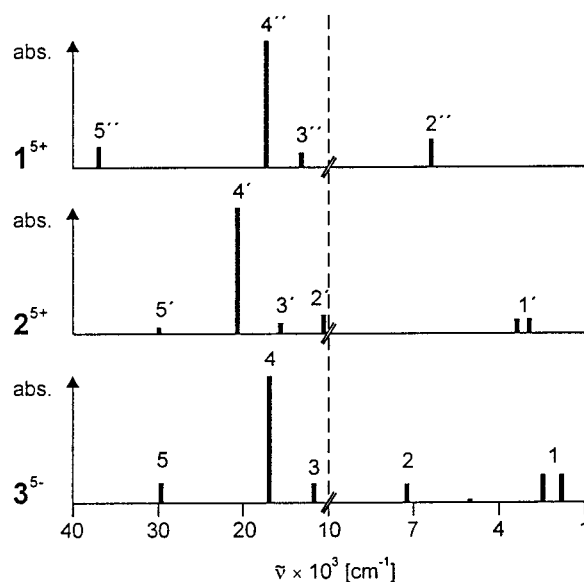
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complex. We assume that this reduction is pyrazine-centered;<sup>26</sup> the very negative peak potential is close to that of free pyrazine ( $E_{1/2} = -2.6$  V) which suggests<sup>27</sup> that  $\sigma$  donation and  $\pi$ -back-bonding are comparable for that diosmium(II) system. The negative reduction potential is also held responsible for the irreversibility due to loss of cyanide.<sup>18,28</sup>

The intense UV absorption for  $3^{6-}$  is attributed to the overlap of intraligand  $\pi \rightarrow \pi^*(\text{pz})$  and  $d(\text{Os}^{\text{II}}) \rightarrow \pi^*(\text{CN})$  MLCT transitions. The appearance of two solvatochromic MLCT transitions in the visible region agrees with observations for  $2^{4+}$  where corresponding features appear at 12 870 and 18 020  $\text{cm}^{-1}$  in aqueous buffered solution.<sup>3a</sup> The solvatochromism as quantified in Table 4 and in the Results section shows that these MLCT absorption values are generally higher in energy as compared to the numbers reported for  $2^{4+}$ ,<sup>3a</sup> reflecting higher lying occupied metal d orbitals in the pentaamminemetal series. The solvatochromic behavior itself is similar to that observed for  $[(\text{L})\text{Os}(\text{CN})_5]^{n-}$  ( $\text{L} = \text{pz}, \text{mpz}^+$ ),<sup>17,18</sup> i.e., the best correlation obtained is clearly that with the acceptor number (AN).<sup>17,18,23</sup> On the other hand, correlations with the donor number (DN)<sup>23</sup> were observed for the  $[(\text{L})\text{M}(\text{NH}_3)_5]^{n+}$  systems ( $\text{M} = \text{Ru}, \text{Os}$ ).<sup>24</sup> This result points to the important role of the negative charge and the 10 lone-pair containing cyanide coligands in the interaction with the solvent medium.

On oxidation to  $3^{5-}$ , a new, broad absorption appears in the near-UV region, which can be assigned to an envelope of LMCT transitions  $\pi(\text{CN}^-) \rightarrow d(\text{Os}^{\text{III}})$ , by comparison with  $\text{Os}(\text{CN})_6^{3-}$ .<sup>29</sup> In the visible region, the bands at 17 430 and 11 900  $\text{cm}^{-1}$  could be the low-energy-shifted components corresponding to the  $d(\text{Os}^{\text{II}}) \rightarrow \pi^*(\text{pz})$  MLCT transitions (see above), in agreement with the expected inductive influence of the  $\text{M}^{\text{III}}$  center and consequent stabilization of  $\pi^*(\text{pz})$ . In an alternative, localized model the band at 11 900  $\text{cm}^{-1}$  is already identified as an intervalence (IV) transition. Whereas two MLCT bands are expected to originate from the symmetric and antisymmetric combinations of the  $(\text{Os}^{\text{II}})_2$ -pyrazine system, the oxidation from  $\text{Os}^{\text{II}}\text{-Os}^{\text{II}}$  to  $\text{Os}^{\text{II}}\text{-Os}^{\text{III}}$  should result in only one  $\text{Os}^{\text{II}}$ -pyrazine chromophore with an intermediate transition energy (17 430  $\text{cm}^{-1}$ ). The band in the NIR region at 7170  $\text{cm}^{-1}$  is definitely assigned to an intervalence transition; a corresponding band at 8300  $\text{cm}^{-1}$  ( $\epsilon = 2200 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\Delta\nu_{1/2} = 4800 \text{ cm}^{-1}$ ) was assigned to a IV transition for  $4^{5-}$  in aqueous solution.<sup>3c</sup> In comparison, the half-absorption width of the asymmetric band in  $3^{5-}$  at 7170  $\text{cm}^{-1}$  is remarkably small, as similarly found for  $1^{5+}$ .<sup>1b</sup>

The various new NIR and IR electronic absorptions appearing on oxidation of  $3^{6-}$  to  $3^{5-}$  are all similar but appreciably lower in energy than those reported for the analogous  $2^{5+}$ .<sup>3a</sup> Figure 4



**Figure 4.** Positions of electronic absorption maxima of  $1^{5+}$  (top),  $2^{5+}$  (middle, from ref 3a, and  $3^{5-}$  (bottom, from ref 3a) in the UV-vis-NIR-IR regions. The major MLCT band (4) has been assigned 100% intensity in each case; the intensities of the other absorptions are indicated accordingly. The numbering scheme for band identification and assignment has been adopted from ref 3a.

illustrates these relations and also shows corresponding transitions of the Creutz-Taube ion  $1^{5+}$ .<sup>2,3a</sup>

We can thus assign the bands in agreement with those reported for  $2^{5+}$ <sup>3a</sup> but which imply weaker metal-pyrazine interaction and thus diminished metal-metal communication because of negative charge and  $\pi$ -accepting effects of the cyanide ancillary ligands. Upon oxidation to the III,III state, Figure 1b shows that the relevant MLCT and IV bands disappear, as expected. The broad band with shoulders in the visible region can be assigned to the manifold of LMCT transitions from cyanides to the  $\text{Os}^{\text{III}}$  centers, as found for the mononuclear and the mixed-valence species. Figure 3 shows that there are no prominent intense bands in the NIR region for  $3^{4-}$ .

It has been shown in several instances that the problem of (de)localization in potentially symmetrical mixed-valent species can be addressed particularly well using information from vibrational spectroscopy.<sup>3a,4c,d,9b,10,14a</sup> The underlying question of symmetry is reflected by the number of vibrational transitions. The present system  $3^{n-}$  offers both the cyanide stretching bands<sup>17</sup> and the pyrazine ring vibrational modes<sup>24</sup> for such an investigation (Figures 2 and 3; Table 3).

First, the  $\nu(\text{CN})$  bands of  $3^{6-}$  can be assigned to E(eq) (2035  $\text{cm}^{-1}$ ) and A(ax) (2080  $\text{cm}^{-1}$ ) modes under pseudo- $C_{4v}$  symmetry; the shoulder at 2052  $\text{cm}^{-1}$  arises probably from splitting of the E mode under the "real"  $C_{2v}$  symmetry. The shift of this band set to higher energy on oxidation is well in agreement with expectations for the symmetrical species  $3^{6-}$  ( $\text{Os}^{\text{II}}_2$ ) and  $3^{4-}$  ( $\text{Os}^{\text{III}}_2$ ), respectively.<sup>4c,d,17,18</sup> For the mixed-valent intermediate  $3^{5-}$  ( $\text{Os}^{\text{III,II}}$ ) the possible overlap with and obscuring by the broad and intense long-wavelength electron absorption band at 1970  $\text{cm}^{-1}$  makes it difficult to clearly identify two or four CN stretching bands (Figures 2 and 3). The former would correspond to a delocalized situation (averaging)<sup>4c,d,9b</sup> on the vibrational time scale of about  $10^{-12}$ – $10^{-13}$  s whereas the latter would indicate a localized structure<sup>29</sup> with individual and only weakly communicating  $(\text{NC})_5\text{Os}^{\text{II}}$  and  $(\text{NC})_5\text{Os}^{\text{III}}$  fragments. The observed features at the less obscured (Figures 2 and 3) high-

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energy side with band maxima at 2080  $\text{cm}^{-1}$  ( $\text{Os}^{\text{II}}$ ) and 2108  $\text{cm}^{-1}$  ( $\text{Os}^{\text{III}}$ ) clearly suggests a localized formulation. In the low-energy region between 1950 and 2050  $\text{cm}^{-1}$  there is some overlap with the electronic transition centered at 1970  $\text{cm}^{-1}$ ; also, the coupling between vibrational and electronic transitions occurring at the same energies has to be considered.

There is one band, however, which is clearly unique to the mixed-valent intermediate state and which appears (Figure 2) and disappears (Figure 3) at 1582  $\text{cm}^{-1}$ , i.e. in the region of aromatic six-membered ring vibrations.<sup>24</sup> This sharp, strong band is thus attributed to a pyrazine ring vibration, the intensity confirming a highly unsymmetrical situation<sup>3a</sup> and thus full valence localization  $[(\text{NC})_5\text{Os}^{\text{III}}(\text{pz})\text{Os}^{\text{II}}(\text{CN})_5]^{5-}$  on the vibrational time scale. Converse arguments were used in the series of ammineosmium complexes where “the very low intensity of the symmetric pyrazine mode in the IR spectrum (1600  $\text{cm}^{-1}$ )” was held to be “consistent with a symmetric delocalized description”.<sup>3a</sup>

The localized model for  $3^{5-}$  would also be in agreement with the observed EPR signals at  $g_{\perp} = 2.0563$  and  $g_{\parallel} = 1.7613$ . These numbers clearly point to mainly metal-centered spin,<sup>30</sup> yet the  $g$  anisotropy is not as large here as for the Creutz-Taube ion ( $g_1 = 2.799$ ,  $g_2 = 2.489$ ,  $g_3 = 1.346$ ),<sup>13a</sup> despite the much higher spin-orbit coupling constant of osmium as compared to ruthenium.<sup>31,32</sup> One factor attenuating the  $g$  anisotropy is probably partial spin delocalization to  $\pi^*$  orbital combinations of the cyanide ligands. In contrast, strong metal-metal interactions can produce close-lying excited states which may result in large  $g$  anisotropy and severe EPR line-broadening due to rapid relaxation; some stable  $\text{Os}_2^{\text{III}}\text{Os}^{\text{II}}$  mixed-valent ions were thus found to be completely EPR-silent, even at 3.5 K.<sup>6a,33</sup> The lack of an EPR signal for the  $\text{Os}^{\text{III}}_2$  species suggests antiferro-

magnetic coupling of low-spin  $d^5$  centers. The average  $g$  value of 1.958 calculated for  $3^{5-}$  is smaller than  $g(\text{electron}) = 2.0023$  and thus points toward excited states lying close to the doublet ground state;<sup>30</sup> the deviation to lower  $g$  factors is unusual for low-spin  $d^5$  systems.<sup>32</sup>

In summary, the presently reported complex  $3^{5-}$  shows a behavior reminiscent—in part—of  $1^{5+}$ . Both systems might be described as delocalized compounds as deduced solely from the IV band widths and the  $K_c$  values. However, in contrast to  $1^{5+}$ , where all the ruthenium-ligand vibrations were averaged in the IR spectrum<sup>1g</sup> (indicating that the delocalization extends to the shorter vibrational time scale), our results show conclusively that this is not the case for  $3^{5-}$ , as a valence-trapped situation is clearly manifest both for cyanide and pyrazine vibrations. On the other hand, the  $3^{5-}$  ion shows an intermediate behavior between the fully delocalized  $2^{5+}$  ion and the fully localized  $4^{5-}$  ion. In acetonitrile solutions of  $3^{5-}$ , the  $\pi$ -acceptor character of cyanides (competitive with pz) is strongly diminished compared to aqueous solutions, thus making the metal more electron rich and favoring the Os-pz-Os interaction. This is also shown by the negative shift of the redox potential of the  $\text{Os}^{\text{II,III}}$  couple when going from water<sup>17</sup> to acetonitrile; as a result, the  $d\pi(\text{Os})$  orbitals can match better in energy with the  $\pi^*(\text{pz})$  orbital of the bridge. Thus, in addition to “internal” factors such as metal type, bridging ligand, and auxiliary coligands, second-sphere interactions can be important in influencing the electronic structure of mixed-valence compounds.<sup>17,18,24,34</sup>

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