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Solvent Dependences of Spectral and Redox Properties of Pyrazine (pz) Complexes of Ruthenium and Osmium Pentaammines: $Ru(NH_3)_5pzCH_3^{3+}$, $Os(NH_3)_5pzCH_3^{3+}$, and $[Ru(NH_3)_5]_2pz^{5+}$

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Near-IR–vis spectra and cyclic voltammetric parameters are reported for the title compounds in the solvent series nitromethane, acetonitrile, propylene carbonate, *N,N*-dimethylformamide, and dimethyl sulfoxide (over which Gutmann donor number (DN) ranges from 2.7 to 29.8). As has been found in related systems, the $E°$ of $(NH_3)_5M^{III/II}$ decreases with donor number, with the magnitude of the response to solvent being quantitatively similar (0.025 ± 0.002 V/DN) for all of the couples examined. (Consequently the stability of $[Ru(NH_3)_5]_2pz^{5+}$ with respect to disproportionation is solvent independent within experimental error.) By contrast, the vis (ν_h) and near-IR (ν_l) absorption bands exhibit very different solvent dependences. For $Ru(NH_3)_5pzCH_3^{3+}$, the position of ν_h is solvent independent, but ν_l exhibits a typical MLCT solvent dependence. For $Os(NH_3)_5pzCH_3^{3+}$, ν_l shifts to longer wavelength with increasing donor number (MLCT character) while ν_h exhibits the opposite behavior. Both vis and near-IR bands of $[Ru(NH_3)_5]_2pz^{5+}$ shift only very slightly with solvent, but the vis band of $[Ru(NH_3)_5]_2pz^{4+}$ is more solvent dependent—about 80% as much as $Ru(NH_3)_5pz^{2+}$. The spectral shifts are discussed in terms of a simplified molecular orbital scheme for the M–pz back-bonding interaction, and the nature of the solvent sensitivity is found to be related to the metal and pyrazine character of the MO's involved in the transition.

Introduction

Metal-to-ligand charge-transfer (MLCT) absorption is commonly observed when a d^6 metal center M is bound to an aromatic nitrogen heterocycle L such as pyridine.[1,2] The energy of the MLCT band maximum is related to the electron-donor ability of the metal and to the electron-acceptor ability of the ligand.[1–3] The band maxima are also usually solvent dependent. The striking solvent sensitivity of the $Ru(NH_3)_5L^{2+}$ series was first noted by Ford et al.[3] Later Curtis et al.[4] found that MLCT band energies for ruthenium(II) ammine complexes correlate with Gutmann donor number (DN)[5] and that the spectral shifts derive in part from changes in ground-state $Ru^{III/II}$ redox potentials with solvent,[4,6] the potential of the bound L/L^- couple being less solvent dependent.[4a]

For most $Ru(NH_3)_5L^{2+}$ complexes only one low-energy band (MLCT in nature) is observed.[3,4] By contrast, for $Ru(NH_3)_5pzCH_3^{3+}$[7,8] and for $Os(NH_3)_5L^{2+}$[7,9] two relatively low energy (vis, near-IR) transitions are found. These have been ascribed to excitation of different πd electron sets on the strongly back-bonding Ru(II) or Os(II) center.[7] In the case of $Ru(NH_3)_5pzCH_3^{3+}$ the position of the visible band (ν_h) was recently found to be solvent independent,[8] while the near-IR band (ν_l) is at longer wavelength in DMSO than in water solvent (as is generally found for $Ru(NH_3)_5L^{2+}$ MLCT bands). In this paper the solvent dependences of the electrochemical and spectral properties of $pzCH_3^+$ complexes of Ru(II) and Os(II) are investigated. In addition the results of analogous studies of the mixed-valence $[Ru(NH_3)_5]_2pz^{5+}$ are reported. The results suggest that, in mononuclear complexes, the degree of M–L electronic interaction (back-bonding) may be tuned to some extent by changing solvent. Such "solvent tuning" has recently been reported for asymmetric mixed-valence complexes.[4b,10] By contrast, in the present work we found little evidence for "solvent tuning" of the symmetric mixed-valence complex $[Ru(NH_3)_5]_2pz^{5+}$.

Experimental Section

Materials. The ligand *N*-methylpyrazinium cation was prepared from pyrazine and neat methyl iodide.[11] The ruthenium(II) complexes were prepared by literature methods.[3,12] The complexes $Os(NH_3)_5L^{3+}$ with L = py and pz were prepared[13] from the $CF_3SO_3^-$ complex[14] and purified by chromatography on SP-Sephadex C-25 (Pharmacia) (product eluted in 0.3–0.4 M HCl or NaCl). L = py: 0.25 g of $[Os(NH_3)_2CF_3SO_3](CF_3SO_3)_2$ was stirred 3 h at room temperature with 2 mL of pyridine containing 6 drops of concentrated triflic acid. L = pz: 0.5 g of $[Os(NH_3)_5CF_3SO_3](CF_3SO_3)_2$ was added to a melt of 0.6 g of pyrazine containing ~3 drops of concentrated triflic acid. After 10 min the melt was allowed to cool, yielding a brown solid. The latter was dissolved in 80 mL of 0.01 M HCl, and the solution was loaded onto the Sephadex column. A similar method was used for L = $pzCH_3^+$ (acetone solvent; $(pzCH_3)CF_3SO_3$ as starting material). However, the crude product obtained on evaporation of solvent acetone was found to be a mixture of the Os(II) and Os(III) complexes: To simplify the purification procedure, the crude product was mixed with aqueous $Na_2S_2O_4$ (moles of $S_2O_4^{2-}$ = moles of total Os(III) initially taken) prior to loading the column. The tripositive Os(II) complex was eluted and isolated as the Cl^- salt. The isolated $Os(NH_3)_5L^{3+}$ yields were routinely low (<15%). The products were characterized by UV–vis spectroscopy and by analyses for metal and anion (E. Norton, BNL).

Vis–near-IR spectra were measured on Cary 210 and 17 spectrophotometers (in the near-IR region against solvent blanks). Electrochemical measurements were made on a BAS 100 electrochemical analyzer. Solvents used were Spectrograde, dried overnight over 3- or 4-Å molecular sieve prior to use.

Results and Discussion

Table I summarizes the results of the cyclic voltammetric studies. For $pzCH_3^+$ complexes the first value given is the $M^{III/II}$ potential and the second is the L/L^- ($pzCH_3^+/pzCH_3$) potential. For the binuclear complex, only the metal-centered redox processes are reported. All of the $M^{III/II}$ potentials have been studied previously in 0.1 M aqueous chloride (vs. NHE): $Ru(NH_3)_5pzCH_3^{4+/3+}$, $E°$ = 0.87 V;[12] $Os(NH_3)_5pzCH_3^{4+/3+}$, $E°$ =

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Table I. $E_{1/2}$ Values vs. Aqueous SCE as a Function of Solvent at 22 ± 2 °C in the Presence of 0.1 M Tetrabutylammonium Hexafluorophosphate[a]

solvent	$Ru(NH_3)_5pzCH_3^{3+}$ 3+/4+ $E_{1/2}$ (ΔE_p), V (mV)	$Ru(NH_3)_5pzCH_3^{3+}$ 3+/2+ $E_{1/2}$ (ΔE_p), V (mV)	$Os(NH_3)_5pzCH_3^{3+}$ 3+/4+ $E_{1/2}$ (ΔE_p), V (mV)	$Os(NH_3)_5pzCH_3^{3+}$ 3+/2+ $E_{1/2}$ (ΔE_p), V (mV)	$[Ru(NH_3)_5]_2pz^{4+}$ 4+/5+ $E_{1/2}$ (ΔE_p), V (mV)	$[Ru(NH_3)_5]_2pz^{4+}$ 5+/6+ $E_{1/2}$ (ΔE_p), V (mV)
CH_3NO_2	≥1.01	~−0.8[b]			0.53 (78)[d]	
CH_3CN	0.94 (80)[c]	−0.73 (90)[c]	0.561	−1.02	0.44 (66)[d]	0.87 (80)[d]
PC	0.86	−0.76	0.46 (87)[c]		0.34 (80)[f]	0.77 (140)[f]
DMF	0.76 (75)[d]	−0.76 (75)[d]	0.39 (75)[e]		0.25 (60)[d]	0.66 (75)[d]
DMSO	0.62 (75)[e]	−0.87 (73)[e]	0.30 (60)[d]	−0.70 (60)[d]	0.10 (60)[d]	0.52 (75)[d]

[a] A Pt-disk electrode was used with the BF_4^-, Cl^-/PF_6^-, and PF_6^- salts of the ruthenium, osmium, and binuclear ruthenium complexes, respectively. The following abbreviations are used: PC, propylene carbonate; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide. [b] Only E_{pc} was observed at −0.79 V (scan rate 300 mV s^{-1}) and at −0.85 V (scan rate 1000 mV s^{-1}). [c] Scan rate 50 mV s^{-1}. [d] Scan rate 100 mV s^{-1}. [e] Scan rate 300 mV s^{-1}. [f] Scan rate 10 mV s^{-1}.

Table II. Absorption Maxima and Half-Bandwidths of Pentaammine Complexes as a Function of Solvent at ~22 °C: λ_{max} ($\Delta\nu_{1/2}$), nm (10^{-3} cm^{-1})[a]

complex		CH_3NO_2, 2.7	BN, 11.9	CH_3CN, 14.1	PC, 15.1	H_2O, 18.1	DMF, 26.6	DMSO, 29.8
$Ru(NH_3)_5py^{2+}$		400 (4.6)	412 (4.8)	407 (4.1)			437 (3.8)	447 (3.7)
$Ru(NH_3)_5pz^{2+}$		450 (3.1)	460 (3.1)	457 (3.1)		472 (3.2)	485 (3.1)	493 (3.1)
$Ru(NH_3)_5pzCH_3^{3+}$	h	541 (4.5)		540 (3.9)	540 (4.0)	538 (4.0)	539 (4.2)	540 (4.6)
	l	800		855	875	877	970 (3.9)	1000 (3.8)
$[Ru(NH_3)_5]_2pz^{4+}$		535 (3.1)	545 (3.1)	545 (2.8)	543	547 (2.6)	574 (2.7)	580 (2.9)
$[Ru(NH_3)_5]_2pz^{5+}$	h	557		562	565	565 (2.3)	568	573
	l	1620		1600	1585	1570 (1.5)	1585	1582
$[Ru(NH_3)_5]_2bpy^{4+}$ [b]						518	585	595
$[Ru(NH_3)_5]_2bpy^{5+}$ [b,c]						520	575	585
$Os(NH_3)_5py^{2+}$						428		456
						555		598
$Os(NH_3)_5pz^{2+}$						460 (3.6)		
						770 (3.3)		
$Os(NH_3)_5pzCH_3^{3+}$	h	458 (5.0)		450 (5.0)		436 (5.1)		426
	l	1050 (2.9)		1100 (2.6)		1110 (2.4)		1200 (2.4)

[a] λ_{max} ± 2 nm and ($\Delta\nu_{1/2}$ ± 0.5) × 10^3 cm^{-1} in the visible region. In the near-IR region λ_{max} ± 5 nm. BN = benzonitrile. For other abbreviations, see Table I. [b] bpy = 4,4′-bipyridine. [c] Data bearing on the solvent dependence of the near-IR intervalence-transfer band are given in: Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *68*, 7828.

0.55 V;[13] $[Ru(NH_3)_5]_2pz^{6+/5+/4+}$, E° = 0.76, 0.37 V in 0.1 M Cl^-[12] and 0.81, 0.40 V in 0.1 M $CF_3SO_3^-$.[15] For solubility reasons[4] a 0.1 M PF_6^- medium was used for the present solvent-dependence studies. In dry, air-free solvents all of the reported redox processes were chemically reversible on the cyclic voltammetric time scale. However, rather large peak separations were commonly encountered for these highly charged species at even moderate sweep rates (see especially the 5+/6+ data in the far-right column).

The ferrocene–ferrocenium couple (Fc^0–Fc^+) has been proposed as a solvent-independent reference.[6] In Figure 1 plots of the $M^{III/II}$ potential (relative to that for $Fc^{+/0}$) vs. solvent donor number are shown.[16] For all of the complexes the slopes are ~−25 mV/DN, as has been found for other pentaammine complexes.[6,17] Interestingly, the solvent dependence of the $M^{III/II}$ potential does not appear to be particularly sensitive to the charge on the complex, to the nature of the ligand, or, including the osmium data, to the metal—but simply to the number of NH_3 groups per metal center.[4,17] For the binuclear complex the disproportionation equilibrium

$$2(5+) \rightleftharpoons (4+) + (6+)$$

is consequently solvent independent with ΔG° for disproportionation being +0.42 ± 0.02 eV for the solvents studied to date (including water). Finally it is noteworthy that the bound $pzCH_3^{+/0}$ reduction potential vs. that of $Fe^{+/0}$ is also solvent dependent. The solvent sensitivity (~−16 mV/DN) is smaller than that of the $M^{III/II}$ couples and similar to that of L = 4-$NCpyCH_3^+$ in $Ru(NH_3)_5L^{3+}$ studied by Curtis et al.[4a] By contrast the $bpy^{0/-}$ potentials in a large number of $M(bpy)_3$ complexes (bpy = 2,2′-bipyridine) are essentially solvent independent (−3 mV/DN or smaller).[18]

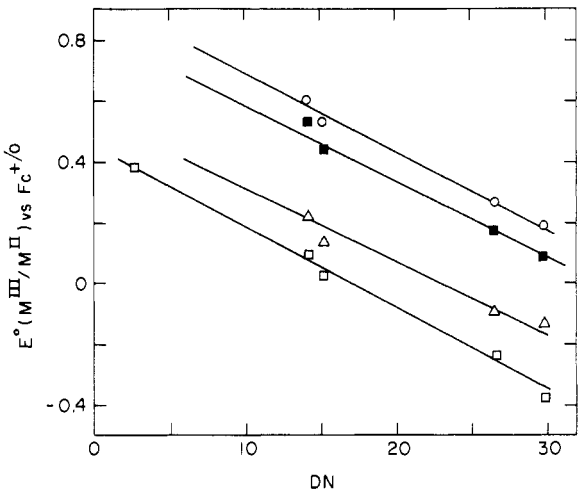

Figure 1. $Ru^{III/II}$ or $Os^{III/II}$ reduction potentials vs. $Fe^{+/0}$ as a function of solvent donor number: $Ru(NH_3)_5pzCH_3^{4+/3+}$, ○; $[Ru(NH_3)_5]_2pz^{6+/5+}$, ■; $[Ru(NH_3)_5]_2pz^{5+/4+}$, □; $Os(NH_3)_5pzCH_3^{4+/3+}$, △.

For the binuclear complex $[Ru(NH_3)_5]_2pz^{4+}$ the pz/pz^- reduction process was inaccessible (<−2 V). It has however been observed for other d^6-M M_2pz complexes in DMF; for M = $Mn(cp)(CO)_2$ the reversible process occurs at ~−1.4 V vs. SCE, considerably positive of that in the ruthenium complex or the free ligand.[19]

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(16) The data plotted were obtained from the values in Table I and values of E° for the ferrocene–ferrocenium couple vs. SCE given in ref 6.
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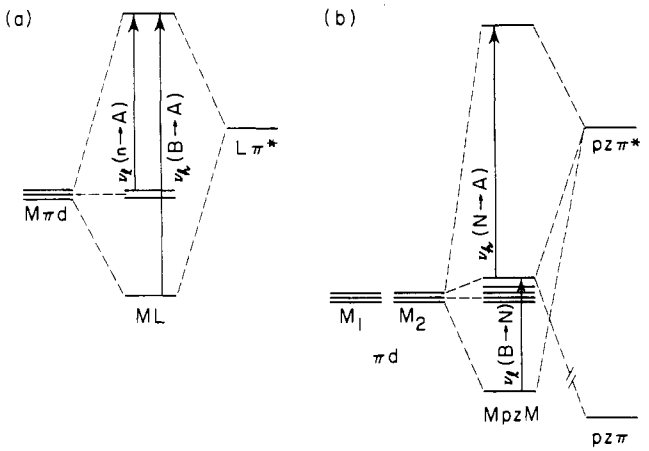

Figure 2. Assignments of the vis–near-IR transitions observed for (a) mononuclear complexes such as $Os^{II}(NH_3)_5L^{2+}$ and $Ru^{II}(NH_3)_5pzCH_3^{3+}$ and (b) binuclear pyrazine complexes. (For $[Ru(NH_3)_5]pz^{4+}$ ν_l cannot occur because level N is doubly occupied in the ground state.) The figures are adapted from ref 21, 7, 8, 20, and 12. As pointed out by Laufer[21] the diagram for the mononuclear complexes is generally applicable for pyridine, pyrazine, etc., while that for the binuclear species varies with L.

Table II summarizes the spectral results obtained in this study. With the exception of the ~1600-nm band[12] of $[Ru(NH_3)_5]_2pz^{5+}$, all of the band reported are approximately Gaussian in shape. Band maxima are given in nm; the numbers in parentheses are bandwidths at half-intensity in 10^3 cm^{-1} units. The spectra of $Os(NH_3)_5L^{2+}$ with L = py and pz were obtained by reducing the Os(III) complex in situ with $Na_2S_2O_4$. The remaining spectra were obtained by dissolving PF_6^-, BF_4^-, or $CF_3SO_3^-$ salts of the complex listed. The first two entries, $Ru(NH_3)_5py^{2+}$ and $Ru(NH_3)_5pz^{2+}$, exhibit the solvatochromic behavior found for a number of complexes of this family[3,4] with the band maximum shifting to longer wavelength as solvent donor number increases. Similar, but smaller, shifts are found for $[Ru(NH_3)_5]_2pz^{4+}$, while the visible (ν_h) band of $[Ru(NH_3)_5]_2pz^{5+}$ shifts very little with solvent. Very strikingly, the visible band for $Ru(NH_3)_5pzCH_3^{3+}$ is solvent independent and that of $Os(NH_3)_5pzCH_3^{3+}$ shifts to *shorter* wavelength with increasing solvent donor number. By contrast, the near-IR bands (ν_l) of both $pzCH_3^+$ complexes do shift to lower energy with increasing DN.

For all of the complexes considered here the vis–near-IR electronic spectra are dominated by the interaction of the metal center with the N-heterocycle. Ford et al.[3] recognized that the filled metal πd (t_{2g} in O_h symmetry) orbitals may interact with empty π* orbitals of the heterocycle, giving ground-state back-bonding and intense metal-to-ligand charge-transfer absorption at relatively low energy.[20,21] For pyrazine complexes the lowest energy π* orbital (ψ_4) interacts strongly with one πd metal orbital. In $Ru(NH_3)_5L^{2+}$ complexes the intense visible band is due to metal-πd to ligand-π* transitions involving these orbitals. Magnuson and Taube noted and interpreted the occurrence of two low-energy bands for $Os^{II}(NH_3)_4ClL^+$ complexes and for $Ru(NH_3)_5pzH^{3+}$.[7] They proposed that transitions originating from both the "π-bonding" d (ν_h) and "nonbonding" d orbitals (ν_l) were being observed, with the energetic difference between the two band maxima reflecting the extent of π back-bonding E_{π^*} in the complex. A recent structural study of the related $Ru(NH_3)_5pzCH_3^{3+}$ complex confirms that back-bonding in such complexes can be very great indeed.[22]

A diagram illustrating the origin of the two transitions is given in Figure 2. In the $Ru(NH_3)_5L^{2+}$ series ν_h is always observed,

Table III. Band Maxima for $Os^{II}(NH_3)_5L$ Complexes in Water

L	λ_1, nm	λ_2, nm	$E°$, V[c]
pyridine (py)	428[a]	555[a]	−2.69
pyrimidine (pm)	458[b]	663[b]	−2.37
pyrazine (pz)	460[a]	770[a]	−2.11
$pzCH_3^+$	435[a]	1150[a]	−0.73

[a] This work. [b] From ref 9. [c] In dimethylformamide solvent: Wiberg, K. B.; Lewis, T. P. *J. Am. Chem. Soc.* **1970**, *92*, 7154. Cf.; Tabner, B. J.; Yandle, J. R. *J. Chem. Soc. A* **1968**, 381. [d] From ref 8; in acetonitrile solvent.

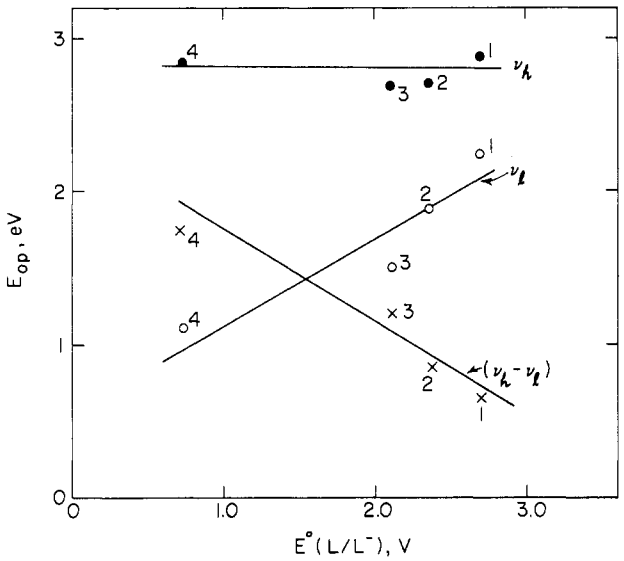

Figure 3. Optical transition energies for $Os^{II}(NH_3)_5L$ complexes in water as a function of the reduction potential of the noncomplexed ligand: 1, pyridine; 2, pyrimidine; 3, pyrazine; 4, $pzCH_3^+$ (data from Table III). The lines are drawn only to guide the eye.

but the weaker low-energy band ν_l is found only for L = $pzCH_3^+$ and some related compounds.[8,23] The right-hand side of Figure 2 illustrates the origins of low-energy bands in binuclear pyrazine complexes. For $[Ru(NH_3)_5]_2pz^{4+}$ the single intense transition allowed (ν_h) involves the three-center nonbonding (N) and antibonding (A) molecular orbitals.[12,21] The former has been postulated to lie above the other nonbonding πd levels (n) because of interaction between the N molecular orbital and the filled pyrazine-π level (ψ_3).[21] When such configuration interaction is neglected, ν_h for the binuclear species corresponds (at least, energetically) to ν_l for the mononuclear complexes. For the mixed-valence complex $[Ru(NH_3)_5]_2pz^{5+}$,[24] ν_h (B → N) is also allowed and, in addition, the electron hole in the N molecular orbital gives rise to ν_l, a transition between bonding (B) and nonbonding (N) molecular orbitals (as well as to even lower energy n → N transitions[24-26]).

(19) (a) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 498. (b) Kaim, W.; Kohlmann, S.; Ernst, S.; Olbrich-Deussner, B.; Bessenbacher, C.; Schulz, A. *J. Organomet. Chem.* **1987**, *321*, 215.
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(22) Wishart, J.; Bino, A.; Taube, H. *Inorg. Chem.* **1986**, *25*, 3318.

(23) (a) Wishart, J., private communication. (b) The absence of ν_l for other $Ru(NH_3)_5L^{2+}$ species is attributed to the small separation between ν_l and ν_h; ν_l (being of much lower intensity) is simply masked by the low-energy tail of ν_h.[8] In addition, the Ru^{II}–L distance being greater for L = py or pz, the intensity of ν_l should be smaller than for L = $pzCH_3^+$.

(24) (a) Here the electronic structure of the mixed-valence complex is considered within the framework of a delocalized model (equivalent metal sites, "class III").[24b] Although the nature of the electronic structure has been a subject of some controversy, the delocalized model affords the best description in light of recent data.[24c,25,26] (b) For a review of the literature up to 1983 see: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, p 19 ff. (c) See: Furholz, U.; Bürgi, H. B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. H. J.; Stead, M. J.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121; and subsequent papers in the series. (d) The spectral assignments for $[Ru(NH_3)_5]_2pz^{5+}$ are consistent with those for the mononuclear species and are internally consistent with one another with the exception of the 850-nm shoulder.[12,25] If this shoulder is assigned as a transition to the quartet n → A state,[25,26] the internally consistent picture is retained. However, there is no independent corroboration of such an assignment and no rationale for the relatively high intensity of such a spin-forbidden (doublet → quartet) transition.

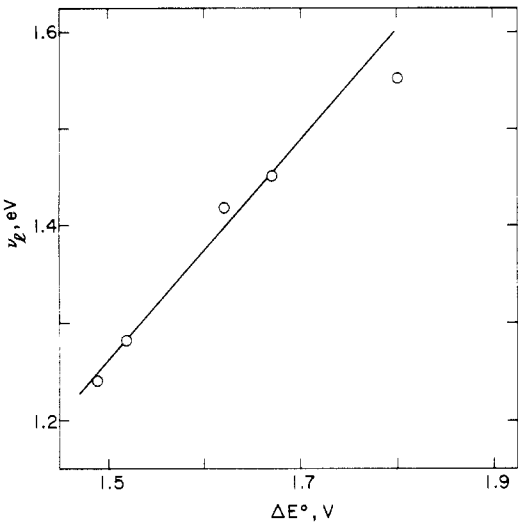

Figure 4. Energy of ν_l for $Ru(NH_3)_5pzCH_3^{3+}$ as a function $\Delta E°$, the difference between metal-centered and ligand-centered redox potentials in Table I, as a function of solvent.

The Taube–Magnuson assignments illustrated in Figure 2a are supported by the behavior of the pentaammineosmium(II) data collected in Table III. As shown in Figure 3, a plot of the spectral data in Table III against the reduction potential of the free ligand, ν_l decreases in energy as the free-ligand redox potential increases.[27] This is expected for an MLCT assignment of ν_l; the molecular orbital A has greater ligand character than the n nonbonding πd osmium(II) orbitals. By contrast, ν_h varies much less[2] with L; as $E°(L/L^-)$ rises, the energy difference (δ_{π^*}) between the zero-order and πd Os(II) and Lπ^* orbitals decreases, the back-bonding interaction increases, and ν_h takes on increasingly more M=L bonding (B) to M=L antibonding (A) character. Thus the energy difference $\nu_h - \nu_l$ increases in parallel. Magnuson and Taube also found a striking effect of protonation (or, here "methylation") on the spectrum of $Os(NH_3)_4Clpz^+$: upon protonation of the complex ν_h *increased* in energy, which led to the conclusion that the πd–L bonding orbital has greater ligand than metal character in $Os(NH_3)_4ClpzH^{2+}$. The present solvent-dependence studies on the analogue $Os(NH_3)_5pzCH_3^{3+}$ support this conclusion: ν_l shifts in the normal sense for an MLCT transition, while ν_h shifts in the opposite sense, as expected for LMCT character. The analogous ruthenium complex exhibits intermediate character—ν_l responds to solvent with MLCT character, while ν_h is solvent independent.

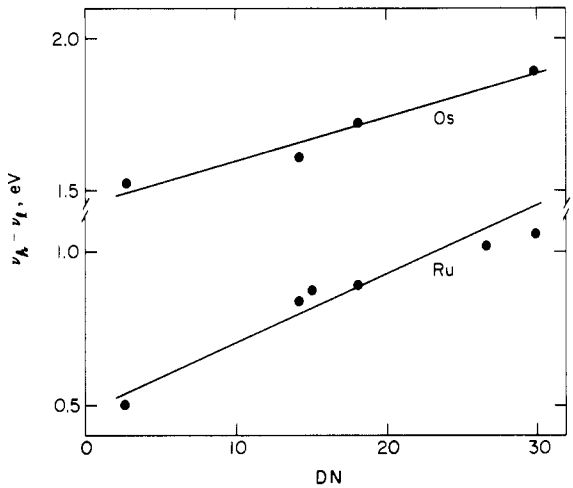

Figure 5. Energy difference between vis and near-IR band maxima for $Os(NH_3)_5pzCH_3^{3+}$ and $Ru(NH_3)_5pzCH_3^{3+}$ complexes as a function of solvent donor number.

For a number of series of complexes the positions of (singlet) MLCT bands have been found to correlate strikingly well with $\Delta E°$, the difference between bound-ligand acceptor ($E°(ML/ML^-)$) and metal donor ($E°(M^+L/ML)$) reduction potential.[28,29] Such correlations are usually obtained in a given solvent by varying L in a homologous series. For $Ru(NH_3)_5pzCH_3^{3+}$ sufficient electrochemical data were obtained to investigate this trend for one complex as a function of solvent. In Figure 4, a plot of the energy of ν_l as a function of $\Delta E°$ (obtained from the difference between metal-centered and ligand-centered redox potentials in Table I) is shown. An excellent correlation, with approximate slope of unity, is found.[27] Earlier Curtis et al. considered analogous data for $Ru(NH_3)_5(4\text{-}NCpyCH_3)^{3+}$ and also found a good correlation.[4a] However, the slope of the analogue of Figure 4 was smaller ($\sim$0.6). Since only ν_h is observed for the $4\text{-}NCpyCH_3^+$ complex, the smaller slope may arise from the B $\rightarrow$ A character of ν_h as discussed above for the Os(II) complexes.[30] Earlier it was noted that both $E°(Ru^{III/II})$ and $E°(pzCH_3^{+/0})$ drop as donor number increases. It is thus worth pointing out that the solvent sensitivity of $\Delta E°$ and of the MLCT maximum (at least for $Ru(NH_3)_5pzCH_3^{3+}$ and $Ru(NH_3)_5NCpyCH_3^{3+}$) arises because the metal-center $E°$ is more solvent dependent than the bound-ligand potential—not simply because the latter is solvent independent.[31]

The differing solvent sensitivities of ν_h and ν_l in the $pzCH_3^+$ (and presumably pzH^+, etc.) complexes indicate that solvent variation may be used to modulate the extent of M–L π back-bonding and the splitting of the πd orbitals on these d^6 complexes. In Figure 5, the difference $\nu_h - \nu_l$ for $Os(NH_3)_5pzCH_3^{3+}$ and $Ru(NH_3)_5pzCH_3^{3+}$ is plotted against solvent donor number.

The visible band (ν_h) of the binuclear complex $[Ru(NH_3)_5]_2pz^{4+}$ is related to ν_l for the mononuclear species in that, for both,

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(26) Ko, J.; Zhang, L.-T.; Ondrechen, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1712. Zhang, L.-T.; Ko, J.; Ondrechen, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 1666. Ondrechen, M. J.; Ko, J.; Zhang, L.-T. *J. Am. Chem. Soc.* **1987**, *109*, 1672.

(27) (a) The absorption maximum gives the energy of the excited state produced with ground-state nuclear configuration (metal–ligand and intraligand bonding, as well as solvation). If the differences in ground- and excited-state structures lie entirely in low-frequency ($h\nu < kT$) modes, then $E_{max} = E^* + \lambda^*$; i.e., the energy of the absorption maximum E_{max} is the sum of λ^*, the excited-state distortion energy, and E^*, the energy of the thermally relaxed excited state. Thus it would be more appropriate to compare E^* (rather than E_{max}) values with redox potentials, donor numbers, etc. The fact that E_{max} correlations such as Figures 3–5 are observed indicates that λ^* is either small compared to E_{max} or not changing greatly (or changing systematically[4b]) through a given series. In earlier work, λ^* was estimated at 2800–3600 cm^{-1} for related mononuclear complexes in water.[8] (b) The correlation of optical MLCT absorption (or emission) energies with $\Delta E°$ varied by changing solvent is somewhat surprising. The excited-state distortion λ^* is a function of intramolecular structural differences (λ_i^*) and solvational differences (λ_0^*). Since λ_0^* is expected to vary with solvent dielectric continuum properties (static and optical dielectric constants) of the solvent, rather than with donor number, trends such as Figure 4 must be attributed to the change in λ_0^* being small relative to the change in E^* induced by solvent variation. In principle, the bandwidths provide information about λ^*, as discussed for related complexes in ref 8. For $Ru(NH_3)_5pzCH_3^{3+}$ ν_l is not well resolved from ν_h for the low donor number solvents. For DMF and DMSO the $\Delta\nu_{1/2}$ values (3900 and 3800 cm^{-1}) are the same within error. For $Os(NH_3)_5pzCH_3^{3+}$ ν_l is much narrower and also narrows significantly (from 2900 to 2400 cm^{-1}) as the band shifts to lower energy with increasing donor number. This pattern would not be predicted from a dielectric continuum model if the extent of charge transfer is independent of solvent. Equally striking is the considerable breadth of ν_h for $Os(NH_3)_5pzCH_3^{3+}$ ($\sim$5000 cm^{-1}).

(28) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1985**, *119*, 61; **1986**, *124*, 152 and references cited therein.

(29) A similar correlation has been noted for emission maxima: Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755.

(30) In contrast to Figure 4a, the B level in the 4-cyanopyridinium complex should be doubly degenerate, and the n level, singly degenerate. This does not affect the arguments given.

(31) It is possible that the solvent dependence of the bound-ligand reduction potential is a consequence of the solvent-dependent π back-donation. Thus the bound ligand is most difficult to reduce in DMSO where back-bonding is most extensive and most easily reduced in low donor number solvents where back-bonding is less extensive.

Table IV. Results of Spectral Analysis (Data for Water)[a]

L	E_{π^*}	δ_{π^*}	β	ϕ	c_M	c_L	Δe_{calcd} h	Δe_{calcd} l	$\Delta(E_{op}/DN)$ h	$\Delta(E_{op}/DN)$ l
					$Os^{II}(NH_3)_5L$					
py	5.4	12.9	9.7	B	0.88	0.47	0.6	0.8		
pm	6.8	8.4	12.1	B	0.83	0.55	0.4	0.7		
pz	8.7	4.7	10.5	B	0.78	0.63	0.2	0.6		
$pzCH_3^+$	13.9	−4.9	11.2	B	0.63	0.78	−0.2	0.4	+8.3	−6.6
	12.3[b]	−2.8[b]	10.8[b]	B	0.66[b]	0.75[b]	−0.1[b]	0.4[b]		
	15.2[c]	−6.8[c]	11.2[c]	B	0.61[c]	0.79[c]	−0.3[c]	0.4[c]		
					$Ru^{II}(NH_3)_5L$					
py[d]		22.2	5.2	B	0.97	0.22	0.9		−11.2[e]	
pz[d]		16.7	6.6	B	0.95	0.33	0.8		−8.3	
$pzCH_3^+$	7.2	4.2	9.0	B	0.78	0.62	0.2	0.6	0	−10
	6.4[b]	6.1[b]	8.9[b]	B	0.81[b]	0.58[b]	0.3[b]	0.7[b]		
	8.5[c]	1.5[c]	9.2[c]	B	0.74[c]	0.68[c]	0.1[c]	0.6[c]		
					$[Ru(NH_3)_5]_2pz^{5+}$					
							(N → A)	(B → N)		
model i[f]	6.4	11.3	7.5	B	0.61	0.51	0.3	−0.1	−2	+0.7
		(11.8[b])		N	0.71	0				
		(11.1[c])		A	0.40	0.82				
model ii[g]	3.4	17.3	5.9	B	0.66	0.37				
				A	0.24	0.94				

[a] The value of E_{π^*} (the B–n separation), δ_{π^*}, and β are given in 10^3 cm^{-1} units. The parameters are defined in footnote 35. For the last two columns, the units are millivolts. [b] For nitromethane solvent. [c] For DMSO solvent. [d] From ref 20. [e] Evaluated from the data in ref 4. [f] Calculated with the assumption that n and N levels are degenerate, i.e. that N is purely nonbonding. [g] Calculated on the assumption that N lies 3000 cm^{-1} above n.[36] If this ordering is a result of L → M π bonding, N is mixed with a (filled) pyrazine π level. Thus, the coefficient of L π^* is zero but that of L π is not. For this reason, no coefficients are given for N.

nonbonding πd (N or n, respectively) is excited to an antibonding MO arising from the back-bonding interaction. As expected from the simple model in Figure 2,[32] the absorption maximum of the dimer (N → A) lies at lower energy than that (B → A) of the monomer $Ru(NH_3)_5pz^{2+}$ (2900–3500 cm^{-1} depending upon solvent). A similar trend has been found[19] for $[Mn(cp)(CO)_2]_2pz$, for which the difference between monomer and dimer maxima is somewhat greater (4200–4900 cm^{-1}). The Mn(I) dimer series also exhibits a solvent sensitivity comparable in magnitude (1500-cm^{-1} range) to that found here for the pentaammine-ruthenium complex. Even greater sensitivity is found[33] for $[W(CO)_5]_2pz$ (range 4300 cm^{-1}), probably reflecting the larger number of carbonyl groups in the latter. (Note that, in contrast to the ammine complexes, the MLCT bands shift to higher energy with donor number for the carbonyl complexes, probably reflecting changes in metal-centered redox potentials as discussed above.[34]) As noted earlier, while the $[Ru(NH_3)_5]_2pz^{4+}$ spectrum is solvent dependent, the sensitivity is smaller than for the mononuclear pyrazine and pyridine complexes in Table II—about 80% as sensitive as the pyrazine monomer.

The solvent insensitivity of the near-infrared band of $[Ru(NH_3)_5]_2pz^{5+}$ has long been recognized.[12] The full range observed here is ~200 cm^{-1}, with the band (assigned B → N in Figure 2) creeping to *higher* energy with donor number. The visible band (N → A in Figure 2) shifts ~500 cm^{-1} in the opposite (i.e. usual) sense with solvent. As can be seen from Figure 2, the dimer ν_h (N → A) transition corresponds (approximately) to ν_l (n → A) of the monomers, and the dimer ν_l (B → N) transition is related to $\nu_h - \nu_l$ of the monomers. Thus, the *directions* of the shifts of the 5+ dimer bands are the same as those for the monomers (see Figure 5). The magnitudes of the solvent shifts are, however, very much smaller. Indeed the 5+ dimer spectrum is reasonably regarded as solvent independent. This solvent insensitivity of the spectrum is to be contrasted with the (quite normal) solvent dependence of the metal-centered electrochemistry (Table I and Figure 1), of the 4+ dimer spectrum, and of the (class II, mixed-valence) $[Ru(NH_3)_5]_2(4,4'\text{-bpy})^{5+}$ spectrum. To discuss these differences, we return to the MO scheme in Figure 2.

The simple molecular orbital scheme indicated in Figure 2 may be used along with the ν_h and ν_l positions[35] to obtain molecular orbital parameters for the mononuclear and 5+ binuclear complexes. Parameters calculated from the spectra obtained in aqueous solutions are given in Table IV. For the mononuclear complexes the observed band maxima were used. For the 5+ dimer two models are considered: in the first (i) the N molecular orbital is assumed to be degenerate with the n πd levels. In the second treatment (ii) N is assumed to lie 3000 cm^{-1} [24c,25,26,36] above n (thus n → A lies at 17 700 + 3000 cm^{-1} and B → n at 6400 − 3000 cm^{-1}). The table compiles values of E_{π^*}, the n–B splitting ($\nu_h - \nu_l$ for the monomers; ν_l for (i)), δ_{π^*}, the zero-order energy difference between πd and L_{π^*} levels, β, the resonance integral, and c_M and c_L, the metal and ligand orbital coefficients in the MO's. For the mononuclear complexes only the absolute values of the lowest (B) MO coefficients are tabulated; in the A level the numerical values are interchanged, and for n, the metal coefficient is unity and the ligand coefficient is zero. For the binuclear 5+ ion, all three sets of MO coefficients are listed (the absolute values of c_M are the same at both ruthenium centers in any given MO) for (i). Within this model, the extent and direction of charge transfer in the optical transitions may be gauged from the difference in the squares of metal MO coefficients of the

(32) In addition, λ^* may be smaller for the binuclear species (as suggested by the smaller $\Delta\nu_{1/2}$ values in Table II).

(33) Lees, A. J.; Fobare, J. M.; Mattimore, E. F. *Inorg. Chem.* **1984**, *23*, 2709.

(34) Chadwick, I.; Diaz, C.; Gonzalez, G.; Santa Ana, M. A.; Yutronic, N. *J. Chem. Soc., Dalton Trans.* **1986**, 1867.

(35) For the mononuclear complexes $\nu_h = (\delta_{\pi^*}^2 + 4\beta^2)^{1/2}$ (bonding-to-antibonding transition, B → A) and $\nu_l = [\delta_{\pi^*} + (\delta_{\pi^*}^2 + 4\beta^2)^{1/2}]/2$ (nonbonding-to-antibonding transition, n → A).[20] For the binuclear complexes $\nu_h = [\delta_{\pi^*} + \delta_{\pi^*}^2 + 8\beta^2)^{1/2}]/2$ (transition between nonbonding and antibonding MO's, N → A) and $\nu_l = [-\delta_{\pi^*} + (\delta_{\pi^*}^2 + 8\beta^2)^{1/2}]/2$ (transition between bonding and antibonding MO's, B → A). The parameters are as follows:[20] $\alpha_L = \langle L|H|L\rangle$, $\alpha_M = \langle M|H|M\rangle$, $\beta = \langle L|H|M\rangle$, and $\delta_{\pi^*} = \alpha_L - \alpha_M$ where M and L denote the single metal πd and ligand π^* orbitals involved in back-bonding within this model. Note that, in addition to the problems discussed in footnote 27, this is a one-electron model applied to a multielectron problem: overlap, repolarization effects, and two-electron integrals are neglected.

(36) (a) A splitting of ca. 3000 cm^{-1} is suggested by results[25] obtained for poly(vinyl alcohol) foils[22a] and Nafion films.[25c] The very low energy spectral features appear to be sample or medium dependent,[22b] as expected within model ii. As a consequence, the values given in Table IV for model ii are most relevant to the media in which the 2000–4000-cm^{-1} features were observed—not necessarily to aqueous room-temperature solutions. (b) These considerations suggest that LMCT (L π → N) should occur near 20 000 cm^{-1}.

orbitals populated in initial and final states. At the right-hand side of the table, calculated charge transferred (Δe) for ν_h and for ν_l may be compared with solvent sensitivity, the slope of the ν vs. donor number plot. (The sign convention for Δe is that $\Delta e = +1.0$ for pure MLCT and $\Delta e = -1.0$ for pure LMCT.) For the mononuclear complexes the calculated Δe values range from ~ 1.0 to <0.0 and track the donor number slopes (−11 to +8 mV/DN) reasonably well. The tabulated MO coefficients provide a consistent picture of the continuum of metal–ligand "back-bonding" interaction ranging from rather weak ground-state charge transfer for $Ru(NH_3)_5py^{2+}$ ($c_M \gg c_L$)[20] where δ_{π^*} is large to extensive "double bonding" for the $pzCH_3^+$ complexes ($c_M \sim c_L$). In Table IV, parameters for the extreme solvents, nitromethane and DMSO, are also included for the $pzCH_3^+$ complexes. The primary effect of changing solvent for a given complex is in δ_{π^*}, the zero-order metal–ligand (πd–L π^*) energy difference, which ranges over 4000–4500 cm^{-1} ($\sim$0.5 eV) for the solvents studied—about two-thirds of the range observed in the electrochemical studies (Figure 1).

In Table IV, models i and ii for $[Ru(NH_3)_5]_2pz^{5+}$ yield rather strikingly different pictures of the ruthenium–pyrazine bonding. When N is assumed degenerate with n (negligible pz → Ru π donation), the value of E_{π^*} obtained is comparable to that in $Ru(NH_3)_5pzCH_3^{3+}$. The MO coefficients obtained lead to rather small Δe_{calcd} values, consistent with low solvent sensitivity. However, the behavior of the monomers (as in Figure 5) leads to the expectation that δ_{π^*} should vary markedly with solvent, and this is not observed. Instead, the δ_{π^*} values for $[Ru(NH_3)_5]_2pz^{5+}$ change only over a small range $\sim$650 cm^{-1} (0.08 eV). This behavior is difficult to reconcile with that of the monomers. It would require that metal and pz energy levels move almost exactly in parallel with solvent. However, model ii, in which the N molecular orbital of $[Ru(NH_3)_5]_2pz^{5+}$ is not strictly nonbonding but rather somewhat antibonding through interaction of N with the filled pz π orbital (ψ_3), can provide a resolution of the dilemma. In this model, an n–N splitting of 3000 cm^{-1} (E_π due to L → M π donation) was taken and the π-back-bonding stabilization E_{π^*} = 3400 cm^{-1} was obtained. The comparable sizes of the two splittings are at first surprising. However, the overall energetics seem consistent with such a pattern: the lowest energy π–π^* transition[12] suggests a $\sim$37 000-cm^{-1} separation between the relevant pyrazine π^* and π levels. In model ii, $\delta_{\pi^*} \sim 17\,000$ cm^{-1} is obtained, suggesting δ_π (the energy difference between πd and pz π^* levels) of the order of 20 000 cm^{-1}.[36b] For the 5+ ion, δ_π and δ_{π^*} are thus comparable, consistent with comparable E_π and E_{π^*}. It is then conceivable that the solvent insensitivity arises from compensating π-bonding (L → M) and back-bonding (M → L) interactions. As solvent donor number increases, the energy of the d electrons rises, and δ_{π^*} decreases while δ_π increases. The increased back-bonding with increasing DN should result in increased B–A splitting and in a decrease in the (unobserved) n → A transition energy. The N molecular orbital, however, *drops* in energy with increasing DN (larger δ_π) because the effect of π interaction is to destabilize this MO and there is less destabilization at larger δ_π. The opposing effects of DN on π^* and π interactions thus tend to maintain constant N → A (ν_h) and B → N (ν_l) transition energies as a consequence of the "amphoteric"[21] nature of pyrazine.

Thus model ii provides a qualitative rationalization of the solvent insensitivity and suggests a significant degree of L → Ru π bonding. It is noteworthy that the spectrum of $[Ru(NH_3)_5]_2pz^{5+}$ is dominated by a Ru(II)-like chromophore; i.e., the purple color is associated with MLCT as is seen for $[Ru(NH_3)_5]_2pz^{4+}$ and the Ru(II) mononuclear complexes. However, in light of model ii, the Ru–pz (and, through it, Ru–Ru) electron delocalization arises through *both* π back-bonding and π bonding, with the importance of the latter reflecting the Ru(III) character of the molecule. The validity of model ii might be tested through a study of the very low energy n → N transitions with medium; the latter should be much more medium dependent than N → A and B → N transitions.[36] In addition, the solvent dependence of the spectrum of the osmium analogue[37,38] would be of interest because the relative dispositions of the πd levels and pyrazine HOMO and LUMO levels are considerably different for osmium ($\delta_\pi \gg \delta_{\pi^*}$) than for ruthenium ($\delta_\pi \sim \delta_{\pi^*}$). Thus L → M donation should play a much less significant role, and a solvent dependence similar to that found for $[Ru(NH_3)_5]_2pz^{4+}$ might be expected.

Solvent effects of several origins arise in mixed-valence systems. For symmetric, valence-trapped (class II) species such as $[(NH_3)_5Ru]_2(4,4'\text{-bpy})^{5+}$ shifts in the MMCT (metal-to-metal charge-transfer) band arise through solvent-dependent reorganizational barriers λ_0*[27,39–41] and, in the MLCT band, through solvent-dependent M–L interaction, as well as λ_0*. For asymmetric class II species such as[4b] $[(bpy)_2ClRu^{II}]pzRu^{III}(NH_3)_5^{4+}$ the differing solvent sensitivities of the two Ru redox sites lead to solvent-dependent MMCT energies (E^*)[27] superposed on the λ_0* variations. In selected asymmetric systems[4b,10] such as $[(bpy)_2ClOs]pzRu(NH_3)_5^{4+}$ the differing solvent sensitivities of the redox moieties may be used to adjust the redox equilibrium

$$Os^{III}\text{–}Ru^{II} \rightleftharpoons Os^{II}\text{–}Ru^{III}$$

to one side or the other. However, among the most interesting of recent applications of solvent effects is the indication that when solvent is used to adjust E^* for MMCT to $\sim$0 in the above system, the mixed-valence ion becomes class III (delocalized).[10] In the present work, the results obtained for the pentaammine monomers indicate that solvent strongly influences the $(NH_3)_5M$–L back-bonding interaction. Results such as those presented in Figure 5 lead to the expectation that it might be possible to solvent-tune the nature of *symmetric* mixed-valence complexes. For example, $[M(NH_3)_5]_2pz^{5+}$ might undergo a transition from class II in nitromethane (low DN, maximal δ_{π^*}, minimal back-bonding) to class III in DMSO (high DN, minimal δ_{π^*}, maximized back-bonding) or $[M(CO)_5]_2pz^+$ might undergo a class II to III transition on changing from DMSO to nitromethane. As discussed above, such tuning is not found for $[Ru(NH_3)_5]_2pz^{5+}$. However, for other metal (ligand) combinations it may be achievable. The study of such transitions in symmetric species could yield a deeper understanding of delocalization mechanisms in bridged mixed-valence systems and lead to a better description of the localized-to-delocalized transition.

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(38) Encouraging in this regard is the fact that Figure 2b provides simple assignments for the binuclear 4+ and 5+ osmium complexes[37a] if the N molecular orbital is placed *below* the n levels (consistent with little Os πd–pyrazine $\pi\psi_3$ interaction, but some πd–pyrazine $\pi^*\psi_6$ interaction). Then for $[Os(NH_3)_5]_2pz^{n+}$ the above model yields the following assignments: (n = 4) 530 nm, N → A; 770 nm, n → A; (n = 5) 500 nm, N → A; 612 nm, n → A; 890 nm, B → n; $\sim$3000 nm, N → n.

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