

Infrared Activity of Symmetric Bridging Ligand Modes in Pyrazine-Bridged Hexaruthenium Mixed-Valence Clusters

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A fully symmetric (A_g) vibrational mode of pyrazine is observed in the infrared spectrum of four pyrazine-bridged hexaruthenium mixed-valence complexes with varying degrees of electronic coupling between clusters. Deuteration of the bridging pyrazine ligand and the accompanying shift in frequency confirm the assignment of this mode. Previous observation of infrared line coalescence in the carbonyl stretching region assigns all of these complexes to Robin–Day class II (partial localization of charge) on the picosecond time scale. The infrared activity of the fully symmetric bridging ligand mode could provide a complementary assignment of these complexes to class II on a faster, femtosecond time scale. However, the extinction coefficient for this band is much greater than that observed in similar asymmetric, non-mixed-valence complexes and suggests that its strong IR activity is due to vibronic enhancement rather than electronic asymmetry.

A number of pyrazine-bridged, two-center mixed-valence complexes have been reported in the literature.^{1–9} The infrared (IR) activity of various symmetric modes of pyrazine (pz) in some of these complexes (including the Creutz–Taube ion, $(\text{NH}_3)\text{Ru}(\mu\text{-pz})\text{Ru}(\text{NH}_3)^{5+}$,⁵ and some Os analogues^{2,3}) has been interpreted as evidence for electronic asymmetry on the time scale of the lifetime of those normal modes. This electronic asymmetry suggests a possible

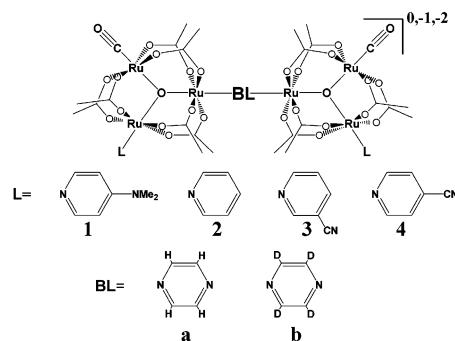


Figure 1. Pyrazine-bridged dimers of carbonyl-substituted trinuclear ruthenium complexes with varying ancillary pyridyl ligands, **L**.

classification of these complexes as Robin–Day¹⁰ class II, or partially localized, mixed-valence complexes.

We have reported IR line coalescence in the Ru-bound C–O stretching peaks of the mixed-valence clusters $\{\text{Ru}_3\text{O}(\text{OAc})_6(\text{L})(\text{CO})\}_2(\mu\text{-pz})^{1-}$ [where **L** = 4-(dimethylamino)pyridine (**1a**), pyridine (**2a**), 3-cyanopyridine (**3a**), or 4-cyanopyridine (**4a**)]^{11–13} (Figure 1). The shape of these IR bands (Figure 2 and Figure 3, for example) has been interpreted in terms of dynamic exchange on the infrared time scale: this interpretation implicitly assigns all of these complexes to class II with varying strength of electronic coupling and varying rates of electron transfer between Ru_3O clusters. Figures 2a and 3a present respective examples of this phenomenon in pyrazine-bridged compounds with stronger (**1a**) and weaker (**4a**) electronic coupling between the two clusters.

IR activity of symmetric pyrazine modes exists in the full IR spectra of the (-1) mixed-valence oxidation states, but the active $\nu_{8a}(\text{pz})$ band (which is the most intense of these bands) in particular is overlapped with cluster acetate bands and is not unambiguously clear. Isotopic substitution of

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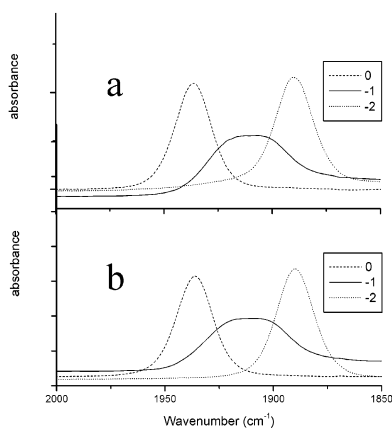


Figure 2. Infrared spectroelectrochemistry in the region 2000–1850 cm^{-1} of (0), (–1), and (–2) oxidation states of **1a** (a) and **1b** (b). Coalescence of C–O stretching vibrational lines has been interpreted as evidence of electron transfer on the time scale of vibrational spectroscopy. Deuteration of the pyrazine bridge has no observable effect on the coalesced line shape.

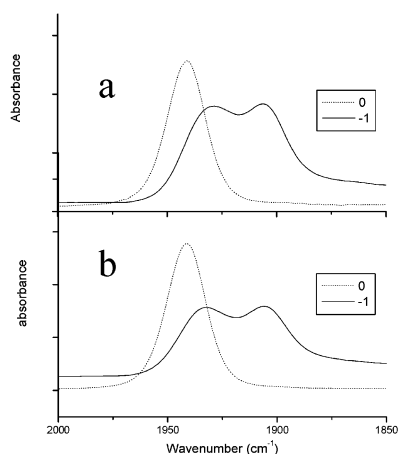


Figure 3. Infrared spectroelectrochemistry in the region 2000–1850 cm^{-1} of (0) and (–1) oxidation states of **4a** (a) and **4b** (b). As in **1a** and **1b**, deuteration of the pyrazine bridge appears to have little or no observable effect on the coalesced line shape.

pyrazine was used to shift this mode in frequency to avoid substantial overlap with the acetate bands.

Synthesis of hexaruthenium clusters with pyrazine- d_4 as bridging ligand (**1b**–**4b**)¹⁴ was achieved following the “cluster as complex, cluster as ligand” scheme reported previously,¹⁵ with pyrazine- d_4 used as received from Aldrich. IR spectroelectrochemistry¹⁶ of three different oxidation states (0, –1, –2) of these clusters reveals spectral changes

(14) Characterization of **1b**–**4b**. **1b**. Calcd for $\text{Ru}_6\text{C}_{44}\text{H}_{56}\text{D}_4\text{O}_{28}\text{N}_6$: C, 31.10; H, 3.30; N, 4.95. Found: C, 30.83; H, 3.46; N, 4.79. ^1H NMR (400 MHz, CDCl_3): 8.96 (4H, dmap-*ortho*), 7.23 (4H, dmap-*meta*), 3.31 (12H, dmap CH_3), 2.20 (12H, acetate CH_3), 2.10 (12H, acetate CH_3), 1.93 (12H, acetate CH_3) ppm. **2b**. Calcd for $\text{Ru}_6\text{C}_{40}\text{H}_{46}\text{D}_4\text{O}_{28}\text{N}_4$: C, 29.20; H, 3.29; N, 3.41. Found: C, 27.99; H, 2.99; N, 3.02. ^1H NMR (400 MHz, CDCl_3): 8.99 (4H, py-*ortho*), 8.21 (2H, py-*para*), 8.09 (4H, py-*meta*), 2.23 (12H, acetate CH_3), 2.13 (12H, acetate CH_3), 1.99 (12H, acetate CH_3) ppm. **3b**. Calcd for $\text{Ru}_6\text{C}_{42}\text{H}_{44}\text{D}_4\text{O}_{28}\text{N}_6$: C, 29.76; H, 2.62; N, 4.96. Found: C, 28.68; H, 2.67; N, 4.34. ^1H NMR (300 MHz, CDCl_3): 8.99 (s, 2H, 2-H on 3-cpy), 8.90 (d, 2H, 6-H on 3-cpy), 8.34 (d, 2H, 4-H on 3-cpy), 8.20 (t, 2H, 3-cpy, 5-H on 3-cpy), 2.26 (12H, acetate CH_3), 2.19 (12H, acetate CH_3), 2.05 (12H, acetate CH_3). **4b**. Calcd for $\text{Ru}_6\text{C}_{42}\text{H}_{44}\text{D}_4\text{O}_{28}\text{N}_6$: C, 29.76; H, 2.62; N, 4.96. Found: C, 30.67; H, 2.98; N, 4.80. ^1H NMR (400 MHz, CDCl_3): 8.73 (4H, cpy-*ortho*), 8.21 (4H, cpy-*meta*), 2.23 (12H, acetate CH_3), 2.16 (12H, acetate CH_3), 2.01 (12H, acetate CH_3).

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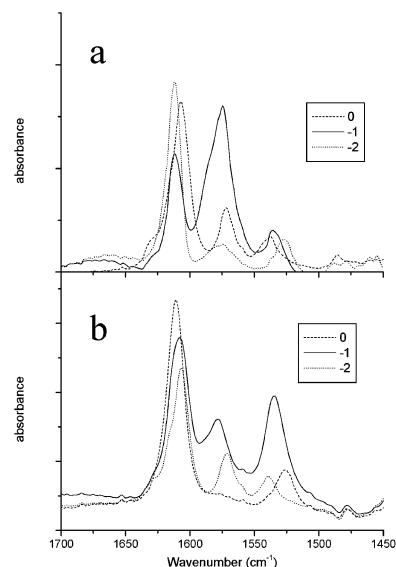


Figure 4. Infrared spectroelectrochemistry in the region 1500–1700 cm^{-1} of (0), (–1), and (–2) oxidation states of **1a** (a) and **1b** (b). A vibrational band unique to the (–1) mixed-valence state shifts in frequency upon deuteration of the bridging pyrazine ligand.

dependent on oxidation state. In the 1450–1700 cm^{-1} region of **1a** (Figure 4a), an absorption only present in the mixed-valence (–1) state is evident, but it is extensively overlapped with the cluster acetate peaks centered at 1579 and 1611 cm^{-1} . In the same region of the spectrum of **1b**[–] (Figure 4b), the absorption in question is shifted to 1535 cm^{-1} , and it is more clearly discernible by virtue of not being overlapped with the most intense acetate bands.

The magnitude of the isotopic frequency shift of the IR band present in only the mixed-valence infrared spectra permits its assignment as the ν_{8a} mode of pyrazine.^{17,18} In free pyrazine (D_{2h} symmetry) this mode is of A_g symmetry and is not IR active. Since both clusters to which pyrazine is a ligand are equivalent in the (0) and (–2) oxidation states of **1**–**4**, this mode remains IR inactive. An inequivalency of the two clusters in the (–1) mixed-valence state could lower the effective electronic symmetry and activate this particular mode.

1[–] is the most strongly coupled mixed-valence complex presented here: the electronic coupling in **1**[–]–**4**[–] is dependent on the donor strength of the ancillary pyridyl ligand, with 4-(dimethylamino)pyridine the strongest donor in **1** and 4-cyanopyridine the weakest in **4**.^{11,13} Since **1**[–] is the most strongly coupled and potentially most delocalized mixed-valence complex, similar IR activity of the A_g ν_{8a} pyrazine mode could be expected in **2**[–]–**4**[–]. Figure 5 shows that the same mode shows activity in the mixed-valence state of **4**, and the isotopic frequency shift in **4b**[–] matches that seen in **1b**[–]. The same behavior is observed in **2**[–] and **3**[–]. Band frequencies in all complexes are summarized in Table 1.

Since there is still some overlap with weak IR bands at almost the same frequency, it is not possible to report exact

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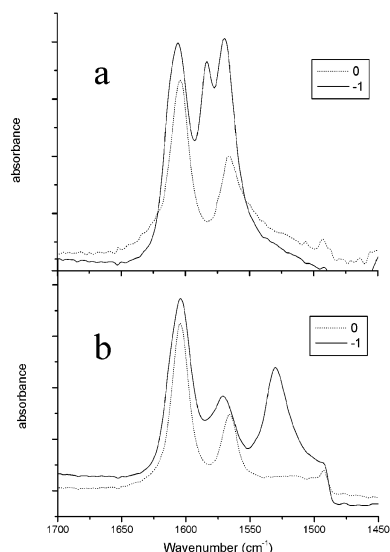


Figure 5. Infrared spectroelectrochemistry of (0) and (-1) states of **4a** (a) and **4b** (b). A similar vibrational band unique to the (-1) mixed-valence state shifts in frequency upon deuteration of pyrazine in the least strongly coupled pyrazine-bridged mixed-valence complex.

Table 1. Positions of Symmetric Pyrazine Vibrational Absorptions Unique to the (-1) Mixed-Valence States of **1a–4a** and **1b–4b**

complex	$\nu_{8a}(\text{pz})$ (cm^{-1})	complex	$\nu_{8a}(\text{pz-d}_4)$ (cm^{-1})
1a ⁻	1585	1b ⁻	1535
2a ⁻	1584	2b ⁻	1534
3a ⁻	1583	3b ⁻	1532
4a ⁻	1583	4b ⁻	1530

extinction coefficients for the ν_{8a} bands of pyrazine- d_4 in **1b**⁻–**4b**⁻. We are currently unable to quantify any difference in the extinction coefficients due to differences in strength of electronic coupling or rate of charge transfer from cluster to cluster, but this does not necessarily mean that there are not small differences which we cannot currently observe due to overlapping bands. It is significant to note, however, that the ν_{8a} band is much more intense than would be expected on the basis of a lowered symmetry at pyrazine alone. Although it is one of the most intense mid-IR bands in the spectra of **1**⁻–**4**⁻, the ν_{8a} band is very weak and not observable in “monomeric” trinuclear complexes $\{\text{Ru}_3\text{O}(\text{OAc})_6(\text{L})(\text{CO})\}\text{pz-d}_4$ and in the neutral, non-mixed-valence oxidation states of asymmetric hexanuclear complexes with two different ancillary pyridyl ligands, $\{\text{Ru}_3\text{O}(\text{OAc})_6(\text{L}_1)(\text{CO})\}(\mu\text{-pz})\{\text{Ru}_3\text{O}(\text{OAc})_6(\text{L}_2)(\text{CO})\}$ where $\text{L}_1 \neq \text{L}_2$. It has been suggested that the large extinction coefficient of this band in similar mixed-valence complexes is due to coupling to the charge-transfer process,^{19,20} and our observations are consistent with this suggestion. In addition to the above examples, the strong IR activity of formally symmetry-forbidden normal modes has been observed in Mulliken charge-transfer complexes²¹ and organic linear-chain conductors²² and attributed to charge-transfer induced vibronic

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enhancement of IR bands regardless of any lowered electronic symmetry.

It is also of interest to note in Figures 2b and 3b that there is little or no effect on the coalescence of C–O IR bands due to isotopic substitution of the pyrazine bridging ligand. This suggests either that the symmetric ν_{8a} pyrazine mode is not a participant in the nuclear reorganization which accompanies the electron transfer from cluster to cluster, or that the small frequency change due to the isotopic substitution is not significant enough to affect the electron-transfer rate as observed in the dynamic broadening of the C–O bands.

Previous estimates of electron transfer rate constants in these complexes based on the partially coalesced C–O infrared bands^{11–13} led to the conclusion that **1**⁻–**4**⁻ are class II species on the time scale of the dynamic spectral exchange process, for which the exchange frequencies have been estimated to be between 1×10^{11} and 2×10^{12} s⁻¹. The electron transfer rate constants have been shown to be strongly correlated with solvent relaxation on a similar time scale.¹¹ Since the vibrational period of the ν_{8a} mode of pyrazine is ca. 20 fs,⁸ an electronic asymmetry in the hexaruthenium clusters on that faster time scale is expected and the formerly A_g mode should be IR active. Indeed, these results provide an example of a mixed-valence system which, unlike previous examples,^{2,3,5} has already been assigned to class II on a slightly slower time scale by observations other than the IR activity of symmetric bridging ligand modes. However, the great intensity of the ν_{8a} band of pyrazine cannot be explained by symmetry-lowering due to localization of charge. The intensity is most likely indicative of the importance of the bridging ligand in mediating the coupling between clusters vis-à-vis a three-state vibronic model which explicitly includes a bridge-based state and symmetric bridge vibrations (which has been successfully applied theoretically^{23,24} and experimentally²⁵ to the Creutz–Taube ion). The success of this model as applied to resonance Raman spectroscopy and the little-acknowledged fact that it can predict the *infrared* activity of symmetric bridge modes due to vibronic coupling call into question the use of these bands to assign near-delocalized mixed-valence complexes to class II.⁸

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