Unusual Redox State Dependent Fermi Resonances in the Infrared Spectra of Trinuclear Ruthenium Clusters with Isocyanide Ligands

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We report unusual redox state dependent band shape effects in the infrared (IR) spectra of trinuclear ruthenium clusters containing terminal isocyanide ligands, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6\text{-}(L)_3]$ (L = xylyl isocyanide (**1**), *tert*-butyl isocyanide (**2**)).
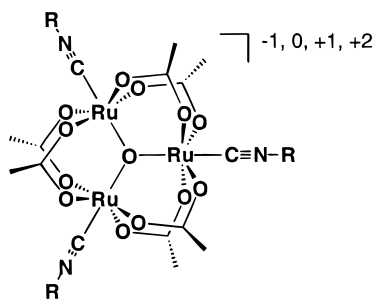
R = Xylyl (**1**), t-Butyl (**2**)

Recently we reported studies of intramolecular electron transfers within the mixed-valence states of the ligand-bridged hexaruthenium clusters $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CO)(L)(\mu\text{-}L')Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(CO)(L)]$ (L' = 1,4-pyrazine, 4,4′-bipyridine; L = substituted pyridine). These studies provided clear evidence of the coalescence of ν(CO) spectral features in the most rapidly exchanging systems.[1,2] In view of the similar properties of CO and isocyanides as ligands and the strong and tunable ν(C≡N) IR chromophore, we have prepared several related isocyanide-substituted trinuclear and ligand-bridged hexaruthenium clusters.[3]

The reflectance IR spectroelectrochemical responses of **1** in the −1, 0, +1, and +2 states[3] in the ν(C≡N) region are presented in Figure 1. Each of the four redox states is addressed by applying an appropriate potential to the working electrode on the basis of the known reduction potentials: $E_{1/2}(+2/+1)$ = +1.31, $E_{1/2}(+1/0)$ = +0.36, $E_{1/2}(0/-1)$ = −0.30 V vs SSCE.[3] In reflectance spectroelectrochemistry, the working electrode also serves as an optical mirror which directs IR radiation from the source, through the sample solution, to the detector.[4]
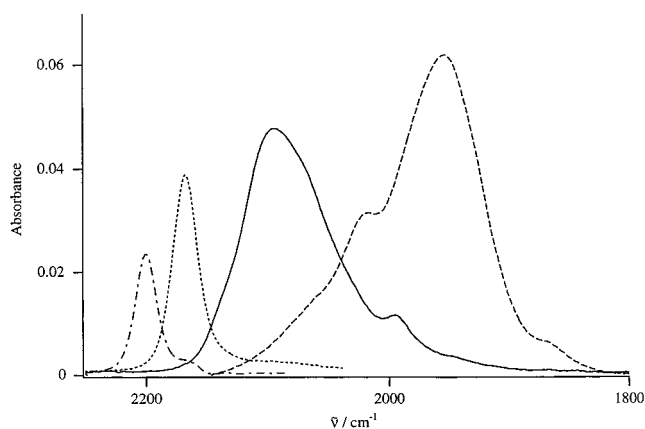
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Figure 1. Reflectance IR spectroelectrochemical responses for **1**^{n}, *n* = +2 (−·−), +1 (···), 0 (−), and −1 (- - -), in CH_2Cl_2 solution, with 0.1 M tetra-*n*-butylammonium hexafluorophosphate supporting electrolyte.

For the neutral isolated $Ru^{III}_2Ru^{II}$ (0) state, the IR spectrum in the ν(C≡N) region shows an unusually broad feature centered at 2094 cm^{-1} and a shoulder at 1990 cm^{-1}. The spectrum for the $Ru^{III}Ru^{II}_2$ (−1) state similarly shows a broad, intense feature centered at 1954 cm^{-1} and a shoulder at 2020 cm^{-1}. These results are in sharp contrast to the spectra of the Ru^{III}_3 (+1) and $Ru^{IV}Ru^{III}_2$ (+2) states, which exhibit single narrow Gaussian bands at 2168 and 2200 cm^{-1}, respectively. The solid-state samples (KBr) show similar spectra overall for the neutral (**1**) and +1 states (**1**$^+$) when compared to those in solution. We have considered whether structural isomerism or structural distortions were contributing to the broad and complex IR line shapes for the neutral and −1 states. Complexes **1** and **1**$^+$ were obtained as crystalline samples, and their crystal and molecular structures were determined by X-ray diffraction.[5] Neither the structure of **1** nor that of **1**$^+$ displays any irregularities. The molecular structures are nearly 3-fold symmetric, and bond distances and angles are normal. The structural comparison of **1** vs **1**$^+$ reveals slightly shorter Ru⋯Ru (3.342(1) Å vs 3.363-(1) Å), Ru−(μ_3-O) (1.926(4) Å vs 1.942(6) Å), and Ru−CNXy (1.991(8) Å vs 2.040(10) Å) distances and slightly longer Ru−O(acetate) (2.044(7) Å vs 2.004(7) Å) distances. The structures of **1** and **1**$^+$ do not provide a clue as to why the ν(C≡N) normal modes should deviate from the usual A_1 + E modes, which would produce an IR spectrum with one (E) band.

We have seriously considered two possible explanations for the structured broad ν(C≡N) bands that only appear for the neutral and −1 states. First, in view of recent reports of the effects of rapid electron transfer on vibrational spectra,[1,2] we considered the possibility of dynamic line broadening of bands associated with the trapped-valence states. These compounds are formally $Ru^{III}_2Ru^{II}$ in their neutral state, and their electronic

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(5) Crystal data for **1**·3C₆H₅NO₂: green prismatic, monoclinic space group *C2/c* (No. 15), a = 25.812(2) Å, b = 15.161(1) Å, c = 17.298(1) Å, β = 113.624(1)°, V = 6202.3(7) Å³, Z = 4; R = 0.067. Crystal data for **1**(CF₃SO₃)·2CF₃SO₃H·CH₃CN·H₂O: green prismatic, orthorhombic space group *Pca2₁* (No. 29), a = 23.42(1) Å, b = 11.645(7) Å, c = 22.620(7) Å, V = 6170(4) Å³, Z = 4; R = 0.053. Details of the crystal structures are reported as Supporting Information at http://pubs.acs.org.

absorption spectra show intense intracluster charge-transfer bands.[3] This explanation, however, seems unlikely since the $Ru^{IV}Ru^{III}_2$ (+2) states, which could also involve intracluster charge transfer, show nothing unusual in their IR spectra. Second, we considered Fermi resonance as an explanation for the structured broad bands. Isocyanide ligands are known to exhibit Fermi resonances in their IR spectra involving the ν-($C\equiv N$) mode and an overtone of another ligand-based mode with the appropriate energy. In the case of the series of methyl isocyanide capped nickel trimers, Fermi resonance was established between the $\nu(C\equiv N)$ fundamental and $2\nu(C-NMe)$.[6] Our initial assumption was that this holds for xylyl isocyanide ligands as well. To identify candidate overtones for Fermi resonance with the $\nu(C\equiv N)$ fundamental, we performed ab initio DFT calculations on the free xylyl isocyanide ligand. The geometry of the molecule was optimized first at the BLYP/6-31+G(d) level of theory.[7,8] The computed IR spectrum was found to be an excellent match to the experimental spectrum. The calculation shows that the single-bond stretch $\nu(C-N)$ lies too low in energy (801 cm^{-1} experimental, 791 cm^{-1} calculated) for its overtone to interact by Fermi resonance with the triple-bond $\nu(C\equiv N)$ fundamental at 2117 cm^{-1}. In the free isocyanide molecule, there is no normal mode of appropriate energy to mix appreciably with the $\nu(C\equiv N)$ mode at 2117 cm^{-1}. This makes it clear why free xylyl isocyanide does not exhibit a Fermi resonance. The situation changes when the $\nu(C\equiv N)$ frequency decreases as a result of complexation to ruthenium. Although the C−N single-bond stretch still lies too low in energy (the lowest energy ν-($C\equiv N$) band is 1954 cm^{-1} for **1**$^-$), there are several other modes that could enter into Fermi resonances with the $\nu(C\equiv N)$ fundamental. As always, the strength of these interactions will depend on the interaction potentials and spatial proximity to the $C\equiv N$ group. The overtone of the B_2 (assuming C_{2v} symmetry) mode at 1021 cm^{-1} (1038 cm^{-1} experimentally) in particular is interesting since it might be expected to resonate with $\nu(C\equiv N)$ fundamentals of both **1** at 2094 cm^{-1} and **1**$^-$ at 2010 (shoulder) cm^{-1}. The frequencies of this mode are expected to be similar for free xylyl isocyanide (1038 cm^{-1}), **1**, and **1**$^-$ since this mode involves a normal coordinate with a primarily $C\equiv N-C$ bending component. The other modes in this frequency range do not involve atomic displacements near the $C\equiv N$ group. The dual requirements for Fermi resonance, energy match of an overtone (or combination band) with another fundamental and spatial proximity of the interacting modes, are fulfilled by the assumption that the overtone of the $C\equiv N-C$ bending mode interacts with the $\nu(C\equiv N)$ fundamental in the 0 and −1 states. The $\nu(C\equiv N)$ bands of **1**$^+$ (2168 cm^{-1}) and **1**$^{2+}$ (2200 cm^{-1}) are shifted to higher energy, so that the Fermi resonance with the bending mode dissipates.

The IR spectra of **2** in the −1, 0, +1, and +2 states in the $\nu(C\equiv N)$ region are shown in Figure 2.[9] The broad, structured bands for the −1 state (2028 cm^{-1} with a shoulder at 2080 cm^{-1}) and the 0 state (2131 cm^{-1} with a shoulder at 2060 cm^{-1}) and the narrow Gaussian bands for the +1 (2195 cm^{-1}) and
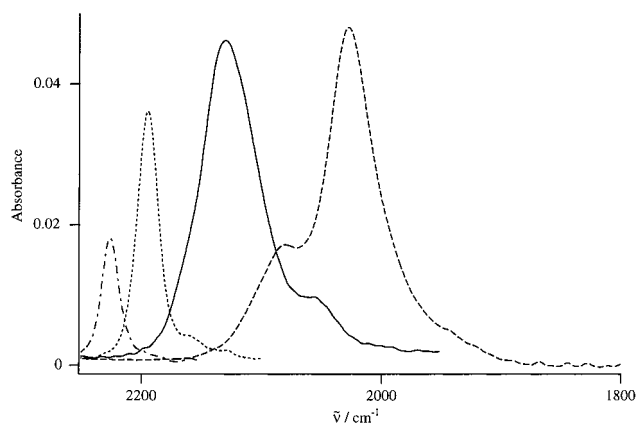

Figure 2. Reflectance IR spectroelectrochemical responses for **2**^{n}, n = +2 (−·−), +1 (···), 0 (—), and −1 (- - -) in CH$_2$Cl$_2$ solution, with 0.1 M tetra-n-butylammonium hexafluorophosphate supporting electrolyte.

+2 states (2225 cm^{-1}) are evident. Even though the IR bands of **2** are shifted higher in energy for each of the four oxidation states by 30−70 cm^{-1}, as expected for an alkyl vs aryl isocyanide, the observed behavior is very similar to that for **1**. Since the details of the normal modes for xylyl vs *tert*-butyl isocyanide are vastly different, it was surprising to find that the *tert*-butyl isocyanide compound **2** exhibits IR spectra that are so strikingly similar to those for **1**, *in all four redox states*. We considered that there was a normal mode of *tert*-butyl isocyanide that was perhaps not identical to the participant mode in xylyl isocyanide but at least similar enough to explain the similar spectroscopic behavior. Ab initio DFT calculations performed for free *tert*-butyl isocyanide offered a possible basis for a Fermi resonance in the neutral and reduced states of **2** but not for the +1 and +2 states. The overtone of the E mode at 1035 cm^{-1} (1042 cm^{-1} experimentally) can undergo Fermi resonance with the fundamental of **2** at 2131 cm^{-1} or **2**$^-$ at 2028 cm^{-1}. This mode also has a $C\equiv N-C$ bending component similar to the B_2 mode in xylyl isocyanide. There are a number of other normal modes that have the right energy to interact through Fermi resonance with $\nu(C\equiv N)$ for the +1 and +2 states of both **1** and **2**. None of these modes, however, involve the bending of the $C\equiv N-C$ group. We believe that this bending mode has unusually high coupling to the $\nu(C\equiv N)$ fundamental because of its close spatial proximity. This bending mode is critical for Fermi resonance to occur. Despite other differences, the energies of this mode happen to be similar in both xylyl isocyanide and *tert*-butyl isocyanide. One way to break the Fermi resonance interaction is to shift the frequency of the fundamental by oxidation of **1** or **2** to the +1 or +2 state.

Finally, we note that the usual way of investigating Fermi resonances is to shift participating normal-mode frequencies by isotope substitution. In the present case, the rich redox chemistry of the $Ru_3(\mu_3$-O) clusters offers a convenient means of effecting shifts in the energy of $\nu(C\equiv N)$ bands of coordinated isocyanide ligands, in and out of Fermi resonance.

Experimental Section

Synthesis of [Ru$^{III}_3$(μ_3-O)(CH$_3$CO$_2$)$_6$(CNXy)$_3$](PF$_6$) (1$^+$PF$_6$$^-$). The parent compound, [Ru$^{III}_2$Ru^{II}(μ_3-O)(CH$_3$CO$_2$)$_6$(CNXy)$_3$] (**1**), was prepared according to the reported method.[3] To a CH$_2$Cl$_2$ solution (50

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(9) Cyclic voltammetry data for **2** in 0.1 M *t*-Bu$_4$NPF$_6$/CH$_2$Cl$_2$ solution: $E_{1/2}(+2/+1)$ = +1.24, $E_{1/2}(+1/0)$ = +0.22, $E_{1/2}(0/-1)$ = −0.58 V vs SSCE.

cm^3) of **1** (50 mg) were added 1 equiv of AgPF$_6$ and a methanolic solution (20 cm^3) of NH$_4$PF$_6$ (1 equiv). The solution was stirred for 30 min in the dark. The color of the solution turned from green to dark green. The resultant solution was evaporated to dryness on a rotary evaporator, the residue was dissolved in a minimal amount of CHCl$_3$, and insoluble materials were removed by filtration. The remaining solution was chromatographed over silica gel (Wakogel C-200) with CHCl$_3$/C$_2$H$_5$OH (98/2, v/v) as the eluting agent. The main dark green fraction was collected and evaporated to dryness. The residue was dissolved in a small amount of CHCl$_3$, and excess *n*-hexane was added to the solution. The deep blue precipitate of **1**(PF$_6$) was isolated by filtration. Yield: 36 mg (63%). Anal. Calcd for **1**(PF$_6$): C, 38.65; H, 3.74; N, 3.47. Found: C, 39.10; H, 3.81; N, 3.51. UV−vis (CH$_3$CN) λ_{max}/nm (ϵ_{max}/cm^{-1} M^{-1}): 734 (9730), 268 (36 600). IR (KBr pellet): ν(CN) = 2168 cm^{-1}. ^{1}H NMR in CD$_3$CN (δ vs TMS): 0.40 (18H, isocyanide methyl), 5.95 (3H, CNXy-*p*), 6.35 (6H, CNXy-*m*), 7.42 (18H, acetate methyl).

Synthesis of [Ru$^{III}_2$Ru^{II}(μ_3-O)(CH$_3$CO$_2$)$_6$(CN-*t*-Bu)$_3$]·H$_2$O (2·H$_2$O). A chloroform solution (50 cm^3) containing [Ru$^{III}_2$Ru^{II}(μ_3-O)(CH$_3$CO$_2$)$_6$(CO)(EtOH)$_2$]^{10} (100 mg) and CN-*t*-Bu (9 equiv) was stirred at 40 °C for 2 d. The color of the solution turned from violet to blue-green. The resultant solution was evaporated to dryness on the rotary evaporator, the blue-green residue was dissolved in a minimal amount of CHCl$_3$, and insoluble materials were filtered off. The solution was chromatographed over silica gel (Wakogel C-200; $\varnothing$ = 2 cm, l = 15 cm) with CHCl$_3$/C$_2$H$_5$OH (96/4, v/v) as the eluting agent. The main green band was collected and evaporated to dryness. Yield: 36 mg (63%). Anal. Calcd for **2**·H$_2$O: C, 34.37; H, 5.04; N, 4.47. Found: C, 34.49; H, 4.64; N, 4.47. IR (KBr pellet): ν(CN) = 2132 cm^{-1}. ^{1}H NMR in CDCl$_3$ (δ vs TMS): 1.79 (27H, isocyanide methyl), 2.17 (18H, acetate methyl).

Synthesis of [Ru$^{III}_3$(μ_3-O)(CH$_3$CO$_2$)$_6$(CN-*t*-Bu)$_3$](PF$_6$) (2$^+$PF$_6^-$). To a CH$_2$Cl$_2$ solution (20 cm^3) of **2**·H$_2$O (30 mg) was added a methanolic solution (20 cm^3) containing AgPF$_6$ (1 equiv) and NH$_4$PF$_6$ (1 equiv). The solution was stirred for 30 min in the dark, during which its color turned from green to blue. The resultant solution was evaporated to dryness on the rotary evaporator. The blue residue was dissolved in a minimal amount of CHCl$_3$, and insoluble materials were filtered off. The remaining solution was chromatographed over silica gel (Wakogel C-200; $\varnothing$ = 2 cm, l = 15 cm) with CHCl$_3$/C$_2$H$_5$OH (97/3, v/v) as the eluting agent. The main blue band was collected and evaporated to dryness, giving a blue product. Yield: 20 mg (58%). Anal. Calcd for **2**(PF$_6$): C, 30.37; H, 4.25; N, 3.94. Found: C, 30.22; H, 4.11; N, 3.90. IR (KBr pellet): ν(CN) = 2194 cm^{-1}. ^{1}H NMR in CD$_3$CN (δ vs TMS): −0.54 (27H, isocyanide methyl), 7.13 (18H, acetate methyl).

Reflectance Infrared Spectroelectrochemistry. IR spectral changes accompanying thin-layer bulk electrolyses were measured using a temperature controlled flow-through reflectance spectroelectrochemical cell.^{4} Path lengths were typically 0.1 mm. The controlled potentials were measured vs an Ag pseudoreference electrode (ca. −0.06 V vs SCE). Spectroelectrochemical experiments were carried out in 0.1 M tetra-*n*-butylammonium hexafluorophosphate solutions using freshly distilled dichloromethane. All solutions were prepared under an atmosphere of nitrogen and deoxygenated completely by N$_2$ gas before injection into the spectroelectrochemical cell. Blank reference solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate were used for Fourier transform IR solvent subtractions. All measurements were performed at room temperature except those for the **2**$^-$ state, which were carried out at −30 °C. The potential was applied with a Hokuto-Denko potentiostat/galvanostat, model HA-501. The IR spectra were acquired on a Jasco IR-810 spectrophotometer.

DFT Calculations. All calculations were performed using the Gaussian 94 program package, available on Purdue University Chemistry Department workstations, or the computing cluster of the Purdue University Computing Center, model IBM RISC 6000/595, which run the D.2 revision of Gaussian 94. The BLYP DFT method was chosen because its calculated vibrational frequencies do not have to be scaled. Calculations with the improved B3LYP potential were also performed, but these results are less reliable because of the uncertainties associated with the scaling factor. A 6-31+G(d) basis set was found to predict vibrational spectra in very good agreement with experimentally determined spectra in a reasonable amount of CPU time. Calculations with significantly larger basis sets (up to 6311++3df,3pd) were also undertaken, but they did not lead to significantly different results. All calculations of IR transition energies and force constants were performed analytically. Geometry optimizations were performed with the "symm=loose" option, which identifies the correct point group even if the initial molecular symmetry is slightly different from that point group. All geometry optimizations were run by starting with several different initial parameter settings to ensure that the global minimum of optimization was reached.

Supporting Information Available: Tables of X-ray experimental details, bond distances, and bond angles, ORTEP drawings of **1** and **1**$^+$, and Gaussian 94 outputs for the DFT calculations of the vibrational spectra of xylyl isocyanide and *tert*-butyl isocyanide. This material is available free of charge via the Internet at http://pubs.acs.org.

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