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# The Onset of Band-Like Properties in the Ligand-Bridged, Trimeric Cluster $\{[(py)_2Ru_3O(OAc)_6(pyr)]_2[Ru_3O(OAc)_6(CO)]\}$

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**Abstract:** The ligand-bridged trimeric cluster $\{[(py)_2Ru_3O(CH_3CO_2)_6(pyr)]_2[Ru_3O(CH_3CO_2)_6(CO)]\}(PF_6)_2$ (py = pyridine, pyr = pyrazine) has been prepared by a reaction between the monomeric clusters $[Ru_3O(CH_3CO_2)_6(py)_2(pyr)]^+$ and $[Ru_3O(CH_3CO_2)_6(CH_3OH)_2(CO)]$. Electrochemical studies show that the trimer has an extraordinary degree of reversible electron-transfer chemistry. Its optical and redox properties are of interest when compared to those of the monomer units which make it up. When its total electron content is low, which is the case, for example, in the 2+ ion mentioned above, its properties are those expected for isolated cluster units where intercluster electronic interactions are weak. However, the results of electrochemical studies suggest that as electron content increases, electronic coupling between the cluster sites is enhanced and the appearance of a series of closely spaced, one-electron waves may signal the appearance of band-like behavior in this discrete chemical system.

## Introduction

The tri-$\mu$-oxo-carboxylate-bridged cluster system $[Ru_3O(OAc)_6(py)_3]^{3+/2+/+/0/-}$ (OAc is acetate; py is pyridine) (Figure 1) is remarkable for the extent of its reversible redox chemistry.[1-3] Spectral studies suggest that the observed "electron-sponge"-like behavior is based on the gain or loss of electrons from molecular levels which are delocalized over the $Ru_3O$ core.[2] The molecular complexity of such systems can be extended since we recently devised synthetic procedures for linking cluster units through bridging ligands as in the dimer i. It is now clear that a systematic synthetic chemistry is available for preparing higher oligomers.

i

One of our long-term interests in molecularly complex metal systems is the possibility of observing and controlling transitions in properties from those of discrete molecules in solution to those more normally associated with the infinite systems of the solid state. In the process of building up higher oligomers based on the ruthenium clusters, an important synthetic intermediate has turned out to be the cluster trimer $[(py)_2Ru_3O(OAc)_6(pyr)]_2[Ru_3O(OAc)_6(CO)]^{2+}$ (Figure 2). We report here the preparation and properties of the trimer for two reasons. One is that linking together the clusters results in the creation of a chemical system which has truly remarkable, reversible electron-transfer properties. The second is that when electron rich, the properties of the trimer are consistent with the beginnings of a band-like electronic structure which may be realizable in higher oligomers.

## Experimental Section

**Measurements.** Electrochemical measurements made were vs. the

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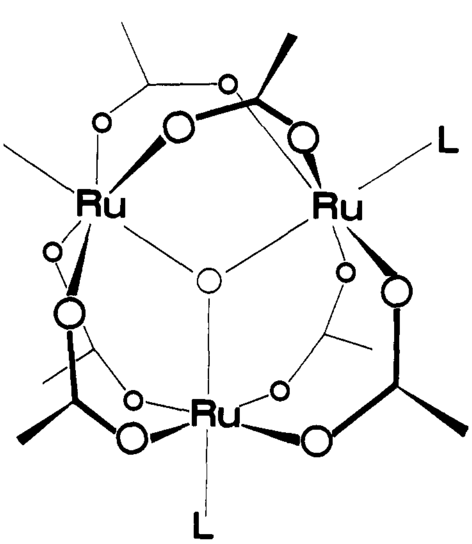


**Figure 1.** Structure of the cluster unit $[Ru_3O(CH_3CO_2)_6(L)_3]$.

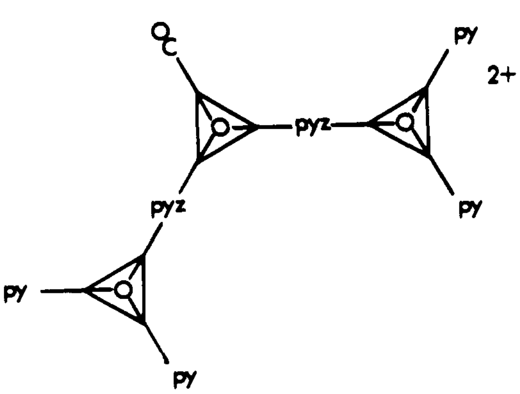


**Figure 2.** Schematic structure of the trimer $\{[(py)_2Ru_3O(OAc)_6(pyr)]_2[Ru_3O(OAc)_6(CO)]\}^{2+}$ (Δ represents the triangular cluster unit shown in Figure 1).

saturated sodium calomel electrode (SSCE) at 22 ± 2 °C and are uncorrected for junction potential effects. A PAR Model 173 potentiostat was used for potential control while a PAR Model 175 Universal Programmer was used as a sweep generator for cyclic voltammetry experiments. Electrochemical reversibility was determined by the ratio of cathodic to anodic peak currents ($i_{p,c}/i_{p,a} = 1$) and the potential separation of the anodic and cathodic peaks ($\Delta E_p$). All voltammetric measurements were carried out at platinum electrodes in solutions deaerated by a stream of dry argon, when necessary.

Ultraviolet, visible, and near-infrared spectra were recorded using Bausch and Lomb Model 210 and Cary Models 14 and 17 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer in KBr pellets at room temperature.

**Materials.** Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques, recrystallized three times from hot ethanol-water mixtures, and vacuum dried at 70 °C for 10 h. Acetonitrile (MCB spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical measurements and used without drying for spectral measurements. Water was deionized and then distilled from alkaline permanganate. All other solvents, which were reagent grade or better, were used without further purification. All pyrazine (pyr) was obtained commercially and used without further purification. Argon was purified by passing it through a heated column of activated catalyst R3-11 (Chemical Dynamics Corp.) and then through drying tubes containing Drierite. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn., and Integral Microanalytical Laboratories, Raleigh, N.C.

**Preparation.** $\mathbf{[Ru_3O(OAc)_6(CH_3OH)_3]^+}$ (**1**, OAc = $CH_3CO_2$). Details of the synthesis of this useful starting material appear elsewhere.[2,3] For isolation of the cluster, a methanol solution was reduced to a minimum volume and six volumes of acetone were added which precipitated the complex as the acetate salt. A blue-green powder was obtained by collecting the precipitate and washing it with ethyl ether, followed by air drying.

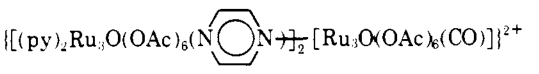
$\mathbf{[Ru_3O(OAc)_6(CO)(CH_3OH)_2]}$ (**2**). The blue-green powder **1**, $[Ru_3O(OAc)_6(CH_3OH)_3](OAc)$ (1.4 g), was dissolved in 100 mL of methanol. The solution was deaerated with argon for 30 min after which 10 g of Zn-Hg amalgam was added to the solution. The reaction was allowed to proceed for 3 h with argon bubbling which stirred the solution. The solution was filtered under argon and the argon atmosphere replaced by carbon monoxide. The yellow-green solution soon became purple. CO was passed through the solution for a total of 3 h, and it was stirred under an atmosphere of CO overnight. The solution was reduced to dryness using a rotary evaporator. The solid which remained was dissolved in a minimum of methanol. Four volumes of benzene were added and the solution was passed through a column of alumina. A purple band was eluted from the column using 20% methanol-benzene (by volume). A green band remained on the column. The purple solution was evaporated to dryness, redissolved in a minimum of hot methanol, and added to 14 volumes of stirring ligroin which precipitated the desired complex, yield 0.530 g (41%). Anal. Calcd for **2**, $Ru_3O_{16}C_{15}H_{26}$: C, 23.53; H, 3.42. Found: C, 22.87; H, 3.88.

$\mathbf{[Ru_3O(OAc)_6(CO)(pyr)_2]}$ (**3**). $[Ru_3O(OAc)_6(CO)(CH_3OH)_2]$ (111.9 mg, 0.146 mmol) was added along with 117 mg of pyrazine (1.46 mmol) to a closed flask containing 70 mL of $CH_3OH$. The resulting solution was stirred for several hours. The solvent was removed on a rotary evaporator and the residue was dissolved in $CH_2Cl_2$. Chromatography on alumina using $CH_2Cl_2$ as eluent gave an isolable blue fraction which was collected, leaving behind green-colored bands on the column. The blue solution was reduced to a minimum volume and filtered into stirred ligroin. The resultant precipitate was collected and air dried, yield 45.45 mg (36%). Anal. Calcd for $Ru_3O_{14}C_{21}H_{26}N_4$: C, 29.27; H, 3.04; N, 6.50. Found: C, 29.09; H, 3.00; N, 6.23.

$\mathbf{\{[Ru_3O(OAc)_6(py)_2(pyr)]_2[Ru_3O(OAc)_6(CO)]\}(PF_6)_2}$ (**4**). $[Ru_3O(OAc)_6(CO)(CH_3OH)_2]$ (**2**, 64 mg, 0.084 mmol) and 117.7 mg (0.168 mmol) of $[Ru_3O(OAc)_6(py)_2(pyr)](PF_6)^2$ were dissolved in 35 mL of $CH_2Cl_2$ which contained 5 mL of $CH_3OH$. The solution was stirred for 3 days in a stoppered flask after which the solvent was removed on a rotary evaporator without heating. The residue was dissolved in $CH_2Cl_2$ and chromatographed on Bio-Beads, S-X1 (Bio-Rad Laboratories). The first band, dark green in color, was collected and reduced to a minimum volume. A blue band, presumably containing $[Ru_3O(OAc)_6(py)_2(pyr)]^+$, was eluted from the column after the green band. The green solution was slowly added to 50 mL of stirred ligroin. The precipitate which appeared was collected, washed with ligroin and ethyl ether, air dried, and stored under vacuum, yield 160 mg (68%). Anal. Calcd for $Ru_9O_{40}C_{65}H_{82}N_8P_2F_{12}$: C, 27.73; H, 2.94; N, 3.98. Found: C, 27.90; H, 2.90; N, 3.77.

## Results and Discussion

The preparation of the cluster trimer ii (Figure 2) is



$$\{[(py)_2Ru_3O(OAc)_6(N\bigcirc N)]_2[Ru_3O(OAc)_6(CO)]\}^{2+}$$

ii

straightforward in that it involves the displacement of weakly bound methanol groups either from $[Ru_3O(OAc)_6(CO)(CH_3OH)_2]$ by $[Ru_3O(OAc)_6(py)_2(pyr)]^+$ (pyr is pyrazine) (eq 1) or from $[Ru_3O(OAc)_6(py)_2(CH_3OH)]^+$ by $[Ru_3O(OAc)_6(CO)(pyr)_2]$. Clusters like $[Ru_3O(OAc)_6(CO)(pyr)_2]$ and $[Ru_3O(OAc)_6(py)_2(pyr)]^+$ are of course able to act as ligands because only a single nitrogen site of the diazine ligand is bound.

$$\begin{aligned}&[Ru_3O(OAc)_6(CO)(CH_3OH)_2]\\&\quad + 2[Ru_3O(OAc)_6(py)_2(pyr)]^+\\&\rightarrow \{[(py)_2Ru_3O(OAc)_6(pyr)]_2\,[Ru_3O(OAc)_6(CO)]\}^{2+}\\&\qquad + 2CH_3OH \quad (1)\end{aligned}$$

$$\begin{aligned}&[Ru_3O(OAc)_6(CO)(pyr)_2]\\&\quad + 2[Ru_3O(OAc)_6(py)_2(CH_3OH)]^+\\&\rightarrow \{[(py)_2Ru_3O(OAc)_6(pyr)]_2\,[Ru_3O(OAc)_6(CO)]\}^{2+}\\&\qquad + 2CH_3OH \quad (2)\end{aligned}$$

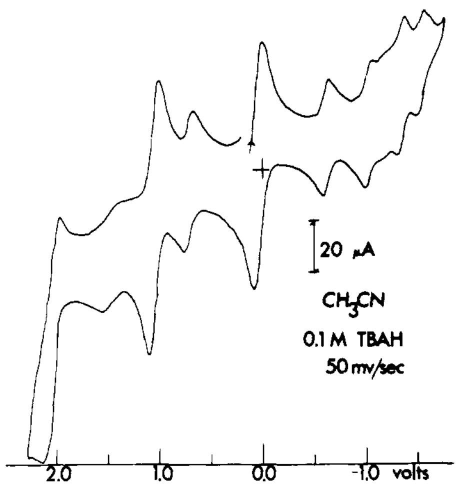


Figure 3. Cyclic voltammogram of $\{[(py)_2Ru_3O(OAc)_6(pyr)]_2[Ru_3O(OAc)_6(CO)]\}^{2+}$ at room temperature in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$-$CH_3CN$ vs. the SSCE at a scan rate of 500 mV/s.

**Table I.** Ultraviolet-Visible Spectra

| compd | $\lambda_{max}$, nm | $\epsilon$ | solvent |
|---|---|---|---|
| $Ru_3O(OAc)_6(CO)(MeOH)_2$ | 555 | 2650 | $CH_3OH$ |
| | 375 sh | 1900 | |
| | 227 | 15 200 | |
| | 580 | 3960 | acetone |
| | 575 | | $CH_3CN$ |
| $Ru_3O(OAc)_6(CO)(py)_2$[a] | 585 | 4590 | $CH_2Cl_2$ |
| | 345 | 6570 | |
| $Ru_3O(OAc)_6(CO)(pyr)_2$ | 593 | 6280 | $CH_2Cl_2$ |
| | 406 | 10 000 | |
| $\{[Ru_3O(OAc)_6(py)_2(pyr)]_2$-$[Ru_3O(OAc)_6(CO)]\}(PF_6)_2$[b] | 693 | 6935[b] | $CH_2Cl$ |
| | 630 sh | 6235[b] | |
| | 458 | 6270[b] | |
| | 325 sh | 6800[b] | |
| $[Ru_3O(OAc)_6(py)_2(pyr)]$[a] | 910 | 10 200 | |
| | 425 | 8870 | |
| | 393 | 9370 | |
| | 240 | 25 175 | |
| $[Ru_3O(OAc)_6(py)_2(pyr)](PF_6)$[a] | 692 | 6200 | |
| | 325 sh | 9560 | |
| | 243 | 21 800 | |

[a] Reference 2. [b] The $\epsilon$ value quoted is calculated per cluster unit.

**Table II.** Electrochemical Data on the Trimeric Cluster $\{[Ru_3O(OAc)_6(py)_2(pyr)]_2[Ru_3O(OAc)_6(CO)]\}(PF_6)_2$ and Related Monomeric Clusters in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$-$CH_3CN$ at 22 ± 2 °C vs. the SSCE[a]

| | $E_{1/2}$, V[b] | | | |
|---|---|---|---|---|
| trimer | $[Ru_3O(pyr)_2(CO)]$[b] | $[Ru_3O(py)_2(pyr)]^+$ | $[Ru_3O(py)_2(CO)]$ | $[Ru_3O(CH_3OH)_2(CO)]$ |
| 2.05[c] | | 2.03 | | |
| 1.49[d] | 1.36[e] | | 1.26 | 1.44 |
| 1.06 | | 1.04 | | |
| 0.72 | 0.69 | | 0.62 | 0.70 |
| 0.04 | | 0.00 | | |
| −0.63 | −0.66 | | −0.88 | −0.74[f] |
| −1.05 | | | | |
| −1.21[g] | −1.30 | | | |
| −1.37 | | −1.20 | | |
| −1.56 | | −1.88 | | |

[a] Saturated sodium chloride calomel electrode; sweep rate = 200 mV/s. [b] $[Ru_3O(L)_2L'] \equiv [Ru_3O(OAc)_6(L)_2L']$. [c] $\Delta E_p = 160$ mV. [d] $\Delta E_p = 120$ mV. [e] $\Delta E_p = 105$ mV. [f] $\Delta E_p = 112$ mV. [g] $\Delta E_p = 100$ mV.

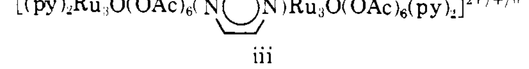
The preparation of the cluster trimer involves the assembly of a series of multiple electron redox sites by chemical binding. As can be seen by the cyclic voltammogram in Figure 3, the resulting material is spectacular in terms of the extent of its multiple electron transfer behavior. There is a series of ten one- or two-electron waves in the potential region from +2.2 to −1.7 V (in $CH_3CN$ vs. the SSCE). Given the extent of its reversible redox chemistry, the system surely deserves the epithet "electron sponge." In principle, the multiple redox behavior of such compounds could be exploitable to a number of ends including the establishment of potential ranges for biochemical redox couples which are not electrochemically active.

Perhaps the most interesting feature of the cyclic voltammogram in Figure 3 is the behavior at negative potentials where the electron content of the cluster sites is high. In this potential region a series of closely spaced one-electron waves appears which may signal the beginning of band-like behavior. A complete transition to a band-like state may occur in higher oligomers, and such materials may truly be capable of functioning as "floating" electrodes when dissolved in solution.

Actually, most of the features in the cyclic voltammogram in Figure 3 are more or less predictable given the properties of related dimers and of the component clusters which make up the trimer. Spectral data for the trimer and for related monomeric clusters are summarized in Table I and electrochemical data in Table II. The $E_{1/2}$ values in Table II were calculated from the average value of the anodic and cathodic peak potentials, $E_{1/2} = \frac{1}{2}(E_{p,a} - E_{p,c})$, for a given wave. The observed peak splittings were in the range 60-80 mV independent of sweep rate except for some excessively large peak splittings which are noted in Table II.

The spectral and redox potential data support the view that the cluster trimer contains weakly interacting $[Ru_3O(OAc)_6(py)_2]$- and -$[Ru_3O(OAc)_6(CO)]$- groups when the electron content of the system is relatively low. Earlier work has shown that compared to non-CO-containing clusters, CO clusters like $[Ru_3O(OAc)_6(CO)(py)_2]$ are electron deficient.[2] Intramolecular transitions between cluster electronic levels are shifted to higher energy ($\lambda_{max}$ at 910 nm for $[Ru_3O(OAc)_6(py)_2(pyr)]$ compared to 585 nm for $[Ru_3O(OAc)_6(CO)(py)_2]$) and the potentials for the cluster +2/+1, +/0, and 0/− couples are shifted from 1.04, 0.00, and −1.20 to 1.26, 0.62, and −0.88 V (Table II). The origin of the electron deficiency appears to lie in strong Ru to CO back-bonding which has a profound effect on the electronic structure of the cluster.[2]

In the low-energy visible spectral region where there is a series of intracluster electronic transitions,[2,4] the spectrum of the trimer (Figure 4) is essentially the sum of the spectrum of $[Ru_3O(OAc)_6(pyr)_2(CO)]$ and twice the spectrum of $[Ru_3O(OAc)_6(py)_2(pyr)]^+$. In the trimer, $\pi^*(pyr) \leftarrow$ cluster transitions are observed at 458 and 400 nm (sh) which are red shifted compared to bands at 406 and 385 nm for $[Ru_3O(OAc)_6(py)_2(pyr)]^+$ and $[Ru_3O(OAc)_6(py)_2(CO)]$. The red shift, which is also observed in the dimers iii,[4] has been


$$[(py)_2Ru_3O(OAc)_6(N\bigcirc N)Ru_3O(OAc)_6(py)_2]^{2+/+/0}$$

iii

attributed to stabilization of the Cluster to Ligand Charge Transfer (CLCT) excited state by a remote metal site.[5-7]

Cyclic voltammograms for the clusters $[Ru_3O(OAc)_6(CO)(pyr)_2]$ and $[Ru_3O(OAc)_6(py)_2(pyr)]^+$ are shown in Figure 5. When the voltammograms are added and certain special effects which arise in ligand-bridged dimers are taken into account, the redox properties of the cluster trimer can be understood from Figures 3 and 5 and the data in Table II.

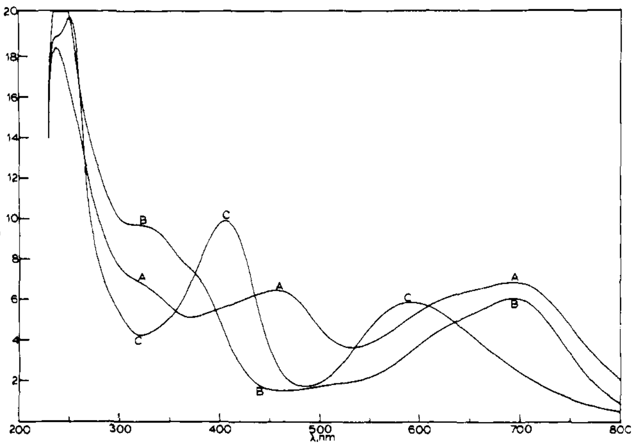
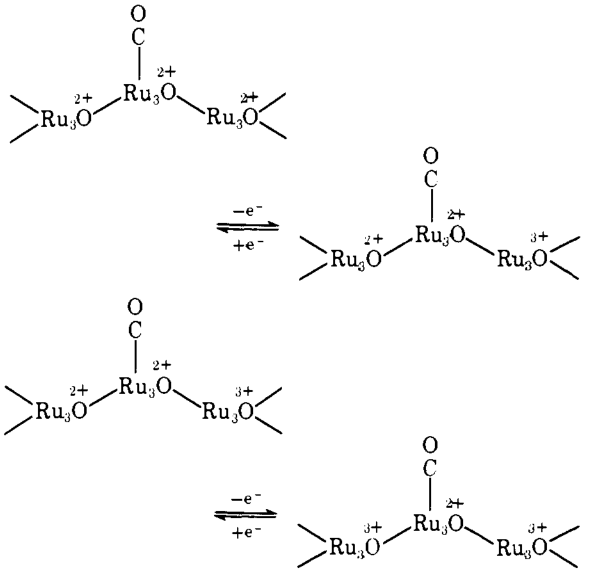


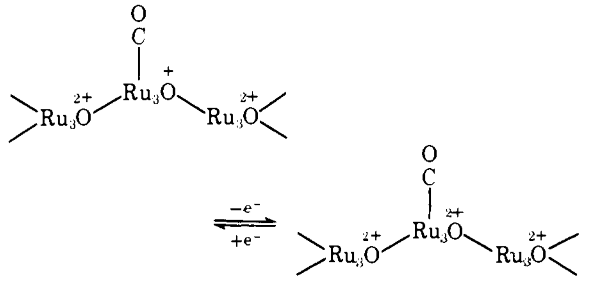
**Figure 4.** UV-visible absorption spectra in methylene chloride from 800 to 240 nm of (A) trimer; (B) $[Ru_3O(OAc)_6(py)_2(pyr)]^+$; (C) $[Ru_3O(OAc)_6(CO)(pyr)_2]$.

Starting at the most oxidizing potentials, the waves in the cyclic voltammogram in Figure 3 can be assigned to the following processes.

$E_{1/2}$ = **2.05 V (eq 3).** At this wave both the terminal cluster sites as 2+ ions $[(py)_2Ru_3O(OAc)_6]-^{2+}$ are oxidized to 3+ ions. The bridging cluster is in the 2+ state. Interactions between the terminal cluster sites are sufficiently weak that the two one-electron transfer processes are unresolvable by cyclic voltammetry.


(3)

$E_{1/2}$ = **1.49 V (eq 4).** An oxidation occurs at the bridging carbonyl cluster. The large peak splitting may be associated with loss of CO. The $[Ru_3O(OAc)_6(CO)(pyr)_2]^{+/0}$ couple is chemically reversible on the cyclic voltammetry time scale but, following oxidation to the + cluster, CO is displaced by a solvent molecule:[2]


(4)

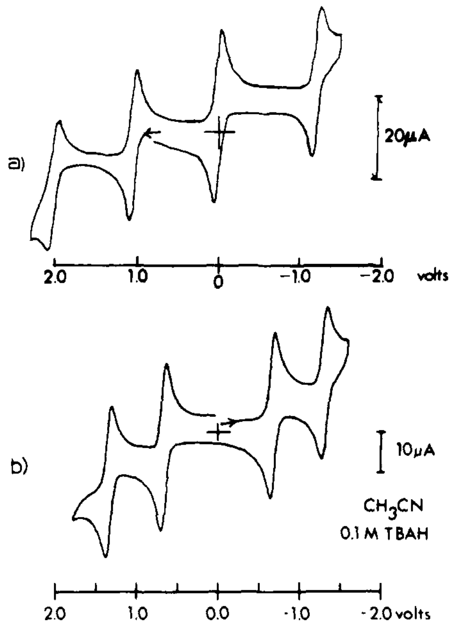
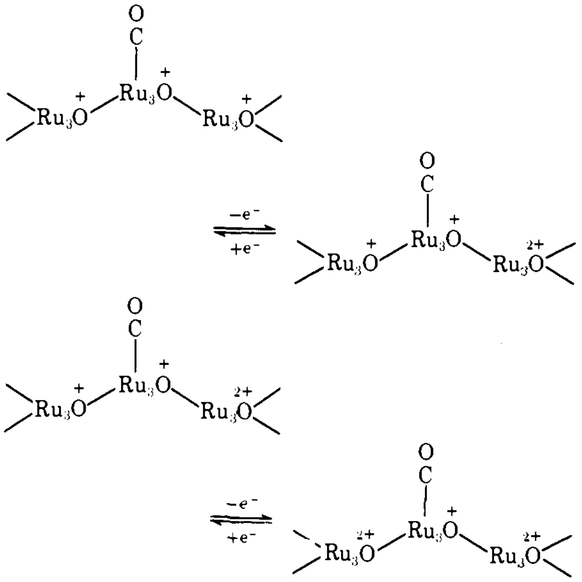


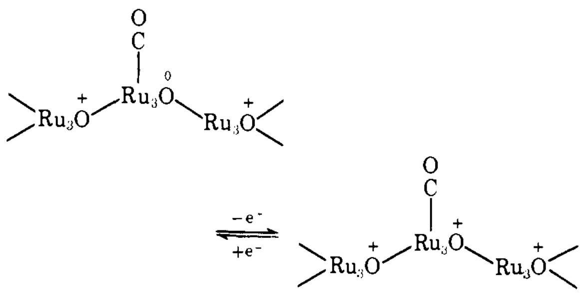
**Figure 5.** Cyclic voltammograms at room temperature in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)\text{-}CH_3CN$ at a scan rate of 500 mV/s vs. SSCE for (a) $[Ru_3O(OAc)_6(py)_2(pyr)]^+$; (b) $[Ru_3O(OAc)_6(pyr)_2(CO)]$.

$$[Ru_3O(OAc)_6(CO)(pyr)_2]^+ + CH_3CN \rightarrow Ru_3O(OAc)_6(pyr)_2(CH_3CN)]^+ + CO$$

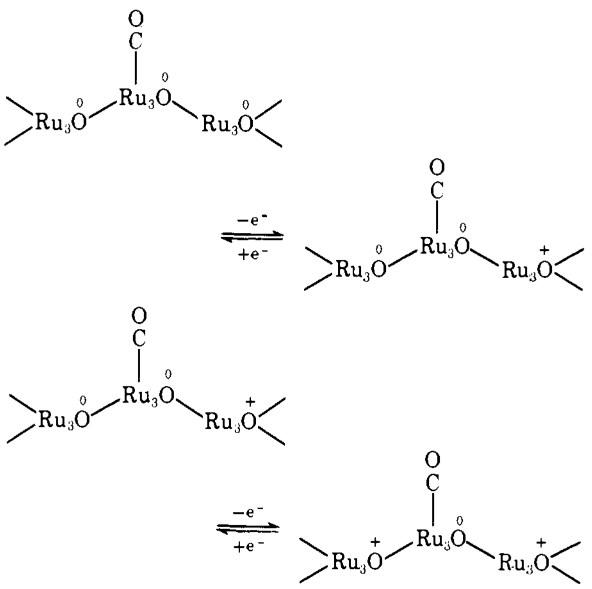
$E_{1/2}$ = **1.06 V (eq 5).** One-electron oxidation-reduction occurs at the two terminal clusters. The two one-electron waves are unresolvable by cyclic voltammetry.


(5)

$E_{1/2}$ = **0.72 V (eq 6).** One-electron oxidation-reduction occurs at the bridging carbonyl cluster.


(6)

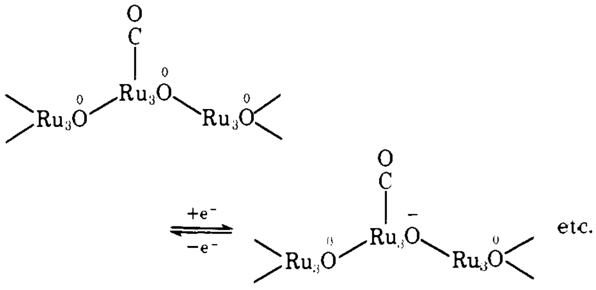
**$E_{1/2}$ = 0.04 V (eq 7).** In the pyrazine-bridged dimer i there



(7)

is a splitting of $\Delta E_{1/2}$ = 140 mV between the 2+/+ and +/0 waves indicating that significant cluster-cluster electronic interactions across pyrazine are beginning to appear. In the trimer, the terminal cluster-cluster separation is appreciably longer so that electrostatic effects, which do help determine the magnitude of the splitting,[5a] are relatively unimportant. If the large peak splitting of 85 mV observed for this wave arises from two one-electron waves which are nearly resolvable, there is an appreciable electronic interaction between the terminal clusters in the trimer as well.

**$E_{1/2}$ = −0.63, −1.05, −1.21, −1.37, −1.56 V (eq 8).** This

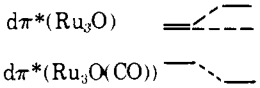


etc. (8)

series of five one-electron waves which occur within a potential range of 0.9 V signals the onset of band-like behavior. For the isolated clusters, reduction of $[Ru_3O(OAc)_6L_3]$ to $[Ru_3O(OAc)_6L_3]^-$ in the potential range −0.6 to −1.30 V involves the addition of electrons to the delocalized $Ru_3O$ levels, $d\pi^*(Ru_3O)$, which are largely antibonding in character with regard to the cluster core.[2,4] For the pyrazine complex $[Ru_3O(OAc)_6(py)_2(pyr)]^-$, a second reduction, apparently at $\pi^*$(pyr), occurs at −1.88 V.[2] In the absence of strong intercluster electronic interactions, it would be predicted from Table II that four waves should appear in the cyclic voltammogram, one-electron waves at −0.66 and −1.30 V and two closely spaced one-electron waves at ∼−1.20 V. In fact, there are five one-electron waves at −0.63, −1.05, −1.21, −1.37, and −1.56 V. There are no additional waves out to −2.0 V, the solvent background limit, and apparently the $\pi^*$(pyr) reductions are shifted cathodically and lost in the solvent background.

An inference that can be drawn from the data is that strong intercluster interactions begin to appear when the electron content of the system is high. The same observation has been made for the dimer i, where, as noted above, $\Delta E_{1/2}$ = 140 mV for the 2+/+ and +/0 couples, but for the 0/− and −/2− couples, $\Delta E_{1/2}$ increases to 270 mV.

It is reasonable that electronic interactions should increase with electron content. The antibonding $d\pi^*(Ru_3O)$ levels which are populated in the cathodic region are largely $d\pi$ in character, have spatial character along the bridging pyrazine ligands, and are near in energy to the $\pi^*$(pyr) levels. Strong cluster-cluster electronic interactions would then have their origin in $d\pi^*(Ru_3O)$-$\pi^*$(pyr)-$d\pi^*(Ru_3O)$ mixing. Mixing of the three sets of $d\pi^*(Ru_3O)$ orbitals would lead to a new set of molecular levels in which there is appreciable $\pi^*$(pyr) character.



Because of the redox asymmetry induced by the CO group and the two different chemical sites (bridging and terminal), the lowest level is probably largely $d\pi^*(Ru_3O(CO))$ in character. The first electron in the cathodic region would be added to this level followed by the addition of four more electrons to the manifold of closely spaced intercluster levels.

If the analysis given here is correct, the electrochemical experiments are very revealing. They suggest that cluster-cluster electronic interactions lead to a series of closely spaced one-electron levels. Although the spacings between levels are relatively large (∼200 mV), the implication is clear that we are observing the onset of band-like properties in a discrete chemical system. In oligomers containing a sufficient number of cluster sites, the spacings between levels may become small leading to true band properties and to metallic or semiconductor-like intramolecular conductivity properties in solution and/or in the solid state.

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