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Mixed-Valence State of a Pyrazine-Bridged Dimer of Oxocarboxylatotriruthenium Complexes with a Nitrosyl Ligand

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Supporting Information

ABSTRACT: Three new pyrazine-bridged dimers of oxoacetatotriruthenium with an NO ligand are synthesized. These complexes show two types of stable mixed-valence states. The ν(NO) stretches for five oxidation states were obtained, and the intramolecular electron-transfer rate within the mixed-valence state is evaluated from the IR spectral line-shape simulation based on Bloch-type analysis, which is the first application of this method to a spectator ligand of NO.

Intramolecular electron transfers are fundamentally important properties of mixed-valence complexes.[1] It is important to determine the intramolecular electron-transfer rates within mixed-valence complexes. Intramolecular electron-transfer rates have been semiclassically estimated by analyzing the intervalence charge-transfer band.[2] However, these estimations are based on certain assumptions, and thus the obtained rate constants are inherently inaccurate. We have recently developed a more direct method of estimating these rates from IR spectral line-shape simulation based on Bloch-type analysis.[3–9]

Previously, estimations of the electron-transfer rate within a mixed-valence[10] state were carried out for pyrazine (pz)-,[3–7] 4,4′-bipyridine-,[4] and bipyrimidine-bridged[8] oxoacetatotriruthenium dimers with CO as the spectator ligand. However, there have been quite a few reports of such estimations being carried out for compounds other than complexes with CO.[11,12]

To use a ligand as the spectator ligand for this method, the ligand must show a strong single peak in IR spectra, and the peak must show an appropriate shift when the complex is reduced or oxidized. Nitrosyl (NO^+), which is isoelectronic with CO, is a good candidate for this purpose. Oxoacetatotriruthenium complexes with an NO ligand, $[Ru_3O(CH_3CO_2)_6(NO)(L)_2](PF_6)$ (L = pyridine and 4-methylpyridine), have been reported by Toma and co-workers.[13] The NO ligand in these complexes acts as a "noninnocent ligand" whose redox, NO^+/NO^0, strongly interacts with a redox of the Ru_3 core. It is inappropriate to express a redox state in terms of an oxidation state of the Ru_3 core, such as $Ru^{III,III,III}$. For example, the monocation form of the complexes should be represented by the two contributing structures, $Ru^{III,III,III}NO^0$ and $Ru^{III,III,II}NO^+$. Therefore, for clarity, we describe the state as $\{Ru_3NO\}^{16}$, where the superscript stands for the number of electrons in the metal d and π^*(NO) orbitals; this expression is similar to that used by Enemark and Feltham.[14] These complexes have a single ν(NO) band at ca. 1870 cm^{-1}, and the band is shifted to ca. 1785 cm^{-1} upon reduction of the complexes. This behavior appears to be suitable for the IR spectral line-shape analysis of a mixed-valence state of a pz-bridged dimer with an NO ligand.

In this paper, we report the synthesis, cyclic voltammetry, and IR spectroelectrochemistry of pz-bridged dimers of Ru_3 complexes with an NO terminal ligand, $[\{Ru_3O(CH_3CO_2)_6(NO)(L)\}_2(\mu\text{-pz})](PF_6)_2$ [L = *N*,*N*′-dimethylaminopyridine (dmap), **1**; pyridine (py), **2**; 4-cyanopyridine (cpy), **3**] (Chart 1).

The dimers **1**−**3** were synthesized directly by bubbling NO gas through a CH_2Cl_2 solution of the corresponding CO dimer, $[\{Ru_3O(CH_3CO_2)_6(CO)(L)\}_2(\mu\text{-pz})]$. These complexes were isolated as a PF_6^- salt of the dication, and the electron configuration of the isolated state can be described as $[\{Ru_3NO\}^{16}\{Ru_3NO\}^{16}]^{2+}$, hereafter abbreviated as $\{16;16\}^{2+}$.

Each complex (**1**−**3**) exhibits four reversible single-electron redox waves in the region of +0.3 to −1.1 V vs SSCE (sodium-saturated calomel electrode), which corresponds to the $\{16;16\}^{2+}/\{17;16\}^+$, $\{17;16\}^+/\{17;17\}^0$, $\{17;17\}^0/\{18;17\}^-$, and $\{18;17\}^-/\{18;18\}^{2-}$ redox processes, as well as one reversible two-electron redox wave corresponding to the $\{15;15\}^{4+}/\{16;16\}^{2+}$ redox process at +1.5 V in its cyclic voltammogram, as shown in Figure1. The redox potentials are summarized in Table S1 in the Supporting Information.

The pz-bridged dimers of triruthenium complexes with CO[4,5] have only one mixed-valence state, which corresponds to the $Ru_3^{III,III,II}{-}Ru_3^{III,II,II}$ state; in contrast, the present complexes show two mixed-valence states, $\{17;16\}^+$ and $\{18;17\}^-$, hereafter abbreviated as MV1 and MV2, respectively. A splitting of the redox couples involving a mixed-valence state is a good indicator of the stability of the mixed-valence state. The redox splitting for MV1, $\Delta E_1 = |E_{1/2}(\{16;16\}^{2+}/\{17;16\}^+) - E_{1/2}(\{17;16\}^+/\{17;17\}^0)|$, and that for MV2, $\Delta E_2 = |E_{1/2}(\{17;17\}^0/\{18;17\}^-) - E_{1/2}(\{18;17\}^-/\{18;18\}^{2-})|$, are summarized in Table 1. Both splittings depend on the electron-donating ability of the ancillary ligand. ΔE_1 values for **1**−**3** are 350, 280, and 200 mV, respectively, which correspond to comproportionation constants of 8.3×10^5, 5.4×10^4, and 2.4×10^3, respectively. The splitting is larger for the complex with electron-donating ancillary ligands, dmap > py > cpy. The same trend is also observed for the corresponding carbonyl dimers. On the other hand, ΔE_2 values for **1**−**3** are 160, 250, and 330 mV, respectively, which correspond to comproportionation constants of 5.1×10^2, 1.7×10^4, and 3.8×10^5, respectively. These trends show a reverse dependence on the electron-donating ability of the ancillary ligands. The sums of ΔE_1 and ΔE_2 are almost constant, 510−530 mV, and thus the two redox splittings are complementary.

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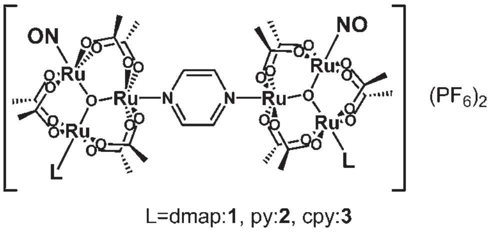
Chart 1



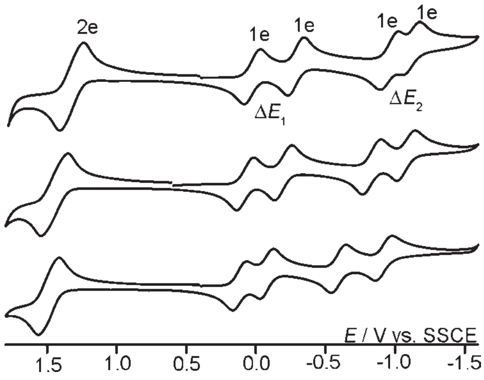


Figure 1. Cyclic voltammograms of the NO dimers **1** (top), **2** (middle), and **3** (bottom) in dichloromethane. Potentials were referenced to the SSCE.

Table 1. Redox Splitting for the Mixed-Valence State of pz-Bridged Triruthenium Dimers

complex	ΔE_1/mV	ΔE_2 /mV
$[\{Ru_3O(CH_3CO_2)_6(NO)(dmap)\}_2(\mu\text{-pz})](PF_6)_2$ (**1**)	350	160
$[\{Ru_3O(CH_3CO_2)_6(NO)(py)\}_2(\mu\text{-pz})](PF_6)_2$ (**2**)	280	250
$[\{Ru_3O(CH_3CO_2)_6(NO)(cpy)\}_2(\mu\text{-pz})](PF_6)_2$ (**3**)	200	330
$[\{Ru_3O(CH_3CO_2)_6(CO)(dmap)\}_2(\mu\text{-pz})]$	440	
$[\{Ru_3O(CH_3CO_2)_6(CO)(py)\}_2(\mu\text{-pz})]$	380	
$[\{Ru_3O(CH_3CO_2)_6(CO)(cpy)\}_2(\mu\text{-pz})]$	250	

The complementary relationship between the redox splittings can be explained as follows. The electronic interaction in a mixed-valence state depends on the amount of difference in the charge density and the distance between the locations where the charge changes during the electron transfer within the mixed-valence state. For a pz-bridged dimer, a major contributing factor is the amount of the electron density change on the ruthenium coordinated by pz. Because the NO ligand strongly coordinates to the ruthenium, the isolated state, $\{Ru_3NO\}$,[16] can be regarded as $\{Ru\text{-}NO\}^6Ru_2^{III,III}$. The MV1 is a mixed-valence state concerned with the $\{Ru\text{-}NO\}^6Ru_2^{III,III}$ and $\{Ru\text{-}NO\}^6Ru_2^{III,II}$ states, and the electron density change is due to a distribution of the added electron to the $\{Ru\text{-}NO\}^6Ru_2^{III,III}$ state, and an electron added to the $\{Ru\text{-}NO\}^6Ru_2^{III,II}$ state contributes to the electronic interaction in MV2. Although the valence electron on the $\{Ru\text{-}NO\}^6Ru_2$ unit is delocalized over the two rutheniums, an inequality of the valence due to a difference in the basicity of the attached ligands is observed. The electron-withdrawing ligand gathers the electron density to the attached ruthenium. The first reduction of the $\{Ru\text{-}NO\}^6Ru_2^{III,III}$ unit, which is correlated to the interaction in MV1, occurs mainly on the ruthenium coordinated by the electron-withdrawing ligand; on the other hand, the second reduction, which is also correlated to the interaction in MV1, occurs on the other ruthenium. Because the dmap ligand is more electron-donating than pz, ΔE_1 for **1** is relatively large, whereas its ΔE_2 is small. The complementary relation may be reminiscent that the one mixed-valence state involves electron transfer and the other does hole transfer. However, in such a case, the dependencies of interactions for both mixed-valence states on the ligand basicity are the exact opposite to the result.

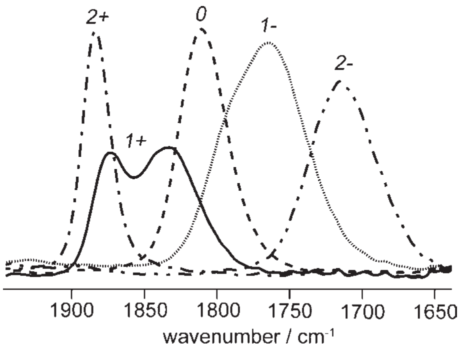


Figure 2. IR spectra of **3** for different oxidation states in dichloromethane at −35 °C: $\{16;16\}^{2+}$ (dash-dotted line), $\{17;16\}^+$ (solid line), $\{17;17\}^0$ (dashed line), $\{18;17\}^-$ (dotted line), and $\{18;18\}^{2-}$ (dash-double dotted line).

The vibrational spectrum of complex **3** in each oxidation state was obtained by using IR spectroelectrochemistry.[15] The $\nu(NO)$ stretches for five oxidation states, $\{16;16\}^{2+}$ to $\{18;18\}^{2-}$, were observed at 1900−1650 cm^{-1}, as is shown in Figure 2. The homovalence states, that is, the isolated state $\{16;16\}^{2+}$, the doubly reduced state $\{17;17\}^0$, and the quadruply reduced state $\{18;18\}^{2-}$, show a single $\nu(NO)$ band at 1884, 1811, and 1715 cm^{-1}, respectively, as expected from the fact that both Ru_3 units have the same electron configuration. The band shifts toward lower wavenumber upon reduction of a unit. The shifts per reduction of the unit, 73 and 96 cm^{-1}, are slightly larger than those for the corresponding CO dimers, ~50 cm^{-1}. On the other hand, the mixed-valence states, that is, the singly reduced state, MV1, and the triply reduced state, MV2, show complicated spectra. The singly reduced state, MV1, shows two $\nu(NO)$ bands at 1874 and 1833 cm^{-1}. The former is characteristic of the $\{Ru_3NO\}^{16}$ state, and the latter is characteristic of the $\{Ru_3NO\}^{17}$ state; however, these peaks were close to each other and partially coalesced. A fast intramolecular electron transfer between the two Ru_3 units in the MV1 state is responsible for this broadening in the same manner as that of the carbonyl dimers. In the triply reduced state, MV2, a single broad coalesced peak was observed at 1765 cm^{-1}, indicating a much faster intramolecular electron transfer in the MV2 state.

The intramolecular electron-transfer rate for the MV1 state was preliminarily estimated by Bloch-type analysis. Figure 3 illustrates the observed and simulated IR spectra of the MV1 state for complex **3**. This is the first example of the estimation of the intramolecular electron-transfer rate of a complex with a spectator ligand other than the CO ligand. The rate constant is estimated to 8×10^{11} s^{-1}.[16] The rate constant is much larger than that of the corresponding CO dimer, 1×10^{11} s^{-1}, even though the redox splitting for the NO dimer is smaller than that for the CO dimer.[17]

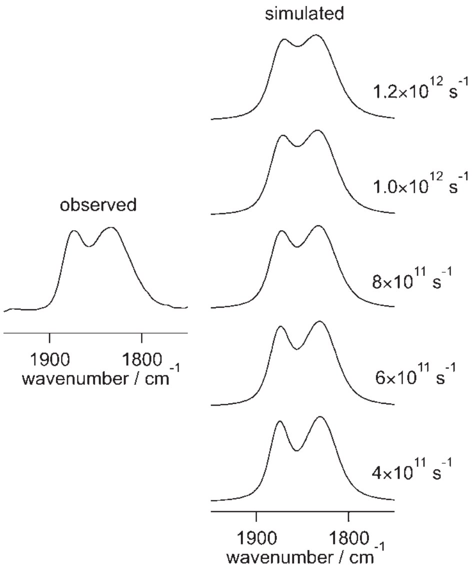


Figure 3. Comparison of observed and simulated IR spectra for the MV1 state of **3** as a function of the intramolecular electron-transfer rate constant.

The IR spectra of **1** and **2** in the five oxidation states are shown in Figures S3 and S4 in the Supporting Information. These are similar to those of **3**, although the lower wavenumber shifts for the higher reduced states of **1** are slightly larger.

In summary, we have synthesized novel pz-bridged oxoacetatotriruthenium dimers with an NO ligand, which show two mixed-valence states. The ν(NO) spectra for five oxidation states were obtained, and the intramolecular electron-transfer rate within a mixed-valence state has been evaluated. An intervalence charge-transfer band study of these mixed-valence states is now in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic procedures, NMR spectra of **1**−**3**, details of spectroelectrochmical measurement, IR spectra of **1** and **2** in the five oxidation states, and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655–2685. (b) Day, P.; Hush, N. S.; Clark, R. J. H. *Philos. Trans. R. Soc., A* **2008**, *366*, 5–14.(c) *Electron Transfer in Inorganic, Organic and Biological Systems, Advances in Chemistry Series*; Bolton, J. R., Mataga, N., McLendon, G., Eds.; American Chemical Society: Washington, DC, 1991.

(2) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–444. (c) Sutin, N. S. *Prog. Inorg. Chem.* **1983**, *30*, 441–498.

(3) (a) Breedlove, B. K.; Yamaguchi, T.; Ito, T.; Londergan, C. H.; Kubiak, C. P. *Comprehensive Coordination Chemistry II: from Biology to Nanotechnology*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, U.K., 2004; Vol. 2, pp 717−729. (b) Glover, S. D.; Goeltz, J. C.; Lear, B. J.; Kubiak, C. P. *Eur. J. Inorg. Chem.* **2009**, 585–594. (c) Glover, S. D.; Goeltz, J. C.; Lear, B. J.; Kubiak, C. P. *Coord. Chem. Rev.* **2010**, *254*, 331–345. (d) Glover, S. D.; Lear, B. J.; Salsman, J. C.; Londergan, C. H.; Casey, H.; Kubiak, C. P. *Philos. Trans. R. Soc., A* **2008**, *366*, 177–185. (e) Londergan, C. H.; Kubiak, C. P. *Chem.—Eur. J.* **2003**, *9*, 5962–5969. (f) Ito, T.; Yamaguchi, T.; Kubiak, C. P. *Macromol. Symp.* **2000**, *156*, 269–275.

(4) (a) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Washington, J.; Kubiak, C. P. *Science* **1997**, *277*, 660–663. (b) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Kido, H.; Zavarine, I. S.; Richmond, T.; Washington, J.; Kubiak, C. P. *J. Am. Chem. Soc.* **1999**, *121*, 4625–4632.

(5) Yamaguchi, T.; Imai, N.; Ito, T.; Kubiak, C. P. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1205–1212.

(6) Ito, T.; Imai, N.; Yamaguchi, T.; Hamaguchi, T.; Londergan, C. H.; Kubiak, C. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 1376.

(7) (a) Lear, B. J.; Glover, S. D.; Salsman, J. C.; Londergan, C. H.; Kubiak, C. P. *J. Am. Chem. Soc.* **2007**, *129*, 12772–12779. (b) Londergan, C. H.; Salsman, J. C.; Ronco, S.; Kubiak, C. P. *Inorg. Chem.* **2003**, *42*, 926–928. (c) Londergan, C. H.; Salsman, J. C.; Ronco, S.; Dolkas, L. M.; Kubiak, C. P. *J. Am. Chem. Soc.* **2002**, *124*, 6236–6237.

(8) Ohtsu, H.; Kitazume, J.; Yamaguchi, T. *Dalton Trans.* **2011**, *40*, 7502−7504.

(9) (a) Salsman, J. C.; Ronco, S.; Londergan, C. H.; Kubiak, C. P. *Inorg. Chem.* **2006**, *45*, 547–554. (b) Londergan, C. H.; Salsman, J. C.; Lear, B. J.; Kubiak, C. P. *Chem. Phys.* **2006**, *324*, 57–62. (c) Salsman, J. C.; Kubiak, C. P. *J. Am. Chem. Soc.* **2005**, *127*, 2382–2383. (d) Lear, B. J.; Kubiak, C. P. *Inorg. Chem.* **2006**, *45*, 7041–7043. (e) Zavarine, I. S.; Kubiak, C. P. *J. Electroanal. Chem.* **2001**, *495*, 106–109. (f) Wittrig, R. E.; Kubiak, C. P. *J. Electroanal. Chem.* **1995**, *393*, 75–86.

(10) Although the triruthenium cluster core, $\mathrm{Ru_3^{III,III,II}}$ or $\mathrm{Ru_3^{III,II,II}}$, itself is in a mixed-valence state, the term "mixed valence" in this report is used only for a mixed-valence state between the cluster.

(11) (a) Nishiumi, T.; Nomura, Y.; Higuchi, M.; Yamamoto, K. *Chem. Phys. Lett.* **2003**, *378*, 18–23. (b) Nishiumi, T.; Nomura, Y.; Chimoto, Y.; Higuchi, M.; Yamamoto, K. *J. Phys. Chem. B* **2004**, *108*, 7992–8000.

(12) (a) Meesuk, L.; Jayasooriya, U. A.; Cannon, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 2009–2016. (b) Ohto, A.; Tokiwa-Yamamoto, A.; Abe, M.; Ito, T.; Sasaki, Y.; Umakoshi, K.; Cannon, R. D. *Chem. Lett.* **1995**, *24*, 97–98. (c) Koley, M.; Sarkar, B.; Ghumaan, S.; Bulak, E.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2007**, *46*, 3736–3742. (d) Fujino, T.; Hoshino, Y.; Eto, M.; Yukawa, Y.; Fiedler, J.; Kaim, W. *Chem. Lett.* **2003**, *32*, 274–275. (e) Sheiring, T.; Kaim, W.; Olabe, J. A.; Parise, R.; Fiedler, J. *Inorg. Chim. Acta* **2000**, *300−302*, 125–130.

(13) (a) Toma, H. E.; Alexiou, A. D. P.; Dovidauskas, S. *Eur. J. Inorg. Chem.* **2002**, 3010–3017. (b) Toma, H. E.; Alexiou, A. D. P.; Formiga, A. L. B.; Nakamura, M.; Dovidauskas, S.; Eberlin, M. N.; Tomazela, D. M. *Inorg. Chim. Acta* **2005**, *358*, 2891–2899.

(14) (a) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339–406. (b) Roncaroli, F.; Videla, M.; Slep, L. D.; Olabe, J. A. *Coord. Chem. Rev.* **2007**, *251*, 1903–1930.

(15) The spectra show isosbestic points for each one-electron reduction, and the stability of the complex during the measurement was confirmed by a spectrum at the initial potential after measurement. See the Supporting Information.

(16) Because the line width of the ν(NO) stretch of the {18;18} state is very broad, the fitting of the spectrum in the MV2 state is not as sensitive to the rate constant for this region. Rate constants of more than 4×10^{11} s^{-1} can reproduce the observed spectrum.

(17) Because of the noninnocent nature of an NO ligand, it is difficult to determine an exact valence of the ruthenium cluster. Thus, we do not determine which one of MV1 and MV2 corresponds to the mixed-valence state of the CO dimer.