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Remarkable Stabilization of a Ligand-Based Mixed-Valence State in the Metal-Based Mixed Valent $Ru_2^{II,III}M^{II}(\mu_3\text{-O})$ (M = Co, Ni) Trinuclear Cluster Complexes

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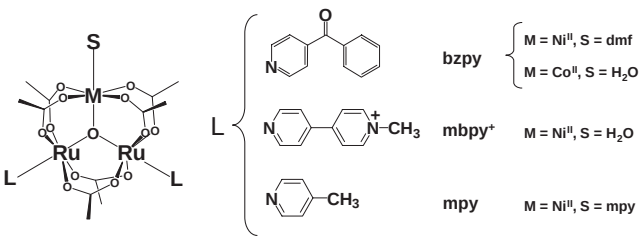
Two consecutive one-electron reductions of the mixed-metal trinuclear complexes $[Ru^{III}_2M^{II}(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(S)(bzpy)_2]$ {(M = Co, S = H_2O) and (M = Ni, S = *N*,*N*′-dimethylformamide); bzpy = 4-benzoylpyridine} in acetonitrile give stable "double" mixed-valence states where both $Ru_2^{II,III}$ and $(bzpy^-)(bzpy)$ states coexist. Splitting of the ligand-based redox waves, $(bzpy)_2/(bzpy^-)(bzpy)/(bzpy^-)_2$, is 0.35 and 0.34 V for the Co and Ni complexes, respectively.

We have previously reported that the overlapped reduction waves of the three or two chemically equivalent ligands, $mbpy^+$ (*N*-methyl-4,4′-bipyridinium ion), in oxo-centered trinuclear ruthenium cluster complexes $[Ru_3(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(mbpy^+)_3]^{4+1}$ and $[Ru_3(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(L)(mbpy^+)_2]^{n+}$ ($n = 2$, L = CO; $n = 3$, L = pyrazine, pyridine (py), imidazole, 4-(dimethylamino)pyridine)[2] show small ($\Delta E_{1/2} < 0.1$ V) but distinctive splitting in acetonitrile.[3] Splitting of the overlapped waves may be taken as a measure of the extent of the inter-ligand electronic communication through the large triruthenium cluster core. It has been concluded that the π-system, based on the $d\pi(Ru_3)$–$p\pi(O)$ interaction, of the trinuclear core provides an effective pathway to the communication.[1–4] Splitting of the waves is, however, much smaller than those of the metal-center-based redox waves of these trinuclear complexes[5,6] or of more general ligand-bridged dinuclear complexes.[7] In the case of the trinuclear complexes, for example, the redox waves for the $Ru_3^{III,III,III}/Ru_3^{II,III,III}$ and $Ru_3^{II,III,III}/Ru_3^{II,II,III}$ processes of $[Ru_3(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(py)_3]^+$ are separated by $\Delta E_{1/2} = 1.27$ V.[5,6]

We thought that by changing the triruthenium center to mixed-metal Ru_2M (M; Mg^{II}, Co^{II}, Ni^{II}, and Zn^{II}) center[8–11] the splitting would become more significant, since the π-system is more effectively localized in the Ru–(μ_3-O)–Ru moiety. In fact, the carbonyl complex, $[Ru_3(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(CO)(mbpy^+)_2]^{2+}$, manifests relatively large splitting of the overlapped mbpy-based redox waves ($\Delta E_{1/2} \approx 0.1$ V), because Ru–CO is not effectively involved in the Ru–O–Ru π system. In the present study, in addition to $mbpy^+$ ($E_{1/2}$ of the free ligand in acetonitrile is −0.94 V vs Ag/AgCl), 4-(benzoyl)pyridine (bzpy), which has a more negative redox potential (−1.46 V (E_{pc})), was chosen as a redox-active ligand. Although $[Ru_2^{III,III}Ni(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(H_2O)(mbpy^+)_2]^{2+}$ showed negligible splitting of the $mbpy^+$-based reduction waves ($(mbpy^+)_2/(mbpy^+)(mbpy)/(mbpy)_2$) in the $(mbpy^+)$-Ru^{III}-(μ_3-O)-$Ru^{III}(mbpy^+)$ moiety, the bzpy derivative $[Ru_2Ni(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(H_2O)(bzpy)_2]$ and its Ru_2Co analogue showed surprisingly large splitting of the bzpy-based reduction waves $(bzpy)_2/(bzpy^-)(bzpy)/(bzpy^-)_2$ ($\Delta E_{1/2} =$ 0.34 and 0.35 V for the Ni and the Co complexes, respectively). This paper describes the redox behavior of the new complexes $[Ru_2M(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(S)(L)_2]^{n+}$ {L = bzpy ($n = 0$): M = Co and S = H_2O, M = Ni and S = dmf; L = $mbpy^+$ ($n = 2$): M = Ni and S = H_2O} (Scheme 1). A Ru_2Ni complex with three 4-methylpyridine (mpy) ligands, $[Ru_2Ni(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(mpy)_3]$, was also prepared as a reference compound.

Figure 1 shows the cyclic voltammograms (CV) of the bzpy complexes of the Ni and the Co complexes in 0.1 mol dm^{-3} $TBAPF_6$–acetonitrile. The two oxidation waves in the positive potential region of the Ni complex (Fig. 1a) (+0.55 and +1.66 V vs Ag/AgCl) are assigned to the stepwise one-electron oxidation of the diruthenium moiety from $Ru_2^{III,III}$ to $Ru_2^{IV,IV}$. Four one-electron reduction waves (−0.86, −1.14, −1.48, and −1.70 V) involve the stepwise one-electron reduction of the $Ru_2^{III,III}$ core to $Ru_2^{II,II}$ and the successive reductions of the two bzpy ligands {$(bzpy)_2$ to $(bzpy)(bzpy^-)$}



Scheme 1. Structures of the complexes that were used in this study.

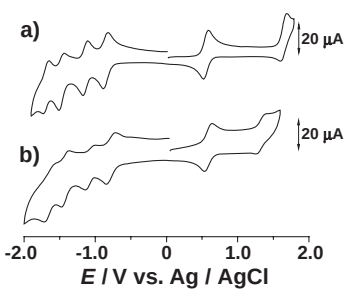


Fig. 1. Cyclic voltammograms (CV) of (a) $[Ru_2Ni(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(dmf)(bzpy)_2]$ and (b) $[Ru_2Co(\mu_3\text{-O})(\mu\text{-CH}_3COO)_6(H_2O)(bzpy)_2]$ in 0.1 mol dm^{-3} $TBAPF_6$–acetonitrile (scan rate, 100 mV s^{-1}).

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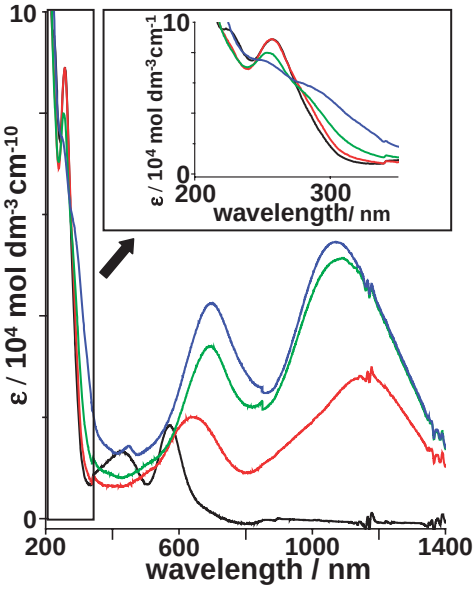

Fig. 2. Change in the spectra of $[Ru_2Ni(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(dmf)(bzpy)_2]$ at different applied potentials (black line at 0.0 V; red line at −1.00 V; green line at −1.30 V, and blue line at −1.65 V) in 0.1 mol dm^{-3} $TBAPF_6$–acetonitrile.

and {(bzpy)(bzpy$^-$) to (bzpy$^-$)$_2$}. For the assignments of these four reduction waves, spectroelectrochemical studies were useful. Figure 2 shows the electronic spectra taken at the three electrode potentials where the three consecutive reduced species are predominant. The inset is the spectral change in the ligand π–π^* transition region. Although the spectra given in Fig. 2 do not necessarily represent the pure chemical species of the certain oxidation states, the general trend in the spectral changes is certainly informative. While a new near infra-red band centered around 1170 nm develops upon the first reduction, the spectrum in the ligand π–π^* transition region remains almost unchanged. The second reduction, however, causes a significant spectral change in the ligand π–π^* transition region together with further increase in the near infra-red band, which slightly shifts to higher energy side. Further change in the π–π^* transition region was observed upon the third reduction with only a small change in the near infra-red region. The fourth reduction was spectroelectrochemically irreversible. These spectral changes are best explained by considering that the second and the third reduction waves involve ligand reduction steps and the first one involves the reduction of the diruthenium core. The spectroelectrochemically reversible nature of the third reduction step is consistent with the assignment of the ligand-based reduction, since the reduction of the $Ru_2^{II,III}$ core to the $Ru_2^{II,II}$ state is generally irreversible.[1,2] In dichloromethane, the 4-benzoylpyridinenickel(II) complex shows a similar CV as that observed in acetonitrile.

The 4-benzoylpyridinecobalt(II) complex in acetonitrile also shows similar CV pattern in the region < 0 V (Fig. 1b). The four reduction waves as well as the oxidation wave at +0.59 V were assigned as those of the 4-benzoylpyridinenickel(II) complex. An oxidation wave was observed at around +1.37 V that corresponds to the Co^{II}/Co^{III} process. This wave shifts to +1.28 V on addition of pyridine, as pyridine quickly coordinates to the cobalt center.

Table 1 summarizes the electrochemical data of the four mixed metal complexes based on the assignment given above. From the comparison of the redox potentials of the bzpy complexes with those of the mpy (4-methylpyridine) complex, the corresponding redox potentials of the Ru–O–Ru core appear at more negative potentials for the mpy complex, and the assignment of the redox waves of the bzpy complexes based on the spectrophotometric measurements is reasonable. Table 1 shows unusually large splitting of the bzpy-based reduction waves, which is 0.35 and 0.34 V for the Ru_2Co and Ru_2Ni complexes, respectively, in acetonitrile. The large splitting indicates that there is significant stabilization of the ligand-(bzpy)-based mixed-valence state; the comproportionation constant[12] is 8.2×10^5 (M = Co) and 5.6×10^5 (M = Ni). In dichloromethane, splitting of the ligand-based reduction waves of the Ni complex is 0.31 V. It should be noted that ligand reduction takes place at the oxidation level of the mixed-valent $Ru_2^{II,III}$ state. Thus, the two-electron reduced state is a unique double mixed-valence state $Ru_2^{II,III}$–(bzpy)(bzpy$^-$). The corresponding mbpy$^+$ complex $[Ru_2Ni(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)(mbpy^+)_2]^{2+}$ did not show any significant splitting in the ligand mbpy$^+$ reduction waves (Table 1). In this case, the ligand reduction process precedes the $Ru_2^{III,III}(\mu\text{-}O)$ core reduction. It is possible that the interaction between the two mixed-valence states, more specifically the interaction between the two unpaired electrons, causes unusually high stability of the ligand-based mixed-valence state. Attempts to isolate a series of the reduced species have not been successful so far, and further discussion about their electronic structures based on magnetic and other measurements is not feasible. We have also measured the CV of the complexes with diamagnetic metal ions, $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)(bzpy)_2]$ (M = Mg^{II}, Zn^{II}). Although similar splitting in ligand reduction

Table 1. Redox Potentials ($E_{1/2}$ vs Ag/AgCl)[a] and (ΔE_p)[a] of $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CH_3CN)(L)_2]^{n+}$ (M = Co, Ni) and $[Ru_2Ni(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(mpy)_3]$

M	S[b),c)]	L[d)]	$Ru_2^{II,II}/Ru_2^{II,III}$	$Ru_2^{II,III}/Ru_2^{III,III}$	$Ru_2^{III,III}/Ru_2^{III,IV}$	$Ru_2^{III,IV}/Ru_2^{IV,IV}$	$(L)_2/LL^-$	$LL^-/(L^-)_2$
Co	CH_3CN	bzpy	−1.62 (214)	−0.80 (134)	0.59 (112)	1.37 (262) ($Co^{II/III}$)	−1.07 (144)	−1.42 (114)
Ni	CH_3CN	bzpy	−1.70 (E_{pc})	−0.86 (92)	0.55 (102)	1.66 (98)	−1.14 (96)	−1.48 (100)
	CH_2Cl_2	bzpy	—	−0.93 (140)	0.50 (124)	1.71 (106)	−1.24 (118)	−1.55 (136)
	CH_3CN	mbpy$^+$	−1.96 (E_{pc})	−1.15 (70)	0.57 (80)	1.66 (93)	−0.76 (70)	
	CH_3CN	mpy	−1.93 (E_{pc})	−1.05 (69)	0.43 (72)	1.60 (100)	—	—

a) $E_{1/2} = (E_{pa} + E_{pc})/2$ (in V), $\Delta E_p = E_{pa} - E_{pc}$ (in mV). b) 0.1 mol dm^{-3} $TBAPF_6$–CH_3CN or 0.1 mol dm^{-3} $TBAPF_6$–CH_2Cl_2 ($TBAPF_6$ = tetra(*n*-butyl)ammonium hexafluorophosphate). c) Coordinated solvent is assumed to be replaced by CH_3CN in CH_3CN solutions. d) $n = 0$ for L = bzpy and $n = 2$ for L = mbpy$^+$.

waves appears, the irreversible nature of the redox waves means that quantitative evaluation of the splitting cannot be performed.

Significant splitting of the ligand-based redox waves of mononuclear complexes has been observed for some chelating ligands, such as 2,2′-bipyridine and catecholato ligands.[13,14] Through-space interactions possibly by the contribution of metal π-orbitals are favorable for these chelating ligands.[3] However, for monodentate ligands, no significant splitting has been observed for d^6 metal complexes, such as *cis*-[Ru(bpy)$_2$(mbpy$^+$)$_2$]$^{4+}$[15] and [Re(CO)$_3$Cl(bzpy)$_2$].[16] The present observation is thus significant because the two monodentate ligands which are separated by the sterically bulky trinuclear cluster core show considerably large splitting of their redox waves.

Observation of the well separated ligand reduction waves of the complexes [Ru$_2$M(μ_3-O)(μ-CH$_3$COO)$_6$(S)(bzpy)$_2$] (M = Co (S = H$_2$O), Ni (S = dmf)) indicates that the dπ–pπ conjugate system is expanded to the ligand π-orbitals. The ligand π-orbitals may have some metal dπ character, and conversely the Ru–O–Ru π system mixes to some extent with ligand π orbitals.

Experimental

Preparation of the Complexes. [Ru$_2$Ni(μ_3-O)(μ-CH$_3$COO)$_6$(dmf)(bzpy)$_2$]·C$_6$H$_5$CH$_3$ (1) (dmf = *N*,*N*′-Dimethylformamide): A mixture of the triaqua complex [Ru$_2$Ni(μ_3-O)(μ-CH$_3$COO)$_6$(H$_2$O)$_3$] (100 mg, 0.154 mmol) and bzpy (100 mg, 0.546 mmol) in acetonitrile (50 cm^3) was stirred at 50 °C for 1 h. The resulting reddish purple solution was filtered and evaporated to dryness. The residue was then dissolved in toluene (20 cm^3). To the solution was added dmf (1 cm^3), and the mixture was stirred for 10 min. Reddish purple solid that was obtained by adding a large amount of pentane was filtered. Recrystallization twice from dichloromethane by adding pentane gave a crystalline solid. Yield, 37 mg (26.3%). Anal. Calcd for C$_{46}$H$_{51}$N$_3$O$_{16}$NiRu$_2$: C, 47.52; H, 4.42; N, 3.61%. Found: C, 47.79; H, 4.08; N, 3.81%.

[Ru$_2$Co(μ_3-O)(μ-CH$_3$COO)$_6$(H$_2$O)(bzpy)$_2$]·0.1C$_6$H$_5$CH$_3$ (2): This complex was prepared by the method similar to that of the corresponding Ni complex described above, except using [Ru$_2$Co(μ_3-O)(μ-CH$_3$COO)$_6$(H$_2$O)$_3$] instead of [Ru$_2$Ni(μ_3-O)(μ-CH$_3$COO)$_6$(H$_2$O)$_3$]. The residue was dissolved in toluene (20 cm^3), and 2 cm^3 of dmf was added. From 200 mg of the aquacobalt(II) complex and 200 mg (1.09 mmol) of bzpy, 214.4 mg of reddish purple residue was obtained. About the half of the residue (100 mg) was used for purification from toluene/dmf by adding pentane. Recrystallization finally gave 19.2 mg of reddish purple solid (12.8%). Anal. Calcd for C$_{36.7}$H$_{38.8}$N$_3$O$_{16}$CoRu$_2$: C, 43.01; H, 3.82; N, 2.73%. Found: C, 43.27; H, 3.83; N, 3.09%.

[Ru$_2$Ni(μ_3-O)(μ-CH$_3$COO)$_6$(H$_2$O)(mbpy$^+$)$_2$](PF$_6$)$_2$·5H$_2$O (3): A mixture of [Ru$_2$Ni(μ_3-O)(μ-CH$_3$COO)$_6$(H$_2$O)$_3$] (100 mg, 0.154 mmol) and (mbpy$^+$)[PF$_6$] (145.8 mg, 0.924 mmol) in methanol (50 cm^3) was stirred for 3 h at room temperature. The reddish purple precipitate was recrystallized from acetone by adding diethyl ether to obtain reddish purple solid. Yield 81.9 mg (42.5%). Anal. Calcd for C$_{36}$H$_{52}$N$_2$O$_{19}$F$_{12}$P$_2$NiRu$_2$: C, 31.63; H, 3.83; N, 2.05%. Found: C, 31.60; H, 3.58; N, 2.25%.

[Ru$_2$Ni(μ_3-O)(μ-CH$_3$COO)$_6$(mpy)$_3$]·0.3CH$_2$Cl$_2$ (4): A mixture of [Ru$_2$Ni(μ_3-O)(μ-CH$_3$COO)$_6$(H$_2$O)$_3$] (50 mg, 0.077 mmol) and mpy (3 cm^3) in acetonitrile (30 cm^3) was stirred for 1 d at room temperature. The bluish purple residue was recrystallized three times from dichloromethane by adding *n*-pentane to obtain microcrystalline solid. Yield 77.9 mg (84.5%). Anal. Calcd for C$_{30.3}$H$_{39.6}$N$_3$O$_{13}$Cl$_{0.6}$NiRu$_2$: C, 38.86; H, 4.26; N, 4.49; Cl, 2.27%. Found: C, 38.34; H, 4.41; N, 4.58; Cl, 1.82%.

Measurements. Electronic absorption spectra were recorded on a HITACHI U-3000 spectrophotometer. Cyclic voltammetry was performed with a BAS CV-50W potentiostat. The working and the counter electrodes were a glassy carbon disk (3 mm in diameter) and a platinum wire, respectively. The reference electrode was Ag/AgCl (3 mol dm^{-3} NaCl) against which the half-wave potential of Fc/Fc$^+$ ($E_{1/2}$(Fc$^{0/+}$)) was 0.435 V. The sample solution was prepared in 0.1 mol dm^{-3} TBAPF$_6$ (tetra(*n*-butyl)ammonium hexafluorophosphate) acetonitrile solution. Spectroelectrochemistry was carried out by using an optically transparent thin-layer electrode cell (thickness, 2 mm) at room temperature with an Ar-purged 0.1 mol dm^{-3} TBAPF$_6$–acetonitrile solution as a solvent and a platinum mesh as a working electrode.

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