Enhanced Kinetic Lability of Ru(III) Centers in Oxo-Centered Mixed-Metal Ru_2M Trinuclear Complexes (M = Zn and Mg)

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Oxo-centered carboxylate-bridged trinuclear complexes of the type $[M_3(\mu_3\text{-O})(\mu\text{-RCO}_2)_6L_3]^{n+}$ constitute an important class of compounds in transition metal chemistry.[1] They are known with a wide variety of metal ions (M), bridging carboxylate anions (RCO_2^-), and monodentate terminal ligands (L) as well as with mixed-valence[2] and mixed-metal[3−6] combinations. Kinetic studies on terminal ligand substitution reactions for this family[6−8] as well as oxo-bridged dinuclear metal complexes with related core structures[9,10] have provided a good measure for the reactivity of metal centers which strongly couple through the oxide ion, the kinetic rates clearly reflecting the nature of metal ions, metal oxidation states, and possibly the extent of metal−metal interactions. Two or three identical terminal ligands in the homonuclear complexes undergo substitution with bulk solvent molecules or added ligands by a dissociative (D) or dissociative interchange (I_d) mechanism,[6−8] and the rate constants are increased as compared to those for mononuclear complexes due to the trans-labilizing effect of the central oxide bridge.[4a,6−10] For mixed-metal cases, their ligand-substitution properties have been less explored[6] and remain open to further investigation.

In the present study, we investigated for the first time substitution reactions of terminal pyridine ligands for mixed-metal trinuclear $Ru^{III}{}_2Zn^{II}$ and $Ru^{III}{}_2Mg^{II}$ complexes, namely, $[Ru_2Zn(O)(CH_3CO_2)_6(py)_3]$ (**1**), $[Ru_2Zn(O)(CH_3CO_2)_6(py)_3]\cdot py$ (**1·**py), and $[Ru_2Mg(O)(CH_3CO_2)_6(py)_2(H_2O)]$ (**2**), where py = pyridine. Site-distinctive ligand-substitution properties of the mixed-metal clusters and the effect of the divalent metal ions (Zn and Mg) on kinetics at the Ru(III) centers are described.

Experimental Section

Materials. The Ru_2Zn complexes $[Ru^{III}{}_2Zn^{II}(O)(CH_3CO_2)_6(py)_3]$ (**1**) and $[Ru^{III}{}_2Zn^{II}(O)(CH_3CO_2)_6(py)_3]\cdot py$ (**1·**py) were prepared according to the reported procedures.[5a] Deuterated solvents, CD_3CN (99% deuterated), CD_2Cl_2 (99%), py-d_5 (C_5D_5N, 100%), and other chemicals were used as received.

$[Ru^{III}{}_2Mg^{II}(O)(CH_3CO_2)_6(py)_2(H_2O)]$ (2). The tris(aqua) complex $[Ru_2Mg(O)(CH_3CO_2)_6(H_2O)_3]$[5a] (200 mg, 0.284 mmol) was suspended in CH_3CN (30 cm^3), and pyridine (3 cm^3) was added with stirring at room temperature. The mixture was stirred for 24 h, and the solvent was removed by rotary evaporator. Crystallization of the resultant solid from CH_2Cl_2/*n*-pentane gave crystalline complex **2**, which was collected by filtration, washed with *n*-pentane, and dried in vacuo (191 mg). Yield, 85.3%. Anal. Calcd for $[Ru_2Mg(O)(CH_3CO_2)_6(py)_2(H_2O)]\cdot H_2O$: C, 33.41; H, 4.08; N, 3.54. Found: C, 33.43; H, 4.17; N, 3.60. Spectroscopic data for **2** are provided in the Supporting Information.

Physical Measurements. Infrared spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. Ultraviolet−visible (UV−vis) spectra were taken on a Hitachi U-3410 spectrophotometer. ^1H NMR spectra were obtained on JEOL JNM-EX 270 NMR spectrometer with a variable-temperature controller at 270.15 MHz.

Kinetics. Two independent kinetic measurements were employed to study pyridine-exchange reactions to occur at the two kinds of metal centers, i.e., two Ru(III) centers and one M(II) center.

First, the py exchange reaction at the Zn(II) center was examined for **1·**py. The complex was dissolved in CD_2Cl_2, and the ^1H NMR spectra were recorded over the temperature range between −90 and +20 °C.

Second, the py/py-d_5 exchange reactions at Ru(III) centers were studied for **1** and **2**. To a deuterated solvent (CD_2Cl_2 or CD_3CN) containing **1** or **2** ([complex] = $(1.8−4.1) \times 10^{-3}$ mol dm^{-3}) was added a large excess amount of py-d_5 (0.36−0.55 mol dm^{-3}) at room temperature just before the acquisition of ^1H NMR data. Before the sample was placed into the NMR cell compartment, a desired temperature was achieved [30.0, 32.5, 35.0, 37.5, 40.0, and 42.5 (±0.1) °C]. ^1H NMR spectra were recorded at a specific time interval (10−30 min, depending on the reaction rate). No sign of decomposition was observed for **1** and **2** during kinetic runs on the basis of UV−vis and ^1H NMR spectra. Intensity changes of the 2,6-H resonances of coordinated and dissociated pyridine ligands were followed, from which the rate constant k (=R/m) was determined using McKay type eq 1,[11]

$$\ln\{(I_t - I_\infty)/(I_0 - I_\infty)\} = -\{(2m + n)/(2mn)\}Rt + \text{constant} \quad (1)$$

where m and n are the initial concentration of complex and py-d_5, respectively; I is equal to $p/(p + q)$, where p and q are relative intensities of the ^1H NMR resonances of the coordinated and dissociated pyridine ligands, respectively.

Results

The present mixed-metal complexes display two principal features in solution in terms of exchange reactions for terminal

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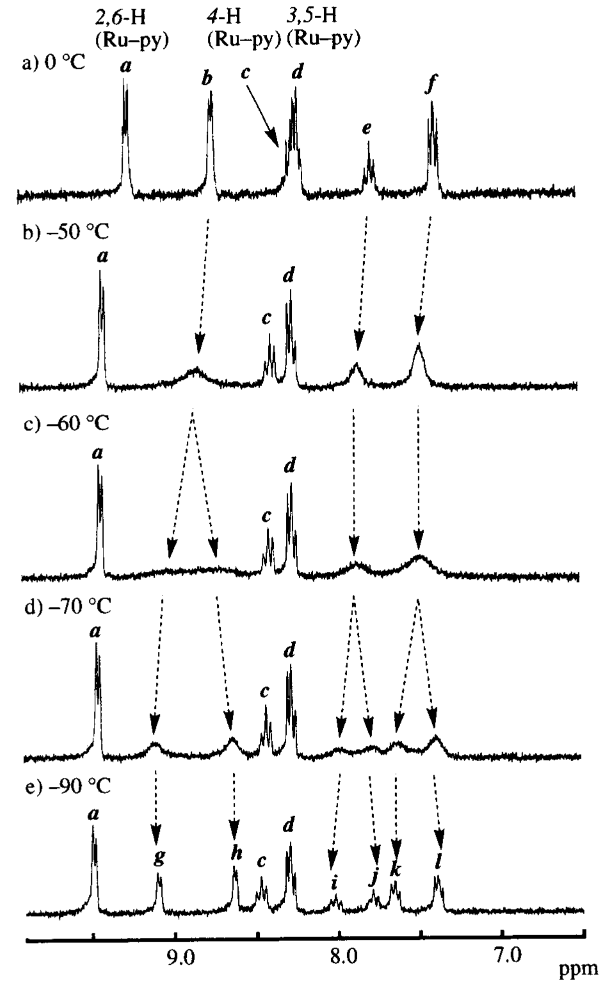

Figure 1. Variable-temperature ^{1}H NMR spectra, demonstrating pyridine-exchange reactions at the Zn(II) center of **1**·py in CD_2Cl_2. See text for the signal assignments.

ligands: one is a rapid exchange (NMR time scale) of pyridine at the Zn(II) center with an equivalent amount of free pyridine observed for **1**·py, and the other corresponds to much slower kinetics on two Ru(III) centers for **1** and **2**, substitution of pyridine with added py-d_5.

Ligand-Exchange Reactions at Zn(II). A variable-temperature ^{1}H NMR study for **1**·py established that an exchange of the pyridine at the Zn(II) center with a bulk pyridine molecule occurs on the NMR time scale. Figure 1 shows temperature-dependent ^{1}H NMR spectra of **1**·py in CD_2Cl_2. At 0 °C, a spectrum of the fast-exchange limit[12] is obtained, consisting of six sharp resonances of pyridine molecules (Figure 1a, resonances *a*−*f*, in which *c* and *d* are accidentally overlapped). These involve two sets of signals due to Ru-py (*a*, *c*, and *d*) and rapidly exchanging ones (*b*, *e*, and *f*) as subsequently evidenced by dynamic NMR. Upon cooling, the latter set of signals becomes broadened (Figure 1b−d) and finally split into nine distinct signals at −90 °C (Figure 1e). The exchange reaction at Ru(III) centers is negligible due to its much slower kinetics (see below). The dynamic behavior is fully reversible over the temperature range studied, and the exchange rate constant calculated from 2,6-H signals at the coalescence temperature (−50 °C) is $\sim 10^2$ s^{-1}.[13]

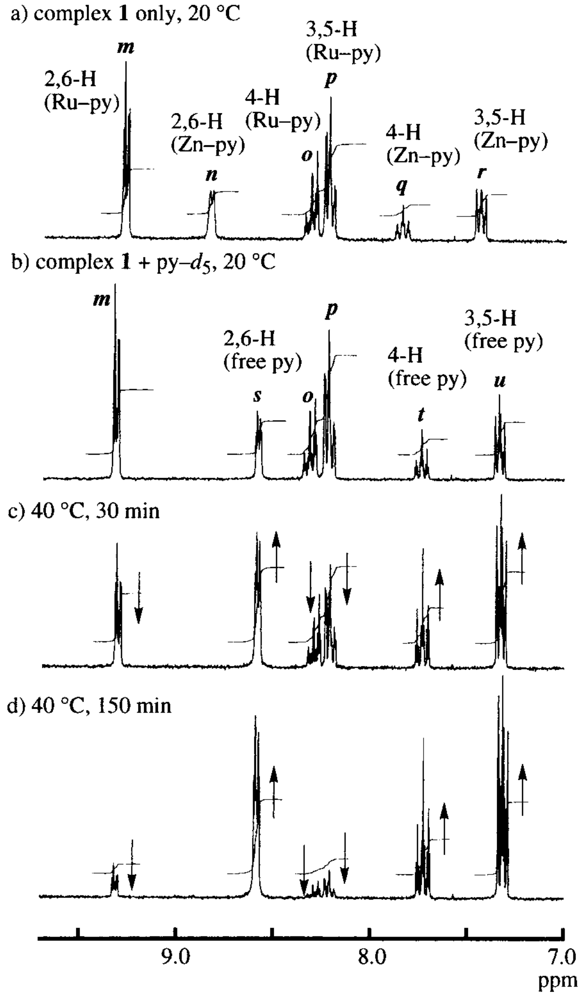

Figure 2. ^{1}H NMR spectral variations due to a py/py-d_5 exchange reaction at Ru(III) centers of **1** (3.7×10^{-3} mol dm^{-3}) in CD_3CN: (a) 20 °C, **1** only; (b) 20 °C, immediately after the addition of py-d_5 (0.75 mol dm^{-3}); (c) 40 °C for 30 min; (d) 40 °C for 150 min.

Ligand-Exchange Reactions at Ru(III). Figure 2 presents ^{1}H NMR spectral variations for **1** in CD_3CN, demonstrating substitution of terminal pyridine ligands at Ru(III) centers with py-d_5. Complex **1** dissolved in CD_3CN reveals two sets of resonances for pyridine (Ru-py and Zn-py) in a 2/1 intensity ratio at 25 °C (Figure 2a). None of the resonances are consistent with those of a free pyridine [δ 8.57 (d, 2H), 7.73 (t, 1H), and 7.33 (t, 2H)], thus confirming that coordinated pyridine remains intact upon dissolution. On the addition of a large excess of py-d_5 (Figure 2b), the resonances of Zn-py (*n*, *q*, and *r* in Figure 2a) were replaced by those of free py (*s*, *t*, and *u*), while Ru-py resonances remain unchanged (*m*, *o*, and *p*). This feature corresponds to substitution of pyridine taking place specifically at Zn(II), eq 2,

$$[\mathrm{Ru_2Zn(O)(CH_3CO_2)_6\{(py)_{Ru}\}_2(py)_{Zn}}] + \text{py-}d_5 \rightarrow [\mathrm{Ru_2Zn(O)(CH_3CO_2)_6\{(py)_{Ru}\}_2(py\text{-}}d_5)_{\mathrm{Zn}}] + \mathrm{py} \quad (2)$$

where $(py)_{Ru}$ and $(py)_{Zn}$ represent pyridine coordinated to Ru and Zn centers, respectively. With increasing the temperature (40 °C), substitution of the Ru-py ligands with py-d_5, eq 3, is then observed, which is evidenced by a decrease of Ru-py and an increase of free py signals (Figure 2c,d).

The exchange rate constants for eq 3 were obtained at several temperatures by first-order kinetic treatments for 2,6-H signals

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(12) This spectral pattern is consistent with that for $[Ru_2Mg(O)(CH_3CO_2)_6(py)_3]$·py in $CDCl_3$ at room temperature.[5b]

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Table 1. Summary of Activation Parameters and Rate Constants for py/py-d_5 Exchange Reactions at Ru(III) Centers of **1** and **2** and Related Triruthenium Complexes (**3** and **4**)

complex	solvent	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	k(25 °C)^a/s^{-1}	refs
$[Ru_2Zn(O)(CH_3CO_2)_6(py)_3]$ (**1**)	CD_3CN	112 ± 11	+53 ± 36	8.7×10^{-5}	this work
	CD_2Cl_2	106 ± 12	+35 ± 38	1.1×10^{-4}	this work
$[Ru_2Mg(O)(CH_3CO_2)_6(py)_2(H_2O)]$ (**2**)	CD_3CN	91 ± 19	−15 ± 61	1.2×10^{-4}	this work
	CD_2Cl_2	105 ±11	+34 ± 37	1.5×10^{-4}	this work
$[Ru_3(O)(CH_3CO_2)_6(py)_3]^+$ (**3**)	CD_3CN	123 ± 6	+41 ± 19	2.4×10^{-7}	*b*
$[Ru_3(O)(CH_3CO_2)_6(CO)(py)_2]$ (**4**)	CD_3CN	126 ± 9	+52 ± 27	2.7×10^{-7}	*b*

[a] Calculated from activation parameters. [b] Reference 8.

$$[Ru_2Zn(O)(CH_3CO_2)_6\{(py)_{Ru}\}_2(py\text{-}d_5)_{Zn}] + 2\cdot py\text{-}d_5 \rightarrow [Ru_2Zn(O)(CH_3CO_2)_6\{(py\text{-}d_5)_{Ru}\}_2(py\text{-}d_5)_{Zn}] + 2\cdot py \quad (3)$$

m (Ru-py) and s (free py) using eq 1.[14] For Ru_2Mg complex **2**, the reaction was monitored similarly.[15] Table 1 lists the thermodynamic and kinetic parameters of **1** and **2** along with those of the corresponding reactions for (μ_3-oxo)triruthenium complexes **3**[8] and **4**[8,16] for comparison. It can be seen that the activation parameters are almost the same between **1** and **2** within experimental error, suggesting identical contribution of Zn(II) and Mg(II) to the py/py-d_5 substitution at Ru(III).

Discussion

The present mixed-metal $Ru^{III}_2M^{II}$ complexes exhibit site-distinctive kinetics in terminal ligand exchange reactions due to the nonequivalent metal centers, e.g., inert Ru(III) and labile M(II) ions. Few reports on multinuclear metal complexes exhibiting varied kinetic rates depending on the nature of metal centers are available at present.[17]

Most interestingly, the py/py-d_5 exchange reactions at Ru(III) centers in **1** and **2** are unusually fast (up to 480 ×, 25 °C) as compared to the analogous reactions for (μ_3-oxo)triruthenium complexes **3** and **4** (Table 1). The *divalent* metal ions in the trinuclear cores thus play a crucial role in the enhancement of kinetic rates at Ru(III) centers. It should be noted that in a mixed-metal complex $[Ru^{III}_2Rh^{III}(O)(CH_3CO_2)_6(H_2O)_3]^+$ which involves a trivalent Rh center, no acceleration effect of Rh(III) was observed for substitution ($H_2O \rightarrow CD_3OD$) at Ru(III).[6] Large $\Delta H^{\ddagger}$ and positive (or near zero) $\Delta S^{\ddagger}$ values for **1** and **2** (Table 1) suggest a dissociative interchange mechanism. The mechanism is also supported by the weak dependence of activation parameters on solvents (CD_3CN and CD_2Cl_2), along with virtually no dependence of the rate constants on the concentration of py-d_5 (Supporting Information). Structural data further support the dissociative nature and the faster kinetics of **1**: a preliminary EXAFS analysis shows that the Ru−N(py) distance of **1** [2.22(11) Å in CH_2Cl_2, Ru K edge][18] is longer than the corresponding distances of a crystallographically characterized triruthenium complex $[Ru_3(O)(C_6H_5CO_2)_6(py)_3]PF_6$ (**5**, 2.134(8) Å)[19] and diruthenium complex $[Ru_2(O)(CH_3CO_2)_2(py)_6](PF_6)_2$ (**6**, 2.208(11) and 2.162(13) Å),[9] in which slower py/py-d_5 exchange reactions have been observed [$k = 2.2 \times 10^{-4}$ s^{-1} for **5** (50 °C)[19] and 4.9×10^{-6} s^{-1} for **6** (60 °C)[9]]. We note that the significant influence of divalent metal ions attached on the μ_3-oxo bridge in **1** and **2** can be related to observations for (μ-oxo)diruthenium(III) complexes with a $\{Ru_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2\}^{2+}$ core, in which the electronic, magnetic, and redox properties are dramatically tuned through modifications of the oxo bridge, e.g., protonation[20] and divalent-metal association.[21]

Conclusions

This work provides a rare example of site-distinctive ligand-exchange properties of mixed-metal trinuclear complexes. It was found that dissociative substitution of terminal pyridine ligands at Ru(III) centers in trinuclear Ru_2M complexes is substantially enhanced by a remote divalent metal ion M. This work also stresses the great importance of oxo-bridge modulation in kinetics and other properties of oxo-bridged, coupled metal assemblies. In order to fully understand the tuning ability of M, more detailed structural and mechanistic investigations are required with use of a range of M throughout the series,[4,5] and efforts along this line are currently being made.

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Supporting Information Available: Spectroscopic data for **2**; ^1H NMR spectra demonstrating py/py-d_5 exchange reactions for **2**, first-order plots, Eyring plots, and a summary of rate constants for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Rate constants obtained under various conditions are provided in the Supporting Information.

(15) We assume that the aqua ligand on the Mg site in **2** is most likely to be replaced by py-d_5 upon dissolution of the complex into a solution containing a large excess amount of py-d_5 and it exchanges with bulk py-d_5 on the NMR time scale at room temperature. In a separate experiment, we observe a very broad ^1H NMR signal (9.15 ppm) at −30 °C assignable to the Mg-coordinated py (2,6-H) for **2** in CD_2Cl_2 containing 100 equiv of normal pyridine. The signal becomes sharp upon cooling (−80 °C) while it disappears at elevated temperatures (over 0 °C) due to the complete averaging of the signal with that of free pyridine (8.60 ppm, 2,6-H).

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