SUPPORTING MATERIALS MADE AVAILABLE TO REVIEWERS

Electron Transfer on the Infrared Vibrational Time Scale in 1,4-Pyrazine and 4,4'-Bipyridine Bridged Ruthenium Cluster Charge Transfer Complexes

Tasuku Ito*, Tomohiko Hamaguchi, Haruko Nagino, Tadashi Yamaguchi, Hiroaki Kido,[a]

Department of Chemistry, Tohoku University, Aoba, Aramaki, Aoba-ku,

Sendai 980-8578, Japan;

Igor S. Zavarine, Todd Richmond, John Washington, and Clifford P. Kubiak* [b]

Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393, USA.

*To whom correspondence should be addressed

[a] Present address : College of Engineering, Nihon University, Koriyama 963-8642, Japan

[b] Present address : Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0358

X-ray data collection and structure determination

Crystals used in the X-ray analysis were obtained as dark deep green prisms by layering a solution of [$Ru_3(\mu_3\text{-}O)(CH_3COO)_6(CO)$(dmap)(pyrazine)] (3 mg/2 mL), EtOH/$CHCl_3$ (1/1, 2 mL), and an EtOH solution of [$Ru_3(\mu_3\text{-}O)(CH_3COO)_6(CO)$(dmap)($H_2O$)] (3 mg/2 mL) and allowing the layers to diffuse together over two weeks. The crystals of [{$Ru_3(\mu_3\text{-}O)(CH_3COO)_6(CO)$(dmap)}$_2$(pyrazine)] (**1**) were obtained as chloroform solvates and deteriorated quickly in air owing to the loss $CHCl_3$. Crystallinity therefore was not ideal. Intesity data were collected for three specimens. The best data obtained are as follows. A specimen with dimension of $0.50 \times 0.10 \times 0.70$ mm^3 was sealed in a thin-walled Lindemann glass capillary along with small amount of mother liquor. The specimen was mounted on a Rigaku AFC 7S four circle diffractometer. Crystallographic and structural data are summarized in Table S1.

A total of 7171 independent reflections in the range $3 < 2\theta < 45°$ were measured at room temperature by using a 2θ -ω scan at a scan rate of 4.0° min^{-1}. Intensity data were corrected for Lorentz and polarization effects, and for absorption (ψ scan method). The structure was solved by automatic Paterson analysis (DIRDIF 94 PATTY) and expanded by alternate difference Fourier syntheses and full matrix least-squares refinement. All non-hydrogen atoms within [{$Ru_3(\mu_3\text{-}O)(CH_3COO)_6(CO)$(dmap)}$_2$(pirazine)] were unambiguously located. The molecule lies on a crystallographic inversion center. Some of the chloroform molecules were severely disorded. Anisotropic temperature factors were applied to most of non-hydrogen atoms within the Ru_3 dimer. The final refinement gave $R = 0.112$ and $R_W = 0.113$ for 3484 independent reflections having $I > 3\sigma(I)$ and 437 independent parameters. All calculations were performed using teXsan crystallographic software. An ORTEP drawing of the complex is presented in Figure S1.

Table S1. Crystallographic data for $[\{Ru_3O(CH_3CO_2)_6(CO)(dmap)\}_2pz]\cdot 3CHCl_3$

Formula	$C_{47}H_{63}O_{28}N_6Ru_6Cl_9$
Formula weight	2085.55
a (Å)	14.075(7)
b (Å)	16.450(5)
c (Å)	12.85(2)
α (°)	93.40(6)
β (°)	112.23(6)
γ (°)	88.09(3)
V (Å^3)	2748(4)
Space Group	triclinic $P\bar{1}$ (No.2)
Z value	1
D_{calc} (g/cm^3)	1.331
μ (cm^{-1})	11.04
Transmission coefficient	0.7534 - 1.0000
R	0.112
R_w	0.113
Goodness of fit indicator	5.84

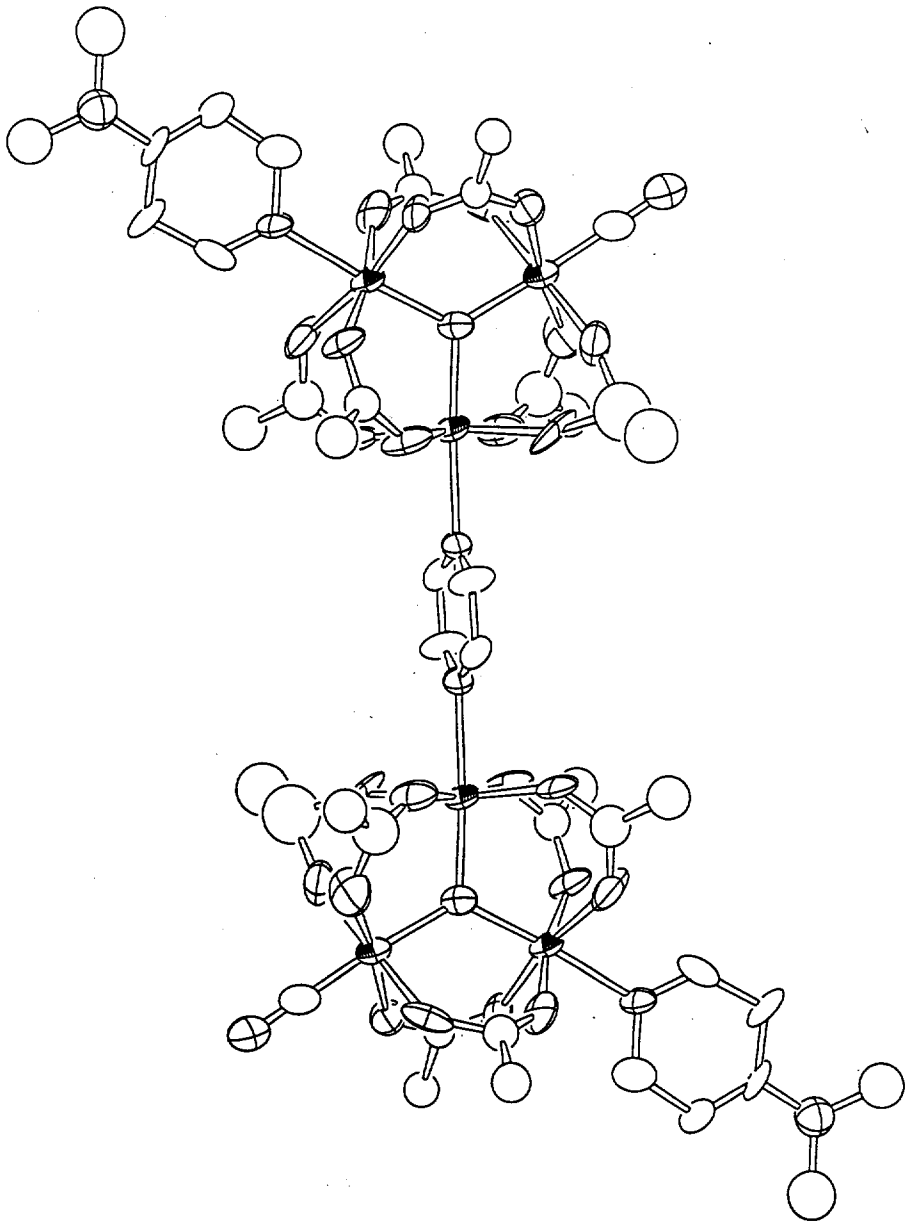

Figure S1.