Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Trans-heteroleptic carboxylate-bridged paddlewheel diruthenium(II, II) complexes with 2,6-bis(trifluoromethyl)benzoate ligands

Yoshihiro Sekine,[a,b] Wataru Kosaka,[a,b] Hirohisa Kano,[c] Changxiao Dou,[b]
Taiga Yokoyama,[b] and Hitoshi Miyasaka*[a,b]

a) Institute for Material Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

b) Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan

c) Department of Chemistry, Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

Corresponding author*
Prof. Dr. Hitoshi Miyasaka
Institute for Materials Research, Tohoku University
2–1–1 Katahira, Aoba-ku, Sendai 980-8577, Japan
E-mail: miyasaka@imr.tohoku.ac.jp
Tel: +81-22-215-2030
FAX: +81-22-215-2031

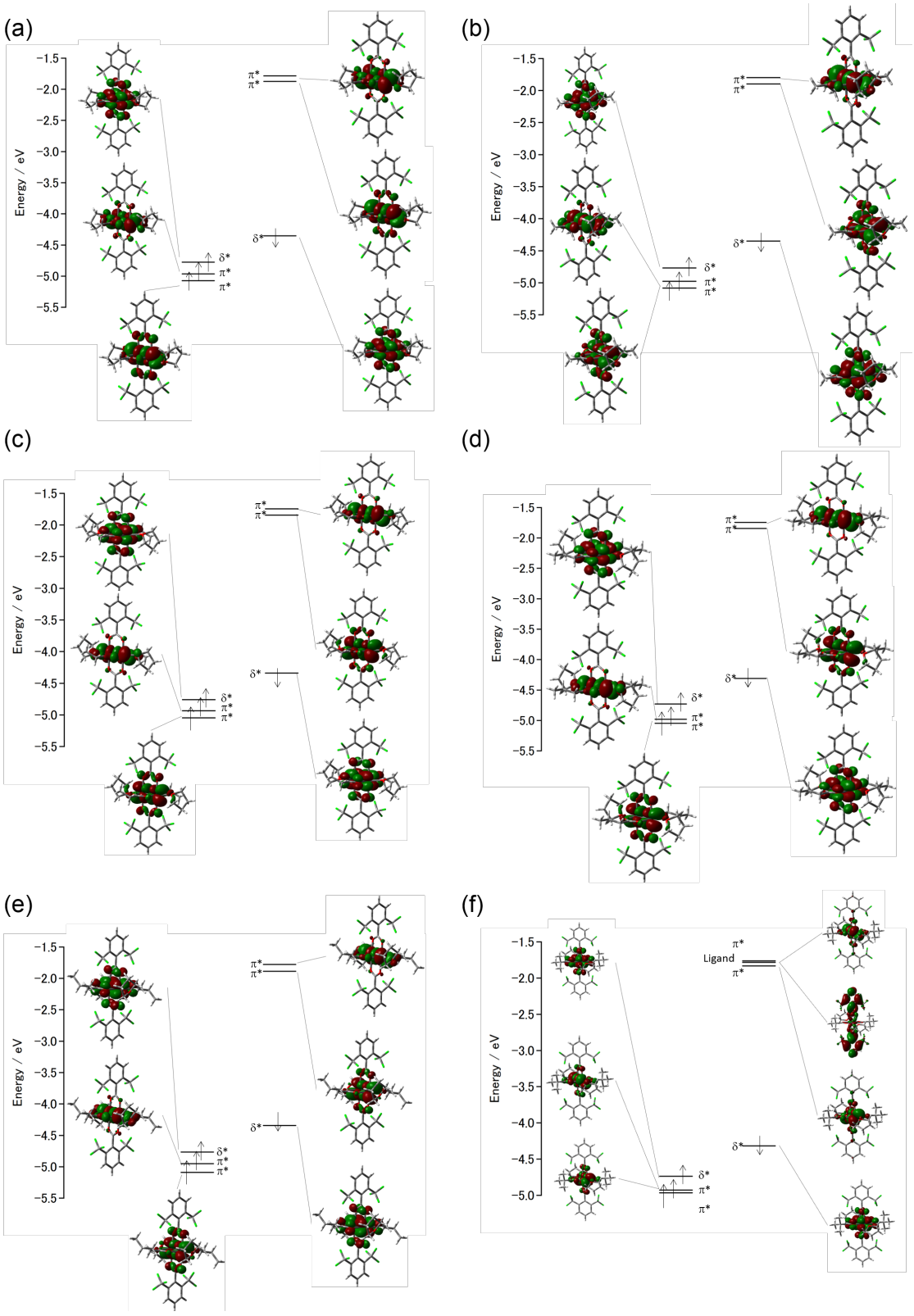

Figure S1. Frontier orbitals associated with π* and δ* orbitals of the diruthenium unit and their energy levels (eV) for **1** (a and b for $[Ru(1)_2]$ and $[Ru(2)_2]$, respectively), **2** (c), **3** (d), **4** (e), **5** (f), and **6** (g), where the β electron on the δ* orbital corresponds to the HOMO level of compound.

Table S1. Relevant bond lengths around Ru centers in heteroleptic and previously reported homoleptic $[Ru_2^{II,II}(F_xPhCO_2)_4(THF)_2]$ and related compounds (where O_{eq} means oxygen atoms of equatorial positions) and dihedral angles (°) between the least-squares planes defined by the phenyl ring of the benzoate ligand and the carboxylate-bridging mode (i.e. atom set of Ru_2O_2C) (Set-1 and Set-2: benzoate ligands structurally determined as asymmetric groups)

Compound	Ru-Ru/Å	Averaged Ru-O_{eq}/Å	Ru-O_{ax}/Å	Set-1	Set-2	Ref
$[Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(CH_3CO_2)_2(THF)_2]$ (unit 1)	2.2637(13)	2.066	2.327(4)	78.1		This work
(unit 2)	2.2638(13)	2.067	2.345(4)	76.5		This work
$[Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(C_2H_5CO_2)_2(THF)_2](THF)$	2.2696(6)	2.073	2.324(3)	67.0		This work
$[Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(C_3H_7CO_2)_2(THF)_2]$	2.2676(4)	2.066	2.3386(16)	70.5		This work
$[Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(C_4H_9CO_2)_2(THF)_2]$	2.2638(4)	2.068	2.3506(18)	79.1		This work
$[Ru_2^{II,II}(2,6\text{-}CF_3PhCO_2)_2(C(CH_3)_3CO_2)_2(THF)_2]$	2.2632(6)	2.068	2.339(4)	53.2		This work
$[Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(2,3,5,6\text{-}F_4PhCO_2)_2(THF)_2]$	2.2760(5)	2.069	2.351(2)	70.9	43.5	This work
$[Ru_2^{II,II}(CH_3CO_2)_4(THF)_2]$	2.261(3)	2.060	2.391(5)			1
$[Ru_2^{II,II}(CF_3CO_2)_4(THF)_2]$	2.276(3)	2.073	2.268(6)			2
$[Ru_2^{II,II}(PhCO_2)_4(THF)_2]$	2.2642(8)	2.065	2.314(4)			3
$[Ru_2^{II,II}(o\text{-}FPhCO_2)_4(THF)_2]$	2.2669(2)	2.067	2.312(2)	37.5	17.7	4
$[Ru_2^{II,II}(m\text{-}FPhCO_2)_4(THF)_2]$	2.2691(4)	2.065	2.331(2)	3.2	19.5	4
$[Ru_2^{II,II}(p\text{-}FPhCO_2)_4(THF)_2]$	2.2691(4)	2.061	2.331(2)	19.5	15.8	4
$[Ru_2^{II,II}(2,3,5,6\text{-}F_4PhCO_2)_4(THF)_2]$	2.2731(3)	2.065	2.298(2)	36.7	26.3	4

[a] averaged value. $PhCO_2^-$ = benzoate, *o*-$FPhCO_2^-$ = *o*-fluorobenzoate, *m*-$FPhCO_2^-$ = *m*-fluorobenzoate, *p*-$FPhCO_2^-$ = *p*-fluorobenzoate, 2,3,5,6-$F_4PhCO_2^-$ = 2,3,5,6-tetrafluorobenzoate.

Simulation of magnetic data

The magnetic susceptibility for $S = 1$ centers with zero-field splitting (D) and a temperature independent paramagnetic (χ_{TIP}) contribution can be expressed as in eqn. (1)[5]

$$\chi = (2Ng^2\beta^2/3k_BT)[\{\exp(-D/k_BT)+(2k_BT/D)(1-\exp(-D/k_BT))\}/(1+2\exp(-D/k_BT))+TIP \quad (1)$$

where β is Bohr magneton. The abrupt increase of χ at low temperature that can be observed in Figure 2 for the present compounds **1**-**6** is probably attributed to inter-molecular interactions and/or an extrinsic paramagnetic impurity (ρ) of a ubiquitous $Ru_2^{II,III}$ species ($S = 3/2$). These effects was taken into account by eqn. (2) in a mean-field approximation level.

$$\chi' = (1-\rho)(\chi/1-(2zJ/Ng^2\beta^2)\chi)+\rho(5Ng_{imp}^2\beta^2/4k_BT) \quad (2)$$

where z is the number of neighbours and J is the magnitude of the intermolecular interaction. The value of g_{imp} is assumed to be 2.0 by convention. In order to minimize the usual problems of refining many parameters (g, D, zJ, χ_{TIP}, ρ), the least-squares calculation was performed in a parameter range of $g = 2.0$ and $zJ = 0$ based on previously reported magnetic data.

References in ESI

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