Supporting Information

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Unusual Magnetic Properties of the Edge-sharing Biocahedral Dirhenium(IV) Complex of Pyridine-2-thiolate

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Experimental

Magnetic susceptibility measurements were performed on powdered samples over the temperature range 2.0-300 K in an applied field of 0.3 T using a Quantum Design MPMS5S SQUID magnetometer. Corrections for diamagnetic contributions were applied by using Pascal’s Constants.

UV-visible spectra were recorded on a Jasco V-560 or a Shimadzu UV-1600 spectrophotometer at 20 °C. The 1H NMR spectra were obtained at 400 MHz with a JEOL JNM-GX400 spectrometer.

Cyclic voltammetry was performed with a Hokuto HA-301 potentiostat and a Hokuto HB-104 function generator equipped with a Yokokawa 3086 X-Y recorder. The working and the counter electrodes were a glassy-carbon disk and a platinum wire, respectively. Cyclic voltammograms were recorded at a scan rate of 50 mV/s. The sample solutions (ca. 0.5 mM) in 0.1 M n-Bu4NPF6-CH2Cl2 were deoxygenated with a stream of argon. The reference electrode was Ag/AgCl and the half-wave potential of Fc+/Fc (E1/2(Fc+/0) vs Ag/AgCl) was +0.49 V.

Controlled-potential coulometry was carried out in 0.1 M n-Bu4NPF6-CH2Cl2 with a standard H-type cell with a Hokuto HA-310 potentiostat and a Fuso Model 1119 integrator. The working electrode was made of platinum foil, and the working compartment was separated from the counter compartment by a sintered-glass disk.

Crystal structure analyses: Single crystal X-ray diffraction data were collected on a Quantum CCD area detector coupled with a Rigaku AFC7 diffractometer (for 1a·CH2Cl2, 1b and (PPN)[2a]·3CH2Cl2) and Rigaku/MSC Mercury CCD diffractometer (for (Et4N)[2a]) with graphite monochromated MoKα radiation (λ = 0.71069 Å). 1a·CH2Cl2: crystal dimensions 0.15 × 0.10 × 0.10 mm3, triclinic, space group P1-, a = 9.058(2), b = 11.981(3), c = 13.617(2) Å, α = 98.544(1), β = 99.981(3), γ = 109.4057(7) °, V = 1376.4(6) Å3, Z = 2, T = 296 K, ρcalcd = 2.376 g cm−3, 2θmax = 55.38 °, μ(MoKα) = 9.507 mm−1, symmetry-related absorption correction (transmission coefficient: 0.1826, 0.3865). Reflections: 11986 collected, 5904 unique (Rint = 0.042), 4351 observed [I>2σ(I)]; 325 parameters refined with R = 0.0466 [I>2σ(I)], wR2 = 0.1448 (all data), GOF = 1.391, residual electron density: +2.15, -2.42 eÅ−3. 1b: crystal dimensions 0.25 × 0.12 × 0.04 mm3, monoclinic, space group P21/m, a = 8.889(1), b = 14.811(3), c = 10.4333(2) Å, β = 99.4180(5) °, V = 1355.1(3) Å3, Z = 2, T = 296 K, ρcalcd = 2.205 g cm−3, 2θmax = 54.96 °, μ(MoKα) = 9.455 mm−1.
symmetry-related absorption correction (transmission coefficient: 0.2834, 0.6851). Reflections: 11750 collected, 3167 unique ($R_{int} = 0.035$), 166 parameters refined with $R = 0.0310$ [$I>\sigma(I)$], $wR_2 = 0.0989$ (all data), GOF = 1.035, residual electron density: +1.15, -1.01 eÅ$^{-3}$. (PPN)[2a]$\cdot$3CH$_2$Cl$_2$: crystal dimensions 0.60 $\times$ 0.40 $\times$ 0.10 mm$^3$, monoclinic, space group $P2_1/c$, $a = 13.072(2)$, $b = 13.4544(8)$, $c = 37.2835(9)$ Å, $\beta = 98.2243(6)$°, $V = 6490.0(9)$ Å$^3$, $Z = 4$, $T = 296$ K, $\rho_{calc} = 1.733$ g cm$^{-3}$, $\mu$(MoK$\alpha$) = 4.279 mm$^{-1}$, symmetry-related absorption correction (transmission coefficient: 0.2897, 0.6519). Reflections: 45721 collected, 13410 unique ($R_{int} = 0.036$), 10573 observed [$I>\sigma(I)$]; 730 parameters refined with $R = 0.0580$ [$I>\sigma(I)$], $wR_2 = 0.1670$ (all data), GOF = 1.330, residual electron density: +2.71, -2.26 eÅ$^{-3}$. (Et$_4$N)[2a]: crystal dimensions 0.20 $\times$ 0.20 $\times$ 0.20 mm$^3$, monoclinic, space group $Cc$, $a = 22.255(3)$, $b = 8.518(1)$, $c = 20.832(3)$ Å, $\beta = 121.132(3)$°, $V = 3380.1(9)$ Å$^3$, $Z = 4$, $T = 93$ K, $\rho_{calc} = 2.024$ g cm$^{-3}$, $\mu$(MoK$\alpha$) = 7.596 mm$^{-1}$, symmetry-related absorption correction (transmission coefficient: 0.0840, 0.2189). Reflections: 13709 collected, 3822 unique ($R_{int} = 0.050$), 3612 observed [$I>\sigma(I)$]; 215 parameters refined with $R = 0.0433$ [$I>\sigma(I)$], $wR_2 = 0.1027$ (all data), GOF = 1.030, residual electron density: +1.95, -2.01 eÅ$^{-3}$. All crystal structures were solved by heavy-atom method by using DIRDIF94.$[1]$ The positional and thermal parameters of non-H atoms were refined anisotropically by the full-matrix least-squares method for 1a$\cdot$CH$_2$Cl$_2$ and (PPN)[2a]$\cdot$3CH$_2$Cl$_2$, whereas Re, Cl, S and O atoms in the complex anion were refined anisotropically and the rest of atoms were refined isotropically by the full-matrix least-squares method for (Et$_4$N)[2a]. For 1b, N11-C16 atoms in pyridine ring (1) were refined isotropically and the rest of atoms were refined anisotropically by the full-matrix least-squares method. All calculations were performed using TEXSAN.$[2]$ Magnetic Susceptibility: The magnetic susceptibility in an applied magnetic field is represented by the following van Vleck equation:$[3]$

$$\chi = N \sum_J (2J + 1) \exp \left( - \frac{E_J}{k_B T} \right) \left[ g_J J J + \alpha_J \right]$$

where $k_B$, $J$, and $g_J$ are the Bohr magneton, the total angular momentum, and the Landé $g$-factor, respectively, and $E_J$ is the energy level with the momentum $J$. The constant $\alpha_J$ is derived from the van Vleck constant paramagnetism and is written as

$$\alpha_J = \frac{\mu_B^2}{6(2J + 1)} \left[ \frac{F(J + 1)}{E_{J+1} - E_J} + \frac{F(J)}{E_{J-1} - E_J} \right]$$

where $F(J)$ is

$$F(J) = \frac{[(L + S + 1)^2 - J]^2}{J^2 - (S - L)^2}.$$
Assuming the two-energy-level system of the ground state \(^1\text{A}_1\text{g} (J = 0)\) and the first excited state \(^3\text{B}_1\text{u} (J = 1)\), the equation (S1) reduces to

\[
\chi_{\alpha \mu} = \frac{\alpha_0 + \left\{ \frac{g_J^2 \mu_B^2}{k_B T} + \alpha_1 \right\} \exp\left(\frac{-E_1}{k_B T}\right)}{1 + 3\exp\left(\frac{-E_1}{k_B T}\right)}
\]  

(S4)

In consideration of the Curie-Weiss paramagnetism \((C/T)\) of impurities in a proportion \(n\) and temperature-independent term \((\chi_{\text{TIP}})\), the total magnetic susceptibility of the complex 1a is given by the following equation,

\[
\chi = (1 - n)N \frac{\alpha_0 + \left\{ \frac{g_J^2 \mu_B^2}{k_B T} + \alpha_1 \right\} \exp\left(\frac{-E_1}{k_B T}\right)}{1 + 3\exp\left(\frac{-E_1}{k_B T}\right)} + \chi_{\text{TIP}} + n \frac{C}{T}.
\]

References


Figure S1. Cyclic voltammogram of the major isomer of [Re₂Cl₂O(py)t]₄ (1a) in 0.1 M TBAPF₆-CH₂Cl₂ with a scan rate of 50 mV/s
Figure S2. $^1$H NMR spectra of $[\text{Re}_2\text{Cl}_2\text{O}(\text{pyt})_4]$ in CDCl$_3$; a) minor isomer (1b), b) major isomer (1a).
**Figure S3.** UV-vis spectra of 1a (■) and 1b (■■) in CH$_2$Cl$_2$.

$\lambda$/nm ($\varepsilon$/M$^{-1}$cm$^{-1}$): (1a) 258 (30600), 322 sh (12900), 409 (4930), 491 sh, 582 (9010); (1b) 262 (30000), 320 sh (11800), 405 sh (3350), 483 sh, 573 (7260).
**Figure S4.** UV-vis spectra of [Et₄N][2a] in CH₂Cl₂. \( \lambda / \text{nm} \) (\( \varepsilon / \text{M}^{-1} \text{cm}^{-1} \)): 384 (6950), 418 sh, 475 sh (ca 5200), 516 sh, 578 (2980), 692 sh.