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 ($E_{1/2}(\text{Fc}^+/\text{Fc})$ 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 Mo_{K α} radiation ($\lambda = 0.71069 \text{ \AA}$). **1a**·CH₂Cl₂: crystal dimensions $0.15 \times 0.10 \times 0.10 \text{ mm}^3$, triclinic, space group *P*1-, $a = 9.058(2)$, $b = 11.981(3)$, $c = 13.617(2) \text{ \AA}$, $\alpha = 98.544(1)$, $\beta = 89.981(3)$, $\gamma = 109.405(7)^\circ$, $V = 1376.4(6) \text{ \AA}^3$, $Z = 2$, $T = 296 \text{ K}$, $\rho_{\text{calcd}} = 2.376 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 55.38^\circ$, $\mu(\text{Mo}_{K\alpha}) = 9.507 \text{ mm}^{-1}$, symmetry-related absorption correction (transmission coefficient: 0.1826, 0.3865). Reflections: 11986 collected, 5904 unique ($R_{\text{int}} = 0.042$), 4351 observed [$I > 2\sigma(I)$]; 325 parameters refined with $R = 0.0466$ [$I > 2\sigma(I)$], $wR_2 = 0.1448$ (all data), GOF = 1.391, residual electron density: +2.15, -2.42 e $\text{\AA}^{-3}$. **1b**: crystal dimensions $0.25 \times 0.12 \times 0.04 \text{ mm}^3$, monoclinic, space group *P*2₁/*m*, $a = 8.889(1)$, $b = 14.811(3)$, $c = 10.4333(2) \text{ \AA}$, $\beta = 99.4180(5)^\circ$, $V = 1355.1(3) \text{ \AA}^3$, $Z = 2$, $T = 296 \text{ K}$, $\rho_{\text{calcd}} = 2.205 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 54.96^\circ$, $\mu(\text{Mo}_{K\alpha}) = 9.455 \text{ mm}^{-1}$,

symmetry-related absorption correction (transmission coefficient: 0.2834, 0.6851). Reflections: 11750 collected, 3167 unique ($R_{\text{int}} = 0.035$), 2362 observed [$I > 2\sigma(I)$]; 166 parameters refined with $R = 0.0310$ [$I > 2\sigma(I)$], $wR_2 = 0.0989$ (all data), $\text{GOF} = 1.035$, residual electron density: +1.15, -1.01 $\text{e}\text{\AA}^{-3}$. (PPN)[**2a**] $\cdot 3\text{CH}_2\text{Cl}_2$: crystal dimensions $0.60 \times 0.40 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 13.072(2)$, $b = 13.4544(8)$, $c = 37.2835(9) \text{ \AA}$, $\beta = 98.2243(6)^\circ$, $V = 6490.0(9) \text{ \AA}^3$, $Z = 4$, $T = 296 \text{ K}$, $\rho_{\text{calcd}} = 1.733 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 55.50^\circ$, $\mu(\text{Mo}_{\text{K}\alpha}) = 4.279 \text{ mm}^{-1}$, symmetry-related absorption correction (transmission coefficient: 0.2897, 0.6519). Reflections: 45721 collected, 13410 unique ($R_{\text{int}} = 0.036$), 10573 observed [$I > 2\sigma(I)$]; 730 parameters refined with $R = 0.0580$ [$I > 2\sigma(I)$], $wR_2 = 0.1670$ (all data), $\text{GOF} = 1.330$, residual electron density: +2.71, -2.26 $\text{e}\text{\AA}^{-3}$. (Et_4N)[**2a**]: crystal dimensions $0.20 \times 0.20 \times 0.20 \text{ mm}^3$, monoclinic, space group Cc , $a = 22.255(3)$, $b = 8.518(1)$, $c = 20.832(3) \text{ \AA}$, $\beta = 121.132(3)^\circ$, $V = 3380.1(9) \text{ \AA}^3$, $Z = 4$, $T = 93 \text{ K}$, $\rho_{\text{calcd}} = 2.024 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 54.96^\circ$, $\mu(\text{Mo}_{\text{K}\alpha}) = 7.596 \text{ mm}^{-1}$, symmetry-related absorption correction (transmission coefficient: 0.0840, 0.2189). Reflections: 13709 collected, 3822 unique ($R_{\text{int}} = 0.050$), 3612 observed [$I > 2\sigma(I)$]; 215 parameters refined with $R = 0.0433$ [$I > 2\sigma(I)$], $wR_2 = 0.1027$ (all data), $\text{GOF} = 1.030$, residual electron density: +1.95, -2.01 $\text{e}\text{\AA}^{-3}$. 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** $\cdot\text{CH}_2\text{Cl}_2$ and (PPN)[**2a**] $\cdot 3\text{CH}_2\text{Cl}_2$, 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_4N)[**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]

$$\chi = N \frac{\sum_J (2J+1) \exp\left(-\frac{E_J}{k_B T}\right) \left\{ \frac{g_J^2 \mu_B^2 J(J+1)}{3k_B T} + \alpha_J \right\}}{\sum_J (2J+1) \exp\left(-\frac{E_J}{k_B T}\right)}, \quad (\text{S1})$$

where μ_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 α_J is derived from the van Vleck constant paramagnetism and is written as

$$\alpha_J = \frac{\mu_B^2}{6(2J+1)} \left[\frac{F(J+1)}{E_{J+1} - E_J} + \frac{F(J)}{E_{J-1} - E_J} \right], \quad (\text{S2})$$

where $F(J)$ is

$$F(J) = \frac{[(L+S+1)^2 - J^2][J^2 - (S-L)^2]}{J}. \quad (\text{S3})$$

Assuming the two-energy-level system of the ground state $^1A_{1g}$ ($J = 0$) and the first excited state $^3B_{1u}$ ($J = 1$), the equation (S1) reduces to

$$\chi = \frac{\alpha_0 + \left\{ \frac{2g_J^2 \mu_B^2}{k_B T} + \alpha_1 \right\} \exp\left(-\frac{E_1}{k_B T}\right)}{1 + 3 \exp\left(-\frac{E_1}{k_B T}\right)} \quad (S4)$$

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

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

References

- [1] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits The DIRDIF94 Program System. Technical Report: Crystallography Laboratory, University of Nijmegen: The Netherlands, 1994.
- [2] teXsan: Crystal Structure Analysis Package. Molecular Structure Corporation: The Woodlands, TX 77381, USA, 1999.
- [3] J. H. Van Vleck, Theory of Electric and Magnetic Susceptibilities (Clarendon, Oxford, 1932)

Figure S1. Cyclic voltammogram of the major isomer of $[\text{Re}_2\text{Cl}_2\text{O}(\text{py})_4]$ (**1a**) in $0.1 \text{ M TBAPF}_6\text{-CH}_2\text{Cl}_2$ with a scan rate of 50 mV/s

Figure S2. ^1H 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_2Cl_2 .
 λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): (**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. λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 384 (6950), 418 sh, 475 sh (ca 5200), 516 sh, 578 (2980), 692 sh.