Supporting Information for

Strong antiferromagnetic coupling of the cobalt(II)–semiquinone radical in a dinuclear complex with 2,2′-bipyrimidine ligands

Jin-Hua Wang,[a] Jing-Wei Dai,[b] Zhao-Yang Li,[a] and Masahiro Yamashita[a,c,d]*

[a]*School of Materials Science and Engineering, Nankai University, 38 Tongyan Road, Haihe Educational Park, Jinnan District, Tianjin 300350, P. R. China*

[b]*State Key Laboratory of Medicinal Chemical Biology, Nankai University, 94 Weijin Road, Nankai District, Tianjin 300071, P. R. China*

[c]*WPI-Advanced Institute for Materials Research (AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

[d]*Department of Chemistry, Graduate School of Science, Tohoku University, 980-8578 Sendai, Japan*

E-mail: zhaoyang@nankai.edu.cn (Z. Y. Li)

1. General methods

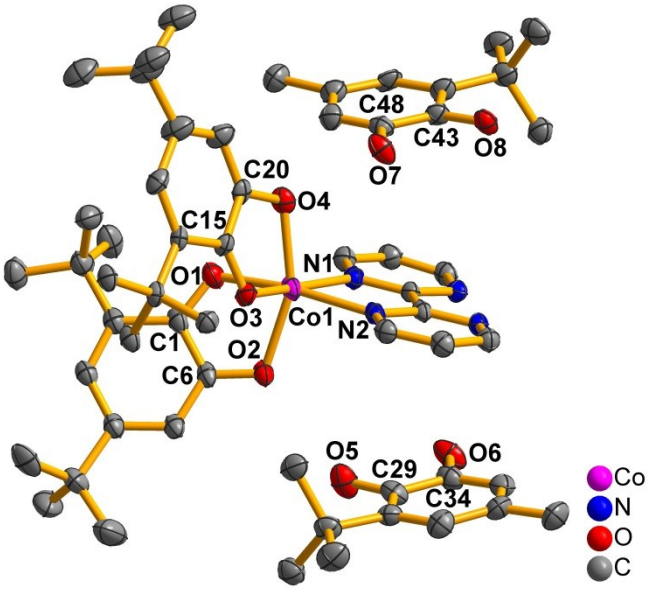
1.1 Materials and methods

The reagents and solvents used were commercially available and without further purification. Thermogravimetric analysis (TGA) was carried out on a Rigaku standard TG-DTA analyzer from room temperature to 700 °C in argon atmosphere with a heating rate of 10 °C min^{-1}. Elemental analysis (C, H, and N) was performed on a vario EL cube elemental analyzer. Powder X-ray diffraction (PXRD) was performed on a Rigaku Miniflex 600 at room temperature. The direct current magnetic susceptibilities were measured for polycrystalline samples on a Quantum Design superconducting quantum interference device (SQUID) magnetometer operated between 1.8 and 300 K.

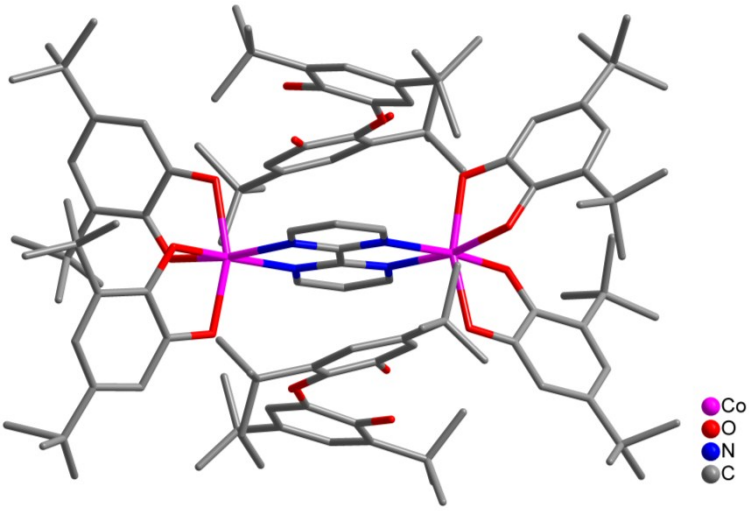
1.2 X-ray crystallography

Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku Miniflex 600 at room temperature. The single-crystal XRD study of complex **1** was performed on a Rigaku diffractometer equipped with charge-coupled device (CCD) area detector with a graphite monochromator. The unit cell parameters and full data set were obtained using Cu-K_α radiation (λ = 1.54 Å). The data were corrected by a semi-empirical method using SADABS. SAINT was used for data integration. The structure was solved by direct methods using SHELXS and refined with SHELXL of the SHELXTL-97 package [1]. The final refinements were performed by using full matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms on F^2. The uncoordinated solvent molecules were disordered and were removed using the SQUEEZE algorithm in PLATON [2]. The results of this treatment are appended to the CIF file. A summary of the crystallographic data and structure refinement of **1** are listed in Table 1. Selected bond lengths and angles are given in Table 2.

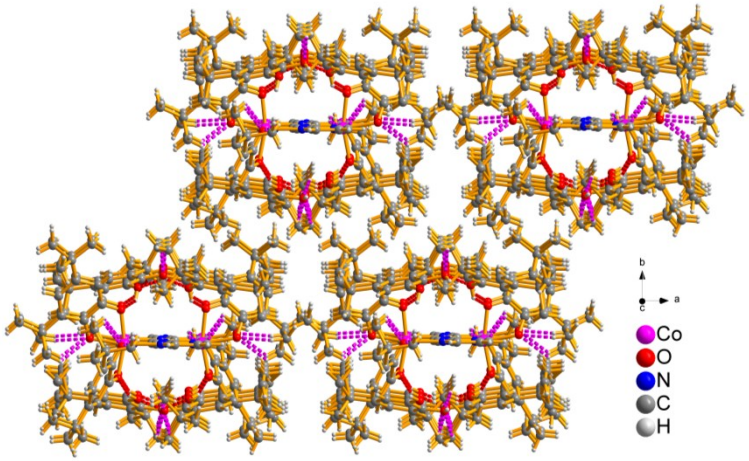
2. X-ray structure determination



(a)



(b)



(c)

Fig. S1 (a) A perspective view of the coordination geometry of **1** at 100 K (Thermal ellipsoids are drawn at the 30% probability level). (b) The molecular structure of **1**. (c) Packing diagram of the dinuclear units in complex **1**.

Table S1 Hydrogen bond geometries in the crystal structures at 100 K for **1**.

D–H···A	H···A (Å)	D···A (Å)	D–H···A(°)
O5–H5B···O2	1.65	2.465(16)	163
O6–H6···O5	1.92	2.666(8)	147'
O7–H7···O4	1.82	2.641(12)	164
O8–H8···O7	2.04	2.731(7)	139'
Intra-C9–H9C···O1	2.45	3.143(11)	127
Intra-C10–H10A···O1	2.38	3.089(10)	128
Intra-C22–H22C···O3	2.34	2.997(15)	124
Intra-C24–H24A···O3	2.39	3.011(12)	120
Intra-C38–H38C···O6	2.43	3.059(7)	121
Intra-C51–H51C···O8	2.22	2.880(6)	123

3. Infrared spectroscopy

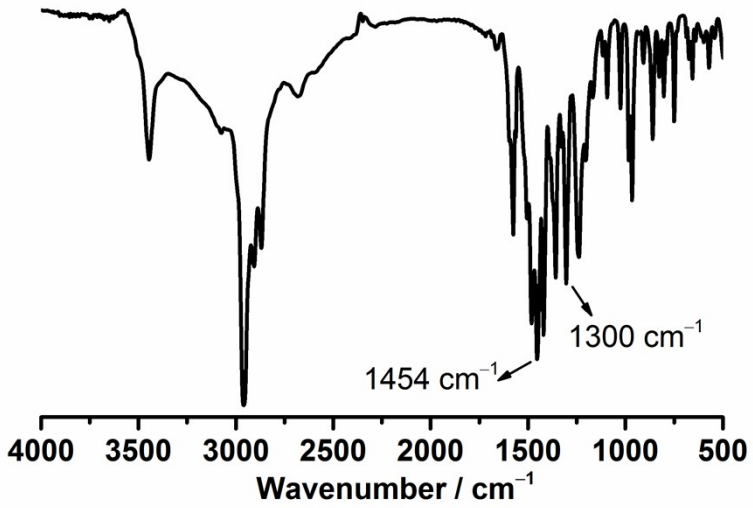


Fig. S2 IR spectra between 500 and 4000 cm^{-1} for complex **1**.

4. Thermogravimetric analysis (TGA)

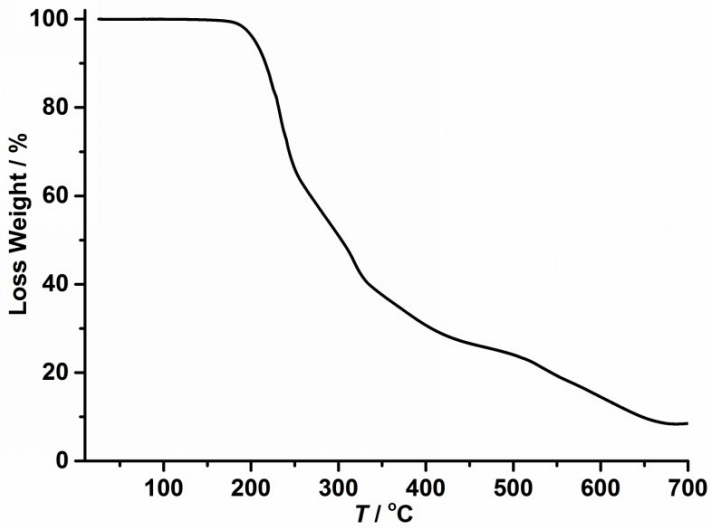
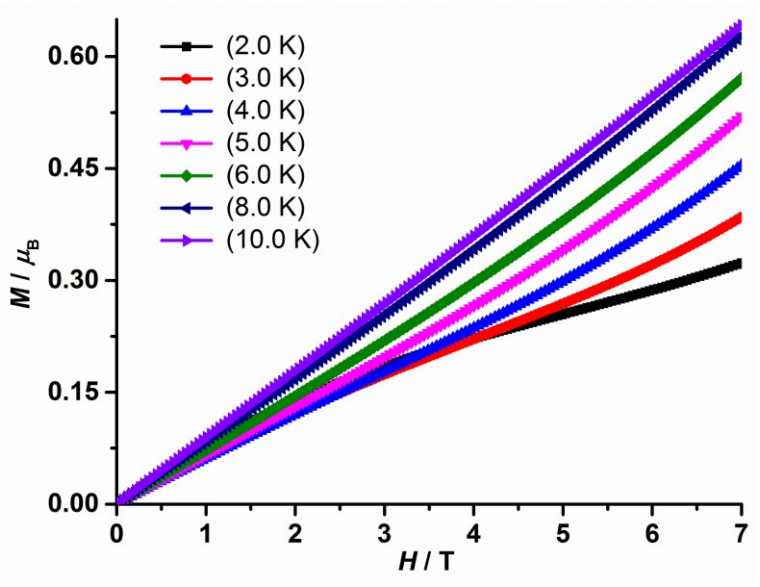


Fig. S3 TGA curve of **1**.

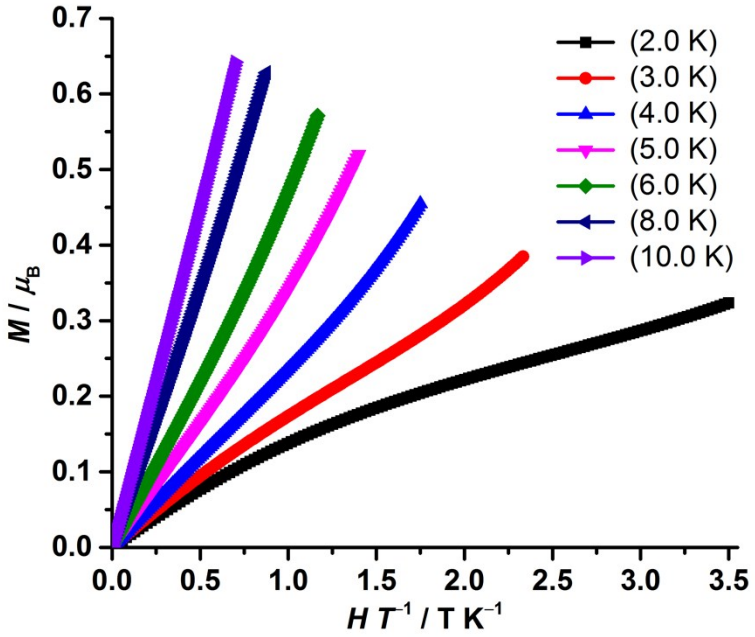
5. Magnetic properties

Table S2 Selected antiferromagnetic coupling between 3d metal ions and semiquinone radical.

M (3d) – R (semiquinone radical)	*J*	Ref
Cu(II) – R	-64.0 cm^{-1}	3
Fe(II) – R	-83 cm^{-1}	4
Fe(II) – R	-127 cm^{-1}	5
Fe(III) – R	-206 cm^{-1}	6
Mn(II) – R	-41.3 cm^{-1}	7
Ni(II) – R	-87.8 cm^{-1}	7
Ni(II) – R	-364 cm^{-1}	8
Ni(II) – R	-382 cm^{-1}	5
Ni(II) – R	-320 cm^{-1}	5
Co(II) – R	-18 cm^{-1}	9
Co(II) – R	0 cm^{-1}	10
Co(II) – R	-7 cm^{-1}	11
Co(II) – R	-594 cm^{-1}	12
Co(II) – R	-90.25 cm^{-1}	This work



(a)



(b)

Fig. S4 (a) SQUID magnetization M (μ_B) plotted versus external magnetic field H (T) plot under 2.0–10.0 K for **1**. (b) M vs. H/T data plot in the range of 0–7 T under 2.0–10.0 K for **1**.

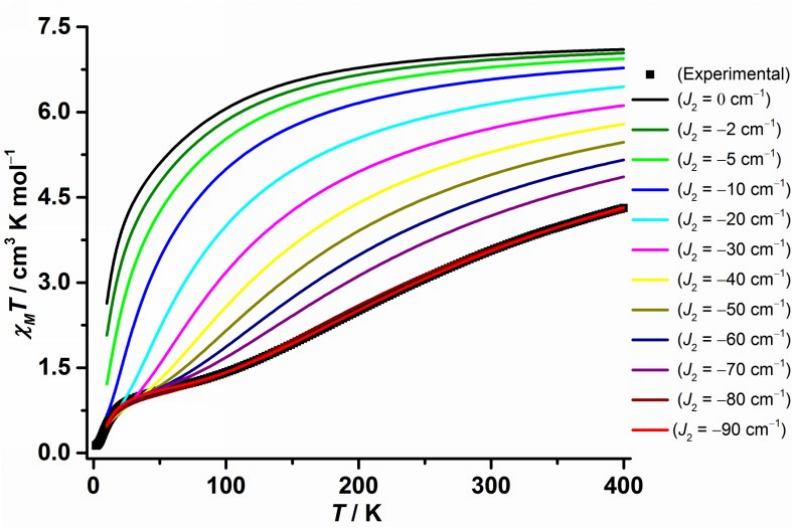


Fig. S5 The $\chi_M T$ vs. T simulations for **1** where the $g_R = 2.0$, $g_{CoII} = 2.49$, $D_{CoII} = 87.41$ cm^{-1}, $zJ' = 0.02$ cm^{-1}, $J_1 = -2.67$ cm^{-1} and $J_3 = -2.14$ cm^{-1} were fixed and the J_2 values were varied (lines).

6. References

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