Supporting Information for

## On Balancing the QTM and the Direct Relaxation Processes in Single-Ion Magnets - the Importance of Symmetry Control

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	1			2			
Bonds	Å	Angles	0	Bonds	Å	Angles	0
Co(1)-O(1)	1.8637(9)	O(1)-Co(1)-O(2)	124.62(3)	Co(1)-O(1)	1.8374(11)	O(1)-Co(1)-O(2)	129.76(5)
Co(1)-O(1A)	1.8637(9)	O(1A)-Co(1)-O(2)	124.62(3)	Co(1)-O(2)	1.8701(10)	O(1)-Co(1)-O(3)	124.87(5)
Co(1)-O(2)	1.8346(14)	O(1)-Co(1)-O(1A)	110.77(6)	Co(1)-O(3)	1.8943(11)	O(2)-Co(1)-O(3)	105.27(5)

Table S1. Selected bond lengths (Å) and angles (°) for complexes 1 and 2.

Symmetry transformations used to generate equivalent atoms: A -x, y, -z+1/2

 Table S2. The best results fitted for 1 under 1500 Oe dc field by a generalized Debye model.

	1	
$T/\mathrm{K}$	au / s	α
2.00	5.89×10 <sup>-2</sup>	0.16
2.29	1.90×10 <sup>-2</sup>	0.11
2.60	5.61×10 <sup>-3</sup>	0.07
2.90	1.91×10 <sup>-3</sup>	0.05
3.20	7.43×10 <sup>-4</sup>	0.04
3.51	3.19×10 <sup>-4</sup>	0.03
3.85	$1.47 \times 10^{-4}$	0.04
4.13	6.66×10 <sup>-5</sup>	0.06
4.35	4.41×10 <sup>-5</sup>	0.03



Figure S1. (a) Packing arrangements of complexes 1 (a) and 2 (b). The dashed lines show the nearest intermolecular Co…Co separation. Hydrogen atoms and cations are omitted for clarity.



**Figure S2**. Temperature dependence of the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) ac susceptibility for **1** under zero dc field. The lines are guides to the eyes.



**Figure S3**. Temperature dependence of the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) ac susceptibility for **2** under zero dc field. The lines are guides to the eyes.



**Figure S4**. Frequency dependence of the in-phase ( $\chi'$ ) ac susceptibility for **1** at 2 K under different dc fields. The lines are guides to the eyes.



**Figure S5**. Frequency dependence of the out-of-phase ( $\chi''$ ) ac susceptibility for **1** at 2 K under different dc fields. The lines are guides to the eyes.



**Figure S6**. Frequency dependence of the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) ac susceptibility for **2** at 2 K under different dc fields. The lines are guides to the eyes.



**Figure S7**. Temperature dependence of the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) ac susceptibility for **1** under 1500 Oe dc field. The lines are guides to the eyes.



**Figure S8.** Frequency dependence of the in-phase  $\chi'$  (top) and out-of-phase  $\chi''$  (bottom) components of the alternating-current (ac) susceptibility for the complex **1** measured under 1500 Oe dc field in the temperature range of 2.00–4.35 K. The lines are guides to the eyes.



Figure S9. Cole-Cole plots for 1 at 1500 Oe dc field. The solid lines represent the best fit to the data.



**Figure S10**. Power law analysis in the form  $ln(\tau)$  vs ln(T). The solid line represents the best fits to the data.

${}^{4}\Psi_{0}$ 0.00.0 ${}^{4}\Psi_{1}$ 309.2434.0 ${}^{4}\Psi_{2}$ 991.51221.4 ${}^{4}\Psi_{3}$ 3851.33522.0 ${}^{4}\Psi_{4}$ 4648.65529.8		1	2
${}^{4}\Psi_{1}$ 309.2434.0 ${}^{4}\Psi_{2}$ 991.51221.4 ${}^{4}\Psi_{3}$ 3851.33522.0 ${}^{4}\Psi_{4}$ 4648.65529.8	${}^{4}\Psi_{0}$	0.0	0.0
${}^{4}\Psi_{2}$ 991.51221.4 ${}^{4}\Psi_{3}$ 3851.33522.0 ${}^{4}\Psi_{4}$ 4648.65529.8	${}^{4}\Psi_{1}$	309.2	434.0
${}^{4}\Psi_{3}$ 3851.33522.0 ${}^{4}\Psi_{4}$ 4648.65529.8	${}^{4}\Psi_{2}$	991.5	1221.4
<sup>4</sup> Ψ <sub>4</sub> 4648.6 5529.8	${}^{4}\Psi_{3}$	3851.3	3522.0
	${}^{4}\Psi_{4}$	4648.6	5529.8

Table S3. The relative energies of ground and low-lying Quartet spin eigenstates (cm<sup>-1</sup>).

Table S4. The relative energies of ground and first excited Kramers doublets (KD) (cm<sup>-1</sup>).

	1	2
$KD_0$	0.0	0.0
$KD_1$	218.27	211.8

**Table S5.** The occupation number (occ), orbital energy (oe) and contributions (%) of five metal 3d atomic orbitals to the active orbitals  $\varphi_1$ - $\varphi_5$  of **1**.

	occ (a.u.)	oe (eV)	$d_{z2}$	$d_{xz}$	$d_{yz} \\$	d <sub>x2-y2</sub>	$d_{xy}$	other
φ1	1.499	0.000	5.3	89.1	0.0	3.5	0.0	2.1
φ <sub>2</sub>	1.467	0.424	0.0	0.0	2.0	0.0	95.7	2.3
φ3	1.421	0.986	15.6	0.7	0.0	80.0	0.0	3.7
φ4	1.372	2.051	74.2	8.4	0.0	12.2	0.0	5.2
φ5	1.241	3.711	0.0	0.0	92.0	0.0	2.0	6.0



Figure S11. The dc magnetizations and susceptibilities of 1 and 2 reproduced with the calculated spin Hamiltonian parameters.



**Figure S12.** The CASSCF energy diagram and perspective views of the active orbitals (mainly 3d metal orbitals) as well as the electronic configuration of the ground quartet (S = 3/2) state of **2** 

	occ (a.u.)	oe (eV)	$d_{z2}$	$d_{xz}$	$d_{yz} \\$	d <sub>x2-y2</sub>	$d_{xy}$	other
$\phi_1$	1.50586	0.000	10.8	81.5	0.8	4.9	0.0	2.0
$\phi_2$	1.46421	0.545	0.0	0.1	1.7	0.1	95.8	2.3
φ3	1.42300	1.110	7.3	2.0	0.1	86.5	0.2	3.9
φ4	1.41057	1.516	72.3	14.9	5.5	3.0	0.2	4.1
φ5	1.19636	4.346	5.3	0.0	85.7	1.1	1.6	6.3

**Table S6.** The occupation number (occ), orbital energy (oe) and contributions (%) of five metal 3d atomic orbitals to the active orbitals  $\varphi_1$ - $\varphi_5$  of **2**.

**Table S7.** Qualitative analysis of the contribution of the SOC between the ground and the two lowest excited Quartets to the magnetic anisotropy based on CAS (7e, 5o)/TZ results of **1**.

	main single excitation	$\Delta m_1$	$\Delta m_{\rm s}$	contribution
$\left< {}^{4}\Phi_{1} \left  H_{soc}^{e\!f\!f} \right  {}^{4}\Phi_{0} \right>$	$\phi_2(d_{xy}) \Longrightarrow \phi_3(d_{x2-y2})$	0	0	negative D
	$\phi_1(d_{xz}) \Rightarrow \phi_5(d_{yz})$	0	0	negative D
$\left< {}^{4}\Phi_{2} \left  H^{e\!f\!f}_{soc} \right  {}^{4}\Phi_{0} \right>$	$\phi_1(d_{xz}) \Longrightarrow \phi_3(d_{x2-y2})$	±l	±1	positive D
\ I I /	$\phi_1(d_{xz}) \Longrightarrow \phi_4(d_{z2})$	±l	±1	positive D
	$\phi_2(d_{xy}) \Longrightarrow \phi_5(d_{yz})$	±1	±1	positive D



**Figure S13.** Composition of the wavefunctions corresponding to the ground  $({}^{4}\Psi_{0})$  and first two excited  $({}^{4}\Psi_{1})$  and  ${}^{4}\Psi_{2}$  Quartets of **2**.

**Table S8.** Qualitative analysis of the contribution of the SOC between the ground and the two lowest excited Quartets to the magnetic anisotropy based on CAS(7e, 5o)/TZ results of **2**.

	main single excitation	$\Delta m_1$	$\Delta m_{\rm s}$	contribution
$\left< {}^{4}\Phi_{1} \left  H_{soc}^{e\!f\!f} \right  {}^{4}\Phi_{0} \right>$	$\phi_2(d_{xy}) \Longrightarrow \phi_3(d_{x2-y2})$	0	0	negative D
	$\phi_1(d_{xz}) \Rightarrow \phi_5(d_{yz})$	0	0	negative D
$\left< {}^4\Phi_2 \left  H^{e\!f\!f}_{soc} \right  {}^4\Phi_0 \right>$	$\phi_1(d_{xz}) \Rightarrow \phi_3(d_{x2-y2})$	±1	±l	positive D
\ I I /	$\phi_1(d_{xz}) \Rightarrow \phi_4(d_{z2})$	±1	±1	positive D
	$\phi_2(d_{xy}) \Longrightarrow \phi_5(d_{yz})$	±1	±1	positive D

Equation (S1) describes the relationship between the main values of g tensor of a KD and the related tunneling gap  $\Delta_{tun}$ .

$$\mu_{X} = \frac{1}{2} g_{X} \mu_{B}, \ \mu_{Y} = \frac{1}{2} g_{Y} \mu_{B}, \ \mu_{z} = \frac{1}{2} g_{Z} \mu_{B} \ (S1-a)$$
$$\Delta_{tun} = \left[ (\mu_{X} H_{X})^{2} + (\mu_{Y} H_{Y})^{2} \right]^{\frac{1}{2}} \qquad (S1-b)$$
$$\Delta_{tun} = \frac{1}{2} \left[ \mu_{B} \left( g_{X}^{2} H_{X}^{2} + g_{Y}^{2} H_{Y}^{2} \right)^{\frac{1}{2}} \right] \qquad (S1-c)$$

Equation (S2) describes the relationship between the main values of g tensor of a KD and the related  $\mu_{\text{QTM}}$ .

$$g_{XY} = \left(g_X^2 + g_Y^2\right)^{1/2}$$
 (S2-a)

$$\mu_{QTM} = 1/3(|\mu_X| + |\mu_Y| + |\mu_Z|)$$
 (S2-b)

$$|\mu_{\alpha}| = \left| \left\langle -n \left| \mu_{\alpha} \right| n \right\rangle \right| \qquad \alpha = X, Y, Z$$
 (S2-c)

$$g_{X,Y} = 2\left\langle -n \left| \mu_{X,Y} \right| n \right\rangle / \mu_B$$
 (S2-d)

$$\left\langle -n \left| \mu_{X,Y} \right| n \right\rangle = \frac{g_{X,Y}}{2} \mu_B$$
 (S2-e)

$$\mu_{QTM} = 1/6 (g_X + g_Z) \mu_B \tag{S2-f}$$

A semi-quantitative analysis of the relaxation rates of QTM and direct processes in 1 and 2.

$$\tau_{\text{tun}}^{-1} = \frac{C_1 \Delta_{\text{tun}}^2}{1 + C_2 \Delta E^2} \quad (S3-a)$$

$$H_{\text{zeeman}} = -\overline{H} \cdot \overline{\mu} \quad (S3-b)$$

$$\Delta E \approx H_{dc,Z} \cdot \left| \mu_{Z,a} - \mu_{Z,b} \right| \quad (S3-c)$$

$$H_{dc,Z} \cdot \left| \mu_{Z,a} - \mu_{Z,b} \right| = H_{dc,Z} \cdot g_Z \mu_B \approx H_{dc} \cdot g_Z \mu_B \quad (S3-d)$$

$$\downarrow$$

$$\Delta E \approx H_{dc,Z} \cdot g_Z \mu_B \approx H_{dc} \cdot g_Z \mu_B \quad (S3-e)$$

$$\downarrow$$

$$\tau_{\text{tun}}^{-1} \approx \frac{C_1 \Delta_{\text{tun}}^2}{1 + C_3 g_Z^2 \cdot H^2} \approx \frac{C_1 \Delta_{\text{tun}}^2}{C_3 g_Z^2 \cdot H^2} \approx \frac{C_1 \Delta_{\text{tun}}^2}{C_3 g_Z^2 \cdot H_{dc}^2} = \frac{B_1}{B_2 \cdot H_{dc}^2} \quad (S3-f)$$

The relaxation rate due to QTM between two quantum-mechanical state  $|a\rangle$  and  $|b\rangle$ ,  $\tau^{-1}_{tun}$ , could be expressed as eqn (S3-a)<sup>S1</sup> where C<sub>1</sub> and C<sub>2</sub> are system-specific parameters.  $\Delta E$  is the

energy difference between  $|a\rangle$  and  $|b\rangle$ . If  $|a\rangle$  and  $|b\rangle$  are the two components a KD under strictly zero magnetic field,  $\Delta E$  must be zero. In actual environment, small magnetic field, with internal or external source, always exists and thus  $\Delta E$  is determined by the Zeeman interaction between the small magnetic field and magnetic moment of the metal ion (eqn (S3-b)).

One common source of the internal field is the magnetic dipolar interaction due to other metal ions in the crystal. The applied dc field,  $H_{dc}$ , to suppress QTM, is the external field. Usually the strength of  $H_{dc}$  is larger than that of internal field by several orders of magnitude. Thus, if a dc fiels is applied, it is reasonable to only take into account of  $H_{dc}$  to estimate  $\Delta E$ . For metal ions of strong easy-axis anisotropy, the component of magnetic moment along the easy-axis direction ( $\mu_z$ ) is significantly larger than those of transeval directions ( $\mu_{x,y}$ ), i.e.,  $g_z >> g_{x,y}$ . Therefore, the Zeeman interaction, which is in principle a dot product between two vectors (magnetic field and magnetic component), could be approximated as the product of Z component of  $H_{dc}$  ( $H_{dc,z}$ ) and that of magnetic moment of the metal ion ( $\mu_z$ ) in the systems of this work (eqn(3-c) and eqn(3-d)).

To facilitate the following analysis,  $H_{dc}$  is assumed to be applied along the Z direction and thus  $\Delta E$  for a KD under real environment could be approximately determined by the product of the magnitude of  $H_{dc}$  and  $g_z$  (eqn(S3-e)). Based on these assumptions and approximations, the dependence of  $\tau^{-1}_{tun}$  on  $H_{dc}$  could be derived as eqn(S3-f). In addition, the tunneling gap ( $\Delta_{tun}$ ) in eqn(S3-a) for a KD is expressed as eqn(S1-c).

In the aspect of direct process, its relaxation rate could be expressed as eqn(S4-a)<sup>S2</sup> where C<sub>3</sub> is the system-specific parameter and  $\Delta E$  is the same as in the case of QTM. The operator  $V_I$  is a timedependent perturbing Hamiltonian which induces the direct transition between  $|a\rangle$  and  $|b\rangle$ . In the aspect of spin-lattice coupling,  $V_I$  is the first-order contribution to the dynamic modulation of the crystalline electric potential generated by lattice vibration <sup>S2</sup>, i.e., phonon.

In the case of KD under strictly zero magnetic field,  $\tau^{-1}_{direct}$  must be zero due to the zero values of both  $\Delta E$  and  $\langle a|V_I|b \rangle$  attributed to the time-reversal symmetry<sup>S2</sup>. However, in real condition, small magnetic field always exists and it could work as another perturbation leading to non-zero values of both  $\Delta E$  and  $\langle a|V_I|b \rangle$ . In this condition,  $\tau^{-1}_{direct}$  could be reformulated as eqn(S4-b)<sup>S2</sup> where  $\Delta E$ ' is the energy gap between ground and excited doublets. As mentioned before, the magnitude of internal magnetic field is quite small and the resulted direct transition

within the doublet is usually negligible. In other words, the influence of direct process on the relaxation of magnetization is only worthy of being treated when external dc field is applied. Based on these conditions, the dependence of  $\tau^{-1}_{direct}$  on  $H_{dc}$  could be derived as eqn(S4-c) under the approximation of eqn(S3-e).

$$\vec{H}_{dip,i} = C_7 \bullet \frac{\mu_i}{r_i^3} \quad (S5-a)$$

$$\vec{H}_{dip,total} \approx C_7 \bullet \sum_{i \in NB} \frac{\mu_i}{r_i^3} \approx C_7 \bullet \vec{\mu}_i \bullet \sum_{i \in NB} \frac{1}{r_i^3} = C_8 \bullet \sum_{i \in NB} \frac{1}{r_i^3} = C_8 \bullet R \quad (S5-b)$$

$$R = \sum_{i \in NB} \frac{1}{r_i^3} \quad (S5-c)$$

The internal magnetic field  $H_{dip}$ , felt by a given metal ion and attributed to the dipolar interaction with the magnetic moment of another neighbouring ion i, is of the order of  $\mu_i/r_i^3$  (eqn(S5-a)) <sup>S2</sup>. Since  $H_{dip}$  scales inversely as the third power of the distance r, the total  $H_{dip}$  could be approximated as the sum of the contributions from the nearest-neighbouring (NB) ions (eqn(S5-b)). As shown in our *ab initio* results, the magnetic anisotropies as well as the magnetic moments of the Co(II) ions in these two compounds are quite close to each other. Therefore the effect of local magnetic moment of Co(II) ion on  $H_{dip}$  could be assumed to be equal (eqn(S5-b)). Based on these considerations, the total internal field, i.e.,  $H_{dip, total}$ , could be described by a parameter R (eqn(S5c)) in a semi-quantitative manner (eqn(S5-b)). The R parameters of 1 and 2 are shown in Table S9.

Table S9. The R parameters of 1 and 2 based on the corresponding crystal structures.

1	r (in Å) <sup>a</sup>	n <sup>b</sup>	
	10.80	2	
	13.13	4	
	13.79	2	$R = 4.12 \times 10^{-3} \text{ Å}^{-3}$
2	r (in Å)	n	
	10.00	2	
	11.45	1	
	11.69	2	
	12.25	2	$R = 5.01 \times 10^{-3} \text{ Å}^{-3}$

<sup>a</sup> the distance between the central Co(II) and a given NB Co(II). <sup>b</sup> the number of a given type of NB Co(II)

In order to facilitate the theoretical derivation, the total internal dipolar field (eqn(S5-b)) is assumed to be isotropic, i.e., its components along the three Cartesian directions are all the same, equal to one third of the magnitude of eqn(S5-b). Since **1** and **2** possess the same coordination number and donor atoms as well as similar ligand fields, all the system-specific parameters  $C_1$ - $C_8$  in the eqns above are assumed to be equal in these two compounds.

At first, based on eqn(S1-c) and eqn(S5-b), the tunneling gaps of **1** and **2** could be approximated as eqn(S6-a) and eqn(S6-b) respectively. Then, under the assumption of eqn(S3-f) the relaxation rates of QTM in these two compounds could be described as eqn(S6-c) and eqn(S6-d) respectively.

$$\begin{split} &\Delta_{hun,1} = \frac{1}{3} \times \frac{1}{2} C_8 \times \mu_B \Big[ (0.9559 \times 4.1175 \times 10^{-3})^2 + (1.7742 \times 4.1175 \times 10^{-3})^2 \Big]^{\frac{1}{2}} \\ &= \frac{C_8 \times \mu_B}{6} \times 8.2981 \times 10^{-3} \qquad (\text{S6-a}) \\ &\Delta_{nun,2} = \frac{1}{3} \times \frac{1}{2} C_8 \times \mu_B \Big[ (1.0548 \times 5.0061 \times 10^{-3})^2 + (1.9678 \times 5.0061 \times 10^{-3})^2 \Big]^{\frac{1}{2}} \\ &= \frac{C_8 \times \mu_B}{6} \times 11.177 \times 10^{-3} \qquad (\text{S6-b}) \\ &\tau_{\text{tun,1}}^{-1} \approx \frac{C_1 \times \left(\frac{C_8 \times \mu_B}{6}\right)^2 (8.2981 \times 10^{-3})^2}{C_3 g_{Z,1}^2 \cdot H_{dc,1}^2} \qquad (\text{S6-c}) \\ &\tau_{\text{tun,2}}^{-1} \approx \frac{C_1 \times \left(\frac{C_8 \times \mu_B}{6}\right)^2 (11.177 \times 10^{-3})^2}{C_3 g_{Z,2}^2 \cdot H_{dc,2}^2} \qquad (\text{S6-d}) \\ &\frac{\tau_{\text{tun,1}}^{-1}}{\tau_{\text{tun,2}}^{-1}} \approx \frac{g_{Z,2}^2 \cdot H_{dc,1}^2}{g_{Z,1}^2 \cdot H_{dc,1}^2} \times \left(\frac{8.2981}{11.177}\right)^2 = 1 \qquad (\text{S7-a}) \\ &\downarrow \\ &\left(\frac{H_{dc,2}}{H_{dc,1}}\right)^2 \approx \left(\frac{11.177}{8.2981}\right)^2 \times \left(\frac{g_{Z,1}}{g_{Z,2}}\right)^2 = \left(\frac{11.177}{8.2981}\right)^2 \times \left(\frac{9.7699}{9.4839}\right)^2 = 1.9238 \quad (\text{S7-b}) \\ &\downarrow \\ \\ &\frac{H_{dc,2}}{H_{dc,1}} \approx 1.387 \quad (\text{S7-c}) \end{aligned}$$

In order to suppress the QTM of **1** and **2** to the same degree (eqn(S7-a)), different dc fields,  $H_{dc,1}$  and  $H_{dc,2}$  for **1** and **2** respectively, are needed(eqn(S7-b)). The relationship between these two dc fields could be described as eqn(S7-c).

$$\tau_{direct,1}^{-1} \approx C_6 \bullet H_{dc,1}^4 \bullet T \quad (S8-a)$$
  
$$\tau_{direct,2}^{-1} \approx C_6 \bullet H_{dc,2}^4 \bullet T \quad (S8-b)$$
  
$$\frac{\tau_{direct,2}^{-1}}{\tau_{direct,1}^{-1}} \approx \left(\frac{H_{dc,2}}{H_{dc,1}}\right)^4 = 1.387^4 = 3.701 \quad (S8-c)$$

With eqn(S7-c), the relaxation rates of direct process of **1** and **2**, at these two dc fields respectively, could be expressed as eqn(S8-a) and eqn(S8-b) under the approximation of eqn(S4-c). As shown by eqn(S8-c), to suppress the QTM of **2** to the same degree as **1**, larger dc field is required for **2**. This larger dc field could induce stronger direct process of **2**, whose rate may be as large as around 4 multiples of that of **1**.

## **References:**

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(S2) A. Abragam and B. Bleaney. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon Press: Oxford, 1970.