Electronic Supporting Information

Ising-type magnetic anisotropy and single molecule magnet behaviour in mononuclear trigonal bipyramidal Co(II) complexes

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Synthesis

Chemicals were purchased from Aldrich and used without further purification. Me_6 tren and all cobalt complexes were synthesized according to literature procedures or minor alterations thereof. All solvents were from BDH and were used as received. All manipulations were conducted under standard benchtop conditions.

Synthesis of $[Co(Me_6tren)Cl](ClO_4)$ (1)

CoCl₂·6H₂O (0.200 g, 0.84 mmol) was dissolved in EtOH (20 ml) at 55 °C. Me₆tren (0.214 g, 0.92 mmol) dissolved in EtOH (10 ml) was added dropwise with stirring, forming a blue solution that was stirred overnight at room temperature. NaClO₄·H₂O (0.118 g, 0.84 mmol) was added with stirring inducing precipitation of pale blue [Co(Me₆tren)Cl](ClO₄) (1) (0.336 g, 95%), which was isolated by filtration and dried in air. Crystals suitable for X-ray analysis were formed upon cooling a hot MeOH solution of 1. Elemental analysis (%), observed (calculated for CoC₁₂H₃₀N₄Cl₂O₄) C, 33.81 (34.03) H, 7.08 (7.15) N, 13.05 (13.24). MS ESI⁺ (MeOH): *m/z* 324.20 [Co(Me₆tren)Cl]⁺. IR (KBr) v/cm⁻¹: 3431 (w), 2983 (m), 2903 (m), 2852 (m), 2795 (w), 2017 (w), 1486 (s), 1475 (s), 1461 (s), 1435 (m), 1359 (w), 1300 (s), 1248 (w), 1174 (m), 1091 (s), 1053 (s), 1023 (m), 1006 (m), 938 (m), 913 (m), 807 (m), 778 (m), 742 (w), 622 (s), 602 (m), 573 (w), 486 (m), 411 (w), 382 (w).

Synthesis of $[Co(Me_6 tren)Br]Br(2)$

CoBr₂·6H₂O (0.100 g, 0.30 mmol) was dissolved in EtOH (20 ml) at 55 °C. Me₆tren (0.077 g, 0.33 mmol) dissolved in EtOH (5 ml) was added dropwise with stirring, forming a blue solution that was stirred overnight at room temperature. This was reduced in volume to 10 ml, yielding royal blue [Co(Me₆tren)Br]Br (**2**) (0.107 g, 80%) upon addition of petroleum ether, which was isolated by filtration and dried in air. An X-ray structure has previously been reported. Elemental analysis (%), observed (calculated for CoC₁₂H₃₀N₄Br₂) C, 32.18 (32.21) H, 6.78 (6.76) N, 12.38 (12.53). MS ESI⁺ (MeOH): m/z 368.10 [Co(Me₆tren)Br]⁺. IR (KBr) v/cm⁻¹: 3436 (w), 2987 (m), 2927 (m), 2873 (s), 2778 (w), 1485 (s), 1474 (s), 1456 (s), 1395 (m), 1354 (w), 1293 (s), 1275 (s), 1238 (m), 1170 (m), 1098 (s), 1061 (m), 1050 (m), 1032 (m), 1016 (s), 999 (s), 933 (s), 911 (m), 802 (m), 771 (s), 742 (w), 598 (w), 585 (w), 482 (m), 402 (w), 379 (w).

Synthesis of [Zn_{1-x} Co_x(Me₆tren)Cl](ClO₄)

The preparation of the pure Zn and the Co diluted complexes (x = 0, 0.05 and 0.1) were performed with same method as for 1 by using the corresponding Co/Zn molar ratio. Single crystals of the pure (colorless) and the diluted complexes (very pale blue) were obtained. The crystal structure of the pure Zn complex was solved (see below) and the structure was found isotructural to 1. The diluted

compounds have the same cell parameters as the pure Zn one. All measurements were made on collection of single crystals of the diluted compounds.

Physical measurements

IR data were measured on KBr pellets using a PerkinElmer FTIR spectrometer. Variable temperature (300 - 2 K) magnetic data were measured on powdered samples of **1** and **2** in an eicosane matrix in 1.0 and 0.1 T fields using a Quantum Design MPMS5 SQUID magnetometer. The data were corrected for the diamagnetic contribution of the sample holder and eicosane, and the diamagnetism of the sample estimated according to Pascal's constants. Low temperature (2 - 6 K) variable field (0 - 5.5 T) measurements were carried out in the same manner. Modeling of magnetic susceptibility and magnetization data was performed by matrix diagonalization methods using home made software

High-Frequency EPR measurements were performed on a multifrequency spectrometer operating in a double-pass configuration. A 110 GHz frequency was generated with a Phase-Locked Dielectric Resonator Oscillators associated to an active multiplication chain, from Virginia Diodes Inc., and then multiplied by a doubler, a tripler or a sextupler to obtain 221, 331 or 662 GHz respectively. The 475 and 575 GHz spectra were obtained using 95 and 115 GHz Gunn oscillators from Radiometer Physics GmbH together with quintuplers. The detection was performed with a hot electron InSb bolometer (QMC Instruments). The exciting light was propagated with a Quasi-Optical set-up (Thomas Keating) outside the cryostat and with the help of a corrugated waveguide inside it. The main magnetic field was provided by a superconducting magnet and low temperatures were supplied by a VTI from Cryogenic. The measurements were done on powdered samples pressed into pellets in order to limit torqueing effects. However, discrepancies on the intensities between calculated spectra and experimental ones seem to indicate that some torqueing was still present. Calculated spectra were obtained with the SIM program from H. Weihe (Univ. of Copenhagen).

Structural information

X-ray diffraction data was collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97¹ and refined against F^2 by full-matrix least-squares techniques using SHELXL-97² with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a

¹⁾ Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**.

²⁾ Sheldrick, G. M. SHELXL-97, Program for the refinement of crystal structures from diffraction data, University of Göttingen, Göttingen, Germany, **1997**.

³⁾ Farrugia, L. J. J. Appl. Cryst., 1999, 32, 837.

⁴⁾ Flack H. D. Acta Cryst. 1983, A39, 876.

riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.³

The absolute configuration was determined by refining the Flack's⁴ parameter using a large number of Friedel's pairs.

The crystal data collection and refinement parameters are given in Table S1.



Figure S1. View of the Co-Co distances. Each Co is surrounded by twelve others ; 6 neighbours placed at the vertices of an octahedron and belonging to two adjacent (ab) planes along the c axis (d(Co-Co) = 7.95 Å (black)) and 6 next neighbours forming a regular hexagon and belonging to the same (ab) plane (d(Co-Co) = 9.89 Å (red)).

Compound	[Co(Me ₆ tren)Cl](ClO ₄) 1	[Co(Me ₆ tren)Br]Br 2	[Zn(Me ₆ tren)Cl](ClO ₄)
Empirical formula	C ₁₂ H ₃₀ Cl ₂ Co N ₄ O ₄	C ₁₂ H ₃₀ Br ₂ Co N ₄	$C_{12}H_{30}Cl_2N_4O_4Zn$
M _r	424.23	449.15	430.67
Crystal size, mm ³	0.21 x 0.20 x 0.19	0.32 x 0.18 x 0.18	0.21 x 0.20 x 0.19
Crystal system	trigonal	cubic	trigonal
Space group	<i>R 3c</i>	P 2 ₁ 3	<i>R 3c</i>
a, Å	9.891(5)	12.0262(4)	9.9025(3)
b, Å	9.891(5)	12.0262(4)	9.9025(3)
c, Å	33.183(5)	12.0262(4))	33.1835(12)
α, °	90	90	90
β, °	90	90	90
γ, °	120	90	120
Cell volume, Å ³	2811(2)	1739.34(17)	2818.0(2)
Z ; Z'	6 ; 1/3	4 ; 1/3	6;1/3
Т, К	100(1)	100(1)	100(1)
F ₀₀₀	1338	908	1356
μ, mm ⁻¹	1.223	5.576	1.614
θ range, °	2.68 - 37.32	2.40 - 36.28	2.67 - 36.71
Reflection collected	13 201	21 073	9 823
Reflections unique	2 790	2 791	2 197
R _{int}	0.0226	0.0501	0.0241
GOF	1.048	0.989	1.059
Refl. obs. $(I > 2\sigma(I))$	2 537	2 508	1 810
Parameters	72	549	72
Flack's parameter	0.031(12)	0.010(5)	0.006(10)
wR ₂ (all data)	0.0801	0.0295	0.0639
R value $(I > 2\sigma(I))$	0.0287	0.0212	0.0283
Largest diff. peak and hole (eÅ ⁻³)	-0.423 ; 1.024	-0.531 ; 0.563	-0.413 ; 0.858

Table S1. Crystallographic data and structure refinement details for compounds

Table S2. Selected bond lengths [Å] and angles [°] for compounds (cf. Figure 1. for the labels). All esds are estimated using the value of the full covariance matrix of least square.

	1		1
	$[Co(Me_6tren)Cl](ClO_4)$ 1	[Co(Me ₆ tren)Br]Br 2	$[Zn(Me_6tren)Cl](ClO_4)$
Co - N(1)	2.176(3)	2.2089(15)	2.184(3)
Co – N(2)	2.1519(12)	2.1342(9)	2.1614(16)
Co – X(1)	2.2821(7)	2.4512(3)	2.2881(9)
N(2) – Co – N(2)'	117.733(19)	117.772(12)	118.08(2)
N(1) – Co – N(2)	81.26(4)	81.34(2)	81.97(4)
N(1) – Co – X(1)	180	180	180

N(2) - Co – X(1)	98.74(4)	98.66(2)	98.03(4)
d [Co – (N(2) N(2)' N(2)''')]	0.327	0.321	0.302

Symmetry code : (') -y, x-y, z ; (''') -x+y, -x, z.



Figure S2. Experimental (O) and calculated (—) χ T vs.T and $1/\chi$ vs. T (inset) for 1 (top) and 2 (bottom). See fit parameters in the text



Figure S3. EPR spectra at T = 15 K for 1 at v = 475 and 575 GHz, experimental (top) and calculated (bottom) for $g_x = g_y = 2.15 \pm 0.10$, $g_z = 2.2 \pm 0.2$ and $D = -8.12 \pm 0.06$ cm⁻¹.



Figure S4. Comparison between the experimental (top) and the calculated (bottom) spectra for **1** considering D > 0 and D < 0 cases with the same *g* values for three different frequencies. The simulation of the spectra leads to the right resonance positions with negative and positive D values but the discrepancy with the experimental intensities is much more important when D is positive, especially for the spectra recorded with the highest frequencies



Figure S5. EPR spectra at T = 15 K for **2** at v = GHz, experimental (top) and calculated (bottom) for $g_x = g_y = 2.1 \pm 0.1$, $g_z = 2.0\pm0.1$ and $D = -2.40 \pm 0.05$ cm⁻¹

Table S3. Energies (cm⁻¹) of the first four excited quartet states computed at the CAS(7,5)SCF and CAS(7,5)NEVPT2 (10Q-40D) level for the two complexes, note that ${}^{4}\Phi_{3}$ and ${}^{4}\Phi_{4}$ are degenerate

	[Co(Me ₆ tren)Cl](ClO ₄) 1	[Co(Me ₆ tren)Cl](ClO ₄) 1	$[Co(Me_6tren)Br]Br$ 2	[Co(Me ₆ tren)Br]Br 2
	CASSCF	NEVPT2	CASSCF	NEVPT2
$^{4}\Phi_{0}$	0	0	0	0
$^{4}\Phi_{1}$	2521	3861	3077	4612
$^{4}\Phi_{2}$	4118	6162	4627	6829
$^{4}\Phi_{3}, ^{4}\Phi_{4}$	4549	6524	4947	7184



 $\Box \Box \Box \Box \Box \Box$ S6. Main determinants and their coefficients (for 1) in the wave functions of the ground state (${}^{4}\Phi_{0}$) and in the three excited quartet states (energetically classified from lowest to highest from top to bottom) that contribute significantly to the *D* value. The coefficients of the orbitals decrease from left to right. ${}^{4}\Phi_{3}$ and ${}^{4}\Phi_{4}$ are degenerate so we have chosen a specific combination of the two corresponding wave functions.

The contributions of the excited states to the D value result from the following interactions:

- (i) The main contribution of the first excited state $({}^{4}\Phi_{1})$ arises from $\sum_{i} \hat{1}_{Z_{i}} \cdot \hat{s}_{Z_{i}}$ operator that couples the two determinants (d) and (e) with the determinants (b) and (c) of $({}^{4}\Phi_{0})$ and contributes negatively to the *D* value.
- (ii) The two contributions through $\sum_{i} \hat{l}_{Z_{i}} \cdot \hat{s}_{Z_{i}}$ of the second excited state (⁴ Φ_{2}) which is spanned by the same determinants (d) and (e) but with opposite sign coefficients cancel.
- (iii) The main contribution of the third degenerate excited state (the two states may be obtained from any linear combinations between ${}^{4}\Phi_{3}$ and ${}^{4}\Phi_{4}$) essentially arises from the $\frac{1}{2}\sum_{i} \hat{1}_{+_{i}} \hat{s}_{-_{i}} + \hat{1}_{-_{i}} \hat{s}_{+_{i}}$ operator that couples (f) with (a) and contributes positively to the *D* value.

Since $({}^{4}\Phi_{1})$ is much lower in energy than $({}^{4}\Phi_{3})$ and $({}^{4}\Phi_{4})$, its large negative contribution is not compensated by the two positive contributions of $({}^{4}\Phi_{3})$ and $({}^{4}\Phi_{4})$ and the overall *D* value is negative.



Figure S7. Magnetization *vs.* field on a single crystal of **1** with its easy axis aligned with the field at T = 30 mK and for two different sweep rates (top) and at a sweep rate of 0.002 T/s and two different temperatures (bottom). For the clarity of the plots, only two sweep rates and two temperatures are shown.



Figure S8. (top) $M = f(\mu_0 H)$ for the Co chloride complex diluted in the diamagnetic Zn compound (10%). Fixing the g value at 2.24, it is possible to fit the data for five different temperatures with D = -7.3 cm⁻¹ and a Co percentage of 9%, which is in perfect agreement with the dilution used during the synthesis and the D value of the pure complex; (bottom) $\chi_M T = f(T)$ for the 10% diluted sample



Figure S9. Magnetization *vs.* field on a single crystal of $[Zn_{0.9}Co_{0.1}(Me_6tren)Cl](ClO_4)$ with its easy axis aligned with the field at T = 30 mK and different sweep rates



Figure S10. Magnetization *vs.* field on a single crystal of $[Zn_{0.95}Co_{0.05}(Me_6tren)Cl](ClO_4)$ with its easy axis aligned with the field at T = 30 mK and different sweep rates (top); the inset shows the detailed features in the -0.2 – 0.2 T region and $dM/dH = f(\mu_0 H)$ at T = 30 mK and a sweep rate of 0.07 T/s (bottom).