Supporting Information

Tuning the Ising-type anisotropy in trigonal bipyramidal Co(II) complexes

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Experimental Section

General procedures: All starting materials were obtained commercially and were used without further purification unless otherwise stated. Elemental analyses for C, H, N were performed on a Thermo Scientific Flash analyzer. IR spectra were recorded on a Bruker TENSOR-27 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) sample holder in the 4000–500 cm⁻¹ range. NMR spectra were recorded on a Bruker Aspect 300 NMR spectrometer. X-ray diffraction data were collected by using a Bruker Kappa VENTURE PHOTON 100 diffractometer with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Magnetic data were collected using a Quantum Design MPMS XL7 SQUID magnetometer.

Synthesis:

tris(2-(isopropylthio)ethyl)amine : NS₃^{iPr}



c: Na / Me₂HCOH / 298 K; Me₂HCSH / Me₂COH / 360 K

Scheme 1. Ligand synthesis.

Tris(2-chloroethyl)amine hydrochloride (i). A 250 mL two-necked round-bottom flask, which was fitted with a dropping funnel and a reflux condenser, was charged with thionyl chloride (52 mL, 0.70 mol) and chloroform (80 mL). A solution of triethanolamine (29.80 g, 0.20 mol) in 50 mL of chloroform was added dropwise to this solution. The addition was carried out at ambient temperature for 1 h. The reaction continued at room temperature until gas evolution stopped, and then the mixture was heated at reflux for 4 h. After cooling to room temperature, a white solid precipitate was formed, which was filtered and washed with CHCl₃ (50 × 3 mL) and dried overnight in a vacuum oven. Tris(2-chloroethyl)amine hydrochloride (**i**) was obtained in 80 % yield (38.56 g).

Tris(2-chloroethyl)amine (ii). Sodium hydroxide (2.00 g, 0.05 mol) was added portionwise to a solution of compound **i** (12.05 g, 0.05 mol) and 30 mL of water. The reaction was stirred for 1 h. The solution was extracted with CHCl₃ (20×3 mL) and the organic layer was further washed with (20×3 mL) distilled water, dried over anhydrous MgSO₄. The solvent was removed and the heavy oil product was obtained by vacuum-distillation (7.26 g, 71% yield).

tris(2-(isopropylthio)ethyl)amine (iii). (Cautions: The 2-Propanethiol used in this synthesis is a poisonous gas with an obnoxious odor. All procedures must be carried out in an efficient fume hood. The apparatus must be connected to a series of washing bottles charged with chromic acid mixture or other absorbing solutions.) All glassware must be previously dried. A two-necked flask was equipped with a reflux condenser topped with a drying tube (CaCl₂) and a 500-mL dropping funnel

with external warming bath. With stirring, anhydrous 2-Propanol (200 mL) was added and refluxed at 360 K, followed by sodium (2.30 g, 0.10 mol) in small portions. Upon reaction of all the sodium, the flask was allowed to cool to room temperature. 2-Propanethiol (9.29 mL, 0.10 mol), and 50 mL of warm anhydrous 2-Propanol were poured into the dropping funnel, which was heated by warm water. The solution was added dropwise with stirring to the sodium iso-propoxide solution during a 1 h period. The warming bath was then drained off, and a solution of N(CH₂CH₂Cl)₃ (ii) (6.81 g, 0.033 mol) of dissolved in 20 mL of anhydrous 2-Propanol was placed in the dropping funnel. The sodium iso-propoxide solution was heated to 323-333 K, and slowly added over 4 h. The mixture was then refluxed for 1 h, and cooled to room temperature. The NaCl, which precipitates, was filtered, and the solution was concentrated under reduced pressure. The residue was diluted with diethyl ether, filtered, concentrated, and vacuum-distilled. The ligand was collected at 408-413 K /2 torr to yield 7.91 g (0.023 mol) of product (74.1% yield). ¹H NMR (CDCl₃, 300 MHz, ppm from TMS): 1.183-1.279 (18H, (CH₃)₂CHS-); 2.92 (3H, (CH₃)₂CHS-); 2.62 (6H, Me₂CHSCH₂CH₂-); 2.69 (6H, Me₂CHSCH₂CH₂-). MS-ESI: m/z caled for C₁₈H₃₉NS₃: 323.2, found: 324.1.

[Co(NS_3^{iPr})Cl] (BPh₄). To a hot solution of CoCl₂ (65.1 mg, 0.5 mmol) in 1-butanol (3 mL) sulfur NS₃^{iPr} (194.2 mg, 0.6 mmol) in 1-butanol (1 mL) were added followed by NaBPh₄ (171.1 mg, 0.5 mmol) in1-butanol (2 mL). Then the solution was cooled down to room temperature at ambient condition. A purple precipitate was formed, it was filtered, washed with 1-butanol and petroleum ether, and dried in vacuum at room temperature. Yield, 78.7%, 290 mg. X-ray quality crystals were obtained by vapor diffusion of diethyl ether into an ethanol/acetone (v/v 1:1) solution of **1**. Elem Anal. Calcd: C, 62.77; H, 7.29; N, 1.8. Found: C, 62.33; H, 7.00; N, 1.76. IR (KBr): 3468 (s), 3053 (s), 2981 (s), 1579 (w), 1477 (m), 1455 (m), 1423 (m), 1368 (w), 737 (s), 709 (s), 611 (m) cm⁻¹.

Single Crystal X-ray Diffraction Studies. X-ray diffraction data was collected by using a Kappa VENTURE PHOTON 100 Bruker diffractometer with IµS microfocus 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 flash frozen 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 riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.³ The crystal data collection and refinement parameters are given in Table S1. CCDC 1061993 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via

http://www.ccdc.cam.ac.uk/Community/Requestastructure.

Table	S1.	Selected	bond	distances	and	D	values	in	cm ⁻¹	experimentally	determined	and
calcul	ated	by ab init	<i>tio</i> usin	g CASSCI	F met	ho	d.					

Complexes	Co- Cl /Å	Co-S (eq)/Å	Co-N (ax)/Å	D(ex) /cm ⁻¹	D(calc) /cm ⁻¹	E/D
		2.397				
$[\operatorname{Co}(NS_3^{iPr})\operatorname{Cl}]^+(a)$	2.255	(av)	2.263		-23.0	0.09
		2.368		-19.9		
$[\operatorname{Co}(NS_3^{iPr})\operatorname{Cl}]^+(b)$	2.265	(av)	2.408		-13.1	0.08

Table S2. Details for the structure solution and refinement of $[Co(NS_3^{iPr})Cl](BPh_4)$ (top)

	$[\operatorname{Co}(NS_3^{iPr})\operatorname{Cl}]$ (BPh ₄)
Formula	C ₃₉ H ₅₃ BNS ₃ CoCl
$M_{\rm r} ({\rm g \ mol}^{-1})$	737.19
Crystal system	Triclinic
Space group	P-1
Crystal Color	Pink
<i>T</i> (K)	100(1)
<i>a</i> (Å)	11.5577 (5)
<i>b</i> (Å)	18.1837 (8)
<i>c</i> (Å)	18.2006 (8) Å
α (°)	97.507 (2)
β (°)	92.728 (2)
γ (°)	92.840 (2)
$V(\text{\AA}^3)$	3782.0 (3)
Z; Z'	4: 2
$\rho_{\text{calcd}} (\text{g} \cdot \text{cm}^{-3})$	1.295
$\mu (\mathrm{mm}^{-1})$	0.72
F(000)	1564
reflns collected	153139
reflns unique	24980
GOF on F^2	1.01
$R_1[I > 2\sigma(I)]$	0.043
$wR_2(all data)$	0.089

and Selected bond length for $[Co(NS_3^{iPr})Cl]^+$ a, and b (bottom)

Bond	$[\operatorname{Co}(NS_3^{iPr})\operatorname{Cl}]^+ \operatorname{a}/\operatorname{A}$	$Co(NS_3^{iPr})Cl]^+ b / Å$
Co-S1	2.4120(5)	2.3646(5)
Co-S2	2.3907(5)	2.3785(5)
Co-S3	2.3881(5)	2.3618(5)
Co-N(ax)	2.2632(14)	2.4078(14)
Co-Cl	2.2549(5)	2.2655(5)

Table S3. Cole-cole fit parameters for $[Co(NS_3^{iPr})Cl](BPh_4)$, slow relaxation process (top) and fast

	Slow process							
т	χο	χs	α	τ				
1.8	0.60655	0.04996	0.11613	0.035960405				
2	0.64742	0.05104	0.11311	0.021673529				
2.25	0.73203	0.07352	0.13037	0.010603178				
2.375	0.75822	0.08038	0.09804	0.004831523				
2.5	0.74157	0.05737	0.10427	0.002552686				
2.75	0.68920	0.04134	0.09190	0.000862512				
3	0.74640	0.08366	0.12477	0.000271624				
3.25	0.65083	0.08264	0.12318	0.000162255				
3.5	0.59318	0.10883	0.08033	0.000100015				

relaxation process (bottom)

	Fast process						
Т	χο	χs	α	τ			
1.8	1.27049	0.04323	0.39044	0.002806275			
2	1.06812	0.04504	0.37278	0.001863941			
2.25	0.86153	0.03648	0.34488	0.001275364			
2.375	0.70654	0.03464	0.27036	0.000690317			
2.5	0.66204	0.03677	0.27586	0.000454918			
2.75	0.59858	0.04188	0.22443	0.000176098			
3	0.45248	0.01175	0.29063	8.39391E-05			
3.25	0.45978	0.00600	0.19207	2.74887E-05			
3.5	0.44403	0.01211	0.24820	9.3066E-06			

The fit of the $\chi' = f(v)$, $\chi'' = f(v)$ and $\chi'' = f(\chi')$ were carried out using the following equations using

a home made program:

$$\chi'(v_{ac}) = \chi_{\infty} + \frac{(\chi_0 - \chi_{\infty})[1 + (2\pi v_{ac}\tau)^{1-\alpha}\sin(\alpha\pi/2)]}{1 + 2(2\pi v_{ac}\tau)^{1-\alpha}\sin(\alpha\pi/2) + (2\pi v_{ac}\tau)^{2(1-\alpha)}}$$
$$\chi''(v_{ac}) = \frac{(\chi_0 - \chi_{\infty})(2\pi v_{ac}\tau)^{1-\alpha}\cos(\alpha\pi/2)}{1 + 2(2\pi v_{ac}\tau)^{1-\alpha}\sin(\alpha\pi/2) + (2\pi v_{ac}\tau)^{2(1-\alpha)}}$$

Where χ_{∞} is the adiabatic susceptibility (at $v_{ac} \rightarrow \infty$), χ_0 is the isothermal susceptibility (at $v_{ac} \rightarrow 0$) and τ is the average relaxation time of magnetization.

	$\Delta E({}^{4}A_{2}-{}^{4}A_{1})$	$\Delta E({}^{4}A_{2}-{}^{4}E_{1})$	$\Delta E({}^{4}A_{2}-{}^{4}E_{2})$	$\Delta E(^{4}A_{2}-^{4}E_{3})$
$[\operatorname{Co}(NS_3^{iPr})\operatorname{Cl}]^+$ a	2718.694	4589.493	4938.234	5657.119
$\left[\operatorname{Co}(NS_{3}^{iPr})\operatorname{Cl}\right]^{+}\mathrm{b}$	3221.023	4905.981	5162.937	5370.92
$[Co(Me_6tren)Cl]^+$	3486.571	5206.69	5583.809	5589.198

Table S4. Energy difference between the ground state and the different quadruplets for $[Co(NS_3^{iPr})Cl]^+$ a, and b.

Magnetic Measurements. The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Dc analysis was performed on polycrystalline samples wrapped in eicosane under a field between 0.1 and 1 T and between 1.8 and 300 K. Ac susceptibility measurements were carried out under an oscillating field of 3 Oe and ac frequencies ranging between 0.1 and 1500 Hz within a dc filed of 2 kOe. Diamagnetic corrections were applied for the sample holder and the eicosane.



Figure S1. Temperature dependence of the χ T product (O (exp), – (best fit)) of [Co(NS_3^{iPr})Cl](BPh₄).





Figure S2. Magnetization at variable temperatures for $[Co(NS_3^{iPr})Cl](BPh_4)$ vs. μ_0H (top; the solid lines correspond to theoretical fits with the best D, E and g parameters), vs. μ_0H/T (middle) and vs. μ_0H (bottom; the solid lines correspond to the average of the calculated values considering the spin Hamiltonian parameters obtained from the *ab initio* calculations D = -23 and -13 cm⁻¹; we assumed g = 2.43 and the E/D values of 0.09 has no dramatic impact on the shape of the curves).



Figure S3. Powder EPR spectra recorded at 5 K at four frequencies, showing the signals corresponding to g_{1eff} and g_{2eff} (top) and powder EPR spectra recorded at 460 GHz and four different temperatures (bottom). At 5 K, only the signals corresponding to g_{1eff} and g_{2eff} are visible (at 4.7 and 4.8 T respectively). At higher temperature, a third signal can be followed, corresponding to g_{3eff} (at 7.2 T).



Figure S4. Deconvolution of the $\chi' = f(T)$ and $\chi'' = f(T)$ curves and the corresponding cole-cole at 1.8 K. The least square fit parameters R1 and R2 for X' and X'' = f(frequency) curves are 1.9×10^{-5} and 7.1×10^{-4} respectively.



Figure S5. Deconvoluted out of phase χ " data for $[Co(NS_3^{iPr})Cl](BPh_4)$ (d.c. applied field = 2000 Oe) as a function of wave frequency at difference temperatures for the fast processes (top) and the slow processes (bottom).



Figure S6. Cole-cole plots for $[Co(NS_3^{iPr})Cl](BPh_4)$ (d.c. applied field = 2000 Oe), calculated curves for the slower relaxation processes (top), the faster process (middle), and experimental data (\bullet) and fit (—) bottom.

Micro-SQUID Measurements. Magnetization measurements on oriented single crystals were carried out with an array of micro-SQUIDs.⁴ This magnetometer works in the temperature range of 0.04 to 7 K and in fields of up to 0.8 T with sweeping rates as high as 0.28 Ts⁻¹ and exhibits field stability of better than T. The time resolution is approximately 1 ms. The field can be applied in any direction of the micro-SQUID plane with precision greater than 0.1° by separately driving three orthogonal coils. In order to ensure good thermalization, a single crystal was fixed with apiezon grease.

Computational details

Theoretical calculations were performed to validate the experimental values of D obtained. We used the experimental geometries for our study. The ab initio calculations were done using the two-step approach implemented in the MOLCAS code.⁵ The first step consists in calculating the non-relativistic Born–Oppenheimer Hamiltonian using complete active space self-consistent field (CASSCF) methods.⁶ The second step is taking into account the spin-orbit coupling (SOC) using the Spin-Orbit Restricted Active Space-State Interaction (SO-RASSI) method.⁷ The values of D are reported in Table 1 and are in good agreement with the experimental values obtained.

Experimental structures were used for calculations. The position of the hydrogen atoms was optimized using DFT calculations (UB3LYP/6-311g). For CASSCF calculations, the active space contains seven electrons in 10 orbitals (five 3d orbitals plus five diffuse 4d orbitals).^{5b,5d,5e} The ground electronic state was described by a state-specific calculation while excited states (nine quartets and 40 doublets) were obtained using state-average calculations. ANO-RCC basis set was used with the following contraction scheme: 6s5p4d2f1g for Co, 5s5p3d1f for Cl and S, 6s3p2d1f for N, 6s3p for C and 2s for H. All the calculated electronic states were included in the SO-RASSI

calculations.5e,8

References

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

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

(3) Farrugia, L. J. J. Appl. Crystallogr. 1999, 837-838.

(4) Wernsdorfer, W. Supercond. Sci. Technol. 2009, 22, 064013.

(5) (a) Maurice, R.; Bastardis, R.; Graaf, C. d.; Suaud, N.; Mallah, T.; Guihéry, N. J. Chem. Theory Comput. 2009, 5, 2977-2984; (b) Aquilante, F.; De Vico, L.; Ferré, N.; Ghigo, G.; Malmqvist, P.-Å.; Neogrády, P.; Pedersen, T. B.; Pitoňàk, M.; Reiher, M.; Roos, B.; Serrano-Andrés, L.; Urban, M.; Veryazov, V.; Lindh, R. J. Comput. Chem. 2010, 31, 224-247; (c) Roos, B. O.; Malmqvist, P.-A. Phys. Chem. Chem. Phys. 2004, 6, 2919-2927; (d) Karlstroem, G.; Lindh, R.; Malmqvist, P.-A.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimmelpfennig, B.; Neogrady, P.; Seijo, L. Comput. Mater. Sci. 2003, 28, 222-239; (e) Malmqvist, P. A.; Roos, B. O.; Schimmelpfennig, B. Chem. Phys. Lett. 2002, 357, 230-240.

(6) Roos, B. O.; Taylor, P. R.; Siegbahn, E. M. Chem. Phys. 1980, 48, 157-173.

(7) (a) Maurice, R.; de Graaf, C.; Guihéry, N. Phys. Rev. B 2010, 81, 214427; (b) Chibotaru, L. F.; Ungur, L.; Aronica,

C.; Elmoll, H.; Pilet, G.; Luneau, D. J. Am. Chem. Soc. 2008, 130, 12445-12455.

(8) Bolvin, H. ChemPhysChem 2006, 7, 1575-1589.