Supporting Information

The Ligand Field of the Azido Ligand: Insights into Bonding Parameters and Magnetic Anisotropy in a Co(II)-Azido Complex

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Table S1. Crystallographic Details for 1.

Chemical formula sum	$C_{36}H_{39}ClCoN_{16}O_4$
M_r	854.21
T (K)	100(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	P-1
a, b, c (Å)	11.276(2)
	11.683(2)
	16.883(3)
α,β, γ (deg)	94.091(3)
	110.732(3)
	113.868(3)
V (Å^3)	1971.6(5)
Z	2
D_{calc} (g cm^{-3})	1.439
μ (mm^{-1})	0.565
meas. Θ-range (deg)	1.24-25.08
Indexbereich	-13<h<13
	-13<k<12
	-20<l<20
F(000)	886
meas. refl	20221
indep. refl.	6987
data / restraints / parameter	6987 / 0 / 526
Goodness-of-fit on F^2	1.002
Final R indices [$F^2 > 2\sigma (F^2)$] R_1; wR_2	0.0429; 0.0953
R indices (all data) R_1; wR_2	0.0789; 0.1214

R_{int}	0.0451
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	0.699; -0.469

Table. S2 *Ab-initio* ligand field orbital energies e_{LF} (in cm-1)[a] from CASSCF and NEVPT2 calculations on the $[Co^{II}(tbta)N_3]^{1+}$ complexes with geometries from X-data and from a DFT-geometry optimization.

	CASSCF	NEVPT2
	e_{LF}	e_{LF}
X-ray(SMM) $[Co^{II}(tbta)N_3]^{1+}$	0,130(e) 3562,3931(e) 7662(a_1)	0,268(e) 4224,4666(e) 8914(a_1)
X-ray(SMM) $[Co^{II}(tbta)]^{2+}$ [b]	0,194(e) 3236,4912(e) 5019(a_1)	0,46(e) 4367,5570(e) 5713(a_1)
DFT-optimized[c] $[Co^{II}(tbta)N_3]^{1+}$	0,289(e) 3910,4390(e) 7239(a_1)	0,327(e) 4536,4999(e) 8256(a_1)

[a] Orbital notations given in parenthesis pertain to the irreducible representations of the approximate trigonal C_3 trigonal point group of the complex; energy splitting of the degenerate components are due to additional off-axial distortions; [b] Model complex preserving the X-ray(SMM) geometry of $[Co^{II}(tbta)N_3]^{1+}$ obtained on removal of the N_3^- ligand; [c] BP86 exchange correlation potential, def2-TZVP basis set. VDW10 van-der-Waals corrections for non-bonding interactions following L. Goerigk and S. Grimme. J. Chem. Theory Comput., 6:107, 2010 , polarizable solvent continuum COSMO(Water) for charge compensation.

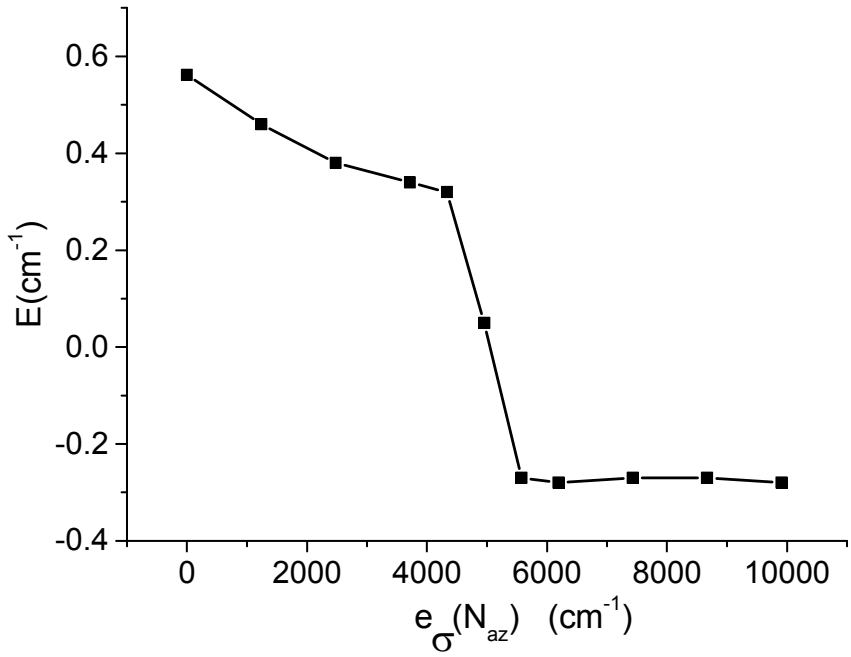

Figure S1. Variation of *E* on the σ-donor strength of the axial ligands in **1**; ligand field parameters to construct the graph are those resulting from a one-to-one mapping of NEVPT2 results on ligand field theory: B = 965 cm^{-1}, C/B = 4.53, $e_\sigma(N_{amine})$ = 3223 cm^{-1}, $e_\sigma(N_{tbta})$ = 4169, $e_{\pi s}$ = 1404 cm^{-1}; ζ_{eff} = 515 cm^{-1}; $e_\sigma(N_{az})$ was varied, while keeping the $e_{\pi s}(N_{az})/e_\sigma(N_{az})$ = 0.39 and $e_{\pi c}(N_{az})/e_\sigma(N_{az})$ = 0.33 constant and adopting the X-ray structure of **1**.

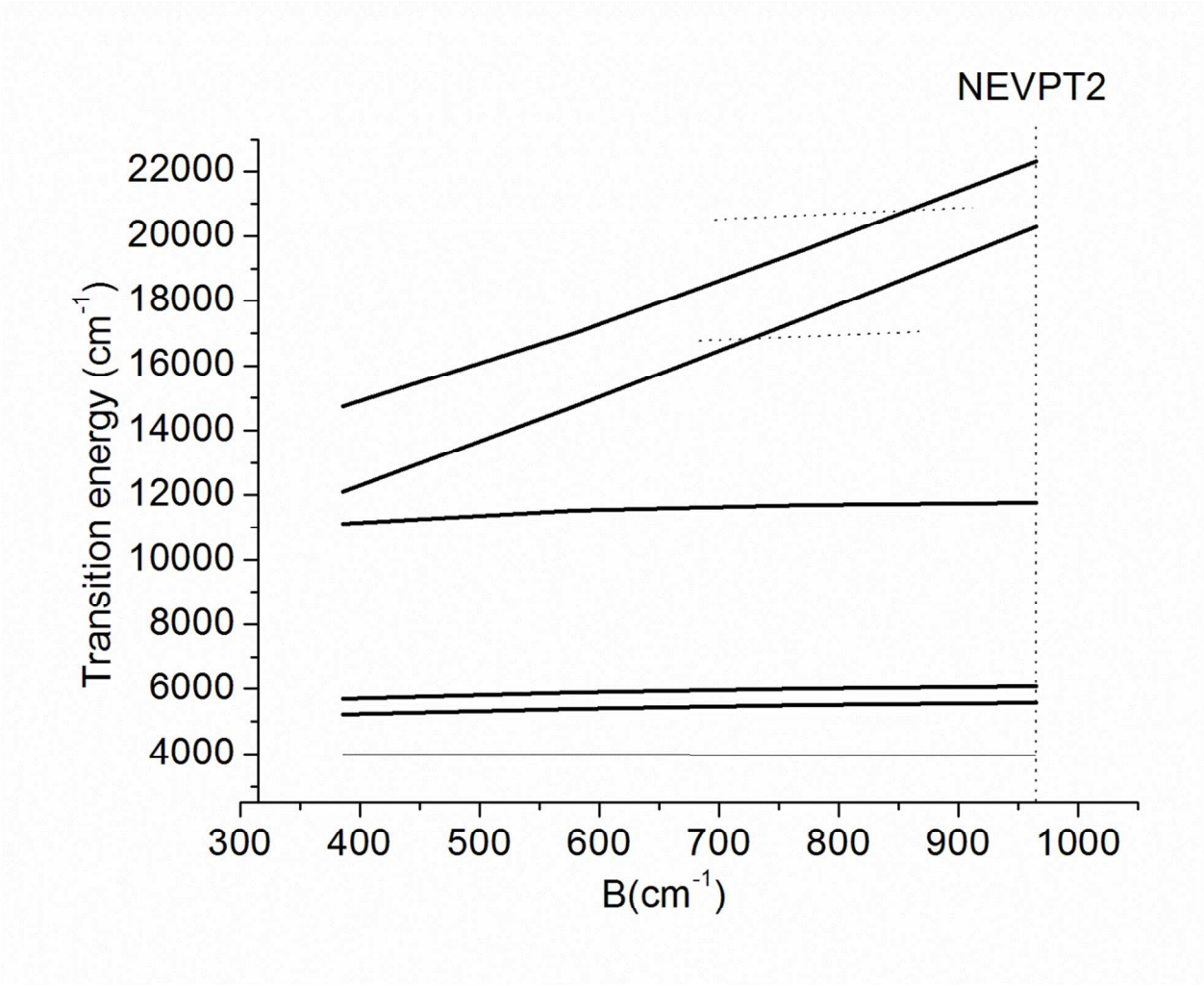

Figure S2. Term energies in dependence of B. Reference set of ligand field parameters to construct the plot adopted from a one-to-one mapping of NEVPT2 results on ligand field theory are B = 965 cm^{-1}, $e_{\sigma}(N_{amine})$ = 3223 cm^{-1}, $e_{\sigma}(N_{az})$ = 6193 cm^{-1}, $e_{\pi s}(N_{az}) = e_{\pi c}(N_{az})$ = 2348 cm^{-1}, $e_{\sigma}(N_{tbta})$ = 4169, $e_{\pi s}$ = 1404 cm^{-1}. Restricting point group symmetry to C_{3v} off-linearity of N_3^- has been neglected taking an average over the two parameters $e_{\pi s}(N_{azide})$ = 2437, $e_{\pi c}(N_{azide})$ = 2018 cm^{-1}.

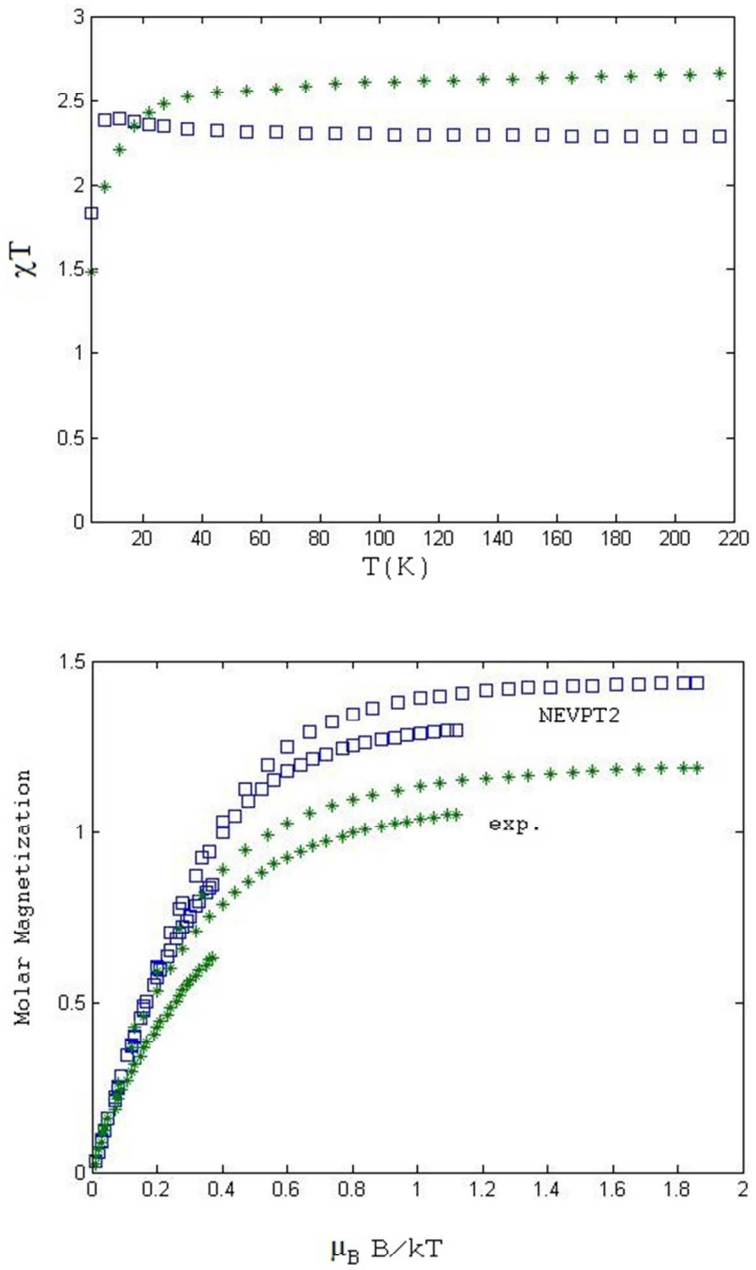

Figure S3. Magnetic susceptibility (top) and field dependent magnetizations (bottom) for **1** from NEVPT2 calculations (squares) vs experimental ones (stars).

DFT optimized geometry of 1 (def2-TZVP basis, BP86 functional, van der Waals corrections for non-bonding interactions)

Total energy (Hartree): −3256.797222377427

XYZ-coordinates

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Co  1.73471325751829     -0.15730496002931     13.19929232294752
  N   2.20352861788305      0.37374583926109     15.00247939724975
  N   0.26079214464436     -1.51240330079863     13.37223931180129
  N   1.17779866215465      1.47519704665106     12.17182373339841
  N   3.43692876403539     -0.95342858870329     12.47855342202501
  N   1.22167969108624     -0.92196006244056     10.91598732673465
  C   2.15132743148122     -2.03677753145518     10.67148145140276
  C   1.46739855836981      0.24701658152097     10.05525153048191
  C   -0.19151414503180     -1.33207239246550     10.95496577082667
  N   4.66323968365930     -0.79872296067177     12.94508480221730
  N   5.46116841812165     -1.47868290780581     12.11009015072196
  C   4.75921292600785     -2.05918469693594     11.09931694290069
  C   6.91626544545047     -1.46604629005938     12.29690586118963
  N   0.45967993997114      3.39261821515594     11.61496616689624
  N   0.80788070903078      2.64284846160503     12.66818708620317
  C   0.58794636455679      2.71235379942449     10.44278981401510
  C   -0.10357935267254      4.73516506810016     11.81671702260450
  N   0.83157985666599      1.14913800873723     16.77184775354089
  N   1.48387727507574      0.76681240642293     15.88400270340003
  N   -0.14054895117030     -2.12350468282906     14.47353968486670
  N   -1.13837925786162     -2.93326689903323     14.09823199746360
  C   -0.46933515167240     -1.93164658680031     12.29344369814910
  C   -1.37551343987738     -2.85997188448476     12.75967106924646
  C   -1.79286704921331     -3.81169921633939     15.07744657383667
  C   3.44544698487084     -1.72173765726949     11.34527286753492
  C   1.06228010023642      1.47058975686206     10.80802859593239
  C   -2.71014242147635     -6.07016745967700     14.42723925055629
  C   -2.53459321248716     -7.41411830204663     14.08130379329347
  C   -1.60286165243213     -5.26547978101258     14.71653952364457
  C   -2.17074589359985      5.33772143808222     10.49716322760798
  C   -3.55560936372780      5.30563610990962     10.30344567949920
  C   -1.60134585826454      4.72752115338426     11.62070683180128
  C   -0.31385914071968     -5.81456492857604     14.65275395270916
  C   -1.24859154972394     -7.95630246076714     14.01545565042733
  C   -0.13763845424519     -7.15337720255145     14.30174060680243
  C   7.61245452118845     -0.77479277857807     11.14744683519808
  C   7.24393562794777      0.52591059044494     10.77358140119311
  C   8.63218425917077     -1.43015809594145     10.44827413378647
  C   -2.42869639342930      4.08217990611512     12.55123033541506
  C   -4.37606308292356      4.65849840414935     11.23131297643658
  C   9.28496537312453     -0.79002117918075      9.38933325257053
  C   -3.81031003734331      4.04673993137394     12.35667896210567
  C   7.88922280867807      1.16173405822026      9.71192001832455
  C   8.91297196313399      0.50462650870536      9.01824802022508
  H   -3.71364142413684     -5.64261967811276     14.47178605806692
  H   -1.52865453110006      5.84161191497943      9.77165515826159
  H   -2.85725306136879     -3.54893959551676     15.11164205170922
  H   -1.34003381817269     -3.56176195028257     16.04479403456750
  H   5.23271820025940     -2.63797525746070     10.31538912631782
  H   2.29667483741623     -2.23934179796909      9.59806877551991
  H   1.71632303837089     -2.94398686730626     11.11643633919041
  H   0.94752628611028      0.17852452847201      9.08637030948868
  H   2.54628450258768      0.28873748804446      9.84386226431914
  H   -0.45415035513065     -2.02631954469206     10.14040454674008
  H   -0.80851306473934     -0.43022006412527     10.82524873819465
  H   0.34043280433377      3.14825301489236      9.48257566306606
  H   -1.10916123386160     -9.00245274970869     13.73974990951779
  H   -3.99210700565526      5.78478731460217      9.42598415700804
  H   8.91471008337629     -2.44542881878492     10.73187555883839
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H	0.38897601590443	5.41213782344259	11.10902403876049
H	0.17577299239990	5.02672476769809	12.83580072862914
H	-4.44822539647123	3.54527728700239	13.08592902765712
H	7.25721778188586	-2.50365870984177	12.39784880510994
H	7.08740260442104	-0.95133703434181	13.25088433825929
H	-1.98822279880093	3.60598608395687	13.42978346133430
H	7.59490112820431	2.17200589870069	9.42543570414783
H	10.07951265399661	-1.30793095488632	8.85037557302702
H	-2.13617381941329	-3.45352194290562	12.26714020224631
H	6.44678751489331	1.04245329027343	11.31212280528728
H	9.41660363551948	1.00182097634486	8.18818041190482
H	-5.45653105339853	4.63151023609804	11.08042426079066
H	0.86796833810739	-7.57359203999778	14.25284205214767
H	0.55410660198923	-5.19073468273746	14.87593767488704
H	-3.40348143371831	-8.03403141351089	13.85674671582072

Table S4 Spin-Hamiltonian parameters from coupled perturbed DFT calculations:

Complex:	**1**			**2**		
Functional	g_i	D/cm^{-1}	E/D	g_i	D	E/D
B3LYP	2.075 2.077 2.107	-2.442	0.032	2.091 2.094 2.106	-1.762	0.216
BP86	2.058 2.059 2.082	-2.469	0.036	2.067 2.072 2.083	-2.106	0.263

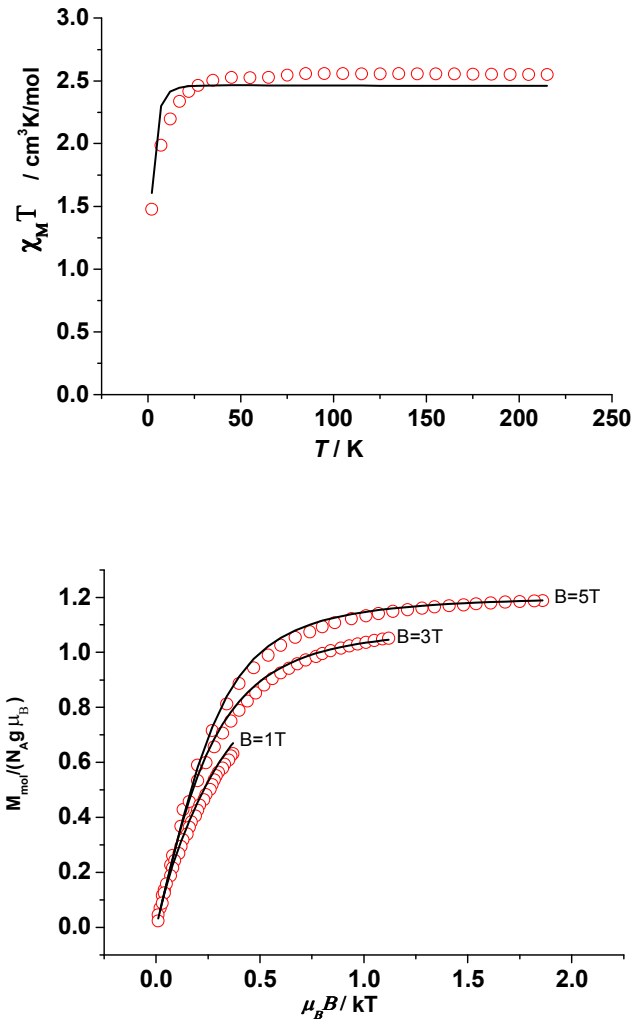

Figure S4. Magnetic susceptibility (top) and magnetization (bottom) for $[Co^{II}tbta\ N_3]^{1+}$ from experiment (open circles) and from *ab initio* based ligand field calculations (solid lines). Computed values are based on LF parameters deduced from a 1-to-1 mapping of LF theory on a converged CASSCF wave function and NEVPT2 diagonally corrected energies with a parameter set of Table 4 following a scaling of the bonding parameters of the N_3 ligand by a factor of 1.15 (values for the parameters are given in bold face type in Table 4); B=965 cm^{-1} (taken from the mapping), ζ_{eff}=511 cm^{-1} (from adjustment of the energies of spin-orbit split sublevels).