Can continuous symmetry measure TPR6 measure the axial magnetic anisotropy in the hexacoordinated Co(II) SIMs?

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Electronic Supplementary Information

Table S1 Experimental magnetic anisotropy parameter D (cm^{-1}) for series of hexacoordinated mononuclear Co(II) coordination compounds are taken from the corresponding references (column Ref.). TPR6 and OC6 are continuous symmetry measures of the structure deformation towards ideal trigonal prismatic (TP) and octahedral (OC) symmetry, correspondingly, calculated with SHAPE 2.1 program [1]). Atomic coordinates are taken from Cambridge structure database (for compounds with listed CSD code) or from CIF files from supplementary materials of the corresponding articles (marked with "-" in CSD code column).

Compound	D_{exp}	OC6	TPR6	Δ	CSD code	Ref
$Co(Cl_2Gm)_3(BC_6H_3\text{-}3,5\text{-}(CF_3)_2)_2$	-65	15.720	0.128	-15.592	YUFZOQ10	[2]
$[Co^{II}(tppm)][BPh_4]_2$	-97.2	15.893	0.554	-15.339	WOWNUU	[3]
$Co(Cl_2Gm)_3(B\textit{n}\text{-}C_{16}H_{33})_2$	-65	12.431	0.557	-11.874	PUQNIA	[2]
$[Co^{II}(tppm)][ClO_4]_2\cdot 2CH_3CN\cdot H_2O$	-80.7	14.920	0.588	-14.332	HIRLAY	[4]
$[Co^{II}(PzOx)_3(BC_6H_5)]Cl$	-82	16.272	0.828	-15.444	QIWKAK	[5]
$[Co^{II}(AcPzOx)_3(BC_6H_5)DMF]_2(B_{10}Cl_{10})$	-85	15.245	0.862	-14.383	FUGQEG	[6]
$[Co^{II}(TFIMTH)](NO_3)_2$	-72	11.882	0.866	-11.016	BOJHIS01	[7]
$[Co(AcMeImd)_3BPh]ClO_4$	-102.5	13.462	0.905	-12.557	FOFLAQ	[8]
$[Co^{II}(pprz)]$	-31	10.866	1.382	-9.484	AYAQIC	[9]
$\{Na[Co(ctam)]\}(BPh_4)_3$	-75.8	9.293	1.793	-7.500	TARXOC	[10]
$[Co^{II}(AcPyOx)_3BC_6H_5]ClO_4$	-86	10.042	2.006	-8.036	CAWCUB	[11]
$[HNEt_3][Co^{II}Co^{III}_3(bhpm)_6]$	-115	9.548	2.221	-7.327	GEXQIL	[12]
$[Co^{II}(hpy)][BPh_4]_2\cdot 3CH_2Cl_2$	-107.5	8.237	2.471	-5.766	WOWPAC	[3]
$[Co(tlt)]X\cdot S$ ($X = BF_4^-$) 4	-127.6	7.373	2.757	-4.616	-	[13]
$[Co(tlt)]X\cdot S$ ($X = ClO_4^-$. $S = 2CH_3OH$) 3	-116.0	7.301	3.016	-4.285	-	[13]
$[H(NEt_3)]^+[Co^{II}Co^{III}_3(hpmp)_6]$-	-24.7	7.778	3.171	-4.607	QUJGEJ	[14]
$[Co(tlt)]X\cdot S$ ($X = ZnCl_4^{2-}$. $S = CH_3OH$) 2	-87.20	6.875	3.185	-3.690	-	[13]
$[Co(ctam)][CoCl_4]$	-11	6.789	3.240	-3.549	TARXIW	[10]
$[H(DBU)]^+[Co^{II}Co^{III}_3(hpmp)_6]^-$	-35.2	7.521	3.339	-4.182	QUJGOT	[14]
$[Co(tlt)]X\cdot S$ ($X = CoCl_4^{2-}$.$S = CH_3CN$) 1	-60.60	5.833	3.835	-1.998	-	[13]
$[H(NEt_3)]^+[Co^{II}Co^{III}_3(L^2\ R)_6]^-$	-21.6	7.248	4.406	-2.842	QUJGUZ	[14]
$[Co(pntdt)(CH_3CN)](ClO_4)_2$	-25.80	12.849	5.14	-7.709	ZUWGUW	[15]
$[Co(bggn)(NCS)_2]\cdot DMSO$	-78.7	10.11	5.4	-4.710	-	[16]
$[Co(bggn)Cl_2]\cdot H_2O$	-68.4	11.29	6.15	-5.140	PODCIX	[17]
$[Co(doym)_2](ClO_4)_2$	-66.4	5.89	6.352	0.462	BENBAA	[18]
$[Co(nah)_2]$	-18.4	5.906	6.559	0.653	BECDOF	[19]
$[Co(hch)_2]\cdot 2THF$	-30.4	5.539	7.109	1.570	BECDIZ	[19]
{[Co(bmb)(2.2′-bipy)]·0.5DMF}n	-56.2	6.818	7.269	0.451	IDOPAV	[20]
$[Co(hbah)_2]\cdot CH_2Cl_2$	-27.4	4.991	7.823	2.832	BECDUL	[19]
$[Co(pyrtpy)_2](BPh_4)_2$	-53.6	4.476	9.1	4.624	ECIJOS	[21]
$[Co(bbp)_2][Co(NCS)_4]\cdot 4DMF$	39.00	4.718	9.286	4.568	CUPHIH	[22]
$[Co(C_n\text{-terpy})_2](BF_4)_2$	47.50	4.11	9.389	5.279	SONDUX	[23]

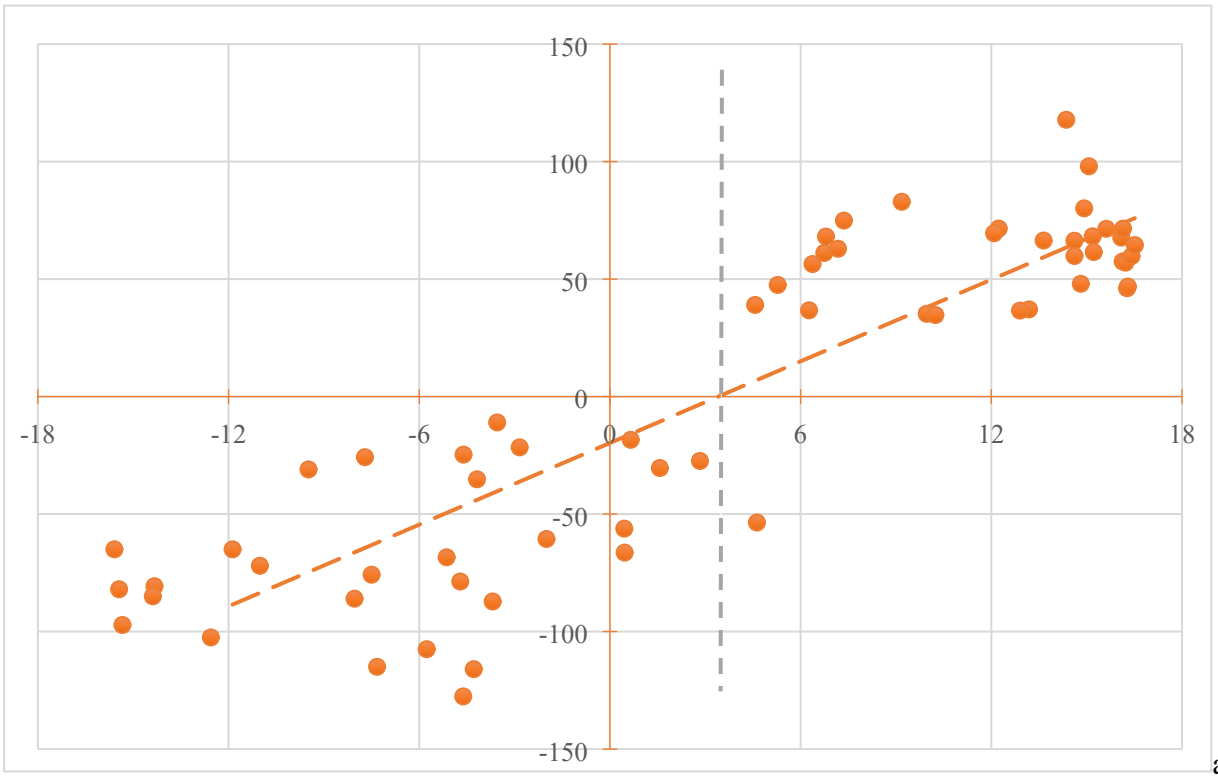
$[Co(2\text{-}Himap)_2]$	36.70	3.243	9.508	6.265	LEPFAQ	[24]
$[Co(HATN)(hfac)_2]\cdot(CH_2Cl_2)$	60.00[a]	1.8	10.495	8.695	PIBDUC	[25]
$[Co(dmoyp)_2](ClO_4)_2\cdot MeCN$	56.40	4.368	10.742	6.374	BEMZUR	[18]
$[Co(dmoyp)_2](ClO_4)_2$	68.10	4.085	10.882	6.797	BEMZOL	[18]
$[Co(ddoyp)_2](ClO_4)_2$	61.10	4.206	10.95	6.744	BEMZIF	[18]
$[Co(ddoyb)_2](ClO_4)_2$	74.90	4.043	11.405	7.362	BENBEE	[18]
$[Co(ddoym)_2](ClO_4)_2$	62.90	4.311	11.486	7.175	BEKXEX	[18]
$[Co(phf)Cl_2]$	35.2	1.853	11.82	9.967	KUYZEM	[26]
$[Co(tlt)(NCS)_2]$	34.70	1.799	12.039	10.24	-	[13]
$[Co(dimphen)(NCS)_2]$	82.90	2.977	12.158	9.181	UKACUH	[27]
$[Co(mtpd)_4(NO_3)_2]$	71.50	0.58	12.811	12.231	NIBQEX	[28]
$[Co(bbp)(NCS)_2(DMF)]\cdot 2DMF$	69.50	1.395	13.483	12.088	CUPHED	[22]
$[Co(hfac)_2(bpy)]$	37.10	0.677	13.863	13.186	YOZQEM	[29]
$[Co(mtxqn)_2(SCN)_2]$	36.60	1.231	14.134	12.903	ROZGUL	[30]
$[Co(biq)(\mu_{1.5}\text{-}dca)_2]_n$	66.40	0.665	14.310	13.645	URANUZ	[31]
$Et_4N[Co(hfac)_3]$	117.80	0.182	14.539	14.357	EXEHUM	[32]
$[Co^{II}(^{Me}bik)_2(NCSe)_2]$	66.32	0.169	14.784	14.615	-	[33]
$[Co^{II}(^{Me}bik)_2(NCS)_2]$	59.84	0.171	14.787	14.616	-	[33]
$[Co(bmim)_4(tcm)_2]$	80.10	0.16	15.082	14.922	-	[34]
$[Co(py)_4(Cl)_2]\cdot H_2O$	68.20	0.344	15.533	15.189	QELMEZ02	[35]
$[Co(abpt)_2(tcm)_2]$	48.00	0.855	15.670	14.815	EQINID	[36]
$[Co(phpl)_4(NO_3)_2]$	71.40	0.168	15.787	15.619	LECWAS01	[28]
cis-[Co(dmphen)$_2$(NCS)$_2$]·0.25EtOH	98.00	0.908	15.977	15.069	PEMMUR	[37]
$[Co(py)_4(Br)_2]$	61.50	0.881	16.104	15.223	CURSUG	[35]
$[Co(hfac)_2(MBIm)_2]$	67.65	0.096	16.185	16.089	VUJZEI	[38]
$[Co(hfac)_2(DMF)_2]$	71.47	0.093	16.236	16.143	VUJZIM	[38]
$\{[Co(bimb)(H_2O)_4]\cdot(pmb)\cdot 2DMF\}_n$	57.5	0.134	16.266	16.132	IDOQUQ	[20]
$[Co(bim)_4(tcm)_2]$	46.10	0.078	16.349	16.271	-	[34]
$[Co(acac)_2(H_2O)_2]$	57.00	0.149	16.369	16.220	CODAAC03	[39]
$[Co(py)_4(SCN)_2]$	46.80	0.103	16.399	16.296	ITCPCO03	[35]
$[Co(hfac)_2(Spy)_2]$	59.78	0.051	16.464	16.413	VUJZAE	[38]
$[Co(hfac)_2(MeCN)_2]$	64.46	0.062	16.578	16.516	VUJYUX	[38]

[a] this compound was excluded from correlation, see below.

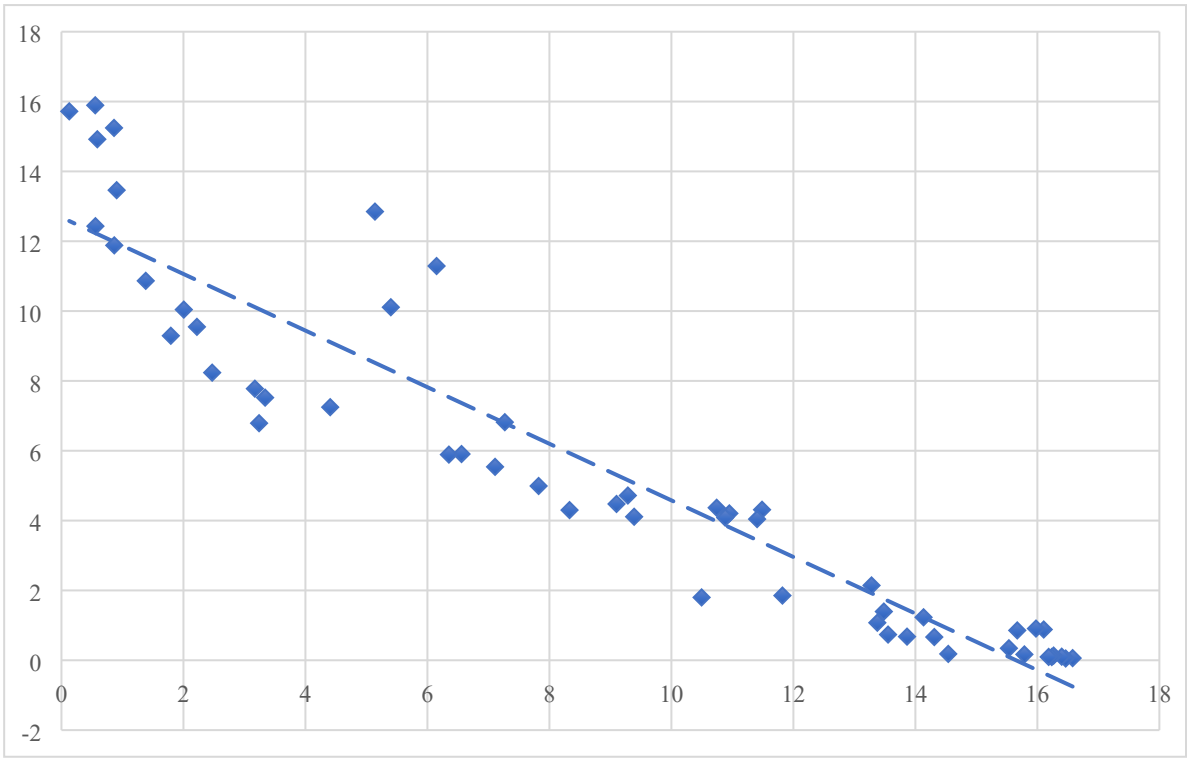
Ligand names from the compound's formula:

Gm – glyoxime; tppm - tris[6-(1*H*-pyrazol-1-yl)pyridin-2-yl]methanol; PzOx – pyrazoloxime; AcPzOx - 2-acetylpyrazoloxime; TFIMTH - $(P(S)\{[N(CH_3)N{=}CHC_3N_2H_3]_3)\}$; AcMeImd - 1-(1-methyl-1H-imidazol-2-yl)ethanone oxime; pprz - 6,6′-((1*Z*)-((piperazine-1,4-diylbis(propane-3,1-diyl)) bis(azanylylidene))bis(methanylylidene))bis(2-methoxyphenol; ctam - 6,6',6"-(cyclohexane-1,3,5-triyltris((azanylylidene)methylylidene))tris(N-t-butylpyridine-3-carboxamide); AcPyOx - 2-acetylpyridineoxime; bhpm - 4-bromo-2-((2-hydroxy-1-phenylethylimino)methyl)phenol; hpy - tris(2,2′-bipyrid-6-yl)methanol); tlt - tris(pyridylhydrazonyl)phosphorylsulfide; hpmp - 2-((2-hydroxy-1-phenylethylimino methyl)phenol); DBU - 1,8-diazabicyclo[5.4.0]undec-7-ene; pntdt - 1,5,13,17,22-pentaazatricyclo[15.2.2.17,11]docosa-7,9,11(22)-triene; bggn - biscondensation product of diacetyl and 2-hydrazinyl-4,6-dimethylpyrimidine; doym - 2,6-bis(4,5-dihydro-1,3-oxazol-2-yl)-4-(4-methylphenyl)pyridine; nah - nicotinic acid(6-hydroxymethyl-pyridin-2-ylmethylene)hydrazide; hch - 3-hydroxy-naphthalene-2-carboxylic acid (6-hydroxymethyl-pyridin-2-ylmethylene) hydrazide; bmd - 2,2′-[benzene-1,4-diylbis(methanediylsulfanediyl)]dibenzoic acid; hbah - 2-hydroxy-benzoic acid(6-hydroxymethyl-pyridin-2-ylmethylene)hydrazide; pyrtpy - 4′-pyrrolidine-2,2′:6′,2″-terpyridine; bbp - 2,6-bis(1*H*-benzo[*d*]imidazol-2-yl)pyridine; C_n-terpy - 4′-alkoxy-2,2':6′,2″-terpyridine; 2-Himap - *o*-[(1*H*-imidazol-2-yl)methylideneamino]phenol; HATN - 5,6,11,12,17,18-hexaazatrinaphthylene; hfac – hexafluoroacetylacetone; dmoyp - 2,6-bis(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)pyridine; ddoyp - 2,6-bis(4,5-dihydro-1,3-oxazol-2-yl)pyridine; ddoyb - 2,6-bis(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-4,4'-bipyridine; ddoym - 2,6-bis(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-4-(4-methylphenyl)pyridine; phf - 1,1′-bis(1-((pyrid-2-ylmethylene)hydrazono)ethyl)ferrocene; dimphen - [1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane]; mtpd – 4-methylpyridine; bbp - 2,6-bis(1*H*-benzo[*d*]imidazol-2-yl)pyridine;

bpy - 2,2′-dipyridyl; mtxqn - 8-methoxyquinoline; biq - 2,2′-biquinoline; dca - dicyanamide anion; ^{Me}bik = bis(1-methylimidazol-2-yl)ketone; bmim - 1-benzyl-2-methylbenzimidazole; tcm - tricyanomethanide ion; py – pyridine; abpt - 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole; phpl - 3-phenylpyrazole; dmphen - 2,9-dimethyl-1,10-phenanthroline; MbIm - 5,6-dimethylbenzimidazole; bimb - 1,4-bis(benzoimidazo-1-ly)benzene); pmb - 2,2′-(1,4-phenylenebis(methylene))bis(sulfanediyl)dinicotinic acid; bim - 1-benzylimidazole; acac – acetylacetonate; Spy - 4-styrylpyridine.



a)



b)

Figure S1 a) D *vs* Δ = TPR6-OC6 (difference between continuous symmetry measures TRP6 and OC6), correlation coefficient R = 0.88; b) correlation between OC6 and TPR6 CSMs (R = 0.94)

Computational study for $[Co(HATN)(hfac)_2]\cdot(CH_2Cl_2)$ [25] (CSD code PIBDUC)

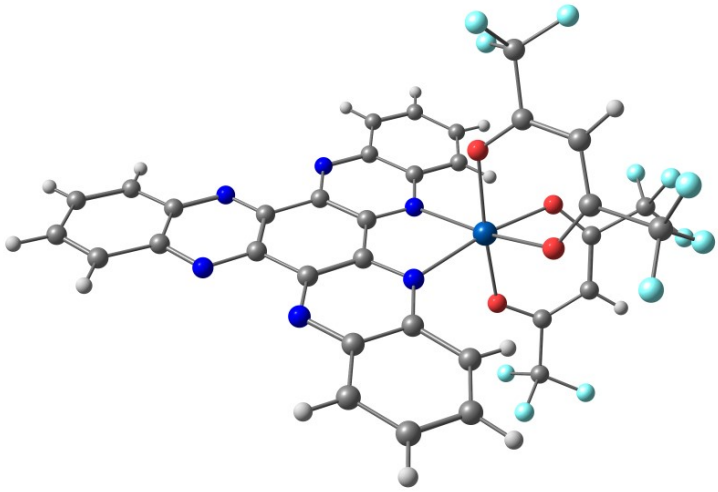


Figure S2. Molecule of the compound $[Co(HATN)(hfac)_2]\cdot(CH_2Cl_2)$ [25] (CSD code PIBDUC) (solvent molecule is excluded, nuclei coordinates are frozen at the positions as found from the single crystal X-ray diffraction study).

Compound $[Co(HATN)(hfac)_2]$ [25] was subjected to quantum-chemical modelling of the zero field splitting parameters (ZFS) at the CAS(7,5) level of theory (details of the calculations are given further). Nuclei coordinates were taken from single crystal X-ray diffraction experiment, corresponding cif-file was obtained from Cambridge Structure Database (CSD)[40].

First five quartet excitations (spin-orbit free excited states) were found at 1060, 1551, 7292, 7418, 7738 cm^{-1}. Calculated energies of the lowest spin-orbit states (Kramers doublets) are 0.0, 109.7, 1135.4, 1345.3 cm^{-1}.

Ground state is well-separated from the quartet excited states, so ZFS spin-Hamiltonian can be considered applicable for this compound. Also applicable is effective Hamiltonian approximation used in ORCA program for extraction of the anisotropy parameters from relativistic states and relativistic energies). Calculated within this approximation anisotropy parameters are: D = +49.5 cm^{-1} with rather high rhombicity, E/D = 0.28.

Calculated composition of the ground spin-orbit (Kramer's) states are: 80% (S=3/2, M_S=+1/2) and 80% (S=3/2, M_S=-1/2), while composition of the first excited Kramer's doublet is 90% (S=3/2, M_S=+3/2) and 90% (S=3/2, M_S=-3/2). Such ordering of the SOC states (stabilization of the states with smaller spin projection value) also supports the easy magnetization plane case and positive value of D parameter for this compound.

Also in agreement with this conclusion are the calculated principal values of g-tensor:

$g_x = 2.398$ $g_y = 2.700$ $g_z = 2.084$ ($g_{iso} =$ 2.394).

This result is in discrepancy with the experimental value evaluated in [25] for this compound by fitting magnetic susceptibility data (-60 cm^{-1}). That's why this compound was excluded from the correlation.

Computational details

ORCA 4 program[41, 42] was employed to perform theoretical calculations of the electronic structure of several Co(II) complexes within post-Hartree–Fock multi-reference wavefunction approach based on state-averaged complete active space self-consistent field calculations (SA-CASSCF)) [43-46]. Scalar relativistic effects were account for using a standard second-order Douglas–Kroll–Hess (DKH) procedure[47]. Segmented all-electron relativistically contracted version of Ahlrichs polarized triple-zeta basis set, def2-TZVP [48-50], was used for all atoms. To improve the calculation time, the resolution of the identity approximation with corresponding correlation fitting of the basis set[51] was employed. The CASSCF active space was constructed from 5 MOs with predominant contributions of 3d-AOs from the Co(II) center and 7 electrons, corresponding to metal ion CAS(7, 5). Ten quartets and 40 doublet states were included in the WF expansion. Spin–orbit effects were included using the quasi-degenerate perturbation theory (QDPT)[52].

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