Supplementary Information to

Precursor molecules for 1,2-diamidobenzene containing cobalt(II), nickel(II) and zinc(II) complexes – Synthesis and magnetic properties

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‡ Equal Contribution

Contents

NMR Spectra

[Zn(II)(bmsab)dme]

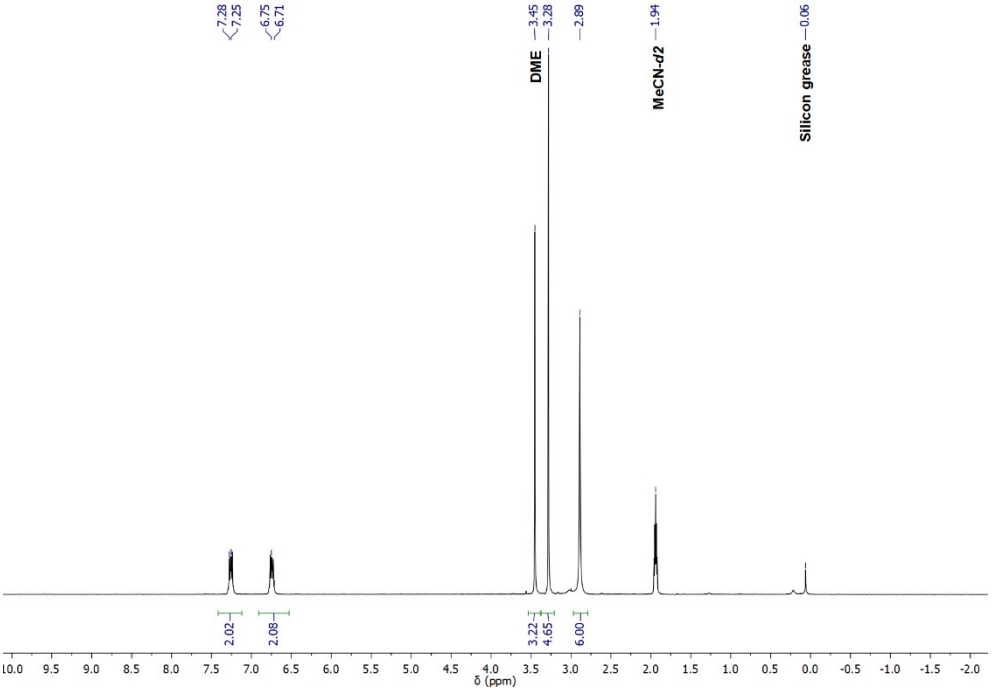

Figure S1: ^{1}H-NMR-Spectrum (250 MHz, MeCN-*d3*, 25 °C) of the heteroleptic Zn(II) precursor **[Zn^{II}(bmsab)dme]** dissolved in deutero-acetonitrile.

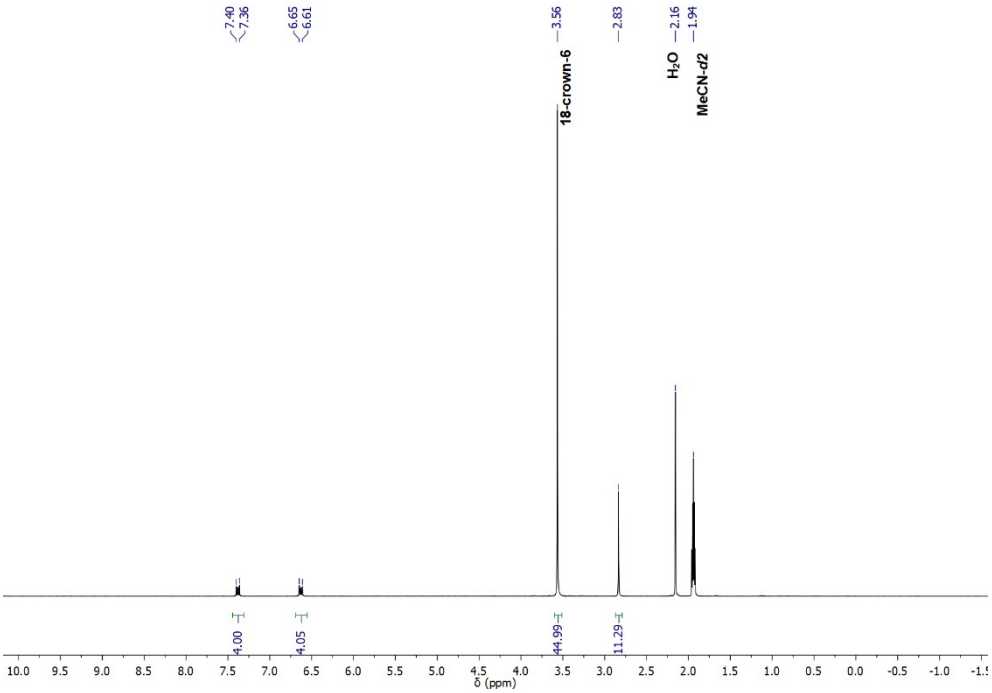

Figure S2: ^{1}H-NMR-Spectrum (250 MHz, MeCN-*d3*, 25 °C) of the homoleptic complex **(K-18-crown-6)$_2$[Zn^{II}(bmsab)$_2$]** dissolved in deutero-acetonitrile.

[Ni(II)(bmsab)dme]

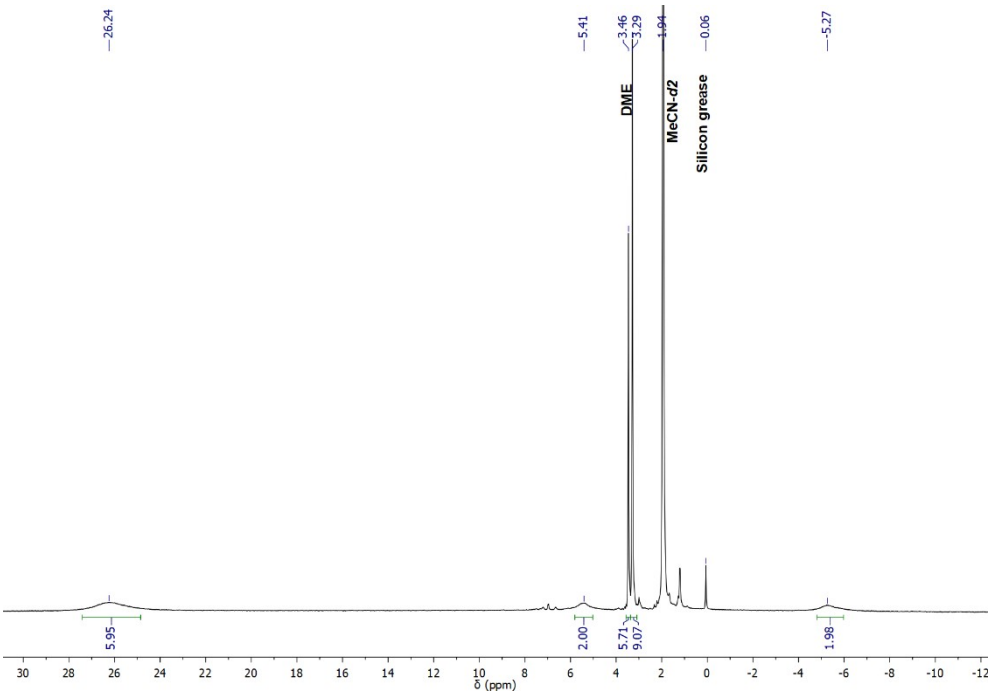

Figure S3: ^{1}H-NMR-Spectra (250 MHz, MeCN-*d3*, 25 °C) of the heteroleptic Ni(II) precursor **[Ni^{II}(bmsab)dme]** dissolved in deutero-acetonitrile.

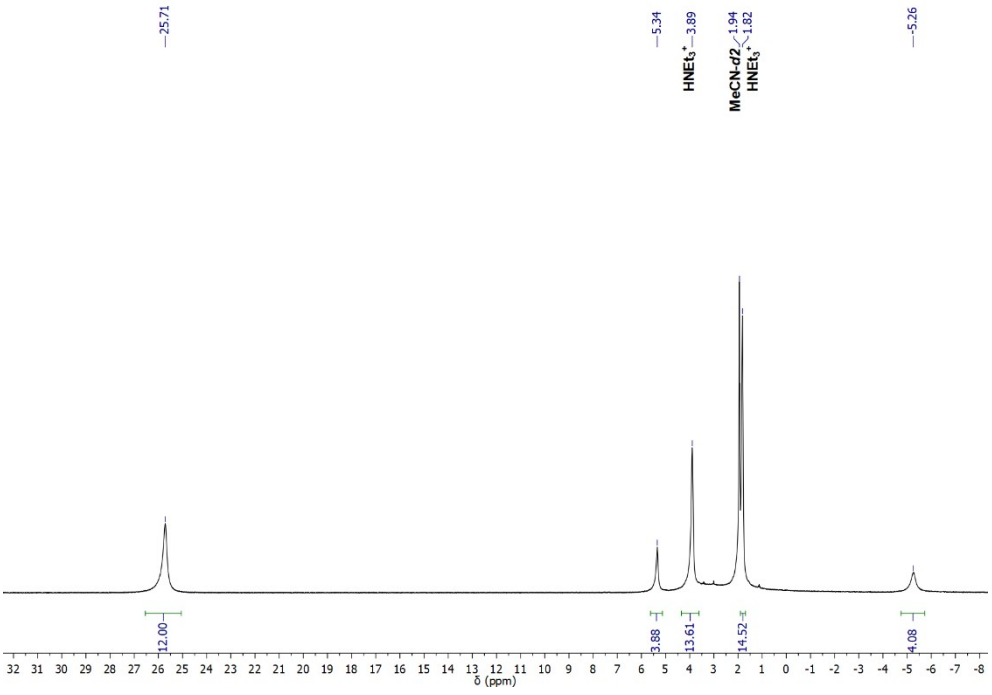

Figure S4: ^{1}H-NMR-Spectrum (250 MHz, MeCN-*d3*, 25 °C) of the homoleptic Ni(II) complex **$(HNEt_3)_2$[Ni^{II}(bmsab)$_2$]** dissolved in deutero-acetonitrile.

[Co(II)(bmsab)dme]

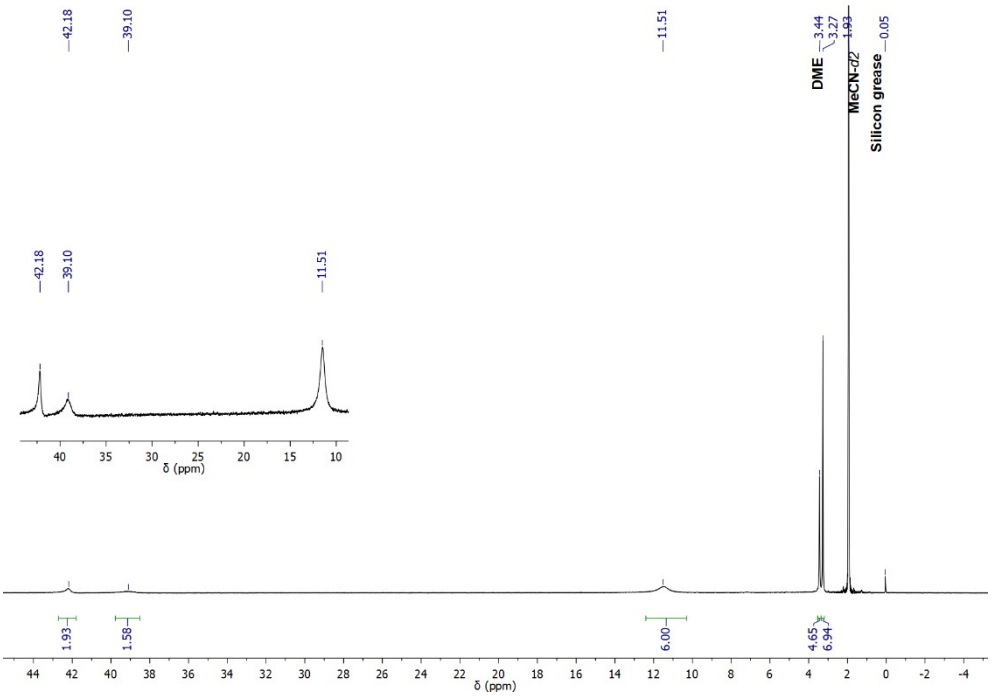

Figure S5: ^{1}H-NMR-Spectrum (250 MHz, MeCN-*d3*, 25 °C) of the heteroleptic Co(II) precursor **[Co^{II}(bmsab)dme]** dissolved in deutero-acetonitrile.

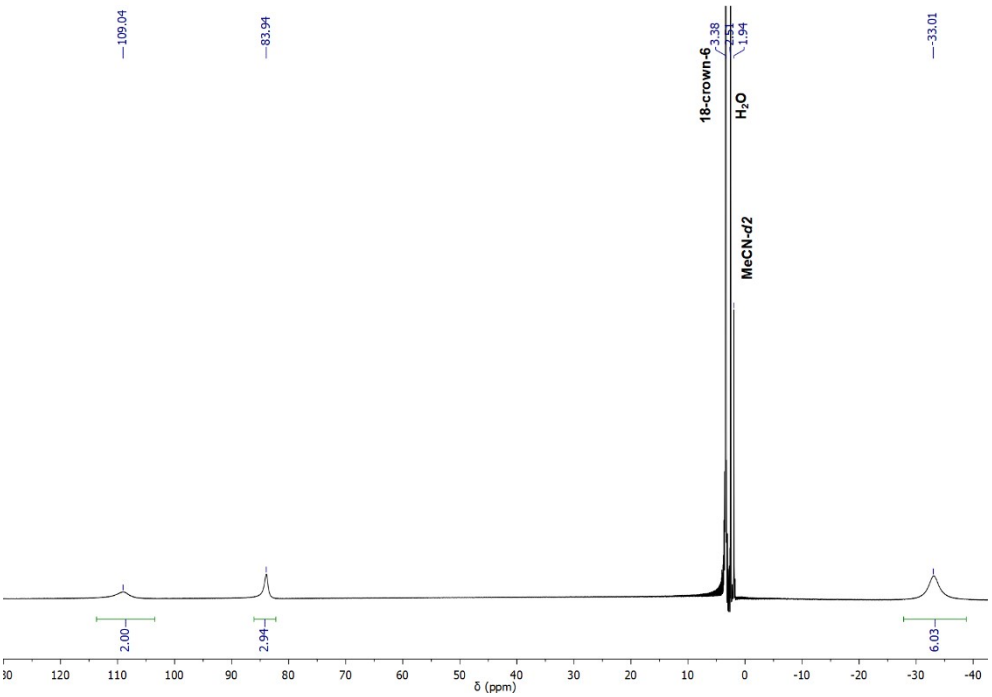

Figure S6: ^{1}H-NMR-Spectrum (250 MHz, MeCN-*d3*, 25 °C) of the homoleptic Co(II) complex **(K-18-crown-6)$_2$[Co^{II}(bmsab)$_2$]** dissolved in deutero-acetonitrile.

UV/Vis/NIR Spectroscopy

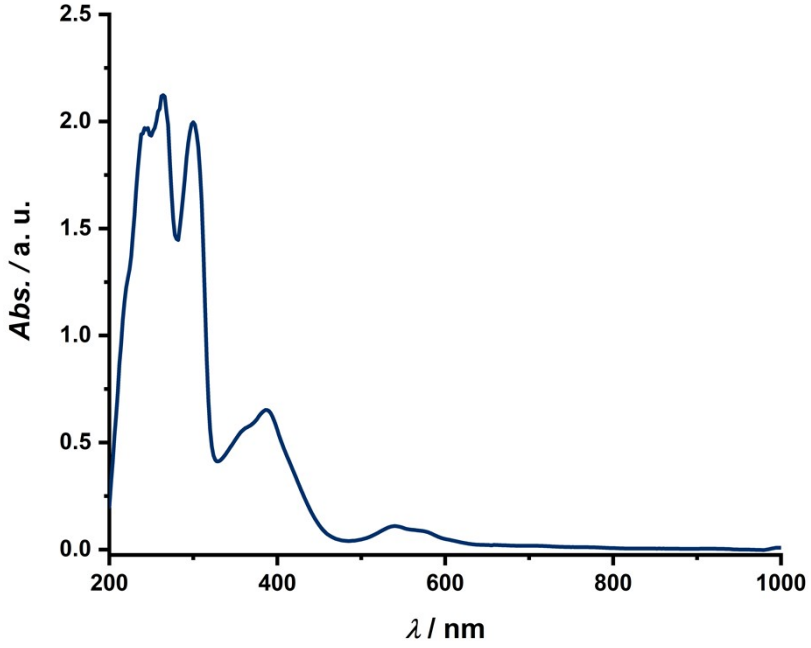

Figure S7: UV/Vis/NIR spectrum of heteroleptic precursor **[Ni^{II}(bmsab)dme] (2)** dissolved in acetonitrile**.**

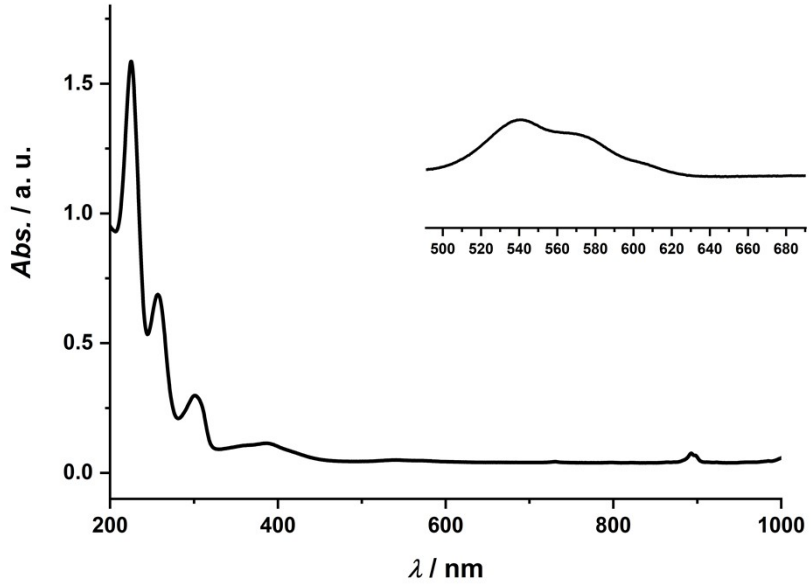

Figure S8: UV/Vis/NIR spectrum of the homoleptic complex **[Ni^{II}(bmsab)$_2$]$^{2-}$** dissolved in acetonitrile. Inset shows the bands between 540 and 570 nm at higher concentration. Compound was re-measured as the weak low-wavelength bands were not mentioned in the original publication[1].

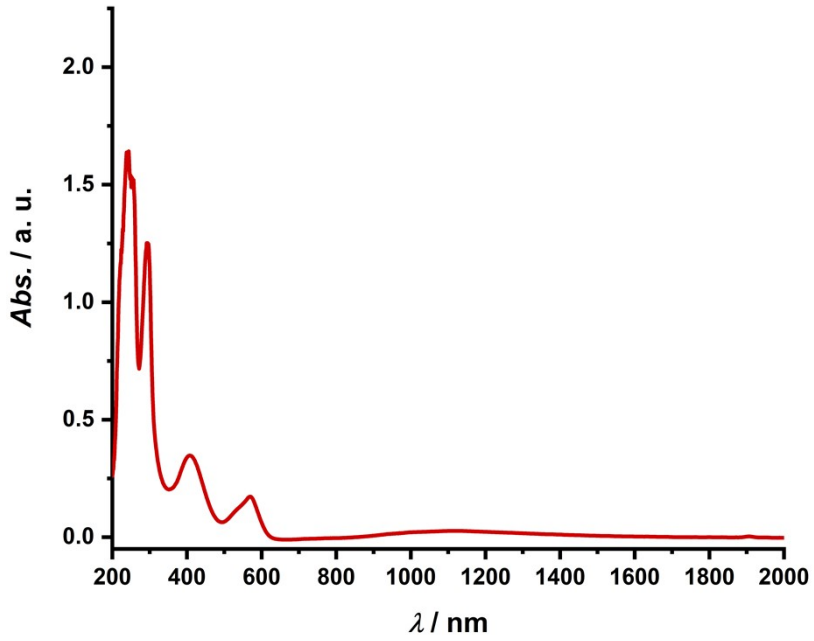

Figure S9: UV/Vis/NIR spectrum of heteroleptic precursor **[Co^{II}(bmsab)dme] (3)** dissolved in acetonitrile.

Table S1: Absorption maxima of acetonitrile solutions of the heteroleptic precursors **2** and **3** and of the corresponding homoleptic complexes. Values for **[Co^{II}(bmsab)$_2$]$^{2-}$** were taken from reference 1.

	Absorption maxima / nm
[Ni^{II}(bmsab)dme] (2)	244, 264, 300, 386, 540, 574
[Ni^{II}(bmsab)$_2$]$^{2-}$	230, 256, 301, 389, 540, 568
[Co^{II}(bmsab)dme] (3)	244 257, 295, 408, 569, 1120
[Co^{II}(bmsab)$_2$]$^{2-}$	234, 259, 305, 561

Magnetism and EPR Spectroscopy

For all measurements potential ferromagnetic impurities were corrected for. To this end, temperature dependent susceptibility measurements were carried out in the temperature regime from 1.8 K up to 50 K at an applied magnetic field of 1000 Oe and from 40 K to 300 K at an applied field at 10000 Oe. The overlap region served for correcting the data for the ferromagnetic impurity. The diamagnetic contribution was estimated on the basis of Pascal's constants.[3]

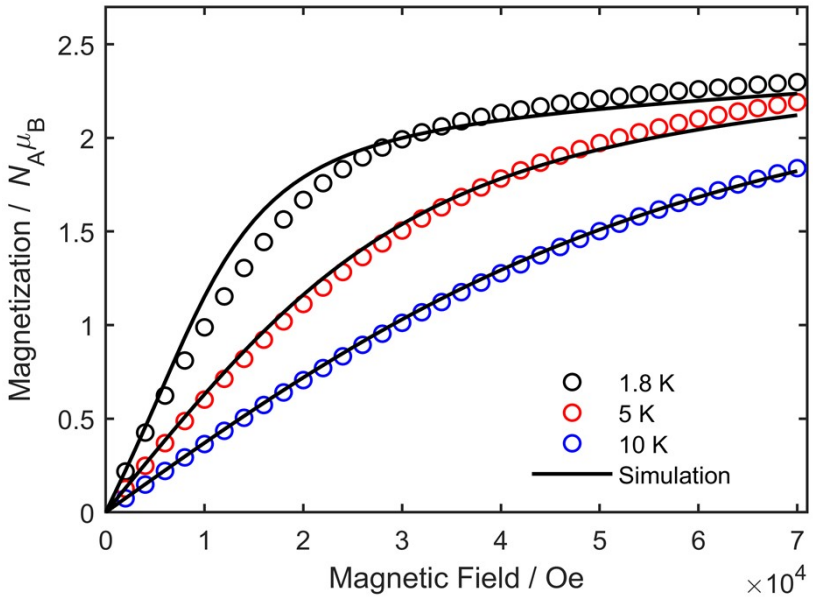

Figure S10. Magnetization curves of the heteroleptic precursor **[Co^{II}(bmsab)dme] (3)** at the indicated temperatures. Experimental values are shown as circles, while spin Hamiltonian simulations at the corresponding temperatures are shown as black lines. Simulations are carried out with the parameters given in the main text.

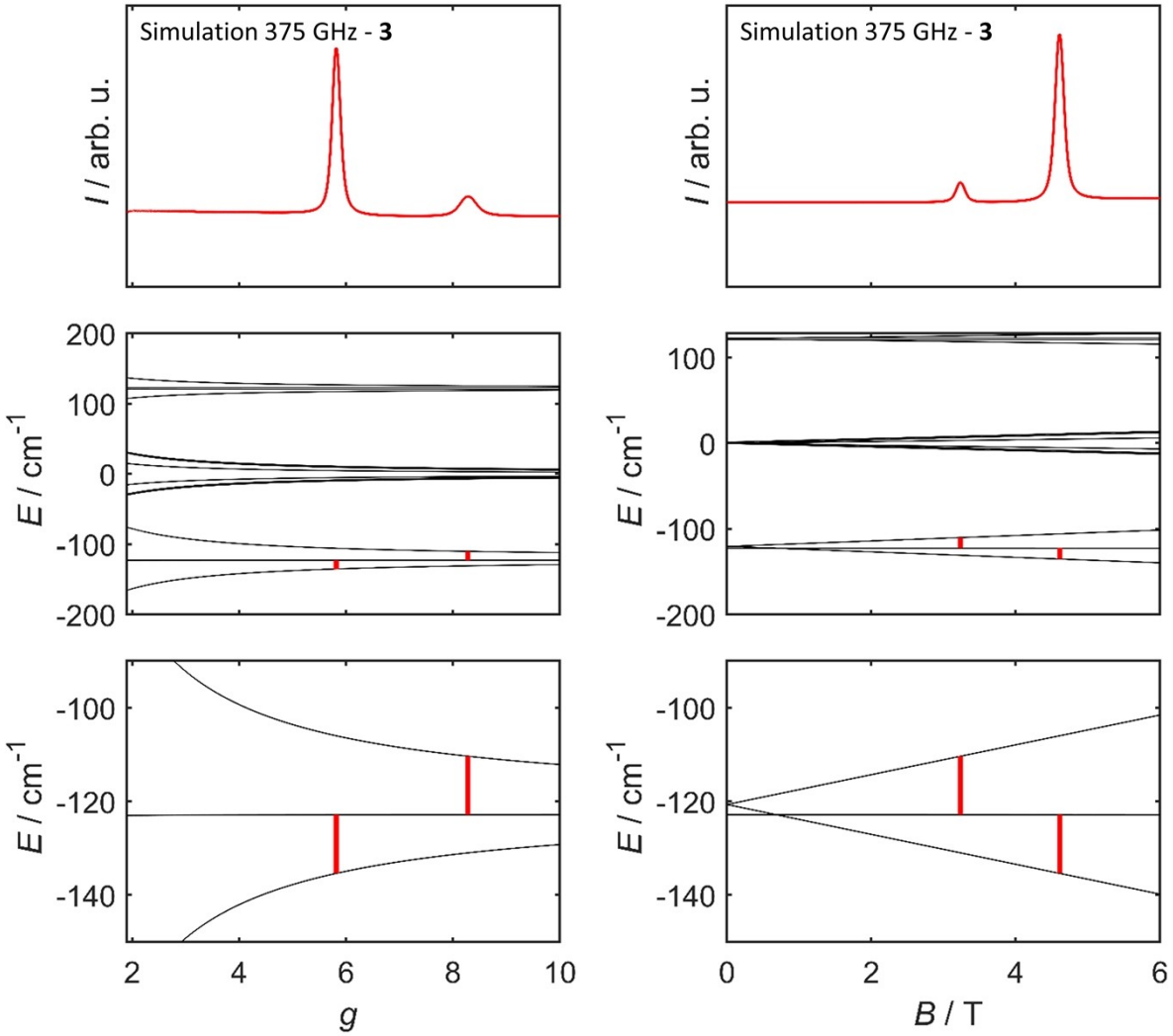

Figure S11: Simulated HFEPR spectrum of **3** (top) as well as the corresponding complete overview of the spin sublevels (middle) and a zoom-in on the region where the transitions that are observed in HFEPR take place. Levels are plotted for the magnetic field in *z*-direction. The red transitions are plotted for a frequency of 375 GHz.

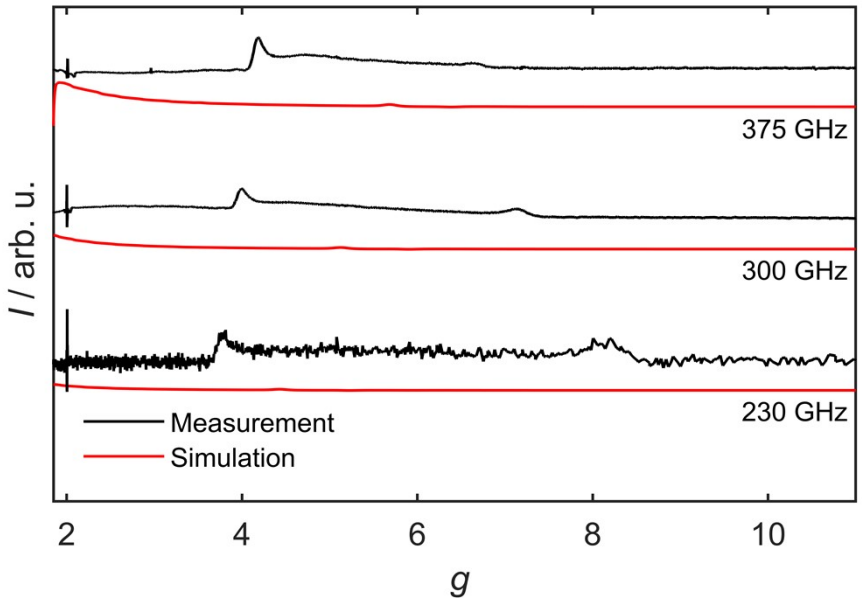

Figure S12. Measured HFEPR spectra of **3** at the indicated frequencies at 5 K (black), simulations based on the parameter set, that was obtained on the basis of the magnetometry measurements are shown in red.

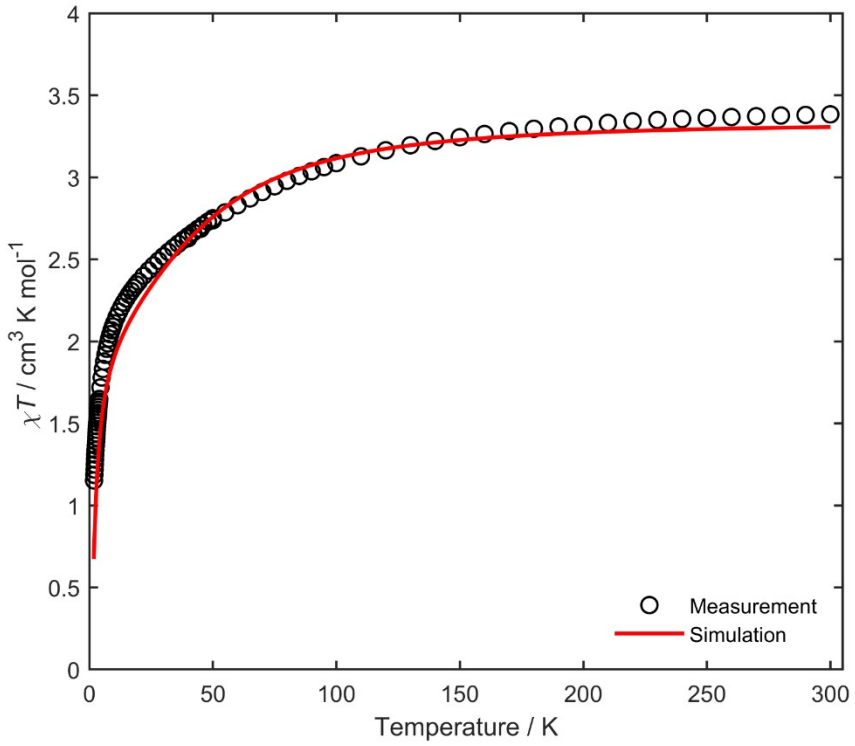

Figure S13. Susceptibility temperature product of **3** as a function of the temperature (black symbols) recorded on pressed powder samples at external fields of 0.1 T ($T < 40$ K) and at 1 T ($T > 40$ K). Lines are fits according to Eq. (1), assuming positive D. The parameters are $S = 3/2$, $g_x = 2.8$, $g_y = 2.7$, $g_z = 2.6$, $D = +50–1$, $E = 0.18D$, $J = +0.8$ cm^{-1}.

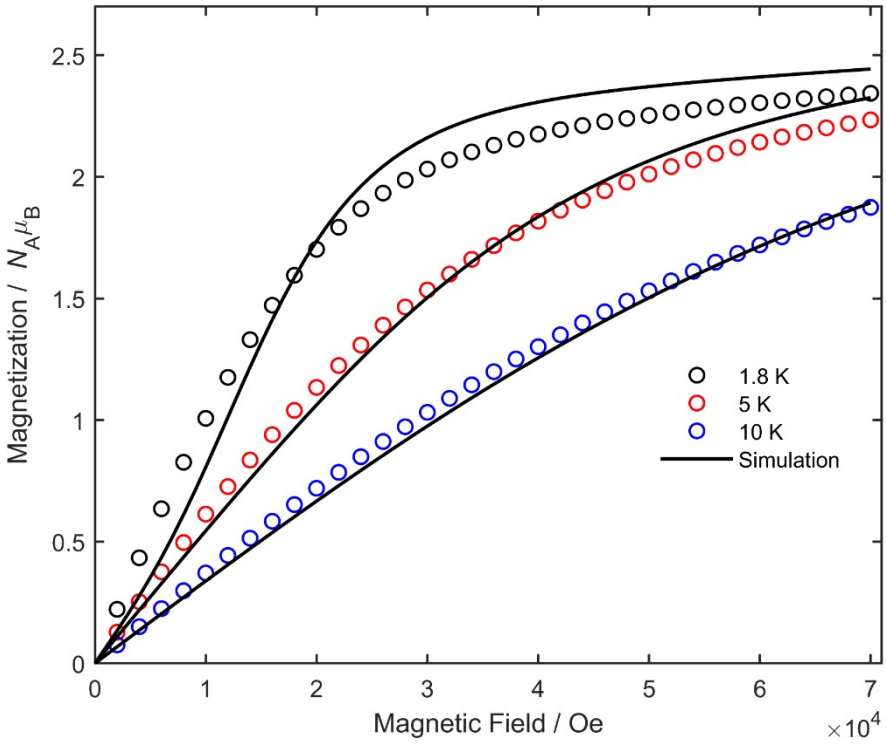

Figure S14. Magnetization curves of **3** at the indicated temperatures. Experimental values are shown as circles, while spin Hamiltonian simulations at the corresponding temperatures are shown as black lines. Lines are fits according to Eq. (1), assuming positive D. The parameters are $S = 3/2$, $g_x = 2.8$, $g_y = 2.7$, $g_z = 2.6$, $D = +50–1$, $E = 0.18D$, $J = +0.8$ cm^{-1}.

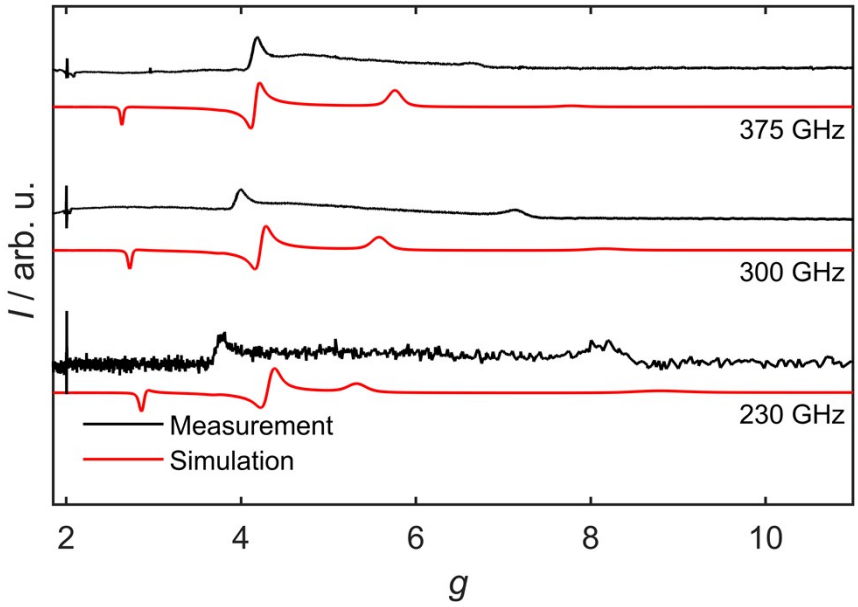

Figure S15. Measured HFEPR spectra of **3** at the indicated frequencies at 5 K (black), simulations based on the parameter set, that was obtained assuming positive D. The parameters are $S = 3/2$, $g_x = 2.8$, $g_y = 2.7$, $g_z = 2.6$, $D = +50$, $E = 0.18D$, $J = +0.8$ cm^{-1}.

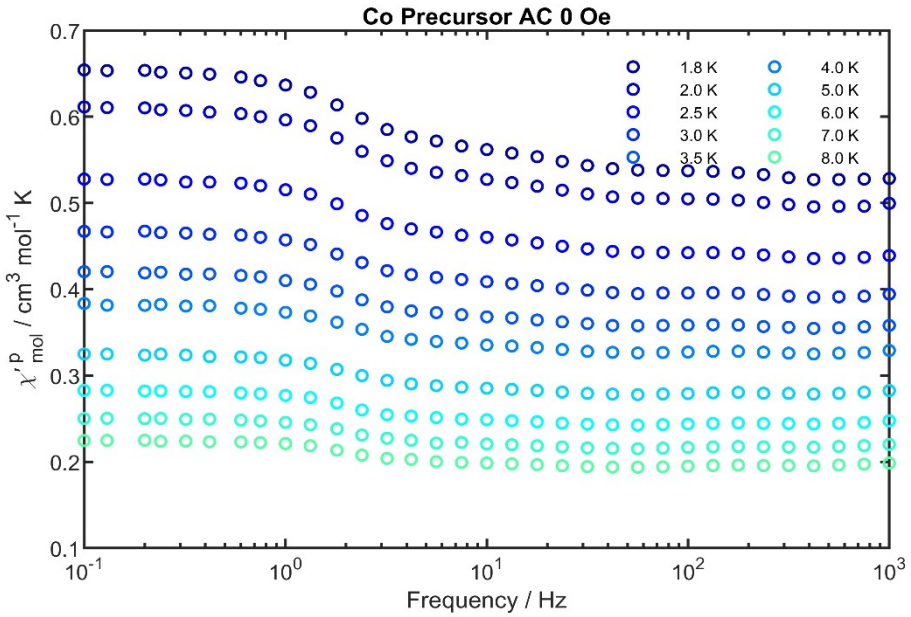

Figure S16: In-phase component of the dynamic susceptibility of the heteroleptic precursor **[Co^{II}(bmsab)dme] (3)** at the indicated temperatures in zero applied magnetic field.

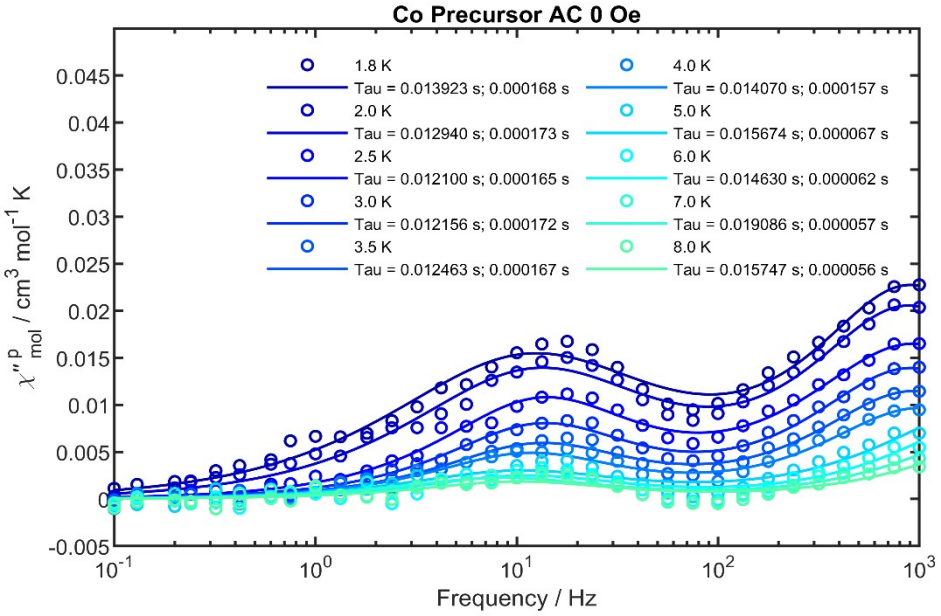

Figure S17. Out-of-phase component of the dynamic susceptibility of the heteroleptic precursor **[Co^{II}(bmsab)dme] (3)** at the indicated temperatures in zero applied magnetic field. The solid lines are fits based on modified Debye functions. Two relaxation processes with different relaxation times are visible and hence two relaxation times are given at each temperature. Since the magnitude of $X``$ is only approx. 3% of $X`$, the out-of-phase signal is attributed to an impurity.

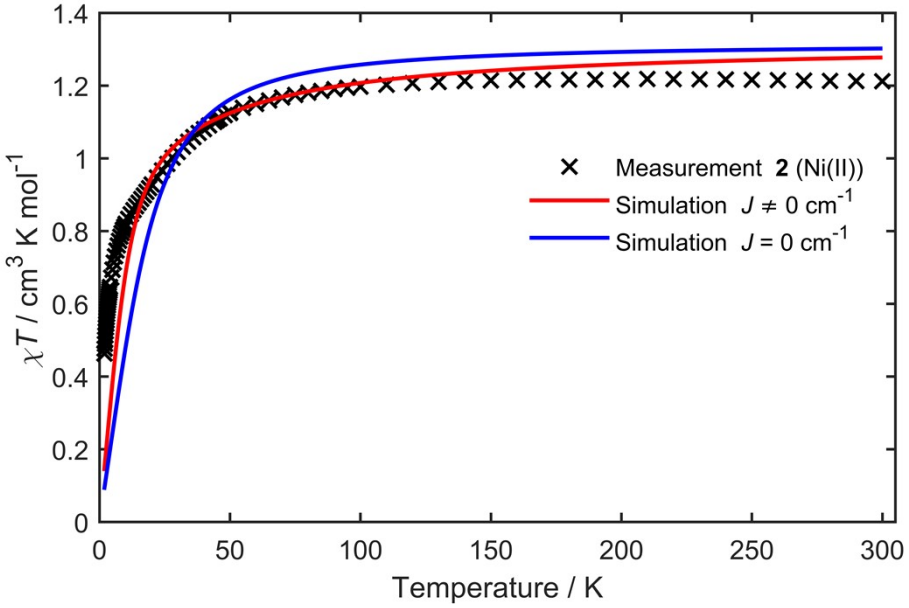

Figure S18. Temperature-susceptibility curve of **2** (black symbols) and the corresponding simulations based on the assumption of a **positive** *D* parameter. The parameters are given in table 1 in the main text.

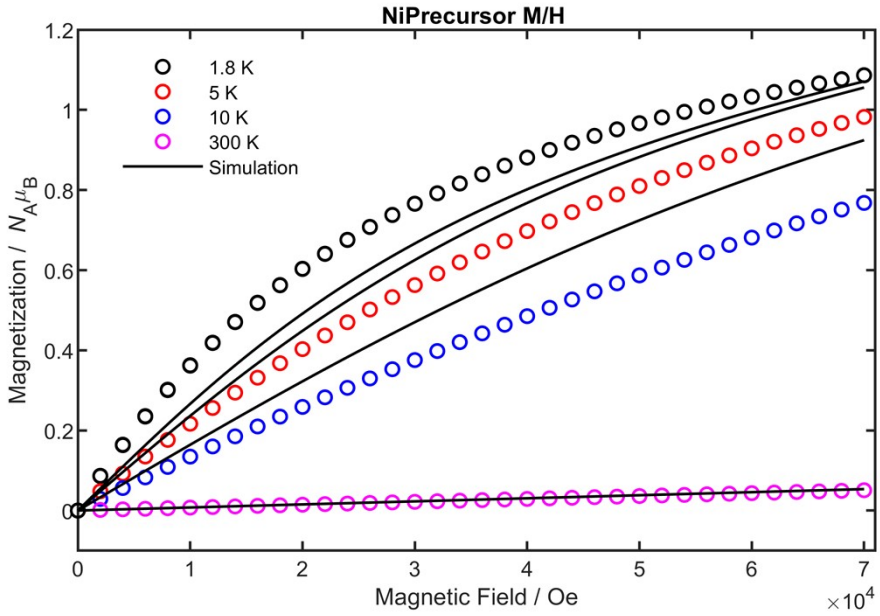

Figure S19. Magnetization curves of the heteroleptic precursor **[Ni^{II}(bmsab)dme] (2)** plotted as magnetic moment versus field at the temperatures indicated. Measurements are shown as circles, while the simulations are shown as black solid lines. The simulations are based on the parameters given in table 1 in the main text, that feature a **positive** ZFS *D* parameter.

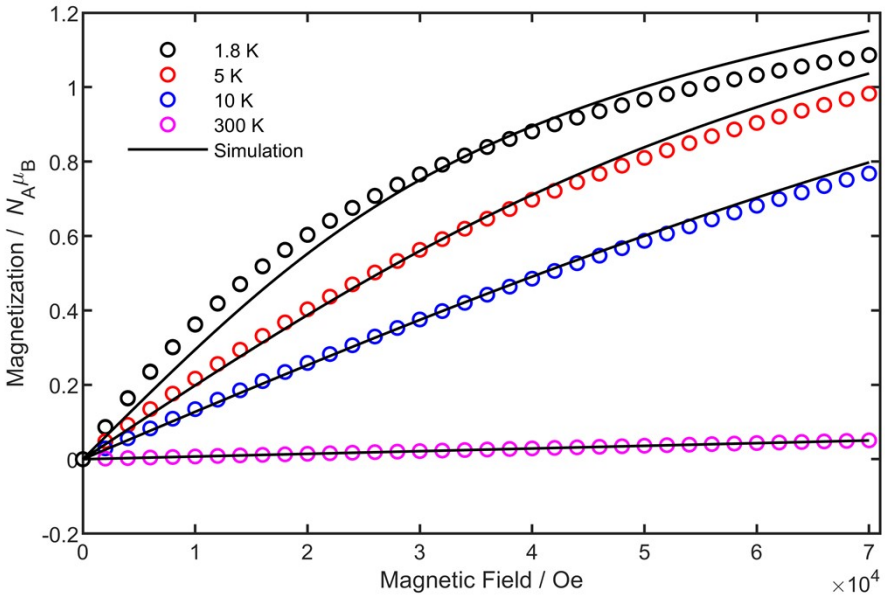

Figure S20. Magnetization curves of **[Ni^{II}(bmsab)dme] (2)**, measured at the indicated temperatures (circles). The corresponding simulations are based on eq. (1) and are carried out under the assumption of a **negative** ZFS *D* parameter (see table 1 in the main text).

Theoretical Calculations

Table S2: Geometry optimized coordinates of the dimer of [Co^{II}(bmsab)dme] (**3**)

C	-2.17194417265913	1.38773331712138	-0.66167156160106
C	-2.02569144086611	0.26227930860450	-1.46743940300876
C	-0.80546664054372	-0.41467862063060	-1.51814083365710
C	0.26922016617229	0.01462865790177	-0.73575717723295
C	0.11950904377610	1.16930825988355	0.08330969167759
C	-1.09907142639480	1.85027550723508	0.10198935452665
N	1.27665988739635	1.50659334429055	0.78780135455300
N	1.54510846294699	-0.56145843551830	-0.67636113283559
S	1.52819686832365	2.82179374685961	1.68596952874434
S	1.99405953850836	-1.91327066057873	-1.42811114871310
O	3.42049638976900	-2.06399580448456	-1.03873534603296
O	1.68156807927113	-1.94946458121166	-2.85562270884415
O	2.98756815701559	2.75775555298036	1.95240647082242
O	0.98090087378496	4.05241363824771	1.12326916974625
C	0.72310626242939	2.56491356126601	3.25628332207351
H	1.14664806641852	1.67324386382787	3.73263717720399
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H	0.91983201133665	3.46267886173947	3.85672238374351
C	1.11570310230877	-3.27256383505711	-0.67513616279642
H	1.42588509058300	-4.17727040661226	-1.21357847200737
H	0.03747032595934	-3.10686639157592	-0.79588123080473
H	1.38591347464604	-3.33420228413205	0.38524532086950
Co	2.87210839048619	0.51063486075688	0.30602132592870
Co	8.10494763941323	0.44664209144323	-0.02758298367423

N	9.53485514426795	1.64759928904898	-0.64631655181494
N	9.62862711402653	-0.70324253118249	0.35285723527638
C	10.88359636657700	-0.15953039860739	0.06991359697640
C	10.83476671026517	1.16425352726627	-0.44913157349414
C	12.02957876210667	1.84309357503096	-0.70129811762825
C	12.11747195904398	-0.79028922590319	0.24654454209305
C	13.30019302680738	-0.10525036273773	-0.03710608772865
C	13.25601555883683	1.20746009126320	-0.49761926703988
S	9.34918624990524	-2.00157594399785	1.26899607030303
S	9.16322816048632	3.12441912740337	-1.17482087798023
O	9.85799309493200	4.20048181783893	-0.46946578240176
O	7.67929338629405	3.13432772722569	-1.15869388521643
O	10.05401568797966	-3.20925669111458	0.84828600179937
O	7.86729939486348	-2.04404522748735	1.33361207689649
C	9.64428619618119	3.23297908543561	-2.89076393144071
H	10.72754987730580	3.07743238036375	-2.96974040558823
H	9.37801417162808	4.24495580336781	-3.22242387950170
H	9.09921736273626	2.47396171906110	-3.46428197977608
C	9.92172116229228	-1.62212334831236	2.91783712307161
H	10.99948492404168	-1.41738093723920	2.87858396541010
H	9.72480025149097	-2.51419599977512	3.52638896488608
H	9.36962958469633	-0.75395476218679	3.29676453146503
H	14.18121500562967	1.75202856663391	-0.69980956966359
H	14.25983266487323	-0.60759738527450	0.10495509947863
H	12.14042311228269	-1.82795436622615	0.58607672578481
H	12.00157531987217	2.88658127220759	-1.02002074635411
H	-1.19244141353321	2.76823701299268	0.68495987752328
H	-3.11980512053288	1.93036208577091	-0.63962274787623
H	-2.85722967459856	-0.08477643829525	-2.08505228371346
H	-0.67154675266653	-1.25589059132461	-2.20084536583545
O	3.94381240322947	-0.44002736961659	1.81718385617624
O	4.27738337171699	1.38570228424658	-0.94443161513391
O	6.74429867744392	-0.24329968289577	-1.40573533696585
O	7.11160448815042	1.28771535394828	1.61056984396902
C	4.63150138234371	0.73298085900108	-2.17027658952806
C	6.12562383548379	0.62417669825032	-2.36067585807435
H	4.19781649861794	1.29417303282394	-3.01561870091068
H	4.15986562081246	-0.25827639360772	-2.14181527890436
H	6.61925511540135	1.60068935726547	-2.24610170816365
H	6.32876280662816	0.24167736292904	-3.37598575779728
C	5.37262466678175	-0.37951175994488	1.73394945752986
C	5.78658213449800	1.03678281802498	2.07421654613076
H	5.69274476880404	-0.65996661310129	0.71962862945773
H	5.81460828533048	-1.11265087718414	2.42188673157321
H	5.76024497933216	1.19728277513057	3.16493991356996
H	5.08632083455057	1.76136848802302	1.62765982294522
C	7.58366611053974	2.56939236789123	2.04095229599588
H	8.59743768660885	2.70621248732490	1.64813103594031
H	7.59390166277574	2.60294645802595	3.14182052425951
H	6.93748270711994	3.36517878107150	1.64285981335688
C	6.64790706476600	-1.64587145794885	-1.70979812483770
H	7.14806509722943	-2.18055353040274	-0.89278958277866
H	7.15942961223852	-1.84664287573950	-2.66435532205642
H	5.59216812057380	-1.95115546008760	-1.75856507277939
C	4.36069970680566	2.82163607570336	-1.00288123721798
H	3.98304884558788	3.20305440127265	-0.04608484477271
H	3.72031738042752	3.19099612587963	-1.81948439452224
H	5.40351306776757	3.13688457189061	-1.15355097823860
C	3.45373761080967	-1.73310682887760	2.17123055496050
H	2.36192780953904	-1.64780483174086	2.24825965929386
H	3.86927099875721	-2.02889411844408	3.14686273916225
H	3.71738923850300	-2.46864836350450	1.39713910099187

Table S3: Geometry optimized coordinates of the dimer of [Ni^{II}(bmsab)dme] (**2**)

C	-2.41153260405356	-1.56912438633710	-0.45277335909900
C	-1.44947137420889	-2.57803335981877	-0.41444961860252
C	-0.28065164152776	-2.39264788197286	0.32549551052697
C	-0.04483030505014	-1.19903299304718	1.01184600520192
C	-1.04970891024789	-0.19378520966813	1.00343972252671
C	-2.22368328506621	-0.38901227217491	0.26443698165884
N	-0.79020514712642	0.88505353127155	1.82571049814743
N	1.16292141391144	-1.00084854630877	1.75502459503339
S	-1.04769878505435	2.44826335837773	1.60526645293588
S	2.37830201761216	-0.33859436111325	0.93350750650956
O	2.11366386673913	1.15989552600689	0.91571427855176
O	3.67497654181682	-0.70201795583891	1.50269715629093
O	-0.00646366841998	2.99792892912958	2.54893799159446
O	-2.41916283062264	2.91108623916944	1.77866528206369
C	-0.52859716485310	2.90793749800774	-0.03584833185692
H	0.51159780303574	2.58270199233792	-0.16373722761809
H	-1.19857200146862	2.42493470561289	-0.75914218499921
H	-0.62761580365158	3.99940550081624	-0.09611917716932
C	2.38506647333566	-0.82484593327934	-0.77924251230232
H	3.20525932178801	-0.25082488590967	-1.22912113582328
H	2.59348558647450	-1.89996672262790	-0.83331040087975
H	1.42479309411565	-0.58096974585909	-1.24753716033261
Ni	0.95433872833217	0.99814051272680	2.70467891029761
Ni	1.84530121671680	-1.68941617946164	7.80438021981633
N	2.45756000397915	-1.00783143334707	9.74718737054579
N	0.64040938619024	-2.97095870277441	8.92615520692147
C	0.78577697064341	-2.70476350163611	10.30467257608697
C	1.69730483357278	-1.70268819956313	10.71918843819232
C	1.86703125485077	-1.46322360979426	12.08906510851616
C	0.03483137470484	-3.38636344704467	11.27071816344425
C	0.19972244613345	-3.12079377846247	12.62822741766560
C	1.12427381761392	-2.16093209593032	13.03916220584939
S	1.42127957982514	-4.24974719216434	8.32190471635309
S	1.96089776698822	0.46188576136712	9.33124312193903
O	3.07314202750215	1.35841641543844	9.02914238754538
O	1.01410795318692	0.23251770350216	8.15696830844904
O	0.58903435082267	-5.09486699924007	7.47333450231418
O	2.61759176534448	-3.62878338126440	7.61451731227159
C	0.95171781065534	1.23520246230612	10.57725136401232
H	1.57394494339891	1.45508115549082	11.45231682470127
H	0.60546001460464	2.16619444326993	10.11012890759700
H	0.10897867753288	0.58402704213020	10.83619555969878
C	2.12107867339298	-5.27340850075970	9.60037683991074
H	1.31191520760887	-5.76690299974250	10.15077998426117
H	2.72398381824366	-6.01169166829298	9.05593824923727
H	2.74468343025618	-4.66541922368584	10.26601753769605
H	1.27228532185880	-1.95645893219895	14.10226431362266
H	-0.39559906246174	-3.66479392910269	13.36557894876154
H	-0.69577735120463	-4.12564089497457	10.93208633135440
H	2.61212215575493	-0.72648441941887	12.39980228237365
H	-2.99288959901541	0.38735175615616	0.28247472197809
H	-3.33082323498282	-1.71047919953640	-1.02668576912279
H	-1.61034219712005	-3.51462111404897	-0.95317666891915
H	0.47784731113686	-3.17849866212615	0.37380806298465
O	2.70215015626574	1.28680134159278	3.81170131826375
O	0.09629862683883	0.54333226867521	4.59593545502371
O	0.84476332345982	-1.91086193433305	5.95116270371907
O	3.42863601741664	-0.80189884934440	6.71155096411310

C	-0.75318740425191	-0.59854447769621	4.65499678765783
C	-0.49626580742574	-1.44153904676831	5.88605138268570
H	-1.81157888978446	-0.28717447751395	4.62894730290768
H	-0.56230861349847	-1.17155117284486	3.73801753972748
H	-0.65501445071370	-0.86256298889643	6.80563009165638
H	-1.19450042870373	-2.29752499701648	5.89770412220169
C	3.22313192416625	0.15026994307754	4.50815079297047
C	3.23872860536113	0.42204711478838	6.00127757506873
H	2.54913344790726	-0.69040074586138	4.30644840077944
H	4.20832991405527	-0.11327411723460	4.09456809045406
H	4.01160463006407	1.14584297010914	6.30246275309181
H	2.26825414751498	0.82969216794383	6.30718135495679
C	4.74362379944648	-1.01262333882591	7.21203440272617
H	4.75685648238666	-2.01590498300291	7.65566219947945
H	5.47679760984541	-0.96776290100410	6.39046302360583
H	4.97969611452955	-0.26157215759323	7.98172099930291
C	1.15577844132776	-2.95522422189299	5.02672457536483
H	2.19120521331501	-3.25109519239290	5.22493096657049
H	0.50459645612563	-3.82434681978645	5.20734610423545
H	1.06304623970056	-2.59699138159747	3.98964048834178
C	-0.35826033477558	1.65062473665268	5.36950677525989
H	0.37925057189448	2.45188418609938	5.24536344955538
H	-1.33066451216956	2.00495672102360	4.99204078518407
H	-0.41753289659283	1.37583873491320	6.43303729978493
C	3.69372424973093	2.18449907080729	3.32236058286495
H	3.16658782498299	3.03951060921793	2.88172391194458
H	4.32930443968630	2.53430613549672	4.15115941652469
H	4.30058310834947	1.69032558861675	2.54958405526095

Table S4: Geometry optimized coordinates of a monomer of [Co^{II}(bmsab)dme] (**3**)

C	-2.19151332888963	1.54502478055777	-0.76951699494450
C	-2.11560572225804	0.37404699208314	-1.51783096963480
C	-0.93977282574000	-0.38063199219201	-1.53123491102012
C	0.15770490825229	0.02139757817011	-0.76814502279532
C	0.07890846639089	1.21997257600586	-0.00299520176916
C	-1.09250936193602	1.97800706214016	-0.02382934473963
N	1.25971510286133	1.51872448233941	0.68040979262480
N	1.39666767915459	-0.62101017528714	-0.67081878471816
S	1.56213965382915	2.80367437016868	1.60966594206090
S	1.80716410536431	-2.02817558856260	-1.35624094593096
O	3.22342420087157	-2.19980921215948	-0.96486118702991
O	1.45483470800917	-2.13328186187655	-2.76902635842285
O	3.00159018614659	2.65664061645316	1.92641736728799
O	1.09958872703541	4.07377526953002	1.05516052500207
C	0.68265041633267	2.56081546286745	3.14345421003667
H	1.04689402274802	1.64336671696346	3.62002324188797
H	-0.39255911484424	2.49755067075780	2.93153039759837
H	0.89863697452223	3.43897558012330	3.76578907817116
C	0.88127863532502	-3.30169124951764	-0.50959940066481
H	1.15090429704992	-4.25125408798880	-0.98977610055924
H	-0.19096242991350	-3.10303640585810	-0.63544603478196
H	1.15522119722905	-3.30535926176922	0.55188022778349
Co	2.75892684730556	0.35025842261651	0.29835060317680
H	-1.12726069214234	2.92690413847056	0.51471631582195
H	-3.10416800971954	2.14556372844355	-0.77780699678231
H	-2.96750586719577	0.04927742122371	-2.11980500029516
H	-0.85622358470969	-1.26350759615999	-2.16779140699939
O	4.09159711804263	-0.58894350692586	1.61082823518099
O	4.52620393106247	1.20149619433527	-0.36880127933417
C	5.41053873987273	-0.41591066789432	1.09616956125700
C	5.52532076929153	1.01084158621825	0.62825343080781
H	5.57348633997946	-1.12121839692460	0.26291707731904
H	6.14725478633303	-0.61210486479247	1.89365063095556
C	4.49051277562548	2.52194146765533	-0.91370343632217
H	4.21429889300810	3.24540813741713	-0.13251032862800
H	3.72783917340321	2.51881378782238	-1.70217041602418
H	5.47130190235317	2.76457421286937	-1.35207218480673
C	3.83990095052100	-1.90056487807503	2.10488952951051
H	2.83194119112543	-1.88871851910953	2.53911243475090
H	4.57072656022420	-2.14714232285183	2.89172227669593
H	3.88319074047076	-2.62906013746079	1.28135733642837
H	6.52350912668518	1.18444653683397	0.19153434636185
H	5.35276781092229	1.71623293333955	1.45859974548331

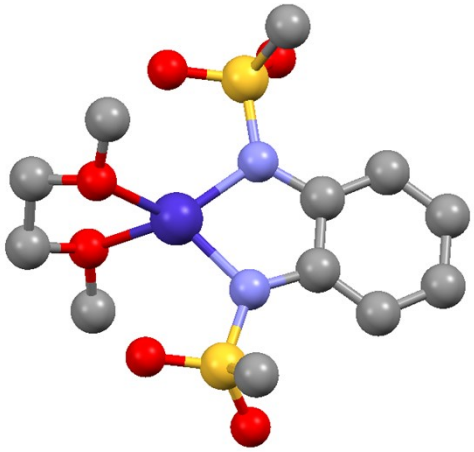

Figure S21. Theoretical structure of the monomeric version of **[Co^{II}(bmsab)dme]** (**3**). The geometry was optimized on the DFT level as described in the methods section. Oxygen is shown in red, nitrogen in light blue, carbon in grey, sulphur in yellow and cobalt in dark blue. Hydrogens are omitted for clarity.

Table S5: Geometry optimized coordinates of a monomer of [Ni^{II}(bmsab)dme] (**2**)

C	-2.12984541227537	1.66147748067818	-0.67324192384354
C	-2.15790885222230	0.49633374681991	-1.43602418164405
C	-1.01764492247316	-0.30314125652167	-1.52732349299228
C	0.13444317847929	0.05631192400950	-0.82963909317531
C	0.17575351352567	1.24783929065300	-0.05266575323563
C	-0.97107447765635	2.04805582256844	0.00381505761442
N	1.41327631363942	1.48341468528358	0.55564568603678
N	1.34450385416381	-0.62517987104299	-0.80524697618916
S	1.67441170264651	2.70274747410769	1.59159840380800
S	1.77084653226392	-2.03428361331264	-1.46410480166600
O	3.18887527202903	-2.13535059983552	-1.02818235314463
O	1.45396489094959	-2.17910758116830	-2.87896393328867
O	3.10685021788850	2.62993332063226	1.92912953558479
O	1.14950829134064	3.98448645770398	1.12081878092020
C	0.78652706132857	2.30253458882889	3.09023670896369
H	1.19907044978299	1.37648031048001	3.50756388044154
H	-0.28077267190638	2.19246320427397	2.85805000712790
H	0.94408105245141	3.14502586826155	3.77625979000271
C	0.87464505108284	-3.31594567505241	-0.60300831680767
H	1.19584112039648	-4.26771705425180	-1.04594781851104
H	-0.20034857924972	-3.16453917236287	-0.76524822057649
H	1.11968595047535	-3.27566641138077	0.46463711958138
Ni	2.79622390320207	0.14516810632813	0.10767654777504
H	-0.94023904362095	2.99432461640257	0.54557772624874
H	-3.01500936414760	2.29971202271324	-0.61687998605814
H	-3.06135560159601	0.21479548842670	-1.98160783907254
H	-1.00509323009623	-1.18996598673576	-2.16499480509851
O	4.03239515396560	-0.50493266785312	1.65803519150110
O	4.53143124380023	1.11920225265342	-0.38701950824789
C	5.39167376947838	-0.26609986268394	1.30153223840188
C	5.45228654068376	1.11142884954304	0.70149666231455
H	5.72105001253480	-1.03156613458706	0.57707104694780

H	6.02731042886321	-0.32004133554983	2.20162384762265
C	4.40598909609990	2.39382915755207	-1.02057322254822
H	4.02139643326295	3.13356633078433	-0.30379669200028
H	3.69715020134237	2.27071884434735	-1.84823773584008
H	5.38639510993647	2.70239690151997	-1.41680570754520
C	3.80209288865301	-1.80983191662681	2.17306303567640
H	2.75169883078704	-1.84881602486925	2.48920649216687
H	4.44889755929292	-1.98632188344348	3.04752513539977
H	3.98354368735200	-2.57009819635445	1.39712568900596
H	6.46967811602823	1.31965774168801	0.32887359096857
H	5.14635472751677	1.87301075737280	1.43540018737453

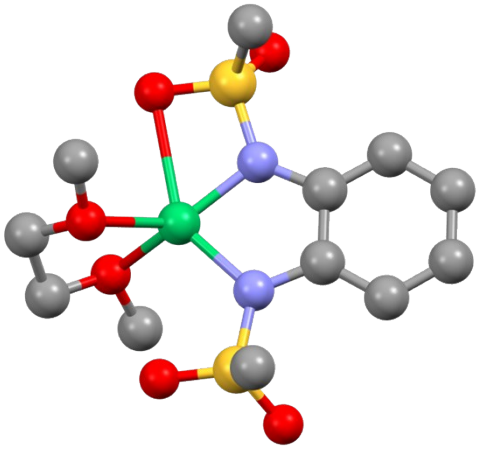

Figure S22. Theoretical structure of the monomeric version of **[Ni^{II}(bmsab)dme]** (**2**). The geometry was optimized on the DFT level as described in the methods section. Oxygen is shown in red, nitrogen in light blue, carbon in grey, sulphur in yellow and nickel in green. Hydrogens are omitted for clarity.

Table S6: Comparison of the relevant bond length of the calculated structure of **3** to the experimental structure of the corresponding homoleptic complex.[1,2]

Bond	**3** Center 1	**3** Center 2	[Co(II)(bmsab)$_2$(K-18-c-6)$_2$ Ligand 1	Co(II)(bmsab)$_2$(K-18-c-6)$_2$ Ligand 2	Co(II)(bmsab)$_2$(HNEt$_3$)$_2$ Ligand 1	Co(II)(bmsab)$_2$(HNEt$_3$)$_2$ Ligand 2
Co-N1	1.967	1.942	2.005	2.026	2.004	1.998
Co-N2	1.946	1.969	2.008	1.995	2.010	2.013
C-N1	1.401	1.396	1.418	1.415	1.414	1.409
C-N2	1.397	1.401	1.411	1.410	1.418	1.415

Table S7: Individual contributions to the *D*-tensor for **3**, Co(II)-center 1. Calculations were carried out on CASSCF/NEVPT2 level, with a def2-TZVPP basis set for the metal center and the first coordination sphere.

Mult	Root	D	E
4	1	-54.207	0.059
4	2	7.849	1.286
4	3	2.964	1.741
4	4	5.887	-3.195
4	5	0.258	0.154
4	6	0.095	0.035
4	7	0.004	0.002
4	8	0.008	0.001
4	9	0.006	-0.002
2	0	-0.134	0.362
2	1	0.551	0.206
2	2	-0.025	0.019
2	3	-0.291	-0.232
2	4	0.151	-0.017
2	5	0.369	0.005
2	6	5.836	-0.013
2	7	-3.082	-1.893
2	8	-1.521	1.043

Table S8: Individual contributions to the *D*-tensor for **3**, Co(II)-center 2. Calculations were carried out in accordance with Co(II)-center 1 on a CASSCF/NEVPT2 level. Again, a def2-TZVPP basis set for the metal center and the first coordination sphere was used.

Mult	Root	D	E
4	1	-50.614	0.071
4	2	7.768	-5.177
4	3	4.063	4.217
4	4	5.858	-0.021
4	5	0.040	-0.000
4	6	0.165	0.112
4	7	0.002	-0.002
4	8	0.011	0.004
4	9	0.009	-0.002
2	0	1.101	-0.012
2	1	-0.706	0.210
2	2	-0.006	0.009
2	3	-0.107	-0.046
2	4	-0.050	-0.015
2	5	0.454	-0.002
2	6	5.944	-0.012
2	7	-3.352	-0.288
2	8	-1.559	0.014
2	9	-0.008	-0.009

Table S9: Individual contributions to the *D*-tensor for **2**, Ni(II)-center 1. As for the previous two tables, calculations were carried out on CASSCF/NEVPT2 level with a def2-TZVPP basis set for the metal center and the first coordination sphere.

Mult	Root	D	E
3	1	-58.659	-0.660
3	2	21.817	-21.600
3	3	19.870	18.539
3	4	0.779	-0.077
3	5	0.710	-0.521
3	6	0.321	0.346
3	7	0.044	0.039
3	8	0.042	-0.012
3	9	-0.003	0.001
1	0	0.082	0.004
1	1	0.006	-0.000
1	2	16.237	0.020
1	3	-6.883	6.903
1	4	-6.695	-6.650
1	5	-0.424	0.204
1	6	-0.012	0.013
1	7	-0.178	0.101
1	8	-0.019	-0.018
1	9	-0.029	0.002

Table S10: Individual contributions to the *D*-tensor for **2**, Ni(II)-center 2. As for center 1, calculations were carried out again on CASSCF/NEVPT2 level with a def2-TZVPP basis set for the metal center and the first coordination sphere.

Mult	Root	D	E
3	1	-38.184	-4.178
3	2	14.264	-8.020
3	3	12.677	11.591
3	4	0.110	-0.166
3	5	-0.052	-0.009
3	6	0.006	-0.001
3	7	0.000	0.000
3	8	0.001	-0.002
3	9	-0.003	-0.000
1	0	0.005	-0.006
1	1	0.004	-0.001
1	2	15.691	0.033
1	3	-7.012	7.063
1	4	-7.122	-7.125
1	5	-0.005	-0.001
1	6	-0.227	0.180
1	7	-0.092	0.064
1	8	-0.125	-0.115
1	9	-0.139	-0.044

Sample Inputs for ORCA Calculations

Sample input for a CASSCF calculation, used for the calculation of the spin Hamiltonian parameters for **2** and **3** as well as for the monomeric structures.

```
! def2-TZVP autoaux PATOM Normalprint RI-NEVPT2
! tightscf slowconv
! MORead
%moinp "desiredfilefrompreviouscalc.gbw"
%pal
 nprocs 20
end
%scf
MaxIter 500
end
%maxcore 15000
%casscf
nel 7 or 8
norb 5
mult 4,2 or 3,1
nroots 10,10 or 10,9
Trafostep ri
rel
dosoc true
gtensor true
dtensor true
end
end

%coords
CTyp xyz
Charge 0
Mult 4 or 3
Units Angs
Coords
      Coordinates of each molecule. One center is exchanged for Zn instead
      of Co or Ni. Here the
          newgto "def2-TZVPP" end
          newauxgto "def2/J" end
      keywords were used for the atoms, where different basis sets were
      needed
end
end
```

Sample input for the broken symmetry DFT calculations used in this work

```
! PBE0 def2-SVP def2/J
! RIJCOSX

%pal
 nprocs 10
end
%scf
Flipspin 0
FinalMs 0.0
MaxIter 1000
end

%maxcore 15000

%coords
CTyp xyz
Charge 0
Mult 7 or 5
Units Angs
Coords
      Coordinates of each molecule. Metalcenters have to be in first
      positions of the coordinates. Here also the
          newgto "def2-TZVPP" end
          newauxgto "def2/J" end
      keywords were used for the atoms, where different basis sets were
      needed
end
end
```

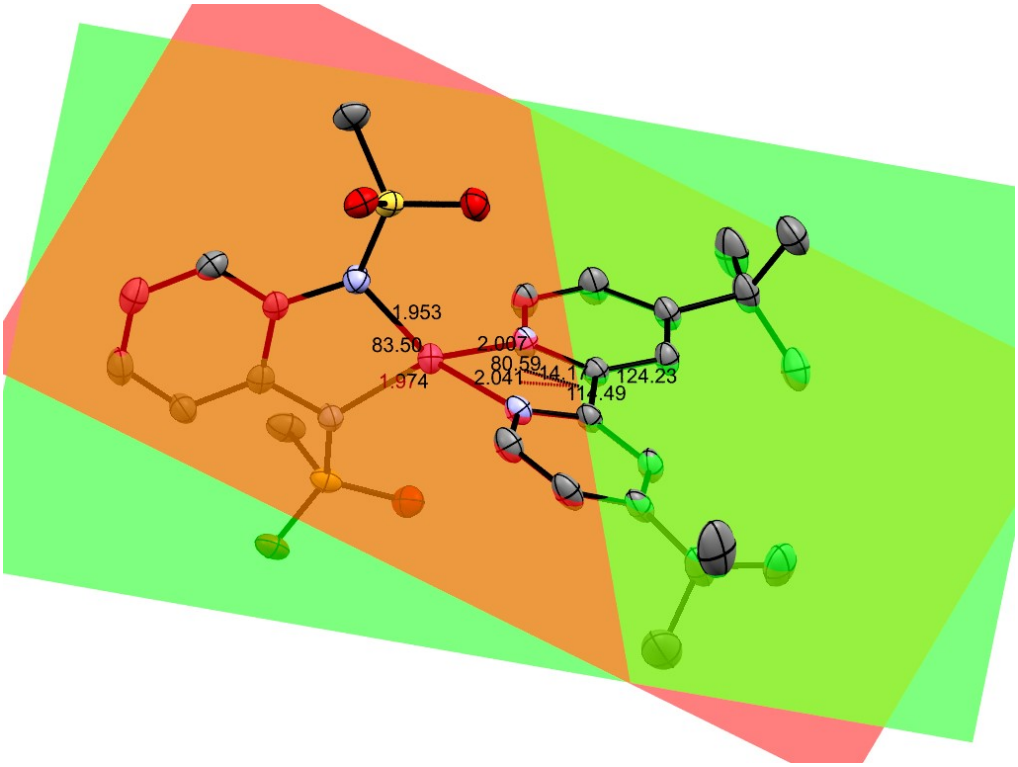

Figure S23. Bond distances and angles in the crystal structure of Zn^{II}(bmsab)DTBBPy.

Analytical data for heteroleptic complex [Zn(bmsab)DTBBPy] (4)

NMR Spectra

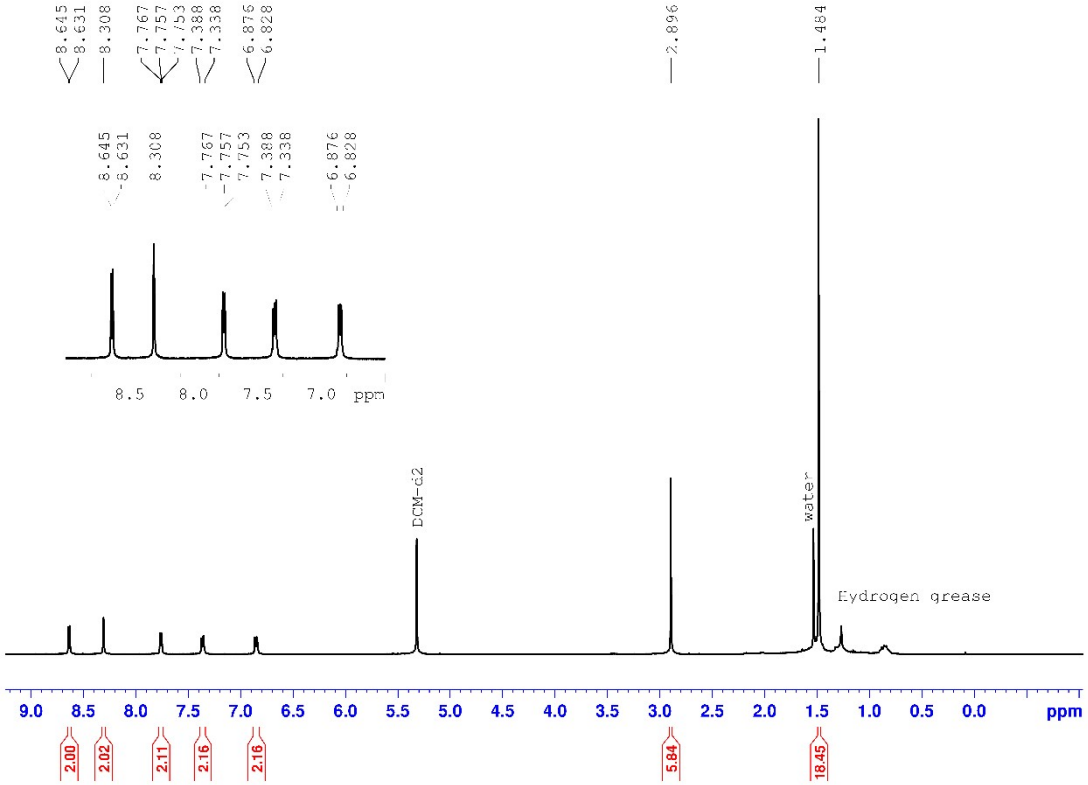

Figure S24. [1]H-NMR-Spectrum (400 MHz, DCM-*d2*, 25 °C) of the heteroleptic Zn(II) complex **Zn(bmsab)DTBBPy 4** dissolved in deutero-dichloromethane.

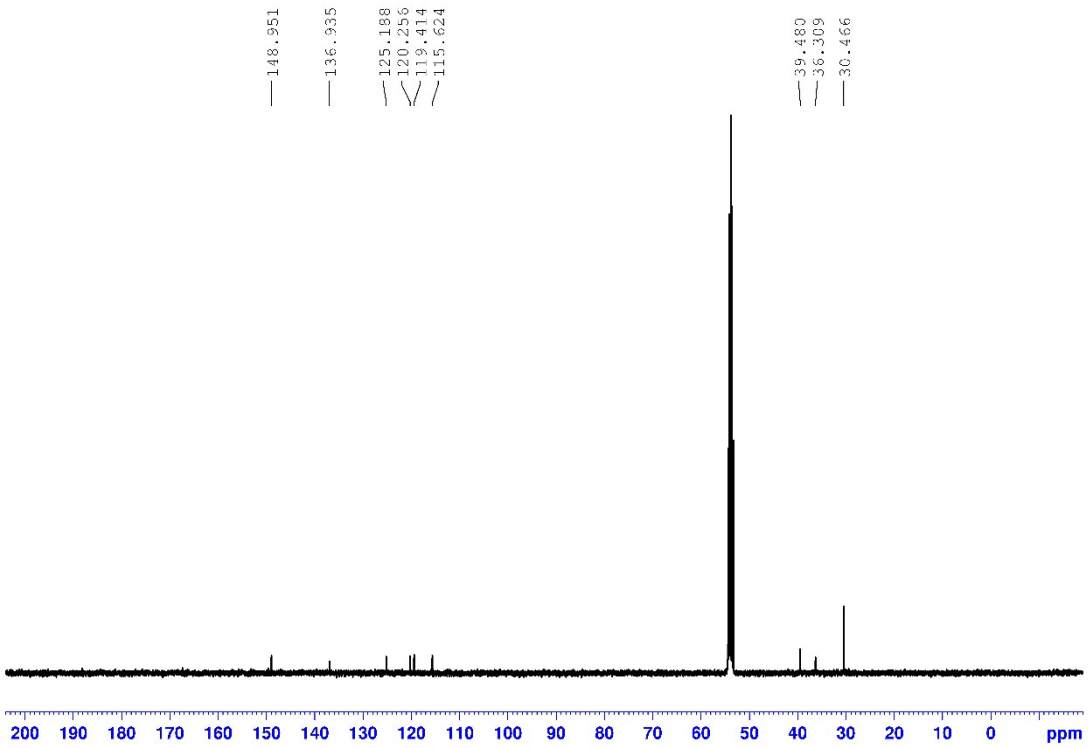

Figure S25. ^{13}C-NMR-Spectrum (100 MHz, DCM-*d2*, 25 °C) of the heteroleptic Zn(II) complex **Zn(bmsab)DTBBPy 4** dissolved in deutero-dichloromethane.

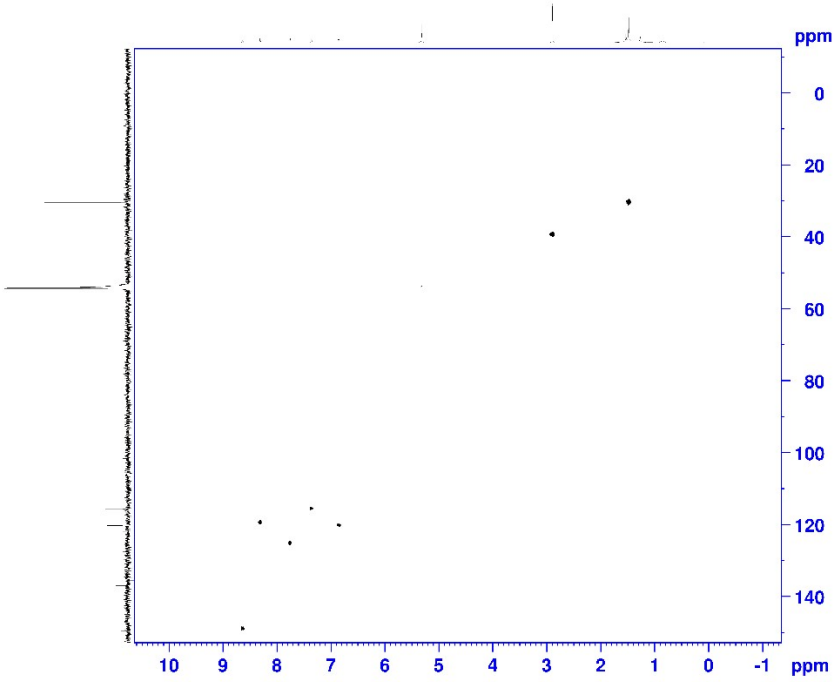

Figure S26. ^{1}H-^{13}C-HSQC-NMR-Spectrum of the heteroleptic Zn(II) complex **Zn(bmsab)DTBBPy 4** dissolved in deutero-dichloromethane.

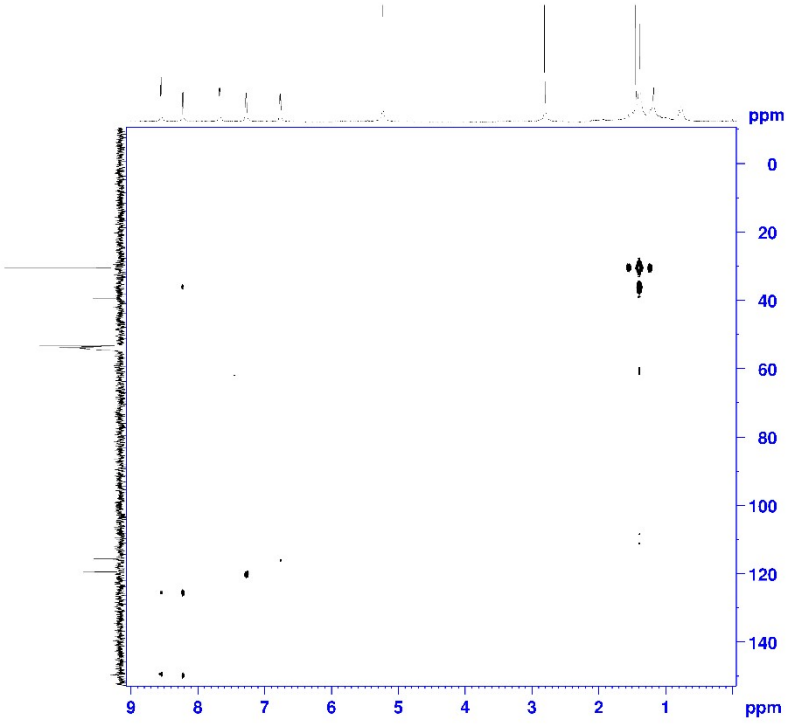

Figure S27. ^{1}H-^{13}C-HMBC-NMR-Spectrum of the heteroleptic Zn(II) complex **Zn(bmsab)DTBBPy 4** dissolved in deutero-dichloromethane.

Mass Spectrometry

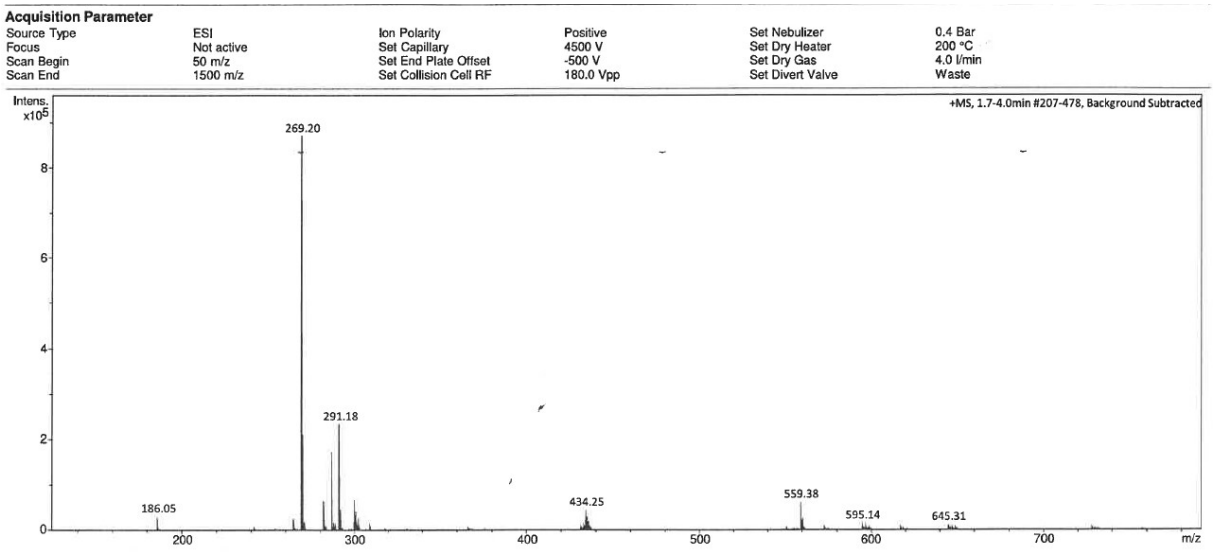

Figure S28. ESI(+)-Mass-spectrum of **Zn(bmsab)DTBBPy 4** measured on a Bruker micrOTOF-Q

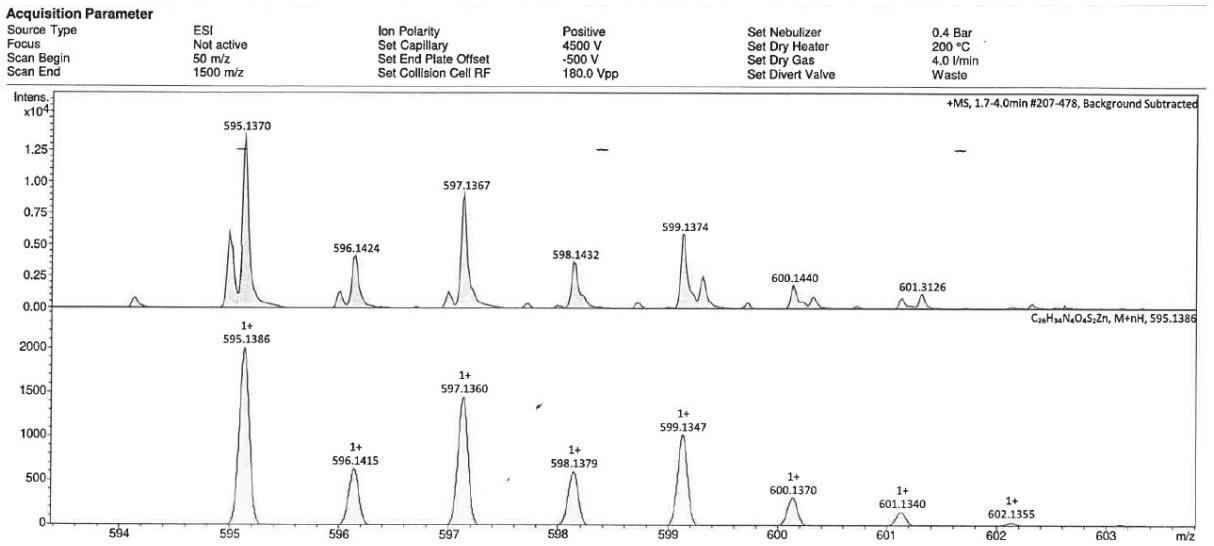

Figure S29. ESI(+)-mass-spectrum of the molecular ion of **Zn(bmsab)DTBBPy 4** (top) with calculated isotope pattern (bottom).

X-ray Diffraction Data

Table S11 Crystallographic Data of Zn^{II}(bmsab)DTBBPy.

Chemical formula	$C_{26}H_{34}N_4O_4S_2Zn$
Formula Mass	596.06
Crystal System	Monoclinic
Space Group	*P*2(1)/*c*
a / Å	6.8118(4)
b / Å	17.4551(9)
c / Å	28.7818(17)
α / °	90
β / °	95.371(2)
γ / °	90
Unit cell Volume ($Å^3$)	3407.1(3)
Z	4
Density ($g \cdot cm^{-3}$)	1.162
Radiation type	MoK_α
Absorption coefficient μ / mm^{-1}	0.875
Crystal Size / mm	0.653 x 0.121 x 0.073
F(000)	1248
Measured reflections	26211
Unique reflections	6939
R_{int}	0.0404
S	1.025
Final R indices [I>2σ]	R1 = 0.0371, wR2 = 0.0814
Final R indices (all data)	R1 = 0.0565, wR2 = 0.0857
Largest diff. peak and hole / ($eÅ^{-3}$)	0.296 & -0.309

References

(1) Bamberger, H.; Albold, U.; Dubnická Midlíková, J.; Su, C.-Y.; Deibel, N.; Hunger, D.; Hallmen, P. P.; Neugebauer, P.; Beerhues, J.; Demeshko, S. *et al.* Iron(II), Cobalt(II), and Nickel(II) Complexes of Bis(sulfonamido)benzenes: Redox Properties, Large Zero-Field Splittings, and Single-Ion Magnets. *Inorg. Chem.* **2021**, *60*, 2953–2963.

(2) Rechkemmer, Y.; Breitgoff, F. D.; van der Meer, M.; Atanasov, M.; Hakl, M.; Orlita, M.; Neugebauer, P.; Neese, F.; Sarkar, B.; van Slageren, J. A four-coordinate cobalt(II) single-ion magnet with coercivity and a very high energy barrier. *Nat. Commun.* **2016**, *7*, 268.

(3) Bain, G. A.; Berry, J. F. Diamagnetic Corrections and Pascal's Constants. *J. Chem. Educ.* **2008**, *85*, 532.