Electronic Supplementary Material (ESI) for Dalton Transactions
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Supplementary material

Probing differences in binding of methylbenzylamine enantiomers to chiral cobalt(II) salen complexes

Sepideh Zamani,[a] Emma Carter,[b] Damien M. Murphy[b] and Sabine Van Doorslaer*[a]

1) Simulation of EPR spectra of the mono- and bis-MBA ligated SS-R cases.

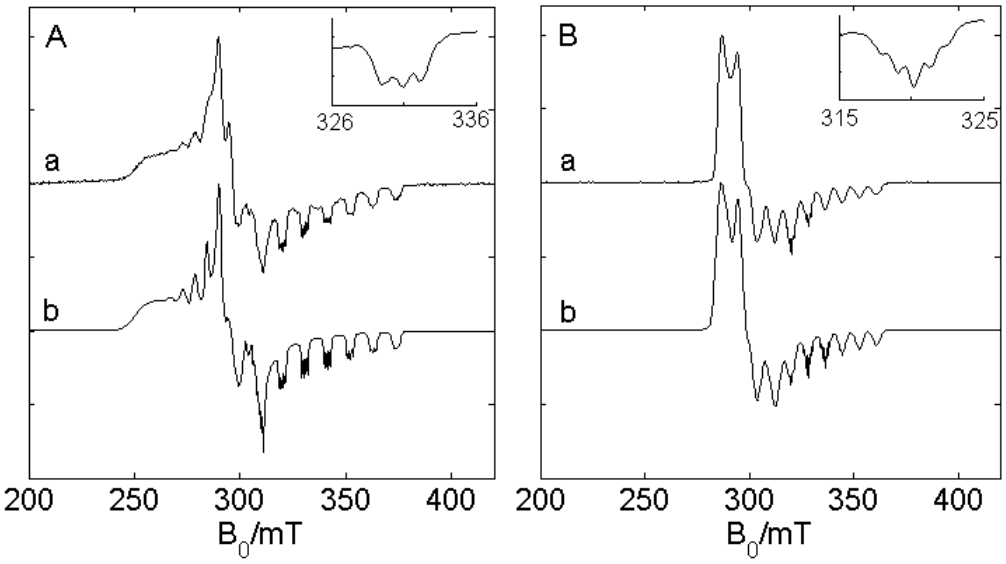

Figure S1. *(**A**) Experimental (a) and simulated (b) X-band CW-EPR spectrum of a frozen toluene solution of S,S-[Co(**1**)]:R-MBA (1:1.5). Inset: enlargement of high-field part showing the splitting into three lines due to the ^{14}N hyperfine interaction. (**B**) (a) Difference EPR spectrum of the spectrum of S,S-[Co(**1**)]:R-MBA in a 1:30 and 1:1.5 ratio and (b) its simulation. Inset: enlargement of high-field part showing the splitting into five lines due to the hyperfine interaction with two ^{14}N nuclei. The simulations were performed using the parameters given in Table 1 (main text). The spectra were recorded at 50 K.*

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2) Simulation of the HYSCORE spectra

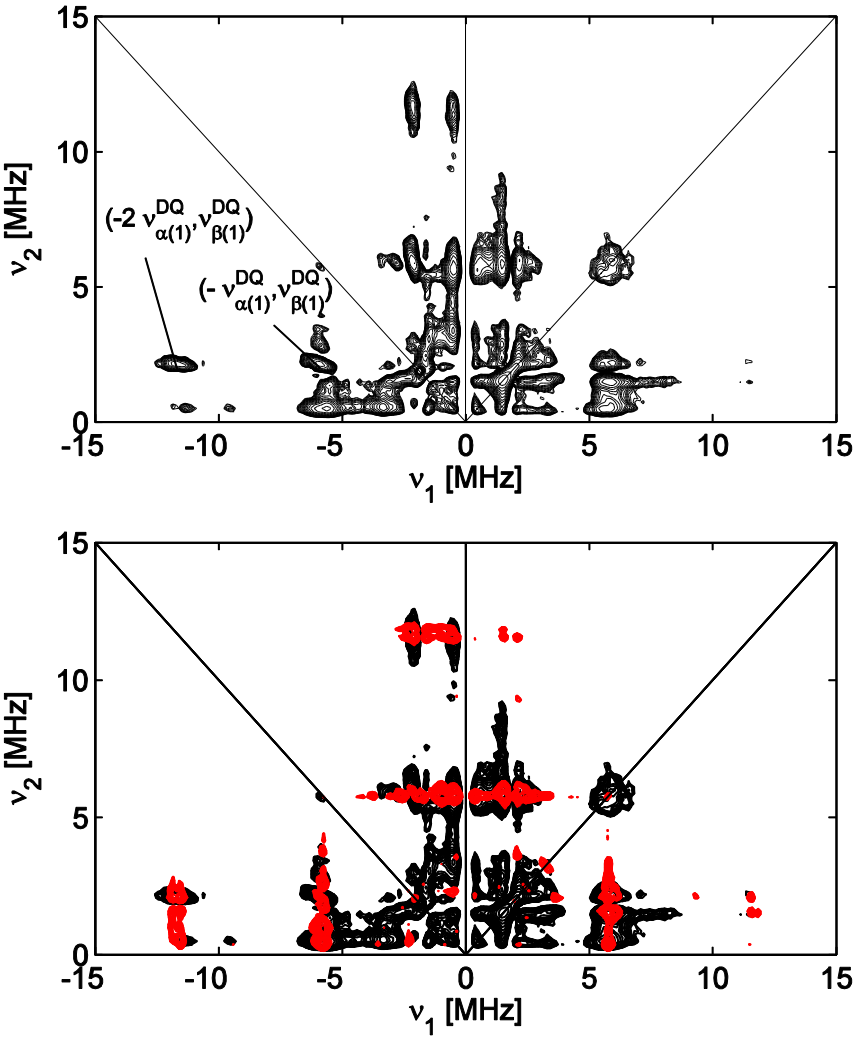

Figure S2. *The experimental X-band HYSCORE spectrum of [S,S-[Co(**1**)](S-MBA) taken at an observer position corresponding to* $g \approx g_z$, $m_I = -5/2$ (τ = 176 ns) *is depicted (top). Contributions from two equivalent* ^{14}N(**1**) *nuclei are observed. The simulation (red) is represented in the bottom spectrum in comparison with the experiment (black). The simulation parameters are shown in Table 2 (main text). The spectrum was taken at 6 K.*

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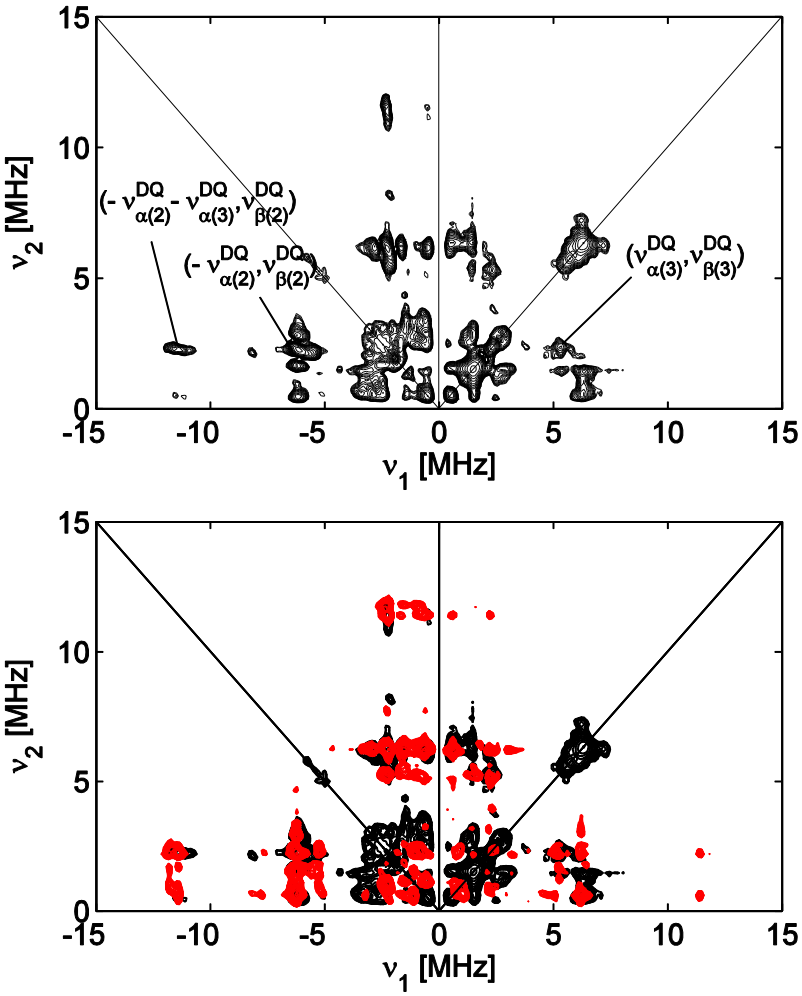

Figure S3. *The experimental X-band HYSCORE spectrum of S,S-[Co(**1**)](R-MBA) taken at an observer position corresponding to* $g \approx g_z$, m_I= -5/2 (τ= 176 ns) *is depicted (top). Contributions from two inequivalent* ^{14}*N(**1**) nuclei are observed. The simulation (red) is represented in the bottom spectrum in comparison with the experiment (black). The simulation parameters are shown in Table 2 (main text). The spectrum was taken at 6 K.*

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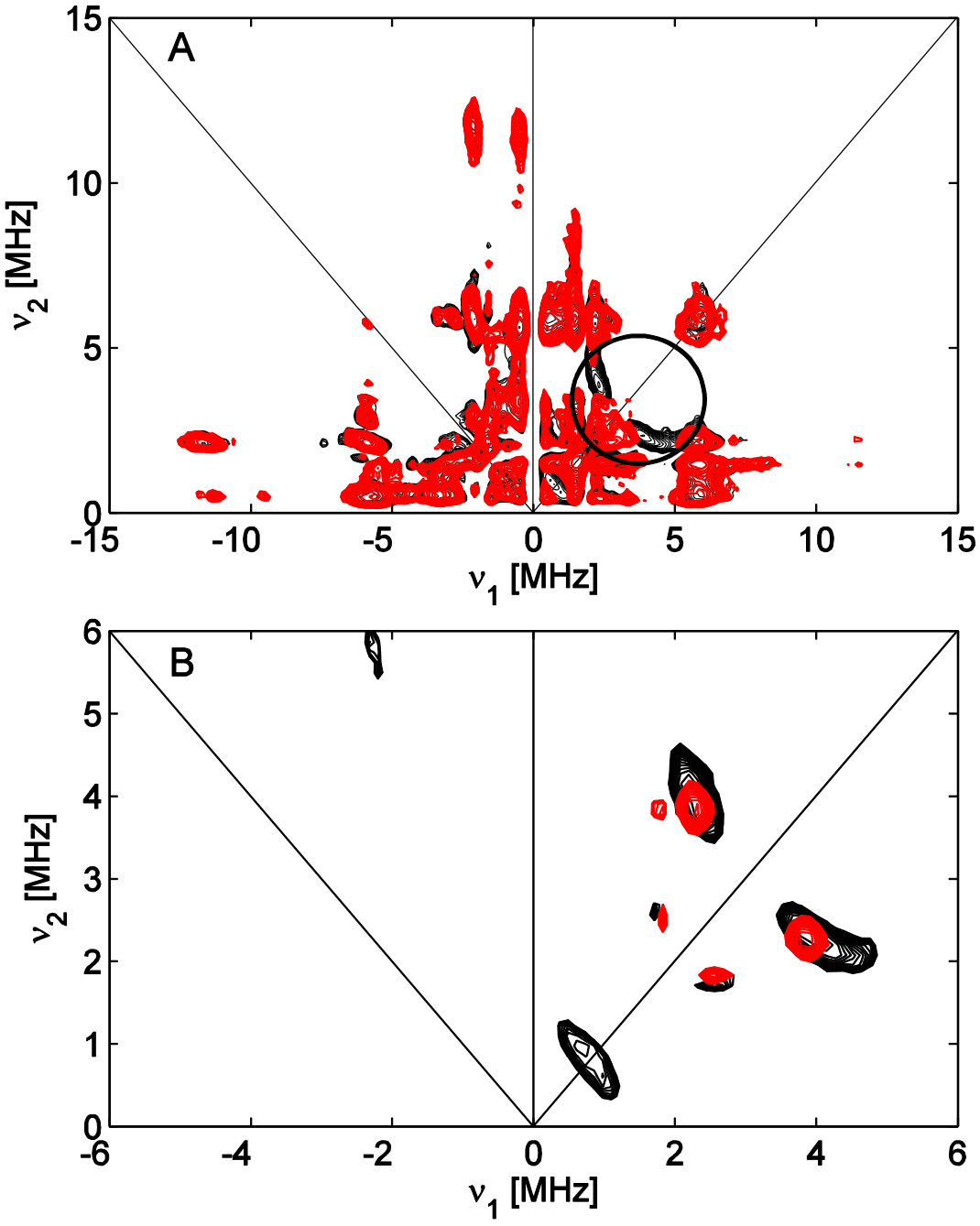

Figure S4. *(**A**) Comparison between the experimental X-band HYSCORE spectrum of S,S-[Co(**1**)] in neat S-MBA (black) and S,S-[Co(**1**)]:S-MBA (1:1.5) mixture (red). The spectra are taken at an observer position corresponding to $g \approx g_z$, m_I= -5/2 (τ = 176 ns). (**B**) X-band HYSCORE spectrum of S,S-[Co(**1**)](S-MBA)$_2$ (black) obtained by subtraction of the spectra in Figure S4**A**. The corresponding simulation is marked in red. The ^{14}N spin-Hamiltonian parameters used for this simulation are presented in Table 2 (main text).*

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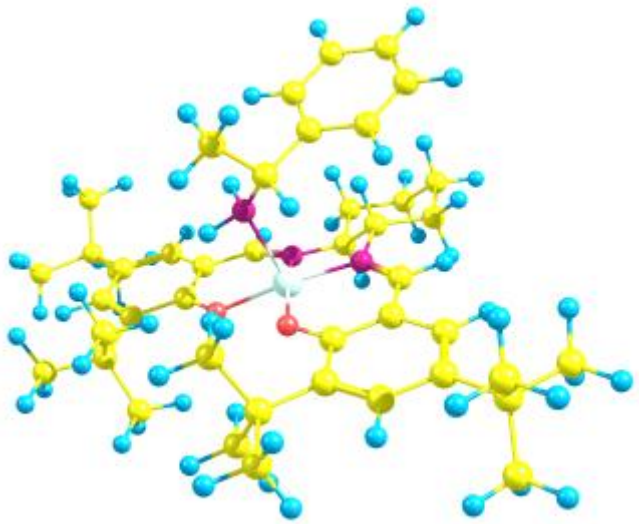
3) DFT computations

A. Coordinates of optimized structures

HETEROCHIRAL PAIRS

S,S-[Co(**1**)](*R*-MBA)



Coordinates (in Å)

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C	-0.363648	1.312256	5.909141
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Co	-0.353249	-0.521493	0.585129
N	-1.659413	0.821463	0.711948
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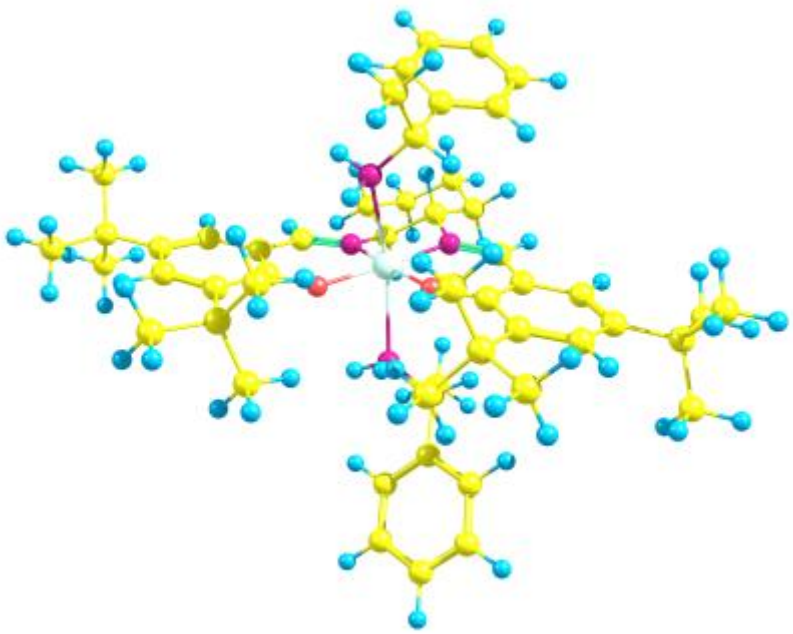
S,S-[Co(**1**)](*R*-MBA)$_2$



Coordinates (in Å)

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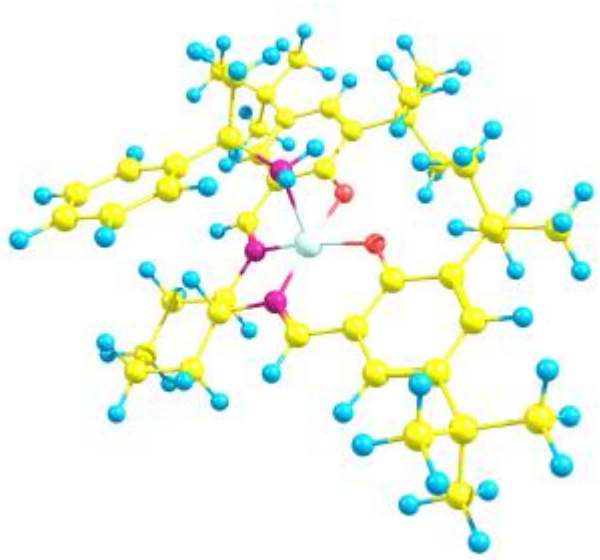
HOMOCHIRAL PAIR

R,R-[Co(**1**)](*R*-MBA)



Coordinates (in Å)

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C	4.319356	-2.761182	-0.819357
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N	1.279024	1.370361	-1.138518
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C	-5.707841	0.015669	0.018026
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C	2.097055	-4.012180	-0.544308
C	1.166262	-4.188803	-1.772381
C	6.696801	-1.733089	-1.132561
C	7.200710	-3.181814	-0.962315
N	0.347859	0.126011	1.666985
C	1.485965	0.731566	2.400261
C	1.794418	-0.018627	3.712960
C	1.263865	2.216603	2.662176
C	2.307619	3.137536	2.430477
C	2.145288	4.503905	2.718493
C	0.928070	4.974373	3.241712
C	-0.119252	4.066842	3.481116
C	0.050717	2.700386	3.199336
C	1.251258	-3.939015	0.752553
C	2.990062	-5.268477	-0.446946
C	-4.610359	-4.087428	0.493570
C	-2.533213	-3.238533	1.588569
C	-7.636082	1.019030	-1.273515
C	-7.486714	1.344632	1.228692
C	7.342402	-0.863204	-0.023255
C	7.162332	-1.218968	-2.519177
H	3.239568	1.796383	-1.684964
H	0.082763	3.236745	0.373508
H	-2.967005	2.847074	-0.478601
H	0.338253	2.545210	-2.590356
H	5.092019	0.512834	-1.370819
H	-5.065317	2.069986	-0.280771
H	-5.934738	-2.113245	0.316764
H	4.799196	-3.743107	-0.730126
H	2.292312	3.985075	-0.688712
H	2.603475	3.597452	-2.406781
H	-1.582868	4.153349	-2.059330
H	-1.887765	4.600942	-0.356198
H	1.826917	5.974268	-2.137161

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H	0.723385	5.018776	-3.154408
H	-0.601736	6.399530	-1.554558
H	0.304203	5.731362	-0.175280
H	-0.535300	0.273171	2.176923
H	0.476293	-0.896275	1.631048
H	2.367804	0.636523	1.732266
H	2.006735	-1.089504	3.512349
H	2.680781	0.415310	4.218442
H	0.936785	0.041571	4.415303
H	-0.782867	2.009351	3.406257
H	3.262733	2.776431	2.015896
H	-1.075509	4.423530	3.894693
H	0.796401	6.044372	3.465625
H	2.973467	5.204791	2.529652
H	6.863100	-0.164532	-2.688400
H	8.268596	-1.271688	-2.605892
H	6.724787	-1.829303	-3.336178
H	6.924416	-3.603993	0.025720
H	6.800848	-3.855557	-1.747725
H	8.307507	-3.205441	-1.036378
H	7.037470	-1.214137	0.984499
H	8.450775	-0.910651	-0.082077
H	7.046697	0.201961	-0.113405
H	3.603577	-5.421661	-1.358711
H	3.673499	-5.231996	0.426860
H	2.347317	-6.164965	-0.327625
H	0.497025	-3.315829	-1.885615
H	1.762671	-4.302329	-2.701818
H	0.538932	-5.097899	-1.655763
H	0.530696	-3.102781	0.698829
H	0.679743	-4.880739	0.893473
H	1.903641	-3.801883	1.640837
H	-2.176998	-4.281143	1.728284
H	-1.650641	-2.577401	1.510802
H	-3.113878	-2.951680	2.490434
H	-2.287717	-4.661296	-0.791421
H	-3.240805	-3.558107	-1.838272
H	-1.714044	-2.980578	-1.076252
H	-5.217630	-3.842024	1.389448
H	-5.282337	-4.087305	-0.389614
H	-4.234603	-5.123345	0.623424
H	-6.911215	2.285551	1.112300
H	-8.563825	1.613141	1.272458
H	-7.205569	0.895257	2.203711
H	-7.967334	-1.633365	-0.538103
H	-7.863176	-1.400957	1.239228
H	-9.162149	-0.602551	0.304114
H	-8.714884	1.283867	-1.257934
H	-7.065050	1.949441	-1.469191
H	-7.463974	0.331716	-2.127597

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B. Spin density distribution

In the picture below, the spin density distribution is plotted for the heterochiral pair *S*,*S*-[Co(1)](*R*-MBA). We observe a positive spin density on the cobalt and MBA nitrogen, whereas negative spin density is found for the nitrogens of ligand (**1**). Furthermore, it is clear that the unpaired electron resides predominantly in a d_{z2} orbital of the cobalt atom, agreeing with the earlier assignment of the ground state of the complex.

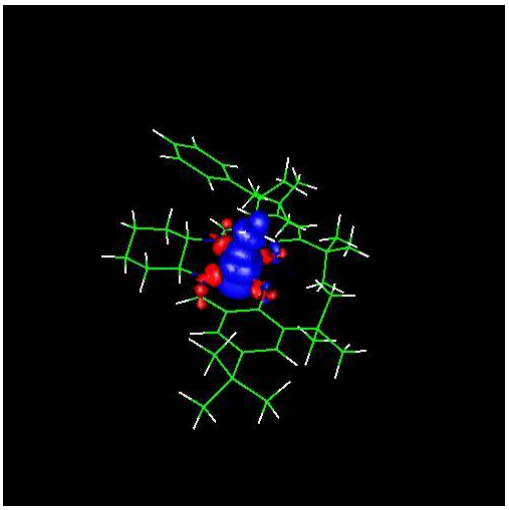

Figure S5. Spin density distribution computed for heterochiral pair *S*,*S*-[Co(1)](*R*-MBA). Blue is positive spin density, red is negative spin density. The contour levels are put at 0.001 and -0.001 respectively.