Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material for: *Ab initio* paramagnetic NMR shifts via point-dipole approximation in a large magnetic-anisotropy Co(II) complex

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Table S1 Tensorial ranks of the hyperfine shielding terms in paramagnetic substances in higher than doublet multiplicity spin states according to Ref. [S1]

			Contributions to $S > 1$[a]		
Term name	Term in $\sigma_{\varepsilon\tau}$	Number	rank-0	rank-1	rank-2
σ_{orb}	σ_{orb}	0	x	x	x
σ_{con}	$g_e A_{\mathrm{con}} \langle S_\varepsilon S_\tau \rangle$	1	x	-	x
σ_{dip}	$g_e \sum_b A^{\mathrm{dip}}_{b\tau} \langle S_\varepsilon S_b \rangle$	2	x	x	x
$\sigma_{\mathrm{con,2}}$	$g_e A_{\mathrm{PC}} \langle S_\varepsilon S_\tau \rangle$	3	x	-	x
$\sigma_{\mathrm{dip,2}}$	$g_e \sum_b A^{\mathrm{dip,2}}_{b\tau} \langle S_\varepsilon S_b \rangle$	4	x	x	x
σ_{as}	$g_e \sum_b A^{\mathrm{as}}_{b\tau} \langle S_\varepsilon S_b \rangle$	5	-	x	x
$\sigma_{\mathrm{con,3}}$	$\Delta g_{\mathrm{iso}} A_{\mathrm{con}} \langle S_\varepsilon S_\tau \rangle$	6	x	-	x
$\sigma_{\mathrm{dip,3}}$	$\Delta g_{\mathrm{iso}} \sum_b A^{\mathrm{dip}}_{b\tau} \langle S_\varepsilon S_b \rangle$	7	x	x	x
$\sigma_{\mathrm{c,aniso}}$	$A_{\mathrm{con}} \sum_a \Delta\tilde{g}_{\varepsilon a} \langle S_a S_\tau \rangle$	8	x	x	x
σ_{pc}	$\sum_{ab} \Delta\tilde{g}_{\varepsilon a} A^{\mathrm{dip}}_{b\tau} \langle S_a S_b \rangle$	9	x	x	x

[a] Rank-0, 2, and 1 contributions correspond to the isotropic shielding constant and anisotropic symmetric as well as antisymmetric terms, respectively.

Table S2 Breakdown of paramagnetic shielding (ppm) obtained in the full quantum-chemical approach according to Table S1 the Co(II) clathrochelate system corresponding to the static PBE/def2-SVP optimised structure of Figure 1 in the main text. This structure has been used for the calculation of the hyperfine coupling tensors. For the ZFS- and g-tensors, the NEVPT2 results of the PBE0/def2-TZVP, ECP structure of the cage have been used.

Atom	Distance to Co (Å)	1	2	3	4	6	7	8	9	Full QC
Cage N	2.05	-24374.16	14.15	-62.96	-16.40	-3923.09	2.28	-1346.31	15.99	-29690.50
Cage C	2.87	-690.35	16.94	3.56	0.93	-111.11	2.73	-38.13	19.01	-796.44
Cage B	3.09	84.72	-101.23	-8.16	-5.89	13.64	-16.29	4.68	-113.85	-142.38
C 1	4.70	60.49	-31.43	-3.31	-1.88	9.74	-5.06	3.34	-35.35	-3.47
C 2	5.49	-6.54	-18.08	-1.66	-1.05	-1.05	-2.91	-0.36	-20.34	-51.98
C 3	6.99	2.61	-9.33	-0.85	-0.53	0.42	-1.50	0.14	-10.49	-19.52
C 4	7.96	0.67	-5.42	-0.48	-0.31	0.11	-0.87	0.04	-6.10	-12.37
C 5	9.42	0.19	-3.49	-0.31	-0.20	0.03	-0.56	0.01	-3.92	-8.25
C 6	10.48	0.03	-2.19	-0.19	-0.12	0.01	-0.35	0.00	-2.47	-5.28
C 7	11.90	0.03	-1.61	-0.15	-0.09	0.01	-0.26	0.00	-1.81	-3.88
C 8	13.02	0.02	-1.08	-0.10	-0.06	0.00	-0.17	0.00	-1.22	-2.61
C 9	14.42	0.02	-0.85	-0.09	-0.05	0.00	-0.14	0.00	-0.96	-2.06
C 10	15.56	0.00	-0.60	-0.05	-0.03	0.00	-0.10	0.00	-0.68	-1.46
C 11	16.95	0.00	-0.51	-0.02	-0.01	0.00	-0.08	0.00	-0.57	-1.20
C 12	18.12	0.00	-0.37	-0.02	-0.01	0.00	-0.06	0.00	-0.42	-0.88
C 13	19.49	0.00	-0.32	0.00	-0.01	0.00	-0.05	0.00	-0.36	-0.74
C 14	20.68	0.00	-0.25	-0.02	-0.01	0.00	-0.04	0.00	-0.28	-0.58
C 15	22.04	0.02	-0.21	-0.02	-0.01	0.00	-0.03	0.00	-0.24	-0.49
C 16	23.23	0.02	-0.17	-0.02	-0.01	0.00	-0.03	0.00	-0.19	-0.39
H 1	5.16	2.95	-23.40	-2.21	-1.33	0.47	-3.77	0.16	-26.32	-53.44
H 2	5.39	-2.09	-16.42	-1.49	-0.92	-0.34	-2.64	-0.12	-18.47	-42.49
H 3	7.32	-0.59	-8.37	-0.76	-0.47	-0.10	-1.35	-0.03	-9.41	-21.07
H 4	7.89	0.02	-4.80	-0.42	-0.27	0.00	-0.77	0.00	-5.40	-11.65
H 5	9.67	-0.01	-3.40	-0.29	-0.19	0.00	-0.55	0.00	-3.82	-8.26
H 6	10.42	0.00	-1.97	-0.17	-0.11	0.00	-0.32	0.00	-2.21	-4.77
H 7	12.10	0.00	-1.62	-0.14	-0.09	0.00	-0.26	0.00	-1.82	-3.94
H 8	12.97	0.00	-0.98	-0.09	-0.05	0.00	-0.16	0.00	-1.10	-2.39
H 9	14.58	0.00	-0.87	-0.08	-0.05	0.00	-0.14	0.00	-0.98	-2.13
H 10	15.53	0.00	-0.56	-0.05	-0.03	0.00	-0.09	0.00	-0.63	-1.35
H 11	17.09	0.00	-0.52	-0.05	-0.03	0.00	-0.08	0.00	-0.58	-1.27
H 12	18.09	0.00	-0.35	-0.01	-0.01	0.00	-0.06	0.00	-0.39	-0.81
H 13	19.61	0.00	-0.33	-0.01	-0.01	0.00	-0.05	0.00	-0.37	-0.77
H 14	20.65	0.00	-0.23	0.00	-0.01	0.00	-0.04	0.00	-0.26	-0.54
H 15	22.14	0.00	-0.22	0.00	-0.01	0.00	-0.04	0.00	-0.25	-0.52
H 16	23.57	0.00	-0.16	0.00	0.00	0.00	-0.03	0.00	-0.18	-0.37

Anisotropy parameters of a 3×3 second-rank tensor

As the PDA is made for the second-rank part of the HFC tensor, the rank-zero part is removed to obtain a traceless tensor. The eigenvalues of the traceless tensor are sorted according to their absolute values as:

$$|A_{11}| \leq |A_{22}| \leq |A_{33}|. \tag{S1}$$

In this way, the sorting of the eigenvalues is unique and natural. The axiality and rhombicity are then obtained according to common formulae:

$$\Delta A_{\mathrm{ax}} = A_{33} - (A_{11} + A_{22})/2 \tag{S2}$$

$$\Delta A_{\mathrm{rh}} = A_{11} - A_{22}. \tag{S3}$$

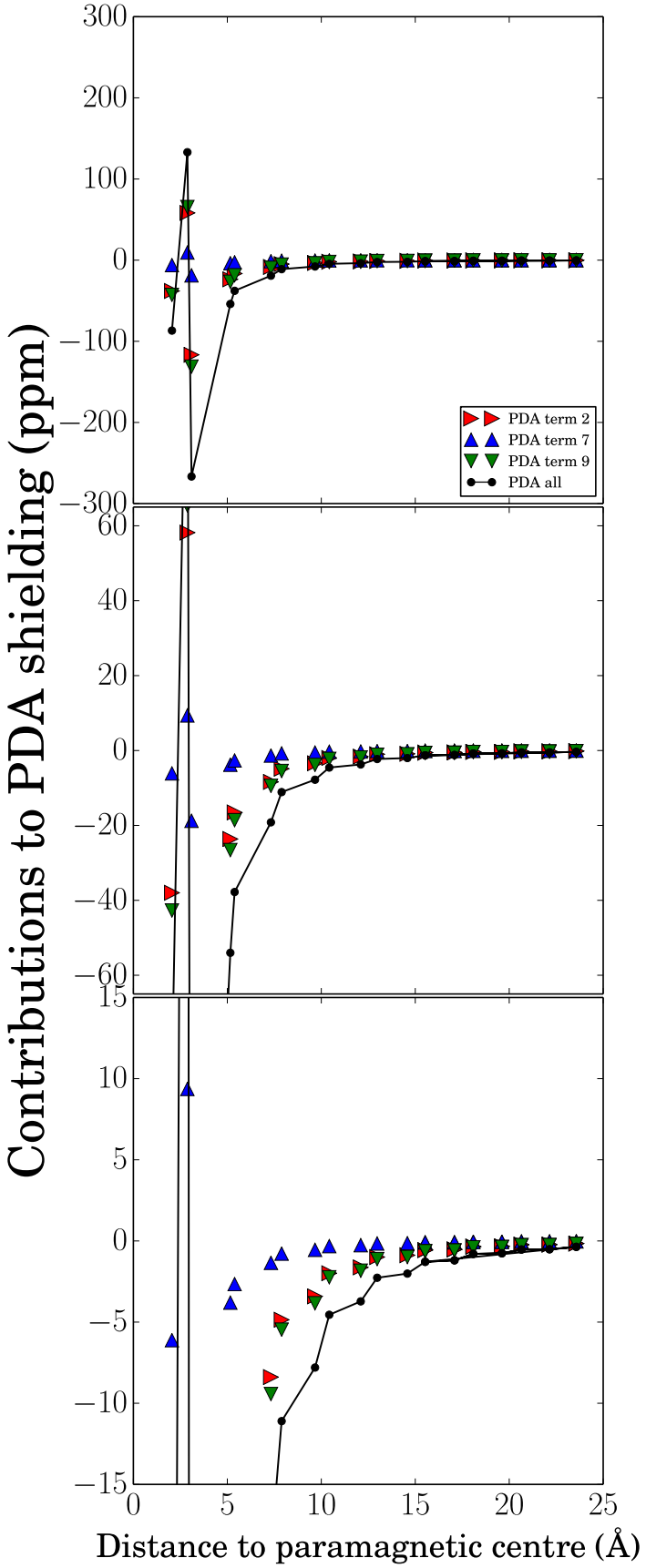

Figure S1 Calculated individual physical contributions at $T = 300$ K to the point-dipole approximation (PDA) to the shielding constant as a function of the distance from the paramagnetic centre. ^{13}C, ^{11}B nuclei of the cage and and only the ^{1}H nuclei of the tail are included to avoid unnecessary clutter of the plot, since there is only little difference between the nuclei in the PDA for H and C that are close to each other in space. The break-down is made according to the terms listed in Table S1. The different panels (top, middle, down) represent the same data in increasing magnification of the vertical axis.

References

[S1] T. O. Pennanen and J. Vaara, *Phys. Rev. Lett.*, 2008, **100**, 133002.