Supporting information

Table S1. Tensor parameters and shift of metal ion from starting position for the 10 subsets (from a total of 100) resulting in the largest number of peak pairings, using 2D and 3D data of $^{15}N/^{13}C$-ε186/θ complexed with Dy^{3+}, Er^{3+} and Tb^{3+}, respectively, and their diamagnetic reference spectra.

2D ε186/θ/Dy^{3+}

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg	d / Å
37	40.0	5.8	25	78	14	0.9
34	37.8	6.1	27	76	27	1.1
32	29.2	1.3	23	81	69	2.0
31	39.5	6.0	26	78	18	0.8
30	33.0	5.2	25	77	17	1.6
29	34.3	6.5	27	85	135	2.1
29	32.7	0.9	23	86	163	2.4
28	34.1	1.4	22	81	156	1.7
28	24.0	0.7	23	87	144	3.3
28	43.3	6.8	28	79	16	1.0

3D ε186/θ/Dy^{3+}

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg	d / Å
46	39.4	4.0	27	79	23	0.7
45	36.8	3.5	26	78	31	1.0
45	39.3	4.5	27	79	21	0.7
43	36.8	3.5	26	78	29	1.0
43	38.6	4.5	28	78	28	0.7
42	34.0	2.5	26	79	36	1.1
40	38.2	4.1	27	79	29	0.7
39	40.6	3.2	29	79	18	0.7
39	39.9	0.3	27	79	47	0.5
38	37.5	5.2	25	79	8	1.1

2D ε186/θ/Er^{3+}

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg	d / Å
77	-11.1	-4.0	24	90	41	0.4
77	-10.8	-3.4	25	91	44	0.2
77	-10.4	-3.9	22	91	46	0.8
77	-10.4	-3.6	23	90	47	0.8
76	-11.4	-4.1	24	90	41	0.6
76	-11.2	-4.0	23	91	42	0.6
76	-11.1	-4.0	24	90	41	0.5
76	-11.1	-3.9	23	91	42	0.6
76	-11.0	-3.8	23	91	43	0.5
76	-10.9	-3.6	23	92	43	0.5

3D ε186/θ/Er^{3+}

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg	d / Å
78	-10.5	-4.3	24	90	41	0.6
78	-10.5	-4.4	23	91	40	0.8
78	-10.5	-4.4	23	91	40	0.8
78	-10.5	-4.3	23	91	41	0.7
78	-10.5	-4.3	23	91	41	0.7
78	-10.5	-4.3	23	91	41	0.7
78	-10.5	-4.5	23	90	42	0.8
78	-10.5	-4.5	23	90	42	0.8
78	-10.5	-4.5	23	90	42	0.8
78	-10.5	-4.4	23	90	42	0.8

2D ε186/θ/Tb^{3+}

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg	d / Å
56	27.7	3.7	19	84	3	0.6
55	27.9	4.0	19	84	4	0.7
54	28.6	4.8	20	84	-3	0.5
53	28.0	5.1	18	85	2	1.3
52	29.5	5.2	20	84	6	0.7
52	27.5	4.7	17	85	2	1.2
51	29.7	6.4	20	85	-1	0.6
50	27.1	3.0	22	84	-10	0.2
49	28.1	4.7	20	85	-13	1.0
49	27.9	4.7	20	85	-11	0.8

3D ε186/θ/Tb^{3+}

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg	d / Å
63	27.8	5.9	20	84	0	0.7
63	27.6	5.8	20	84	0	0.7
63	27.6	5.8	20	84	0	0.7
63	27.3	5.7	20	84	0	0.8
63	27.3	5.7	20	84	-1	0.7
63	27.3	5.7	20	84	0	0.7
63	27.3	5.7	20	84	0	0.7
63	27.3	5.7	20	84	0	0.7
62	27.9	5.6	20	84	-3	0.7
62	27.6	5.8	20	84	1	0.7

Table S2. Tensor parameters determined by Echidna for randomly varied structures, using 2D data of $^{15}N/^{13}C$-ε186/θ complexed with Dy^{3+}, Er^{3+} and Tb^{3+}, respectively, and the diamagnetic reference. Structural variation was obtained by random displacement of the N and H atomic coordinates following a Gaussian distribution with σ = 0.5, 1.0, 1.5 and 2.0 Å along each coordinate. Tensors and paramagnetic resonance assignments were determined using Echidna for 10 different randomized structures.

2D ε186/θ/Dy^{3+} σ = 0.5 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
30	34.6	4.2	23	79	26
30	34.5	4.1	28	80	154
28	40.9	2.0	27	77	153
28	33.3	3.6	27	83	35
28	36.1	3.7	28	79	126
26	39.3	5.4	33	84	41
25	24.0	2.0	23	89	129
25	30.4	1.1	25	81	16
25	39.1	3.8	29	78	176
24	36.9	8.3	27	78	30

2D ε186/θ/Dy^{3+} σ = 1.0 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
22	27.2	2.9	25	81	44
20	20.4	1.3	28	76	86
20	36.8	15.7	29	77	38
19	42.0	5.3	30	78	150
18	25.7	1.1	23	83	4
18	27.1	12.9	22	91	134
17	20.7	5.0	20	93	73
16	41.5	18.9	26	80	18
9	51.5	29.7	18	81	146
5	2.1	1.1	0	1	2

2D ε186/θ/Er^{3+} σ = 0.5 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
76	-10.2	-4.0	24	89	43
74	-11.5	-5.5	24	89	40
73	-10.9	-4.3	24	90	44
72	-10.7	-3.9	22	90	38
71	-10.0	-3.9	21	91	44
71	-10.5	-3.6	25	88	44
71	-10.0	-3.4	25	90	40
70	-10.6	-4.2	22	91	31
68	-10.3	-3.9	22	92	34
64	-10.3	-5.7	22	87	41

2D ε186/θ/Er^{3+} σ = 1.0 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
65	-10.9	-4.4	30	90	37
61	-10.9	-2.9	23	91	41
60	-12.3	-7.7	20	84	46
60	-11.2	-4.8	21	90	37
59	-10.9	-1.8	25	89	40
59	-9.1	-4.2	22	91	44
59	-10.8	-4.1	22	89	41
57	-10.0	-1.3	24	94	52
57	-11.2	-3.9	25	90	33
57	-9.4	-4.5	25	86	44

2D ε186/θ/Tb^{3+} σ = 0.5 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
49	24.3	4.7	21	84	9
48	28.8	6.5	21	84	11
47	22.6	4.1	18	86	11
47	26.6	6.8	20	83	13
45	24.9	3.6	18	86	14
45	24.9	4.2	20	84	12
44	25.3	5.1	19	84	12
43	22.8	4.6	24	84	10
42	23.5	4.2	21	84	27
40	25.8	5.6	20	86	12

2D ε186/θ/Tb^{3+} σ = 1.0 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
37	27.0	4.5	22	81	4
35	29.3	6.0	23	83	178
33	29.2	7.7	21	84	170
33	24.8	6.7	20	82	5
32	18.2	1.0	25	86	38
32	26.6	4.8	23	85	177
31	20.7	3.0	21	87	14
31	19.4	1.1	13	83	27
29	22.2	3.4	21	79	166
27	18.2	4.7	27	84	127

2D ε186/θ/Dy^{3+} σ = 1.5 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
19	18.3	8.5	29	85	137
16	18.5	6.4	24	111	52
16	39.1	17.8	24	84	156
15	21.2	10.9	23	84	122
14	27.6	12.3	30	81	125
8	34.2	26.2	50	128	164
8	56.5	55.4	18	93	116
7	42.8	16.5	15	89	85
6	73.3	49.9	161	98	4
2	90.4	42.8	28	98	164

2D ε186/θ/Dy^{3+} σ = 2.0 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
14	19.4	2.4	7	92	46
14	18.0	4.6	35	84	62
10	15.2	8.9	42	74	33
9	2.3	30.3	111	132	177
7	-2.3	4.3	0	0	0
5	0.4	37.9	-17	167	30
5	29.3	20.8	27	90	43
5	6.3	1.7	-1	2	101
5	16.7	7.0	50	153	102
3	0.5	0.1	0	0	179

2D ε186/θ/Er^{3+} σ = 1.5 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
56	-12.5	-4.2	24	90	40
54	-10.2	-4.4	27	90	43
52	-11.2	-7.6	25	84	41
52	-8.4	-5.1	25	99	50
51	-10.1	-4.8	21	90	46
50	-9.8	-4.9	23	88	43
47	-10.5	-2.8	24	88	26
47	-9.8	-6.6	16	96	48
45	-10.0	-5.6	22	88	29
44	-10.9	-2.3	23	86	19

2D ε186/θ/Er^{3+} σ = 2.0 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
47	-9.7	-3.2	20	95	36
45	-8.0	-2.3	11	90	65
45	-8.5	-5.7	22	94	42
44	-9.7	-4.0	20	84	35
44	-9.7	-3.8	23	100	30
43	-7.1	-4.9	24	91	46
43	-10.5	-4.4	24	88	40
41	-10.4	-2.8	20	96	46
40	-10.5	-2.9	24	84	35
39	-4.2	-4.0	17	91	48

2D ε186/θ/Tb^{3+} σ = 1.5 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
31	21.8	4.2	24	86	14
30	17.1	2.8	21	90	26
30	11.6	2.6	15	79	150
29	29.2	8.2	24	78	167
28	17.3	4.7	30	84	32
25	16.4	0.2	18	75	54
25	20.1	0.8	17	91	159
22	22.5	5.0	26	86	133
21	22.4	6.7	25	80	158
9	42.8	14.8	35	56	191

2D ε186/θ/Tb^{3+} σ = 2.0 Å

#peaks	Δχ_ax	Δχ_rh	α / deg	β / deg	γ / deg
28	21.0	7.1	27	79	146
26	17.8	5.8	23	87	19
25	14.6	1.7	11	83	108
24	20.3	4.3	26	79	139
22	16.8	2.3	23	74	22
21	10.9	1.9	19	90	146
21	16.0	6.9	28	64	60
20	13.1	8.7	-1	163	33
9	43.1	143.7	81	134	138
6	57.5	23.7	-3	66	97

Figure S1. Results of Table S2 visualized in Sanson-Flamsteed projections, with the principal axes of the magnetic susceptibility tensors shown in brown (x-axis), purple (y-axis) and blue (z-axis). The crystal coordinates (PDB code 1J53) were used as the reference coordinate system. No results are shown for cases where the number of initial peak pairings was below 10, since a minimum of 10 initial assignments was the requirement for random subset sampling.

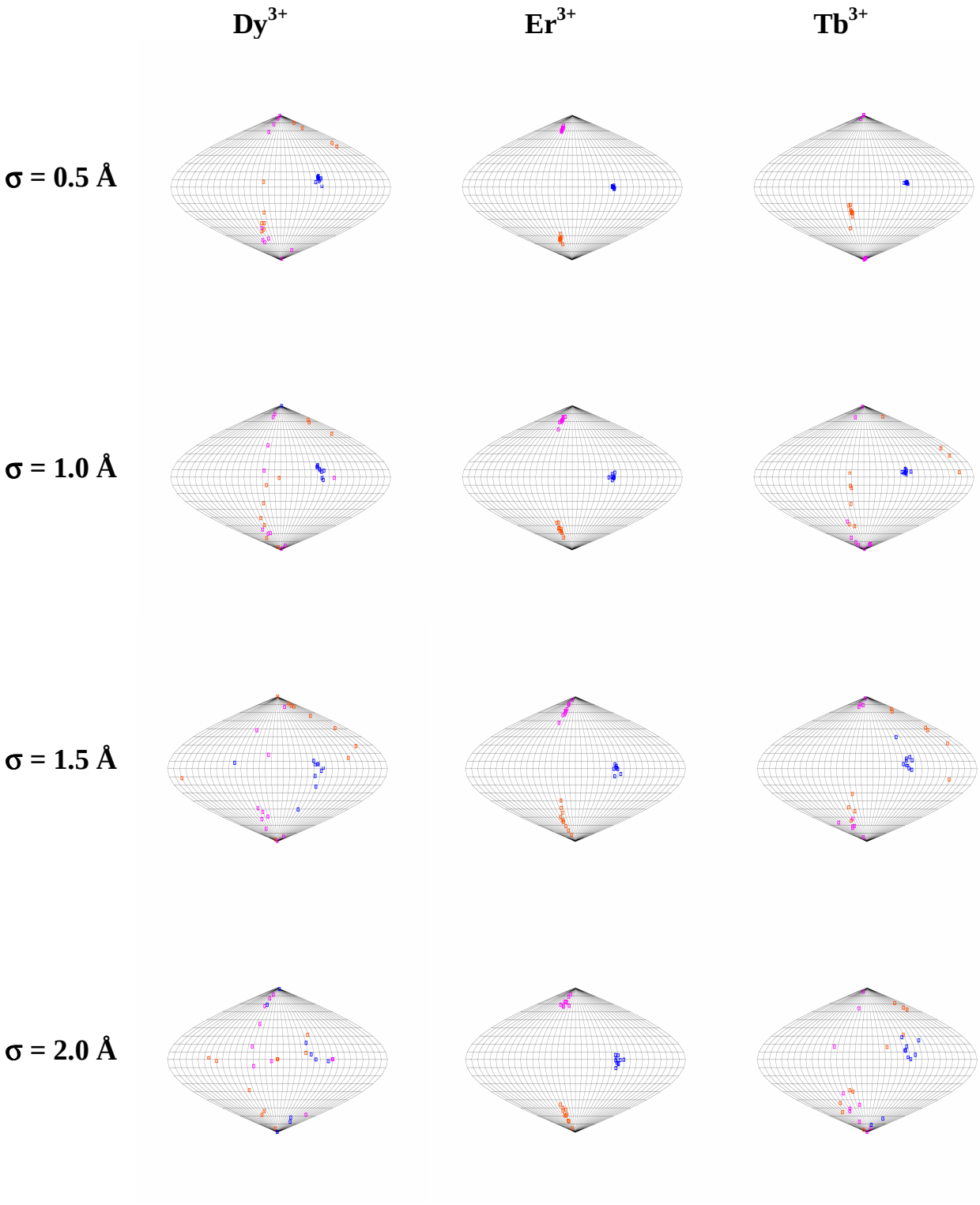

Table S3. Chemical shifts of $^{15}N/^{13}C$-labeled ε186 complexed to unlabeled θ and different lanthanide ions at pH 7.2 and 25 °C.[a]

	diamagnetic (La)			paramagnetic (Dy)			paramagnetic (Er)			paramagnetic (Tb)		
residue	C'	N	HN	C'	N	HN	C'	N	HN	C'	N	HN
1 MET												
2 SER												
3 THR	174.1			174.1			174.1			174.2		
4 ALA	177.3	127.1	8.43	177.3	127.1	8.43	177.4	127.1	8.46	177.4	127.2	8.51
5 ILE	176.7	121.3	8.33	176.6	121.2	8.30	176.8	121.3	8.37	176.8	121.3	8.41
6 THR	173.4	119.8	8.59	173.5	119.9	8.61	173.5	119.9	8.65	173.7	120.0	8.73
7 ARG	174.2	125.6	8.26	174.0	125.5	8.11	174.5	125.8	8.40	174.3	125.7	8.35
8 GLN	174.5	124.9	9.36		124.9	9.41	174.8	125.1	9.54	174.8	125.1	9.65
9 ILE	174.1	122.5	9.14					123.0	9.60		122.5	9.21
10 VAL	175.7	129.7	9.02									
11 LEU		126.6	8.49									
12 ASP	173.8											
13 THR	174.7	114.5	8.01									
14 GLU	177.6	118.5	8.79									
15 THR	174.1	111.2	8.94									
16 THR	172.0	107.5	8.97									
17 GLY	170.6	104.9	7.64									
18 MET	173.6	113.4	7.90				173.4					
19 ASN	175.8	119.0	9.09				175.8	118.7	8.86			
20 GLN	175.3	121.6	9.02				175.3	121.6	9.01	174.8		
21 ILE	175.4	117.1	7.57	175.4			175.5	117.0	7.59	175.1	116.6	7.36
22 GLY	173.4	112.1	8.29	173.4	112.1	8.21	173.4	112.1	8.34	173.0	111.7	7.93
23 ALA	181.3	124.5	8.36	181.7	124.8	8.53	181.3	124.5	8.34	181.0	124.3	8.15
24 HIS		121.5	8.33		121.6	8.15		121.6	8.39		121.1	7.66
25 TYR	174.7			176.6						175.3		
26 GLU	177.5	120.6	5.60	179.1	122.0	6.69	177.2			178.2	121.0	5.77
27 GLY	173.2	111.8	8.15	175.9	113.5	9.80	172.6	111.5	7.82	174.6	112.6	8.88
28 HIS	173.6	120.9	8.48		123.7	11.17		120.3	7.95		122.4	9.73
29 LYS	177.2	113.4	8.52									
30 ILE	175.7	121.6	9.65									
31 ILE	174.7	117.1	8.89									
32 GLU	174.8	122.6	7.47									
33 ILE	174.0	124.6	8.60									
34 GLY	170.9	115.5	9.28									
35 ALA	175.6	125.3	9.54									
36 VAL	174.4	113.8	8.83				175.5			174.0		
37 GLU	175.2	121.7	6.48	175.5			175.6	122.6	7.31	175.5	121.3	5.79
38 VAL	175.2	130.2	9.57	175.6	130.5	9.64	175.4	130.4	9.88	175.6	130.5	9.84
39 VAL	177.0	125.5	8.94	177.6	125.8	9.40	177.0	125.6	9.02	177.5	125.8	9.32
40 ASN	174.3	128.6	9.46	174.9	129.1	9.81	174.3	128.6	9.48	174.8	129.0	9.81
41 ARG	173.1	106.3	8.96	174.2	107.1	9.70	173.1	106.1	8.87	173.9	106.9	9.59
42 ARG	175.1	117.3	7.68	176.2	118.2	8.48	175.1	117.2	7.63	175.8	117.9	8.27
43 LEU	178.7	125.6	8.78	179.2	126.8	9.99	178.9	125.6	8.69	178.9	126.3	9.49
44 THR	177.2	114.7	7.84	177.0	114.9	8.07	177.4	115.0	8.08	176.9	114.7	7.93
45 GLY	173.9	111.7	9.96	173.1	111.3	9.82	174.4	112.0	10.32	173.2	111.3	9.69
46 ASN	173.3	119.7	8.02	171.7	119.0	7.30	174.1	120.2	8.48	172.1	119.1	7.43
47 ASN	174.1	123.6	7.68		121.6	5.83		124.5	8.49		122.1	6.25
48 PHE	172.9	122.0	9.15									
49 HIS	172.8	127.0	7.54									
50 VAL	172.8	119.7	8.53									
51 TYR		119.2	8.04									
52 LEU	174.3						173.3					
53 LYS		120.8	8.31					120.0	7.67			
54 PRO												
55 ASP												
56 ARG	174.5			177.8			173.8			176.7		
57 LEU	178.5	120.0	8.73		123.3	11.62	177.4	119.2	8.02		122.1	10.60
58 VAL	176.0	125.5	10.75					124.3	9.57			
59 ASP		128.8	9.25									
60 PRO	178.7											

61	GLU	179.2	118.1	9.19										
62	ALA	179.7	124.1	7.54										
63	PHE	178.1	118.7	8.03										
64	GLY	173.3	105.8	7.73										
65	VAL	177.3	119.1	7.14										
66	HIS	177.3	113.2	7.13										
67	GLY	174.3	111.6	8.45										
68	ILE	173.1	125.4	10.64										
69	ALA		125.6	7.85										
70	ASP													
71	GLU	177.8						177.1						
72	PHE	174.2	114.5	6.93	175.9			173.4	113.7	5.99	175.8			
73	LEU	177.3	116.0	7.27	179.4	118.3	9.97	176.6	115.0	6.24	179.0	118.0	9.54	
74	LEU	177.5	114.6	6.83	178.6	116.3	8.56	177.1	114.0	6.14	178.4	116.0	8.27	
75	ASP	176.7	115.4	7.78	177.4	116.4	8.79	176.3	115.1	7.31	177.2	116.3	8.67	
76	LYS		120.5	7.13		120.9	7.65		120.1	6.64		121.3	8.06	
77	PRO	176.3			177.1			176.1			176.9			
78	THR		108.2	8.38		109.1	9.03		108.1	8.23		108.9	8.85	
79	PHE	177.9			178.4			177.9						
80	ALA	180.0	117.6	8.56	180.0	117.9	9.19	180.1	117.4	8.38	180.0			
81	GLU		115.3	7.63	177.4	115.6	7.92	177.6	115.5	7.56		115.5	7.80	
82	VAL	176.1			175.4	112.2	7.30	176.3	112.5	7.47	175.6			
83	ALA		123.7	7.79		123.4	7.39		123.9	7.82		123.5	7.47	
84	ASP	178.0												
85	GLU	179.8	121.1	8.37	178.5			180.2			178.9			
86	PHE	176.7	120.2	8.88	175.2	118.9	7.58	177.4	120.6	9.26	175.8	119.4	8.02	
87	MET	177.4	117.9	8.94	176.3	116.9	7.86	177.9	118.3	9.41	176.8	117.2	8.26	
88	ASP	177.9	116.8	8.09	176.9	116.0	7.15	178.4	117.3	8.57	177.3	116.4	7.55	
89	TYR	176.8	120.0	7.61		118.8	6.16	177.4	120.4	8.13	175.9	119.3	6.72	
90	ILE	176.3	108.3	7.51	174.9			176.8	108.9	8.12	175.6	107.5	6.51	
91	ARG	177.7	120.4	7.93	177.0	119.3	6.78	178.1	120.9	8.42	177.4	119.8	7.30	
92	GLY	173.8	114.4	8.58	173.1	113.6	7.76	174.0	114.6	8.92	173.5	114.0	8.20	
93	ALA	176.0	123.7	8.24	175.3	123.0	7.28	176.4	123.9	8.60	175.8	123.5	7.81	
94	GLU	174.8	119.3	8.00	174.0	118.6	7.46	175.1	119.6	8.24	174.8	119.1	7.97	
95	LEU	175.2	129.2	9.43		128.2	8.28		129.8	9.76		129.1	9.20	
96	VAL	174.4	125.6	9.01										
97	ILE		123.1	8.27										
98	HIS	176.2												
99	ASN	174.9	126.1	8.35										
100	ALA	177.0	118.9	6.80										
101	ALA	180.8	116.4	8.85										
102	PHE		118.9	7.84										
103	ASP	179.2												
104	ILE	177.8	119.4	9.27										
105	GLY	175.8	105.2	7.84										
106	PHE	177.6	118.3	7.22										
107	MET	176.2	119.6	8.66	175.6			176.4			175.5			
108	ASP	179.3	116.6	9.02	179.3	115.9	8.11	179.4	116.8	9.27		115.9	8.19	
109	TYR	178.4	122.4	7.47	178.9	122.6	7.45	178.3	122.4	7.50	178.4			
110	GLU	181.1	120.4	8.36	181.5	121.0	8.97	181.0	120.3	8.29	181.1	120.6	8.41	
111	PHE	180.8	117.6	8.95	180.8	117.7	8.97	180.9	117.6	9.03	180.6	117.5	8.75	
112	SER	177.6	119.0	8.61	178.0	119.1	8.68	177.6	119.1	8.63	177.8	119.0	8.49	
113	LEU	178.5	124.0	7.74	178.9	124.6	8.17	178.4	123.9	7.68	178.7	124.2	7.85	
114	LEU	177.0	114.7	7.52	177.1	115.0	7.78	177.0	114.6	7.49	176.9	114.8	7.59	
115	LYS	176.0	112.7	7.84	176.1	112.8	8.02	176.0	112.6	7.82	176.0	112.6	7.88	
116	ARG	175.2	117.7	8.74	175.0	117.6	8.73	175.2	117.8	8.76	175.0	117.6	8.67	
117	ASP	175.2	117.9	8.53		117.9	8.43	175.3	118.1	8.58	175.1	117.9	8.43	
118	ILE		121.5	7.72					121.6	7.79		121.4	7.51	
119	PRO	175.3						175.5						
120	LYS		116.0	8.31	178.0			179.0	116.2	8.45				
121	THR	175.4			174.4	123.9	9.31	175.7	125.1	10.54	174.9			
122	ASN	176.2	116.0	8.94		115.1	7.89	176.3	116.2	9.19		115.5	8.32	
123	THR	175.8	109.5	8.25	175.0			176.0	109.6	8.45	175.3			
124	PHE	174.6	116.8	7.36	173.8	115.9	6.56	174.9	117.0	7.61	174.2	116.3	6.92	
125	CYS	173.5	123.1	8.03	172.5	122.2	7.10	173.6	123.3	8.29	173.1	122.6	7.57	
126	LYS	175.2	121.3	7.78	174.1	120.4	6.94	175.5	121.6	8.04	174.9	120.9	7.51	
127	VAL	175.2	125.1	8.67		124.1	7.71	175.3	125.4	8.84	175.0	124.8	8.37	
128	THR	171.4	130.1	9.86	170.4			171.3	130.1	9.98	171.6	130.0	9.85	
129	ASP	178.2	124.9	8.58		123.9	7.78		124.7	8.44		125.1	8.74	

130	SER	177.3	121.6	8.95										
131	LEU	177.8	125.4	8.43				177.2			178.3			
132	ALA	181.2	122.1	6.84	181.3			180.8	121.6	6.37	181.7	122.3	7.07	
133	VAL	178.0	118.1	7.57	178.9	118.4	7.82	177.4	117.5	7.01	179.1	118.9	8.43	
134	ALA	178.7	122.3	8.16	179.6	123.4	9.32	178.2	121.5	7.35	179.7	123.7	9.68	
135	ARG	178.3	115.7	8.65	178.4	116.1	8.84	178.0	115.3	8.14	178.7	116.4	9.31	
136	LYS	178.3	117.4	7.40	178.8	117.6	7.63	178.0	117.1	7.04	178.9	117.9	7.91	
137	MET	176.4	117.6	7.68	177.2	118.3	8.34	176.0	117.2	7.27	177.1	118.4	8.44	
138	PHE		117.0	8.54		117.7	9.22		116.6	8.13		117.7	9.28	
139	PRO													
140	GLY	174.1			173.7			174.0			174.0			
141	LYS		117.8	7.29		117.6	7.26		117.7	7.09		117.9	7.44	
142	ARG													
143	ASN	173.8												
144	SER	174.6	110.3	6.98										
145	LEU	178.7	122.1	9.11										
146	ASP	178.7	116.0	8.69										
147	ALA	181.3	124.4	7.51										
148	LEU	178.9	120.2	8.41										
149	CYS	176.8	117.3	8.63				175.5						
150	ALA	180.8	120.0	7.41				180.0	118.9	6.16				
151	ARG	177.5	119.6	7.82	180.2			176.8	118.7	6.87	179.3			
152	TYR	173.3	114.1	7.60	176.4	117.3	11.31	172.6	113.1	6.59		116.3	10.13	
153	GLU	175.6	117.3	7.70	178.7	120.3	10.73	174.8	116.6	6.91	177.4			
154	ILE	175.4	120.0	8.29		123.8	12.55	174.4	119.1	7.28		122.3	10.91	
155	ASP		127.1	8.70				175.9	126.6	7.94				
156	ASN	176.3						175.8	124.3	8.21				
157	SER	175.1	117.3	8.68				175.0	116.9	8.27				
158	LYS	176.5	121.5	8.54					121.3	8.27				
159	ARG	177.4	119.0	7.54										
160	THR	174.4	110.3	8.53										
161	LEU	174.4	119.1	6.55										
162	HIS	175.7	114.4	8.21										
163	GLY		107.9	8.81										
164	ALA	179.6												
165	LEU	176.6	117.0	6.52										
166	LEU		118.5	6.37										
167	ASP													
168	ALA	178.0												
169	GLN	177.6	118.6	7.98										
170	ILE		118.3	8.35										
171	LEU	178.0												
172	ALA	179.1	122.0	8.66										
173	GLU	180.8	116.7	7.88										
174	VAL	176.8	121.9	8.88										
175	TYR	179.6	122.4	9.83				178.6						
176	LEU	179.3	120.8	8.66	182.1			178.6	119.8	7.67				
177	ALA	180.5	123.2	7.61	183.2	126.6	11.48	179.8	122.3	6.66				
178	MET	177.7	117.4	8.53	179.7	120.2	11.96	177.1	116.5	7.57	179.3			
179	THR	175.4	104.2	7.33	176.9	106.1	9.64	175.0	103.6	6.68	176.6	105.8	9.19	
180	GLY	174.7	109.5	7.44	176.0	111.1	9.21	174.3	109.1	6.97	175.7	110.8	8.82	
181	GLY	174.4	108.6	8.29	175.5	109.9	9.67	174.1	108.2	7.93	175.2	109.6	9.35	
182	GLN	176.3	119.9	8.36	177.3	121.0	9.50	176.1	119.6	8.05	177.0	120.7	9.22	
183	THR	174.4	115.4	8.32	175.2	116.4	9.24	174.2	115.2	8.07	175.0	116.1	9.01	
184	SER	174.4	117.9	8.39	175.0	118.7	9.16	174.2	117.8	8.18	174.9	118.6	8.97	
185	MET	175.0	122.7	8.46	175.5	123.3	9.15	174.8	122.5	8.27	175.4	123.2	8.98	
186	ALA		130.5	7.98		131.1	8.53		130.4	7.82		130.9	8.40	

[a] NMR resonances of ε186 in complex with unlabeled θ were assigned at 25 ^{o}C in the presence of diamagnetic and paramagnetic lanthanide ions. The diamagnetic HNCO spectrum was recorded of the complex between ^{15}N/^{13}C-labeled ε186 and unlabeled θ which had been titrated with 1 equivalent of La^{3+}. Most of the peaks were assigned using the chemical shifts reported previously for the di-Mg^{2+} form at 30 ^{o}C (De Rose et al. (2003) *Biochemistry*, **42**, 3635-3644). Additional assignments were obtained from a 3D HNCA spectrum and a 3D NOESY-^{15}N-HSQC spectrum recorded of a complex in which ε186 was ^{15}N/^{2}H-labeled. This resulted in the assignment of 161 out of 169 HNCO peaks (there are 180 non-proline residues in ε186). The ^{15}N chemical shifts of several residues, particularly those near the metal-binding site, changed by up to about 0.5 ppm with respect to the di-Mg^{2+} and the metal-free form. The ^{15}N/^{13}C-labeled sample was further used to measure HNCO spectra in the presence of 1 equivalent of Dy^{3+}, Tb^{3+}, and Er^{3+}, respectively. Compared with the diamagnetic HNCO spectrum, the number of cross-peaks in these

paramagnetic spectra was greatly reduced due to paramagnetic relaxation enhancement. Observable cross-peaks were from amide protons located beyond a certain cutoff distance r_{cutoff} from the metal ion. This distance was about 15.5 Å for Dy^{3+}, and 15.0 Å for Tb^{3+} and Er^{3+}. In all three cases, an initial set of 15 to 20 peaks could be identified that were shifted from well-resolved cross-peaks in the diamagnetic HNCO spectrum by similar ppm values in all three dimensions. The pseudocontact shifts (PCS) derived from these paramagnetic/diamagnetic peak pairs were used to fit the $\Delta\chi$ tensor parameters and predict PCS values for all $^{13}C'$, ^{15}N, and $^{1}H^{N}$ nuclei in ε186 using Mathematica (Wolfram Research) routines. This allowed the identification of new assignments. The procedure was repeated iteratively and resulted in the confident assignment of 77 out of 81 HNCO peaks for the Dy^{3+}, 97 out of 104 HNCO peaks for the Er^{3+}, and 77 out of 89 HNCO peaks for the Tb^{3+} sample, respectively.