Supplementary Information

Thiol, Disulfide, and Trisulfide Complexes of Ru Porphyrins: Potential Models for Iron-Sulfur Bonds in Heme-Proteins

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Table S1. Thiol, sulfide, disulfide, and trisulfide ^{1}H NMR data used for the calculation of the "ring-current shielding shift".

Table S2. ^{1}H NMR titration of Ru(TMP)(MeCN)$_2$ with MeSSMe in C_6D_6. Legend: M, Ru(TMP); A, MeCN; B, MeSSMe.

Figure S1. ^{1}H-^{1}H COSY NMR (400 MHz, C_6D_6) spectrum of in situ sample of Ru(TMP)(^{n}PrSS^{n}Pr)$_2$ (from ^{n}PrSS^{n}Pr : (Ru(TMP)(MeCN)$_2$ = 5). Assignments: a–c, a' – c', see diagram (top); f, Me group of free ^{n}PrSS^{n}Pr; n, free MeCN; w, residual H_2O.

Figure S2. ^{1}H-^{1}H COSY NMR (400 MHz) spectrum of in situ sample of Ru(T-*p*Me-*P*P)(^{n}PrSS^{n}Pr)$_2$ (from ^{n}PrSS^{n}Pr : Ru(T-*p*Me-*P*P)(MeCN)$_2$ = 10). Assignments: a–c, a' – c', see diagram (top); f, Me group of free ^{n}PrSS^{n}Pr; n, free MeCN; w, residual H_2O.

Figure S3. *p*-Me (mesityl) region of the ^{1}H NMR (300 MHz) during titration of Ru(TMP)(MeCN)$_2$ with MeSSMe in C_6D_6. See Table S2 for experimental conditions. Legend: M, Ru(TMP); A, MeCN; B, MeSSMe.

Figure S4. Upfield region of the ^{1}H NMR (300 MHz) during titration of Ru(TMP)(MeCN)$_2$ with MeSSMe in C_6D_6. See Table S2 for experimental conditions. Assignments: a, Ru(TMP)(CH_3CN)$_2$; b, Ru(TMP)(CH_3CN)(MeSSMe); c, Ru(TMP)(MeCN)(C$H_3$$\underline{S}$SMe); d, Ru(TMP)(C$H_3$$\underline{S}$SMe)$_2$.

Table S1. Thiol, sulfide, disulfide, and trisulfide ^{1}H NMR data used for the calculation of the "ring-current shielding shift".[a]

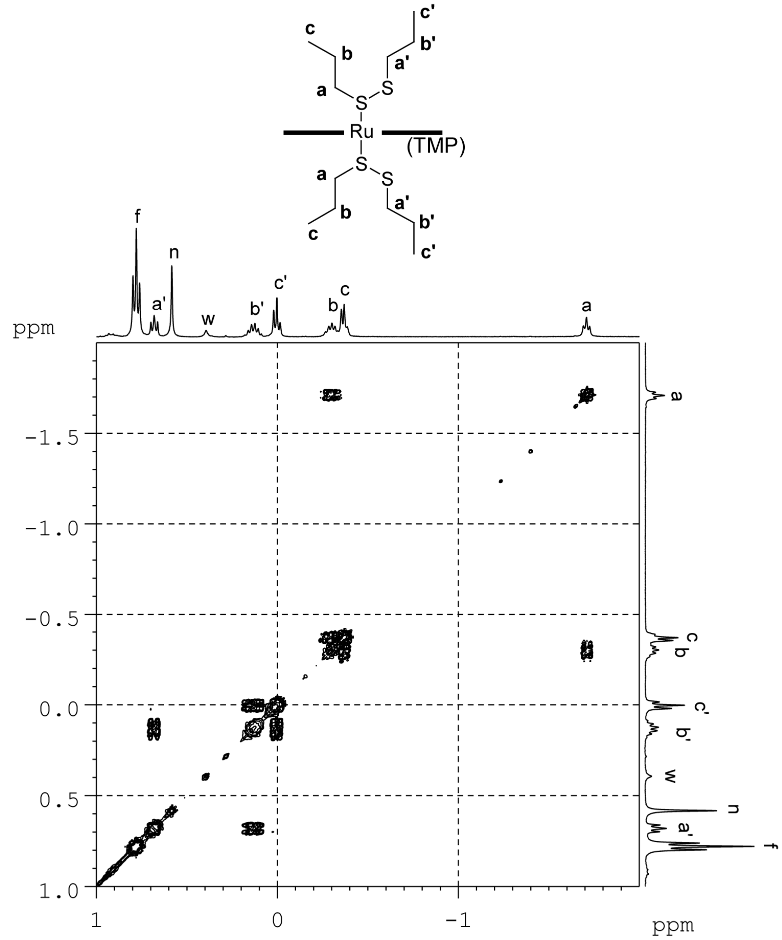
Compound		Alkyl Chain						p-C_6H_4X		
	S*H*	C^1*H*	C^2*H*	C^3*H*	C^4*H*	C^5*H*	C^6*H*	*o-H*	*m-H*	*p-X*
MeSH	0.80 (q)	1.49 (t)	–	–	–	–	–	–	–	–
EtSH	1.06 (t)	2.07 (m)	0.94 (t)	–	–	–	–	–	–	–
^{n}PrSH	1.02 (t)	2.07 (m)	1.29 (m)	0.71 (t)	–	–	–	–	–	–
^{i}PrSH	1.33 (d)	2.73 (m)	1.04 (d)	–	–	–	–	–	–	–
^{t}BuSH	1.61 (s)	–	1.20 (s)	–	–	–	–	–	–	–
BnSH	1.39 (t)	3.25 (t)	–	–	–	–	–	7.03 (m)	7.03 (m)	7.03 (m, X = *H*)
PhSH	3.00 (s)	–	–	–	–	–	–	6.97 (m)	6.86 (m)	6.86 (m, X = *H*)
MeSMe	–	1.72 (s)	–	–	–	–	–	–	–	–
BnSBn	–	3.34 (s)	–	–	–	–	–	7.07 (m)	7.07 (m)	7.07 (m, X = *H*)
MeSSMe	–	1.96 (s)	–	–	–	–	–	–	–	–
EtSSEt	–	2.35 (q)	1.07 (t)	–	–	–	–	–	–	–
^{n}PrSS^{n}Pr	–	2.40 (t)	1.54 (m)	0.78 (t)	–	–	–	–	–	–
^{t}BuSS^{t}Bu	–	–	1.21 (s)	–	–	–	–	–	–	–
BnSSBn	–	3.34 (s)	–	–	–	–	–	7.06 (m)	7.06 (m)	7.06 (m, X = *H*)
MeSS^{t}Bu	–	2.05 (s)	1.18 (s)	–	–	–	–	–	–	–
MeSSSMe	–	2.06 (s)	–	–	–	–	–	–	–	–
BnSSSBn	–	3.72 (s)	–	–	–	–	–	7.05 (m)	7.05 (m)	7.05 (m, X = *H*)

[a] δ values in ppm (C_6D_6, room temperature, under air).

Table S2. ^{1}H NMR titration of Ru(TMP)(MeCN)$_2$ with MeSSMe in C_6D_6. Legend: M, Ru(TMP); A, MeCN; B, MeSSMe.[a, b]

Entry	C_B	C_B/C_{Ru}	Integration values for o-Me signals[c]			% Species distribution			K_2/K_1[e]
	/mmol L^{-1}		MA_2	MAB[d]	MB_2	MA_2	MAB	MB_2	
1-	0.00	0.00	24	0	0	100	0	0	–
2-	1.09	0.42	17.69	4.34 (2.16 + 2.18)	1.97	73.7	18.1	8.2	1.84
3-	2.15	0.83	10.51	6.02 (3.00 + 3.02)	6.58	43.8	25.1	27.4	1.90
4-	2.68	1.04	8.86	6.98 (3.55 + 3.43)	8.52	36.9	29.1	35.5	1.55
5-	3.20	1.25	6.82	6.34 (3.17 + 3.17)	10.15	28.4	26.4	42.3	1.72
6-	3.71	1.45	4.37	5.69 (2.74 + 2.95)	12.50	18.2	23.7	52.1	1.69
7-	4.21	1.66	3.58	5.30 (2.64 + 2.66)	15.41	14.9	22.1	64.2	1.96
8-	4.72	1.87	2.40	4.08 (2.04 + 2.04)	16.82	10.0	17.0	70.1	2.43
9-	5.21	2.08	1.58	3.53 (1.70 + 1.82)	18.89	6.6	14.7	78.7	2.40
10-	5.70	2.28	0.91	2.64 (1.44 + 1.20)	20.40	3.8	11.0	85.0	2.67
11-	7.15	2.91	0	~0	~24	0	< 1	~100	–
									2.0 ± 0.4

[a] Data at 25.0 ± 0.1 °C, under Ar. [b] C_{Ru} = 2.65 – 2.46 x 10^{-3} mol L^{-1} (decrease in total Ru concentration during titration is due to dilution on addition of MeSSMe solution). [c] Integration values normalized against total integration of the *p*-Me signals (calibrated to 12 protons). [d] Integration values for each *o*-Me signal of MAB species are given in parentheses. [e] $K_2/K_1 = [MA_2]\cdot[MB_2]/[MAB]^2$.



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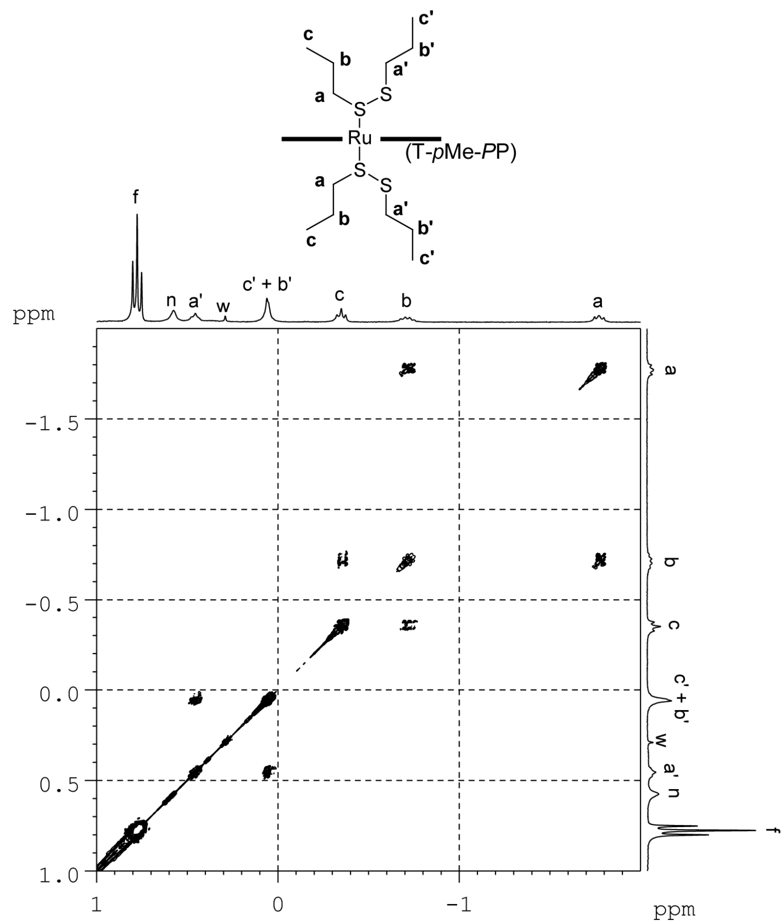

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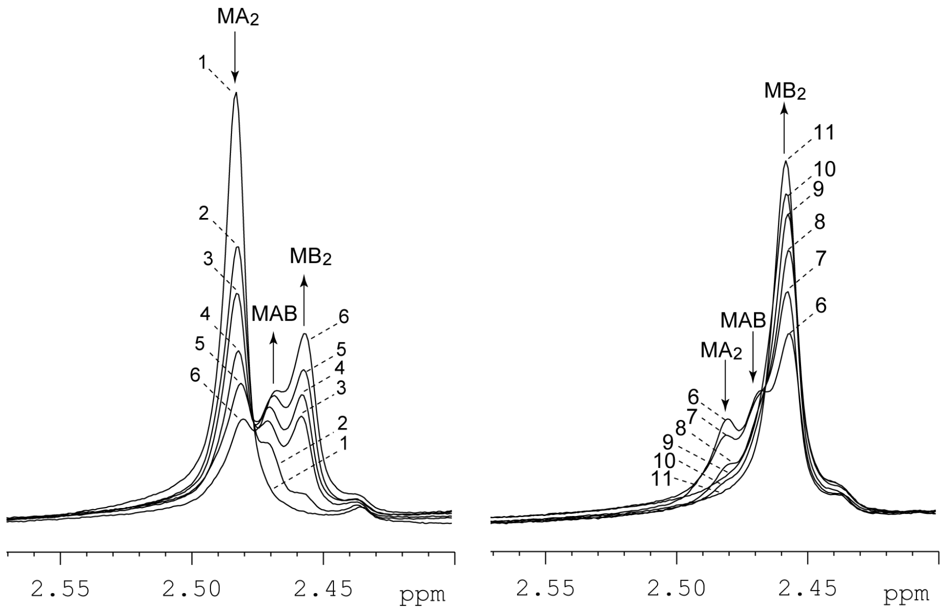

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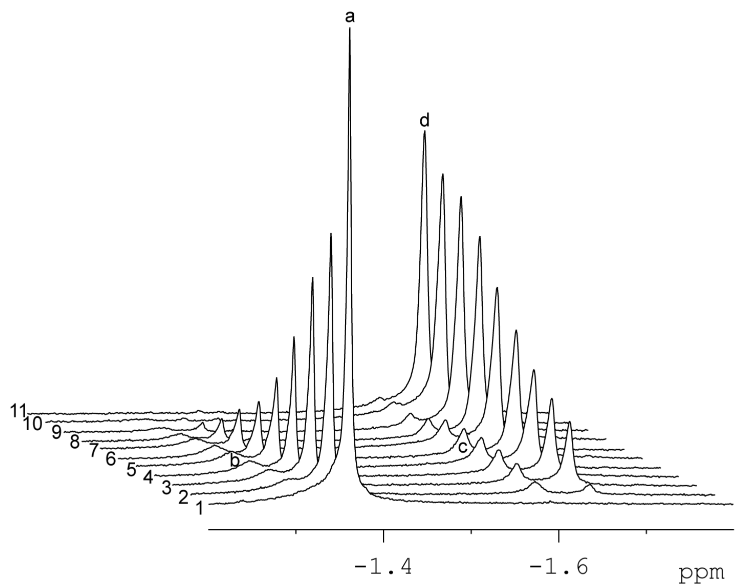

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