Electronic supplementary information (ESI)

Oxocomplexes of Mo(VI) and W(VI) with 8-Hydroxyquinoline-5-Sulfonate in Solution: Structural Studies and the Effect of the Metal Ion on the Photophysical Behaviour

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Table S1. ^{1}H NMR parameters [a] for 8-HQS and its complexes with Mo(VI) and W(VI) (298 K)

	H-2	H-3	H-4	H-6	H-7	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$	$J_{6,7}$
8-HQS [b]									
pH*=2.1	9.17	8.28	9.74	8.36	7.53	5.0	8.6	1.2	8.3
pH*=3.0	9.14	8.21	9.65	8.33	7.49	5.0	8.6	1.2	8.3
pH*=4.0	9.00	7.98	9.32	8.21	7.33	5.4	8.8	1.2	8.2
pH*=5.0	8.96	7.85	9.15	8.16	7.27	4.4	8.8	1.2	8.2
pH*=6.5	8.95	7.81	9.09	8.14	7.25	4.2	8.7	1.0	8.2
pH*=7.0	8.95	7.81	9.08	8.13	7.24	4.2	8.7	1.0	8.2
Mo(VI)/8-HQS									
complex **a** [c] (pH* 3.8)									
δ	9.15	7.92	9.16	8.15	7.03	4.8	8.6	-	8.3
Δδ	0.15	-0.06	-0.16	-0.06	-0.30				
complex **b** [c] (pH* 3.8)									
δ	8.74	7.66	9.04	8.28	7.47	4.9	8.7	1.3	8.3
Δδ	-0.26	-0.32	-0.28	0.07	0.14				
complex **c** [d] (pH* 5.3)									
δ	9.18	7.94	9.18	8.18	7.05	4.3	6.7	- [e]	8.3
Δδ	0.22	0.09	0.03	0.02	-0.22				
W(VI)/8-HQS									
complex **a** [f] (pH* 4.6)									
δ	9.06	8.05	9.43	8.25	7.39	5.0	8.8	- [e]	8.2
Δδ	0.10	0.20	0.28	0.09	0.12				
complex **b** [f] (pH* 4.6)									
δ	8.83	7.75	9.13	8.37	7.58	4.9	8.7	1.2	8.2
Δδ	-0.13	-0.10	-0.02	0.21	0.31				
complex **c** [g] (pH* 7.0)									
δ	9.24	8.00	9.24	8.25	7.10	- [e]	- [e]	- [e]	8.3
Δδ	0.29	0.19	0.16	0.12	-0.14				

[a] δ values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_H=1.3) as internal reference; J values in Hz.
[b] 10 mmol dm^{-3} 8-HQS solution.
[c] 5:10 mmol dm^{-3} Mo(VI)–8-HQS solution.
[d] 10:10 mmol dm^{-3} Mo(VI)–8-HQS solution.
[e] not observed due to the broadness of the signals.
[f] 10:10 mmol dm^{-3} W(VI)–8-HQS solution.
[g] 5.0:10 mmol dm^{-3} W(VI)–8-HQS solution.

Table S2. ^{13}C NMR parameters [a] for 8-HQS and its complexes with Mo(VI) and W(VI) (298 K)

	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
8-HQS [b]									
pH*=2.1	146.17	124.17	144.77	131.58	132.34	115.74	151.56	131.39	127.66
pH*=3.1	146.23	124.82	143.63	133.59	131.68	114.64	153.26	131.29	127.48
pH*=4.0	148.09	124.75	140.34	136.33	130.81	113.22	154.91	130.91	127.07
pH*=5.0	149.59	124.71	137.78	138.60	130.16	112.14	156.29	130.49	126.84
pH*=6.5	150.19	124.71	136.79	139.54	129.81	111.73	156.91	130.35	126.78
pH*=7.0	150.12	124.67	136.69	139.59	129.91	111.72	157.14	130.04	126.75
Mo(VI)/8-HQS									
complex **a** [c] (pH* 3.8)									
δ	151.08	125.26	139.26	142.02	131.88	112.37	162.59	127.08	125.92
Δδ	2.99	0.51	-1.08	5.69	1.07	-0.85	7.68	-3.83	-1.15
complex ***b*** [c] (pH*3.8)									
δ	149.64	124.77	139.63	141.28	131.13	114.29	164.27	126.70	125.92
Δδ	1.55	0.02	-0.71	4.95	0.32	1.07	9.36	-4.21	-1.15
complex **c** [d] (pH* 5.3)									
δ	151.07	125.26	139.18	142.04	131.92	112.32	164.40	127.10	126.48
Δδ	1.48	0.55	1.40	3.44	1.76	0.18	8.11	-3.39	-0.36
W(VI)/8-HQS									
complex **a** [e](pH* 4.6)									
δ	151.47	125.54	139.84	142.46	132.09	113.82	162.88	131.30	127.45
Δδ	1.88	0.83	2.06	3.68	1.93	1.68	6.59	0.81	0.61
complex ***b*** [e] (pH*4.6)									
δ	147.59	124.94	139.84	141.73	131.91	113.96	163.54	131.18	127.45
Δδ	-2.00	0.23	2.06	3.13	1.75	1.82	7.25	0.69	0.61
complex **c** [f] (pH* 6.8)									
δ	151.46	125.31	139.58	142.42	132.02	113.47	164.04	127.47	127.31
Δδ	1.34	0.64	2.89	2.83	2.11	1.75	6.90	-2.57	0.56

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference; *J* values in Hz.

[b] 10 mmol dm^{-3} 8-HQS solution.

[c] 5:10 mmol dm^{-3} Mo(VI)–8-HQS solution.

[d] 10:10 mmol dm^{-3} Mo(VI)–8-HQS solution.

[e] 5:10 mmol dm^{-3} W (VI)–8-HQS solution.

[f] 10:10 mmol dm^{-3} W (VI)–8-HQS solution.

Table S3. ^{95}Mo NMR parameters [a] for the Mo(VI)/8-HQS complexes (298 K)

	δ ^{95}Mo	$\Delta\nu_{1/2}$ /Hz
Mo(VI)/8-HQS		
complex **a** [b] (pH* 3.8)	88	600
complex **b** [b] (pH* 3.8)	109	940
complex **c** [c] (pH* 5.3)	36	410

[a] δ values, in ppm, relative to external reference Na_2MoO_4 2 mol dm^{-3}, pH* dissolution (pH* 9.0).

[b] 5:10 mmol dm^{-3} Mo(VI)–8-HQS solution.

[c] 10:10 mmol dm^{-3} Mo(VI)–8-HQS solution.

Table S4. ^{183}W NMR parameters [a] for the W(VI)/8-HQS complexes (298 K)

	δ ^{183}W
W(VI)/8-HQS	
complex **a** [b] (pH* 4.6)	20.7
complex **b** [b] (pH* 4.6)	63.3
complex **c** [c] (pH* 6.8)	-74.5

a δ values, in ppm, relative to external reference Na_2WO_4 2 mol dm^{-3}, pH* dissolution (pH* 9.5).
b 5:10 mmol dm^{-3} W(VI)–8-HQS solution.
c 10:10 mmol dm^{-3} W(VI)–8-HQS solution.

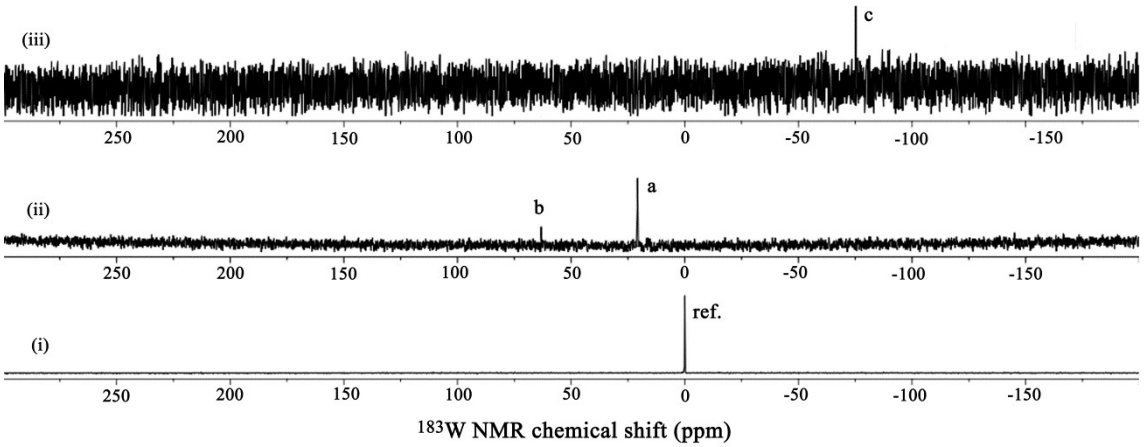

Figure S1. ^{183}W NMR spectra (20.825 MHz) of D_2O solutions of (i) Na_2WO_4 2 mol dm^{-3}, pH* 9.8 (external reference), (ii) W(VI)/8-HQS 5:10 mmol dm^{-3}, pH* 4.6, (iii) W(VI)/8-HQS 10:10 mmol dm^{-3}, pH* 7.0, temp 298 K.