

**Trinuclear ruthenium-dioxolene complexes based on the bridging ligand hexahydroxytriphenylene: electrochemistry, spectroscopy, and near-infrared electrochromic behaviour associated with a reversible seven-membered redox chain**

Christopher S. Grange, Anthony J. H. M. Meijer\* and Michael D. Ward\*

*Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK*

*Email: [m.d.ward@sheffield.ac.uk](mailto:m.d.ward@sheffield.ac.uk); [a.meijer@sheffield.ac.uk](mailto:a.meijer@sheffield.ac.uk)*

**Supporting information:** tables of calculated electronic spectra for the complexes  $[1]^{n+}$  (n = 6, 5, 4, 3, 2, 1, 0)

[1]<sup>6+</sup>

## Coordinates

153

H 0.27870 5.58096 -2.49710  
H 4.71527 -3.02603 -2.51887  
H -7.34336 -4.25509 -1.80101

## Computed Spectral Data

**Table Error! Bookmark not defined.S1: Selected transitions for [1]<sup>6+</sup> with major contributing transitions. Cut-off for oscillator strength 0.04. HOMO (H) is orbital no. 348.**

No.	Energy (cm <sup>-1</sup> )	Wavelength (nm)	Osc. Strength	Major contribs
10	10737.73328	931.295250053	0.1829	H-5->LUMO (21%), H-4->LUMO (26%), H-3->L+1 (31%)
11	10744.99232	930.666090974	0.1841	H-5->LUMO (26%), H-4->LUMO (20%), H-3->L+2 (30%)
20	13475.19792	742.104127848	0.4144	H-9->LUMO (41%), H-5->L+2 (13%), H-4->L+1 (12%)
21	13483.26352	741.660206015	0.4173	H-10->LUMO (41%), H-5->L+1 (13%), H-4->L+2 (14%)
23	14120.44592	708.192932196	0.409	H-10->LUMO (-17%), H-9->LUMO (21%)
24	14123.67216	708.03116121	0.4085	H-10->LUMO (21%), H-9->LUMO (17%)
28	14920.55344	670.216425967	0.1663	H-7->L+1 (36%), H-6->L+2 (36%)
29	14925.3928	669.999117209	0.1674	H-7->L+2 (-36%), H-6->L+1 (36%)
47	20193.84272	495.200449892	0.0531	H-16->LUMO (36%), H-15->L+1 (33%), H-15->L+2 (12%)
48	20195.45584	495.160895561	0.053	H-17->LUMO (37%), H-15->L+1 (13%), H-15->L+2 (32%)
59	24562.97824	407.116755236	0.0677	H-17->L+2 (32%), H-16->L+1 (32%)
60	24566.20448	407.063289249	0.068	H-17->L+1 (32%), H-16->L+2 (32%)
61	24965.45168	400.553538072	0.0357	H-2->L+4 (-31%), H-1->L+3 (42%), HOMO->L+4 (10%)
62	24968.67792	400.501781954	0.0435	H-2->L+3 (-20%), H-1->L+4 (36%), HOMO->L+3 (14%)
63	24979.1632	400.333666902	0.0598	H-2->L+3 (-10%), H-2->L+5 (14%), H->L+5 (56%)
97	28811.93632	347.078373662	0.0398	H-5->L+6(62%), H-4->L+6 (12%)
98	28825.64784	346.913278602	0.0358	H-4->L+7 (70%)

99	28835.32656	346.796835444	0.038	H-5->L+8 (47%), H-4->L+8 (25%)
178	33129.452	301.84622432	0.0378	H-7->L+3 (13%), H-7->L+4 (10%), H-6->L+3 (18%), H-1->L+14 (13%)
179	33139.13072	301.758066151	0.0374	H-7->L+5(15%),H-6->L+4 (14%)

[1]<sup>5+</sup>

## Coordinates

153

H -0.25523 5.51040 2.48531  
H -4.67190 -2.97336 2.50339  
H 7.34927 -4.23744 1.80586

## Computed Spectral Data

**Table Error! Bookmark not defined.S2: Selected transitions for [1]<sup>5+</sup> with major contributing transitions. Cut-off for oscillator strength 0.04. HOMO (H) on the  $\alpha$ -manifold is orbital no. 349.**

No.	Energy (cm <sup>-1</sup> )	Wavelength (nm)	Osc. Strength	Major contribs
7	6255.67936	1598.54740381	0.1852	HOMO( $\alpha$ )->LUMO( $\alpha$ ) (83%)
8	6262.9384	1596.69461223	0.1849	HOMO( $\alpha$ )->L+1( $\alpha$ ) (83%)
11	8400.3224	1190.43050062	0.2518	HOMO( $\beta$ )->LUMO( $\beta$ ) (38%)
12	8418.06672	1187.92120954	0.2346	H-1( $\alpha$ )->L+1( $\alpha$ ) (12%), H-1( $\beta$ )->LUMO( $\beta$ ) (33%)
24	12303.26624	812.792294739	0.2563	H-6( $\alpha$ )->LUMO( $\alpha$ ) (29%), H-5( $\alpha$ )->L+1( $\alpha$ ) (30%)
25	12303.26624	812.792294739	0.2512	H-6( $\alpha$ )->L+1( $\alpha$ ) (29%), H-5( $\alpha$ )->LUMO( $\alpha$ ) (30%)
31	14034.95056	712.506963046	0.0577	H-6( $\beta$ )->LUMO( $\beta$ ) (13%), H-5( $\beta$ )->L+1( $\beta$ ) (25%), H-4( $\beta$ )->L+1( $\beta$ ) (26%)
32	14043.82272	712.05683804	0.0555	H-7( $\beta$ )->LUMO( $\beta$ ) (13%), H-5( $\beta$ )->L+2( $\beta$ ) (24%), H-4( $\beta$ )->L+2( $\beta$ ) (18%), H-2( $\beta$ )->L+2( $\beta$ ) (14%)

36	15184.29856	658.575037924	0.1935	H-9( $\alpha$ )->LUMO( $\alpha$ ) (14%), H-9( $\alpha$ )->L+1( $\alpha$ ) (19%), H-8( $\alpha$ )->LUMO( $\alpha$ ) (21%), H-7( $\alpha$ )->L+1( $\alpha$ ) (21%)
37	15200.42976	657.87613626	0.1878	H-9( $\alpha$ )->LUMO( $\alpha$ ) (22%), H-9( $\alpha$ )->L+1( $\alpha$ ) (15%), H-8( $\alpha$ )->L+1( $\alpha$ ) (18%), H-7( $\alpha$ )->LUMO( $\alpha$ ) (20%)
42	16470.76176	607.1364607	0.0818	H-9( $\alpha$ )->LUMO( $\alpha$ ) (31%), H-9( $\alpha$ )->L+1( $\alpha$ ) (11%), H-8( $\alpha$ )->L+1( $\alpha$ ) (19%), H-7( $\alpha$ )->LUMO( $\alpha$ ) (19%)
43	16489.31264	606.453417333	0.0813	H-9( $\alpha$ )->LUMO( $\alpha$ ) (12%), H-9( $\alpha$ )->L+1( $\alpha$ ) (34%), H-8( $\alpha$ )->LUMO( $\alpha$ ) (17%), H-7( $\alpha$ )->L+1( $\alpha$ ) (17%)
95	23181.34096	431.381429455	0.0428	H-2( $\alpha$ )->L+2( $\alpha$ ) (33%), H-2( $\beta$ )->L+3( $\beta$ ) (11%)
96	23207.95744	430.886691595	0.0412	H-3( $\alpha$ )->L+3( $\alpha$ ) (12%)
97	23219.24928	430.677145476	0.0561	H-3( $\alpha$ )->L+3( $\alpha$ ) (11%), H-3( $\alpha$ )->L+4( $\alpha$ ) (16%)

[1]<sup>4+</sup>

## Coordinates

153

H 5.45645 0.69641 2.48340  
H -3.30416 4.39571 2.50360  
H -3.73390 -7.70151 1.77920

## Computed Spectral Data

**Table Error! Bookmark not defined.S3: Selected transitions for [1]<sup>4+</sup> with major contributing transitions. Cut-off for oscillator strength 0.04. HOMO (H) is orbital no. 349.**

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Major contribs
4	6078.23616	1645.21412738	0.1989	HOMO->LUMO (39%)
5	6087.10832	1642.81617384	0.1996	HOMO->L+1 (39%)
6	7067.88528	1414.85035535	0.037	H-4->LUMO (57%)
7	7072.72464	1413.88227437	0.0374	H-4->L+1 (56%)
13	11308.77776	884.268858423	0.3632	H-4->LUMO (16%)
14	11317.64992	883.575660202	0.3645	H-5->L+1 (10%), H-4->L+1 (16%)
16	12417.79776	805.295769288	0.5862	H-8->LUMO (20%), H-8->L+1 (15%), H-7->LUMO (15%), H-7->L+1 (20%)
17	12424.25024	804.877542454	0.5869	H-8->LUMO (15%), H-8->L+1 (20%), H-7->LUMO (20%), H-7->L+1 (15%)
45	21681.13936	461.230373273	0.0603	H-5->L+2 (21%), H-4->L+2 (15%), H-4->L+3 (18%)
46	21692.4312	460.990283099	0.0561	H-6->L+2 (10%), H-6->L+3 (25%), H-4->L+3 (14%), H-4->L+4 (15%)
47	21699.69024	460.836071363	0.1103	H-6->L+4 (11%), H-5->L+4 (23%), H-4->L+2 (13%), H-4->L+4 (19%)
52	22711.11648	440.313007456	0.0436	H-5->L+5 (10%), H-4->L+5 (23%)
53	22719.18208	440.156690711	0.0424	H-6->L+7 (17%), H-4->L+6 (21%)
55	23360.39728	428.074911575	0.1247	H-18->LUMO (10%), H-18->L+1 (26%), H-17->LUMO (25%)
56	23364.43008	428.001024025	0.1254	H-18->LUMO (26%), H-18->L+1 (10%), H-17->L+1 (26%)
84	26147.86864	382.440348683	0.0431	HOMO->L+13 (92%)
96	27416.58752	364.74269428	0.0351	HOMO->L+17 (51%), HOMO->L+20 (28%)
97	27423.04	364.656872469	0.0351	HOMO->L+18 (52%), HOMO->L+21 (25%)

[1]<sup>3+</sup>

## Coordinates

153

H 4.70575 -2.70173 2.44225  
H -0.04995 5.45905 2.42209  
H -7.61249 -3.86309 1.79461

## Computed Spectral Data

**Table Error! Bookmark not defined.S4: Selected transitions for [1]<sup>3+</sup> with major contributing transitions. Cut-off for oscillator strength 0.04. HOMO (H) on  $\alpha$ -manifold is orbital no. 350.**

No.	Energy (cm <sup>-1</sup> )	Wavelength (nm)	Osc. Strength	Major contribs
8	8330.95824	1200.34211095	0.164	H-6( $\beta$ )->LUMO( $\beta$ ) (14%), H-1( $\beta$ )->L+1( $\beta$ ) (19%), HOMO( $\beta$ )->LUMO( $\beta$ ) (35%)
9	8760.85472	1141.44114012	0.5216	H-1( $\beta$ )->LUMO( $\beta$ ) (18%), HOMO( $\beta$ )->L+1( $\beta$ ) (52%)
10	9157.68224	1091.97936093	0.3741	H-1( $\alpha$ )->LUMO( $\alpha$ ) (75%)
11	10328.0008	968.241598122	0.0559	H-4( $\beta$ )->LUMO( $\beta$ ) (42%), HOMO( $\beta$ )->L+1( $\beta$ ) (23%)
14	12858.17952	777.71507113	0.0679	H-4( $\beta$ )->L+1( $\beta$ ) (27%), H-3( $\beta$ )->L+1( $\beta$ ) (11%), H-2( $\beta$ )->LUMO( $\beta$ ) (11%), H-1( $\beta$ )->L+1( $\beta$ ) (12%)
22	14564.05392	686.622011627	0.0542	H-8( $\beta$ )->LUMO( $\beta$ ) (51%), H-6( $\beta$ )->LUMO( $\beta$ ) (10%)
66	19489.71584	513.09111339	0.0402	H-4( $\alpha$ )->L+2( $\alpha$ ) (14%), H-1( $\alpha$ )->L+2( $\alpha$ ) (43%)
70	20142.22288	496.469533655	0.0595	H-6( $\alpha$ )->L+2( $\alpha$ ) (11%)
74	20651.9688	484.215335441	0.0373	H-6( $\beta$ )->L+3( $\beta$ ) (-10%), H-4( $\beta$ )->L+3( $\beta$ ) (19%), HOMO( $\beta$ )->L+3( $\beta$ ) (10%)
81	21730.33952	460.186091009	0.0418	H-4( $\beta$ )->L+6( $\beta$ ) (15%)

[1]<sup>2+</sup>

## Coordinates

153

H 5.21302 1.40777 2.40331  
H -3.83779 3.80301 2.41052  
H -2.75517 -8.16568 1.72327

## Computed Spectral Data

**Table Error! Bookmark not defined.S5: Selected transitions for [1]<sup>2+</sup> with major contributing transitions. Cut-off for oscillator strength 0.04. HOMO (H) is orbital no. 350.**

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Major contribs
2	6573.464	1521.26793423	0.122	H-5->LUMO (17%), H-3->LUMO (14%), H-1->LUMO (50%)
4	7741.36288	1291.76220712	0.0357	H-5->LUMO (10%), H-3->LUMO (80%)
7	9919.07488	1008.15853504	0.5306	H-5->LUMO (63%), H-1->LUMO (10%)
8	10447.37168	957.178542728	0.218	H-7->LUMO (65%)
12	12073.39664	828.267330079	0.0906	H-9->LUMO (67%)
16	13764.75296	726.493241765	0.1112	H-8->LUMO (80%)
31	18137.11472	551.355612752	0.0508	H-5->L+4 (13%), H-4->L+3 (10%), H-4->L+4 (24%), H-1->L+5 (20%)
32	18157.27872	550.74332196	0.1391	H-5->L+3 (14%), H-4->L+3 (24%), H-4-> <b>Error! Bookmark not defined.</b> +4 (10%), H-1->L+6 (21%)
36	18554.9128	538.940824341	0.0587	H-7->L+1 (36%), H-2->L+1 (20%), HOMO->L+7 (11%)
38	19352.60064	516.726417603	0.0386	H-4->L+5 (30%)



[1]<sup>1+</sup>

## Coordinates

153

H -5.07155 -2.18882 2.32640  
H 4.39588 -3.30881 2.33312  
H 1.63090 8.45806 1.70597

## Computed Spectral Data

**Table Error! Bookmark not defined.S6: Selected transitions for [1]<sup>1+</sup> with major contributing transitions. Cut-off for oscillator strength 0.04. HOMO (H) for  $\alpha$ -manifold is orbital no. 351.**

No.	Energy (cm <sup>-1</sup> )	Wavelength (nm)	Osc. Strength	Major contribs
2	5428.95536	1841.97499093	0.2824	H-1( $\beta$ )->LUMO( $\beta$ ) (89%)
5	8687.45776	1151.08473345	0.0798	H-5( $\beta$ )->LUMO( $\beta$ ) (72%)
6	8747.1432	1143.23039778	0.1	H-4( $\beta$ )->LUMO( $\beta$ ) (51%), H-2( $\beta$ )->LUMO( $\beta$ ) (16%)
10	9478.69312	1054.99775902	0.0471	H-7( $\beta$ )->LUMO( $\beta$ ) (35%), H-6( $\beta$ )->LUMO( $\beta$ ) (46%)
12	9751.3104	1025.50319801	0.0378	H-4( $\beta$ )->LUMO( $\beta$ ) (-16%), H-3( $\beta$ )->LUMO( $\beta$ ) (63%)
65	16971.63552	589.218404332	0.0529	H-8( $\alpha$ )->LUMO( $\alpha$ ) (14%), H-7( $\beta$ )->L+1( $\beta$ ) (14%), H-2( $\beta$ )->L+1( $\beta$ ) (21%)

[1]<sup>0+</sup>

## Coordinates

153

H -5.07155 -2.18882 2.32640  
H 4.39588 -3.30881 2.33312  
H 1.63090 8.45806 1.70597

## Computed Spectral Data

**Table Error! Bookmark not defined.S7: Selected transitions for [1]<sup>0+</sup> with major contributing transitions. Cut-off for oscillator strength 0.04. HOMO (H) is orbital no. 351**

No.	Energy (cm <sup>-1</sup> )	Wavelength (nm)	Osc. Strength	Major contribs
1	7586.50336	1318.13030661	0.0809	H-1->LUMO (25%), H-1->L+1 (13%), HOMO->LUMO (35%)
2	7610.70016	1313.93955743	0.0807	H-1->LUMO (23%), H-1->L+2 (21%), HOMO->LUMO (13%), HOMO->L+1 (19%)
34	15627.1	639.913995559	0.0497	H-8->LUMO (18%), H-6->L+1 (10%), H-3->L+1 (18%)
35	15633.55248	639.649882059	0.0822	H-8->L+1 (17%), H-3->LUMO (11%), H-2->L+5 (10%)
36	15649.68368	638.99055115	0.096	H-7->L+2 (22%), H-6->L+2 (13%), H-3->L+2 (13%)
63	18425.05664	542.739172822	0.0914	H-5->L+4 (15%), H-5->L+5 (18%), H-4->L+3 (12%)
101	22064.25536	453.221730661	0.0512	H-7->L+7 (-10%), H-6->L+8 (16%)
102	22067.4816	453.155470174	0.0517	H-8->L+6 (21%), H-7->L+6 (12%)
115	23205.53776	430.931620867	0.0497	H-3->L+15 (40%)
118	23332.97424	428.578024265	0.0374	H-11->LUMO (47%), H-10->L+1 (11%)
134	24551.6864	407.303996845	0.0733	H-8->L+15 (10%), H-7->L+15 (Error! Bookmark not defined.0%), H-7->L+17 (13%), H-6->L+15 (12%), H-6->L+17 (17%)
135	24559.752	407.170235269	0.0699	H-8->L+15 (17%), H-8->L+16 (18%), H-7->L+16 (17%), H-6->L+16 (14%)
137	24671.86384	405.320006014	0.0555	H-12->L+1 (48%)
138	24696.8672	404.90965591	0.0536	H-12->L+2 (50%), H-10->L+2 (10%)
143	25448.58112	392.949216023	0.0623	H-12->L+3 (16%), H-12->L+4 (18%)
144	25455.84016	392.837161812	0.0429	H-12->L+5 (22%)
145	25464.71232	392.700293423	0.067	H-12->L+5 (34%), H-5->L+10 (10%)
157	26011.56	384.444454696	0.1711	H-12->L+1 (10%)
158	26026.88464	384.218093649	0.1674	
163	26334.99056	379.722938469	0.0593	H-5->L+12 (22%), H-3->L+12 (22%)
164	26350.3152	379.502101743	0.0543	H-4->L+14 (22%), H-3->L+13 (21%)
167	26375.31856	379.142340111	0.039	H-4->L+17 (15%)
173	26555.988	376.562905511	0.0423	H-5->L+13 (25%), H-5->L+14 (15%), H-4->L+14 (11%)
175	26744.72304	373.905535871	0.0976	H-5->L+15 (10%), H-4->L+15 (14%), H-4->L+16 (11%), H-1->L+24 (12%), HOMO->L+24 (14%)
176	26750.36896	373.826619549	0.0953	H-5->L+17 (15%), H-1->L+24 (15%), HOMO->L+24 (13%)

193	27424.65312	364.635423327	0.0868	H-10->L+6 (10%), H-9->L+6 (10%), H-1->L+27 (14%)
194	27431.91216	364.538933403	0.0854	H-9->L+7 (13%), HOMO->L+27 (15%)