Electronic Supplementary Information for Dalton Transactions

Nitrite reduction by copper complexes

John G. Woollard-Shore,[a] Jason P. Holland,[a,b] Michael W. Jones,[a] and Jonathan R. Dilworth[a]

[a] Department of Chemistry, University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford, United Kingdom, OX1 3TA. E-mail: michael.jones@chem.ox.ac.uk; jon.dilworth@chem.ox.ac.uk; Tel: +44 1865 272690.

[b] Current Address: Memorial Sloan-Kettering Cancer Center, Department of Radiology, 1275 York Avenue, New York, United States of America, NY10065. E-mail: hollanj3@mskcc.org or jasonpholland@gmail.com; Tel: +1.646.888.3083; Fax: 1.646.422.0408

DFT Optimised Cartesian Coordinates

Cartesian coordinates for complexes **11** (η^1-$\underline{N}O_2$ and η^1-$\underline{O}NO$), **12** (η^1-$\underline{O}NO$) and **19** (η^1-$\underline{N}O_2$ and η^1-$\underline{O}NO$) are provided in Tables S1 – S5, respectively. The coordinates were optimised by using the uB3LYP/6-31+G(d,p) methodology in are sufficiently close to allow rapid re-optimisation. In all cases frequency analysis should be performed to ensure that the calculated structures correspond to local minima on the potential energy surface.

Table S1. uB3LYP/6-31+G(d,p) optimised Cartesian coordinates of complex **11** (η^1-$\underline{N}O_2$)

Atomic number	*x*	*y*	*z*
6	2.113712	-0.78741	1.076595
6	1.218637	-0.61245	2.306754
7	-0.18814	-0.88919	1.931098
29	-0.49441	0.027008	0.038737
7	-0.29605	2.093123	-0.05353
6	1.025255	2.360726	-0.66497
6	2.059665	1.427113	-0.0266
7	1.61069	0.00483	-0.08175
6	1.952356	-0.63632	-1.38379
6	0.972219	-1.76444	-1.72168
7	-0.41066	-1.2421	-1.62604
1	-0.82921	-0.54783	2.647412
1	-0.35902	-1.89488	1.883442
1	1.57849	-1.26131	3.114145
1	1.264772	0.416631	2.677388
1	3.151885	-0.52033	1.314248
1	2.115158	-1.84301	0.787382
1	-1.09503	-1.98897	-1.4987
1	-0.67816	-0.774	-2.49315
1	1.204831	-2.1679	-2.71389
1	1.065979	-2.59038	-1.01006
1	1.889526	0.132573	-2.16084
1	2.98604	-1.00743	-1.38083
1	-1.07423	2.455307	-0.6065
1	-0.37578	2.556899	0.852527
1	1.346842	3.402159	-0.54703
1	0.938494	2.169657	-1.73932
1	3.04129	1.548163	-0.50326
1	2.18128	1.700253	1.02664
7	-2.42298	0.013127	0.03575
8	-2.94982	-1.10104	0.146064
8	-3.06473	1.057209	-0.11225

Table S2. uB3LYP/6-31+G(d,p) optimised Cartesian coordinates of complex **11** (η^1-ONO)

Atomic number	*x*	*y*	*z*
6	1.874296	-0.78824	-1.44614
6	0.668089	-1.58438	-1.95231
7	-0.54351	-0.74931	-1.79847
29	-0.40438	0.217129	0.058328
7	-0.35462	-0.97091	1.801057
6	1.06049	-1.08026	2.219471
6	1.923059	-1.29243	0.97225
7	1.631592	-0.26184	-0.06897
6	2.39334	0.997853	0.181325
6	1.661964	2.213825	-0.39312
7	0.26891	2.211754	0.10811
1	-1.40354	-1.30018	-1.78155
1	-0.64506	-0.10781	-2.58597
1	0.842147	-1.89973	-2.98768
1	0.524752	-2.49417	-1.36105
1	2.788846	-1.39474	-1.47648
1	2.03476	0.068728	-2.10774
1	-0.3379	2.801179	-0.46174
1	0.218385	2.608173	1.047619
1	2.208859	3.127782	-0.13329
1	1.621528	2.163981	-1.48573
1	2.487968	1.120415	1.26499
1	3.410996	0.926419	-0.22456
1	-0.93358	-0.54374	2.524194
1	-0.76033	-1.89462	1.642592
1	1.235769	-1.89536	2.931469
1	1.33044	-0.14831	2.726187
1	2.98985	-1.29287	1.231166
1	1.69659	-2.27416	0.544868
8	-2.19544	0.717649	0.29298
7	-3.01348	-0.24712	-0.17562
8	-4.17871	-0.03564	0.013209

Table S3. uB3LYP/6-31+G(d,p) optimised Cartesian coordinates of complex **12** (η^1-ONO)

Atomic number	*x*	*y*	*z*
29	-0.12196	0.026683	0.148759
7	1.632681	-0.24594	-0.89745
6	1.951477	1.031618	-1.60393
6	0.684136	1.713267	-2.11956
7	-0.32003	1.867774	-1.0412
6	1.419565	-1.3616	-1.86778
6	0.510369	-2.43305	-1.27094
7	-0.76131	-1.8452	-0.78235
6	2.705622	-0.59654	0.082387
6	2.534886	0.176094	1.388821
7	1.158458	0.028693	1.914452
8	-1.5683	0.389248	1.279322
7	-2.78584	0.11971	0.772809
1	2.467662	1.685778	-0.89776
1	2.648373	0.845969	-2.43198
1	0.229056	1.113001	-2.91356
1	0.946149	2.682816	-2.56872
1	2.381752	-1.79789	-2.16659
1	0.967677	-0.94478	-2.7705
1	1.00336	-2.91678	-0.42145
1	0.325639	-3.21997	-2.01689
1	2.648593	-1.67071	0.272406
1	3.695728	-0.40337	-0.35124
1	3.286316	-0.16135	2.117888
1	2.715326	1.24277	1.223987
6	0.84392	1.112165	2.877729
1	-0.20278	1.02746	3.17138
1	1.488543	1.04625	3.765406
1	0.992678	2.084683	2.405023
6	0.984292	-1.26437	2.616773
1	-0.0612	-1.36237	2.915688
1	1.24209	-2.09937	1.960691
1	1.621767	-1.31621	3.510974
6	-1.42126	-2.78177	0.161318
1	-2.35715	-2.34181	0.506575
1	-1.63624	-3.74196	-0.32843
1	-0.77671	-2.96061	1.024093
6	-1.69583	-1.60839	-1.91127
1	-2.59004	-1.11537	-1.5273
1	-1.23347	-0.96613	-2.66444
1	-1.97665	-2.55736	-2.39021
6	-1.66556	2.095556	-1.62013

1	-2.39493	2.185335	-0.81436
1	-1.68319	3.01496	-2.22261
1	-1.95175	1.25248	-2.25121
6	-0.0015	3.024906	-0.17188
1	-0.70251	3.040195	0.665071
1	1.012896	2.94173	0.224834
1	-0.07981	3.970041	-0.72827
8	-3.68904	0.429024	1.502477

Table S4. uB3LYP/6-31+G(d,p) optimised Cartesian coordinates of complex **19** (η^1-$\underline{N}O_2$)

Atomic number	*x*	*y*	*z*
29	-0.05372	-0.01323	-0.14626
7	-0.00967	0.016611	2.127735
6	-1.20153	-0.74873	2.544383
6	-2.30645	-0.49211	1.559734
7	-2.06044	-0.13677	0.312805
6	-3.3018	-0.03677	-0.31847
6	-3.63708	0.317423	-1.63169
6	-4.98662	0.328899	-1.96102
6	-5.98527	0.004014	-1.0192
6	-5.66894	-0.34227	0.289738
6	-4.31193	-0.35428	0.614873
7	-3.63679	-0.63202	1.801992
6	-0.07294	1.447481	2.488555
6	0.730393	2.225973	1.486426
7	0.888611	1.81374	0.242327
6	1.649697	2.794794	-0.39642
6	2.118222	2.876082	-1.71354
6	2.875033	3.990608	-2.05205
6	3.163804	5.005877	-1.11598
6	2.703596	4.941967	0.194453
6	1.944947	3.819212	0.528917
7	1.344793	3.416908	1.719714
6	1.261435	-0.62216	2.521318
6	1.614816	-1.67827	1.514212
7	1.189087	-1.64111	0.264807
6	1.770367	-2.74128	-0.37338
6	1.662166	-3.19705	-1.69333
6	2.377402	-4.33907	-2.0321
6	3.177269	-5.02304	-1.09303
6	3.289471	-4.58765	0.222729
6	2.571846	-3.43833	0.55634
7	2.439842	-2.73326	1.749803
7	-0.30079	-0.05575	-2.06175
8	-0.27941	1.000465	-2.6978
8	-0.63817	-1.13449	-2.55558
1	-4.05922	-0.91117	2.676744
1	1.343058	3.930021	2.590458
1	2.890593	-2.95506	2.626812
1	-0.93627	-1.81246	2.523077
1	-1.5109	-0.51005	3.573307
1	-2.87525	0.568853	-2.36051
1	-5.28214	0.593932	-2.97121

1	-7.0272	0.025776	-1.32307
1	-6.43817	-0.58917	1.014725
1	0.273269	1.632492	3.516759
1	-1.12287	1.758367	2.438214
1	1.86963	2.109573	-2.43689
1	3.249528	4.088599	-3.06618
1	3.757371	5.860073	-1.42674
1	2.924208	5.724486	0.913732
1	1.218374	-1.03489	3.540562
1	2.038935	0.150697	2.520224
1	1.037299	-2.67535	-2.40783
1	2.317817	-4.71858	-3.04739
1	3.71738	-5.91208	-1.40363
1	3.902973	-5.1149	0.946606

Table S5. uB3LYP/6-31+G(d,p) optimised Cartesian coordinates of complex **19** (η^1-ONO)

Atomic number	*x*	*Y*	*z*
29	-0.06689	0.010168	0.098118
7	-0.1014	-0.05912	-2.14414
6	0.251131	-1.44821	-2.51047
6	1.271121	-1.96229	-1.53755
7	1.369049	-1.49737	-0.30584
6	2.385382	-2.23978	0.304977
6	2.928201	-2.16744	1.594493
6	3.949155	-3.05675	1.906454
6	4.432452	-3.99519	0.970943
6	3.911591	-4.07421	-0.31567
6	2.885413	-3.17971	-0.62259
7	2.154102	-2.96545	-1.78801
6	0.898872	0.932295	-2.60513
6	0.919087	2.078012	-1.63426
7	0.569429	1.917637	-0.37292
6	0.749855	3.153383	0.246387
6	0.517547	3.554533	1.567845
6	0.791582	4.87932	1.883772
6	1.27826	5.787946	0.920267
6	1.508218	5.405118	-0.39671
6	1.233599	4.072891	-0.70936
7	1.323407	3.349595	-1.89816
6	-1.48552	0.293656	-2.53577
6	-2.42363	-0.27862	-1.51294
7	-2.02728	-0.49702	-0.27494
6	-3.14488	-0.94709	0.424413
6	-3.29263	-1.30906	1.768671
6	-4.55422	-1.72517	2.175008
6	-5.64219	-1.78326	1.277837
6	-5.51028	-1.42179	-0.05883
6	-4.242	-1.00137	-0.46202
7	-3.7399	-0.57201	-1.69081
8	-0.33367	0.176316	1.940395
7	0.803063	0.146525	2.646803
8	0.640537	0.331755	3.826883
1	2.248424	-3.4773	-2.65436
1	1.649417	3.702476	-2.78739
1	-4.26711	-0.46737	-2.54673
1	-0.66084	-2.05219	-2.43625
1	0.607134	-1.52159	-3.54879
1	2.559843	-1.44128	2.30895
1	4.388965	-3.02892	2.898498

1	5.231481	-4.67049	1.260863
1	4.2847	-4.79313	-1.0384
1	0.698873	1.268846	-3.63293
1	1.878127	0.43987	-2.60838
1	0.145317	2.855155	2.307293
1	0.628401	5.226887	2.898979
1	1.478722	6.813605	1.214087
1	1.880675	6.107158	-1.13612
1	-1.72481	-0.04882	-3.55341
1	-1.56484	1.387182	-2.53277
1	-2.45486	-1.23655	2.452857
1	-4.71189	-2.00824	3.210999
1	-6.61001	-2.11467	1.641236
1	-6.35091	-1.4629	-0.74431

Figure S1. A graph showing the initial rate of NO_2^- catalytic turnover versus experimental reduction potential, *E*(SCE) / V for complexes **11** – **19**. Non-linear regression analysis (excluding complexes **15**, **17** and **19**) gives an excellent fit with a regression coefficient R^2-value of 0.980. The mechanistic details which relate complex redox potential and catalytic turnover rate remain uncertain.