Electronic Supplementary Information

Mechanistic Study on reduction of nitric oxide to nitrous oxide using a dicopper complex

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Table of Contents

Figure S1. Optimized structures of all intermediates in the closed-shell singlet, open-shell singlet and triplet states. Distances are given in a unit of Å.

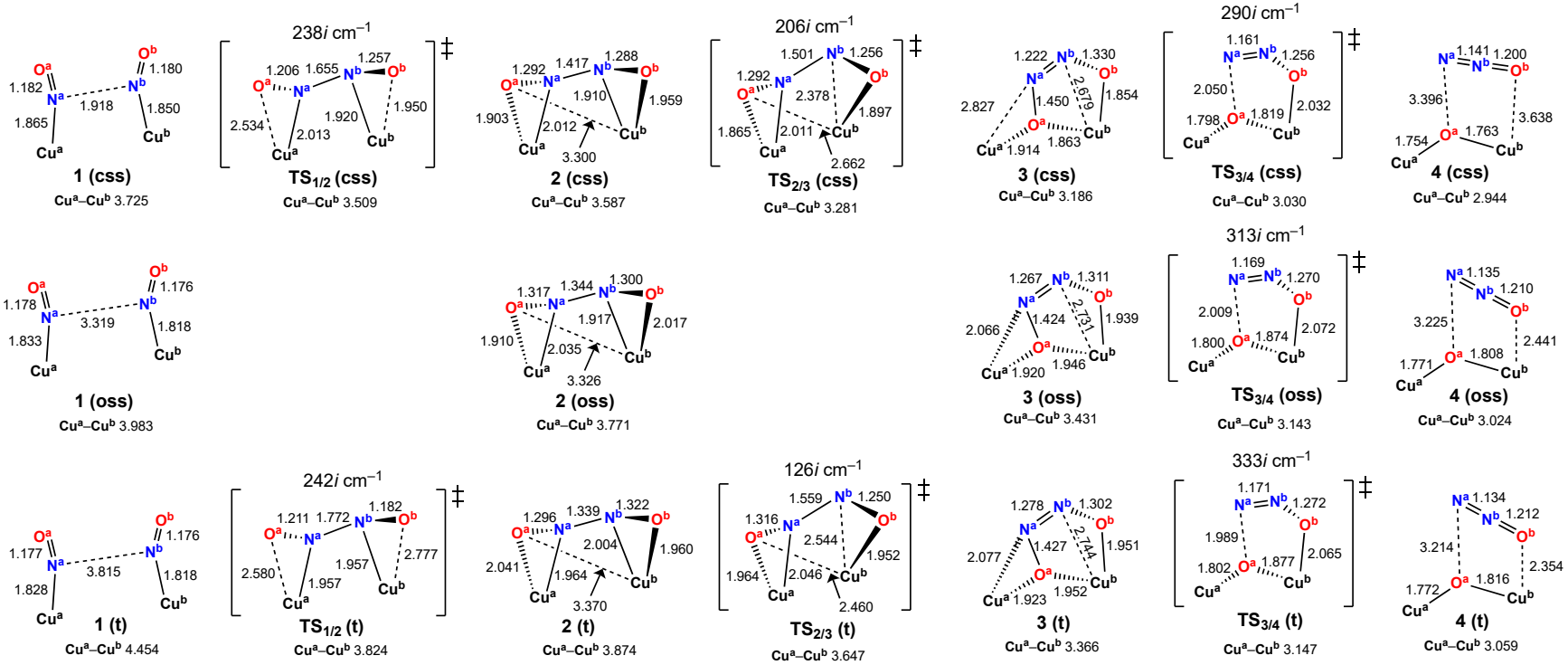


Figure S2. Optimized structures of neutral-, mono-anion- and di-anion N_2O_2 species.

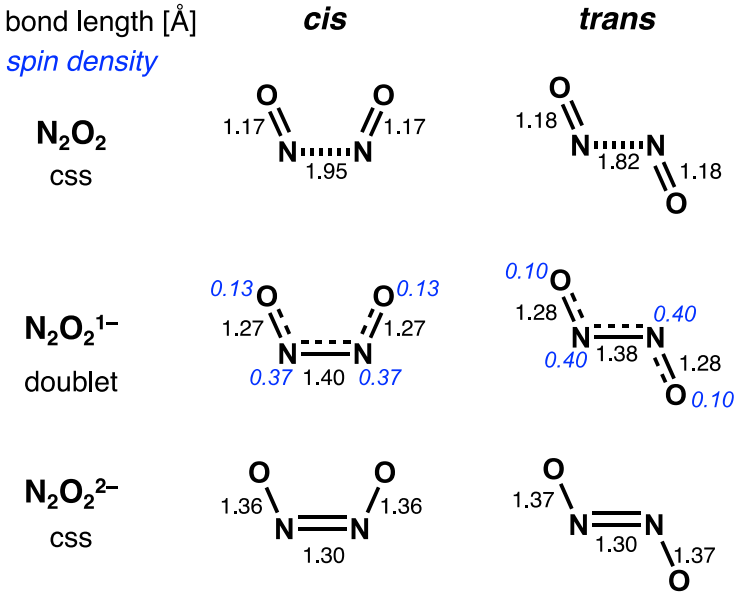


Table S1. Calculated Mulliken charges of all intermediates.

Closed-shell singlet

	1	**$TS_{1/2}$**	**2**	**$TS_{2/3}$**	**3**	**$TS_{3/4}$**	**4**
Cu^a	0.33	0.31	0.33	0.32	0.43	0.44	0.41
Cu^b	0.28	0.24	0.25	0.32	0.38	0.36	0.48
N^a	0.09	0.11	0.12	0.08	0.11	0.04	-0.08
N^b	0.09	0.08	0.13	0.11	0.11	0.29	0.35
O^a	-0.07	-0.09	-0.24	-0.21	-0.46	-0.57	-0.54
O^b	-0.07	-0.17	-0.24	-0.17	-0.29	-0.22	-0.21

Open-shell singlet

	1	**$TS_{1/2}$**	**2**	**$TS_{2/3}$**	**3**	**$TS_{3/4}$**	**4**
Cu^a	0.31	-	0.34	-	0.44	0.51	0.45
Cu^b	0.30	-	0.29	-	0.39	0.38	0.41
N^a	0.05	-	0.13	-	0.07	0.04	-0.08
N^b	0.06	-	0.14	-	0.07	0.24	0.40
O^a	-0.04	-	-0.30	-	-0.40	-0.60	-0.60
O^b	-0.03	-	-0.28	-	-0.32	-0.28	-0.21

Triplet

	1	**$TS_{1/2}$**	**2**	**$TS_{2/3}$**	**3**	**$TS_{3/4}$**	**4**
Cu^a	0.32	0.35	0.41	0.41	0.44	0.51	0.45
Cu^b	0.30	0.35	0.26	0.35	0.40	0.38	0.41
N^a	0.06	0.02	0.26	0.05	0.05	0.04	-0.07
N^b	0.06	0.09	0.00	0.07	0.08	0.24	0.40
O^a	-0.04	-0.10	-0.25	-0.27	-0.40	-0.58	-0.59
O^b	-0.03	-0.04	-0.31	-0.17	-0.30	-0.28	-0.21

Table S2. Calculated Mulliken spin densities of all intermediates.

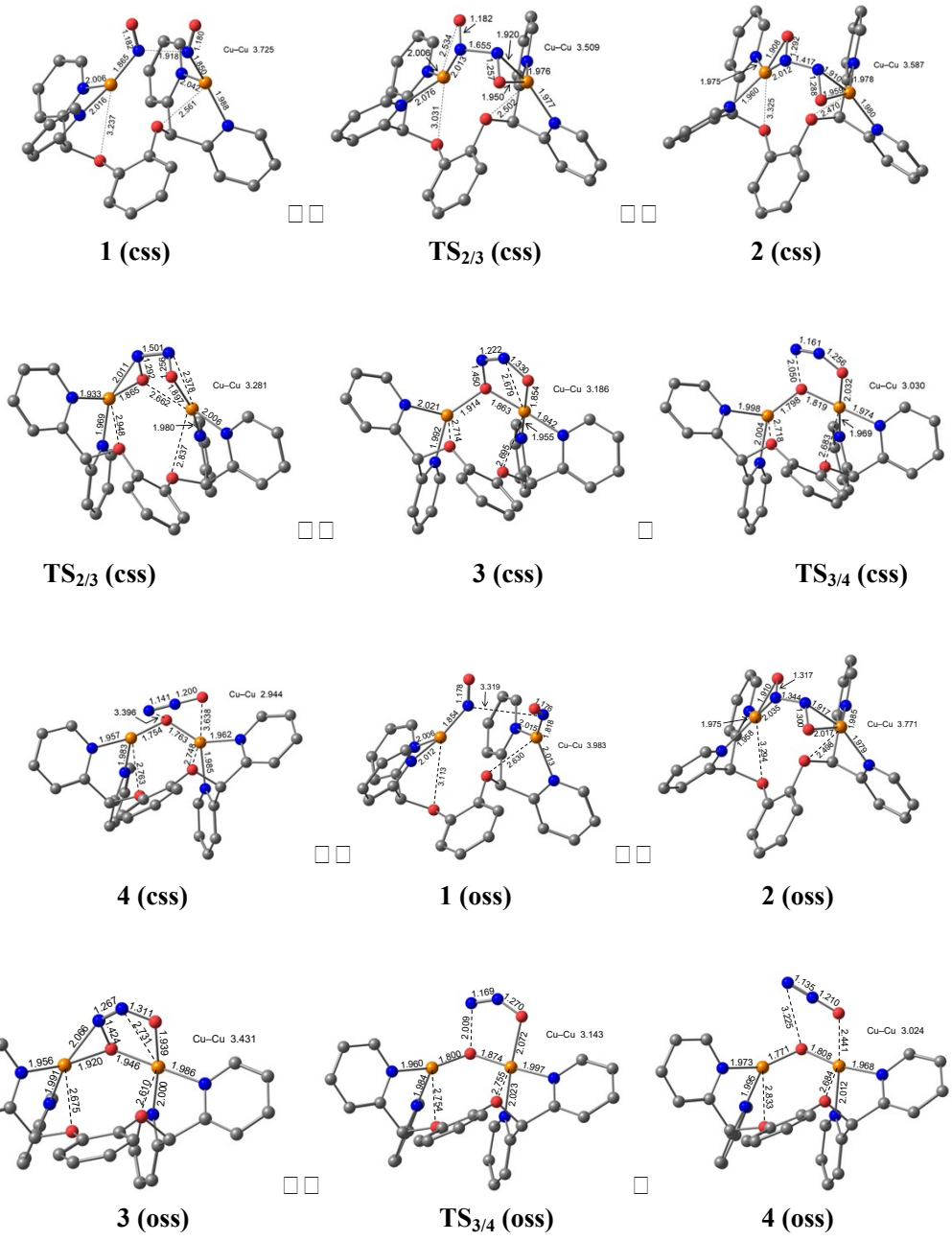
Open-shell singlet

	1	**$TS_{1/2}$**	**2**	**$TS_{2/3}$**	**3**	**$TS_{3/4}$**	**4**
Cu^a	0.01	-	0.37	-	0.53	0.62	0.51
Cu^b	-0.01	-	-0.34	-	-0.57	-0.56	-0.61
N^a	0.60	-	-0.17	-	0.02	0.02	-0.02
N^b	-0.61	-	0.11	-	0.03	0.03	0.01
O^a	0.38	-	0.00	-	0.03	-0.05	0.16
O^b	-0.38	-	0.03	-	-0.05	-0.08	-0.01

Triplet

	1	**$TS_{1/2}$**	**2**	**$TS_{2/3}$**	**3**	**$TS_{3/4}$**	**4**
Cu^a	0.01	0.26	0.48	0.45	0.53	0.62	0.50
Cu^b	0.01	0.06	0.38	-0.32	0.59	0.56	0.59
N^a	0.62	0.45	0.40	0.77	0.00	-0.05	0.02
N^b	0.61	0.29	-0.10	0.49	0.09	0.01	-0.01
O^a	0.38	0.51	0.44	0.44	0.20	0.39	0.55
O^b	0.38	0.34	0.10	0.11	0.20	0.09	0.02

Figure S3. Overall structures of all intermediates. The color of the balls indicates the type of atom, gray (C), blue (N), red (O), and orange (Cu). H atoms are omitted for clarity. Distances are given in a unit of Å.

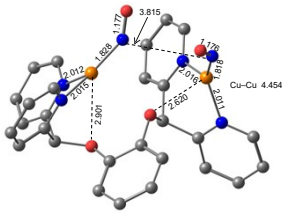


1 (css) **$TS_{2/3}$ (css)** **2 (css)**

$TS_{2/3}$ (css) **3 (css)** **$TS_{3/4}$ (css)**

4 (css) **1 (oss)** **2 (oss)**

3 (oss) **$TS_{3/4}$ (oss)** **4 (oss)**



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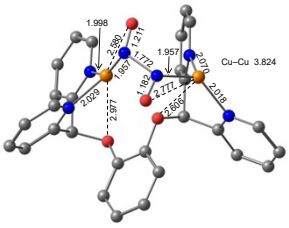

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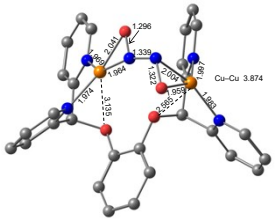

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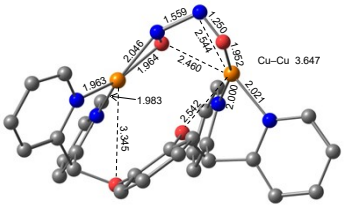

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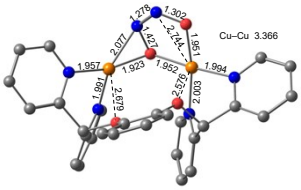

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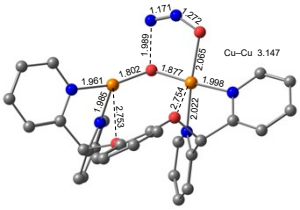
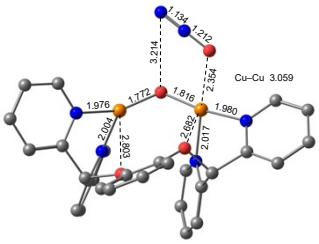


$TS_{3/4}$ (t)



4 (t)