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SUPPORTING INFORMATION

Mechanistic Analysis of Water Oxidation Catalyzed by Mononuclear Copper in Aqueous Bicarbonate Solutions

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Theoretical Methods

Calculations were performed at the density functional level of theory (DFT) using the local M11-L[1] functional. All calculations employed a basis set consisting of the Stuttgart relativistic pseudopotential[2] for copper atoms, augmented with 3 f functions having exponents of 5.10, 1.275, and 0.32, and the 6-311+G(d,p)[3] basis set for all other atoms. All structures were fully optimized accounting for aqueous solvation effects using the SMD continuum solvent model.[4] Following optimization, intrinsic reaction coordinate (IRC) calculations were performed to verify the connection between transition state structures and their associated minima, and frequency calculations were performed to calculate thermal contributions to Gibbs free energies for all structures; frequencies having values of less than 50 cm^{-1} were replaced by values of 50 cm^{-1} to avoid errors associated with the breakdown of the quantum-mechanical harmonic-oscillator approximation for such normal mode partition functions. All calculations were performed with the *Gaussian09* suite of electronic structure programs.[5]

For reactions in solution, standard free energies refer to a 1 M standard-state concentration for all species other than water. Compared to the conventional 1 atm standard state for gas-phase calculations, this requires the introduction of a concentration-change term of RTln(24.5), which is equal to 1.9 kcal/mol at 298 K. The corresponding concentration-change term for water molecules must reflect the 55.56 M concentration of the bulk solvent, and thus includes an additional 2.4 kcal/mol energy correction (total of 4.3 kcal/mol).[6]

For the computation of free energies associated with protonation or deprotonation reactions, the experimental proton solvation energy of –264.0 kcal/mol was used, which is appropriate for a common 1M H^+ concentration in both the gas phase and aqueous solution.[7,8] Free energies for acid/base reactions were used to compute pK_a values according to

$$pK_a = \frac{\Delta G_{aq}}{RT\ln(10)}$$

where ΔG_{aq} refers to the standard state free energy associated with the deprotonation reaction

$$AH_{aq} \rightarrow A^-_{(aq)} + H^+_{(aq)}$$

where AH is an acid, A^- is the conjugate base, H^+ is a proton, and all concentrations are taken to be 1 M.[9,10] As our interest here is in reactions taking place in aqueous solution buffered to a pH value of 8.2 (not the pH of 0 that would correspond to a 1 M proton concentration), we must correct for the reduced concentration of H^+ in all relevant free energies of reaction. This correction reduces the free energy of the aqueous proton by pH*1.36 kcal/mol, or about 11.2 kcal/mol for the experimental pH.

We also consider electrochemical reactions of the form

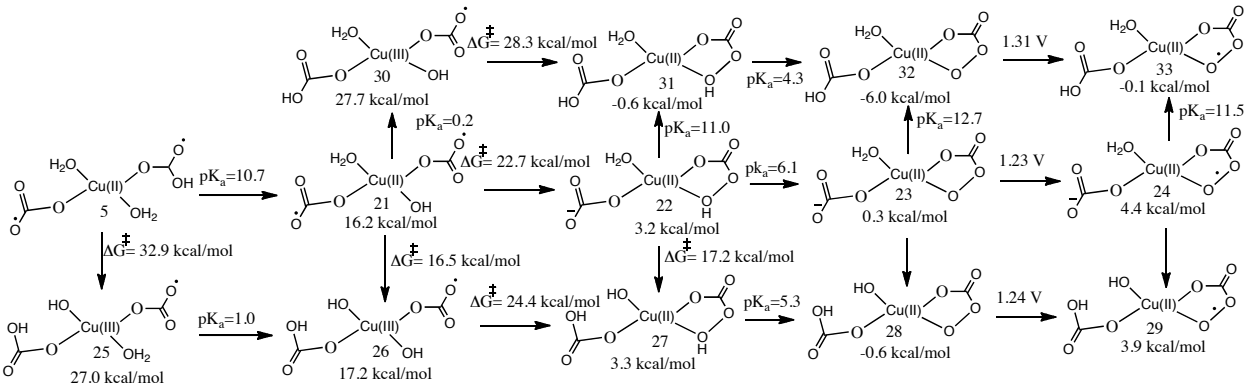
$$O_{(aq)} + n_e e^-_{(g)} + n_p H^+ \rightarrow R_{(aq)}$$

where O is the oxidized species, R is the reduced species, n_e is the number of electrons being transferred and n_p is the number of protons transferred. The standard reduction potential of this class of reaction ($E^o_{O|R}$) can be calculated using the equation

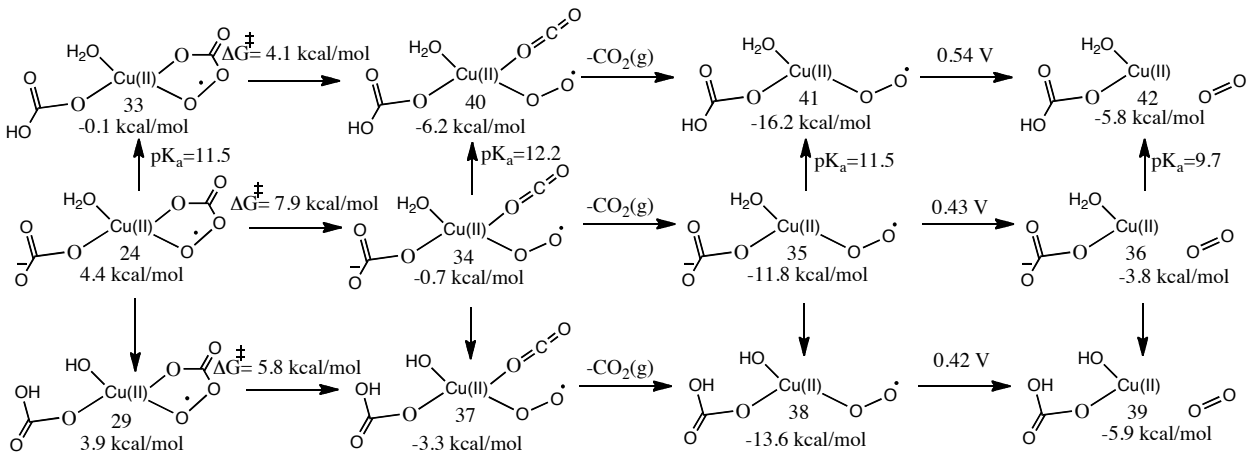
$$E^o_{O|R} = -\frac{\Delta G^o_{O|R} - \Delta G^o_{SHE}}{n_e F}$$

where $\Delta G^o_{O|R}$ is the standard state free energy of the redox reaction, F is the Faraday constant and ΔG^o_{SHE} is the free energy of standard hydrogen electrode (SHE), which we take as 4.28 eV.[11,12] An additional n_p*pH*0.0591V term can be added to the potential to account for a pH different from 0.

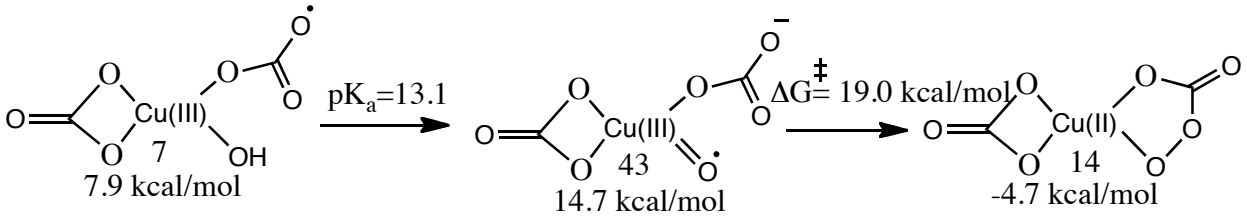
Alternative reaction sequence schemes



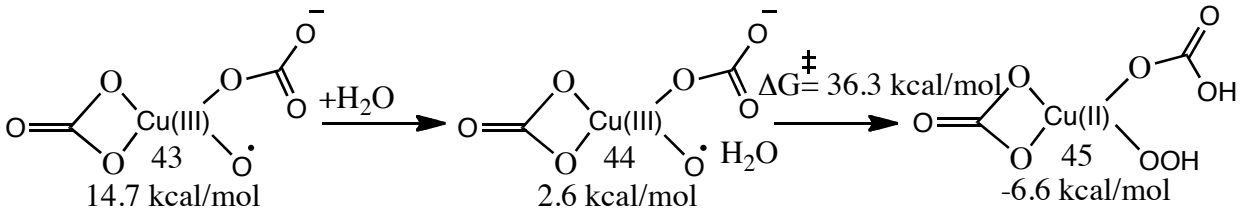
Scheme S1. Possible steps leading to the formation of a peroxycarbonate copper complex with a *monodentate* carbonate group and a water derived ligand at the newly open site (most favorable tautomers shown). The energies for all $2e^-$ oxidized structures and free energies of activation are given relative to **12**; the energies for all $3e^-$ oxidized structures are given relative to **16**. All energies are reported for pH = 8.2.



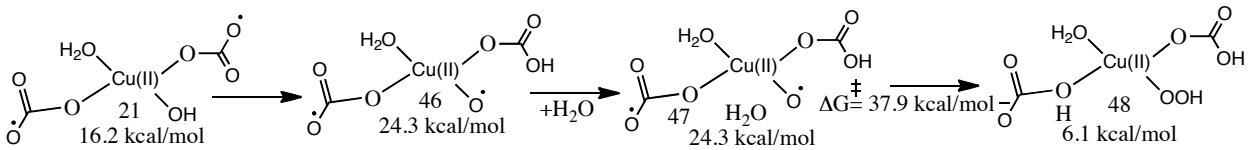
Scheme S2. Continuation from Scheme S1. The energies for all $3e^-$ oxidized structures and free energies of activation are relative to **16**; the energies for all $4e^-$ oxidized structures are relative to **19**. All energies are reported for pH = 8.2.



Scheme S3. Alternative mechanism for the formation of complex **14** involving deprotonation of the hydroxo-group in **7** and subsequent formation of an O–O bond. The energies of all structures and transition states are relative to **12** at pH = 8.2.



Scheme S4. Mechanism for the formation of a peroxo group via water nucleophilic attack on **43**. The energies of all structures and transition states are relative to **12** at pH = 8.2.



Scheme S5. Mechanism for the formation of a peroxo group via water nucleophilic attack on an oxo tautomer of **21**. The energies of all structures and transition states are relative to **12** at pH = 8.2.

Cartesian coordinates (Å)

Cartesian coordinates for all minima and transition-state structures reported in the main text follow. Electronic energies at the SMD/M11-L/SDD|6-311+G(d,p) are provided for each optimized structure.

1 (E_h = –879.440 31)

Cu	0.00037300	-0.00054600	-0.00541400
O	-0.52774600	-1.93197500	0.20237700
O	0.52837900	1.93061200	-0.21307600
H	0.14221100	2.41912700	0.51287700
H	-1.48423400	-1.88369300	0.02098800
O	1.76256800	-0.68298000	-0.09415900
C	2.83900700	-0.05719600	0.00949700
O	3.89824400	-0.86021100	-0.03692700
O	3.00414700	1.14804300	0.14278500
H	1.48256000	1.88333300	-0.02000000
H	-0.15070600	-2.41905800	-0.52919200
H	4.67723700	-0.30808500	0.04593700
O	-1.76087600	0.68288700	0.08384700
C	-2.83932000	0.05785400	-0.00147200
O	-3.00797500	-1.14834000	-0.12189200
O	-3.89656800	0.86302000	0.04952700
H	-4.67739100	0.31182400	-0.02162400

2 (E_h = –802.524 05)

Cu	-0.33516700	0.21943500	-0.06302900
O	1.27040700	-0.81797100	-0.08935700
O	0.55334800	2.00068100	-0.09127500
H	0.29698700	2.47757900	0.69690600
O	-2.11873600	0.82249800	0.02226300
C	-2.55057500	-0.39684600	0.03919400
O	-1.58918900	-1.25041700	-0.02909800
O	-3.73816200	-0.69501400	0.11388700
H	1.48572000	1.74517200	0.04720800
C	2.44255400	-0.40941000	0.01911200
O	2.83966500	0.74810100	0.09326800
O	3.33097700	-1.40114500	0.05524100
H	4.19878300	-1.00269600	0.13446500

3 (E_h = –725.605 37)

Cu	0.00042100	0.00077900	-0.00061000
O	-1.59846700	1.07203300	0.00024400
O	1.59727000	-1.07220600	0.00004500
C	2.31599200	-0.00023300	0.00027800
O	1.60032400	1.07329900	-0.00065800
O	3.54491400	-0.00223600	0.00139300
C	-2.31617600	-0.00085000	0.00035300
O	-1.60009900	-1.07357400	-0.00046300
O	-3.54533200	0.00067300	0.00117800

4 (E_h = –878.300 91)

Cu	-0.00002700	-0.00006000	-0.38101300
O	0.47795900	1.70096500	-0.40194900
O	-0.47833000	-1.70121600	-0.40180000
H	0.29743600	-2.16240600	-0.08110300
H	1.72053300	1.47071300	0.54719800
O	-1.71836800	0.55351400	-0.41768000
C	-2.69354200	0.09133300	0.27535000
O	-2.55494400	-1.05926400	0.87730500
O	-3.73460400	0.70178900	0.36777000
O	1.71790500	-0.55399000	-0.41621000
C	2.69385400	-0.09084800	0.27529000
O	2.55528100	1.05955300	0.87713400
O	3.73490200	-0.70153600	0.36704700
H	-1.71961900	-1.47012300	0.54774700
H	-0.29782100	2.16212900	-0.08123300

5 (E_h = –878.071 51)

Cu	0.00013400	0.00010100	0.00175900
O	-0.50544400	1.91386800	-0.21230700
O	0.50569700	-1.91368400	0.21341900
H	0.05529400	-2.42670900	-0.45783200
H	-1.44559300	1.96830700	0.00273800
O	1.76774100	0.70060000	0.10448100
C	2.85342400	0.09974600	-0.00383900
O	3.90178000	0.83489000	0.04099100
O	3.06022200	-1.10095200	-0.14856900
H	1.44477100	-1.96880200	-0.00597800
H	-0.05869900	2.42651400	0.46169100
O	-1.76743800	-0.70100200	-0.10098700
C	-2.85347900	-0.09986000	0.00176900
O	-3.06081700	1.10133200	0.14160900
O	-3.90165800	-0.83524700	-0.04353700

6 (E_h = –801.860 78)

Cu	-0.28737600	0.23792100	-0.07043800
O	1.19764600	-0.77471600	-0.22359700
O	0.52931600	1.80080400	-0.22131800
H	0.06822700	2.38615300	0.38044900
O	-1.97653900	0.83307500	0.02077400
C	-2.41806800	-0.38694500	0.07228000
O	-1.40138000	-1.18350500	0.03367900
O	-3.57405300	-0.70775200	0.14511500
H	1.92955100	1.28769700	0.24949700
C	2.41926800	-0.49902800	0.03470000
O	2.73540200	0.72499100	0.36287800
O	3.28072500	-1.35011200	-0.02116900

7 (E_h = –801.171 51)

Cu	-0.21797900	0.46184100	-0.17568800
O	1.44408500	0.00959500	-0.79619200
O	0.26702800	2.09536900	0.24212800
O	-1.92893400	0.64195900	0.35868600
C	-2.17367100	-0.59123400	0.03474900
O	-1.08541700	-1.10717000	-0.43547100
O	-3.23320100	-1.14633900	0.15057600
C	2.20729500	-0.52536800	0.04977600
O	1.80625500	-0.69542000	1.24109100
O	3.34803600	-0.90700800	-0.18177200
H	1.17683700	2.17830800	-0.04456500

8 (E_h = –725.417 13)

Cu	0.00001500	0.00010900	-0.05868300
O	1.46779400	-1.05060400	-0.00396300
O	-1.46800400	1.05061100	-0.00405500
C	-2.22486200	-0.00010200	0.03174000
O	-1.46789500	-1.05058400	-0.00431500
O	-3.42663000	-0.00014000	0.09085100
C	2.22488900	-0.00003900	0.03180600
O	1.46802500	1.05063600	-0.00416800
O	3.42663700	-0.00021000	0.09071600

9 (E_h = –725.144 23)

Cu	-0.00012000	-0.06881300	-0.00001000
O	-1.58641900	1.06496000	0.00001600
O	1.71638900	-1.07291100	0.00004200
C	2.28871800	0.03304900	0.00000500
O	1.58651500	1.06498000	-0.00005300
O	3.53958300	0.10783100	0.00002000
C	-2.28917600	0.03315300	0.00001000
O	-1.71581300	-1.07253200	0.00000600
O	-3.53947800	0.10746900	-0.00000700

TS structure for water displacement leading from **5** to **10** (E_h = –878.065 60)

Cu	0.00088400	-0.14316000	-0.07415400
O	1.76018900	-0.70482100	-0.43264600
O	0.75019600	2.48437400	-0.47895600
H	-0.01951500	2.52965900	0.08604100
O	-1.66856900	0.70219300	0.10646500
C	-2.79882000	0.18015300	0.07413500
O	-3.08971100	-1.00938400	-0.00565300
O	-3.80224300	0.97148800	0.13075600
H	1.42130900	2.09284600	0.08568800
C	2.74560300	-0.15942200	0.08999100
O	2.76277500	0.83171800	0.82546700
O	3.91236700	-0.63006100	-0.11869000
O	-0.54561700	-2.13376200	0.16594500
H	-1.50152000	-2.07125900	0.05395500
H	-0.24170900	-2.61794800	-0.60148100

10 (E_h = –801.604 28)

Cu	0.28128400	0.22599200	0.07049400
O	1.98097900	0.81954600	0.00786100
O	-1.21061000	-0.81734900	0.22547800
C	-2.37951900	-0.46016100	-0.05504300
O	-2.78441900	0.61980700	-0.45412500
O	-3.28638400	-1.35083800	0.10579800
C	2.43125500	-0.39046800	-0.07117600
O	1.40954500	-1.18404900	-0.03549500
O	3.57655900	-0.71680100	-0.16491900
O	-0.50788500	1.93636200	0.04875100
H	-1.45756200	1.78479300	-0.08310300
H	-0.43236700	2.31179500	0.92930700

TS structure for carbonate coordination leading from **7** to **11** (E_h = –801.168 57)

Cu	-0.11099200	0.50248400	-0.19877400
O	1.52812700	0.05135900	-0.87234900
O	0.39496100	2.10972400	0.28770700
O	-1.81471700	0.63713400	0.42731900
C	-2.07442400	-0.56284800	0.01377400
O	-1.01839700	-1.03210300	-0.56256200
O	-3.12387700	-1.13243000	0.14496600
C	2.00465900	-0.62110400	0.10101000
O	1.23566800	-0.66810000	1.11152000
O	3.08783000	-1.17185700	0.09150600
H	1.32059300	2.18186700	0.05087300

11 (E_h = –801.169 31)

Cu	-0.05636700	0.47818300	-0.20531300
O	1.56667400	-0.00733000	-0.91563200
O	0.50466400	2.08193000	0.26129100
O	-1.75717200	0.65118900	0.47838600
C	-2.09148200	-0.50700600	0.01451700
O	-1.09010900	-1.00941700	-0.61596100
O	-3.16910700	-1.02197100	0.16155600
C	1.95292300	-0.65420500	0.13038400
O	1.06935100	-0.58515800	1.05242200
O	3.00697600	-1.23926500	0.21738300
H	1.41579300	2.14014700	-0.03088900

12 (E_h = –1065.779 67)

Cu	0.27728800	-0.05297600	0.09980100
O	1.39062900	-1.16670800	-0.99976100
O	-0.01709700	-1.38979400	1.54529800
O	-0.41397800	1.45331300	1.06864700
C	-0.13026600	2.22932300	0.08235200
O	0.43106500	1.58037900	-0.87944600
O	-0.36067600	3.42670200	0.05452400
H	-0.96208700	-1.59263700	1.45529500
C	2.42656100	-0.79595400	-0.33120400
O	2.10108600	0.01007300	0.62309000
O	3.56756000	-1.15531500	-0.56144400
O	-1.44104000	-0.31685100	-0.81383600
C	-2.46163600	-0.84931200	-0.32918400
O	-2.58656100	-1.37400900	0.77572100
O	-3.48544800	-0.83871100	-1.08806600
H	0.42845500	-2.20803200	1.32086200

TS structure for O–O bond formation leading from **7** to **13** (E_h = –801.158 91)

Cu	0.26422500	0.16454800	-0.04514600
O	-1.23160800	-0.95452400	-0.04579100
O	-0.91583600	1.56240000	-0.11252500
O	1.95400800	0.93651000	0.02201000
C	2.48611800	-0.24202900	0.02945400
O	1.57388400	-1.15017100	-0.03309900
O	3.68019200	-0.45259900	0.08611200
C	-2.37831400	-0.45853400	0.02016900
O	-2.56168000	0.83162400	0.04752800
O	-3.42112800	-1.09294600	0.06831700
H	-0.93200500	1.98913900	0.75106000

13 (E_h = –801.187 58)

Cu	0.27416000	0.08483600	0.00864700
O	-1.25902700	-0.98936800	0.11371000
O	-1.23567900	1.51041000	-0.02182400
O	1.92714500	0.97039200	-0.03480300
C	2.56600100	-0.15768400	-0.01949700
O	1.76618400	-1.16284600	0.01292800
O	3.78865200	-0.24177100	-0.03454900
C	-2.38629900	-0.49387200	-0.00322000
O	-2.49088800	0.88027500	-0.09746100
O	-3.46714000	-1.02337400	-0.05986400
H	-1.26282800	1.89935300	0.86046300

14 (E_h = –800.734 62)

Cu	-0.21806900	0.08727300	0.00001100
O	1.32343500	-1.02607000	-0.00008300
O	1.02713400	1.46604000	0.00003700
O	-1.93141300	0.99405200	-0.00008700
C	-2.51704100	-0.15348300	-0.00001900
O	-1.67777800	-1.13410200	0.00010700
O	-3.73706600	-0.30344800	-0.00001100
C	2.39860300	-0.39152900	-0.00004000
O	2.34611000	0.94661600	0.00004600
O	3.52890900	-0.85069100	-0.00000600

15 (E_h = –800.539 49)

Cu	0.21043100	0.07062100	-0.01626800
O	-1.20988500	-0.98424600	0.00552000
O	-0.91852400	1.43366000	0.01746400
O	1.76804900	0.96580600	-0.00765800
C	2.42028000	-0.15487300	0.00630800
O	1.55688600	-1.12008300	-0.01113600
O	3.61494400	-0.27426800	0.03095100
C	-2.31583800	-0.35776000	0.00770000
O	-2.24619000	0.97062800	0.00123900
O	-3.40642300	-0.86302400	0.01208700

16 (E_h = –800.530 55)

Cu	0.23970600	0.05670300	0.00014600
O	-1.33507700	-1.03174900	0.00017600
O	-1.11521400	1.44654100	-0.00003300
O	1.87825100	0.98339600	-0.00007300
C	2.53257200	-0.13369900	0.00009300
O	1.73998500	-1.14931800	-0.00033200
O	3.75363500	-0.20636300	-0.00008700
C	-2.41499000	-0.45789400	0.00045700
O	-2.32550000	1.00476500	-0.00009900
O	-3.55320200	-0.80912600	-0.00049600

TS structure for CO_2 extrusion leading from **16** to **17** (E_h = –800.522 29)

Cu	0.26919300	0.08352200	0.00228600
O	-1.49092800	-1.14132600	0.13152500
O	-0.98664100	1.50961600	0.02150300
O	2.00767800	0.98920000	0.01143500
C	2.55765100	-0.17187300	-0.01621600
O	1.67950900	-1.12708200	-0.04326900
O	3.76673800	-0.37130900	-0.01742300
C	-2.56751700	-0.69375400	0.01044100
O	-2.22525600	1.21691000	-0.01276100
O	-3.71952500	-0.72955500	-0.09496700

17 (E_h = –611.940 87)

Cu	-0.46137200	-0.19949700	0.00002700
O	-2.99917700	-0.21555300	0.00048100
O	-2.07807300	0.68974900	-0.00074700
O	1.07813000	1.10026900	0.00043100
C	1.85220800	0.07948700	0.00004100
O	1.20234100	-1.04498800	-0.00017100
O	3.08009600	0.13408500	-0.00012300

18 (E_h = –461.460 30)

Cu	1.13851900	-0.00194200	-0.00007100
O	-0.48878800	1.10304200	0.00019900
C	-1.16076900	0.00963500	0.00008600
O	-0.38647900	-1.03846900	0.00022700
O	-2.38128800	-0.06476000	-0.00023300

References

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