

CHEMISTRY

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Supporting Information

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How Does Cu^{II} Convert into Cu^I? An Unexpected Ring-Mediated Single-Electron Reduction

**Davide Barreca,^[b] Ettore Fois,^[a] Alberto Gasparotto,^[c] Roberta Seraglia,^[b]
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How Does Cu^{II} Convert into Cu^I? An Unexpected Ring-Mediated Single-Electron Reduction

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Distances (Å)	[Cu(hfa) ₂ (TMEDA)]	[Cu(hfa)(TMEDA)] ⁺
Cu-N	2.062	2.016
Cu-O	1.976	1.913

Table S1. Comparison of the equatorial Cu-O and Cu-N distances for the [Cu(hfa)₂(TMEDA)] parent complex and the [Cu(hfa)(TMEDA)]⁺ ion in the calculated M06/D95+* minimum energy structures.

Tests of the adopted computational protocol

Unless otherwise specified, results reported in the text refer to M06/aug-cc-pVTZ wavefunctions and M06/D95+* optimized geometries. Convergence vs. basis set size was checked (Table S2), while Cu pseudopotential effects were previously tested.^[S1] The PBE0^[S2] hybrid functional yielded comparable results for structural parameters, electronic structure and energy differences pertaining to the [Cu(II)(hfa)(TMEDA)]⁺ → (Hhfa)[Cu(I)(TMEDA(-H))] ⁺⁺ reaction (Tables S3, S4, S5). Test calculations with the PBE functional^[S3] also led to similar optimized structures (Table S4). Tests at the MP2 and CCSD(T) levels of theory were performed on the smaller [Cu(TMEDA(-H))] ⁺⁺ system (Table S5).

Energies (kcal/mol)	D95+*	D95++**	6-311++g **	aug-cc-pVTZ
ΔE_r	39.0	36.6	36.0	34.5
ΔE_{TS}	62.3	60.2	60.5	59.8

Table S2. Energy differences for the [Cu(II)(hfa)(TMEDA)]⁺ (initial state) to (Hhfa)[Cu(I)(TMEDA(-H))] ⁺⁺ (final state) reaction calculated with the M06 hybrid density functional and different basis sets. ΔE_r = reaction energy = E(final state) - E(initial state); ΔE_{TS} = E(transition state) - E(initial state).

Energies (kcal/mol)	PBE^[S3]	PBE0^[S2]	M06^[S4]
ΔE_r	29.9	42.1	34.5
ΔE_{TS}	51.9	59.9	59.8

Table S3. Energy differences for the [Cu(II)(hfa)(TMEDA)]⁺ (initial state) to (Hhfa)[Cu(I)(TMEDA(-H))] (final state) reaction calculated with different density functional approximations and the aug-cc-pVTZ basis set. ΔE_r = reaction energy = E(final state) - E(initial state); ΔE_{TS} = E(transition state) - E(initial state).

d(Å)	PBE/pw	PBE^[S3]	PBE0^[S2]	M06^[S4]
Cu-N	2.090	2.079	2.063	2.046
Cu-N*	1.956	1.947	1.924	1.929
Cu-O*	3.000	3.013	3.087	2.911
Cu-O	1.875	1.874	1.870	1.873
Cu-C*	2.146	2.149	2.103	2.125
C*-H	1.473	1.475	1.487	1.459
Cu-H*	1.991	2.000	2.038	2.004
N*-C*	1.460	1.467	1.462	1.459
N-C1'	1.501	1.500	1.485	1.485
C1'-C1	1.531	1.537	1.528	1.525
C3-N	1.492	1.494	1.479	1.481
O*-H*	1.238	1.240	1.212	1.227

Table S4. Geometrical parameters for the optimized geometries of the transition state with different density functionals and the D95+* basis set (columns 2-4). The values calculated with the PBE functional and plane waves basis set (PBE/pw) are also reported for comparison. Atom labeling as in Figures 2 and 5a.

Tests for the geometry of $[\text{Cu}(\text{TMEDA}(-\text{H}))]^+$

In the search of the minimum energy structure of the ion detected at $m/z = 178.05250$ in the ESI/MS² spectrum of $[\text{Cu}(\text{hfa})(\text{TMEDA})]^+$ (Figure 1a), alternative geometries with respect to the six-membered ring N,C bidentate $[\text{Cu}(\text{TMEDA}(-\text{H}))]^+$ adduct (structure **(a)**, Figure 5) have been tested. The calculated energy minima, corresponding to a four-membered ring cycle (structure **(b)**) and to a N-monodentate system (structure **(c)**), are shown in Figures S1 and S2 respectively, whereas the relative energies of these candidate structures with respect to the most stable geometry (the six-membered ring system, structure **(a)**) are reported in Table S5. In all cases, copper exhibits a Cu(I) d^{10} configuration.

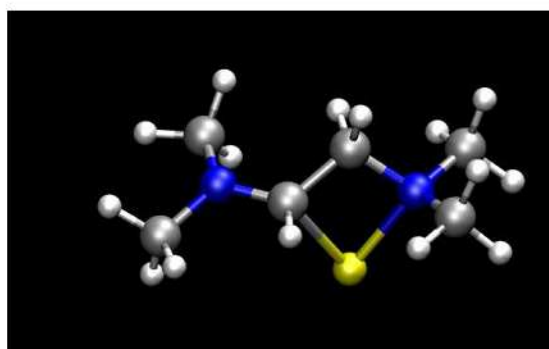


Figure S1. Four-membered ring structure **(b)** for the $m/z = 178.05250$ ion. Colors as in Figure 1.

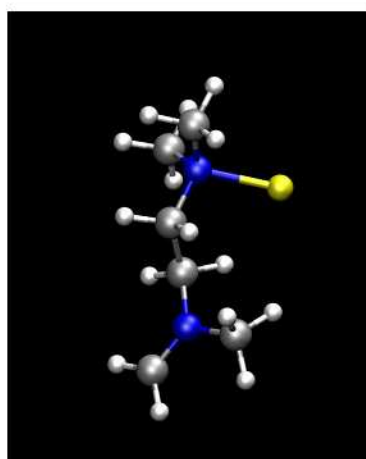


Figure S2. N-monodentate structure **(c)** for the $m/z = 178.05250$ ion. Colors as in Figure 1.

ΔE (kcal/mol)	MP2 D95+*	PBE0 D95+*	M06 D95+*	M06 aug-cc-pVTZ	CCSD(T) D95+* ⁽¹⁾	CCSD(T) D95+* ⁽²⁾
$\Delta E_{(b)}$	14.7	11.1	13.0	12.4	14.2	14.1
$\Delta E_{(c)}$	41.7	31.9	30.2	28.8	35.7	40.0
BE				118.8	101.0	

Table S5. Relative energies ΔE of structures **(b)** and **(c)** with respect to the six-membered ring minimum energy structure **(a)** of the $[\text{Cu}(\text{TMEDA}(-\text{H}))]^+$ ion calculated at different levels of theory, and binding energy (BE) of the minimum energy structure **(a)**. ⁽¹⁾: Energies calculated with CCSD(T) wavefunctions and M06 optimized geometries. ⁽²⁾: Energies calculated with CCSD(T) wavefunctions and MP2 optimized geometries.

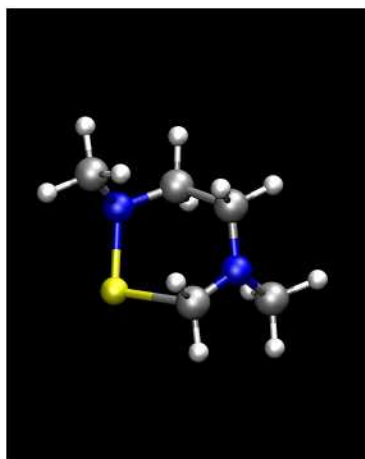


Figure S3. Minimum energy structure calculated for the $m/z = 163.02911$ ion of the MS^3 spectrum (compare Figure 1).

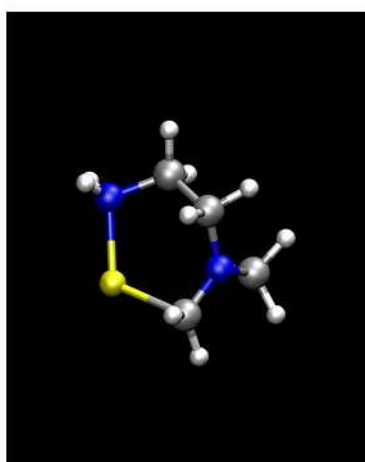


Figure S4. Minimum energy structure calculated for the $m/z = 150.02125$ ion of the MS^3 spectrum (compare Figure 1).

NBO results

Natural Bond Orbital (NBO) wavefunction analyses^[S5] were performed on the M06/aug-cc-pVTZ wavefunctions for the M06/D95+* optimized structures with the NBO 3.1 package^[S5] interfaced with G09.^[S6]

Donor	Acceptor	E(2) (kcal/mol)
Lp N	4p Cu	14.3
Lp N	4s Cu	15.3
Lp N*	4s Cu	4.0
π C*-N*	4s Cu	11.0
π C*-N*	4p Cu	3.5
d-Cu	π^* C*-N*	9.5

Table S6. NBO second order perturbation energies E(2) calculated for the six-membered ring minimum energy structure of $[Cu(TMEDA(-H))]^{+}$. Energies in kcal/mol. Atom labels in figure 5a. Lp = lone pair.

References

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