

Supplementary information

For

Copper complexes supported by an N_2S -tridentate ligand inducing efficient heterolytic O–O bond cleavage of alkylperoxide

Tetsuro Tano,^a Kaoru Mieda,^b Hideki Sugimoto,^a Takashi Ogura^b and Shinobu Itoh^{*a}

^a *Department of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: Shinobu@mls.eng.osaka-u.ac.jp*

^b *Research Institute of Picobiology, Graduate School of Life Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan.*

Synthesis

[Cu^{II}(L^{N2S})(Cl)](BF₄) (2^{N2S}•Cl). Cu^{II}Cl₂ (8.6 mg, 64 μmol) was added to a CH₃CN solution of L^{N2S} (15 mg, 64 μmol). After stirring the solution for 10 min at room temperature, NaBF₄ (7.0 mg, 64 μmol) was added to the solution. Addition of CH₂Cl₂ (30 mL) to the solution gave a white powder that was removed by filtration. The filtrate was concentrated to give green oily material. Single crystals were obtained for the X-ray analysis by diffusion of *n*-hexane into a CH₂Cl₂ solution of the green material (73 % yield, 20 mg). FT-IR (KBr) 1084 cm⁻¹ (BF₄⁻); ESI-MS (pos.) *m/z* = 334.0, calcd for [Cu^{II}(L^{N2S})(Cl)]⁺ 334.0; Anal. Calcd for [Cu^{II}(L^{N2S})(Cl)]BF₄•0.1H₂O (C₁₃H_{20.2}BClCuF₄N₂O_{0.1}S): C, 36.83; H, 4.80; N, 6.61. Found: C, 36.64; H, 4.76; N, 6.60.

[Cu^{II}(L^{N2S})(N₃)](BF₄) (2^{N2S}•N₃). To a methanol solution of L^{N2S} (12 mg, 51 μmol) was added Cu^{II}SO₄•5H₂O (13 mg, 51 μmol), when the color of solution turned dark blue. After stirring for 5 min, NaN₃ (3.3 mg, 51 μmol) was added to give the green solution. Then, NaBF₄ (5.6 mg, 51 μmol) was added to the solution, and the mixture was stirred for additional 5 min. Insoluble material was then removed by filtration. The filtrate was concentrated to give green oily material. Single crystals were obtained for the X-ray analysis by diffusion of *n*-hexane into a CH₂Cl₂ solution of the green material (67 % yield, 15 mg). FT-IR (KBr) 2078 cm⁻¹ (N₃⁻), 1073 cm⁻¹ (BF₄⁻); ESI-MS (pos.) *m/z* = 299.2, calcd for [Cu^I(L^{N2S})]⁺ 299.1; Anal. Calcd for [Cu^{II}(L^{N2S})(N₃)]BF₄•0.13H₂O (C₁₃H_{20.26}BClCuF₄N₅O_{0.13}S): C, 36.22; H, 4.74; N, 16.25. Found: C, 35.91; H, 4.75; N, 16.56.

[Cu^{II}(L^{N2S})(NO₂)(OTf)] (2^{N2S}•NO₂). To a methanol solution of L^{N2S} (6.5 mg, 23 μmol) was added Cu^{II}SO₄•5H₂O (6.0 mg, 23 μmol), when the color of solution turned dark blue. After stirring for 5 min, NaNO₂ (1.6 mg, 23 μmol) was added to give the green solution. Then, NaOTf (4.0 mg, 23 μmol) was added to the solution, and the mixture was stirred for additional 5 min. Insoluble material was then removed by filtration, and the filtrate was concentrated to give green oily material. Single crystals were obtained for the X-ray analysis by diffusion of *n*-hexane into a CH₂Cl₂ solution of the green material (43 % yield, 5.0 mg). FT-IR (KBr) 1477 cm⁻¹ (NO₂⁻), 1248, 1158 and 1030 cm⁻¹ (OTf⁻); ESI-MS (pos.) *m/z* =

448.2, calcd for $[\text{Cu}^{\text{II}}(\text{L}^{\text{N}2\text{S}})(\text{OTf})]^+$ 448.0; Anal. Calcd for $\text{Cu}^{\text{II}}(\text{L}^{\text{N}2\text{S}})(\text{NO}_2)(\text{OTf}) \cdot 0.5\text{H}_2\text{O}$
($\text{C}_{14}\text{H}_{21}\text{ClCuF}_3\text{N}_3\text{O}_{5.5}\text{S}_2$): C, 33.36; H, 4.20; N, 8.34. Found: C, 33.24; H, 3.96; N, 8.30.

Table S1. X-ray Crystallographic Data of Copper(I) Complexes **1^{N2S}**.

Compound	1^{N2S}
formula	C ₁₃ H ₂₀ CuF ₆ N ₂ PS
formula weight	444.88
crystal system	monoclinic
space group	<i>P</i> 2 ₁ /n (#14)
<i>a</i> , Å	9.0976(3)
<i>b</i> , Å	15.0804(6)
<i>c</i> , Å	12.5185(5)
<i>α</i> , deg	90
<i>β</i> , deg	105.9955(9)
<i>γ</i> , deg	90
<i>V</i> , Å ³	1650.6(1)
<i>Z</i>	4
<i>F</i> (000)	904.00
<i>D</i> _{calcd} , g/cm ⁻³	1.790
<i>T</i> , K	103
crystal size, mm	0.500 x 0.400 x 0.400
<i>μ</i> (MoKα), cm ⁻¹	16.071
2 <i>θ</i> _{max} , deg	54.9
no. of reflns measd	3774
no. of reflns obsd	3774 (All reflections)
no. of variables	217
<i>R</i> 1 ^a	0.0302
<i>wR</i> 2 ^b	0.1122
GOF	1.031

^a *RI* = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b *wR2* = $[\sum w (|F_o|^2 - |F_c|^2)^2 / \sum w (F_o^2)^2]^{1/2}$

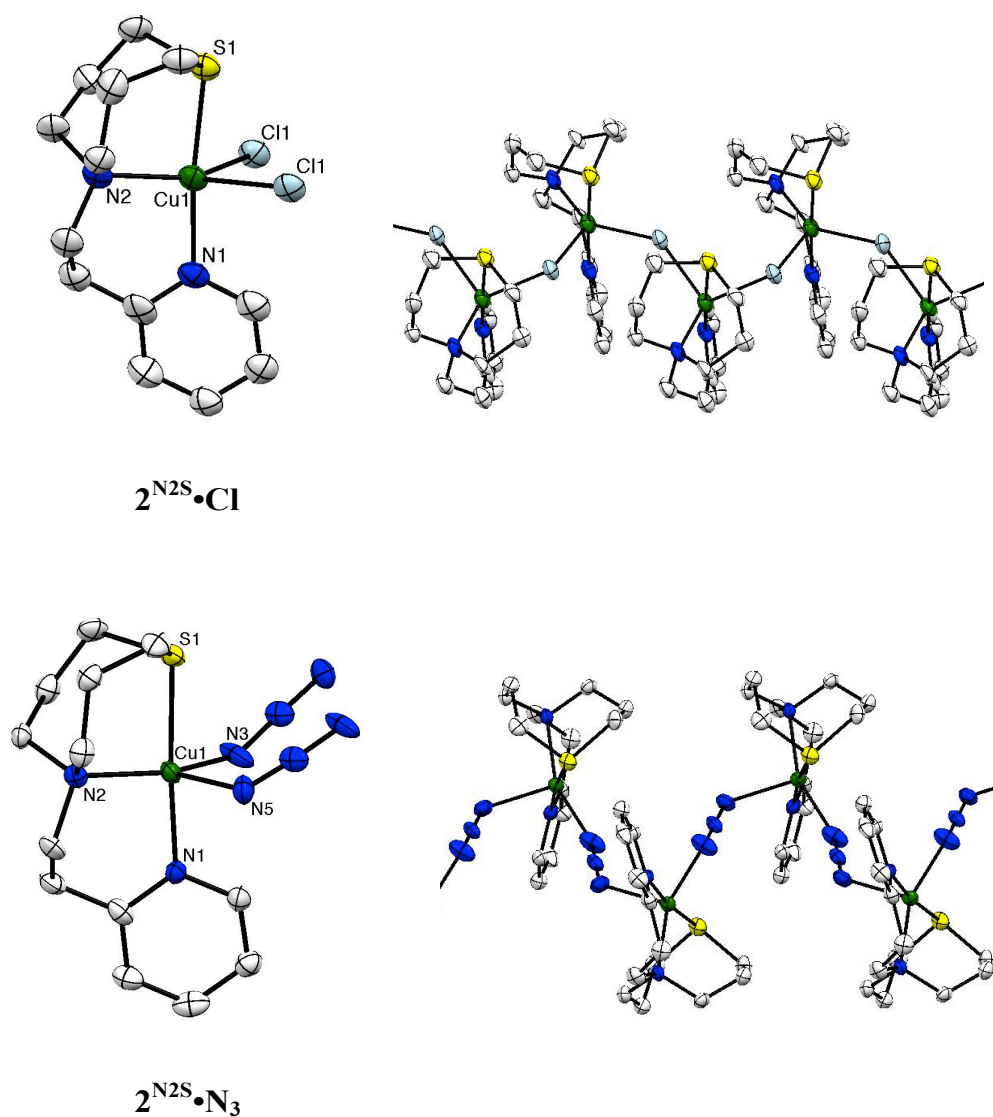


Fig. S1 ORTEP drawings of $2^{N_2S} \cdot Cl$ and $2^{N_2S} \cdot N_3$ (left) and their linear chain structures (right) showing 50 % probability thermal ellipsoids. Counter anion (BF_4^-) and hydrogen atoms are omitted for clarity.

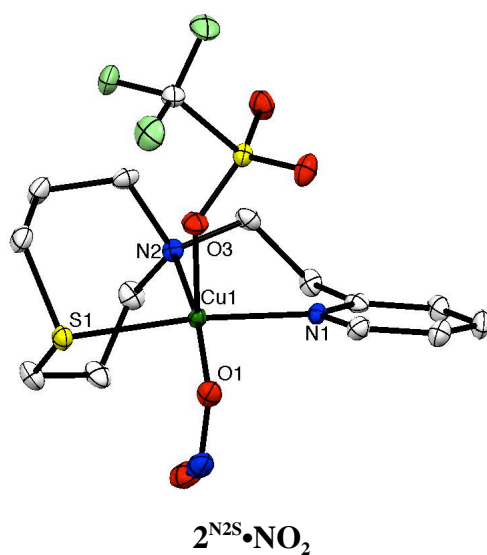


Fig. S2 ORTEP drawings of $2^{N2S} \cdot NO_2$ showing 50 % probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table S2. X-ray Crystallographic Data of Copper(II) Complexes **2^{N2S}•Cl**, **2^{N2S}•N₃**, **2^{N2S}•NO₂** and **2^{N2S}•OTf**.

Compound	2^{N2S}•Cl	2^{N2S}•N₃
formula	C ₁₃ H ₂₀ BClCuF ₄ N ₂ S	C ₂₆ H ₄₀ B ₂ Cu ₂ F ₈ N ₁₀ S ₂
formula weight	422.18	857.49
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)
<i>a</i> , Å	10.430(2)	19.271(2)
<i>b</i> , Å	22.179(5)	7.1058(4)
<i>c</i> , Å	7.084(2)	25.114(2)
<i>α</i> , deg	90	90
<i>β</i> , deg	92.797(3)	103.692(2)
<i>γ</i> , deg	90	90
<i>V</i> , Å ³	1636.6(5)	3341.2(4)
<i>Z</i>	4	4
<i>F</i> (000)	860.00	1752.00
<i>D</i> _{calcd} , g/cm ⁻³	1.713	1.704
<i>T</i> , K	103	103
crystal size, mm	0.600 x 0.200 x 0.100	0.400 x 0.400 x 0.100
<i>μ</i> (MoKα), cm ⁻¹	16.627	14.808
2 <i>θ</i> _{max} , deg	55.0	55.0
no. of reflns measd	15561	31522
no. of reflns obsd	3744 (All reflections)	7660 (All reflections)
no. of variables	228	491
<i>RI</i> ^a	0.1626	0.0561
<i>wR2</i> ^b	0.4008	0.1528
GOF	1.000	1.142

$$^a RI = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum w (|F_o|^2 - |F_c|^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

Table S2. X-ray Crystallographic Data of Copper(II) Complexes **2^{N2S}•Cl**, **2^{N2S}•N₃**, **2^{N2S}•NO₂** and **2^{N2S}•OTf** (continued).

Compound	2^{N2S}•NO₂	2^{N2S}•OTf
formula	C ₁₄ H ₂₂ CuF ₃ N ₃ O ₆ S ₂	C ₁₅ H ₂₀ CuF ₈ N ₂ O ₆ S ₃
formula weight	513.01	598.05
crystal system	triclinic	monoclinic
space group	<i>P</i> -1 (#2)	<i>P</i> 2 ₁ /c (#14)
<i>a</i> , Å	7.6907(4)	7.172(2)
<i>b</i> , Å	8.7410(5)	20.845(4)
<i>c</i> , Å	15.2512(7)	15.117(3)
<i>α</i> , deg	84.088(2)	90
<i>β</i> , deg	78.235(2)	103.769(4)
<i>γ</i> , deg	74.662(2)	90
<i>V</i> , Å ³	966.66(8)	2195.0(7)
<i>Z</i>	2	4
<i>F</i> (000)	526.00	1212.00
<i>D</i> _{calcd} , g/cm ⁻³	1.713	1.810
<i>T</i> , K	103	103
crystal size, mm	0.400 x 0.300 x 0.100	0.500 x 0.200 x 0.200
<i>μ</i> (MoKα), cm ⁻¹	14.124	13.673
2 <i>θ</i> _{max} , deg	54.9	55.0
no. of reflns measd	9398	21107
no. of reflns obsd	4363 (All reflections)	5020 (All reflections)
no. of variables	262	298
<i>RI</i> ^a	0.0377	0.0749
<i>wR2</i> ^b	0.1430	0.2053
GOF	1.188	1.083

$$^a RI = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum w (|F_o|^2 - |F_c|^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $2^{N_2S} \cdot Cl$, $2^{N_2S} \cdot N_3$, and $2^{N_2S} \cdot NO_2$.

$2^{N_2S} \cdot Cl$			
Cu(1)–Cl(1)	2.388(3)	Cu(1)–Cl(1)*	2.572(3)
Cu(1)–S(1)	2.310(3)	Cu(1)–N(1)	2.016(8)
Cu(1)–N(2)	2.068(8)		
Cl(1)–Cu(1)–Cl(1)*	98.50(9)	Cl(1)–Cu(1)–S(1)	85.52(9)
Cl(1)–Cu(1)–N(1)	90.0(3)	Cl(1)–Cu(1)–N(2)	140.2(3)
Cl(1)*–Cu(1)–S(1)	81.65(9)	Cl(1)*–Cu(1)–N(1)	94.3(3)
Cl(1)*–Cu(1)–N(2)	119.9(3)	S(1)–Cu(1)–N(1)	173.4(3)
S(1)–Cu(1)–N(2)	89.6(3)	N(1)–Cu(1)–N(2)	96.9(3)
$2^{N_2S} \cdot N_3$			
Cu(1)–S(1)	2.3306(13)	Cu(1)–N(1)	2.036(4)
Cu(1)–N(2)	2.078(4)	Cu(1)–N(5)*	2.265(4)
Cu(1)–N(3)	2.029(4)		
S(1)–Cu(1)–N(1)	173.24(10)	S(1)–Cu(1)–N(2)	88.85(11)
S(1)–Cu(1)–N(5)*	91.71(11)	S(1)–Cu(1)–N(3)	86.51(13)
N(1)–Cu(1)–N(2)	96.98(14)	N(1)–Cu(1)–N(5)*	90.39(14)
N(1)–Cu(1)–N(3)	86.78(15)	N(2)–Cu(1)–N(5)*	102.36(13)
N(2)–Cu(1)–N(3)	155.92(15)	N(5)*–Cu(1)–N(3)	101.39(15)
$2^{N_2S} \cdot NO_2$			
Cu(1)–S(1)	2.3343(10)	Cu(1)–O(1)	2.012(2)
Cu(1)–N(1)	2.037(3)	Cu(1)–N(2)	2.076(3)
Cu(1)–O(5)	2.343(3)		
S(1)–Cu(1)–O(1)	85.01(8)	S(1)–Cu(1)–N(1)	172.73(7)
S(1)–Cu(1)–N(2)	89.03(8)	S(1)–Cu(1)–O(3)	89.65(10)
O(1)–Cu(1)–N(2)	92.05(15)	O(3)–Cu(1)–N(2)	102.01(13)
O(1)–Cu(1)–N(1)	88.17(10)	N(1)–Cu(1)–N(2)	97.52(10)

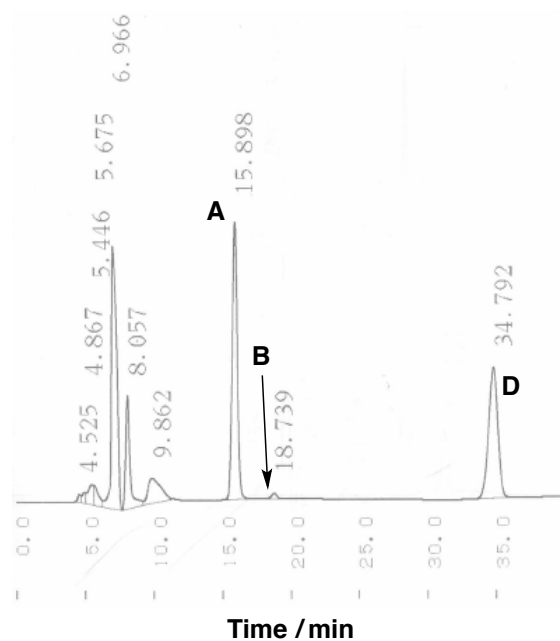


Fig. S3 HPLC diagram of the organic products derived from the reaction of 1^{N2S} (0.5 mM) and cumene hydroperoxide (CmOOH, 0.5 mM). **Peak A**: cumyl alcohol (CmOH); **Peak B**: acetophenone (PhC(O)Me); **Peak D**: anisole (internal standard).

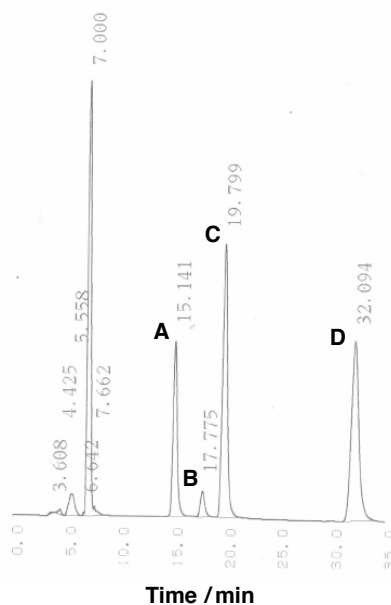


Fig. S4 HPLC diagram of the organic products derived from the reaction of 1^{N3} (0.5 mM) and cumene hydroperoxide (CmOOH, 0.5 mM). **Peak A**: cumyl alcohol (CmOH); **Peak B**: acetophenone (PhC(O)Me); **Peak C**: CmOOH; **Peak D**: anisole (internal standard).

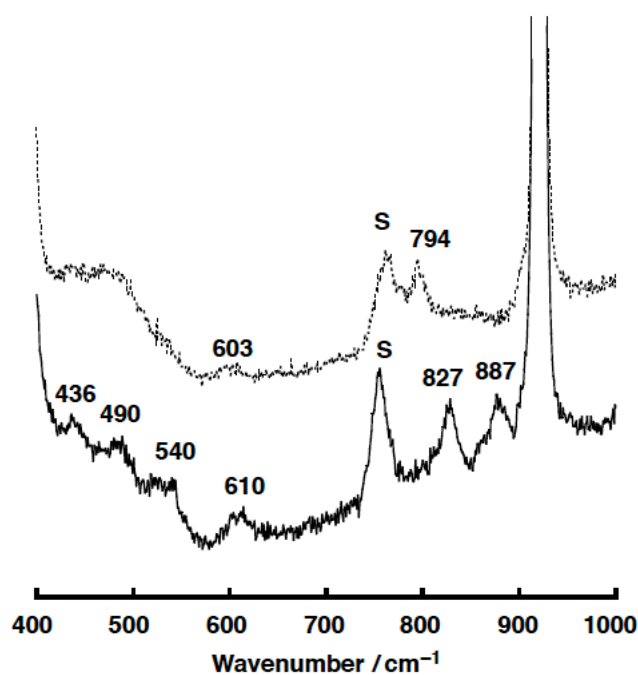


Fig. S5 Resonance Raman spectra of the intermediate derived from the reaction of 1^{N2S} (3.0 mM) with CmOOH (3.0 mM) generated by using Cm 16 O $_2$ H (solid line, below) and Cm 18 O $_2$ H (dotted line, above) obtained with $\lambda_{max} = 441.6$ nm in CH $_3$ CN at -40°C ; s denotes the solvent band.

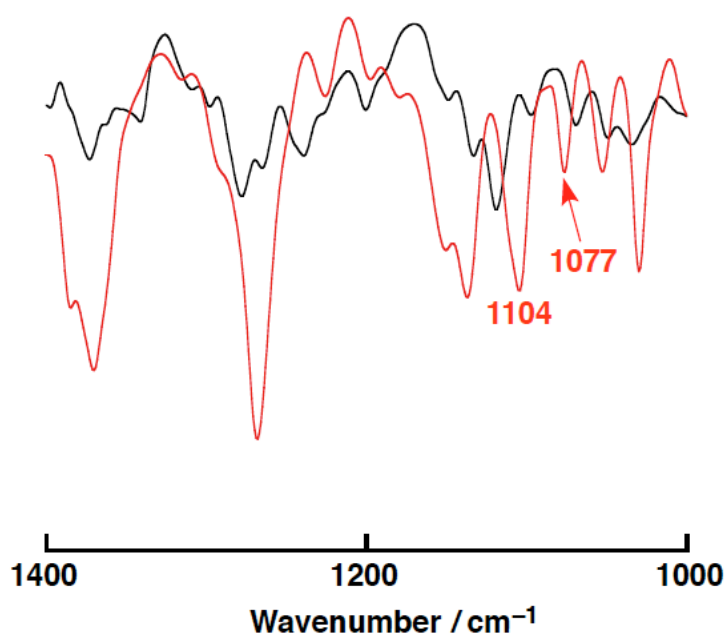


Fig. S6 IR spectra of ligand oxidation product L N2SO (red line) and L N2S (black line).

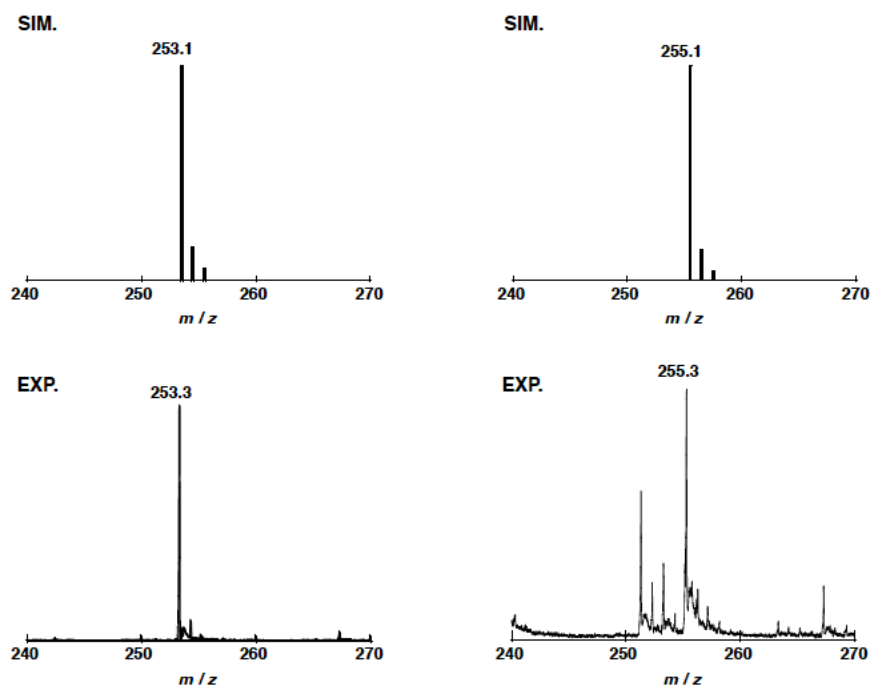


Fig. S7 Experimental (bottom) and simulated (top) peak envelopes in the positive-ion ESI-MS spectra of the ligand oxidation product derived from the reaction mixture of 1^{N2S} and CmOOH in acetone. (left) with Cm 16 O $_2$ H and (right) with Cm 18 O $_2$ H.

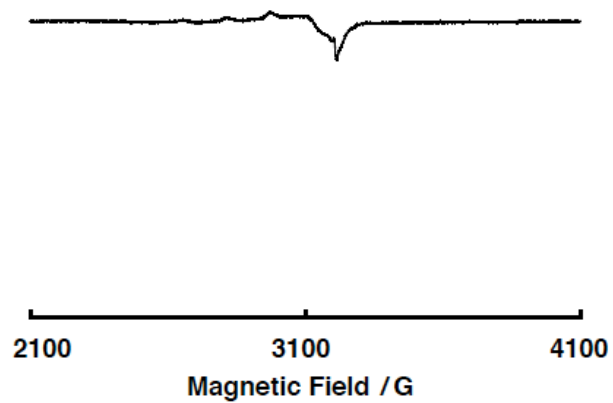


Fig. S8 The EPR spectrum of the final reaction mixture of **1**^{N2S} (0.5 mM) with an equimolar amount of CmOOH in acetone (after warming up to 30 °C). A small amount of copper(II) byproduct (9 % based on the starting copper complex) is involved.