Supporting information

Cleavage of the C-S bond with the formation of a binuclear copper complex with 2-thiolato-3-phenyl-5-(pyridine-2-ylmethylene)-3,5-dihydro-4H-imidazole-4-on. A new mimic of the active site of N_2O reductase

Supplementary materials and methods.

All preparations were carried out in reagent grade solvents. All chemicals used in the syntheses were obtained from Acros or Aldrich and were used without further purification. 2-thioxo-3-phenyl-5-(pyridine-2-ylmethylene)-3,5-dihydro-4H-imidazole-4-on was synthesized according to the previously reported procedure [A.G. Majouga, E.K. Beloglazkina, S.Z. Vatsadze, A.A. Moiseeva, F.S. Moiseev, K.P. Butin and N.V. Zyk. *Mend. Comm.*, *2004*, **14**, 115]

Elemental analyses were carried out on a Vario MICRO cube CHNS/O Elementar. ^{1}H NMR spectra were recorded on a *Bruker AV* 400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent. Data are reported in the following order: chemical shift (δ) values are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ = 7.26 ppm for ^{1}H NMR); coupling constants (*J*) are given in Hertz (Hz). X-ray diffraction was measured with a CAD4 diffractometer at 293 K [graphite monochromator, l(MoKα) = 0.71073 Å, w-scan with a step of 0.3°]. The structure was solved by a direct method SIR2002 (solution, Burla, M.C., Camalli, M., Carrozzini, B., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R., J. Appl. Cryst, *2003*, **36**, 1103) and JANA2000 (refinement, Petricek, V., Dusek, M. & Palatinus L. (2000). Jana2000. Structure Determination Software Programs. Institute of Physics, Praha, Czech Republic. This program is available free of charge via http://jana.fzu.cz/). Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC 723648 contain supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.uk/ conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

Electrochemistry

Ferrocene (Aldrich), anhydrous CH_3CN and anhydrous dimethylformamide (Aldrich) were used as received. Cyclic voltammetric studies were carried out using an Autolab PGSTAT20 potentiostat, using a three-electrode arrangement in a single compartment cell. A glassy carbon working electrode, a Pt wire secondary electrode and a saturated calomel reference electrode (chemically isolated from the test solution *via* a bridge tube containing electrolyte solution and

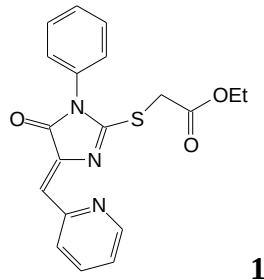
fitted with a porous Vycor frit) were used in the cell. Experiments were performed under an atmosphere of argon. Sample solutions were prepared under an atmosphere of argon using Schlenk line techniques and consisted of a 0.2 M $[NBu_4][BF_4]$ solution as the supporting electrolyte and a 1 mM solution of the test compound. Redox potentials were referenced *vs*. the Fc^+/Fc couple, which was used as an internal standard. Compensation for internal resistance was not applied.

Electrochemical studies in the presence of N_2O and control experiments in the absence of N_2O were carried out in CH_3CN solution in the presence of 0.1 M $[NBu_4][ClO_4]$ as supporting electrolyte on a 0.2 mM sample solution. Measurements were carried out on a PI-50-1.1. potentiostat in a three-electrode cell with a glassy carbon (2 mm in diameter) disk polished by Al_2O_3 as working electrode, Pt plate as a secondary electrode and Ag/AgCl/KCl(sat.) as reference electrode.

UV/Vis spectroelectrochemical experiments were carried out with an optically transparent electrochemical (OTE) cell (modified quartz cuvette, optical pathlength 0.5 mm). A three-electrode configuration, consisting of a Pt/Rh gauze working electrode, a Pt wire secondary electrode (in a fritted PTFE sleeve) and a saturated calomel electrode (chemically isolated from the test solution *via* a bridge tube containing electrolyte solution and terminated in a porous frit) were used in the cell. The potential at the working electrode was controlled by a Sycopel Scientific Ltd. DD10M potentiostat. UV/Vis data were recorded on a Perkin Elmer Lambda 16 spectrometer. The cavity was purged with nitrogen gas and cooled down to 0 °C, temperature control at the sample was achieved by flowing cooled nitrogen gas across the surface of the cell. Sample solutions were prepared under an atmosphere of argon using Schlenk line techniques and consisted of a 0.2 M $[NBu_4][BF_4]$ solution as the supporting electrolyte and a 0.54 mM solution of the test compound. The test species in solution was reduced at constant potential and the redox process was considered complete when consecutive spectra were identical. The reversibility of the process was investigated by applying a potential at the working electrode sufficient to re-oxidise the electrogenerated product. The process was considered to be reversible, under the conditions of the experiment, if the spectral profile of the starting material was reproduced.

Synthesis of the ligands 1-5 (general procedure)

2-Thioxo-3-phenyl-5-(pyridine-2-ylmethylene)-3,5-dihydro-4H-imidazole-4-on (1.12 g, 0.004 mol) and corresponding methyl or ethyl ester of 2-bromoacetic (**1**), 2-bromopropionic (**2**), 2-bromo butyric (**3**), 3-bromopropionic (**4**) or 5-bromovaleric (**5**) acid (0.004 mol) were dissolved in a water/ethanol mixture (1:1, 10 ml). A solution of NaOH (0.16 g, 0.004 mol in 10 ml H_2O) was slowly added at room temperature and resulting mixture was refluxed for two hours. The solid formed was collected by filtration, washed with ethanol and dried under vacuum.



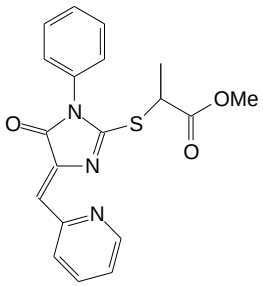
1

Ethyl [[(4Z)-5-oxo-1-phenyl-4-(2-pyridylmethylene)-4,5-dihydro-1*H*-imidazol-2-yl]thio]-acetate 1. M.p. 168 °C.

^{1}H NMR δ_H [400.13 MHz, DMSO-d_6, 298 K]: 8.76 (d, J = 7.8 Hz, 1H, $H_{\alpha'}$-Py), 8.68 (d, J = 4.1 Hz, 1H, H_{β}-Py), 7.78 (td, J_1 = 7.4 Hz, J_2= 1.8 Hz, 1H, $H_{\gamma'}$-Py), 7.48 (m, 4H), 7.36 (m, 5H, Ph), 7.21 (s, 1H, CH=), 4.23 (q, J = 6.8 Hz, 2H, -CH_2-), 4.05 (s, 2H, CH_2), 1.27 (t, J = 6.9 Hz, 3H, CH_3).

IR (KBr, ν, cm^{-1}): 1735 (C=O), 1640 (C=N), 1600 (C=C).

Anal. Calc. for $C_{19}H_{17}N_3O_3S$: C 62.11%; H 4.66%; N 11.44%. Found: C 62.31%; H 4.60%; N 11.57%.



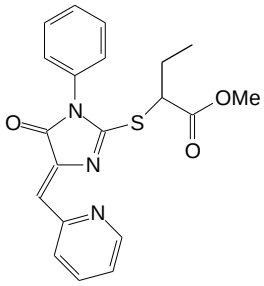
2

Methyl 2-[[(4Z)-5-oxo-1-phenyl-4-(2-pyridylmethylene)-4,5-dihydro-1*H*-imidazol-2-yl]thio]-propionate 2. M.p. 137 °C.

^{1}H NMR δ_H [400.13 MHz, DMSO-d_6, 298 K]: 8.83 (d, J = 9.0 Hz, 1H, $H_{\alpha'}$-Py), 8.71 (d, J = 4.4Hz, 1H, H_{β}-Py), 7.81 (td, J_1 = 7.6 Hz, J_2 = 1.7 Hz, 1H, $H_{\gamma'}$-Py), 7.36-7.57 (m, 6H), 7.24 (s, 1H, CH=), 4.68 (q, J = 7.4 Hz, 1H, -CH-), 3.80 (s, 3H, CH_3), 1.73 (d, J = 7.4 Hz, 3H, CH_3).

IR (KBr, ν, cm^{-1}): 1740 (C=O), 1640 (C=N), 1595 (C=C).

Anal. Calc. for $C_{19}H_{17}N_3O_3S$: C 62.11%; H 4.66%; N 11.44%. Found: C 61.81%; H 4.77%; N 11.32%.



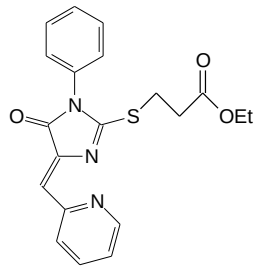
3

Methyl 2-[[(4Z)-5-oxo-1-phenyl-4-(2-pyridylmethylene)-4,5-dihydro-1*H*-imidazol-2-yl]thio]-butanoate 3. M.p. 124 °C.

^{1}H NMR δ_H [400.13 MHz, DMSO-d_6, 298 K]: 8.81 (d, J = 8.0 Hz, 1H, $H_{\alpha'}$-Py), 8.70 (d, J = 4.0 Hz, 1H, H_{β}-Py), 7.81 (td, J_1 = 7.9 Hz, J_2 = 1.5 Hz, 1H, $H_{\gamma'}$-Py), 7.35-7.57 (m, 6H), 7.23 (s, 1H, CH=), 4.66 (q, J = 7.3 Hz, 1H, -CH-), 2.66 (q, J = 7.3 Hz, 2H, -CH_2-), 3.78 (s, 3H, CH_3), 1.72 (d, J = 7.4 Hz, 3H, CH_3).

IR (KBr, ν, cm^{-1}): 1735 (C=O), 1635 (C=N), 1600 (C=C).

Anal. Calc. for $C_{20}H_{19}N_3O_3S$: C 62.99%; H 4.99%; N 11.02%. Found: C 60.82%; H 4.84%; N 10.57%.

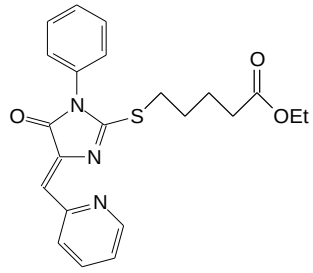


Ethyl 3-[[(4Z)-5-oxo-1-phenyl-4-(2-pyridylmethylene)-4,5-dihydro-1*H*-imidazol-2-yl]thio]-propanoate 4. M.p. 134 °C.

^{1}H NMR δ_H [400.13 MHz, DMSO-d_6, 298 K]: 8.83 (d, J = 8.0 Hz, 1H, $H_{\alpha'}$-Py), 8.72 (d, J = 4.6 Hz, 1H, H_{β}-Py), 7.78 (td, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 1H, $H_{\gamma'}$-Py), 7.56-7.55 (m, 6H), 7.24 (s, 1H, CH=), 4.21 (q, J = 7.0 Hz, 2H, -CH_2-), 3.60 (t, J = 6.9 Hz, 2H, CH_2), 2.96 (t, J = 6.9 Hz, 2H, CH_2),1.29 (t, J = 6.9 Hz, 3H, CH_3).

IR (KBr, ν, cm^{-1}): 1725 (C=O), 1640 (C=N), 1600 (C=C).

Anal. Calc. for $C_{20}H_{19}N_3O_3S$: C 62.99%; H 4.99%; N 11.02%. Found: C 62.83%; H 5.09%; N 11.12%.



Ethyl 5-[[(4Z)-5-oxo-1-phenyl-4-(2-pyridylmethylene)-4,5-dihydro-1*H*-imidazol-2-yl]thio]-pentanoate 5. M.p. 94 ^{o}C.

^{1}H NMR δ_H [400.13 MHz, DMSO-d_6, 298 K]: 8.84 (d, J = 8.0 Hz, 1H, $H_{\alpha'}$-Py), 8.71 (d, J = 4.8 Hz, 1H, H_{β}-Py), 7.81(td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H, $H_{\gamma'}$-Py), 7.24-7.54 (m, 6H), 7.23 (s, 1H, CH=), 4.14 (q, J = 7.1 Hz, 2H, -CH_2-), 3.36 (t, J = 7.0 Hz, 2H, -CH_2-), 2.40 (t, J = 7.5 Hz, 2H, -CH_2-), 1.80-1.95 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H, CH_3).

IR (KBr, ν, cm^{-1}): 1735 (C=O), 1635 (C=N), 1600 (C=C).

Anal. Calc. for $C_{22}H_{21}N_3O_3S$:: C 65.53%; H 5.66%; N 10.26%. Found: C 63.55%; H 5.46%; N 9.71%.

Synthesis of coordination compound 6 from ligands 1-5 and $CuCl_2 \cdot 2H_2O$ (general procedure)

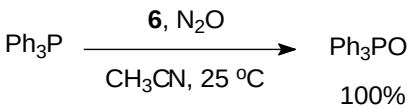
To a solution of 0.068 mmol of ligand **1-5** in 5-10 ml of CH_2Cl_2 (placed in a 1 cm diameter glass tube) pure EtOH (2 ml) was slowly added to form a diphasic system. Then a solution of 1 eq. of $CuCl_2 \cdot 2H_2O$ (0.068 mmol) in 2–3 ml of EtOH was added down the side of the tube, without mixing the ligand and salt solutions. Thereafter the tube was covered and kept for crystalline solid precipitation. The solid was filtered and dried in air to give the product as brown crystals (yield 46-57%). M.p. > 340 °C.

UV-vis (DMF): λ_{max} (ε x 10^{-3}/dm^{-3} mol^{-1} cm^{-1}): 783 (0.754), 424 (24.143), 389 (23.049), 370 (20.998), 305 (19.490).

IR (KBr, ν, cm^{-1}): 1770 (C=O), 1640 (C=N), 1600 (C=C).

Anal. Calc. for $C_{30}H_{22}ClCu_2N_6O_2S_2 \cdot CH_2Cl_2$: C, 45.96; H, 2.99; N, 10.37. Found: C, 45.93; H, 2.75; N, 10.58%.

Triphenylphosphine oxidation in the presence of complex 6



A solution of of Ph_3P (0.5 g, 2 mmol) and complex **6** (0.072 g, 0.1 mmol) in CH_3CN (10 ml) was placed in a two-neck flask equipped with the gas supply pipe and condenser. N_2O (medical quality; from Criogen, http:/cryogen-firma.ru/) was bubbled through the solution for 4 h at room temperature with a gas

flow rate ~1 l/h. After evaporation of the solvent the mixture was analyzed by ^{1}H and ^{31}P NMR spectroscopy. The control experiment was carried out in the absence of complex **6** under the same conditions. The yield of Ph_3PO was estimated based on the integral intensity of Ph_3P (-5 p.p.m) and Ph_3PO (29 p.p.m.) peaks in ^{31}P NMR spectra.

Table 1S. Summary of Crystallographic Information for compound **6**.

Crystal data

Chemical Formula	$C_{28}H_{30}ClCu_2N_6O_3S_2$
Molecular weight	725.25
Crystal system	Monoclinic
Space group	C*2/c*
Cell constants (Å)	*a* = 12.234 (3) *b* = 23.877 (4) *c* = 19.9656 (24) β = 99.020 (14)
Volume (Å^3)	5760.0(17)
Z	4
D_{calc}, g·cm^{-3}	1.672
Radiation	MoKα
Wavelenghth (Å)	0.71073
No. of reflections for cell parameter determination	23
θ range (°)	15.11 - 18.59
Linear absorption coefficient (cm^{-1})	17.58
Temperature (K)	293
Crystal form	Distorted hexagonal prism
Crystal size (mm)	0.33 x 0.17 x 0.12
Colour	dark red

Data collection

Program package	
Solution	SIR2002
Refinement	JANA2000
Diffractometer	CAD4, Graphite monochromator
Data collection method	□-1.33□ scans
Absorption correction	Gaussian (crystal shape)
Absorption correction Tmin/Tmax	0.766/0.846
No. of measured reflection	9183
No. of independent reflection	8280

No. of observed reflection	4769
Criteria for observed reflections	$I > 3\sigma(I)$
θ limits (^{o})	2 - 28.0
Range of *h*, *k*, *l*	$-16 \rightarrow h \rightarrow 15$
	$0 \rightarrow k \rightarrow 31$
	$0 \rightarrow l \rightarrow 26$
R_{int}	0.026
No. of standard reflections for intensity correction	2
Frequency of standard reflections (min)	120

Refinement

Refinement on	F
R/R_w $(I > 3\,\theta(I))$	0.052/0.072
Goodness of fit	1.53
No. of reflections used in refinement	3595
No. of refined parameters	410
Weighting scheme	$w = (\sigma^2(F) + (0.01225F)^2)^{-1}$
θ/θ_{max}	0.022
σr_{max} (e/Å^{-3}) positive/negative	0.75/-0.31

Table 2. Bond lengths (Å) and angles (deg) in complex **6**.

Atoms	Distance	Atoms	Distance	Atoms	Angle
Cu1–Cu2	2.5620(10)	C102–O1	1.217(9)	N5 Cu1 N4	91.9(2)
Cu1–Cl1	2.4644(16)	C102–C103	1.476(9)	N5 Cu1 S1	132.0(3)
Cu2–Cl1	2.4613(18)	C103–C104	1.335(9)	N4 Cu1 S1	96.17(19)
Cu1–N11	1.939(5)	C103–N11	1.388(8)	N5 Cu1 Cl1	113.0(2)
Cu1–N13	2.055(5)	C104–C105	1.444(9)	N4 Cu1 Cl1	106.0(2)
Cu1–S2	2.2524(19)	C105–N13	1.364(8)	S1 Cu1 Cl1	109.94(7)
Cu2–N21	1.931(5)	C105–C106	1.408(9)	N5 Cu1 Cu2	90.68(16)
Cu2–N23	2.070(5)	C106–C107	1.373(11)	N4 Cu1 Cu2	165.2(2)
Cu2–S1	2.259(2)	C107–C108	1.384(12)	S1 Cu1 Cu2	92.91(6)
N11–C101	1.318(8)	C108–C109	1.382(10)	Cl1 Cu1 Cu2	59.68(6)
C101–S1	1.680(7)	N13–C109	1.353(9)	N2 Cu2 N1	93.9(2)
C101–N12	1.393(9)	N21–C201	1.323(8)	N2 Cu2 S2	134.42(18)
N12–C102	1.384(8)	C201–S2	1.684(6)	N1 Cu2 S2	93.79(17)
N12–C110	1.460(9)	C201–N22	1.390(9)	N2 Cu2 Cl1	100.89(17)
C110–C111	1.467(13)	N22–C202	1.372(9)	N1 Cu2 Cl1	109.70(18)
C111–C112	1.196(19)	N22–C210	1.492(9)	S2 Cu2 Cl1	118.32(8)

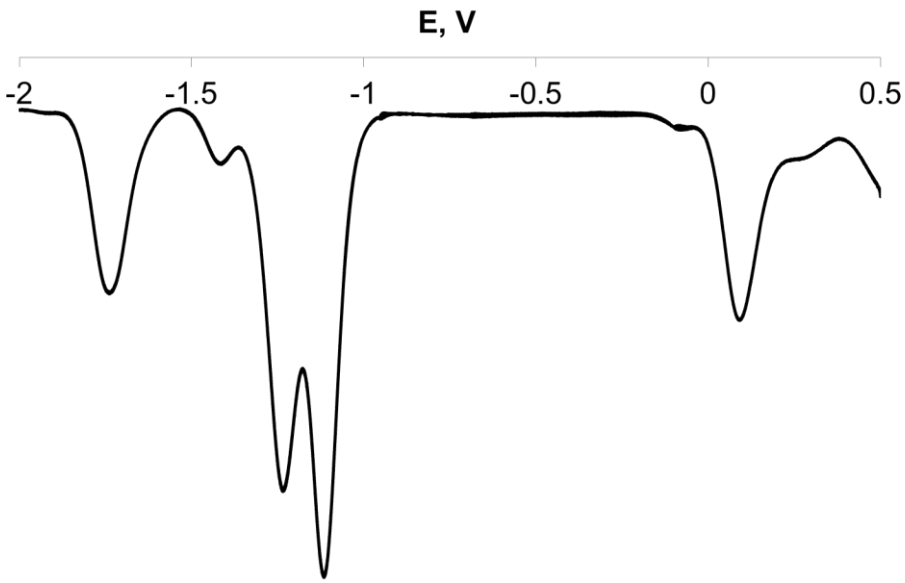


Figure 1S. Square wave voltammogram of complex **6**. 10^{-3} M, DMF, 0.2 M Bu_4NBF_4, 100 mV/s (GC working electrode, Pt wire secondary electrode, saturated calomel reference electrode, room temperature, Ar atmosphere, $E^{1/2}$ (Fc^+/Fc) = +0.49 V).

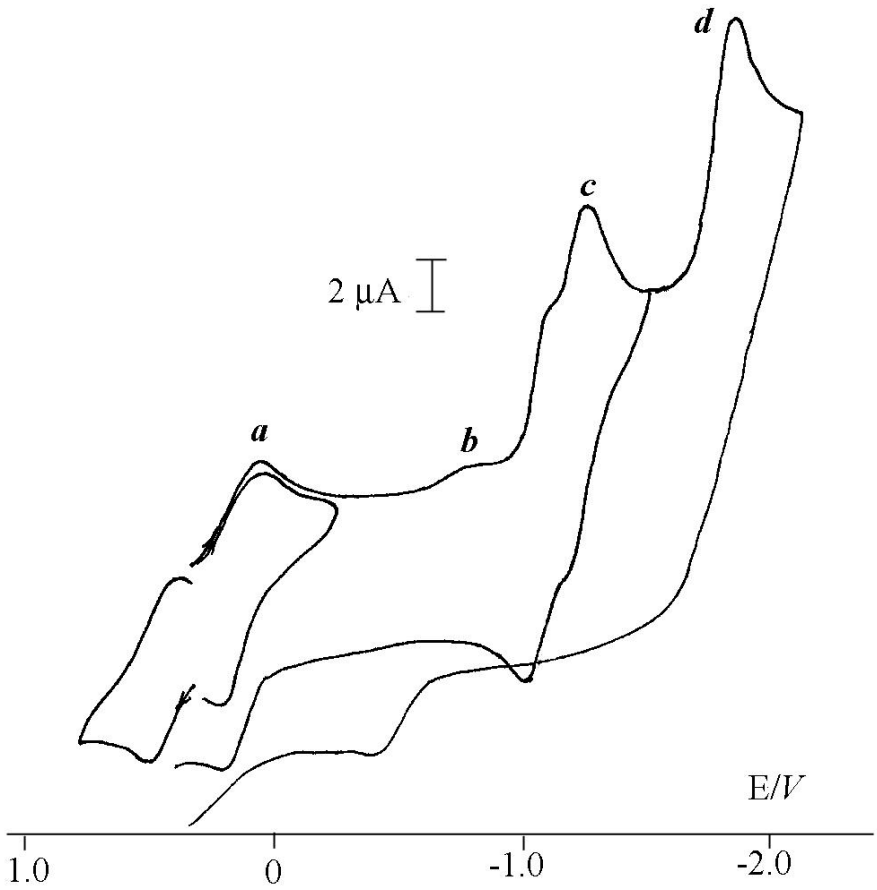


Figure 2S. Cyclic voltammogram of complex **6** ($5 \cdot 10^{-4}$ M) in CH_3CN solution in the presence of 0.1 M Bu_4NClO_4 recorded at 0.2 Vs^{-1}. (GC working electrode, Pt plate secondary electrode, Ag | AgCl | KCl(sat.) reference electode, room temperature, Ar atmosphere, $E^{1/2}$ Fc^+/Fc = +0.29 V).

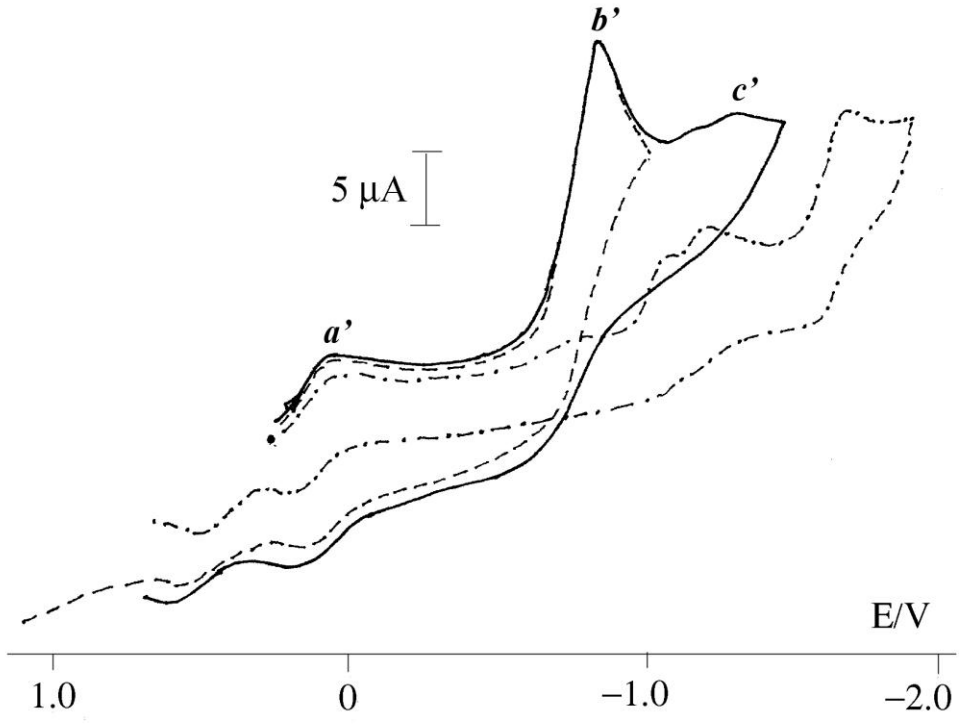
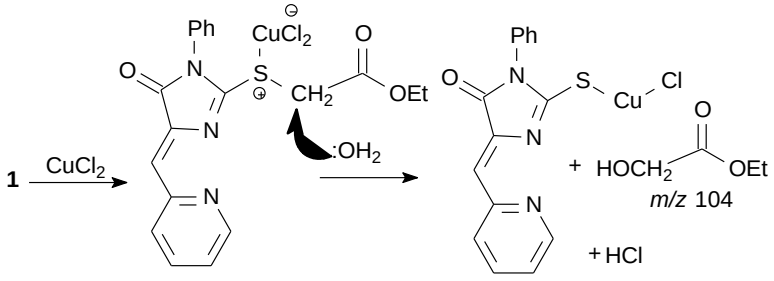
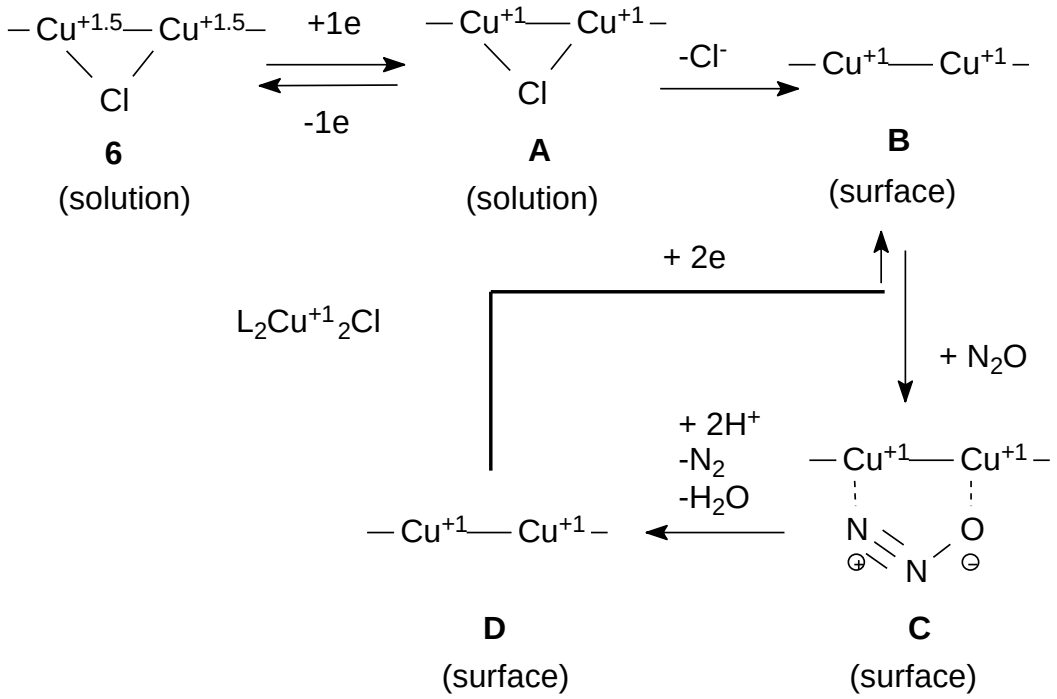


Figure 3S. Cyclic voltammograms of complex **6** ($2 \cdot 10^{-4}$ M) in CH_3CN solution saturated by N_2O in the presence of 0.1 M Bu_4NClO_4 as supporting electrolyte recorded at 0.02 Vs^{-1} (solid and dashed lines) and at 0.2 Vs^{-1} (dash-dotted line) (GC working electrode, Pt plate secondary electrode, Ag | AgCl | KCl(sat.) reference electode, room temperature, Ar atmosphere, $E^{1/2}$ Fc^{+}/Fc = +0.29 V).



Scheme 1S. A proposed mechanism of the C-S bond cleavage reaction of ligand **1**.



Scheme 2S. A proposed mechanism of the N_2O interactions with **6** in an electrochemical cell.

We suppose that the one electron reduced product **A** eliminates the chloride anion with the formation of the neutral complex **B** adsorbed on electrode surface which then binds N_2O to the vacant coordination positions forming the intermediate **C**. This intermediate is protonated by the solvent molecule or by a tetraalkyl ammonium cation of the supporting electrolyte [*(a)* Eds. M. M. Baizer, H. Lund, *Organic Electrochemistry. An Introduction and a Guide* (2nd Edition), Marcel Dekker Inc., Marcel Dekker : New York. 1983. Chapter 7.5; (b) J. A. Morales-Morales, C. Frontana, M. Aguilar-Martınez, J. A. Bautista-Martınez, F. J. Gonzalez, I. Gonzalez, *J. Phys. Chem. A, 2007*, **111**, 8993; (c) F. J. Arévalo, P. G. Molina, M. A. Zón, H. Fernández, *J. Electroanal. Chem., 2008*, **619-620**, 46] giving a water molecule, N_2 and the Cu^{2+}-containing intermediate **D**, which is then electrochemically reduced closing the catalytic cycle.

Apparently, only N_2 (not NH_3) is forming under the catalytic N_2O reduction, because the NH_3 re-oxidation peak at E_{pa} ~ +1.0 B is not observed in the CV reverse scan in the anodic region.