Supporting Information

for

Dioxygenation of cysteamine to hypotaurine at a tris(pyrazolyl)borate iron(II) unit – cysteamine dioxygenase mimicking?

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1. Methods

All experiments were carried out in a dry argon atmosphere using a MBraun glovebox and/or standard Schlenk techniques. Solvents were purified employing a MBraun Solvent Purification System SPS. Deuterated solvents were purified using appropriate techniques. NMR spectra were recorded on a Bruker AV 400 NMR spectrometer (^{1}H 400.13 MHz) and AV 300 NMR spectrometer (^{1}H 300 MHz). Chemical shifts are reported in ppm relative to residual proton signals of CD_2Cl_2 (5.32 ppm) and D_2O (4.79 ppm), respectively. EPR spectra were recorded on liquid samples with a ERS 300 X-Band EPR spectrometer. Mass spectra (ESI) were recorded on an Agilent Technologies 6210 Time-of-Flight LC-MS instrument. Microanalyses were performed on a Leco CHNS-932 elemental analyser. Magnetic susceptibility measurements were carried out using the Evans NMR method.

2. Synthesis of 1

Triethylamine (35 µL, 226 µmol) was added to a suspension of cysteamine (19.4 mg, 226 µmol) in 15 mL dichloromethane, and the reaction mixture was stirred for 4 h. Subsequently, $Tp^{Me,Ph}FeCl$ (130 mg, 226 µmol) in 10 mL dichloromethane was added, and the reaction mixture was stirred overnight. All volatiles were then removed in vacuo, and the residue was extracted twice with 10 mL of diethylether. Thereafter the resulting pale yellow powder was washed with hexane (10 mL) to give analytically pure **1** (60 mg, 43 % yield, 97 mmol). Crystals of **1** suitable for single crystal X-ray diffraction studies were obtained by slowly evaporating the volatiles from a saturated solution of **1** in dichloromethane. Elemental analysis (%) calc. for $C_{32}H_{34}BFeN_7S$ (615.20 g•mol^{-1}): C 62.46, H 5.57, N 15.93; found: C 63.12, H 5.62, N 15.34; IR: [KBr]: $\tilde{\nu}$ = 3358 (m), 3290(w), 3126 (w), 3055(m), 2967 (m), 2923 (m), 2868 (m), 2547 (m), 1578 (m), 1542 (vs), 1480 (m), 1450 (s), 1431 (s), 1414 (vs), 1362 (m), 1343 (m), 1194 (vs), 1175 (vs), 1073 (vs), 782 (vs), 764 (vs), 697 (vs), 640 (s), 531 (m) cm^{-1}; ^{1}H-NMR (300.13 MHz, CD_2Cl_2): δ = 50.16 (3H, Pz-*H*), 20.71 (9H, Pz-CH_3), 5.85 (6H, -CH_{Ph}), 5.65 (3H, -CH_{Ph}), -6.73 (6H, -CH_{Ph}) ppm; μ_{eff} = 5.36 µB (in benzene at r.t.).

3. Analysis of the oxygenated product

A solution of **1** (50 mg, 81 μmol) in 10 mL CH_2Cl_2 was purged with O_2 for 5 min and stirred for an additional 12 h under an O_2 atmosphere. A 3 M HCl solution (5 mL) was added, and the two-phase mixture was stirred for 3 h; during this time the aqueous layer turned pale yellow. The aqueous layer was separated and all volatiles were removed from it in vacuo. The residue was dissolved in methanol and the solution stirred with chelex resin (Chelex 100 sodium form) overnight. Then the solution, containing the organic reaction products, was filtered off the precipitated iron complexes, and the solvent was removed in vacuo. The white residue was washed twice with toluene to remove the decomposition product of the ligand, 5,3-methylphenylpyrazole. A ^{1}H-NMR spectrum of the oxygenation product was recorded. ^{1}H-NMR (400.13 MHz, MeOD): δ = 3.25 (t, 2H, -C*H*NH_2), 2.60 (t, 2H, -C*H*$_2$S) ppm.

4. ESI-TOF measurements of the reaction of 1 with dioxygen.

20 mg of **1** (32 mmol) were dissolved in CH_2Cl_2 (20 mL). The argon atmosphere of the resulting solution was replaced by O_2 ($^{16}O_2$, $^{18}O_2$) and stirred overnight. The reaction mixture was then diluted with dichloromethane and transferred into an ESI vial under an inert atmosphere. Mass spectra (ESI) were recorded on an Agilent Technologies 6210 Time-of-Flight LC-MS instrument. Acetonitrile was used as the eluent.

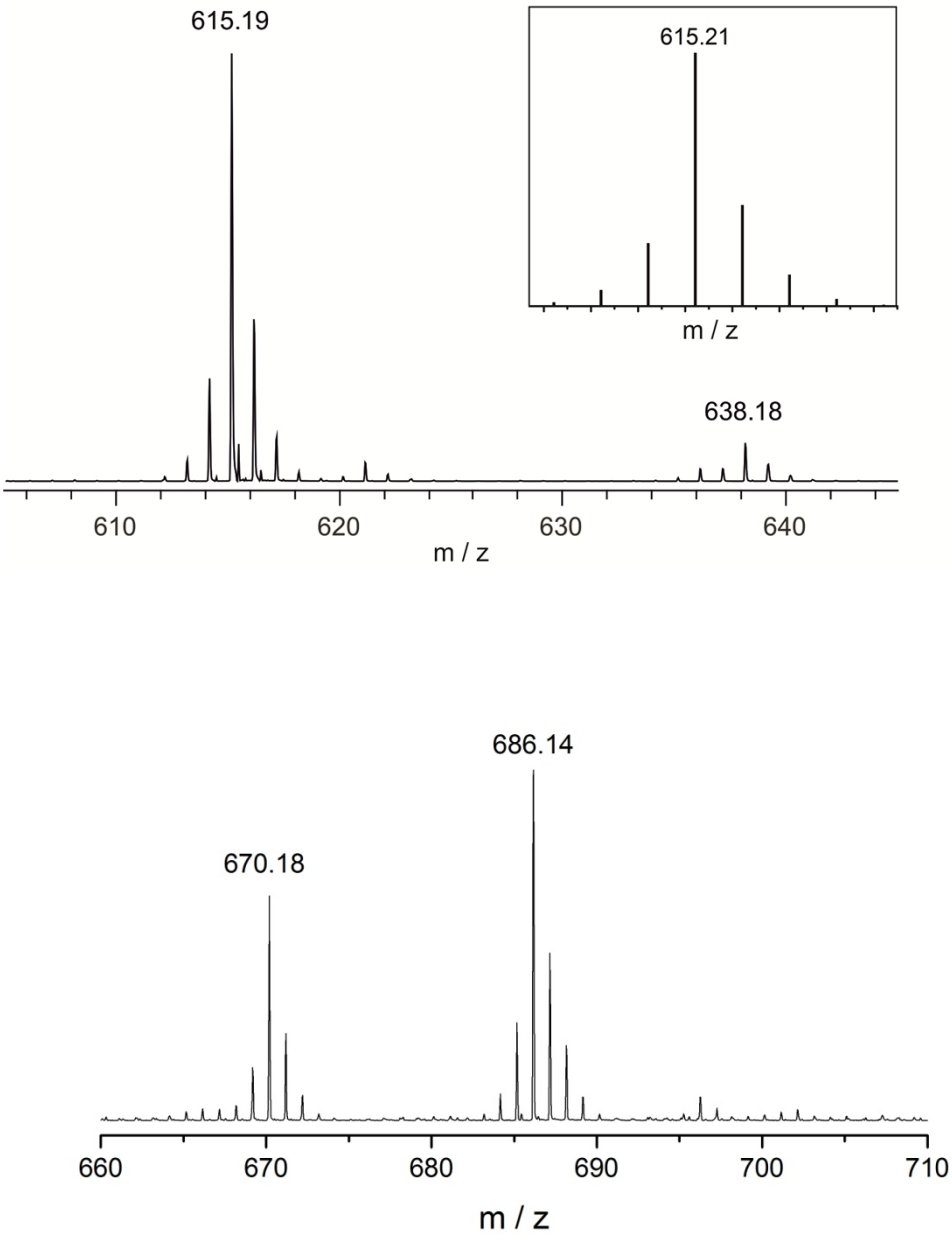

Figure S1. Section of the ESI-TOF spectrum recorded before (top) and after (bottom) the reaction of **1** with $^{16}O_2$ in dichloromethane.

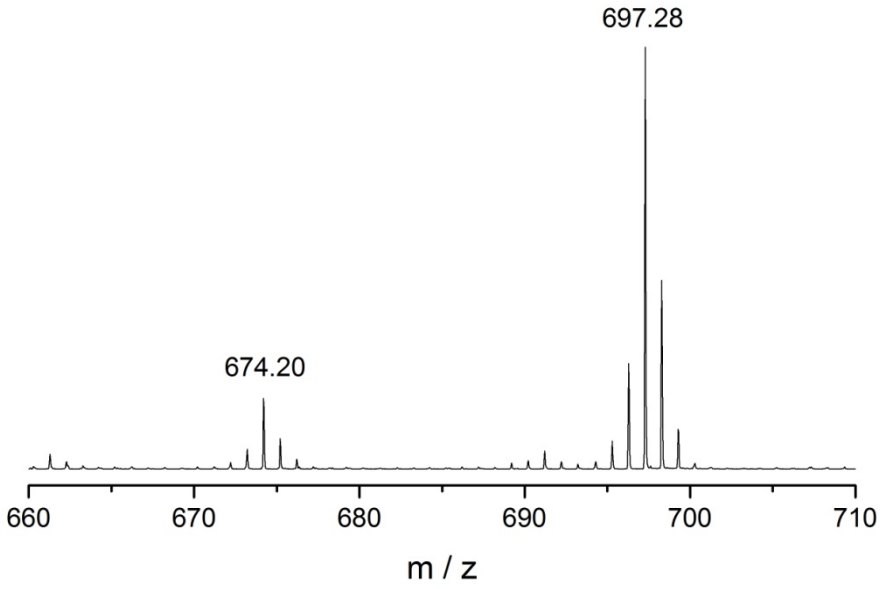

Figure S2. Shift of the m/z = 670.17 peak upon usage of $^{18}O_2$ instead of $^{16}O_2$.

5. Crystallographic data of 1

X-ray structure analysis of **1**: $C_{32}H_{34}BFeN_7S$, *M*r = 615.20 g*mol^{-1}, monoclinic, space group $P2_1/n$, a = 9.3767(6), b = 16.0545(6), c = 19.6816(15) Å, β = 95.438(2)°, V = 2942.1(3) Å^3, Z = 4, T = 100(2) K, F(000) = 1276, μ = 0.619 mm^{-1}, Θ = 4.65 – 29.21°, reflections collected 29804, independent reflections 7869 [*R*int = 0.0530], GoF = 1.086, *R*1 = 0.0475, *wR*2 = 0.1012, largest diffraction peak/hole 0.84/-0.52 e Å^{-3}. The crystal was mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the diffractometer (Stoe IPDS 2Θ). MoK_α radiation, λ = 0.71073 Å. The structure was solved by direct methods (SHELXS-97),[1] refined versus F^2 (SHELXL-97)[2] with anisotropic temperature factors for all non-hydrogen atoms. Multi-scan absorption correction was applied to the data[3]. All hydrogen atoms were added geometrically and refined by using a riding model. CCDC-1044609 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, Universität Göttingen, 1997.

2 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997.

3. A. L. Spek, J. Appl. Cryst. 36, 7-13, 2003.