Supporting Information

Towards Biocompatible Dinitrosyl Iron Complexes: Appended Sugar Thiolates

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Experimental Details

General Methods and Materials

All reagents, including 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride ($IMesH^+Cl^-$), sodium *tert*-butoxide (NaO^tBu), sodium methoxide (MeONa) 1-thio-β-D-glucosetetraacetate, 1-thio-β-D-glucose sodium salt and CoTPP were purchased from Sigma-Aldrich Chemical Co. and were used as received. Air-free conditions were maintained during synthesis, isolation, and storage of products through the use of standard Schlenk-line techniques (N_2 atmosphere) and an Ar-filled glove box. The NHC stabilized IMes-TNIC, $[(IMes)Fe(NO)_3]^+$, $[(bme\text{-}dach)Co]_2$, and complex **3** were synthesized according to literature procedures.[1,2] Complex **4** was synthesized in a slightly modified literature procedure in which the solvent used was THF instead of acetonitrile.[3] Bovine coronary venular endothelial cells (CVECs) were kindly gifted by Professors Cynthia J. Meininger and Andreea Trache at Texas A&M Health Science Center. CVECs were cultured in GIBCO® Dulbecco's Modified Eagle Medium: Nutrient Mixture F-12 (DMEM/F-12) (Invitrogen, Carlsbad, CA) mixed with 10% fetal bovine serum (Sigma Aldrich, St. Louis, MS), 100 U/mL penicillin - 100 U/mL streptomycin - 0.25 mg/mL amphotericin B (Lonza, Walkersville, MD), and 20 units/mL heparin (Midwest Vet Supply, Lakeville, MN).

Physical Measurements

Infrared spectra were recorded on a Bruker Tensor 27 FTIR spectrometer in CaF_2 solution cells with a path length of 0.1 mm. Mass spectrometry (ESI-MS) was performed by the Laboratory for Biological Mass Spectrometry at Texas A&M University. Nanoelectrospray ionization in positive mode was performed using an Applied Biosystems QSTAR Pulsar (Concord, ON, Canada) equipped with a nanoelectrospray ion source. Solution was flowed at 700 nL/min through a 50 μm ID fused-silica capillary that was tapered at the tip. Electrospray needle voltage was held at 1900 V. Elemental analyses of crystalline samples were determined by Atlantic Microlab, Inc., Norcross, GA. EPR spectra were typically recorded in frozen THF using a Bruker ESP 300 equipped with an Oxford ER910 cryostat operating at 10 K. Doublet was used to simulate spectral parameters.

X-ray Crystallography

X-ray diffraction (XRD) data collections were carried out using a Buker APEX2 using MoKα radiation (0.7107 Å). All crystals were coated in paraffin oil, mounted on a nylon loop, and paced under streaming N_2 (110/150 K). The space groups were determined by systematic absences and intensity statistics, and structures were solved by direct methods and refined by full-matrix least-squares on F^2. Anisotropic displacement parameters were employed for all non-hydrogen atoms; H atoms were placed at idealized positions and refined with fixed isotropic displacement parameters. The following programs were used: cell refinement, data collection, data reduction, APEX2; [4] absorption correction, SADABS; [5] structure solutions, SHELXS-14; [6] and structure refinement, SHELXL-97.[7] The final data presentation and structure plots were generated in X-Seed Version 2.0. CIF files were prepared for publication using WinGX and its included programs.

References

(1) Hsieh, C. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2010**, *132*, 14118-14125.

(2) Hess, J. L.; Conder, H. L.; Green, K. N.; Darensbourg, M. Y. *Inorg. Chem.* **2008**, *47*, 2056-2063.

(3) Skodje, K.M.; Williard, P. G.; Kim, E. *Dalton Trans.,* **2012**, *41*, 7849-7851.

(4) APEX2, version 2009.7-0; Bruker AXS Inc.: Madison, WI, 2007.

(5) Sheldrick, G. M. SADABS: Program for Absorption Correction of Area Detector Frames; Bruker AXS Inc.: Madison, WI, 2001.

(6) Sheldrick, G. M. SHELXS-97: Program for Crystal Structure Solution; Universität Göttingen: Göttingen, Germany, 1997.

(7) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; Universität Göttingen: Göttingen, Germany, 1997.

Synthesis and Characterization

Synthesis of complex 1

A 0.10 mmol (0.054 g) portion of $[(IMes)Fe(NO)_3]^+$ and 0.10 mmol (0.036 g) of 1-thio-β-D-glucosetetraacetate were weighed and dissolved in 10 mL of THF in a 100 mL Schlenk flask. A color change from green to brown resulted within time of mixing and the formation of complex **1** was confirmed by IR spectroscopy. The solution was filtered through Celite, and **1** (0.066 g, 83%) was isolated as a brown powder by recrystallization of THF solutions of **1** with cold hexanes or pentane. X-ray quality crystals of **1** were obtained from THF solutions layered by hexanes at -35 °C. IR (THF, cm^{-1}) υ(Me-C(O)O): 1759 (s), 1749 (sh) cm^{-1} υ(NO): 1768 (sh), 1718 (s) cm^{-1}. Elemental Anal. calculated for $C_{35}H_{43}FeN_4O_{11}S$ (found) : C, 53.64 (53.21); H, 5.53 (5.42); N, 7.15 (6.73). $C_{35}H_{43}FeN_4O_{11}S$ (MW = 783 g/mol) $^+$ESI-MS: m/z = 784 $[M + H]^+$. Room temperature EPR measurements showed an isotropic signal at g = 2.03.

Upon exposure to air for 3 h, **1** converted to an unidentified species that has the appearance of a mononitrosyl iron complex. IR (DMSO, cm^{-1}) υ(NO): 1663.

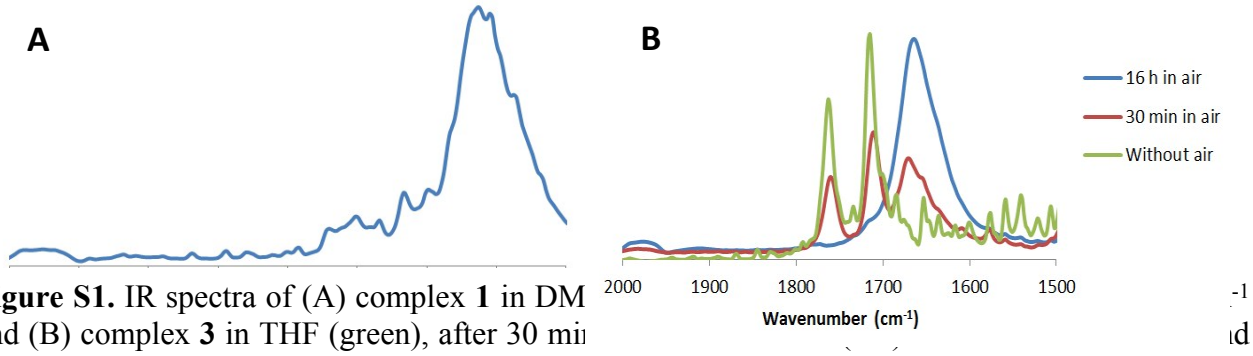


Figure S1. IR spectra of (A) complex **1** in DM -1 and (B) complex **3** in THF (green), after 30 mi d air (blue). The same species at 1665 cm^{-1} appears here as well.

Deprotection of complex 1 to give complex 1′ and the direct synthesis of 1′

In a 100 mL Schlenk flask, 0.040 g (0.05 mmol) of complex **1** was mixed with excess (0.40 mmol, 0.022 g) of MeONa and the solid mixture was dissolved in 20 mL of MeOH. The deprotection proceeded with changes in the IR pattern of complex **1**, and was complete in ca. 2 h. Direct synthesis of complex **1′** was achieved by reacting 0.10 mmol (0.054 g) of $[(IMes)Fe(NO)_3]^+$ and 0.10 mmol (0.022 g) of 1-thio-β-D-glucose sodium salt in THF. The

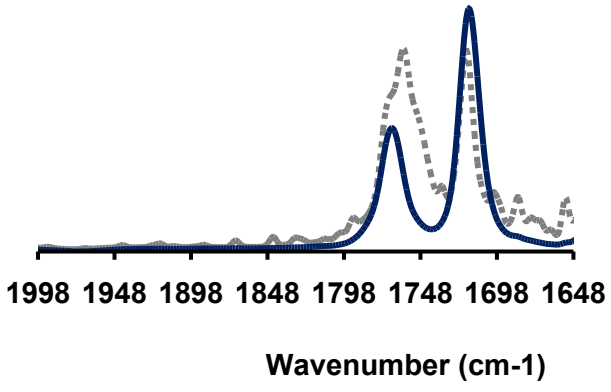


Figure S2. IR spectrum of complex **1′** in THF: ν(NO) 1768 (sh), 1716 cm^{-1}. Dotted-line inset: IR spectrum of complex **1** (THF).

reaction was complete within time of mixing as confirmed by IR spectroscopy and a greenish brown product was obtained in powder form in good yield (crude yield > 75%). IR (THF, cm^{-1}) υ (NO): 1768 and 1716 cm^{-1}. $C_{27}H_{35}FeN_4O_7S$(MW = 615 g/mol) $^+$ESI-MS: m/z = 638 $[M + Na]^+$.

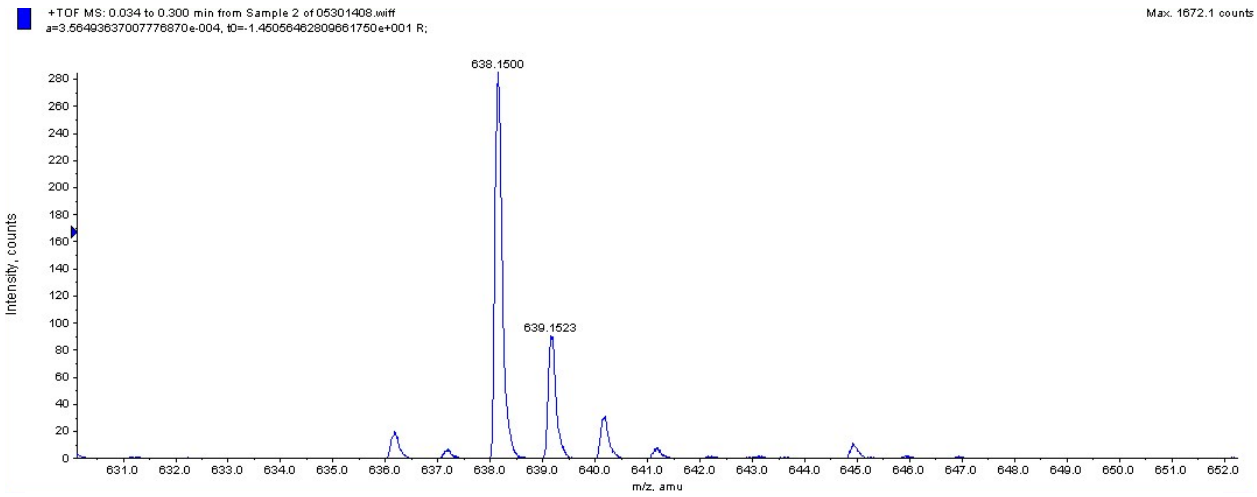


Figure S3. $^+$ESI-MS isotope bundle for the parent ion of **1'**, where m/z = 638 $[M + Na]^+$.

Synthesis of complex 2

The Roussin's Red Ester type dimeric complex **2**, $(\mu\text{-}(SR))_2[Fe(NO)_2]_2$, where R = acetylated thiosugar units, was synthesized by the room temperature reaction of 1 mmol of 1-thio-β-D-glucosetetraacetate with 1 mmol of freshly prepared $Fe(CO)_2(NO)_2$ (isolated by vacuum transfer to a flask immersed in liquid N_2) in ~ 30 mL THF solution. The reaction was complete in about 12 h as monitored by IR spectroscopy. A brown powdery product was obtained in good yield (0.36 g, 75.1%), by recrystallizing concentrated THF solutions (~ 5 mL) of **2** with cold hexanes (~20 mL). Room temperature EPR measurements showed no signal in DCM. However, a rhombic signal with g_x=2.043, g_y=2.030, g_z=2.013 appeared in DMSO solution. IR (THF, cm^{-1}) υ(NO): 1787, 1750 cm^{-1} υ(Me-C(O)O): 1759, 1749 cm^{-1}.

Elemental Anal. calculated for $C_{28}H_{38}Fe_2N_4O_{22}S_2$●THF (found) : C, 37.30 (37.63); H, 4.50 (4.41); N, 5.44 (4.65). $C_{28}H_{38}Fe_2N_4O_{22}S_2$ (MW = 958 g/mol) $^+$ESI-MS: m/z = 959 $[M + H]^+$, 980 $[M + Na]^+$.

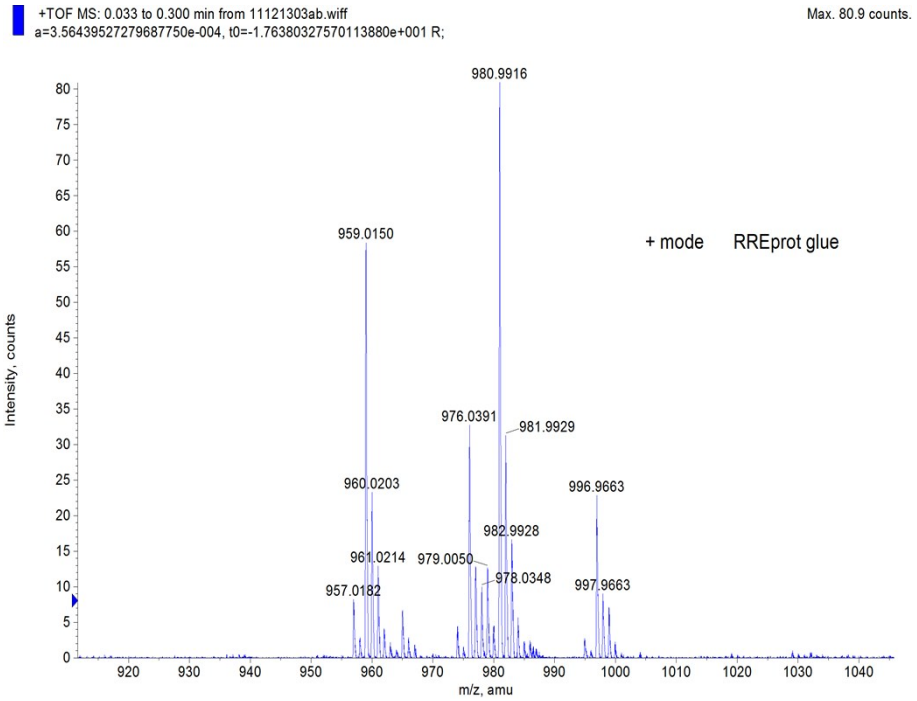
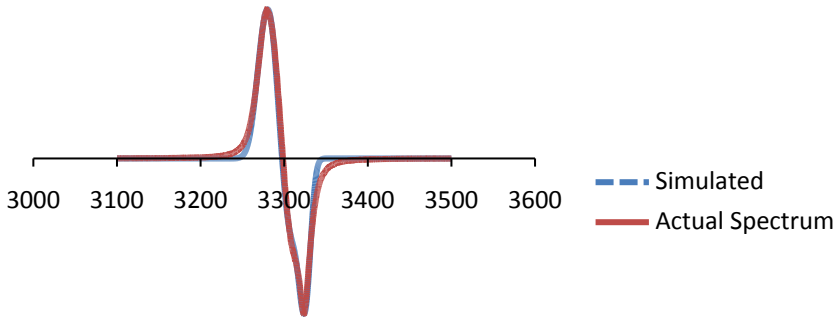


Figure S4. $^+$ESI-MS Isotope bundle for the parent ion of **2** where m/z = 959 $[M + H]^+$ and 980 $[M + Na]^+$.



[G]

Figure S5. Overly of X-band EPR spectrum of complex **2** in DMSO solution at 295 K (red) and that of the simulated spectrum (blue dotted line).

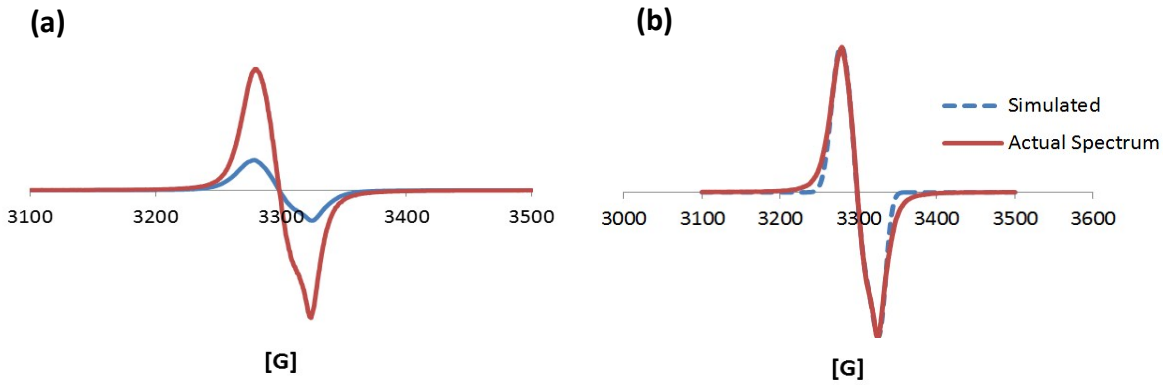


Figure S6. (a) Overlay of the X-band EPR spectrum of complex **2** in DMSO solution (red) with complex **2** in DMSO and media (blue) at 295 K. (b) Overlay of X-band EPR spectrum of **2** in DMSO and media (red) and that of the simulated spectrum (blue dotted line).

NO-trapping experiments

Complex **1** was used in NO trapping experiments with Co(TPP). Into a 50 mL Schlenk flask, 0.060 mmol (0.050 g) of **1** was weighed out and dissolved in 10 mL of THF. This was transferred *via* cannula into a different flask containing 0.12 mmol (0.081 g) of CoTPP in 10 mL THF. Loss of NO bands was seen over 48 hours in the IR monitor. In order to isolate the (TPP)Co(NO), the solution was concentrated to ca. 5 mL, and MeOH was added. Careful decanting of the red supernatant showed a dark purple precipitate. The residue was dried in *vacuo* and re-dissolved in dichloromethane. The IR spectrum of this dichloromethane solution showed a strong absorption peak at 1683 cm^{-1} for (TPP)Co(NO). $^{+}$ESI-MS: m/z = 671 $[(TPP)Co]^{+}$. UV-Vis (DCM): 410 nm, 534 nm.

Complex **1** (0.025 mmol, 0.019 g) and **2** (0.025 mmol, 0.023 g) were individually reacted with 0.10 mmol (0.056 g) of $[(bme\text{-}dach)Co]_2$ in THF solutions separately. Loss of NO bands in the IR monitor was seen over ~24 h for **1** and over ~12 h for **2**. The resulting solution was

dried *in vacuo* and washed x2 with Et_2O. The remaining solid was re-dissolved in dichloromethane, of which the IR showed a strong, broad band at 1601 cm^{-1}, indicating the formation of (bme-dach)Co(NO). When the reactions were carried out in DCM, loss of the NO bands was seen over ~48 h for **1** and ~24 h for **2**. $^{+}$ESI-MS:m/z = 308 $[M + H]^{+}$, 277 [M-NO].

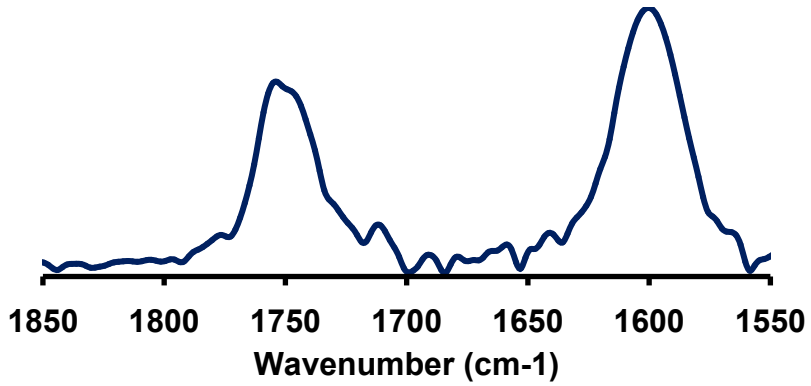


Figure S7. IR spectrum resulting from complete reaction of **1** or **2** with $[(bme\text{-}dach)Co]_2$ in THF: ν(NO) 1601 cm^{-1} indicates the formation of (bme-dach)Co(NO).

Quatification of NO Trapped by $[(bme\text{-}dach)Co]_2$

A series of DCM solutions of Co(bme-dach)NO were prepared with concentrations ranging from 3-14 mM. A calibration curve (below) was created using the intensities of the ν_{NO} band at 1601 cm^{-1} and the concentrations. Complex 1 (0.008 g, 0.008 mmol) and 2 (0.008 g, 0.01 mmol) were separately mixed with an excess of $[Co(bme\text{-}dach)]_2$ and stirred in DCM for 24 h. The reaction mixture was then dried *in vacuo* and the solid residue dissolved in 5 mL DCM. IR of **1** revealed the formation of Co(bme-dach)NO (0.002 g, 0.005 mmol) ca. 0.5 moles Co(bme-dach)NO per mole **1**, while **2** showed the formation of Co(bme-dach)NO (0.007 g, 0.02 mmol) in a ratio of 2.7 moles Co(bme-dach)NO per mole **2**.

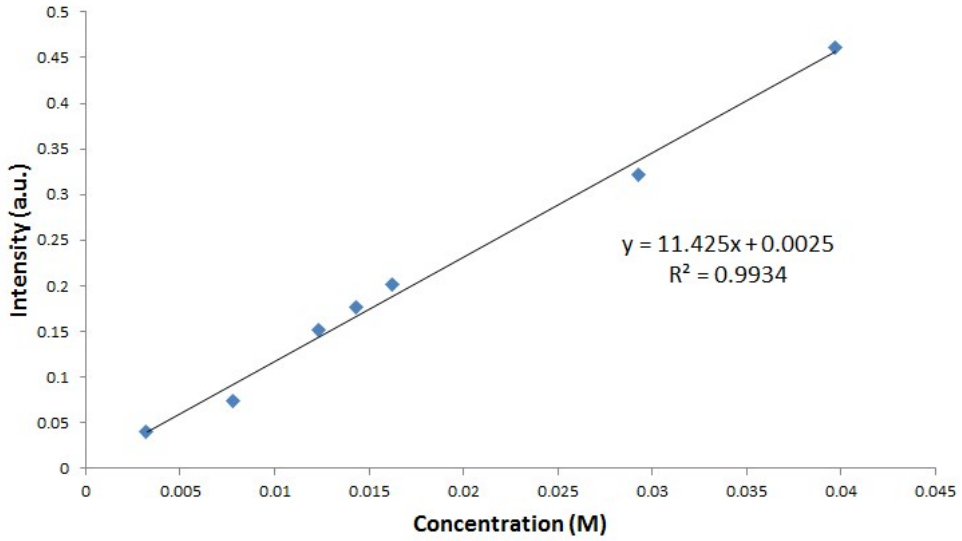


Figure S8. Plot of the intensity of the ν_{NO} vs. concentration of Co(bme-dach)NO for concentrations ranging from 3-14 mM. This plot was used to calculate the moles of NO transferred from **1** and **2** following a 24-h stir of either **1** or **2** with $[Co(bme\text{-}dach)]_2$ in DCM. For **1**, 0.5 moles of the Co(bme-dach)NO were formed per mole of complex, while for **2**, 2.7 moles of the Co(bme-dach)NO were formed per mole of complex.

Griess assay analysis

The release of NO from the compounds under physiological conditions was quantitatively measured by the Griess assay (Invitrogen) following the manufacturer's protocol. For each measurement, compounds **1-4** were mixed with the media, which was taken from 96-wells with and without cells, and incubated at 37 °C with 5% CO_2. NO under physiological conditions converts to nitrite (NO_2^-), which induces formation of azo dye that absorbs at 548 nm. Specific absorbance at 548 nm was measured and corrected with blank measurement and with absorbance at 690 nm with a Spectra Max M5 plate reader.

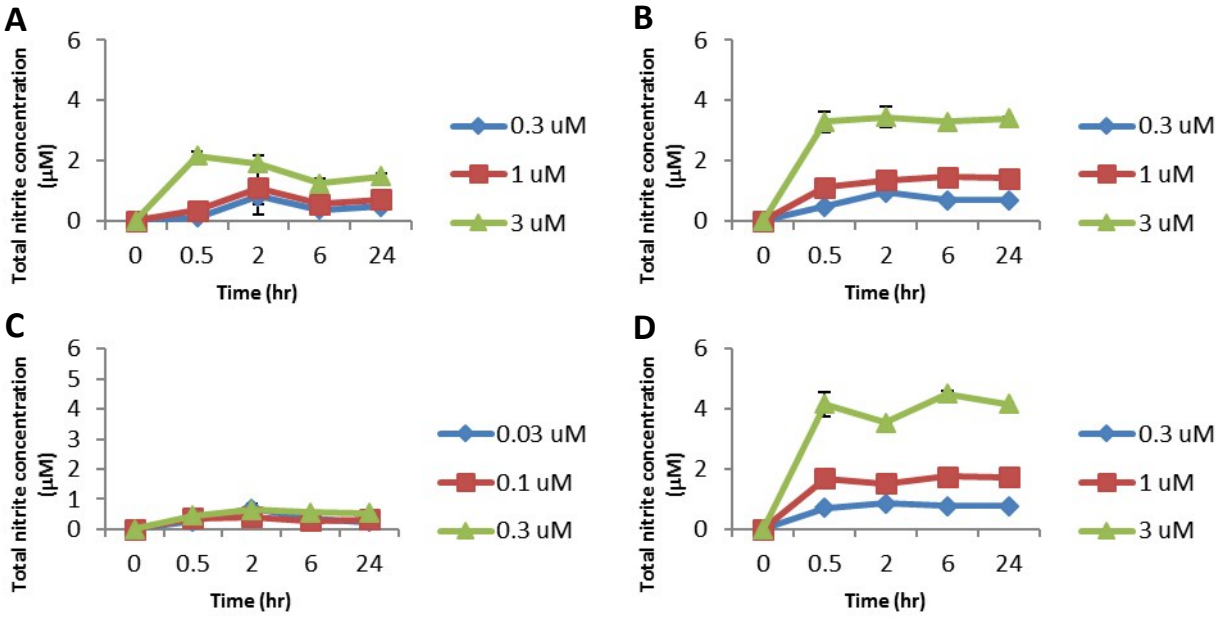


Figure S9. Griess assay results for addition of **1** (A), **2** (B), **3** (C), and **4** (D) to the medium in presence of cells at concentrations of 0.3 μM (blue), 1 μM (red) and 3 μM (except for **3** (C), where 0.03, 0.1 and 0.3 μM concentrations were used due to high cytotoxicity). Total nitrite concentration correlates to the NO concentration.

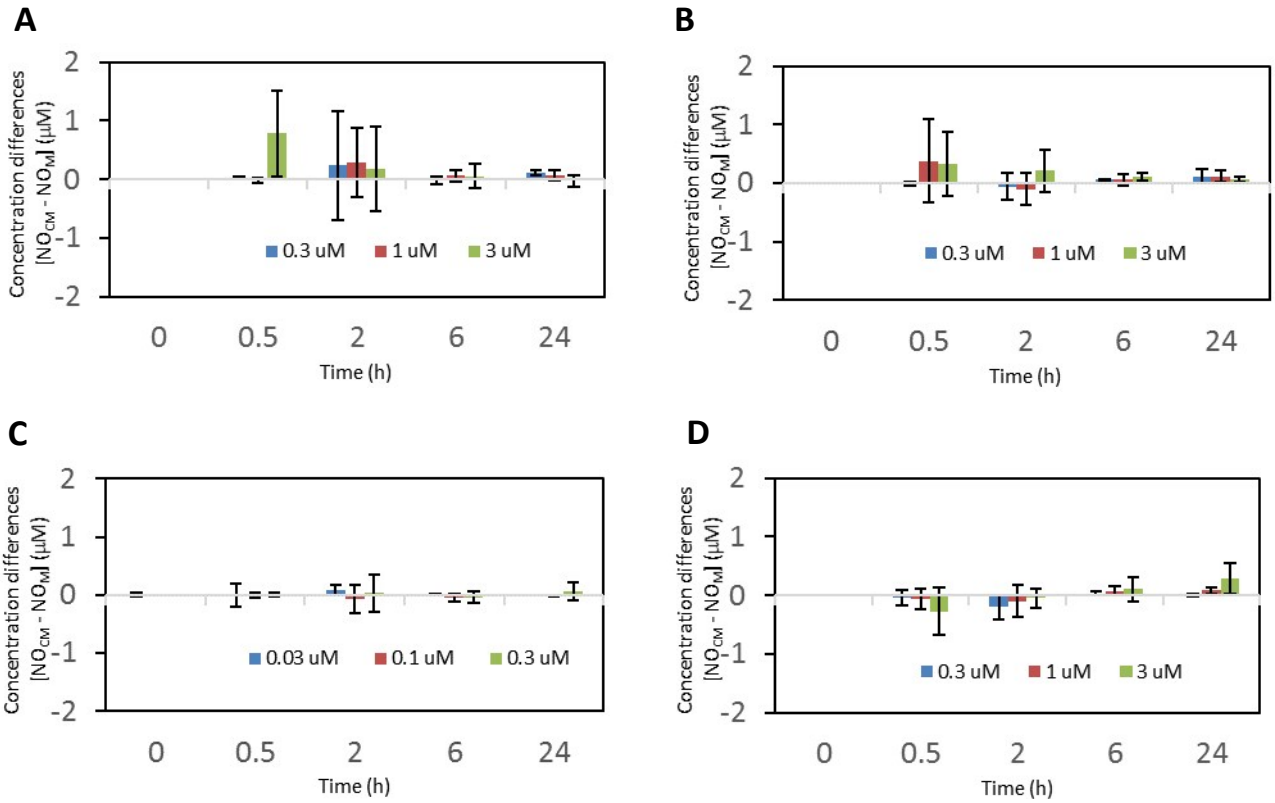


Figure S10. Differential of NO release to media with and without out cells for complexes **1-4**, A-D, respectively. Negative nitrite concentrations are indicative of cellular uptake of NO. The values were calculated by subtracting the amount of nitrite in the media alone (NO_M) from that found in the presence of cells (NO_{CM}).

Cell viability studies

Bovine coronary venular endothelial cells (CVECs) were cultured in GIBCO®Dulbecco's Modified Eagle Medium: Nutrient Mixture F-12 (DMEM/F-12) from Invitrogen (Invitrogen, Carlsbad, CA), along with 10% FBS, 100 U/mL penicillin - 100 U/mL streptomycin - 0.25 mg/mL amphotericin B (Lonza, Walkersville, MD), and 20 units/mL heparin (Midwest Vet Supply, Lakeville, MN). For cytotoxicity experiments, cells were trypsinized and quenched with media. Trypsin was removed after centrifugation at 250 G for 5 minutes. Resuspended cells were plated (10×10^3 cells/well) in a 96-well plate coated with 1.5 % bovine gelatin. Cells were incubated at 37 °C in a humidified atmosphere containing 5% CO_2 for 24 h to adhere. The medium was replaced with fresh medium 1 h prior to the addition of formulations at desired concentrations. The cells were incubated with the formulations for 72 h. MTS combined reagent was added to each well (Cell Titer 96® Aqueous Non-Radioactive Cell Proliferation Assay, Promega Co., Madison, WI). The cells were then incubated with the reagent for 2 h at 37 °C in a humidified atmosphere containing 5% CO_2 protected from light. Absorbance was measured at 490 nm using SpectraMax M5 (Molecular Devices Co., Sunnyvale, CA). The cell viability was calculated based on the relative absorbance to the control-untreated cells.

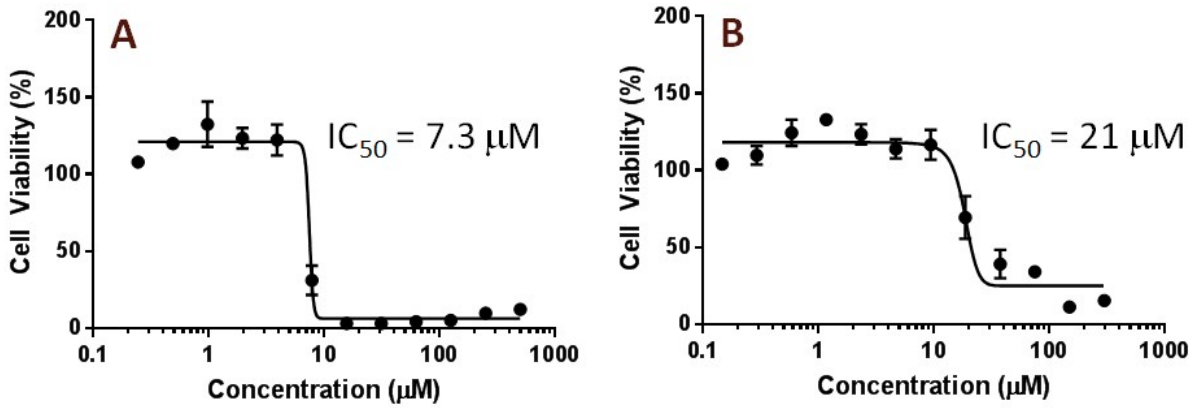


Figure S11. Cell viability vs. concentration of complex for **3** (A) and **4** (B). Each sample was diluted by a dilution factor of 2. There were ca. 12 ranges of concentrations (high – low) and each concentration was done in a set of triplets. Each dot on the plot represents the average of the three readings at that specific concentration.

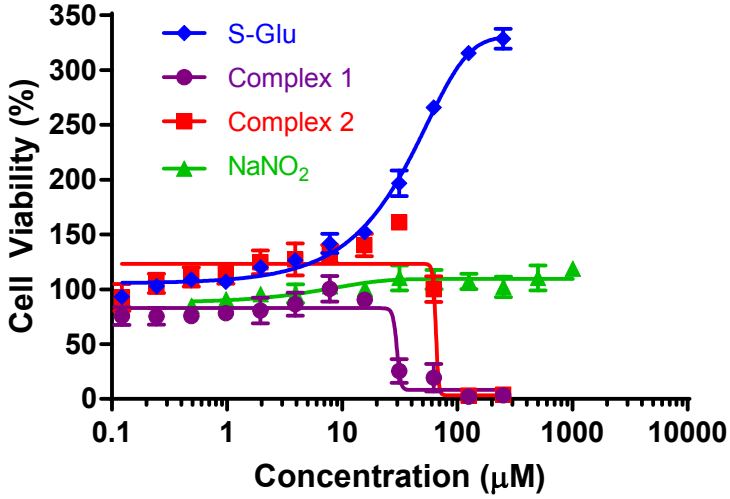


Figure S12. Overlay of cell viability plots for **1** and **2** (purple and red, respectively) with the thiosugar (S-Glu, blue) and sodium nitrite (green). These experiments were carried out in the same manner as outlined in Figure S11. The overlay visually supports the claim that the increase in proliferation at low concentrations can be attributed to the thiosugar moiety itself.

Table S1. Crystal data and structure refinement for complex 1.

Identification code	glu	
Empirical formula	C35 H43 Fe N4 O11 S	
Formula weight	783.64	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.0301(13) Å	α = 90°.
	b = 16.641(2) Å	β = 90°.
	c = 25.460(4) Å	γ = 90°.
Volume	3826.0(9) $Å^3$	
Z	4	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.511 mm^{-1}	
F(000)	1644	
Crystal size	0.560 x 0.530 x 0.250 mm^3	
Theta range for data collection	1.462 to 34.998°.	
Index ranges	-14<=h<=14, -26<=k<=26, -41<=l<=41	
Reflections collected	196391	
Independent reflections	16862 [R(int) = 0.0666]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16862 / 2 / 486	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0898	
R indices (all data)	R1 = 0.0414, wR2 = 0.0949	
Absolute structure parameter	0.021(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.437 and -0.229 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for complex **1**.

Fe(1)-N(1)	1.647(13)	C(5)-C(6)	1.392(2)
Fe(1)-N(2)	1.6772(17)	C(5)-C(10)	1.502(3)
Fe(1)-N(1A)	1.701(5)	C(6)-C(7)	1.387(3)
Fe(1)-C(1)	2.0482(16)	C(6)-H(6)	0.9500
Fe(1)-S(1)	2.2743(5)	C(7)-C(8)	1.395(2)
S(1)-C(22)	1.8033(15)	C(7)-C(11)	1.503(2)
O(1)-N(1)	1.154(15)	C(8)-C(9)	1.396(2)
O(2)-N(2)	1.174(2)	C(8)-H(8)	0.9500
O(3)-C(23)	1.4227(19)	C(9)-C(12)	1.504(2)
O(3)-C(22)	1.4348(17)	C(10)-H(10A)	0.9800
O(4)-C(28)	1.344(2)	C(10)-H(10B)	0.9800
O(4)-C(27)	1.441(3)	C(10)-H(10C)	0.9800
O(5)-C(28)	1.218(4)	C(11)-H(11A)	0.9800
O(6)-C(30)	1.351(2)	C(11)-H(11B)	0.9800
O(6)-C(24)	1.442(2)	C(11)-H(11C)	0.9800
O(7)-C(30)	1.197(3)	C(12)-H(12A)	0.9800
O(8)-C(32)	1.357(2)	C(12)-H(12B)	0.9800
O(8)-C(25)	1.4394(19)	C(12)-H(12C)	0.9800
O(9)-C(32)	1.201(3)	C(13)-C(14)	1.390(3)
O(10)-C(34)	1.3583(19)	C(13)-C(18)	1.399(2)
O(10)-C(26)	1.4421(18)	C(14)-C(15)	1.391(3)
O(11)-C(34)	1.202(2)	C(14)-C(19)	1.516(3)
N(3)-C(1)	1.3601(19)	C(15)-C(16)	1.395(3)
N(3)-C(2)	1.388(2)	C(15)-H(15)	0.9500
N(3)-C(4)	1.4415(19)	C(16)-C(17)	1.387(3)
N(4)-C(1)	1.354(2)	C(16)-C(20)	1.514(3)
N(4)-C(3)	1.387(2)	C(17)-C(18)	1.400(2)
N(4)-C(13)	1.441(2)	C(17)-H(17)	0.9500
C(2)-C(3)	1.346(3)	C(18)-C(21)	1.499(3)
C(2)-H(2)	0.9500	C(19)-H(19A)	0.9800
C(3)-H(3)	0.9500	C(19)-H(19B)	0.9800
C(4)-C(5)	1.386(2)	C(19)-H(19C)	0.9800
C(4)-C(9)	1.395(2)	C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800	N(1)-Fe(1)-N(2)	112.3(8)

C(20)-H(20C)	0.9800	N(2)-Fe(1)-N(1A)	121.3(3)
C(21)-H(21A)	0.9800	N(1)-Fe(1)-C(1)	105.0(8)
C(21)-H(21B)	0.9800	N(2)-Fe(1)-C(1)	106.29(8)
C(21)-H(21C)	0.9800	N(1A)-Fe(1)-C(1)	108.0(3)
C(22)-C(26)	1.535(2)	N(1)-Fe(1)-S(1)	113.0(6)
C(22)-H(22)	1.0000	N(2)-Fe(1)-S(1)	109.01(5)
C(23)-C(27)	1.510(2)	N(1A)-Fe(1)-S(1)	101.1(3)
C(23)-C(24)	1.526(2)	C(1)-Fe(1)-S(1)	110.97(5)
C(23)-H(23)	1.0000	C(22)-S(1)-Fe(1)	101.73(5)
C(24)-C(25)	1.519(2)	C(23)-O(3)-C(22)	111.53(11)
C(24)-H(24)	1.0000	C(28)-O(4)-C(27)	114.62(19)
C(25)-C(26)	1.524(2)	C(30)-O(6)-C(24)	117.96(16)
C(25)-H(25)	1.0000	C(32)-O(8)-C(25)	117.05(14)
C(26)-H(26)	1.0000	C(34)-O(10)-C(26)	117.85(12)
C(27)-H(27A)	0.9900	O(1)-N(1)-Fe(1)	169(2)
C(27)-H(27B)	0.9900	O(2)-N(2)-Fe(1)	172.68(18)
C(28)-C(29)	1.496(5)	C(1)-N(3)-C(2)	111.37(13)
C(29)-H(29A)	0.9800	C(1)-N(3)-C(4)	125.30(13)
C(29)-H(29B)	0.9800	C(2)-N(3)-C(4)	123.18(13)
C(29)-H(29C)	0.9800	C(1)-N(4)-C(3)	111.67(14)
C(30)-C(31)	1.501(3)	C(1)-N(4)-C(13)	124.89(13)
C(31)-H(31A)	0.9800	C(3)-N(4)-C(13)	123.34(13)
C(31)-H(31B)	0.9800	N(4)-C(1)-N(3)	103.83(13)
C(31)-H(31C)	0.9800	N(4)-C(1)-Fe(1)	127.95(11)
C(32)-C(33)	1.501(3)	N(3)-C(1)-Fe(1)	127.94(11)
C(33)-H(33A)	0.9800	C(3)-C(2)-N(3)	106.58(15)
C(33)-H(33B)	0.9800	C(3)-C(2)-H(2)	126.7
C(33)-H(33C)	0.9800	N(3)-C(2)-H(2)	126.7
C(34)-C(35)	1.495(2)	C(2)-C(3)-N(4)	106.52(15)
C(35)-H(35A)	0.9800	C(2)-C(3)-H(3)	126.7
C(35)-H(35B)	0.9800	N(4)-C(3)-H(3)	126.7
C(35)-H(35C)	0.9800	C(5)-C(4)-C(9)	122.69(14)
N(1A)-O(1A)	1.171(5)	C(5)-C(4)-N(3)	119.04(14)
		C(9)-C(4)-N(3)	118.26(14)
C(4)-C(5)-C(6)	117.65(15)	C(18)-C(13)-N(4)	118.58(15)
C(4)-C(5)-C(10)	120.90(17)	C(13)-C(14)-C(15)	117.72(16)

C(6)-C(5)-C(10)	121.44(18)	C(13)-C(14)-C(19)	121.43(16)
C(7)-C(6)-C(5)	121.88(16)	C(15)-C(14)-C(19)	120.83(18)
C(7)-C(6)-H(6)	119.1	C(14)-C(15)-C(16)	121.79(18)
C(5)-C(6)-H(6)	119.1	C(14)-C(15)-H(15)	119.1
C(6)-C(7)-C(8)	118.80(15)	C(16)-C(15)-H(15)	119.1
C(6)-C(7)-C(11)	120.08(16)	C(17)-C(16)-C(15)	118.63(16)
C(8)-C(7)-C(11)	121.09(16)	C(17)-C(16)-C(20)	121.3(2)
C(7)-C(8)-C(9)	121.20(15)	C(15)-C(16)-C(20)	120.1(2)
C(7)-C(8)-H(8)	119.4	C(16)-C(17)-C(18)	121.77(17)
C(9)-C(8)-H(8)	119.4	C(16)-C(17)-H(17)	119.1
C(4)-C(9)-C(8)	117.76(14)	C(18)-C(17)-H(17)	119.1
C(4)-C(9)-C(12)	120.77(14)	C(13)-C(18)-C(17)	117.33(16)
C(8)-C(9)-C(12)	121.47(15)	C(13)-C(18)-C(21)	121.54(15)
C(5)-C(10)-H(10A)	109.5	C(17)-C(18)-C(21)	121.13(16)
C(5)-C(10)-H(10B)	109.5	C(14)-C(19)-H(19A)	109.5
H(10A)-C(10)-H(10B)	109.5	C(14)-C(19)-H(19B)	109.5
C(5)-C(10)-H(10C)	109.5	H(19A)-C(19)-H(19B)	109.5
H(10A)-C(10)-H(10C)	109.5	C(14)-C(19)-H(19C)	109.5
H(10B)-C(10)-H(10C)	109.5	H(19A)-C(19)-H(19C)	109.5
C(7)-C(11)-H(11A)	109.5	H(19B)-C(19)-H(19C)	109.5
C(7)-C(11)-H(11B)	109.5	C(16)-C(20)-H(20A)	109.5
H(11A)-C(11)-H(11B)	109.5	C(16)-C(20)-H(20B)	109.5
C(7)-C(11)-H(11C)	109.5	H(20A)-C(20)-H(20B)	109.5
H(11A)-C(11)-H(11C)	109.5	C(16)-C(20)-H(20C)	109.5
H(11B)-C(11)-H(11C)	109.5	H(20A)-C(20)-H(20C)	109.5
C(9)-C(12)-H(12A)	109.5	H(20B)-C(20)-H(20C)	109.5
C(9)-C(12)-H(12B)	109.5	C(18)-C(21)-H(21A)	109.5
H(12A)-C(12)-H(12B)	109.5	C(18)-C(21)-H(21B)	109.5
C(9)-C(12)-H(12C)	109.5	H(21A)-C(21)-H(21B)	109.5
H(12A)-C(12)-H(12C)	109.5	C(18)-C(21)-H(21C)	109.5
H(12B)-C(12)-H(12C)	109.5	H(21A)-C(21)-H(21C)	109.5
C(14)-C(13)-C(18)	122.63(15)	H(21B)-C(21)-H(21C)	109.5
C(14)-C(13)-N(4)	118.67(14)	O(3)-C(22)-C(26)	107.84(11)
O(3)-C(22)-S(1)	108.82(10)	O(5)-C(28)-O(4)	122.1(3)
C(26)-C(22)-S(1)	112.48(10)	O(5)-C(28)-C(29)	126.6(2)
O(3)-C(22)-H(22)	109.2	O(4)-C(28)-C(29)	111.3(3)

C(26)-C(22)-H(22)	109.2	C(28)-C(29)-H(29A)	109.5
S(1)-C(22)-H(22)	109.2	C(28)-C(29)-H(29B)	109.5
O(3)-C(23)-C(27)	108.77(13)	H(29A)-C(29)-H(29B)	109.5
O(3)-C(23)-C(24)	107.72(12)	C(28)-C(29)-H(29C)	109.5
C(27)-C(23)-C(24)	114.93(13)	H(29A)-C(29)-H(29C)	109.5
O(3)-C(23)-H(23)	108.4	H(29B)-C(29)-H(29C)	109.5
C(27)-C(23)-H(23)	108.4	O(7)-C(30)-O(6)	124.29(19)
C(24)-C(23)-H(23)	108.4	O(7)-C(30)-C(31)	126.5(2)
O(6)-C(24)-C(25)	105.93(12)	O(6)-C(30)-C(31)	109.3(2)
O(6)-C(24)-C(23)	109.16(13)	C(30)-C(31)-H(31A)	109.5
C(25)-C(24)-C(23)	109.50(12)	C(30)-C(31)-H(31B)	109.5
O(6)-C(24)-H(24)	110.7	H(31A)-C(31)-H(31B)	109.5
C(25)-C(24)-H(24)	110.7	C(30)-C(31)-H(31C)	109.5
C(23)-C(24)-H(24)	110.7	H(31A)-C(31)-H(31C)	109.5
O(8)-C(25)-C(24)	107.43(12)	H(31B)-C(31)-H(31C)	109.5
O(8)-C(25)-C(26)	109.37(13)	O(9)-C(32)-O(8)	123.67(17)
C(24)-C(25)-C(26)	111.64(12)	O(9)-C(32)-C(33)	126.15(18)
O(8)-C(25)-H(25)	109.5	O(8)-C(32)-C(33)	110.17(17)
C(24)-C(25)-H(25)	109.5	C(32)-C(33)-H(33A)	109.5
C(26)-C(25)-H(25)	109.5	C(32)-C(33)-H(33B)	109.5
O(10)-C(26)-C(25)	107.66(12)	H(33A)-C(33)-H(33B)	109.5
O(10)-C(26)-C(22)	107.97(11)	C(32)-C(33)-H(33C)	109.5
C(25)-C(26)-C(22)	108.72(12)	H(33A)-C(33)-H(33C)	109.5
O(10)-C(26)-H(26)	110.8	H(33B)-C(33)-H(33C)	109.5
C(25)-C(26)-H(26)	110.8	O(11)-C(34)-O(10)	123.76(15)
C(22)-C(26)-H(26)	110.8	O(11)-C(34)-C(35)	124.65(15)
O(4)-C(27)-C(23)	108.67(14)	O(10)-C(34)-C(35)	111.59(14)
O(4)-C(27)-H(27A)	110.0	C(34)-C(35)-H(35A)	109.5
C(23)-C(27)-H(27A)	110.0	C(34)-C(35)-H(35B)	109.5
O(4)-C(27)-H(27B)	110.0	H(35A)-C(35)-H(35B)	109.5
C(23)-C(27)-H(27B)	110.0	C(34)-C(35)-H(35C)	109.5
H(27A)-C(27)-H(27B)	108.3	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5		
O(1A)-N(1A)-Fe(1)	170.0(7)		

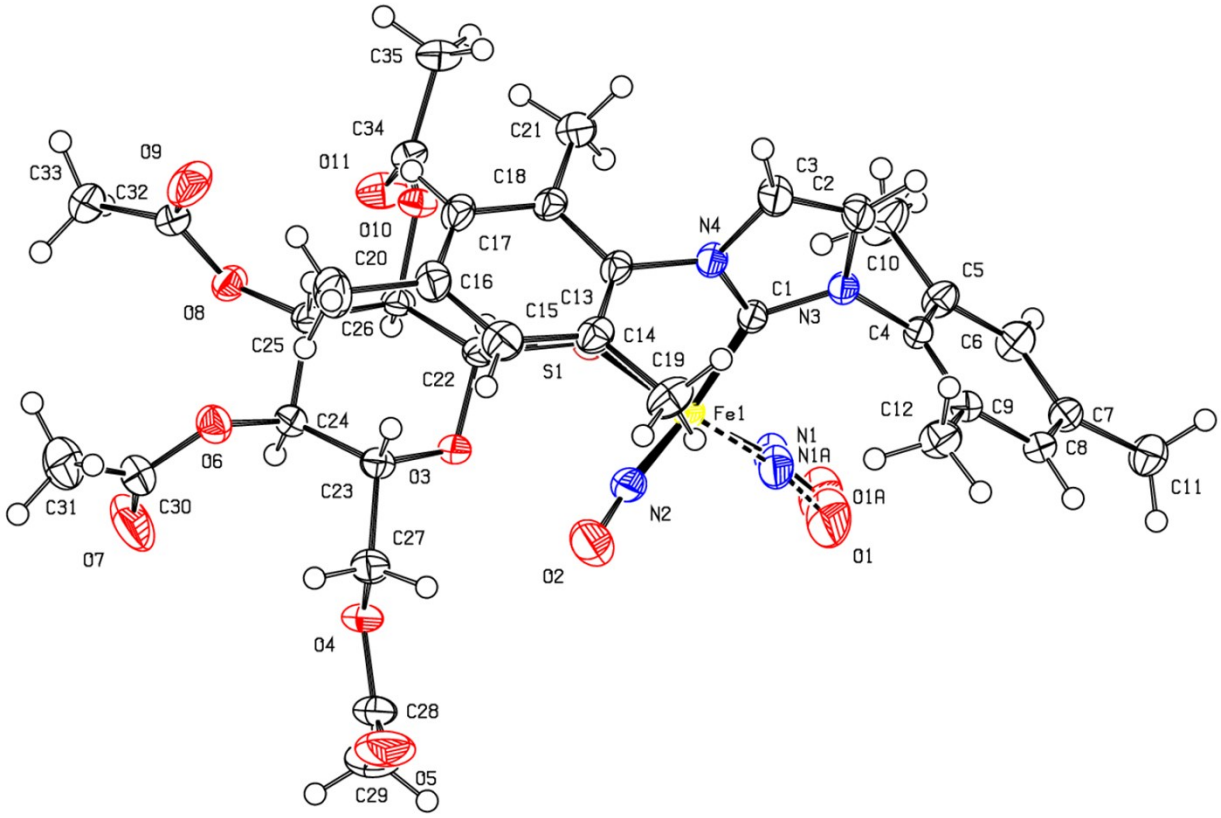


Figure S13. ORTEP drawing and labeling scheme of complex **1** with thermal ellipsoids drawn at 50% probability.

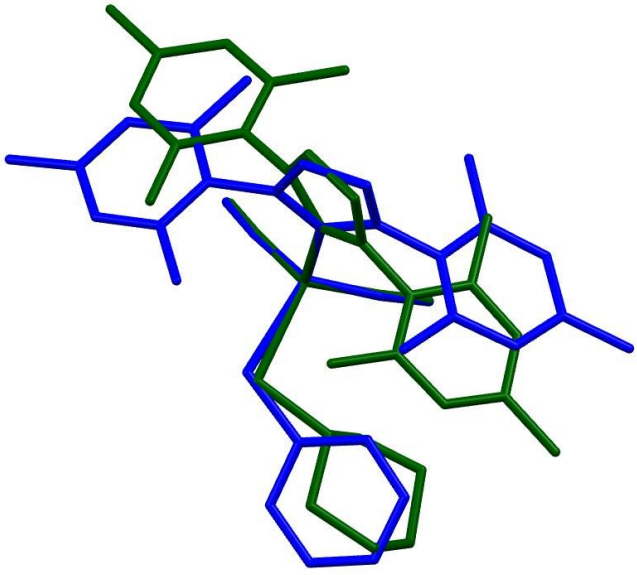


Figure S14. Overlay of Complex **1** (green) and Complex **3** (blue). The acetyl groups on the thioglucose have been omitted for clarity.