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PAPER

Structure and Nitrite Reduction Reactivity Study of Bio-inspired Copper(I)-nitro Complexes in Steric and Electronic Considerations of Tridentate Nitrogen Ligand†

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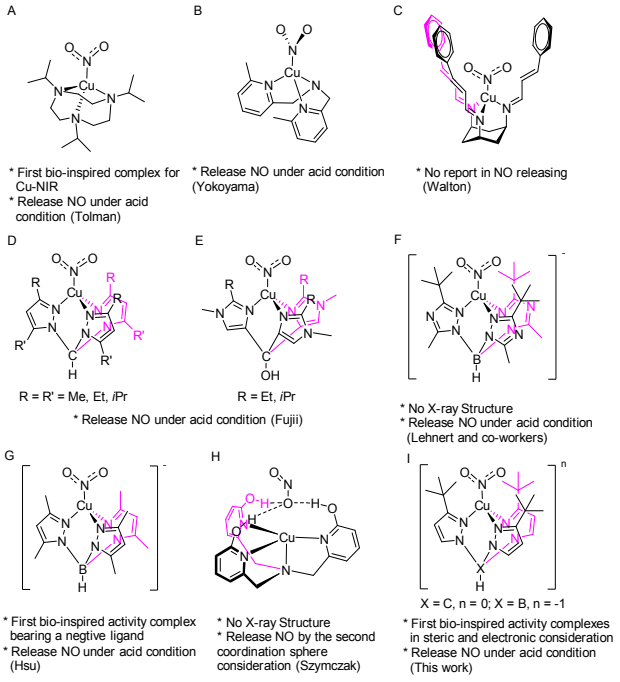
Two copper(I)-nitro complexes [Tpm$^{3\text{-}tBu}$Cu(NO$_2$)] (**1**) and [(Ph$_3$P)$_2$N][Tp$^{3\text{-}tBu}$Cu(NO$_2$)] (**2**), containing steric bulky neutral tris(3-tert-butylpyrazolyl)methane and anionic hydrotris(3-tert-butylpyrazolyl)borate lignads, have been synthesized and characterized. Complex **2** adopts a unique κ^2-binding mode of Tp$^{3\text{-}tBu}$ around copper(I)-nitro environment in solid state and shows four-coordinated tetrahedral geometry surrounded by a nitro and three pz$^{3\text{-}tBu}$ groups in solution. Both complexes **1** and **2** allow for the stoichiometric reduction of NO_2^- to NO with H^+ addition. The results of this efforts show the increasing steric bulky and electronic donation properties on the nitrogen ancillary ligand will improve the nitrite reduction ability on the copper(I)-nitro model complexes.

Introduction

Copper-containing nitrite reductases (Cu-NIRs) catalyze the reduction of nitrite to nitric oxide (NO), a key step in denitrification.[1-5] Base on numerous spectroscopic and crystallographic studies, the catalysis mechanisms of Cu-NIRs will involve formation of copper(I)-nitro (N-bound) or -nitrito (O-bound) core species in type 2 center.[6-18] The type 2 active site of Cu-NIRs contains a copper ion ligated by three histidines that are in a facial conformation.[3] Due to the complexity of the Cu-NIRs enzyme structures, chemists have tried to use some relatively simple ligands to model the environment of the type 2 copper center. However, because of the instability of copper(I)-nitro complexes, only a few copper(I)-nitro complexes have been synthesized and fully characterized.[19-27] Despite the instability issue, using simple ligands, Tolman and co-workers successfully synthesized [(^{i}Pr-TACN)Cu(NO$_2$)],[20] which forms NO$_{(g)}$ by reaction with acid, generating the first functional biomimetic model of the copper center in Cu-NIRs. To explore the electronic influences of compounds of this type, various N3 donating ancillary ligands have been made and their complexes have been fully characterized by neutral ligand such as tris(pyrazolyl)methane (Tpm),[24, 25] and tris(4-imidazolyl)carbinol (TIC),[24] or by negative ligand such tris(pyrazolyl)borate (Tp)[25] or tris(triazolyl)borate[28] tridentate ligands in model copper(I)-nitro complexes (Scheme 1). Recently, the first example of a monomeric copper(I)-nitrito complex, containing two bidentate nitrogen ligands, was described, but its reduction ability of NO_2^- to NO was not evaluated.[29]



Scheme 1. Structural Illustrations of specific Tpm, Tp, and other Cu(I) nitrite complexes bearing in N3 ligand environment.

A few Cu(II)-nitrito complexes with Tp ligand have been characterized by X-ray crystallography showing either a symmetric

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† Electronic Supplementary Information (ESI) available: Includes detailed information about the characterization spectrum, theoretical calculations, and X-ray structure determinations (CCDC 1576739-1576740). see DOI: 10.1039/x0xx00000x

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or asymmetric η^2-O,O coordination mode of the NO_2^- ligand depending on the pyrazolyl substituents.[30, 31] However, these compounds do not support nitric oxide formation from nitrite.[32] Very recently, electron-deficient β-diketiminate copper(II)-nitrito complex also show the activation of nitrite through the oxygen atom transfer pathway or thiol reduction.[27, 33] Two phosphine ligands supported copper(I)-nitrito complexes, have described by our group and others, could release NO under acidic condition act as functional model of Cu-NIRs.[34, 35]

In order to understand how electronic issue will affect the nitrite reduction ability in the bio-inspired copper(I)-nitro model of Cu-NIRs, we first reported and examined the electronic rich anionic $[(Ph_3P)_2N][Tp^{Me2}Cu(NO_2)]$ complex which is more effective model compound for nitrite reduction to NO than neutral $[Tpm^{Me2}Cu(NO_2)]$ analogue.[25] However, steric hindrance influences discussion in Tp^{RR} type copper(I)-nitro complexes still remains an unknown entity. Since Tp^{Me2} and $Tp^{3\text{-}tBu}$ ligands have similar electronic donating ability, as is evident from similar value in the $[Tp^{R,R}Cu(CO)]$ stretching frequencies (νCO: 2066 cm^{-1} for Tp^{Me2}; 2069 cm^{-1} for $Tp^{3\text{-}tBu}$).[36] Therefore, the $Tp^{3\text{-}tBu}$ will be chosen to explore how the steric change in the ligand from Tp^{Me2} to $Tp^{3\text{-}tBu}$ alters the structures and the spectral properties of copper(I)-nitro complexes (Chart 1). The electronic effect between the neutral $Tpm^{3\text{-}tBu}$ and anionic $Tp^{3\text{-}tBu}$ was also investigated. The synthesis of two new copper(I)-nitro complexes $[Tpm^{3\text{-}tBu}Cu(NO_2)]$ (**1**) and $[(Ph_3P)_2N][Tp^{3\text{-}tBu}Cu(NO_2)]$ (**2**) are described here, both could evolve $NO_{(g)}$ upon protonation and act as bio-inspired compounds for Cu-NIRs.

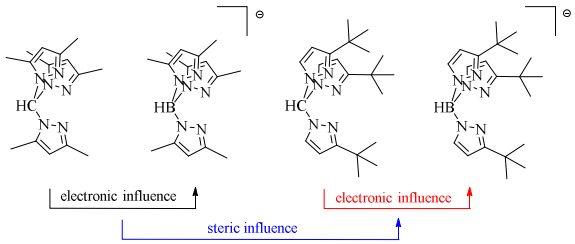


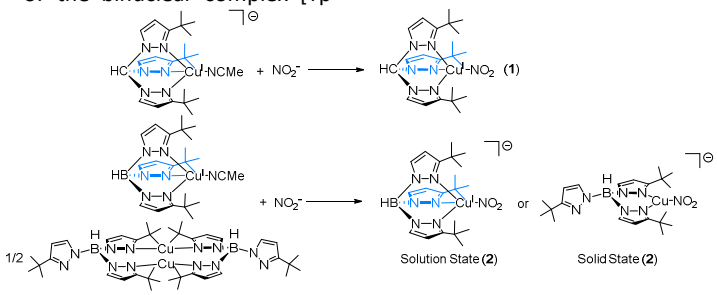
Chart 1. Comparisons of the Tpm^{Me2}, Tp^{Me2}, $Tpm^{3\text{-}tBu}$ and $Tp^{3\text{-}tBu}$ ligand sets.

Results and discussion

The neutral copper(I)-nitro complex $[Tpm^{3\text{-}tBu}Cu(NO_2)]$ (**1**) was prepared through the reaction of $[Tpm^{3\text{-}tBu}Cu(CH_3CN)](BF_4)$[37] with $NaNO_2$ and isolated as a yellow solid. For comparison to neutral $Tpm^{3\text{-}tBu}$ ligand, the mononuclear complex $[Tp^{3\text{-}tBu}Cu(CH_3CN)]$[38] or the binuclear complex $[Tp^{3\text{-}tBu}Cu]_2$[38] react with $[(Ph_3P)_2N](NO_2)$ $[(Ph_3P)_2N$ = bis-(triphenylphosphine)iminium] in THF yielded a yellow solution that deposited an mononuclear copper(I)-nitro complex $[(Ph_3P)_2N][Tp^{3\text{-}tBu}Cu(NO_2)]$ (**2**) as pale yellow prism upon cooling to -20 °C (Scheme 2). The anionic copper(I)-nitro species is rarely reported due to their instability and air-sensitivity.[21] Only two examples were described separately by Lehnert and his co-workers[28] and our lab[25], but only our lab reported crystallographic structure of anionic copper(I)-nitro complex $[(Ph_3P)_2N]$ $[Tp^{Me2}CuNO_2]$. The FAB-MS data of **1** shows a positive molecular ion peaks (*m/z* = 445.16) which is corresponding to the loss of coordinated NO_2^- (Fig. S1, ESI†). On the other hand, the ESI-MS data of anionic complex **2** displays a negative molecular ion peaks (*m/z* = 490.37) contains coordinated NO_2^- (Fig. S2, ESI†). UV-vis spectra of **1** and **2** contain diagnostic metal-to-ligand charge-transfer bands at 320 nm (ε = 4200 $M^{-1}cm^{-1}$) and 295 nm (ε = 4292 $M^{-1}cm^{-1}$), respectively.

Complexes **1** and **2** were obtained as single crystals and investigated by X-ray crystallography (see Table 1), indicating that both complexes are mononuclear. As shown in Fig. 1, complex **1** has a C3 pseudoaxis along the $C_{methine}\cdots Cu\cdots N$ atoms with a symmetric disorder of nitrite molecule. The $Tpm^{3\text{-}tBu}$ tridentate ligand bound to copper ion in a κ^3-manner and the nitrite ion is bound to copper in a N coordination manner. The coordination geometry of copper atom in complex **1** is described as tetrahedral environment. The Cu-$N_{nitrite}$ distance of 1.921(9) Å in complex **1** is longer than the $[Tpm^{Me2}Cu(NO_2)]$ [1.833(6) Å][24] due to the steric hindrance of 3-tert-butyl compared to 3-methyl.

Complex **2** shows a Y-shape coordinated environment by two nitrogen of the anion $Tp^{3\text{-}tBu}$ ligand in a κ^2-manner and the N-bound nitrite ion as shown in Fig. 2, is a new binding mode for Tp ligand in copper-nitrite chemistry. Very recently, a potential relevance anionic three coordinate Cu(I) nitro complex bearing a β-dikitiminate ligand was reported by Warren.[27] Two pyrazolyl rings of $Tp^{3\text{-}tBu}$ ligand are binding to copper(I)-nitro core and the third pyrazolyl ring is hanging away from the copper(I) core. The steric hindrance and charge consideration of the $Tp^{3\text{-}tBu}$ ligand presumably are responsible for adoption of this unusual binding mode.[38] The average distance of Cu-N_L of complex **2** is 1.993 Å which is shorter than related bis(pyrazolyl)methane ligand Cu(II) (bis-nitrito) complex (2.005 Å)[32] due to the electronic consideration of ligand effect. The IR analysis (KBr pellets) also supports the different structural properties between **1** and **2**. The NO_2^- stretching bands of **1** appear at 1306, 1282 cm^{-1}, and **2** at 1319, 1293 cm^{-1}. The higher NO_2^- frequencies in **2** are due to the three-coordinated copper(I)-nitro environment.



Scheme 2. Method for synthesis of copper(I)-nitro complexes **1** and **2**

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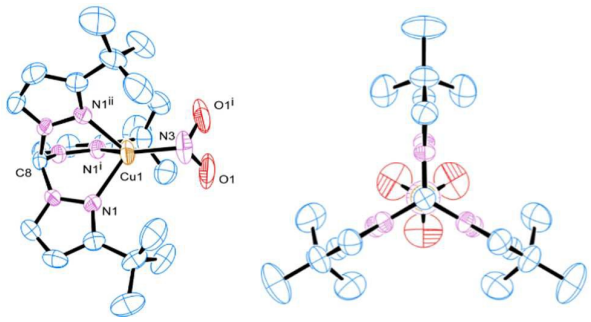

Fig. 1 ORTEP drawing of the X-ray structure of [Tpm$^{3\text{-}t\text{Bu}}$Cu(NO$_2$)] (**1**) (50% ellipsoids; hydrogen atoms not shown for clarity) and the projections along their C3-pseudoaxis.

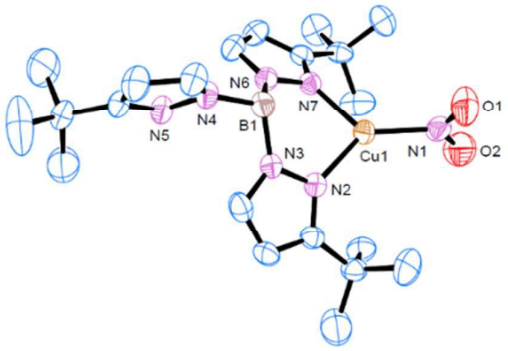

Fig. 2 ORTEP drawing of an anion of the X-ray structure of [(Ph$_3$P)$_2$N][Tp$^{3\text{-}t\text{Bu}}$Cu(NO$_2$)] (**2**) (50% ellipsoids; hydrogen atoms not shown for clarity).

The solution structures of complex **1** and **2** were confirmed by NMR and IR analysis. Interestingly, measurements of **1** carried out in solution and solid states give consistent results, whereas the structure of **2** in solution disagrees with that in the solid state (see Table 2). The ^{1}H NMR spectrum of complex **2** reveals only one type of pz$^{3\text{-}t\text{Bu}}$ signals, implying the symmetrical κ^3-coordinated nature of Tp$^{3\text{-}t\text{Bu}}$ in solution. To obtain better understanding of its solution behavior, complex **2** was then subjected to the variable temperature NMR studies (333 K to 173 K; THF-d^8 as NMR solvent). The chemical shifts for pz$^{3\text{-}t\text{Bu}}$ were observed to be temperature independent (Fig. S4, ESI†). Furthermore, the IR spectrum of **2** recorded in DMSO exhibits the NO_2^- stretching bands at 1299 and 1270 cm^{-1}, similar to the peaks shown in [(PPh$_3$)$_2$N][Tp^{Me,Me}Cu(^{14}NO$_2$)][25], consistent with a more electron-rich copper center. The facts suggest that complex **2** in solution has a Cu(I) center surrounded by three pz$^{3\text{-}t\text{Bu}}$ moieties and a NO_2^- group thus adopts a distorted tetrahedral geometry (see Scheme 2).

The dispersion-corrected DFT calculations were performed to shed more light on the structural variation from solid state to solution. The B3LYP-D3/6-31g* approach in Gaussian 09 program was exploited to obtain the optimized structures. The polarized continuum model (PCM) was employed to mimic solvation. The tetra-coordinated structures of [Tp$^{3\text{-}t\text{Bu}}$Cu(NO$_2$)]$^-$ and [Tp^{Me2}Cu(NO$_2$)]$^-$ are respectively about 8 and 12 kcal/mol more stable than the tri-coordinated isomers with/without the consideration of solvent effects. According to the crystal structural analysis of **2**, interaction between the N atom on the uncoordinated pz$^{3\text{-}t\text{Bu}}$ and the H atom on [(Ph$_3$P)$_2$N]$^+$ can be found. Therefore, the effect of the counterion [(Ph$_3$P)$_2$N]$^+$ was further taken into account in the gas-phase calculation. To our surprise, in the presence of [(Ph$_3$P)$_2$N]$^+$, the tetra-coordinated structure of **2** is not a minimum on the energy surface. Instead, the equilibrium geometry obtained after optimization shows the dissociation of one of the pz$^{3\text{-}t\text{Bu}}$ fragments, thereby leading to a trigonal planar arrangement of the Cu(I) center. The shortest distance between [Tp^{Me2}Cu(NO$_2$)]$^-$ and [(Ph$_3$P)$_2$N]$^+$ was found to be 2.432 Å (Fig. S5, ESI†). On the other hand, the tetra-coordinated structure of [(Ph$_3$P)$_2$N][Tp^{Me2}Cu(NO$_2$)] was calculated to be 18.7 kcal/mol more stable than the tri-coordinated one (Fig. S6, ESI†). Consequently, the structural variation of **2** can be attributed to both the steric effect and the necessity to neutralize the negative charge on the ligand. For the tetra-coordinated isomers, the average Cu–N bond length between Cu and pz$^{3\text{-}t\text{Bu}}$ in [Tp$^{3\text{-}t\text{Bu}}$Cu(NO$_2$)]$^-$ is 0.06 Å longer than that in [Tp^{Me2}Cu(NO$_2$)]$^-$ (Fig. S7, ESI†). Hence, the anionic Tp$^{3\text{-}t\text{Bu}}$ ligand is much easier to be attracted by [(Ph$_3$P)$_2$N]$^+$ and undergo dissociation of one pz$^{3\text{-}t\text{Bu}}$ arm.

Table 1. Selected Bond Distance (Å) and Angles (deg) for **1**, **2**, and Known Relevant Copper(I)-Nitro Complexes

	Cu-N$_{nitro}$	N-O	Cu-N$_L$	O-N-O	N$_L$-Cu-N$_{nitro}$	N$_L$-Cu-N$_L$	ref
[Tpm$^{3\text{-}t\text{Bu}}$Cu(NO$_2$)] (**1**)	1.921(9)	1.264(9) 1.264(9)	2.112(4) 2.112(4) 2.112(4)	96.2(7)	125.93(9) 125.93(9) 125.93(9)	89.06(13) 89.06(13) 89.06(13)	this work
[(Ph$_3$P)$_2$N][Tp$^{3\text{-}t\text{Bu}}$Cu(NO$_2$)] (**2**)	1.925(4)	1.224(3) 1.224(4)	1.985(3) 2.001(3)	122.8(3)	131.53(13) 131.98(13)	96.33(12)	this work
[Tpm^{Me,Me}Cu(NO$_2$)]	1.883(6)	1.176(7) 1.278(7)	2.051(3) 2.051(3) 2.124(5)	117.4(5)	126.7(1) 126.7(1) 128.4(2)	86.2(2) 87.6(1) 87.6(2)	24
[(PPh$_3$)$_2$N][Tp^{Me,Me}Cu(NO$_2$)]	1.927(5)	1.212(9) 1.290(12) 1.161(10)^a 1.332(13)^a	2.070(3) 2.078(5) 2.103(4)	116.7(7) 116.8(8)^a	121.07(19) 126.38(19) 128.2(2)	89.17(16) 90.19(14) 90.51(17)	25
NaNO$_2$		1.240(3)		114.9(5)			39

^{a} Oxygen atoms in the copper-bound nitro were found to be disordered.

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Table 2. Comparisons on the Vibrational Frequencies of **1**, **2**, and Known Relevant Copper(I)-Nitro Complexes

compound	FT-IR cm^{-1}(KBr) $\nu(NO_2)$	FT-IR cm^{-1}(Solution, DMSO) $\nu(NO_2)^a$	ref
$[Tpm^{3\text{-}tBu}Cu(^{14}NO_2)]$ (**1**)	1306, 1282, 821	1303, 1283	this work
$[Tpm^{3\text{-}tBu}Cu(^{15}NO_2)]$	1285, 1256, 814		
$[(Ph_3P)_2N][Tp^{3\text{-}tBu}Cu(^{14}NO_2)]$ (**2**)	1319, 1293, 812	1299, 1270	this work
$[(Ph_3P)_2N][Tp^{3\text{-}tBu}Cu(^{15}NO_2)]$	1300, 1265, 820		
$[Tpm^{Me,Me}Cu(^{14}NO_2)]$	1312, 1289, 824	-	24
$[Tpm^{Me,Me}Cu(^{15}NO_2)]$	1289, 1262, 814		
$[(PPh_3)_2N][Tp^{Me,Me}Cu(^{14}NO_2)]$	1302, 1284, 806	1299, 1268[b]	25
$[(PPh_3)_2N][Tp^{Me,Me}Cu(^{15}NO_2)]$	1284, 1265, 805		

[a] Due to the complexity on the fingerprint region, only show the ν_s(N-O) and ν_{as}(N-O) values.
[b] This work.

Table 3. Yields of NO generation of **1**, **2** and known copper(I)-nitro complexes.

Complex	NO yield	Ref
$Tpm^{Me2}CuNO_2$	52.3±3.7 [a] 32.0 [b]	24, 25
$[(Ph_3P)_2N][Tp^{Me2}Cu(NO_2)]$	83.3±2.3 [a]	25
$Tpm^{3\text{-}tBu}Cu(NO_2)$ (**1**)	80.0 [a] 86.4±0.5 [c]	This work
$[(Ph_3P)_2N][Tp^{3\text{-}tBu}Cu(NO_2)]$ (**2**)	93.0 [a] quantitative [c]	This work
$[(Ph_3P)_2N][Ttz^{3\text{-}tBu,5Me}Cu(NO_2)]$	93.0[c]	28

[a.] Addition of 6 equiv. acetic acid and detection from GC-TCD method.
[b] Addition of 4 equiv. acetic acid and detection from the intensities of the EPR signals.
[c] Addition of 4 equiv. acetic acid and detection from UV band of Co(TPP).

Cyclic voltammetry measurements were conducted to assess the ligand properties of the neutral and anionic copper(I)-nitro complexes. Complex **2** exhibits an irreversible wave with an E_{pa} of 0.08 V (Fig. S8, ESI†), which is nearly the same as the Tp^{Me2} copper(I)-nitro analogue.[25] These results provide another evidence that $Tp^{3\text{-}tBu}$ and Tp^{Me2} have identical coordination modes toward the Cu(I)-NO_2 fragment in solution. Besides, the two ligands are evaluated to possess similar electronic donating abilities according to the electrochemical data. In contrast, the cyclic voltammetry of **1** contains an irreversible wave at E_{pa} = 0.16 V (Fig. S9, ESI†),which is significantly higher than that of **2**. This finding indicates the electronic influences of the tridentate ligands dominate the redox properties of the copper(I)-nitro complexes. The irreversible oxidation behavior ($Cu^{I/II}$) of complexes **1** and **2** may due to the coordinate geometry changed via a classical EC mechanism.

In order to probe the viability of **1** and **2** as functional Cu-NIRs models under anaerobic conditions, the CH_2Cl_2 solution of **1** or **2** was treated with 4 equiv. of acetic acid at ambient temperature, color change observed from yellow to blue-green. The results show that complex **2** is highly reactive toward acids, as shown by the immediate color change that occurs when the complex is subjected to acidic conditions. In contrast, **1** reacts more slowly with acid. For the reactivity toward oxygen, we observed complex **2** is extremely air sensitive and that **1** is air- and moisture-stable in the solid state but air-sensitive in solution. These properties may be a consequence of the different electronic nature of the Cu-NO_2 cores of **1** and **2** which has been observed earlier in the studies of $[Tpm^{Me2}CuNO_2]$ and $[(PPh_3)_2N][Tp^{Me2}CuNO_2]$.[25]

To confirm the NO generation ability from these reactions, the generating NO gas was trapped with Co(TPP) (TPP = tetra-phenylporphyrinato) complex that has high affinity for NO (Fig. S10). From the vial-to-vial gas-trapping experiment and UV detection, it was estimated that about 86% and quantitative yield of NO were trapped for complexes **1** and **2**, respectively. Comparisons of the NO evolution results demonstrate that the more steric bulky and electron-rich complex **2** is a more effective model compound for nitrite reduction than the neutral complex **1** and known copper(I)-nitro complexes[25] (see Table 3), and is a good functional bio-inspired Cu-NIRs model. Importantly, no N_2O gas is found by known GC-TCD method[25] and the blue-green copper(II) product $[Tpm^{3\text{-}tBu}Cu(OAc)_2]$ (**3**) as well as $[Tp^{3\text{-}tBu}Cu(OAc)]$ (**4**)[31] are generated as products in the respective reaction of **1** and **2** (Fig. S11 and S12, ESI†). Complexes **3** and **4** prepared via these routes are identical (by UV-vis, IR, and ESI-MS, S11-S14) with samples prepared directly from copper(II) acetate.

Summary and conclusions

In summary, two copper(I)-nitro complexes bearing steric bulky neutral $Tpm^{3\text{-}tBu}$ and anionic $Tp^{3\text{-}tBu}$ were synthesized and exam their nitrite reduction ability. Crystallographic evidence of complex **1** shows a four-coordinated distorted tetrahedral environment and moderate NO generation ability. Complex **2** contains a copper(I)-nitro core in a unique three-coordinated environment in solid state, protonation of which to release NO gas quantitatively is of interest within the context of the chemistry of the biological denitrification process. Our work

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shows that the steric bulky on the ancillary ligand will improve the nitrite reduction ability on the copper(I)-nitro model complexes.

Experimental section

General considerations

All manipulations involving copper(I) complexes were carried out under an atmosphere of purified dinitrogen in the dry box, or using standard Schlenk techniques. Chemical reagents were purchased from Aldrich Chemical Co. Ltd., Lancaster Chemicals Ltd., or Fluka Ltd. All the reagents were used without further purification, apart from all solvents that were dried over Na (Et_2O, THF) or CaH_2 (CH_2Cl_2, CH_3CN) and then thoroughly degassed before use. The mononuclear copper(I) complexes [$Tpm^{3\text{-}tBu}Cu(CH_3CN)](BF_4)$[37] and [$Tp^{3\text{-}tBu}Cu(CH_3CN)$][38] or the dinuclear complex [$Tp^{3\text{-}tBu}Cu]_2$[38] were prepared as described in the literature. IR spectra were recorded on a Varian FT-IR 640 or Brucker Alpha FT-IR spectrometer. UV-vis spectra were recorded on an Agilent 8453 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were acquired on a Varian Gemini-200 proton/carbon FT NMR or a Varian Gemini-500 proton/carbon FT NMR spectrometer. Elemental analyses were performed using a Heraeus CHN-OS Rapid Elemental Analyzer. ESI mass spectra were collected on a Waters ZQ 4000 mass spectrometer. Cyclic voltammetry measurements were taken in 10^{-4} M MeCN solutions using 0.1 M (Bu_4N)(PF_6) as supporting electrolyte and referenced to $Fc^{+/0}$. A platinum wire counter electrode, a glassy carbon working electrode, and an Ag/AgCl (MeCN) reference electrode were used. Gas chromatography thermal conductivity detector (GC-TCD) experiments were performed by using a Agilent/HP 6890 GC with TCD & FID, Porpak Q column (6 ft, 20 mL/min flow rate, 30°C, nitrogen carrier gas), and TCD detector.

[$Tpm^{3\text{-}tBu}Cu(NO_2)$] (1)

A solution of [$Tpm^{3\text{-}tBu}Cu(CH_3CN)](BF_4)$ (0.203 g, 0.435 mmol) in 15 mL methanol was added to a solution of sodium nitrite (0.150 g, 2.175 mmol) in 10 mL methanol followed by stirring 1 hr. The reaction mixture was evaporated under vacuum at room temperature to remove solvent. The resulting precipitates formed were washed by MeOH to give a yellow solid 0.160 g (75%) of product. 1H-NMR(d_3-acetonitrile): δ8.25 (s, 1H, *H*C($Tpm^{3\text{-}tBu}$)$_3$), 7.57 (d, 3H, 5-*H*pz), 6.27 (d, 3H, 4-*H*pz), 1.29(s, 27H, *Me*2pz). IR(KBr, cm^{-1}; $\nu(NO_2)$): 1306, 1282. IR (solution, DMSO, cm^{-1}; $\nu(NO_2)$): 1303, 1283. ESI-MS: m/z = 445.16 [$Tpm^{3\text{-}tBu}Cu]^+$. Anal. Calcd for $C_{22}H_{34}CuN_7O_2$: C, 53.70; H, 6.96; N, 19.92. Found: C, 53.76; H, 7.01; N, 19.89.

[$(Ph_3P)_2N$][$Tp^{3\text{-}tBu}Cu(NO_2)$] (2)

Method A: In glove box, a solution of [$(Ph_3P)_2N$](NO_2) (0.393 g, 0.672 mmol) in 1.4 mL acetone was added to a solution [$Tp^{3\text{-}tBu}Cu]_2$ (0.300 g, 0.336 mmol) in 0.5 mL THF followed by stirring 2 hrs. The solution was kept at -20°C for 3 days under a N_2 atmosphere to yield yellow crystals (0.276 g, 0.269 mmol, 40 %). 1H NMR (d_6-acetone): δ 7.58~7.78 (m), 6.9 (d, 3H, 5-*H*(pz)), 6.01 (d, 3H, 4-*H*(pz)), 1,31(s, 27H, C*Me*). IR (KBr, cm^{-1}; $\nu(NO_2)$): 1319, 1293. IR (solution, DMSO, cm^{-1}; $\nu(NO_2)$): 1299, 1270. ESI-Mass(-): m/z = 490.37 [$Tp^{3\text{-}tBu}Cu(NO_2)]^-$. Anal. Calcd for $C_{57}H_{64}BCuN_8O_2P_2$: C, 66.50; H, 6.27; N, 10.88. Found: C, 66.38; H, 6.57; N, 10.45.

Method B: In glove box, a solution of [$(Ph_3P)_2N$](NO_2) (0.361 g, 0.618 mmol) in 6 mL acetone was added to a solution [$Tp^{3\text{-}tBu}Cu(CH_3CN)$] (0.300 g, 0.618 mmol) in 5 mL THF followed by stirring 2 hrs. The solution was kept at -20°C for 3 days under a N_2 atmosphere to yield yellow crystals (0.128 g, 0.125 mmol, 20 %).

[$Tpm^{3\text{-}tBu}Cu(O_2CCH_3)_2$] (3)

To a stirred methanol solution (15 mL) of $Tpm^{3\text{-}tBu}$ (0.200 g, 0.522 mmol) at r.t. and under nitrogen, $Cu(O_2CCH_3)_2$ (0.063 g, 0.348 mmol) was added. After approximately 12 h the solvent was removed by a rotary evaporator. The residue was extracted with diethyl ether, and undissolved powder was filtered off using Celite. The filtrate was evaporated under reduced pressure to give a blue-green solid 0.121 g (41%) of product. IR (solution, CH_3CN, cm^{-1}): 3377br [ν(O-H)], 2961, 2916, 2866, 1528 [ν(COO)], 1456 [ν(COO)], 1365, 1252, 1160, 1056, 803, 759. ESI-MS: m/z = 504.16 [$Tpm^{3\text{-}tBu}Cu(O_2CCH_3)]^+$. UV-vis ($CH_3CN$)[$\lambda_{max}$, nm($\varepsilon$, cm^{-1} M^{-1})]: 223 (10714), 253 (2192), 672 (53).

X-ray Crystal Structure Determinations

All single-crystal X-ray diffraction data were accumulated using a Bruker Nonius Kappa CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The data collection was executed using the *SMART* program.[40] Cell refinement and data reduction were made with the *SAINT* program.[41] The structure was determined using the *SHELXTL/PC* program[42] and refined using full-matrix least squares. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at calculated positions and included in the final stage of refinement with fixed parameters.

Computational Details

All calculations were executed using Gaussian 09 program package at the B3LYP–D3 level with the 6–31g* basis set.[43-45] The polarized continuum model (PCM) was employed to mimic systems in solution of acetone and DMSO.[46-48] The vibrational frequencies were analyzed at the same level to confirm all the optimized structures are corresponding to the local minima.

Detection of NO generated from 1 or 2

Method A : A solution of **1** (0.029 g, 0.059 mmol) in CH_2Cl_2 (0.9 mL) was prepared in a small vial capped with a rubber septum. A solution of acetic acid (21 μL) in CH_2Cl_2 (0.1 mL) was then introduced with a syringe at room temperature. The solution changed immediately from light-yellow to blue-green. A solution of **2** (0.061 g, 0.059 mmol) in CH_2Cl_2 (0.9 mL) was prepared in a small vial capped with a rubber septum. A solution of acetic acid (21 μL) in CH_2Cl_2 (0.1 mL) was then introduced with a syringe at room temperature. The solution changed immediately from light-yellow to blue-green. Analysis of the headspace gas by a TCD indicated that NO had been generated (80.0 for **1** and 93.0 for **2**). The NO generation data are obtained by using three different experiments (see Table 3). NO concentrations were determined by using a calibration curve correlating responses to known concentrations of NO gas mixed with N_2 (120, 100, 80, 60, and 40 ppm of NO in N_2); molar quantities were calculated using the ideal gas equation.

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Method B : A mixture of **1** (0.003 g, 5.955 X 10^{-6} mol) and [Co(TPP)] (0.004 g, 5.955 X 10^{-6} mol) in MeOH (4 mL) was placed in a septum sealed vial. Acetic acid (2.2 μL, 3.573 X 10^{-5} mol) was injected to this solution via a syringe. The mixture was kept for 60 minutes at room temperature and then the UV/Vis spectrum of the resultant mixture was recorded. The data showed the formation of [Co(NO)TPP]. A mixture of **2** (0.006 g, 5.95 X 10^{-6} mol) and [Co(TPP)] (0.004 g, 5.95 X 10^{-6} mol) in MeOH (4 mL) was placed in a septum sealed vial. Acetic acid (2.2 μL, 3.57 X 10^{-5} mol) was injected to this solution via a syringe. The mixture was kept for 60 minutes at room temperature and then the UV/Vis spectrum of the resultant mixture was recorded. The data showed the formation of [Co(NO)TPP].

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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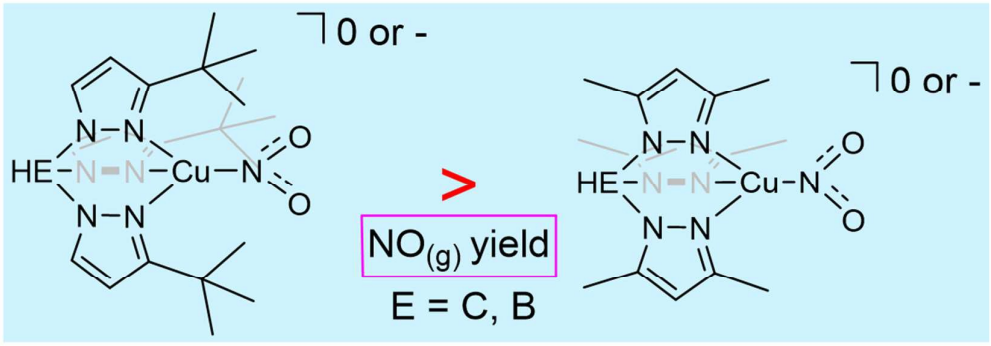

Reactivity in Solution State

Two bio-inspired cooper(I)-nitro complexes bearing steric bulky neutral $Tpm^{3\text{-}t\text{Bu}}$ and anionic $Tp^{3\text{-}t\text{Bu}}$ were synthesized to release NO gas under acid condition.

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