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Investigation of the Nitric Oxide Reduction of the Bis(2,9-Dimethyl-1,10-phenanthroline) Complex of Copper(II) and the Structure of $[Cu(dmp)_2(H_2O)](CF_3SO_3)_2$

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The reaction between nitric oxide (NO) and the Cu(II) complex $Cu(dmp)_2(H_2O)^{2+}$ (**1**, dmp = 2,9-dimethyl-1,10-phenanthroline) has been quantitatively examined in solution. In neutral or alkaline aqueous solutions or in methanol, **1** ($E_{1/2}$ = 0.58 V vs NHE in water) is reduced by NO to give the corresponding cuprous species $Cu(dmp)_2^+$ plus RONO (R = H, CH_3). The analogous reaction for $Cu(phen)_2(H_2O)^{2+}$ (**2**, phen = 1,10-phenanthroline) ($E_{1/2}$ = 0.18 V) is much slower and does not go to completion. In aqueous solutions, the conjugate base of **1** reacts with NO at a slower rate. At low pH, the cuprous complex $Cu(phen)_2^+$ reacts quantitatively with NO_2^- in the reverse reaction to give **2** plus NO, detected with a NO-sensitive electrode. The crystal structure of the triflate salt of **1** was determined, and the cupric ion was found to be 5-coordinate with two bidentate dmp ligands and one H_2O ligand. The triflate salt of **1**, $[Cu(dmp)_2(H_2O)](CF_3SO_3)_2$, crystallizes in the orthorhombic system, space group *Pbca*, with $a = 20.531(4)$ Å, $b = 21.342(8)$ Å, $c = 15.345(5)$ Å, $V = 6723(4)$ Å^3, $Z = 8$, and $R = 0.051$ ($R_w = 0.053$). Kinetics studies for the NO reduction of **1** show the reaction to be first order in [NO], to be slower in basic media, and to be inhibited by higher concentrations of different buffers. This behavior is rationalized in terms of a mechanism where NO must form an inner sphere complex with Cu(II), but such binding at the fifth coordination site is inhibited by prior binding to OH^- or to the conjugate base of the buffer.

Introduction

Nitric oxide has significant roles as an intercellular signaling agent in mammalian biology, e.g. in blood pressure control and in neuronal communication.[2] It has also been identified as a cytotoxic agent in immune response and claimed to have numerous other physiological roles in normal and disease states.[2] In its bioregulatory functions, the principal targets for NO are metal centers, primarily heme and non-heme iron,[3] but other transition metals are potential targets.[4] Metal−NO adducts may also play important roles in the nitrosation reactions of various nucleophiles such as thiols (RSH) to give *S*-nitrosothiols (RSNO) which have been proposed as important carriers of nitric oxide equivalents in cellular systems.[5]

NO has been demonstrated to be a reductant in reactions with Co(II) and Fe(II) halides as well as with Fe(III) porphyrins and ferriheme proteins.[6] Given the importance of Cu(I/II) couples in biological redox systems,[7] the Cu−NO interaction may also be of interest; indeed qualitative aspects of NO reactions of different types of copper proteins have been reported.[8] Furthermore, a substantial fraction of the bacterial nitrite reductases (which catalyze reduction of NO_2^- to NO) are copper enzymes.[9] Described here is a quantitative investigation of the oxidation of NO by the copper(II) complex $Cu(dmp)_2(H_2O)^{2+}$ (**1**, dmp = 2,9-dimethyl-1,10-phenanthroline). The reduction potential for **1** (0.58 V vs NHE in water)[10] is substantially more positive than most other cupric complexes, apparently because of steric effects from the dmp 2,9-methyl substituents. For comparison, the less distorted bis(1,10-phenanthroline)copper(II) analogue $Cu(phen)_2(H_2O)^{2+}$ (**2**, phen = 1,10-phenanthroline) is a weaker oxidant (0.18 V).[10] The product of the Cu(II) oxidation of NO

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is CH_3ONO in methanol solution and is NO_2^- in water, the reverse of the conversions catalyzed by nitrite reductases.[9]

Experimental Section

Materials. The copper starting materials $CuCl_2$ and $Cu(CF_3SO_3)_2$ as well as the ligands neocuproine (dmp) and 1,10-phenanthroline were obtained from Aldrich. Buffer solutions were prepared from $NaHCO_3$, from Na_2HPO_4 (Aldrich), and from "Tris" (tris(hydroxymethyl)-aminomethane) (Sigma). Methanol was distilled from CaH_2 under N_2 prior to use. Nitric oxide gas was obtained from Matheson Gas Products and was passed through a column of KOH pellets to remove higher nitrogen oxides. The complexes $[Cu(phen)_2]X_2$, $[Cu(phen)_2]X$, $[Cu(dmp)_2]X_2$, and $[Cu(dmp)_2]X$ were synthesized with X = Cl or CF_3SO_3 (triflate) according to published methods.[11] The elemental analysis (Quantitative Technologies Inc.) of the triflate salt of the copper(II) dmp complexes proved to be consistent with the formulation $[Cu(dmp)_2(H_2O)](CF_3SO_3)_2$. Calculated for $C_{28}H_{24}O_7N_4S_2F_6Cu$: C, 45.24; H, 3.30; N, 7.04. Found: C, 45.18; H, 3.17; N, 6.85.

Instrumentation. Absorption spectra were recorded with an OLIS-modified CARY 118 spectrometer or a HP 8452A diode array spectrometer. Emission spectra were recorded with a SPEX Fluorolog 2 fluorometer equipped with a Hamamatsu R928A water-cooled PMT. Cyclic voltammograms were recorded with a BAS 100B/W voltammetric analyzer. Low-current electrochemical measurements of [NO] also required a PA-1 preamplifier (BAS) using NO sensitive electrodes. The two types of NO electrodes used were a commercially available World Precision Instrument (WPI) electrode and a Ni(TPMPy) coated-carbon electrode manufactured by Dr. Setsuko Kudo in this laboratory. Experimental details of such electrochemical measurements of NO have been described elsewhere.[12] Kinetic measurements were performed with an Applied Photophysics model SX-18MV stopped-flow spectrometer.

Procedures. All buffer solutions were prepared according to standard procedures. Aqueous solutions for kinetics measurements were degassed by subjecting the samples to at least three freeze−pump−thaw (f-p-t) cycles, or more conveniently, by evacuating the samples on the vacuum line for several cycles at room temperature. Both sample handling techniques gave identical kinetics results. Nitric oxide solutions were prepared in 150 mL flasks adapted with Teflon stopcocks and electrode adapters (injection ports) for anaerobic use. Solutions were allowed to equilibrate with NO by stirring under various P_{NO} for at least 30 min. The copper solutions were backfilled with Ar after degassing. Methanol solutions were degassed by the f-p-t technique, and those containing the copper complexes were then backfilled with Ar. The NO solutions were prepared by repeatedly exposing the evacuated methanol solution to a various P_{NO} for a short period while stirring. The latter process was repeated until no changes were observed on the manometer (∼3−4 times). Solubilities of NO in water and CH_3OH were taken as 1.8×10^{-3} and 1.4×10^{-2} M atm^{-1}, respectively, at 25 °C according to literature values.[13] All solutions for the stopped-flow experiments were transferred from their flasks to the reactant syringes by argon-purged Hamilton airtight syringes (10 mL) with Teflon plungers. Stopped-flow kinetics experiments were carried out under pseudo-first-order conditions with excess NO (at least 10-fold) and $[CuL_2^{2+}] \sim 5 \times 10^{-5}$ M. Absorbance changes were monitored at 455 and 440 nm, the respective λ_{max} for the reaction products $Cu(dmp)_2^+$ (**3**) and $Cu(phen)_2^+$ (**4**).

Titration experiments to determined the pK_a values of the coordinated H_2O of **1** and **2** were carried out spectroscopically. Aqueous copper solutions (30 mL, ∼0.5 mM) were prepared at an initial pH ∼ 5, and then 0.05 M NaOH solution was added (1−2 drops were required for a ΔpH of ∼0.2) to the stirred copper solution dropwise to obtain the desired pH. A small aliquot was drawn from the solution to record the UV−vis absorption spectrum in a 1 cm quartz cell and was then returned to the bulk solution for the next pH determination. The pH was monitored by a Corning pH electrode which was calibrated over pH range 4−10 with standard buffers.

Table 1. Crystallographic Parameters for $[Cu(dmp)_2(H_2O)](CF_3SO_3)_2$

empirical formula	$C_{30}H_{26}CuF_6N_4O_7S_2$
fw	796.2
color/habit	green/prism
crystal size, mm	0.85 × 0.23 × 0.65
crystal system	orthorhombic
space group	*Pbca* (No. 61)
a, Å	20.531(4)
b, Å	21.342(8)
c, Å	15.345(5)
V, Å^3	6723(4)
Z	8
T (°C)	20
ρ_{calc}, g/cm^3	1.57$_3$
λ (Mo Kα), Å	0.710 73
F(000), electrons	3240
abs coeff (μ), cm^{-1}	8.6
no. of obsd reflcns, $I > 3\sigma(I)$	3620
R^a	0.051
$R_w{}^b$	0.053

[a] $R = \Sigma\Delta|F|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(\Delta|F|)^2/\Sigma w(|F_o|)^2]^{1/2}$.

The reduction potentials of the cupric complexes were measured by cyclic voltammetry, which gave $E_{1/2}$ values of 0.59 ± 0.01 and 0.17 ± 0.01 V (vs NHE in pH 5.2 water) for **1** and **2**, respectively, in slightly acidic aqueous solutions, consistent with literature values (0.58 and 0.18 V, respectively).[9] In most cases, the chloride salts were used for kinetics experiments in aqueous solutions; the triflate salts were used for experiments in methanol owing to their higher solubilities in those solvents. Identical kinetics results were obtained with the chloride and triflate salts.

Structure Determination of $[Cu(dmp)_2(H_2O)](CF_3SO_3)_2$. Crystals suitable for X-ray determination were grown from an acetone/ether solution. A unique room-temperature four-circle diffractometer data set was measured at 295 K ($2\theta_{max} = 50°$ with $2\theta/\theta$ scan mode; monochromatic Mo Kα radiation, $\lambda = 0.710\ 73$ Å; 5732 independent reflections, 3620 with $I > 3\sigma(I)$ considered "observed" and used in the full-matrix least-squares refinement on $|F|$ after Gaussian absorption correction and solution by Patterson/Fourier methods). Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{eq})_H$ being included at estimated values for the ligand and difference map sites for the water molecule. Triflate ($CF_3SO_3^-$) "thermal motion" was very high; the oxygen atoms of triflate were resolved into two rotationally disordered sets for which site occupancies refined to 0.86(1) (and complement). Conventional residuals at convergence ($R = \Sigma\Delta|F|/\Sigma|F_o|$; $R_w = [\Sigma w(\Delta|F|)^2/\Sigma w(|F_o|)^2]^{1/2}$) were 0.051 and 0.053, respectively. Neutral atom complex scattering factors were employed; the Xtal 3.4 program system was used.[14] Selected details of crystal data collection are listed in Table 1. The atomic coordinates and the isotropic displacement coefficients, U_{eq}, are listed in the Supporting Information.

Results and Discussion

Comparison of Crystal Structures. The structure of $[Cu(dmp)_2(H_2O)](CF_3SO_3)_2$ (Figure 1) is similar to that reported previously for $[Cu(dmp)_2(NO_3)](CCl_3CO_2)$.[15] Both cations can be described as having distorted trigonal bipyramid coordination geometries with Cu, O (water or nitrate), and one N from each ligand (N(11) and N(12′)) defining the trigonal plane.[16] The axial sites are occupied by the remaining ligand nitrogens. The

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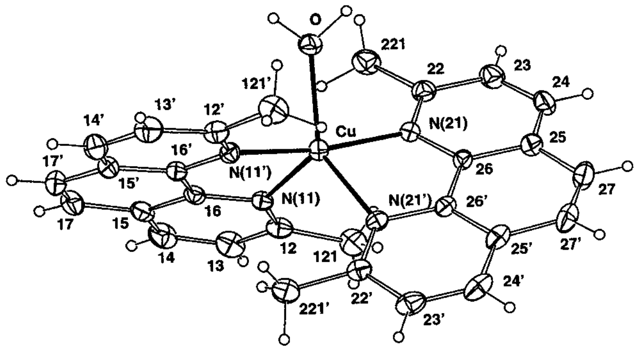

Figure 1. Molecular structure and numbering of atoms of the $\mathrm{Cu(dmp)_2(H_2O)^{2+}}$ cation. Thermal ellipsoids are shown at 20% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{[Cu(dmp)_2(H_2O)](CF_3SO_3)_2}$

Cu−O	2.075(4)
Cu−N(11)	2.123(4)
Cu−N(11′)	1.970(4)
Cu−N(21)	1.988(4)
Cu−N(21′)	2.112(4)
O−Cu−N(11)	118.1(1)
O−Cu−N(11′)	86.1(2)
O−Cu−N(21)	85.4(1)
O−Cu−N(21′)	132.5(1)
N(11)−Cu−N(11′)	82.0(2)
N(11)−Cu−N(21)	104.4(2)
N(11)−Cu−N(21′)	109.3(2)
N(11′)−Cu−N(21)	171.1(2)
N(11′)−Cu−N(21′)	102.1(2)
N(21)−Cu−N(21′)	81.8(2)

Cu−O bond length for the aquo complex **1** (2.075(4) Å) is somewhat shorter than the nitrato analogue (2.15(4) Å), but the Cu−N bond lengths of the two complexes are similar, ranging from 1.970(4) to 2.123(4) Å for the aquo complex and from 2.03(1) to 2.14(1) Å for the nitrato complex. Selected bond distances and angles are listed in Table 2. The sums of the bond angles for the trigonal plane (i.e. Cu, O, N(11), N(21′) atoms of aquo complex; see Figure 1) for both the aquo and nitrato complexes are ∼360°, consistent with the trigonal bipyramid geometry.

The crystal structure of $\mathrm{[Cu(phen)_2(H_2O)](BF_4)_2}$ has also been reported.[17] The $\mathrm{Cu(phen)_2(H_2O)^{2+}}$ cation can also be described as having a distorted trigonal bipyramid geometry. One clear difference between the two complexes is the substantially longer Cu−O bond distance (2.238(8) Å) in the structure of **2** compared to that of **1** (2.075(4) Å). In contrast, the Cu−N distances in the trigonal plane are shorter for the phen complex (2.041(7) vs 2.112(4) Å), while the Cu−N distances to the axial N are similar (∼1.98 Å). The other important structural difference between the phen complex and the dmp complex is the degree of distortion of the N−Cu−N bond angles toward the tetrahedral geometry. The sum of the bond angles defining the trigonal plane is significantly smaller for the phen complex (335 vs ∼360°). This structural difference is reflected in the difference in the dihedral angle (between the nitrogen planes of the ligands). The structure of the phen complex gives a dihedral angle of 31°, while that of the dmp complex gives a dihedral angle of 72°, much closer to the ideal value of 90° for a tetrahedral complex.

Equilibrium Constant Measurements. The equilibrium constants K for the reactions between $\mathrm{CuL_2}^{2+}$ and NO (eq 1) can be calculated as 5.0×10^{-11} M^2 and 5.9×10^{-18} M^2, respectively, for **1** and **2** from the known potential[18] $E°(\mathrm{NO_2}^-/\mathrm{NO}) = 1.20$ V and the measured values for $E_{1/2}(\mathrm{CuL_2}^{2+/+})$ (0.59 and 0.17 V for L = dmp and phen, respectively). Experimentally, when **1** was equilibrated under 1.0 atm P_{NO} (for at least 30 min with stirring) the amount of **1** converted to the $\mathrm{Cu(dmp)_2}^+$ ($\lambda_{max} = 455$ nm; $\epsilon = 6160$ M^{-1} cm^{-1})[19] increased with pH (pH 3.8, 50%; pH 4.5, 91%; pH 4.8, 95%; pH 5.1, 97%), consistent with eq 1. At pH 4.5, the average experimental K_1 value from three trials was 6.5 (±0.9) × 10^{-11} M^2, which corresponds to a $\Delta E°$ (between the two redox couples) value of − 0.60 V, within experimental uncertainty of the − 0.61 V calculated from electrochemical data.

$$\mathrm{CuL_2}^{2+} + \mathrm{NO} + \mathrm{H_2O} \overset{K}{\rightleftharpoons} \mathrm{Cu_2}^{+} + \mathrm{NO_2}^{-} + 2\mathrm{H}^{+} \qquad (1)$$

For the unsubstituted phen analogue **2**, the experimental K_2 obtained in pH 8.6 (Borax/HCl buffer) was 3.4×10^{-20} M^2. The much smaller value is consistent with the more negative value of $\Delta E°$, although applying the Nernst equation to K gives a ΔE of −1.15 V in significant disagreement with that (−1.02 V) from electrochemical measurements. The error here is likely due to the instability of $\mathrm{Cu(phen)_2}^+$ in aqueous solutions, giving a larger uncertainty in the extinction coefficient of the cuprous complex. It is unlikely that the error is due to the electrochemical data for $\mathrm{Cu(phen)_2}^{2+}$, since the $E_{1/2}$ value measured in this laboratory reproduced the literature values.[9]

The reversibility of the latter reaction was demonstrated by adding the cuprous complex $\mathrm{Cu(phen)_2}^+$ to a deaerated, acidic (pH 4.5 acetate buffer) solution of excess sodium nitrite and monitoring the formation of NO quantitatively using a nitric oxide specific electrode[12] calibrated in situ by adding aliquots of NO solution independently standardized by the myoglobin method.[20] The experimentally determined concentrations of NO so generated were 51 and 42 μM, in reasonable agreement with $\mathrm{Cu(phen)_2}^+$ concentrations, 49 and 47 μM, respectively, introduced to the solution. Under these conditions the reaction was effectively quantitative with a 1:1 stoichiometry. Similarly, addition of a 14 μM nitrite to a deaerated pH 4.5 acetate buffer solution of excess $\mathrm{Cu(phen)_2}^+$ resulted in quantitative formation of NO (14 μM). Such production of NO parallels the reactivities of certain cuprous nitrito complexes which have been proposed as models for nitrite reductase.[21]

pK_a of Coordinated Water for $\mathrm{CuL_2(H_2O)^{2+}}$. In the solid state, $\mathrm{Cu(phen)_2}^{2+}$ and $\mathrm{Cu(dmp)_2}^{2+}$ ions are present as 5-coor-

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(16) (a) The deviation from trigonal bipyramidal geometry can be evaluated from the τ parameter.[16b] A true TBP would have a value of 1.0 while a regular tetragonal pyramid would have a τ value of 0. The τ parameter for the triflate salt of **1** is 0.64. The electronic absorption spectra of methanol solutions of **1** and **2** show single, very broad, d−d bands with maxima at ∼750 and ∼740 nm, respectively. On the basis of previously reported structure/spectra correlations for pentacoordinate Cu(II) complexes,[16c] these data are consistent with distorted TBP structures for both ions in solution. (b) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356. (c) Dittler-Klingemann, A. M.; Orvig, C.; Hann, F. E.; Thaler, F.; Hubbard, C. D.; van Eldik, R.; Shindler, S.; Fabian, I. *Inorg. Chem.* **1996**, *35*, 7793−7803.

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dinate species with H_2O occupying the fifth coordination site similar to other Cu(II) complexes with distorted trigonal bipyramidal geometry. For example, McMillin and co-workers have reported the crystal structure of $[Cu(tmbp)_2](ClO_4)_2$ (tmbp = 4,4′,6,6′-tetramethyl-2,2′-bipyridine),[22] where both $Cu(tmbp)_2(H_2O)^{2+}$ and $Cu(tmbp)(ClO_4)^+$ ions were isolated in the solid state. The ubiquity of pentacoordination, even with the weakly ligating ClO_4^- ion, suggests that such cupric complexes will be 5-coordinate in solution as well. This is supported by the optical spectra of **1** and **2** in aqueous solution; both ions display visible region absorptions which tail off to 800 nm, consistent with other 5-coordinate trigonal bipyramidal copper(II) complexes.[23]

The coordinated water of $CuL_2(H_2O)^{2+}$ is likely to have relevant acid/base chemistry (eq 2); therefore, the pK_a's of the complexes were determined, since the two forms are likely to respond differently to NO. These appear to be the first measurements of pK_a's for bis(phen) copper(II) complexes $CuL_2(H_2O)^{2+}$, although pK_a values for 1:1 CuL complexes of phen and other bidentate ligands have been long known.[24] During the course of this work, Fabbrizzi et al.[23] reported the pK_a (8.8) for the analogous 5-coordinate complex $Cu(Me\text{-}bpy)_2(H_2O)^{2+}$ (Me-bpy = 5-methyl-2,2′-bipyridine).

$$CuL_2(H_2O)^{2+} \overset{K_a}{\rightleftharpoons} CuL_2(OH)^+ + H^+ \qquad (2)$$

The visible range absorption spectra of both aqueous **2** and aqueous **1** change with solution pH over certain ranges consistent with the above equilibrium. For example, when dilute aqueous NaOH was added to a solution of **2**, the ligand field absorption band at 650 nm decreased and a new band appeared at 535 nm. The difference spectra clearly show the isosbestic point at 580 nm, indicating the presence of two species in solution. A plot of absorbance ratio ($\lambda_{650}/\lambda_{535}$) vs pH gave a typical titration curve, and a pK_a value of 11.1 ± 0.2 was visually estimated from the midpoint of the region of steepest slope. Similarly titration of aqueous $Cu(dmp)_2(H_2O)^{2+}$ over the pH range of 6.1 to 10.8 resulted in a decrease of the ligand field absorption band at 740 nm and appearance of a new one at 620 nm with an isosbestic point at 685 nm. Plotting the absorbance ratio A_{740}/A_{620} changes vs pH gave a typical titration curve from which the pK_a value of 8.6 ± 0.2 was estimated.

The higher pK_a value for $Cu(phen)_2(H_2O)^{2+}$ relative to that for $Cu(dmp)_2(H_2O)^{2+}$ can be rationalized by comparing Cu−O (water) bonding. The crystal structure of the triflate salt of the $Cu(dmp)_2(H_2O)^+$ ion revealed a Cu−O bond distance of 2.075(4) Å, while that of BF_4^- salt of the $Cu(phen)_2(H_2O)^+$ ion gave a Cu−O bond distance of 2.238(8) Å.[17] The stronger Cu−O bond of the dmp complex should render it more acidic.

Nitric Oxide Reduction of 1. Addition of excess NO to deaerated solutions of **1** in water, neat methanol, or methanol/dichloromethane mixtures led to rapid, quantitative reduction to $Cu(dmp)_2^+$ as observed from spectral changes. The formation of methyl nitrite (CH_3ONO) for the reaction in $MeOH/CH_2Cl_2$ was confirmed qualitatively by GC−MS (CH_3ONO; *m*/*z* 44, 46, 60,61), and GC analysis demonstrated that the mole ratio of $Cu(dmp)_2^+$ to MeONO formed is unity. Formation of nitrite ion (NO_2^-) in aqueous solution was confirmed by the Griess test.[20] Generation of H^+ was qualitatively confirmed by noting that unbuffered aqueous solutions became considerably more acidic as the reaction proceeded. No absorption changes were observed in neat acetonitrile or dichloromethane, confirming the requirement for a protic reactant such as methanol or water, i.e.,

$$\underset{(\mathbf{1})}{Cu(dmp)_2(H_2O)^{2+}} + NO + ROH \rightarrow \underset{(\mathbf{3})}{Cu(dmp)_2^{\ +}} + RONO + H^+ + H_2O \qquad (3)$$

The reduction of **1** could be conveniently followed over time by using a stopped flow spectrometer for rapid mixing of the components and tracking the formation of **3** at the 455 nm λ_{max} of its metal to ligand charge transfer (MLCT) absorption band. When NO was present in large excess, the formation of **3** followed simple first-order kinetics in various media (eq 4) and the rate behavior was independent of the initial concentration of **1**. Furthermore, addition of 5 × 10^{-5} M $NaNO_2$ had no effect on the reaction profile with NO present, and no reaction was observed (on the time scale of the stopped flow experiment) when NO was absent. The (pseudo) first-order rate constants k_{obs} so determined proved to be a linear function of nitric oxide concentration with a zero intercept, indicating simple first-order dependence on [NO] (eq 5)

$$\frac{d[Cu(dmp)_2^{\ +}]}{dt} = -\frac{d[Cu(dmp)_2^{\ 2+}]}{dt} = k_{obs}[Cu(dmp)_2^{\ 2+}] \qquad (4)$$

$$k_{obs} = k_{NO}[NO] \qquad (5)$$

The majority of the kinetics studies were carried out in aqueous or methanol solutions, so the kinetic effect of solvent concentration could not be probed under such conditions. However, some rate measurements were carried out in mixed CH_2Cl_2/MeOH solutions to assess the rate dependence on [MeOH]. At low methanol concentrations under $P_{NO} = 1$ atm, a linear relationship between the k_{obs} and [MeOH] is evident with values of (4.1 ± 0.3) × 10^{-3} s^{-1} and (8.4 ± 0.4) × 10^{-3} for 1.0% and 2.0% MeOH, respectively. However, above ∼3%, k_{obs} values increased nonlinearly, suggesting that MeOH activity is affected by changes in the bulk solvent as methanol becomes a significant fraction. That MeOH, not its conjugate base methoxide ion, is the predominant nucleophile under these (mixed solvent) conditions was confirmed by adding CF_3CO_2H (2.6 mM) to the 2.0% MeOH solution noted above. The effect on k_{obs} was relatively small (6.7 × 10^{-3} s^{-1}).

Since the reaction depicted in eq 3 involves generation of H^+ in a protic medium (one equivalent in MeOH, two in water), careful attention was directed toward evaluating possible kinetic roles of acid and base, including general base catalysis. Specific acid or base catalysis will be reflected in rates responding primarily to changes in pH, general base or acid catalysis will be reflected by rates responding to changing buffer concentrations at constant pH. The observations described above for mixed $MeOH/CH_2Cl_2$ solutions indicated that added acid had little effect on the overall rate of eq 3, suggesting that in these "neutral" or acidic mixed solvent media, the conjugate base of MeOH is at most a minor player. In contrast, Hoshino et al.[25]

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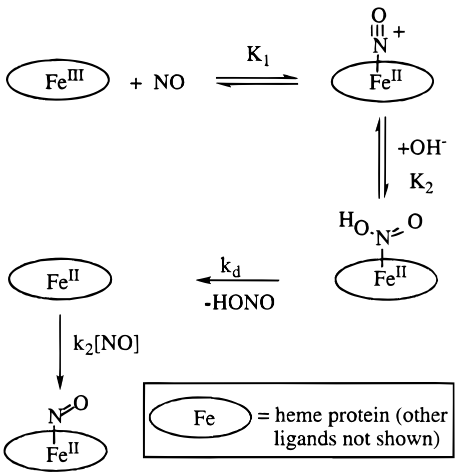
[22] Burke, P. J.; Henrick, K.; McMillin, D. R. *Inorg. Chem.* **1982**, *21*, 1881−1886.

[23] De Santis, G.; Fabbrizzi, L.; Iacopino, D.; Pallavicini, P.; Perotti, A.; Poggi, A. *Inorg. Chem.* **1997**, *36*, 827−832.

[24] (a) Gustafson, R. L.; Martell, A. E. *J. Am. Chem. Soc.* **1959**, *81*, 525−529. (b) Ryland, L. B.; Ronay, G. S.; Fowkes, F. M. *J. Phys. Chem.* **1959**, *62*, 798−801.

[25] Hoshino, M.; Maeda, M.; Konishi, R.; Seki, H.; Ford, P. C. *J. Am. Chem. Soc.* **1996**, *118*, 5702−5707.

Scheme 1



have described the kinetics of the reductive nitrosylations of several ferrihemoproteins $Fe^{III}(P)$ ($Fe^{III}P$ = metmyoglobin, Fe^{III}cytochrome *c*, or methemoglobin) in aqueous media and clearly demonstrated that these reaction rates are strongly catalyzed by hydroxide ion in the pH range 6−9. This behavior was interpreted in terms of rate-limiting attack by OH^- on Fe^{III} coordinated NO according to a mechanism such as outlined in Scheme 1.

Similar kinetic behavior might be anticipated for the NO reduction of **1**; however, this does not appear to be the case under analogous conditions in buffered aqueous solutions. For solutions at fixed concentrations of NO (9.0×10^{-4} M) and Tris buffer (2 mM) and an initial 5×10^{-5} M concentration of **1**, k_{obs} values actually *declined* ∼70% over the pH range 7−9 (Figure 2). This rate/pH profile argues against any form of specific base catalysis over this pH region. This pH regime overlaps with the pK_a of **1** (8.6), so the changing nature of the substrate would be one possible explanation for decreased rates at higher pH. Notably, for the conditions specified, k_{obs} appears to have limiting values of ∼0.6 s^{-1} at lower pH and ∼0.1 s^{-1} at higher pH (see below)

However, the picture is considerably more complicated. Attempts to use other buffers in order to probe higher pH regions immediately gave indications that the buffers were playing a serious role with regard to the kinetics of this system, i.e., the reaction rates varied with the nature and concentration of the buffers. Although one might suspect general base catalysis as a player, the kinetics fingerprint of such catalysis would be rising k_{obs} values with increasing buffer concentrations.[26] In contrast, the opposite was seen, so general base catalysis is also not considered to be an important contributor to the kinetics under these conditions. With Tris, phosphate, and carbonate buffers, increasing concentrations generally resulted in slower rates, suggesting that the buffer may be reversibly binding to the copper(II) (see below). Some representative k_{obs} values are summarized in Table 3.

Given the highly labile nature of copper(II) centers, one must consider the possibility that solution species, such as buffer anions (or other conjugate bases), may coordinate to the site on **1** occupied by H_2O. In such a case, each buffer may have specific effects on the kinetics of the reaction with NO as indeed was observed (Table 3). The simple model in Scheme 2 attempts to account for this possibility by treating buffer complexation as a "dead end" equilibrium.

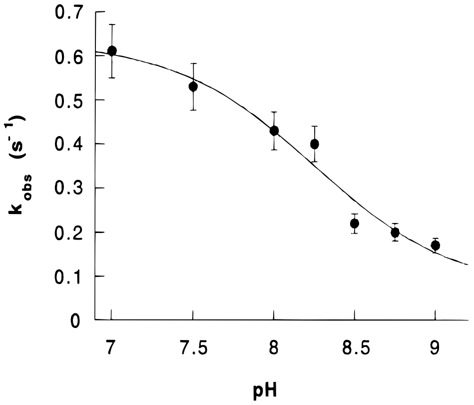


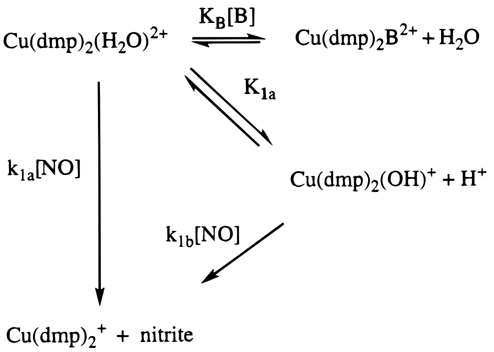
Figure 2. pH dependence data fitted to eq 8 (see text). [$Cu(dmp)_2^{2+}$] = 5.0×10^{-5} M; [NO] = 9.0×10^{-4} M.

Table 3. Representative k_{obs} Values; [$Cu(dmp)_2^{2+}$] = 5.0×10^{-5} M, [NO] = 9.0×10^{-4} M

buffer	pH	$[B]_T$, mM	k_{obs} (s^{-1})[a]	k_{obs}/[NO] (M^{-1} s^{-1})
carbonate	9.0	2.0	0.084	93
		5.0	0.026	29
		10.0	0.017	19
phosphate	6.5	1.0	0.32	356
	6.5	100	0.090	100
Tris	7.0	2.0	0.61	678
	7.5	2.0	0.53	589
	8.00	2.0	0.43	478
		100	0.22	244
	8.25	2.0	0.40	444
	8.50	2.0	0.22	244
	8.75	2.0	0.20	222
	9.00	2.0	0.17	189
		5.0	0.12	133
		10.	0.046	51
		20.	0.031	34

[a] Experimental uncertainties ∼10% for a series of experiments under the same conditions.

Scheme 2



This model leads to the equation

$$k_{obs} = \frac{k_{1b}K_{1a} + k_{1a}[H^+]}{[H^+] + K_{1a} + K_B[B][H^+]}[NO] \qquad (6)$$

which predicts that a plot of k_{obs}^{-1} vs [B] at a constant pH should be linear with a slope of $K_B[H^+]/C_1$ and an intercept of C_2/C_1, where $C_1 = (k_{1b}K_{1a} + k_{1a}[H^+])[NO]$ and $C_2 = [H^+] + K_{1a}$. Such a plot is shown in Figure 3 for the Tris and carbonate/bicarbonate buffers at pH 9.0. These plots give similar intercepts, consistent with the model suggesting that inhibition of Cu(II) reduction by the buffer is by simple coordination and that the K_B for carbonate buffer is about 4-fold larger than K_B

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[26] Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964.

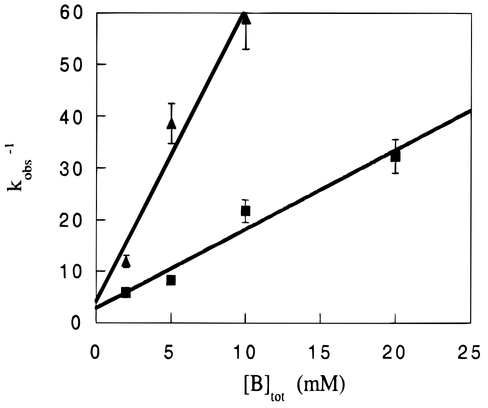


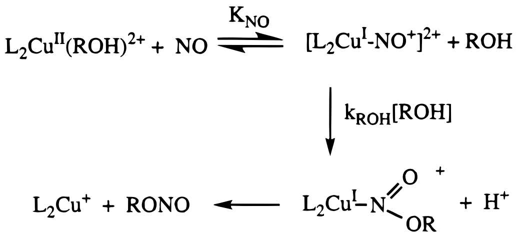
Figure 3. Plots of $1/k_{obs}$ vs total buffer concentration ($[B]_T$) for carbonate (▲) and Tris (■) at pH 9.

for Tris under these conditions. On the basis of this model, the slope/intercept ratio equals $K_B[H^+]/([H^+] + K_{1a})$, and values of 4.5×10^2 and 1.5×10^2 M^{-1} can be calculated for the K_B values for carbonate and Tris, respectively. The K_B so determined for Tris can be used to fit the data in Figure 2 to eq 6, and this was done by allowing the values of K_a, k_{1a}, and k_{1b} to iterate. The solid curve in Figure 2 represents such a (best) fit based on the values $pK_a = 8.2 \pm 0.2$, $k_{1a} = 914$ (±58) M^{-1} s^{-1}, and $k_{1b} = 77$ (±67) M^{-1} s^{-1}. Such a fit indicates that the model described in Scheme 2 is consistent with the kinetics behavior of this system. However, it should be emphasized that the experimental uncertainties in numbers derived from intercepts such as those of Figure 3 are large and that the values derived from such a fit are (at best) approximate.

Nitric Oxide Reduction of 2. The rate of the reaction between NO and the bis(phenanthroline) complex **2** proved to be much slower than that for **1** under comparable conditions. For example, **2** is a least 4 orders of magnitude less reactive than is **1** under the same conditions (9.0×10^{-4} M [NO in pH 8.0 aqueous phosphate buffer (100 mM)), and the reaction does not go to completion. Analogous behavior was seen in neat methanol ($k_{obs} < 10^{-6}$ s^{-1}) where only partial reduction was observed for a solution of $Cu(phen)_2^{2+}$ under NO for several days. The behavior of $Cu(phen)_2^{2+}$ can be rationalized by its reduction potential which is 0.4 V less positive than that of **1**, presumably because the methyl substituents in dmp destabilize the Cu(II) state through steric interaction with one another or with the fifth ligand. Yandell et al. invoked the same argument to rationalize the substantially larger rate constant (ca. 5 orders of magnitude) observed for the outer sphere oxidation of ferrocytochrome *c* by $Cu(dmp)_2^{2+}$ than that by $Cu(phen)_2^{2+}$.[27] In addition, the Cu(II)/Cu(I) structural changes are apparently reflected in the much slower $Cu^{2+/+}$ self-exchange rate constant for $Cu(phen)_2^{2+/+}$ than for $Cu(dmp)_2^{2+/+}$ (by ~400×). The structural barrier energies for electron transfer for **1** and **2** have been estimated at 19 and 34 kJ/mol, respectively.[27]

Mechanistic Considerations. The results described above for the NO reduction of aqueous $Cu(dmp)_2(H_2O)^{2+}$ can be rationalized in terms of an inner sphere mechanism such as illustrated by Scheme 3. The three steps depicted are (i) the reversible equilibrium displacement of solvent ROH (H_2O or ROH) from the copper(II) coordination sphere by NO to form an inner sphere complex copper(II)−nitric oxide complex which is activated toward nucleophilic attack by ROH (step ii) owing to charge transfer from NO to the metal ($Cu^{II}-NO \leftrightarrow Cu^I-NO^+$). Dissociation of the RONO complex (step iii) would be rapid owing to the preference of the cuprous complexes for tetrahedral coordination. Other examples of nucleophilic attack on coordinated NO include the hydroxide reaction with Ru(II)-coordinated NO to give the corresponding nitro complexes[28] and alcohols reacting with Ir(III)-coordinated NO to give isolable alkyl nitrite complexes.[29] Attempts to observe formation of the putative inner sphere complex $Cu(dmp)_2(NO)^{2+}$ when a dichloromethane solution of **1** was exposed to an atmosphere of NO, conditions where there was little net reaction, gave no spectral evidence of a new species. Similarly, examining the early stages of the spectral changes when reactive aqueous solutions were mixed in the stopped-flow kinetics spectrophotometer gave no obvious indication of this intermediate. These (negative) observations can be explained by at least two alternatives: either spectral changes between **1** and the intermediate are quite small, or K_{NO} has a relatively small value. The first-order dependence of the reaction rate on [NO] would be consistent with the latter alternative, since in such a case, the apparent second-order rate constant k_{NO} simply equals $K_{NO}k_{ROH}$ in the absence of other complicating equilibria. While [ROH] is not a variable in aqueous or methanolic solution, the kinetics dependence on [MeOH] in methanolic dichloromethane agrees with this model.

Scheme 3



The inner sphere mechanism would also appear to be favored by the conclusions that buffer anions or conjugate bases substantially inhibit the NO reduction of **1** in aqueous solution as does the formation of the hydroxo conjugate base of **1**. This scheme is qualitatively consistent with the analysis of the reductive nitrosylation of various ferrihemoproteins carried out by Hoshino et al.;[25] however, there are certain key differences. First, in that case, the K_{NO} for formation of the ($Fe^{III}-NO \leftrightarrow Fe^{II}-NO^+$) complex is large and measurable so that under P_{NO} = 1 atm, the nitrosyl complex formation is nearly complete. Second, the dominant nucleophile in that mechanism is not neutral water, but hydroxide ion, although the NO reduction of methemoglobin does show a pH independent pathway as well.

The apparent absence of a $[OH^-]$ dependent activation step for NO reduction of **1** may have a more convoluted explanation. If the conjugate base $Cu(dmp)_2(OH)^+$ is not active toward reaction with NO (i.e., acid dissociation of **1** also is a dead-end equilibrium), the residual reactivity seen at higher pH (i.e. the k_{1b} term in Scheme 2) might instead be due to reaction of OH^- with $Cu(dmp)_2(NO)^{2+}$ as in Scheme 4. This would give the following expression for k_{obs} (which has the same form with respect to pH as eq 6), i.e.,

$$k_{obs} = \frac{k_{H_2O}[H^+] + k_{OH}K_w}{[H+] + K_{1a} + K_B[B][H^+]}K_{NO}[NO] \qquad (7)$$

The two alternatives are not differentiated by the kinetics data.

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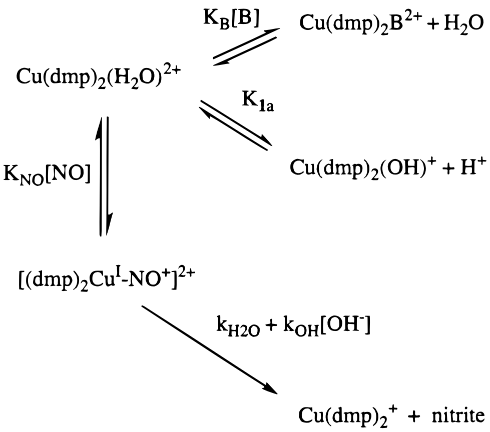
[27] Augustin, M. A.; Yandell, J. K. *Inorg. Chem.* **1979**, *18*, 577−583.

[28] Rhodes, M. R.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 629−635 and references therein.

[29] Reed, C.; Roper, W. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1243.

Scheme 4



The above evidence points to an inner sphere mechanism such as Schemes 3 or 4, involving NO coordination *before* reduction occurs as seen for reductive nitrosylations of ferrihemes and ferriheme proteins first described by Wayland[6] and studied quantitatively by Hoshino et al.[25] However, the viability of an alternative mechanism involving outer sphere electron transfer from NO to **1** in the first step followed by rapid hydrolysis of NO^+ (eqs 8 and 9) needs to be considered.

$$\mathrm{Cu(dmp)_2}^{2+} + \mathrm{NO} \underset{k_{-\mathrm{os}}}{\overset{k_{\mathrm{os}}}{\rightleftharpoons}} \mathrm{Cu(dmp)_2}^{+} + \mathrm{NO}^{+} \qquad (8)$$

$$\mathrm{NO}^{+} + \mathrm{H_2O} \xrightarrow{k_{\mathrm{hyd}}} + \mathrm{H}^{+} + \mathrm{HNO_2} \qquad (9)$$

Two limiting cases can be considered, both of which would display rates with a first-order dependence on [NO]. One pathway might involve a reversible equilibrium (eq 8) followed by rate-limiting hydrolysis of the nitronium ion. In this case, the second-order rate constant would be $k_{NO} = K_{os}k_{hyd}$, where $K_{os} = k_{os}/k_{-os}$. At the other extreme, k_{os} would be rate limiting and the electron transfer is effectively irreversible owing to rapid hydrolysis of nitronium ion. The latter would appear more likely given the expectation that k_{hyd} is quite large.[31] In either case, the reaction rate would be expected to be slower when an anion (buffer conjugate base or hydroxide) is coordinated to the Cu(II) instead of H_2O owing to the (likely) lower reduction potential of a $Cu(dmp)_2B^+$ species. Thus, without observation of an inner sphere complex of NO as was seen during the reductive nitrosation of the ferriheme systems, it is not a simple matter to discount the outer sphere mechanism.

However, for an outer sphere mechanism, the maximum rate constant by which NO reduction of **1** would occur is k_{os}, and a value for this can be estimated from the Marcus cross relation,[32] $k_{os} \sim (k_{11}k_{ex}K_{os})^{1/2}$, where k_{11} is the $Cu(dmp)_2^{2+}/Cu(dmp)_2^+$ self-exchange rate constant, k_{ex} is the self-exchange rate constant for NO^+/NO, and K_{os} the equilibrium constant for eq 10. The $E_{1/2}$ for the NO^+/NO couple has been reported as -1.20 V in aqueous solution,[33] and this would give $\Delta E° = -0.61$ V for eq 10, or $K_{os} = 5.4 \times 10^{-11}$. The value of k_{11} has been reported as 2.0×10^5 M^{-1} s^{-1},[34] and $\Delta G_{ex}^{\ddagger}$ has been estimated as 17.5 kcal/mol in accord with predictions of Marcus theory,[35] the latter exchange being slow (estimated $k_{ex} = (kT/h)(e^{-\Delta G^{\ddagger}/RT}) \cong 1.3$ M^{-1} s^{-1} at 298 K) owing to the large reorganization energies for this process. These values when inserted into the cross relation give an estimate of $\sim 3 \times 10^{-3}$ M^{-1} s^{-1} for k_{os}, which is more than 5 orders of magnitude smaller than the value of k_{NO} measured at lower pH's. Thus, on this basis, the outer sphere reaction mechanism appears unlikely in the present case.

Conclusion

The kinetics of the reduction of $Cu(dmp)_2^{2+}$ and $Cu(phen)_2^{2+}$ by nitric oxide have been examined in solution. Both cupric complexes are five-coordinate in the solid state, similar to other known trigonal bipyramidal cupric complexes, as well as in solution phase. In aqueous solutions both complexes exist in two forms, with water or hydroxide as the fifth coordinating ligand depending on the solution pH. The pK_a of the coordinated water of the dmp complex is more acidic than that of the phen complex by ~2.5 pK_a units, consistent with its shorter Cu−O bond in the solid state (2.07 vs 2.24 Å).

In aqueous solutions $Cu(dmp)_2(H_2O)^{2+}$ reacts with NO in a second-order reaction at least an order of magnitude faster than does $[Cu(dmp)_2(OH)]^+$. Similarly, the presence of buffers such as Tris, carbonate and phosphate inhibit the reaction consistent with possible coordination of the conjugate base with copper(II). There is no evidence for either general or specific base catalysis of the reaction, although, the pK_a of the acidic protons of the coordinated water may obscure such a pathway. The kinetics in mixed CH_3OH/dichloromethane solutions suggest that the reaction under those conditions are first order in methanol. These results are consistent with an inner sphere mechanism where a $Cu(dmp)_2(NO)^{2+}$ complex is formed in undetectable concentrations and undergoes reaction with solvent (H_2O or CH_3OH) leading to formation of $Cu(dmp)_2^+$ plus nitrite (HONO or CH_3ONO). The much higher reactivity of the bis(dmp) complex relative to that of the bis(phen) complex can largely be attributed to the greater stability of copper(I) in the former case owing to relief of steric strain between interligand methyls upon forming the tetrahedral Cu(I) species.

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Supporting Information Available: For the crystal stucture of $[Cu(dmp)_2(H_2O)](CF_3SO_3)_2$, tables of cation non-hydrogen positional and isotropic displacement parameters and structure refinement details, bond lengths and angles, anisotropic displacement parameters of non-hydrogen atoms and hydrogen coordinates, and isotropic displacement parameters are available (5 pages). Ordering information is given on any current masthead page.

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(30) Although there is considerable uncertainty in the value of k_{1b} estimated from the analysis used to fit the model described by Scheme 2 to the data described in Figure 2, the residual reactivity at the higher pH was confirmed (qualitatively) by nonsystematic studies which demonstrated that the reactivity of **1** toward NO at pH 10 and 11 is comparable to or even somewhat higher than that at pH 9 under otherwise analogous conditions.

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