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Variable Nitric Oxide Reactivity of Tropocoronand Cobalt(III) Nitrite Complexes as a Function of the Polymethylene Linker Chain Length

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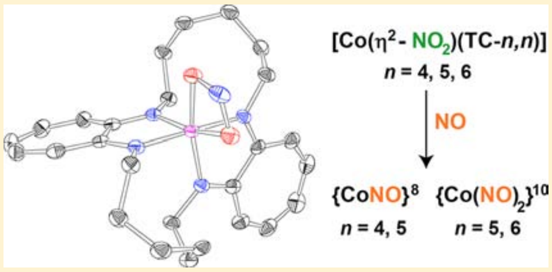
S *Supporting Information*

ABSTRACT: The size-dependent reactivity of cobalt tropocoronands $[\text{TC-}n,n]^{2-}$ is manifest in the NO chemistry of the cobalt(III) nitrite complexes $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-}n,n)]$ (n = 4–6), the synthesis and characterization of which are reported for the first time. Complete conversion of $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-4,4})]$ to the cobalt mononitrosyl $[\text{Co(NO)(TC-4,4)}]$ occurs upon exposure to NO(g). In contrast, addition of NO(g) to $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-5,5})]$ generates both cobalt mono- and dinitrosyl adducts, and addition of nitric oxide to $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-6,6})]$ converts this complex to the dicobalt tetranitrosyl species $[\text{Co}_2(\text{NO})_4(\text{TC-6,6})]$. In the latter complex, two tetrahedral cobalt dinitrosyl units are bound to the aminotroponeiminate poles of the $[\text{TC-6,6}]^{2-}$ ligand. These results significantly broaden the chemistry of cobalt tropocoronands with nitric oxide and the nitrite anion.

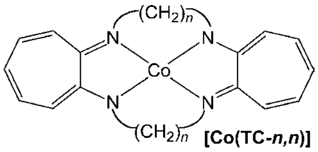


INTRODUCTION

The many functions of physiological nitric oxide (NO), which frequently involve metal ions,[1] have stimulated research into the chemistry of NO as well as that of other nitrogen oxides with coordination compounds. Studies of the biological chemistry of nitrite ion, for example, have implicated NO_2^- in storage and transport pathways for biological NO in the cardiovascular system.[2−4] Nitrite reductases that convert NO_2^- to NO at heme iron or copper active sites occur in both eukaryotes and bacteria.[2,5−9] The preservation of nitrite reductase activity in such a broad range of organisms is an indication of the ubiquity of the relationship between NO_2^- and NO in biology.

Cognizant of these investigations, we have been studying the chemistry of nitrogen oxides with first-row transition-metal complexes of the tropocoronands (TCs), a tetraazamacrocyclic ligand system. Recently, we reported[10] the dependence of the nitric oxide reactivity of cobalt(II) tropocoronands, $[\text{Co(TC-}n,n)]$, on the polymethylene linker chain lengths (Chart 1; n = 3–6). $[\text{Co(TC-}n,n)]$ (n = 4, 5) complexes with shorter chain lengths form simple $[\text{Co(NO)(TC-}n,n)]$ (n = 4, 5) adducts upon exposure to NO(g), whereas $[\text{Co(TC-6,6)}]$, with longer polymethylene linker chains, forms the neutral dicobalt tetranitrosyl complex $[\text{Co}_2(\text{NO})_4(\text{TC-6,6})]$, in which both cobalt centers are coordinated by two nitrosyl ligands and two aminotroponeiminate nitrogen atoms of the tropocoronand macrocycle in a pseudotetrahedral manner.[10] The presence of this complex in the reaction mixture was deduced by IR spectral analysis and crystallographic study of independently prepared material. The IR spectrum revealed ν_{NO} stretches corresponding to species that eluded isolation and structural characterization, and the cobalt(III) nitrite adduct $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-6,6})]$ was the only product that could be isolated and structurally characterized directly from the reaction.[10] The discovery of nitrite formation spurred our interest in the potential interconversion between cobalt nitrosyls and cobalt nitrites. We therefore extended our investigation to examine the size dependence of the reactivity of $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-}n,n)]$ (n = 4–6) complexes with NO(g). The results, including the synthesis and characterization of the starting nitrite complexes, are described in the present report.

Chart 1



EXPERIMENTAL METHODS

General Considerations. Air- and moisture-sensitive materials were handled in an MBraun glovebox under a nitrogen atmosphere. Reagents were used as purchased, without further purification, with the exception of NO. NO obtained from Airgas was purified according to published methods.[11] The NO was passed through an Ascarite column and a 6 ft coil containing silica gel at −78 °C to remove impurities, collected, and stored under nitrogen. ^{15}NO was purchased from Cambridge Isotope Laboratories and purified similarly. All gas transfers were performed using gastight syringes under a nitrogen atmosphere. Methylene chloride and tetrahydrofuran were purified by passage through activated alumina and stored over 4 Å molecular sieves under a nitrogen atmosphere prior to use. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, stored

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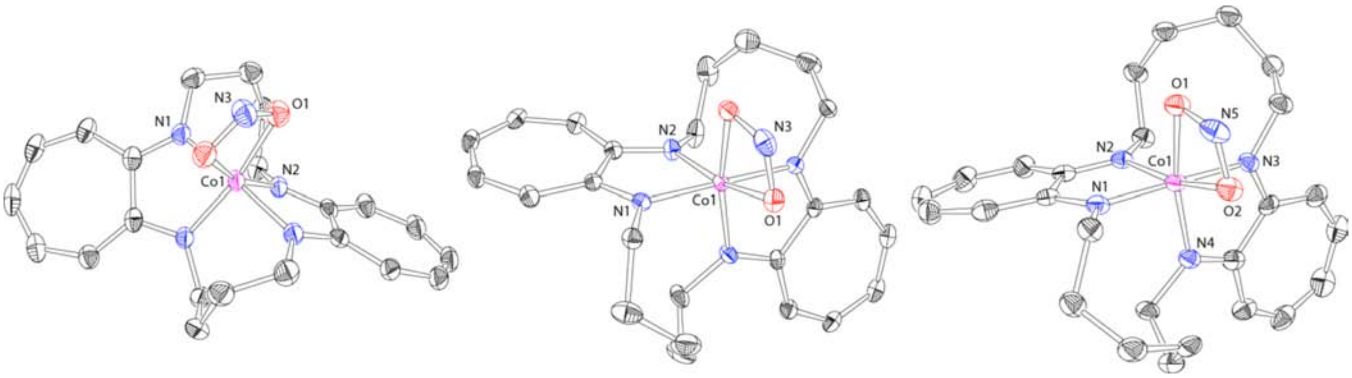


Figure 1. Thermal ellipsoid plots for [Co(η^2-NO_2)(TC-4,4)] (left), [Co(η^2-NO_2)(TC-5,5)] (middle), and [Co(η^2-NO_2)(TC-6,6)] (right), depicted at 50% probability. One of the two [Co(η^2-NO_2)(TC-6,6)] molecules in the asymmetric unit, hydrogen atoms, and solvent molecules are omitted for clarity.

under a nitrogen atmosphere, and used without further purification. The syntheses of H_2TC-6,6,[12,13] [Co(TC-4,4)],[14] [Co(TC-5,5)],[14] and [Co(TC-6,6)][14] are described elsewhere.

Synthesis of [Co(η^2-NO_2)(TC-4,4)]. To a solution of [Co(TC-4,4)] (100 mg, 0.25 mmol) in methylene chloride was added $AgNO_2$ (42 mg, 0.27 mmol) in the dark. The reaction was left to stir overnight, resulting in a color change to brown and the formation of a precipitate. The solution was filtered through Celite, and the precipitate was washed with methylene chloride. The filtrate was collected, and the solvent was removed in vacuo to give the desired product as a brown powder. X-ray-quality crystals were obtained by recrystallization from CH_2Cl_2/Et_2O at −30 °C (16 mg, 14% yield): ^{1}H NMR (CD_2Cl_2) δ 1.59 (m, 4H, CH_2), 1.77 (m, 4H, CH_2), 3.53 (t, J = 9.2 Hz, 4H, CH_2), 3.79 (d, J = 11.2 Hz, 4H, CH_2), 6.12 (t, J = 10.4 Hz, 2H, ArH_δ), 6.59 (d, J = 15.2 Hz, 4H, ArH_β), 6.86 (t, J = 10.4 Hz, 4H, ArH_γ); IR (KBr) ν_{NO} 1172 cm^{-1}; UV−vis (CH_2Cl_2) λ, nm (ε, M^{-1} cm^{-1}) 288 (71400), 299 (sh), 412 (49678), 482 (sh), 519 (sh), 813 (1311). Anal. Calcd for $C_{22}H_{26}N_5O_2Co\cdot0.13CH_2Cl_2$: C, 57.52; H, 5.73; N, 15.16; Cl, 1.92. Found: C, 57.17; H, 5.48; N, 14.83; Cl, 1.67. The presence of residual methylene chloride was confirmed by ^{1}H NMR spectroscopy, and the quantity used for the computed elemental composition was adjusted for the best fit to the results.

Synthesis of [Co(η^2-NO_2)(TC-5,5)]. To [Co(TC-5,5)] (50 mg, 0.12 mmol) in ~7 mL of methylene chloride was added silver nitrite (18 mg, 0.12 mmol). The solution was allowed to stir for 8 h and then filtered through Celite to remove Ag^0. The filtrate was layered with pentane and left to crystallize at −30 °C. The desired product was isolated as brown crystals (34 mg, 62% yield): ^{1}H NMR (CD_2Cl_2) δ 1.12−1.18 (m, 2H, CH_2), 1.77−2.05 (m, 10H, CH_2), 2.17−2.22 (m, 2H, CH_2), 2.76 (d, J = 14 Hz, 2H, CH_2), 3.53−3.60 (m, 2H, CH_2), 3.79 (dd, J = 14.6 Hz, 3 Hz, 2H, CH_2), 6.00 (t, J = 9 Hz, 2H, ArH_δ), 6.56 (d, J = 11.2 Hz, 2H, ArH_β), 6.72 (t, J = 10.2 Hz, 2H, ArH_γ), 6.95 (t, J = 10.2 Hz, 2H, ArH_γ), 7.04 (d, J = 11.6 Hz, 2H, ArH_β); IR (KBr) ν_{NO} 1176 cm^{-1}; UV−vis (CH_2Cl_2) λ, nm (ε, M^{-1} cm^{-1}) 283 (38296), 406 (23268), 475 (sh), 497 (sh), 745 (sh), 949 (1111). Anal. Calcd for $C_{24}H_{30}N_5O_2Co$: C, 60.12; H, 6.31; N, 14.61. Found: C, 60.41; H, 6.08; N, 14.74.

Synthesis of [Co(η^2-NO_2)(TC-6,6)]. To a solution of [Co(TC-6,6)] (50 mg, 0.11 mmol) in methylene chloride was added silver nitrite (17 mg, 0.11 mmol). The suspension was allowed to stir overnight and then filtered through Celite to remove Ag^0. The filtrate was concentrated, layered with diethyl ether, and placed at −30 °C to crystallize. The desired product was obtained as brown crystals (36 mg, 66% yield): ^{1}H NMR (CD_2Cl_2) δ 1.10−1.17 (m, 2H, CH_2), 1.50−1.54 (m, 4H, CH_2), 1.70−1.72 (m, 2H, CH_2), 1.95−1.98 (m, 2H, CH_2), 2.10−2.13 (m, 6H, CH_2), 2.31−2.34 (m, 2H, CH_2), 2.91−2.93 (m, 2H, CH_2), 3.74−3.76 (m, 2H, CH_2), 3.83−3.85 (m, 2H, CH_2), 6.06 (t, J = 9 Hz, 2H, ArH_δ), 6.54 (d, J = 11.2 Hz, 2H, ArH_β), 6.69 (t, J = 10 Hz, 2H, ArH_γ), 6.85−6.93 (m, 4H, ArH_γ + ArH_β); IR (KBr) ν_{NO} 1169 cm^{-1}; UV−vis (CH_2Cl_2) λ, nm (ε, M^{-1} cm^{-1}) 280 (44450), 396 (28325), 473 (14442), 585 (sh), 938 (1742). Anal. Calcd for $C_{26}H_{34}N_5O_2Co\cdot0.09CH_2Cl_2$: C, 60.81; H, 6.69; N, 13.59. Found: C, 60.91; H, 6.77; N, 13.22. The presence of residual methylene chloride was confirmed by ^{1}H NMR spectroscopy, and the quantity used for the computed elemental composition was adjusted for the best fit to the results.

Physical Measurements. ^{1}H NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer. Optical spectra were obtained on a Varian Cary 50 Bio UV−vis spectrophotometer in 6SQ Starna cells. Solutions were prepared under a nitrogen atmosphere. FT-IR spectra were recorded on a Thermo Nicolet Avatar 360 spectrometer running the *OMNIC* software package.

X-ray Crystallography. Crystals were mounted in Paratone N oil and frozen at 100 K under a cold nitrogen stream controlled by a Cryopad low-temperature apparatus. Data were collected on a Bruker APEX CCD X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) controlled by the *APEX2* software package.[15] Empirical absorption corrections were performed with *SADABS*.[16] The structures were solved by direct methods using *SHELXS-97* and refined by full-matrix least squares on F^2 using the *SHELXL-97* program incorporated into the *SHELXTL* software package.[17] Possible higher symmetries were evaluated by *PLATON*.[18] Non-hydrogen atoms were located and their positions refined anisotropically. Hydrogen atoms were assigned idealized positions and given thermal parameters 1.2 times the thermal parameters of the atoms to which they are attached.

NO Reactions. Methylene chloride solutions (13−15 mg, 0.028−0.030 mmol) of [Co(η^2-NO_2)(TC-*n*,*n*)] (n = 4−6) were set up to stir under a nitrogen atmosphere in septum-capped vials. A gastight syringe was used to remove a 5 mL volume of headspace from the vials, and subsequently excess NO or ^{15}NO (5 mL, 0.2 mmol) was injected into the headspace. The reactions were allowed to stir overnight, after which time they were evaporated to dryness in vacuo, and KBr pellets for IR, or CD_2Cl_2 samples for ^{1}H NMR, spectral analysis were prepared from the resultant solid material. A solution IR time course was conducted in an analogous manner, except that aliquots were removed from the reaction solution by a gastight syringe and injected into a CaF_2 solution IR cell. The cell was sealed and removed from the glovebox, and the solution was analyzed by IR spectroscopy.

■ RESULTS

The nitrite complexes [Co(η^2-NO_2)(TC-*n*,*n*)] (n = 4−6) were prepared by oxidation of the [Co(TC-*n*,*n*)] (n = 4−6) precursors with $AgNO_2$ (Figure 1 and Tables 1 and S1−S3 in the Supporting Information, SI). X-ray-quality crystals of the [Co(η^2-NO_2)(TC-*n*,*n*)] complexes were isolated in 14%, 62%, and 66% yields for n = 4−6, respectively. All three complexes contain octahedral cobalt(III) centers, with the nitrite ligands bound in a bidentate fashion through the oxygen atoms.

Table 1. Crystallographic Parameters for [Co(η^2-NO_2)(TC-4,4)], [Co(η^2-NO_2)(TC-5,5)], and [Co(η^2-NO_2)(TC-6,6)]

	[Co(η^2-NO_2)(TC-4,4)]	[Co(η^2-NO_2)(TC-5,5)]	[Co(η^2-NO_2)(TC-6,6)]·Et_2O
empirical formula	$C_{22}H_{26}CoN_5O_2$	$C_{24}H_{30}CoN_5O_2$	$C_{56}H_{76}Co_2N_{10}O_5$
fw	451.41	479.46	1087.13
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$P2_1/c$
a (Å)	13.186(6)	15.9717(17)	14.5809(14)
b (Å)	15.794(7)	13.0636(14)	12.7705(12)
c (Å)	9.718(4)	10.3826(11)	28.256(3)
β (deg)	102.575(7)	90.910(2)	93.057(2)
V (Å^3)	1975.1(15)	2166.0(4)	5254.0(9)
Z	4	4	4
ρ_{calc} (g/cm^3)	1.518	1.470	1.374
temperature (K)	100(2)	100(2)	100(2)
μ(Mo Kα) (mm^{-1})	0.900	0.825	0.691
θ range (deg)	2.04−26.37	2.01−26.78	1.40−26.43
cryst size (mm^3)	0.40 × 0.05 × 0.05	0.14 × 0.08 × 0.03	0.35 × 0.10 × 0.05
completeness to θ (%)	100.0	100.0	99.8
max, min peaks (e/Å^3)	0.764 and −0.381	0.603 and −0.375	0.741 and −0.532
GOF[a]	1.086	1.053	1.026
total no. of data	16194	19369	90211
no. unique data	2022	2319	10787
R1 (%)[b]	5.03	3.85	5.88
wR2 (%)[c]	9.46	7.38	11.67

[a] GOF = $[\sum w(F_o{}^2 - F_c{}^2)^2/(n - p)]^{1/2}$, where n is the number of data and p is the number of refined parameters. [b] R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. [c] wR2 = $\{\sum [w(F_o{}^2 - F_c{}^2)^2] / \sum [w(F_o{}^2)^2]\}^{1/2}$.

[Co(η^2-NO_2)(TC-4,4)] and [Co(η^2-NO_2)(TC-5,5)] crystallize in monoclinic space group $C2/c$ with a crystallographically required C_2 symmetry axis passing through the cobalt center and the nitrogen atom of the nitrite ligand. The asymmetric units of [Co(η^2-NO_2)(TC-4,4)] and [Co(η^2-NO_2)(TC-5,5)] each contain half of the molecule as a result. [Co(η^2-NO_2)(TC-6,6)] crystallizes in $P2_1/c$ with two molecules of the cobalt(III) nitrito complex and a disordered diethyl ether molecule in the asymmetric unit.

The cobalt(III) centers of the three [Co(NO_2)(TC-n,n)] (n = 4−6) complexes have similar coordination environments. The Co−O distances are 2.019(3) and 2.0237(17) Å for [Co(η^2-NO_2)(TC-4,4)] and [Co(η^2-NO_2)(TC-5,5)], respectively. Average distances of 2.006(3) and 2.012(3) Å are observed for the Co−O bonds in the two crystallographically distinct [Co(η^2-NO_2)(TC-6,6)] molecules. Average distances between the cobalt center and the tropocoronand nitrogen atoms are 1.88, 1.89, and 1.90 Å for [Co(η^2-NO_2)(TC-n,n)] (n = 4−6), respectively. The Co−N_{TC} bond distances in [Co(η^2-NO_2)(TC-n,n)] (n = 4−6) are shorter by an average of 0.037 Å for tropocoronand nitrogen atoms located trans to oxygen atoms of the nitrite ligands. The disparity between Co−N_{TC} bond lengths within individual molecules is attributed to the weaker trans influence of coordinated nitrite ion than of the aminotroponeiminate ligand. The geometric parameters of the [Co(η^2-NO_2)(TC-6,6)] complex presented in this work are comparable to those observed for the cobalt(III) nitrite complex that was isolated from a [Co(TC-6,6)]/NO reaction mixture, described previously.[10]

We employed vibrational spectroscopy to probe the dependence of the reactivity of [Co(η^2-NO_2)(TC-n,n)] (n = 4−6) complexes with NO(g) on the polymethylene linker chain lengths (Figure 2). Exposure of [Co(η^2-NO_2)(TC-4,4)] to NO(g) resulted in the appearance of a strong band at 1592 cm^{-1} in the IR spectrum corresponding to ν_{NO} of [Co(NO)(TC-4,4)] (Figure 2a,b).[19] The analogous reaction with ^{15}NO shifted this band to 1571 cm^{-1}. The expected isotope shift, based the simple harmonic oscillator model, is calculated to be 1563 cm^{-1}. Complete consumption of [Co(η^2-NO_2)(TC-4,4)] occurred during the reaction, as determined by the disappearance of the nitrite ligand band at 1172 cm^{-1}. There was no spectroscopic evidence that a compound containing a dinitrosylcobalt moiety had formed. The reaction mixture was examined by ^{1}H NMR spectroscopy (Figure S1 in the SI), but because the ^{1}H NMR spectra of [Co(η^2-NO_2)(TC-4,4)] and [Co(NO)(TC-4,4)] are nearly identical, no useful information could be obtained. We grew crystals from the [Co(η^2-NO_2)(TC-4,4)]/NO reaction mixture to confirm conversion to a cobalt mononitrosyl, and we were able to characterize the [Co(NO)(TC-4,4)] species (Figure S2 in the SI). This compound crystallizes in space group $P2_1/c$. Unit cell parameters of the species isolated from the reaction mixture are a = 12.7081(13) Å, b = 16.0180(16) Å, c = 9.8503(10) Å, β = 104.057(2)°, and V = 1945.1(3) Å^3, comparable to values reported previously.[19] The metrical parameters for [Co(NO)(TC-4,4)] from the [Co(η^2-NO_2)(TC-4,4)] reaction are analogous to the published values.[19]

We next exposed [Co(η^2-NO_2)(TC-5,5)] to NO(g) and observed the formation of products containing both mono- and dinitrosyl units by IR spectroscopy (Figure 2c,d). The cobalt mononitrosyl adduct is characterized by a strong band corresponding to the ν_{NO} stretch at 1606 cm^{-1} in the IR spectrum of the reaction mixture. This band shifted to 1570 cm^{-1} upon labeling with ^{15}NO(g), which is comparable to the 1577 cm^{-1} value predicted by the simple harmonic oscillator model. The cobalt dinitrosyl species was identified by its ν_{NO} stretches at 1809 and 1732 cm^{-1}, which appear at 1764 and 1689 cm^{-1} upon ^{15}NO isotope labeling. The calculated isotope shift values are 1776 and 1700 cm^{-1}. We expect the identity of the cobalt dinitrosyl adduct to be [$Co_2(NO)_4$(TC-5,5)], by analogy to the [$Co_2(NO)_4$(TC-6,6)] complex described in previous work.[10] The persistence of a band at 1176 cm^{-1} in the spectra of [Co(η^2-NO_2)(TC-5,5)]/NO and ^{15}NO(g) reaction mixtures led us to conclude that [Co(η^2-NO_2)(TC-5,5)] was incompletely consumed in the reaction. ^{1}H NMR spectroscopic analysis of the reaction mixture revealed only peaks corresponding to the [Co(η^2-NO_2)(TC-5,5)] starting material (Figure S3 in the SI) and similarly indicated that consumption of this cobalt(III) nitrite complex is incomplete in the presence of NO(g). IR studies reveal more about the identities of the products formed than ^{1}H NMR experiments because little material is required to detect metal nitrosyl moieties by IR owing to the high oscillator strength of nitrosyl stretching modes.

As in the [Co(η^2-NO_2)(TC-5,5)]/NO reaction, exposure of [Co(η^2-NO_2)(TC-6,6)] to NO(g) also resulted in formation of a dinitrosyl adduct (Figure 2e,f). The ν_{NO} stretching frequencies for the cobalt dinitrosyl appeared at 1799 and 1720 cm^{-1}, and these bands shift to 1770 and 1693 cm^{-1}, respectively, in the ^{15}NO isotope labeling study. For

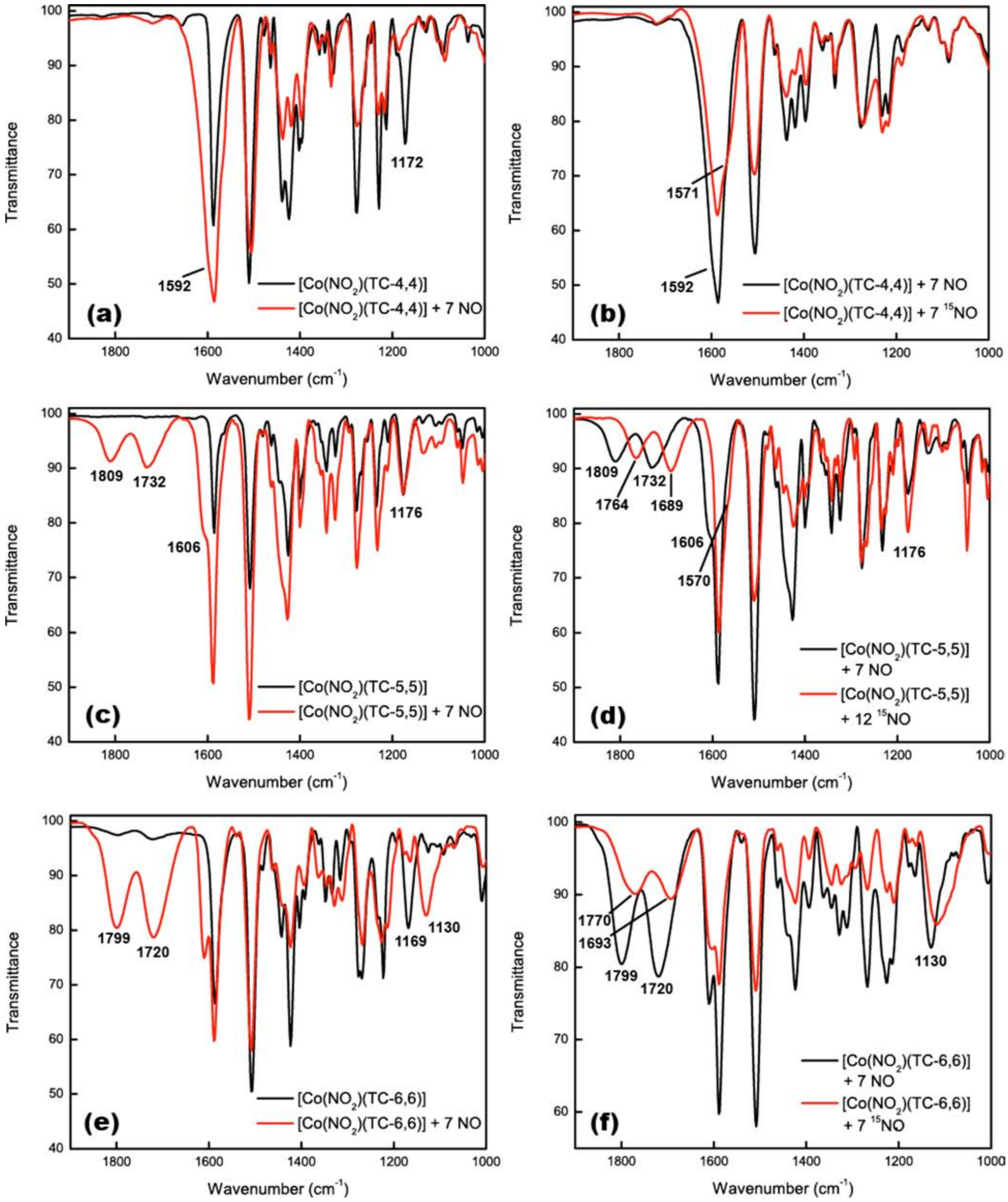


Figure 2. IR spectroscopic comparisons of the reactions of [Co(η^2-NO$_2$)(TC-4,4)], [Co(η^2-NO$_2$)(TC-5,5)], and [Co(η^2-NO$_2$)(TC-6,6)] with NO(g) (a−e, respectively) and ^{15}NO(g) (b−f, respectively). Spectra of the cobalt(III) nitrite starting materials are shown in black. NO(g) reaction spectra are shown in red. ^{15}NO(g) reaction spectra are shown in blue. Stretches for ν_{NO} are labeled.

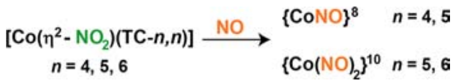
comparison, the calculated ν_{NO} stretching frequencies for the ^{15}NO-labeled cobalt dinitrosyl are 1766 and 1689 cm^{-1}. The bands assigned to ν_{NO} stretches of a cobalt dinitrosyl adduct compare well with bands at 1799 and 1722 cm^{-1} in independently prepared [Co$_2$(NO)$_4$(TC-6,6)], suggesting [Co$_2$(NO)$_4$(TC-6,6)] to be a viable product of the [Co(η^2-NO$_2$)(TC-6,6)]/NO reaction.[10] A band appeared at 1610 cm^{-1} in the IR spectrum of the reaction between [Co(η^2-NO$_2$)(TC-

6,6)] and NO(g) and shifted minimally to 1602 cm^{-1} when $^{15}NO(g)$ was used. Additionally, the band assigned to ν_{NO} of {Co(η^2-NO_2)} in the [Co(η^2-NO_2)(TC-6,6)] starting material shifted from 1169 to 1130 cm^{-1} upon reaction with natural abundance NO(g). The band shifted to 1117 cm^{-1} upon exposure of the starting complex to $^{15}NO(g)$. A [Co(NO)(η^1-NO_2)(TC-6,6)] complex may form in the reaction with NO and could give rise to these bands in the IR spectrum. The computed ν_{NO} value for [Co(^{15}NO)(η^1-NO_2)(TC-6,6)], based on a simple harmonic oscillator model, is 1581 cm^{-1}, sufficiently close to the observed ν_{NO} stretch at 1602 cm^{-1} to support this suggestion. The deviation may be the result of vibrational coupling of the nitrosyl stretching mode with the N–O bands of the coordinated nitrite. Analysis of the [Co(η^2-NO_2)(TC-6,6)]/NO reaction mixture by ^1H NMR spectroscopy revealed a spectrum with peaks corresponding only to the [Co(η^2-NO_2)(TC-6,6)] starting material (Figure S4 in the SI). Thus, IR spectroscopy is again superior to ^1H NMR spectral studies at identifying products, aided by the intensity of the nitrosyl stretching modes.

■ DISCUSSION

[Co(η^2-NO_2)(TC-*n,n*)] (*n* = 4–6) complexes react with NO(g) in a size-dependent manner, with exclusive *mono*nitrosyl formation occurring only with [Co(η^2-NO_2)(TC-4,4)]. Both mono- and dinitrosyl adducts form in the reaction of [Co(η^2-NO_2)(TC-5,5)] with NO(g), and exposure of [Co(η^2-NO_2)(TC-6,6)] to NO(g) led to cobalt *di*nitrosyl formation (Scheme 1). The increasing preference toward *di*nitrosyl formation with increasing tropocoronand linker length parallels the chemistry of cobalt(II) tropocoronands with NO(g).[10,19] ^{15}NO isotope labeling studies support the assignment of the mono- and dinitrosyl species, and deviations from the calculated values for the isotope shifts may be explained by the vibrational coupling of Co–N and N=O stretches. The complete conversion of [Co(η^2-NO_2)(TC-4,4)] to the nitrosyl product in the presence of NO(g) differs from the chemistry of [Co(η^2-NO_2)(TC-5,5)] and [Co(η^2-NO_2)(TC-6,6)], which showed little reactivity with NO. The differences in conversion may be accounted for by greater accessibility of the cobalt(III) center in [Co(η^2-NO_2)(TC-4,4)] to NO(g), compared to that in [Co(η^2-NO_2)(TC-5,5)] and [Co(η^2-NO_2)(TC-6,6)]. The longer linker chains in [Co(η^2-NO_2)(TC-5,5)] and [Co(η^2-NO_2)(TC-6,6)] provide greater steric impedance, controlling NO(g) access to the metal center (Figure 3).

Scheme 1. Conversion of Cobalt(III) Nitrite Tropocoronand Complexes [Co(η^2-NO_2)(TC-*n,n*)] (*n* = 4–6) to the Corresponding Cobalt Nitrosyls Depending on the Ring Size of the Tropocoronand Ligand



A dependence of cobalt(III) tropocoronand reactivity on the linker chain length was previously encountered for metal–carbon bond homolysis reactions of the alkyl complexes [CoMe(TC-3,3)] and [CoMe(TC-4,4)].[20] Bond homolysis occurred >13 times faster in [CoMe(TC-4,4)] than in [CoMe(TC-3,3)], probably due to greater ring strain in the larger of the two square-pyramidal tropocoronand complexes.[20] A size dependence was also observed for reactions of [CoEt(TC-3,3)] and [CoMe(TC-4,4)] with CO. The CO insertion product [Co(COMe)(TC-4,4)] formed readily from [CoMe(TC-4,4)], whereas [CoEt(TC-3,3)] did not react under similar conditions.[20] This difference in reactivity reflects the flexibility of $[TC\text{-}4,4]^{2-}$, which allows CO to bind the cobalt center cis to the coordinated methyl group.[20]

We note an important feature of the nitrite-to-nitrosyl exchange described herein. Isotopic labeling studies with ^{15}NO indicate external NO(g) to be the source of the nitrosyl ligands in the newly formed cobalt mono- and dinitrosyl complexes; nitrite is not directly converted to NO in these reactions. Direct conversion of nitrite to nitrosyl would lead to the appearance of bands corresponding to natural abundance [Co(NO)(TC-*n,n*)] (*n* = 4, 5) and [$Co_2(NO)_4$(TC-*n,n*)] (*n* = 5, 6) species in the IR spectra of the $^{15}NO(g)$ reactions with [Co(η^2-NO_2)(TC-*n,n*)]. The absence of such bands indicates that external NO is the nitrosyl source.

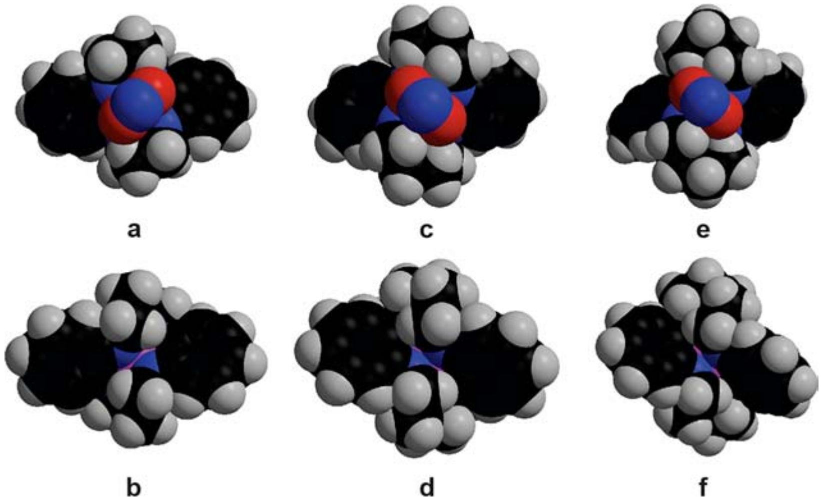


Figure 3. Space-filling models of [Co(η^2-NO_2)(TC-4,4)] (a and b), [Co(η^2-NO_2)(TC-5,5)] (c and d), and [Co(η^2-NO_2)(TC-6,6)] (e and f). The view down the Co–N_{NO_2} vector is shown in the top row, and the bottom row shows the view up the Co–N_{NO_2} vector. Access to the cobalt center (magenta) is reduced with increasing tropocoronand linker chain length.

Previous reports detailing reactions of cobalt(III) centers with NO(g) describe reductive nitrosylation pathways, whereby cobalt(III) reacts with NO to form species that are formally $\{Co^{III}-NO^-\}$ adducts.[21−26] A reductant such as butylamine is sometimes utilized in these reactions.[23] We propose that, in reductive nitrosylation reactions between $[Co(\eta^2\text{-}NO_2)(TC\text{-}n,n)]$ (n = 4−6) and NO(g), nitrite may provide the electrons for cobalt mononitrosyl formation, generating $^\bullet NO_2$ as a byproduct. Similar chemistry has been described for reductive nitrosylation reactions of iron(III) porphyrins in the presence of nitrite ion.[27−30]

Taking into account the spectroscopic data described herein, we hypothesize that binding of NO to the cobalt center occurs with a concomitant change to monodentate coordination of the nitrite ligand, forming a transient $[Co(NO)(\eta^1\text{-}NO_2)(TC\text{-}n,n)]$ adduct. The NO_2^- ion can serve as an electron source and the complex may convert to a $\{Co^{III}(NO^-)(^\bullet NO_2)\}$ species by internal electron transfer. At this stage, the tropocoronand in the $[TC\text{-}4,4]^{2-}$ complex would fit stably about the metal nitrosyl. The $^\bullet NO_2$ radical could then dissociate, generating [Co(NO)(TC-4,4)]. The larger $[Co(\eta^2\text{-}NO_2)(TC\text{-}n,n)]$ (n = 5, 6) complexes may experience unfavorable steric interactions between the methylene groups of the tropocoronand linker chains in the $\{Co^{III}(NO^-)(^\bullet NO_2)\}$ species, forcing the ligand to bend away from the metal center and exposing an additional site for NO binding with dissociation of $^\bullet NO_2$. Because such steric interactions are most pronounced in $[Co(\eta^2\text{-}NO_2)(TC\text{-}6,6)]$, the $\{Co(NO)_2\}^{10}$ dinitrosyl adduct is the favored product. We have no evidence for the formation of a $\{Co(NO)_2\}^9$ species. Experimental studies to test the proposed reaction pathways were precluded by our inability to completely characterize all reaction products and to block side reactions.

Bands assigned to ν_{NO} stretches of cobalt dinitrosyl species throughout this discussion correspond well with the IR spectroscopic features of the dicobalt tetranitrosyl complex $[Co_2(NO)_4(TC\text{-}6,6)]$, described in recent work.[10] Comparable IR spectroscopic features are reported for the products of $[Co(i\text{-}Pr_2ATI)]$ and $[Co(^RDATI)]$ (ATI = aminotroponiminate; DATI = dansyl aminotroponiminate) reactions with NO(g),[31−33] as well as for $[Co(NO)_2(Ar\text{-}nacnac)]$, where Ar-nacnac is a bulky β-diketiminate ligand.[34] We conclude from these similarities that the species generated in the reactions of $[Co(\eta^2\text{-}NO_2)(TC\text{-}5,5)]$ and $[Co(\eta^2\text{-}NO_2)(TC\text{-}6,6)]$ with NO(g) are indeed $\{Co(NO)_2\}^{10}$ species.

■ CONCLUSIONS

We established the size-dependent reactivity of $[Co(\eta^2\text{-}NO_2)(TC\text{-}n,n)]$ (n = 4−6) with NO(g), which parallels to a degree the NO(g) reactivity of $[Co(TC\text{-}n,n)]$ (n = 4−6).[10,19] Mononitrosyl formation is favored for the $[Co(\eta^2\text{-}NO_2)(TC\text{-}4,4)]$/NO reaction, whereas $[Co(\eta^2\text{-}NO_2)(TC\text{-}5,5)]$ forms both mono- and dinitrosyl species in the presence of NO(g). Dinitrosyl formation predominates in the NO chemistry of $[Co(\eta^2\text{-}NO_2)(TC\text{-}6,6)]$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of structurally determined bond lengths and angles for $[Co(\eta^2\text{-}NO_2)(TC\text{-}n,n)]$ (n = 4−6), ^1H NMR spectra of the reactions of $[Co(\eta^2\text{-}NO_2)(TC\text{-}4,4)]$, $[Co(\eta^2\text{-}NO_2)(TC\text{-}5,5)]$, and $[Co(\eta^2\text{-}NO_2)(TC\text{-}6,6)]$ with NO(g), a thermal ellipsoid plot of [Co(NO)(TC-4,4)] isolated from the $[Co(\eta^2\text{-}NO_2)(TC\text{-}4,4)]$/NO reaction, and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Tennyson, A. G.; Lippard, S. J. *Chem. Biol.* **2011**, *18*, 1211−1220.

(2) Dejam, A.; Hunter, C. J.; Schechter, A. N.; Gladwin, M. T. *Blood Cell. Mol. Dis.* **2004**, *32*, 423−429.

(3) Gladwin, M. T.; Crawford, J. H.; Patel, R. P. *Free Radical Biol. Med.* **2004**, *36*, 707−717.

(4) Tota, B.; Quintieri, A. M.; Angelone, T. *Curr. Med. Chem.* **2010**, *17*, 1915−1925.

(5) Averill, B. A. *Chem. Rev.* **1996**, *96*, 2951−2964.

(6) Basu, S.; Grubina, R.; Huang, J.; Conradie, J.; Huang, Z.; Jeffers, A.; Jiang, A.; He, X.; Azarov, I.; Seibert, R.; Mehta, A.; Patel, R.; King, S. B.; Hogg, N.; Ghosh, A.; Gladwin, M. T.; Kim-Shapiro, D. B. *Nat. Chem. Biol.* **2007**, *3*, 785−794.

(7) Cutruzzolà, F.; Rinaldo, S.; Castiglione, N.; Giardina, G.; Pecht, I.; Brunori, M. *Bioessays* **2009**, *31*, 885−891.

(8) Suzuki, S.; Kataoka, K.; Yamaguchi, K. *Acc. Chem. Res.* **2000**, *33*, 728−735.

(9) Suzuki, S.; Kataoka, K.; Yamaguchi, K.; Inoue, T.; Kai, Y. *Coord. Chem. Rev.* **1999**, *190−192*, 245−265.

(10) Kozhukh, J.; Lippard, S. J. *J. Am. Chem. Soc.* **2012**, *134*, 11120−11123.

(11) Lorkovic, I. M.; Ford, P. C. *Inorg. Chem.* **2000**, *39*, 632−633.

(12) Zask, A.; Gonnella, N.; Nakanishi, K.; Turner, C. J.; Imajo, S.; Nozoe, T. *Inorg. Chem.* **1986**, *25*, 3400−3407.

(13) Imajo, S.; Nakanishi, K.; Roberts, M.; Lippard, S. J.; Nozoe, T. *J. Am. Chem. Soc.* **1983**, *105*, 2071−2073.

(14) Jaynes, B. S.; Doerrer, L. H.; Liu, S.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 5735−5744.

(15) *APEX2*, version 4.0; Bruker AXS, Inc.: Madison, WI, 2008.

(16) Sheldrick, G. M. *SADABS: Area-Detector Absorption Correction*; University of Göttingen: Göttingen, Germany, 2001.

(17) Sheldrick, G. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

(18) Speck, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001.

(19) Franz, K. J.; Doerrer, L. H.; Spingler, B.; Lippard, S. J. *Inorg. Chem.* **2001**, *40*, 3774−3780.

(20) Jaynes, B. S.; Ren, T.; Masschelein, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 5589−5599.

(21) Franke, A.; Roncaroli, F.; van Eldik, R. *Eur. J. Inorg. Chem.* **2007**, *2007*, 773−798.

(22) Cheng, S.-H.; Su, Y. O. *Inorg. Chem.* **1994**, *33*, 5847−5854.

(23) Dózsa, L.; Pénzeli, P. *React. Kinet. Catal. Lett.* **1995**, *55*, 121−126.

(24) Pukhovskaya, S.; Guseva, L.; Golubchikov, O. *Russ. Chem. Bull.* **2007**, *56*, 743−747.

(25) Roncaroli, F.; van Eldik, R. *J. Am. Chem. Soc.* **2006**, *128*, 8042−8053.

(26) Zhu, X.-Q.; Li, Q.; Hao, W.-F.; Cheng, J.-P. *J. Am. Chem. Soc.* **2002**, *124*, 9887−9893.

(27) Fernandez, B. O.; Ford, P. C. *J. Am. Chem. Soc.* **2003**, *125*, 10510−10511.
(28) Fernandez, B. O.; Lorkovic, I. M.; Ford, P. C. *Inorg. Chem.* **2004**, *43*, 5393−5402.
(29) Fernandez, B. O.; Lorkovic, I. M.; Ford, P. C. *Inorg. Chem.* **2003**, *42*, 2−4.
(30) Ford, P. C.; Fernandez, B. O.; Lim, M. D. *Chem. Rev.* **2005**, *105*, 2439−2456.
(31) Lim, M. H.; Kuang, C.; Lippard, S. J. *ChemBioChem* **2006**, *7*, 1571−1576.
(32) Franz, K. J.; Singh, N.; Lippard, S. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2120−2122.
(33) Franz, K. J.; Singh, N.; Spingler, B.; Lippard, S. J. *Inorg. Chem.* **2000**, *39*, 4081−4092.
(34) Tonzetich, Z. J.; Héroguel, F.; Do, L. H.; Lippard, S. J. *Inorg. Chem.* **2011**, *50*, 1570−1579.