Influence of Tetraazamacrocyclic Ligands on the Nitric Oxide Reactivity of their Cobalt(II) Complexes

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S *Supporting Information*

ABSTRACT: The reactions of cobalt(II) complexes of tetraazamacrocyclic tropocoronand (TC) ligands with nitric oxide (NO) were investigated. When [Co(TC-5,5)] was allowed to react with NO(g), the {CoNO}^{8} mononitrosyl [Co(NO)(TC-5,5)] was isolated and structurally characterized. In contrast, a {Co(NO)$_2$}^{10} species formed when [Co(TC-6,6)] was exposed to NO(g), and the nitrito [Co(NO$_2$)(TC-6,6)] complex was structurally and spectroscopically characterized from the reaction mixture. The {Co(NO)$_2$}^{10} species was assigned as the bis(cobalt dinitrosyl) complex [Co$_2$(NO)$_4$(TC-6,6)] by spectroscopic comparison with independently synthesized and characterized material. These results provide the first evidence for the influence of tropocoronand ring size on the nitric oxide reactivity of the cobalt(II) complexes.

Nitric oxide (NO) regulates a diverse array of biological processes, including the function of the immune, circulatory, and nervous systems.[1] A variety of chemical motifs serve as targets for nitric oxide and its redox relatives in biology, inspiring studies of the inorganic and coordination chemistry of NO.[2] Recent contributions have provided insights into the interactions between nitric oxide and transition metal centers bearing thiolate,[3] porphyrin,[4] phosphine,[5] N-heterocyclic carbene,[6] and non-porphyrinic amine ligands.[7]

Previously, we described the synthesis and chemistry of transition metal tropocoronand (TC) complexes (Chart 1), in which the ligand provides a tunable scaffold for controlling the geometry at the metal center. The tetraazamacrocyclic TC architecture can support metal complexes in square-planar, tetrahedral, square-pyramidal, trigonal-bipyramidal, and octahedral coordination environments with no change in the nature of the aminotroponeimate (ATI) N-donor atoms.[8] The electronic properties are tuned by variations in the lengths of the polymethylene linker chains. A twist from square-planar to increasingly more tetrahedral geometries is similarly induced by lengthening the linker chains. Structural profiles for metal complexes with linker chain lengths ranging from 3 to 6 methylene units have been established for cobalt(II) and nickel(II),[8d,9] and from 3 to 5 methylene units for copper(II).[8c]

Previously, we described the NO reactivity of [Co(TC-3,3)] and [Co(TC-4,4)] complexes and the formation of {CoNO}^{8} species that result upon exposure of the cobalt(II) complexes to NO(g).[8a] In the present study we wished to assess the NO reactivity of cobalt(II) coordinated by tropocoronand ligands

Chart 1. The Tropocoronand Scaffold Binds Metals in a Variety of Geometries, Which Can Be Tuned by Changing the Number (*m,n*) of Methylene Groups in the Linker Chains That Connect the Aminotroponeimate Units
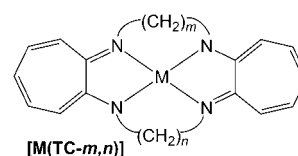
having longer linker chains. Specifically, we sought to characterize reaction products of nitric oxide with [Co(TC-5,5)] and [Co(TC-6,6)], to determine whether there is a point at which tropocoronand size can affect NO reactivity. We discovered unprecedented size-dependence of cobalt(II) tropocoronand reactivity with NO(g). Specifically, we find preferential formation of {CoNO}^{8} species from the reaction of [Co(TC-5,5)] and NO(g), whereas exposure of [Co(TC-6,6)] to NO(g) results in {Co(NO)$_2$}^{10} formation. The cobalt(III) nitrite complex [Co(NO$_2$)(TC-6,6)] was subsequently isolated from the reaction mixture (Figure 1).
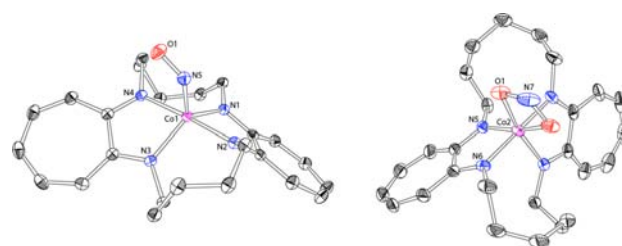

Figure 1. Left: Thermal ellipsoid plot for [Co(NO)(TC-5,5)]. Right: Thermal ellipsoid plot for [Co(NO$_2$)(TC-6,6)]. Ellipsoids are depicted at 50% probability. Hydrogen atoms are omitted for clarity.

Addition of excess NO(g) to the headspace of a [Co(TC-5,5)] methylene chloride solution led to formation of [Co(NO)(TC-5,5)] (Figure 1, left; Tables S1, S2). As with [Co(NO)(TC-4,4)], reported previously,[8a] the nitrosyl ligand in [Co(NO)(TC-5,5)] lies in the equatorial plane of an idealized trigonal bipyramid. The Co−N−O angle is 129.48(13)°. The degree of nitrosyl bending in [Co(NO)-(TC-5,5)] is comparable to the 128.9(6)° and 134.9(9)° bend angles of the disordered nitrosyl in the [Co(NO)(TC-4,4)]

crystal structure. In contrast, the nitrosyls of [Fe(NO)(TC-5,5)][10] and [Mn(NO)(TC-5,5)],[11] also bound in equatorial positions of idealized trigonal bipyramids, have bend angles of 174.3(4)° and 174.1(3)°, respectively.

The infrared spectrum of [Co(NO)(TC-5,5)] reveals a ν_{NO} stretch at 1622 cm^{-1}, which shifts to 1585 cm^{-1} when ^{15}NO(g) is used in the synthesis (Figure S1). The calculated value, based on the simple harmonic oscillator approximation, is 1592 cm^{-1}. As in the infrared spectrum for the reaction of [Co(TC-4,4)] with NO(g) (Figure S2), low-intensity bands appear at 1731 and 1809 cm^{-1}, reflecting the presence of small quantities of a putative $\{Co(NO)_2\}^{10}$ adduct that may form in the [Co(TC-5,5)]/NO reaction mixture. ^{15}N$_2$O was not observed by EI-MS analysis of the headspace of the [Co(TC-5,5)] reaction with ^{15}NO(g) (Figures S3, S4). The cobalt mononitrosyl is the only species isolable from the reaction between [Co(TC-5,5)] and NO(g).

In light of the NO reactivity of [Co(TC-n,n)] (n = 3, 4, 5), we were interested to discover that a stable [Co(NO)(TC-6,6)] species does not form when [Co(TC-6,6)] is exposed to nitric oxide. Only crystals of the starting material could be isolated when the complex was allowed to react with 1 equiv of NO for 3 h. Recrystallization after exposure of [Co(TC-6,6)] to 2.5 equiv of NO(g) for 2 h led to formation of brown blocks, the composition of which was crystallographically determined to be a 2:1 mixture of [Co(TC-6,6)] and [Co(NO$_2$)(TC-6,6)] (Figure 1, right; Tables S1, S3). The nitrite ion is bound in a bidentate manner through its oxygen atoms to the cobalt center in the [Co(NO$_2$)(TC-6,6)] complex, and the tropocoronand ligand folds back to accommodate an octahedral geometry at cobalt(III). A crystallographically required C_2 symmetry axis passes through the nitrite nitrogen (N7) atom and the cobalt center (Co2). The asymmetric unit contains one complete [Co(TC-6,6)] molecule and one-half [Co(NO$_2$)(TC-6,6)]. The Co−O distance in [Co(NO$_2$)(TC-6,6)] is 2.0027(17) Å, and the average distance between the cobalt center and the tropocoronand nitrogen atoms is 1.90 Å. The O1−N7−O1A angle is 110.5(3)°, and the O1−Co2−O1A angle is 63.13(11)°.

Infrared spectroscopic analysis of the reaction mixture containing [Co(TC-6,6)] and NO revealed bands at 1799 and 1720 cm^{-1}, corresponding to ν_{NO} stretches of a putative dinitrosyl species. The bands shifted to 1762 and 1687 cm^{-1}, respectively, upon isotopic labeling with ^{15}NO (Figure S5). By comparison with independently prepared [Co(NO$_2$)(TC-6,6)],[12] we can assign the band at 1169 cm^{-1} in the natural abundance NO reaction spectrum to the asymmetric N−O stretch of nitrite in [Co(NO$_2$)(TC-6,6)].[13] This band shifts to the 1140 cm^{-1} region in the ^{15}NO reaction spectrum, where other bands obscure it (Figure S5).

A timecourse study in methylene chloride solution by IR spectroscopy revealed that the reaction between [Co(TC-6,6)] and 3 equiv of NO(g) proceeds through what is likely to be a metastable [Co(NO)(TC-6,6)] intermediate (Figure 2) with ν_{NO} at 1621 cm^{-1}, a band that increases in intensity over ~20 min and then begins to disappear. The features assigned to ν_{NO} stretches of the dinitrosyl do not appear immediately, but instead increase in intensity over time, concomitant with the disappearance of the ν_{NO} stretch of the putative [Co(NO)(TC-6,6)] species. Any nitrite stretches of [Co(NO$_2$)(TC-6,6)] that may be present are masked by methylene chloride.

In order to confirm that a neutral coordination complex containing a $\{Co(NO)_2\}^{10}$ core is accessible in the [TC-6,6]$^{2-}$ coordination environment, we prepared the dicobalt tetra-

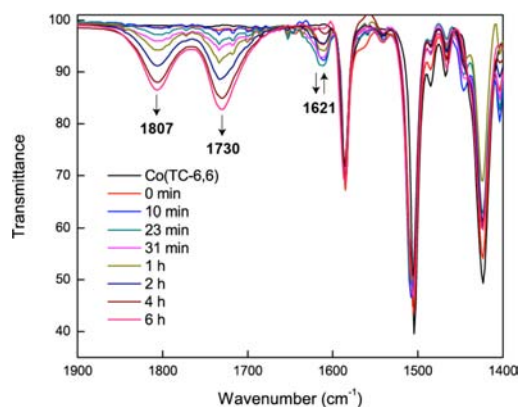**Figure 2.** Solution IR timecourse for the reaction between [Co(TC-6,6)] and 3 equiv of NO, recorded in CH$_2$Cl$_2$. A band at 1621 cm^{-1}, assigned to ν_{NO} of a putative [Co(NO)(TC-6,6)] complex, increases in intensity over 23 min and subsequently decreases in intensity with time. Bands at 1730 and 1807 cm^{-1} increase in intensity over the course of the experiment, and they are assigned to ν_{NO} of an overall neutral coordination environment about the $\{Co(NO)_2\}^{10}$ fragment. Minor deviations from ν_{NO} values reported in the text are attributed to solvent effects on the nitrosyl stretching frequencies.

nitrosyl complex [Co$_2$(NO)$_4$(TC-6,6)], determined its structure, and then compared its infrared spectroscopic features with those of the [Co(TC-6,6)]/NO reaction mixture.

The structure of [Co$_2$(NO)$_4$(TC-6,6)] is presented in Figure 3 and Tables S1 and S4. Both cobalt atoms are coordinated in a pseudo-tetrahedral manner with Co−N$_{NO}$ bond distances of 1.6575(11) and 1.6897(12) Å for the linear and bent nitrosyls of the $\{Co(NO)_2\}^{10}$ fragment, respectively. The plane formed by cobalt and the nitrogen and oxygen atoms of the bent nitrosyl makes a 74° angle to the plane of the aminotroponeiminate ring. The oxygen atom of the bent nitrosyl is 3.34 Å from the aromatic ring of the aminotroponeiminate on the adjacent cobalt atom.
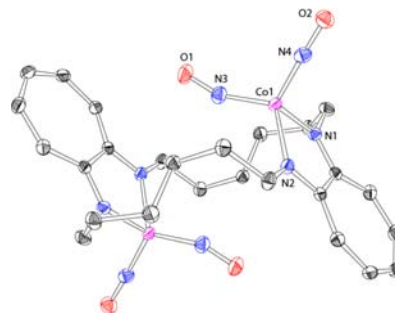

Figure 3. Thermal ellipsoid plot for [Co$_2$(NO)$_4$(TC-6,6)], depicted at 50% probability. Hydrogen atoms are omitted for clarity.

The ν_{NO} stretches of [Co$_2$(NO)$_4$(TC-6,6)] occur at 1799 and 1722 cm^{-1}, matching very well ν_{NO} stretches at 1799 and 1720 cm^{-1} in the IR spectrum of the [Co(TC-6,6)]/NO reaction mixture (Figure S6). This result confirms the above assignment of the [Co(TC-6,6)]/NO reaction product.

The reaction of [Co(TC-5,5)] with NO(g), to form the $\{CoNO\}^8$ complex [Co(NO)(TC-5,5)], is analogous to the chemistry of [Co(TC-3,3)] and [Co(TC-4,4)] with nitric oxide. The geometry of the pentacoordinate product is nicely accommodated by the [TC-5,5]$^{2-}$ ligand. In contrast, the putative cobalt mononitrosyl that might form in the reaction of

$[Co(TC-6,6)]$ with $NO(g)$ appears to be metastable at best, readily converting to the dinitrosyl adduct. This result suggests that the $[TC-6,6]^{2-}$ ligand in a putative cobalt mononitrosyl complex would not be able to avoid unfavorable intraligand steric interactions involving atoms within the polymethylene linker chains. The consequence is addition of a second NO, which enables dinitrosyl formation and a more favorable, extended conformation of the chains (Figure 3).

Nitrosyl stretches for $[Co_2(NO)_4(TC-6,6)]$ that is formed in the $[Co(TC-6,6)]$/NO reaction occur at energies similar to those previously reported for other nitrogen-bound $\{Co(NO)_2\}^{10}$ fragments. In $[Co(NO)_2(Ar-nacnac)]$ (where Ar-nacnac is a bulky β-diketiminate ligand, the anion of $[(2,6-$ diisopropylphenyl)$NC(Me)]_2CH]$), the ν_{NO} stretches appear at 1801 and 1706 cm^{-1} in benzene-d_6 solution.[14] The ν_{NO} stretching frequencies for $[Co(NO)_2(i-Pr_2ATI)]$ occur at 1809 and 1730 cm^{-1},[15] and bands in the ranges 1833−1838 and 1755−1760 cm^{-1} are observed in spectra of the related $[Co(NO)_2(^{R}DATI)]$ complexes (DATI = dansyl aminotroponeiminate).[15] The authors attribute the shift to higher energy in the DATI species to the electron-withdrawing nature of the sulfonamide-substituted ligands. As in the reaction between $[Co(TC-6,6)]$ and NO, cobalt mononitrosyl formation and subsequent decay are observed spectroscopically upon exposure of $[Co(^{R}DATI)]$ to nitric oxide.[15]

The formation of a $\{Co(NO)_2\}^{10}$ species from $[Co(TC-6,6)]$ and $NO(g)$ most likely involves reductive nitrosylation, and oxidized species must therefore arise to balance the electron count. That is, generation of a $\{Co(NO)_2\}^{10}$ adduct from a d^7 cobalt(II) center and 2 equiv of •NO requires an additional electron. Another equivalent of •NO may supply the required electron, for example, and convert to the highly reactive nitrosonium cation. The formation and reactivity of such oxidized products may account for the difficulty in isolating and characterizing the $\{Co(NO)_2\}^{10}$ species directly from the $[Co(TC-6,6)]$/NO reaction mixture. It is possible that nitrite is generated in the reaction via attack of free NO on the coordinated nitrosyl of a metastable $[Co(NO)(TC-6,6)]$ adduct, with concomitant release of $N_2O(g)$. Such attack of free $NO(g)$ on coordinated NO has been described in the literature, and a mechanism for this transformation has been discussed.[16] In support of this mechanism, we were able to detect $^{15}N_2O$ in the headspace gas of the reaction between $[Co(TC-6,6)]$ and $^{15}NO(g)$ following analysis by EI-MS (Figure S7). More detailed mechanistic studies to probe the $[Co(TC-6,6)]$/NO reaction pathway were precluded by the complexity of the reductive nitrosylation process and the difficulty in fully characterizing the reaction products.

The difference in reactivity between $[Co(TC-5,5)]$ and $[Co(TC-6,6)]$ with $NO(g)$ is a major finding of this study. Cobalt(III) nitrite is absent from the $[Co(TC-5,5)]$/NO reaction solution, and we note the proclivity toward cobalt *mono*nitrosyl formation. In contrast, nitrite formation and a cobalt *di*nitrosyl adduct characterize the chemistry of $[Co(TC-6,6)]$ with $NO(g)$. This example is the first to demonstrate true size-dependent reactivity of cobalt(II) tropocoronands, and it reveals the preference for the smaller $[Co(TC-n,n)]$ (n = 3, 4, 5) complexes to form mononitrosyl adducts upon exposure to $NO(g)$. The dinitrosyl units in $[Co_2(NO)_4(TC-6,6)]$, which forms in the NO reactions of $[Co(TC-6,6)]$, are supported by the extension of the polymethylene linker chains in the larger $[TC-6,6]^{2-}$ tropocoronand ligand.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Experimental methods; crystallographic tables; infrared spectroscopic comparison of the reactions between $[Co(TC-4,4)]$ and NO or ^{15}NO; infrared spectroscopic comparison of the reactions between $[Co(TC-5,5)]$ and NO or ^{15}NO; infrared spectroscopic comparison of $[Co(NO_2)(TC-6,6)]$ and reactions between $[Co(TC-6,6)]$ and NO or ^{15}NO; infrared spectroscopic comparison of $[Co_2(NO)_4(TC-6,6)]$ and the $[Co(TC-6,6)]$/NO reaction; data for EI-MS analysis of the reaction headspace of $[Co(TC-6,6)]$ and ^{15}NO; 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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