3722 *Inorg. Chem.* **2000,** *39,* 3722−3723

# Nitrosyl Transfer from Manganese to Iron in Tropocoronand Complexes

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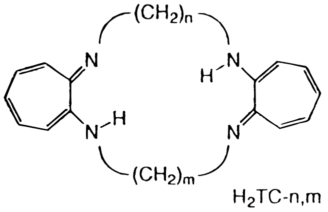
*Received April 4, 2000*

## Introduction

We recently described examples of NO disproportionation promoted by manganese[1] and iron[2] tropocoronand (TC-n,m) complexes. By limiting the stoichiometry of added NO, discrete {MnNO}[6] and {FeNO}[7] compounds were isolated and characterized. During our investigation, we uncovered nitrosyl transfer from [Mn(NO)(TC-5,5)] to [Fe(TC-5,5)], affording [Fe(NO)(TC-5,5)] as shown in eq 1.



H$_2$TC-n,m

$$\mathrm{M(NO) + M' \rightleftharpoons M'(NO) + M} \qquad (1)$$

An early example of intermolecular NO transfer occurred between $[Co(NH_3)_5(NO)]^{2+}$ and $Cr^{2+}$.[3] Since then, two general mechanisms have been advanced for this overall reaction (eqs 2 and 3).[4] In the first case, formation of a nitrosyl-bridged

$$\mathrm{M(NO) + M' \rightleftharpoons M(\mu\text{-}NO)M' \rightleftharpoons M'(NO)} \qquad (2)$$

$$\mathrm{M(NO)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M + NO} \xrightarrow{k_2,\, \mathrm{M'}} \mathrm{M'(NO)} \qquad (3)$$

dimetallic intermediate facilitates direct transfer of NO from one metal center to another.[5−7] Evidence for this mechanism was based mostly on product analysis and the observation that coordinatively unsaturated acceptors were favored.[5] Detailed kinetic analysis of NO transfer between cobalt dimethylglyoximate complexes and hemoglobin revealed that dissociation of nitric oxide (eq 3) from cobalt leads to NO transfer to hemoglobin.[8,9] This result suggested that such a mechanism might generally describe NO transfer between metal centers.[8,9]

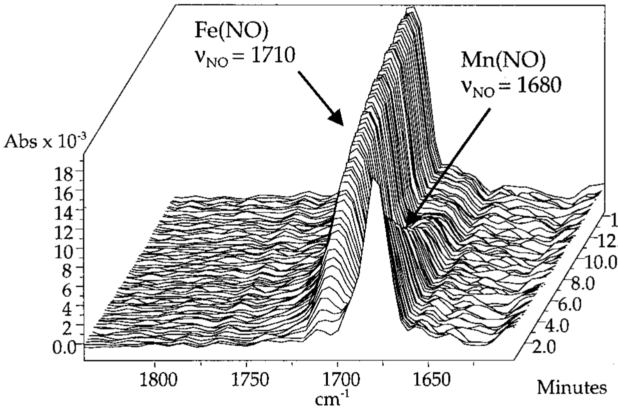


**Figure 1.** The NO stretching region of IR spectra collected in situ at room temperature during the reaction of [Mn(NO)(TC-5,5)] with [Fe(TC-5,5)] in THF. The initial concentration of each compound was 6.5 mM. The band at 1680 cm$^{-1}$ corresponds to $\nu_{NO}$ of [Mn(NO)(TC-5,5)]. This signal decayed within 10 min as a new band at 1710 cm$^{-1}$ emerged, indicating formation of [Fe(NO)(TC-5,5)].

To determine the mechanism of nitrosyl transfer between [Mn(NO)(TC-5,5)] and [Fe(TC-5,5)] we monitored the reaction by in situ IR spectroscopy. The results are described in this note.

## Experimental Section

**General Considerations.** All reactions were performed under strict anaerobic conditions in an $N_2$-filled glovebox or by using standard Schlenk techniques under an Ar atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under nitrogen. The compounds [Mn(NO)(TC-5,5)][1] and [Fe(TC-5,5)][2] were prepared as described previously.

**Reaction Protocol.** In situ IR sample monitoring was performed with a ReactIR 1000 from ASI Applied Systems. The details of the experimental setup have been described elsewhere.[2] The IR probe was inserted through a well-sealed adapter into a custom-made flask equipped with a gas-inlet adapter, a septum-sealed joint, and a stir bar. Under an Ar atmosphere, the flask was charged with 5 mL of a 13 mM THF solution of [Mn(NO)(TC-5,5)] at ambient room temperature. After monitoring was initiated with ReactIR 2.0 software, 5 mL of a 13 mM THF solution of [Fe(TC-5,5)] was added to the flask by syringe. The final concentration of each species was therefore 6.5 mM. A spectrum was collected every 2.6 s for 28 min.

## Results

The strong NO stretching band provides a convenient spectroscopic signal with which to monitor formation of metal nitrosyls. When a solution of [Fe(NO)(TC-5,5)] ($\nu_{NO} = 1710$ cm$^{-1}$, THF) was added to a solution of [Mn(THF)(TC-5,5)] no change occurred in the 1710 cm$^{-1}$ IR spectral band, indicating that iron does not transfer NO to Mn(II). When a solution of [Mn(NO)(TC-5,5)] ($\nu_{NO} = 1680$ cm$^{-1}$, THF) was mixed with a solution of [Fe(TC-5,5)], however, the band at 1680 cm$^{-1}$ was replaced by a band at 1710 cm$^{-1}$. This result indicates that the Mn-bound nitrosyl ligand was transferred quantitatively to Fe(II) to form [Fe(NO)(TC-5,5)]. Figure 1 displays in situ IR spectra taken after equimolar amounts of [Mn(NO)(TC-5,5)] and [Fe(TC-5,5)] were combined at room temperature. Within 10 min, the Mn nitrosyl stretching mode at 1680 cm$^{-1}$ was replaced by a band at 1710 cm$^{-1}$, which is the signature of the Fe nitrosyl compound.

The two mechanisms depicted in eqs 2 and 3 to describe this NO transfer reaction can, under favorable circumstances, be distinguished by the reaction order with respect to the concen-

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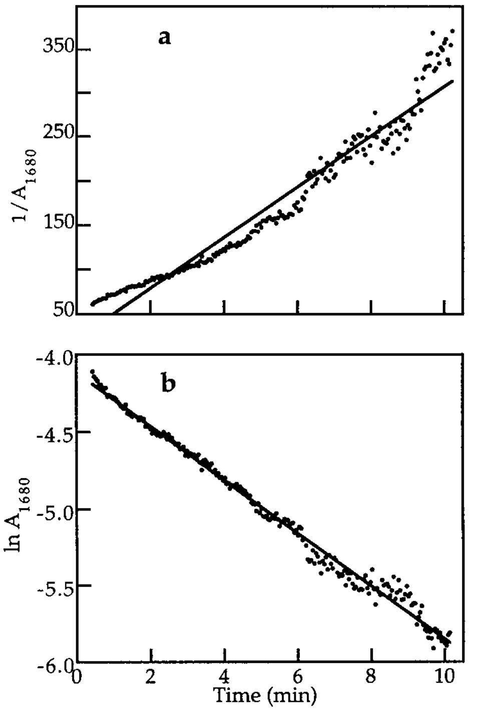

**Figure 2.** (a) Plot of the inverse of the absorbance at 1680 cm$^{-1}$ vs time. A fit of the data to a straight line gives a residual $R = 0.972$. (b) Plot of ln of the absorbance at 1680 cm$^{-1}$ vs time. The best-fit line has a $y$-intercept at $-4.114(7)$ and a slope ($-k_{obs}$) of $-0.174(1)$ min$^{-1}$ with a residual $R = 0.995$.

trations of the metal complexes. If the mechanism in eq 2 were operative, formation of a nitrosyl-bridged species would require that the reaction be first order in both [MnNO] and [Fe]. Equation 3 describes a process that is either first- or second-order overall, depending on conditions. Application of a steady-state analysis to eq 3 yields the rate law given by eq 4.[10] In the

$$\frac{-\mathrm{d}[\mathrm{MnNO}]}{\mathrm{d}t} = \frac{k_1 k_2[\mathrm{MnNO}][\mathrm{Fe}]}{k_{-1}[\mathrm{Mn}] + k_2[\mathrm{Fe}]} \tag{4}$$

limit where $k_{-1}[\mathrm{Mn}] \ll k_2[\mathrm{Fe}]$, the reaction depends only on [MnNO], whereas if $k_{-1}[\mathrm{Mn}] \gg k_2[\mathrm{Fe}]$, the reaction would show a dependence on [Fe] as well as [MnNO]. If the reaction did not obey first-order kinetics, therefore, the mechanisms described by eqs 2 and 3 would be indistinguishable.

Because the experiment utilized equimolar quantities of MnNO and Fe, the second-order rate expression for eq 2, $v = k[\mathrm{MnNO}][\mathrm{Fe}]$, reduces to $v = k[\mathrm{MnNO}]^2$.[10] The dependence on [MnNO] should, therefore, distinguish the two mechanisms, with a first-order dependence on [MnNO] indicating eq 3 in the limit where $k_{-1}[\mathrm{Mn}] \ll k_2[\mathrm{Fe}]$. Because absorbance is proportional to concentration, the absorbance of the Mn(NO) stretch at 1680 cm$^{-1}$ was used for kinetic analysis.

Figure 2a shows data plotted as $1/A_{1680}$ vs time. A straight-line fit of the data reveals poor agreement with second-order kinetics. The data agree much better with first-order dependence on [MnNO], as shown by a plot of ln $A_{1680}$ versus time (Figure 2b). This analysis, therefore, reveals the likely pathway for NO transfer to be NO dissociation from Mn prior to reaction with Fe. A more definitive proof would require more extensive kinetic studies.

To test the dissociation hypothesis further, THF solutions of approximately equimolar amounts of [Fe($^{15}$NO)(TC-5,5)] and [Mn($^{14}$NO)(TC-5,5)] were mixed. Given the evidence for a dissociative mechanism described above, the reaction should completely scramble the NO ligands to afford a mixture of Fe($^{15}$NO), Fe($^{14}$NO), Mn($^{15}$NO), and Mn($^{14}$NO) species. Figure 3 shows the solution IR spectrum after 15 min. The bands at 1710 and 1648 cm$^{-1}$ indicate Fe($^{14}$NO) and Mn($^{15}$NO), respectively, whereas the more intense band at 1680 cm$^{-1}$ arises from the overlapping signals of Fe($^{15}$NO) and Mn($^{14}$NO).

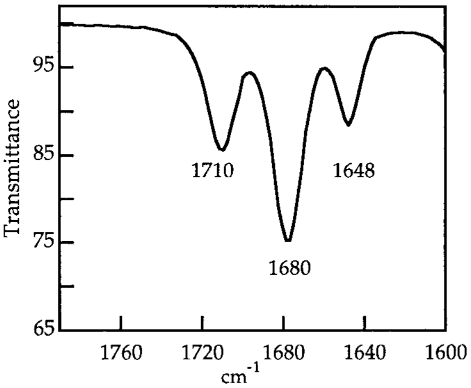

**Figure 3.** IR spectrum in THF solution taken 15 min after mixing approximately equimolar solutions of [Fe($^{15}$NO)(TC-5,5)] and [Mn(NO)(TC-5,5)] (both compounds, $\nu_{NO} = 1680$ cm$^{-1}$). New bands appear at 1710 and 1648 cm$^{-1}$, indicating formation of [Fe(NO)(TC-5,5)] and [Mn($^{15}$NO)(TC-5,5)], respectively.

Although neither [Fe(NO)(TC-5,5)] nor [Mn(NO)(TC-5,5] readily loses NO in solution or the solid state, as previously reported,[1,2] the evidence of NO dissociation discovered here implies that such a reaction does occur.

## Discussion

A kinetic analysis of the nitrosyl transfer reaction observed between Mn and Fe tropocoronand complexes presented here suggests a mechanism that involves dissociation of Mn-bound NO prior to formation of Fe(NO)(TC-5,5)] (eq 3). Both [Fe(NO)(TC-5,5)] and [Mn(NO)(TC-5,5)] are stable species and do not lose NO under moderate conditions of heat and vacuum.[1,2] This stability suggested that a dissociative mechanism would be unlikely to account for exchange of $^{14}$NO for labeled $^{15}$NO that was observed previously.[1,2] The current study demonstrates that such a mechanism may be feasible, although it does not directly address the exchange of NO at a single metal center and, therefore, cannot exclude the possibility of an associative pathway for that reaction.

These manganese and iron mono-nitrosyl species are activated by their metal centers for further reactivity with nitric oxide. The reaction pathways of NO disproportionation are similar for the two metal compounds, up to the formation of metal nitrosyl-nitrito {M(NO)(NO$_2$)} intermediates, which are stable at −78 °C. At room temperature, the lability of the nitrosyl and nitrito ligands differs for the two metal centers, however. Whereas Mn loses NO to afford a Mn nitrito product [Mn(NO$_2$)(TC-5,5)],[1] Fe retains the nitrosyl and NO$_2$ dissociates. Free NO$_2$ attacks the ligand to give the final nitrosyl product, [Fe(NO)(TC-5,5-NO$_2$)].[2]

The NO transfer reaction described here reflects this difference in affinity for NO by Fe and Mn. The fact that NO transfers only from Mn to Fe and not in the reverse direction demonstrates the much higher affinity of iron for nitric oxide. The kinetic analysis corroborates speculation that NO dissociation provides a general pathway for intermolecular NO transfer reactions.[8]

**Acknowledgment.** This work was supported by a grant from the National Science Foundation.

IC000360N