Remote Control of NO Reactivity through Redox Switching in Dinuclear Cyano-Bridged Complexes

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The binding of NO to transition metals and further reactivity are of concern to coordination chemists, in particular for elucidating the role of NO in diverse physiological functions.[1] Thus, the electrophilicity of NO^+ and its redox interconversions to NO or NO^- become of interest for some biologically relevant low-spin d^6 systems.[2]

Among the few mechanistic studies of base additions to bound NO^+ in mononuclear species like $\{X_5MNO\}$[3] are the reactions of OH^- with the pentacyanonitrosylmetalate ions (M = Fe, Ru, Os).[4] A rate-determining addition of OH^- to bound nitrosyl is followed by deprotonation and formation of nitro complexes. For other X coligands (NH_3, halides, polypyridines, etc.) and other nucleophiles (SH^-, thiolates, ammines, hydroxylamine, etc.) a similar mechanism is operative, although the initial adduct formations are followed by fast irreversible redox steps. With these systems mainly equilibrium and spectroscopic data but no detailed kinetic studies are available.[3]

We prepared a set of dinuclear complexes containing the pentacyanonitrosylmetalate fragments, bridged through one of the cyanides to a pentaammineruthenium moiety. To control the reactivity of bound NO^+, we studied the rate of addition of OH^-, with the result that the metal−nitrosyl electrophilicity can be dramatically altered by switching the oxidation states of the distant $Ru(NH_3)_5$ moiety. We took advantage of the properties of the mononuclear fragments[5] and of the studies on dinuclear complexes of the $[(NH_3)_5Ru{-}NC{-}M(CN)_5]^n$ type, which have been widely used because of interest in intermetallic electronic coupling, mixed valence, and photoinduced electron- and energy-transfer properties.[6] We show that the substitution of one cyanide by NO^+ induces drastic electronic rearrangements in the dinuclear systems, which can be gauged by spectroscopic, electrochemical, and kinetic measurements.

The complexes were prepared by mixing equimolar solutions of the mononuclear reactants:

$$[M(CN)_5NO]^{2-} + [Ru^{II}(NH_3)_5H_2O]^{2+} \leftrightarrow [(NH_3)_5Ru^{II}{-}NC{-}M(CN)_4NO] + H_2O \quad (1)$$

The products, hereafter named $\mathbf{I}_M$, showed new absorption bands, not seen in either of the reactants, at 618 ($\mathbf{I}_{Fe}$), 640 ($\mathbf{I}_{Ru}$), and 538 nm ($\mathbf{I}_{Os}$).[7] The molar absorbances were $10^{-3}\epsilon = 3.2$, 3.6, and 4.0 $M^{-1}\ cm^{-1}$, respectively, suggesting an assignment to MLCT transitions from Ru(II) to a delocalized π-molecular orbital comprising the $\{NC{-}M(CN)_4NO\}$ moiety (see below). Through mole-ratio procedures,[8] a 1:1 stoichiometry was defined for eq 1 and the equilibrium constants were $10^{-6}K_1 = 5.0$, 1.5, and 5.0 M^{-1} (same order). The complexes are of inner-sphere type indeed, as no new bands develop upon mixing the pentacyanonitrosylmetalates with $[Ru(NH_3)_6]^{2+}$. From the electrochemical data (Table 1), the wave at 0.28 V for complex $\mathbf{I}_{Os}$ corresponds to redox activity at the $Ru(NH_3)_5$ center; the value is positively shifted by ca. 0.3 V compared to the $[Ru(NH_3)_5H_2O]^{2+,3+}$ couple, as expected by coordination of a π-acceptor ligand, namely the $\{NC{-}Os(CN)_4NO\}$ moiety. On the other hand, a small shift to negative potentials is observed for the nitrosyl-centered reduction wave, compared to the mononuclear species, suggesting that the electron depletion associated with σ-coordination to the $Ru^{II}(NH_3)_5$ fragment is more than compensated by the π-back-donation of Ru(II). Remarkably, the upward shift in the energy of the electronic absorption band when going from the ruthenium to the osmium complex is of 0.41 V, close to the difference in nitrosyl reduction potentials, 0.34 V. This confirms the MLCT assignment and shows that the charge transfer from Ru(II) includes mainly the nitrosyl group as the acceptor site. Table 1 also shows IR and Raman data for $\mathbf{I}_{Os}$. The broad IR band at 2145 cm^{-1} for aqueous $[Os(CN)_5NO]^{2-}$ shifts to 2138 cm^{-1} for $\mathbf{I}_{Os}$, and a new band at 2113 cm^{-1} appears.[9] We assign them to nonbridging and bridging ν(CN) stretchings, respectively. Although an increase in ν(CN) is expected upon coordination of metal fragments to the N end of cyanide, a decrease was found for systems where π-back-bonding is operative;[10,11] this is now the case for Ru(II). The back-donation extends to the distant NO ligand, as ν(NO) also decreases. The Raman results for $\mathbf{I}_{Os}$ (2138, 2120 cm^{-1}) agree with the IR picture; now, a third peak is detected at 2160 cm^{-1}, corresponding to the $\nu(CN)_{ax}$ stretching.[4] The bridging mode at 2120 cm^{-1} is confirmed by the strong enhancement obtained upon excitation with a wavelength (514.5 nm) close to the maximum of the electronic absorption band of $\mathbf{I}_{Os}$ (no resonance is observed with 632.8 and 547.9 nm light); moreover, the enhancement extends also to ν(NO), which was absent in $[Os(CN)_5NO]^{2-}$. Even the deformation mode of coordinated ammine in Ru(II) is enhanced,

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(1) Feelisch, M.; Stamler, J. S., Eds. *Methods in Nitric Oxide Research*; Wiley: 1996.

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(3) Bottomley, F. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1989; Vol. 2, p 115.

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(5) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

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(7) $\mathbf{I}_{Os}$ was obtained as a solid by mixing 0.2 mmol of the mononuclear reactants in 2 mL of an aqueous solution, pH 4.75, under argon. The solid was filtered off, dissolved again in water, and poured into a Sephadex G-25 column. The fractions with $\lambda_{max} = 538$ nm were dried in a rotavap.

(8) Reilley, C, N,; Sawyer, D. T. *Experiments for Instrumental Methods*; McGraw-Hill: New York, 1961.

(9) The resolution pattern in aqueous solution is poor compared to solid IR measurements. However, the correspondence is fair: for the solids, the absorptions at 2166, 2156, and 2142 cm^{-1} ($K_2[Os(CN)_5NO]$. H_2O) transform into 2131, 2120, and 2110 cm^{-1} upon formation of $\mathbf{I}_{Os}$.

(10) (a) Coe, B. J.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1995**, *34*, 3600. (b) Bignozzi, C. A.; Argazzi, R.; Schoonover, J. R.; Dyer, R. B.; Scandola, F. *Inorg. Chem.* **1992**, 31, 5260. (c) Watzky, M. A.; Endicott, J. F.; Song, X.; Lei, Y.; Macatangay, A. *Inorg. Chem.* **1996**, *35*, 3463.

(11) Most probably, $\mathbf{I}_{Os}$ is formed through the bridging of a cyanide ligand cis to NO, as suggested by predictable relative basicities, and consistently with structural data in related complexes (cf.: Chen, Z. N.; Wang, J. L.; Qiu, J.; Miao, F. M.; Tang, W. X. *Inorg. Chem.* **1995**, *34*, 2255).

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Table 1. Spectroscopic (UV−vis, IR and Raman) and Electrochemical Characterization and Kinetic Reactivity toward OH^- for $K_2[Os(CN)_5NO]\cdot H_2O$, $[(NH_3)_5Ru^{II}-NC-Os^{II}(CN)_4NO]$ ($\mathbf{I}_{Os}$), and $[(NH_3)_5Ru^{III}-NC-Os^{II}(CN)_4NO]^+$ ($\mathbf{II}_{Os}$) Complexes

			IR[a]		Raman[c]		
compd	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[a]	E°_{red},[b] V vs NHE	ν_{CN},[e] cm^{-1}	ν_{NO}, cm^{-1}	ν_{CN},[e] cm^{-1}	ν_{NO}, cm^{-1}	k_{OH^-},[d] (M^{-1} s^{-1})
$K_2[Os(CN)_5NO]$	427 (89) 314 (97)	−0.492[f]	2145 (eq)	1894	2154 (eq) 2170 (ax)		1.4×10^{-4} [g]
$\mathbf{I}_{Os}$	538 (4000)	0.280[h] −0.520[i]	2138 (eq) 2113 (br)	1884	2138 (eq) 2120 (br) 2160 (ax)	1880	1.2×10^{-4}
$\mathbf{II}_{Os}$	295 (1823)		2140 (eq)	1906	2164 (eq) 2190 (br)	1895	15

[a] In aqueous solution, pH = 4.5, $I = 0.1$ M. [b] Obtained by square wave voltammetry, $I = 0.1$ M. [c] In aqueous solution, pH = 4.5 (buffer HOAc/NaOAc), $[Os(CN)_5NO^{2-}] = 10^{-2}$ M; $[\mathbf{I}_{Os}] = [\mathbf{II}_{Os}] = 5 \times 10^{-3}$ M, $I = 0.1$ M, CH_3CN 1% as internal standard. [d] $[\mathbf{I}_{Os}] = [\mathbf{II}_{Os}] = 10^{-4}$ M; $[OH^-] = 0.63-2.25 \times 10^{-4}$ M, $I = 0.5$ M. [e] Assignments in parentheses. [f] $E^\circ = -0.102$ and -0.182 V for the nitrosyl-centered reduction of $[Fe(CN)_5NO]^{2-}$ and $[Ru(CN)_5NO]^{2-}$, respectively. [g] $k_{OH^-} = 0.55$ and 0.95 M^{-1} s^{-1} for the $[Fe(CN)_5NO]^{2-}$ and $[Ru(CN)_5NO]^{2-}$, respectively. [h] $E^\circ = 0.270$ and 0.280 V for the reduction at the $Ru(NH_3)_5$ center of $\mathbf{I}_{Fe}$ and $\mathbf{I}_{Ru}$, respectively. [i] $E^\circ = -0.110$ and -0.180 V for the nitrosyl-centered reduction of $\mathbf{I}_{Fe}$ and $\mathbf{I}_{Ru}$, respectively.

at 1257 cm^{-1}.[12] The electrochemical, UV−vis, IR, and Raman results prove that the peaks at 2113 (IR) and 2120 (Raman) cm^{-1} corrrespond to the bridging cyanide, and that the electronic communication, as indicated by the intense visible band, comprises the overall delocalized system, from Ru(II) up to the distant NO.

The kinetics of addition of OH^- to $\mathbf{I}_{Os}$ (eq 2) showed a second-order rate law, first order in each of the reactants, with $k_{OH^-} = 1.2 \times 10^{-4}$ M^{-1} s^{-1}.

$$[(NH_3)_5Ru^{II}-NC-Os(CN)_4NO] + 2\ OH^- \leftrightarrow [(NH_3)_5Ru^{II}-NC-Os(CN)_4NO_2]^{-2} + H_2O \quad (2)$$

Compared to the value for the $[Os(CN)_5NO]^{2-}$ ion,[4] the decrease of k_{OH^-} for eq 2 is very small (Table 1), despite the decrease in ν(NO).[3,13] The more positive charge in $\mathbf{I}_{Os}$ should favor an *increase* in rate, but this is more than compensated by the π-donor ability of Ru(II), as discussed above. The product of the reaction showed the disappearance of the intense visible band of $\mathbf{I}_{Os}$ and the appearance of a new absorption at $\lambda = 347$ nm, assignable to the nitro compound.

Upon oxidation with peroxydisulfate, $\mathbf{I}_{Os}$ leads to $\mathbf{II}_{Os}$ (eq 3).[14] The conversion is associated with the disappearance of the intense visible band; also, $\mathbf{I}_{Os}$ is recovered upon reduction of $\mathbf{II}_{Os}$ with ascorbic acid. A mole-ratio experiment showed a net one-electron oxidation product. The shifts in the IR and Raman spectra are consistent with the role of Ru changing from electron donor to electron acceptor when going from oxidation state II to III. Thus, the upward shifts in ν(CN) and ν(NO) reflect the lower population of π^* orbitals on both ligands, as well as the increased σ-acid ability of Ru(III).[10a,15] A significant upward Raman shift is detected with $\mathbf{II}_{Os}$ for the bridging ν(CN) mode, compared to $\mathbf{I}_{Os}$.[16]

$$2[(NH_3)_5Ru^{II}-NC-Os(CN)_4NO] + S_2O_8^{\ 2-} \leftrightarrow 2[(NH_3)_5Ru^{III}-NC-Os(CN)_4NO]^+ + 2SO_4^{\ 2-} \quad (3)$$

By measuring the reaction of OH^- with $\mathbf{II}_{Os}$, the rate constant was 15 M^{-1} s^{-1}, under the same conditions as for eq 2.[17] The rate increase of 5 orders of magnitude is certainly remarkable and reflects the electron flow away from the NO ligand upon coordination to Ru(III), as indicated by the spectroscopic changes, and in agreement with the positive charge of $\mathbf{II}_{Os}$. Evidently, the energy of the delocalized LUMO, mainly located at the N atom of nitrosyl,[18] is drastically lowered, favoring attack by OH^-. The above-mentioned spectroscopic and kinetic changes can be reversibly driven by redox cycling at the Ru center.

Few systems with a related behavior have been documented. The rate of hydrolysis of nitriles bound to the $Ru(NH_3)_5$ fragment was enhanced by 10^6 upon oxidation of Ru(II) to Ru(III).[19] However, in these mononuclear species the redox active center is close to the chemically active site. To our knowledge, the only reported example for a dinuclear remote system was a rhenium complex containing a cobaltocene-based phosphine and carbonyl ligands; here, the electrophilicity at bound carbonyl was increased by 2−3 orders of magnitude for different nucleophiles through a $1e^-$ oxidation of the cobaltocene unit.[20] We show an amplification of these effects, now operating on NO at long distances, with a strong communication between the reactive and redox sites. Thus, a control of the reactivity of bound NO^+ could be obtained by incorporating charged species, either covalently bound or in a strong, specific interaction with the first coordination sphere of an iron-enzyme target. In this context, an extension of OH^- addition chemistry to other biochemically relevant nucleophiles such as the thiolates is straightforward.[21]

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(12) Nakamoto, K. *Infrared and Raman Spectra of Inorganic Compounds*; Wiley: New York, 1986.

(13) A general correlation predicts that *k* values for the addition reactions to NO should decrease with decreasing ν(NO).[3] This statement should be applied with caution, particularly when complexes with unequal charges and/or different metal centers are considered (cf. refs 3, 4).

(14) $\mathbf{II}_{Os}$ was prepared by taking a solution of $\mathbf{I}_{Os}$ and mixing with 1 equiv of peroxydisulfate. It was dried in a rotavap, redissolved in water, and poured again into the G-25 column. The fraction with $\lambda_{max} = 295$ nm was dried in the rotavap.

(15) The single IR peak at 2140 cm^{-1} for $\mathbf{II}_{Os}$ probably relates to the unresolved nonbridging cyanides; remarkably, no new bridging mode is detected, as was the case with a related binuclear complex.[6a] This is probably associated with weak dipolar changes.

(16) ν(CN) for the nitrile stretching in $[Ru^{II,III}(NH_3)_5(benzonitrile)]^{2,3+}$ shifts from 2188 to 2267 cm^{-1}, when Ru(II) is oxidized to Ru(III) (cf.: Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 227 and ref 12).

(17) During the reaction of $\mathbf{II}_{Os}$ with OH^-, ν(NO) disappeared and ν(CN) shifted to 2039 cm^{-1}. Also, the product showed an intense band at 530 nm, probably related to LMCT from cyanides to Ru(III). The presence of the nitro group is related to new bands at 1447 and 866 cm^{-1}.[12]

(18) Bottomley, F.; Grein, F. *J. Chem. Soc., Dalton Trans.* **1980**, 1359.

(19) Constable, E. C. *Metals and Ligand Reactivity*; VCH: Weinheim, 1996; p 65.

(20) Lorkovic, I. M.; Wrighton, M. S.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6220.

(21) The rates of addition of SH^- were greater than those for OH^- by about 2 orders of magnitude, for the three pentacyanonitrosylmetalates.[6]