# Electrophilic Behaviour of the Co-ordinated Nitrosyl Cation

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*Summary* It is proposed that co-ordinated $NO^+$ having $\nu(NO) > 1886\ cm^{-1}$ or $F(N\text{–}O) > 13{\cdot}8$ mdyn Å$^{-1}$ will behave as an electrophile.

IN contrast to free $NO^+$, which is very readily attacked by nucleophiles [*e.g.* for $NO^+ + 2OH^- \rightleftharpoons NO_2^- + H_2O$, $K = 2{\cdot}3 \times 10^{31}$ (ref. 1)], nucleophilic attack at co-ordinated $NO^+$ is relatively rare. The hydrolysis of $[Fe(CN)_5NO]^{2-}$ (ref. 1) was an isolated example until relatively recently, when nucleophilic attack at $[M(CN)_5NO]^{2-}$ (M = Ru, Os);[2,3] $[RuX(A\text{–}A)_2NO]^{n+}$ [A–A = 2,2′-bipyridyl or *o*-phenanthroline; X = $NO_2$, Cl, Br ($n$ = 2), or pyridine ($n$ = 3)];[4,5] $[RuCl(das)_2NO]^{2+}$ (das = *o*-phenylenebisdimethylarsine);[6,7] $[Ru(NH_3)_5NO]^{3+}$;[8] and $[IrCl_3L_2NO]^+$ (L = $Ph_3P$ or $Ph_3As$)[9] was demonstrated. Unsuccessful attempts to attack co-ordinated $NO^+$ with nucleophiles have been reported.[9,10] We propose a general relation between $\nu(NO)$ or, more accurately, the N–O force constant (these crudely but conveniently measuring the electron density at the co-ordinated nitrogen atom of $NO^+$ [11]) which correlates the existing scattered examples of the electrophilic behaviour of co-ordinated $NO^+$ and allows prediction of such reactivity. This relation is partly prompted by one recently advanced for reactions of co-ordinated CO with $RNH_2$.[12]

The Table lists $\nu(NO)$ and $F(N\text{–}O)$ (where the latter can be determined) for a selection† of reactive and unreactive complexes. The reactions of $[IrCl_5NO]^-$, $[IrBr_5NO]^-$, $[RuOH(NO_2)_4NO]^{2-}$, and *cis*-$[RuCl(NH_3)_4NO]^{2+}$ are reported here for the first time. Several of the complexes in the Table are known, from *X*-ray studies, to contain linear MNO groups,[13] and therefore co-ordinated $NO^+$. It can be confidently assumed, from their high $\nu(NO)$ frequencies,

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† We have 'selected' examples in the sense that only one member of a series stands for all. For example, all $[RuX(bipy)_2NO]^{n+}$ complexes are reactive, and have similar $\nu(NO)$; *trans*-$[MOH(NH_3)_4NO]^{2+}$ (M = Ru, Os; X = $OH^-$, Cl, Br, $NH_2$) are unreactive, and all have $\nu(NO) < 1878\ cm^{-1}$.

TABLE

Stretching frequencies, force constants, and reactivities of some complexes containing $NO^+$

| Complex | $\nu$(NO) $cm^{-1a}$ | *F* (N–O) | Nucleophile |
|---|---|---|---|
| $K[IrCl_5NO]$ | $2006^b$ | 16·0 | $OH^-$, $NH_3$, $N_3^-$ |
| $[IrBr_5NO]^-$ | 1953 | 15·1 | $OH^-$, $NH_3$, $N_3^-$, $N_2H_4$ |
| $[IrCl_3(PPh_3)_2NO]ClO_4$ | $1945^b$ | — | $MeO^-$, $EtO^{-d}$ |
| $[Fe(CN)_5NO]^{2-}$ | 1938 | 14·7 | $OH^{-e}$ |
| $[Ru(NH_3)_5NO]^{3+}$ | 1925 | 14·6 | $OH^-$, $NH_3$, $N_2H_4$, $NH_2OH$ |
| $[RuCl(bipy)_2NO]^{2+}$ | $1927^c$ | 14·5 | $OH^-$, $N_3^{-f}$ |
| $K_2[Ru(CN)_5NO]$ | $1927^b$ | — | $OH^{-g}$ |
| *cis*-$[RuCl(NH_3)_4NO]^{2+}$ | 1920 | — | $NH_2OH$ |
| $K_2[Os(CN)_5NO]$ | $1905^b$ | — | $OH^{-h}$ |
| $[RuOH(NO_2)_4NO]^{2-}$ | 1902 | 14·1 | $OH^-$, $N_2H_4$ |
| $[RuCl_5NO]^{2-}$ | 1886 | 13·9 | No reaction |
| $[RuCl(das)_2NO]^{2+}$ | 1886 | 13·8 | $OH^-$, $N_2H_4$, $N_3^{-i}$ |
| *trans*-$[RuOH(NH_3)_4NO]^{2+}$ | 1878 | 13·5 | No reaction |
| $[Os(NH_3)_5NO]^{3+}$ | 1885 | 13·4 | No reaction |
| $[OsOH(NH_3)_4NO]^{2+}$ | 1833 | 12·3 | No reaction |

[a] In aqueous solution, except where noted. [b] Nujol mull. [c] Acetone solution, ref. 5. [d] Ref. 9. [e] Ref. 1. [f] refs. 4 and 5. [g] Ref. 2. [h] Ref. 3. [i] Refs. 6 and 7.

the other complexes contain $NO^+$ also. It is seen, from the Table, that all reactive complexes have $\nu(NO) > 1886$ $cm^{-1}$, $F(N–O) > 13·8$ mdyn $Å^{-1}$. The borderline between reactive and unreactive complexes is less clear cut than for carbonyls.[12] $[RuCl_5NO]^{2-}$ (unreactive) has a marginally greater N–O force constant than (reactive) $[RuCl(das)_2NO]^{2+}$. This may reflect an inadequacy in the three-atom approximation used for the force-constant calculations. Where possible, all spectra have been measured in solution. This is important, since, for example, $K_2[RuCl_5NO]$ has $\nu$(NO) 1910 $cm^{-1}$ in the solid state, but 1886 $cm^{-1}$ in solution. Since we find there is often a decrease in the N–O frequency on dissolution of anionic nitrosyls, the extremely insoluble complexes $[M(CN)_5NO]^{2-}$ (M = Ru, Os) may lie closer to the borderline of reactivity than the Table implies.

The Table contains a reasonable range of six-co-ordinated complexes and of nucleophiles. Although not all permutations of nucleophiles and complexes have been investigated, some discrimination by the nucleophile is apparent. For instance, $N_3^-$ reacts with $[RuCl(A–A)_2NO]^{2+}$ [4,7] and $[IrBr_5NO]^-$, but not with $[Ru(NH_3)_5NO]^{3+}$. $NH_3$ reacts slowly with $[Ru(NH_3)_5NO]^{3+}$, giving a mixture of products, but with $[IrBr_5NO]^-$ dinitrogen and an amminebromoiridium(III) complex are obtained instantaneously. The role of the nucleophile is being investigated. However, from the results we propose those complexes of $NO^+$ with $\nu(NO) > 1886$ $cm^{-1}$, $F(N–O) > 13·8$ mdyn $Å^{-1}$ will show electrophilic behaviour of the co-ordinated $NO^+$.

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