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Metal–Nitrosyl Complexes as a Source of New Vasodilators: Strategies Derived from Systematic Chemistry and Nitrosyl Ligand Reactivity

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A series of nitrosyl complexes of empirical formula $K_n[M(CN)_5NO]$, where M = V, Cr, Mn and Co and $n=3$, or M = Mo and $n=4$, have been prepared which are notional analogues of the widely used vasodilator sodium nitroprusside. Their reactivity towards common nucleophiles (OH^-, NH_2R, NHR_2, HS^- and RS^-), acid and photolysis has been investigated to elucidate the desired properties required of new metal nitrosyls which may have some potential as new non-cyanide-based vasodilators.

Keywords: Nitric oxide complexes, vasodilators, nitrosyls, nitroprusside analogues

INTRODUCTION

Recent studies have shown that the small molecule nitric oxide is an important species in cell signalling.[1-3] It is released by various cell types in close proximity to the vascular cell wall by synthase enzymes inducing vasodilation.[1-3] As a consequence, there is a resurgent interest in the efficient delivery of this reactive small gaseous molecule within a clinical environment. Recent animal studies have begun to consider delivering it directly to the lung.[4] However, due to the third-order kinetics of NO oxidation[5] to NO_2 (Eqn [1]), this method of administering nitric oxide would have to be restricted to low concentrations.

$$2NO + O_2 \rightarrow 2NO_2 \qquad [1]$$

A further complication with the use of nitric oxide in gaseous form is the redox equilibrium which exists for its major degradation product, nitrogen dioxide. This equilibrium releases other oxides of nitrogen such as nitrous acid and nitric acid which are themselves toxic (Eqn [2]).

$$N_2O_4 \rightleftarrows 2NO_2 + H_2O \rightleftarrows HNO_3 + HNO_2 \qquad [2]$$

Common therapies overcome these problems by forming stable compounds of nitric oxide operating as vasodilators through the pro-drug philosophy.[6] One of the most important compounds in this series is sodium pentacyanonitrosylferrate(II) or sodium nitroprusside. The oxidation of nitric oxide in this complex is prevented by the formation of a metal complex which stabilizes the small molecule.[6] Although this compound has been well received clinically, there are a number of problems associated with its use, namely reduced activity due to photolysis[7] and its oxidative breakdown due to the action of an activated immune system,[6] both of which release cyanide from the otherwise inert low-spin d^6 iron complex.

Sodium nitroprusside is best formulated as a nitrosonium complex (NO^+).[8] Thus nitric oxide is not just released from the substitution-inert metal centre but requires to be reductively eliminated from the coordination sphere of the metal[9] (Eqns [3], [4]). This creates a two-step mechanism which may explain the biphasic response[10] of the complex in many studies.

$$[Fe(CN)_5NO]^{2-} + RS^- \rightarrow [Fe(CN)_5OH_2]^{3-} + RSNO \qquad [3]$$

$$RSNO \rightarrow \tfrac{1}{2}RSSR + NO \qquad [4]$$

The chemistry can be simplified by representing it as sulphydryl-induced reduction of the nitrosonium cation to nitric oxide generated locally

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(Eqn [5])

$$NO^+ + RS^- \rightarrow NO + \tfrac{1}{2}RSSR \qquad [5]$$

The increased medicinal interest in nitric oxide has led to a desire to produce nitrosyl complexes which are both safe (i.e. not cyanide-based) and are targeted towards specific tissue types (e.g. gut). Although nitric oxide can coordinate to metals in at least five different modes (Fig. 1),[11] the important bonding mode is as the nitrosonium cation.

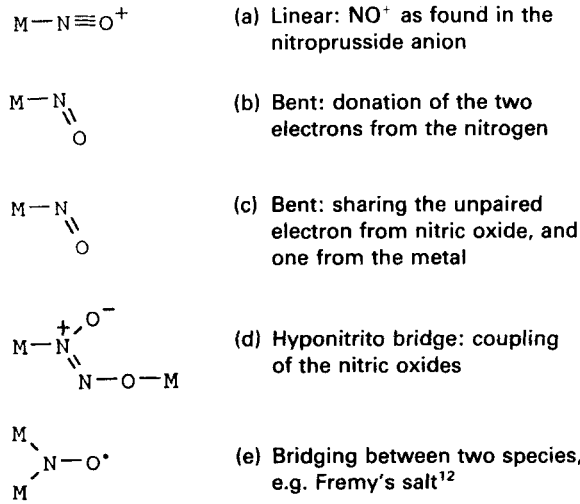


Figure 1 The five common binding modes for nitric oxide.

A simple approach for the preparation of new complexes would be to use systematic chemistry. This approach is investigated here via the preparation of some simple analogues of sodium nitroprusside which maintain the ligand set, while altering the metals. Although these species would be viewed as clinically unacceptable since they contain the toxic cyanide ligand, they can provide details of the desired qualities required of a potential therapeutic agent. In this paper, we present a study of the known analogues of sodium nitroprusside $[(M(CN)_5NO]^{n-}$ where M = V, Cr, Mn, Co and Mo). Their chemistry and physical properties may provide a clear rationale of the properties desired of new nitric-oxide-containing species of medicinal value.

EXPERIMENTAL

All chemicals were commercially obtained unless otherwise stated.

Potassium pentacyanonitrosylvanadate(I),[13] potassium pentacyanonitrosylchromate(I),[14] potassium pentacyanonitrosylmanganate(I),[15] potassium hyponitritobispentacyanocobaltate(III)[16] and potassium pentacyanonitrosylmolybdate(0)[17] were prepared by published methods. The oxidation states of the vanadate, chromate, manganate and molybdate follow the nitroprusside anion where the nitric oxide ligand is formally the nitrosonium cation (NO^+).

Kinetic measurements

Preliminary investigations were carried out using standard solutions (10^{-4} M, 10^{-3} M and 3×10^{-3} M) of each complex. The UV–visible spectrum was recorded (200–850 nm) on a Unicam SP800 spectrophotometer, care being taken to note any reaction which occurrs on dissolution (e.g. for the cobalt and molybdenum complexes). The standard solutions were doped with a small volume (0.1 ml in 3.0 ml) of reagent (H^+, OH^-, ethylamine, diethylamine, HS^- and cysteine). The amines required to be buffered and solutions of cysteine were adjusted to pH 8, i.e. above the pK_a of the thiol.

The kinetics of pentacyanonitrosylmanganate(I) with H^+ were studied at 384 nm, at pH 3–4 in phthalate/HCl buffer at 302 K, 1.0 M KCl, on a Pye–Unicam SP8-100 spectrophotometer. A fixed amount of the complex was weighed directly into a standard flask (25 ml). Buffer was added and the complex was dissolved and made up to the mark. The cuvette was filled and the spectrum monitored at 384 nm. the reaction was followed at pH values of 1.87, 2.02, 2.14, 2.31, 2.63 and 2.82 (pH range 2.00–3.00) and at pH values of 3.04, 3.12, 3.40, 3.50 and 3.61 (pH range 3.00–4.00). The remaining solution was used to obtain an accurate pH value and to verify that the buffer was operating satisfactorily.

The kinetics of hyponitritobispentacyanocobaltate(III) with H^+ were studied at 290 nm, at pH 8–9 in borax buffer at 303 K, 1.0 M KCl on a Pye–Unicam SP8-100 spectrophotometer. The method used followed that for the manganese complex over the pH values 7.99, 8.10, 8.15, 8.20, 8.47 and 9.03.

Isolation of the product derived from acid-treated $[Mn(CN)_5NO]^{3-}$

Concentrated hydrochloric acid was added dropwise to a filtered aqueous solution of pentacyanonitrosylmanganate(I) (1 g in 5 ml), whereupon

Table 1 The IR stretching frequencies ν(CN) and ν(NO), metal–nitrosyl bond angles and bond lengths derived from X-ray analysis for sodium nitroprusside and its five notional analogues.

Compound	ν(CN) (cm^{-1})	ν(NO) (cm^{-1})	N=O (ppm)	M—N=O angle (deg)	Ref.
$[V(CN)_5NO]^{3-}$	2095	1530	129	176	23
$[Cr(CN)_5NO]^{3-}$	2137	1645	Disordered	180	24
$[Mo(CN)_5NO]^{4-}$	2130	1595	123	175	25
$[Mn(CN)_5NO]^{3-}$	2129	1730	121	174	26
$[Fe(CN)_5NO]^{2-}$	2130	1925	113	178	27
$[Co(CN)_5NO]_2^{6-}$ [a]	2205	1114, 1052, 971	Bis(hyponitrito)-	—	28

[a] The cobalt analogue is a bis(hyponitritocobalt) dimer (Co—NO=N—O—Co).

the solution turned yellow and a gas was evolved (H_2). A concentrated solution of cobalt chloride was added and a red precipitate formed. This was collected on a filter and washed with hot water (70 °C), ethanol and diethyl ether, and dried in a desiccator.

Infrared: $\nu(H_2O)$ 3500–3400 cm^{-1} strong,
1600 cm^{-1} medium
ν(CN) 2180 cm^{-1} strong
ν(NO) 1880 cm^{-1} strong

Found:
Co 16.5; Mn 13.2; C 17.0; H 1.4; N 22.3%

Expected for $Co[Mn(CN)_5NO].5H_2O$:
Co 16.2; Mn 15.1; C 16.5; H 2.8; N 23.1%

Isolation of the product derived from H^+-treated $[Co(CN)_5]_2N_2O_2^{6-}$

The cobalt complex (1 g) was dissolved in 25 ml of water and allowed to stand for 30 min. A 10 ml portion of this solution was removed and added to a concentrated solution of silver nitrate, precipitating a yellow–white powder. This was collected and washed with hot water (70 °C), ethanol and diethyl ether, and dried in a desiccator under vacuum.

Infrared: $\nu(H_2O)$ 3550–3450 cm^{-1} weak,
1600 cm^{-1} weak
ν(CN) 2160 cm^{-1} strong

Found: C 14.7; H 0.2; N 16.6%
Expected for $AG_4[Co(CN)_5]_2.4H_2O$:
or $Ag_2[Co(CN)_5OH_2].H_2O$:
C 14.2; H 0.4; N 16.6%

RESULTS AND DISCUSSION

The chemistry of sodium nitroprusside is dominated by the nitrosyl (NO^+) ligand. Although it is inert to hydrolysis,[7] it reacts with hydroxide,[18] primary amines, secondary amines,[19–21] hydrogen sulphide[22]; and thiols[9] via nucleophilic attack to produce a variety of products. This profile of chemical reactivity is important to the discovery of new vasodilators as there is strong evidence to support the hypothesis that it is the reactivity of the nitroprusside anion towards cysteinyl residues *in vivo* which gives rise to its hypotensive properties (Eqns [3]–[5]).

A series of five compounds with empirical formula $[M(CN)_5NO]^{n-}$ (where M = V, Cr, Mn and Co and $n = 3$, or M = Mo and $n = 4$) has been prepared which are notional analogues of sodium nitroprusside. These complexes allow the reactivity of the nitrosyl ligand to be modified by the electronic environment of the different metals. Correlation of the reactivity of these species with simple physical measurements derived from their infrared and X-ray data (Table 1) should make it possible to develop a simple set of chemical tests for putative therapeutic agents which contain coordinated nitric oxide and which are expected to operate through a mechanism similar to that of sodium nitroprusside.

The infrared ν(NO) stretch is a useful guide to the subtle bonding adopted by the ligand, allowing a reasonable assessment of the nature of the coordinated nitric oxide (NO^-, $NO^\bullet$ or NO^+; Table 2).[11,31] Sodium nitroprusside has the highest stretching frequency of the six complexes in this study (Table 1), indicating that it has the shortest N–O bond and contains a well developed NO^+ ligand. As the N–O bond length increases, considerable overlap occurs between the infrared stretching frequencies of the linear and bent geo-

Table 2 The expected range of infrared stretching frequencies for complexes containing coordinated nitric oxide in linear (NO^+), bent (NO^-) and bridging configurations (μ^2, μ^3 and hyponitrito-)[11,29]

Structure	ν(NO)(cm^{-1})
Linear	1940–1575
Bent	1750–1575
Bridging	1600–1040

metries (Table 2), making a quick assignment more difficult. The species prepared here have all been previously subjected to X-ray analysis,[24–28] where it was observed that all but one of the analogues prepared has a linear metal–nitrosyl, the cobalt complex being a bis(hyponitrito) complex (Fig. 1d: $[(Co(CN)_5)_2N_2O_2]^{6-}$). In this compound two nitric oxides couple to form a bridge.

Reactivity Towards Acids and Bases

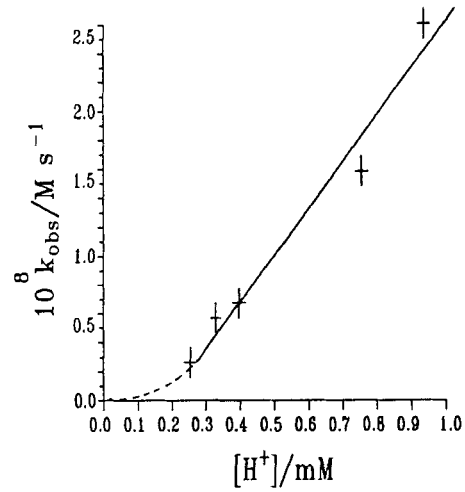
Of the nitrosyl complexes prepared, $[V(CN)_5NO]^{3-}$ hydrolyses in both acid (pH <3, VO_2^+) and base (pH>11, VO_4^-) and $[Cr(CN)_5NO]^{3-}$, and $[Mo(CN)_5NO]^{4-}$ hydrolyse in acid only. (Unlike iron(II) (nitroprusside) and cobalt(III) complexes, the vanadium, chromium, molybdenum and manganese species do not have a d^6 low-spin configuration and are therefore more susceptible to hydrolysis in aqueous solution.) The dissociation of the chromium and molybdenum species have been studied, with the lability of the cyanide ligands being greater than that of the nitrosyl.[30–32] In these instances it is known that the axial cyanide is the first to dissociate and the nitrosyl is the last ligand to leave the coordination sphere of the chromium (Eqns [6], [7]).

$$[Cr(CN)_5NO]^{3-} + 5H_2O \rightarrow [Cr(OH_2)_5NO]^{2+} + 5CN^- \quad [6]$$

$$[Cr(OH_2)_5NO]^{2+} + H_2O \rightarrow [Cr(OH_2)_6]^{3+} + NO^- \quad [7]$$

The reaction of the pentacyanonitrosylmanganate anion in acid and base has been reported[33] but not extensively studied.

In acid, the manganese complex acts as a reducing agent, producing an unstable $[Mn(CN)_5NO]^{2-}$ anion (Eqn [8]), which has a strong ν(NO) at 1880 cm^{-1}.



$$[(NC)_5Mn\text{-}NO]^{3-} + H^+ \xrightarrow{\text{fast}} [(NC)_5Mn\text{-}NO^{H}]^{2-}$$

$$[(NC)_5Mn\text{-}NO^{H}]^{2-} \xrightarrow{\text{slow}} [(NC)_5Mn\text{-}NO]^{2-} + 1/2H_2$$

Figure 2 The reaction kinetics for the reaction of $[Mn(CN)_5NO]^{3-}$ with H^+ at 384 nm, pH 3–4, phthalate/HCl buffer, 302 K, 1.0 M KCl. The kinetics are first-order in H^+ and independent of the metal complex. Above pH 4, the kinetics were found to be independent of both complex concentration and pH. $k_{obs} = 2.5 \times 10^{-5}\ s^{-1}$.

$$[Mn(CN)_5NO]^{3-} + H^+ \rightarrow [Mn(CN)_5NO]^{2-} + \tfrac{1}{2}H_2 \quad [8]$$

The kinetics of this process have been investigated (384 nm, pH 3–4, phthalate/HCl buffer, 302 K, 1.0 M KCl) and found to be first-order in H^+ and independent of the complex concentration (Fig. 2). Above pH 4 and below pH 2 the kinetics were found to be independent of both complex concentration and pH.

A mechanism can be constructed whereby there is rapid protonation of the complex at the nitrosyl, with the slow elimination and reduction of hydrogen (Fig. 2). The rate-determining step is governed by the concentration of $[Mn(CN)_5NOH]^{2-}$ which is equivalent to the H^+ concentration.

The unstable product of the reaction of $[Mn(CN)_5NO]^{3-}$ and H^+ is of some interest as it has a ν(NO) (1880 cm^{-1}) comparable with that of the nitroprusside anion (1947 cm^{-1}) and a band in the visible region at 385 nm indicative of π–π^*

M–NO, suggesting the presence of a nitrosonium ligand.

In base, $[Mn(CN)_5NO]^{3-}$ decomposes to form manganese dioxide. However, because of the precipitation of MnO_2 on the cuvette windows no kinetic analysis was possible. However, by using a method reported previously to test the photostability of the nitroprusside anion,[7] it was possible to estimate the amount of cyanide released from the manganese complex during its reaction with base. In this crude experiment only 10% of the cyanide ligand could be accounted for in the reaction.

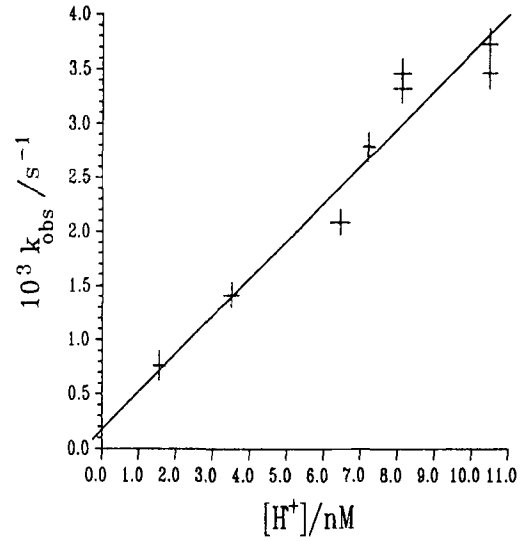
The hyponitrito complex of cobalt is stable in base but hydrolyses in acid (pH <9) to form $[(Co(CN)_5)_2]^{4-}$ or $[Co(CN)_5OH_2]^{2-}$, depending on its concentration. The kinetics were investigated (290 nm, pH 8–9, borax buffer, 303 K, 1.0 M KCl); first-order kinetics were observed (Fig. 3). A mechanism is constructed which relies on the protonation of the hyponitrito bridge as the rate-determining step inducing bridge cleavage, allowing the 'nitric oxide' ligand to leave the coordination sphere of the otherwise low-spin d^6 substitution-inert cobalt via a simple dissociative mechanism. The products of bridge cleavage follow the degradation of *N*-nitrosohydroxylamine-*N*-sulphonates[34] where degradation forms sulphate and nitrous oxide (N_2O) (Eqn [9]).

$$(Co(CN)_5)—NO—N—O—(Co(CN)_5) + H^+ \rightarrow (Co(CN)_5)_2 + N_2O + OH^- \quad [9]$$

Reactivity Towards Amines and Thiols

A facet of the chemistry of sodium nitroprusside which is important to its vasodilatory properties is its reactivity towards amines, hydrogen sulphide and organic thiols.[9,21,22,35] The compounds prepared showed no reactivity towards amines or simple thiols such as cysteine. There was no reaction with hydrogen sulphide except for $[V(CN)_5NO]^{3-}$, in which case the reaction probably proceeds as a result of slow reductive degradation of $[V(CN)_5NO]^{3-}$ *in solution, releasing the* cyanide anion which ligates to the parent complex by expanding its coordination sphere (Eqn [10]). The product observed in the UV-visible spectrum was consistent with $[V(CN)_6NO]^{4-}$.[36]

$$[V(CN)_5NO]^{3-} + H_2S \xrightarrow{\text{steps}} [V(CN)_6NO]^{4-} \quad [10]$$



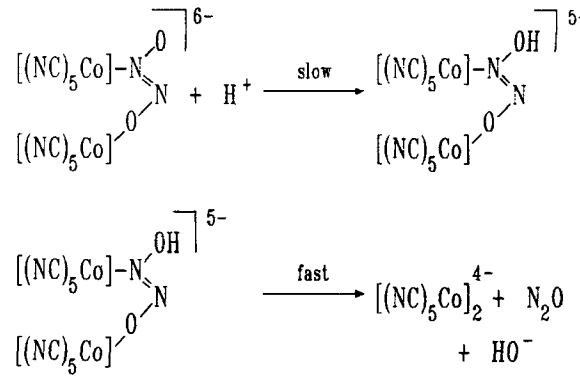


Figure 3 The reaction kinetics for the reaction of $[[Co(CN)_5]_2N_2O_2]^{6-}$ with H^+ at 290 nm, pH 8–9, borax buffer, 303 K, 1.0 M KCl. The kinetics are first-order in H^+ and cobalt complex. $k_{obs} = 3.3 \times 10^5$ M^{-1} s^{-1}.

In this reaction there is no evidence to support a direct interaction of coordinated NO with HS^- in a similar manner to sodium nitroprusside.[22]

The physical characteristics (Table 1) of the complexes prepared indicate that, apart from the cobalt complex, they are all isostructural with the nitroprusside anion. Using a method developed previously to study the photodecomposition of the nitroprusside anion,[7] it can be shown that all the complexes prepared here are also photolytically unstable at pH 7.2, liberating the cyanide ligand. The chemistry of the five compounds is, however, completely different from that of the parent complex. Of the species prepared, the manganese analogue shows behaviour closest to the nitroprusside anion when reacting with base. Its product with acid, which has a ν(NO) of

1880 cm^{-1}, would have been an important compound had it been more stable. It should be possible to prepare chemical analogues of sodium nitroprusside using metal–ligand sets which do not favor a strong back-bonding arrangement with the nitric oxide ligand (Eqn [11], right).

$$Fe^{3+}—N{=}O \leftrightarrow Fe^{2+}—N{=}O^{+} \qquad [11]$$

X-ray analysis of the six compounds (Table 1) would suggest that they can all be considered as nitrosonium complexes, by virtue of the linear nature of the M—N=O (it should be noted that disorder around the nitrogen environment in the X-ray patterns is known to occur with nitrosyl species,[24,29] further complicating the identification of linear species). However, this formulation is not sufficient to allow us to predict their chemistry. As such, structural information alone cannot be used to screen compounds. The prediction of metal complexes with nitrosonium cations from infrared data (Table 2) is known to be difficult below 1700 cm^{-1}.

This study suggests that the potential analogues of sodium nitroprusside could be screened quickly in a preliminary manner using a combination of infrared spectroscopy (in preference to X-ray analysis) and a series of simple chemical tests in order to identify likely compounds prior to animal studies. What is required is a ν(NO) stretching frequency greater than 1800 cm^{-1} indicative of a linear nitrosonium cation with a relatively short N—O bond length (<120 ppm). The potential of any given compound can probed using a set of simple chemical tests involving nucleophilic attack at the coordinated nitric oxide by hydroxide, primary amines and thiols (Eqns [12]).

$$M—NO + 2OH^{-} \rightarrow M—NO_2 + H_2O$$

$$M—NO + NH_2R \rightarrow M—OH_2 + ROH + N_2 \qquad [12]$$

$$M—NO + RS^{-} \rightarrow M—OH_2 + \tfrac{1}{2}RSSR + NO^{\cdot}$$

There is an alternative mechanism whereby nitric oxide complexes can act as vasodilators, namely the facile breakdown of the complex in the bloodstream into its constituent parts, including nitric oxide. Two of the more stable species prepared, $[Cr(CN)_5NO]^{3-}$ and $[Mn(CN)_5NO]^{3-}$, were submitted for biological testing in case they operated through this latter, less desirable, mechanism; however, neither showed any hypotensive action. The chemistry of coupled nitric oxide bridge complexes (e.g. bis(hyponitrito) complexes) is also expected to be of little value in providing a method of protecting nitric oxide. Release of the ligand occurs as a consequence of protonation rather than by nucleophilic attack. More important, however, is that the nitric oxide ligand is modified during release to generate nitrous oxide (N_2O).

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