



Nitric Oxide: A Unique Coordinating Molecule

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Abstract: Nitric Oxide (NO) has one unpaired electron in $\Pi(\pi)$ antibonding molecular orbital which is highly reactive as it is located in higher energy level. The $\Pi(\pi)$ -antibonding orbital can take up one electron forming NO^- or can loss its unpaired electron to form NO^+ ion whose common example is $\text{NO}^+\text{HSO}_4^-$ known as Nitrosonium Hydrogen Sulphate. Nitric oxide can coordinate to metal ions in low oxidation state as neutral (NO), cataionic (NO^+) or anionic (NO^-) coordinating molecule. The formation of a coordinate bond with metal atom as neutral (NO) anionic (NO^-) and (NO^+) molecule makes it a unique donor molecule. In a previous paper¹ we have reported the formation of aquomono nitrosylbis Biguanidimum Cobalt (III) sulphate hydrate,

$[\text{Co}(\text{BigH})_2(\text{NO}^-)(\text{H}_2\text{O})]\text{SO}_4 \cdot 1.5\text{H}_2\text{O}$ in which NO has been found to be coordinated as NO^- group. In diamagnetic $\text{K}_3[\text{Co}(\text{CN})_5(\text{NO})]$ and $\text{Na}_2[\text{Co}(\text{NO}_2)_4(\text{NO})(\text{OH})]$ the NO has been reported as NO^+ group.² In most of the nitrosyls, mixed nitrosyl and carbonyl complexes, NO has been found to be coordinated as three electron NO^+ donor atom in which one of the I^* antibonding molecular orbital electron is transferred to metal atom and highest occupied non bonding electron pair localised at N atom form σ coordinate bond to metal atom and filled t_2g set of non bonding pair of electron forms backbonding to vacant antibonding (I^*) orbital of NO^+ to make it highly strong Π acceptor ligand.³

I. INTRODUCTION

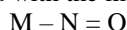
The ligand NO ($:\ddot{\text{N}}::\ddot{\text{O}}: \leftrightarrow :\ddot{\text{N}}::\ddot{\text{O}}^+$) might seem very simple compared to ligands containing N, O donor groups, but actually it possesses some of the most perplexing problems in complex chemistry. One source of difficulties is that it contain partly filled shell, NO^+ being isoelectronic with N_2 and CO and hence a very stable molecule, where as NO contains one and NO^- two Π antibonding electrons. Another reason for the complications is that not only NO potentially ambidentate but there is X-ray crystallographic evidence⁴ that the line NO sometimes forms a smaller angle than 180° with the direction to the central ion. Finally there is some evidence that dimeric forms of NO may be involved in certain complexes.

NO often shows a tendency to lose an electron to give NO^+ . The ionization potential for NO is much lower than for comparable molecules, viz., CO, N_2 , etc. With its relatively low ionization potential one can readily understand the formation of the ionic compound $\text{NO}^+\text{HSO}_4^-$, known as “Chamber crystals”, as well as NO^+BF_4^- , $\text{NO}^+\text{ClO}_4^-$, $\text{NO}^+\text{FeCl}_4^-$, $\text{NO}^+\text{SbCl}_6^-$, $(\text{NO}^+)_2\text{PtCl}_6^-$ etc., all of which gave ionizing solutions in appropriate solvents. Nitrosonium perchlorate is perhaps the most stable nitrosonium compounds.⁵ The crystals structure shows it to be a true salt, isomorphous with $\text{NH}_4^+\text{ClO}_4^-$ and $\text{H}_3\text{O}^+\text{ClO}_4^-$ but unlike these it is immediately hydrolysed in water.

Electronic configuration of nitric oxide molecule has been used to rationalize the two important reactions, namely combination with free radicals and formation of ionic nitrosonium compounds with some poly atomic anions. **A third reaction and froms the point of this study, the most important, is that of nitric oxide with transition metals to form a very diverse series of compounds.** There are a number of ways in which NO could combine with metal. So far there is no direct evidence for the bond occurring between metal and oxygen and although bonding between the metal and the NO Π bond system of cobalt nitrosyl diethyl-di-thiocarbamate is now beyond

question; this type of bonding has not been demonstrated in other compounds. There are three plausible methods of combination through nitrogen.

- (i) Nitrogen forms a normal coordinate bond with the metal leaving the three electron N–O bond intact.



Such bond should confer reactivity and paramagnetism on the compound. The NO stretching frequency should be not far removed from that of nitric oxide at 1878 cm^{-1} . Examples of this class are very rare perhaps the only example being $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]$.

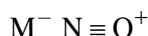
- (ii) Coordinate bond as in (i) together with transfer of an electron from the metal to the nitric oxide.



There are relatively few compounds which illustrate this bond type, primarily because of the tendency of nitric oxide to realize the NO^+ state. There is however no doubt of its occurrence in some cobalt compounds such as

$\text{K}_3\text{Co}(\text{CN})_5\text{NO}$ and $[\text{Co}(\text{NH}_3)_5\text{NO}](\text{NO}_3)_2$. A low NO stretching frequency (1100 cm^{-1}) is expected in keeping with the formal N–O double bond.⁶

- (iii) Coordinate bond as in (i) together with transfer of an electron from nitric oxide to the metal.



This is by far the commonest type of bonding in the metal nitrosyls.⁷

Magnetic and infra red absorption studies have been most useful in systematizing and interpreting the properties of the nitrosyls.

II. Magnetic Measurements

In sodium nitroprusside, we can consider the possibility of NO bonding in the three ways mentioned above. The observed diamagnetism permits an unequivocal assignment to the formula $(\text{CN})_5\text{Fe}^0\text{NO}^+$. This is in keeping with the chemical evidences. The chromium compound $\text{K}_3\text{Cr}(\text{CN})_5\text{NO}\cdot\text{H}_2\text{O}$ has a magnetic moment of 1.87 B.M. at 25°C .⁸ This follows directly from coordination of NO^+ and the one unpaired electron of Cr(I) in a spin paired configuration. The other possibilities, NO or NO^- should give rise to three unpaired electrons. By far the greatest majority of nitrosyls however are diamagnetic showing if nothing else that the neutral NO is unimportant as a donor.

III. Infrared Spectroscopy

Ideally an I.R. study of molecule is an analysis of all the possible modes of vibration in the molecule. For a many atom system this must be very complicated, but a study of large number of compounds having s groups in common shows that particular group absorbs over a narrow range of frequencies irrespective of the rest of the molecule. In accordance with this the nature of L and M should have little effect on NO in the compound L_xMNO . Lewis et al⁹ have shown that the cationic (NO^+) stretching frequency falls in the range between $1940\text{--}1575\text{ cm}^{-1}$, where as the anionic NO^- stretching band is observed in the range between $1200\text{--}1000\text{ cm}^{-1}$, whereas nitrosonium ion (NO^+) absorbs at about 2220 cm^{-1} and NO (nitric oxide) absorbs at 1876 cm^{-1} . Infra red spectroscopy therefore can give highly significant information on the way in which the NO bonds.

Waddington and Klanberg¹⁰ measured the NO stretching frequencies of nitrosyl compounds such as NOBF_3Cl (2335 cm^{-1}), NOSbF_5Cl (2300 cm^{-1}), NOSbClO_4 (1900 cm^{-1}) and NOAsClO_4 (1860 cm^{-1}). The first two frequencies represents the free NO^+ ion where as the latter two frequencies are near those of coordinated neutral and cationic (NO^+).

The diamagnetism of $\text{K}_3\text{Co}(\text{CN})_5\text{NO}$ could be explained in terms of either $(\text{CN})_5\text{Co(I)}\text{NO}^+$ or $(\text{CN})_5\text{Co(III)}\text{NO}^-$, but the infra red absorption shows the latter to be correct.

The red brown substance obtained by adding NaNO_2 to a cold solution of CoCl_2 was originally formulated as $\text{Na}_2[\text{Co}(\text{NO}_2)_4\text{NO}\cdot\text{H}_2\text{O}]$ by Nast and Rohmer¹¹ showed it to be $\text{Na}_2[\text{Co}(\text{NO}_2)_4\text{OH}\cdot\text{NO}^+]$ since this compound exhibits a cationic NO^+ stretching band 1720 cm^{-1} .

The red and black pentammine nitrosyl cobalt nitrate $[\text{Co}(\text{NH}_3)_5\text{NO}](\text{NO}_3)_2$ have been studied by i.r. spectroscopy and it has been established that the black series exhibits the NO stretching frequency at 1170 cm^{-1} and therefore does not have a cationic NO^+ group. The red series, on the other hand, is monomeric and exhibits a NO stretching frequency between $1195\text{ and }1045\text{ cm}^{-1}$ and therefore the structure must be $[\text{Co}(\text{NH}_3)_5\text{NO}^-]_2\text{X}_2$.¹²

According to Raynor¹³ the red and black nitrosyl pentammines of cobalt, previously considered as having the NO formally bonded as NO^- have been reformulated as $[(\text{NH}_3)_5\text{Co N}_2\text{O}_2\text{Co}(\text{NH}_3)_5]^{4+}$ (with a trans hyponitrite bridging group and M–N bond) and $[\text{Co(I)}\text{NO}(\text{NH}_3)_5]^{2+}$ (with a NO^+ group) respectively. Similar hyponitrite bridging structures are proposed for the nitrosylpentacyanocobalt ion and Ru and Fe nitrosyls.

Feltham and Nyholm¹⁴ have studied a new series of six coordinated mono nitrosyl complexes of cobalt. These complexes stabilized by using the bidentate ligands ethylenediamine and o-phenylenabis(dimethylarsine) are of the type $[\text{Co X NOL}_2]^+$ where X = Cl, Br, I, NO_3 , CNS; L = das, en, etc. The infra red and electronic spectra of these nitrosyl complexes show these to be complexes of Cobalt(III). From i.r. studies, the above compounds of

cobalt can be described in terms of a model which consists of a Co(III) ion coordinated to NO⁻ and other five ligands.

Jackson *et al*¹⁵ have prepared a variety of interesting nitrosyl complexes of cobalt. These compounds fit in the general formula CoL_q(NO)_rX_s. These compounds fall in two categories (1) [CoL_x(NO)]X₂ where L = tetraziridine, ethylenediamine, pyridine, *o*-phenylenediamine and (2) [CoL_x(NO)₂]X where L = *p*-touldine, aniline, triphenylphosphine. Magnetic data indicate that all these compounds are diamagnetic (or very slightly paramagnetic due in all probability to small amount of spin free cobalt(II) impurities). It seems reasonable conclude that compounds have diamagnetic ground state.

Reinhard Nast¹⁶ has studied the neutral or cationic nitrosyl compounds of cobalt(II) chelates. The title compounds are prepared from cobalt chelates of β-dicarbonyl compounds or the corresponding mono or dithiocarbonyl compounds. It is prepared by the action of dry NO on cobalt(II) acetylacetonate in CH₂Cl₂. It has the magnetic moment μ_{eff} = 0.87 B.M. Nitrosyl cobalt bis(salicylidine ethylenediamine) μ_{eff} = 1.5 B.M. was prepared in 80% yield by treating a solution of oxygen free cobalt bis(salicylidine ethylenediamine) in CHCl₃ with NO.

Cobalt nitrosyl halides show many similarities to their iron analogues. The parent compound Co(NO)₂I is dimeric but as Co⁻¹ had a d¹⁰ configuration, there is no need to invoke metal-metal interaction to account for the observed diamagnetism. In solution, triphenylphosphine breaks the chloride bridges of [Co(NO)₂Cl]₂ to give the diamagnetic monomer [Co(NO)₂Cl.P₃] and fused triphenyl-phosphine again eliminates chlorine to give [Co(NO)(P₃)₃] isoelectronic with the nitrosyl carbonyl and phosphite compound [Co(OP₃)₂Cl₂]¹⁷. The reaction with the bidentate ligand *o*-phenathroline is more complex and leads to the salt [Co(NO)₂Phen]⁺ [Co(NO)₂Cl₂]⁻¹⁸.

Ruthenium forms a large number of nitrosyl complexes, most of which are remarkably stable, and in which the NO group is tenaciously held by the metal. No paramagnetic compounds are known and i.r data proves bonding as NO⁺. The metal atom is formally Ru(II) i.e., d⁶, in the great majority of compounds and spin pairing appears to be the rule.

The tetrammine nitrosyls are an interesting group of compound obtained by treating K₂RuNOCl₅ with ammonia.¹⁹ The aquo compound [Ru(NH₃)₄NO.H₂O]³⁺ is difficult to prepare as it readily changes to [Ru(NH₃)₄NO.OH]²⁺ even in water. The ammonia is readily replaced by ethylenediamine to give [Ru(en)₂NOX]X₂ where X = OH, Cl, Br, I, but can never be replaced entirely by pyridine.

Levitus and Raskovan²⁰ have investigated the nature of the green compound K₂[Pt(NO₂)₄]HCl, obtained by the action of conc. HCl on K₂[Pt(NO₂)₄] at 0°C and have found to be a nitrosyl derivative with the formula K₂[Pt(NO)(NO₂)₃Cl₂] analogous to six coordinated nitrosyl compound obtained by Griffith, Lewis and Wilkinson²¹ in which NO⁺ group is present with frequency at about 1725 cm⁻¹ in addition to coordinated nitro group.

Merer and Frasar²² studied the formation and dissociation of copper(II) nitrosyl complex in non-aqueous solvents.

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