

# Study of stability of the complexes and Bond strength dependency on Binding modes of ligands like NO—

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**Abstract - Generally Nitrosyl ligands containing compounds are viewed as derivative of the various complexes, NO<sup>+</sup> i.e. nitrosyl cation is similar electronic system with CO thus the bonding between a nitrosyl ligand and a metal follows the same principles as the bonding in complexes of carbonyl. The nitrosyl cation serves as a two-electron donor to the metal and accepts electrons from the metal via special bonding that is called back bonding. The compounds Co(NO)(CO)<sub>3</sub> and Ni-Carbonyl illustrate the analogy between NO<sup>+</sup> and CO. Similarly, two NO groups are isoelectronic with three CO groups. This trend is illustrated by the isoelectronic pair Fe(CO)<sub>2</sub>(NO)<sub>2</sub> and [Ni(CO)<sub>4</sub>].<sup>[2]</sup> These complexes are double electronic and, incidentally, both obey the rule which is known as 18 electronic rule. The formal description of nitric oxide as NO<sup>+</sup> does not match certain measurable and calculated properties. In an alternative description, nitric oxide serves as a 3-electron donor, and the metal-nitrogen interaction is a multiple bond say triple bond. In This Paper it has been tried to figure out the dependency of bond strength and stability of the nitrosyl compounds on their binding modes with central Metal atom.**

**Keywords: Nitrosyl Ligand, Isoelectronic, Carbonyl**

## I. INTRODUCTION

Prototypes for such compounds are the organic nitroso compounds<sup>1</sup>, such as nitrosobenzene. A complex with a bent NO ligand is *trans*-[Co(en)<sub>2</sub>(NO)Cl]<sup>+</sup>. Trends in structure and bonding are usually analyzed using the Enemark-Feltham approach.<sup>[3]</sup> In their framework, the factor that determines the bent vs linear NO ligands in octahedral complexes is the sum of electrons of pi-symmetry. Complexes with "pi-electrons" in excess of 6 tend to have bent NO ligands. Thus, [Co(en)<sub>2</sub>(NO)Cl]<sup>+</sup>, with seven electrons of pi-symmetry (six in t<sub>2g</sub> orbitals and one on NO), adopts a bent NO ligand, whereas [Fe(CN)<sub>5</sub>(NO)]<sup>3-</sup>, with six electrons of pi-symmetry, adopts a linear nitrosyl<sup>2</sup>. Linear and bent NO ligands can be distinguished using infrared spectroscopy. Linear M-N-O groups absorb in the range 1650–1900 cm<sup>-1</sup>, whereas bent nitrosyls absorb in the range 1525–1690 cm<sup>-1</sup>. The differing vibrational frequencies reflect the differing N-O bond orders for linear (triple bond) and bent NO (double bond).

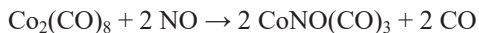
## II. BRIDGING NITROSYL LIGANDS

Nitric oxide can also serve as a bridging ligand. In the compound [Mn<sub>3</sub>(η<sup>5</sup>C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>(μ<sub>2</sub>-NO)<sub>3</sub>(μ<sub>3</sub>-NO)], three NO groups bridge two metal centres and one NO group bridge to all three.<sup>[2]</sup>

## III. MATERIALS AND METHODS

Most complexes containing the NO ligand can be viewed as derivatives of the nitrosyl cation, NO<sup>+</sup>. The nitrosyl cation is isoelectronic with carbon monoxide, thus the bonding between a nitrosyl ligand and a metal follows the same principles as the bonding in carbonyl complexes. The nitrosyl cation serves as a two-electron donor to the metal and accepts electrons from the metal via back-bonding.<sup>3</sup> The compounds Co(NO)(CO)<sub>3</sub> and Ni(CO)<sub>4</sub> illustrate the analogy between NO<sup>+</sup> and CO. Similarly, two NO groups are isoelectronic with three CO groups. This trend is illustrated by the isoelectronic pair Fe(CO)<sub>2</sub>(NO)<sub>2</sub> and [Ni(CO)<sub>4</sub>].<sup>[2]</sup> These complexes are isoelectronic and, incidentally, both obey the 18-electron rule. The formal description of nitric oxide as NO<sup>+</sup> does not match certain measurable and calculated properties. In an alternative description, nitric oxide serves as a 3-electron donor, and the metal-nitrogen interaction is a triple bond

Nitrosyl complexes can be prepared by many routes. Direct formation from nitric oxide is common. The nitrosylation of cobalt carbonyl is illustrative:



In such approaches one must guard against the tendency of nitric oxide to be oxidized by air. Replacement of ligands by the nitrosyl cation may be accomplished using nitrosyl tetrafluoroborate,  $[\text{NO}][\text{BF}_4]$ . Other indirect methods are indirect with the NO group deriving from some other species, often accompanied by oxidation and reduction reactions. A classic example is provided by the brown ring test in which the nitrate ion is the source of a nitric oxide ligand. Nitrosyl chloride is also useful, being applicable to  $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$ .

#### IV. REACTIONS

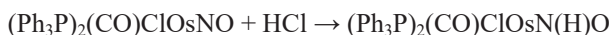
An important reaction is the acid/base equilibrium:



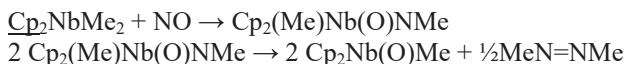
This equilibrium serves to confirm that the linear nitrosyl ligand is, formally,  $\text{NO}^+$ , with nitrogen in the oxidation state +3



Since nitrogen is more electronegative than carbon, metal-nitrosyl complexes tend to be more electrophilic than related metal carbonyl complexes. Nucleophiles often add to the nitrogen.<sup>[1]</sup> The nitrogen atom in bent metal nitrosyls is basic, thus can be oxidized, alkylated, and protonated, e.g.:



In rare cases, NO is cleaved by metal centers:



#### V. DISCUSSION

The value of the Mn-N(NO) bond indices is greater for Mn complex containing linear Mn-N(NO) group than the Co-N(NO) bond indices for Co complex containing bent Co-N-O bond. The sum of the Mn-N(NO) sigma bond component (0.3691) is smaller than Co-N(NO) sigma bond component (0.4854) whereas the Mn-N(NO) pi bond component (1.2450) are greater than the Co-(NO) pi component (0.0418). The largest difference between the component of M-N(NO) bonds occur with the M(dpi)-N component s. One could conclude from the result that the bent No ligand is a better sigma donar and relatively worst pi acceptor, than the linear No ligands. The bending of the nitrosyl ligand decrease the M-N pi or back bonding. Sigma donation tends to raise the N-O bond indices since electron are removed from anti bonding sigma orbital of No, while pi back bonding tends to decrease the N-O bond indices because the electron enter in to the antibonding pi orbital. The increasing value of N-O(bent)bond strength ( $w_{\text{N-O}} = 2.3100$ ) above N-O (linear) bond strength ( $w_{\text{N-O}} = 1.6713$ ) confirm the poor sigma donor and better pi acceptor abilities of the linear NO.

Table - Bond Strength (Wiberg indices) for  $[\text{Co}(\text{NH}_2)_4\text{NO}]^{2-}$  and  $[\text{Mn}(\text{NH}_2)_4\text{NO}]^{2-}$ 

Bond	$[\text{Co}(\text{NH}_2)_4\text{NO}]^{2-}$	$[\text{Mn}(\text{NH}_2)_4\text{NO}]^{2-}$
M-N(NO)	0.5273	1.6141
$\sigma$	0.4854	0.3691
$\pi$	0.0418	1.2450
M-N(NH <sub>2</sub> )	0.3315	0.2752
N-O	2.3100	1.6713

## REFERENCES

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