



## RESEARCH ARTICLE

### STRUCTURAL STUDIES ON MIXED LIGAND NITROSYL COMPLEXES OF TRANSITION METALS CHROMIUM AND IRON

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#### ABSTRACT

There has been a considerable interest in the transition metal nitrosyls and the reactions of the nitrosyl ligand. Thus no can function as an electron donor giving  $\text{NO}^+$  or an electron acceptor, giving  $\text{NO}^-$  and  $\text{N}_2\text{O}_2^{2-}$ . Another stimulus to investing NO reactivity has been the developments in pollution control. Largely steaming from attempts to remove, or at least diminish the concentration of  $\text{NO}^-$  in exhaust gases, emitted by the internal combustion engines. The long search for  $\text{NO}^-$  complexes predicted as by Sidgwick, culminated in the complex,  $[\text{Ir}(\text{Cl})(\text{CO})(\text{NO})(\text{Ph}_3)_2]\text{BF}_4$ . In this case  $\text{NO}^+$  is believed to be coordinated as a Lewis acid accepting an electron pair from the weak base Iridium. Cyano nitrosyl complexes have drawn a distinction from other metal nitrosyl, although they are not basically different from other nitrosyl complexes. Among these  $[\text{M}(\text{CN})_5\text{NO}]^{\text{m}+}$  species have received attention. A diamagnetic cyano nitrosyl complex of composition  $\text{Ag}_3[\text{Re}(\text{CN})_6(\text{NO})]$  is also reported. This red brown compound on further reduction with sodium amalgam gives very green  $[\text{Fe}(\text{NO})_2(\text{CN})_2]^{2-}$ . Different physical methods used so far for the elucidation of structural aspects of the starting complexes along with the trends observed with the alike complexes of the other transition metals. Therefore, some general comments of results of X-ray diffraction studies, magnetic measurements along with electronic spin resonance, vibration electronic, photo-electronic and mass spectra redox properties and kinetic studies are used. The synthesis bonding and reactivity of the nitrosyl complexes are complexed and varied. Mononitrosyl complexes containing  $\{\text{MNO}\}^n$  group having cyanide as coligand are comparatively less explored regarding substitution reaction keeping the (MNO) moiety intact.

**Key words:** Cyano Nitrosyl Complex, Mixed Ligand And Transition Metal

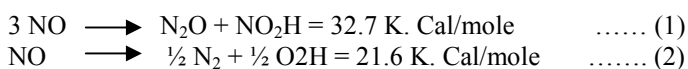
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#### INTRODUCTION

Transition metal nitrosyl complexes (1,2) had been known for over a century and since then nitrosyl chemistry continues to be a source of interest to chemists. However, in comparison to the related metal carbonyl complexes, they have been very little investigated due to the following possible reasons:

- (i) The majority of metal carbonyl synthesis are based on the use of CO itself. Excess CO is seldom harmful in these reactions, and high pressure, high temperature conditions are always available for kinetically sluggish transformation. In contrast, these later conditions are seldom tolerable with nitric oxide due to its thermodynamic instability (3) (equation 1 & 2) and its tendency to function as an oxidizing agent.

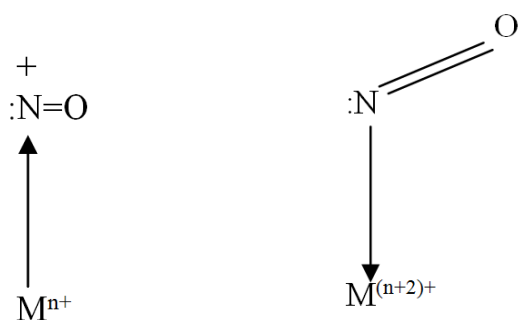


These limitations have motivated the development of new approaches for introducing NO group into metal complexes (vide infra).

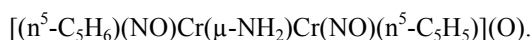
- (ii) Another reason for this in attention was almost certainly their apparent lack of reactivity. On the one hand, M-NO bond is very strong, and the ligand displacement reactions, which are so important in the chemistry of metal carbonyl complexes were not found in the metal nitrosyl complexes.

Recently, there has been a considerable interest in the transition metal nitrosyls and the reactions of the nitrosyl ligand. This is pretty due to increase in understanding of the way in which NO binds to a metal, which is subtly different to the situation involving CO, principally, because NO has an additional electron. Thus NO can function as an electron donor, giving  $\text{NO}^+$ , or an electron acceptor, giving  $\text{NO}^-$  and even  $\text{N}_2\text{O}_2^{2-}$ . Another

stimulus to investigating NO reactivity has been the developments in pollution control (4), largely stemming from attempts to remove, or at least diminish the concentration of NO in exhaust gases, emitted by the internal combustion engines. Further, interest has arisen from the possibility of producing organo-nitrogen compounds from NO, in reactions assisted or moderated by transition metal catalysts (4). During the past few decades, two surprisingly unusual and toxic molecules namely nitric oxide (NO) and carbon monoxide (CO) have been shown to play critical roles as signaling molecules in various biological pathways. Although the chemistry of these two "inorganic" molecules has been studied by researchers involved in chemistry, atmospheric science, toxicology and forensic science for quite some time, their occurrence in human physiology and in recent years their utility as drugs have added new paradigms in biology and medicine. Both molecules are known to be toxic: CO enjoys notoriety as the silent killer and NO as the source of smoke in polluted urban air. That very low concentrations these two gaseous molecules are nevertheless essential for life therefore comes as a shocker where the hyponitrite ion is asymmetrically bonded to the two cobalt moiety in a trans arrangement (8). The long search for NO<sup>-</sup> complexes predicted as early as 1934 by Sidgwick (1), culminated in the complex, [Ir(Cl)(CO)(NO)(Ph<sub>3</sub>)<sub>2</sub>] BF<sub>4</sub>. In this case NO<sup>+</sup> is believed to be co-ordinated as a Lewis acid accepting an electron pair from the weak base iridium (I). In other words, the co-ordinated nitrosyl group can be treated as NO<sup>-</sup> in the formal oxidation state of iridium as +3. In other words two canonical forms may be depicted as follows:



Thus, it is generally assumed that in the bent form of co-ordinated NO (when NO is co-ordinated as NO<sup>-</sup>), it functions as one electron donor. Besides, these two extreme formulations of terminal bonding of nitrosyl group, the nitrosyl group like CO, can form bridges between, two or three metal atoms. For example, it acts as doubly bridging group in the compound.



This is formed by the attack of borohydride upon Cr(n<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(Cl)(NO)<sub>2</sub>. No can act even as triply bridging group (11) as has been observed in the complexes [Mn<sub>3</sub>(n<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>4</sub>](11). Cyanonitrosyl complexes have drawn a distinction from other metal nitrosyls, although they are not basically different from other nitrosyl complexes. Among these, [M(CN)5(NO)]<sup>n+</sup> species have received special attention. A

survey on the existing literature suggests formation of these species from different transition metals as shown in Table 1.

**Table 1.**

V	Cr	Mn	Fe
--	Mo	--	Ru
--	--	Re	Os

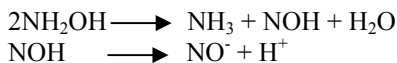
In other stereochemistry, nickel forms [Ni(NO)(CN)<sub>3</sub>]<sup>2-</sup> of tetrahedral geometry (12), and vanadium gives K<sub>4</sub>[V(NO)(CN)<sub>6</sub>] of pentagonal bipyramidal geometry (13, 14). A diamagnetic cyanonitrosyl complex of composition Ag<sub>3</sub>[Re(CN)<sub>7</sub>(NO)] is also reported (15). A dimeric cyanonitrosyl complex of manganese of composition [Mn(NO)<sub>2</sub>(CN)<sub>2</sub>]<sup>4+</sup> has been reported by H. Behrens and co-worker (16). Reduction of this compound with potassium in liquid ammonia gives another compound of composition [Mn(NO)<sub>2</sub>(CN)<sub>2</sub>]<sup>3-</sup>. An interesting nitrosyl complex of iron, [Fe(NO)<sub>2</sub>(CN)<sub>2</sub>]<sup>1-</sup> is reported to be synthesized from the reaction of [Fe(NO)<sub>2</sub>(X)]<sub>2</sub> (x-halide, and cyanide ion)(17). This red-brown compound on further reduction with sodium-amalgam gives grey green, [Fe(NO)<sub>2</sub>(CN)<sub>2</sub>]<sup>2-</sup>. Two compounds of cobalt in tetrahedral stereochemistry, such as K<sub>3</sub>[Co(NO)(CN)<sub>3</sub>] and Na[Co(NO)<sub>2</sub>(CN)]<sup>2-</sup> have also been reported (18).

#### Method of preparation of cyanonitrosyl complexes

The cyanonitrosyl complexes synthesizing using typically different methods. Each method is suitable for a particular transition metal as summarized below:

a) **Alkaline hydroxylamine method:** Hieber and co-workers first employed the use of hydroxyl ammonium chloride as nitrosyl agent (19) tracing back an observation made by Vonderhilde and Hofman (20). The use of hydroxylamine in the synthesis of metal nitrosyl utilizes hydroxylamine in the basic solution. Molybdate, cyanide and KOH react with hydroxylamine hydrochloride in aqueous medium to give a violet product of composition, K<sub>4</sub>[Mo(NO)(CN)<sub>5</sub>].2H<sub>2</sub>O(21). There was some controversy to formulate this compound and an alternate octa-coordinated structure, K<sub>4</sub>[Mo(NO)(OH)<sub>2</sub>(CN)<sub>5</sub>] was proposed by Griffith, Lewis and Wilkinson (21). X-ray studies finally confirm the hexa-coordinated structure and composition of the compound is really K<sub>4</sub>[Mo(NO)(CN)<sub>5</sub>].2H<sub>2</sub>O. The complex is also accessible directly from K<sub>4</sub>[Mo(CN)<sub>6</sub>](22). Wilkinson and co-workers then utilized this procedure for other oxometallate anions. Thus with CrO<sub>4</sub><sup>2-</sup>, the green complex, K<sub>4</sub>[Cr(NO)(CN)<sub>5</sub>].H<sub>2</sub>O was isolated (23). Bhattacharya and co-worker reported the preparation of K<sub>3</sub>[Re(CN)<sub>5</sub>(NO)].2H<sub>2</sub>O by taking perrhenate (VII), ReO<sub>4</sub><sup>1-</sup>, excess of CN<sup>-</sup>, KOH and hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCL). The same authors (24) recently reported the preparation of some new molybdenum (II) cyanonitrosyl complexes, R<sub>2</sub>[Mo(NO)(CN)<sub>5</sub>].2H<sub>2</sub>O (R=Ph<sub>4</sub>P or Bu<sub>4</sub>N) using Na<sub>2</sub>MoO<sub>4</sub>.2H<sub>2</sub>O, KCN and NH<sub>2</sub>OH, HCL in alkaline medium maintaining pH 8. Ammonium vanadate (NH<sub>4</sub>VO<sub>3</sub>), cyanide and base react with hydroxylamine to produce a vanadium nitrosyl (27), originally formulated erroneously as [V(NO)(CN)<sub>5</sub>]<sup>5-</sup>. This has been now characterized structurally (28) as [V(NO)(CN)<sub>5</sub>]<sup>3-</sup>. When this reaction is performed under H<sub>2</sub>S, the product was claimed to be K<sub>4</sub>[V(NO)(CN)<sub>6</sub>].H<sub>2</sub>O. Although the CN and NO stretching frequencies closely

resemble those of  $[\text{V}(\text{NO})(\text{CN})_5]^{3-}$ , the cell constants differ and the compound is diamagnetic (29). The source of nitrosyl group in the alkaline hydroxylamine medium has been attributed to the following sequence of purely formal reactions (28-30).



Basic conditions are suggested to be required to displace the second reaction towards "NO".

**b) The reaction of nitrooxide on cyano complex of a transition metal:** Nitric oxide reacts with  $\text{K}_4[\text{Ni}_2(\text{CN})_6]$  in liquid ammonia suspension to form a deep violet  $\text{K}_2[\text{Ni}_2(\text{CN})_6(\text{NO})]$  (19).

**c) Preparation of nitrosyl complexes involving substitution of cyano groups in parent cyanonitrosyl complexes:** Sarkar and Maurya (31) reported the preparation of some cationic dinitrosyl complexes of vanadium in (-1) oxidation state by taking parent compound  $\text{K}_3[\text{V}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$  with orthophenanthroline / dipyriddy in 1:4 mole ration and shaking for 24 hours. The red violet colored compound so precipitate were of composition  $[\text{V}(\text{NO})_2(\text{o-phen})_2] \cdot \text{CN}$  and  $[\text{V}(\text{NO})_2(\text{dipy})_2] \cdot \text{CN}$ , respectively. The same authors synthesized some compounds of composition,  $[\text{V}(\text{CN})_4(\text{L-L})(\text{NO})]^{2-}$ , where L-L = o-phen or dipy, by taking  $\text{K}_4[\text{V}(\text{CN})_6\text{NO}]$  in aqueous medium and the organic ligand dissolved in ethanol in a reaction vessel, after continuous stirring of the reaction mixture around temperature 35-40°C under nitrogen atmosphere. The compounds of aforesaid composition as yellow mass were obtained. Maurya and co-woker (32) have reported the synthesis of come novel cyanonitrosyl complexes of chromium (I) by the interaction of pentacyanonitrosylchromate (I) with different nitrogen, oxygen and sulphur donor ligands in aqueous acetic acid medium. On the basis of different physic-chemical studies suitable structures have been proposed. A molybdenum (O) nitrosyl complex of composition  $[\text{Mo}(\text{NO})_2(\text{CN})_2(\text{phen})] \cdot 2\text{H}_2\text{O}$  has been investigated by Hattacharya et.al.(33). They prepared this compound by adding hot aqueous solution of phenanthroline into a freshly prepared solution of  $[\text{Mo}(\text{NO})_2(\text{CN})_2(\text{CN})_4]^{2-}$  with stirring at 50°C.

**d) The reaction of nitric acid on a cyano complex of a transition metal:** This method has been first employed for preparation of sodium pentacyanonitrosylferrate(II), commonly called sodium nitroprusside, by nitric acid on sodium hexacyanoferrate(II),  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  (34). The same method has been applied for preparation of analogous ruthenium and osmium complexes<sup>(35)</sup>. Treatment of  $\text{Na}_3[\text{Re}(\text{CN})_5(\text{H}_2\text{O})]$  with moderately strong nitric acid is reported to yield a cyanonitrosyl complex of rhenium having composition  $\text{Na}_2[\text{Re}(\text{CN})_5(\text{NO})]$  (36). A diamagnetic cyanonitrosyl complex of rhenium of suggested composition,  $\text{Ag}_3[\text{Re}(\text{CN})_5(\text{NO})]$  (contaminated with  $\text{AgCN}$ ), obtained when  $\text{K}_3[\text{Re}(\text{CN})_9]$  was warmed with 2 molar nitric acid.

**e) Preparation using redox reactions:** It is note worthy to mention that the use of nitric acid as a nitrosylating agent has been successfully applied to the synthesis of nitroprusside and its ruthenium and osmium analogous, in the same formal oxidation state, that is, +2. Although oxidation state of the central metal attached with NO has got no sense in the real

sense of the term, yet a formalism containing  $(\text{MNO})^{n+}$  would avoid an extreme formalist of NO either as  $\text{NO}^+$  or  $\text{NO}^-$  (vide infra). In this sense, by following the same process of preparation, Fe, Ru and Os give  $(\text{MNO})^{3+}$  in their complexes. Contrary to this using hydroxylamine method of preparation, chromium gives  $(\text{CrNO})^{2+}$  group where as molybdenum gives  $(\text{MoNO})^+$  moiety. This prompted Griffith (28) to reduce the  $(\text{CrNO})^{2+}$  group containing compound,  $\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_5]$ , (using polarographic method of reduction) to isolate a blue reduced species  $\text{K}_4[\text{Cr}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$  analogous to  $\text{K}_4[\text{Mo}(\text{NO})(\text{CN})_5]$ . There have been several attempts to isolate one electron oxidation product (37,38) of  $\text{K}_4[\text{Mo}(\text{NO})(\text{CN})_5]$  to obtain  $[\text{Mo}(\text{NO})(\text{CN})_5]^{3-}$ , but the pure green product,  $\text{PPh}_4[\text{Mo}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$  was isolated only recently by Sarkar and co-workers (37) using air as oxidizing agent. Similarly the purple colored complex  $\text{K}_3[\text{Mn}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$  on oxidation with bromine or nitric acid gives yellow  $\text{K}_2[\text{Mn}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$  (39). The reduction of sodium nitroprusside with sodium in liquid ammonia yields other yellow compound,  $\text{Na}_3[\text{Fe}(\text{NO})(\text{CN})_5] \cdot 2\text{NH}_3$ , as an unstable solid (40). The corresponding tetraethylammonium salt, when treated with acetic acid in acetonitrile converts it into a blue colored complex (41),  $(\text{Et}_4\text{N})_2[\text{Fe}(\text{NO})(\text{CN})_4]$ . Gray-green (42),  $[\text{Fe}(\text{NO})(\text{CN})_2]^{2-}$  has been prepared by the sodium-amalgam reduction of paramagnetic red-brown  $[\text{Fe}(\text{NO})_2(\text{CN})_2]^{-1} \cdot [\text{Mn}(\text{NO})_3(\text{CO})]$  reacts with KCN in liquid ammonia to give a deep yellow diamagnetic anion,  $[\text{Mn}(\text{NO})_2(\text{CN})_2]^{4-}$  having a metal-metal bond. Reduction of this complex with potassium in liquid ammonia gives the unstable product (43)  $[\text{Mn}(\text{NO})_2(\text{CN})_2]^{3-}$ .

#### Physical studies of cyanonitrosyl complexes of transition metals

**Structure and bonding:** As the emphasis in this thesis is made on "Synthesis and Structural Studies of some mixed-ligand Nitrosyl Complexes of first row Transition Metals-Chromium and Iron", which has been explored using some substitution reactions, hence it is proper to discussed briefly different physical methods used so far, for the elucidation of structural aspects of the starting complexes alongwith the trends observed with the alike complexes of the other transition metals. The shapes of the complex ions are of great interest which can account for a indication of the relative strength of chemical reactivities in these complexes (vide infra). Therefore, some general comments on results of X-ray diffraction studies, magnetic measurement alongwith e.s.r. vibrational electronic, photoelectronic and mass spectra, redox properties and kinetic studies are viewed here.

**The  $\{\text{M}(\text{NO})_m\}^n$  formalism:** Before going to the different physical studies pertaining to structure and bonding of nitrosyl complexes, one must be aware about the inorganic functional group notation (44) for nitrosyl complexes. For understanding the complex behaviour of metal nitrosyl compounds, these are conveniently classified as derivatives of the appropriate inorganic functional group  $\{\text{M}(\text{NO})_m\}^n$ , eq.  $\{\text{M}(\text{NO})\}^n$  or  $\{\text{M}(\text{NO})_2\}^n$  or  $\{\text{M}(\text{NO})_3\}^n$ ; the value of 'n' corresponds to the number of 'd' electrons on the metal, when the nitrosyl ligand is formally considered to be bounds as  $\text{NO}^+$ .

**(I) Electronic Spectra:** Attempts to correlate the structural information with a unified description of the bonding in metal nitrosyl complexes formally remain not much of significance. This is due to the fact that, whether nitrosyl

group is positive or negative. This means that how many 'd' electrons are present in the compound. Till today we do not have any formal answer to this problem regarding the formal oxidation state of the metal ion involved. It is only recently that a meaningful alternative description of the bonding in metal complexes is developed. This is originated from the analysis of the structures of the triatomic species of the non-transition element using the correlation method by Walse's and 'p' orbitals in the valance shell of the atoms and suggested that the concept should be in general applicable. Mingos and Ibers (48) have first applied this concept to understand the M-N-O angles in the metal nitrosyl complexes. Pierpont and Eisenberg (49) and Mingos (50) have utilized these concepts in attempts to interpret the geometries of tetragonal metal nitrosyl complexes. In a six-coordinated complexes of MNO group, the maximum symmetry is  $C_{4v}$  and accordingly the modification of the molecular orbital diagram for the linear triatomic species, MNO, will change in  $[M(NO)L_5]$  as shown in Fig. 1.1. It is experimentally different to know the ground state configuration of the diamagnetic complexes in the series  $[M(NO)L_5]$ . However, e.s.r. technique has been widely employed to investigate the ground state electronic configuration of paramagnetic complexes, especially  $K_3[Cr(NO)(CN)_5]$ . Although there is no complete agreement on the interpretation of the e.s.r. data of this complex made by several groups, yet the successful explanation of most of the e.s.r. parameters is consistent with the assignment of  ${}^2B_2$  ground state expected from the electronic configuration  $(2e)^4(1b_2)^1$ . Manoharan and Gray (51), using the information from the know cycstal structure of  $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ , assign the observed electronic transition of a series of cyanonitrosyl complexes. Through the agreement between observed electronic transitions energies is not very good, yet the model they have used can accommodate a wide variety of experimental facts, is interesting. The obtained results of Manoharan and Gray are shown in Table 1.2.

(II) **Mass Spectral Studies:** Mass spectral studies on nitrosyl compound have involved the measurement of physical quantities of such ionization energies (52-54), metal-ligand dissociation energies (55) and the investigation of fragmentation pattern (56-59). For a series of compound,  $[Fe(NO)_2(CO)L]$  and  $[CO(NO)(CO)_2L]$ , a linear correlation is found between the first ionization energy of the corresponding ligand, L(52,53). An invrease in the  $\pi$ -bonding ability of L brings about a decrease in the first ionization energy of the complex. Calculation of the first ionization energies of  $[Fe(NO)_2(CO)L]$  and  $[CO(NO)(CO)L]$  have also been made (54) and shown to be a good agreement with the measured values. The fragmentation patterns of  $[M(NO)_2X]_n$  where X-Cl, Br and I for M=Co and C-Cl and Br for M=Fe have been investigated (57). The nitrosyl group are removed stepwise from the iron compounds, giving  $[Fe_2X_2]^+$ , but the spectra of the cobalt species show higher abundances of mononuclear ions containing notrosyl groups. These results are said to show that the ion compounds contain metal-metal bonds which add to the stability of the di-nuclear fragments. An interesting rearrangement has been observed in the mass spectra of several organometallic nitrosyls (56). In the fragmentation pattern of  $[CpV(NO)_2CO]$ , the ion  $VO^+$  is observed, and in that of  $[CpFe(NO)_2]$ , the ion  $Cp_2FeO^+$ . Meta stable peaks show that these ions are formed in the following processes.

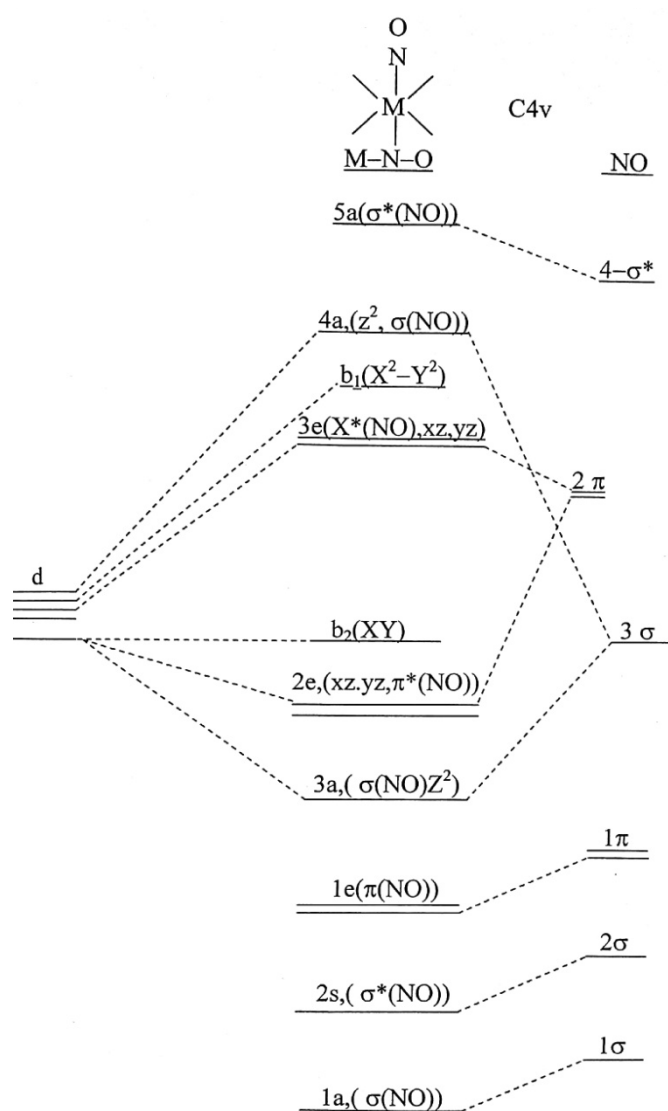
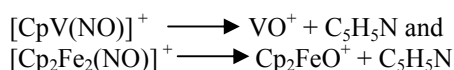


Fig. 1. The M.O. diagram for six coordinate complexes with linear M-N-O group, Z axis is coincident with M-N bond



Similar rearrangements do not occur in the mass spectra of  $[CpNi(NO)]$  or  $[CpM(NO)(CO)_2]$ , where M=Cr, MO and W. The different behavior is suggested to occur because the intermediate ions,  $[CpV(NO)]^+$  and  $[Cp_2Fe_2(NO)]^+$  contain an even number of electron, whereas  $[CpNi(NO)]^+$  and  $[CpM(NO)]^+$  contain an odd number of electrons. Maurya et.al (60) have carried out the mass spectral study of bis (acetylacetonato) nitrosylchromium (I),  $[Cr(NO)(acac)_2]$  at ionization energy 70e.v. and acceleration voltage 1500V. Besides the parent ion peak at  $m/z$  280, fragment ions like  $No^+$ ,  $Cr^+$ ,  $Cr(acac)^+$ ,  $CrNO(acac)^+$ ,  $Cr(acac)_2^+$  and  $Cr(acac)_3^+$  are also observed. On the basis of such results the compound is confirmed to be monomeric.

(III) **Electronic Spin resonance studies:** Most of the work in this field is related with the investigation of e.s.r. spectrum of  $[Cr(NO)_5(NO)]^3+$ . Several groups (61-60) have tried to interpret spectrum, but there is no complete agreement on the interpretation of the observed data. As an outcome of these investigations, the important experimental results may be summarized as below:

Table 2. Electronic Spectra of  $[M(CN)_5NO]^{n-}$  in aqueous solution

Complex	Observed maximum (cm <sup>-1</sup> )		Calculated Energies (cm <sup>-1</sup> )		Bond Agreement
$[C(CN)(NO)]^{2-}$	12,900	1.15	9,200		$^1A_1 \rightarrow ^1E(2b_2 \rightarrow 7e)$
	21,160	36.5	19,000		$^1A_1 \rightarrow ^1A_2(2b_2 \rightarrow 3b)$
	32,470	1000	30,100		$^1A_1 \rightarrow ^1A_1(6e \rightarrow 7e)$
	37,470	5200	23,260		$^1A_1 \rightarrow ^1E(2b_2 \rightarrow 8e)$
$[Cr(CN)_5(NO)]^{3-}$	13,700	8	12,660		$^2B_2 \rightarrow ^2E(6e \rightarrow 2b_2)$
	15,380	1.5	13,890		$^2B_2 \rightarrow ^2E(2b_2 \rightarrow 2e)$
	22,200	72	26,550		$^2B_2 \rightarrow ^2B_2(6e \rightarrow 7e)$
	27,320	59	28,260		$^2B_2 \rightarrow ^2B_2(2b_2 \rightarrow 3b_1)$
	37,300	1100	37,420		$^2B_2 \rightarrow ^2E(5e \rightarrow 3b_2)$
	43,480	3600	35,680		$^2B_2 \rightarrow ^2E(2b_2 \rightarrow 8e)$
$[Mn(CN)_2(NO)]^{3-}$	18,520	22.0	14,900		$^1A_1 \rightarrow ^1E(2b_2 \rightarrow 7e)$
	24,490	60	24,200		$^1A_1 \rightarrow ^1A_1(6e \rightarrow 7e)$
	28,980	111.4	26,500		$^1A_1 \rightarrow ^1A_1(2b_2 \rightarrow 3b_1)$
	37,850	1000	37,770		$^1A_1 \rightarrow ^1E(2b_2 \rightarrow 5a_1)$
	42,550	4500	41,490		$^1A_1 \rightarrow ^1E(6e \rightarrow 3b_1)$
	45,450	500	40,470		$^1A_1 \rightarrow ^1E(2b_2 \rightarrow 8e)$
$[Mn(CN)_5(NO)]^{2-}$	12,050	19	7,820		$^2B_2 \rightarrow ^2E(6e \rightarrow 2b_2)$
	18,600	20	18,350		$^2B_2 \rightarrow ^2E(2b_2 \rightarrow 7e)$
	25,960	1700	26,170		$^2B_2 \rightarrow ^2B_2(6e \rightarrow 7e)$
	28,860	120	32,530		$^2B_2 \rightarrow ^2B_1(2b_2 \rightarrow 3b_1)$
	32,280	880	28,830		$^2B_2 \rightarrow ^2E(6e \rightarrow 2b_2)$
	37,030	2400	38,740		$^2B_2 \rightarrow ^2E(6e \rightarrow 5a_1)$
	48,540	23800	45,050		$^2B_2 \rightarrow ^2E(2b_2 \rightarrow 8e)$
	20,080	8	20,540		$^1A_1 \rightarrow ^1E(2b_2 \rightarrow 2e)$
$[Fe(CN)_5(NO)]^{2-}$	25,380	25	25,090		$^1A_1 \rightarrow ^1A_1(6e \rightarrow 7e)$
	30,300	40	30,770		$^1A_1 \rightarrow ^1A_1(2b_2 \rightarrow 3b_1)$
	37,800	900	37,750		$^1A_1 \rightarrow ^1E(2b_2 \rightarrow 5a_1)$
	42,000	700	37,750		$^1A_1 \rightarrow ^1E(6e \rightarrow 3b_1)$
	50,000	24000	4,900		$^1A_1 \rightarrow ^1E(2b_1 \rightarrow 8e)$

Table 3.

Compound	Electron configuration $[MNO]^{n+}$	Expected number of unpaired electron(s)	Expected mag. Moment (spin only value) (B.M.)	Observed mag. Moment (B.M.)	Ref.
$K_3[VNO(CN)_5] \cdot 2H_2O$	$\{VNO\}^4$	0	0	Dimagnetic	28
$K_4[VNO(CN)_6] \cdot 2H_2O$	$\{VNO\}^4$	0	0	Dimagnetic	30
$K_3[CrNO(CN)_5] \cdot 2H_2O$	$\{CrNO\}^5$	1	1.73	1.87	24
$K_4[CrNO(CN)_5] \cdot 2H_2O$	$\{CrNO\}^6$	0	0	Dimagnetic	33
$K_3[MnNO(CN)_5] \cdot 2H_2O$	$\{MnNO\}^5$	0	1.73	1.73	37
$K_2[MnNO(CN)_5] \cdot 2H_2O$	$\{MnNO\}^6$	1	1.73	1.73	37
$Na_2[FeNO(CN)_5] \cdot 2H_2O$	$\{FeNO\}^6$	0	0	Dimagnetic	37
$(Et_4N)_2[FeNO(CN)_5]$	$\{FeNO\}^7$	1	1.73	1.75	38
$K_4[Mo(NO)(CN)_5]$	$\{MoNO\}^6$	0	0	Dimagnetic	22
$(PPh_4)_3[Mo(NO)(CN)_5] \cdot 2H_2O$	$\{MoNO\}^5$	1	1.73	1.96	36
$\{Cr(NO)(CN)_2(\text{dipy})\}$	$\{CrNO\}^5$	1	1.73	1.60	42
$\{Cr(NO)(CN)_2(\text{o-phen})\}$	$\{CrNO\}^5$	1	1.73	1.67	42

N\* = number of electron in d-orbit

D = Diamagnetic

- The 'g' and Chromium hyperfine tensor has slight deviation from axial symmetry.
- The nitrogen hyperfine tensor has slight deviation from axial symmetry.
- The nitrogen hyperfine tensor is highly anisotropy and  $g_t < g_l$ .

The e.s.r. parameters for other hexa-coordinated complexes of the family  $[Cr(NO)L_5]$  (70-77) are as expected and depend on the electro negativity of L. The 'g' value comes closer to free electron value when there is more delocalization. This is also reflected in NO stretching frequency. The acid hydrolysis of  $[Cr(NO)_5(NO)]^{3-}$  has been followed by e.s.r. method (79) by which it can be shown that the successive replacement of cyanide groups by water takes place. Sometimes e.s.r. spectroscopy can firmly predict the stereochemistry of a complex. This has been exemplified by the study of the oxidized species,  $[Mo(CN)_5(NO)]^{3-}$ , which was not isolated at the time (37), but the e.s.r. parameters obtained for the oxidized species in the host of  $K_3[Co(CN)_6]$  supports the information of parent d6-diamagnetic complex as

$[Mo(CN)_5(NO)]^{4+}$ , rather than  $[Mo(NO)(CN)_5(OH)_2]^{4+}$ , which was later verified by X-ray studies. The e.s.r. studies on  $[Mn(CN)_5(NO)]^{2-}$ , has been studied in detail (79-82) because of the interest in the ordering of the energy levels in the corresponding Cr(I) and Fe(II) complexes. There is controversy existed to attribute the spin density in the NO group, where one group believes this due to spin-orbit coupling, whereas the other group feels that the spin polarization mechanism is most likely. Surprisingly,  $\gamma$ -radiation of the diamagnetic  $K_3[Mn(CN)_5(NO)]^{2-}$  (81) produced the oxidized  $[Mn(CN)_5(NO)]$  species by simple electron addition, whereas intrapruiside losses an electron on irradiation.

**(IV)Magnetic measurement studies:** An advanced understanding of the bonding scheme of nitrosyl complexes is required for the theoretical knowledge of the magnetic properties of the nitrosyl complexes. Hence, various bonding scheme based on molecular orbital approach developed, so far, would be reviewed here. The X-ray structural results allow a qualitative picture of the bonding in transition

metal nitrosyl to be derived. However, molecular orbital calculations have been carried out in attempts to place the bonding in nitrosyl complexes on a more quantitative basis. Johnson and McCleverty (5) have reviewed the molecular orbital calculations carried out by Manoharan and Gray (83) on the pentacyanonitrosyl compounds  $[M(CN)_5(NO)]^n$ . The energy level scheme derived by them is present in Fig. 1.2.

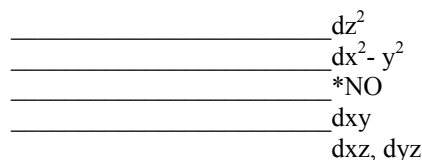


Fig. 2.

It has been used as basis for quantitative bonding discussions for other complexes of general formula  $[M(NO)L_5]^{n+}$ , where L are ligands such as  $NH_3$  and  $H_2O$ . A certain amount of controversy (84-86) over the ordering of the  $dz^2$  and  $dx^2-y^2$  levels of Gray's scheme still exists. J.H. Enermark and R.D. Fertham (87) recently developed an alternative description of the bonding in metal nitrosyl complexes utilizing the molecular orbital correlation method. For six coordinated complexes of the MNO group, where maximum symmetry is  $C_{4v}$ , the molecular orbital diagram derived by them are presented in Fig. 1.1. The important features of this molecular diagram are following:

The orbital  $3a_1$  is primarily localized on the N atom of the NO ligand and is  $\sigma$ -bonding with respect to the MNO group. The degenerate  $2e$  orbital, consisting primarily of metal  $dxz$ ,  $dyz$  and the  $\pi^*$  orbital of the NO ligand, is bonding with respect to M and N and is ant bonding between N and O. The  $1b_2$  orbital is localized on the metal ( $dxy$ ) and is non-bonding. Thus an MNO complexes with the electronic configuration  $93a_1)2(2e)_4$  has three bonding interaction between the metal and the NO group. This situation corresponds to the usual back bonding model used in describing the bonding of  $NO^+$  or CO with transition metal. The presence or absence of electrons in the  $1b_2$  orbit will be of minor consequence as far as the MNO group concerned. In advancement of the bonding scheme of nitrosyl complexes, the observed magnetic moment values are quite expected. Taking into account, the metal and nitrosyl group together (because of the fact that nitric oxide is itself paramagnetic with respect to one unpaired electron), the number of total electrons present in this group are given in Table 1.3, alongwith the expected number of unpaired electrons and the observed magnetic moment values. The strong covalent nature of M-NO bonding is now certain from the studies of other physico-chemical measurements and X-ray structural analysis. The bonding scheme presented in Fig. 1.1, shows the nature of this interaction. Though cyanide group in most of its complexes behave as a good  $\pi$ -bonding ligand in cyanonitrosyl complexes, the strong interaction between metal ion and nitrosyl group is enough to cause the separation of bonding, non-bonding and anti bonding orbital to a large extent. In these hexa-coordinated complexes maximum symmetry expected to  $C_{4v}$  leading to a strong tetragonal distortion. Thus the ordering of these orbitals according to Fig. 1.1 is  $(2e) < (1b_2) < (3e)$ . The bonding orbitals below  $2e$  will accommodate the ligand electrons. Thus filling up of the d electrons on the metal will start from '2e' level. Rationalization of the bonding scheme has been done mainly on the consideration that the nitrosyl ligand is as  $NO^+$ .

It is convenient to classify MNO complexes by the number of d-electrons present in the complex. Thus an MNO complex with electronic configuration  $(3a_1)^2(2e)^4$  would be written as  $\{MNO\}^4$ , one with an electron configuration  $(3a_1)_2(2e)\{MNO\}^4(1b_2)^2$  would be  $\{MNO\}^6$  and so forth. This method of designating the number of d-electrons present in MNO complexes corresponds to the familiar number of d-electrons on the metal when the nitrosyl ligand is formally considered to be  $NO^+$ . In this formalism, the cyanonitrosyl complexes may contain the electronic configuration  $\{MNO\}^n$  where the values of n may be 4,5,6 or 7 which directly count the number of d-electrons. Obviously complexes containing  $n=4$  or 6 will show diamagnetism and for  $n=5$  or 7, paramagnetism with respect to one unpaired electrons, is expected. The magnetic moment values are present in Table 3. For the complexes containing  $d^5$  configuration, the spin-orbit coupling constant would contribute in the measured magnetic moment value. The spin orbit-coupling constant for Mo(I), Mn(II) and Cr(I) are  $-450$ ,  $-300$  and  $-190$   $cm^{-1}$ , respectively, which will affect the magnetic moment values a bit greater than the spin only value at room temperature (88). The observed result for the Cr and Mo complexes described here follow this trend. However for the manganese complex the magnetic moment measurement of  $K_2[Mn(NO)(CN)_5]$  I the solution gives the value corresponding to spin only formula. Interestingly, the magnetic moment value of its silver salt, measured in the solid state gives a sub-normal magnetic moment of 0.55 B.M. only (38). The reason for this anomaly is difficult to explain. The last two compounds given in Table 1.3 also show unusually low magnetic moment due to polymeric nature of the complexes (32).

**(V) X-ray diffraction studies:** Recent X-ray structural studies revealed that although most transition metal nitrosyl contain essentially linear M-N-O bond angles, which are very close to  $180^\circ$ . It is useful, however, to discuss the older bonding concept before considering how nitric oxide bonds to a metal in either linear or a bent fashion. Besides acting as a double or triply bridging ligand, nitric oxide has usually been regarded as bonding to a metal in one of the following ways.

- (i) By donation of one electron from an antibonding nitric oxide orbital to the metal followed by additional electron pair donation from  $NO^+$ .
- (ii) By donation of two electron to the metal from neutral NO.
- (iii) By acceptance of one electron from the metal followed by electron pair donation from  $NO^+$ .

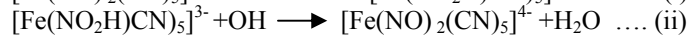
In these three cases, nitric oxide function as (i) a three electron donor, (ii) a two electron donor and (iii) a one electron donor. These ideas concerning the bonding modes of NO have been regarded as valid for many years. The X-ray structural studies have, however, suggested that they must be modified. Thus, although, nitrosyl complexes may still be regarded in terms of  $NO^+$  and  $NO^-$ , the former label is now given to those species which contain linear M-N-O bond angles (close to  $180^\circ$ ), while the later is assigned to the compound with at M-N-O bond close to  $120^\circ$ . The ways in which  $NO^+$  and  $NO^-$  bind to metals to give rise to linear and bent nitrosyl, respectively, may be visualized in the following simple terms. Donation of one electron from nitric oxide to a metal results in the formation of  $NO^+$ , the nitrogen atom of  $NO^+$  is  $sp$ -hybridised, so that subsequent donation of an electron pair to the metal results in the formation of an M-N-O bond angle of  $180^\circ$ . Alternatively

donation of one electron from the metal, functioning as a Lewis base to nitric oxide, results in the generation of NO<sup>-</sup>. In these species the nitrogen atom is sp<sup>2</sup>-hybridised, so that donation of an electron pair by NO<sup>-</sup> results in an M-N-O bond angle of 120°. It must be pointed out that M-N-O bond angle in metal nitrosyls may deviate from 180° or 120° for a number of reasons. Kettle (89) has suggested that because of the two – orbitals of each of the carbonyl ligands in M(CO)<sub>3</sub> system are non degenerate, the metal M, will back donate to them to different extents. Thus the M-C-O bond angles in M(CO)<sub>3</sub> system will deviate from linearity. Using the same reasoning Enemark (90) has shown that even in mononitrosyl species, the M-N-O bond angle will deviate (91) from 120°. However, deviation from the expected angles in both NO<sup>+</sup> and NO<sup>-</sup> species may occur because of packing effects in the crystal lattice. Originally, the presence of NO<sup>+</sup>, NO or NO<sup>-</sup> in compound was inferred from the position of the nitrosyl stretching in the infrared spectrum. However, the X-ray structural results have shown that the validity of assigning these labels solely on the basis of infrared spectroscopy must be seriously questioned. The fact that nitric oxide can bond to a metal in a linear and a bent fashion means that isomerism can occur in nitrosyl complexes, solely because of the presence of the different bond angles in the isomers. An interesting example having both linear and bent NO group is the compound [Co(NO)(L)<sub>2</sub>(Cl)<sub>2</sub>] (where L=phosphine ligand). This compound is reported to have two isomers, one having linear NO<sup>+</sup> group and the other bent NO<sup>-</sup> group (92).

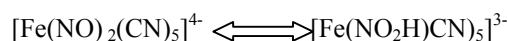
The two bonding modes of nitric oxide not only result in different M-N-O bond angle, but also in different M-NO bond length. Bonding of the nitric oxide as NO<sup>+</sup> allows the metal to back donate electrons to the π\* NO orbitals causing the M-N bond to gain considerable multiple bond character. The M-N bond length will, therefore, be much shorter than that of a single M-N bond. In contrast, limited back donation from the metal will occur when NO<sup>-</sup> is bonded, so that the M-N bond length in bent nitrosyls will not be as short as those in linear nitrosyls. Some of the points discussed above, as well as other effects observed in the bonding of metal nitrosyls are best illustrated by a consideration of the X-ray structural results in some cyanonitrosyl complexes (Table 4).

Interestingly, in all these complexes, the M-N-O group attachment is linear. Among the hexa-coordinated complexes, the shortest M-N bond length is found for (FeNO)<sup>3+</sup> and the largest has been encountered in (CrNO)<sup>2+</sup> group considering the first transition series. The reported C-N distance for all these complexes is of constant value, whereas for the N-O distance one can observe some variations. The expected trend is observed for the (MoNO)<sup>+</sup> and (MoNO)<sup>2+</sup> groups with respect to Mo-N and N-O bond distance. The insensitiveness of C-N bond distance is suggestive that the stabilization of the metal is mainly done by the nitrosyl group. Quite expectedly, vibrational spectroscopy can explain this trend along with the change in M-O bond distance. The penta-coordinated complex containing (FeNO)<sup>2+</sup> group has a tetragonal pyramidal structure. The short Fe-N distance is suggestive of strong trans directing effect of the coordinated nitrosyl group, and by virtue of this effect, the compound was isolated at low pH (93). The only known hepta-coordinated complex is pentagonal bipyramidal in nature and through the stability of this compound was some time thought unusual, it can now be explained easily on the basis of structural data in the bonding scheme.

**(vi) Kinetic studies:** The kinetic of the reactions of the nitroprusside ion [Fe(NO)(CN)<sub>5</sub>]<sup>2-</sup> with various substrates have been widely studied. The simplest reaction studied is that of the nitroprusside ion with OH<sup>-</sup>, which has long been known to result in the formation of [Fe(NO)<sub>2</sub>(CN)<sub>5</sub>]<sup>4-</sup>. Detailed thermodynamic and kinetic investigations (94) suggested that the mechanism of the reaction is as follows:

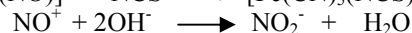
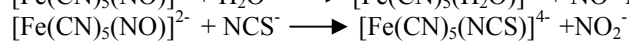
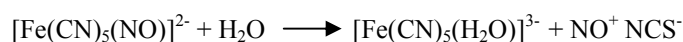


The rate determining step is reaction (i). The pK<sub>a</sub> value for the equilibrium,

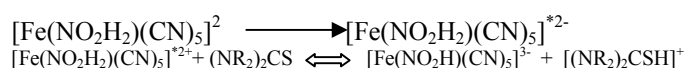


has been estimated to be about 6.4 (95).

The nitroprusside ion and SH<sup>-</sup> react via a mechanism similar to that outlined above. [Fe(NOS)(CN)<sub>5</sub>]<sup>4-</sup> which is unstable in solution, is formed via an intermediate which possibly contains the NOSH group (96). The deep blue solutions generated when mixtures of [Fe(NO)(CN)<sub>5</sub>]<sup>2-</sup> and NCS<sup>-</sup> are irradiated, may also be made by acidification of a basic solution of the two reactions (97,98). The species responsible for the deep blue colour is suggested by kinetic studies to be [Fe(NCS)(CN)<sub>5</sub>]<sup>4-</sup>, formed by the reaction of [Fe(NO)<sub>2</sub>(CN)<sub>5</sub>]<sup>4-</sup> or [Fe(H<sub>2</sub>O)(CN)<sub>5</sub>]<sup>3-</sup> with thiocyanate ion. The nitrous acid present in the reaction reduces the deep blue species to the related trianion, [Fe(NCS)(CN)<sub>5</sub>]<sup>3-</sup> (99).



An investigation (100) of the kinetics of the reactions of [Fe(NO)(CN)<sub>5</sub>]<sup>2-</sup>, with thioureas, particularly (NH<sub>2</sub>)<sub>2</sub>CS, (Me<sub>2</sub>N)<sub>2</sub>CS and (EtNH)<sub>2</sub>CS has allowed the following mechanism to be proposed.

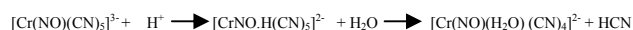


The hydrolysis of [Cr(NO)(CN)<sub>5</sub>]<sup>3-</sup> has been studied by e.s.r. (78) and electro-chemical studies (101). The e.s.r. spectra of all equation products [Cr(NO)(H<sub>2</sub>O)<sub>x</sub>(CN)<sub>5-x</sub>]<sup>x-3</sup> have been observed and the processes,



shown to be first order (78).

Polarography showed that the first reaction in the sequence is also first order. The rate determining step being the loss of the first CN<sup>-</sup> ligand (101). The mechanism suggested for the formation of the monoquo complex is



**(vii) Infrared Spectroscopy:** Recent X-ray studies presented in Table 1.5, reveals the presence of linear M-NO group and thus the coordinated NO group can be regarded as NO<sup>+</sup>. Thus infrared spectra of this series of complexes are widely used to obtain the information about the nature of metal to ligand bonding.

Table 4.

Compound	M-N (A°)	N-O (A°)	M-N-O bond angle (degree)	Coordination number	Coordination configuration	Functional group
K <sub>2</sub> [V(NO)(CN) <sub>5</sub> ].2H <sub>2</sub> O	1.662	1.294	171.4	6	{VNO} <sup>4</sup>	(VNO) <sup>2+</sup>
K <sub>4</sub> [V(NO)(CN) <sub>6</sub> ].H <sub>2</sub> O	1.680	1.165	164.2	7	{VNO} <sup>4</sup>	(VNO) <sup>2+</sup>
K <sub>3</sub> [Cr(NO)(CN) <sub>5</sub> ].H <sub>2</sub> O	1.990	1.210	Linear	6	{CrNO} <sup>5</sup>	(CrNO) <sup>2+</sup>
[Co(en) <sub>3</sub> ][Cr(NO)(CN) <sub>5</sub> ]	1.710	1.210	176.0	6	{CrNO} <sup>5</sup>	(CrNO) <sup>2+</sup>
K <sub>3</sub> [Mn(NO)(CN) <sub>5</sub> ].2H <sub>2</sub> O	1.660	1.210	174.0	6	{MnNO} <sup>6</sup>	(MnNO) <sup>2+</sup>
Na <sub>2</sub> [Fe(NO)(CN) <sub>5</sub> ]	1.653	1.124	175.7	6	{FeNO} <sup>6</sup>	(FeNO) <sup>3+</sup>
Ba[Fe(NO)(CN) <sub>5</sub> ]	1.710	1.110	166.0	6	{FeNO} <sup>6</sup>	(FeNO) <sup>3+</sup>
(Et <sub>4</sub> N) <sub>2</sub> [FeNO(CN) <sub>4</sub> ]	1.669	1.157	174.7	5	{FeNO} <sup>7</sup>	(FeNO) <sup>2+</sup>
K <sub>4</sub> [Mo(NO)(CN) <sub>5</sub> ]	1.950	1.230	Linear	6	{MoNO} <sup>7</sup>	(MoNO) <sup>1+</sup>
(PPh <sub>4</sub> ) <sub>3</sub> [Mo(NO)(CN) <sub>5</sub> ].2H <sub>2</sub> O	1.921	1.195	Linear	6	{MoNO} <sup>5</sup>	(MoNO) <sup>2+</sup>

Table 5. Infrared spectral data of the cyanonitrosyl anions in the solid state (in cm<sup>-1</sup>)

Compound	V(CN)	V(NO)	δ(M-N-O)	V(M-N)
K <sub>4</sub> [V(CN) <sub>5</sub> NO].2H <sub>2</sub> O	2150, 2080	1530	-	-
K <sub>4</sub> [V(CN) <sub>6</sub> NO].H <sub>2</sub> O	2095, 2100	1508	631	620
K <sub>3</sub> [Cr(CN) <sub>5</sub> NO].2H <sub>2</sub> O	2020, 2120	1630	612	621
K <sub>4</sub> [Cr(CN) <sub>5</sub> NO].2H <sub>2</sub> O	2095, 2177	1470	627	645
K <sub>3</sub> [Mn(CN) <sub>5</sub> NO].2H <sub>2</sub> O	2124, 2129	1706	660	660
K <sub>2</sub> [Mn(CN) <sub>5</sub> NO]	2150, 2100	1885	550	628
Na <sub>2</sub> [Fe(CN) <sub>5</sub> NO]	2144, -	1940	663	496
(Et <sub>4</sub> N) <sub>2</sub> [Fe(CN) <sub>5</sub> NO]	2111, 2122	1755	-	-
K <sub>4</sub> [Mo(CN) <sub>5</sub> NO]	2120, 2106	1450	589	604, 595
	2097, 2080			
(PPh <sub>4</sub> ) <sub>3</sub> [Mo(CN) <sub>5</sub> NO]	2040, 2023	1580	-	-

Table 6. Infrared spectra of Pentacyanonitrosyl complexes (14<sub>NO</sub> and 15<sub>NO</sub>) (cm<sup>-1</sup>)

Compound	14 <sub>NO</sub> complex			15 <sub>NO</sub> complex		
	V(NO)	V(M-N)	δ(M-N-O)	V(NO)	V(M-N)	δ(M-N-O)
K <sub>3</sub> [Cr(CN) <sub>5</sub> NO].H <sub>2</sub> O	1643	620	610	1610	617	600
	1635			1590		
K <sub>3</sub> [Mn(CN) <sub>5</sub> NO].2H <sub>2</sub> O	1741	663	663	1704	660	651
	1733		653	1694		646
K <sub>3</sub> [M(CN) <sub>5</sub> NO].2H <sub>2</sub> O	1736	663	663	-	-	-
	1728		653			
K <sub>3</sub> [Mn(CN) <sub>5</sub> NO]	1711	659	659	1675	661	648
	1695			1663		
Ag <sub>2</sub> [Mn(CN) <sub>5</sub> NO]	1888	628	628	1850	620	620

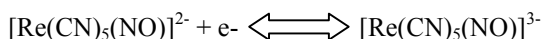
Although much is known about the nitrosyl stretching frequency, that is, the nature of ligand vibration, it is only recently that some efforts are made to locate the associated  $\nu(\text{M-NO})$  and  $\delta(\text{M-N-O})$  modes. Characterization of these low frequency vibrations would reflect more directly to the state of the metal-ligands bonding. The first meaningful work on this aspect was done by during et.al. (102) on the hexa-coordinated ruthenium nitrosyl halo down to the frequency of 50 cm<sup>-1</sup>. Contrary to the carbonyl compounds the  $\nu(\text{M-NO})$  and  $\delta(\text{M-N-O})$  is general appear to low intensity and thus poses additional problem. Furthermore, dealing with the hydrated salt of cyanonitrosyl metallate, considerable difficulties are encountered in locating these vibrations because of the presence of librational modes due to water and vibrations due to  $\nu(\text{M-NO})$  and  $\delta(\text{M-N-O})$ . Recently to avoid the complexity due to the presence of water of crystallization, infrared studies are made on anhydrous complexes (Table 1.5). For the relative position between the metal-nitrogen stretching and metal nitrosyl deformation mode, assignments are made from deducing the results obtained from the studies of carbonyl and cyano complexes. In metal carbonyl complexes,  $\nu(\text{M-NO})$  is lower than  $\delta(\text{M-N-O})$ . The same order is usually obtained for complexed cyanides. However, unequivocal assignment of these vibrations require N<sup>15</sup> and C<sup>13</sup> substitution data alongwith Raman polarization data.

Some of the work on N<sup>15</sup> substitution are done by Miki et.al (103). Using a linear three body model, they assign the higher wave number band to the M-N stretching vibration and to the lower one, M-N-O bending vibration in the lower frequency range. These assignments are definitely more realistic than the assignments done on tentative basis as presented in Table 1.5. The work of Miki et.al. on cyanonitrosyl metallates are summarized in Table 6. Taking representative example as amine complexes, (m-NH<sub>3</sub>), a single bond stretching frequency appears much lower (104) than those appeared for (M-NO) inspite of the fact that the mass of the NO group is larger NH<sub>3</sub> group. This represents a considerable  $\pi$ -back bonding in nitrosyl complexes.

**(viii) Redox Properties:** The one electron reduction of [Cr(NO)(CN)<sub>5</sub>]<sup>3-</sup>, was first demonstrated by Wilkinson and co-worker (21). They used the polarographic method of reduction and could not be able to isolate the oxidized product at that times. Few years later, Griffith using same method have been able to isolate, [Cr(NO)(CN)<sub>5</sub>]<sup>4-</sup>. Cotton and co-workers have isolated the one electron oxidized product of [Mn(CN)<sub>5</sub>(NO)]<sup>3-</sup>, using bromine or nitric acid as oxidizing agent (38). The extra stability achieved by coordinated nitric oxide for a particular metal can be seen from the isoelectronic redox system for the manganese



complex (Table 7). The nitroprusside analogue of Rhenium (105) shows reduction, which is reversible one, as may be expressed:

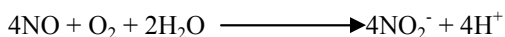


Jakab et.al. studied quantitatively one electron oxidation of  $[\text{Re}(\text{CN})_5(\text{NO})]^{4-}$ , which is a reversible one (106). However, several attempts to isolate the oxidized product failed, and it is only recently  $[\text{Mn}(\text{CN})_5(\text{NO})]^{3-}$  has been synthesized and characterized. A comparative study of the electrochemistry of  $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$  at  $\text{NO}^+$  itself has been made (107). The nitrosonium ion shows three reduction waves and these have been interpreted as the formation of NO in the first stage, which then dimerized and reduced to  $\text{N}_2\text{O}_2^{2-}$  in the second part of reduction. The third phase corresponds to three electrons reduction of NO into  $\text{NH}_2\text{OH}$ . The  $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$  anions first undergoes reduction to  $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$ , which undergoes either protonation and reduction via second wave or formation of the complex  $[\text{Fe}(\text{CN})_5(\text{NH}_2\text{OH})]^{3-}$  which has been isolated by the used conventional chemical method (39). This isolation demands a reinterpretation of the earlier electrochemical studies on nitroprusside anion (108, 109).

**Table 7. Standard Electrode Potential**

Couple	$E_0(\text{v})$
$[\text{Cr}(\text{NO})(\text{CN})_5]^{3-} / [\text{Cr}(\text{NO})(\text{CN})_5]^{4-}$	-1.146
$[\text{Mn}(\text{CN})_6]^{4-} / [\text{Mn}(\text{CN})_6]^{5-}$	-1.06
$[\text{Mn}(\text{CN})_5]^{2-} / [\text{Mn}(\text{CN})_5]^{3-}$	+0.597

Both NO and CO are non polar gaseous molecules which are readily diffuse through the lipid bilayers of mammalian cells NO has one unpaired electron in the  $\pi^*$  antibonding level and hence is paramagnetic. This unpaired electron gives rise to its high reactivity; NO readily reacts with dioxygen to afford  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2$  and other  $\text{N}_x\text{O}_y$  species (collectively known as reactive nitrogen species, RNS) which constitute a major portion of smoke in urban air. NO is quite soluble in water (1mm at body temperature) and is converted to  $\text{NO}_2$  (eq.1) and  $\text{NO}_3^-$  through metabolic pathways and is excreted via the urinary path. Although increased concentration of nitrite and nitrate in the urine of patients with chronic inflammation, sepsis or acute microbial infection was noted in the earlier part of twentieth century, their connection with elevated level of NOS activity in the body has only been recently realized. NO also reacts (at diffusion controlled rate) with  $\text{O}_2^+$  (and other ROS) to produce peroxynitrite  $\text{ONOO}^-$ , which causes rapid nitration of aromatic amino acid residues of proteins (such as super oxide dismutase, SOD). These nitrate proteins serves as hall marks of inflammation.



These characteristics are sensitive to various aspects of the electron density distribution so that the boundary between NO- and  $\text{NO}^+$  cases depends on the characteristics considered and the problem concerns only the definition of oxidation state concept rather than the measurement of physically observed parameters. Thus the closest, correspondence to the classical chemical concepts, for example, the oxidation state of a metal atom may be obtained with such observable parameters, which describe the extent to which the electron density is drawn away from an atom or a group. The  $N_{1s}$  value for  $\text{NO}^+$  in  $\text{NOCl}$  is about 409 eV and 406 eV for the neutral NO molecule. The extrapolation of the data for  $\text{NO}^+$  and NO yields the range of

$N_{1s}$  value for  $\text{NO}^-$  in vicinity of 402 eV. Fokesson (111) started a systematic photoelectron spectral study for a series of cyanonitrosyl complexes. The results are tabulated in Table 1.8. The  $N_{1s}$  binding energies for the cyanide group in this series reflect the observation made by (CN) in infrared spectroscopy as discussed earlier. Interestingly, most of the  $N_{1s}$  binding energy for the nitrosyl group falls below 402 eV and hence can be treated as containing the nitrosyl group  $\text{NO}^-$ . According to the arguments put before, the nitrosyl group in nitroprusside can be said to contain a formally positive charged 'N' that is,  $\text{NO}^+$ . However, these data are insufficient in the sense that they do not say anything about the binding energies of the metal electrons. A comparison of a series of a particular metal in its complexes containing different oxidation states having the same coordination number would have been more useful in assessing the charge distribution. Furthermore, the ESCA data of a cyanonitrosyl metallate ions in its consecutive reduced or oxidized state as in some cases it is formed, would supplement the study. The first point of the above use has been studied by Nefedov (112) whereas he compared the  $\text{Fe}_{2p3/2}$  energies in  $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . These data are presented in Table 1.9 along with the data for  $\text{Fe}(\text{n}^5\text{-C}_5\text{H}_5)_2$ .

**Table 8. ESCA data of some of the cyanonitrosyl complexes**

Compound	$\text{Eb}_{N_{1s}}(\text{NO})(\text{eV})$	$\text{Eb}_{N_{1s}}(\text{CN})(\text{eV})$	Electronic configuration $\{\text{MNO}\}^n$
$[\text{V}(\text{CN})_5(\text{NO})]^{3-}$	400.00	398.8	$\{\text{VNO}\}^4$
$[\text{Cr}(\text{CN})_2(\text{NO})]^{3-}$	401.4	399.0	$\{\text{CrNO}\}^4$
$[\text{Mn}(\text{CN})_5(\text{NO})]^{3-}$	401.6	398.3	$\{\text{MnNO}\}^6$
$[\text{Mn}(\text{CN})_5(\text{NO})]^{3-}$	402.1	398.3	$\{\text{MnNO}\}^5$
$[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$	406.0	398.7	$\{\text{FeNO}\}^6$
$[\text{Mo}(\text{CN})_5(\text{NO})]^{4-}$	401.1	398.8	$\{\text{MoNO}\}^6$
$[\text{Mo}(\text{CN})_5(\text{NO})]^{3-}$	400.1	398.8	$\{\text{MoNO}\}^5$

**Table 9. Binding energies (eV) of some iron complexes**

Compound	$\text{Fe}_{2p3/2}(\text{eV})$	$N_{1s}\text{NO}(\text{eV})$
$\text{Fe}(\text{n}^5\text{-C}_5\text{H}_5)_2$	708.0	
$\text{K}_4[\text{Fe}(\text{CN})_6]$	708.8	
$\text{K}_3[\text{Fe}(\text{CN})_6]$	710.3	
$\text{Fe}[\text{Fe}(\text{CN})_5(\text{NO})]$	711.3	402.6
$\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$	711.0	403.6

The trend in  $2P_{3/2}$  according to the above Table suggests that iron in nitroprusside is in high oxidized state compared to even that in  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , meaning thereby that the formal oxidation state of Fe in nitroprusside would be IV. Furthermore, in the absolute sense the  $N_{1s}$  binding energy for NO is even lower for the neutral NO molecule, suggesting that the coordinated nitric oxide even in nitroprusside should be treated as  $\text{NO}^-$ . Attempts have been made by Sarkar and Muller (113) to observe the changes appear in the two adjacent reduced and oxidized species of nitrosyl complexes of Molybdenum. This has been done on the ground to observe the changes occurred in the  $3d_{3/2}$  and  $3d_{5/2}$  binding energies of the molybdenum along with  $N_{1s}$  binding energies of coordinated NO.

For a redox reaction,

$$(\text{MoNO})^n \xrightarrow{e^-} \text{MONO}^{n-1} \quad (n = \text{number of 'd' electrons}),$$

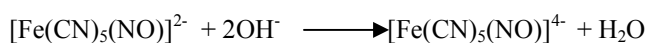
the overall electronic distribution in MoNO moiety will change. The release of an electron may take place (i) from the molybdenum ion, (ii) from the nitrosyl ligand (iii) an inseparable withdrawn of an electron from both the centres, that is from MNO group. From the crystallographic data of

$K_4[Mo(NO)(CN)_5]$  and  $(PPh_4)_3[Mo(NO)(CN)_5] \cdot 2H_2O$  (vide Table 1.4), it is known that the Mo-N bond in the oxidized species  $MoNO^5$  is shorter than that of  $MoNO^6$  group containing compound. This shortening is due to a stronger Mo-NO attachment in the former species than the later. The stronger attachment can only be visualized by the increase back donation from Mo – NO, leading thereby accumulation of more electron density on NO. The observed trend present in Table 1.8, justifies these arguments. It is interesting to note that there is overall no electronic change of the cyanide group present as co-ligand in both the complexes. X-ray photoelectron spectrum of  $[Cr(NO)(acac)_2]$  in the binding energy range (365 – 415 eV) has been studied by Maurya et al. (60). They observed the  $N_{1s}$  binding energy of the co-ordinated NO group is 401.8 eV which is comparable to that reported for potassium pentacyanonitrosylchromate(I) (111). The slight increase in the value may be due to the neutral nature of the complex. It appears, therefore, that NO in this compound is present as  $NO^+$  just to comparing the  $N_{1s}$  value of  $K_3[Cr(NO)(CN)_5]$ , where co-ordination of nitric oxide as  $NO^+$  is already established by X-ray studies (114).

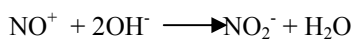
**Reactivity of co-ordinated nitric oxide:** The study of the reactivity of the metal nitrosyls compare to the metal carbonyl complexes is rare. This is due to the fact that the co-ordinated nitric oxide is very firmly bound with the metal and the ligand displacement reactions are not found so commonly as these happen with the metal carbonyls. Due to the enormous studies on the metal carbonyls having industrial significance in recent years, many facets concerning the reactivity of nitrosyl complexes have emerged. Two things are of prime importance in these studies. The first one is to deal with the environment pollution caused by nitric oxide and the second one is the development of newer catalytic system of industrial applicability.

**(i)Reduction and Disproportion:** One electron reduction of  $[Fe(CN)_5(NO)]^{2-}$  gives brown,  $[Fe(CN)_5(NO)]^{3-}$  which ultimately affords  $[Fe(CN)_5(NO)]^{2-}$ . The reduction of  $Fe^{III} NO^6$  moiety has been explained to proceed via  $Fe^{II} NO^7$  in the brown complex, which ultimately changes to  $Fe^I NO^7$  (115). The reduction commonly occurs at the metal centre (116) and there are some examples, where reduction takes place on the co-ligand sites (117). In non-protic media multi-electron reduction of  $[Fe(CN)_5(NO)]^{2-}$  gives  $[Fe(CN)_5(NO)]^{3-}$ ,  $[Fe(CN)_4(NO)]^{2-}$ ,  $[Fe(CN)_4(NO)]^{3-}$ ,  $[Fe(CN)_3(NO)]^{3-}$  and  $[Fe(CN)_3(NO)]^{4-}$ . Using dispersed platinum metals oxide or metal gauze as catalyst, the reduction of NO to either ammonia or di-nitrogen has been achieved. This heterogeneous reduction is used in treatment of automobile exhaust gas pollution (118). Using some sodium and Iridium nitrosyl and carbonyl complexes, mixtures of NO and CO may be disproportionate into  $N_2O$  and  $CO_2$  (119, 120).

**(ii)Nucleophilic Attack:** This is most well known reactivity of the nitrosyl complexes, which can be classified exemplified by the following reaction (121).

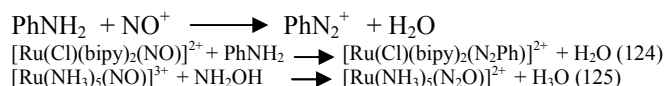


This reaction has an equilibrium constant of  $1.5 \times 10^6$ , which may be compared to the value of  $2.3 \times 10^{31}$  for the parent reaction:

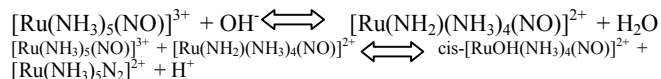


Clearly, co-ordinated  $NO^+$  in  $[Fe(CN)_5(NO)]^{2-}$  is a much weaker electrophile than free  $NO^+$ . The corresponding ruthenium and osmium analogues behave similarly (122, 123).

A number of reactions are known, where a lot of nucleophiles have been used instead of  $OH^-$  and the general reactivity is of the same nature as given below:

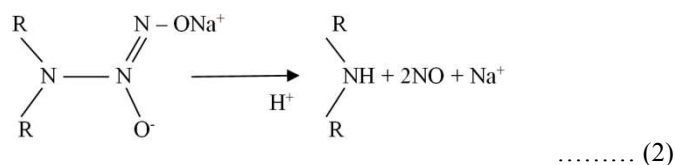


The formation of novel intermediate entities using this type of nucleophilic attack has been demonstrated by Bottomley and co-workers (126, 127) which is shown below:



**Exogenous NO- and CO- donors:** Although glycerine trinitrate (GTN) and sodium nitroprusside (SNP) have been used for many decades to control hypertension systematic research on exogenous NO- donors has gained significant momentum following the discovery of the physiological roles of NO. In recent years the cytoprotective role of CO has also inspired synthesis of designed CO- donors to impede tissue injury during oxidative and inflammatory stress.

**NO- donating drugs:** Organic nitrates such as glycerin trinitrate (GTN) and nitrites such as isoamyl nitrite (IMN) are most widely used for blood pressure control. Selected doses of these compounds are metabolized in human to produce NO at desired levels Glycerin trinitrate is employed as pills ointments, sprays and patches to induce vasodilation. Isoamyl nitrite is also used in the hospitals as an inhalant antidote for cyanide poisoning. NO generated from isamyl nitrite competes with CN as the home site of cytochrome – C oxidize and exerts its inhibitory effects. Sodium nitroprusside is the oldest inorganic compound used as an exogenous NO – donor. Although loss of cyanide ligands from sodium nitro prusside in the body often limits its use in tackling prolong hypertension, intravenous injections of sodium nitro prusside are sometimes used in the hospitals to combat hypertensive emergency. The S-Nitroso-N-acetylated penicillamine (SNAP) has been employed as a NO-donor drug in animals for protection against hemorrhagic shock. The diethyl amino NONO ate (diazemium diolates such as DEA-NO commonly known as NONO ates) produces 2-equivalent of NO-via a pH-dependent pathway.



Recently it has been demonstrated that though a co-ordinated nitrosyl remains intact, yet it can activate the metal centre so that dimethylformamide can be bonded to the metal as carbamide moiety (135). The use of dinitrosyl molybdenum derivatives have been made for the olefin metathesis reaction involving the intermolecularexchange of alkylidene units between alkene via cleavage of C = C bond as co-catalyst (136, 137). A very useful synthetic procedure has been observed where co-ordinated NO may be transferred to the other metal (138), for example,

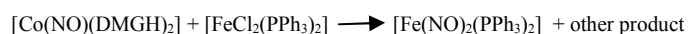
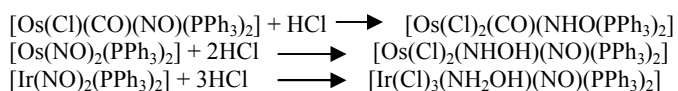


Table 10.

Electronic configuration {MNO} <sup>n</sup> (where n is number of d electrons)	Coordination number	Relative chemistry with representative known species
With 'CN' group	6 and 7	Poorly known [V(CN) <sub>5</sub> (NO)] <sup>3-</sup> [V(CN) <sub>6</sub> (NO)] <sup>4-</sup>
d <sup>4</sup> without 'CN' group	5, 6 and 7	Fairly known [V(DTC) <sub>2</sub> (NO)] [MoCl <sub>4</sub> (NO)] <sup>-</sup> [MoCl <sub>5</sub> (NO)] <sup>2-</sup> and [Mo(DTC) <sub>3</sub> (NO)]
With 'CN' group	6	Poorly known [Cr(CN) <sub>5</sub> (NO)] <sup>3-</sup>
d <sup>5</sup> without 'CN' group	6	Moderately known [Cr(NO)L <sub>5</sub> ] <sup>2-</sup> ,
With 'CN' group	6	Well known [Fe(CN) <sub>5</sub> (NO)] <sup>2-</sup> and its derivatives
d <sup>6</sup> without 'CN' group	6	Well known [RuX <sub>5</sub> (NO)] <sup>2-</sup>
With 'CN' group	5 and 6	Poorly known [Fe(CN) <sub>4</sub> (NO)] <sup>2-</sup> and [Fe(CN) <sub>5</sub> (NO)] <sup>3-</sup>
d <sup>7</sup> without 'CN' group	6	Moderately known [FeL <sub>5</sub> (NO)] <sup>2+</sup> ,
With 'CN' group	6	Poorly known [Pt(CN) <sub>5</sub> (NO)] <sup>2-</sup>
d <sup>8</sup> without 'CN' group	5 and 6	Widely known [Mn(CO) <sub>4</sub> (NO)] <sup>2+</sup> [Mn(CO) <sub>4</sub> (NO)], [MnL <sub>2</sub> (NO) <sub>2</sub> X] and [Co(NO)L <sub>2</sub> X <sub>2</sub> ]
With 'CN' group	4	Unknown Fairly known [Fe(NO) <sub>2</sub> X <sub>2</sub> ] and [Co(NO)(L)(SR) <sub>2</sub> ] <sub>2</sub>
d <sup>9</sup> without 'CN' group	4	Poorly known K <sub>2</sub> [Ni(CN) <sub>3</sub> (NO)]
With 'CN' group	4	Most widely known [Mn(NO) <sub>3</sub> L], [Fe(NO) <sub>2</sub> (CO)L], [Fe(NO) <sub>2</sub> L <sub>2</sub> ], [Co(NO)(CO) <sub>2</sub> L], [Ni(NO)X] <sub>n</sub> , [Ni(CO)L <sub>2</sub> X] and [Fe(NO) <sub>2</sub> (RNC) <sub>2</sub> ]

(iii) **Electrophilic Attack:** By the mode of attack, it is evident that the activity of the co-ordinated NO would be associated just in the opposite direction as encountered in nucleophilic attack. This attack is therefore, associated with the nitrosyl (139 – 143) complexes where M-N-O group is bent or in other words the nitrosyl group contains formally NO<sup>-</sup>. The extent of protonation on this group depends on the formal oxidation state of the metal and the trends observed are shown below:



The above cited nucleophilic and electrophilic attacks suggest a broad division like the linear M-N-O group containing NO<sup>+</sup> should be unstable in alkaline medium, whereas, the bent M-N-O group containing NO<sup>-</sup> should be unstable in acidic medium. From the synthetic point of view, the cyanonitrosyl complexes prepared in acidic medium should behave like nitroprusside anion, and which is in fact found to be true (144 – 150). Contrary to this the cyanonitrosyl prepared using alkaline hydroxylamine method, though somewhat unstable in acidic medium, do not contain bent nitrosyl group (vide supra). Nevertheless, it has been demonstrated that complexes containing the same moiety can be isolated in alkaline as well as acidic medium (37). This once more reflects our lack of understanding about the variation of actual electron density in the linear M-N-O group. Attempts (151 – 155) are being made to answer this uncertainty, however, a complete answer is still awaited.

The synthesis, bonding and reactivity of the nitrosyl complexes are complexed and varied. Mononitrosyl complexes {MNO}<sup>n</sup> group having cyanide as co-ligand are comparatively less explored regarding substitution reactions keeping the (MNO) moiety intact. As described in the preceding part of the chapter, a fairly balanced physico-chemical study along with X-ray structural data are not available, but for accounting the reactivity of these complexes, there is definitely a paucity of data compared to other nitrosyl derivatives. Among the cyanonitrosyl complexes, it is only nitroprusside anion which received much attention in all aspects. The comparative rate of attention regarding substitution reaction in nitrosyl complexes containing cyano group as co-ligand as well as without cyano group are summarized in Table 1.10. An examination of the Table shows that except for d<sup>6</sup> configuration the cyanonitrosyl chemistry of other electronic configuration is very poorly studied with respect to their reactivity and substitution reactions. This is due to the fact that on populating electrons in the antibonding orbitals (vide supra) cause destabilization of the bonding between metal and nitrosyl centres enhancing thereby the reactivity of the co-ordinated NO group. Keeping these possibilities in mind different substitution reactions were carried out by changing the substituent, to get slight modification of the electronic distribution in the (MNO) group depending on the nature of donor and π-acceptor capabilities of the substituent ligands. These maneuvering sometimes lead to restrict the uncontrollable reactivity of the co-ordinated NO group or the reverse. From the viewpoints discussed above, it is obvious that the nitrosyl complexes containing d<sup>6</sup> electronic configuration do not feel any destabilization because the

highest occupied orbital is non-bonding. However, maximum studies on this electronic configuration were made on two grounds. Firstly, from the theoretical consideration this electronic configuration can act some sort of base line from which a comparison can be made for the other containing more number of 'd' electrons. Secondly, it is merely coincidental that nitrosyl complexes of this configuration existed long back (by the celebrated example of nitroprusside and easily recognized class of nitrosyl ruthenium (III) compounds) before the bonding scheme were devised, which resulted the development of nitrosyl chemistry on this electronic configuration. The existing theories on different nitrosyl complexes do not suggest anything of the  $d^4$  – and  $d^5$  – electronic configuration. This is partly responsible for the paucity of nitrosyl complexes with these configuration and so when they are recently being explored, gave interesting results. As it is often discussed earlier that in cyanonitrosyl complexes stabilization rest mainly on the nitrosyl group which indicates the cyanide co-ligand should be mobile in nature and can be displaced by other ligand of interest. A judicious choice of different ligands containing different donor sites would be of much preparative interest and with their nature of perturbation on the (MNO) moiety one can think a bit differently to see whether a particular condition for the introduction of nitrosyl group is very much specific or not. In the preparative sense, only very little nitrosyl complexes of chromium (I) are reported. As acid hydrolysis of  $[\text{CrNO}(\text{CN})_5]^{3+}$  (94) has been followed using e.s.r. technique and also by polarography. It would be of interest to see whether the different equation products can be isolated using different nitrogen donors. This type of nitrosyl derivatives are mostly known with ruthenium complexes containing  $d^6$  configuration. As  $d^5$  chromium (I) and  $d^6$  ruthenium (II) complexes contain the highest populated orbital of non-bonding nature, a comparative chemistry in light of bonding theories would be interesting. From the Table 1.10, it is evident that complexes containing  $(\text{CrNO})^{2+}$  moiety are mostly of the cationic type. Anionic complexes is restricted to only on the preparation of  $[\text{Cr}(\text{NO})(\text{CN})_5]^{3-}$ . It would be of interest to see whether other anions of different complexing abilities would be synthesized or not. The studies of a series of this type of species, if possible, would open a new way to monitor their complexing abilities using e.s.r. technique. Besides, non-electrolytic complexes containing  $(\text{CrNO})^{2+}$  moiety is very little known. Further, mixed-ligand cyanonitrosyl complexes of  $\{\text{FeNO}\}^6$  electronic configuration, which are expected to be biologically active are also very little known. The complexes thus synthesized would require an attention of re-activities, which can be dealt using different physic-chemical techniques. Thus a correlation can be made on the changes noticed with the help of existing theories in hand.

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