Electronic Structure and Chemical Bonding in Cyanonitrosyl Complexes of Transition Metals*

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The electronic structure of central ions in complexes of the $[M(CN)_5NO]^{n-}$ type and the character of metal ligand bond were interpreted using the radioisotopic exchange method and by the IR-spectroscopic investigations [4]. Investigations of kinetics of the isotopic exchange reaction in the system: $[M(CN)_5NO]^{n-}$ — $^{14}CN^-$ where M = Cr, Mn, Fe and Co, have shown that the effective valency state of central ions in the complexes investigated is 3+. The stabilization of metal oxidation state in the pentacyanonitrosyl complexes of chromium, manganese and iron as compared with hexacyanide complexes is due to the increase of stability of M—NO bond, because of the additional π-bond (dative or covalent type). The appearance of π-bond M—NO, alongside the σ-bond was confirmed in the complexes of chromium, manganese and iron by investigations of kinetics and mechanism of exchange reaction as well as the very comprehensive examination of infrared spectra. The investigations of the IR-spectra demonstrated the close relationship between values and position of frequencies characteristic for N—O and M—N fundamental vibrations and π- or σ-bonds participation in information of M—N and N—O bonding. The above investigations permitted the construction of a general model of coordination in the NO group of the pentacyanonitrosyl complexes of the first transition metal series.

The unusual properties of nitrogen oxide as a complex ligand aroused an interest in the structure and properties of nitrosyl complexes. Out of a number of nitrosyl complexes the pentacyanonitrosyl complexes of transition metals, having a general formula $[M(CN)_5NO]^{n-}$ are of particular interest.

A great amount of the investigations of the structure of these compounds (Griffith, Lewis and Wilkinson wrote most extensively on the subject [1—6]) showed that the NO group may be coordinated in these complexes in three different ways. (Table 1.)

The first type of coordination does not require a change in the oxidation state of the central ion but it is very rare owing to the presence of an unpaired electron in NO group. The second and the third type of coordination may be accepted only on the assumption that the oxidation state of the metal is changed by one or two units.

A model of NO coordination shown above was arrived by the investiga-

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tions of the IR-spectra and magnetic measurements. The authors mentioned above — with regard to the values of NO valence frequencies and magnetic susceptibilities of cyanonitrosyl complexes given in Table 2 — have suggested the following electronic configurations of some compounds.

The assumption of such a NO coordination model does not agree, in our opinion, with the optical and chemical properties of these compounds. Since

Table 1

Type of coordination	Character of the coordinated NO group
I. $[(CN)_5M{-}\dot{N}{\equiv}O{:}]^{n-}$	A NO molecule is coordinating with an electron pair, maintaining its neutral character.
II. $[(CN)_5M{-}N{\equiv}O{:}]^{n-}$	NO or NO^- groups are coordinating with an electron pair and simultaneous reduction of metal by one or two degrees occurs.
III. $[(CN)_5M{-}\ddot{N}{=}\underset{\cdot\cdot}{\ddot{O}}]^{n-}$	NO group coordinates with an electron pair and simultaneous oxidation of metal by one degree occurs.

Table 2

Compound	ν^{NO} (cm^{-1})	μ (BM)	d_ε	Electronic configuration
				D^2SP^3
$K_3[Cr(CN)_5NO]$	1640	1.87	5	⇅ ⇅ ↑ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅
$K_3[Cr(CN)_6]$	—	3.87	3	↑ ↑ ↑ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅
$K_3[Mn(CN)_5NO]$	1730	0.0	6	⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅
$K_3[Mn(CN)_6]$	—	2.95	4	⇅ ↑ ↑ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅
$Na_2[Fe(CN)_5NO]$	1940	0.0	6	⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅
$K_3[Fe(CN)_6]$	—	1.7	5	⇅ ⇅ ↑ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅
$K_3[Co(CN)_5NO]$	1125	0.0	6	⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅
$K_3[Co(CN)_6]$	—	0.0	6	⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅

the electronic structure of these compounds was given mainly on the ground of magnetic studies, we have decided to approach this problem more generally, by application of radioisotopic exchange methods as well as by examination of electronic and IR-absorption spectra.

In the course of the extensive studies of exchange reactions in a homogeneous system:

$$[M(CN)_5NO]^{n-} — {}^{14}CN^-$$

we have found the reaction to be of a photochemical character, which was revealed by the increased reaction rate under the influence of light [7—10]. (Table 3.)

Table 3

Compound	Concentration (mole CN/l)		pH	R_S/R_C	
	$[M(CN)_5NO]^{n-}$	KCN		*trans* CN	*cis* CN
$K_3[Cr(CN)_5NO]$	0.0779	0.0532	10.2	1.11	
$K_3[Mn(CN)_5NO]$	0.4925	0.2078	10.6	17.85	
$Na_2[Fe(CN)_5NO]$	0.5010	0.2078	10.7	1.31	1.12
$K_3[Co(CN)_5NO]$	0.4995	0.2078	11.4	1.07	5.13

R_S — exchange reaction at standart illumination,
R_C — exchange reaction in the dark.

Table 4

Compound	Concentration (mole CN/l)		$R \cdot 10^6$		Ionic strength I
	$[M(CN)_5NO]^{n-}$	KCN	*trans* CN	*cis* CN	
$K_3[Cr(CN)_5NO]$	0.0390	0.0532	0.101		0.1
	0.0779	0.0532	0.142		0.15
	0.0779	0.2128	0.257		0.3
$K_3[Mn(CN)_5NO]$	0.2650	0.1901	2.34		0.51
	0.5045	0.1997	2.46		0.79
	0.4990	0.9985	5.50		1.55
$Na_2[Fe(CN)_5NO]$	0.0501	0.2078	1.44	0.23	0.24
	0.2505	0.2078	7.80	0.40	0.36
	0.5010	0.0208	4.65	0.49	0.17
$K_3[Co(CN)_5NO]$	0.0499	0.2078	1.28	0.36	0.17
	0.2497	0.2078	4.58	0.37	0.51
	0.2497	0.0208	2.87	0.47	0.32

The spectrophotometric and conductometric studies of irradiated solutions have shown that the increase of the exchange reaction rate under the influence of the light does not result from decomposition of the complex compound in the circumstances of exchange reaction [11]. The kinetics of exchange reaction was also examined with respect to the effect of reagent concentration, pH, ionic strength and temperature on the exchange reaction rate [7—11]. (Table 4 and 5.)

The above investigations have shown that the apparently „inert“ $K_3[Cr(CN)_5NO]$, $K_3[Mn(CN)_5NO]$ and $Na_2[Fe(CN)_5NO]$ complexes show a significant increase of the exchange reaction rate under the influence of light.

According to these studies, the exchange reaction proceeds in these complexes through a heptacoordinated transition stage. Coordination of a seventh ligand (H_2O molecule or CN^- ion) is due to the transition of the electron pair forming a π-bonding metal—NO into NO orbitals. A free *d*-orbital of the metal may then be used for coordination of the seventh ligand, according to the association mechanism S_N2 [8—10]. (Table 6.)

Table 5

Compound	Concentration (mole CN/l)		$R \cdot 10^6$		pH
	$[M(CN)_5NO]^{n-}$	KCN	*trans* CN	*cis* CN	
$K_3[Cr(CN)_5NO]$	0.0779 0.0779	0.0532 0.0532	0.142 0.148		10.6 9.0
$K_3[Mn(CN)_5NO]$	0.4925 0.4728	0.2078 0.2078	2.50 2.21		10.6 8.5
$Na_2[Fe(CN)_5NO]$	0.5010 0.5010	0.2078 0.2078	41.10 6.70	1.71 0.98	10.7 8.0
$K_3[Co(CN)_5NO]$	0.4995 0.4995	0.2078 0.2078	5.90 15.90	1.59 2.01	11.4 8.0

Table 6

1	$[M(CN)_5NO]^{n-}$	$\overset{h\nu}{\rightleftarrows}$	$\{[M(CN)_5NO]^{n-}\}^*$
2	$\{[M(CN)_5NO]^{n-}\}^* + {}^{14}CN^-$	$\rightleftarrows$	$[M(CN)_5({}^{14}CN)NO]^{(n+1)-}$
3	$[M(CN)_5({}^{14}CN)NO]^{(n+1)-}$	$\rightleftarrows$	$[M(CN)_4({}^{14}CN)NO]^{n-} + CN^-$
4	$H^+ + {}^{14}CN^-$	$\rightleftarrows$	$H^{14}CN$

where M = Cr, Mn and Fe

A possible $d\pi$—$p\pi$ interaction, which is an evidence of a double bond between the NO group and central ion, prevents the coordination of NO^+ ions in these compounds. The results obtained in the course of these investigations suggested the hypothesis claiming that in these complexes the NO^- ion in chromium and manganese complexes, or a neutral NO molecule in iron complex, is a coordinating molecule. In this coordination a σ-bond is involved and an additional π-bond formed by a free electron pair of the NO^- ion or by odd electrons of the neutral NO molecule and of the metal. In the first case a π-bonding of a dative type is formed alongside of a σ-bonding, and in the latter — a covalent π-bond results [11—12].

The studies on exchange reaction in the $K_3[Co(CN)_5NO]$ complexes have shown that exchange proceeds according to a dissociation mechanism S_N1 [8—10]. (Table 7.)

A rate-controlling stage in this mechanism is the complex ion dissociation combined with aquation. A $d\pi$—$p\pi$ interaction is not possible in this complex, since both the non-bonding cobalt d-orbital and antibonding NO orbital are closed.

The exchange reaction rate (R) at pH 8—9, — increasing from chromium to cobalt — shows, that M—NO binding force is decreasing with decrease of a π-bonding force. (Table 8.)

It should be added that in the iron and cobalt complexes a *trans* effect of the NO group interaction is observed (Table 4 and 5), revealed by the increased

Table 7

1	$[Co(CN)_5NO]^{3-}$	$\overset{h\nu}{\rightleftarrows}$	$\{[Co(CN)_5NO]^{3-}\}^*$
2	$\{[Co(CN)_5NO]^{3-}\}^* + H_2O$	$\rightleftarrows$	$[Co(CN)_4(H_2O)NO]^{2-} + CN^-$
	$\{[Co(CN)_5NO]^{3-}\}^* + H_3O^+$	$\rightleftarrows$	$[Co(CN)_4(H_2O)NO]^{2-} + HCN$
3	$[Co(CN)_4(H_2O)NO]^{2-} + {}^{14}CN^-$	$\rightleftarrows$	$[Co(CN)_4({}^{14}CN)NO]^{3-} + H_2O$

Table 8

	$K_3[Cr(CN)_5NO]$	$K_3[Mn(CN)_5NO]$	$Na_2[Fe(CN)_5NO]$		$K_3[Co(CN)_5NO]$	
			trans CN	*cis* CN	*trans* CN	*cis* CN
$R \cdot 10^6$ mole CN/l . min	0.148	2.21	6.70	0.98	15.90	2.01
$E_{activ.}$ kcal/mole	29.8	19.7	14.7	24.6	8.1	21.2

mobility of the CN group (in *trans* position to NO) as compared with the remaining four groups. Thus it may be assumed that the M—NO bond in iron and cobalt complexes is polarized to a high degree and therefore the electron pair forming a π-bond is nearer to the nitrogen atom.

In order to obtain further proofs confirming the validity of the conclusions drawn on the ground of exchange reactions, the absorption spectra of cyanonitrosyl complexes were examined in ultraviolet, visible and infra-red ranges. A comparison of the electronic absorption spectra of these complexes with the spectra of mother hexacyano complexes or others of the same symmetry, shows that the coordination of the NO group does not cause the reduction of metals in nitrosyl complexes. (Table 9.)

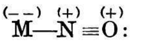
Table 9

Compound	Band position (cm^{-1})			
$[Cr(NH_3)_6]^{3+}$	—	28500	21500	15300
$K_3[Cr(CN)_5NO]$	36400	26700	22000	13530
$K_3[Mn(CN)_6]$	47700	30300	19600	10000
$K_3[Mn(CN)_5NO]$	45500	29400	18500	10800
$K_4[Fe(CN)_6]$	46100	31200	20100	—
$K_3[Fe(CN)_6]$	38500	31880	23530	—
$Na_2[Fe(CN)_5NO]$	36400	30300	25000	20000
$K_3[Co(CN)_5NO]$	30800	26400	22700	—
$[Co(en)_3]^{3+}$	29600	—	21400	—
$K_3[Co(CN)_5OH]$	—	26310	—	—

Interpretation of the electronic spectra on the basis of the M. O. theory demonstrates that in contrast with cobalt there is a high probability of M—NO π-bonding formation alongside the σ-bond in the cyanonitrosyl complexes of chromium, manganese and iron [13—14].

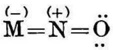
The most convincing data were supplied by the studies of IR-spectra from 400 to 5000 cm^{-1} [11—15].

Since the formation of a π-bond depends on the possibility of $d\pi$—$p\pi$ or $p\pi$—$d\pi$ interaction, it was anticipated that the changes of the M—N and N—O bond order brought about by this interaction will be reflected in the character of the spectrum, thus enabling us to determine which one of the possible structure is the most probable:



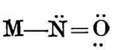
$\overset{(--)}{M}—\overset{(+)}{N}\equiv\overset{(+)}{O}:$

a



$\overset{(-)}{M}=\overset{(+)}{N}=\underset{\cdot\cdot}{\ddot{O}}$

b

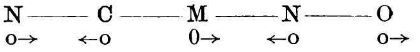


$M—\ddot{N}=\underset{\cdot\cdot}{\ddot{O}}$

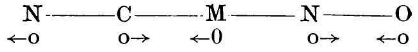
c

Adopting the numeration of the observed frequencies similar to that given by Jones [16—17] for hexacyano complexes of a $[M(CN)_6]^{n-}$ type, ν_6^{NO}, ν_7^{MNO} and ν_8^{MN} have been identified in the investigated frequency range. (Table 10.)

We assume that the frequencies observed are due to vibration of the metal and ligands atoms according to a simplified scheme (*I* and *II*):



I



II

Table 10

Compound	Frequencies (cm^{-1})			d_ε
	ν_6^{NO}	ν_7^{MNO}	ν_8^{MN}	
$K_3[Cr(CN)_5NO]$	1640	610	621	3
$K_3[Mn(CN)_5NO]$	1730	622	518	4
$Na_2[Fe(CN)_5NO]$*	1940	663	496	5
$K_3[Co(CN)_5NO]$	1125	(834)	417	6

* The IR-spectrum of $Na_2[Fe(CN)_5NO]$ has been earlier investigated by Bor [18]. His results agree with ours.

It may be observed that the increase of ν_6^{NO} and ν_8^{MN} is caused by the increase of the N—O and M—N bonding strength, respectively. According to Jones' assumption [16—17], which applies to hexacyano complexes and the validity of which is supposed alone in the case of the compounds of the type: $[M(CN)_5NO]^{n-}$ the M—NO σ-bonding strength should increase with the increase of the frequency values ν_6^{NO}, ν_7^{MNO} and ν_8^{MN}, while on the other hand, the π-bonding strength should increase with the increase of ν_7^{MNO} and ν_8^{MN} but it should decrease with the increase of ν_6^{NO}

Characteristic shifts of ν_6^{NO} showing a varying character of M—NO π-bonding in these compounds, deserve particular attention. As was mentioned earlier, the participation of a π-bond in the M—NO bond has some effect on the character of the N—O bonding, or, strictly speaking, on its bond order. It is interesting to compare the N—O bond order in NO^+, NO (neutral) and NO^- single or double-bonded in the complex of a $[M(CN)_5NO]^{n-}$ type. (Table 11.)

The above data confirm that the weakest π-bond occurs in the iron complex in which nitrogen—oxygen bond is the strongest one.

ν_6^{NO} and the N—O bond order (0.75) are very low in the cobalt complex and suggest the existence of a single nitrogen—oxygen bond in this compound.

Table 11

Character NO group	ν_0^{NO} (cm^{-1})	k_{NO} 10^{-5} (dynes/cm)	N—O bond order
$[:N\equiv O:]^+$	2275	22.56	3
$[:N\overset{\cdots}{\equiv}O:]$	1876	15.32	2.04
$[=N=\ddot{O}]^-$	1640—1940	10.55—16.36	1.5—2.18
$[-\underset{..}{\ddot{N}}-\underset{..}{\ddot{O}}:]^-$	1125	5.48	0.75

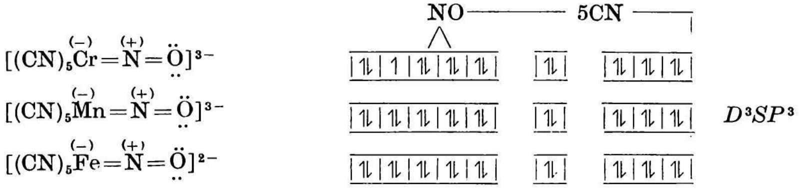
Such bonding, if simultaneously no Co—NO π-bonding is observed, indicates a $Co-\ddot{N}-\ddot{O}:$ structure. A possibility of binding the NO molecule analogously to olefin complexes should be alternatively considered. With this type of coordination the nonlinear linking of the NO group is possible.

Summing up the model of the NO group coordination admits, in principle, two kinds of M—NO bonds in $[M(CN)_5NO]^{n-}$ compounds:

1° — coordination of the NO (neutral) or NO^- ion double-linked with the central ion by a σ-bond and by additional π-bond of a dative or covalent type.

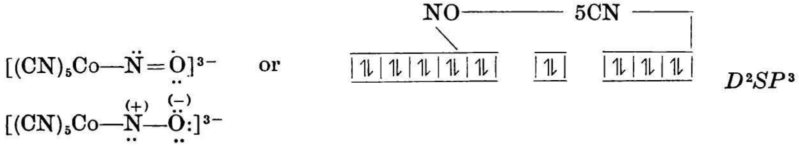
2° — coordination of the NO^- ion with the help of a single σ-bond. When NO^- is coordinated in this way, the M—NO bond may be also considered as an olefin bond.

Accordingly, the electronic structure of the complexes investigated should be presented as follows:


$[(CN)_5\overset{(-)}{Cr}=\overset{(+)}{N}=\underset{..}{\ddot{O}}]^{3-}$

$[(CN)_5\overset{(-)}{Mn}=\overset{(+)}{N}=\underset{..}{\ddot{O}}]^{3-}$

$[(CN)_5\overset{(-)}{Fe}=\overset{(+)}{N}=\underset{..}{\ddot{O}}]^{2-}$


$[(CN)_5Co-\ddot{N}=\underset{..}{\dot{O}}]^{3-}$ or

$[(CN)_5Co-\underset{..}{\overset{(+)}{N}}-\underset{..}{\overset{(-)}{\ddot{O}}}:]^{3-}$

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