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THE NITROPRUSSIDE ION

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A. INTRODUCTION

The chemical and physical properties of the nitroprusside ion (pentacyanonitrosylferrate(III)), $(NC)_5FeNO^{2-}$, have attracted considerable interest during various periods in chemical history. Compounds containing $(NC)_5FeNO^{2-}$ were characterized in the mid-19th century[1]. At this time and soon afterwards much of the chemistry of the ion was qualitatively described. In the period between 1910 and 1930 an Italian group of chemists centered about Cambi, Scagliarini and their co-workers virtually dominated the investigation of the chemistry of the ion. They prepared and characterized a wide variety of compounds which result from reactions between bases and $(NC)_5FeNO^{2-}$. These reactions involve the addition of bases to the NO moiety of $(NC)_5FeNO^{2-}$, and thus attention has been directed to that functional group. Questions relating to the structural and electronic properties of $(NC)_5FeNO^{2-}$ and in particular to the NO moiety are pertinent in an analysis of the chemical reactivity of the ion. Questions of this nature have only recently been resolved. With this information available it is expected that there will be renewed interest in the chemistry of $(NC)_5FeNO^{2-}$ and related nitrosyl complexes. This review article attempts to indicate areas of the chemistry of $(NC)_5FeNO^{2-}$ which would be fruitful for investigation.

B. STRUCTURE AND SPECTRAL PROPERTIES

The NO moiety dominates the chemical and spectral properties of $(NC)_5FeNO^{2-}$ and most attention has been directed towards its electronic and structural characterization.

(i) X-ray study

The crystal structure of $Na_2[(NC)_5FeNO]\cdot 2H_2O$ has only recently been determined[2]. The crystal is orthorhombic with space group P_{nnm}. The $(NC)_5FeNO^{2-}$ ion has approximate C_{4v} symmetry. The Fe-N distance is 1.63 ± 0.02 Å. This bond length is comparable with distances of between 1.57 and 1.71 Å observed for Roussin's black salt[3], $Cs[Fe_4S_3(NO)_7]$, and Roussin's red ethyl ester[4]. The rather short Fe-N bond distance suggests the presence of a large amount of triple bond character in this bond. The N–O distance is 1.13 ± 0.02 Å. The N–O bond distances observed in NOX, where X is a halogen, are 1.14 ± 0.02 Å. The five C–N distances are 1.16 ± 0.02 Å and do not differ from the C–N bond distances in other cyanide complexes[5]. The Fe–C distances are equivalent for all of the cyanides at 1.90 ± 0.02 Å. This implies that no special structural characteristics exist for the axial or equitorial cyanides. The Fe–N–O angle is within experimental error 180°, which has important consequences in terms of the nature of the bond between the iron and the NO moiety. The $N\text{–}Fe\text{–}C_{\text{equatorial}}$ angle is 96°, slightly larger than the expected 90°.

(ii) Ultraviolet and visible spectra

The very short Fe–N bond distance is a distinguishing structural characteristic of complexes of NO with transition metal ions. This short distance indicates that the electronic structure $Fe \equiv NO$ occurs. The triple bond is composed of one σ-bond utilizing an empty metal d-orbital and the nitrogen lone pair and two π-bonds utilizing the empty π^*-orbital of NO and the filled metal ion d-orbitals. This assignment would predict a Fe–N–O bond angle of 180° which is experimentally observed.

Although there are a large number of papers in the literature containing interpretations and/or results on the electronic spectrum of $(NC)_5FeNO^{2-}$ and related compounds, there appears to have been considerable disagreement on an unambiguous interpretation of the spectrum[6-18]. The major disagreement centers about the ordering of the energy levels approximated by the d_{xy}, d_{yz}, d_{xz}, d_{z^2}, $d_{x^2-y^2}$ and π^*NO orbitals of the ion. Manoharan and Gray have recently carried out an extensive SCCC-MO calculation on the $(NC)_5FeNO^{2-}$ ion[19]. The two highest-filled molecular orbitals in the ground-state of the ion are represented by the symbols 6e and $2b_2$, the ground state being $(6e)^2(2b_2)^2$. The 6e level is mainly d_{xz} and d_{yz} but contains 24.8% π^*NO and a small percent of the πCN, π^*CN and σCN orbitals, while the $2b_2$ level is 84.5% d_{xy}, 13.9% πCN and 1.6% π^*CN. The lowest-unfilled molecular orbital (7e) contains 72.5% π^*NO and small contributions from the d_{xy}, d_{yz}, d_{xz}, σCN, πCN and π^*CN orbitals. The primary contributions to the next two higher molecular orbitals come from the $d_{x^2-y^2}$ and d_{z^2} orbitals. Thus the ordering of the two highest filled and three lowest unfilled orbitals in $(NC)_5FeNO^{2-}$, as represented by their major orbital contributions, are $d_{xz}, d_{yz} < d_{xy} < \pi^*NO < d_{x^2-y^2} < d_{z^2}$. It should be noted that there is considerable π^*NO character to the orbital represented by d_{xz}, d_{yz} (6e) which indicates a large amount of back-bonding from the iron to the NO moiety. However, the ion can formally be considered to contain iron(II) and NO^+, which is consistent with the observation that $(NC)_5FeNO^{2-}$ is diamagnetic[20]. Contributions to the $6e(d_{xz}, d_{yz})$ and $2b_2(d_{xy})$ molecular orbitals from unfilled orbitals on cyanide (π^*CN) are small. This indicates that there is little back-bonding from iron to the cyanides. The final charge distribution is calculated to be

$$[Fe^{+0.3166}(CN)_4{}^{-2.2000}(CN)^{-0.5809}(NO)^{+0.4643}].$$

The following assignments have been made for the electronic spectrum of $(NC)_5FeNO^{2-}$ [19]: 20,080 cm^{-1} (480 mμ) $d_{xy} \rightarrow \pi^*NO$; 25,380 cm^{-1} (394 m$\mu$) $d_{xz}, d_{yz} \rightarrow \pi^*NO$; 30,300 cm^{-1} (330 m$\mu$) $d_{xy} \rightarrow d_{x^2-y^2}$; 37,800 cm^{-1} (264 m$\mu$) $d_{xz}, d_{yz} \rightarrow d_{z^2}$; 42,000 cm^{-1} (238 m$\mu$) $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$; and 50,000 cm^{-1} (200 mμ) $d_{xy} \rightarrow \pi^*CN$. Note that the long wavelength absorption bands (480 mμ and 394 mμ) involve a transition to a molecular orbital containing primarily the antibonding orbital (π^*NO) on the NO^+ while the other transitions do not. This should have important consequences in the photochemistry of $(NC)_5FeNO^{2-}$.

(iii) Infrared studies

A substantial number of infrared studies have been carried out on nitrosyl complexes and $(NC)_5FeNO^{2-}$ in particular[21-27]. Table 1 contains a summary of the pertinent NO and CN stretching frequency data in the literature. The NO stretching frequency can be compared with those of NO (1878 cm^{-1})[28] and NO^+ (2220 cm^{-1})[29]. Bonding of either of these species to a metal ion center will lower the observed frequency. Upon examination of a wide variety of NO stretching frequencies in complexes Wilkinson *et al.*[23,30] have concluded that if the frequency lies in the range 1650 to 2000 cm^{-1} the NO moiety can formally be considered to be coordinated as NO^+. However, from a comparison of the CN

TABLE 1

INFRARED DATA ON $(NC)_5FeNO^{2-}$

Frequency, cm⁻¹		*Ref.*
NO stretch	*CN stretch*	
1925	2140	21
1938	2152	22
1925	—	23
1938	—	23
1944	2182, 2169, 2155	20
1939	2173.4, 2161.6, 2156.7, 2143.4	24
—	2170, 2160, 2148	25
1940	2144	26
1939	2173, 2159, 2142	27

stretching frequencies of $Fe(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$, and $(NC)_5FeNO^{2-}$ it is possible to conclude that the oxidation state of the iron in $(NC)_5FeNO^{2-}$ is plus three or four[22]. Tosi and Danon[25] conclude that the high CN stretching frequency of $(NC)_5FeNO^{2-}$ compared to other $(NC)_5Fe^{II}X$ complexes ($X = NH_3, H_2O, NO_2{}^-$ and $SO_3{}^{2-}$) indicates less π-bonding in the Fe–C bond for $(NC)_5FeNO^{2-}$. The splitting of the CN stretch band is consistent with the C_{4v} symmetry[20,24] of $(NC)_5FeNO^{2-}$.

The far infrared region has been studied by several groups of workers. Tosi and Danon[25] find two groups of bands at 470, 497, 515 cm⁻¹ and 420, 435, 450 cm⁻¹, which are attributed to Fe–C–N bending and Fe–C stretching[31]. B. Jezowska-Trzebiatowska and J. Ziolkowski[26] have determined the Fe–C–N bending (518 cm⁻¹), Fe–N–O bending (663 cm⁻¹), Fe–C stretching (422 cm⁻¹) and Fe–N stretching (496 cm⁻¹) frequencies[32]. No clear structural distinctions have been drawn from the observed frequencies.

(iv) Mössbauer studies

Numerous Mössbauer studies of $Fe(CN)_6{}^{4-}$ and complexes of the type $(NC)_5Fe^{II}X$ have been carried out[33,34]. Table 2 shows values of the isomer shift (σ) and quadrapole coupling (ΔE) for a number of these complexes[34]. The isomer

TABLE 2

RESULTS OF MÖSSBAUER STUDIES OF $(NC)_5Fe^{II}X$ COMPLEXES[34]

Compound	ΔE *(cm/sec)*	σ *(cm/sec)*
$K_4[Fe(CN)_6]$	0.000	+0.008
$Na_3[(NC)_5FeH_2O]$	0.080	+0.015
$Na_4[(NC)_5FeNO_2]$	0.089	+0.010
$Na_3[(NC)_5FeNH_3]$	0.070	+0.019
$Na_5[(NC)_5FeSO_3]$	0.080	+0.010
$Na_2[(NC)_5FeNO]$	0.185	−0.012

shift results from the interaction of the nuclear charge distribution and electrons with a finite probability of being in the region of the nucleus (s-electrons). Compounds containing $(NC)_5FeNO^{2-}$ have the largest electron density at the nucleus of any octahedral or substituted octahedral complex studied. Thus π-bonding from the iron(II) to the ligands appears to give a strong contribution to the s-electron distribution at the nucleus. This argument appears to be consistent if the isomer shifts of the isoelectronic series $Fe(CN)_6{}^{4-}$, $(NC)_5FeCO^{3-}$ and $(NC)_5FeNO^{2-}$ are compared. In this series back-bonding from the iron(II) to the ligand is in the order $NO^+ > CO > CN^-$. The nuclear quadrapole splitting, ΔE, for $(NC)_5FeNO^{2-}$ is double that of any other $(NC)_5Fe^{II}X$ complex. Ballhausen and Gray[35] have suggested that this is confirmation of heavy back-bonding in $(NC)_5FeNO^{2-}$.

C. ADDITION AND SUBSTITUTION REACTIONS

The addition reactions that will be considered are those obeying the general equation

$$(NC)_5FeNO^{2-} + X^n = (NC)_5FeNO(X)^{n-2}$$

The ligand notation NO(X) is used to signify that X may bind at either the oxygen or nitrogen. Any detailed interpretation of these reactions requires information about the oxidation state of the iron and the NO moiety. There is persuasive evidence to support the view that $(NC)_5FeNO^{2-}$ can be considered formally as an iron(II) complex which is a carrier of the nitrosonium ion, NO^+ (see section B-ii, page 386). Therefore it is profitable to examine reactions involving the addition of bases to $(NC)_5FeNO^{2-}$ in light of the chemistry of the reactions of nitrous acid, HNO_2, which in many instances involves the nitrosonium ion, NO^+, or nitrous acidium ion, $H_2NO_2{}^+$, as an intermediate[36].

(i) Hydroxide

Cambi and Szegö spectrally characterized the equilibrium for the $(NC)_5FeNO^{2-}$–OH^- reaction as[37]

$$(NC)_5FeNO^{2-} + 2OH^- = (NC)_5FeNO_2{}^{4-} + H_2O\,.$$

Several groups of workers have determined the equilibrium concentration quotient for this reaction. Values obtained are 1.0×10^6 (298 °K, 0.5 *M* KCl)[38], $0.7_4 \times 10^5$ (293 °K)[39], and 1.5×10^6 (298 °K, 1.0 *M* NaCl)[40]. The thermodynamic parameters, ΔH° and ΔS° are -16.2 ± 0.9 kcal/mole and -26.1 ± 3.0 e.u[40]. The equilibrium concentration quotient for this reaction is strongly dependent on the nature and concentration of the inert electrolyte, which explains the slight differences observed. This behaviour is observed for many equilibria involving only negatively or positively charged ions.

It is interesting to compare the equilibrium quotient for this reaction with that of the aqueous equilibrium

$$NO^+ + 2OH^- = NO_2^- + H_2O.$$

The equilibrium constant for this reaction is 2.3×10^{31} if a value of 5×10^6 (293 °K)[36] is used as the equilibrium quotient for the reaction $NO^+ + H_2O = HNO_2 + H^+$. Comparison with the equilibrium quotient for the reaction in which NO^+ is formally bound to an iron(II) center (approximately 10^6) clearly indicates that NO^+ is highly stabilized against conversion to NO_2^- by OH^- in $(NC)_5FeNO^{2-}$. Also high concentrations of H^+ are required to produce appreciable concentrations of NO^+ from NO_2^-, while $(NC)_5FeNO^{2-}$ is a source of NO^+ at low acid concentrations. Thus the $(NC)_5FeNO^{2-}$ ion provides a unique opportunity to explore the chemistry of NO^+ under conditions where H^+ is not competing with it for base sites.

Once $(NC)_5FeNO_2^{4-}$ is produced from the reaction between $(NC)_5FeNO^{2-}$ and OH^- the following reaction occurs

$$(NC)_5FeNO_2^{4-} + H_2O = (NC)_5FeH_2O^{3-} + NO_2^-.$$

The equilibrium constant for this reaction is $(3.0 \pm 0.1) \times 10^{-4}$ (298 °K, 1.0 *M* NaCl). The thermodynamic parameters, $\Delta H°$ and $\Delta S°$ are 12.3 ± 0.2 kcal/mole and 25.2 ± 0.7 e.u[40].

Table 3 summarizes the kinetic parameters for the reactions of the $(NC)_5FeNO^{2-}$–OH^- system[40]. The rate of formation of $(NC)_5FeNO_2^{4-}$ from $(NC)_5FeNO^{2-}$ and OH^- is first-order in the concentrations of both reactants. A reasonable mechanism would be the slow reaction of a OH^- with $(NC)_5FeNO^{2-}$ followed by a rapid reaction in which a OH^- removes a H^+ from the resulting species to yield H_2O and $(NC)_5FeNO_2^{4-}$. Oxygen-18 exchange[41] and infrared studies[42] on $(NC)_5FeNO_2^{4-}$ indicate that the NO_2^- group is bound as the nitro, Fe–NO_2, and not the nitrito, Fe–ONO, ligand.

(ii) Hydrogen sulfide and HS- containing compounds

The purple–violet coloration resulting when $(NC)_5FeNO^{2-}$ is reacted with compounds containing an ionizable SH group has long been used as a color test

TABLE 3

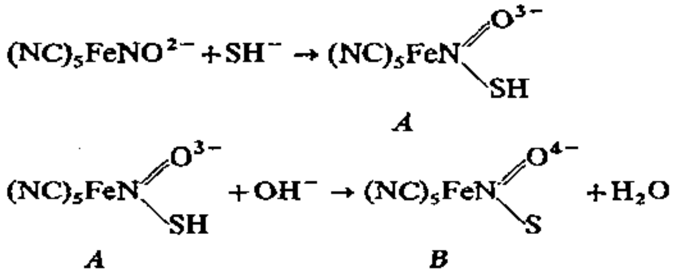
SUMMARY OF KINETIC DATA FOR $(NC)_5FeNO^{2-}$–OH^- REACTIONS[40]

Reaction	*Rate law*	k[a] $M^{-1}Sec^{-1}$	$\Delta H^{\ddagger}$ *kcal/mole*	$\Delta S^{\ddagger}$ *e.u.*
$(NC)_5FeNO^{2-} + 2OH^- = (NC)_5FeNO_2^{4-} + H_2O$	$k[(NC)_5FeNO^{2-}][OH^-]$	0.55	12.6	−17.5
$(NC)_5FeNO_2^{4-} + H_2O = (NC)_5FeH_2O^{3-} + NO_2^-$	$k[(NC)_5FeNO_2^{4-}][H_2O]$	1.4×10^{-4}	21.6	−3.6
	$k[(NC)_5FeH_2O^{3-}][NO_2^-]$	0.46	9.3	−28.8

[a] Bimolecular rate constant at 298 °K, $\mu = 1.0$ (NaCl).

for such groups. In 1850 Playfair observed a transient reddish coloration when $(NC)_5FeNO^{2-}$ and HS^- were mixed[43]. Reactions also occur when aqueous basic solutions containing Na_2Se or Na_2Te are mixed[44] with $(NC)_5FeNO^{2-}$. The former reaction results in a deep blue-green solution and the latter a black solution.

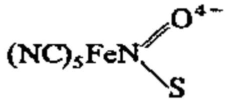
On the basis of electro-titrations the mechanism for the reaction between $(NC)_5FeNO^{2-}$ and HS^- has been postulated to be



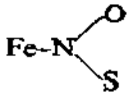
$$(NC)_5FeNO^{2-} + SH^- \rightarrow \underset{A}{(NC)_5FeN\begin{smallmatrix} \nearrow O^{3-} \\ \searrow SH \end{smallmatrix}}$$

$$\underset{A}{(NC)_5FeN\begin{smallmatrix} \nearrow O^{3-} \\ \searrow SH \end{smallmatrix}} + OH^- \rightarrow \underset{B}{(NC)_5FeN\begin{smallmatrix} \nearrow O^{4-} \\ \searrow S \end{smallmatrix}} + H_2O$$

in which both species *A* and *B* are observed. The structure of the final product of the reaction was postulated as



$$(NC)_5FeN\begin{smallmatrix} \nearrow O^{4-} \\ \searrow S \end{smallmatrix}$$

by analogy with the OH^-–$(NC)_5FeNO^{2-}$ system[45]. The kinetics of this reaction have been studied[46]. The rate of formation of species *A* is first-order in the concentrations of both HS^- and $(NC)_5FeNO^{2-}$. The bimolecular rate constant at 298 °K and $\mu = 1.0$ (NaCl) is $170\ M^{-1}sec^{-1}$ and the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, are 7.2 kcal/mole and −24 e.u. The increased rate constant in the SH^-–$(NC)_5FeNO^{2-}$ reaction as compared to the OH^-–$(NC)_5FeNO^{2-}$ case results primarily from a decrease in $\Delta S^{\ddagger}$, while $\Delta S^{\ddagger}$ is approximately the value expected from a purely electrostatic contribution[47]. The interesting rate data is that for the conversion of species *A* to *B*[46]. The reaction appears to be unidirectional and first-order in the concentration of species *A*. The first-order rate constant at 298 °K and $\mu = 1.0$ (NaCl) is $1.3 \times 10^{-2}\ sec^{-1}$, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 19.4 kcal/mole and −3 e.u. respectively. At room temperature the half-life of the reaction is about 55 seconds. This seems unusually long for a reaction which simply involves a proton transfer. Coupled with the observation that the rate constant is independent of pH between 11.5 and 12.8 it seems reasonable to suggest that the reaction involves a rate determining rearrangement of the HS^- adduct of NO^+ followed by the rapid loss of a proton[46,48]. It would be speculative to say what this rearrangement might be, but a change from  Fe–N$\begin{smallmatrix} \nearrow O \\ \searrow S \end{smallmatrix}$ to Fe–S–N–O bonding is attractive. This problem remains to be resolved.

Some evidence exists for the elimination of a CN^- from $(NC)_5FeNOS^{4-}$ (species *B*) to form[46] $H_2O(NC)_4Fe^{II}NOS^{3-}$. This type of elimination does not readily occur with $(NC)_5FeNO_2^{4-}$. However, the detailed mechanism by which species *B* slowly decomposes remains to be studied.

Alkaline solutions of mercaptans readily react with $(NC)_5FeNO^{2-}$,

$$(NC)_5FeNO^{2-} + RS^- \rightarrow (NC)_5FeNO(SR)^{3-}$$

giving red-purple solutions[49]. In fact this type of reaction has long been used as a test for the amino acid cysteine[50], $NH_2CH(CH_2SH)CO_2H$. The pK of the SH group in this compound is 8.3 and thus the determination is done in mildly basic solution. It should be noted that the $(NC)_5FeNO^{2-}$–OH^- reaction becomes competitive if the solution is too basic (see section C–*i*, page 389).

Among others, studies have been made of the reactions between $(NC)_5FeNO^{2-}$ and glutathione[51], and substituted mercaptopurines and mercaptopyrimidines[52].

(iii) Sulfite

A deep red coloration occurs when solutions of SO_3^{2-} and $(NC)_5FeNO^{2-}$ are combined; this is commonly called the Boedeker reaction[53]. The color is intensified by increasing the concentration of the inert electrolyte (*e.g.* NaCl, KCl)[54]. There is a specific cation effect with effectiveness of color intensification $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$[55]. The color of the solutions gradually fades on heating to ultimately yield $(NC)_5FeSO_3^{5-}$, which can be isolated as the potassium or sodium salt[56]. The equilibrium

$$(NC)_5FeNO^{2-} + SO_3^{2-} = (NC)_5FeNO(SO_3)^{4-}$$

has recently been studied with a wide variety of inert electrolytes in both aqueous and non-aqueous solutions, and the structure of $(NC)_5FeNO(SO_3)^{4-}$ examined[55,57,58,59]. Infrared analysis of salts of $(NC)_5FeNO(SO_3)^{4-}$ indicates that the bonding of the SO_3^{2-} to NO^+ is through the oxygen[58], $(NC)_5Fe{-}NO{-}SO_3^{4-}$. Using temperature-jump relaxation techniques a preliminary study of the Boedeker reaction has been carried out[60]. At 298 °K and $\mu = 1.0$ (NaCl) the first-order rate constant is 820 sec^{-1} and from the published equilibrium concentration quotients the bimolecular rate constant is 107 $M^{-1}sec^{-1}$.

There is a similarity between the Boedeker reaction and the first step postulated in the Raschig synthesis of hydroxylamine, NH_2OH. Seel and Knorre[61] have studied the kinetics of the reaction between NO_2^- and HSO_3^-. The rate law, which is $-d[NO_2^-]/dt = k[NO_2^-]\,[HSO_3^-]^2/1+k'[SO_3^{2-}]$, implies that the nitrososulfonate ion, $ONSO_3^-$, is an intermediate in the reaction.

(iv) Ketones and compounds containing acidic hydrogens

Table 4 contains a partial list of reactions that are reported to occur between $(NC)_5FeNO^{2-}$ and ketones and related compounds. In some cases the workers simply reported a positive or negative reaction for a compound without reporting the nature of the observation.

If slightly alkaline solutions containing ketones or other compounds containing "acidic" hydrogen bound to carbon are mixed with $(NC)_5FeNO^{2-}$ a coloration (usually red) develops, which often rapidly fades. The resulting solution usually contains $(NC)_5FeH_2O^{3-}$ and the oxime of the organic compound. For example it has been suggested that the sequence of reactions in the $(NC)_5FeNO^{2-}$-propanone system are[62,71]:

$$CH_3C(=O)CH_3 + OH^- \rightleftharpoons CH_3C(=O)CH_2^- + H_2O$$

$$(NC)_5FeNO^{2-} + CH_3C(=O)CH_2^- \rightarrow \underset{C}{(NC)_5FeNO[=CHC(=O)CH_3]^{4-}} + H^+$$

$$(NC)_5FeNO[=CHC(=O)CH_3]^{4-} \rightarrow (NC)_5FeH_2O^{3-} + \left\{\begin{matrix} CH_3C(=O)C(=NO)H^{-1} \\ CH_3C(=O)C(=NOH)H \end{matrix}\right\}$$

Since red salts containing species *C* have been isolated, this anion is assumed to give rise to the red coloration in solution. The kinetics of these reactions have been studied by several workers[71,75,76]. The rate of formation of $(NC)_5FeNO[=CHC(=O)CH_3]^{4-}$ is found to be either first-order in the concentrations of propanone[71] and OH^- or propanone[76], OH^- and $(NC)_5FeNO^{2-}$ depending on the concentrations of the reactants. These rate laws are common in reactions involving the enolization of propanone and indicate that the enolization of prapanone or reaction of the enolate form with $(NC)_5FeNO^{2-}$ is rate determining. In the latter case the bimolecular rate constant for the reaction between $CH_3C(=O)CH_2^-$ and $(NC)_5FeNO^{2-}$ can be calculated if the equilibrium concentration quotient for the enolization of propanone is known. Assuming a value[77] of 10^{-6}, this rate constant is 5×10^5 $M^{-1}sec^{-1}$ at 298 °K and $\mu = 1.0$ (NaCl, NaOH)[76]. This is large compared to analogous rate constants in the OH^- (0.55 $M^{-1}sec^{-1}$) and HS^- (170 $M^{-1}sec^{-1}$) systems.

The kinetics of the decomposition of $(NC)_5FeNO[=CHC(=O)CH_3]^{4-}$, species *C*, have been studied for propanone as well as the analogous reactions in the butanone and 3-pentanone-$(NC)_5FeNO^{2-}$ systems[76]. The rate law in the propanone case is $-d[C]/dt = k[C]$. If k is assumed to be $k_1[H_2O]$, $k_1 = 2.9 \times 10^{-4}$ $M^{-1}sec^{-1}$ (298 °K, $\mu = 1.0$ NaCl), $\Delta H^{\ddagger} = 17.8$ kcal/mole and $\Delta S^{\ddagger} = -15$ e.u. However, the rate law in both the butanone and 3-pentanone cases is $-d[C]/dt = k_2[C][OH^-] + k_3[C][OH^-]$[ketone], indicating that either OH^- or the enolate form of the ketone can displace the ligand from species *C*. In the butanone case $k_2 = 0.65$ $M^{-1}sec^{-1}$ and $k_3 = 3.3$ $M^{-1}sec^{-1}$, and for the 3-pentanone case $k_2 = 0.50$ $M^{-1}sec^{-1}$, $\Delta H^{\ddagger} = 8.8$ kcal/mole, $\Delta S^{\ddagger} = -30$ e.u. and $k_3 = 8.4$ M^{-1}-

TABLE 4

REACTIONS OF $(NC)_5FeNO^{2-}$ WITH BASIC LIGANDS

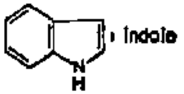
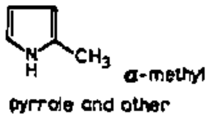
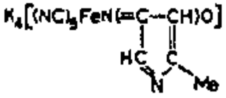
Reactant	*Intermediates*[a] *Isolated*	*Products*[b]	*Ref.*
$CH_3C(=O)CH_3$	$Na_4[(NC)_5FeC_3H_4O_2N]$-red	$CH_3C(=O)C(=NOH)H$	62, 66, 70, 44
$CH_3C(=O)C_6H_5$	$Na_4[(NC)_5FeC_8H_6O_2N] \cdot H_2O$-red	$HC(=NOH)C(=O)C_6H_5$	63, 44, 71
$CH_3C(=O)C_6H_4Br$	$Na_4[(NC)_5FeC_8H_5BrO_2N] \cdot H_2O$-red	$HC(=NOH)C(=O)C_6H_4Br$	63, 44, 71
$CH_3C(=O)CH_2C(=O)CH_3$	$Na_4[(NC)_5FeC_5H_6O_3N]$-red	$CH_3C(=O)C(=NOH)C(=O)CH_3$[c]	63
$CH_3C(=O)C(=O)OH$	red salt	$CH(=NOH)C(=O)C(=O)OH$	64
$NCCH_2C(=O)OCH_2CH_3$	unstable red salt	$NCC(=NOH)C(=O)OCH_2CH_3$	64
$NCCH_2C_6H_5$[d]	unstable red salt	$NCC(=NOH)C_6H_5$	64
p-$O_2NC_6H_4CH_2CN$	unstable red salt	p-$O_2NC_6H_4C(=NOH)CN$	64
$CH_3C(=O)CH_2C(=O)OH$	—	red coloration	66, 67
C_6H_5NHOH	—	—	64
CH_3CH_2NO	—	ethylnitrolic acid	64
 indole	$K_4[(NC)_5Fe(C_8H_6ON_2)]$-violet $K_3[(NC)_5Fe(C_8H_7ON_2)]$-indigo	—	64
α-methylindol	red salt	—	64
$NH_2C(=S)NH_2$	$(NC)_5Fe^{II}X$, X = nitrosothiocarbamic acid	—	65, 49
derivative of thiourea	red-violet salts	—	44
 α-methyl pyrrole and other derivatives		—	68

TABLE 4 *(continued)*

Reactant	*Intermediates*[a] *Isolated*	*Products*[b]	*Ref.*
HC(=O)H	$Na_6[(NC)_5FeN(OH)C(OH)NOFe(CN)_5]$	—	70, 73
Thiamine (Vitamin B_1)	—	green solution	69
$(O_2N)_2C_6H_4$	—	violet-red coloration	70
RCH_2NHCH_2-R′	—	blue to violet-base	72
α, β, γ diketones	—	red coloration	44
carvone, pulegone, ionone, citral, piperazine, piperidine, uracil, 4-methyl uracil, 5-methyl uracil and allantoin	—	—	44
pyrocatechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol and hydroxyhydroquinone	—	green solution – base blue solution – acid	44
phenylhydrazones, $PhNHNH_2$, and glucose	—	—	74

[a] Intermediates usually isolated from methanol.

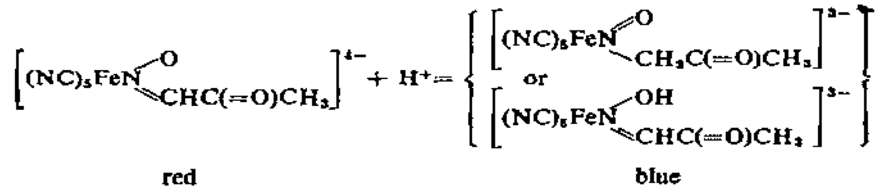
[b] $(NC)_5FeH_2O^{3-}$ formed in most cases.

[c] Decomposes to $CH_3C(=O)OH$ and $CH_3C(=O)C(=NOH)H$ in base.

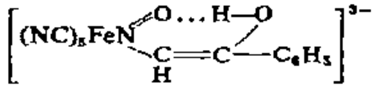
[d] Other derivatives of $C_6H_5CH_2CN$ give similar results.

$\sec^{-1}$, $\Delta H^* = 5.0$ kcal/mole. All rate constants are at 298 °K and $\mu = 0.5$ NaCl.

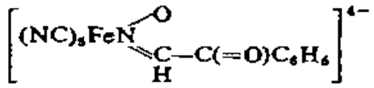
When species C is treated with acetic acid the solution becomes blue-violet[62]. The equilibrium involved is thought to be[63,71]



The same type of equilibrium has been proposed to account for the variation in color with pH for a number of $(NC)_5FeNO^{2-}$-ketone systems[63]. Cambi and his coworkers first investigated the acetophenone-$(NC)_5FeNO^{2-}$ system and proposed an equilibrium between species analogous to those described above to account for the pH dependent color changes observed. An infrared investigation has been made on salts of the blue acetophenone complex[71]. On the basis of a medium strength band at 1930 cm^{-1} corresponding to the nitrosyl absorption and a weak carbonyl band at 1684 cm^{-1} the following structure was suggested:

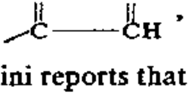


Salts of the red form show no N=O absorption, but bands corresponding to NO^- at 1175 cm^{-1} and 1155 cm^{-1} are observed. The suggested structure is:



It would be interesting to have an X-ray analysis of these and related salts in order to confirm these structures.

Pavolini[44] has studied a wide variety of reactions between $(NC)_5FeNO^{2-}$ and organic compounds. Aldehydes and ketones which are α, β unsaturated readily react with $(NC)_5FeNO^{2-}$ (ionone and citral) while ketones which are not α, β unsaturated do not react (menthone and citronellal). Reactions also occur between molecules having the group

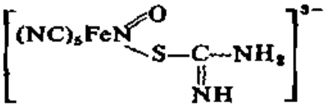


, and $(NC)_5FeNO^{2-}$.

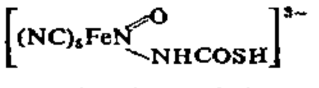
Pavolini reports that α-methyl iodole does not react, but other workers report that it does[64]. Some aromatic dinitroderivatives, m-dinitrobenzene, and polyhydric phenols react (see Table 4, page 394).

Thiourea[65,49] and derivatives of thiourea[44] react with $(NC)_5FeNO^{2-}$. It has been suggested that the structure of the ion resulting when the thiourea-$(NC)_5$-

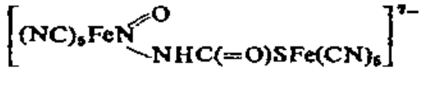
$FeNO^{2-}$ reaction is carried out in methanol with sodium methoxide present is[65]:



Cambi made a complete study of the reaction[49]. Nitrogen was evolved and the Fe:N ratio of the product was 1:7. By analogy with the reaction of NO_2^- with thiourea, where N_2 and SCN^- are produced by way of NH_2COSH, Cambi postulated that the product contains:



If the reaction is carried out in methanol with sodium methoxide present an orange-yellow salt is also formed. The salt is postulated to contain:



It would be interesting to have both chemical and X-ray work done on these salts to unequivocally determine their structures.

D. OXIDATION–REDUCTION PROPERTIES

The reduced forms of $(NC)_5FeNO^{2-}$ offer an opportunity to study the chemical properties of unusual oxidation states of nitrogen bound to an iron center.

(i) Polarographic studies

A polarographic study of $(NC)_5FeNO^{2-}$ has been carried out by Kolthoff and Toren[38]. At the dropping mercury electrode $(NC)_5FeNO^{2-}$ gives three reduction waves. The first two waves involve one electron each as calculated from the n in Ilkovic's equation, are independent of the hydrogen ion concentration in the pH range 6 to 10, and are reversible. The third wave is irreversible, and the value of n is 1.2 at pH 5.9_5 and 2.3 at pH 9.0_2. The first two reductions are postulated to correspond to the reactions:

$$(NC)_5FeNO^{2-} + e = (NC)_5FeNO^{3-}$$
$$(NC)_5FeNO^{3-} + e = (NC)_5FeNO^{4-}$$

where these species may be protonated.

Salts of $(NC)_5FeNO^{3-}$ have been prepared[78] and the ion will be discussed in detail later (see section D-*ii*, page 398). The $(NC)_5FeNO^{4-}$ ion has been reported, but is not well characterized[78]. Kolthoff and Toren suggested the possibility of the second wave corresponding to the decomposition of $(NC)_5FeNO^{4-}$ yielding $H_2N_2O_2$ ($N_2O_2^{2-}$ in this pH region) and $(NC)_5FeOH^{4-}$. However it is unlikely that this reaction would be reversible. Therefore it seems probable that the nitroxyl radical, NOH, or its anion, NO^-, can be stabilized on an iron(II) atom. The reaction corresponding to the third reduction wave has not been established, but it occurs at −1.2 volts *vs.* S.C.E., while the first two waves occur at −0.4 and −0.6 volts *vs.* S.C.E. The $(NC)_5FeNO^{2-}$ ion is not oxidized at a platinum electrode.

Another polarographic study of $(NC)_5FeNO^{2-}$ reports that the second and third waves involve two and four faradays per mole[79] of $(NC)_5FeNO^{2-}$.

(ii) The $(NC)_5FeNO^{3-}$ and $(NC)_5FeNOH^{2-}$ ions

The pK of $(NC)_5FeNOH^{2-}$ in water has been determined to be 6.5 ± 0.2 at 293 °K by spectral measurements[80]. Aqueous solutions containing $(NC)_5FeNOH^{2-}$ are blue (absorbance maximum at 625 mμ), and $(NC)_5FeNO^{3-}$ are yellow-brown (absorbance maximum at 450 mμ). Magnetic susceptibility measurements on aqueous solutions containing the one-electron reduction product of $(NC)_5FeNO^{2-}$ (probably $(NC)_5FeNOH^{2-}$) prepared by adding NO to $(NC)_5FeNH_3{}^{3-}$ in excess acetic acid indicate that the ion has one unpaired electron[81]. On the basis of chemical evidence such as *(i)* aqueous OH^- reacts in the absence of air to give $(NC)_5FeH_2O^{3-}$ and *(ii)* CN^- reacts to give $Fe(CN)_6{}^{4-}$ it is proposed that the odd electron is localized on the NO moiety[5]. However, this evidence does not unequivocally preclude the possibility of the unpaired electron being localized on the iron center.

Manoharan and Gray have discussed the electronic structure of $(NC)_5FeNO^{3-}$ (see B-*ii*, page 386). They suggest that the unpaired electron lies in a molecular orbital of primarily π^*NO character (72.53% π^*NO) containing some d_{xy}, d_{yz}, d_{zx}, σCN, πCN and π^*CN contributions. It is suggested that the ^{13}C splitting observed by some workers supports this assignment[82,83]. An analysis of the electron spin resonance (ESR) spectrum of $(NC)_5FeNO^{3-}$ indicates that the unpaired electron density is in a π^*NO orbital with less than 8% of the spin density on the iron[84].

ESR studies of the spectrum of $(NC)_5FeNOH^{2-}$ in *N,N*-dimethylformamide (DMF)–acetic acid at room temperature and 77 °K have been carried out[80]. The spectrum is essentially identical to those obtained by electrolytic reduction of $(NC)_5FeNO^{2-}$ in DMF and attributed[82,85,86] to $(NC)_5FeNO^{3-}$. Hockings and Bernal[82] observed their solutions to be blue with an absorbance band at 16,500 cm^{-1} (607 mμ, $\varepsilon_{max} = 1500\ M^{-1}cm^{-1}$) and another band, not clearly resolved, at 25,000 cm^{-1} (400 mμ, $\varepsilon_{max} = 5000\ M^{-1}cm^{-1}$). The same spectrum was obtained when $(NC)_5FeNO^{2-}$ was photo-irradiated in DMF. ESR experiments have been carried out on 2-Mev electron irradiated powders[17] of $Na_2[(NC)_5FeNO]\cdot 2H_2O$ and γ-irradiated single crystals[87] of $Na_2[(NC)_5FeNO]\cdot 2H_2O$. On the basis of the latter work and related work on electrolytically reduced $(NC)_5FeNO^{3-}$ in DMF (blue solution) it has been suggested that the spin density on the nitrogen of the nitrosyl group is 7.4% and that the unpaired electron density resides primarily in a $3d_{z^2}$ orbital[14,88]. This means that the ordering of the d orbitals is d_{xz}, d_{yz} <

$d_{xy} < d_{z^2} < d_{x^2-y^2}$ and the π^*NO orbital is less stable than the d_{z^2} orbital. Manoharan and Gray have presented persuasive arguments against this assignment[19].

It has also been suggested that metal nitrosyls with one or more electrons in molecular orbitals derived mainly from π^*NO will have a bent M–N–O bond[19]. This has been observed in a X-ray examination[88] of $Co[S_2CN(C_2H_5)_2]_2NO$, but a crystallographic study of salts of the reduced form of $(NC)_5FeNO^{2-}$ still remain to be carried out.

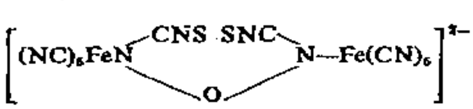
(iii) Photochemical reactions

In the presence of light $(NC)_5FeNO^{2-}$ undergoes numerous reactions, many of which are undefined. It is reported that irradiation of a neutral solution of $(NC)_5FeNO^{2-}$ results in a pH decrease, which increases to nearly the original value when irradiation ceases[89]. The action of direct sunlight on $(NC)_5FeNO^{2-}$ ultimately yields Berlin blue, HCN and NO[56]. The immediate products of the photodecomposition of $(NC)_5FeNO^{2-}$ are apparently[90] NO and $(NC)_5FeH_2O^{3-}$. It is reported that $(NC)_5FeNO^{2-}$ is photoreduced in aqueous solution[5] to $(NC)_5FeNO^{3-}$. No blue coloration, $(NC)_5FeNOH^{2-}$, is observed when $(NC)_5FeNO^{2-}$ is irradiated with moderate intensity light in water over long periods of time. However, when $(NC)_5FeNO^{2-}$ is irradiated in the presence of thiocyanate[91], thiosulfate[92], thiourea[90] and aniline[93], to name a few, a blue color develops.

In the thiocyanate case the color does not develop if irradiated (normal tungsten light) SCN^- is mixed with fresh $(NC)_5FeNO^{2-}$ or *vice versa.* Since SCN^- begins to absorb in the ultraviolet at 280 mμ (thiourea 320 mμ) and there is no transmission through pyrex below 360 mμ, the observed reaction must result from the immediate products of the excitation[60] of $(NC)_5FeNO^{2-}$. It has been proposed that the blue coloration in the irradiated $(NC)_5FeNO^{2-}$–SCN^- case is due to

$$\left[(NC)_5FeNO\begin{matrix}OH\\CNS\end{matrix}\right]^{3-}$$

and that by cleavage of water the ion is converted to a green complex[90,91]



$$\left[(NC)_5FeN\begin{matrix}CNS\ SNC\\O\end{matrix}N—Fe(CN)_5\right]^{3-}$$

However, there appears to be no firm evidence to support these assignments[94]. The spectrum for the blue species formed is the same for both thiocyanate and thiourea ($\lambda_{max} = 580$–590 mμ)[60]. The maximum nearly corresponds to that of $(NC)_5Fe^{III}H_2O^{2-}$. The photochemical course of these reactions may be intimately involved with the fact that excitation with low energy light (long wavelength) involves a transition to a molecular orbital containing primarily the antibonding orbital (π^*NO) on the NO^+. A further study of the mechanism of these photochemical reactions would prove extremely interesting.

E. ANALOGOUS OF $(NC)_5FeNO^{2-}$

The $(NC)_5FeNO^{2-}$ ion is one of large number of diamagnetic pentacyanonitrosyl complexes that can be prepared. Table 5 summarizes some of the complexes which have heen prepared; infrared NO stretching frequencies and the % π^*NO character of 6e molecular orbitals are cited, (see B-*ii*, page 386 for spectral designations). Examination of an isoelectronic series: $(NC)_5FeNO^{2-}$, $(NC)_5MnNO^{3-}$ and $(NC)_5VNO^{5-}$, indicates that the NO stretching frequency decreases as the π^*NO character of the 6e molecular orbital increases, which is consistent with a greater tendency for M → π^*NO intramolecular transfer of electronic density in going from iron to vanadium. This tendency should certainly be reflected in the chemical properties of the ion.

TABLE 5

DATA ON DIAMAGNETIC $(NC)_5MNO^{n-}$ COMPLEXES

Complex	*NO stretch* *cm^{-1}*	*% π^*NO* *in 6e level*[99]
$(NC)_5FeNO^{2-}$	1939[24]	24.79
$(NC)_5MnNO^{3-}$	1725[20]	42.22
$(NC)_5CrNO^{4-}$	1515[95]	—
$(NC)_5VNO^{5-}$	1575[96]	76.68
$(NC)_5RuNO^{2-}$	1920[97]	—
$(NC)_5MoNO^{4-}$	1455[98]	—

Some chemical properties of the ruthenium analogue of $(NC)_5FeNO^{2-}$, $(NC)_5RuNO^{2-}$, have been reported[100] and a more thorough investigation of the chemistry of the ion should prove interesting.

REFERENCES

1 L. Playfair, *Proc. Roy. Soc.* (London), 5 (1849) 846; *Phil. Mag.*, 36 (1850) 197; *Liebigs Ann. Chem.*, 74 (1850) 317.
2 P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, 2 (1963) 1043.
3 G. Johansson and W. N. Lipscomb, *Acta Cryst.*, 11 (1958) 594.
4 J. T. Thomas, J. H. Robertson and E. G. Cox, *Acta Cryst.*, 11 (1958) 599.
5 W. P. Griffith, *Quart. Revs.*, 16 (1962) 188.
6 L. E. Orgel, *J. Inorg. Nucl. Chem.*, 2 (1956) 315.
7 I. Bernal and S. E. Harrison, *J. Chem. Phys.*, 34 (1961) 102.
8 H. B. Gray and C. J. Ballhausen, *J. Chem. Phys.*, 36 (1962) 1151.
9 H. B. Gray, I. Bernal and E. Billig, *J. Am. Chem. Soc.*, 84 (1962) 3404.
10 H. B. Gray, P. T. Monoharan, J. Pearlman and R. F. Riley, *Chem. Comm.* (London), (1965) 62.
11 Y. J. Israeli, *Bull. Soc. Chim. France*, 5 (1964) 1145.
12 D. A. C. McNeil, J. B. Raynor and M. C. R. Symons, *Proc. Chem. Soc.* (London), (1964) 364.
13 B. Jezowska-Trzebiatowska, J. Ziolkowski and W. Wojciechowski, *Bull. Acad. Polon. Sci., Sér. Sci. Chim.*, 11 (1963) 567; *Chem. Abstr.*, 60 (1964) 11499.
14 D. A. C. McNeil, J. B. Raynor and M. C. R. Symons, *J. Chem. Soc.*, (1965) 410.

15 H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, 40 (1964) 910.
16 J. Danon, *J. Chem. Phys.*, 41 (1964) 3378.
17 J. Danon, P. A. Muniz and H. Panapucci, *J. Chem. Phys.*, 41 (1964) 3651.
18 B. Jezowska-Trzebiatowska and J. Ziolkowski, *Chem. Zvesti*, 19 (1965) 177; *Chem. Abstr.*, 63 (1965) 1464.
19 P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, 87 (1965) 3340.
20 F. A. Cotton, R. R. Monchamp, R. J. M. Henry and R. C. Young, *J. Inorg. Nucl. Chem.*, 10 (1959) 28.
21 F. A. Miller and C. H. Wilkins, *Anal. Chem.*, 24 (1952) 1253.
22 E. F. G. Herington and W. Kynaston, *J. Chem. Soc.*, (1955) 3555.
23 J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 7 (1958) 32.
24 G. Bor, *J. Inorg. Nucl. Chem.*, 17 (1961) 174.
25 L. Tosi and J. Danon, *Inorg. Chem.*, 3 (1964) 150.
26 B. Jezowska-Trzebiatowska and J. Ziolkowski, *Bull. Acad. Polon. Sci. Sér. Sci. Chim.*, 12 (1964) 503.
27 W. Beck and H. S. Smedal, *Z. Naturforsch.*, 20b (1965) 109.
28 E. L. Saier and A. Pozefska, *Anal. Chem.*, 26 (1954) 1079.
29 D. J. Millen and D. Watson, *J. Chem. Soc.*, (1957) 1369.
30 W. P. Griffith, J. Lewis and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 7 (1958) 38.
31 L. H. Jones, *J. Chem. Phys.*, 36 (1962) 1209.
32 L. H. Jones, *Inorg. Chem.*, 2 (1963) 777.
33 E. Fluck, W. Kerler and W. Neuwirth, *Z. Anorg. Allgem. Chem.*, 333 (1964) 235 and references cited therein.
34 J. Danon, *J. Chem. Phys.*, 41 (1964) 3378 and references cited therein.
35 C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 2 (1963) 426.
36 T. A. Turney and G. A. Wright, *Chem. Revs.*, 59 (1959) 497.
37 L. Cambi and L. Szegö, *Atti. Accad. Nazl. Lincei*, 5 (1927) 737; *Gazz. Chim. Ital.*, 58 (1928) 64, 71; *Chem. Abstr.*, 22 (1928) 2722.
38 I. M. Kolthoff and P. E. Toren, *J. Am. Chem. Soc.*, 75 (1953) 1197.
39 P. Zuman and M. Kabát, *Chem. Listy*, 48 (1954) 358.
40 J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, 5 (1966) 573.
41 D. X. West, *Dissertation Abstr.*, 25 (1965) 5552.
42 D. X. West, *J. Inorg. Nucl. Chem.*, 29 (1967) 1163.
43 N. V. Sidgwick, *The Chemical Elements ond Their Compounds II*, Oxford University Press, London, 1950, p. 1345 and references cited therein.
44 T. Pavolini, *Boll. Chim. Farm.*, 69 (1930) 713; *Chem. Abstr.*, 25 (1931) 2933.
45 G. Scagliarini and P. Pratesi, *Atti. Accad. Nazl. Lincei*, 8 (1928) 75; *Chem. Abstr.*, 23 (1929) 573.
46 P. A. Rock and J. H. Swinehart, *Inorg. Chem.*, 5 (1966) 1078.
47 A. A. Frost and R. G. Pearson, *Kinetics and Mechanisms*, 2nd ed., John Wiley and Sons, Inc., New York, N.Y., 1962, p. 145.
48 J. O. Edwards, private communication.
49. L. Cambi, *Atti. Accad. Nazl. Lincei*, 24 (1915) 434; *Chem. Abstr.*, 10 (1916) 1351.
50 G. Scagliarini, *Atti. V. Congr. Nazl. Chim. Pura. Appli. Rome*, 1935, Pt. I (1936) 546; *Chem. Abstr.*, 31 (1937) 3407.
51 G. Scagliarini and G. Avoni, *Atti. Accad. Nazl. Lincei*, 24 (1936) 215; *Chem. Abstr.*, 31 (1937) 4276.
52 J. Vachek, *Pharmazie*, 15 (1960) 707; *Chem. Abstr.*, 57 (1962) 15244.
53 C. Boedeker, *Liebigs Ann. Chem.*, 117 (1861) 193.
54 I. Fages, *Compt. Rend.*, 134 (1902) 1143.
55 W. Moser, R. A. Chalmers and A. G. Fogg, *J. Inorg. Nucl. Chem.*, 27 (1965) 831 and references cited therein.
56 *Gmelin's Handbuch der Anorganischen Chemie, Iron 59B*, Verlag Chemie, GmbH, Berlin, 1938, p. 903.
57 A. G. Fogg, A. D. Jones and W. Moser, *J. Inorg. Nucl. Chem.*, 28 (1966) 2428.
58 A. G. Fogg, A. H. Norbury and W. Moser, *J. Inorg. Nucl. Chem.*, 28 (1966) 2753.

59 A. G. Fogg, W. Moser and R. A. Chalmers, *Anal. Chim. Acta*, 36 (1966) 248.
60 J. H. Swinehart, unpublished results.
61 von F. Seel and H. Knorre, *Z. Anorg. Allgem. Chem.*, 313 (1961) 70.
62 L. Cambi, *Atti. Accad. Nazl. Lincei*, 22 (1912) 376; *Chem. Abstr.*, 7 (1913) 2551; *Chem. Zent.*, I (1913) 1756.
63 L. Cambi, *Atti. Accad. Nazl. Lincei*, 23 (1914) 812; *Chem. Abstr.*, 9 (1915) 452; *Chem. Zent.*, II (1914) 1099.
64 L. Cambi, A. Cagnasso and T. Ricci, *Gazz. Chim. Ital.*, 61 (1931) 3; *Chem. Abstr.*, 25 (1931) 2383.
65 K. A. Hoffmann, *Liebigs Ann. Chem.*, 311 (1900) 28.
66 N. O. Engfeldt, *Biochem. Z.*, 159 (1925) 257; *Chem. Abstr.*, 20 (1926) 927.
67 P. Fischer, *Phar. Zentralhalle*, 75 (1934) 189; *Chem. Abstr.*, 28 (1934) 3433.
68 G. Scagliarini, *Atti. Accad. Nazl. Lincei*, 24 (1936) 294; *Chem. Abstr.*, 31 (1937) 7421.
69 H. Wachsmuth, *J. Pharm. Belg.*, 5 (1950) 300; *Chem. Abstr.*, 45 (1951) 4292.
70 B. v. Bitto, *J. Soc. Chem. Ind.*, 11 (1892) 847.
71 K. W. Loach and T. A. Turney, *J. Inorg. Nucl. Chem.*, 18 (1961) 179.
72 F. Feigl, *Spot Tests in Organic Chemistry*, Elsevier, Amsterdam, 1966, p. 251.
73 R. Brunner, *Z. Anorg. Allgem. Chem.*, 190 (1930) 384.
74 W. Parri, *Giorn. Farm. Chim.*, 73 (1924) 153; *Chem. Abstr.*, 18 (1924) 3564.
75 M. Z. Yampol'skii and B. E. Geller, *Tr. Komis po Analit. Khim.*, 13 (1963) 78.
76 J. H. Swinehart and W. G. Schmidt, *Inorg. Chem.*, 6 (1967) 232.
77 J. Hine, *Physical Organic Chemistry*, McGraw-Hill Inc., New York, N.Y., 1956, p. 227.
78 K. A. Hoffmann, *Z. Anorg. Allgem. Chem.*, 12 (1896) 146.
79 P. Lanza and A. Corbellini, *Atti Accad. Nazl. Lincei*, 13 (1952) 406; 14 (1953) 65; *Chem. Abstr.*, 47 (1953) 9179.
80 J. D. W. van Voorst and P. Hemmerich, *J. Chem. Phys.*, 45 (1966) 3914.
81 W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, (1958) 3995.
82 E. F. Hockings and I. Bernal, *J. Chem. Soc.*, (1964) 5029.
83 J. Danon, R. P. A. Muniz and A. O. Caride, *J. Chem. Phys.*, 46 (1967) 1210.
84 H. Beinert, D. V. Dervartanian, P. Hemmerich, C. Veeger and J. D. W. van Voorst, *Biochem. Biophys. Acta.*, 96 (1965) 530.
85 I. Bernal and E. F. Hockings, *Proc. Chem. Soc.*, (1962) 361.
86 J. B. Raynor, *Nature*, 201 (1964) 1216.
87 D. A. C. McNeil, J. B. Raynor and M. C. R. Symons, *Proc. Chem. Soc.*, (1964) 364.
88 P. R. H. Alderman, P. G. Owston and J. M. Rowe, *J. Chem. Soc.*, (1962) 668.
89 R. P. Mitra, D. V. S. Jain, A. K. Banerjee and K. V. R. Chari, *J. Inorg. Nucl. Chem.*, 25 (1963) 1263.
90 O. Baudisch, *Science*, 108 (1948) 443.
91 N. Tarugi, *Ann. Chem. Applic.*, 16 (1926) 407; 17 (1927) 519; *Chem. Abstr.*, 21 (1927) 865.
92 A. Casolari, *Rend. Soc. Chim. Ital.*, 5 (1914) 294; *Chem. Abstr.*, 9 (1915) 1435.
93 V. G. Belikov and V. N. Bernshtein, *Sb. Nauchn. Dokl.*, (1960) 38; *Chem. Abstr.*, 59 (1963) 12182.
94 L. Cambi, *Ann. Chim. Applic.*, 17 (1927) 55; *Chem. Abstr.*, 21 (1927) 1941.
95 W. P. Griffith, *J. Chem. Soc.*, (1963) 3286.
96 W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, (1959) 1632.
97 N. M. Sinitsyn and O. R. Zvagintsev, *Dokl. Akad. Nauk. SSSR*, 145 (1962) 109.
98 R. F. Riley and L. Ho, *J. Inorg. Nucl. Chem.*, 24 (1962) 1121.
99 P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, 5 (1966) 823.
100 *Gmelin's Handbuch der Anorganischen Chemie, Ruthenium No. 63*, Verlag Chemie, GmbH, Berlin, 1938, p. 88.