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Properties and Structure of Nitroprusside $[Fe(CN)_5NO]^{2-}$ Ion and Its Reduction and Oxidation Products

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The following nitrosylcyanate iron complexes being the reduction products of the $[Fe(CN)_5NO]^{2-}$ ion were obtained: $Cd[Fe(CN)_5NOH]\cdot 2DMF$, $Cd_2[Fe(CN)_5NO]_3\cdot(formamide)_x$, $K_4Na_2[Fe_2(CN)_{10}(NO)_2]$ and $Na_5[Fe(CN)_5NO_2]$. The complex $Cd[Fe(CN)_5NO]_2\cdot 4H_2O$, the oxidation product of nitroprusside ion, was synthesized. Their magnetic properties, EPR, electronic and infrared spectra were examined. The character of the Fe–ligand bondings, especially of the Fe–NO one was determined and the molecular orbital order was established.

Introduction

The chemical or electrolytic reduction as well as the irradiation with γ-Rays or with electron stream of the diamagnetic nitroprusside lead to the formation of the paramagnetic compounds[1–14].

Their structure, not always properly identified, was up to now studied mainly by the EPR method and the results were interpreted in terms of analogies with any of the possible structures of nitroprusside.

Hockins and Bernal[4–5] who studied by the EPR method the electrolytic reduction product of nitroprusside in dimethylformamide (blue compound) assigned by them with the formula $[Fe(CN)_5NO]^{3-}$ proposed the following molecular orbitals order: e^4, b_2^2, b_1^1, a_1, (π *NO). Manoharan and Gray[15] assuming the same composition of that complex, have assigned it the structure with the unpaired electron on the (π* NO) orbital. Griffith[16,17] represented the same opinion. He suggested the following series of compounds: $[Fe(CN)_5NO]^{2-}$, $[Fe(CN)_5NO]^{3-}$ and $[Fe(CN)_5NO]^{4-}$, in which the NO group coordinates subsequently as NO^+, NO^0 and NO^- (or ON). The existence of that last complex was not confirmed, anyway. Van Voorst and co.[18,19] suggest the existence of two forms in the acid–basic equilibrium:

$$\underset{\text{blue compound}}{[Fe(CN)_5NOH]^{2-}} + OH^- \rightleftharpoons \underset{\text{brown compound}}{[Fe(CN)_5NO]^{3-}} \qquad (1)$$

Van Voorst and co. have interpreted the EPR results on the basis of the molecular orbital scheme given by Manoharan and Gray[15]. Many authors[1,6,10,12,20,21] however, doubt about the existence of the protonated form, and consider it to be the $[Fe(CN)_5NO]^{3-}$ ion, with the unpaired electron on the $a_1(d_{z^2})$ orbital. Reynor and Symons[10] oppose the reaction (1) to the reaction

$$[Fe(CN)_5NO]^{3-} + 2\,OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{5-} + H_2O \qquad (2)$$

which is analogous to the known reaction of nitroprusside with OH^- ions[23,24]

$$[Fe(CN)_5NO]^{2-} + 2\,OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + H_2O \qquad (3)$$

The reaction products of nitroprusside $[Fe(CN)_5NOH]^{2-}$, $[Fe(CN)_5NO]^{3-}$ and $[Fe(CN)_5NO_2]^{5-}$ were never isolated in the pure form, and moreover, the conventional research methods, (EPR) were the cause of the controversial opinions about their structure and even about their composition. The nitroprusside oxidation product was not obtained up to the present either. There were some suggestions, however, that during the photolysis of the $[Fe(CN)_5NO]^{2-}$ solution[24] the complex $[Fe(CN)_5NO]^-$ is formed, which may be one of the γ-irradiation products of nitroprusside[25]. In the reported work we have obtained and isolated all the reduction and oxidation products of nitroprusside in the solid phase. We have employed several methods, such as magnetic measurements, EPR, electronic and vibrational spectroscopy as well as reactivity measurements by the isotopic exchange method, which allowed us to obtain the model of structure and bonding of the NO group in iron nitrosylcyanate complexes, consistent with the experiments.

Experimental

Synthesis

Electrolytic reduction products of the $[Fe(CN)_5NO]^{2-}$ ion

Synthesis of $Cd[Fe(CN)_5NOH]\cdot 2DMF$. The 5×10^{-3} m/l $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ solution in dimethylformamide (DMF) was reduced on the mercury catode with tetraethylammonium chloride as the basic electrolyte. As the result of the monoelectronic reduction the blue compound $[Fe(CN)_5NOH]^{2-}$ is formed, mistakenly determined by the authors[5] as $[Fe(CN)_5NO]^{3-}$. From the reduced solution the blue cadmium salt $Cd[Fe(CN)_5NOH]\cdot 2DMF$ was isolated by the CdI_2 in DMF. In the case of higher electrolytic solution concentrations the needed cadmium salt was isolated with the CdI_2 solution in DMF, with the acetic acid added. After filtration, the complex salt was washed with alcohol and ether and dried under vacuum. Reduction and other operations were performed under argon atmosphere. *Analysis:* found, % Fe 11.91, % CN 27.10, % Cd 23.44; calcd. for $Cd[Fe(CN)_5NOH]\cdot 2DMF$, 11.74, 27.33, 23.64.

Synthesis of $Cd_3[Fe(CN)_5NO]_2\cdot(formamide)_x$. The monoelectronic reduction on the mercury electrode of the $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ solution in formamide (concentration over 10^{-3} m/l) gives rise to the formation of the brown compound $[Fe(CN)_5NO]^{3-}$. The tetraethylammonium chloride was used as the basic electrolyte.

From the reduced solution the brown salt $Cd_3[Fe(CN)_5NO]_2\cdot(formamide)_x$ was isolated using the CdI_2 in formamide. The salt was next filtered off, washed with alcohol and dried under vacuum. The reduction and all other operations were carried out under argon atmosphere. The amount of the bonded formamide molecules was not stoichiometric. From the analysis the Cd:Fe:CN = 2.88:2:10.1 ratio was determined, which confirmed the composition of the compound.

Synthesis of $Na_6[Fe_2(CN)_{10}(NO)_2]$ and $K_4Na_2[Fe_2(CN)_{10}(NO)_2]$. $Na_6[Fe_2(CN)_{10}(NO)_2]$ and $K_4Na_2[Fe_2(CN)_{10}(NO)_2]$ were obtained by the monoelectronic reduction of the nonaqueous sodium nitroprusside in nonaqueous methanole on the mercury cathode. Well dried NaI or KI were used as the basic electrolytes (sodium salt or potassium–sodium salt were obtained, respectively). During reduction the brown precipitate settled down, which was filtered off, washed with the mixture of nonaqueous methanol and ethanol, and finally only with nonaqueous ethanol. The precipitate was dried under vacuum. The reduction and all other activities were performed under argon atmosphere. *Analysis:* calcd. for $Na_6[Fe_2(CN)_{10}(NO)_2]$, % Na 24.22, % Fe 19.60, % CN 45.72; found, 24.51, 19.48, 45.66. Calcd. for $K_4Na_2[Fe(CN)_{10}(NO)_2]$, % Na 7.19, % K 24.85, % Fe 17.33, % CN 40.92; found, 41.01, 7.26, 24.66, 17.62.

Products of the nitroprusside with sodium amalgam or with the metallic sodium

Synthesis of $Na_5[Fe(CN)_5NO_2]$ and $Na_4[Fe(CN)_5NO(OCH_3)]$. During reduction of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ in methanol and of non-aqueous $Na_2[Fe(CN)_5NO]$ in non-aqueous methanol with sodium amalgam or with metallic sodium the yellow precipitates liberated. The precipitates were filtered off, washed with methanol and dried under vacuum. All activities were performed under argon atmosphere. On the basis of the EPR and IR spectra the compound formed from the hydrated initial compounds was assigned the formula $Na_5[Fe(CN)_5NO_2]$, and the compound formed in the non-aqueous medium was assigned the formula $Na_4[Fe(CN)_5NO(OCH_3)]$. We failed, however, in preparing these compounds in the pure form.

Oxidation products of the $[Fe(CN)_5NO]^{2-}$ion

Synthesis of $[Fe(CN)_5NO]^-$ and $Cd[Fe(CN)_5NO]_2\cdot 4H_2O$. $K_2Na[Fe(CN)_5NO_2]$, formed in the oxidation reaction of sodium nitroprusside with the potassium hypermanganate in basic medium[26] was used as the substrate. The fixed amount of $K_2Na[Fe(CN)_5NO_2]\cdot H_2O$ was dissolved in small volume of water. Next, the nitric acid was added to the solution under mixing, until change of its colour from red to yellow. The formed $[Fe(CN)_5NO]^-$ ion is unstable in the strongly acid solution. To enhance the stability of a complex in the solution the pH should be increased over 4.

Cadmium salt of the $[Fe(CN)_5NO]^-$ ion was precipitated fast from the strongly acid solution with the cadmium nitrate excess.

The precipitate was filtered off, washed with water and alcohol and dried in the dessiccator over P_2O_5. Reaction was carried out and the product was stored in the darkness because of the sensitivity to the light of the complex formed. *Analysis:* calcd. for $Cd[Fe(CN)_5NO]_2\cdot 4H_2O$, % Fe 18.12, % CN 42.21, % Cd 18.24; found, 18.01, 42.09, 18.41.

Dehydration of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$. The non-aqueous sodium nitroprusside was obtained by dessiccation of the powdered $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ in the vacuum dryer at 100° C, for about 2 weeks. The dryness was checked by the spectroscopic methods in infrared.

Dehydration of CH_3OH and C_2H_5OH. Methyl and ethyl alcohols were initially dehydrated with calcium oxide, and next with metallic magnesium. The resulting dehydrated alcohols contain 10^{-4} % water, according to Lund and Bjerrum[27].

Magnetic and Spectroscopic Measurements

For the magnetic susceptibility measurements the Gouy method was employed at four field intensities, over the temperature range 77°–300° K.

The EPR spectra were measured on a JES-ME-3X JEOL spectrometer. To the temperature measurements the standard VT-3 unit was applied. The studies were performed over the temperature range 100°–300° K.

The absorption spectra were measured in the range 50,000–10,000 cm^{-1}, on the recording UNICAM-SP-700 spectrophotometer.

The IR spectra were measured in the range 700–4000 cm^{-1} in KBr mulls and in the slurry in nujol, on the Perkin–Elmer 121 spectrophotometer.

Results and Discussion

Structure and Properties of the Reduction Products of the $[Fe(CN)_5NO]^{2-}$ Ion

Electrolytic reduction of sodium nitroprusside – depending on the reaction conditions – leads to the formation of $[Fe(CN)_5NOH]^{2-}$ and $[Fe(CN)_5NO]^{3-}$ ions, isolated in the form of cadium salts $Cd[Fe(CN)_5NOH]$ 2DMF and $Cd_3[Fe(CN)_5NO]_2 \cdot (formamide)_x$ or gives rise to the formation of $K_4Na_2[Fe_2(CN)_{10}(NO)_2]$ or $Na_6[Fe_2(CN)_{10}(NO)_2]$. Reduction of the methanol solutions of $Na_2[Fe(CN)_5NO]$ with sodium amalgam or with metallic sodium gives rise to the formation of two compounds, $Na_5[Fe(CN)_5NO_2]$ and $Na_4[Fe(CN)_5NO(OCH_3)]$. All the reduction products of the $[Fe(CN)_5NO]^{2-}$ ion are paramagnetic, their magnetic moments corresponding to one unpaired electron (Table I, Figure 1).

Low value of the magnetic moment of complexes $Na_5[Fe(CN)_5NO_2]$ and $Na_4[Fe(CN)_5NO(OCH_3)]$ may be caused by their instability and hence by the presence of diamagnetic decomposition products, *e.g.* $Na_4[Fe(CN)_5NO_2]$. Nevertheless, the magnetic moments and the EPR spectra (Table II) confirmed the existence of the paramagnetic bondings $Na_5[Fe(CN)_5NO_2]$ and $Na_4[Fe(CN)_5NO(OCH_3)]$.

In the IR spectra of these compounds over the range 700–2100 cm^{-1} no vibrations beside the frequencies characteristic for NO_2 and CN groups were observed. In the case of $Na_4[Fe(CN)_5NO(OCH_3)]$ the frequency derivating from the OCH_3 group was stated (Table III).

That proved the assumed structures to be correct.

The EPR[28] spectra of $[Fe(CN)_5NOH]^{2-}$ ions in dimethylformamide (blue compound) and of $[Fe(CN)_5NO]^{3-}$ ion in formamide (brown compound) are identical at room temperature. Identical are also the powder spectra of their cadmium salts at 300–100° K. The Hamiltonian spin parameters for these complexes are gathered in Table II.

TABLE I. Magnetic Moments of the Reduction and Oxidation Products of Nitroprusside.

Compound	μ_{eff}(BM)	Θ °K^a
$Cd[Fe(CN)_5NOH] \cdot 2DMF$	2.30	–31
$K_4Na_2[Fe_2(CN)_{10}(NO)_2]$	1.96	–44
$Na_5[Fe(CN)_5NO_2]$	0.8	–
$Na_4[Fe(CN)_5NO(OCH_3)]$	0.9	–
$Cd[Fe(CN)_5NO]_2 \cdot 4H_2O$	1.74	–43

^{a}The Θ value was determined from the relationship $1/\chi_M$ = f(T) over the range in which the Curie–Weiss law is obeyed.

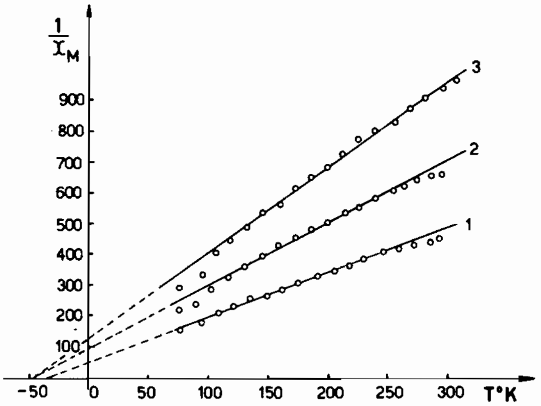


Figure 1. Relation $1/\chi_m$ = f(T) for (1) $Cd[Fe(CN)_5NOH] \cdot 2DMF$, (2) $K_4Na_2[Fe_2(CN)_{10}(NO)_2]$ and (3) $Cd[Fe(CN)_5NO]_2 \cdot 4H_2O$.

These parameters proved the unpaired electron density to be localized mainly on the $a_1(d_{z^2})$ iron orbital[2,3,6–12,21,28]. That conclusion is in full agreement with the results of the infrared spectra of these compounds[32]. Small changes in valence vibration frequency of the NO group, when compared with those of nitroprusside (Table III) indicate the additional electron to be localized mainly on iron orbitals. The lowering of the frequency as well as the decay of the ν^{CN}_{ax} in comparison with ν^{CN}_{equ} proved that orbital to be $a_1(d_{z^2})$. The weakening of the σ bondings along the "z" axis is the further consequence. The σ-donor properties of cyanates, stronger that those of the NO group, cause the greater weakening of the Fe–CN$_{ax}$ bonding than of the Fe–NO one. The considerable lowering of the ν^{CN}_{ax} frequency, when compared with the ν^{NO} at the transition from $[Fe(CN)_5NO]^{2-}$ to $[Fe(CN)_5NO]^{3-}$ and to $[Fe(CN)_5NOH]^{2-}$ (Table III) as well as the increased kinetic mobility of the CN$_{ax}$ groups in the reaction products of nitroprusside[30] fully confirmed our arguments.

The examination of the IR spectra of $Cd[Fe(CN)_5NOH] \cdot 2DMF$ with substituted ^{15}N in the NO group[32] proved the bands at 1798 cm^{-1} and 1778 cm^{-1} (Table III) to derive from the vibrations of the NO group. Those frequencies were attributed to the deformation vibrations of the NOH group. Anyway, the interaction of two adjacent NOH group in the mode given below cannot be excluded:

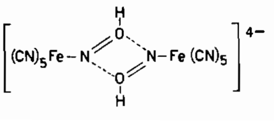


TABLE II. Spin Hamiltonian Parameters of the Reduction Products of Nitroprusside.

Compound	T °K	Spin Hamiltonian Parameters[a]
$[Fe(CN)_5NOH]^{2-}$ in DMF solution	293	$g_{av} = 2.024$ $A_{av} = 15.1$
	100	$g_{\perp} = 2.031, g_{\parallel} = 2.005, A_{\perp} = 14.1, A_{\parallel} = 17.0$
$Cd[Fe(CN)_5NOH]\cdot 2DMF$ powder spectrum of diluted $Cd[Fe(CN)_5NO]$	100	$g_{\perp} = 2.031, g_{\parallel} = 2.005, A_{\perp} = 14.1, A_{\parallel} = 17.0$
$Cd_3[Fe(CN)_5NO]_2\cdot$(formamide)$_x$ powder spectrum of diluted $Cd[Fe(CN)_5NO]$	100	$g_{\perp} = 2.031, g_{\parallel} = 2.006, A_{\perp} = 14.3, A_{\parallel} = 17.1$
$[Fe(CN)_5NO]^{3-}$ in formamide + CH_3COOH solution	293	$g_{av} = 2.024, A_{av} = 15.1$
	100	$g_{\perp} = 2.031, g_{\parallel} = 2.005, A_{\perp} = 14.1, A_{\parallel} = 17.0$
$[Fe(CN)_5NO]^{3-}$ in formamide solution	293	$g_{av} = 2.024, A_{av} = 15.2$
	100	$g_1 = 1.93, g_2 = g_3 = 2.01$
$Na_5[Fe(CN)_5NO_2]$ powder spectrum	77	$g_1 = 1.9282, g_2 = 1.9993, g_3 = 2.008$ (ref. 10)
	100	$g_1 = 1.93, g_2 = g_3 = 2.01$
$K_4Na_2[Fe_2(CN)_{10}(NO)_2]$ powder spectrum	100	$g_{av} = 1.98$

[a] Tensor components A(^{14}N) in Gauss ($\bar{\nu}$ = 9.20 GHz).

In such a case also two valency vibration frequencies of the NO group should be expected, $\nu^{NO}_{as} = 1925$ cm^{-1} and $\nu^{NO}_{s} = 1798$ cm^{-1}.

The studies on the electronic absorption spectra of complexes $[Fe(CN)_5NOH]^{2-}$ and $[Fe(CN)_5NO]^{3-}$ indicated their acid–basic equilibrium according to the reaction 1.

The absorption spectrum of the formamide solution of $[Fe(CN)_5NO]^{3-}$ (brown solution) turned to be identical with that of $[Fe(CN)_5NOH]^{2-}$ in dimethylformamide (blue solution) after the acetic acid was added (Table IV).

The results of the above reported investigations allow us to consider the bands of the smaller wavenumbers in the absorption spectra of complexes $[Fe(CN)_5NO]^{3-}$ and $[Fe(CN)_5NOH]^{2-}$ (Table IV), as the transitions of electrons from orbitals $a_1(d_{z^2})$ to orbitals (π^* NO).

The acid-basic equilibrium between the examined compounds was confirmed also by the electron paramagnetic rezonance spectra[28]. The EPR spectra of the frozen solutions of $[Fe(CN)_5NOH]^{2-}$ and $[Fc(CN)_5NO]^{3-}$ in DMF and in formamide with CH_3COOH are identical (Table III). Whereas, during the freezing of the $[Fe(CN)_5NO]^{3-}$ formamide solution without H^+ ions, the changes in the EPR spectrum are observed. The spectrum obtained at 120° K differs from the powder spectrum of cadmium salt of that ion, but is identical with EPR spectra of complexes $Na_4[Fe(CN)_5NO(OCH_3)]$ and $Na_5[Fe(CN)_5NO_2]$ (Table II). Thus, the acceptor properties for the electron pair of the NO group in the reduced form of nitroprusside similar as in the nitroprusside[29] should be expected, as well as the formation of $[Fe(CN)_5NO(OR)]^{n-}$, resulting from interaction with a solvent (OR–formamid or its part capable to the coordination via the oxygen atom). The spin Hamiltonian parameters (Table II) calculated from the EPR spectra are in good agreement with the assumption about the unpaired electron density to be localized mainly on the nitrogen atom of either NO_2[10,11,12,28] or NO(OR) group[28].

The molecular orbital order proposed by us for complexes of the type $[Fe(CN)_5NO_2]^{n-}$ at assumption of the C_{4v} symmetry will be as follows: $b_2(d_{xy})$, $e(d_{xz},d_{yz})$, (π^* NO_2), $b_1(d_{x^2-y^2})$, $a_1(d_{z^2})$, (π^* CN).

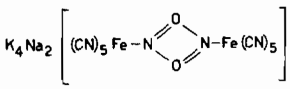
Such molecular orbitals order we have established from the absorption and vibrational spectra of the series of iron(II) and iron(III) complexes of the type $[Fe(CN)_5X]^{n-}$ [X = NO_2^-, H_2O, pyridine, NH_3, *etc.*[32]].

The properties of the NO group observed in [Fe

TABLE III. Frequencies of IR Absorption Spectra of Reduction and Oxidation Products of Nitroprusside.

Compound	Frequencies Observed (cm^{-1})	Assignements
Cd[Fe(CN)$_5$NOH]·2 DMF	2173 vs 2149 vs	ν^{CN}_{equ}
	2077 s	ν^{CN}_{ax}
	1925 vs 1910 sh	ν^{NO}
	1798 m 1778 m	ν^{NOH}
Cd$_3$[Fe(CN)$_5$NO]$_2$·formamide	2135 s 2110 s	ν^{CN}_{equ}
	2072 vs	ν^{CN}_{ax}
	1920 vs	ν^{NO}
Cd[Fe(CN)$_5$NO]·2H$_2$O	2172 m 2158 m	ν^{CN}_{equ}
	2141 s	ν^{CN}_{ax}
	1935 vs	ν^{NO}
Cd[Fe(CN)$_5$NO]$_2$·4H$_2$O	2180 vs	ν^{CN}_{equ}
	2162 vs	ν^{CN}_{ax}
	1960 vs	ν^{NO}
K$_4$Na$_2$[Fe$_2$(CN)$_{10}$(NO)$_2$]	2105 vs	ν^{CH}_{equ}
	2040 vs	ν^{CN}_{ax}
	1610 vs, sh	ν^{NO}_{as}
	1589 vs	ν^{NO}_{s}
Na$_5$[Fe(CN)$_5$NO$_2$]	2022 sh, 2040 vs	ν^{CN}
	1277 s	$\nu^{NO_2}{}_{as}$
	1239 s	$\nu^{NO_2}{}_{s}$
	840 m	δ^{NO_2}
Na$_4$[Fe(CN)$_5$NO(OCH$_3$)]	2040 vs	ν^{CN}
	1360 s, 1320 s, 1280 s, 1242 s	ν^{NO_2}
	2920, 2845, 1465, 1085, 1005	Vibrations of the OCH$_3$ Group

(CN)$_5$NO]$^{3-}$, such as ability of bonding of the hydrogen ion by the oxygen atom of the NO group and the possibility of nitrogen interaction with oxygen (*e.g.* from a solvent) suggest the following mode of the bonding between two monomers forming the dimer:



Such a bonding of the NO groups results in weakening of the nitrogen–oxygen π-bonding and in appear-

TABLE IV. Electronic Absorption Spectra of Pentacyanonitrosyl Iron Complexes.

Compound	Absorption max. (ε)	Location cm^{-1}	Notes
$[Fe(CN)_5NOH]^{2-}$	2740	30 000 sh	solvents:
	1050	25 000 sh	DMF, formamide + CH_3COOH
	1840	16 500	
$[Fe(CN)_5NO]^{3-}$	3590	36 400	formamide
	2133	28 200	
	540	21 700	
	(245)	17 900 sh	
$[Fe(CN)_5NO]^{1-}$	(12520)	49 000 sh	H_2O; pH = 4.1–7.0
	1194	35 400	
	(693)	31 400 sh	
	730	29 000	
	795	25 100	
$[Fe(CN)_5NO]^{2-}$	24000	50 000	ref.[31]
	700	42 000	
	900	37 800	
	40	30 300	
	25	25 380	
	8	20 080	

ance of two valency vibration frequencies of the NO group, $\nu^{NO}_{as} = 1610\ cm^{-1}$ and $\nu^{NO}_{s} = 1589\ cm^{-1}$, remarkably lowered in comparison with the monomeric form $\nu^{NO} = 1920\ cm^{-1}$ (Table III). Simultaneously, in comparison to the monomeric forms, there is an increase in the contribution of π-orbitals to the Fe–CN bonding; ν^{CN}_{ax} and ν^{CN}_{equ} are lowered from 2077 cm^{-1} and from 2135, 2110 cm^{-1} to 2044 and 2105 cm^{-1}, respectively.

The frequencies ν^{CN}_{equ}, ν^{CN}_{ax}, ν^{FeC} and δ^{FeCN} observed in the IR spectrum of a dimer could be compared with the respective frequencies observed in the infrared spectra of some Fe(II) cyanate complexes, *e.g.* in $Na_4[Fe(CN)_5NO_2]$.[32] That is the result of the enlarged delocalization of the unpaired electron towards the NO group, in comparison with the monomer. Further result is also the lowering of the *g* parameter value calculated from the EPR spectrum of that compound[28] below 2 (Table II). The small exchange integral value causes the relation $1/\chi_M = f(T)$ in the examined temperature range to deviate very little from the straight-line (Figure 1).

The complexes $K_4Na_2[Fe_2(CN)_{10}(NO)_2]$ and $Na_6[Fe_2(CN)_{10}(NO)_2]$ exist in the solid only. It has been stated that the formation of dimers of that type as well as of $[Fe(CN)_5(NO)OR]^{n-}$ is quite important in isotopic exchange reaction mechanisms in the systems: $[Fe(CN)_5NO]^{3-}$–$^{14}CN^-$ and $[Fe(CN)_5NOH]^{2-}$–$^{14}CN^-$ in formamide and dimethylformamide solutions[30]. The absorption spectrum of $K_4Na_2[Fe_2(CN)_{10}(NO)_2]$ in formamide or dimethylformamide solution is the spectrum of the respective monomeric form, depending on the hydrogen ion concentration (Table IV).

Structure and Properties of Oxidation Products of Sodium Nitroprusside

The nitrosylcyanate iron complexes react with OH^- ions (reactions 2 and 3), giving rise to the formation of the respective $[Fe(CN)_5NO_2]^{n-}$ complexes.

To that series of complexes belongs also $[Fe(CN)_5NO_2]^{3-}$ formed in the oxidation reaction of nitroprusside in basic medium. The reactions 2 and 3 suggested the existence of the nitrosylcyanate compound $[Fe(CN)_5NO]^-$ which is the product of nitroprusside oxidation. That compound we succeeded to obtain in the reaction $[Fe(CN)_5NO_2]^{3-} + H_2O \rightarrow [Fe(CN)_5NO]^- + 2OH^-$, whose rate increases considerably with increasing hydrogen ion concentration, and we have isolated it as the salt $Cd[Fe(CN)_5NO]_2 \cdot 4H_2O$. Magnetic properties of that compound indicated the one unpaired electron (Table I, Figure 1) and the IR spectrum confirmed the presence of the NO group ($\nu^{NO} = 1960\ cm^{-1}$, Table III). Small increase of the ν^{NO} frequency in comparison with nitroprusside indicated the oxidation of $[Fe(CN)_5NO]^{2-}$ ion to $[Fe(CN)_5NO]^-$ to be caused by the breaking off of the electron from $b_2(d_{xy})$ orbital. That orbital does not contribute to the Fe–NO π-bonding and is less stable than the $e(d_{xy}, d_{yz})$ orbital. That leads to the decay of the $Fe(CN)_{equ}$ π-bondings and in the consequence to the mobility equivalence of all coordinated cyanate groups[30].

The changes of the respective frequencies in the IR spectra of the series of $[Fe(CN)_5NO]^{n-}$ complexes and the comparison of these spectra with those of the series of iron(II) and iron(III) compounds of the type $[Fe(CN)_5X]^{n-}$ ($X \neq NO$) confirmed the π-acceptor properties of the coordinated cyanates and of the NO group. That was also the proof of the great delocalization of the electron density towards the NO group[32] (because of the d_π–p_π Fe–NO interaction). Hence, the remarkable contribution of the (π^* NO) orbital to the formation of the molecular orbitals of the complex should be concluded.

The molecular orbital scheme calculated for $[Fe(CN)_5NO]^{2-}$ by Fenske[33] proved the π-acceptor character of the summary π-bonding and anti-bonding effect of cyanates and of the NO group on the $2B_2$ and 8E metal orbitals. Hence, their energy with respect to *d* orbitals of the free ion is lowered. σ-donor properties of the CN groups are stronger than those of the NO group, characterised by the stronger π-acceptor properties, and due to this the 8E orbital is more stabile than the $2B_2$ one. On the basis of our studies on the series of cyanonitrosyl iron complexes we have stated the following molecular orbitals order and the electronic configuration of nitroprusside, *i.e.* of the initial product for all the compounds reported here: $[e(d_{xz}, d_{yz}) + (\pi^* NO)]^4$, $b_2(d_{xy})^2$, $a_1(d_{z^2})$, $b_1(d_{x^2-y^2})$, $\pi^*(NO)$, $\pi^*(CN)$.

The total effect of the coordinated CN and NO groups on the e and b_2 metal orbitals is the π-acceptor (Figure 2a). Both the reduction and oxidation processes of nitroprusside do not change either the character or the coordination mode of the NO group. The increase or decay of the electron density caused by these processes is running mainly in the iron ion. Oxidation process of the $[Fe(CN)_5NO]^{2-}$ ion, giving rise to the $[Fe(CN)_5NO]^-$ leads to the loss of electron from the b_2 orbital. The reduction process, which gives rise to the $[Fe(CN)_5NO]^-$, leads to the loss of electron from the b_2 orbital. In the reduction process, which gives rise to the formation of $[Fe(CN)_5NO]^{3-}$ and $[Fe(CN)_5NOH]^{2-}$, the additional electron occupies the a_1 orbital.

From the above molecular orbitals order it follows that in the absorption spectra of complexes $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_5NO]^-$ two first bands of the lowest wavenumber are the transitions from orbitals b_2 to antibonding orbitals a_1^* and b_1^*. The energy of the latter transition is responsible for the $10D_q$ parameter value. Two subsequent bands are also the transitions of the crystal field ($e^b \rightarrow a^*$ and $e^b \rightarrow b_1^*$ and $e^b \rightarrow b_1^*$), and the next bands are the electron transitions from the b_2 to antibonding (π^* NO) orbitals. In the absorption spectrum of the complex $[Fe(CN)_5NO]^-$ the transition $b_2{}^b \rightarrow e$ (π^* NO) is overlapped by the very intense $b_2{}^b \rightarrow e$ (π^* CN) band.

The oxidation of nitroprusside is accompanied by the general stabilization of molecular orbitals with contribution of the metal *d* orbital. However, the simultaneous decay of the $Fe–CN_{equ}$ π-bondings follows, which causes some destabilization of the b_2 orbital in comparison with the energy of the free metal ion (Figure 2a and 2b). However, with the increase of the positive charge at the central ion the greater destabilization of the σ-antibonding b_1^* orbital will follow in comparison with the b_2 orbital. Hence, the $10D_q$ parameter value in $[Fe(CN)_5NO]^-$ should be higher than in $[Fe(CN)_5NO]^{2-}$. The diminished electron number on the central ion diminishes also the possibility of π-interactions along the "z" axis. The stronger acceptor properties of ligands bonded along that axis are the cause, that the destabilization of the $e(\pi^b)$ orbital will be accompanied by the same energy increase on the a_1^* orbital. And that is why the energy difference between those levels in $[Fe(CN)_5NO]^-$ should not be very different from that in $[Fe(CN)_5NO]^{2-}$.

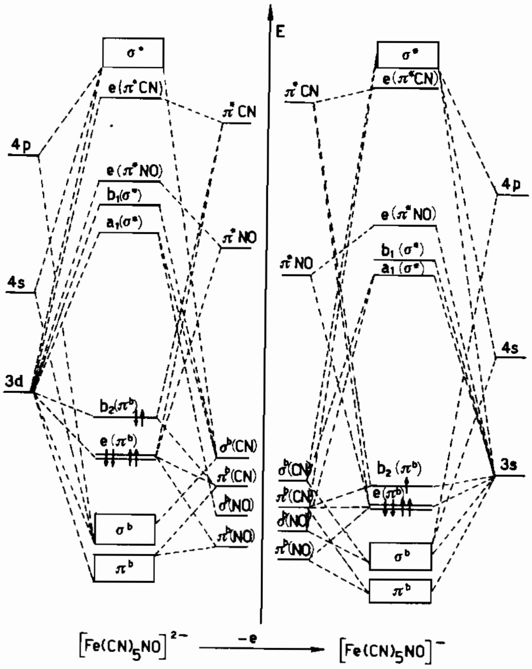


Figure 2. The relative changes of molecular orbitals energy at transition from (a) $[Fe(CN)_5NO]^{2-}$ to (b) $[Fe(CN)_5NO]^-$.

Due to the simultaneous studies on the structure of numerous nitroprusside derivatives and its oxidation and reduction products, we succeeded in explaining the controversial electronic structure of nitrosylcyanate complexes and of the NO group.

We would like also to point out the importance of the application of versatile methods such as electronic absorption spectra, IR, EPR, magnetic susceptibility *etc.* which allow one to explain fully the electronic and molecular structure and the character of bonding. The studies on reactivity of these compounds with application of radioisotopic exchange methods proved also to be important. Only such versatile approach to the problem, and a comparison of the results allowed us to draw the real conclusions and to propose the molecular orbital scheme consistent with the experiments.

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