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On the Reactivity of Tetracyanonitrosylferrate(2−). I. Stereochemically Controlled Intramolecular Electron Transfer

JAN FIEDLER and JIŘÍ MAŠEK

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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Complexes $Fe(chel)(CN)_3NO^-$ (chel = bpy, phen) were prepared from $Fe(CN)_4NO^{2-}$ generated by 1-electron reduction of the nitroprusside ion. The increase of the coordination number from 5 in $Fe(CN)_4NO^{2-}$ to 6 in $Fe(CN)_3(chel)NO^-$ causes an intramolecular electron transfer from Fe to NO group which represents a new example of the stereochemical control of valence.

Introduction

Complexes containing nitrosyl group NO as one of the ‘non-innocent’ ligands have attracted considerable interest in the past. Several attempts have been made to correlate the structure, physical and chemical properties of transition metal nitrosyls with the formal oxidation state of the nitrosyl group. In 1974 Enemark and Feltham [1] developed a method utilizing MO diagrams of molecular fragments MNO placed in different ligand fields which enables us to elucidate to a large extent relationships among structure, bonding and reactivity of metal nitrosyl complexes. Their principle of ‘stereochemical control of valence’ [1] is based on the concept that the overall stereochemistry of the complex can determine the metal-ligand charge distribution, the geometry of MNO moiety and its chemical reactivity. This principle can be extremely useful if the energies of the metal d orbitals and the π^* orbitals of the NO ligand are similar. In such cases the change in the structure of the coordination sphere can evoke the intramolecular metal to nitrosyl or opposite electron transfer which significantly influences the reactivity of the MNDO moiety. From the point of view of homogeneous catalysis, the importance of being able to control the electron density distribution within the complex by means of stereochemical factors, such as *e.g.* coordination number, is evident.

In order to verify the validity of the above principle, we chose $[Fe(CN)_4)NO]^{2-}$ ion as a model system with the electron configuration $\{MNO\}^7$*. $Fe[(CN)_4NO]^{2-}$ is formed in acidic or neutral solution from the anion $[Fe(CN)_5NO]^{3-}$ obtained by one-electron reduction of the nitroprusside ion [2–4]. The reaction $[Fe(CN)_5NO]^{3-}$ (1) + $H^+ \rightleftarrows$ $[Fe(CN)_4NO]^{2-}$ (2) + HCN is connected with the transition from the formal electron configuration $Fe^{II}–NO^0$ in (1) to the configuration $Fe^I–NO^+$ in (2) [5, 6]. If the coordination number of (2) is increased by coordination of the sixth ligand a transfer of the electron density from metal d orbitals to π_{NO}^* orbitals is expected in accordance with the principle of the stereochemical control of valence [1, 7]. As changes in electron density delocalization can be readily followed electrochemically, we used electrochemical methods to follow the reaction route and identify the reaction products.

Experimental

All electrochemical experiments were performed using a multipurpose electrochemical instrument GWP 673 (Academy of Sciences, G.D.R.). Tektronix 5103N oscilloscope was used as a recording device for fast scan voltammetry.

Both electrochemical experiments on a dropping mercury or platinum microelectrode and electrolyses on a mercury pool were carried out in a universal electrolytic vessel employing a counterelectrode in the anodic compartment separated by sintered glass. The electrolysis potential was controlled potentiostatically using a three electrode system. A saturated aqueous calomel electrode was used as a reference electrode. Potentials in nonaqueous solutions were determined using bis(biphenyl)chromium(I) iodide as a pilot substance [8].

IR spectra were recorded on the Perkin-Elmer Model 257 spectrophotometer.

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*Symbol introduced in [1]. The exponent denotes the sum of electrons in metal d orbitals and π_{NO} orbitals.

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TABLE I. Half-wave Potentials and Electron Consumption of Redox Reactions of $\{Fe(NO)\}^7$ Containing Species.

$E_{1/2}$ vs SCE Complex	Aqueous buffer pH 7		CH_2Cl_2		DMF	
	oxidn.	redn.	oxidn.	redn.	oxidn.	redn.
$[Fe(CN)_4NO]^{2-}$	not detected	−0.55(1e)	−0.66(1e)*	−1.23(1e)*	not measured	not measured
$[Fe(CN)_5NO]^{3-}$	−0.33(1e)	−1.46(3e)	not detected	not detected	not measured	not measured
$[Fe(bpy)(CN)_3NO]^-$	+0.2(1e)	−0.58(3e)	−0.01(1e)	−1.38(1e)	−0.02(1e)	−1.49(1e)
$[Fe(phen)(CN)_3NO]^-$	+0.18(1e)	−0.60(3e)	+0.01(1e)	−1.45(1e)	+0.03(1e)	−1.5(1e)

*Values from ref. [12].

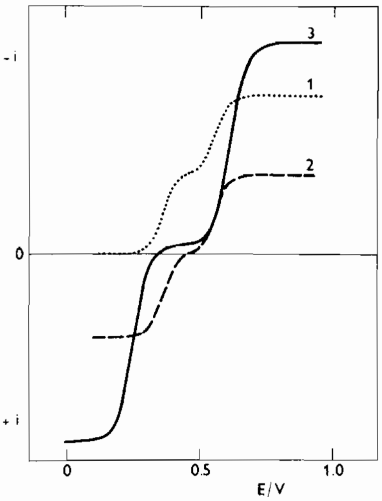

Fig. 1. Polarographic curves obtained in the course of preparation of $[Fe(bpy)(CN)_3NO]^-$. Britton–Robinson buffer; pH 7.0; 1:10^{-3} *M* $[Fe(CN)_5NO]^{2-}$; 2: after reductive electrolysis on passing 1F/mol; 3: after reaction with bpy.

Magnetic measurements were carried out at room temperature using a simple apparatus described in [9].

Britton–Robinson buffer solutions were employed for maintaining the pH value in aqueous medium.

Dichloromethane (CH_2Cl_2) was dried under P_2O_5 and freshly distilled. N,N-dimethylformamide (DMF) was purified by azeotropic distillation with benzene and successive fraction distillation under reduced pressure. Tetra-n-butylammonium perchlorate dried under vacuum was used in concentration 0.1 *M* as a supporting electrolyte for measurements in non-aqueous media.

Other chemicals used were of analytical grade.

$[Fe(CN)_4NO]^{2-}$ ion (blue species) was generated from $[Fe(CN)_5NO]^{2-}$ in a neutral or slightly acidic medium by a large area electrolysis at the potential of the limiting current of the first reduction wave of the nitroprusside ion. For preparative purposes, $[Fe(CN)_4NO]^{2-}$ was obtained by a careful one-electron stoichiometry chemical reduction of sodium nitroprusside with use of $Na_2S_2O_4$ or $NaBH_4$ as a reducing agent.

All manipulations with air sensitive solutions were carried out using the Schlenk type glassware technique under argon [10].

Results

Reactions with monodentate ligands in aqueous media

The reactivity of $[Fe(CN)_4NO]^{2-}$ towards selected inorganic and organic ligands was examined in aqueous buffer solutions of pH 4 to 8. No interaction was detected with thiosulphate (SCN^-), ammonia (NH_3), triphenylphosphinoxide ($(C_6H_5)_3PO$), triisopropylphosphine ($[(CH_3)_2CH]_3P$), pyridine (C_5H_5N) even when the ligands were added in a great excess (100 fold).

Reactions with bidentate ligands in aqueous media

The $[Fe(CN)_4NO]^{2-}$ ion in neutral or acidic aqueous solution reacts with aromatic di-imines 2,2-bipyridine (bpy) and 1,10-phenanthroline (phen). Figure 1 shows the polarographic pattern in the course of a typical experiment in which $Fe(CN)_4NO^{2-}$ (curve 2) is generated electrochemically from the nitroprusside ion $Fe(CN)_5NO^{2-}$ (curve 1) and then reacted with 2,2′-bipyridine (curve 3). The corresponding half-wave potentials are given in Table I. The third nitroprusside ion wave with $E_{1/2} = -1.46$ V and the waves corresponding to the unreacted free bipyridine in the region of −1.2 V are not shown in Fig. 1. It is seen that with the addition of bipyridine the polarographic waves of the reduced nitroprusside system (curve 2) are replaced by a new cathodic wave of the reaction product and by an anodic wave corresponding to CN^- ions (curve 3; the small cathodic wave at the potential of the first nitroprusside wave is due to small quantities of the nitroprusside ion generated during the reaction presumably by disproportionation of the reduced system as an unimportant side reaction).

TABLE II. NO–Stretching Frequencies.

Compound	ν_{NO} (cm^{-1})	medium
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	1935*	KBr
$[Et_4N]_3[Fe(CN)_5NO]$	1568*	nujol
$[Et_4N]_2[Fe(CN)_4NO]$	1746*	nujol
$[Ph_4P][Fe(bpy)(CN)_3NO]$	1640	KBr
$[Ph_4P][Fe(CN)_3NO(phen)]$	1630	KBr

*Values from ref. [11].

The overall height of the anodic wave corresponds to two free cyanide ions per molecule of the complex, from which it follows that on the way from $[Fe(CN)_5NO]^{2-}$ to the chelate species two CN^- ions are released and replaced by one chelate molecule. Thus the composition of the newly formed complex ions corresponds to the stoichiometric formula $[Fe(chel)(CN)_3NO]^-$ (chel = bpy, phen). As the reaction mixture contained in addition to CN^- ions an excess of bipyridine or phenanthroline and, in small amounts, products of side reactions, especially $[Fe(chel)_3]^{2+}$, the complexes were isolated for further measurements by precipitation with tetraphenylphosphonium or tetraphenylarsonium ions. The solids formed in this way can be recrystallized from organic solvents, such as ethanol-diethylether mixture.

Electrochemistry of $[Fe(chel)(CN)_3NO]^-$

A) Aqueous medium

The $[Fe(bpy)(CN)_3NO]^-$ ion is reduced in aqueous medium in a one three-electron irreversible wave (the number of electrons was confirmed coulometrically). The half-wave potential at pH = 7.0 is –0.58 V (*vs.* SCE). The number of protons consumed in the reduction was determined by coulometry in nonbuffered solution: the anodic wave of hydroxyl ions arising during the electrolysis at the potential of the cathodic wave of the complex corresponds to 1 OH^- per 1 electron. Thus it can be concluded that in analogy with $[Fe(CN)_5NO]^{3-}$ ion [2] the nitrosyl ligand in $[Fe(bpy)(CN)_3NO]^-$ is reduced to hydroxylamine. The phenanthroline analogue ($E_{1/2}$ = –0.61 V at pH = 7.0). exhibits similar behaviour. In unbuffered perchlorate media the complexes show a positive anodic wave merging with the anodic mercury dissolution and corresponding to the 1-electron oxidation of the complexes.

B) Nonaqueous medium

Electrochemical behaviour of both $[Fe(bpy)(CN)_3NO]^-$ and $[Fe(CN)_3NO(phen)]^-$ ion is similar in CH_2Cl_2 as well as in DMF solution. The half-wave potentials of the polarographic waves are summarized in Table I. A one-electron slightly semireversible anodic wave is obtained at positive potentials. A cathodic one-electron wave at negative potentials has a reversible shape, but cyclic voltammetry in the sweep rate range 100 mV/s to 100 V/s exhibits no anodic peak; this indicates that the reversible reduction is followed by a fast inactivation process.

Infrared Spectra

The measured values of NO-stretching frequencies in $[PPh_4][Fe(bpy)(CN)_3NO]$ and $[PPh_4][Fe(CN)_3NO(phen)]$ are compared with literature data for $[Fe(CN)_5NO]^{2-}$, $[Fe(CN)_5NO]^{3-}$ and $[Fe(CN)_4NO]^{2-}$ in Table II.

Magnetic Measurements

Magnetic susceptibility of $[PPh_4][Fe(bpy)(CN)_3NO]$ was measured at the temperature 298 K. The value of gram susceptibility χ_g is 2.65×10^{-6} cm^3 g^{-1}. Molar susceptibility after correction for diamagnetism using data in [13] is then $\chi_m' = 2.15 \times 10^{-3}$ cm^3 mol^{-1}. Assuming that the substance is 'magnetically dilute' the effective magnetic moment in Bohr magnetons can be evaluated: $\mu_{eff} = 2.83 (\chi_m'T)^{1/2} = 2.27$.

Reactivity in Nonaqueous Solution

The anion $[Fe(CN)_4NO]^{2-}$ can be also obtained in nonaqueous medium by electrochemical reduction of tetrabutylammonium nitroprusside [12]. We have checked the reactivity of the solution obtained by the large area electrolysis of $[NBu_4]_2[Fe(CN)_5NO]$ in dichloromethane at the potential of the limiting current of the first reduction wave. No interaction has been found with phosphines, pyridine nor with bipyridine and phenanthroline.

Discussion

The results show that the enhancement of the coordination number from five in $[Fe(CN)_4NO]^{2-}$ to six in $[Fe(CN)_3(chel)NO]^-$ causes considerable changes in physico-chemical properties, such as redox behaviour and NO–stretching frequency which were followed in this study.

The most significant changes regarding the redox behaviour are observed in the reduction pattern obtained in aqueous media. In the absence of the chelate there exists in the solution a rapid equilibrium $[Fe(CN)_4NO]^{2-} + CN^- \rightleftarrows [Fe(CN)_5NO]^{3-}$ the components of which are reduced at largely different potentials and electron consumption [2], *viz.*, $[Fe(CN)_4NO]^{2-}$: $E_{1/2} \sim -0.55$ V, 1e; $[Fe(CN)_5NO]^{3-}$: $E_{1/2} \sim -1.46$ V, 3e. In the presence of chelate ligands $[Fe(CN)_4NO]^{2-}$ is slowly and irreversibly converted into the hexacoordinate species $[Fe(CN)_3(chel)NO]^-$ which is reduced under consumption of 3 electrons in the same way as the hexacoordinate species $[Fe(CN)_5NO]^{3-}$, but at potentials by about 800 mV more positive. This large shift of the reduction potentials between both six-coordinate species can be accounted for by the difference in charge type (3– and 1–, respectively) and in σ-π donor-acceptor properties of the coordination sphere (the chelate ligands are poorer σ-donors and better π-acceptors than the cyanide ions which in the chelate complexes causes a partial withdrawal of the electron density from the $\{Fe(NO)\}^7$ fragment at which the redox changes are localized). For the same reasons the oxidation of the chelate species takes place at more positive potential (near +0.2 V) than that of $[Fe(CN)_5NO]^{3-}$ (–0.33 V). On the other hand, the difference in charge type and σ-π donor-acceptor properties of the coordination sphere cannot explain the observed difference in the consumption of electrons in the reduction of the pentacoordinate species $[Fe(CN)_4NO]^{2-}$ (1e) and hexacoordinate species $Fe(CN)_5NO^{3-}$ or $[Fe(CN)_3(chel)NO]^-$ (3e). This behaviour must therefore be ascribed to the change in preponderant localization of the odd electron in the $\{Fe(NO)\}^7$ fragment, *viz.*, assuming that in the pentacoordinate species the odd electron is localized at the metal atom and consequently the fragment can be viewed formally as $\{Fe^I–NO^+\}^7$ whereas with hexacoordinate species the odd electron is localized at the nitrosyl group and the fragment has a formal configuration $\{Fe^{II}–NO^o\}^7$. This is in accordance with the formerly observed 'typical behaviour' of the free and coordinated nitrosyl group in cases where the coordination causes just a minor perturbance of the electronic properties of this group, as *e.g.* in nitroprusside and derived ions [2, 18]: the species which can be viewed as containing formally the NO^+ group, *i.e.* free NO^+, $[Fe(CN)_5NO]^{2-}$, $[Fe(CN)_4NO]^{2-}$, undergo a 1-electron reduction, while species containing formally the NO^o group, *i.e.* free NO, $[Fe(CN)_5NO]^{3-}$ and $[Fe(chel)(CN)_3NO]^-$ are in aqueous media reduced at more negative potentials with the uptake of 3 electrons to free or coordinated NH_2OH. The formation of hydroxylamine species from the nitrosyl group is not possible in aprotic media and therefore in these media even with the NO^o containing species only a 1-electron reduction is observed.

The anion $[Fe(bpy)(CN)_3NO]^-$ can be reversibly oxidized to the neutral species $[Fe(bpy)(CN)_3NO]$. This complex has been referred to by Sarkar, Singh and Mishra [15], but the described properties of the complex are at variance with those found by us with the complex obtained by oxidation of $[Fe(bpy)(CN)_3NO]^-$ [16]. We tried to reproduce the procedure described in [15] and we obtained $[Fe(bpy)_3]^{2+}$ ion as the main reaction product. A similar negative result has been found by Aymonino and coworkers [17].

Changes in NO stretching frequencies (see Table II) which can be considered as a measure of the electronic occupation of the π^*-NO orbitals [14, 18] show also that the transition from penta- to hexacoordination is accompanied by a transfer of electron density from the iron to the nitrosyl group. The decrease of the ν_{NO} value when going from the pentacoordinate $[Fe(CN)_4NO]^{2-}$ to the hexacoordinate species is smaller in case of the $[Fe(chel)(CN)_3NO]^-$ species than with the $[Fe(CN)_5NO]^{3-}$ ion, which is due to the above mentioned difference in σ-π donor-acceptor properties between the chelate ligands and CN^- ions.

The value of the effective magnetic moment of $[PPh_4][Fe(bpy)(CN)_3NO]$ $\mu_{eff} = 2.27$ B.M. confirms the presence of one unpaired electron in the complex. While for the ions $[Fe(CN)_5NO]^{3-}$ and $[Fe(CN)_4NO]^{2-}$ the spin only value 1.73 B.M. has been reported [11] the increased value observed by us is evidently due to the orbital contribution arising in the chelate complex.

In conclusion it can be stated that the results obtained in this study represent another example of the validity of the stereochemical control of valence and show the usefulness of this principle both in elucidating and predicting the properties of nitrosyl complexes containing the $\{M(NO)\}^{7-8}$ fragments.

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