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On the Reactivity of Tetracyanonitrosylferrate(2−).
II. Formation and Properties of Mixed Ligand Complexes with Aromatic Di-imines

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Abstract

Preparation, UV-Vis, IR and ESR spectra, electrochemical redox and magnetic properties of novel complexes obtained by interaction of the tetracyanonitrosylferrate(2−) with 2,2′-bipyridine or 1,10-phenanthroline are described in detail. The results corroborate the previously suggested validity of stereochemical control of valence with these complexes.

Introduction

In our previous paper [1] dealing with the intramolecular electron transfer in the course of transition from the pentacoordinated to hexacoordinated $\{FeNO\}^7$ type species, we described the reaction resulting in the formation of the aromatic di-imine-cyanonitrosyl complexes:

$$[Fe(CN)_4NO]^{2-} + \text{chel} \longrightarrow CN^- + [Fe(\text{chel})(CN)_3NO]^-$$

chel = bpy (2,2′-bipyridine) or phen (1,10-phenanthroline). The complex anion $[Fe(\text{chel})(CN)_3NO]^-$ can be readily converted to the neutral species $[Fe(\text{chel})(CN)_3NO]$ using a convenient oxidizing agent (such as bromine) in nonaqueous medium.

A more detailed account of the preparation procedures and of physical and chemical properties of the novel complexes is given in this paper.

Experimental

Chemicals

All chemicals used for preparative purposes were of analytical reagent grade, with the exception of diethylether from which peroxides had to be removed. Purification of solvents for electrochemical measurements was described in the previous paper [1].

Preparation of Tetraphenylphosphonium (2,2′-bipyridine)tricyanonitrosylferrate(1−)

298 mg (1 mmol) of sodium nitroprusside dihydrate in 50 ml of water was reduced under stirring with 5 ml of 0.1 M solution of sodium dithionate and immediately 318 mg (2 mmol) of 2,2′-bipyridine dissolved in 2 ml of acetone was added. The mixture was stirred for several min, until the dark blue colour changed to red-brown. Then a solution of 210 mg (0.5 mmol) of tetraphenylphosphonium bromide in 10 ml of water was added to the reaction mixture. The precipitate formed was filtered, washed several times with small portions of water, and then dissolved in 15 ml of ethanol. The resulting brown solution was filtered and diethylether was carefully added until brown crystals began to form. The product was recrystallized using ethanol/diethylether mixture. All manipulations were carried out in Schlenk-type glassware under argon. The product in solid state is stable on air but solutions slowly decompose. *Anal.* Calc. for $[Ph_4P][Fe(bpy)(CN)_3NO]$: C, 67.39; H, 4.28; N, 12.74. Found: C, 67.16; H, 4.33; N, 12.56.

Preparation of Tetraphenylphosphonium Tricyanonitrosyl(1,10-phenanthroline)ferrate(1−)

298 mg (1 mmol) of sodium nitroprusside dihydrate in 50 ml of water was reduced with 5 ml of 0.1 M solution of sodium dithionite and immediately 360 mg (2 mmol) of 1,10-phenanthroline dissolved in 2 ml of ethanol was added. The mixture was stirred until the dark blue colour changed to red-brown. Then a solution of 210 mg (0.5 mmol) of tetraphenylphosphonium bromide in 10 ml of water was added to the reaction mixture. The precipitated crude product was filtered, washed several times with small portions of water, and dissolved in 20 ml of acetonitrile. The solution was filtered into a polyethylene or polyethylene-coated glass flask and brought to crystallization by careful addition of diethylether. Brown crystals were filtered and the product recrystallized from an acetonitrile/diethylether mixture. Sensitivity to air was the same as with the

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bipyridine complex. *Anal.* Calc. for [Ph_4P] [$Fe(CN)_3$-NOphen]: C, 68.53; H, 4.13; N, 12.30. Found: C, 68.25; H, 4.41; N, 12.09.

Tetraphenylarsonium (2,2′-bipyridine)tricyanonitrosylferrate(1−) and Tetraphenylarsonium Tricyanonitrosyl (1,10-phenanthroline)ferrate(1−)

This was prepared by the same procedure as the tetraphenylphosphonium salts, using tetraphenylarsonium chloride instead of tetraphenylphosphonium bromide.

Preparation of (2,2′-Bipyridine)tricyanonitrosylferrate

660 mg (1 mmol) of tetraphenylphosphonium (2,2′-bipyridine)tricyanonitrosylferrate(1−) was dissolved in 100 ml of deaerated dichloromethane and the intensively stirred solution was oxidized by 25 μl (0.5 mmol) of bromine in 10 ml CH_2Cl_2. Dichloromethane was evaporated *in vacuo* and the solid residue was extracted five-times with 2 ml of methanol. The remaining solid was dissolved in 200 ml of dichloromethane and filtered. The crystals of [Fe(bpy)$(CN)_3$NO] as white needles were isolated from the solution by evaporation *in vacuo*. The product must be stored under argon. *Anal.* Calc. for Fe(bpy)$(CN)_3$NO: C, 48.78; H, 2.52; N, 26.25. Found: C, 48.53; H, 2.52; N, 26.12.

UV-Vis spectra were measured on a Specord M 40 spectrophotometer (Carl Zeiss, Jena, GDR). IR spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Magnetic susceptibilities were determined at room temperature using a simple apparatus described in [2]. ESR spectra were measured with a Varian E-4 spectrometer. The apparatus for electrochemical experiments was described in our previous paper [1].

Results and Discussion

Ultraviolet and Visible Spectra

Figures 1 to 3 show the electronic spectra of the synthesized complexes in acetonitrile solution. Comparative spectra of free bipyridine, phenanthroline and tetraphenylphosphonium bromide are also given.

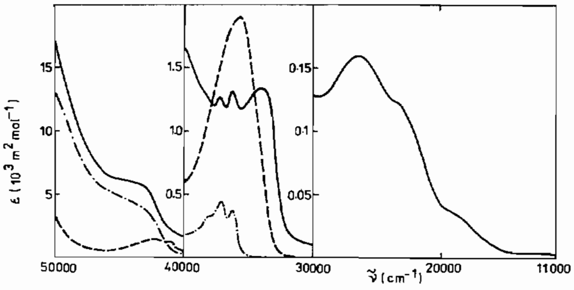

Fig. 1. UV-Vis spectra of [Ph_4P][Fe(bpy)$(CN)_3$NO] (——), 2,2′-bipyridine (– – –) and [Ph_4P]Br (– · – ·) (CH_3CN solution, 25 °C).

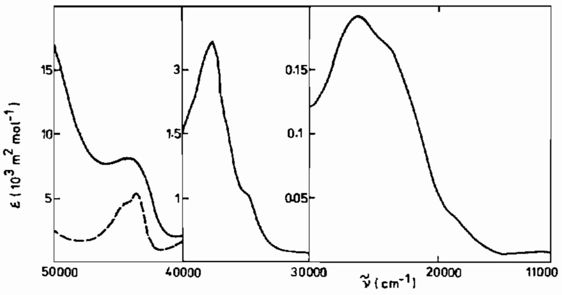

Fig. 2. UV-Vis spectra of [Ph_4P][$Fe(CN)_3$NOphen] (——) and 1,10-phenanthroline (– – –) (CH_3CN solution, 25 °C).

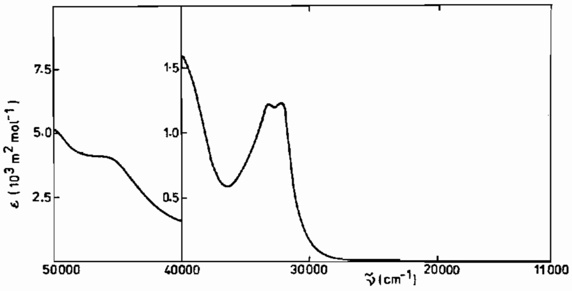

Fig. 3. UV-Vis spectrum of [Fe(bpy)$(CN)_3$NO] (CH_3CN solution, 25 °C).

The anionic complexes [Ph_4P][Fe(bpy)$(CN)_3$NO] and [Ph_4P][$Fe(CN)_3$NOphen] exhibit in the near-UV and visible regions very similar spectra, consisting of overlapping bands with maxima at 26 300 cm^{-1} (ϵ (molar absorptivity) = 160 m^2 mol^{-1}) and at 26 100 cm^{-1} (ϵ = 190 m^2 mol^{-1}) for the bipyridine complex and for the phenanthroline analogue respectively. These bands disappear completely when the anionic complex is oxidized to the neutral species Fe(bpy)-$(CN)_3$NO (Fig. 3). Hence these absorption bands can be assigned to ligand-to-metal charge transfers (LMCT) corresponding to the transition of the unpaired electron localized in the π^*(NO) orbital to vacant metal $d_{(z^2,\, x^2-y^2)}$ orbitals. It can be assumed that in these complexes there is a 'bent' structure of the M–N–O bond predicted for $\{M\text{–}NO\}^{7-8}$ type of hexacoordinated nitrosyl complexes [3, 4].

The ultraviolet region of the spectra of investigated complexes is characterized by: 1, intraligand $\pi \rightarrow \pi^*$ absorption bands of coordinated diimine ligands, 2, absorption bands of tetraphenylphosphonium in the case of the anionic complexes, and 3, a strong absorption at the highest wavenumbers.

The absorption maxima corresponding to the lower energy transition in coordinated diimines exhibit in the case of $\{Fe(NO)\}^7$ complexes (34200 cm^{-1}/ϵ = 1350 m^2 mol^{-1} for [Ph_4P][Fe(bpy)$(CN)_3$-NO] and 37500 cm^{-1}/ϵ = 3400 m^2 mol^{-1} for [Ph_4P]-[$Fe(CN)_3$NOphen] a small shift to lower wavenumbers in comparison with free bipyridine and phenanthroline. Such a shift is common for bipyridine and phenanthroline metal complexes, and is ascribed to the influence of a positive charge on the metal on the energy levels of π-conjugated systems [5]. In the case of the $\{Fe-(NO)\}^6$ type $[Fe(bpy)(CN)_3NO]$ species the shift to a lower energy of the $\pi \rightarrow \pi^*$ transition is much greater and a splitting of the band to two maxima is also observed. In addition to the influence of the higher positive charge on iron in the oxidized form of the complex, the enhancement of the ligand field in the $Fe-NO^+$ type of the complex results in a stronger interaction between π, π^*(bpy) and d(Fe) orbitals of corresponding symmetry.

The band corresponding to the higher energy $\pi \rightarrow \pi^*$ intraligand (bpy, phen) transition is overlapped in the studied complexes by more intensive bands of the tetraphenylphosphonium cation and by a further intensive absorption in the highest energy region of the spectra (Figs. 1–3). This latter absorption, which arises in both anionic and electroneutral complexes, is probably due to the metal-to-ligand charge transfer (MLCT) from $d_{(xy,xz,yz)}$ iron orbitals to the π^*-chelate orbitals. This assignment is supported by the fact that no such intensive absorption bands have been found in pentacyanonitrosyliron complexes of any oxidation state [6]. Furthermore, the oxidation of the $[Fe(bpy)(CN)_3NO]^-$ anion to electroneutral $[Fe(bpy)(CN)_3NO]$ species increases the experimentally observed energy of the transition (44000 cm^{-1} for $[Fe(bpy)(CN)_3NO]^-$ and 46500 cm^{-1} for $[Fe(bpy)(CN)_3NO]^0$), in agreement with increasing electrostatic influence of the positive charge on iron. Some contribution of the transition d(xy) $\rightarrow \pi^*$(CN) which is responsible for the most intensive band in the nitroprusside spectrum [7, 8] must also be considered in analyzing this shortest wavelength region of the spectra.

Infrared Spectra

Values of NO and CN stretching frequencies, assessed from infrared spectra of the prepared compounds in KBr pellets, are summarized in Table I.

Slightly raised NO stretching frequencies in both types of complexes (1) to (4) and (5) when compared with the isoelectronic pentacyano complexes $[Fe(CN)_5NO]^{3-}$ (ν(NO) = 1568 cm^{-1}) and $[Fe(CN)_5NO]^{2-}$ (ν(NO) = 1935 cm^{-1}) [9] demonstrate that the substitution of cyanides by bipyridine or phenanthroline diminishes the electron density on nitrosyl. This is in accordance with the fact that cyanide ions behave as ligands with stronger σ-donor and poorer π-acceptor ability than bipyridine or phenanthroline.

TABLE I. NO and CN Stretching Frequencies, in cm^{-1}.

Compound	ν(NO)	ν(CN)
(1) $[Ph_4P][Fe(bpy)(CN)_3NO]$	1642	2091
(2) $[Ph_4As][Fe(bpy)(CN)_3NO]$	1642	2091
(3) $[Ph_4P][Fe(CN)_3NOphen]$	1632	2090
(4) $[Ph_4As][Fe(CN)_3NOphen]$	1632	2090
(5) $[Fe(bpy)(CN)_3NO]$	1947	2115

Magnetic Properties

Magnetic properties of the paramagnetic species $[Ph_4P][Fe(bpy)(CN)_3NO]$ and $[Ph_4P][Fe(CN)_3NOphen]$ were followed using the Gouy method and ESR spectrometry; the neutral complex $[Fe(bpy)(CN)_3NO]$ is diamagnetic.

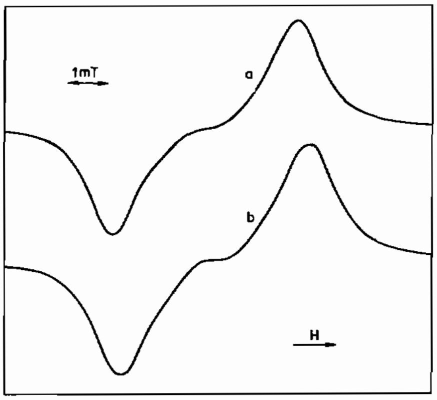

Fig. 4. ESR spectra of $[Ph_4P][Fe(bpy)(CN)_3NO]$ (curve 1) and $[Ph_4P][Fe(CN)_3NOphen]$ (curve 2), (concentration 5 × 10^{-3} M in CH_3CN solution, 25 °C).

ESR spectra of the complexes in dichloromethane solution are given in Fig. 4. The spectra of both compounds are very similar and represent an apparently poorly-resolved triplet with a g-factor of 2.0010 (± 0.003) for the bipyridine complex and 2.0016 (± 0.003) for the phenanthroline analogue. The splitting arises from the interaction between the unpaired electron and the nitrogen nucleus ^{14}N (I = 1) in the nitrosyl ligand.

The measurement of the magnetic susceptibility at the room temperature gives the following values of molar susceptibilities: $\chi_M = 2.15 \times 10^{-9}$ m^3 mol^{-1} for $[Ph_4P][Fe(bpy)(CN)_3NO]$ [1] and $\chi_M = 1.45 \times 10^{-9}$ m^3 mol^{-1} for $[Ph_4P][Fe(CN)_3NOphen]$ (values corrected for diamagnetism). The use of the formula for the effective magnetic moment of a "magnetically dilute" material $\mu_{eff} = 2830 (\chi_M T)^{1/2}$ leads to the values which are significantly greater (2.83 and 1.85) than the spin-only value of 1.73 B.M. This result is inconsistent with the g-values evaluated from ESR spectra measured in CH_2Cl_2 solution, which are close for both complexes to the free electron value g = 2.0023. Hence it is necessary to conclude that in the solid samples there exists an interaction between the magnetic centers.

Electrochemistry

Polarographic behaviour of the $[Fe(bpy)(CN)_3NO]^-$ and $[Fe(CN)_3NOphen]^-$ ions was described in our previous paper [1]. In aprotic media the complexes exhibit one anodic (slightly semireversible) and one cathodic (reversible) one-electron wave. In aqueous solution an irreversible, three-electron reduction is observed in which the coordinated NO^0 group is reduced to hydroxylamine.

As mentioned in the previous paper [1], the electrode reduction of the $[Fe(chel)(CN)_3NO]^-$ ion in aprotic media is followed by a fast inactivation process. In order to detect the products of the coupled reaction, the large area electrolysis on a mercury pool electrode was performed. Polarographic curves in the course of the electrolysis in dichloromethane are presented in Fig. 5. During the electrolysis at the potential of the cathodic wave the original characteristic pattern disappears and new anodic waves of the products are formed.

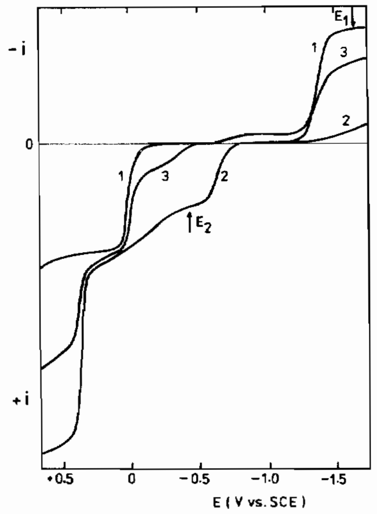

Fig. 5. Electrolysis of $[Ph_4P][Fe(bpy)(CN)_3NO]$ in CH_2Cl_2 solution. Concentration 10^{-3} M, supporting electrolyte 10^{-1} M $Bu_4N\ ClO_4$; (1) before electrolysis; (2) after reduction by 1 F/mol at potential E_1; (3) after reoxidation at potential E_2.

The most positive wave ($E_{1/2} = +0.30$ V) can be ascribed to the free bipyridine. Hence it follows that the bipyridine ligand is released from a primary reduction product and a tetracoordinated iron species is formed which can be oxidized in the more negative anodic wave ($E_{1/2} = -0.70$ V). This oxidation wave reaches only approximately 50% of the original wave height. Reverse reoxidation at the potential of this wave leads only to a partial regeneration of the initial complex (curve 3). Hence it follows that the species $[Fe(CN)_3NO]^{2-}$ formed after releasing bipyridine from the primary reduction product decomposes partially to some unidentified products yielding several anodic waves in the potential region between the two main anodic waves (curves 2 and 3). Thus the following overall scheme characterizes the redox behaviour in aprotic media:

$$\begin{tikzcd}
{[Fe(bpy)(CN)_3NO]} \arrow[r, shift left, "1e^-"] \arrow[r, leftarrow, shift right] & {} & \\
{[Fe(bpy)(CN)_3NO]^-} \arrow[rr, shift left, "1e^-"] \arrow[rr, leftarrow, shift right] & & {[Fe(bpy)(CN)_3NO]^{2-}} \arrow[d, "-bpy"', "fast"] \\
{[Fe(CN)_3NO]^-} \arrow[u, "+bpy"'] \arrow[rr, shift left, "1e^-"] \arrow[rr, leftarrow, shift right] & & {[Fe(CN)_3NO]^{2-}} \arrow[r] & ?
\end{tikzcd}$$

In DMF solution the side reaction is less significant and about 80% conversion in the sense of the indicated cycle can be achieved. Attempts to isolate the tricyanonitrosyliron(2–) salt failed, presumably due to the extreme instability of the species.

Polarography of the chemically prepared (see Experimental) complex $[Fe(bpy)(CN)_3NO]$ resembles that of the corresponding anionic complex, with self-evident difference in the position of the waves with respect to the zero-current line (Fig. 6).

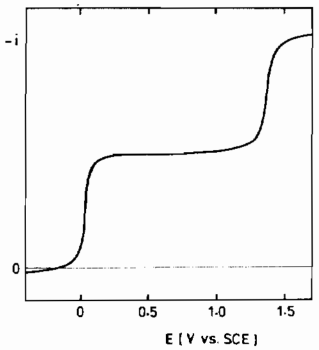

Fig. 6. Polarogram of the complex $[Fe(bpy)(CN)_3NO]$ in CH_2Cl_2 solution. Concentration 10^{-3} M, supporting electrolyte 10^{-1} M $Bu_4N\ ClO_4$.

Conclusions

The previously described [1] rearrangement of the electron density distribution between the iron atom of the nitrosyl group, which is achieved by increasing the coordination number of the $\{Fe(NO)\}^7$ moiety from 5 to 6 in the course of the reaction of tetracyanonitrosylferrate(2–) with 2,2′-bipyridine or 1,10-phenanthroline, is consistent with the results of the study of physical, chemical and electrochemical properties of the reaction products. The formulation of the atomic and electronic configuration of the anion $[Fe(chel)(CN)_3NO]^-$ as a hexacoordinated $\{Fe^{II}\text{–}NO^0\}^7$ species with the unpaired electron localized predominantly of the nitrosyl ligand, and accordingly with the bent structure of the M–N–O bond was proved as such by the following evidence:

1. Presence of the strong LMCT bands in the Vis and near UV region of the spectra of $[Fe(chel)(CN)_3NO]^-$, unlike the much weaker absorption of $[Fe(CN)_4NO]^{2-}$ in the visible spectrum [10, 11] assigned to MLCT $d_{(x^2-y^2)} \rightarrow \pi^*(NO)$ transition [12].
2. Relatively low values of NO stretching frequencies in IR spectra of $[Fe(chel)(CN)_3NO]^-$, which indicate an increased electron density in $\pi^*(NO)$ orbitals due to occupation by the unpaired electron.
3. Ability of the coordinated nitrosyl in the $[Fe(chel)(CN)_3NO]^-$ species to be reduced by 3 electrons to hydroxylamine in aqueous solution, typical for NO^0 configuration but not for NO^+ (see discussion in part I of this series).

Properties of the oxidized form $[Fe(bpy)(CN)_3NO]$ show that this complex contains a linearly-bonded nitrosyl group in the formal oxidation state NO^+, similar to the isoelectronic nitroprusside ion.

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