

Mechanism of Deactivation Processes of Excited Iron(III) Thiocyanato Complexes with Benacen-Type Ligands

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The complexes $[\text{Fe}(4\text{-R-benacen})(\text{CH}_3\text{OH})(\text{NCS})]$, where 4-R-benacen²⁻ are tetradentate open-chain *N,N'*-ethylenebis(4-R-benzoylacetoneiminato) N_2O_2 -ligands (R=H, Cl, Br, OCH_3), are redox stable in the dark in methanolic solutions. Irradiation of the complexes into intraligand and/or ligand-to-metal charge-transfer bands induces a series of photophysical and photochemical deactivation processes leading to Fe(II) and CH_2O as final products in a 2 : 1 molar ratio. Formation of polystyrene containing bonded NCS group when irradiating the complexes in the presence of styrene monomer used as a radical scavenger indicates that the primary photoreduction of Fe(III) to Fe(II) is accompanied by the oxidation of NCS^- ligand to $\bullet\text{NCS}$ radical. 4-R-benacen-ligands behave as an innocent moiety virtually not participating in the photoinduced redox processes. The quantum yield of Fe(II) formation $\Phi_{\text{Fe(II)}}$ decreases significantly with increased wavelength of the incident radiation, and is slightly influenced by the peripheral groups R of the 4-R-benacen-ligands.

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1. INTRODUCTION

Contrary to halogeno and the majority of pseudohalogeno ligands, thiocyanato anion NCS^- can coordinate to the central atom both through its nitrogen and sulphur terminal atoms. Up-to-now performed photochemical investigations of thiocyanato complexes have documented that they can undergo at least five types of radiation-induced reactions, namely,

- (i) photosubstitution of NCS^- anion, usually for a solvent molecule [1, 2], and photoanation substitution of a solvent molecule for an NCS^- anion [3];
- (ii) thiocyanato-isothiocyanato photoisomerization [4];
- (iii) primary photooxidation of NCS^- anion to $\bullet\text{NCS}$ radical associated by the central atom photoreduction followed by several fast reactions of the $\bullet\text{NCS}$ radical, for example, its reaction with NCS^- anion forming the detectable anion-radical $(\text{NCS})_2^{\bullet-}$ [1], dimerization yielding the molecule $(\text{NCS})_2$ [5], redox reaction with a solvent molecule [6], initiation of polymerization by attacking a monomer molecule [7] and so forth;
- (iv) photochemical decomposition of NCS^- ligand through a sulphur atom loss [8] or formation of NCS^- ligand initiated by photodecomposition of N_3^- ligand and subsequent reaction of the nitrene intermediate with CS_2 [9];

- (v) photochemical reaction not involving NCS^- ligand, such as an electron ejection from the central atom (frequent process occurring at photoelectrochemical solar cells [10, 11]) or photosubstitution of other ligands [12].

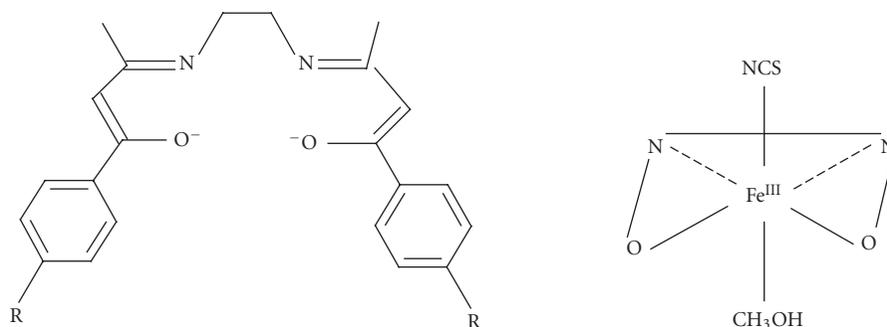
Along with potentially useful applications of thiocyanato complexes, “adverse” utilization of iron(III) thiocyanate as a camouflaging agent able to mask cocaine and facilitate thus its transport from Columbia to other countries [13] may be presented.

In this contribution, the results on photochemical properties of the complexes $[\text{Fe}(4\text{-R-benacen})(\text{CH}_3\text{OH})(\text{NCS})]$ are presented. The structures of 4-R-benacen²⁻ where R=H, Cl, Br, CH_3O (further on generally abbreviated as N_2O_2 -ligands) and the central atom environment in the investigated complexes are depicted in Scheme ??.

2. EXPERIMENTAL

2.1. Reagents and solutions

Methanol (Lachema, reagent grade) was dried before use by distillation from magnesium activated with iodine. The spin trapping agents 2,3,5,6-tetramethyl nitrosobenzene (nitrosodurene, ND) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were obtained from Aldrich. DMPO was freshly



SCHEME 1: Schematic representation of 4-R-benacen²⁻ ligands (R=H, Cl, Br, CH₃O) and a mode of the ligands coordination to the central atom Fe(III).

redistilled before use and stored under argon in a freezer. Monomeric styrene was distilled before use and stored in a freezer. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals) and 1,10-phenanthroline (phen, Aldrich) were used directly without prior purification. The other chemicals were of analytical grade, purchased from Lachema, and used as received.

The Schiff bases H₂(benacen), H₂(4-Cl-benacen), H₂(4-Br-benacen), and H₂(4-CH₃O-benacen) were available from our previous work [14, 15], their purity was checked by elemental analysis, melting point, ¹³C-NMR and ¹H-NMR spectra.

Solutions of [Fe(N₂O₂)(CH₃OH)(NCS)] were prepared *in situ* diluting 40 mL of stock methanolic solution of $c\{[\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})_2](\text{NO}_3)\} = 3.00 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ to 600 mL volume by dried methanol, adding 0.175 g of solid KNCS, and stirring at ambient temperature. Oxygen was removed from the photolyte solutions by purging with solvent-saturated argon 30 minutes prior and during irradiation.

2.2. Apparatus

Solutions of investigated complexes were photolysed in a three-chamber thermostated (20 ± 1 °C) quartz photoreactor. A low-pressure germicidal lamp G8T5 or a high-pressure 150 W Hg-lamp (applied photophysics) were used as radiation sources. Radiation of the high-pressure lamp was monochromatized passing through solution filters [16].

Electronic absorption spectra were recorded on a Specord 200 spectrophotometer using 1.00 or 0.10 cm quartz cells. EPR spectra were measured using a computer controlled Bruker EMX instrument (operating at X-band, with 100-kHz field modulation) equipped with a quartz flat cell optimized for the Bruker TM cylindrical EPR cavity. IR spectra of a solid polystyrene residue were scanned by KBr tablets technique on an FTIR spectrometer Nicolet Magna 750.

2.3. Irradiation and product analysis

The radiation intensities were periodically measured with ferrioxalate actinometry [17].

Progress of the photoredox processes was monitored by UV-VIS spectrophotometry as time evolution of $c(\text{Fe}^{\text{II}})$ and $c(\text{CH}_2\text{O})$. Iron(II) was determined in the form of [Fe(phen)₃]²⁺, formaldehyde CH₂O as 3,5-diacetyl-1,4-dihydropyridine. The total amount of photolysis was limited to less than 5% to avoid an inner filter effect. Details on the photolysis, analytical procedures, and experimental data processing are described elsewhere [14–16].

In EPR measurements, the prepared methanol solutions were carefully deoxygenated by an argon stream and irradiated directly in the cavity of EPR spectrometer by an HPA 400/30S lamp (Philips) at $\lambda \geq 300$. Spectrometer settings, a mode of simulations of the individual components of the EPR spectra, and the software used are given elsewhere [18].

Polystyrene formed within 30-minute irradiation of a solution prepared by adding 15 mL of styrene to 110 mL of $c[\text{Fe}(\text{benacen})(\text{CH}_3\text{OH})(\text{NCS})] = 2.00 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ in argon atmosphere was separated as a solid residue using an MPW-type centrifuge (5500 rps) and washed twice with 5 mL of dry methanol.

3. RESULTS AND DISCUSSION

3.1. Spectral properties and photoredox efficiency of complexes

Single crystal X-ray diffraction investigations related to iron(III) complexes with thiocyanato ligands or benacen-type ligands and solution studies show that

- (i) NCS⁻ anion is coordinated to the Fe(III) central atom through its nitrogen [19];
- (ii) benacen-type ligands form the equatorial plane of the complexes and two monodentate ligands are bonded in the axial positions [19];
- (iii) in the majority of its high-spin complexes, the central atom Fe(III) is hexacoordinated both in the solid state and solutions [19, 20].

Based on the literature data and our previous results obtained by a standard spectrophotometric titration [21], the composition of the complexes investigated within this work can be described as [Fe(N₂O₂)(CH₃OH)(NCS)].

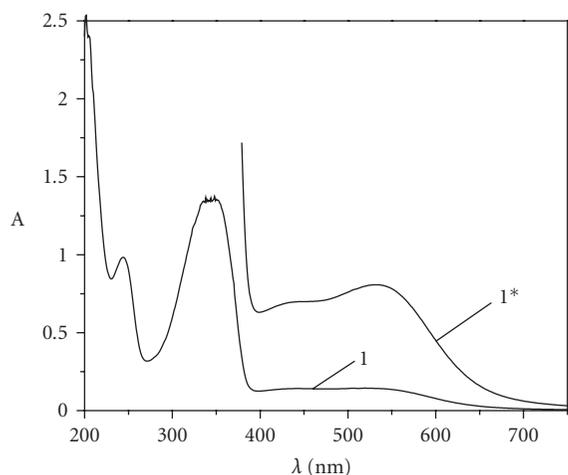


FIGURE 1: Electronic absorption spectrum of 2.0×10^{-4} M $[\text{Fe}(\text{benacen})(\text{CH}_3\text{OH})(\text{NCS})]$ (1, 1*) in methanol measured in 0.2 cm (1) and 1.0 cm (1*) cells.

Typically, the electronic absorption spectra of the complexes $[\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})(\text{NCS})]$ consist of several broadbands and shoulders. As an example, absorption spectrum of $[\text{Fe}(\text{benacen})(\text{CH}_3\text{OH})(\text{NCS})]$ is shown in Figure 1. The spectral data for all complexes are listed in Table 1.

Based on previously published data [14–16], bands in the visible region can be attributed to ligand-to-metal charge-transfer (LMCT) transitions $\text{O}2\text{p}$ or $\text{N}(2\text{p}) \rightarrow \text{Fe}3\text{d}$, the ultraviolet bands in the regions of 210–280 nm and 300–360 nm to the intraligand transitions $\text{IL}(\pi \rightarrow \pi^*)$ localized predominantly on the phenyl rings and on $\text{C}=\text{N}$ fragments of the N_2O_2 -ligands, respectively. Due to their spin-forbidden nature, ligand-field (LF) bands were not observed in solution spectra.

Irradiation of methanolic solutions of the investigated complexes by UV or visible radiation gives rise to the photoreduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$. The integral quantum yields of $\text{Fe}(\text{II})$ formation $\Phi_{\text{Fe}(\text{II})}$ depend on the wavelength of the excitation radiation and on the peripheral groups R of the N_2O_2 -ligands (Table 1). Blank experiments confirmed that the complexes $[\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})(\text{NCS})]$ do not undergo spontaneous redox changes in methanolic solutions in the dark.

Before starting discussion on the wavelength dependence of quantum yield of $\text{Fe}(\text{II})$ formation, it seems to be worth pointing out two specific features, namely,

- (i) the absorption of a photon of 254 nm or 313 nm is associated with IL excitation localized on equatorial benacen-type ligand while it is an axial ligand undergoing the primary photoredox process;
- (ii) inner complex physical deactivations are extremely fast for iron complexes and no radiation deactivation has been observed for such complexes up to now.

Taking these observations into account, the observed decrease in the quantum yield $\Phi_{\text{Fe}(\text{II})}$ with increasing incident

radiation wavelength may be understood and summarized as a consequence of three main factors:

- (1) very efficient internal conversion and/or intersystem crossing from energy higher IL to photoredox reactive LMCT states of the complexes;
- (2) rate constants of the said photophysical partial deactivations are higher than that of rovibrational cooling with a consequence that LMCT states populated from IL states have a higher content of rovibrational energy than those populated directly by visible irradiation;
- (3) the higher the difference between the rovibrational energy of a given LMCT state and the threshold energy of the primary photoproducts formation, the higher the probability of their separation (or, *vice versa*, the lower the probability of their recombination in the solvent cage), that is, the higher $\Phi_{\text{Fe}(\text{II})}$.

Since the investigated complexes provide no luminescence, continuous photolysis does not allow to distinguish between the photoredox reactivity of individual spin-forbidden quartet and spin-allowed sextet LMCT states forming the manifold of states participating in redox deactivation processes.

Contrary to a theoretically justified and experimentally evidenced correlation of electrochemical reduction potentials for $\text{Fe}(\text{III})$ reduction and Hammett substituent constants of the groups R [22], a general unpredictability of quantum yields on such R-groups related parameters was explained in [23]. The main reason lies in the fact that electrochemical outer-sphere electron transfer occurs, in general, from the ground state of molecules and all usual parameters reflect molecular properties in this state. On the other hand, photochemical (frequently inner-sphere) electron transfer occurs from an excited state differing from the ground state in the structure, energy content, and electronic distribution.

3.2. Radical intermediate identification

To identify radicals formed in the irradiated solutions, EPR spin trapping and radical scavenging by a monomer were applied to $[\text{Fe}(\text{benacen})(\text{CH}_3\text{OH})(\text{NCS})]$.

The EPR spectra of $[\text{Fe}(\text{benacen})(\text{CH}_3\text{OH})(\text{NCS})]$ measured in methanol before photoexcitation revealed the formation of paramagnetic EPR signal characterized with the following hyperfine splittings: $a_{\text{N}} = 1.363$ mT, $a_{\text{H}}^{\beta} = 0.775$ mT, $a_{\text{H}}^{\gamma} = 0.16$ mT; g -value = 2.0059, which are attributed to $\cdot\text{DMPO-OCH}_3$ adduct, in accordance with literature data [24]. This adduct is usually observed in systems of iron(III) complexes containing DMPO, a mechanism of its generation is proposed elsewhere [24], and it is not formed in a photochemical step. Continuous irradiation ($\lambda > 300$ nm) of $[\text{Fe}(\text{benacen})(\text{CH}_3\text{OH})(\text{NCS})]$ causes a decrease in the $\cdot\text{DMPO-OCH}_3$ signal intensity without appearing any new EPR signal both at a short and prolonged irradiation. No EPR signal was observed using the ND spin trap as well.

Irradiation in the presence of monomeric styrene (soluble in methanol) gave rise to polystyrene (sparingly soluble in methanol) formation. In IR spectra of the polystyrene scanned after its isolation and purification, a sharp band

TABLE 1: Electronic absorption spectral data (type of transition, absorption band maxima λ_{\max} or shoulders λ_{sh} , and corresponding molar absorption coefficients, ϵ) for methanolic solutions of $2.00 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})(\text{NCS})]$, and quantum yields of Fe(II) formation $\Phi_{\text{Fe(II)}}$ at the excitation wavelength λ_{exc} .

R	λ_{\max} or λ_{sh} , nm (ϵ , $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)			λ_{exc} , nm			
	IL(phenyl)	IL(C=N)	LMCT	254	313	365	436
				$\Phi_{\text{Fe(II)}} \times 10^3$			
H	240.7 (23400)	334.1 (30900) 350sh (28000)	440sh (700) 543.2 (900)	36	12	0.36	0.20
Cl	248.0 (22900)	318.8 (25700) 360sh (19500)	460sh (1500) 541.9 (1960)	68	9.1	1.3	1.1
Br	251.0 (22400)	319.1 (26300) 365sh (14800)	441sh (1900) 537.6 (2290)	46	8.0	4.4	0.91
CH ₃ O	269.0 (39800)	335.7 (42000) 359sh (36400)	450sh (1800) 558.9 (2040)	48	7.5	2.7	1.9

at 1750 cm^{-1} was observed which is typical for covalently bonded SCN-group [25]. Such a results is generally taken as an indication of $\cdot\text{NCS}$ radical formation and its involvement in radical initiation of polymerization.

3.3. Final products determination

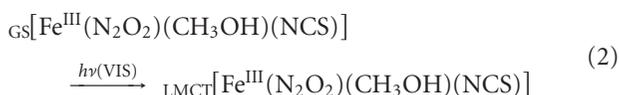
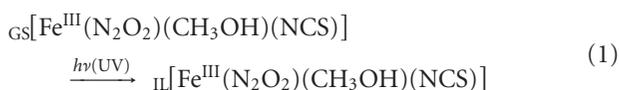
A molar ratio of iron(II) and formaldehyde as the final products of photoredox processes $\text{Fe(II)} : \text{CH}_2\text{O}$ approached a typical 2 : 1 value.

Introducing oxygen into the systems after switching off the irradiation led to a slow reappearance of the parent iron(III) complex spectra.

3.4. Mechanism of photoinduced processes

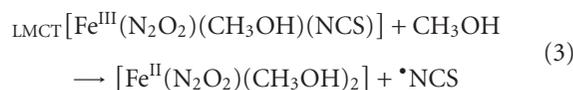
Based on the above spectra interpretation, radicals identification, molar ratio of the final products determination, and literature data [26, 27], processes occurring in the irradiated systems may be described (in the following equations, GS means the ground state) as follows. Composition of the complexes is written in a mode meeting the stoichiometry requirements, actual composition may vary within the processes due to kinetic lability of the complexes.

At UV-VIS irradiation of the investigated systems, spin-allowed IL or LMCT excited sextet states of complexes (1) and (2) are populated:



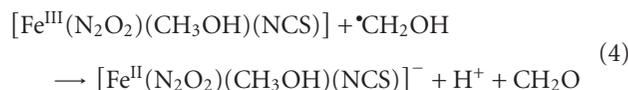
Of all the accessible excited states of the complexes, only LMCT sextet (populated directly by visible light absorption)

and spin-forbidden LMCT quartet states (reached by inter-system crossing from energy higher IL states) possess the electron distribution suitable for an inner-sphere reduction of Fe(III) to Fe(II). The use of styrene and formation of polystyrene containing covalently bonded SCN-group indicates that within the primary photoredox step, the central atom reduction of Fe(III) to Fe(II) is associated with the ligand NCS⁻ oxidation to its radical:



In spite of the absence of EPR evidence of the radical $\cdot\text{CH}_2\text{OH}$, its formation by an intermolecular or intramolecular methanol oxidation cannot be *a priori* ruled out, contrary, given the formaldehyde formation, it must be taken into account.

The radical product(s) can participate in a number of subsequent processes (e.g., back electron-transfer reactions, radicals interconversions). As documented by the value $E^{\circ}(\cdot\text{CH}_2\text{OH}/\text{CH}_2\text{O}) = -1.180 \text{ V}$, the radical $\cdot\text{CH}_2\text{OH}$ is able to reduce ground state Fe(III) forming thus the final products Fe(II) and CH₂O:



The ratio of $c(\text{Fe}^{\text{II}}) : c(\text{CH}_2\text{O}) = 2 : 1$ determined in the irradiated $[\text{Fe}^{\text{III}}(\text{benacen})(\text{CH}_3\text{OH})(\text{NCS})]$ indicates that the reduction of Fe(III) by $\cdot\text{CH}_2\text{OH}$ (4) is responsible for the above ratio.

4. CONCLUSIONS

(1) The paper deals with photoredox behaviour of the complexes $[\text{Fe}(\text{4-R-benacen})(\text{CH}_3\text{OH})(\text{NCS})]$ where 4-R-benacen²⁻ are *N,N'*-ethylenebis(4-R-benzoylacetoneimino) ligands (R=H, Cl, Br, OCH₃). When irradiated in

methanolic solutions into their IL or LMCT bands, the complexes undergo photoredox changes affording Fe(II) and formaldehyde CH₂O as final products formed in a 2 : 1 molar ratio. The quantum yields of the formation of the final products depend both on the incident radiation wavelength and the tetradentate groups R.

(2) Application of styrene as a radical scavenger evidences that [•]NCS radicals are formed as intermediates; formation of CH₂O indicates an involvement of [•]CH₂OH radicals in the photoredox processes.

(3) It is shown that the tetradentate ligands behave as an innocent part of the complexes. A mechanism of photophysical and photochemical deactivation steps is proposed.

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