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Different Photoredox Reactivity of Structurally Similar Iron(III) Complexes

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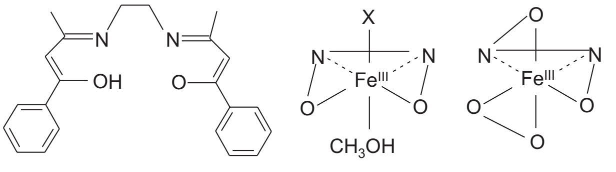
Iron(III) complexes [Fe(benacen)X]^q containing a redox innocent tetradentate open-chain N_2O_2-ligand benacen (*N,N'*-ethylenebis(benzoylacetoneiminato) and a couple of monodentate CH_3OH + F^-, CH_3OH + I^-, CH_3OH + N_3^-, (q = 0); 2 CH_3OH (q = 1) or bidentate $C_2O_4^{2-}$ (q = –1) ligands are redox stable in the dark. Under the impact of ultraviolet and/or visible radiation, the complexes undergo photochemical reactions, yielding Fe^{II} and formaldehyde CH_2O as final products. As intermediates, radicals $^\bullet CH_2OH$ and solvated electrons were identified by EPR spin trapping technique. Efficiency of the photoredox processes, expressed by the quantum yield of net Fe^{II} formation, $\Phi_{Fe^{II}}$, is strongly wavelength and monodentate/bidentate ligand dependent.

INTRODUCTION

Compounds forming a family of structurally similar derivatives often exhibit similar physical and chemical properties. Within the family, trends in several such properties can be predicted and mutual correlations can be found, most of them frequently based on free energy involving relationships. The majority (if not all) of such trends concern compounds in their ground state and belong to textbook information. Passing into the excited state realm gives rise to a new situation, in which the common ground-state based chemical knowledge fails in the prediction of photoreactivity and some properties and reactivity parameters seem to be, in principle, unpredictable.[1,2]

This paper aims to demonstrate significant differences in photochemical behaviour for a structurally very close group of complexes, namely solvated [Fe(benacen)X]^q, where benacen is a dianionic Schiff base open-chain N_2O_2-tetradentate *N,N'*-ethylenebis(benzoylacetoneiminato) ligand, and X are monodentate CH_3OH + N_3^-, CH_3OH + I^-, CH_3OH + F^-, 2 CH_3OH or bidentate $C_2O_4^{2-}$ ligands. Structures of the H_2benacen and the coordination polyhedron of the complexes are schematized in Figure 1.



H_2(benacen) [Fe(N_2O_2)(CH_3OH)X] [Fe(N_2O_2)(C_2O_4)]$^-$

Figure 1. Schematic structure of H_2(benacen) and coordination polyhedra of the complexes [Fe(benacen)(CH_3OH)X]^q (X = CH_3OH, q = 1; X = F, I, or N_3, q = 0) and [Fe(benacen)(C_2O_4)]$^-$.

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Differences in the photoredox behaviour of the complexes are documented in terms of the spin trapping EPR identification of radical intermediates, mole ratio of the final products formed, and wavelength dependence of the quantum yield of net Fe^{II} formation ($\Phi_{Fe^{II}}/\lambda_{irr}$).

EXPERIMENTAL

The Schiff base H_2benacen was synthesized using a general procedure[3] by condensation of benzoylacetone with ethane-1,2-diamine in 2:1 mole ratio in methanol. Its purity was checked by elemental analysis, melting point, ^{13}C NMR and ^{1}H NMR spectra.

Methanol (Lachema, reagent grade) was dried before use by distillation from $Mg(OCH_3)_2$. Ethane-1,2-diamine (Lachema) was distilled at a reduced pressure prior to use. 5,5-Dimethyl-1-pyrrolidine-*N*-oxide, (DMPO, Aldrich) was freshly distilled before use and stored under argon in a freezer. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals), 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene, ND, Sigma), NaN_3 (Sigma), and 1,10-phenanthroline (phen, Aldrich) were used without further purification. Other chemicals were of analytical grade, purchased from Lachema and used as received.

The complexes $[Fe(benacen)(CH_3OH)F]$, $[Fe(benacen)(CH_3OH)I]$, $[Fe(benacen)(CH_3OH)N_3]$, and $K[Fe(benacen)(C_2O_4)]$ were prepared in methanol *in situ* from stock methanolic solution of $[Fe(benacen)(CH_3OH)_2](NO_3)$ and solid $[N(C_2H_5)_4]F$, KI, NaN_3, and $K_2C_2O_4$, by the method described in our previous papers.[4,5]

Solutions of investigated complexes were photolysed by radiation of 254 nm in a two-chambered quartz photoreactor equipped with a low pressure Germicidal Lamp G8T5 and at 313 nm, 366 nm or 436 nm in a three-compartment temperature-controlled (20 ± 1 °C) quartz photoreactor (Applied Photophysics), radiation of the high-pressure 150 W Hg-lamp being monochromatized by solution filters.[4] The irradiated solutions were deoxygenated by purging with methanol-saturated argon 30 minutes prior and during irradiation. The intensity of the incident monochromatized radiation was determined with ferrioxalate actinometry[6] performed before and after a series of photolytic experiments.

The course of photoredox changes was monitored by electronic absorption spectroscopy as time evolution of $c(Fe^{II})$ and $c(CH_2O)$. At Fe^{II} determination, at suitable irradiation intervals (some tens of seconds), a 2 ml aliquot of irradiated solution was transferred from a photoreactor to a quartz cell containing 0.02 ml of 30 % H_3PO_4 and a few crystals of solid 1,10-phenanthroline. After incorporating Fe^{III} into phosphato complexes and Fe^{II} into $[Fe(phen)_3]^{2+}$, the concentration of Fe^{II} in the irradiated sample was calculated from the absorbance measured at 512 nm using a value[6] of 1.12×10^4 mol^{-1} dm^3 cm^{-1} for the molar absorption coefficient of $[Fe(phen)_3]^{2+}$. Absorption of Fe^{III} phosphates in the region $\lambda \geq 500$ nm can be neglected.

Formaldehyde CH_2O was determined following its conversion to 3,5-diacetyl-1,4-dihydrolutidine, for which the molar absorption coefficient at 412 nm is 8.00×10^3 mol^{-1} dm^3 cm^{-1}.

EPR spectra were measured on a Bruker 200D spectrometer (Germany) interfaced to an Aspect 2000 computer (Germany) using freshly prepared solutions containing spin traps DMPO or ND.

Electronic absorption spectra were recorded on a Specord 200 spectrophotometer using 1.00 or 0.10 cm quartz cells. IR spectra were scanned on a FT spectrometer Nicolet, Magna 750, in Nujol mulls.

More details on the experiments performed, measurement conditions, analytical procedures and experimental data processing are provided elsewhere.[4,7]

RESULTS AND DISCUSSION

Electronic absorption spectra of all investigated complexes consist of broad intraligand bands located in the UV region at 230–260 nm and 300–370 nm, which are attributed to intraligand (IL) $\pi \rightarrow \pi^*$ transitions localized on the phenyl rings and on the azomethine C=N fragment of the benacen ligand, respectively, and ligand-to-metal charge transfer (LMCT) bands in the visible region are attributed to O(2p) → Fe(3d) electron transfer. In the case of azido complex, photons with $\lambda \leq 270$ nm are absorbed also by N_3^- anions, $\varepsilon_{254\,nm}(N_3^-) \cong 100$ mol^{-1} dm^3 cm^{-1} in methanol.[8] Owing to their spin-forbidden nature, bands of the ligand field (LF) states are not detectable in solution spectra. The spectra of the investigated complexes are shown in Figure 2. It is obvious that due to their nature, the bands of IL transitions are only slightly influenced by other ligands while the bands of LMCT transitions are more sensitive to these ligands.

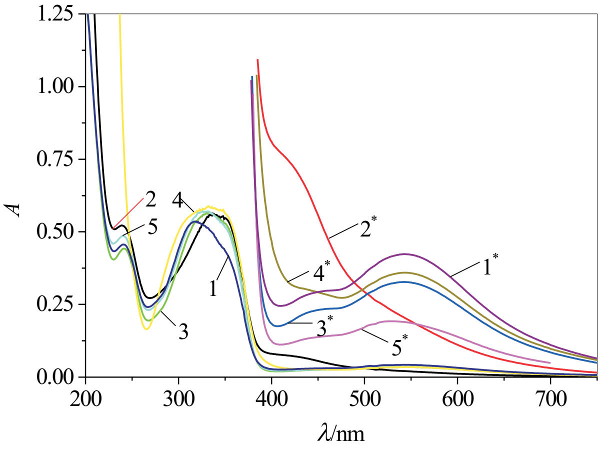

Figure 2. Electronic absorption spectra of $[Fe(benacen)(CH_3OH)F]$ (1, 1*), $[Fe(benacen)(CH_3OH)I]$ (2, 2*), $[Fe(benacen)(CH_3OH)N_3]$ (3, 3*), $[Fe(benacen)(CH_3OH)_2]^+$ (4, 4*), and $[Fe(benacen)(C_2O_4)]^-$ (5, 5*) in methanol, measured in 0.10 cm (1–5) or 1.00 cm (1*–5*) cells. Concentration of all complexes was 2.00×10^{-4} mol dm^{-3}.

TABLE I. Quantum yields of Fe^{II} formation, $\Phi_{Fe^{II}}$, in irradiated methanolic solutions of iron(III) complexes

Complex		$\Phi_{Fe^{II}}$			
	λ_{irr} =	254 nm	313 nm	366 nm	436 nm
[Fe(benacen)(CH_3OH)F]		0.00049	0.00006	<0.00001	<0.00001
[Fe(benacen)(CH_3OH)I]		0.027	0.010	0.0055	0.0032
[Fe(benacen)(CH_3OH)N_3]		0.0018	0.018	0.00090	0.00047
[Fe(benacen)$(CH_3OH)_2]^+$		0.065	0.035	0.0089	0.0043
[Fe(benacen)$(C_2O_4)]^-$		0.079	0.047	0.037	0.033

Control experiments proved that the complexes in the ground state (GS) do not undergo spontaneous redox changes in methanolic solutions.

Irradiation of methanolic solutions of the investigated complexes by ultraviolet or visible radiation led to the photoreduction of Fe^{III} to Fe^{II}. The quantum yields of net Fe^{II} formation, $\Phi_{Fe^{II}}$, depend on the wavelength of the incident radiation and on the monodentate/bidentate ligands present (Table I).

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

[Fe(benacen)(CH_3OH)F]

The [Fe(benacen)(CH_3OH)F] complex exhibits high redox stability not only in the ground state (which is a typical feature of iron(III) fluoro complexes) but also in excited states. When irradiating the complex with $\lambda_{irr} \geq$ 366 nm, the photoreduction of Fe^{III} to Fe^{II} is almost undetectable; even in the case of applying energy-higher UV radiation, the efficiency of Fe^{II} formation is still very low. The mole ratio $n(Fe^{II}) : n(CH_2O) \cong 2 : 1$ and the presence of $^\bullet CH_2OH$ radicals identified by EPR spin trapping evidence that the redox processes obey a general mechanism consisting of the following processes (for the sake of simplicity, spin-states of the complexes and non-redox chemical deactivations are not included; ic and isc mean internal conversion and intersystem crossing, respectively):

$$_{GS}[Fe^{III}(benacen)(CH_3OH)F] \xrightarrow{h\nu(UV)} {}_{IL}[Fe^{III}(benacen)(CH_3OH)F] \quad (1)$$

$$_{IL}[Fe^{III}(benacen)(CH_3OH)F] \xrightarrow{ic/isc} {}_{LMCT}[Fe^{III}(benacen)(CH_3OH)F] \quad (2)$$

$$_{GS}[Fe^{III}(benacen)(CH_3OH)F] \xrightarrow{h\nu(Vis)} {}_{LMCT}[Fe^{III}(benacen)(CH_3OH)F] \quad (3)$$

$$_{LMCT}[Fe^{III}(benacen)(CH_3OH)F] \rightarrow [Fe^{II}(benacen)F]^- + H^+ + {}^\bullet CH_2OH \quad (4)$$

$$[Fe^{III}(benacen)(CH_3OH)F] + {}^\bullet CH_2OH \rightarrow [Fe^{II}(benacen)F]^- + H^+ + CH_2O \quad (5)$$

Owing to the high electrode potential $E^o(F_2/F^-)$, the possibility of fluorine atoms formation can be ruled out.

The course of processes (1) to (3) follows from the spectra and photopohysical deactivation modes applied in excited Fe^{III} complexes.[9] From the viewpoint of electron density distribution, the only excited states suitable for inner-complex redox decomposition (4) are LMCT states (both spin-allowed sextets and spin-forbidden quartets, which are, however, due to the absence of luminescence, indistinguishable).

Reaction (5) is supported by thermodynamic parameters and the so far gained experience.[9] As documented by the value of $E^o(^\bullet CH_2OH/CH_2O) = -1.180$ V,[10] the radical $^\bullet CH_2OH$ is a strong reducing agent able to further reduce Fe^{III} in subsequent secondary thermal redox steps (5), thus forming the final products Fe^{II} and CH_2O.

The ratio $n(Fe^{II}) : n(CH_2O) = 2 : 1$ shows that the reduction of Fe^{III} by $^\bullet CH_2OH$ (5) is the main (if not the only) reactivity mode of $^\bullet CH_2OH$. Its transformation to $HOCH_2–CH_2OH$ or other products would increase the mentioned ratio. It is worth noting that no such products have been found so far in irradiated methanolic solutions of Fe^{III} complexes.[9]

Macrocyclic and open-chain tetradentate ligands behave as »redox innocent« ligands, apparently not participating in the occurring redox processes.[1,11] This conclusion is supported by the dark reoxidation of Fe^{II} in our system, expressed by stoichiometry:

$$4\ [Fe^{II}(benacen)F]^- + O_2 + 4\ H^+ + 4\ CH_3OH \rightarrow 4\ [Fe^{III}(benacen)(CH_3OH)F] + 2\ H_2O \quad (6)$$

[Fe(benacen)(CH_3OH)I]

When compared to its fluoro analogue, different experimental results were obtained for the iodo complex [Fe^{III}(benacen)(CH_3OH)I]. This complex exhibits substantially higher redox reactivity, observable even at irradiation with visible light. Also here $n(Fe^{II}) : n(CH_2O) \cong 2 : 1$, which supports the mechanism similar to that given by Eqs. (1) to (5). In analogy with the fluoro complex, the quantum yield of Fe^{II} formation decreases significantly with decreasing photon energy of incident radiation.

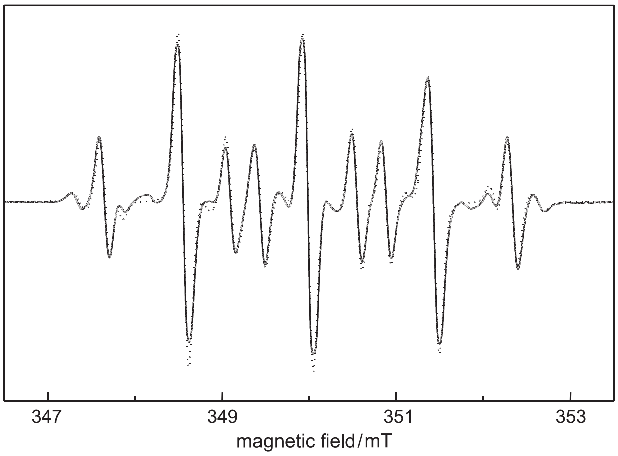

Figure 3. Experimental (solid line) and simulated (dotted line) EPR spectra measured upon continuous irradiation (λ_{irr} > 300 nm) of 1×10^{-3} mol dm^{-3} [Fe(benacen)(CH_3OH)I] in methanol-benzylchloride solution (vol. ratio 1:1) in the presence of excess of iodide ($c(I^-) = 1 \times 10^{-2}$ mol dm^{-3}) saturated with ND spin trap. The simulated EPR spectrum was calculated as a linear combination of three individual EPR spectra (see text).

A new feature lies in identification of solvated electrons, evidenced by EPR spin trapping using nitrosodurene, ND, as a spin trap and benzylchoride as an electron scavenger in the irradiated system of the complex.[12,13] Thus, deconvolution of the EPR signal and its simulation explicitly showed (Figure 3) the presence of three intermediates in irradiated 1×10^{-3} mol dm^{-3} [Fe(benacen)(CH_3OH)I], namely $^\bullet$ND-CH_2OH (a_N = 1.444 mT; a_H(2H) = 1.188 mT; g = 2.0054), e^-(solv) in the forms of $^\bullet$ND-$CH_2C_6H_5$ (a_N = 1.44 mT; a_H(2H) = 0.89 mT), and of $^\bullet$ND-ND radical (a_N = 1.385 mT; a_H(2H) = 0.772 mT; g = 2.0056).[12] Measurements at various concentrations of free I^- anions showed a decrease in the EPR signal of $^\bullet$ND-CH_2OH with an increase of $c(I^-)$, suggesting a fast consumption of $^\bullet CH_2OH$ radicals by these anions. The same concentration effect was observed using the spin trap DMPO.

The formation of solvated electrons and their reactions are expressed by (7) and (8):

$$^\bullet CH_2OH + I^- \rightarrow ICH_2OH + e^- \rightarrow HI + CH_2O + e^- \quad (7)$$

$$_{GS}[Fe^{III}(N_2O_2)(CH_3OH)I] + e^- \rightarrow [Fe^{II}(N_2O_2)(CH_3OH)I]^- \quad (8)$$

No sign of accumulation of I_3^- anions during irradiation was observed in electronic absorption spectra, *i.e.,* iodide ligands were not oxidized to iodine atoms within the redox processes.

[Fe(benacen)(CH_3OH)N_3]

As the final products of photoredox processes occurring in irradiated solutions of [Fe(benacen)(CH_3OH)N_3], CH_2O and Fe^{II} were formed. When applying radiation of 313 nm, 366 nm or 436 nm, $n(CH_2O) : n(Fe^{II}) \cong 1 : 2$, which mimics the situation expressed by Eqs. (1) to (5). However, at irradiation of 254 nm, $n(CH_2O) : n(Fe^{II}) \cong 2 : 1$.

The $\Phi_{Fe^{II}} / \lambda_{irr}$ dependence of the [Fe(benacen)-(CH_3OH)N_3] complex differs from that of the other investigated complexes. It reaches the highest value at 313 nm and decreases to lower values both when increasing (to 254 nm) and decreasing (to 366 nm and 436 nm) the energy of incident photons. Such photochemical dependence was named[14] »bell-shaped«. Along with the commonly encountered[5] decrease in $\Phi_{Fe^{II}}$ with increasing radiation wavelength, the drop in $\Phi_{Fe^{II}}$ with decreasing radiation wavelength deserves an explanation.

Part of the 254 nm photons is absorbed by the anion N_3^- populating excited $_{(n\rightarrow\pi^*)}N_3^-$ while one of possible deactivation modes is its decomposition producing the nitrene intermediate anion N^-.

$$_{(n\rightarrow\pi^*)}N_3^- \rightarrow N_2 + N^- \quad (9)$$

As previously rationalized,[15] this electronically unsaturated anion is extremely reactive and abstracts electrons and/or atoms from the surrounding molecules, in our case from methanol molecules producing additional formaldehyde

$$N^- + 2\ CH_3OH \rightarrow CH_2O + CH_3O^- + NH_3 \quad (10)$$

The sequence initiated by azide excitation and terminated by formaldehyde formation (10) was proven independently by 254 nm irradiation of a methanolic solution of 2.0×10^{-3} mol dm^{-3} NaN_3 in the absence of iron(III) complex. Under such irradiation, formaldehyde was formed with the quantum yield approaching 1×10^{-2}. This »extra-produced« formaldehyde causes the observed high mole ratio $n(CH_2O) : n(Fe^{II}) \cong 2 : 1$ in the system of [Fe(benacen)(CH_3OH)N_3] irradiated by incident radiation with 254 nm. No such azide decomposition was observed when irradiating methanolic solutions of NaN_3 at 313 nm, 366 nm or 436 nm.

A decrease in $\Phi_{Fe^{II}}$ with decreasing the incident radiation wavelength is thus a consequence of opening a new chemical deactivation channel not involving the central atom and competing with the common Fe^{III} photoreduction. This channel is a decomposition of azido group, which occurs only using 254 nm incident irradiation populating directly an excited state of this group. The other possibility lies in an indirect population of (n→π*) excited state localized on the azide ligand/anion from energy higher IL excited states of the complex. Irrespective of the mode of excited azide population, its reaction does not involve the central atom Fe^{III} and thus reduces the quantum yield of its reduction to Fe^{II}. Moreover, oxidation of the photochemically produced Fe^{II} by nitrene intermediates cannot be excluded either.

Upon irradiation of 5×10^{-3} mol dm^{-3} [Fe(benacen)(CH$_3$OH)N$_3$] in the presence of ND or DMPO spin traps, EPR signals of $^{\bullet}$CH$_2$OH-DMPO and $^{\bullet}$CH$_2$OH-ND, respectively, were observed. The *N-tert*-butyl-α-phenylnitrone (PBN) spin trap, which was successfully applied[14,16] in aqueous solutions of azido complexes of cytochrome *c*, $[Co(CN)_5N_3]^{3-}$ and $[Co(NH_3)_5N_3]^{2+}$ forming PBN-N$_3$ adduct, gave only the $^{\bullet}$CH$_2$OH-PBN adduct in the presence of methanol.[16] Thus, PBN is not suitable for distinguishing between the primary formation of $^{\bullet}$CH$_2$OH or $^{\bullet}$N$_3$ radicals in methanolic solution due to a faster reaction of N$_3$ with methanol (11)

$$N_3^{\bullet} + CH_3OH \rightarrow HN_3 + {}^{\bullet}CH_2OH \qquad (11)$$

than with PBN. The course of reaction (11) was investigated[17] and supported also by the electrode potentials[18] $E^o(^{\bullet}CH_2OH/CH_3OH) = 1.29$ V and $E^o(^{\bullet}N_3/N_3^-) = 1.32$ V.

It should be pointed out, however, that contrary to PBN, the use of ND gave a stable spin adduct with $N_3^{\bullet}$ radical also in methanol.[16] The absence of any sign of the $^{\bullet}$ND-N$_3$ adduct signal in our system may be taken as a proof that within irradiation of [Fe(benacen)(CH$_3$OH)N$_3$], predominantly (if not exclusively) coordinated CH$_3$OH molecules undergo photooxidation.

IR spectra of solid residues obtained by vacuum room-temperature evaporation of methanol from solutions of [Fe(benacen)(CH$_3$OH)N$_3$] irradiated at 254 nm or 313 nm showed no characteristic peak (centred at about 875 nm[19]) attributable to a triple $Fe^V\equiv N$ bond, *i.e.*, Fe^V nitrido complexes were not formed. This is in agreement with the observation[11,19] that such complexes are stable only at low temperatures and in the case of complexes with macrocyclic (cyclam, porphyrin) ligands.

[Fe(benacen)(CH$_3$OH)$_2$]$^+$

This complex is present in solutions in the absence of »well-coordinated« acido ligands, *i.e.,* when the counter anions are, *e.g.*, ClO$_4^-$ or NO$_3^-$. The complex behaves similarly to fluoro complex under the influence of radiation, the mole ratio of $n(Fe^{II}) : n(CH_2O) \cong 2 : 1$ at all applied wavelengths and the only radical identified was $^{\bullet}$CH$_2$OH; the difference lies in a significantly higher quantum yield of Fe^{II} formation. Identification of the $^{\bullet}$CH$_2$OH radical (and the absence of CH$_3$O$^{\bullet}$ signal) may be taken as evidence that instead of free (non-coordinated) CH$_3$OH or CH$_3$O$^-$ anions, coordinated CH$_3$OH molecules take part in the primary electron transfer process, and, consequently, the primary redox process is of inner-sphere nature.[13,20] The mechanism expressed by Eqs. (1) to (5) may be applied to [Fe(benacen)(CH$_3$OH)$_2$]$^+$ as well.

[Fe(benacen)(C$_2$O$_4$)]$^-$

The [Fe(benacen)(C$_2$O$_4$)]$^-$ complex differs from the above mentioned complexes at least in three features. It contains a »bent« benacen ligand with the donor oxygen atoms of the oxalato ligand coordinated in the *cis*-position[21] (Figure 1); oxalato ligand is a typical redox irreversible ligand (once being oxidized to C$_2$O$_4^-$ and decomposed to CO$_2$ molecule and CO$_2^-$ anion, it cannot be reverted to the parent C$_2$O$_4^{2-}$ anion); in some of oxalato-containing complexes the quantum yield of the central atom reduction does not depend on the incident radiation wavelength (at least over a certain spectral region, a typical example is the ferrioxalate actinometer and also »bell-shaped« dependence observed in some cases (they can be exemplified[22] by [Fe(phen)$_2$(C$_2$O$_4$)]$^+$). The quantum yields for the [Fe(benacen)(C$_2$O$_4$)]$^-$ complex in Table I are, in general, higher than those for the other investigated complexes. This can be attributed to the mentioned redox irreversibility of the oxalato ligand. A relatively small wavelength effect on the quantum yield can be rationalized as a consequence of different excited states forming the manifold of redox reactive LMCT states participating in the primary photoredox deactivation steps.[23]

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SAŽETAK

Različita fotoredoks reaktivnost strukturno sličnih kompleksa željeza(III)

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Kompleksi željeza(III) [Fe(benacen)X]^q koji sadrže redoks nereaktivni tetradentatni N_2O_2 ligand otvorenoga lanca benacen(*N,N'*-etilenbis(benzoilacetoniminato)) i par monodentatnih liganada CH_3OH + F^-, CH_3OH + I^-, CH_3OH + N_3^-, (q = 0); 2 CH_3OH (q = 1); ili didentatni $C_2O_4^{2-}$ (q = –1) ligand, u mraku su redoks stabilni. Pod djelovanjem ultraljubičastoga i/ili vidljivoga zračenja dolazi do fotokemijskih reakcija i kao krajnji produkti nastaju željezo(II) i formaldehid CH_2O. Metodom EPR spinske stupice kao intermedijeri identificirani su radikali $^{\bullet}CH_2OH$ i solvatirani elektroni. Učinkovitost fotoredoks-procesâ, izražena kvantnim prinosom neto formiranja Fe^{II}, $\Phi_{Fe^{II}}$, jako je ovisna o valnoj duljini i monodentatnom/didentatnom ligandu.