Photochemical behaviour of iron(III) oxalato complexes with N,N′-ethylenebis(benzoylacetoneiminato) Schiff base derivatives

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Abstract

The complexes $Na[Fe(4-R-benacen)(C_2O_4)]$, where 4-R-benacen^{2-} are tetradentate chelating 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. Continuous irradiation of such solutions by ultraviolet and/or visible radiation leads to photophysical and photochemical deactivation processes yielding Fe(II) and CH$_2$O as final products. However, the molar ratio of Fe(II): CH$_2$O is much lower than that being typical for other methanolic iron(III) complexes. Using EPR spin trapping technique $^•$CH$_2$OH and a methine carbon localized radicals ($=$C$^{•-}$) of the benacen-ligand were identified in the irradiated solutions of the benacen-containing complex as intermediates. Contrary, carbon dioxide anion radicals CO$_2$ C$^{•-}$ radicals were found in a system with structurally similar $Na[Fe(salen)(C_2O_4)]$, where salen^{2-} is N,N′-ethylenebis (salicylaldiminato) N_2O_2-ligand. The efficiency of the photoredox processes, expressed by the quantum yield of Fe(II) formation, $\Phi_{Fe(II)}$ slightly decreases with increased wavelength of the incident radiation, and is influenced by the peripheral groups R of the tetradentate ligands. Contrary to the salen-containing complex, 4-R-benacen-ligands did not behave as innocent ones and participated in radical photoprocesses.
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1. Introduction

The oxalato anion $C_2O_4{}^{2-}$ exhibits three particular features when acting as a ligand in photochemical processes. The first one lies in the up-to-now known mechanisms of photochemical reactivity of oxalato complexes that have not included photosubstitutions or photoisomerizations but almost solely photoredox processes involving decomposition of oxalato ligands [1,2]. A further typical attribute is its redox irreversibility, i.e. contrary to the majority of redox reactive ligands, oxalato anions $C_2O_4{}^{2-}$ once being oxidized to $C_2O_4{}^{•-}$ or $CO_2{}^{•-}$ radicals cannot be reverted to $C_2O_4{}^{2-}$. Very detailed data on the mechanism of the photoredox decomposition of $[Fe(C_2O_4)_3]^{3-}$ occurring in $Na_2Mg[Al(C_2O_4)_3]\cdot9H_2O$ or $K_3[Al(C_2O_4)_3]\cdot3H_2O$ single crystal hosts were revealed by EPR technique [3]. It was shown that the primary redox products of the photolysis are $[Fe(C_2O_4)_2]^{2-}$ and $C_2O_4{}^{•-}$ coupled by antiferromagnetic interaction. In solutions the radical $C_2O_4{}^{•-}$ is released from the coordination sphere. Both the radicals $C_2O_4{}^{•-}$ or

$CO_2{}^{•-}$ as a product of its decomposition can react with another Fe(III), forming the final products Fe(II) and CO_2. A third characteristic quality of oxalato complexes is their ability to provide all three types of wavelength dependences of the photoredox quantum yield (further abbreviated as Φ/λ dependence), particularly

(i) a wide-range wavelength nearly independent Φ exemplified by $[Fe(C_2O_4)_3]^{3-}$ [4];
(ii) the most frequently observed gradual decrease in Φ with increasing λ ($[Co(NH_3)_4(C_2O_4)]^+$ can serve as an example [1]);
(iii) a "bell-shaped" Φ/λ dependence with a maximum quantum yield value at a certain wavelength and its gradual decrease both in higher and lower wavelength sides, represented by $[Fe(phen)_2(C_2O_4)]^+$ [5]. In spite of the fact that these three types of the Φ/λ dependence have been tentatively rationalized [6,7], several questions remain open and further results are needed to answer the questions definitely.

In addition to theoretical significance, the photochemical investigation of oxalato complexes is stimulated by its environmental importance [8–10].

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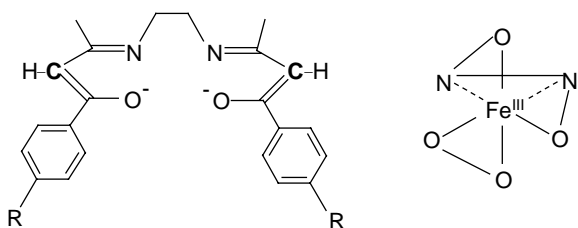*E-mail address:* jozef.sima@stuba.sk (J. Šima).

Fig. 1. Schematic representation of 4-R-benacen^{2-} ligands (R = H, Cl, Br, CH$_3$O) and a mode of the ligands coordination to the central atom Fe(III). Methine carbons are marked as C.

In this contribution, the results on photochemical properties of the complexes Na[Fe(4-R-benacen)(C$_2$O$_4$)] are presented. The structures of 4-R-benacen^{2-} (R = H, Cl, Br, CH$_3$O) and the central atom environment in the investigated complexes are depicted in Fig. 1.

2. Experimental

2.1. Reagents and solutions

The Schiff bases H$_2$ (benacen), H$_2$(4-Cl-benacen), H$_2$(4-Br-benacen) and H$_2$(4-CH$_3$O-benacen) were available from our previous works [11,12], their 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$_3$)$_2$. 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 redistilled before use and stored under argon in a freezer. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals) and 1,10-phenanthroline (phen, Aldrich) were used without further purification. The other chemicals were of analytical grade, purchased from Lachema and used as received.

Solutions of Na[Fe(4-R-benacen)(C$_2$O$_4$)] were prepared in situ from stock methanolic solutions of *trans*-[Fe(4-R-benacen)(CH$_3$OH)$_2$](NO$_3$), NaOCH$_3$, and H$_2$C$_2$O$_4$ so as to obtain solutions with the initial molar ratio c([Fe(4-R-benacen)(CH$_3$OH)$_2$]$^+$):c(H$_2$C$_2$O$_4$):c(NaOCH$_3$) = 1:1.2:4. They were kept in the dark and purged with argon 30 min prior and during irradiation.

2.2. Apparatus

Solutions of investigated complexes were photolysed in a three-compartment thermostated (20 ± 1 °C) quartz photoreactor. As radiation sources, a low pressure Germicidal Lamp G8T5 or a high pressure 150 W Hg-lamp (applied photophysics) were used. Radiation of the high-pressure lamp was monochromatized using solution filters [11]. Electronic absorption spectra were recorded on a Specord 200 spectrophotometer using 1.00 or 0.10 cm quartz cells. The EPR

spectra were measured using a computer controlled Bruker EMX instrument (operating at X-band, using 100 kHz field modulation) equipped with a quartz flat cell optimized for the Bruker TM cylindrical EPR cavity.

2.3. Irradiation and product analysis

The intensity of the incident monochromatized radiation was periodically determined with ferrioxalate actinometry [8].

Progress of the photoredox processes was monitored by UV–vis spectrophotometry as time evolution of c(Fe(II)) and c(CH$_2$O). Iron(II) was determined in the form of [Fe(phen)$_3$]$^{2+}$, formaldehyde CH$_2$O as 3,5-diacetyl-1,4-dihydrolutidine. The total amount of photolysis was limited to less than 5% to avoid an innerfilter effect. Details on the photolysis, analytical procedures and experimental data processing are described elsewhere [12,13].

In EPR mesurements, the prepared methanol solutions were carefully deoxygenated by an argon stream and irradiated directly in the cavity of EPR spectrometer by a 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 described in our previous paper in this Journal [14].

3. Results and discussion

3.1. Wavelength dependence of Fe(III) photoreduction quantum yields

In the majority of high-spin iron(III) complexes, the central tom Fe(III) is hexacoordinated both in the solid state and solutions [15,16]. The composition of the complexes present in methanol under given conditions was determined by a standard spectrophotometric titration of methanolic solutions of *trans*-[Fe(4-R-benacen)(CH$_3$OH)$_2$](NO$_3$) with H$_2$C$_2$O$_4$ in the presence of NaOCH$_3$ keeping the titrated complex concentration at 2.00×10^{-4} mol dm^{-3}, that of NaOCH$_3$ at 8.00×10^{-4} mol dm^{-3}, and increasing the concentration of H$_2$C$_2$O$_4$ from 2.00×10^{-5} mol dm^{-3} to 8.00×10^{-4} mol dm^{-3}. Evaluating the spectral data it was found that at the concentration ratio c([Fe(4-R-benacen)(CH$_3$OH)$_2$]$^+$):c(H$_2$C$_2$O$_4$):c(NaOCH$_3$) = 1:1.2:4 practically all Fe(III) is present in the form of anionic complex [Fe(4-R-benacen)(C$_2$O$_4$)]$^-$.

Typically, the electronic absorption spectra of the complexes [Fe(4-R-benacen)(C$_2$O$_4$)]$^-$ consist of several broad bands and shoulders. As an example, a UV–vis absorption spectrum of [Fe(benacen)(C$_2$O$_4$)]$^-$ and for comparison that of [Fe(benacen)(CH$_3$OH)$_2$]$^+$ are shown in Fig. 2.

Based on previously published data [11–13,17,18] bands in the visible region can be attributed to ligand-to-metal charge transfer (LMCT) transitions O2p or N(2p) → Fe3d,
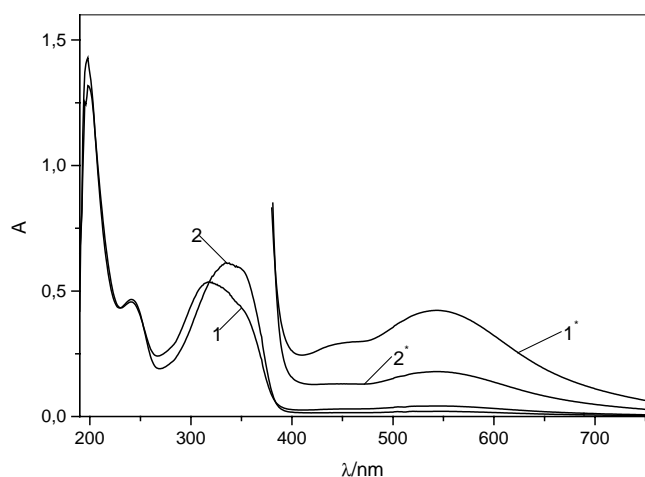
Fig. 2. Electronic absorption spectra of 2.0×10^{-4} Na[Fe(benacen) (C_2O_4)] (2, 2′) and [Fe(benacen)(CH$_3$OH)$_2$](NO$_3$) (1, 1′) in methanol measured in 1.0 cm (1, 2) and 0.1 cm (1′, 2′) quartz cells.

the ultraviolet bands in the regions of 210–280 nm and 300–360 nm to the intraligand transitions IL ($\pi \rightarrow \pi^*$) localized predominantly on the phenyl rings and on C=N fragments of the 4-R-benacen-ligands, respectively. Owing to their spin-forbidden nature, bands of ligand field (LF) states were not observed in solution spectra.

Irradiation of methanolic solutions of the investigated complexes by UV–vis radiation gives rise 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 excitation radiation and on the peripheral groups R of the 4-R-benacen-ligands (Table 1). Blank experiments confirmed that the complexes [Fe(4-R-benacen)(C$_2$O$_4$)]$^-$ do not undergo spontaneous redox changes in methanolic solutions in the dark.

Based on the rationalization published in [6,19,20], the observed decrease in the quantum yield $\Phi_{Fe(II)}$ with increasing incident radiation wavelength may be understood and summarized as a consequence of very efficient internal con-

version and/or intersystem crossing from energy higher IL to photoredox reactive LMCT states of the complexes, and a proportionality of the rovibrational energy content and the energy of absorbed photon. Thus, the higher the difference between the rovibrational energy of a given LMCT state and the threshold energy of the primary photoproducts formation, the higher probability of their separation, i.e. the higher $\Phi_{Fe(II)}$.

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

A comparison of the quantum yields $\Phi_{Fe(II)}$ for [Fe(4-R-benacen)(C$_2$O$_4$)]$^-$ and those for their structural analogues [Fe(4-R-benacen)(CH$_3$OH)X], where X = F, Cl, Br, I or N$_3$ [11,12,18–20] leads to two conclusions stating that (i) the photoredox reactivity of the oxalato complexes are significantly higher, (ii) a slope of Φ/λ plot is of lower value. These phenomena may be a consequence of two effects, namely of a higher ability of oxalato ligand to undergo photodecomposition and the above mentioned redox irreversibility of oxalato ligand.

3.2. EPR spin trapping

To identify radicals formed in the irradiated solutions, EPR spin trapping method was applied to [Fe(benacen)-(C$_2$O$_4$)]$^-$ and, for comparison, to [Fe(salen)(C$_2$O$_4$)]$^-$ complexes exploiting the spin traps DMPO and ND.

The EPR spectra measured in methanol solutions of [Fe(benacen)(C$_2$O$_4$)]$^-$ and [Fe(salen)(C$_2$O$_4$)]$^-$ complexes before photoexcitation revealed the formation of paramagnetic EPR signal characterized with hyperfine splittings $a_N = 1.363$ mT, $a_H^\beta = 0.775$ mT, $a_H^\gamma = 0.16$ mT; g-value $= 2.0059$, which is attributed to $^\bullet$DMPO-OCH$_3$ adduct, in accord with literature data [21–23]. This adduct is not formed in a photochemical step, a mechanism of its generation is offered elsewhere [23].

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 2.00×10^{-4} mol dm^{-3} [Fe(4-R-benacen)(C$_2$O$_4$)]$^-$, and quantum yields of Fe(II) formation, $\Phi_{Fe(II)}$ in methanolic solutions of [Fe(4-R-benacen)(C$_2$O$_4$)]$^-$ irradiated by radiation with the excitation wavelength λ_{exc}

R	λ_{max} or λ_{sh} (nm) (ε, mol^{-1} dm^3 cm^{-1})			λ_{exc} (nm)			
	IL(phenyl)	IL(C=N)	LMCT	$\Phi_{Fe(II)} \times 10^3$			
				254	313	365	436
H	240,7 (23400) 350sh (28000)	334,1 (30900) 543,2 (900)	440sh (700)	79	47	37	33
Cl	248,0 (22900)	318,8 (25700) 360sh (19500)	460sh (1500) 541,9 (1960)	21	3.1	1.9	1.4
Br	251,0 (22400)	319,1 (26300) 365sh (14800)	441sh (1900) 537,6 (2290)	11	4.9	3.3	2.8
CH$_3$O	269,0 (39800)	335,7 (42000) 359sh (36400)	450sh (1800) 558,9 (2040)	39	7.0	6.5	5.0

Continuous irradiation ($\lambda > 300$ nm) of [Fe(benacen)(C_2O_4)]$^-$ complex causes a decrease in the $^\bullet$DMPO-OCH$_3$ signal intensity. Simultaneously, new six-line EPR signal was generated, described by parameters $a_N = 1.44$ mT, $a_H{}^\beta = 2.175$ mT; g-value $= 2.0058$, characteristic for $^\bullet$DMPO-CH$_2$OH adduct [21,22]. Additionally, prolonged photoexcitation led to the formation of further carbon-centered adduct $^\bullet$DMPO-C(methine) with unusual high value of beta-hydrogen splitting constant ($a_N = 1.592$ mT, $a_H{}^\beta = 2.81$ mT; g-value $= 2.0042$). The analysis of nitrogen and hydrogen hyperfine splittings, as well as a lower g-value, allowed us to propose that $^\bullet$DMPO-C(methine) is produced by DMPO addition with radical species obtained via hydrogen abstraction from benacen ligand [24,25].

Fig. 3 illustrates the experimental EPR spectrum measured during 25 min of irradiation in methanolic solutions [Fe(benacen)(C_2O_4)]$^-$ in the presence of DMPO spin trap. The experimental spectrum was simulated by superposition of three individual EPR components corresponding to $^\bullet$DMPO-OCH$_3$ (S1; relative concentration of 51.5%), $^\bullet$DMPO-CH$_2$OH (S2; 42.9%) and $^\bullet$DMPO-C(methine) (S3; 5.6%) as shown in Fig. 3. The radical $^\bullet$DMPO-C(methine) has not been observed in analogous systems up to now [2,11,12,18–20].

Irradiation of methanolic solution of [Fe(benacen)-(C_2O_4)]$^-$ saturated with nitrosodurene resulted in the formation of very low intensity EPR signal corresponding to $^\bullet$ND-CH$_2$OH ($a_N = 1.440$ mT, $a_H{}^\beta$(2H) $= 1.19$ mT; g-value $= 2.0054$), and simultaneously also $^\bullet$ND-CH$_2$R radical was produced ($a_N = 1.336$ mT, $a_H{}^\beta$(2H) $= 0.796$ mT; g-value $= 2.0054$), which was previously attributed to photoproduct of ND in methanol [12].

The photochemical behaviour of [Fe(salen)(C_2O_4)]$^-$ in methanol solution in the presence of DMPO was quite different. During continuous irradiation we monitored a substantial decrease in $^\bullet$DMPO-OCH$_3$ signal intensity, and finally its total disappearance. However, no paramagnetic signals were monitored upon prolonged continuous irradiation. Remarkably, when the irradiation was stopped after 25 min of photoexcitation, we observed the formation of a six-line EPR signal characterized by splittings $a_N = 1.447$ mT, $a_H{}^\beta = 1.711$ mT; g-value $= 2.0054$, which corresponds to the adduct of DMPO with $CO_2{}^{\bullet-}$ radical [26]. Fig. 4 represents the experimental EPR spectrum of the adduct measured (in dark) after 25 min exposure of [Fe(salen)(C_2O_4)]$^-$ in methanol solution, along with the corresponding simulation.

3.3. Final products determination

A molar ratio of iron(II) and formaldehyde as the final products of photoredox processes, Fe(II):CH$_2$O was substantially lower (0.74:1 in a system of the [Fe(benacen)(C_2O_4)]$^-$ complex irradiated at 365 nm) than the typical 2:1 ratio determined in other systems [2,12,18].

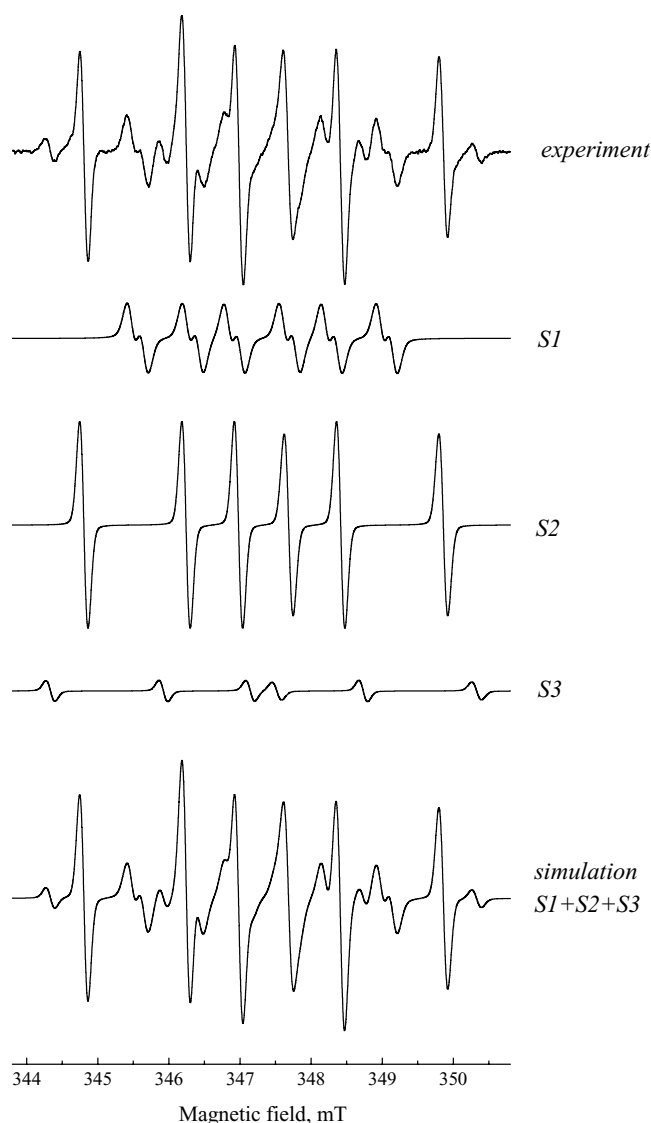Fig. 3. The experimental EPR spectrum measured in methanolic solution Na[Fe(benacen)(C_2O_4)] in the presence DMPO spin trap during 25 min of photoexcitation, c(DMPO) $= 0.01$ mol dm^{-3}). The simulation of experimental spectrum was calculated by the superposition of three individual simulations: S1: $^\bullet$DMPO-OCH$_3$ ($a_N = 1.363$ mT, $a_H{}^\beta = 0.775$ mT, $a_H{}^\gamma = 0.16$ mT; g-value $= 2.0059$); S2: $^\bullet$DMPO-CH$_2$OH ($a_N = 1.44$ mT, $a_H{}^\beta = 2.175$ mT; g-value $= 2.0058$); S3: $^\bullet$DMPO-C(methine) ($a_N = 1.592$ mT, $a_H{}^\beta = 2.81$ mT; g-value $= 2.0042$).

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

3.4. Mechanism of photo-induced processes

Based on the above spectra interpretation, radicals identification, molar ratio of the final products determination and literature data [12,19,20], processes occurring in the irradiated systems may be expressed (in the following equations, GS means the ground state, N_2O_2 denotes benacen-type ligands). Composition of the complexes is written in a mode
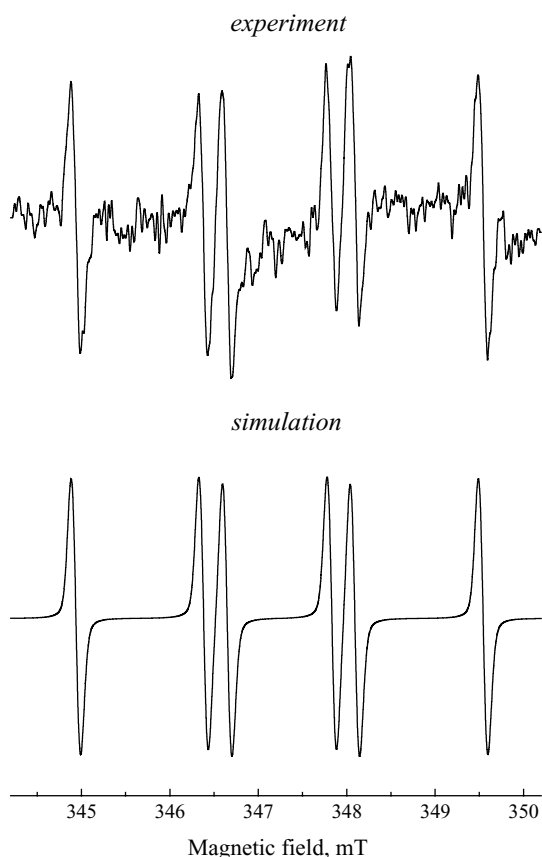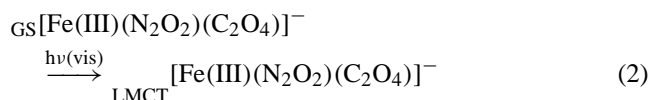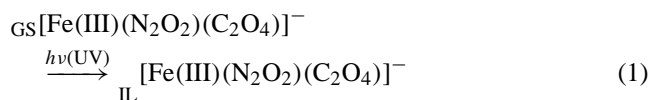
experiment

simulation

Fig. 4. The experimental EPR spectrum measured in methanolic solution of Na[Fe(salen)(C_2O_4)] in the presence of DMPO spin trap after 25 min of irradiation, c(DMPO) = 0.01 mol dm^{-3}. Simulation was calculated using EPR parameters a_N = 1.447 mT, a_H^β = 1.711 mT; g-value = 2.0054.

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:

$$_{GS}[Fe(III)(N_2O_2)(C_2O_4)]^-$$
$$\xrightarrow[IL]{h\nu(UV)} [Fe(III)(N_2O_2)(C_2O_4)]^- \qquad (1)$$

$$_{GS}[Fe(III)(N_2O_2)(C_2O_4)]^-$$
$$\xrightarrow[LMCT]{h\nu(vis)} [Fe(III)(N_2O_2)(C_2O_4)]^- \qquad (2)$$

Of all accessible excited states of the complexes, only LMCT sextet (populated directly by visible light absorption) and spin forbidden LMCT quartet states (reached by intersystem crossing from energy higher IL states) possess the electron distribution suitable for an inner-sphere reduction of Fe(III) to Fe(II). Spin trapping EPR measurements document that along with a commonly occurring photooxidation

of CH_3OH to $^\bullet CH_2OH$ radical

$$_{LMCT}[Fe(III)(N_2O_2)(C_2O_4)]^- + CH_3OH$$
$$\rightarrow [Fe(II)(N_2O_2)(C_2O_4)]^{2-} + {}^\bullet CH_2OH \qquad (3)$$
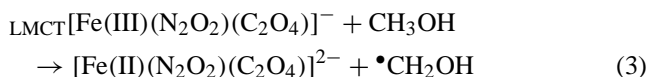
also the hydrogen atom abstraction from a methine carbon of the benacen-ligand occurs

$$*Fe(III) + =CH- \rightarrow Fe(II) + =C^{\bullet-} + H^+ \qquad (4)$$
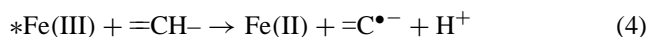
where $*$Fe(III) means excited Fe(III) complex.

Such a new feature has not been observed before in the photochemistry of complexes with benacen-type ligands; these ligands behaved as an innocent moiety not participating in photoredox processes. Electrophilic substitutions localized on methine carbon are known for some decades and were utilized for preparative purposes [27]. Such reactions occurred, however, due to an attack of a strong electrophilic agent on the carbon atom.

A difference in the photochemical behaviour of the benacen complexes with two monodentate axial ligands and those with a bidentate ligand lies probably in a different strain put on the benacen-type ligands. In the former case the benacen-type ligands can adopt the most advantageous structure allowing for effective π-conjugation. In the latter type the benacen-type ligands are forced to distort, π-conjugation is weakened and the (methine) C–H bond becomes more susceptible to react. The mentioned changes in the ligand shape are reflected also in part of the UV spectra (Fig. 2) corresponding to IL(C=N) transitions. The formation of the methine carbon localized radical via (methine) C–H reaction with primarily oxidized oxalato ligand

$$=CH- + CO_2^{\bullet-} \rightarrow =C^\bullet- + HCO_2^- \qquad (5)$$

may be involved, too. Such process would explain the fact that the $CO_2^{\bullet-}$ radical was not detected in the system of benacen-containing complex. Reactivity of the (methine) C–H bond may be enhanced owing to changes in electron density distribution due to population of a benacen-localized IL excited state.

No (methine) C–H bond is present in the complexes with salen-containing ligand which explains the absence of methine carbon localized radical in the EPR spectra. On the other hand, the $CO_2^{\bullet-}$ radical was found in the system of [Fe(salen)(C_2O_4)]$^-$ complex. Based on the standard potential value $E^\circ(CO_2/CO_2^{\bullet-}) = -1.930$ V [28], the $CO_2^{\bullet-}$ radical is a strong reducing agent able to reduce Fe(III)

$$[Fe(III)(N_2O_2)(C_2O_4)]^- + CO_2^{\bullet-}$$
$$\rightarrow [Fe(II)(N_2O_2)(C_2O_4)]^{2-} + CO_2 \qquad (6)$$
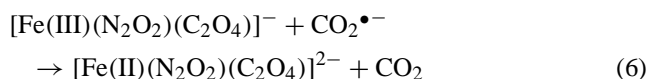
Such reduction is taken into account when rationalizing properties of the ferrioxalate-based actinometer.

The close vicinity of the radical $CO_2^{\bullet-}$ to a reactive (methine) C–H bond enables a competitive reaction (5) to occur in the complexes with benacen-type ligands. It does not involve the central atom reduction, lowering thus the concen-

tration of Fe(II) formed, i.e. contributing to the determined low molar ratio of $c(Fe(II)):c(CH_2O)$.

The radical product(s) can participate in a number of subsequent processes. As documented by the value $E^\circ(^\bullet CH_2OH/CH_2O) = -1.180\,V$ [29], also the radical $^\bullet CH_2OH$ is able to reduce Fe(III) forming thus the final products Fe(II) and CH_2O

$$[Fe(III)(N_2O_2)(C_2O_4)]^- + {}^\bullet CH_2OH$$
$$\rightarrow [Fe(II)(N_2O_2)(C_2O_4)]^{2-} + H^+ + CH_2O \qquad (7)$$
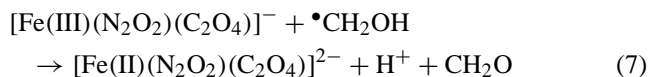
The ratio of $c(Fe(II)):c(CH_2O) = 0.74:1$ determined in the irradiated $[Fe(III)(benacen)(C_2O_4)]^-$ shows that the reduction of Fe(III) by $^\bullet CH_2OH$ (7) is of less importance than in analogous systems with monodentate ligands.

The fate of methine carbon localized radical is not known in detail, it may, however, react with CH_3OH molecule yielding $^\bullet CH_2OH$ and benacen ligand. Given a number of radicals involved in secondary dark reactions and in general their high reactivity, other processes leading to the formation of CH_2O and Fe(II) or to reoxidation of Fe(II) to Fe(III) cannot be excluded.

The slow appearance and persistence of the $CO_2^{\bullet-}$ radical in the system of $[Fe(III)(salen)(C_2O_4)]^-$ call attention to the importance of kinetic aspects of its reactivity.

Acknowledgements

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