

**PHOTOREDOX CHEMISTRY OF IRON(III) OXALATO COMPLEXES WITH  
*N,N'*-1,1-*R*<sub>2</sub>-ETHYLENEBIS(*R'*-SALICYLIDENEIMINATO) LIGANDS****Mário Izakovič and Jozef Šima\****Department of Inorganic Chemistry, Slovak Technical University,  
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Received 16-03-2004

**Abstract**

The complexes  $\text{Na}[\text{Fe}(\text{R}'\text{-sal-}\text{R}_2\text{-en})(\text{C}_2\text{O}_4)]$ , where  $\text{R}'\text{-sal-}\text{R}_2\text{-en}^{2-}$  are tetradentate open-chain *N,N'*-1,1-*R*<sub>2</sub>-ethylenebis(*R'*-salicylideneiminato)  $\text{N}_2\text{O}_2$ -ligands ( $\text{R} = \text{H}$  or  $\text{CH}_3$ ;  $\text{R}' = \text{H}$ , 5-Cl, 5-Br, 3,5-Br<sub>2</sub>, 3-OCH<sub>3</sub> or 4-OCH<sub>3</sub>), are redox stable in methanolic solutions in the dark. Continuous irradiation of such solutions by ultraviolet and/or visible light leads to photophysical and photochemical deactivation processes yielding Fe(II), CO<sub>2</sub> and CH<sub>2</sub>O as final products. Using EPR spin trapping technique, carbon dioxide anion radicals  $\text{CO}_2^{\bullet-}$  were identified in methanolic solutions of the complexes irradiated at  $\lambda_{\text{irr}} > 300$  nm. Tetradentate ligands behave as innocent moiety not participating in redox processes of the complexes. The efficiency of the photoredox processes, expressed by the quantum yield of Fe(II) formation,  $\Phi_{\text{Fe(II)}}$ , slightly decreases with increased wavelength of the incident radiation, and is influenced by the peripheral groups *R* and *R'* of the tetradentate ligands. A mechanism of the primary photochemical and subsequent thermal reactions is proposed.

**Key words:** Iron(III) complexes, photochemistry, mechanism**Introduction**

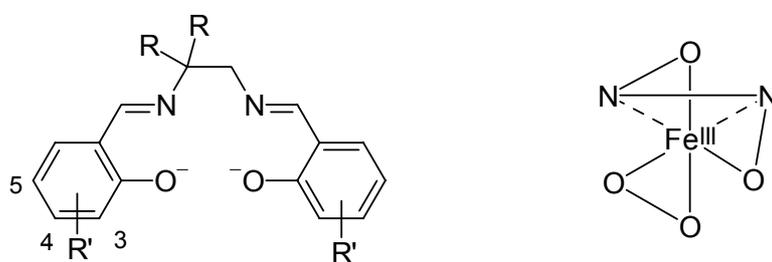
Electronically excited oxalato complexes of redox reactive transition metals exhibit three particular features. The first one lies in the fact that they undergo almost exclusively photoredox deactivation processes involving primary oxidation of oxalato ligands to the radical anion  $\text{C}_2\text{O}_4^{\bullet-}$  and its subsequent decomposition to the radical anion  $\text{CO}_2^{\bullet-}$  and molecule CO<sub>2</sub> with no photosubstitutions or photoisomerizations observed.<sup>1,2</sup> A further typical attribute is the redox irreversibility of the oxalato ligand which being once oxidized it cannot be reverted to  $\text{C}_2\text{O}_4^{2-}$ . As documented by solid state<sup>3</sup> and solution<sup>4</sup> photolysis of  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , both radical anions  $\text{C}_2\text{O}_4^{\bullet-}$  and  $\text{CO}_2^{\bullet-}$  can react with Fe(III) forming the final products Fe(II) and CO<sub>2</sub>.<sup>4</sup> A third characteristic quality of oxalato complexes is their ability to provide all three types of wavelength dependences of the photoredox decomposition quantum yield (further abbreviated as  $\Phi/\lambda$  dependence), i.e. nearly independent  $\Phi$  in a wide range of wavelengths, exemplified<sup>5</sup> by

$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , a frequently observed gradual decrease in  $\Phi$  with increasing  $\lambda$  such as that observed<sup>1</sup> for  $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^+$ , and a “bell-shaped”  $\Phi/\lambda$  dependence with a maximum quantum yield value at a certain wavelength and its gradual decrease both in higher and lower wavelength sides<sup>6</sup> represented by  $[\text{Fe}(\text{phen})_2(\text{C}_2\text{O}_4)]^+$ .

It should be noted that these three types of  $\Phi/\lambda$  dependence have been tentatively rationalized,<sup>7,8</sup> but several questions remain open and further results are needed to answer the questions definitely.

Along with their theoretical significance, photochemical processes of iron(III) oxalato complexes are of practical importance too as documented by numerous works from environmental area.<sup>4,9-11</sup>

In this contribution, the results on photochemical properties of the complexes  $\text{Na}[\text{Fe}(\text{R}'\text{-sal-R-en})(\text{C}_2\text{O}_4)]$  are presented. The structure of  $\text{R}'\text{-sal-R-en}^{2-}$  ligands ( $\text{R} = \text{H}$  or  $\text{CH}_3$ ;  $\text{R}' = \text{H}$ , 5-Cl, 5-Br, 3,5-Br<sub>2</sub> or 4-CH<sub>3</sub>O) and the central atom environment in the investigated complexes are depicted in Fig. 1. For the sake of simplicity, the tetradentate ligands will be further abbreviated as  $\text{N}_2\text{O}_2$  when discussed in general. The simplest ligand ( $\text{R} = \text{R}' = \text{H}$ ) is denoted salen.



**Figure 1.** Schematic representation of  $\text{R}'\text{-sal-R-en}^{2-}$  ligands ( $\text{R} = \text{H}$  or  $\text{CH}_3$ ;  $\text{R}' = \text{H}$ , 5-Cl, 5-Br, 3,5-Br<sub>2</sub>, 3-CH<sub>3</sub>O or 4-CH<sub>3</sub>O) and a mode of the ligands coordination to the central atom.

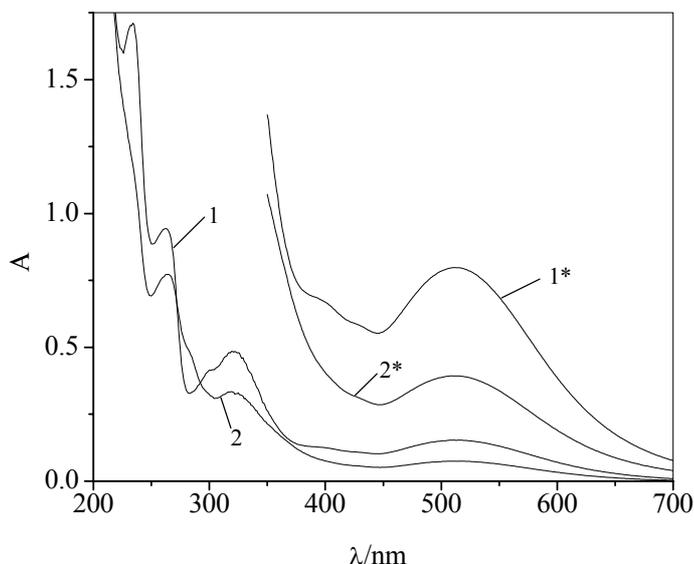
## Results and discussion

### *Wavelength dependence of quantum yields of Fe(II) formation*

In the majority of high-spin iron(III) complexes, the central atom Fe(III) is hexacoordinated both in the solid state and solutions.<sup>12,13</sup> The molecular structure of  $[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]^-$  is given.<sup>14</sup> The composition of the complexes present in methanol under given conditions was determined by a standard spectrophotometric titration<sup>15</sup> of methanolic solutions of  $\text{trans-}[\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})_2](\text{NO}_3)$  with  $\text{H}_2\text{C}_2\text{O}_4$  in the presence of

NaOCH<sub>3</sub> keeping the titrated complex concentration at  $2.00 \times 10^{-4} \text{ mol dm}^{-3}$ , that of NaOCH<sub>3</sub> at  $8.00 \times 10^{-4} \text{ mol dm}^{-3}$ , and increasing the concentration of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> from  $2.00 \times 10^{-5} \text{ mol dm}^{-3}$  to  $8.00 \times 10^{-4} \text{ mol dm}^{-3}$ . Evaluating the spectral data it was found that at the concentration ratio  $c([\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})_2]^+) : c(\text{H}_2\text{C}_2\text{O}_4) : c(\text{NaOCH}_3) = 1 : 1.2 : 4$  practically all Fe(III) is present in the form of anionic complex  $[\text{Fe}(\text{N}_2\text{O}_2)(\text{C}_2\text{O}_4)]^-$ .

Typically, the electronic absorption spectra of the complexes  $[\text{Fe}(\text{N}_2\text{O}_2)(\text{C}_2\text{O}_4)]^-$  consist of several broad bands and shoulders, the spectral band maxima/shoulders and extinction coefficients are slightly influenced by the group R and R' of the N<sub>2</sub>O<sub>2</sub>-ligands. As an example, a UV and VIS absorption spectrum of  $[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]^-$  and for comparison that of  $[\text{Fe}(\text{salen})(\text{CH}_3\text{OH})_2]^+$  are shown in Fig. 2. The spectral properties of all investigated complexes are described in Table 1.



**Figure 2.** Electronic absorption spectra of  $2.00 \times 10^{-4} \text{ mol dm}^{-3}$   $[\text{Fe}(\text{salen})(\text{CH}_3\text{OH})_2](\text{NO}_3)$  (1, 1\*) and  $\text{Na}[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]$  (2, 2\*) in methanol measured in 0.2 cm (1, 2) and 1.0 cm (1\*, 2\*) quartz cells.

Based on previously published data,<sup>16-19</sup> bands in the visible region can be attributed to ligand-to-metal charge transfer (LMCT) transitions  $\text{O}2\text{p} \rightarrow \text{Fe}3\text{d}$ , the ultraviolet bands in the regions of 210 - 300 nm and 300 - 350 nm to the intraligand transitions  $\text{IL}(\pi \rightarrow \pi^*)$  localized predominantly on the phenyl rings and on C=N fragments of the N<sub>2</sub>O<sub>2</sub>-ligands, respectively. Owing to their spin-forbidden nature, bands of ligand field (LF) states are not seen in solution spectra. Electronic spectral data of the complexes are listed in Table 1.

**Table 1.** Wavelength of bands maxima ( $\lambda_{\max}$ ) or shoulders ( $\lambda_{\text{sh}}$ ) and corresponding  $\log \epsilon$  (extinction coefficients  $\epsilon$  are expressed in  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ) in electronic absorption spectra of methanolic solutions of  $[\text{Fe}(\text{R}'\text{-sal-R-en})(\text{C}_2\text{O}_4)]^-$ .

$\text{R}'\text{-sal-R-en}^{2-}$			$\lambda_{\max}$ or $\lambda_{\text{sh}}$ ( $\log \epsilon$ )	
<b>R</b>	<b>R'</b>	<b>IL(phenyl)</b>	<b>IL(C=N)</b>	<b>LMCT</b>
H	H	234sh(4.63); 264.9(4.29); 284sh(4.07)	318.9(3.92); 351sh(4.05)	425sh(3.12); 514.8(3.29)
H	5-Cl	234.0(4.69); 263.3(4.31)	302.9(4.09); 322.6sh(4.06)	441sh(3.39); 370sh(3.69); 520.1(3.61)
H	5-Br	238.8(4.71); 265sh(4.28)	304.5(4.11); 322sh(4.09)	441sh(3.43); 401sh(3.47); 521.0(3.67)
H	3,5-Br <sub>2</sub>	214.0(4.55); 270sh(4.29)	311.7(4.04)	415.0(3.43); 442sh(3.40); 527.1(3.57)
H	3-OCH <sub>3</sub>	227.0(4.65); 275.0(4.39)	310.8(4.10); 345sh(3.91)	455.6(3.47); 566.4(3.56)
H	4-OCH <sub>3</sub>	244.9(4.53); 280.7(4.52)	308.2(4.34); 387.1(3.64)	412.8(3.59); 470.8(3.66); 514sh(3.62)
CH <sub>3</sub>	H	265.9(4.57); 299.0(4.18)	318.2(4.18); 399sh(3.52)	430sh(3.45); 519.7(3.61)

**Table 2.** Quantum yields of Fe(II) formation,  $\Phi_{\text{Fe(II)}}$ , in irradiated methanolic solutions of  $2.00 \times 10^{-4} \text{ mol dm}^{-3} [\text{Fe}(\text{R}'\text{-sal-R-en})(\text{C}_2\text{O}_4)]^-$ .

$\text{R}'\text{-sal-R-en}^{2-} / \lambda_{\text{irr}}$ (nm)		254	313	366	436
<b>R</b>	<b>R'</b>	$\Phi_{\text{Fe(II)}} \times 10^3$			
H	H	7.5	2.7	2.4	2.2
H	5-Cl	12.2	2.2	1.6	1.1
H	5-Br	7.2	3.6	1.8	1.1
H	3,5-Br <sub>2</sub>	29.5	6.8	4.5	2.3
H	3-OCH <sub>3</sub>	10.7	3.8	3.4	2.7
H	4-OCH <sub>3</sub>	16.0	3.8	2.2	1.4
CH <sub>3</sub>	H	4.8	2.0	1.2	1.2

Irradiation of methanolic solutions of the investigated complexes by UV or visible radiation gives rise to the photoreduction of Fe(III) to Fe(II). The overall quantum yields of Fe(II) formation,  $\Phi_{\text{Fe(II)}}$  depend on the wavelength of the incident radiation and on the peripheral groups R of the  $\text{N}_2\text{O}_2$ -ligands (Table 2). Blank experiments confirmed that the complexes  $[\text{Fe}(\text{N}_2\text{O}_2)(\text{C}_2\text{O}_4)]^-$  do not undergo spontaneous redox changes in methanolic solutions in the dark.

Based on the published rationalization,<sup>7,20,21</sup> the observed decrease in the quantum yield  $\Phi_{\text{Fe(II)}}$  with increasing incident radiation wavelength may be understood and summarized as a consequence of very efficient internal conversion 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 and thus  $\Phi_{\text{Fe(II)}}$ .

A comparison of the quantum yields  $\Phi_{\text{Fe(II)}}$  for  $[\text{Fe}(\text{N}_2\text{O}_2)(\text{C}_2\text{O}_4)]^-$  and those<sup>16-20</sup> for their structural analogues  $[\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})\text{X}]$ , where X = F, Cl, Br, I or N<sub>3</sub> leads to two conclusions stating that *i*) the photoredox reactivity of the oxalato complexes are significantly higher, *ii*) a slope of  $\Phi/\lambda$  plot is of lower value. These phenomena may be a consequence of both a higher ability of oxalato ligand to undergo photodecomposition and the above mentioned redox irreversibility of oxalato ligand.

#### EPR spin trapping

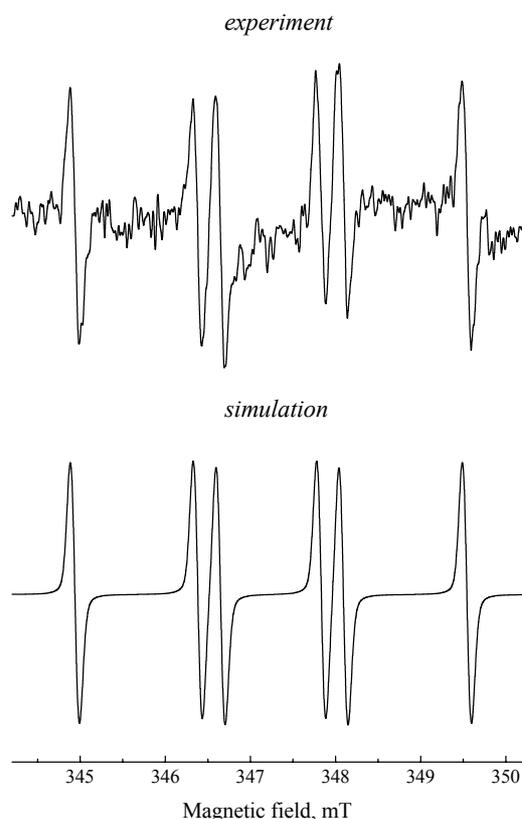
To identify radicals formed in the irradiated solutions, EPR spin trapping method was applied to the complex  $[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]^-$  exploiting the spin traps 5,5-dimethyl-1-pyrrolidine-*N*-oxide (DMPO) and 2,3,5,6-tetramethylnitrosobenzene (ND).

Irradiation of methanolic solution of  $[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]^-$  saturated with nitrosodurene resulted in the formation of very low intensity EPR signal corresponding to  $\bullet\text{ND-CH}_2\text{OH}$  ( $a_{\text{N}} = 1.440$  mT,  $a_{\text{H}}(2\text{H}) = 1.19$  mT;  $g$ -value = 2.0054).

The EPR spectra measured in a methanolic solution of  $[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]^-$  in the presence of DMPO before photoexcitation revealed the formation of paramagnetic EPR signal characterized with 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 is attributed to  $\bullet\text{DMPO-OCH}_3$  adduct, in accord with literature.<sup>22-24</sup> This adduct is not formed in a photochemical step; a mechanism of its generation is given elsewhere.<sup>24</sup>

During continuous irradiation of  $[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]^-$  in methanol in the presence of DMPO a substantial decrease in  $\bullet\text{DMPO-OCH}_3$  signal intensity, and finally its total disappearance was monitored. However, no paramagnetic signals appeared upon prolonged continuous irradiation. Remarkably, when the irradiation was stopped after 25 minutes of photoexcitation, we observed the formation of a six-line EPR signal (Fig. 3) characterized by splittings  $a_{\text{N}} = 1.447$  mT,  $a_{\text{H}} = 1.711$  mT;  $g$ -value = 2.0054, which

corresponds to the adduct of DMPO with  $\text{CO}_2^{\bullet-}$  radical.<sup>25</sup> The experimental and simulated spectra using the above constants (Fig. 3) match well.



**Figure 3.** The experimental EPR spectrum measured in methanolic solution of  $\text{Na}[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]$  in the presence of DMPO spin trap after 25 minutes of irradiation,  $c(\text{DMPO}) = 0.01 \text{ mol dm}^{-3}$ . Simulated spectrum was calculated using EPR parameters  $a_{\text{N}} = 1.447 \text{ mT}$ ,  $a_{\text{H}} = 1.711 \text{ mT}$ ;  $g\text{-value} = 2.0054$ .

#### *Final products determination*

A molar ratio of iron(II) and formaldehyde as the final products of photoredox processes,  $\text{Fe(II)} : \text{CH}_2\text{O}$  was substantially lower (0.75:1 in a system of the  $[\text{Fe}(\text{salen})(\text{C}_2\text{O}_4)]^-$  complex irradiated at 365 nm) than the typical 2:1 ratio determined in other systems.<sup>2,17,19</sup> This fact clearly shows that along with photooxidation of  $\text{CH}_3\text{OH}$  associated with  $\text{Fe(III)}$  photoreduction, also other molecule(s) must be photooxidized. This is supported by EPR measurements discussed above.

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

*Mechanism of photoinduced processes*

Based on the above spectra interpretation, radicals identification, molar ratio of the final products determination and literature data,<sup>17,20,21</sup> processes occurring in the irradiated systems may be expressed (GS means the ground state). 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.

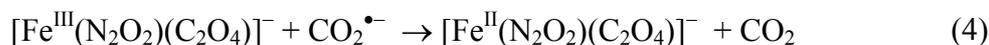
At UV-Vis irradiation of the investigated systems, spin-allowed IL or LMCT excited sextet states of complexes (1, 2) are populated:



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). Finding of  $\text{CO}_2^{\bullet-}$  radicals by spin trapping EPR measurements suggests that the primary photochemical process is oxalato ligand oxidation, the stoichiometry of which can be written as



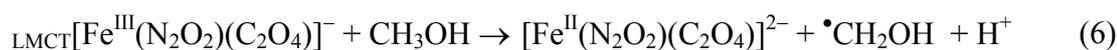
Based on the standard potential value  $E^\circ(\text{CO}_2/\text{CO}_2^{\bullet-}) = -1.930 \text{ V}$ ,<sup>26</sup> the  $\text{CO}_2^{\bullet-}$  radical is a strong reducing agent able to reduce Fe(III) also in the ground state of complexes.



The slow appearance and persistence of the  $\text{CO}_2^{\bullet-}$  radical in our system call attention to the importance of kinetic aspects of its reactivity. Other reactions of the radical  $\text{CO}_2^{\bullet-}$  such as hydrogen abstraction



cannot be excluded. The radical  $\bullet\text{CH}_2\text{OH}$  may, however, form via an outer-sphere process (6) too



As documented by the value  $E^\circ(\bullet\text{CH}_2\text{OH}/\text{CH}_2\text{O}) = -1.180 \text{ V}$ ,<sup>27</sup> the radical  $\bullet\text{CH}_2\text{OH}$  is able to reduce Fe(III) forming thus the final products Fe(II) and  $\text{CH}_2\text{O}$



The ratio of  $c(\text{Fe}^{\text{II}}) : c(\text{CH}_2\text{O}) = 0.75 : 1$  determined in the irradiated  $[\text{Fe}^{\text{III}}(\text{salen})(\text{C}_2\text{O}_4)]^-$  shows that the reduction of Fe(III) by  $\bullet\text{CH}_2\text{OH}$  (7) is of less importance than in analogous systems with monodentate ligands.

### Conclusions

Investigation of photochemical reactivity of the complexes  $\text{Na}[\text{Fe}(\text{R}'\text{-sal-R-en})(\text{C}_2\text{O}_4)]$  dissolved in methanol was performed by the method of continuous photolysis at four wavelength. A mechanism comprising the primary photodeactivation processes and subsequent thermal redox reactions occurring in the irradiated systems is proposed. It is based on EPR spin trapping identification of the radicals formed, determination of the final reaction products, and on literature data. It was found that the tetradentate salen-type ligands obviously behave as innocent moiety not participating in redox processes of the complexes. The quantum yield of Fe(II) formation,  $\Phi_{\text{Fe(II)}}$ , slightly decreases with increased wavelength of the incident radiation, and is influenced by the peripheral groups R and R' of the salen-type ligands.

### Experimental

#### Chemicals and solutions

The Schiff bases  $\text{H}_2(\text{salen})$ ,  $\text{H}_2(5\text{-Cl-salen})$ ,  $\text{H}_2(5\text{-Br-salen})$ ,  $\text{H}_2(3\text{-CH}_3\text{O-salen})$ ,  $\text{H}_2(4\text{-CH}_3\text{O-salen})$ ,  $\text{H}_2(3,5\text{-Br}_2\text{-salen})$ , and  $\text{H}_2(\text{sal}-(\text{CH}_3)_2\text{-en})$  were available from our previous works.<sup>16,17</sup> Their purity was checked by elemental analysis, melting point,  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR spectra.

Methanol (Lachema, reagent grade) was dried before use by distillation from  $\text{Mg}(\text{OCH}_3)_2$ . The spin trapping agents ND and DMPO were obtained from Aldrich. DMPO was freshly redistilled before use and stored under argon in a freezer.  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  (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  $\text{Na}[\text{Fe}(\text{N}_2\text{O}_2)(\text{C}_2\text{O}_4)]$  were prepared *in situ* from stock methanolic solutions of *trans*- $[\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})_2](\text{NO}_3)$ ,  $\text{NaOCH}_3$ , and  $\text{H}_2\text{C}_2\text{O}_4$  to obtain solutions with the initial molar ratio  $c([\text{Fe}(\text{N}_2\text{O}_2)(\text{CH}_3\text{OH})_2]^+) : c(\text{H}_2\text{C}_2\text{O}_4) : c(\text{NaOCH}_3) = 1 : 1.2 : 4$ . They were kept in the dark and purged with argon 30 minutes prior and during irradiation.

### Apparatus

Solutions of investigated complexes were photolysed in a three-compartment thermostated ( $20 \pm 1$  °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.<sup>15</sup> Electronic absorption spectra were recorded on a Specord 200 spectrophotometer using 1.00 or 0.20 cm quartz cells. The EPR spectra were measured with 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.

### Irradiation and product analysis

The intensity of the incident monochromatized radiation was periodically determined with ferrioxalate actinometry.<sup>5</sup>

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  $[\text{Fe}(\text{phen})_3]^{2+}$ , and formaldehyde  $\text{CH}_2\text{O}$  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, spectral measurements, analytical procedures and experimental data processing are described elsewhere.<sup>17,18,28</sup>

### Acknowledgements

The financial support of this work by grants of the Slovak Grant Agency VEGA 1/925/02 is appreciated. The authors thank Prof. Brezová (Department of Physical Chemistry, Slovak Technical University) for EPR spectra measurement and simulation.

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## Povzetek

Kompleksi  $\text{Na}[\text{Fe}(\text{R}'\text{-sal-R}_2\text{-en})(\text{C}_2\text{O}_4)]$ , kjer so  $\text{R}'\text{-sal-R}_2\text{-en}^{2-}$  štirivezni  $N,N'$ -1,1- $\text{R}_2$ -etilenbis( $\text{R}'$ -salicilideniminato)  $\text{N}_2\text{O}_2$ -ligandi ( $\text{R} = \text{H}$  ali  $\text{CH}_3$ ;  $\text{R}' = \text{H}$ , 5-Cl, 5-Br, 3,5- $\text{Br}_2$ , 3-O $\text{CH}_3$  ali 4-O $\text{CH}_3$ ), so v metanolnih raztopinah v temnem redoks stabilni. Pri obsevanje teh raztopin z ultravijolično in/ali vidno svetlobo nastanejo Fe(II) spojine,  $\text{CO}_2$  in  $\text{CH}_2\text{O}$ . Z uporabo EPR tehnike spinskega lovljena smo v metanolnih raztopinah teh kompleksov, obsevanih s svetlobo valovnih dolžin  $\lambda_{\text{irr}} > 300$  nm, identificirali anionske radikale  $\text{CO}_2^{\bullet-}$ . Štirivezni ligandi se obnašajo kot nereaktivne skupine in ne sodelujejo v redoks procesih kompleksa. Učinkovitost fotoredoks procesov, izražena s kvantnim izkoristkom Fe(II),  $\Phi_{\text{Fe(II)}}$ , se rahlo zniža pri povečanih valovnih dolžinah, in je odvisna od skupin R in  $\text{R}'$  ligandov. Predlagan je mehanizem primarnih fotokemijskih in nadaljnjih termičnih procesov.