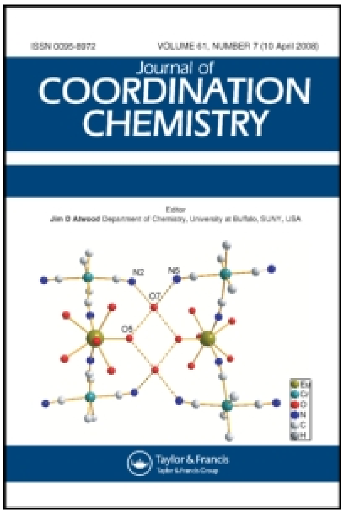

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Effects of wavelength and substituents on iron(III) photoreduction in *trans*-[Fe(R-sal-R`-en)(CH_3OH)(NCS)] complexes

Mário Izakovič; Jozef Šima; Marián Žitňanský

To cite this Article Izakovič, Mário , Šima, Jozef and Žitňanský, Marián(2005) 'Effects of wavelength and substituents on iron(III) photoreduction in *trans*-[Fe(R-sal-R`-en)(CH_3OH)(NCS)] complexes', Journal of Coordination Chemistry, 58: 12, 1039 — 1046

To link to this Article: DOI: 10.1080/00958970500109448

URL: http://dx.doi.org/10.1080/00958970500109448

Journal of Coordination Chemistry
Vol. 58, No. 12, 15 August 2005, 1039–1046

Taylor & Francis
Taylor & Francis Group

Effects of wavelength and substituents on iron(III) photoreduction in *trans*-[Fe(R-sal-R′-en)(CH_3OH)(NCS)] complexes

MÁRIO IZAKOVIČ*, JOZEF ŠIMA and MARIÁN ŽITŇANSKÝ

Department of Inorganic Chemistry, Slovak Technical University,
Radlinského 9, SK-81237 Bratislava, Slovakia

(*Received 6 December 2004*)

Photoredox reactions in irradiated methanolic solutions of *trans*-[Fe(R′-sal-R_2-en)(CH_3OH)(NCS)] complexes, where R′-sal-R_2-en^{2-} are tetradentate open-chain *N*,*N*′-1,1-R_2-ethylenebis(R′-salicylideneiminato) ligands (R = H or CH_3; R′ = H, 5-Cl, 5-Br, 3,5-Br_2, 3-OCH_3, 4-OCH_3), have been explored and a mechanism suggested. The complexes are redox-stable in the dark in methanol. Continuous irradiation of solutions in the region of intraligand (IL) or ligand-to-metal charge transfer (LMCT) transitions leads to photoreduction of Fe(III) to Fe(II) and formation of formaldehyde (CH_2O). Formation of polystyrene-containing bonded NCS, when irradiating the complexes in the presence of styrene used as a radical scavenger, indicates that the primary photoreduction of Fe(III) to Fe(II) is accompanied by oxidation of NCS^- to the $^{\bullet}$NCS radical. R′-sal-R_2-en ligands have little effect on the photoinduced redox processes. The quantum yield of Fe(II) formation, $\Phi_{Fe(II)}$, as a quantitative parameter of photoredox efficiency, decreases significantly with increasing wavelength of incident radiation, and is slightly influenced by the peripheral groups, R, of R′-sal-R_2-en.

Keywords: Iron(III) complexes; Photochemistry; Thiocyanate; Quantum yield; Wavelength dependence; Peripheral group effect

1. Introduction

The thiocyanate anion can coordinate to a metal ion as a unidentate through sulfur (usually to second- and third-row transition metals) or nitrogen (first-row transition metals), and as a bridging ligand through both S and N [1, 2]. The crystal structure of [Fe(L)(NCS)(H_2O)], where L = *N*,*N*′-bis(2-hydroxyphenylmethyleneimino)-1,3-diaminopropane anion, was reported recently [3]. In this complex, the Fe(III) ion has a slightly distorted octahedral geometry and is coordinated by two N and two O donors of the tetradentate ligand and an N atom of the thiocyanate anion, together with a water molecule. The structure complies with those of other iron(III) thiocyanato

---

*Corresponding author. Email: mario.izakovic@stuba.sk

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500109448

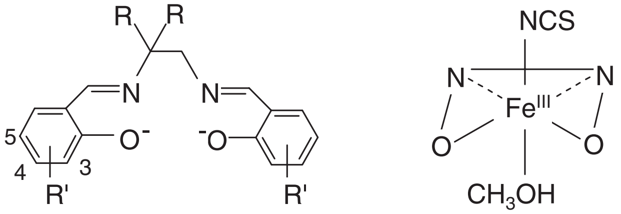

Figure 1. Schematic representation of R′-sal-R_2-en^{2-} ligands (R = H or CH_3; R′ = H, 5-Cl, 5-Br, 3,5-Br_2, 3-OCH_3 or 4-OCH_3) and mode of ligand coordination to Fe(III).

complexes [4]. A survey of structural data shows that the mode of coordination of NCS^- depends on the hardness/softness of the metal ion, steric factors, the solvent and effects of electromagnetic radiation.

Previous photochemical investigations of thiocyanato complexes have shown that they can undergo at least five types of radiation-induced reactions. These include non-redox photosubstitution of NCS^-, usually for a solvent molecule [5, 6] and photoanation substitution of the NCS^- anion [7], non-redox thiocyanato–isothiocyanato photoisomerization [8], and primary photooxidation of NCS^- to $^\bullet NCS$ radicals. The latter concerns photoreduction of the central atom followed by several fast reactions of the $^\bullet NCS$ radical, such as its reaction with NCS^- to form the anion-radical $(NCS)_2^{\bullet-}$ [5], dimerization to $(NCS)_2$ [9], redox reaction with a solvent molecule [10], initiation of polymerization [11], and so on. In addition, photochemical decomposition of NCS^- through loss of the sulfur atom [12] and subsequent reaction of the nitrene intermediate [13], a photochemical reaction not involving NCS^-, such as an electron ejection from the central metal (a frequent process in photoelectrochemical solar cells [14, 15]) or photosubstitution of another ligand [16] can occur.

In this contribution, the photochemical properties of the complexes [Fe(R′-sal-R_2-en)(CH_3OH)(NCS)], where R′-sal-R_2-en^{2-} are tetradentate open-chain *N*,*N*′-1,1-R_2-ethylenebis(R′-salicylideneiminato) ligands (R = H or CH_3; R′ = H, 5-Cl, 5-Br, 3,5-Br_2, 3-OCH_3, 4-OCH_3, are reported. The structures of R′-sal-R_2-en^{2-} (generally referred to as N_2O_2 ligands) and the central metal environment of the complexes investigated are depicted in figure 1.

2. Experimental

The Schiff bases H_2(salen), H_2(5-Cl-salen), H_2(5-Br-salen), H_2(3-CH_3O-salen), H_2(4-CH_3O-salen), H_2(3,5-Br_2-salen), H_2(3,5-Me_2-salen) and H_2(Br_2-sal$(Me)_2$en) were available from previous investigations [17, 18]. Methanol (Lachema, reagent grade) was dried before use by distillation from $Mg(OCH_3)_2$. The spin trapping agents 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene, ND) and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were obtained from Aldrich. DMPO was freshly distilled before use and stored under argon in a freezer. 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 without further purification. $K[Cr(NH_3)_2(NCS)_4]$ was prepared from $NH_4[Cr(NH_3)_2(NCS)_4] \cdot H_2O$ by metathesis, following a literature procedure [19]. Other chemicals were of analytical grade, purchased from Lachema and used as received.

Solutions of [Fe(N_2O_2)(CH_3OH)(NCS)] were prepared *in situ* by diluting 40 cm^3 of stock methanol solution of [Fe(N_2O_2)(CH_3OH)$_2$](NO_3) (3.00×10^{-3} mol dm^{-3}) to 600 cm^3 with dry methanol, adding 0.175 g of solid KNCS and stirring at ambient temperature. Oxygen was removed from the solutions by purging with solvent-saturated argon for 30 min before and during irradiation.

2.1. *Apparatus*

Solutions of complexes were photolysed in a three-chamber thermostatted (20 ± 1°C) quartz photoreactor. A low-pressure G8T5 germicidal lamp and a high-pressure 150 W Hg-lamp (Applied Photophysics) were used as radiation sources. Radiation from the high-pressure lamp was monochromatized using solution filters [20]. Electronic spectra were recorded on a Specord 200 spectrophotometer using 1.00 or 0.20 cm quartz cells. EPR spectra were measured using a computer-controlled Bruker EMX instrument (operating at X-band frequencies, with 100 kHz field modulation) equipped with a flat quartz cell optimized for the Bruker EPR cavity. IR spectra of solid polystyrene residues (KBr disks) were recorded on a Nicolet Magna 750 FTIR spectrophotometer.

2.2. *Irradiation and product analysis*

The intensity of the incident light was determined by ferrioxalate [21] or Reinecke's salt actinometers [19]. Progress of the photoredox processes was monitored by electronic spectrophotometry over time, following the formation of Fe^{II} and CH_2O. Iron(II) was determined as $[Fe(phen)_3]^{2+}$ and formaldehyde using 3,5-diacetyl-1,4-dihydrolutidine. Photolysis was limited to less than 5% to avoid any inner filter effect. Details of the photolysis, analytical procedures and experimental data processing are described elsewhere [17, 18, 20].

In EPR measurements, the methanol solutions were deoxygenated by an argon stream and irradiated directly in the cavity of the EPR spectrometer by an HPA 400/30S lamp (Philips) at $\lambda \geq 300$ nm. Spectrometer settings, mode of simulation of EPR spectra and the software used are given elsewhere [22].

Polystyrene, formed within 30 min of irradiation of a solution prepared by adding 15 cm^3 of styrene to 110 cm^3 of [Fe(salen)(CH_3OH)(NCS)] (2.00×10^{-4} mol dm^{-3}) in an argon atmosphere, was separated as a solid residue using an MPW 310 centrifuge (9000 rpm) and washed twice with 5 cm^3 of dry methanol.

3. Results and discussion

3.1. *Spectroscopy*

Single-crystal X-ray and solution studies of iron(III) complexes with thiocyanate or salen ligands show that the NCS^- anion coordinates nitrogen [3, 4], salen ligands form the equatorial plane of the complex and two monodentate ligands are bonded in axial positions [3, 4], and in the majority of its high-spin complexes Fe(III) is hexacoordinated both in the solid state and in solution [4, 23]. Based on the literature data and our previous results obtained by a standard spectrophotometric titration [24], the composition of the complexes investigated have the stoichiometry [Fe(N_2O_2)(CH_3OH)(NCS)].

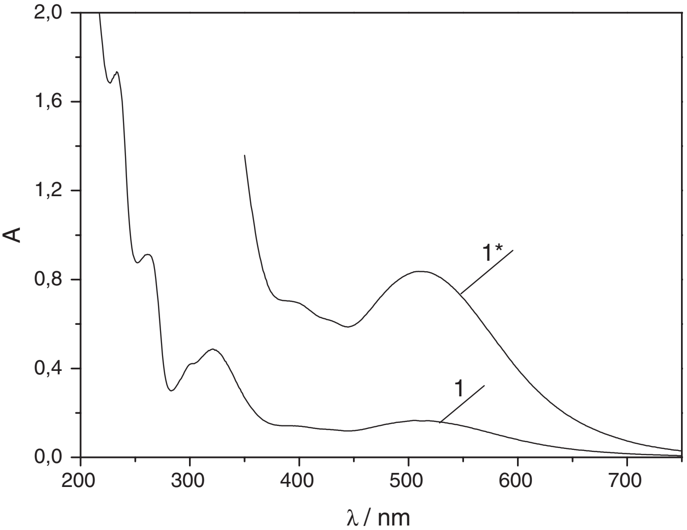

Figure 2. Electronic absorption spectra of [Fe(salen)(CH_3OH)(NCS)] (2.0×10^{-4} M) in methanol measured in 0.2 cm (1) and 1.0 cm (1*) cells.

Table 1. Electronic absorption data for methanol solutions of [Fe(R′-sal-R-en)(CH_3OH)(NCS)] (2.00×10^{-4} mol dm^{-3}).

		λ_{max} or λ_{sh}, nm (ε/mol^{-1} dm^3 cm^{-1})		
R	R′	IL (phenyl)	IL (C=N)	LMCT
H	H	233sh (43 300); 262sh (22 800)	300 (10 470); 320 (12 150); 400 (3470)	430 (3070); 510 (4180)
H	5-Cl	255sh (23 210)	316 (11 570)	440sh (3100); 520 (4180)
H	5-Br	239sh (30 800)	304sh (7700)	530 (5790)
H	3,5-Br_2	241sh (33 600); 270sh (17 600)	312 (10 220)	417 (3240); 445 (3510); 530 (5860)
H	3-OCH_3	223sh (48 200); 276 (24 400)	311sh (8880)	457 (3260); 560 (3940)
H	4-OCH_3	245 (30 670); 282 (28 170)	310 (19 000); 390 (4260)	500 (5070)
$(CH_3)_2$	3,5-Br_2	286 (10 800); 225sh (41 740)	320 (3150)	430 (5020); 560sh (2000)

Electronic spectra of the complexes typically show several broad bands and shoulders. For example, the absorption spectrum of [Fe(salen)(CH_3OH)(NCS)] is shown in figure 2. Spectroscopic data for all complexes are listed in table 1. Based on published data [17, 18, 20], bands in the visible region can be attributed to ligand-to-metal charge transfer (LMCT) transitions O2p or N(2p) → Fe3d, and the ultraviolet bands in the regions of 210–290 and 300–360 nm to the intraligand transitions IL($\pi \rightarrow \pi^*$) localized predominantly on the phenyl rings and C=N fragments of the ligands. Because of their spin-forbidden nature, ligand field (LF) states were not observed in solution spectra.

Table 2. Quantum yields for Fe(II) formation, $\Phi_{\mathrm{Fe(II)}}$, in irradiated methanol solutions of [Fe(R′-sal-R-en)(CH_3OH)(NCS)] ($2.00 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$) at excitation wavelength λ_{irr}, Hammett constants σ(R′) of the peripheral groups R′ [26] and half-wave potentials $E_{1/2}(\mathrm{Fe^{3+}/Fe^{2+}})$/V for the complexes [24].

				$\Phi_{\mathrm{Fe(II)}} \times 10^3$			
R	R′	$E_{1/2}(\mathrm{Fe^{3+}/Fe^{2+}})$/V	σ(R′)	254 nm	313 nm	366 nm	436 nm
H	H	−0.540	0.00	1.9	1.2	0.17	0.098
H	5-Cl	−0.475	0.23	3.9	0.81	0.34	0.021
H	5-Br	−0.490	0.23	29.6	5.2	4.7	0.96
H	3,5-Br_2	−0.435	0.46	13.2	1.6	0.27	0.011
H	3-OCH_3	−0.465	0.12	5.1	0.17	0.15	0.015
H	4-OCH_3	−0.560	−0.27	5.1	0.17	0.15	0.015
$(CH_3)_2$	H			50.0	10.6	6.4	0.63

3.2. *Wavelength dependence of quantum yields*

Irradiation of methanol solutions of the complexes by UV or visible radiation gives rise to photoreduction of Fe(III) to Fe(II). Integral quantum yields for Fe(II) formation, $\Phi_{\mathrm{Fe(II)}}$, depend on the wavelength of the radiation and on the peripheral groups, R, of the ligands (table 2). Blank experiments confirmed that the complexes [Fe(N_2O_2)(CH_3OH)(NCS)] do not undergo spontaneous redox changes in methanol solution in the dark. Two features are noteworthy. Absorption of a photon at 254 nm or 313 nm is associated with IL excitation localized on salen while it is an axial ligand undergoing the primary photoredox process, and inner complex physical deactivations are extremely fast for iron complexes; no radiation deactivation has been observed for such complexes to date. Taking these observations into account, the observed decrease in the quantum yield with decreasing energy of incident photons may be understood and summarized in terms of three main factors: very efficient internal conversion and/or intersystem crossing from higher energy IL to photoredox reactive LMCT states of the complexes; rate constants for the partial photophysical deactivations are higher than that of vibrational cooling with the consequence that LMCT states populated from IL states have a higher vibrational energy than those populated directly by visible irradiation; and the greater the difference between the vibrational energy of a given LMCT state and the threshold energy of the primary photoproduct formation, the greater the probability of their separation (or, vice versa, the lower the probability of their recombination), i.e. the higher the values of $\Phi_{\mathrm{Fe(II)}}$. As the complexes exhibit no luminescence, continuous photolysis does not allow us to distinguish between photoredox reactivity of individual spin-forbidden quartet and spin-allowed sextet LMCT states forming the manifold of states participating in redox deactivation processes.

3.3. *Peripheral group effects*

The term "peripheral group effect" denotes an influence of the electronic properties of the atom or group bonded on the periphery of ligands on chemical processes involving the central atom [25]. Electronic properties of peripheral groups are usually characterized by Hammett or Taft constants [26]. Observed trends in chemical behavior can be viewed as being a consequence of variation in peripheral group properties only for homologous sets of compounds having similar size and ligand skeleton, the same chromophore and charge.

The substituents, R, on the phenyl ring in salen complexes influence photoredox changes localized on the central atom (table 2), although R is sited as far away as seven σ-bonds from Fe(III). The higher the energy of the absorbed photon, the greater the part of it that can be utilized for redox decomposition. Higher energies can thus cause a change in electron configuration at a significant distance from the central atom.

The results listed in table 2 show that the quantum yields do not correlate with any relevant ground-state parameters of the complexes or their substituents. Contrary to a theoretically justified and experimentally evidenced correlation of electrochemical Fe(III) reduction potentials and Hammett substituent constants of the groups R [27], no relationship between quantum yields and R group parameters was found. This phenomenon has, however, been explained [28]. Although peripheral groups influence the ability of the central atom to undergo redox changes, quantum yields do not correlate with Hammett constants. The reason lies in the fact that the quantum yield is a statistical–kinetic parameter reflecting the rate of all deactivation processes and not only the rate of photoredox deactivation. A second reason lies in the fact that values of σ(R) express the electronic effects of R groups in the ground state but quantum yields represent electron transfer in the excited state.

3.4. *Radical intermediate identification*

To identify radicals formed in the irradiated solutions, EPR spin trapping and radical scavenging by a monomer were applied to [Fe(salen)(CH_3OH)(NCS)]. EPR spectra of [Fe(salen)(CH_3OH)(NCS)] measured in methanol before photoexcitation revealed an EPR signal characterized by hyperfine splitting, $a_N = 1.363\,\mathrm{mT}$, $a_H^{\beta} = 0.775\,\mathrm{mT}$, $a_H^{\gamma} = 0.16\,\mathrm{mT}$, $g = 2.0059$, attributed to the $^{\bullet}$DMPO–OCH_3 adduct, in accord with literature data [27]. This adduct is usually observed in iron(III) complexes containing DMPO, and a mechanism for its generation is proposed elsewhere [29]; it is not formed in a photochemical step. Continuous irradiation ($\lambda > 300\,\mathrm{nm}$) of [Fe(salen)($CH_3OH$)(NCS)] causes a decrease in $^{\bullet}$DMPO–OCH_3 signal intensity without the appearance any new EPR signals either at short or prolonged irradiation times. No high-quality EPR signal was observed using the ND spin trap.

Irradiation in the presence of styrene gave rise to polystyrene. IR spectra of the isolated polystyrene showed a sharp band at $1750\,\mathrm{cm}^{-1}$, typical of a covalently bonded SCN group [29]. This is generally taken as an indication of $^{\bullet}$NCS formation and its involvement in radical initiation of polymerization.

3.5. *Final products and mechanism*

The mol ratio of iron(II) and formaldehyde as final products of the photoredox processes approached a value of 2 : 1. Introducing oxygen into the system after switching off the irradiation gave rise to the slow reappearance of the parent iron(III) complex. Irradiation of [Fe(salen)(CH_3OH)(NCS)] in methanol in the presence of oxygen led to over-stoichiometric formation of formaldehyde, with Fe(II) : CH_2O reaching 1 : 3 with 30 min of irradiation at 313 nm. [Fe(salen)(CH_3OH)(NCS)] therefore acts as a catalyst for methanol oxidation. Electronic spectra scanned at certain intervals showed, however, that the complex decomposes.

Based on the spectra, radical identification, molar ratio of the final products and literature data [30, 31], processes occurring in the irradiated systems may be described (in the following equations, GS refers to the ground state). The composition of the complexes is written in a mode meeting stoichiometry requirements; the actual composition may vary in the processes due to kinetic lability.

With irradiation, spin-allowed IL or LMCT excited sextet states of the complexes are populated, equations (1) and (2), respectively.

$$_{\mathrm{GS}}[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)(NCS)}] \xrightarrow{h\nu(UV)} {}_{\mathrm{IL}}[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)(NCS)}] \quad (1)$$

$$_{\mathrm{GS}}[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)(NCS)}] \xrightarrow{h\nu(VIS)} {}_{\mathrm{LMCT}}[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)(NCS)}] \quad (2)$$

Of all accessible excited states of the complexes, only the LMCT sextet (populated directly by visible light absorption) and spin-forbidden LMCT quartet states (reachable by intersystem crossing from higher energy IL states) possess an electron distribution suitable for inner-sphere reduction of Fe(III) to Fe(II). The formation of polystyrene containing covalently bonded SCN indicates that in the primary photoredox step, reduction of Fe(III) to Fe(II) is associated with oxidation of NCS$^-$, equation (3):

$$_{\mathrm{LMCT}}[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)(NCS)}] + \mathrm{CH_3OH} \rightarrow [\mathrm{Fe^{II}(N_2O_2)(CH_3OH)_2}] + {}^{\bullet}\mathrm{NCS} \quad (3)$$

Despite the absence of EPR evidence for the radical $^{\bullet}$CH$_2$OH, its formation by an inter- or intramolecular methanol oxidation cannot be *a priori* ruled out, and given the formation of formaldehyde, it must be taken into account. The radical product(s) can participate in a number of subsequent processes (e.g. back electron transfer reactions, radical interconversions). As documented by the value $E^0(^{\bullet}\mathrm{CH_2OH}/\mathrm{CH_2O}) = -1.180\,\mathrm{V}$, the radical $^{\bullet}$CH$_2$OH is able to reduce Fe(III), thus forming the final products Fe(II) and CH$_2$O, equation (4).

$$[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)(NCS)}] + {}^{\bullet}\mathrm{CH_2OH} \rightarrow [\mathrm{Fe^{II}(N_2O_2)(CH_3OH)(NCS)}]^- + \mathrm{H^+} + \mathrm{CH_2O} \quad (4)$$

The ratio $\mathrm{Fe^{II}} : \mathrm{CH_2O} = 2 : 1$ determined in the experiment reported indicates that the reduction of Fe(III) by $^{\bullet}$CH$_2$OH (equation (4)) is responsible for the above ratio.

Acknowledgements

The financial support of the Slovak Grant Agency VEGA is (grant No. 1/2452/05) acknowledged.

References

[1] S.C. Fung, H.G. Drickamer, *Proc. Natl. Acad. Sci. USA*, **62**, 38 (1969).
[2] A.M. Golub, H. Kohler, V.V. Skopenko, *Chimija Psevdogologenidov*, Vyšša škola, Kyjev (1981).
[3] Z.L. You, H.-L. Zhu, W.-S. Liu, *Acta Cryst.*, **E60**, m794 (2004).
[4] M. Melník, I. Ondrejkovičová, V. Vančová, *Rev. Inorg. Chem.*, **17**, 55 (1997).
[5] B. Mainusch, A. Karocki, D.M. Guldi, Z. Stasicka, F. Wastestian, *Inorg. Chim. Acta*, **255**, 87 (1997).
[6] H.J. Kuhn, S.E. Braslavsky, R. Schmidt, *Pure Appl. Chem.* (In press).
[7] J. Sýkora, J. Šima, *Coord. Chem. Rev.*, **107**, 115 (1990).
[8] G.L. Geoffroy, M.S. Wrighton, *Organometallic Photochemistry*, p. 87, Academic Press, New York (1979).
[9] T. Imamura, T. Jin, T. Suzuki, M. Fujimoto, *Chem. Lett.*, 847 (1985).
[10] J. Šima, *Pol. J. Chem.*, **66**, 936 (1992).
[11] G. Ferraudi, *Inorg. Chem.*, **19**, 438 (1980).
[12] J.E. Moser, D. Noukalis, U. Bach, Y. Tachibana, D.R. Klug, J.R. Durrant, R. Humprey-Baker, M. Graetzel, *J. Phys. Chem. B*, **102**, 3649 (1998).
[13] H. Henning, K. Hofbauer, K. Handke, R. Stich, *Angew. Chem.*, **109**, 373 (1997).
[14] C.G. Garcia, A.S. Polo, N.Y. Muramaki Iha, *J. Photochem. Photobiol. A: Chem.*, **160**, 87 (2003).
[15] P.A. Anderson, F.R. Klene, T.J. Meyer, J.A. Moss, G.F. Strousse, J.A. Treadway, *J. Chem. Soc., Dalton Trans.*, 3820 (2002).
[16] E. Zinato, In *Concepts of Inorganic Photochemistry*, A.W. Adamson, P.D. Fleischauer (Eds), p. 143, Wiley, New York (1975).
[17] M. Izakovič, J. Šima, V. Brezová, *J. Photochem. Photobiol. A: Chem.*, **167**, 81 (2004).
[18] J. Šima, V. Brezová, *Coord. Chem. Rev.*, **229**, 27 (2002).
[19] E.E. Wegner, A.W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
[20] J. Šima, *J. Chin. Chem. Soc.*, **46**, 993 (1999).
[21] S.L. Murov, *Handbook of Photochemistry*, p. 119, Marcel Dekker, New York (1973).
[22] V. Brezová, T. Tarábek, D. Dvoranová, A. Staško, S. Biskupič, *J. Photochem. Photobiol. A: Chem.*, **155**, 179 (2003).
[23] S. Funahashi, Y. Inada, *Bull. Chem. Soc. Jpn*, **75**, 1901 (2002).
[24] J. Šima, J. Mrázová, A. Kotočová, *Pol. J. Chem.*, **72**, 2079 (1998).
[25] C. Hansch, A. Leo, R.W. Taft, *Chem. Rev.*, **91**, 165 (1991).
[26] J. Šima, *Coord. Chem. Rev.*, **159**, 195 (1997).
[27] A. Kotočová, J. Šima, *Chem. Papers*, **48**, 175 (1994).
[28] F. Chen, Y. Xie, J. He, J. Zhao, *J. Photochem. Photobiol. A: Chem.*, **138**, 139 (2001).
[29] J. Coates, In *Encyclopedia of Analytical Chemistry*, R.A. Meyers (Ed.), p. 10815, Wiley, Chichester (2002).
[30] J. Šima, *Commun. Inorg. Chem.*, **13**, 277 (1992).
[31] J. Šima, *Roum. Chem. Quart. Rev.*, **7**, 159 (1999).