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Scientific paper

Effect of Fluoro-containing Ligand and/or Fluoride on Photoredox Stability of Iron(III) Complexes

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Abstract

Photochemical behaviour of iron(III) complexes [Fe(4-R-benacen)X(CH_3OH)] where X = Cl or F, and 4-R-benacen(2-) are *N,N'*-ethylenebis(4-R-benzoylacetoneiminato) ligands with R = H, Cl or F, was investigated in methanolic solutions by steady-state photolysis at four different wavelengths. The course of photoredox processes was followed by UV-VIS spectrophotometry and spin-trapping EPR. It was found that both the axial coordination of a fluoride anion to the iron(III) central atom and the presence of the fluorine atoms of the equatorial 4-F-benacen ligand increased the photoredox stability of the iron(III) central atom when compared with analogous chloro complexes with unsubstituted benacen or 4-Cl-benacen ligands. Quantum yield of Fe(II) formation decreased with increasing wavelength of the incident radiation. Spin-trapping EPR documented the presence of $^{\bullet}CH_2OH$ radicals in irradiated systems. ^{19}F-NMR showed that fluorine atoms of 4-F-benacen ligand did not interact with the central atom. A mechanism of the photodeactivation processes is proposed.

Keywords: photoredox stabilization, iron(III) complexes, benacen, fluoroligand, mechanism.

1. Introduction

Fluoro complexes belong to less popular objects of photochemical investigation. One of the reasons lies in the fact that contrary to the other acido ligands, coordinated fluoride anion obviously does not undergo photooxidation. Another reason originates in the history of inorganic photochemistry. At the advent of photochemistry of coordination compounds, A. W. Adamson formulated his famous "rules of photochemical reactivity" enabling the photochemist to predict the course, stereochemistry and relative efficiency of some photochemical processes.[1] When applied to fluoro complexes, the applicability of the rules, however, failed.

Our focus on fluoro iron(III) complexes was driven by the known fact on redox stabilization of the ground state iron(III) oxidation state by fluoride anions and by experimental observation on different general tendency to undergo redox processes in excited state(s) than that in the ground state. To exemplify the above findings, several known data showing that for numerous complex series, the ground state redox reactivity follows an order indicated by the electrode potential values whilst the photoredox reactivity, expressed in quantum yield values, decreases in the order chloro > iodo > bromo complexes.[2,3] Insufficient number of data has not allowed to put fluoro complexes in the right position in the mentioned order.

Stemming from our experience with complexes containing tetradentate Schiff base open-chain equatorial benacen-type ligands (Fig. 1), further abbreviated as N_2O_2, and two monodentate axial ligands, this work is a continuation of our previous studies[4–6] and is aimed at investigating the effect of the fluorine atom presence both as an axial acido ligand and as part of tetradentate fluoro-N_2O_2-ligands on the photoreactivity of iron(III) complexes.

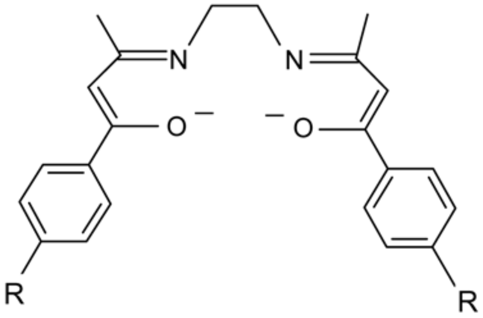

Figure 1. Schematic structure of 4-R-benacen ligands (R = H, Cl or F).

2. Experimental

The Schiff bases H_2benacen, H_2(4-Cl-benacen) and H_2(4-F-benacen) were synthesized from the respective aldehydes and ethane-1,2-diamine according to the procedure given by Jacobsen.[7] 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 $Mg(OCH_3)_2$. 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. Lithium chloride (Lachema) was dried before use at 105 °C for 2 hours. Potassium tris(oxalato)-ferrate(III) (Oxford Organic Chemicals), 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene *ND*, Sigma), tetraethylammonium fluoride, $[N(C_2H_5)_4]F \cdot 3H_2O$ (Sigma) 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.

The irradiated complexes $[Fe(N_2O_2)(CH_3OH)F]$ and $[Fe(N_2O_2)(CH_3OH)Cl]$ were prepared in methanol *in situ* from stock methanolic solution of $[Fe(N_2O_2)(CH_3OH)_2](NO_3)$ and solid $[N(C_2H_5)_4]F \cdot 3H_2O$ or LiCl as described before.[5,6]

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.[8] 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 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, 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 few crystals of solid 1,10-phenanthroline in suitable intervals of irradiation (some tens of seconds). 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 of $1.12 \cdot 10^4$ L mol^{-1} cm^{-1} for the molar absorption coefficient of $[Fe(phen)_3]^{2+}$. The absorption of Fe(III) phosphates in the region $\lambda \geq 500$ nm can be neglected.

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

Coordination of the fluoride anions to the central atom Fe(III) was monitored by potentiometric titration of $2.0 \cdot 10^{-4}$ mol L^{-1} $[Fe(4\text{-}F\text{-}benacen)(CH_3OH)_2]^+$ with $2.0 \cdot 10^{-3}$ mol L^{-1} $[N(C_2H_5)_4]F$ at the ionic strength $I(NaClO_4) = 0.1$ mol L^{-1}. In these titrations, a Radelkis (type 211/1) pH meter in combination with a fluoride-ion selective electrode (Radelkis, model OP-F-O711P) was used.

Solutions of $[Al(4\text{-}F\text{-}benacen)(CH_3OH)F]$ for ^{19}F-NMR spectra measurements were prepared by dissolving solid anhydrous $AlCl_3$ and H_2(4-F-benacen) in $CHCl_3$ so as the molar ratio of $c(Al^{3+}) : c(H_2(4\text{-}F\text{-}benacen)) = 0.3 : 1; 0.6 : 1; 1 : 1; 2 : 1$ or $5 : 1$; $c(Al^{3+}) = 2 \cdot 10^{-2}$ mol L^{-1}. The ^{19}F-NMR spectra were recorded on a Varian VXR-300 spectrometer operating at 282.194 MHz for fluorine. Fluorine shifts were referenced against trifluoroacetic acid (shift = –76.5 ppm) used as external standard.

The 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 0.20 cm quartz cells.

More details on the experiments performed, measurements conditions, analytical procedures and experimental data processing are described elsewhere.[4–6]

3. Results and Discussion

The average number of F^- anions coordinated to the central atom Fe(III) in investigated complexes was determined by a standard potentiometric method.[9] The experimental constants $a = -356.6$ mV and $b = 30.0$ mV for

$$E = a + b \ln\{1 / c_{\text{free}}(F^-)\} \qquad (1)$$

were determined from the E vs $c_{\text{free}}(F^-)$ plot at the total tetraethylammonium fluoride concentration, $c_{\text{total}}(F^-)$, ranging from $5.0 \cdot 10^{-5}$ mol L^{-1} to $5.0 \cdot 10^{-4}$ mol L^{-1} and maintaining $c([Fe(4\text{-}F\text{-}benacen)(CH_3OH)_2]^+) = 2.00 \cdot 10^{-4}$ mol L^{-1}.

The concentration of uncoordinated F^- anions, $c_{\text{free}}(F^-)$, was calculated using the above equation (1) from the experimental potential values E measured in each solution. The number of the F^- anions coordinated to the central atom Fe(III), $c_{\text{coord}}(F^-)$, was calculated as a difference $c_{\text{coord}}(F^-) = c_{\text{total}}(F^-) - c_{\text{free}}(F^-)$. It is obvious that in the range of $c_{\text{total}}(F^-) : c(Fe^{III}) = 1.1 : 1$ to $2.0 : 1$, just one F^- ligand is coordinated to the iron(III) central atom (Table 1).

Given the known tendency of high-spin Fe(III) to form hexacoordinated complexes both in the solid state and solutions and that of tetradentate N_2O_2-ligands to form their equatorial plane,[10,11] the composition of the complex present in methanol at such conditions can be

Table 1: Total concentration of tetraethylammonium fluoride, $c_{total}(F^-)$, measured potential values of fluoride-selective electrode, E, and calculated number of F^- ligands coordinated to the central atom, $c_{coord}(F^-) : c(Fe^{III})$, obtained for the systems with the initial $c([Fe(4\text{-}F\text{-}bena\text{-}cen)(CH_3OH)_2]^{2+})$ = 2.00 × 10^{-4} mol L^{-1} in methanol, the ionic strength I = 0.1 mol L^{-1} $NaClO_4$.

$c_{total}(F^-) \times 10^4$, mol L^{-1}	0.532	1.046	1.569	1.744	1.918	2.092	2.441	2.964	3.313	3.836	4.020
E, mV	106.4	103.6	24.0	1.3	13.8	28.0	48.0	71.4	81.9	94.4	98.3
$c_{coord}(F^-) : c(Fe^{III})$	0.265	0.521	0.771	0.840	0.905	0.962	1.01	1.05	1.06	1.06	1.01

expressed as [Fe(4-F-benacen)(CH_3OH)F] with CH_3OH and F^- bonded in the axial positions and the benacen ligand in the equatorial plane. The other studied complexes showed identical behavior.

Since the ability of the fluorine atoms of the tetradentate 4-F-benacen ligand to interact with the iron(III) central atom cannot be a priori excluded, it was investigated by ^{19}F-NMR using diamagnetic aluminium(III) instead of high-spin iron(III). As follows from the ^{19}F-NMR spectra scanned for solutions of H_2(4-F-benacen) and aluminium chloride containing solutions with the molar ratio c(H_2(4-F-benacen)): $c(Al^{III})$ = 1 : 0.3; 1 : 0.6; 1 : 1, 1 : 2 and 1 : 5, peaks of ^{19}F atoms (located at about –110 ppm *versus* –76.5 ppm for trifluoroacetic acid used as standard) did not change their position due to the presence of aluminium(III). This fact, along with a relatively very low orbital energy of the fluorine-atoms lone pairs can be taken as an evidence that these fluorine atoms are not involved in iron(III) complexes formation and their effects to photochemical behaviour of the complexes is only a consequence of their electron withdrawing effect.

Electronic absorption spectra of all investigated complexes are logically very similar and are interpreted based on detailed analysis of CD and absorption spectra of several groups of transition metal complexes with Schiff base N_2O_2-ligands.[12–14] The spectra consist of broad intraligand bands located in the UV region centered at 230–260 nm and 300–370 nm which are attributed to intraligand (IL) π → π* transitions localized on the phenyl rings and on the azomethine C=N fragment of tetradentate ligand, respectively, and ligand-to-metal charge transfer (LMCT) bands in the visible region attributed O2p → Fe3d electron transfer. Owing to their spin-forbidden nature, bands of ligand field (LF) states are not detectable in solution spectra. For illustration, the spectra of [Fe(benacen)(CH_3OH)F] and [Fe(4-F-benacen)(CH_3 OH)Cl] are shown in Figure 2.

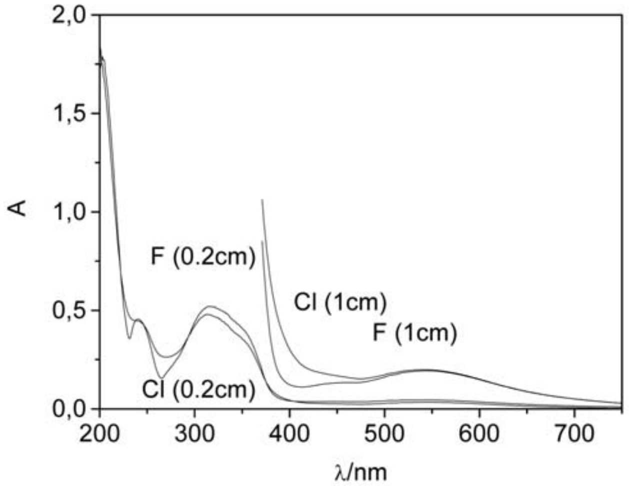

Figure 2. Electronic absorption spectra of [Fe(benacen)(CH_3OH)F] and [Fe(4-F-benacen)(CH_3OH)Cl] in methanol; c(complex) = 2.00 × 10^{-4} mol L^{-1}, path cell = 1.00 cm or 0.20 cm.

Control experiments proved that all investigated complexes are redox stable in the dark. Irradiation of methanolic solutions of the investigated complexes by ultraviolet or visible radiation leads to the photoreduction of Fe(III) to Fe(II). The integral quantum yields of Fe(II) formation, $\Phi_{Fe(II)}$, depend on the wavelength of the incident radiation, the nature of the monodentate ligands X^-, and group R of N_2O_2-ligands (Table 2).

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

Searching for radicals formed in irradiated methanolic solutions of [Fe(benacen)(CH_3OH)F] and [Fe(4-F-be-

Table 2: Quantum yields of Fe(II) formation, $\Phi_{Fe(II)}$ in irradiated methanolic solutions of iron(III) complexes

Complex/λ_{irr}	**254 nm**	**313 nm**	**366 nm**	**436 nm**
	$\Phi_{Fe(II)}$			
[Fe(benacen)(CH_3OH)F]	0.00049	0.00006	< 0.00001	< 0.00001
[Fe(benacen)(CH_3OH)Cl]	0.045	0.0018	0.00090	0.00047
[Fe(4-Cl-benacen)(CH_3OH)F]	0.00075	0.00010	0.00002	< 0.00001
[Fe(4-Cl-benacen)(CH_3OH)Cl]	0.026	0.0022	0.00085	0.00065
[Fe(4-F-benacen)(CH_3OH)F]	0.00065	0.00005	< 0.00001	< 0.00001
[Fe(4-F-benacen)(CH_3OH)Cl]	0.067	0.0031	0.00091	0.00056

nacen)(CH_3OH)F] by spin trapping EPR technique showed that $^{\bullet}CH_2OH$ was the only radical identified in these systems. The adduct of the radical $^{\bullet}CH_2OH$ with the spin trap *ND* gave an EPR spectrum characterized by the splitting constants $a_N = 1.397$ mT and $a_H = 0.772$ mT; for the adduct with *DMPO* the constants $a_N = 1.518$ mT and $a_H = 2.134$ mT were calculated from its spectrum. The experimental EPR spectra and those published before match well.[5,15]

The complexes [Fe(benacen)(CH_3OH)F], [Fe(4-Cl-benacen)(CH_3OH)F] and [Fe(4-F-benacen)(CH_3OH)F] exhibit a high redox stability not only in their ground state but also in excited states. When applying $\lambda_{irr} \geq 366$ nm, the photoreduction of Fe(III) to Fe(II) is almost undetectable and even in case of higher energy UV radiation, the efficiency of Fe(II) formation is still very low when compared to analogous chloro complexes. It should be mentioned that the finding of iron(III) photoredox stabilization due to the presence of fluorine atoms is of empirical nature and to rationalize it, further experiments and their theoretical analysis must be done.

The molar ratio of $c(Fe^{II}) : c(CH_2O) \cong 2 : 1$ and the presence of $^{\bullet}CH_2OH$ radicals identified by EPR spin trapping documents 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):

$$_{GS}[Fe^{III}(N_2O_2)(CH_3OH)F] \xrightarrow{h\nu\,(UV)} {}_{IL}[Fe^{III}(N_2O_2)(CH_3OH)F] \quad (2)$$

$$_{IL}[Fe^{III}(N_2O_2)(CH_3OH)F] \xrightarrow{ic\,/\,isc} {}_{LMCT}[Fe^{III}(N_2O_2)(CH_3OH)F] \quad (3)$$

$$_{GS}[Fe^{III}(N_2O_2)(CH_3OH)F] \xrightarrow{h\nu\,(VIS)} {}_{LMCT}[Fe^{III}(N_2O_2)(CH_3OH)F] \quad (4)$$

$$_{LMCT}[Fe^{III}(N_2O_2)(CH_3OH)F] + CH_3OH \rightarrow [Fe^{II}(N_2O_2)(CH_3OH)F]^- + H^+ + {}^{\bullet}CH_2OH \quad (5)$$

$$_{GS}[Fe^{III}(N_2O_2)(CH_3OH)F] + {}^{\bullet}CH_2OH \rightarrow [Fe^{II}(N_2O_2)(CH_3OH)F]^- + H^+ + CH_2O \quad (6)$$

A course of the processes (2) – (4) follows from the spectra and photophysical deactivation modes applied in excited Fe(III) complexes.[16] From the viewpoint of electron density distribution, the only excited states suitable for inner-complex redox decomposition (5) are LMCT states. The non-emissive nature of the complexes (a general feature of Fe(III) complexes) represents a level of ambiguity for more specific identifying the LMCT states populated and involved in the redox decomposition processes, none of spin-allowed sextet and spin-forbidden quartet manifolds can be a priori excluded.

The reaction (6) is supported by thermodynamic parameters and up-to-now obtained experience.[16,17] As documented by the value of $E^o(^{\bullet}CH_2OH/CH_2O) = -1.180$ V, the radical $^{\bullet}CH_2OH$ is a strong reductant able to reduce Fe(III) in subsequent secondary (dark) redox steps (6) forming thus the final products Fe(II) and CH_2O.

The ratio of $c(Fe^{II}) : c(CH_2O) = 2 : 1$ shows that the reduction of Fe(III) by $^{\bullet}CH_2OH$ (6) 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 should be reminded that no such products have been found so far in irradiated methanolic solutions of Fe(III) complexes.[16]

Owing to the high electrode potential $E(F_2/F^-)$, a possibility of fluorine atoms formation via the oxidation of fluoride anions may be ruled out and the same is supposed for oxidation of Cl^- axial ligands in chloro complexes. It is worth pointing out that the photoredox stabilization of iron(III) does not stem from the redox stability of F^- (Cl^-) axial ligand, since it is a methanol molecule which undergoes photooxidation. An idea on the redox non-reactivity of Cl^- is acceptable based on the fact that even in case of iodo iron(III) complexes with benacen or salen-type ligands, no evidence of iodine atoms was found.[5]

Previous findings documented that macrocyclic and open-chain tetradentate ligands behave as "redox innocent" ligands apparently not participating in the occurring redox processes.[16] This conclusion is supported by dark reoxidation of Fe(II) in our system expressed by stoichiometry

$$4\,[Fe^{II}(N_2O_2)F]^- + O_2 + 4\,H^+ + 4\,CH_3OH \rightarrow 4\,[Fe^{III}(N_2O_2)(CH_3OH)F] + 2\,H_2O \quad (7)$$

and observed as a reappearance of the original spectra of iron(III) complexes.

The significant wavelength dependence of the quantum yield (Table 2) deserves a short explanation. As found and rationalized for several iron complexes,[18] *ic* and/or *isc* processes are extremely fast occurring in femtosecond timescale. Thus, within the sequence IL($\pi \rightarrow \pi^*$, phenyl) → IL($\pi \rightarrow \pi^*$, azomethine) → LMCT (O2p → Fe3d) vibrational energy accumulates. Due to this fact, directly populated LMCT (O2p → Fe3d) states possess a lower vibrational energy content than the LMCT states reached by *ic* and/or *isc* transitions from energy higher IL states. The higher vibrational energy content (assuming the identical constant threshold energy for Fe(III)–O bond cleavage) the higher kinetic energy of the primary products of the redox decomposition, and consequently the lower the probability of their recombination, i.e. the higher quantum yield of net redox process. It should, however, be pointed out that the interplay of kinetic and thermodynamic effects is not definitely solved for non-emitting compounds and hope may come from the application of ultrafast techniques.

4. Acknowledgement

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Povzetek

V članku opisujemo fotokemično obnašanje železovih(III) kompleksov [Fe(4-R-benacen)X(CH_3OH)] kjer je X = Cl or F, in 4-R-benacen(2–) so *N,N'*-etillenebis(4-R-benzoilacetoniminato) ligandi z R = H, Cl or F, v metanolni raztopini pri štirih različnih valovnih dolžinah. Potek fotoredoks procesa smo zasledovali z UV-VIS spektrometrijo in EPR s spinskim lovljenjem. Ugotovili smo, da fluoridni ligand v aksialnem položaju in tudi prisotnost fluorovih atomov v ekvatorialnem 4-F-benacen ligandu poveča fotoredoks stabilnost centralnega železovega(III) iona v primerjavi z kloro kompleksi z nesubstituiranim benacenom ali 4-Cl-benacen ligandi. Kvantni izkoristek za nastanek Fe(II) se zmanjšuje z naraščajočo valovno dolžino vpadne svetlobe. Z metodo EPR s spinskim lovljenjem smo določili prisotnost $^{\bullet}CH_2OH$ radikalov v obsevanih sistemih. ^{19}F-NMR je pokazala, da fluorovi atomi 4-F-benacen liganda nimajo interakcij s centralnim železovim atomom. Predlagamo mehanizem fotodeaktivacijskih procesov.