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Photochemistry of iron(III) complexes

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Contents

Abstract

In this paper, the photochemical properties of ferric complexes are reviewed. The complexes are classified according to the bonding properties of their ligands into classes with unidentate, chelating and macrocyclic ligands. Proteins containing the central atom Fe(III), due to their peculiar properties, are discussed in a separate section. In addition to solution photochemistry, the photoredox processes occurring in microheterogeneous systems, polymer matrices and solid complexes are discussed. In each type of complex the main directions for photochemical research are specified and the current knowledge is evaluated. Practical aspects of the photochemistry of ferric complexes are documented. © 1997 Elsevier Science S.A.

Keywords: Iron(III) complexes; Photochemistry; acacen, dianion of *N*,*N*′-ethylenebis(acetylacetoneimine); benacen, dianion of *N*,*N*′-ethylenebis(benzoylacetoneimine); bpy, 2,2′-bipyridine; CFC, chlorofluorocarbon; 3-Clpy, 3-chloropyridine; cyt, cytochrome; dcbpy, 4,4′-dicarboxy-2,2′-bipyridine; dib, 1,4-diisocyanobenzene; DMF, *N*,*N*-dimethylformamide; DMG, anion of dimethylglyoxime; DMSO, dimethylsulphoxide; edta, tetraanion of ethylenediaminetetraacetic acid; ES, excited state; GS, ground state; HAOX, 2-hydroxyacetophenonoximate anion; HGl, glucose; IL, intraligand; IPCT, ion pair charge transfer; LMCT, ligand-to-metal charge transfer; Mb, myoglobin; MMCT, metal-to-metal charge transfer; NADH, nicotinamide adenine dinucleotide; OEP, dianion of octaethylpor-

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phyrin; ox, oxalate dianion; Pc, dianion of phthalocyanine; phen, 1,10-phenanthroline; PPh_3, triphenylphosphine; py, pyridine; [15]pyaneN_5, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-1(18),14,16-triene; [15]pydieneN_5, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene; pyz, pyrazine; RK, anion of kojic acid derivatives; SDS, sodium dodecylsulphate; TDCPP, meso-tetra(2,6-dichlorophenyl)porphyrin; TdPc, dianion of tetrakis(dodecylsulphonamido)phthalocyanine; TIM, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; TMPyP, hexacation of tetrakis(*N*-methyl-4-pyridinio)porphyrin; TPP, dianion of tetraphenylporphyrin; TPPC, hexaanion of tetrakis(4-carboxyphenyl)porphyrin; TPPS, hexaanion of tetrakis(4-sulphonatophenyl)porphyrin; tz, tetrazine; UroP, decaanion of uroporphyrin

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1. Introduction

Iron(III) forms mostly hexacoordinated, high-spin, labile (an exception are complexes with strong ligand-field ligands, such as CN^-, bpy, phen, macrocyclic ligands) complexes which undergo thermal or photochemical reduction of Fe(III) to Fe(II) [1]. In their electronic absorption spectra, the spin-forbidden ligand-field (LF) bands are generally very weak and hidden in the tails of intense spin-allowed ligand-to-metal charge transfer (LMCT) and/or intraligand (IL) bands [2]. In polynuclear mixed-valence complexes, metal-to-metal charge transfer (MMCT) can be identified; in some systems, the ion pair charge transfer (IPCT) nature has been attributed to the bands which are missing in the spectra of the individual ions. The overwhelming majority of iron(III) complexes provide no luminescence at either room or lower temperatures, which is related to the short lifetime of their excited states.

Iron complexes were the most frequently investigated compounds in the area of the photochemistry and photophysics of inorganic compounds until the end of the 1960s. This fact can be clearly demonstrated by the number of papers quoted in the comprehensive monograph on the photochemistry of inorganic compounds [1], in which the chapter devoted to iron compounds is concluded by more than 300 quoted papers (less than 130 papers were published at the same time for the complexes of platinum metals).

The oil crisis and attempts to exploit solar energy as an alternative energy source at the beginning of the 1970s shifted the attention of inorganic photochemists to intensely coloured, redox-reactive, luminescent complexes with longer excited state lifetimes. From the viewpoint of the quantity of published articles, during the last two decades the complex $[Ru(bpy)_3]^{2+}$ and its derivatives have overshadowed the photochemistry of the other inorganic complexes, iron complexes included.

Virtually all the results published up to 1970 are gathered and evaluated in Ref. [1]. Many original papers appeared thereafter and some reviews and monographs also deal with various aspects of the photochemistry of iron compounds [3–12]. Most papers quoted in this review were published in the last 10 years, but some important sources issued before the year 1986, which are necessary for a formulation of more general conclusions, are also referred to. For simplicity, iron(III) complexes are grouped according to the bonding properties of their ligands. Particular cases of biologically important proteins are discussed separately. Some practical aspects of the photochemistry of iron(III) complexes conclude the article.

2. Complexes with unidentate ligands

In studying the photochemical properties of Fe(III) complexes with unidentate ligands, attention has been focused on four main topics:
(1) the identification of the primary photoredox step;
(2) the energy transfer processes and their chemical consequences;
(3) the wavelength dependence of the quantum yield of Fe(II) formation;
(4) the electron transfer processes in dinuclear-bridged complexes and ion pairs.

The difficulties emerging in area (1) have their origin in the kinetic lability of Fe(III) complexes. Attempts to rationalize the photochemical reactions occurring in systems of chloroferric complexes will illustrate the matter. In the literature, we can find tentative proposals for four modes of the primary electron transfer step, each involving the absorption of a photon by the Fe(III) complex as the primary photophysical step.

(1) An outer-sphere electron transfer from an anionic oxidizable ligand X^- (such as Cl^-, Br^-, NCS^-) to the central atom Fe(III) within an ion pair [1,7]

$$^*Fe^{3+}(solv).X^- = Fe^{2+}(solv) + X^{\cdot} \qquad (1)$$

(2) An inner-sphere electron transfer from a coordinated ligand X^- to the central atom, forming the radical $X^{\cdot}$ and an Fe(II) complex, e.g. in $[FeCl_4]^-$

$$^*[FeCl_4]^- = FeCl_2 + Cl^- + Cl^{\cdot} \qquad (2)$$

This mode is similar to the generally accepted release of the oxidized ligand $X^{\cdot}$ from the LMCT excited states of the inert halogeno complexes of Co(III), Ir(IV), etc. [1,9].

(3) An outer-sphere electron transfer from an organic solvent molecule RH to $FeCl_3$

$$^*FeCl_3 + RH = FeCl_2 + HCl + R^{\cdot} \qquad (3)$$

Such formation of electron paramagnetic resonance (EPR) detectable radicals $R^{\cdot}$ was supposed to occur in solutions of $FeCl_3$ in non-polar uncoordinating solvents, in which $FeCl_3$ does not undergo any observable ionization (e.g. in aromatics) [1,9].

(4) An outer-sphere electron transfer from an anion X^- located in the secondary coordination sphere to the excited Fe(III) complex [13–15]

$$^*[FeCl_4]^- + Cl^- = FeCl_2 + Cl^- + Cl_2^- \qquad (4)$$

Based on the study of the composition and structure of Fe(III) complexes in solution [15], which proves the presence of X^- ligands in the primary coordination sphere of Fe(III) complexes, possibility (1) can be excluded as a common mode of photoreaction. However, neither the identification of various radicals, nor the dependence of the quantum yield of Fe(II) and/or radicals formed on the composition of the system [13,14,16–18] allows an unambiguous answer to be given to the question concerning the primary photoredox step or the discrimination between modes (2)–(4). A very detailed study of the processes occurring in irradiated systems containing $[FeCl_4]^-$, free Cl^- and ethanol [14] has led to the conclusion that, in these and analogous systems, the primary photoredox step involves outer-sphere extraction of an electron from an anion Cl^- by the excited complex $[FeCl_4]^-$ leading to the radical $Cl_2^{\cdot-}$ (Eq. (4)).

The photochemistry of complexes was used as a tool to clarify the mechanism of decarboxylation of halocarboxylic acids [19] and carboxylic acids [20–22]. An inner-sphere decomposition was postulated to be the primary photoredox step

$$*Fe^{III}(RCO_2)^{2+} = Fe^{2+} + R^{\cdot} + CO_2 \qquad (5)$$

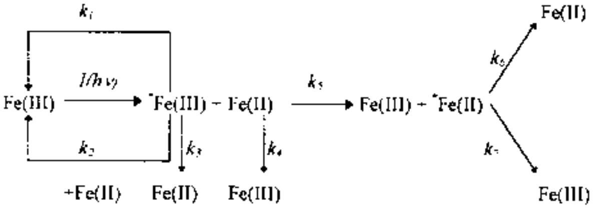
However, no details were given. The irradiation of ferric chloride in water–ethanol mixtures gives rise to the formation of gaseous H_2 [23]; the primary photoredox step is believed to involve homolytic splitting of an Fe^{III}–Cl^- bond.

In the photochemistry of Fe(III) complexes, there are (at least) two perennial problems, namely the mechanisms of the photoreactions of $[Fe(C_2O_4)_3]^{3-}$ and of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_5L]^{q-}$ complexes. The former case will be discussed in Section 3, while the following lines are devoted to the cyano complexes.

The principal problems arising in the study of Fe(III) cyano complexes are that their photochemistry is strongly influenced by the experimental conditions (pH value, presence of other species in the investigated systems, etc.) and complicated photochemical and dark reactions occur simultaneously. If we limit ourselves to the processes involving an excited complex, the question concerning the primary photochemical steps is still difficult to answer. Based on the data reviewed in Refs. [1,7] and the latest results presented in Refs. [24,25], it seems to have been proven definitely that one of the primary steps is Fe(III) reduction, the other being photosubstitution of one of the ligands. The photoreduction of Fe(III) can be accompanied by an inner-sphere photo-oxidation of the ligand L or CN^- or by an outer-sphere oxidation of a molecule located in the secondary coordination sphere (e.g. an alcohol molecule). Not infrequently, hydrated Fe_2O_3 or Prussian blue is formed as the final product of the reactions occurring in systems of irradiated ferric cyano complexes. Of the pentacyano complexes, the complex $[Fe(CN)_5(NO)]^{2-}$ attracts virtually continuous attention. One reason lies in its application in cardiology [25]. The second interesting feature stems from the obscure oxidation state of the central atom and the ligand NO. At present, it is accepted that the complex contains Fe(III) and a neutral NO molecule. However, the results obtained by electron spectroscopy for chemical analysis (ESCA) revealed that the actual positive charge located on the central atom in the complex $[Fe(CN)_5(NO)]^{2-}$ is higher than that in $[Fe(CN)_6]^{3-}$ and both the nitrogen and oxygen atoms in the NO ligand bear a small negative charge [26]. Therefore the complex may also be formulated as $[Fe^{IV}(CN)_5(NO^-)]^{2-}$. Charge transfer photolysis of the complex in methanol produced $[Fe(CN)_5(CH_3OH)]^{2-}$ (in the presence of KOH the complex

$[Fe(CN)_5(CH_3O)]^3$ was formed) and the quantum yield of these photosubstitution products did not depend on the presence of dioxygen in the irradiated systems [27]. The starting complexes and products of the primary photochemical changes underwent further dark and photochemical substitution and/or redox processes yielding a final product composition which depended on the experimental conditions. Electrochemically formed pentacoordinated $[Fe(CN)_4(NO)]^2$ undergoes photochemical oxidation in the presence of oxidizing agents (such as $KMnO_4$ or O_2); however, the evaluation of the mechanism calls for further investigation [28].

Energy transfer and its consequences for redox processes occurring in irradiated systems of Fe(III) complexes were investigated in systems containing chloro complexes or bromo complexes of both Fe(III) and Fe(II) in methanol–ketone (acetone, propiophenone or acetophenone) mixtures [6,18,29,30]. The systems were irradiated with light absorbed only by the Fe(III) complexes ($\lambda_{irr} > 365$ nm). Detailed investigation of the redox properties of such systems led to the conclusion that, in addition to the dark oxidation of Fe(II) by the ketone due to the mutual influence of halogeno and ketone ligands via the central atom [31] (the reaction denoted by the rate constant k_4) and the photoreduction of excited Fe(III)* accompanied by the oxidation of methanol (step k_3), oxidation of Fe(II) sensitized by the excited Fe(III)* complexes (steps k_5 and k_7) also occurred. The processes occurring in these systems can be indicated as follows where Fe(II) and Fe(III) represent the Fe(II) and Fe(III) chloro or bromo complexes and *I*(*hv*) is the intensity of radiation absorbed by the Fe(III) complexes.



(6)

Based on this scheme, the experimentally observed time dependences of the Fe(III) concentration are described by Eq. (7)

$$\{dc(Fe^{III})/dt\}_{exp} = \{dc(Fe^{III})/dt\}_{dark} + I\{[k_5k_7c(Fe^{II}) - k_3(k_6+k_7)]/[(k_1+k_3) + (k_2+k_5)c(Fe^{II})](k_6+k_7)\} \tag{7}$$

For those systems in which the rate of spontaneous (dark) redox change is negligible compared with the photoredox reactions, Eq. (7) can be written in the Stern–Volmer form

$$\phi_{Fe(III)obs} = 1/\phi_{lim} + [(k_1+k_3)(k_6+k_7)/k_5k_7]/c(Fe^{II}) \tag{8}$$

where $\phi_{Fe(III)obs}$ is the experimentally observed quantum yield of Fe(III) formation in the irradiated system and ϕ_{lim} is the limiting quantum yield of the photosensitized oxidation of Fe(II) to Fe(III), obtained from the Stern–Volmer plot for $c(Fe(II)) \rightarrow \infty$. Depending on the composition of the irradiated system and the excitation wavelength, the values of ϕ_{lim} vary from 0.11 to 0.32 [18,29,30]. It is obvious that both the energy transfer process (k_5) and the oxidation of Fe(II)* (k_7) are very effective processes. The data obtained do not discriminate between a long-range resonance or an exchange mechanism for the energy transfer applied in our systems. Kinetic analysis of the spontaneous oxidation of Fe(II) (step k_4 in reaction (6)) showed that the oxidation was second order with respect to the concentration of Fe(II). This might suggest that the redox step is realized either in binuclear Fe(II) complexes or within an encounter of two iron-containing species. The same modes could relate to the energy transfer step k_5.

The transfer of energy from *Fe(III) to Fe(II), followed by subsequent oxidation of *Fe(II), was also observed in acidic aqueous solutions containing both $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$ ions and $(C_4H_9)_4P^-$ ions [32]. The mechanism proposed is analogous to that expressed in reaction (6).

The wavelength dependence of the photoformation of $OH^\cdot$ and $SO_4^{\cdot-}$ radicals was followed in aqueous solutions of $[Fe(H_2O)_5(OH)]^{2+}$ and $[Fe(H_2O)_5(SO_4)]^+$ complexes [33]. The photoreduction of Fe(III) to Fe(II) was not followed directly although its occurrence was declared. Using the technique of radical scavenging, it was found that the quantum yields of both radicals decreased with increasing wavelength of incident radiation. The absolute $SO_4^{\cdot-}$ quantum yield increased from 1.6×10^{-3} at 350 nm to 7.9×10^{-3} at 280 nm (the corresponding values for the $OH^\cdot$ radical were 0.07 at 370 nm and 0.31 at 280 nm). It is very probable that the quantum yield of Fe(II) formation exhibits the same trends (this phenomenon has been known for Fe(III) complexes for many decades) [1]. The decrease in the quantum yield of photosubstitution of the NO ligand for CH_3OH or CH_3O^- ligands in $[Fe(CN)_5(NO)]^{2-}$ with increasing irradiation wavelength [27] is also in accordance with the general trend mentioned.

For ion pairs and dinuclear-bridged mixed-valence complexes, the attention has been focused mainly on two phenomena: the energetics of optical electron transfer (the energy of IPCT and MMCT bands) and photoinduced electron transfer processes in such systems. The spectral properties are correlated with the redox potential values and optical electronegativities of the redox centres involved, the electric properties of the media and other parameters. The experimental data and their theoretical evaluation have been reviewed in many recent articles [34–36].

A representative selection of some recent results on the photoredox chemistry of ion pairs and polynuclear complexes are given in Refs. [7,34,35]. Due to the kinetic lability of the majority of Fe(III) complexes, polynuclear complexes containing an Fe(III) moiety with unidentate ligands are relatively rare.

Irradiation of the complex $[(PPh_3)_3Cu^I\text{–}Cl\text{–}Fe^{III}Cl_3]$ in CH_2Cl_2 into the MMCT band ($\lambda_{irr} = 546$ nm) leads to decomposition to Fe(II) and Cu(II) mononuclear species with a quantum yield ϕ of 0.02 [37]. The small quantum yield was explained as being a consequence of rather effective thermodynamically driven back electron transfer within the photochemically formed dinuclear $[(PPh_3)_3Cu^{II}\text{–}Cl\text{–}Fe^{II}Cl_3]$ intermediate. The electronic absorption spectra, namely the energy of the band maximum of the MMCT band, of the symmetrical complex $[(CN)_5Fe^{III}\text{–}L\text{–}Fe^{II}(CN)_5]^{5-}$, where L ≡ bis(pyridyl)ethylene, are influenced by the presence of cations (Na^+, Ca^{2+}, La^{3+}) which, at low concentrations, preferably bind to the more negative

$\{Fe^{II}(CN)_5\}$ moiety. The absorption of a photon in the MMCT region leads to an electron transfer from Fe(II) to Fe(III), i.e. from the aspects of composition and symmetry, the reactant and product are the same species [38]. Femtosecond and picosecond photolysis of Prussian blue was exploited to study the dynamic processes associated with the wavepacket motion on the ground and MMCT potential energy surfaces [39].

In contrast with the above-mentioned systems in which the Fe(III) complexes themselves absorbed photons and underwent monomolecular or outer-sphere photoredox processes, such complexes can also act as electron transfer quenchers of long-lived excited species, producing Fe(II) and an oxidized product of the electron donor. The complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ were found to play the role of quenchers, whereas excited Zn(Mb) [40], eosin and ethyl eosin [41], $[Zn(TMPyP]^{4-}$ [42] and $[Ru(Pc)L_2]$ [43], where L≡pyridine, DMSO, DMF or CO, acted as electron donors. As an example [40], the reaction

$$^3[Zn^{II}(Mb)]^* + [Fe^{III}(CN)_6]^{3-} \rightarrow [Zn^{II}(Mb^+)] + [Fe^{II}(CN)_6]^{4-} \qquad (9)$$

can be shown. Poly-L-lysine inhibits the reaction due to the formation of a complex with $[Fe(CN)_6]^{3-}$.

The anions $[FeCl_4]^-$ and $[FeBr_4]^-$ luminesce when irradiated into their LF or LMCT bands at 85 K. The maximum of the broad featureless phosphorescence band is localized in the near-IR region (945–1030 nm for $[FeCl_4]^-$; 1005–1050 nm for $[FeBr_4]^-$) and varies slightly with the excitation wavelength [44].

3. Complexes with chelating ligands

Investigations concerning the photochemistry of iron(III) complexes with chelating ligands have dealt with the following main problems:

(1) the tuning and optimization of the photoredox reactivity, e.g. searching out correlations between the photoredox reactivity parameters of excited complexes and the ground state parameters of the complexes, their central atom and ligands;
(2) the mechanisms of detachment of bidentate or polydentate ligands from the coordination sphere of excited iron(III) complexes;
(3) the photodegradation of chelating ligands induced by complexation with iron(III);
(4) the outer-sphere photoinduced electron transfer reactions and optical electron transfer processes in electronically weakly coupled metal complexes (one being an Fe(III) complex) or in binuclear-bridged complexes.

In the chemistry of ground state compounds, the existing knowledge and methods allow the formulation of a number of relationships between the structure, physicochemical properties and chemical behaviour of chemical compounds. Searching out the structure–photoreactivity relationships is still in its infancy except for some more or less successful attempts to find empirically and rationalize theoretically correlations between the excited state (ES) reactivity parameters (rate constant k_q, quantum yield ϕ and threshold energy E_{th}) and the ground state (GS) properties of complexes and their constituents. The state of the art in (1) has been thoroughly considered in Refs. [4,45,46]. Within the framework of this study, the photoredox reactivity of Fe(III) complexes with bidentate and/or open-chain tetradentate ligands was followed. The problems concerning the relationships between the GS and ES parameters of the complexes can be expressed by three questions:

(1) does any correlation exist between the parameters characterizing the electronic properties of polydentate ligands and their ability to undergo photo-oxidation (expressed via the ES parameter $\phi_{Fe(II)}$)?
(2) do the peripheral groups of one ligand influence the tendency of another ligand to undergo photo-oxidation?
(3) is it justifiable and possible to optimize the efficiency of photoredox processes stemming from the GS parameters of the complexes or their constituents?

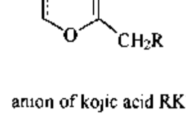
To answer the first question, the complexes $[Fe^{III}(RK)_3]$ (RK, anions of kojic acid or its derivatives) [47–49] were investigated. The distance between the peripheral R groups of the anions and the central Fe(III) atom is five σ-bonds, and the electronic absorption spectra (positions of the LMCT bands) are nearly identical for all the complexes. The overall quantum yields of Fe(II) ($\phi_{Fe(II)}$) are sensitive to the R groups, but there is no correlation between the Hammett constants of the R groups, the potentials of anodic oxidation of the RK^- anions ($E_{pa}(RK^-/RK)$) or their half-wave potentials ($E_{1/2}([Fe(RK)_3]^{0/-})$) [48,50] (for some selected representative data, see Table 1). The molar ratio of $c(Fe^{II})$ to $c(CH_2O)$ is approximately 2 : 1, and the

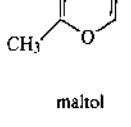
Table 1

Overall quantum yields of Fe(II) formation $\phi(\lambda_{irr}, nm)$ for the complexes $[Fe(RK)_3]$ irradiated in methanol, Hammett constants σ of the peripheral groups R of the kojic acid derivatives, anodic potentials E_{pa} of the oxidation of anions RK^- and half-wave potentials $E_{1/2}$ for the processes $[Fe(RK)_3]+e \Leftrightarrow [Fe(RK)_3]^-$ (both potentials vs. reversible couple ferricenium/ferrocene) [46,47,50]

R	σ(R)	E_{pa}	$E_{1/2}$	ϕ(254)	ϕ(313)	ϕ(365)	ϕ(436)
OH	−0.70	0.36	−0.70	0.16	0.10	0.029	0.018
Cl	−0.19	0.38	−0.66	0.17	0.14	0.061	0.038
N_3	−0.40	0.35	−0.69	nr[a]	nr[a]	0.27	0.16
ScycloC$_6$H$_{11}$	−0.25	0.35	−0.70	0.16	0.15	0.049	<0.0001
SC$_8$H$_{17}$	−0.23	0.395	−0.705	0.30	0.086	0.047	<0.0001
Maltol	−0.18	0.37	−0.80	0.0030	0.0018	0.0016	0.0012

[a] Non-reproducible results probably due to the simultaneous formation of redox-reactive nitrene by decomposition of the azido group.


anion of kojic acid RK⁻


maltol

formation of the $RK^{\cdot}$ and $CH_2OH^{\cdot}$ radicals during irradiation was indicated by spin-trapping EPR. The concentration of the kojic acid derivative H(RK) is, however, constant, and no photo-oxidation product other than CH_2O was found after irradiation. Given the above observations, the proposed mechanism for the redox processes occurring in irradiated methanolic solutions of $[Fe(RK)_3]$ is as follows (for simplicity, possible photophysical processes and photosubstitutions are omitted)

$$_{\rm LMCT}[Fe^{III}(RK)_3]^* \rightarrow [Fe^{II}(RK)_2] + RK^{\cdot} \tag{10}$$

$$[Fe^{II}(RK)_2] + RK^{\cdot} \rightarrow [Fe^{III}(RK)_3] \tag{11}$$

$$RK^{\cdot} + CH_3OH \rightarrow H(RK) + CH_2OH^{\cdot} \tag{12}$$

$$CH_2OH^{\cdot} + [Fe^{III}(RK)_3] \rightarrow CH_2O + H(RK) + [Fe^{II}(RK)_2] \tag{13}$$

The influence of one ligand on the ability of another to undergo photo-oxidation was studied using the complexes *trans*-$[Fe(N_2O_2)X_2]^-$, where $X \equiv Cl^-$, Br^-, NCS^-, N_3^-, CH_3COO^- or CH_3OH and N_2O_2 are non-cyclic, tetradentate, Schiff-base, dianionic ligands of acacen, salen and benacen type [51–54], and *cis*-β-$[Fe(N_2O_2)(OO)]^{q-}$, where $OO \equiv C_2O_4^{2-}$ or RK^- [54–56]. Experiments led to the following conclusions.

(1) The primary photoredox step involves the photoreduction of Fe(III) to Fe(II), accompanied by inner-sphere oxidation of the ligand X^- or OO^{q-}. The fate of the radical products and the mechanisms of the reactions are similar to those expressed by Eqs. (10)–(13). Tetradentate N_2O_2 ligands do not participate in the photoredox or subsequent dark redox processes.

(2) The quantum yields of Fe(II) formation and, therefore, of ligand X^- or OO^{q-} photo-oxidation depend on the periphery of the N_2O_2 ligands. In other words, the electronic properties of the remote parts of one ligand influence the ability of another coordinated ligand to undergo photo-oxidation. This influence applies both in *trans*-complexes, where the electronic effects of the peripheral groups can be transmitted to the central Fe(III) atom and to its bond with the axial X^- ligands via σ- and π-bonding systems, and in *cis*-β-complexes, where due to a strong distortion of the N_2O_2 ligands the effect of π-conjugation (if any) is negligible. The distance between the peripheral groups of the N_2O_2 ligands and the ligands X^- or OO^{q-} is at least seven bonds.

(3) There is no correlation between any relevant GS property (redox potential $E^{\circ}(X^{\cdot}/X^-)$, ionization energy $I(X^-)$, optical electronegativity $\chi(X^-)$, Hammett constants $\sigma(R)$ of the peripheral groups of the N_2O_2 ligands, redox potential of the complexes $E^{\circ}(Fe^{III}/Fe^{II})$, etc.) and $\phi_{Fe(II)}$ (ES reactivity parameter of the complexes).

(4) The observed wavelength dependence of $\phi_{Fe(II)}$ is as expected. However, in the complexes studied, an increase in the photon energy also means an increase in the distance between the site of photon absorption (in the UV region, the absorption of a photon is connected with N_2O_2 intraligand ES formation) and the central atom. Communication between the populated intraligand and photoredox-reactive sextet or quartet LMCT states must be very effective.

(5) Current knowledge does not allow the purposeful tuning and optimization of the efficiency of the photoredox reactions of chemical compounds in general and Fe(III) complexes in particular, which is a sad conclusion, especially in connection with the possible practical applications of photocatalytic processes.

The mechanisms for successive attachment of a polydentate ligand to the central metal atom in the evolution of complex formation have been known for a long time [57,58].

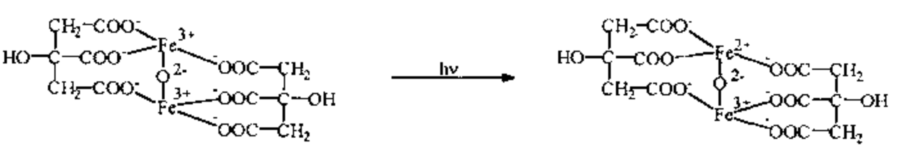
Class (2) photochemical investigations, with the aim to recognize individual steps in the mechanism of detachment of a chelating ligand, have been rather rare, and the majority of the results are linked to photosubstitutions and photoisomerizations [1,6–9,59,60]. Evolution of knowledge in the field of photoredox chemistry can be demonstrated with the anion $[Fe(ox)_3]^{3-}$, the photosensitivity of which has been known for a long time [1,7]. The primary photoredox step occurring from an LMCT state is the homolytic splitting of one Fe(III)–O bond, leading to the formation of the coordinated radical $C_2O_4^-$. The radical can be released from the coordination sphere and either itself, or the radical CO_2^-, can react with another Fe(III), forming the final products Fe(II) and CO_2. The overall quantum yield of Fe(II) is close to 1.2. The presence of Cu(II) ions causes an increase in the quantum yield of Fe(II) via an increasing rate of decomposition of the radical $C_2O_4^-$ [61]. The process can be indicated as follows [7,61]

$$\begin{tikzcd}
 & \mathrm{Fe(II)} + 2\mathrm{CO_2} + \mathrm{Cu(I)} \arrow[r, "\mathrm{Fe(III)}"] & \mathrm{Fe(II)} + \mathrm{Cu(II)} \\
{[\mathrm{Fe^{III}(ox)_3}]^{3-}} \arrow[r, "h\nu"] & {[(\mathrm{ox})_2\mathrm{Fe^{II}}-\mathrm{OCO}-\mathrm{COO^{\cdot}}]^{3-}} \arrow[u, "\mathrm{Cu(II)}"'] \arrow[r, "\mathrm{Fe(III)}"] \arrow[d] & 2\mathrm{Fe(II)} + 2\mathrm{CO_2} \\
 & \mathrm{Fe(II)} + \mathrm{CO_2} + \mathrm{CO_2^-} \arrow[r, "\mathrm{Fe(III)}"] & \mathrm{Fe(II)} + \mathrm{CO_2}
\end{tikzcd} \qquad (14)$$

In connection with the photochemistry of $[Fe(ox)_3]^{3-}$, two observations which are not common in photochemistry are worth mentioning. The first is the formation of non-equilibrium spatial dissipative structures during irradiation of thin layers of solutions of the complex in the presence of $[Fe(CN)_6]^{3-}$. The pattern is formed by Turnbull's blue on a yellow background [62]. The second observation concerns the photodecomposition of $Fe(ox)_3]^{3-}$ occurring in $NaMgAl(ox)_3.9H_2O$ or $K_3[Al(ox)_3].3H_2O$ single crystal hosts studied by the EPR technique [63]. Interpretation of a very detailed study led to the conclusion that the primary redox products of the photolysis are $[Fe^{II}(ox)_2]$ and $C_2O_4^-$ coupled by an antiferromagnetic interaction. No evidence for the formation of the radical CO_2^- was found; in the single crystals, no protonation of $C_2O_4^-$ occurred [62].

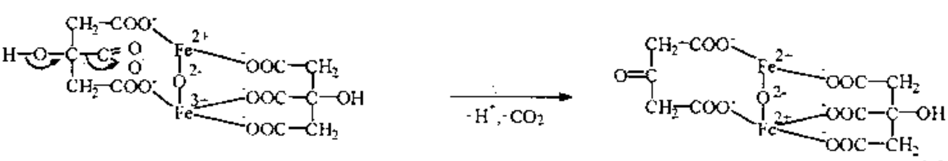
A systematic study of the mechanism of a chelate ligand photoinduced detachment linked to partial photodegradation of the ligand was carried out using Fe(III) carboxylate complexes [59,64–66]. The quantum yields for the photoreduction of these complexes vary with the nature of the carboxylate ligand and the solution pH. The photoreduction of Fe(III) to Fe(II) is accompanied by the oxidative decarboxylation of the carboxylate ligand, and can be observed even in the solid state. The efficiency of the photodecarboxylation in solution depends mainly on two factors:

the pH and the initial ligand-to-metal ratio. While the inclusion of a free carboxylate radical is a virtual necessity in the mechanisms of Fe(III) oxalate systems, where mononuclear complexes are the sole light absorbers, the pH and speciation dependence presented in the Fe(III) hydroxypolycarboxylates [59] justifies a different approach. The simplest mechanism consistent with the data in Ref. [59] involves initial LMCT excitation, followed by the formation of a radical anion carboxylate ligand and Fe(II). At very low pH, no net photoreaction is observed, probably due to non-radiative decay in the chelated mononuclear complex. At moderate pH, the light is absorbed by the dinuclear species, and the carboxylate radical anion is formed in the immediate presence of another Fe(III) ion, which acts as the other half of the dimer



(15)

This allows very rapid completion of the ligand oxidation in a thermal step



(16)

The two Fe(II) ions produced will be released from the carboxylate coordination owing to the lower affinity of Fe(II) for oxygen coordinating sites. The acetonedicarboxylic acid can further undergo two subsequent non-oxidative decarboxylations to form acetone as the ultimate organic product. However, the suggested mechanism needs definitive proof using flash photolysis.

The photodegradation of radiation-transparent organic pollutants present in natural water, induced by complexation with Fe(III), is of great environmental importance. Class (3) photochemical investigations have focused on aminopolycarboxylic and aminopolyphosphonic acids [67–69], which are strong chelating agents widely used for metal cation removal both in industry and in the house and are subsequently dispersed in wastewater. The phototransformation of Fe(III) nitriloacetate (Fe(NTA)) has been studied at 20 °C on monochromatic excitation at different pH [68]. The photochemical behaviour can be adequately described by the following simplified mechanism, involving a redox step between Fe(III) and a carboxylate group

$$Fe^{III}(R_2NCH_2COO) \xrightarrow{h\nu} Fe(II) + R_2NCH_2COO^{\cdot} \rightarrow Fe(II) + R_2N\dot{C}H_2 + CO_2$$

$$\xrightarrow{H_2O} \ldots Fe(II) + HCHO + HNR_2 \qquad (17)$$

where $R \equiv CH_2COO^-$.

The degradation of iminodiacetic acid due to complexation with Fe(III) and subsequent excitation at 365 nm in aqueous solution leads to the photoformation of Fe(II) and formaldehyde (the other final products were not determined) [69]. Contrary to the above-mentioned oxalato complexes, the addition of Cu(II) ions to Fe(III) iminodiacetate complex solution makes the process less efficient. The photodegradation of ethylenediaminetetra-(methylenephosphonic) acid in the presence of Fe(III) was followed by measuring the concentration of phosphate groups formed together with Fe(II) [67]. The final photoproduct is *N*-methylaminomethylene-phosphonic acid, which is photostable under the experimental conditions. Glyphosate, coordinated to Fe(III), undergoes an analogous photodecomposition yielding Fe(II), CO_2 and NH_3 [70].

With regard to the photoredox processes, optical charge transfer transitions between a reducing and an oxidizing metal centre have been studied, either with both metals connected via bridging ligands in a dinuclear complex (inner sphere) [71] or in close contact in separate metal complexes (outer sphere) [72]. Rare outer-sphere transitions of LMCT nature, where L is a ligand of one complex and M is the central atom of another complex, can be observed in ion pairs and in pairs consisting of an ion and a neutral molecular complex. A mixture of neutral bis(*N*-ethylsalicylaldiminato)nickel(II) ($[Ni(Et\text{-}sal)_2]$) and anionic $[Fe(ox)_3]^{3-}$ displays absorption at $\lambda_{max} = 472$ nm. This new long-wavelength absorption band, which is not present in the electronic absorption spectra of the individual complexes, was attributed to an outer-sphere LMCT transition from the coordinated Et-sal of $[Ni(Et\text{-}sal)_2]$ to Fe(III) of $[Fe(ox)_3]^{3-}$. Mixing free Et-sal or [M(Et-sal)], where M ≡ Co(II), Cu(II) or Zn(II), and $[Fe(ox)_3]^{3-}$ shows the same phenomenon. The maximum of the LMCT band is independent of the nature of the metal. A comparison of the energies of the Et-sal to Fe(III) inner-sphere LMCT transition of $[Fe^{III}(Et\text{-}sal)_3]$ and the outer-sphere LMCT transition of $[Ni(Et\text{-}sal)_2]$–$[Fe(ox)_3]^{3-}$ may help to answer questions concerning the character of the LMCT transition.

The unit Fe(III)–O–Fe(III) plays a very important role in biology and chemistry. In this context, the photoredox behaviour of the complex anion $[\{Fe(edta)\}_2O]^{4-}$ was reported [71]. The reversible photolysis of aqueous $[\{Fe(edta)\}_2O]^{4-}$ leads to the evolution of oxygen and the formation of $[Fe(edta)]^{2-}$. It has been concluded that MMCT excitation leads to disproportionation yielding Fe(II) and Fe(IV)=O in the primary photochemical step. Two oxoferryl fragments combine to generate Fe(II) and an O_2 molecule. The quantum yield of Fe(II) formation decreases with increasing wavelength of the incident radiation. This system represents a simple model for the photochemical oxidation of water or oxides. The results presented in Ref. [71] are of considerable interest with regard to the photochemistry of mixed-valence compounds, although in this case the mixed-valence system does not exist in the ground state but is generated by MMCT excitation.

Outer-sphere photoinduced electron transfer reactions, in which the composition and symmetry of the redox-reactive complex are preserved, were found [73] to occur in some homogeneous and micellar systems of the complex $[Fe(bpy)_2(CN)_2]^+$. The quantum yield of photoinduced reduction of Fe(III) to Fe(II) was of the order of 10^{-2} in both aqueous homogeneous and micellar systems. The participation of detergent dodecylsulphate anions DS^- in the electron transfer was suggested

$$[Fe^{III}(bpy)_2(CN)_2]^+ + DS^- \xrightarrow{h\nu} [Fe^{II}(bpy)_2(CN)_2] + DS^{\cdot} \quad (18)$$

In homogeneous systems, the formation of hydroxyl radicals $OH^{\cdot}$ is indicated. However, neither radical was experimentally determined.

4. Complexes with macrocyclic ligands

The basic structural features of iron(III) macrocyclic complexes are the same as for macrocycles of other central atoms. Macrocyclic tetradentate ligands form the equatorial plane of the complexes, and one or two ligands are coordinated in the axial position(s). In binuclear-bridged complexes, the macrocyclic ligands are in a mostly parallel face-to-face position. The iron(III) central atom can be in the low-spin ($S=1/2$), intermediate-spin ($S=3/2$) or high-spin ($S=5/2$) state. The energy difference between the spin states is small and some complexes (e.g. [Fe(TPP)(NCS)(py)] and $[Fe(OEP)(3\text{-}Clpy)_2]ClO_4$) show spin crossovers in the solid state [74]; in solutions of cytochrome *c* the presence of all spin states was found [75]. Luminescence originating from a triplet–sextet intraligand localized excited state was observed for Fe(III) complexes with tetraphenylporphyrin (luminescence maximum $\lambda_{max}=718$ nm, $\phi_{lum}=7\times10^{-5}$, complex irradiated in methylcyclohexane glass at 77 K [76]) and with mesoporphyrin IX dimethyl ester ($\lambda_{max}=681$ nm, complex irradiated in EPA glass (glass consisting of ethanol, ether and isopentane) at 77 K [77]).

Iron macrocyclic complexes, especially those with porphyrin-type ligands, have attracted the interest of a large number of researchers for the following three reasons.

(1) Iron macrocycles act as structural and functional models for the in vivo behaviour of some iron redox enzymes, even though their function is not a consequence of their photochemical reaction. However, rapid photochemical methods can contribute substantially to the understanding and rationalization of the biological processes involving these enzymes.

(2) Iron macrocycles, through reversible changes in the oxidation state of the central iron atom, exhibit very promising photocatalytic properties which can find application in the synthesis of organic compounds and the degradation of some pollutants.

(3) In spite of their seemingly complicated structures, the macrocyclic ligands themselves do not undergo chemical changes within the photoredox reactions of iron(III) macrocyclic complexes; this is a very advantageous property in the investigation and interpretation of the mechanisms of the reactions.

So far, the known photoredox reactions of iron(III) macrocyclic complexes can be classified as follows:

(1) reactions in which the photoreduction of Fe(III) is associated with the photooxidation and subsequent detachment of an axial ligand;

(2) reactions in which an axial ligand is decomposed and part of it remains coordinated to the redox changed central iron atom;
(3) photoredox decomposition of binuclear complexes, forming usually Fe(II) and Fe(IV) macrocyclic complexes;
(4) photoformation of a binuclear-bridged mixed-valence complex induced by irradiation of a mononuclear complex;
(5) outer-sphere photoinduced electron abstraction from a surrounding redox-reactive species (e.g. solvent molecule, triplet excited closed-shell metalloporphyrin) by an Fe(III) macrocyclic complex.

In general, reaction type (1) can be expressed by

$$\mathrm{L{-}Fe^{III}(MC){-}(X^{q-})} \xrightarrow{h\nu} \mathrm{L{-}Fe^{II}(MC)+X^{1-q}} \qquad (19)$$

where L denotes the redox unchanged axial ligand (if any), MC is the macrocyclic ligand and X^{q-} is the axial ligand undergoing photo-oxidation. This type of primary photoredox step was postulated for Fe(III) complexes with various tetraazamacrocycles [78–80] and porphyrins [81–99]. The quantum yields of Fe(II) formation strongly depend on the composition of the primary coordination sphere of the complexes, solvent properties and experimental conditions, and reach values of the order of 10^{-2}–10^{-7} (Table 2). It is assumed that the LMCT states (where L is an axial ligand) are responsible for the primary homolytic axial ligand–Fe(III) bond splitting even in instances when LMCT bands are hidden under an envelope of very intense IL bands or when complexes are irradiated into IL bands. For the low-spin complexes $[\mathrm{Fe(TIM)(CH_3O)(CH_3OH)}]$ and $[\mathrm{Fe(DMG)(CH_3O)(CH_3OH)}]$, the threshold energy for the photoreduction of Fe(III), associated with the oxidation of the CH_3O^- ligand, was measured to be larger than or equal to 2.65 eV [80], which is more than the threshold for LMCT absorption (the complexes absorb photons at energies lower than 1.80 eV). In the absence of oxygen, irradiation of methanolic solutions of the complexes leads to reactions which can, in a simplified form, be expressed by

$$[\mathrm{Fe^{III}(MC)(CH_3O)(CH_3OH)}] \xrightarrow{h\nu} [\mathrm{Fe^{II}(MC)(CH_3OH)}]+\mathrm{CH_3O^{\cdot}} \qquad (20)$$

$$[\mathrm{Fe^{III}(MC)(CH_3O)(CH_3OH)}]+\mathrm{CH_3O^{\cdot}} \rightarrow [\mathrm{Fe^{II}(MC)(CH_3OH)_2}]+\mathrm{CH_2O} \qquad (21)$$

The molar ratio $c(\mathrm{Fe^{II}}):c(\mathrm{CH_2O})=2:1$ determined in these systems [78,80] was taken as clear evidence that other reactions of the methoxy radical $CH_3O^{\cdot}$ (disproportionation to CH_2O and CH_3OH or the formation of $HOCH_2$–CH_2OH) have low, if any, efficiency.

The threshold energies for the high-spin complexes $[\mathrm{Fe([15]pydieneN_5)X_2}]^+$ and $[\mathrm{Fe([15]pyaneN_5)X_2}]^+$ increase with increasing ionization energy of the acido ligand

Table 2
Photoredox properties of excited macrocyclic Fe(III) complexes

Starting complex	Products; efficiency; conditions; notes	Reference
$Fe(TPP)X$, $X \equiv Cl^-$	$Fe^{II}(TPP)$; $\lambda_{irr} > 418$ nm, $\phi = 8 \times 10^{-6}$ for $X \equiv Cl^-$; solvent, MeTHF	[81,82]
$Fe(TPP)N_3$	$Fe^{II}(TPP)$; $N_3^{\cdot}$ identified by spin-trapping EPR; $\lambda_{irr} > 400$ nm; solvent, benzene, toluene, CH_2Cl_2	[83]
$Fe(OEP)(MeIm)(CH_3OH)$	$Fe^{II}(OEP)(MeIm)$; visible light; solvent, CH_2Cl_2; both axial ligands necessary for Fe(III) photoreduction	[84,85]
$Fe(OEP)L$, $L \equiv 1,2\text{-}Me_2Im$, 1-MeIm, 2-MeIm, Im, F^-, Cl^-, Br^-, I^-, ClO_4^-	$Fe^{II}(OEP)$; visible light; Fe(III) reduced only when $L \equiv 2$-MeIm or $1,2\text{-}Me_2Im$; solvent, CH_2Cl_2	[86]
$Fe(TMP)X$, $X \equiv Cl^-$, OH^-	Four-coordinated $Fe^{II}(TMP)$; $\lambda_{irr} > 300$ nm; solvent, aromatic hydrocarbons	[87]
$Fe(P)Cl$, $P \equiv$ TPP, TFPP, TTP, OEP, TMP, TDClP, ProtoIX	$Fe^{II}(P)$; $\lambda_{irr} > 350$ nm, $\phi \sim 10^{-2}$–10^{-3}; solvent, water + pyridine + alcohols or cyclohexene or polystyrene matrices; complexes used as catalysts	[88–95]
$Fe(TPP)(NO_3)$	$[Fe^{III}(TPP)]_2O$; $Fe^{IV}O(TPP^{+})$ formed as an intermediate; $\lambda_{irr} = 350$–450 nm; solvent, benzene	[100,114]
$Fe(P)N_3$, $P \equiv$ TPP, OEP, TMsP	$Fe^{V}N(P)$; $\lambda_{irr} = 514.5$ or 488 nm (laser); $T = 30$ K; solid complexes irradiated; proof of $Fe{\equiv}N$ bond given by Raman spectroscopy; $[Fe(OEP)]_2N$ formed by local heating	[103,104,115]
$Fe(TIM)(CH_3OH)(CH_3O)^{2+}$	$[Fe^{II}(TIM)(CH_3OH)_2]^{2+} + CH_2O$; UV or visible radiation; $\phi_{Fe(II)} \sim 2$, $\phi(CH_2O) \sim 10^{-2}$; solvent, methanol	[78,80]
$Fe(MC)X_2^+$, $MC \equiv [15]pydieneN_5$ or $[15]pyaneN_5$, $X \equiv Cl^-$, Br^-, N_3^-, NCS^-	$Fe^{II}(MC)X^+$, radicals $X^{\cdot}$ scavenged by alcohols; solvent, ACN; threshold energies of Fe(III) photoreduction increase with increase in ionization energy of X^-	[79]
$Fe(P)N_3$, $P \equiv$ OEP, TTP	$[(P)Fe^{III}\text{-}N\text{-}Fe^{IV}(P)]$; $\lambda_{irr} = 413.1$ nm for solid starting complex or radiation from a high pressure Hg lamp for THF solution of complex	[104,115]
$[Fe(P)]_2O$, $P \equiv$ TPP, TPPC, TPPS	$Fe^{II}(P) + Fe^{IV}O(P)$; visible light; $\phi \sim 10^{-4}$; solvent, water, pyridine, hydrocarbons, CH_2Cl_2; FeO(P) behaves as a strong oxidant	[105–111]
$[Fe(TdPc)]_2O$	$Fe^{II}(TdPc)$; products of oxidation unidentified; visible light; $\phi \sim 10^{-2}$; solvent, DMF or THF	[112]

X^- ($X \equiv Cl$, Br, N_3, NCS). Also, in this case, the threshold energies of the photoredox reactions are 0.2–1.6 eV larger than those of the LMCT bands [79].

Usually, only the photoreduction of Fe(III) is followed directly, and it is a priori supposed that it is the ligand X^{q-} which is oxidized in the primary photoredox step. In many cases, research has been directed to practical applications (phototransformation of organic substrates catalysed by a macrocyclic complex) and the mechanisms of the reactions have not been investigated in detail.

Contrary to reactions of class (1), in which Fe(III) is photoreduced to Fe(II), in the atom transfer reactions of class (2) the central atom Fe(III) is, as a rule, oxidized to Fe(IV) or Fe(V). The reactions of class (2) were observed only for porphyrin complexes of Cr(III), Mn(III) and Fe(III) [5]. For Fe(III) complexes, the reactions can be indicated as follows (P, porphyrin)

$$PFe^{III}\text{–}OR \xrightarrow{h\nu} OFe^{IV}(P^+) + R \qquad (22)$$

$$PFe^{III}\text{–}NR \xrightarrow{h\nu} NFe^{V}(P) + R \qquad (23)$$

In the former case (Eq. (22)), the absorption of a photon induces heterolytic bond cleavage within the ligand OR (e.g. a monodentate NO_3^- anion) yielding the formation of an oxo-ferryl π-cation radical, a strong oxidant capable of initiating C–H hydroxylation processes [100] and other photo-oxidations [101,102] (see Section 6). Of the processes discussed in this section, it is the only one involving a redox change localized on both the central atom and the macrocyclic ligand. In the latter case (Eq. (23)), nitridoiron(V) porphyrins with a triple Fe≡N bond are formed when thin films of the corresponding azido complexes [$PFe^{III}N_3$] are irradiated by visible light at approximately 30 K. In this case, it was demonstrated that the formation of π-cation radicals can be ruled out [103,104]. At higher temperatures, the nitridoiron(V) porphyrins convert to the μ-nitrido mixed-valence dimers [$(P)Fe^{III}\text{–}N\text{–}Fe^{IV}(P)$]. Very detailed studies involving isotopically labelled complexes prove that the remaining (O, N) atoms have their origin in the formerly anionic axial ligands.

The third class of photoredox processes of Fe(III) macrocycles involves the photoinduced decomposition of porphyrin and phthalocyanine binuclear-bridged complexes. So far, the attention of various research groups has been focused on the oxo-bridged complexes [$(MC)Fe^{III}\text{–}O\text{–}Fe^{III}(MC)$] due to their highly promising photocatalytic activity (MC ≡ porphyrins TPP, TPPC and TPPS [105–111] and phthalocyanine TdPc [112,113]). The quantum yield of photodisproportionation is rather low (10^{-3}–10^{-5}) and strongly dependent on the wavelength of the incident radiation. The photoredox-reactive excited state(s) is not specified; however, a contribution from a highly distorted MMCT state mixed with an LMCT state can be expected [5,7].

The primary photoredox step is believed to involve iron–oxygen bond splitting

$$[(MC)Fe^{III}(\mu-O)Fe^{III}(MC)] \xrightarrow{h\nu} [Fe^{II}(MC)] + [O=Fe^{IV}(MC)] \qquad (24)$$

The strongly oxidizing oxo-ferryl complex behaves as a two-electron oxidant or as an oxygen atom donor towards amines, hydrocarbons and phosphines (see Section 6). The fact that, in some systems [111,112], the formation of an oxo-ferryl species was not observed does not exclude Eq. (24) as the primary photoredox step. Due to their very fast reactions, the characterization of oxo-ferryl complexes is a difficult task and their formulation as π-cation radicals $[O=Fe^{III}(MC^{+})]$ with strong antiferromagnetic coupling of both paramagnetic centres cannot be excluded [100,114].

There is no direct evidence to indicate that the formation of a binuclear complex (class (4)) on irradiation of a mononuclear complex is a true photochemical reaction involving an excited species with enhanced Lewis acidity or basicity, i.e. a phenomenon found on exciplex and excimer formation [5,6]. The formation of a polynuclear species is usually understood to be a secondary thermal reaction of the reactive species formed in the primary photochemical step. The insertion of class (4) reactions in this section is conditioned by two reasons. Firstly, bearing in mind the mechanisms of exciplex and excimer formation [5,6], there is no reason to exclude an analogous mode of excited species involvement from the reaction of polynuclear complex formation. Secondly, in some cases, dinuclear complexes were prepared for the first time by a photochemical synthetic route. The first binuclear iron macrocyclic complex prepared by photochemical synthesis [115] was the μ-nitrido mixed-valence complex $[(TPP)Fe^{III}(\mu\text{-}N)Fe^{IV}(TPP)]$. Later on an analogous complex with octaethylporphyrin was prepared [104]. In general, it is meaningless to try to find a relationship between the nature of the excited states involved and the ability of mononuclear complexes to undergo polymerization, since the ground state molecules participate in addition reactions leading to polynuclear complex formation.

Outer-sphere electron transfer from a surrounding molecule to an energy-rich excited Fe(III) complex (class (5)) can hardly be omitted in systems containing easily oxidizable molecules. However, this does not apply only to complexes with macrocyclic ligands. In systems with kinetically labile complexes, it is currently generally impossible to distinguish whether the photoreduction of the central atom is associated with the oxidation of a molecule (e.g. alcohol molecule) representing a ligand in the primary coordination sphere or of a molecule from the solvent cage of the excited complex. In all the systems discussed so far containing oxidizable solvent molecules, class (5) reactions should be taken into account at least as an alternative pathway. The situation is clearer in systems in which an outer-sphere electron transfer from an excited inert molecule to the ground state Fe(III) complex occurs. As an example, the photoinduced electron transfer

$$^{3}[Zn^{II}(cyt)]^{*}+[Fe^{III}(UroP)(CN)_2]\rightarrow[Zn^{II}(cyt^{-})]+[Fe^{II}(UroP)(CN)_2] \qquad (25)$$

can be used, in which a long-range electron transfer occurs within a pre-formed electrostatically associated ion pair, consisting of zinc-substituted cytochrome *c* in its highly reducing triplet state and ferric uroporphyrin, with a rate constant of $9.1\times10^{4}\ s^{-1}$ [116]. The constituents of the 1 : 1 complex (zinc-substituted cytochrome and ferric porphyrin) are bound via the electrostatic interaction between the positively charged lysine residues of the cytochrome and the negatively charged carboxylate residues on the porphyrin periphery. The actual charges of the species depend on the pH. In a series of analogous electron transfer processes, a clear observation of the Marcus inverted region was revealed for the thermal processes, but no such region (over the same range of driving force) was found for photoinduced electron transfer.

5. Cytochromes and other iron(III) proteins

From the viewpoint of the inorganic chemist, artificial iron porphyrinato complexes are suitable models of native biologically active enzymes (e.g. cytochromes), since the structure of the site governing their physiological function is identical for both kinds of compounds. However, the actual biological function of the enzymes is tuned by their "organic" protein part. In addition, the protein part contains several sites which can be used to bind certain species, and such a modified enzyme offers new opportunities to investigate the chemical basis of its biological action. These new horizons are one of the main reasons for the very intensive study of the relationships between the structure, chemical properties and biological activity of cytochromes. Cytochromes provide photochemical reactions which are not common in the photochemistry of artificial porphyrinato complexes and this is why their photochemistry is discussed separately.

In the study of photochemical reactions involving cytochromes, two main problems can be specified:

1. the in vivo and in vitro mechanisms of the chemical reactions of cytochromes using photochemical methods as a tool for investigation;
2. the theoretical aspects of the dependence of the kinetic parameters of long-range electron transfer reactions on the edge-to-edge distance between donor and acceptor centres, the difference between their redox potentials, the geometric dispositions for the electron transfer step and the solvent/structural reorganization accompanying the transfer.

Both problems mutually overlap and will be discussed as one topic.

In all photochemical reactions of cytochromes, one of the reaction sites is the central iron atom. The photochemical processes involving cytochromes can be grouped into four categories according to the localization of the redox counterpartner and the mode of its interaction with cytochrome:

1. the photoreduction of Fe(III) associated with the inner-sphere oxidation of an axial ligand coordinated to the central iron(III) atom;
2. the photoreduction of Fe(III) accompanied by the outer-sphere oxidation of an anion forming an ion pair with cytochrome by electrostatic attraction to a positively charged site of the protein part of cytochrome;
3. photoinduced long-range inner-sphere electron transfer between the iron central atom of cytochrome and its redox-reactive partner covalently bound to the protein;

(4) long-range outer-sphere electron transfer quenching of excited molecules by ground state cytochrome.

The photoredox reactions were investigated in homogeneous and microheterogeneous systems (cytochrome embedded in micelles or bilayers).

In the absence of small anionic ligands, which can penetrate to the central Fe(III) atom and coordinate to it, both ferric and ferrous cytochromes *c* (denoted Fe(III)cyt and Fe(II)cyt respectively) contain histidine-18 and methionine-80 as axial ligands at neutral pH. Irradiation of Fe(III)cyt leads to the reduction of Fe(III) associated with the oxidation of the sulphur donor atom of the methionine ligand [95,117,118]. Thermal re-oxidation of Fe(II)cyt to Fe(III)cyt does not lead to the parent Fe(III)cyt. The hexacoordination of the central Fe(III) atom is preserved, but in the axial position tyrosine-67 with an oxygen donor atom becomes coordinated instead of methionine. The photoreduction quantum yield was observed to depend on the pH reaching a maximum value (about 6×10^{-4}) at pH 6. The fate of the oxidized methionine and the potential participation of the protein part in the redox changes are topics still open to investigation. The presence of the biological reductant NADH in irradiated systems of Fe(III)cyt has a strong impact on both the efficiency of photoreduction (the corresponding quantum yield is five times higher than in the absence of NADH) and the mechanism of the thermal redox processes (due to the participation of NADH in these reactions, re-oxidation of Fe(II)cyt yields the parent Fe(III)cyt having histidine-18 and methionine-80 in the axial positions [119]).

Some small ligands can penetrate to the vicinity of the central Fe(III) atom to displace the methionine ligand from the primary coordination sphere and to occupy the axial position. Irradiation of cytochrome *c* in the presence of N_3^- anions induces the formation of the radical $N_3^{\cdot}$ formed by an inner-sphere electron transfer from the coordinated anion N_3^- to the central Fe(III) atom. After its detachment from the Fe(II)cyt formed, the radical $N_3^{\cdot}$ can be identified by spin-trapping EPR [117].

The redox behaviour of ferric cytochrome c_{551} (*Pseudomonas aeruginosa*) exhibits some differences compared with that of cytochrome *c* (horse heart, yeast or tuna). Irradiation of aqueous ferric cytochrome c_{551} in the same conditions as Fe(III)cyt gave no observable photoreduction of Fe(III) to Fe(II); instead the formation of a high-spin Fe(III) compound was observed [118]. A possible reason is that ferric cytochrome c_{551} does not contain a tyrosine residue in the vicinity of the haem group and ferrous cytochrome c_{551} can undergo fast auto-oxidation. In the presence of anions N_3^-, the photochemical behaviour of ferric cytochrome c_{551} is similar to that of Fe(III)cyt.

Fe(III)cyt is a cation with a charge as high as 7+ [120] which can attract anionic species onto the surface of its protein part forming ion pairs. The investigation of systems containing Fe(III)cyt and strongly redox irreversible anions $C_2O_4^{2-}$ [121] or reversible anions RK^- [122] has shown that these anions do not penetrate to the central Fe(III) atom; however, their presence increases the quantum yields of photoreduction of Fe(III)cyt to Fe(II)cyt. It was concluded that the anions are attracted to the positively charged protein part of Fe(III)cyt and, together with the intramolecular transfer of an electron from the methionine axial ligand to the central Fe(III) atom (discussed above), electron transfer from anionic $C_2O_4^{2-}$ or RK^- to the central atom occurs. The higher the number of attracted anions, the higher the probability of electron transfer within such ion pairs and, therefore, the higher the quantum yield of the reaction. For example, using 313 nm excitation, $\phi_{Fe(II)cyt}$ increases from 2.3×10^{-4} (for free hydrated Fe(III)cyt^{7+}) to 5.6×10^{-3} (for ion pairs Fe(III)cyt^{7+}.(OH-K$^-$)$_n$) and 7.0×10^{-3} (for ion pairs Fe(III)cyt^{7+}.($C_2O_4^{2-}$)$_n$). The validity of the proposed reaction model was checked using liposome (in the case of $C_2O_4^{2-}$ anions) and sodium dodecylsulphate (SDS) (in the case of RK^- anions), which can cage both free cytochromes and their ion pairs with the anions in liposome bilayers or SDS micelles. The results obtained can be summarized as follows. Due to the rigidity of the SDS cages containing Fe(III)cyt with on-surface-bound RK^-, the molecules of the geminate pair Fe(II)cyt and $RK^{\cdot}$ cannot separate; thermodynamically driven back electron transfer occurs and the parent reactants Fe(III)cyt and RK^- reappear. In systems containing redox pairs Fe(III)cyt.RK^- embedded in SDS micelles, no net photoredox change is observed on continuous photolysis. However, irradiation of the ion pairs Fe(III)cyt.$C_2O_4^{2-}$ caged in liposome bilayers gives rise to the photoreduction of Fe(III)cyt, since CO_2 molecules, formed from irreversibly oxidized $C_2O_4^{2-}$, do not back react to yield $C_2O_4^{2-}$. In systems containing Fe(III)cyt caged in SDS micelles and $C_2O_4^{2-}$ or RK^- located outside the micelles, no net photochemical change is observed, probably due to the large distance between the reaction centres Fe(III) and the anions (inner diameter of the SDS micelles, Stern layer included, is estimated to be $r > 1500$ pm [123]).

In the systems discussed above, the interaction between Fe(III) and the anions involves the attraction between ions within ion pairs. Several surface-modified cytochromes with redox partners covalently bound to a specific site of the protein (usually at the histidine residue) were prepared, and electron transfer between the redox sites, induced by pulse radiolysis and flash photolysis, was studied [124–127]. Owing to their favourable properties (long-lived emission, substitutional stability, possibility to vary the redox potential value in a relatively large range), ruthenium complexes covalently bound to cytochromes were mainly used as redox partners.

In systems containing histidine-modified cytochromes with a ruthenium redox centre, the kinetic parameters for both spontaneous and photoinduced electron transfer were followed. In photochemical investigations, the excited centre can be, in principle, either an iron or ruthenium centre; however, the excitation of the ruthenium centre prevails. As an example, the electron transfer of ruthenium(II) polypyridine cytochrome *c* labelled at lysine-13 is introduced [124]. The redox changes in the irradiated systems of the labelled ferric cytochromes can be shown as follows

$$\mathrm{Ru(II)–Fe(III)} \xrightarrow{h\nu} {}^*\mathrm{Ru(II)–Fe(III)} \tag{26}$$

$${}^*\mathrm{Ru(II)–Fe(III)} \xrightarrow{k_d} \mathrm{Ru(II)–Fe(III)} \tag{27}$$

$${}^*\mathrm{Ru(II)–Fe(III)} \xrightarrow{k_f} \mathrm{Ru(III)–Fe(II)} \xrightarrow{k_b} \mathrm{Ru(II)–Fe(III)} \tag{28}$$

where k_d, k_f and k_b are the rate constants of deactivation, forward and back electron transfer respectively. In the case of $[(\mathrm{bpy})_2\mathrm{Ru}^{\mathrm{II}}(\mathrm{dcbpy})\ \ \mathrm{Fe}^{\mathrm{III}}\mathrm{cyt}]$, the corresponding rate constants are $k_d = 8 \times 10^6\ \mathrm{s}^{-1}$, $k_f = 1.6 \times 10^7\ \mathrm{s}^{-1}$ and $k_b = 2.6 \times 10^7\ \mathrm{s}^{-1}$. Modification of cytochrome at another lysine group leads to slightly different values of the rate constants [124].

Intramolecular long-range electron transfer was also studied in haemoglobin derivatives [128]. In the human haemoglobin chain, the single sulphydryl group (cysteine-140) was first converted to disulphide and subsequently to its anion radical by the pulse radiolytically generated radical CO_2 . Disulphide radical anion acts as an electron donor and haemoglobin Fe(III) as an electron acceptor.

Outer-sphere electron transfer quenching was observed to occur in some systems containing GS ferric cytochromes together with long-lived excited molecules, such as zinc porphyrins, metal-free porphyrins [129], acridine [130] and Mg(II)-substituted cytochrome peroxidase [131,132]. The rate of dipolar energy transfer, like that of electron transfer, varies strongly with the distance r and is proportional to $r^{\ \ 6}$ [131]. The redox processes occurring in systems containing GS Fe(III)cyt and the intraligand triplet of metal-free porphyrins or Zn(II) porphyrins consist of two steps. The first involves electron transfer from the excited porphyrin to Fe(III)cyt and the second involves back electron transfer from Fe(II)cyt to the GS porphyrin π-cation [130]. The mechanism is believed to be a simple electron transfer. Ferric cytochrome b_5 and cytochrome c quench the excited state of acridine with rate constants of $8.7 \times 10^8\ \mathrm{M}^{\ \ 1}\ \mathrm{s}^{\ \ 1}$ and $1.8 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ respectively [130]. In systems containing ferrous cytochrome b_5 and ferric cytochrome c, ground state electron transfer occurs between the iron central atoms. The interfacial regulation of long-range electron transfer processes between many closed-shell excited metalloporphyrins or magnesium- and zinc-modified proteins and GS Fe(III) proteins was investigated and the results contributed to the understanding of the relationships governing electron transfer in biology [133]. Outer-sphere electron transfer is also responsible for the photodecomposition of the hydroperoxide derivative of biphenyl in the presence of Fe(III)cyt [134]. The reduction of Fe(III)cyt is mediated by electron transfer from a light-induced product of the biphenyl derivative. Details concerning the mechanism of the reduction are not given.

Given the results in Refs. [132,133], it is found that in in vivo systems, an interaction between Fe(III)cyt and cytochrome c peroxidase is a critical prerequisite for electron transfer between these two enzymes. An essential component of biological specificity is the position of the amino acids on the surface of peroxidase which controls enzyme–enzyme recognition.

UV and visible irradiation of ferritin or apoferritin induces the release of Fe(II) into the medium [135,136]. The Fe(II) release depends strongly on the pH, buffer and oxygen concentrations. The quantum yield of Fe(II) formation is of the order of 10^{-3} and markedly increases with the frequency of the incident radiation. The importance of ferritin to skin photobiology has been indicated [134].

Methaemoglobin, metmyoglobin and other ferric protohaem complexes can be excited via their chemical reaction with H_2O_2 and, consequently, provide chemiluminescence. An excited state was formed as a result of electron transfer from an axial ligand to haem iron and its creation was found only for compounds with pentacoordinated haem iron [137].

6. Applications

The theoretical and practical aspects of the photochemical behaviour of chemical compounds and materials strongly overlap. A brief, but comprehensive, evaluation of the perspectives in applied inorganic photochemistry is given in Ref. [138]. There are a number of review papers dealing with the preparation and characterization of photocatalytically active species [139,140]. Use of solar energy to drive chemical processes is still an investigation area of great importance [141]. In nearly all branches of applied photochemistry iron compounds are involved.

Major potential and/or realized applications of the photochemistry of Fe(III) complexes can be grouped into three main categories:

(1) photocatalytic processes aimed at the preparation of required chemical (namely organic) compounds using Fe(III) complexes as photocatalysts;
(2) the photocatalytic destruction of harmful or other undesirable compounds in the presence of Fe(III) complexes playing an active part in decomposition reactions;
(3) the use of Fe(III) complexes as photoinitiators, photostabilizers and photodestructors in polymer chemistry.

In addition, Fe(III) compounds are applied on a smaller scale as photoconductors, active substances of non-conventional photographic materials, etc.

The ability of Fe(III) compounds to act as photocatalysts in the oxidation of alcohols to aldehydes or ketones has been well known for a long time [1]. In recent years, the investigation has been extended to diols which are oxidized in the presence of oxygen and Fe(III) catalyst ($FeCl_3$ or *meso*-porphyrin derivatives) to aldehydes, ketones and acids [11,142–144]. Depending on the system composition and experimental conditions, product formation in 99% yield and turnover numbers of the order of 10^2 were reached in some cases. A characteristic feature of the photolytic reactions of 1,2-diols is the regioselective oxidative cleavage of the 1,2 carbon–carbon bond.

Unsaturated hydrocarbons can be photocatalytically oxidized to alcohols, ketones, aldehydes, epoxides and acids. Iron(III) catalysts (usually *meso*-porphyrin derivatives) can be entrapped in a polymer matrix [90] or dissolved in a non-aqueous solvent [10,101,109,145,146]. Turnover numbers as high as 10^3 and excellent selectivity in product formation were found in some cases (e.g. 100% epoxide formation from 1-methylcyclooctene in photocatalytic oxygenation and 100% alcohol formation from the same alkene in photoinduced auto-oxidation [109]). The photocatalytic oxygenation of α-pinene leads to the formation of six major products [10,101], the ratio of which can be modified by the catalyst used. Based on product analysis, it was concluded that alkenes with strained carbon double bonds give epoxides preferentially, whereas unstrained alkenes undergo mainly allylic oxygenation. Moreover, it was suggested that artificial porphyrinatoiron(III) complexes and microsomal cytochrome P-450 act in a very similar mode [101].

Using $FeCl_3$ instead of iron porphyrins leads, in addition to carbon carbon bond cleavage and oxygenation, to the formation of chloro derivatives [146]. However, such formations of α-chloro or ω-dichloroketones from cycloalkenes are not catalytic but stoichiometric reactions.

The photoaddition of alcohols to epoxides is catalysed by solid Fe_2O_3 or Fe^{3+} ions, and this reaction can be performed in the absence of oxygen [146].

Fe(II) formed by the photoreduction of $Fe(acac)_3$ participates in the addition of O_2 to benzaldehyde to form benzoic peracids and benzoic acid [147]. Irradiation of systems containing salicylic acid and Fe^{3+} ions induces the formation of the hydroxylation products 2,3- and 2,5-dihydroxybenzoic acid. The mechanism of the reaction involves the excited singlet state of methylene blue [148].

From a very critical point of view, the situation in the area of purposeful photochemical transformations of organic substrates may be seen as insufficiently mature to formulate general conclusions. However, it is definitely stimulating, with many potential prospects in chemistry.

The photocatalytic destruction of pollutants in the presence of Fe(III) complexes or iron-doped semiconductor particles appears to be a viable process for pollution control.

Iron oxides, widespread in nature, take part in the photocatalytic processes of pollutant destruction occurring in ecosystems [149]. α-Fe_2O_3 has been found to be stable in the transformations of sulphites, oxalates, formates, haloacetates, peroxosulphates and phenols [19,22,150 152]. The degradation of the organic compounds in aerated iron oxide suspensions could be due to the following: (1) LMCT within the Fe(III) surface, with concomitant oxidation of the organic compound and formation of Fe(II) on the iron surface, which is subsequently re-oxidized in the presence of air; (2) photo-Kolbe-type reactions in which the semiconductor holes are scavenged by pollutant molecules and electrons by the surface iron atoms; (3) $OH^{\cdot}$ radicals resulting from the oxidation of surface OH groups.

The use of Fe(III) ions as dopants to enhance the photocatalytic activity of TiO_2 semiconductors is well documented [21,153 157]. In recent years, there has been increasing interest in the use of doped semiconductors in water purification processes [154]. The semiconductor-sensitized photomineralization of organic pollutants, e.g. alkanes, haloalkanes, aliphatic alcohols, aliphatic and aromatic carboxylic acids, alkenes, haloalkenes, aromatics, haloaromatics, phenols, polymers, surfactants, herbicides, pesticides and dyes, has been successfully studied. The addition of Fe_2O_3 to TiO_2 powder remarkably increases the catalytic activity for NO_x removal from polluted air [158].

Studies on the photolysis of herbicides and pesticides in solution in the presence of Fe(III) ions, resulting in simple inorganic species, e.g. CO_2, Cl^- or NH_3, have demonstrated the major role of Fe(III) species in both the transformation and mineralization of these pollutants [68,159,160]. Considerable attention has been focused on ferric ion-assisted photo-oxidation of haloacetates in connection with the use of haloacetates as possible CFC replacement compounds [19].

Fe(III) porphyrin complexes can act as effective catalysts in the degradation processes of CCl_4 by alcohols in wastes [88,89,161]. The catalytic properties of $[Fe(OEP)]^+$ and [Fe(TDCPP)] complexes have been compared. The catalytic efficiency of [Fe(TDCPP)] is higher than that of $[Fe(OEP)]^+$ which, under comparable conditions, catalyses the photoreduction of CCl_4 with much lower turnover numbers.

Knowledge of the photochemical and photophysical properties of Fe(III) complexes is applied in polymer chemistry in the photoinitiation of polymerization reactions and the photostabilization and photodestruction of polymers.

The radical polymerization of methylmethacrylate, styrene, acrylonitrile, vinylacetate and acrylamide has been initiated by $[Fe(SCN)_3(py)_3]$ and $[Fe^{III}$-HGl] [6,162–164]. Complex initiator is applied in the first step of initiation. The primary radical product is an oxidized ligand, which further reacts with the monomer molecule in a thermal step. Other reactions of the monomer radical result in polymerization. Various iron arene organometallics act as cationic and free radical photoinitiators of epoxide and acrylate polymerization. In the catalytic cycles of polymerization, Fe(III) arenes are formed and involved [165–168].

The photostabilization of light-sensitive polymers involves retardation or elimination of various photoprocesses occurring during polymer decomposition. A dialkyldithiocarbamate complex of Fe(III) acts as an efficient antioxidant reacting with the radical products of polymer destruction [169]. Tris(dibenzoylmethanato) chelates of Fe(III) are quenchers of potentially active excited singlet and triplet states of both aliphatic and aromatic carbonyl compounds and polynuclear aromatic hydrocarbons [170].

Growing interest has been devoted to the problems of photochemical degradation of polymers. Depending on the concentration, $[Fe(HAOX)_3]$ in polyethylene acts as a catalyst of oxidation and hence of polymer destruction, whereas at higher concentrations it functions as an inhibitor of the destruction reaction. Dialkyldithiocarbamate radicals $DTC^{\cdot}$, produced in the irradiation process of the $[Fe(DTC)_3]$ complex, were studied as efficient initiators of polymer oxidation [6,169], as were the $OH^{\cdot}$ radicals generated during the photolysis of $FeCl_3$ [171].

Photochemically active Fe(III) cations and some Fe(III) complexes have been applied in the field of photographic processes. Fe(III) cyano complexes (Turnbull's and Prussian blue) and oxalato complexes are worth mentioning in connection with unconventional photography [172]. Fe(III) complexes with polydentate ligands, such as 1,2-ethylenediamine and *N,N'*-ethylenediaminetetraacetic acid, have been evaluated as silver halide development accelerators [173]. A series of experiments, in which exposed emulsion coatings have been treated with redox buffer solutions composed of citrate complexes and sulphates of Fe(III), have been carried out to investigate the redox stability of the latent-image and latent-subimage centres [174]. Furthermore, the role of Fe(III) photochemically active cations, i.e. impurity ions in commercial photographic emulsions, has been discussed within the framework of the elementary process of latent image formation [175].

Concluding this short review on the applications of Fe(III) complex photochemistry, the photoelectric properties of axially polymerized macrocyclic Fe(III) complexes, e.g. $[PcFe(tz)]_n$, $[PcFe(pyz)]_n$, $[Cl_{16}PcFe(pyz)]_n$, $[Me_8PcFe(dib)]_n$ and

$[Me_8PcFe(Cl_4dib)]_n$, should be commented upon. The electronic influences of the substituents of the macrocycles and of the bridging ligands result in different photoelectric sensitivities [176]. The utilization of the photochemistry of Fe(III) complexes in analytical chemistry is also of interest. Photochemical titration in systems containing Fe(III) complexes has been used for the quantitative determination of various species in solution [177,178], and the rapid photochemical method for the determination of the Fe(II) and Fe(III) contents in minerals using 1,10-phenanthroline has been applied [179].

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