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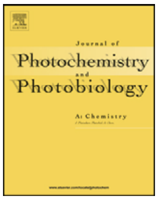

# Photoredox reactions of Cr(III) mixed-ligand complexes

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ABSTRACT

Irradiation of chromium(III) complexes with oxalate and pyridinedicarboxylate ligands (pda = 2,3-, 2,4-, or 2,5-dicarboxylate) leads to diverse behaviors, dictated by light energy, presence of oxygen and the ligand nature. Irradiation within the MC bands is unaffected by $O_2$ and results in ligand substitution. The LMCT excitation is effective only when oxalate is coordinated to Cr(III); then electron transfer from oxalate to central ion generates an intermediate, consisted of a Cr(II)species and the $C_2O_4^{\bullet -}$ radicals. The species undergo fast redox reactions dependent on the presence of $O_2$ and the pda ligand.

(1) In anoxic medium the fast outersphere electron transfer from Cr(II) to solvent, generates hydrated electrons and re-oxidizes the chromium centre to $Cr^{III}$. Then geminate recombination regenerates substrate, whereas competitive release of the $C_2O_4^{\bullet -}$ radical leads to substitution of one oxalate ligand by two water molecules (aquation induced by the LMCT excitation). In the presence of the pda ligand the outersphere electron transfer is accompanied by the innersphere CT, generating Cr(III) coordinated to two radical ligands: $C_2O_4^{\bullet -}$ and $pda^{\bullet 3-}$; the intermediate releases also $e_{aq}^-$, but this reaction is slower than that of the homoleptic oxalate complex. Hydrated electrons are scavenged also by the released radicals. All these processes are completed within microseconds and in consequence, the Cr(III) complexes irradiated in deoxygenated solutions are insensitive to subsequent oxygenation.

(2) When UV-irradiation is carried out in oxygenated medium reaction of Cr(II) species with molecular oxygen competes with the outer- or inner electron transfer observed in anoxic medium. Both these pathways result in generation of chromate(VI). Quantum yield of the Cr(VI) production is sensitive to the presence and structure of pda ligand, decreasing within the series 2,3-pda > 2,4-pda > 2,5-pda.

## 1. Introduction

Current knowledge of chromium(III) photochemistry mostly relates the decay of the metal-centred (MC) excited states [1]. Unfortunately, the contribution of photoredox processes initiated by the charge-transfer (CT) excited state is highly undervalued. The substitution products generated irrespective of the excited state nature and difficulty in detecting unstable Cr(II) species and ligand radicals are probably the reasons. Only in some cases the spectral characteristics of relatively long-living transition complexes $[Cr^{II}(CN)_6]^{4-}$ [2] and $[Cr^{II}(edta^{\bullet})(OH)]^{2-}$ [3] as well as $SCN^{\bullet}$ radicals [4,5] have been reported.

To undergo the photoredox reaction the central atom should coordinate to electron donor good enough for electron transfer towards the Cr centre in the ligand-to-metal charge-transfer (LMCT) excited state. One of the typical complexes representative of this group is trisoxalatochromate(III), $[Cr(C_2O_4)_3]^{3-}$, which photochemistry was studied more intensively from 1950s. Results of these studies were at first ambiguous and only since 1966 [6] it became apparent that UV-irradiation (254 nm) in a vacuum induces a photoredox reaction:

$$[\mathrm{Cr^{III}(C_2O_4)_3}]^{3-} \xrightarrow{h\nu} [\mathrm{Cr^{II}(C_2O_4)_2}]^{2-} + \mathrm{C_2O_4}^{\bullet -} \qquad (1)$$

followed by $CO_2$ production in reaction between substrate and the $C_2O_4^{\bullet -}$ radical:

$$[\mathrm{Cr(C_2O_4)_3}]^{3-} + \mathrm{C_2O_4}^{\bullet -} \rightleftarrows [\mathrm{Cr^{II}(C_2O_4)_3}]^{4-} + 2\mathrm{CO_2} \qquad (2)$$

Recent studies of the $[Cr(C_2O_4)_3]^{3-}$–$C_2O_4^{2-}$–$CrO_4^{2-}$ system [7] revealed that the transient $[Cr^{II}(C_2O_4)_2(C_2O_4^{\bullet -})]^{3-}$ species in aerated medium undergoes oxidation to $Cr^{III}$:

$$[\mathrm{Cr^{II}(C_2O_4)_2(C_2O_4}^{\bullet -})]^{3-} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow [\mathrm{Cr^{III}(C_2O_4)_2(H_2O)_2}]^{-} + \mathrm{C_2O_4}^{\bullet -} + \mathrm{O_2^-} \qquad (3)$$

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and under special conditions also to Cr(VI):

$$[\mathrm{Cr^{II}(C_2O_4)_2(C_2O_4{}^{\bullet -})}]^{3-} \xrightarrow[\mathrm{OH^-}]{\mathrm{O_2}} \mathrm{CrO_4{}^{2-}} + \mathrm{CO_2} + 2\mathrm{C_2O_4{}^{2-}} \tag{4}$$

The latter process (Eq. (4)) needs alkaline medium and a large $O_2$ excess over the Cr(II) concentration [2–4,7,8].

Chromium(III) has a strong tendency to bind not only oxygen-containing functional groups such as oxalate, citrate, malonate, but also ligands with both oxygen and nitrogen donor atoms, like DTA and EDTA [3,9]. The last ligand was recognized as a donor potent enough to induce the photoredox behavior of the $[\mathrm{Cr^{III}edta}]^-$ complex [3,7], but the properties of other N,O-complexes have not yet been studied.

Here we investigated the recently synthesized chromium(III) complexes containing in addition to oxalate also the N,O-bonded 2,3-, 2,4-, or 2,5-pyridinedicarboxylate (pda) ligands, which have an electrophilic character. The complexes are soluble in water and their thermal aquation is slow enough to allow the photochemical investigation. The study is of relevance in relation to the potential use of these compounds as new biochrom sources [10–14].

## 2. Experimental

### 2.1. Reagents

Mixed-ligand complexes containing oxalate and monoprotonated pyridinedicarboxylate ligands (pdaH) and their aqua-derivatives were synthesized as described previously [10,12,13]. Methods of assay of the purity and identity of the complexes are given in Supplementary material. 2,3-Pyridinedicarboxylic acid (quinolinic acid), 99% (Aldrich), 2,4-pyridinedicarboxylic acid (lutidinic acid) 99% (Aldrich), 2,5-pyridinedicarboxylic acid (isocinchomeronic acid) 99% (Aldrich), 70% $HClO_4$ (Aldrich), $NaClO_4{\cdot}H_2O$ (Merck), NaOH (POCh, Poland) and other chemicals were used without further purification. Sephadex DEAE A-25 $[ClO_4{}^-]$ and Sephadex C-25 $[H^+]$ were applied for chromatographic separations. Water utilized in all preparations and other procedures was demineralised and triple distilled. All chromium solutions were freshly prepared for each experiment and stored in the dark to avoid uncontrolled light-induced reactions.

For the continuous photolysis the 2 mM solutions of Cr-complexes at pH 10.5 were used, whereas for laser experiments lower concentrations (0.1–0.4 mM) were applied. In all cases pH was stabilized with Britton-Robinson buffer containing 0.04 M $H_3PO_4$, 0.04 M $H_3BO_3$, 0.04 M $CH_3COOH$ and KOH. Oxygenated and oxygen-free solutions were prepared by 30-min saturation of samples with oxygen or argon, respectively.

### 2.2. Procedures, instrumentation and data analysis

Continuous irradiation was performed using a high-pressure mercury HBO-200 lamp (OSRAM) as a light source, equipped with 10 cm IR water filter. Irradiations were carried out with full light from the mercury lamp or with a cut-off glass filter ($\lambda \geq 300$ nm). Solutions were held in 1-cm quartz cells thermostated at 293 K. Reaction progress was monitored spectrally within 200–800 nm. Spectral detection was made using a Shimadzu UVPC 2100 spectrophotometer in a thermostated chamber at 293 K. The solution pH was measured using a CX-741 (Elmetron, Poland) pH-meter with a glass electrode, calibrated with standard buffers (POCH, Poland).

Quantum yields were measured on home-made computer controlled equipment according to the method described previously [15]. Changes in Cr(VI) concentrations were calculated from absorbance changes at 374 nm.

Laser flash photolysis within nano- to microseconds was carried out using a LKS.60 Spectrometer (Applied Photophysics, UK) equipped with Nd:YAG laser pump source Surlite I-10 (Continuum), operating in fourth harmonic (266 nm, max 75 mJ pulses, 6 ns FWHM). Absorbance changes were monitored using a 150 W Xenon arc lamp supplied with a pulse unit, and a photomultiplier tube R928 (Hamamatsu). Data were recorded on a digital storage oscilloscope HP 54522A (Hewlett-Packard) with 0.5 ns resolution and transferred to a computer for subsequent handling. To increase the output signal-to-noise ratio each experiment was repeated 30 times. The photolysed solution flowed continuously through the Fluorometer Micro Flow Cell type 59-FL UV Quartz (NSG Precision Cells) with chamber length and light path = 4 mm. Rate of the flow was 0.15 $cm^3/s$, ensuring complete replacement of the solution within the detection zone.

### 2.3. Calculations

Factor analysis [16–18] of spectroscopic data was performed using Target 96 M software (MATLAB version). This method uses matrix representation of the spectral data (5). The matrix $\boldsymbol{A}$ consists of $j$ columns, every column of the matrix constitutes an absorption spectrum containing $i$ data points.

$$\boldsymbol{A} = \begin{bmatrix} a_{1,1} & \cdots & a_{1,j} \\ \vdots & \ddots & \vdots \\ a_{i,1} & \cdots & a_{i,j} \end{bmatrix} \tag{5}$$

All the spectra were measured in 1 cm cell, and therefore the absorption matrix can be presented as a matrix product of molar absorption coefficients and concentrations (6):

$$\boldsymbol{A} = \begin{bmatrix} \varepsilon_{1,1} & \cdots & \varepsilon_{1,m} \\ \vdots & \ddots & \vdots \\ \varepsilon_{i,1} & \cdots & \varepsilon_{i,m} \end{bmatrix} \times \begin{bmatrix} c_{1,1} & \cdots & c_{1,j} \\ \vdots & \ddots & \vdots \\ c_{m,1} & \cdots & c_{m,j} \end{bmatrix} = \boldsymbol{E} \times \boldsymbol{C}, \tag{6}$$

where $m$ denotes the number of independent chemical species present in the system, matrix $\boldsymbol{E}$ consists of absorption spectra of the individual components and $\boldsymbol{C}$ of concentrations of all the components in every sample. In order to calculate spectra of individual components an experimental matrix $\boldsymbol{A}$ must be decomposed into two matrices, $\boldsymbol{E}$ and $\boldsymbol{C}$. The decomposition is achieved by the singular value decomposition algorithm [19] (7):

$$\boldsymbol{A} = \boldsymbol{U} \times \boldsymbol{S} \times \boldsymbol{V}^{\mathrm{T}} \tag{7}$$

The matrices $\boldsymbol{U}$, $\boldsymbol{S}$, and $\boldsymbol{V}$ are abstract factors and have the following properties: $\boldsymbol{U}$ consists of the eigenvectors of $\boldsymbol{D} \times \boldsymbol{D}^{\mathrm{T}}$, $\boldsymbol{V}$ consists of the eigenvectors of $\boldsymbol{D}^{\mathrm{T}} \times \boldsymbol{D}$, and $\boldsymbol{S}$ is a diagonal matrix of the singular values; the positive square roots of the eigenvalues of $\boldsymbol{D} \times \boldsymbol{D}^{\mathrm{T}}$ and $\boldsymbol{D}^{\mathrm{T}} \times \boldsymbol{D}$. $\boldsymbol{U}$ and $\boldsymbol{V}$ are orthonormal, with the columns ordered from the most to the least significant eigenvectors. In the absence of experimental error (noise), there will be $m$ (number of components) positive singular values; all the other values are zero [17,18]. The relationship between the chemically relevant matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ and the abstract matrices $\boldsymbol{U}$ and $\boldsymbol{V}^{\mathrm{T}}$ can be established in the following way: For any non singular matrix $\boldsymbol{T}$, the product $\boldsymbol{T} \times \boldsymbol{T}^{-1}$ is the identity matrix, so the term $\boldsymbol{T} \times \boldsymbol{T}^{-1}$ can be introduced to Eqs. (7) and (8).

$$\boldsymbol{A} = \boldsymbol{U} \times (\boldsymbol{T} \times \boldsymbol{T}^{-1}) \times \boldsymbol{S} \times \boldsymbol{V}^{\mathrm{T}} \tag{8}$$

Combinations of Eqs. (6) and (8) yields (9):

$$\boldsymbol{A} = (\boldsymbol{U} \times \boldsymbol{T}) \times (\boldsymbol{T}^{-1} \times \boldsymbol{S} \times \boldsymbol{V}^{\mathrm{T}}) = \boldsymbol{E} \times \boldsymbol{C}, \tag{9}$$

Hence, the matrices $\boldsymbol{E}$ and $\boldsymbol{C}$ can be calculated as follows:

$$\boldsymbol{E} = \boldsymbol{U} \times \boldsymbol{T} \tag{10}$$

$$\boldsymbol{C} = \boldsymbol{T}^{-1} \times \boldsymbol{S} \times \boldsymbol{V}^{\mathrm{T}} \tag{11}$$

**Table 1**
Spectral characteristics of the bisoxalatopyridinedicarboxylate chromium(III) complexes, their aqua derivatives and 2,3-, 2,4-, 2,5-pyridinedicarboxylic acids in 0.1 M $HClO_4$.

| No | Complex | Characteristic bands $\lambda_{max}$ (nm)($\varepsilon_{max}$, $M^{-1}$ $cm^{-1}$) | | |
|---|---|---|---|---|
| | | LMCT (IL for **11–13**) | MC | |
| | | | $^4T_{1g}(^4F,^4P)$ | $^4T_{2g}(^2E_g)$ |
| **1** | $[Cr(C_2O_4)_2(2,3\text{-pdaH})]^{2-a}$ | 268 (4700) | 407 (100) | 551 (79) |
| **2** | $[Cr(C_2O_4)_2(2,4\text{-pdaH})]^{2-a}$ | 280 (5700) | 406 (102) | 550 (79) |
| **3** | $[Cr(C_2O_4)_2(2,5\text{-pdaH})]^{2-a}$ | 271 (6800) | 407 (96) | 552 (76) |
| **4** | $[Cr(C_2O_4)(2,3\text{-pdaH})(H_2O)_2]^a$ | 268 (5615) | 402 (71) | 547 (52) |
| **5** | $[Cr(C_2O_4)(2,4\text{-pdaH})(H_2O)_2]^a$ | 280 (5200) | 403 (70) | 545 (52) |
| **6** | $[Cr(C_2O_4)(2,5\text{-pdaH})(H_2O)_2]^a$ | 270 (5500) | 402 (72) | 546 (53) |
| **7** | $[Cr(2,3\text{-pdaH})_3]^{b,c}$ | 270 (9150) | | 519 (64) |
| **8** | $[Cr(2,4\text{-pdaH})_3]^{c,d}$ | 280 (14,800) | 396 (91.5) | 514 (72) |
| **9** | $[Cr(2,5\text{-pdaH})_3]^{c,e}$ | 272 (16,800) | | 519 (65) |
| **10** | $[Cr(2,4\text{-pdaH})(H_2O)_4]^{2+c,d}$ | 280 (5200) | 403 (42) | 545 (33) |
| **11** | $2,3\text{-pdaH}_2{}^a$ | 268 (4360) | | |
| **12** | $2,4\text{-pdaH}_2{}^a$ | 280 (6300) | | |
| **13** | $2,5\text{-pdaH}_2{}^a$ | 271 (7300) | | |
| **14** | $[Cr(C_2O_4)_3]^{3-f}$ | 270 (3500) | 420 (95) | 570 (73) |
| **15** | *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^{-a,f}$ | | 415 (66) | 560 (50) |
| **16** | $[Cr(H_2O)_6]^{3+f}$ | | 407 (24.6) | 575 (13.4) |

References: [a][14]; [b][10]; [c]this work; [d][13]; [e][12]; [f][7,20].

As the matrices ***U***, ***S***, and ***V*** are not unique factors of matrix ***A*** solutions and there is no mathematical way of choosing the right one, only the chemically relevant solutions (e.g. positive values of absorbance and concentration) should be taken into account [17,18].

## 3. Results and discussion

All pyridinedicarboxylate complexes exhibit acidic properties ($pK_a$ ca. 2) due to the presence of one uncoordinated COOH group [9,11–13]. Therefore at pH < 4 they exist in the acidic ($pdaH^-$), whereas at pH > 4 in the basic ($pda^{2-}$) forms (e.g. $[Cr(C_2O_4)_2(pda)]^{3-}$, $[Cr(C_2O_4)(pda)(H_2O)_2]^-$ and $[Cr(pda)_3]^{3-}$). The protonation–deprotonation reactions do not bring about any detectable change in their UV–vis spectra.

Similarly to other $Cr^{III}$ coordination species, the electronic spectra of the chromium(III) complexes with oxalate and/or 2,3-, 2,4-, 2,5-pyridinedicarboxylate ligands, consist of two metal-centred (MC) bands and one or two LMCT bands (Table 1).

For the $[Cr(C_2O_4)_2(pdaH)]^{2-}$ complexes (**1–3**) the MC bands are localized about 405 and 550 nm, whereas the LMCT bands appear near 270 nm. The MC spectra of all complexes containing the pdaH ligands (**1–10**) are practically independent of the position of the second carboxylic group. Positions of LMCT bands are almost the same as those characteristic of the intraligand transitions bands in the free $pdaH_2$ ligands (**11–13**). Replacement of the pda ligand by oxalate or aqua ligand results in a bathochromic shift of the MC bands accompanied with a significant intensity decrease in the case of aquacomplexes.

Irradiation within the MC and/or LMCT bands revealed that all Cr(III) complexes containing both oxalate and pyridinedicarboxylate (**1–3**), tris-pda (**7–9**) and tris-oxalate (**14**) ligands are photochemically active; an exception was made by the $[Cr(2,4\text{-pda})(H_2O)_4]^+$ (**10**) and *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ (**15**) complexes.

Irradiation of these complexes in weakly alkaline solutions within their MC bands induces subtle spectral changes in band energies and detectable lowering of their intensities, which is consistent with photoaquation, e.g.:

$$[Cr(2,3\text{-pda})_3]^{3-} + 2H_2O \xrightarrow[MC]{h\nu} [Cr(2,3\text{-pda})_2(H_2O)_2]^- + pda^{2-} \quad (12)$$

Similar effects accompany irradiation of the **1–3** and **14** complexes in deoxygenated solutions within their LMCT bands. The spectra of the $[Cr(C_2O_4)_2(pda)]^{2-}$ photoproducts calculated by factor analysis are very similar to each other and to the photoaquation products obtained by the MC excitation (Fig. 1).

The photosubstitution as the only mode was observed, however, only in deoxygenated solutions, whereas UV-irradiation in the presence of molecular oxygen induced generation of additional photoproduct absorbing strongly at about 374 nm (Fig. 2).

The factor analysis calculations demonstrated that the UV-photoproduct that dominates in aerated media is characterized by the intense bands at 374 and 274 nm. This fits well to the $CrO_4{}^{2-}$ spectral characteristic: 373 nm (4800) and 275 nm (3600) [20]. In the case of homoleptic oxalate $[Cr(C_2O_4)_3]^{3-}$ complex (**14**) both bands could be separated (Fig. 3a), substantiating the previous product identification as chromate(VI) [3,4,7]. For the mixed-ligand complexes $[Cr(C_2O_4)_2(pda)]^{3-}$ (**1–3**) the 270-band isolation was impossible because of the very intensive absorption of the pda ligands which overlapped the band (Fig. 3b).

Thus, in presence of $O_2$, the bisoxalatopyridinedicarboxylate **1–3** complexes irradiated within their LMCT bands generate chromate(VI), like trisoxalatochromate(III) [7]. It is characteristic that the Cr(VI) production needs the presence of oxalate ligand coordinated to chromium(III) (**1–3** and **14**); the homoleptic pda complexes and their aqua-derivatives (**7–10**) do not manifest this

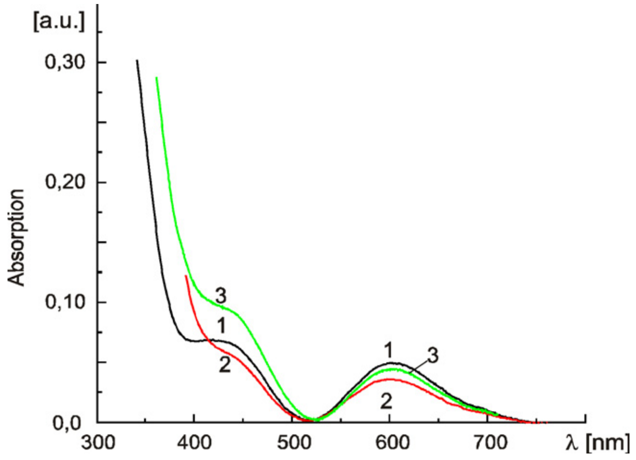


**Fig. 1.** Spectra of the photoaquation products calculated by factor analysis of the spectral changes accompanying UV-irradiation of 2 mM deoxygenated alkaline solution (pH 10.5) of the $[Cr(C_2O_4)_2(pda)]^{3-}$ complexes: 2,3-pda (curve 1), 2,4-pda (curve 2) and 2,5-pda (curve 3).

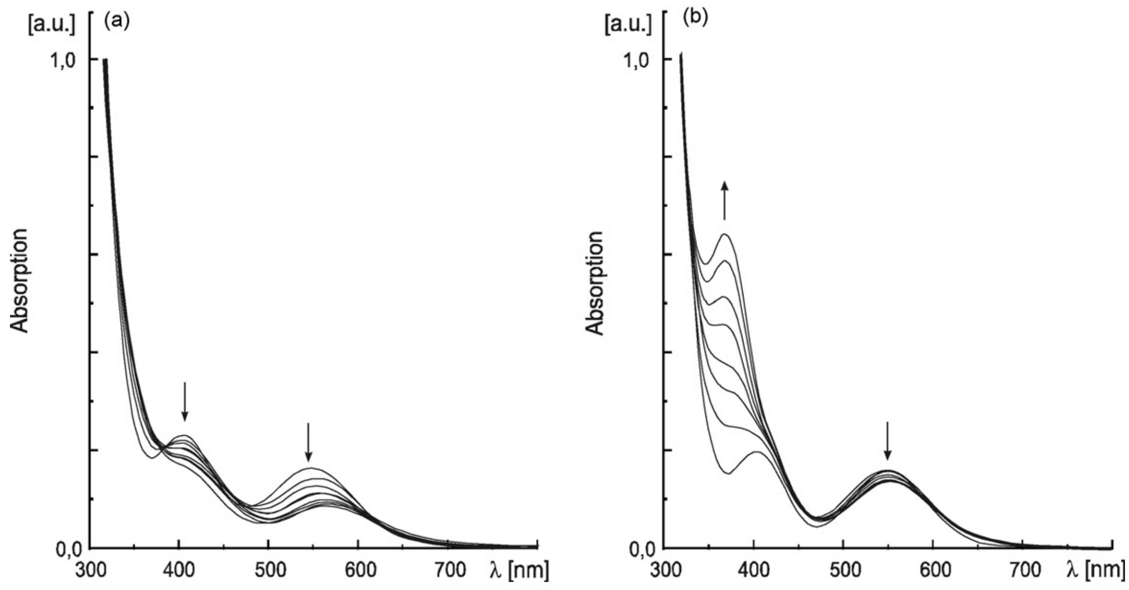


**Fig. 2.** Spectral changes accompanying irradiation of 2 mM $[Cr(C_2O_4)_2(2,5\text{-pda})]^{3-}$ complex in aerated alkaline medium (pH 10.5) by filtered radiation (λ > 300 nm) (a) and by full light of the mercury lamp (b); recorded after every 5 min of irradiation.

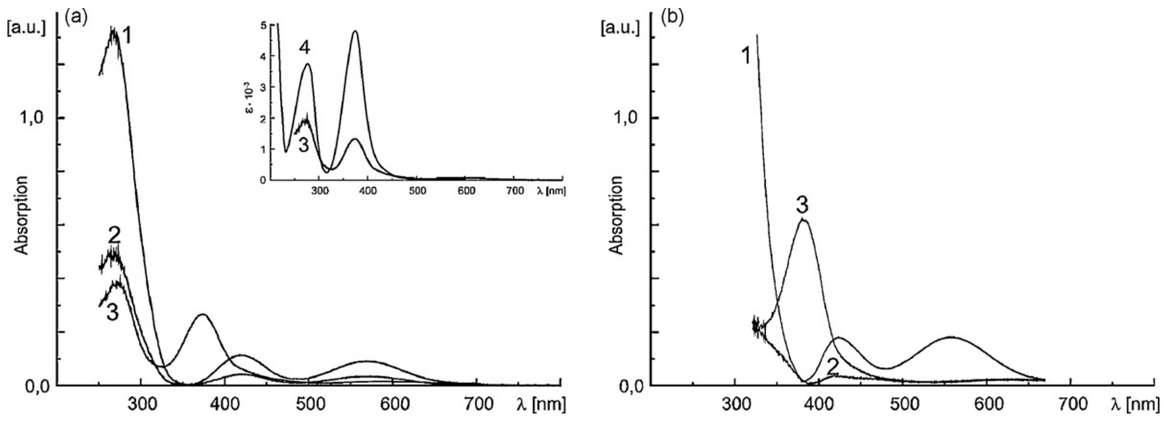


**Fig. 3.** Spectra of the UV-photoproducts isolated by factor analysis of the spectral changes accompanying UV-irradiation of aerated alkaline 2 mM solutions (pH = 10.5) of $[Cr(C_2O_4)_3]^{3-}$ (a) and $[Cr(C_2O_4)_2(2,5\text{-pda})]^{3-}$ (b); curve 1 is identical with the spectrum of the parent complex, curve 2—spectrum of the photoaquation product, while curve 3 corresponds to the spectrum of chromate(VI); the last curve (3) is compared with the $CrO_4^{2-}$ spectrum (4) in the inset.

behavior. However, the quantum yield of the chromate(VI) production is sensitive to the presence of the pyridinedicarboxylate ligand in the mixed oxalato-pdaH complexes, and even depends on its isomeric form (Table 2).

The experiments proved, moreover, that the Cr(III) complexes irradiated in deoxygenated solutions are insensitive to subsequent oxygenation, opposite to behavior observed earlier for the $[Cr(edta)(OH)]^{2-}$ complex [3]. In the case of oxalate complexes **(1–3** and **14)**, the Cr(VI) generation required UV-irradiation in the presence of molecular oxygen. The behavior can be justified by fast decay of the Cr(II) species in deoxygenated solutions of **1–3** and **14.**

To receive more mechanistic information the time-resolved spectra recorded upon the 266-nm laser pulses were interpreted. The experiments revealed, that in all cases the most pronounced transient absorption recorded in microsecond time range is that at long wavelengths (increasing continuously from λ ~ 450 to λ ≥ 600 nm) characteristic of hydrated electrons [21,22]. The $e_{aq}^-$ generation is accompanied by bleaching of the substrate observed at ~ 280 nm and production of relatively long-lived intermediates weakly absorbing at ~330–340 nm for **14,** and within 350–360 for **1–3** complexes (Fig. 4).

The spectral changes presented in Fig. 4 demonstrate that the innersphere electron shifts occurring in consequence of the LMCT

**Table 2**
Effect of the pyridinedicarboxylate ligands on quantum yield of the chromate(VI) production from aerated, alkaline (pH 0.5) solutions of oxalatochromates(III) irradiated by the 254-nm radiation.

| Complex | $[Cr(C_2O_4)_3]^{3-}$ | $[Cr(C_2O_4)_2(pda)]^{3-}$ | | |
|---|---|---|---|---|
| | | 2,3-pda | 2,4-pda | 2,5-pda |
| Rate constant $k_{obs} \times 10^8$ [min$^{-1}$] | 5.75 ± 0.12 | 10.8 ± 0.24 | 8.72 ± 0.12 | 5.82 ± 0.19 |
| Quantum yield × $10^2$ | 1.14 | 2.14 | 1.74 | 1.16 |

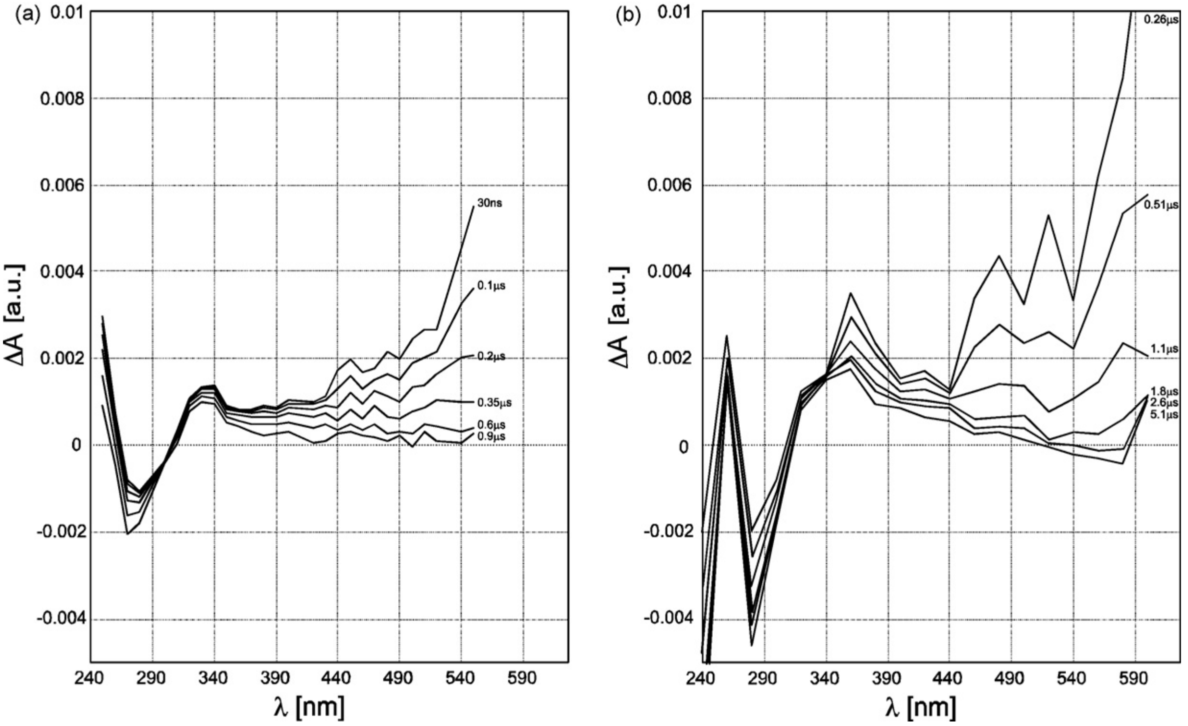


**Fig. 4.** Time-resolved spectra recorded as differences between $A_\tau$ and $A_0$, within microseconds upon flashing by 266-nm laser pulse the deoxygenated alkaline solutions (pH 10.5) of 0.3 mM $[Cr(C_2O_4)_3]^{3-}$ (a) and 0.1 mM $[Cr(C_2O_4)_2(2,3\text{-}pda)]^{3-}$ (b).

excitations:

$$[Cr^{III}(C_2O_4)_3]^{3-} \xrightarrow{h\nu(LMCT)} [Cr^{II}(C_2O_4^{\bullet-})(C_2O_4)_2]^{3-} \qquad (13)$$

$$[Cr^{III}(C_2O_4)_2(pda)]^{3-} \xrightarrow{h\nu(LMCT)} [Cr^{II}(C_2O_4^{\bullet-})(C_2O_4)(pda)]^{3-} \qquad (14)$$

are followed by outersphere electron transfers generating hydrated electrons:

$$[Cr^{II}(C_2O_4{}^{\bullet-})(C_2O_4)_2]^{3-} \rightarrow [Cr^{III}(C_2O_4{}^{\bullet-})(C_2O_4)_2]^{2-} + e_{aq}{}^{-} \qquad (15)$$

$$[Cr^{II}(C_2O_4{}^{\bullet-})(C_2O_4)(pda)]^{3-} \rightarrow [Cr^{III}(C_2O_4{}^{\bullet-})(C_2O_4)(pda)]^{2-} + e_{aq}{}^{-} \qquad (16)$$

The time-resolved spectra of bisoxalatopyridinedicarboxylatochromates(III) are illustrated in Fig. 4b for the 2,3-pdaH ligand, and the spectral changes recorded for the other two pda complexes were similar. The only difference was in the $e_{aq}{}^{-}$ lifetimes, which varied within 0.1 and 0.7 μs depending on the ligand nature (Table 3).

Kinetics of the $e_{aq}{}^{-}$ decay (Table 3) shows that in deoxygenated solutions the $e_{aq}{}^{-}$ decay is much faster in the presence of the chromium(III) complexes than under the same conditions without any complex ($k_{obs} = 2.1 \times 10^5\ s^{-1}$, $\tau = 4.76\ \mu s$); in the presence of molecular oxygen, however, the kinetic parameters are comparable ($k_{obs} = 5.56 \times 10^6\ s^{-1}$, $\tau = 0.18\ \mu s$).

It means, that in aerated media $O_2$ is the main $e_{aq}{}^{-}$ scavenger, whereas in deoxygenated solutions $e_{aq}{}^{-}$ is scavenged either by geminate recombination, or by reaction with other transients or intermediates. The results presented in Fig. 4a and in Table 3 demonstrate that in the case of the homoleptic oxalate complex geminate recombination is dominating:

$$[Cr^{III}(C_2O_4{}^{\bullet-})(C_2O_4)_2]^{2-} + e_{aq}{}^{-} \rightarrow [Cr^{III}(C_2O_4)_3]^{3-} \qquad (17)$$

rate of which is comparable with that characteristic for $e_{aq}{}^{-}$ scavenging by molecular oxygen. In consequence, the yield of the competitive UV-induced aquation (18) has to be low.

$$[Cr^{III}(C_2O_4{}^{\bullet-})(C_2O_4)_2]^{2-} + 2H_2O \rightarrow [Cr^{III}(C_2O_4)_2(H_2O)_2]^{-} + C_2O_4{}^{\bullet-} \qquad (18)$$

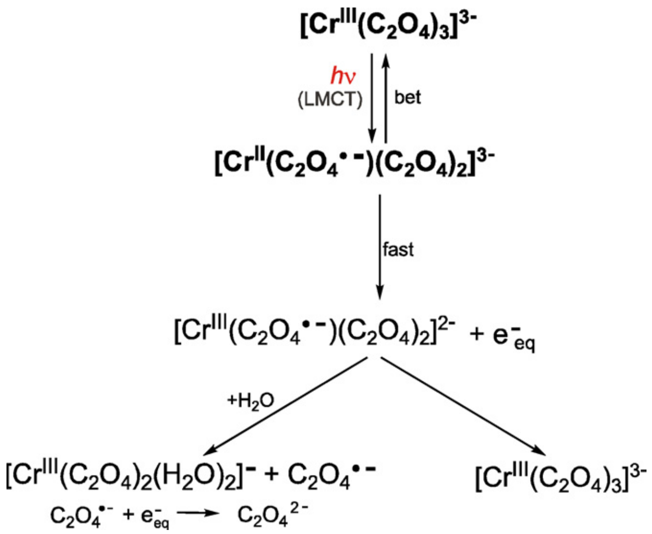
The mechanism proposed for the UV photochemistry of $[Cr^{III}(C_2O_4)_3]^{3-}$ in the absence of molecular oxygen is presented in Scheme 1.

In the presence of the pda ligand in the oxalate complex the rate of the $e_{aq}{}^{-}$ decay in deoxygenated solutions is reduced significantly (Table 3). Distinct from oxalate, pyridine derivatives are known as highly electrophilic ligands, enabling the redox process to be localized on the aromatic group [23,24]. Thus, the $[Cr^{II}(C_2O_4^{\bullet-})(C_2O_4)(pda)]^{3-}$ transient beside the outersphere electron transfer (Eq. (16)) may undergo innersphere electron transfer from the $Cr^{II}$ centre to the pda ligand:

$$[Cr^{II}(C_2O_4{}^{\bullet-})(C_2O_4)(pda)]^{3-} \rightarrow [Cr^{III}(C_2O_4{}^{\bullet-})(C_2O_4)(pda^{\bullet 3-})]^{3-} \qquad (19)$$

**Table 3**
Decay rates and lifetimes of solvated electrons generated upon 266-nm laser pulse in deoxygenated (except of the last column) solutions of the oxalatochromates(III).

| Complex | $[Cr(C_2O_4)_3]^{3-}$ | $[Cr(C_2O_4)_2(pda)]^{3-}$ | | |
|---|---|---|---|---|
| | | 2,3-pda | 2,4-pda | 2,3-pda + $O_2$ |
| Rate constant $k_{obs} \times 10^{-6}$ [$s^{-1}$] | 6.12 | 1.62 | 1.35 | 8.11 |
| Lifetime $\tau = 1/k_{obs}$ [μs] | 0.16 | 0.62 | 0.74 | 0.12 |



**Scheme 1.** Mechanistic pathways of secondary thermal reactions proceeding in deoxygenated alkaline solution of trisoxalatochromate(III) in a consequence of the LMCT excitation.

Electrophilic character of the pda ligand retards the electron transfer to solvent and thus the $e_{aq}^-$ release (Eq. (20))

$$[Cr^{III}(C_2O_4^{\bullet-})(C_2O_4)(pda^{\bullet 3-})]^{3-} \rightarrow [Cr^{III}(C_2O_4^{\bullet-})(C_2O_4)(pda)]^{2-} + e_{aq}^- \quad (20)$$

competes with its scavenging by $[Cr^{III}(C_2O_4^{\bullet-})(C_2O_4)(pda)]^{2-}$ and $C_2O_4^{\bullet-}$ (Eqs. (21)–(23)).

$$[Cr^{III}(C_2O_4^{\bullet-})(C_2O_4)(pda)]^{2-} + e_{aq}^- \rightarrow [Cr^{III}(C_2O_4)_2(pda)]^{3-} \quad (21)$$

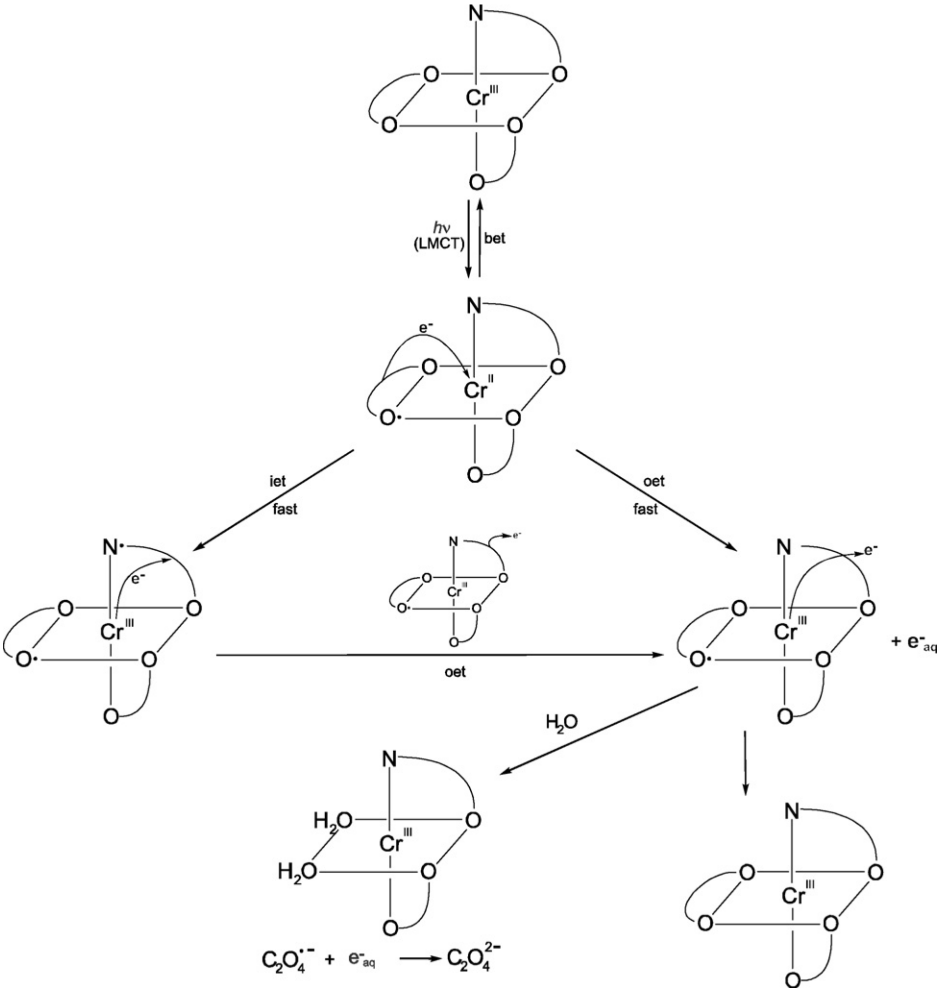
$$[Cr^{III}(C_2O_4^{\bullet-})(C_2O_4)(pda)]^{2-} + 2H_2O \rightarrow [Cr^{III}(C_2O_4)(pda)(H_2O)_2]^- + C_2O_4^{\bullet-} \quad (22)$$

$$C_2O_4^{\bullet-} + e_{aq}^- \rightarrow C_2O_4^{2-} \quad (23)$$

The electron transfer processes following the LMCT excitation in the $[Cr^{III}(C_2O_4)_2(pda)]^{3-}$ complexes are outlined in Scheme 2.

The results presented in Fig. 4 and Table 3 show that in deoxygenated media Cr(II) and other reactive species decay within microseconds after excitation, i.e. fast enough to prevent oxidation by $O_2$, when it reaches irradiated solutions later on (e.g. within minutes).

When, however, the **1–3** and **14** complexes are irradiated in the presence of molecular oxygen its reactions with transients are fast



**Scheme 2.** General outline of the reactive decay of the LMCT state of the bisoxalatopyridinedicarboxylatochromate(III) in deoxygenated solution; pda = 2,3-pda, 2,4-pda or 2,5-pda; iet = innersphere electron transfer; oet = outersphere electron transfer.

enough to scavenge hydrated electrons (Table 3):

$$e_{aq}^{-} + O_2 \rightarrow O_2^{\bullet -} \qquad (24)$$

and other radicals, as $C_2O_4^{\bullet -}$ [25]

$$C_2O_4^{\bullet -} + O_2 \rightarrow 2CO_2 + O_2^{\bullet -} \qquad (25)$$

The $O_2^{\bullet -}$ radical anions produced in reactions (24) and (25) can be responsible for oxidation of Cr(III) species to chromate(VI) in alkaline medium. The reaction should proceed similarly to oxidation of Cr(II) to Cr(VI) by $O_2$, i.e. *via* formation of a superoxo Cr(III) intermediate [26,27].

$$Cr^{3+} + O_2^{\bullet -} \rightarrow CrO_2^{2+} \qquad (26)$$

Especially susceptible should be the intermediate forms, containing ligand radicals (cf. Schemes 1 and 2).

## 4. Conclusions

The results of this paper demonstrate that almost all studied Cr(III) complexes with oxalate and pyridinedicarboxylate ligands (**1–9** and **14** in Table 1) undergo photosubstitution in result of MC excitation. Moreover, the $[Cr(C_2O_4)_3]^{3-}$ and $[Cr(C_2O_4)_2(pda)]^{3-}$ complexes undergo the photoredox mode induced by the LMCT excitation, similarly to other Cr(III) complexes with electron donor ligands [3,7,28–30]. As distinct from other systems, the innersphere electron transfer from the oxalate ligand to the chromium centre is followed by fast outersphere transfer to the solvent and/or innersphere electron transfer to the electrophilic pda ligand. The final result in anoxic media is aquation induced by photoreduction. These reactions are completed within microseconds i.e. are fast enough to prevent subsequent oxygenation of the previously irradiated solutions.

The secondary reactions induced by LMCT excitation are, however, not fast enough to prevent oxidation of photoproducts during their generation in oxygenated solutions and the $[Cr(C_2O_4)_3]^{3-}$ and $[Cr(C_2O_4)_2(pda)]^{3-}$ complexes under such conditions produce chromate(VI), provided that solutions are (at least slightly) alkaline. The Cr(III) superoxo intermediate ($CrO_2^{2+}$) of the Cr(VI) precursor is expected to be formed not only in reaction of Cr(II) with $O_2$ but also Cr(III) with $O_2^{\bullet -}$.

The presence of the oxalate ligand is thus prerequisite of the described redox behavior, whereas the pyridinedicarboxylate ligands modulate the reaction course, rate and yield. Quantum yield of the $Cr^{VI}$ generation decreases within the series 2,3-pda > 2,4-pda > 2,5-pda.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.11.004.

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