Ligand field photochemistry of mixed-ligand cyanochromates. Comparative study of $[Cr(CN)_5(OH)]^{3-}$ and $[Cr(CN)_4(N_3)(OH)]^{3-}$

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Abstract

The novel mixed-ligand cyanochromate, $[Cr(CN)_4(N_3)(OH)]^{3-}$, has been synthesized and its LF-photochemistry has been studied and compared with that of the better known pentacyanohydroxochromate(III). In both the cases the reaction consists in the photosubstitution of one CN^- ligand followed by fast thermal CN^- release leading to the formation of one relatively stable product. The chemical and spectral analysis of the products showed their formulation as triacido-complexes, $[Cr(CN)_3(OH)_n(H_2O)_{3-n}]^{n-}$ and $[Cr(CN)_2(N_3)(OH)_n(H_2O)_{3-n}]^{n-}$, respectively. The results contribute to the discussion on preferential ligand photosolvation.

Keywords: Mixed ligand cyanochromates; Pentacyanohydroxochromate; Azidocyanochromate; LF photochemistry; Photosubstitution

1. Introduction

Mixed-ligand cyanochromates(III), unlike their Fe(II), Fe(III) or Co(III) analogues, are not so common [1]. Recently, a large family of am(m)ine-cyanochromates(III) has been described, most of which are mono- and di-cyano species [2]. Penta- and tetra-cyanochromates are relatively rare and mostly obtained with a poor yield by substitution or photosubstitution of one or two CN^- in $[Cr(CN)_6]^{3-}$ by H_2O, Me_2SO, $MeCN$, NCS^- or NH_3 [2–4]. One exception is $K_3[Cr(CN)_5(OH)] \cdot H_2O$ which can be produced in good yield by the reaction of $[CrCl(NH_3)_5]^{2+}$ with KCN [5].

Recently, we have found that pentacyanohydroxochromate is a good starting material for preparing other mixed-ligand cyanochromates, among those the $[Cr(CN)_4(N_3)(OH)]^{3-}$ complex [6]. This novel compound revealed photochemical activity resembling that of the parent $[Cr(CN)_5(OH)]^{3-}$ ion, for which photoenhancement of the thermal CN^- aquation mode and photoredox behaviour were reported as a result of LF and CT irradiations, respectively [7,8].

This article reports on the LF photochemistry of $[Cr(CN)_4(N_3)(OH)]^{3-}$ and some new aspects of the LF photochemistry of $[Cr(CN)_5(OH)]^{3-}$. The results should provide information on preferential photosolvation behaviour of ligands differing in the π-bonding nature.

2. Experimental

2.1. Materials

Potassium pentacyanohydroxochromate(III) was prepared according to the literature procedure [5] by the reaction of $[CrCl(NH_3)_5]Cl_2$ with KCN followed by separation on a Sephadex G-25 gel column. The only modification was in precipitating $K_3[Cr(CN)_5(OH)] \cdot H_2O$ by means of methanol instead of ethanol. Purity of the samples was checked by IR and UV-VIS spectroscopy. The IR spectrum shows maxima at: round 3500 cm^{-1}, m (ν_{OH}), 2128 cm^{-1}, vs. (ν_{CN}), 1628 cm^{-1}, m (δ_{HOH}), 1541 cm^{-1}, m, 1343 cm^{-1}, m, 1088 cm^{-1}, w, 876 cm^{-1}, m (δ_{CrOH}), 538, vs, b, and 442, vs (ν_{CrCN}). The UV/VIS spectrum (Fig. 1(a)) is characterized by the bands at 435 nm ($\epsilon = 120$, $^4A_2 \rightarrow {}^4T_2$), 364 nm ($\epsilon = 78$, $^4A_2 \rightarrow {}^4T_1$) and 243 nm ($\epsilon = 4100$, LMCT). The data are in agreement with those previously published [5,8–12].

Potassium azidotetracyanohydroxochromate(III) was prepared as follows: 15 ml of aqueous solution containing 5 g of $K_3[Cr(CN)_5(OH)] \cdot H_2O$ and 2 g of NaN_3 was neutralized using 1 M CH_3COOH and the reaction mixture was stirred at room temperature under a permanent monitoring of pH and periodical adjustment to pH ≈ 7 by addition of 1 M CH_3COOH drop by drop. The substitution progress was followed spectrophotometrically by periodical sampling. The

process was carried out until the absorption at $\lambda = 327$ nm stopped increasing. The synthesis consisting in the substitution of one CN^- ligand by the azide ion

$$[Cr(CN)_5(OH)]^{3-} + N_3^- \longrightarrow$$

$$[Cr(CN)_4(N_3)(OH)]^{3-} + CN^- \quad (1)$$
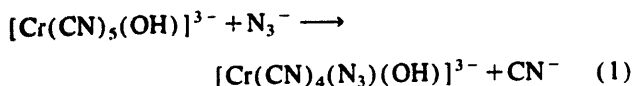
is accompanied by an increase in pH. The progress of this reaction depends strongly on pH, for instance the conversion was about 5% after 10 days at pH ~ 10, whereas at pH ~ 7 it was complete within ca. 4.5 h. The compound was precipitated by pouring the reaction mixture into CH_3OH (1:2 vol) and then into cold (about 4 °C) C_2H_5OH (1:4 vol). The yellow crystals were filtered off and washed with ethanol, dried and stored in a desiccator over KOH. During all operations the samples were protected against intense light. The yield of $K_3[Cr(CN)_4(N_3)(OH)] \cdot H_2O$ was about 3.7 g, i.e. 68% of the theoretical. Analysis gave the Cr:C:N: $(K + Na):H_2O$ ratio of $1.00:(4.12 \pm 0.12):(7.27 \pm 0.13):(2.88 \pm 0.20):(1.26 \pm 0.1)$. Under the described conditions the K:Na ratio was approximately 2.7:0.2. Some amount of the protonated form, $K_2[Cr(CN)_4(N_3)(H_2O)] \cdot H_2O$ could also be coprecipitated. In an effort to precipitate the pure tripotassium salt, a higher concentration of K^+ ions was used, but this led to coprecipitation of CH_3COOK. Recrystallization, however, was found to be ineffective. The IR spectrum of $K_3[Cr(CN)_5(OH)] \cdot H_2O$ shows maxima at: round 3500 cm^{-1}, m (3625, 3551 and 3438 cm^{-1}, ν_{OH}), 2130 cm^{-1} vs (ν_{CN}), 2080 cm^{-1} vs, b and ~ 2035 cm^{-1}, sh (ν^a_{N3}), 1613 cm^{-1}, m (δ_{HOH}), 1350 cm^{-1}, m and 1298 cm^{-1}, m (ν^s_{N3}), 1020 cm^{-1}, w (δ_{CrOH}), 656 cm^{-1}, w (δ_{N3}), 449, s (ν_{CrCN}) and 341 cm^{-1}, m (ν_{CrN3}). The UV/Vis spectrum (Fig. 1(b)) is characterized by the bands at 440 nm ($\epsilon = 217$, $^4A_2 \rightarrow {}^4T_2$), 327 nm ($\epsilon = 2$, 050, LMCT overlaps the $^4A_2 \rightarrow {}^4T_1$ transition), 259 nm ($\epsilon = 5$, 430), 228 nm ($\epsilon = 7$, 340) and 197 nm ($\epsilon = 12$, 360).

Other chemicals were commercial of the available quality.

2.2. Procedures and instrumentation

2.2.1. Product spectra

Product spectra (300–700 nm) were calculated from the spectra of either $[Cr(CN)_5(OH)]^{3-}$ or $[Cr(CN)_4(N_3)-(OH)]^{3-}$ solutions photolyzed at 436 nm. The apparent molar absorption coefficients of all products, $\epsilon'_{p,\lambda,t}$, were calculated by

$$\epsilon'_{p,\lambda,t} = \frac{A_{\lambda,t} - c_s \epsilon_{s,\lambda}}{c_p} \quad (2)$$

where $A_{\lambda,t}$ is the absorbance at λ nm of the solution photolyzed for t min; $\epsilon_{s,\lambda}$ is the molar absorption coefficient of the substrate at wavelength λ; c_s and c_p are concentrations of the substrate and sum of the products, respectively, after t min of irradiation. The substrate conversion was calculated from the decrease in absorbance in the spectral range where product absorption could be neglected, whereas that of the
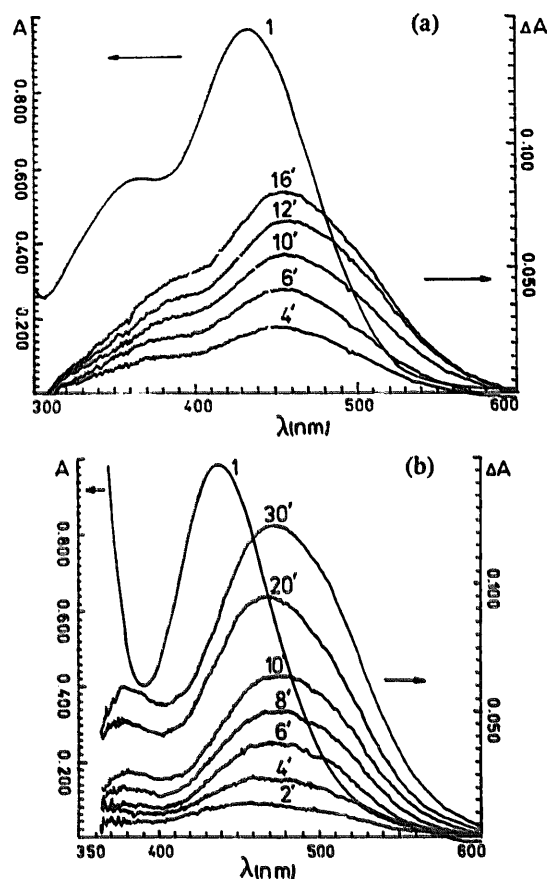

Fig. 1. UV/Vis absorption spectra of the substrate (curve 1) and of the photolysis products (curves 2'–30') for 8.5×10^{-3} M $[Cr(CN)_5(OH)]^{3-}$ (Fig. 1(a)) and 4.5×10^{-3} M $[Cr(CN)_4(N_3)(OH)]^{3-}$ (Fig. 1(b)). The product spectra were calculated from the difference: $A_{\lambda,t} - c_s \epsilon_{s,\lambda}$ (cf. Eq. (2)) upon exposure to 436-nm radiation at 293 K for time shown at each curve.

substrate was appreciable (between 280–320 nm for $[Cr(CN)_5(OH)]^{3-}$, and 350–380 nm for the azide complex).

Since the spectra obtained for the same reagent were practically independent of irradiation time up to about 20 min (cf. Fig. 1) they were averaged and the whole procedure was repeated at least five times. The product spectra were calculated by the same procedure in two laboratories (in Köln and Kraków), by different experimenters (B.M. and H.B.Q.) using two different photochemical equipments and spectrophotometers (Cary 2300 and Shimadzu 2100). In both the cases the results were nearly identical. The calculated product spectra (Fig. 3 and Tables 1 and 2) are averages of at least 50 spectra obtained under similar experimental conditions.

2.2.2. Product analysis

The product composition was determined by simultaneous spectral and electrochemical analyses of the photolyzed solutions. From the former, the actual reactant consumption was calculated, whereas the latter was used to determine the released CN^- ions. The results enabled us to assess the num-

Table 1

Photosubstitution in the $[Cr(CN)_5(OH)]^{3-}$ complex: spectrum of the products, quantum yield, Φ_0, and ratio between the product concentrations, R (Φ_0 determined spectrally from the substrate decay extrapolated to $t = 0$; R = c (released CN^-): c (complex product) averaged for $t \leqslant 20$ min; temperature 293 K and λ_{irr} 436 nm, if not otherwise stated)

Conditions	Product spectrum		Quantum yield	Product ratio
	$\lambda_{max}(1)$, nm(ϵ_{max})	$\lambda_{max}(2)$, nm(ϵ_{max})	Φ_0	R
NaOH 1 M	473 ± 8 (92 ± 15)	370 ± 3 (48 ± 9)		1.92 ± 0.36
pH ~ 13	473 ± 4 (85 ± 9)	371 ± 4 (40 ± 4)	0.062 ± 0.003	2.02 ± 0.28
pH ~ 13, 254 nm aerated			0.17 ± 0.03	
pH ~ 13, 254 nm deaerated			0.14 ± 0.03	
pH 9.6	463 ± 8 (87 ± 9)	~390 ± 6, sh (49 ± 9)		2.04 ± 0.20
pH 8.9	462 ± 9 (100 ± 11)	~386 ± 7, sh (55 ± 5)	0.063 ± 0.004	
pH 8.9, 278 K t_{irr} = 3 min	449 ± 7 (103 ± 2)	~378 ± 2, sh (61 ± 0)	0.058 ± 0.006	1.35 ± 0.13
pH 9.6 → 3.3	451 ± 5 (128 ± 20)	352 ± 3 (112 ± 24)		
KCN 0.01 M	459 ± 6 (97 ± 8)	~375 ± 5, sh (51 ± 3)	0.068 ± 0.00.	
KCN 0.09 M	470 ± 2 (122 ± 4)	370 ± 1 (65 ± 9)		
av. spectrum pH ≥ 8.9, 293 K	467 ± 7 (97 ± 12)	377 ± 10 (51 ± 9)		

Table 2

Photosubstitution in the $[Cr(CN)_4(N_3)(OH)]^{3-}$ complex: spectrum of the product, quantum yield and ratio between the product concentrations (denotation of Φ_0 and R the same as in Table 1; temperature 293 K and λ_{irr} 436 nm, if not otherwise stated)

Conditions	Product spectrum		Quantum yield	Product ratio
	$\lambda_{max}(1)$, nm(ϵ_{max})	$\lambda_{max}(2)$, nm(ϵ_{max})	Φ_0	R
pH ~ 13	474 ± 2 (138 ± 11)	384 ± 2 (59 ± 3)		1.47 ± 0.21
pH ~ 13, 366 nm			0.15 ± 0.03	
pH ~ 13, 254 nm aerated			0.34 ± 0.05	
pH ~ 13, 254 nm deaerated			0.35 ± 0.04	
pH ~ 12	473 ± 10 (136 ± 10)	390 ± 6 (67 ± 8)	0.062 ± 0.004	1.48 ± 0.29
pH 9.6	478 ± 2 (141 ± 10)	382 ± 2 (51 ± 7)		2.14 ± 0.28
pH 8.9	483 ± 10 (140 ± 15)	384 ± 10 (59 ± 11)	0.054 ± 0.003	2.06 ± 0.27
KCN 0.04 M	478 ± 4 (152 ± 15)	388 ± 4 (55 ± 8)		
NaN₃ 0.04 M	482 ± 3 (159 ± 16)	380 ± 2 (61 ± 15)		2.21 ± 0.07
av. spectrum	478 ± 5 (144 ± 15)	385 ± 5 (59 ± 8)		

ber of CN^- ligands in the product complexes. It appeared to be constant within the irradiation times $t \leq 20$ min, whereas it increased at longer times. The value was calculated as an average of those constant values obtained for at least two series under the same conditions.

The electrochemical analysis was made by use of a CN-ion selective electrode of the type OP-CN-7112-OπO350 in the buffered solution pH 12 (0.1 M aminoacetic acid, 0.9 M NaOH, 0.1 M NaCl, saturated AgI). The electrode was calibrated using a standard KCN solution.

Azide ions were analyzed by spectrophotometric determination of an $Fe(III)-N_3^-$ complex (at 460 nm, $\epsilon 3.6_0$ × 103) as well as by oxidation to nitrogen [13,14].

2.2.3. Quantum yield determinations

The equipment and procedure were the same as described before [15]. In all cases irradiations were limited to less than 10% conversion.

3. Results and discussion

3.1. Structure and properties of $[Cr(CN)_4(N_3)(OH)]^{3-}$

The novel complex was synthesized by the substitution reaction (1) and composition of its potassium salt was determined by chemical analyses and IR spectra.

Although the crystals of $K_3[Cr(CN)_4(N_3)(OH)] \cdot H_2O$ were obtained in sizes not appropriate for X-ray structure determination, we assume that the complex was formed in the *cis* configuration. The assumption is based on the *trans* labilizing effect of the CN groups and stereoretentivity typical of the ground-state substitution reactions of chromium(III) complexes [2,4,9–12,16]. In the course of preparation of the azidotetracyanochromate from pentacyanohydroxochromate the cyanide ligand *trans* to OH^- will be less reactive than the ligands on the CN–CN axes. Hence we concluded that the product is formed in the *cis* configuration. The conclusion is supplied by the UV/VIS and IR spectral characteristics of $K_3[Cr(CN)_4(N_3)(OH)] \cdot H_2O$: (i) the extinction coefficient of the $^4A_2 \rightarrow {}^4T_2$ band of the azido is roughly twice the value of the $[Cr(CN)_5OH]^{3-}$ complex (217 and 120 M^{-1} cm^{-1}, respectively); (ii) the stretching mode splittings of coordinated azide vibrations, both ν_a and ν_s, are consistent with the less symmetrical *cis* configuration [17].

3.2. Thermal reaction

Although thermal release of the CN-ligand from $[Cr(CN)_5(OH)]^{3-}$ is acid catalyzed, it is still detectable in alkaline media [7]. Electrochemical monitoring of the CN^- ions released from 8×10^{-3} M $[Cr(CN)_5(OH)]^{3-}$ solutions kept in the dark at 295 K showed a nearly linear increase in the CN^- concentration within at least 90 min with $k_{obs} \cong 2.7 \times 10^{-8}$ s^{-1} in aqueous (pH ~ 9.6) and 2.3×10^{-8} s^{-1} in alkaline (1 M NaOH) solution. The dark CN^- substitution is considerably enhanced by N_3^- ions excess (e.g. at the ratio 2:1 by the factor of 1.5), which leads to CN^- release and the production of $[Cr(CN)_4(N_3)(OH)]^{3-}$ (Eq. (1)) in the ratio of about 1 (experimentally determined 1.16).

The $[Cr(CN)_4(N_3)(OH)]^{3-}$ complex is also susceptible to the thermal CN^- substitution with $k_{obs} \cong 1.6 \times 10^{-8}$ s^{-1} in aqueous, 1.2×10^{-8} s^{-1} in azide (1 M NaN$_3$) and 5.8×10^{-9} s^{-1} in alkaline (1 M NaOH) solution (295 K). No traces of released N_3^- ions were found unless the solution was acidic. In the quantitative treatment of the photochemical results the progress of the dark reaction was taken into account.
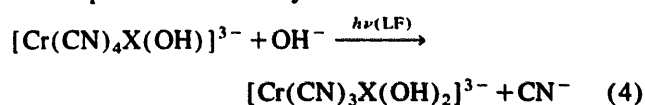
3.3. LF photochemistry

Continuous irradiation of the $[Cr(CN)_5(OH)]^{3-}$ and $[Cr(CN)_4(N_3)(OH)]^{3-}$ complexes within their LF band ($^4A_2 \rightarrow {}^4T_2$) leads to the release of the CN^- ligands and to a bathochromic shift of the UV/Vis spectra (Fig. 1). Isosbestic points were observed for $[Cr(CN)_5(OH)]^{3-}$ at 465 nm and 484 nm, and for $[Cr(CN)_4(N_3)(OH)]^{3-}$ at 467 nm and 482 nm in aqueous and 0.1 M NaOH, respectively. The LF irradiations were ineffective in producing detectable amounts of free N_3^-.

The results are consistent with a photoaquation

$$[Cr(CN)_4X(OH)]^{3-} + H_2O \xrightarrow{h\nu(LF)}$$

$$[Cr(CN)_3X(OH)(H_2O)]^{2-} + CN^- \quad (3)$$
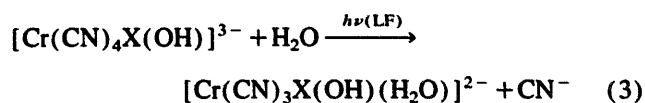
and/or photosubstitution by OH^-

$$[Cr(CN)_4X(OH)]^{3-} + OH^- \xrightarrow{h\nu(LF)}$$

$$[Cr(CN)_3X(OH)_2]^{3-} + CN^- \quad (4)$$

where $X = CN^-$ or N_3^-.

Tetracyanochromates(III), however, are known as thermally unstable species [9–11] and the same seems to be true for the azidotricyanochromate. A fast secondary CN^- substitution leads to the formation of a more stable tricyano [9–11] or azidodicyano species.

To verify this hypothesis the $[Cr(CN)_5OH]^{3-}$ photolysis was performed at 278 K (Fig. 2, Table 1). A transient species was detected which could not be observed at room temperature. Its spectral characteristic, being intermediate between that of the reactant and the tricyano product, as well as the ratio of cyanide released to reactant consumed ($R = 1.35$, Table 1) justify its formulation as tetracyanohydroxochromate(III).

However, irradiations at 293 K resulted not only in different spectral changes but also in the release of two cyanide ligands from one reactant ion consumed (Tables 1 and 2). The results lead to the conlusion that the photosubstitution of the $[Cr(CN)_4X(OH)]^{3-}$ (Eq. (3) or (4)) is followed by fast thermal CN-substitution and generation of one of the triacidochromates $[Cr(CN)_2X(OH)_n(H_2O)_{3-n}]^{n-}$. Their spectra for the same X are similar in shape and differ only within experimental error. They are especially independent of the CN^- or N_3^- ligand excess in the photolyzed solution (Fig. 3, Tables 1 and 2).

The only difference detected was the effect of pH on the $[Cr(CN)_5(OH)]^{3-}$ photolysis (Fig. 3(a), Table 1). The existence of protolytic equilibria among the various $[Cr(CN)_3(OH)_n(H_2O)_{3-n}]^{n-}$ complexes suggested a way for reducing the number of reaction products by shifting the
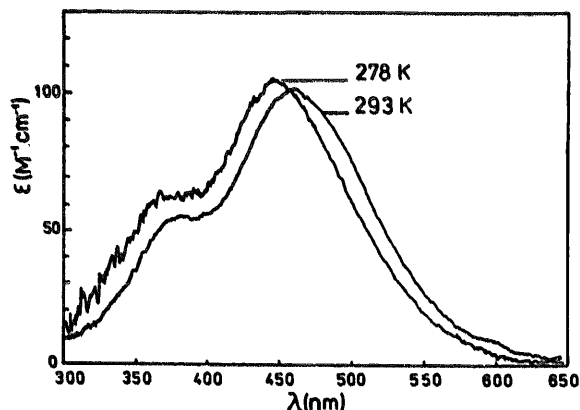

Fig. 2. Spectra of the substitution products of pentacyanohydroxochromate(III) photolysis, recorded at 278 K and at 293 K and calculated by Eq. (2). Conditions for curves: 2.6×10^{-3} M aqueous solution of $[Cr(CN)_5(OH)]^{3-}$ irradiated for 3 min by $\lambda = 436$ nm.
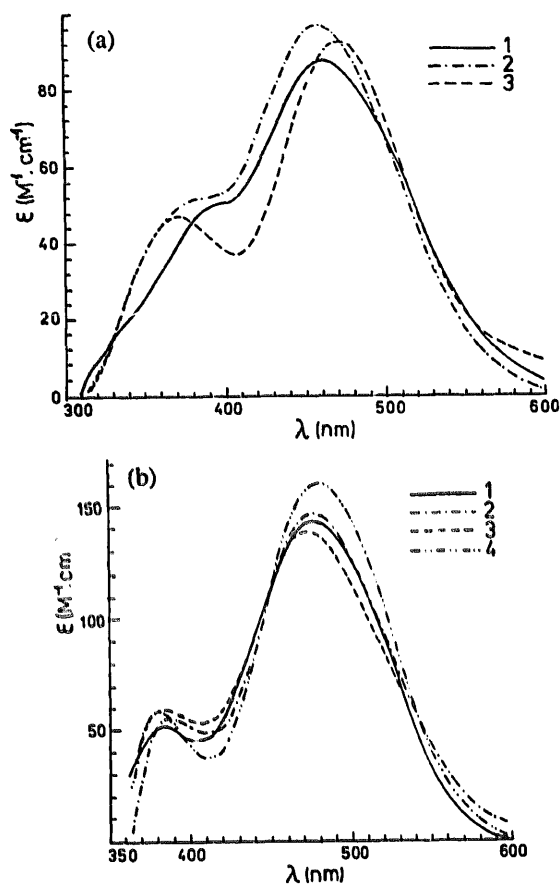
Fig. 3. Spectra of the substitution products generated by 436-nm irradiation at 293 K of $[Cr(CN)_5(OH)]^{3-}$ (Fig. 3(a)) and $[Cr(CN)_4(N_3)(OH)]^{3-}$ (Fig. 3(b)) in aqueous solution (curve 1), in 0.04 M KCN (curve 2), in 0.1 M NaOH (curve 3) and in 0.04 NaN₃ (curve 4).

equilibria towards one side. Acidification of the mixture of $[Cr(CN)_{6-x}(H_2O)_x]^{3-x}$ complexes at pH 3–5, was reported to produce the triaqua form, $[Cr(CN)_3(H_2O)_3]$ [9–11]. Reduction of pH for the examined photolyzed solutions to 3–5 resulted in a hypsochromic shift of $\lambda_{max}(1)$ to 451 ± 5 (128 ± 20) and $\lambda_{max}(2)$ to 352 ± 3 (112 ± 24) (Table 1). The shift is qualitatively consistent with the protonation of the OH⁻ ligands; the spectrum, however, does not correspond exactly to the spectral characteristics of the $[Cr(CN)_3(H_2O)_3]$ complex reported earlier $\lambda_{max}(1)$: 467 (115) and $\lambda_{max}(2)$: 362 (26) [7,9]). However, the isosbestic point found in the acidic solution at about 443 nm and $\epsilon \sim 100$ corresponds well to the earlier data [9–11]. The consistence between the spectra should be recognized as satisfactory because in both the cases they were calculated from different mixtures of several forms. Moreover, the average environment approximation for the $[Cr(CN)_{6-n}$ $(H_2O)_n]^{n-3}$ series showed the best fitting of our spectrum at $n = 2.85$ and 3.22 for $\lambda_{max}(1)$ and $\lambda_{max}(2)$, respectively.

Although LF photochemistry of the chromium(III) complexes has been widely studied both experimentally and theoretically, there are not many reports on complexes with ligands differing in π-bonding such as CN⁻ and N₃⁻ or OH⁻. In particular, only few articles dealing with the pref-

erential ligand photosolvation of negatively charged mixed ligand cyanochromates are known [2,4]. Also the behaviour of the N₃⁻ ligand in preferential ligand photosubstitution has rarely been studied [13].

According to Adamson's rules [18] and Zink's and Wrighton's approaches [19–23], $[Cr(CN)_5(OH)]^{3-}$ and cis-$[Cr(CN)_4(N_3)(OH)]^{3-}$ should dissociate CN⁻, because cyanide is the strong field ligand on the weak field axis. Trans-$[Cr(CN)_4(N_3)(OH)]^{3-}$ should release N₃⁻. The observed reaction mode of the azido complex is in agreement with the assumed cis configuration. The Vanquickenborne-Ceulemans model predicts the axial labilization and CN⁻ release for $[Cr(CN)_5(OH)]^{3-}$ [24–26]. The prediction for cis-$[Cr(CN)_4(N_3)(OH)]^{3-}$ is uncertain due to the numerous possible reaction modes and the lack of angular overlap data for Cr–N₃. However, evaluation made with use of the parameters for the Co–N³⁻ and the procedures from references [24–26] leads to the conclusion that the Cr–N³⁻ labilization is to be expected for $[Cr(CN)_5(N_3)]^{3-}$ and CN⁻ labilization for the cis-$[Cr(CN)_4(N_3)(OH)]^{3-}$ complex.

Quantum yield of $[Cr(CN)_5(OH)]^{3-}$ within the LF band ($^4A_2 \rightarrow {}^4T_2$) amounts to ~0.06 independently of pH within Refs. [9–13], whereas the value found earlier at pH ~14 was 0.09 [8]. Quantum yields at 366 nm and 254 nm are much higher than at 436 nm (Table 1). Similar results were obtained for the $[Cr(CN)_4(N_3)(OH)]^{3-}$ complex (Table 2).

Irradiation within the CT bands leads to a photoredox reaction of both the complexes, which is also accompanied by the substitution of the CN⁻ ligands (Tables 1 and 2, cf. also Ref. [8]). In this case, however, the catalysis by a photoredox generated Cr(II) species contributes to the substitution reaction [8,27].

To conclude, the results show that it is the cyano ligand which undergoes photosubstitution in the LF photolysis of the $[Cr(CN)_4(OH)X]^{3-}$ complexes (X = CN⁻ or N₃⁻). The photoproducts are unstable towards thermal CN⁻ substitution and generate relatively stable triacidochromate(III) products.

Acknowledgements

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