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Optical and photoinduced electron transfer in tris(ethylenediamine)cobalt(III)–cyanometallate ion pairs [1]

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Abstract

The ion pairs $\{[Co(en)_3]^{3+}; [M(CN)_x]^{4-}\}$, where M = Fe, Ru, Os ($x=6$) and M = Mo, W ($x=8$), and $\{[Co(en)_3]^{3+}; [Mn(CN)_5NO]^{3-}\}$, in aqueous solution show up ion pair charge-transfer (IPCT) transitions in the visible and near-ultraviolet spectral regions. On excitation of the IPCT transitions ($\lambda_{irr}=405$ nm), trinuclear complexes *trans*-$\{(en)_2Co[NC{-}M(CN)_{(x-1)}]_2\}^{5-}$ are formed subsequent to an *optical* electron-transfer step with quantum yields close to unity. Excitation of the longest-wavelength ligand-field transition ($\lambda_{irr}=510$ nm) of ion paired $[Co(en)_3]^{3+}$ results in a *photoinduced* electron-transfer reaction leading to the formation of binuclear pentacoordinate $[(en)_2Co{-}NC{-}M(CN)_5]^-$ (M = Fe, Ru, Os) and trinuclear hexacoordinate *trans*−$\{(en)_2Co[NC{-}M(CN)_7]_2\}^{5-}$ (M = Mo, W) complexes. The redox-reactive excited state of $[Co(en)_3]^{3+}$ has a lifetime shorter than 3 ns and is tentatively assigned to the $^5T_{2g}$ ligand-field excited state. © 1997 Elsevier Science S.A.

Keywords: Photo-redox; Cobalt(III); Cyanometallate; Five-coordinate complex; Ion pair

1. Introduction

Photo-redox reactions between thermodynamically stable and substitutionally inert metal complexes resulting in unstable and labile species are of considerable interest with respect to photocatalytic applications [1]. In order to achieve high quantum yields of permanent photoproduct formation it is advantageous to create conditions under which the donor, the acceptor and the chromophore are already present in a relatively stable form prior to light absorption.

These conditions are met for ion pairs of oppositely charged coordination compounds [2]. The synthesis of such ion pairs by simply mixing solutions of appropriate salts allows for a wide variation of spectroscopic, photophysical and photochemical properties of the components. Furthermore, in addition to the individual absorptions of the single components, new electronic transitions between the ions may show up in the ultraviolet and visible spectral regions, which are attributed to charge transfer from the donor to the acceptor ion. Such absorptions are named ion pair charge-transfer (IPCT) bands.

The photochemistry of several ion pairs of coordination compounds has been studied [2–5], including the $\{[Co(en)_3]^{3+}; [Fe(CN)_6]^{4-}\}$ system in aqueous 2–4 M NaCl [6,7]. One of the particularities of the latter system is that the quantum yield of the photo-redox reaction, attributed to a *photoinduced* electron-transfer reaction between ligand-field excited $[Co(en)_3]^{3+}$ and $[Fe(CN)_6]^{4-}$ within an ion pair, has been reported to be close to unity over a wide spectral range. This result is remarkable since $[Co(en)_3]^{3+}$ itself does not undergo any photochemical reaction on irradiation with visible light [8].

Later, Vogler et al. [3] and Haim [9] reported the observation of IPCT transitions in this and related ion pairs with considerable molar extinction coefficients in the near-UV region. $\{[Co(en)_3]^{3+}; [Ru(CN)_6]^{4-}\}$ was shown to undergo an *optical* electron-transfer reaction on irradiation into the IPCT band region with a quantum yield $\Phi=0.1$. The photoproduct was tentatively assigned to a binuclear cyano-bridged cobalt(III)/ruthenium(II) species. Long-wavelength irradiation experiments, however, have not yet been performed for this system. Here, we report a systematic study of the spectroscopic and wavelength-dependent photochemical behaviour of a series of $\{[Co(en)_3]^{3+}; [M(CN)_x]^{4-}\}$ ion pairs in aqueous solution, where M = Fe, Ru, Os ($x=6$) and M = Mo, W ($x=8$), respectively.

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[1] Dedicated to Professor Horst Hennig on the occasion of his 60th birthday.

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2. Experimental details

2.1. Materials

Commercially available samples of $K_4[Fe(CN)_6]\cdot 3H_2O$ (Merck) and $K_4[Ru(CN)_6\cdot 3H_2O$ (Johnson Matthey) were recrystallized from water/methanol. $K_4[Os(CN)_6]\cdot 3H_2O$ [10], $K_4[Mo(CN)_8]\cdot 2H_2O$ [11], $K_4[W(CN)_8]\cdot 2H_2O$ [12], $K_3[Mn(CN)_5NO]\cdot 2H_2O$ [13], $[Co(en)_3](ClO_4)_3$ [14], *trans*-$[Co(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$ [14], and $[Ru(en)_3]Cl_3$ [15] were prepared according to well-known procedures.

2.2. Syntheses

2.2.1. trans-$K_5\{(en)_2Co[NC-M(CN)_{x-1}]_2\cdot 8H_2O\}$ (2a–e)

A freshly prepared 0.05 M aqueous solution of *trans*-$[Co(en)_2Cl_2]Cl$ was added to the same amount of a 0.5 M aqueous solution of $K_4[M(CN)_x]$ (M = Fe, Ru, Os, $x=6$; M = Mo, W, $x=8$). After stirring for 1 h at room temperature the resulting cherry red solution was poured into a ten-fold amount of dry acetone. A red oil precipitated immediately. The opaque solution, containing the excess cyanometallate, was rapidly removed by decanting. The oil was dissolved several times in a minimum of water and reprecipitated by addition of dry acetone. Finally, the oil was allowed to crystallize in a desiccator over KOH. The elemental analyses of the brownish-red or cherry-red products were in convincing agreement with the formulation as $K_5\{(en)_2Co[NC-M(CN)_{(x-1)}]_2\}\cdot 8H_2O$. In a similar procedure, **2b** was isolated after prolonged photolysis of a solution containing 0.001 M $[Co(en)_3](ClO_4)_3$ and 0.01 M $K_4[Ru(CN)_6]$.

2.2.2. $H[(en)_2Co-NC-Ru(CN)_5]\cdot 4H_2O$ (3b)

A 0.05 M aqueous solution of *trans*-$[Co(en)_2Cl_2]Cl$ was allowed to aquate for two days. On stepwise addition of the same amount of a 0.05 M aqueous solution of $K_4[Ru(CN)_6]$, a blue precipitate was formed immediately. This precipitate was filtered off, washed with water and methanol, and dried over KOH. The precipitate is insoluble in water as well as in organic solvents, but soluble under decomposition in both 1 M hydrochloric acid and concentrated aqueous ammonia. On treatment with of a 0.1 M aqueous solution of $K_4[Ru(CN)_6]$ in excess the precipitate dissolves under formation of **2b**. The blue solid shows up two absorption bands at 340 and 610 nm (praying-mantis technique).

The elemental analyses of several independently prepared samples were not entirely satisfactory. The formulation as $H[(en)_2Co-NC-Ru(CN)_5]\cdot 4H_2O$ is the closest to the results of the elemental analyses. The magnetic moment reported for **3b** refers to the experimentally determined cobalt content of the samples (typically 10.4–10.9%).

2.3. Photolyses

The light source was a A-1000 (Amko) lamp-housing, equipped with an ellipsoidal mirror, a 100 W-2 high-pressure mercury lamp (Osram), and a high-intensity grating monochromator (Amko). The absorbed light intensities were determined by ferrioxalate actiometry [16] and by a calibrated Polytec radiometer, equipped with a RkP-345 detector. The reported quantum yields are the result of at least three independent runs. Freshly prepared aqueous solutions of 0.001 M $[Co(en)_3](ClO_4)_3$ and 0.01 M $K_4[M(CN)_x]$, unless otherwise indicated, in 1 cm rectangular or 10 cm cylindrical cells (Hellma) were argon bubbled prior to photolysis and photolyzed under continous stirring. The presence of atmospheric oxygen, however, had no influence on the results of the photochemical experiments.

2.4. Instrumentation

Absorption spectra were recorded on UVIKON 860 (Kontron Instruments), Cary 3 (Varian) and Lambda 900 (Perkin-Elmer) spectrophotometers. IR spectra were obtained by using samples in KBr pellets and a M 80 (Zeiss) IR spectrometer. Magnetic moments were determined on a homemade instrument employing the Gouy method [17]. ^{13}C NMR measurements were performed on a Gemini 200 (Varian) spectrometer.

3. Results

3.1. Spectroscopic properties of the ion pairs

Mixtures of aqueous solutions of $[Co(en)_3](ClO_4)_3$ and $K_4[M(CN)_x]$ (M = Fe, Ru, Os, $x=6$; M = Mo, W, $x=8$) and $K_3[Mn(CN)_5NO]$ show up broad bands in the ultraviolet spectral region in addition to the absorptions of the reactants (Fig. 1 and Table 1). Similar values of the absorption maxima of the ion pairs **1a,b** have been reported previously [3,9]. The assignment of these bands to IPCT transitions is supported by the red shift of its absorption maxima when oxidation of the cyanometallate anion becomes easier. Further support comes from the spectrophotometric studies under systematic variation of the reactant concentrations. The intensity of these bands reaches a maximum when equal amounts of the reactants are present, thus indicating a 1:1 stoichiometry of the absorbing species. Furthermore, deviations from the Lambert–Beer law are observed at concentrations well below 10^{-4} M, which may be attributed to incomplete formation of ion pairs at such low concentrations. The molar extinction coefficients of the additional IPCT bands have been calculated under the assumption of complete ion pair formation with respect to the cationic component (1×10^{-3} M) when the anionic component is present in a ten-fold excess. An ion pair formation constant $K_{IP} = (570\pm 60)\ M^{-1}$ for the ion pair **1c** was calculated from the concentration dependence of the additional absorbance, supporting this assumption.

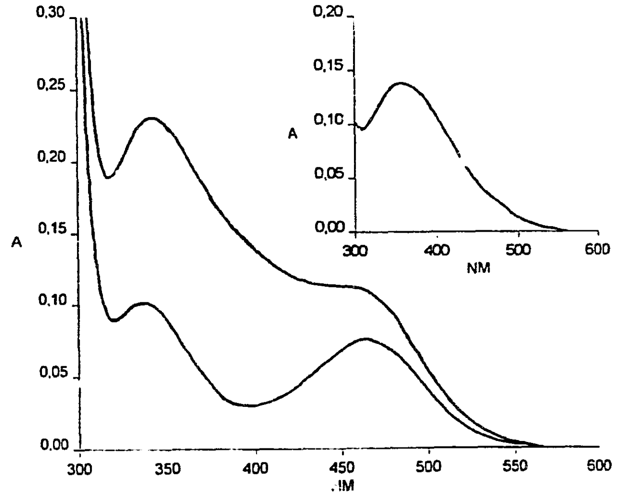

Fig. 1. IPCT absorption in the ion pair {$[Co(en)_3]^{3+}$; $[Os(CN)_6]^{4-}$} in aqueous solution: lower curve, superposition of the absorption spectra of 1.8×10^{-3} M $[Co(en)_3](ClO_4)_3$ and 2.0×10^{-2} M $K_4[Os(CN)_6]$ in aqueous solution (tandem cell; optical path 2×0.437 cm); upper curve, absorption spectrum after mixing; inset, IPCT absorption band (difference spectrum).

3.2. Wavelength-dependent photochemical investigations

3.2.1. Ion pair charge-transfer excitation

Aqueous solutions containing 1×10^{-3} M $[Co(en)_3](ClO_4)_3$ and 1×10^{-2} M $K_4[M(CN)_x]$ (M = Fe, Ru, Os) were irradiated at 405 nm. Under these conditions, the formation of the ion pairs **1a–c** is practically complete with respect to the cationic component. Furthermore, since the cyanometallates do not (M = Ru, Os) or not markedly (Fe) absorb light at this wavelength [18] and the cobalt complex is not light sensitive at wavelengths higher than 370 nm [8], any photoreaction observed may be attributed to the excitation of the optical charge-transfer transitions. Care has been taken for the previously reported thermal reaction of **1a** [6,20]. Several days after mixing the solutions changed in colour from orange to cherry-red. Under the conditions of the photochemical experiments (typical irradiation times were 1–3 min), however, no thermal reaction could have been detected.

After short irradiation times, very intense absorptions in the ultraviolet region, rapidly covering the original absorption features, appeared. No thermal post-irradiation reaction was observable, thus indicating that the final products were formed either immediatly during photolysis or in a very rapid subsequent thermal reaction. The new absorptions are assigned to metal-to-metal (MMCT) charge-transfer transitions in the trinuclear cyano-bridged complexes *trans*-{$(en)_2Co[NC\text{–}M(CN)_5]_2$}$^{5-}$ **2a–c** (Fig. 2 and Table 2). In addition to the intense charge-transfer bands, the spectra show a shoulder at 520 nm which is attributed to a ligand-field transition in the *trans*-{$(en)_2Co(NC)_2$} subunit of **2a–c**.

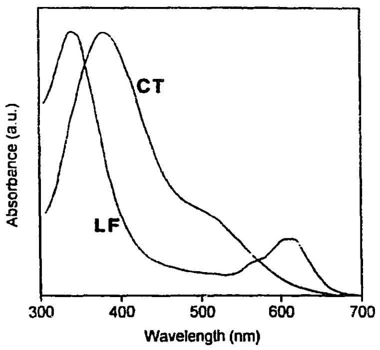

Fig. 2. Absorption spectra of the photolysis products of the ion pair {$[Co(en)_3]^{3+}$; $[Ru(CN)_6]^{4-}$} in aqueous solution (not to scale). CT: IPCT excitation at λ_{irr} = 405 nm. LF: ligand-field excitation at λ_{irr} = 510 nm.

The structurally related binuclear complexes $[Cl(en)_2CoNCFe(CN)_5]^{2-}$ [6], *trans*-$[(NH_3)(en)_2CoNCRu(CN)_5]^-$ [21] and $[(NH_3)_5CoNCRu(CN)_5]^-$ [22], prepared in thermal reactions, have been reported to show up MMCT bands at comparable wavelengths, but with ≈50% lower molar extinction coefficients. In contrast to the latter complex which undergoes an irreversible photo-redox reaction ($\Phi = 0.46$ at λ_{irr} = 366 nm [22]) **2a–c** are stable on MMCT irradiation. A similar drop in photoreactivity on replacing ammine by diamine ligands has been observed for the chromium(III) analogues [23].

The lack of photodecomposition of **2a–c** allowed us to continue the photolyses until no further spectral change was observable. The final spectra are quantitatively identical to those of *trans*-{$(en)_2Co[NC\text{–}M(CN)_5]_2$}$^{5-}$, which were prepared independently in a thermal reaction (see the experimental section). Furthermore, the product of prolonged photolysis of **1b**, which was isolated as the potassium salt, gave

Table 1
Ion pair charge-transfer spectra and redox properties of the ion pairs {$[Co(en)_3]^{3+}$; $[M(CN)_x]^{4-}$} and {$[Ru(en)_3]^{3+}$; $[Ru(CN)_6]^{4-}$} in aqueous solution

No.	Ion pair	λ_{max} (nm)	$\tilde{\nu}_{max}$ (10^3 cm^{-1})	$\tilde{\nu}_{1/2}$ (10^3 cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})	$E^{0\,a}$ (V)
1a	{$[Co(en)_3]^{3+}$; $[Fe(CN)_6]^{4-}$}	414	24.15	9.1	194	0.36
1b	{$[Co(en)_3]^{3+}$; $[Ru(CN)_6]^{4-}$}	338	28.59	10.0	260	0.86
1c	{$[Co(en)_3]^{3+}$; $[Os(CN)_6]^{4-}$}	359	27.86	10.2	195	0.63
1d	{$[Co(en)_3]^{3+}$; $[Mo(CN)_8]^{4-}$}	388	25.77	7.0	53	0.73
1e	{$[Co(en)_3]^{3+}$; $[W(CN)_8]^{4-}$}	427	23.40	8.6	62	0.46
1f	{$[Co(en)_3]^{3+}$; $[Mn(CN)_5NO]^{3-}$}	378	26.46	7.7	27	0.60
1g	{$[Ru(en)_3]^{3+}$; $[Ru(CN)_6]^{4-}$}	690	14.49	6.4	23	0.86

[a] Standard redox potentials of the $[M(CN)_x]^{3-/4-}$ couples [18]; $E^0([Co(en)_3]^{3+/2+}$, low spin) = −0.68 V [19]; $E^0([Ru(en)_3]^{3+/2+})$ = 0.18 V [15] (all values vs. NHE).

Table 2
Metal–metal charge-transfer spectroscopic properties and quantum yields of formation of the cyanobridged complexes *trans*-$\{(en)_2Co[NC\text{–}M(CN)_{(x-1)}]_2\}^{5-}$

No.	Complex	λ_{max} (nm)	$\tilde{\nu}_{max}$ (10^3 cm^{-1})	$\tilde{\nu}_{1/2}$ (10^3 cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})	Φ (λ_{irr}) (nm)
2a	$\{(en)_2Co[NC\text{–}Fe(CN)_5]_2\}^{5-}$	437	22.9	(6)[a]	'200	1.00 (405)
2b	$\{(en)_2Co[NC\text{–}Ru(CN)_5]_2\}^{5-}$	352	28.4	7.7	1400	0.95 (405)
2c	$\{(en)_2Co[NC\text{–}Os(CN)_5]_2\}^{5-}$	377	26.5	8.1	1380	0.98 (405)
2d	$\{(en)_2Co[NC\text{–}Mo(CN)_7]_2\}^{5-}$	484	20.7	6.2	420	0.15 (510)
2e	$\{(en)_2Co[NC\text{–}W(CN)_7]_2\}^{5-}$	545	18.3	5.0	690	0.16 (510)
2f	$\{(en)_2Co[NC\text{–}Mn(CN)_4NO]_2\}^{3-}$	434	23.1	9.2	460	–

[a] Estimated; band is broadened by overlap with a ligand-field band with λ_{max} at about 520 nm.

an elemental analysis in convincing agreement with the formulation $K_5\{(en)_2Co[NCRu(CN)_5]_2\}\cdot 8H_2O$. In the IR spectra of **2a–e**, the CN stretching vibrations are slightly (by 5–10 cm^{-1}) blue shifted with respect to the parent cyanometallates [18] and a shoulder, attributable to the bridging cyanide ligand, is observed at approximately 50 cm^{-1} higher energy. The ^{13}C NMR spectra exhibit a single resonance at $\delta = 48.1$ (**2a–c**) and 48.4 ppm (**2d,e**), assigned to the carbon atoms of the ethylenediamine ligand. The appearance of a single resonance indicates the trans configuration of the bridging cyano groups, whereas the spectra of the corresponding cis compounds should be more complex [24]. In addition, the ^{13}C NMR spectra show resonances at 177–191 (**2a**), 162–165 (**2b**), 153 (**2d**) and 145 (**2e**) ppm, respectively, which are close to the resonances of the free cyanometallates [18]. Interestingly, for **2a** four resonances at 177.3, 178.7, 180.2 and 190.9 ppm with an intensity ratio of 1:2:2:1 have been resolved. While the signals with the highest and lowest chemical shifts are readily assigned to the bridging cyanide and the cyano ligand in the trans position to it [25], the splitting of the signals of the equatorial ligands may be interpreted in terms of the formation of hydrogen bonds between two cyano ligands at each site and the coordinated ethylenediamine ligands.

The photolysis of **1d–f** under the same experimental conditions led to more complex reactions. The characteristic spectral features of **2d–f** could have been observed after short irradiation times. The anions present in excess, however, strongly absorb in the IPCT spectral region and themselves undergo photoreactions resulting in cyanide release [8]. Since an independent excitation of the IPCT transition could not be achieved, no quantitative studies were performed on these systems.

3.2.2. *Ligand-field excitation*

At 510 nm the absorption spectra of the ion pairs **1a–e** are dominated by the $^1T_{1g} \leftarrow {}^1A_{1g}$ (approximately O_h symmetry) ligand-field transition [26] in $[Co(en)_3]^{3+}$ (Fig. 1). Thus, more than 80% of the absorbed number of photons in each case brings about the excitation of the longest-wavelength allowed ligand-field transition of the cobalt complex which is almost completely ion paired under the present experimental conditions. On 510 nm excitation of **1a–c** the colours of the solutions rapidly turned to green (Fe) and blue (Ru,Os), respectively. New intense absorption bands showed up in both the ultraviolet and long-wavelength visible spectral regions (Fig. 2 and Table 3).

While the UV absorption bands could be readily identified as M(II) → Co(III) MMCT transitions owing to the red shift of its absorption maxima with decreasing redox potential of the $[M(CN)_6]^{3-/4-}$ couples (see Table 1), the visible absorption features of the photoproducts **3a–c** are insensitive with respect to the nature of M. Therefore, these absorption bands are tentatively assigned to ligand-field transitions in the cobalt subunit of the photoproducts. The typical absorption features of $[M(CN)_6]^{3-}$ [27] have not been observed in either case. The long-wavelength absorption of **3a** disappeared, accompanied by an intensity decrease and maximum shift in the UV region, after standing in the dark for a short time. The absorption features of the solutions after several minutes resembled those of **2a**. The half-life of **3a** is approximately 3 min under the present experimental conditions. In contrast, **3b,c** were stable over several hours. In order to gain some insight into the nature of the uncommon species **3a–c** its independent synthesis was attempted. On mixing of solutions containing 1×10^{-3} M $[Co(en)_2(H_2O)_2]^{3+}$, obtained from prolonged hydrolysis of $[Co(en)_2Cl_2]^+$ [28], and

Table 3
Metal–metal charge-transfer and ligand-field spectroscopic properties and quantum yields ($\lambda_{irr} = 510$ nm) of formation of the cyanobridged complexes $[(en)_2Co[NCM(CN)_5]^-$

No.	M	Metal–metal charge transfer			Ligand field		Φ
		λ_{max} (nm)	$\tilde{\nu}_{1/2}$ (10^3 cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ_{max} (M$^-$1 cm^{-1})	
3a	Fe	390[a]	6.4	2090	614	586	0.15
3b	Ru	338	7.0	2460	609	594	0.015
3c	Os	345	9.0	2690	614	636	0.14

[a] At 322 nm a shoulder is observed which is attributed to the $^1T_{1g} \leftarrow {}^1A_{1g}$ ligand-field transition in $[Fe(CN)_6]^{4-}$ [26].

1×10^{-3} M $K_4[M(CN)_6]$ the typical absorption features of **3a–c** were observed. Spectrophotometric measurements, performed under systematic variation of the reactant concentrations, indicated a 1:1 stoichiometry of the absorbing species. The Job plots [29] exhibited a triangular shape, thus indicating the practically complete formation of the absorbing species at a 1:1 concentration ratio of $[Co(en)_2(H_2O)_2]^{3+}$ and $[M(CN)_6]^{4-}$. The spectroscopic parameters of **3a–c** obtained by this procedure together with the quantum yields of its formation on 510 nm excitation of **1a–c** are presented in Table 3.

At reactant concentrations higher than about 2×10^{-3} M, blue precipitates of the formulation $H[(en)_2Co–NC–M(CN)_5]\cdot4H_2O$ (M = Ru, Os) were obtained. These precipitates were soluble, after several hours of stirring, in aqueous solutions containing an excess of $K_4[M(CN)_6]$ resulting in stoichiometric amounts, with respect to the cobalt content, of **2b,c** as indicated by the absorption spectra. The ruthenium compound **3b** was isolated in larger amounts (see experimental details) and further characterized. The solid-state diffuse reflectance spectrum shows two absorption bands at the same positions as **3b** in solution. In the IR spectrum the CN-stretching vibration is red shifted by 40 cm^{-1} with respect to $K_4[Ru(CN)_6]$. In addition, a shoulder at 2150 cm^{-1} is observed which may be attributed to bridging cyanide. In a differential thermogravimetric analysis, the loss of all four water molecules in a single step above 400 K was observed. This result may be interpreted in terms of water of crystallization rather than coordinatively bound water molecules. $H[(en)_2Co–NC–Ru(CN)_5]\cdot4H_2O$ exhibits paramagnetism with $\mu = 2.6–2.8\ \mu_B$ ($\mu_B = 9.274\times10^{-24}$ J T^{-1}) at room temperature. The assignment of **3b** to a binuclear cyanobridged complex is supported by the extended X-ray absorption fine structure analyses (EXAFS) of $[Co(en)_3](ClO_4)_3$, **2b**, and **3b** [30]. In each case, the cobalt–nitrogen and cobalt–carbon distances are close to 200 pm and 280 pm, respectively. The cobalt–ruthenium distances in **2b** and **3b** are close to 500 pm, but the intensity of the ruthenium peak in **2b** is approximately twice as high as in **3b** when related to the intensities of the nitrogen peaks. However, when the excitation was performed at the ruthenium edge, the cobalt signals of **2b** and **3b** showed comparable intensities when compared with the cyanide carbon peaks.

Attempts to synthesize the Mo, W and Mn analogues of **3a–c** by the same procedure failed. Instead, after several minutes (W) and hours (Mo, Mn) of reaction the trinuclear species **2d–f** were obtained as indicated by the absorption spectra. Mixtures of $K_3[M(CN)_6]$ (where M = Cr, Co, Fe, Rh) and $[Co(en)_2(H_2O)_2]^{3+}$ did not show remarkable spectral changes over a period of days. Obviously, both a coordination number of six and a four-fold negative charge of the cyanometallate are necessary prerequisites for the formation of **3a–c**.

510 nm excitation of the ion pairs **1d–f** resulted in the formation of **2d–f** (Table 2), in agreement with the observation (see above) that **3d–f** are not stable under the present experimental conditions. Since the octacyanometallates present in excess do not absorb markedly at 510 nm, the quantum yields of formation of **2d,e** could have been determined reliably (Table 2), whereas $[Mn(CN)_5NO]^{3-}$ is photosensitive in that long-wavelength spectral region [8].

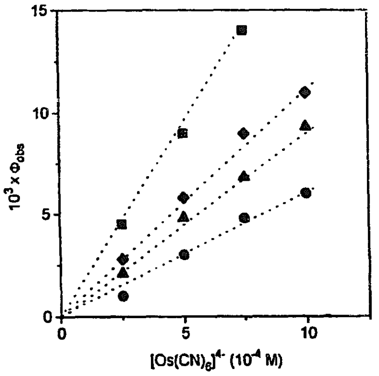

Fig. 3. Dependence of the observed quantum yield at $\lambda_{irr} = 510$ nm on the $[Os(CN)_6]^{4-}$ concentration at various concentrations of $[Co(en)_3]^{3+}$ (squares, 7.5×10^{-3} M; diamonds, 11.2×10^{-3} M; triangles, 15.0×10^{-3} M; circles, 22.5×10^{-3} M).

In order to elucidate whether the excited state of free $[Co(en)_3]^{3+}$ can be dynamically quenched, as has been suggested by Langford and Sasseville [6], solutions containing $2.5–10\times10^{-4}$ M $K_4[Os(CN)_6]$ and an excess, $7.5–22.5\times10^{-3}$ M, of $[Co(en)_3](ClO_4)_3$ were photolyzed at 510 nm. Under these conditions, more than 90% of the $[Os(CN)_6]^{4-}$ is ion paired and more than 94% of the light in each case is absorbed by free mobile $[Co(en)_3]^{3+}$. The observed quantum yields of formation of **3c** (Fig. 3) are almost linearly dependent on the $[Os(CN)_6]^{4-}$ concentration, but decrease with increasing $[Co(en)_3]^{3+}$ concentration. The slopes of the broken lines in Fig. 3 are equal to $(0.13\pm0.02)\times[Co]_0^{-1}$, where [Co] stands for the initial concentration of $[Co(en)_3]^{3+}$. The analogeous $[Ru(CN)_6]^{4-}$ system behaved similarily, but the slopes, $(0.015\pm0.006)\times[Co]_0^{-1}$, were much shallower.

4. Discussion

4.1. Energetic contributions to the IPCT absorption maxima

According to theory [31,32], the Gibbs free energy of the absorption maximum of an IPCT band is given by

$$\Delta G_{IPCT} = hc\tilde{\nu}_{max} = \Delta G_E + \Delta G_{W'} - \Delta G_W + \Delta G_{FC} + \lambda_{so} \quad (1)$$

where ΔG_E is related to the difference in the redox potentials of the donor and acceptor components by the Faraday constant, $\Delta G_{W'} - \Delta G_W$ is the difference in the work terms required for the formation of the successor and precursor pair, respectively, of the optical electron transfer, λ_{so} accounts for spin–orbit splitting effects, and ΔG_{FC} is the Franck–Condon energy, which may be divided into an inner- and an outer-sphere contribution, connected with the vertical electronic transition. Prior to an analysis of the free energy contributions to ΔG_{IPCT} in the ion pairs **1a–f** it has to to be considered that as the result of the optical charge transfer, low spin $[Co(en)_3]^{2+}$ (^2E_g, $t_{2g}^6e_g^1$) is formed owing to the spin conservation rule, whereas the electrochemically determined redox potential refers to the formation of the thermodynamically stable high spin $[Co(en)_3]^{2+}$ ($^4T_{1g}$, $t_{2g}{}^5e_g^2$) configuration. The redox potential referring to the formation of low spin $[Co(en)_3]^{2+}$ has been estimated as −0.68 V vs. NHE [19,32]. Using this value together with the redox potentials of the anions (Table 1) and $\lambda_{so} = 460$ (Fe), 1250 (Ru), and 3000 cm^{-1} (Os) [32], $\Delta G_{FC} = 15.2\text{–}16.7 \times 10^3\ cm^{-1}$ is calculated for **1a–f** from Eq. (1). By analogy, $\Delta G_{FC} = 7.8 \times 10^3\ cm^{-1}$ is obtained for the structurally related ion pair $\{[Ru(en)_3]^{3+}; [Ru(CN)_6]^{4-}\}$ (**1g** in Table 1). The difference of $7.4\text{–}8.9 \times 10^3\ cm^{-1}$ in the Franck–Condon energies of the ion pairs of cobalt(III) on the one hand and ruthenium(III) on the other hand has to be attributed essentially to the difference in the inner-sphere contributions of the cationic components. Since $\Delta G_{FC,in}$ for **1g** can be estimated to be less than $1 \times 10^3\ cm^{-1}$ [32], the total value of $\Delta G_{FC,in}$ for **1a–f** will be in the range $8\text{–}10 \times 10^3\ cm^{-1}$.

Such a large value of $\Delta G_{FC,in}$ points towards considerable structural changes in the first coordination sphere of the cobalt complex as a result of the optical electron transfer. This observation is in line with the results of a theoretical treatment of low spin $[Co(NH_3)_6]^{2+}$, where cobalt–nitrogen bond lengths 6 pm (equatorial) and 24 pm (axial) longer than in the corresponding cobalt(III) complex have been calculated [33]. A similar structural change may reasonably be assumed for the formation of low spin $[Co(en)_3]^{2+}$.

4.2. Photochemical reaction mechanisms

On excitation of the IPCT transitions in the ion pairs **1a–c**, low spin $[Co(en)_3]^{2+}$ (^2E_g) is initially formed together with $[M(CN)_6]^{3-}$:

$$\{[Co(en)_3]^{3+}; [M(CN)_6]^{4-}\} \xrightarrow{h\nu_{IPCT}} \{\text{low spin } [Co(en)_3]^{2+}; [M(CN)_6]^{3-}\} \quad (2)$$

In contrast to the parent $[Co(en)_3]^{3+}$ (d^6), the successor component $[Co(en)_3]^{2+}$ (d^7) is substitutionally labile. Furthermore, the low spin cobalt(II) complex is strongly tetragonally distorted (see above). Thus, one nitrogen of an ethylenediamine ligand at the cobalt(II) centre can be easily replaced by the oxidized cyanometallate ion present in the successor pair of the optical electron transfer (Eq. (3)), resulting in a cyanobridged binuclear complex $[(en)_2LCo^{II}NCM^{III}(CN)_5]^-$, where L is H_2O or monodentate ethylenediamine. Owing to its thermodynamic instability this complex rapidly undergoes back-electron transfer (Eq. (4)) resulting in the formation of its redox isomer.

$$\{\text{low spin } [Co(en)_3]^{2+}; [M(CN)_6]^{3-}\} \rightarrow [(en)_2LCo^{II}NCM^{III}(CN)_5]^- \quad (3)$$

$$[(en)_2LCo^{II}NCM^{III}(CN)_5]^- \rightarrow [(en)_2LCo^{III}NCM^{II}(CN)_5]^- \quad (4)$$

The formation of binuclear cyanobridged complexes on IPCT excitation has also been observed for the ion pairs $\{[Ru(NH_3)_5Cl]^{2+}; [M(CN)_6]^{4-}\}$ and $\{[Os(NH_3)_5Cl]^{2+}; [M(CN)_6]^{4-}\}$ [3,34]. Since the cationic components in the corresponding successor pairs of these systems are d^6 species and therefore much more inert than $[Co(en)_3]^{2+}$, the secondary thermal reactions most likely proceed by different mechanisms.

The observed quantum yields close to unity for **1a–c** indicate that the substitutional reaction (Eq. (3)) is much more rapid than back-electron transfer in the successor pair of the optical electron transfer, i.e. the thermal reversal of Eq. (2). Back-electron transfer would result in the reformation of the initial ion pairs **1a–c** and thus deminish the quantum yields. An alternative route for the secondary reactions involving cage escape of the still oppositely charged components of the successor pair is unlikely, since on one hand the cage-escape yield for the analogous ion pairs $\{[Cr(en)_3]^{3+}; [M(CN)_6]^{4-}\}$ does not exceed a value of 10^{-3} [23] and on the other hand the permanent formation of $[M(CN)_6]^{3-}$ has not been observed for the systems under present investigation.

It is not yet clear how the secondary products $[(en)_2LCo^{III}NCM^{II}(CN)_5]^-$ are converted into the final trinuclear products **2a–c**. Under somewhat different conditions, Langford and Sasseville [6] observed mutarotation of the photoproducts of **1a** when the initial $[Co(en)_3]^{3+}$ was optically active. Ultimate racemization was assumed to occur in secondary photolytic and/or thermal reactions. Polarometric studies have not been performed here, but the instantaneous formation of **2a–c** in the thermal reaction for independent synthesis (see experimental details) together with the lack of slow post-irradiation reactions after photolysis of **1a–c** give some evidence for very rapid conversion of the binuclear secondary photoproducts into the trinuclear species **2a–c** in a thermal reaction (Eq. (5)) by excess $[M(CN)_6]^{4-}$.

$$[(en)_2LCoNCM(CN)_5]^- + [M(CN)_6]^{4-} \rightarrow \{(en)_2Co[NC\text{–}M(CN)_5]_2\}^{5-} + L \quad (5)$$

The reactions on ligand-field excitation of $[Co(en)_3]^{3+}$ in the ion pairs **1a–c** are quite different from those of IPCT excitation: (i) different products were observed; (ii) the quantum yields of product formation are lower than unity; (iii) the quantum yields depend on the redox potentials of the $[M(CN)_x]^{3-/4-}$ couples. Interestingly, the quantum yields for **1d,e** are equal, within the experimental uncertainty, to those for **1a,c**, although the final products are qualitatively different.

The observation that the quantum yields, $\Phi = 0.14$–0.16, are almost independent on M if the redox potentials of the $[M(CN)_x]^{3-/4-}$ couples are $E^0 \leq 0.73$ V and then drop to one tenth for M = Ru, which is more difficult to oxidize, may be interpreted in terms of a redox reaction between the excited $^*[Co(en)_3]^{3+}$ and $[M(CN)_x]^{4-}$ in the ion pairs **1a–e**. Redox reactions on long-wavelength, i.e. beyond the IPCT absorption threshold, irradiation have also been observed for the ion pairs $\{[Co(NH_3)_6]^{3+}; I^-\}$ ($\Phi = 0.0015$ [35]) and $\{[Co(en)_3]^{3+}; htc^-\}$ ($\Phi = 0.16$ [36], corrected for thermal chain reactions [5]), where htc$^-$ is the bis(2-hydroxyethyl)dithiocarbamate ion.

Since the photoproducts on ligand-field excitation of **1a–c** are different from those on IPCT excitation, the $[Co(en)_3]^{2+}$ species in the successor pair of the *photoinduced* electron-transfer reaction (Eqs. (6) and (7)) must be different from that of the *optical* electron transfer (Eq. (2)) which results in low spin $[Co(en)_3]^{2+}$. Most likely, the ground-state ($^4T_{1g}$) high spin species is formed in the primary step of the photoinduced electron transfer. This assumption is supported by our observation that the typical absorption features of **3a** are also observed in the spectra of **1a** during the slow thermal reaction mentioned earlier. The final products **3a–c** are formed under substitution of one ethylenediamine ligand by the oxidized cyanometallate present in the ion pair (Eq. (8)) and subsequent inner-sphere back-electron transfer:

$$\{[Co(en)_3]^{3+}; [M(CN)_6]^{4-}\} \xrightarrow{h\nu_{LF}} \{^*[Co](en)_3]^{3+}; [M(CN)_6]^{4-}\} \tag{6}$$

$$\{[^*Co(en)_3]^{3+}; [M(CN)_6]^{4-}\} \rightarrow \{\text{high spin } [Co](en)_3]^{2+}; [M(CN)_6]^{3-}\} \tag{7}$$

$$\{\text{high spin } [Co(en)_3]^{2+}; [M(CN)_6]^{3-}\} \rightarrow [(en)_2Co^{II}NCM^{III}(CN)_5]^- + en \tag{8}$$

$$[(en)_2Co^{II}NCM^{III}(CN)_5]^- \rightarrow [(en)_2Co^{III}NCM^{II}(CN)_5]^- \tag{9}$$

In contrast, the successor pairs of the photoinduced electron transfer in **1d,e** undergo subsequent thermal reactions by analogy to Eqs. (3)–(5). The possibility cannot be excluded, however, that short-lived intermediates similar to **3a–c** are involved in the secondary reactions leading to the ultimate formation of **2d,e**.

The almost equal, but lower than unity, quantum yields of **1a,c,d,e** on ligand-field excitation could be explained in terms of a competition between the nonradiative decay of the initially excited $^1T_{1g}$ state of $[Co(en)_3]^{3+}$ and the formation of a longer-lived excited state species being able to undergo very rapid redox reactions with the cyanometallates present in the ion pair [7].

The photoinertness of cobalt(III) amine complexes, in contrast with the cobalt(III) cyano complexes, on ligand-field excitation has been attributed to the extremely rapid nonradiative decay of the lowest-energy excited singlet state either directly or via intersystem crossing (ISC) to the triplet manifold [8]. As discussed elsewhere in detail [37,38], there are several lines of evidence that ISC to the $^5T_{2g}$ excited state also occurs. As a result of their spectroscopic and theoretical studies on the $[Co(NH_3)_6]^{3+}$ system, Wilson and Solomon [39] presented some evidence that the latter state is the lowest-energy excited state and that its potential surface crosses that of the lowest triplet state close to its minimum.

The view that in the systems under present investigation the redox-active excited state of $[Co(en)_3]^{3+}$ is the $^5T_{2g}$ state appears to be attractive, since it is the only excited state which can be reduced to ground-state ($^4T_{1g}$) $[Co(en)_3]^{2+}$ in a spin-allowed process, whereas the spin-allowed reduction of the singlet and triplet states should result in low spin (^2E_g) $[Co(en)_3]^{2+}$. The cobalt–nitrogen bond lengths in the quintet state have been calculated to be 12 pm longer than in the ground-state cobalt(III) complex [39], thus being only 6 pm shorter than in the corresponding ground-state cobalt(II) species [40]. The singlet and triplet excited states are expected to be equatorially elongated, but axially compressed with respect to the singlet cobalt(III) ground state [39]. The similarity of the bond lengths between the quintet cobalt(III) and the quartet cobalt(II) states would be connected with only minor inner-sphere reorganization energies [31] when compared with either the ground-state thermal electron-transfer reaction or the optical electron transfer within the ion pairs **1a–e**, thus facilitating the electron-transfer step subsequent to ligand-field excitation.

Despite the plausibility our assumption of the quintet excited state as the redox-reactive state, it cannot be excluded that the reactive state might be a "hot" ground state of $[Co(en)_3]^{3+}$ formed as a result of nonradiative decay from the singlet or triplet manifold [41].

Whatever the nature of the redox-active state of $[Co(en)_3]^{3+}$ is, it must be very short lived. In our quenching experiments (Fig. 3) we observed that the observed quantum yield of **3b** formation, Φ_{obs}, increases with increasing $[Os(CN)_6]^{4-}$ concentration. This may be due to both static and dynamic quenching. Since under the experimental conditions more than 90% of the cyanometallate is ion paired with $[Co(en)_3]^{3+}$, the contribution of this ion paired fraction to Φ_{obs} of **3b** formation has to be considered. The fraction of light absorbed by the ion paired $[Co(en)_3]^{3+}$ is close to $[Os]_0/[Co]_0$ when $[Os]_0 \ll [Co]_0$, where $[Os]_0$ and $[Co]_0$ are the initial concentrations of $[Os(CN)_6]^{4-}$ and $[Co(en)_3]^{3+}$, respectively. Together with the quantum yield of **1b**, $\Phi = 0.14$ (Table 3), the contribution of the ion pairs to Φ_{obs} will be equal to $0.14 \times [Os]_0/[Co]_0$. This accounts completely, within the experimental uncertainty, for the observed quantum yields. Thus, free mobile $[Co(en)_3]^{3+}$ only causes an inner-filter effect, decreasing Φ_{obs} with increasing $[Co(en)_3]^{3+}$ concentration. There is no indication that $^*[Co(en)_3]^{3+}$ is substantially quenched by $[Os(CN)_6]^{4-}$ and the ion pairs in a dynamic process. If it is assumed that on the one hand the redox-reactive state of free mobile $[\mathrm{Co(en)_3}]^{3+}$ is formed with the same efficiency as in the ion pairs and instantaneously quenched on encounter complex formation, and that that on the other hand the encounter complex formation with the quenching species is diffusion controlled ($k_{\mathrm{diff}} \approx 5\times10^9\ \mathrm{M^{-1}\,s^{-1}}$), a 3 ns lifetime of this species would be long enough to increase the observed quantum yield of **3b** by at least 1×10^{-3} at the highest $[\mathrm{Os(CN)_6}]^{4-}$ concentration employed here. This difference is close to the experimental uncertainty of our measurements. Therefore, $\tau \leq 3$ ns may be regarded as the upper limit for the redox-reactive state lifetime. McCusker et al. [38] observed a transient at $\lambda_{\mathrm{max}} = 390$ nm with $\tau = (450 \pm 100)$ ps as the longest-lived component following $[\mathrm{Co(en)_3}]^{3+}$ ligand-field excitation. Most likely, the transient species corresponds to the redox-reactive state observed here. Its short lifetime would explain the lack of dynamic quenching under the present experimental conditions. Based on earlier arguments, given by Wilson and Solomon [39] and Langford [37], the transient absorption has been attributed by McCusker et al. [38] to the $^5\mathrm{T_{2g}}$ state of $[\mathrm{Co(en)_3}]^{3+}$. The assignment to a "hot" ground state, which is unlikely since nuclear relaxation usually proceeds in the 10 ps timescale [31], was not been considered in that work.

A much longer lifetime of 23 ± 4 ns has been inferred by Ismail et al. [42] for an excited state or a chemical intermediate coming from the ligand-field excitation of tris(glycinato)cobalt(III), $[\mathrm{Co(gly)_3}]$, in the presence of $[\mathrm{Ru(CN)_6}]^{4-}$. In this work, however, the possibility of static quenching was not considered. Reinvestigating the $[\mathrm{Co(gly)_3}]$; $\mathrm{Ru(CN)_6}]^{4-}$ system in aqueous solution we have observed an additional outer-sphere charge-transfer band at 350 nm [43]. The formation of stable ($K = 6\ \mathrm{M^{-1}}$) outer-sphere complexes in this system may result in static rather than dynamic quenching of any excited state. Thus, a lifetime of $^*[\mathrm{Co(gly)_3}]$ in the nanosecond timescale would be long enough to account for the observed quantum yield of $\Phi = 0.12$.

Finally, an attempt should be made to obtain some insight into the nature of the intriguing photoproducts **3a–c** which have not been reported so far. The visible and infrared spectra, as well as the elemental analysis and EXAFS results for **3b**, are consistent with binuclear cyanobridged species containing cobalt(III) and ruthenium(II). The DTG results indicate that water molecules are not bound in the first coordination sphere of **3b**. Thus, **3a–c** are most likely pentacoordinate species. A lower symmetry than (idealized) O_{h} would also explain both the unexpectedly high molar extinction coefficients and the unusually long-wavelength positions of the ligand-field transitions in **3a–c**. Examples of pentacoordinate cobalt(III) complexes are rare [44] and do not seem to be well characterized by electronic spectroscopy. The pentacoordinate iron(II) ($\mathrm{d^6}$) complex $[\mathrm{Fe(NO_3)QP}]^+$, where QP is tris(*o*-diphenylphosphinophenyl)phosphine [45], shows similar absorption features as **3a–c** in the long-wavelength region. The absorption ($\tilde{\nu}_{\mathrm{max}} = 9\times10^3\ \mathrm{cm^{-1}}$; $\epsilon_{\mathrm{max}} = 750\ \mathrm{M^{-1}\,cm^{-1}}$) has been assigned to the allowed $(\mathrm{e''})^3(\mathrm{e'})^3 \leftarrow (\mathrm{e''})^4(\mathrm{e'})^2$ transition in the trigonal bipyramidal ligand field, whereas the higher-energy shoulder has been attributed to a forbidden transition involving the same electronic configurations.

A $(\mathrm{e''})^4(\mathrm{e'})^2$ electronic configuration of the $[(\mathrm{en})_2\text{-}\mathrm{CoNC}-]$ subunit of **3a–c** would also explain the paramagnetism ($\mu_{\mathrm{obs}} = 2.6$–$2.8\ \mu_{\mathrm{B}}$; $\mu_{\mathrm{theor}} = 2.83\ \mu_{\mathrm{B}}$, spin-only for two unpaired electrons) observed for **3b**. However, we were unable to crystallize this compound owing to its poor solubility and its instability with respect to the formation of the very stable trinuclear complex **2b**. Therefore, the assignment of **3a–c** to pentacoordinate cobalt(III) complexes can be only tentative.

5. Conclusions

Ion pair formation of $[\mathrm{Co(en)_3}]^{3+}$ and easily oxidizable cyanometallates has been shown to be the origin of the unusual photosensitivity of the cobalt(III) complex on irradiation with visible light. Depending on the irradiation wavelength, the mechanism of the photo-redox reaction switches between *optical* electron transfer ($\lambda_{\mathrm{irr}} = 405$ nm) and *photoinduced* electron transfer ($\lambda_{\mathrm{irr}} = 510$ nm) in a rather narrow spectral region. The well-known photoinertness of cobalt(III) amine complexes on long-wavelength excitation may be understood in terms of very rapid nonradiative decay processes following ligand-field excitation. Interestingly enough, an intermediate, most likely excited, state of $[\mathrm{Co(en)_3}]^{3+}$, which does not undergo ligand substitution, can be intercepted by appropriate donor anions present in an ion pair.

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