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# Pentacyanochromate(III) complexes: ground- and excited-state chemistry

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Dedicated to Arthur Adamson on the occasion of his 80th birthday

## Contents

## Abstract

An overview is presented of the available information on pentacyanochromate(III) complexes, including some recent work in our laboratory. Several aspects of the chemistry of this

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little explored class of anionic compounds are considered, such as the preparative methods, the absorption and emission spectra, and some thermal aquation and anation reactions. The photochemistry is given special attention; various photoaquation and photoanation results are discussed in the light of current models. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In celebrating Arthur Adamson's 80th birthday, it is a pleasure to recall some significant moments that we had the privilege to share in his research group. Most of our photochemical work has developed in the field of chromium(III), and has been primed by the study of $Cr(NH_3)_5(NCS)^{2+}$ [1], the starting step of a long interaction with Art.

The isothiocyanatopentaammine was the first Cr(III) complex to show two simultaneous photosubstitutions on ligand field (LF) excitation, the major reaction being 'antithermal'; furthermore, the quantum yields for the two modes and, more importantly, their ratio changed with the irradiation wavelength, denoting different chemistries for different excited states, not necessarily mimicking the thermal chemistry. The results fitted and strengthened 'Adamson's Rules' that had been formulated a little earlier [2], and have stimulated a great deal of experimental and theoretical research for many years [3–7].

A successive $^{15}N$ labeling study of $Cr(NH_3)_5Cl^{2+}$ [8] established that the rules did predict which $NH_3$ group was actually photolabilized. The complete stereochemical change accompanying ammonia photoaquation testified to the significant distortion of the reacting excited state(s), one of the central issues in chromium(III) photochemistry [3–7]. Significantly, this study closely followed Art's demonstration that if distortion from the octahedron is prevented by cyclic amine ligands, as in *trans*-$Cr(cyclam)Cl_2^+$, the complex is photoinert [9].

The synthesis of $Cr(NH_3)_5(CN)^{2+}$ at our laboratory in Perugia [10] gave access to a new family of complexes, the cyanoam(m)ines, characterized by relatively intense room-temperature solution phosphorescence with lifetimes up to tens or hundreds of microseconds [11]. Again, our findings were just preceded by Adamson's proposal of an additional set of rules for chromium(III), the 'emission rules' [12], which turned out to be obeyed fully by the novel compounds; this circumstance led to a joint investigation of the medium and temperature dependence of the doublet decay rates [13]. Another unusual feature of $Cr(NH_3)_5(CN)^{2+}$ (and of other cyanoammines) was that $NH_3$ photolysis generates a mixture of two isomers rather than a single isomer [11]: in a further collaborative study of emission and photoreaction quenching, the isomeric distribution of products and the apparent activation energy of quantum yields were found to be the same for the quenchable and unquenchable photoreaction, suggesting a common precursor state to all photochemistry in this class of complexes [14].

In general, the photochemical investigations of chromium(III) have been based mainly on cationic am(m)ine complexes, including several $Cr(NH_3)_5X^{z+}$ species, as are those just mentioned above. In contrast, mixed-ligand cyano species, and in particular $Cr(CN)_5X^{z-}$ ions, have received less attention, probably due to preparative difficulties.

The pentacyano complexes may be regarded as the anionic counterpart of the pentaammines, made interesting by a combination of properties of the $CN^-$ ligands, such as the strong coordinate bond, the π back-donation, the *trans* effect, the capability of being protonated, the high LF strength and the large nephelauxetic effect. There appears to be at present sufficient information to delineate the thermal and photochemical behavior of this relatively new series of compounds. This paper surveys the available data on $Cr(CN)_5X^{z-}$ complexes (excluding $Cr(CN)_5(NO)^{3-}$, where the oxidation state of chromium is formally $+1$), and summarizes some recent results from our laboratory [15], with emphasis on the photochemical aspects.

## 2. Preparation of the complexes

The first pentacyanochromate(III) mentioned in the literature was $Cr(CN)_5(H_2O)^{2-}$, described as the product of the initial step in the aquation sequence of $Cr(CN)_6^{3-}$. Its separation in solution from the various anionic, neutral and cationic products of consecutive cyanide release was accomplished by ion-exchange techniques [16,17]. Paradoxically, this species was originally thought to be $Cr(CN)_4(H_2O)_2^-$, arising from a supposedly very fast reaction of the pentacyanoaqua ion; this caused some difficulty in the interpretation of the early photoaquation results of $Cr(CN)_6^{3-}$ [18]. Subsequent studies demonstrated that the complex is actually $Cr(CN)_5(H_2O)^{2-}$ [19].

The conjugate base, $Cr(CN)_5(OH)^{3-}$, was first observed in equilibrium with $Cr(CN)_6^{3-}$ as the result of Cr(II)-catalyzed loss of $CN^-$ from the hexacyanochromate(III) ion in alkaline solution [19,20]. Solid $K_3[Cr(CN)_5(OH)]\cdot H_2O$ was later obtained by reaction of $[Cr(NH_3)_5Cl]Cl_2$ with excess KCN in aqueous solution, followed by purification by gel filtration chromatography and recrystallization from water [21]. For this potassium salt, IR spectral data have also been reported [22]. It was recently realized that in the course of the standard preparation [23] of $K_3[Cr(CN)_6]$ from chromium(III) acetate and KCN, reduced reaction times led to mixtures containing as much as 2/3 $Cr(CN)_5(OH)^{3-}$ and 1/3 $Cr(CN)_6^{3-}$. After gel fractionation, the desired product was precipitated as $K_3[Cr(CN)_5(OH)]\cdot 2H_2O$ [24]. This procedure seems practical in that it does not involve demolition of the starting complex (in principle, any Cr(III) complex) prior to coordination of cyanide.

Protonation can reversibly turn $Cr(CN)_5(OH)^{3-}$ to $Cr(CN)_5(H_2O)^{2-}$. The $pK_a$ value of $Cr(CN)_5(H_2O)^{2-}$ has been reported to be between 8.6 and 9.0 [19,21,24], more than three $pK$ units higher than that of $Cr(NH_3)_5(H_2O)^{3+}$ [25]. The lower acidity of the pentacyano compared with the pentaammine, is related to the higher donor ability of the $CN^-$ ligands and the negative complex charge. Attempts to isolate $Cr(CN)_5(H_2O)^{2-}$ as a solid salt have been unsuccessful.

$Cr(CN)_5(NCS)^{3-}$ was produced in a mixture with all other $Cr(CN)_{6-n}(NCS)_n^{3-}$ anions by interaction of $K_3[Cr(NCS)_6]$ with KCN in acetonitrile [26,27]. Analytical quantities of the $n = 1$ component were separated in solution by either ionophoresis [26] or chromatography on alumina [27], and its $Bu_4N^+$ salt was employed to measure the IR spectrum [28]. A simpler, selective route to the monoisothiocyanato complex has now been devised, consisting of direct anation of $Cr(CN)_5(H_2O)^{2-}$ by $NCS^-$ in buffered (pH 5) aqueous medium [15].

The methanol-substituted species $Cr(CN)_5(MeOH)^{2-}$ was initially obtained by photolyzing $Cr(CN)_6^{3-}$ dissolved in MeOH as the $Ph_4P^+$ salt [29]: the drawbacks of this method, however, were the long irradiation periods and the small product yields. A successive, more convenient preparation was based on thermal labilization of a single cyanide group under bland conditions, promoted by the protons supplied by equimolar amounts of sulfamic acid [30].

Saturation of the above methanolic solutions with $NH_3$ and mild heating readily leads to $Cr(CN)_5(NH_3)^{2-}$ [29]. In a similar manner, smooth reaction of the MeOH complex with added pyridine (py) gives rise to $Cr(CN)_5(py)^{2-}$ [30].

These two complexes cannot be prepared by replacing $H_2O$ in $Cr(CN)_5(H_2O)^{2-}$, by analogy with the syntheses of $Co(CN)_5(NH_3)^{2-}$ and $Co(CN)_5(py)^{2-}$ [31]. The problem is that the affinity of Cr(III) for N-donors relative to O-donors, is lower than that of Co(III). The lability of coordinated MeOH therefore makes $Cr(CN)_5(MeOH)^{2-}$ a suitable intermediate, potentially useful for extending the pentacyanochromate(III) series. An additional advantage of the alcoholic solvent is that its easy removal facilitates product recovery. For this reason, solid $K_3[Cr(CN)_5(NH_3)]$ [29] and $K_3[Cr(CN)_5(py)]\cdot 2H_2O$ [30]. could be isolated.

Another species observed only in solution is $Cr(CN)_5(Me_2SO)^{2-}$, quantitatively formed by heating $Cr(CN)_5(py)^{2-}$ in dimethylsulfoxide; this ion is extremely stable at room temperature [30].

Photosolvolysis of $Cr(CN)_6^{3-}$ in various media has long been known to cause replacement of one $CN^-$ by a solvent molecule. Aqueous systems have been extensively studied in relation to the photosubstitution mechanism on irradiation in the LF region [18,32–35]. The quantum yields for formation of $Cr(CN)_5(H_2O)^{2-}$ range between 0.09 and 0.16: the values were found to increase with increasing excitation wavelength [32,33], temperature ($E_{app} = 12$ kJ mol$^{-1}$ [32]) and pH [33], and to decrease with increasing pressure ($\Delta V^{\ddagger} = 2.7$ cm$^3$ mol$^{-1}$) [34] and viscosity [35].

Photolysis of the $Bu_4N^+$ salt of hexacyanochromate(III) in dimethylformamide (DMF) gave $Cr(CN)_5(DMF)^{2-}$ with a quantum yield of 0.08; this photoproduct was chromatographically isolated in solution [36].

$Cr(CN)_5(MeCN)^{2-}$ was similarly obtained with 0.04 efficiency by photolyzing $Cr(CN)_6^{3-}$ in acetonitrile, although in this case the product was not separated from the reaction mixture [37].

Finally, an early qualitative note [38] describes light-induced spectral changes of dimethylsulfoxide solutions of $Cr(CN)_6^{3-}$, consistent with the formation of $Cr(CN)_5(Me_2SO)^{2-}$.

## 3. Absorption spectra

The LF absorption maxima of the known $Cr(CN)_5X^{z-}$ complexes in various solvents are listed in Table 1 in order of decreasing LF strength of X. For comparison, the parent species with $X = CN^-$ is included. The two bands usually observed are assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions in $O_h$ approximation. Even though in the actual $C_{4v}$ microsymmetry both the $^4T_{2g}$ and $^4T_{1g}$ states are expected to be split into the respective $^4E + {}^4B_2$ and $^4A_2 + {}^4E$ components, no band splittings are perceptible because of the relatively small energy separation between the sublevels. The low-energy bands, reflecting the average LF strength, are generally blue shifted by 3000–3500 $cm^{-1}$ with respect to the corresponding $Cr(NH_3)_5X^{z+}$ complexes, in agreement with the high spectrochemical position of $CN^-$. In some systems the general shift causes the second LF maximum to be obscured by the more intense UV absorptions.

In an early review [39], the spectra of a number of then nonexisting $Cr(CN)_5X^{z-}$ complexes (several of which are still unknown) were calculated by use of the LF theory. It is noteworthy that the anticipation for $X = NH_3$ and $NCS^-$ has been fairly accurate: the experimental long-wavelength maxima closely match the values (396 and 414 nm, respectively) predicted for the $^4B_1 \rightarrow {}^4E$ ($^4T_{2g}$) split component, in agreement with the general observation that, when band splitting is apparent, the stronger absorption is associated with the doubly degenerate $^4E$ state.

Where investigated, medium effects on the positions of the LF bands were found to be considerably larger than those occurring in cationic am(m)ine complexes,

Table 1
Ligand-field absorption maxima (nm) of pentacyanochromate(III) complexes in various solvents (molar extinction coefficients, $M^{-1}$ $cm^{-1}$, in parentheses)

| Complex | Solvent | $^4A_{2g} \rightarrow {}^4T_{2g}$ | $^4A_{2g} \rightarrow {}^4T_{1g}$ | Ref. |
|---|---|---|---|---|
| $Cr(CN)_6^{3-}$ | $H_2O$ | 377 (86) | 307 (60) | [16] |
| | $Me_2SO$ | 386 (78) | 313 (56) | [29] |
| | DMF | 391 (78) | 317 (53) | [29] |
| $Cr(CN)_5(NH_3)^{2-}$ | $H_2O$ | 397 (90) | 320 (54) | [29] |
| | $Me_2SO$ | 406 (77) | 324 (58) | [29] |
| | DMF | 406 (72) | 316 (66) | [29] |
| $Cr(CN)_5(py)^{2-}$ | $H_2O$ | 403 (106) | [a] | [30] |
| | $Me_2SO$ | 411 (79) | 320 (100, sh) | [30] |
| $Cr(CN)_5(NCS)^{3-}$ | $H_2O$ | 416 (171) | [a] | [15][b] |
| $Cr(CN)_5(MeCN)^{2-}$ | MeCN | 424 (107) | 350 (44) | [37] |
| $Cr(CN)_5(H_2O)^{2-}$ | $H_2O$, pH 5 | 428 (110) | 334 (50) | [24] |
| $Cr(CN)_5(MeOH)^{2-}$ | MeOH | 435 (80) | 320 (45) | [30] |
| $Cr(CN)_5(OH)^{3-}$ | $H_2O$, pH 12 | 436 (118) | 368 (73, sh) | [24] |
| $Cr(CN)_5(DMF)^{2-}$ | DMF | 444 (117)[c] | 328 (65)[c] | [36] |
| $Cr(CN)_5(Me_2SO)^{2-}$ | $Me_2SO$ | 453 (98) | 339 (47) | [30] |

[a] Maximum hidden by CT absorptions.

[b] Spectra in MeCN and in $H_2O$ are reported graphically in Ref. [28].

[c] Estimated from figure.

Table 2
UV absorption features of $Cr(CN)_5X^{z-}$ complexes[a]

| X | Solvent | Wavelengths, nm (molar extinction coefficients, $10^3$ $M^{-1}$ $cm^{-1}$) | | | | Ref. |
|---|---|---|---|---|---|---|
| $CN^-$ | $H_2O$ | 264 (5.66) | 259 (5.35)[c] | 230 (1.71) | 219 (3.18) | [15][b] |
| $H_2O$ | $H_2O$, pH 5 | 264 (2.5)[c] | 252 (2.90) | 244 (2.8)[c] | 218 (2.8)[c] | [15] |
| $OH^-$ | $H_2O$, pH 12 | | | 243 (4.1) | | [22] |
| $NH_3$ | $H_2O$ | 263 (2.45)[c] | 251 (3.30) | | 220 (1.95)[c] | [29] |
| py | $H_2O$ | 261 (6.50)[c] | 256[d] (7.00) | 230 (4.5)[c] | 218 (6.25)[c] | [30] |
| $NCS^-$ | $H_2O$ | 319[e] (6.20) | 260 (5.4)[c] | 240 (8.55) | 226 (9.2)[c] | [15][f] |
| MeCN | MeCN | 271 (6.3) | 252 (1.8) | | 223 (5.8) | [37] |

[a] Unless otherwise noted, data refer to charge-transfer transitions involving $CN^-$.

[b] A less detailed spectrum is given in Ref. [40].

[c] Shoulder.

[d] Maximum associated with the $\pi \rightarrow \pi^*$ absorption of pyridine.

[e] $\pi(NCS) \rightarrow e_g^*(Cr)$ charge-transfer band.

[f] Spectra in MeCN and in $H_2O$ are reported graphically in Ref. [28].

which are usually less than 2 nm. The higher transition energies in water can be explained [29,30] by the tightening of the second coordination sphere by hydrogen bonding between $CN^-$ and the $H_2O$ molecules, enhancing the ligand perturbation on the central metal ion. This is clearly related to solvent orientation. While cationic complexes are faced by the oxygen atoms of the solvation shell and, therefore, experience similar interactions in protic and aprotic media, anionic complexes are surrounded by the positive ends of the solvent molecules, appropriately oriented for hydrogen-bond formation if protons are available. Also the changes in the extinction coefficients and in the band intensity ratios (note $Cr(CN)_5(NH_3)^{2-}$) may be ascribed to different degrees of solvent participation in the vibronic interactions that lessen the Laporte restriction to the LF transitions.

The UV region displays several strong absorptions associated with fully allowed transitions, the details of which are collected in Table 2. Common to all the complexes is a main band centered around 250 nm, accompanied by two or three minor features. Assignment of this part of the spectrum is straightforward, given its close resemblance in position, intensity and shape with the charge-transfer (CT) absorption of $Cr(CN)_6^{3-}$. By application of the SCCC MO method and comparison with other transition metal hexacyanides, the direction of the charge shift was originally inferred to be metal-to-ligand, i.e. $t_{2g}(\pi,Cr) \rightarrow t_{1u}(\pi^*,CN)$ [40]. This conclusion was later questioned on the basis of SINDO calculations [41], and the ligand-to-metal character, specifically $t_{1u}(CN) \rightarrow t_{2g}(\pi,Cr)$, was proposed. The photoreduction of Cr(III) upon CT excitation of $Cr(CN)_6^{3-}$ [42] was argued to experimentally support such an interpretation.

The species with X = py [30] and X = $NCS^-$ [15,28] show additional UV features. The 256-nm maximum of the pyridine complex corresponds to $\pi \rightarrow \pi^*$ transitions of the heterocyclic ligand; its high intensity, relative to those of the other ions, denotes overlap with the cyanide-related absorption. The $NCS^-$ compound presents a well-distinct band at longer UV wavelengths, typical of the $\pi(NCS) \rightarrow e_g^*(Cr)$ transitions that characterize thiocyanate-containing complexes [43].

## 4. Emission properties

There are only a few reports of room-temperature solution phosphorescence of $Cr(CN)_5X^{z-}$ complexes: the available data are gathered in Table 3. The emission is moderately intense, narrow and structured, and is characteristic of the $^2E_g \rightarrow ^4A_{2g}$ transition within the $t_{2g}^3$ electron configuration in $O_h$ approximation [44].

In comparison with the $Cr(NH_3)_5X^{z+}$ systems which emit in the 650–680 nm region, the phosphorescence is red-shifted by ca. 2000 $cm^{-1}$. The lowering of the transition energy is caused by the nephelauxetic effect of the cyanide ligands that delocalizes the $t_{2g}(Cr)$ electrons into the low-lying $\pi^*(CN)$ orbitals.

It is notable that the $Cr(CN)_5X^{z-}$ ions luminesce only in dipolar aprotic solvents and not in aqueous media under ambient conditions, paralleling the behavior of $Cr(CN)_6^{3-}$. This is again explained by the specific orientation of the water molecules around anionic complexes, favorable for formation of $CN–H_2O$ hydrogen bonds: a good complex-solvent vibrational coupling is expected to efficiently enhance the nonradiative deactivation of the $^2E_g$ state. On the contrary, the reverse solvent orientation makes the emission of $Cr(NH_3)_5X^{z+}$ cations little sensitive to the protic or aprotic nature of the medium [12,13].

Room-temperature phosphorescence lifetimes have been determined for $Cr(CN)_5(NH_3)^{2-}$ [29] and $Cr(CN)_5(py)^{2-}$ [30] in $Me_2SO$ solution. The decays are monoexponential, with $\tau$ values of several tens of microseconds; i.e. in the upper range of Cr(III) $^2E_g$ lifetimes. Such long-lived emissions enabled accurate doublet-state quenching measurements: the totally inert $Co(sep)^{3+}$ ion (sep = 1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]eicosane) proved an efficient and 'innocent' quencher, with bimolecular rate constants (Table 3) of diffusional order of magnitude [29,30].

Although emission in low-temperature glassy matrices is quite general for chromium(III) [44], this aspect was studied only with $Cr(CN)_5(H_2O)^{2-}$. The phosphorescence spectrum and lifetime of the monoaqua complex were measured in water–ethylene glycol glass at 77 K, in the context of an investigation of the doublet-state radiationless relaxation rates of all the members of the $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ series [45].

Table 3
Solution phosphorescence of pentacyanochromate(III) complexes

| Complex | Medium | $\lambda_{max}$ (nm) | $\tau_{20}$ (μs) | $k_q$ ($M^{-1}$ $s^{-1}$)[a] | Ref. |
|---|---|---|---|---|---|
| $Cr(CN)_5(NH_3)^{2-}$ | $Me_2SO$ | 777 | 32 | $1.9 \times 10^9$ | [29] |
| | DMF | 777 | | | [29] |
| $Cr(CN)_5(py)^{2-}$ | $Me_2SO$ | 774 | 56 | $1.6 \times 10^9$ | [30] |
| $Cr(CN)_5(Me_2SO)^{2-}$ | $Me_2SO$ | 767 | | | [30] |
| $Cr(CN)_5(H_2O)^{2-}$ | $EG/H_2O$[b] | 775 | $(2 \times 10^3)$[c] | | [45] |

[a] Bimolecular rate constants for emission quenching by $Co(sep)^{3+}$ at 20°C.

[b] Ethylene glycol–water (2:1 $v/v$) glass.

[c] $T = 77$ K. Non-exponential decay: a 1500–2500 μs range of lifetimes is given.

Table 4
Rate and activation parameters for ligand substitution reactions of $Cr(CN)_5X^{z-}$ complexes

| Reaction | $10^6$ $k_{25}$, $s^{-1}$ | $\Delta H^{\#}$ (kJ $mol^{-1}$) | $\Delta S^{\#}$ (J $K^{-1}$ $mol^{-1}$) | Ref. |
|---|---|---|---|---|
| $Cr(CN)_5(H_2O)^{2-} + 2H_2O \rightarrow Cr(CN)_3(H_2O)_3 + 2CN^{-}$ [a] | 2.3 ± 0.5 | 136 ± 4 | 105 ± 11 | [15] |
| $Cr(CN)_5(NCS)^{3-} + H_2O \rightarrow Cr(CN)_5(H_2O)^{2-} + NCS^{-}$ [a] | 1.34 ± 0.03[b] | 103 ± 2 | −12 ± 3 | [15] |
| $Cr(CN)_5(H_2O)^{2-} + NCS^{-} \rightarrow Cr(CN)_5(NCS)^{3-} + H_2O$ | 28.9 ± 2.4[c] | 84 ± 1 | −50 ± 3 | [15] |
| $Cr(CN)_5(py)^{2-} + Me_2SO \rightarrow Cr(CN)_5(Me_2SO)^{2-} + py$ | 0.98 ± 0.03[b] | 138 ± 8 | 102 ± 24 | [30] |

[a] pH 5.0; $\mu = 2.00$ ($NaClO_4$).

[b] Extrapolated from data at higher temperatures.

[c] Pseudo-first-order rate constant in 1.00 M $NCS^{-}$ at pH 5.0 and $\mu = 2.00$ ($NaClO_4$).

## 5. Thermal reactions

### 5.1. Ligand solvolysis

In an early study of the stepwise $CN^{-}$ loss of $Cr(CN)_6^{3-}$ in acidic aqueous solution, which ultimately gives $Cr(H_2O)_6^{3+}$, four intermediate $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ products have been observed by means of spectrophotometric measurements and chromatographic separations. The first-step product, erroneously described as the $n = 2$ species [16,17], was later identified as $Cr(CN)_5(H_2O)^{2-}$ [19].

Aquation of $Cr(CN)_5(H_2O)^{2-}$ leads to neutral $Cr(CN)_3(H_2O)_3$ as the first observable complex:

$$Cr(CN)_5(H_2O)^{2-} + 2H_2O \rightarrow Cr(CN)_3(H_2O)_3 + 2CN^{-} \qquad (1)$$

implying that cyanide release of $Cr(CN)_4(H_2O)_2^{-}$ is an exceedingly fast process. The tricyano species was demonstrated to consist exclusively of *fac*-$Cr(CN)_3(H_2O)_3$, and this indicated that reaction sequence (1) is highly stereospecific [16,46,47]. The geometry of $Cr(CN)_4(H_2O)_2^{-}$ was then inferred to be *cis*, in consideration of the *trans* labilizing effect of cyanide that would promote displacement of the only $CN^{-}$ *trans* to another $CN^{-}$ [16]. Subsequent aquation of the other three cyanides is also stereospecific in that it proceeds through *cis*-$Cr(CN)_2(H_2O)_4^{+}$, and occurs in a time scale much longer than that of reaction (1) [46–48]. All steps are characterized by acid-independent and acid-catalyzed pathways, typical of complexes with strongly basic ligands.

The rate of reaction (1) has been measured for various acidities and ionic strengths [16,24]. Its temperature dependence has now been determined in conjunction with anation studies (vide infra) [15]: the pseudo-first-order rate constant for aquation at 25°C and pH 5.0 is given, together with the activation parameters, in

Table 4. Within experimental uncertainty, the $k$ value does not change between pH 4 and 6, suggesting that in this interval the acid-independent path is predominant. By use of literature data [16], the acid-dependent aquation is, in fact, estimated to make up less than 10% of the reactivity at these acidity levels.

Table 4 includes the rate and activation parameters for the aquation reaction:

$$\mathrm{Cr(CN)_5(NCS)^{3-} + H_2O \rightarrow Cr(CN)_5(H_2O)^{2-} + NCS^-} \tag{2}$$

that has been investigated in a range of conditions in order to complement the study of its reverse process, the anation of $Cr(CN)_5(H_2O)^{2-}$ by $NCS^-$ [15].

Rate and activation data (Table 4) have also been obtained for a nonaqueous reaction, such as the solvolysis of $Cr(CN)_5(py)^{2-}$ in $Me_2SO$, which cleanly proceeds to completion according to first-order kinetics [30]:

$$\mathrm{Cr(CN)_5(py)^{2-} + Me_2SO \rightarrow Cr(CN)_5(Me_2SO)^{2-} + py} \tag{3}$$

Other ground-state ligand substitution reactions of $Cr(CN)_5X^{z-}$ systems have occasionally been examined, mostly to test the thermal stability of the substrates subjected to photochemical studies. For example, a $k$ value of $2.3 \times 10^{-8}$ $s^{-1}$ has been reported for the slow release of cyanide from $Cr(CN)_5(OH)^{3-}$ in 1 M NaOH solution at 22°C [22].

Additional, qualitative observations have been made on the acid-induced aquation of the $Cr(CN)_5X^{2-}$ ions with $X = NH_3$ [29] and $X = py$ [30], that eventually leads to the respective $Cr(H_2O)_5X^{3+}$ cationic species. The known spectra of these species were utilized to confirm the composition of the original complexes. By the way, the contrast between the substitution modes of $Cr(CN)_5(py)^{2-}$in aqueous and in aprotic solvents arises from the availability of protons in $H_2O$ but not in $Me_2SO$, determining the order of leaving ability: $CNH \gg py > CN^-$.

### 5.2. Anation

We have recently carried out a quantitative investigation of the interaction of $Cr(CN)_5(H_2O)^{2-}$ with $NCS^-$ in aqueous solution [15]. To our knowledge, this represents the first anation study of an anionic chromium(III) complex, presenting the advantage of reduced outer sphere association between the reactants. Replacement of the $H_2O$ ligand by thiocyanate:

$$\mathrm{Cr(CN)_5(H_2O)^{2-} + NCS^- \rightarrow Cr(CN)_5(NCS)^{3-} + H_2O} \tag{4}$$

naturally occurs in competition with aquation of $CN^-$ (Eq. (1)). Reaction rate measurements have been made at various acidities (pH 4–6), ionic strengths (2.00–5.00, $NaClO_4$) and temperatures (25.0 to 70.0°C), taking advantage of the high sensitivity ensured by the typical, strong CT absorption of the isothiocyanato complex at 319 nm (Table 2).

At a given ionic strength, the pseudo-first-order rate constants, $k_{obs}$, for the appearance of $Cr(CN)_5(NCS)^{3-}$ are adequately described by the kinetic law:

$$k_{obs} = k_a + b[NCS^-]/(c + [NCS^-]) \tag{5}$$

where $k_a$ is the rate constant for the simultaneous formation of $Cr(CN)_3(H_2O)_3$. Fig. 1 exemplifies the dependence of $k_{obs}$ on $[NCS^-]$, and Table 4 reports the rate constant for anation in 1.00 M $NCS^-$ at 25°C, as well as its activation parameters. Nonlinear least-squares fits of $k_{obs}$ gave $k_a$ values in agreement with those directly measured for $CN^-$ aquation in the absence of $NCS^-$. The fairly different activation enthalpies influence the competition between reactions (1) and (4): the lower the temperature, the more preferred the anation by thiocyanate over cyanide aquation becomes.

Two alternative mechanistic explanations of Eq. (5) are possible at present. The first parallels the classic case of the anation of $Co(CN)_5(H_2O)^{2-}$ [49,50], and postulates a dissociative pathway involving a $Cr(CN)_5^{2-}$ intermediate capable to discriminate between $H_2O$ and $NCS^-$. In principle, this interpretation does not seem unreasonable, considering that on passing from $Cr(H_2O)_5X^{z+}$ to $Cr(NH_3)_5X^{z+}$ systems, the ligand substitution mechanisms tend to change from $I_a$ to $I_d$ as a consequence of an increased electron density on the central metal [51,52]. In $Cr(CN)_5X^{z-}$ complexes, the even stronger $\sigma$ donation of $CN^-$ and the negative charge may well push the situation toward the $D$ limit. In this picture, the $b$ parameter of Eq. (5) represents the first-order rate constant for formation of the intermediate, and $c$ describes its relative preference for the two nucleophiles. Accordingly, association with $NCS^-$ would be favored by a factor of 6–7 with respect to $H_2O$.

A second possibility is anation via ligand interchange within ion triplets of the type $Cr(CN)_5(H_2O)^{2-}\cdot Na^+\cdot NCS^-$. This cannot be disregarded at the high ionic strengths for which the curvature of the plots of Fig. 1 becomes evident. In this case, $b$ would represent the rate constant for ligand interchange, while $1/c$ would give the association equilibrium constant. Consistent with this description is the

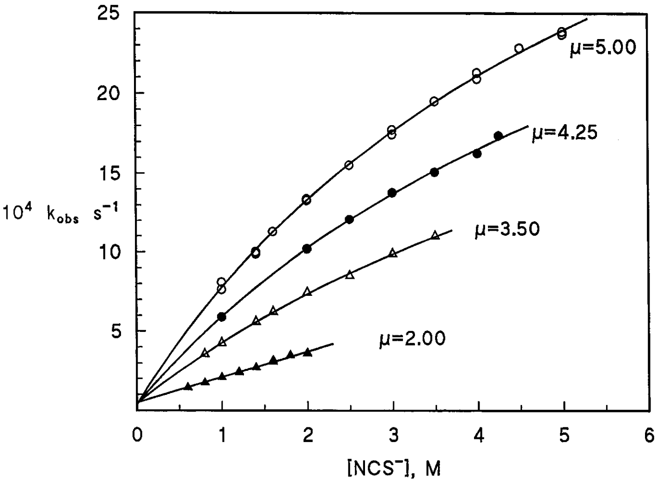


Fig. 1. Pseudo-first-order rate constants for the anation of $Cr(CN)_5(H_2O)^{2-}$ by $NCS^-$ as a function of the thiocyanate ion concentration at 40.0°C, pH 5.0 and various ionic strengths ($NaClO_4$).

Table 5
Photosolvation quantum yields of $Cr(CN)_5X^{z-}$ complexes at 20°C

| Complex | Solvent | $\lambda_{irr}$ (nm)[a] | $\Phi_{CN}$ | $\Phi_X$ | Ref. |
|---|---|---|---|---|---|
| $Cr(CN)_5(H_2O)^{2-}$ | $H_2O$, pH 4.3 | 366 | 0.03 | [b] | [24] |
| | $H_2O$, pH 5.8 | 436 | 0.04 | [b] | [33] |
| $Cr(CN)_5(OH)^{3-}$ | $H_2O$, pH 13 | 436 | 0.06 | [b] | [22] |
| | $H_2O$, pH 13 | 254[c] | 0.17 | [b] | [22] |
| $Cr(CN)_5(NH_3)^{2-}$ | $H_2O$, pH 3.3 | 400 | 0.06 | 0.08 | [29] |
| | $H_2O$, pH 7.2 | 400 | 0.06 | 0.08 | [29] |
| | $Me_2SO$ | 400 | 0.007 | 0.05 | [29] |
| | DMF | 400 | 0.003 | 0.11 | [29] |
| $Cr(CN)_5(py)^{2-}$ | $H_2O$, pH 7.2 | 400 | 0.011 | 0.08 | [30] |
| | $H_2O$, pH 7.2 | 254[d] | 0.015 | 0.10 | [30] |
| | $Me_2SO$ | 400 | 0.002 | 0.04 | [30] |
| $Cr(CN)_5(NCS)^{3-}$ | $H_2O$, pH 5.0[e] | 445 | 0.11 | 0.045 | [15] |

[a] Ligand-field band irradiation, unless otherwise specified.
[b] Solvent photoexchange not investigated.
[c] Charge-transfer band.
[d] Mixed absorption assigned to charge-transfer and py-localized transitions.
[e] Ionic strength 2.00 ($NaClO_4$).

increase, at constant $[NCS^-]$, of both $b$ and $1/c$ with increasing ionic strength. This results in an increase in the observed anation rate constant. The choice between the two alternatives must await further experiments establishing whether or not $b$ is the same in the presence of different nucleophiles.

## 6. Photochemistry

### 6.1. Photosolvation modes and quantum yields

The study of the excited-state reactions of pentacyanochromates(III) has apparently been limited by difficulties in the obtainment of suitable amounts of these materials and, sometimes, by the concurrence of ground-state reactions. Almost all the current information concerns ligand photosubstitution processes following LF band irradiation. The results are summarized in Table 5.

Photolyses of $Cr(CN)_5(H_2O)^{2-}$ were performed in aqueous solutions buffered at pH 4–6, so as to minimize acid-induced cyanide loss, and were shown to yield $Cr(CN)_3(H_2O)_3$ as the sole detectable product [24,33]. The photoreaction stoichiometry is the same as that of the dark aquation reaction [16]. The indication is that primary photosolvation of one $CN^-$ group is accompanied by very fast thermal release of a second cyanide giving rise to the relatively stable tricyano molecule:

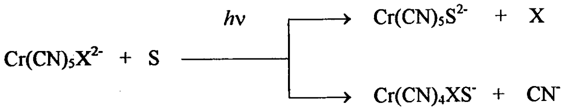
$$Cr(CN)_5(H_2O)^{2-} + H_2O \xrightarrow{h\nu} Cr(CN)_4(H_2O)_2^- + CN^- \quad (6)$$

$$Cr(CN)_4(H_2O)_2^- + H_2O \xrightarrow{kT} Cr(CN)_3(H_2O)_3 + CN^- \qquad (7)$$

Given the same behavior in the course of the photo and thermal aquation, the product of reaction (6) was deduced to originate in both processes with the same *cis* configuration, and to rapidly disappear in reaction (7) because of the ground-state *trans* effect of cyanide [16].

In alkaline solution, the hydroxo complex $Cr(CN)_5(OH)^{3-}$ undergoes $CN^-$ photosolvation [22,33] more efficiently than does its conjugate aqua form in acidic medium. Also in this case the photoprocess is followed by secondary thermal cyanide substitution. In fact, the free $CN^-$ content of photolyzed samples was found to be twice the yield for the disappearance of the starting complex; moreover, reaction (7) was demonstrated to be a dark reaction that could be slowed by lowering the temperature [22]. The congeneric $Cr(CN)_4(N_3)(OH)^{3-}$ anion showed analogous behavior, without any photorelease of $N_3^-$ [22].

Detailed photochemical investigations of $Cr(CN)_5(NH_3)^{2-}$ [29] and $Cr(CN)_5(py)^{2-}$ [30] in various solvents were possible thanks to the availability of solid complex salts. Upon LF excitation, each of these two species undergoes simultaneous replacement of both types of ligands by the solvent S:



(8)

(9)

Table 5 evidences considerable solvent effects on the quantum yields for the two photosolvation modes, and especially on their ratios; these are discussed below.

The same pattern of LF photoreactivity has now been established for $Cr(CN)_5(NCS)^{3-}$ in aqueous medium. Despite the fact that in the presence of the potassium counterion the isothiocyanato complex could be isolated only in solution, its high thermal inertness warranted a study of the concurrent photoaquation of the negatively charged $NCS^-$ and $CN^-$ ligands [15].

The $Cr(CN)_5X^{z-}$ complexes with $X = NH_3$ [29], py [30] and $NCS^-$ [15] are to date the only mixed-ligand chromium(III) anionic species where two competitive photosubstitution modes have been examined. Analogy with the $X = H_2O$ and $OH^-$ systems suggests that water photoexchange may well take place in the latter, and may even represent the major photoreaction: this occurrence, however, was not looked for.

It is seen in Table 5 that the overall substitution quantum yields of pentacyanochromates(III) are of the order of 0.1 or less, as are those of $Cr(CN)_6^{3-}$ [18,32–37]. This confirms the proneness of cyano complexes to a lower level of photoreactivity compared with chromium(III) am(m)mines, the quantum yields of which are usually in the 0.3–0.5 range [3–7]. The difference can be accounted for by the strong coordinate bond of $CN^-$, but also by differences in the excited-state processes in the two groups (vide infra).

## 6.2. Comparison with theory

The above-mentioned findings are adequately rationalized by the Vanquickenborne–Ceulemans, angular overlap model (AOM), whereby the excited-state energies of the various Cr–L bonds are evaluated as a function of the $\sigma_L$ and $\pi_L$ parameters of the two-dimensional spectrochemical series [5]. The model in particular focuses on the lowest excited quartet, long recognized as the main, if not exclusive, precursor to the substitutional photochemistry of chromium(III) [3–7]. The ligands predicted to be preferentially labilized are those with the lowest bonding strengths in such a state, that is $^4E$ for all $Cr(CN)_5X^{z-}$ ions. Table 6 reports the data relevant to the species for which either quantitative or qualitative information exists; note the uppermost $\sigma_{CN}$ and negative $\pi_{CN}$ values that quantify the strong σ donation and fair π acceptance of cyanide.

The predictions are fully verified for the complexes with $X = NH_3$ [29] and py [30], where both possible photoreaction modes were investigated and photosolvation of X was actually found to prevail over that of $CN^-$. According to the model, a general excited-state bond weakening occurs on the X–Cr–CN axis (or, more precisely, on the two planes containing X), caused by the accumulation of σ antibonding electron density. Discrimination between X and $CN^-$ is explained by the comparatively large, initial ground-state strength of the Cr–CN σ bond, that continues to exert its weight in the excited state despite the concomitant loss of the π stabilization of cyanide.

In the case of the recently studied system with $X = NCS^-$ [15], the observation that $\Phi_X < \Phi_{CN}$ (Table 5) is discrepant with the AOM prediction (Table 6). A possible explanation is that the AOM parameters used for $NCS^-$, derived from spectra of am(m)ine complexes [5], may not be fully appropriate for cyano complexes. Only a 10% larger $\sigma_{NCS}$ value would be able to account for the experimental data. Interestingly, the result agrees with Adamson's original rule anticipating loss of the strong-field ligand on the weaker-field axis [2].

The partial results with the other complexes are not inconsistent with the implications of Table 6. Thus, the low $\Phi_{CN}$ of $Cr(CN)_5(H_2O)^{2-}$ [24,33] may well

Table 6
Two-dimensional spectrochemical parameters (units of $10^{-3}$ $cm^{-1}$) for the X ligands and bond energies for the $^4E$ excited state of $Cr(CN)_5X^{z-}$ complexes, calculated by use of the AOM model [5][a]

| X | $\sigma_X$ | $\pi_X$ | $I^*$(Cr–X) | $I^*(Cr–CN)_{ax}$ | $I^*(Cr–CN)_{eq}$ |
|---|---|---|---|---|---|
| $H_2O$ | 5.94 | 0.50 | 8.18 | 9.82 | 14.76 |
| $OH^-$ | 8.66 | 2.25 | 17.66 | 10.98 | 14.18 |
| $NH_3$ | 7.18 | 0.00 | 8.48 | 10.30 | 14.52 |
| py | 5.80 | −0.58 | 7.06 | 9.76 | 14.78 |
| $NCS^-$ | 6.41 | 0.38 | 8.47 | 9.99 | 14.67 |
| DMF | 5.81 | 0.64 | 8.40 | 9.77 | 14.78 |
| $Me_2SO$ | 6.40 | 1.72 | 12.48 | 9.99 | 14.67 |

[a] $\sigma_{CN} = 8.48$; $\pi_{CN} = -0.29$. Ligand-field parameter B taken as 0.55 [39].

denote the preference of this complex for $H_2O$ photoexchange relative to $CN^-$ loss. The somewhat larger cyanide yield of $Cr(CN)_5(OH)^{3-}$ [22,33] would instead reflect the opposite situation: because of the relatively strong $\sigma$ and $\pi$ bonding of $OH^-$ (the high affinity of hydroxide for Cr(III) is well known), the ligand expected to preferentially aquate is $CN^-$.

Also compatible with the prediction is the qualitative observation that the photoproduct of $Cr(CN)_6^{3-}$ appears to undergo secondary photolysis in $Me_2SO$ [38] but not in DMF [36], the latter occurrence being suggested by the spectral isosbestic behavior during full-range irradiation (figure 1 of Ref. [36]). $Cr(CN)_5(Me_2SO)^{2-}$ is, in fact, anticipated to prefer $CN^-$ solvolysis, while DMF exchange would be the major mode for $Cr(CN)_5(DMF)^{2-}$.

It is of interest to compare $\Phi_X/\Phi_{CN}$ for $X = py$ [30] and $X = NH_3$ [29]. For the former complex the quantum yield ratios are $\sim 7$ in $H_2O$ and $\sim 20$ in $Me_2SO$; for the latter, the respective values are $\sim 1.3$ and $\sim 7$. The higher degree of labilization of pyridine is accounted for by the π-acceptor nature of this ligand, expressed by the negative AOM parameter $\pi_{py}$ [53]. The Cr–N σ bonds of the two complexes have similar strengths, and in the excited state are weakened to similar extents; since the $d_{xz}$ and $d_{yz}$ orbitals are π bonding toward py and nonbonding toward $NH_3$, their depletion by the $^4B_1 \rightarrow {}^4E$ transition removes the ground-state π stabilization of py but has no effect on $NH_3$. A parallel behavior is found in the photolysis of $Cr(NH_3)_5(py)^{3+}$, which is to date the only $Cr(NH_3)_5X^{z+}$ species showing $\Phi_X > \Phi_{NH_3}$ [54]. The π-accepting character of the pyridine ligand has been the subject of some controversy [55,56]: the above results confirm such character, and provide an example of how ligand properties can be inferred from photochemical behavior.

A further remark applies to $Cr(CN)_5(py)^{2-}$ as the first Cr(III) complex with two different π-acceptor groups. In the $^4E$ state, the decrease of the σ- and π-bond strengths is similar for $CN^-$ and py; competitive photolabilization is then essentially determined by the large difference in the ground-state σ bonding of these two ligands.

### 6.3. Medium effects

The data for $Cr(CN)_5(NH_3)^{2-}$ [29] and $Cr(CN)_5(py)^{2-}$ [30] attest to the relevance in photochemistry of solvent orientation and hydrogen bonding.

On passing from water to dipolar aprotic media, one aspect of change is the decrease of the total substitution quantum yields, which has been attributed to the need for the molecules of the solvation sphere to rotate during the decay of the reacting state, so as to enable attack by the oxygen atom. While $H_2O$, $Me_2SO$ and DMF have comparable nucleophilicities, solvent reorientation, hence ligand replacement, is inhibited by the increasing viscosity of the medium.

A second aspect is the remarkable increase of the $\Phi_X/\Phi_{CN}$ ratios, essentially due to the fact that $\Phi_{CN}$ decreases by one order of magnitude, far more than does $\Phi_X$.

This can be explained by the capability of coordinated cyanide to hydrogen-bond with the facing H atoms of water; such an interaction would assist interchange of $CN^-$ with $H_2O$, but not with $Me_2SO$ and DMF.

These results show that mixed-ligand anionic complexes are more adapted than cationic ones to enhance solvent effects on the photolabilization of negatively charged groups. Furthermore, they underline the role of chemical factors in photochemistry, in addition to that of electronic factors, and support the associative character of Cr(III) photosubstitution.

### 6.4. Some stereochemical clues

Elucidation of the stereochemistry of L photosubstitution in $CrL_5X$-type complexes is not, in general, a simple task, as it requires identification of the original coordination site of the released ligand in addition to the knowledge of the two possible $CrL_4XS$ isomers. Such pieces of information are lacking for the $Cr(CN)_5X^{z-}$ systems; nevertheless, the available evidence is congruent with (i) the preferential loss of a specific $CN^-$ group that theory predicts to be the one *trans* to X, and (ii) the ubiquitous stereomobility of chromium(III) photolyses [3–7], expected to lead to *cis*-$Cr(CN)_4XS^{z-}$ products.

Thus, one single $Cr(CN)_4(py)(H_2O)^{2-}$ isomer was demonstrated to be largely predominant (95%) as the product of $CN^-$ photoaquation of $Cr(CN)_5(py)^{2-}$, even though its geometry was not established [30].

Consistently, the sequence of reactions (6) and (7) indicates that photolysis of $Cr(CN)_5(H_2O)^{2-}$ gives rise to only one of the $Cr(CN)_4(H_2O)_2^-$ species. It is, in fact, improbable that two isomeric forms be characterized by the same rapid thermal loss of cyanide leading to the same $Cr(CN)_3(H_2O)_3$ isomer. Moreover, the latter was identified as the *fac* isomer [16,17], accessible by stereoretentive thermal aquation (facilitated by the *trans* effect of the two $CN^-$ groups *trans* to each other) only starting from *cis*-$Cr(CN)_4(H_2O)_2^-$: the inferred configuration of the photoproduct then agrees with the theoretical expectation.

Another indirect indication about the position initially occupied by the labilized $CN^-$ may be found in the photobehavior of $Cr(CN)_5(H_2O)^{2-}$ in the presence of [32]ane-$N_8$ (1,5,9,13,17,21,25,29-octaazacyclodotriacontane) [24]. The protonated polyaza macrocycle is known to form adducts with anionic cyano complexes by means of multiple hydrogen bonds between $CN^-$ ligands and ammonium groups. When encircled by the cyclic amine, which very likely assumes a belt arrangement around the complex, both $Co(CN)_6^{3-}$ and $Cr(CN)_6^{3-}$ reduce their $CN^-$ photoaquation yields to 1/3 of the values observed when the hexacyanides are free in solution. The implication is that the supramolecular structure prevents four of the six ligands from escaping the coordination sphere. In contrast, analogous interaction of [32]ane-$N_8$ with $Cr(CN)_5(H_2O)^{2-}$ has no effect on $CN^-$ photorelease. This was taken to indicate that, while the four equatorial cyanides are blocked by the macrocycle, the axial group, which is the one anticipated to be photolyzed, remains free from any hindrance.

### 6.5. Excited-state reactivity

The role of the lowest doublet in chromium(III) photochemistry has been a longstanding question: indications about the possible reactive involvement of this state have frequently been sought in quenching experiments [3–7].

In the largely studied am(m)ine complexes, part of the photoreactivity is usually quenched on complete quenching of the phosphorescent doublet. The unquenchable (or fast) contribution is acknowledged to originate from the short-lived, lowest quartet excited state in competition with intersystem crossing. The quenchable (or slow) component has essentially two alternative explanations: (a) doublet-state reaction, either direct or via tunneling to a ground-state intermediate, and (b) delayed quartet reaction via back intersystem crossing (bisc). The choice between routes a and b for this class of cationic complexes has been a controversial matter, since bisc is allowed by their quartet–doublet energy differences.

In regard to this point, an important peculiarity of pentacyanochromates(III) is the much wider state separation: the combined extreme LF strength and large nephelauxetic effect of the $CN^-$ ligands raise the quartet(s) and depress the doublet(s), respectively. For $Cr(CN)_5(NH_3)^{2-}$ [29] and $Cr(CN)_5(py)^{2-}$ [30] the quartet–doublet gap was estimated to be ca. 9000 $cm^{-1}$, or sufficiently large to preclude pathway b. The observation that complete doublet quenching in $Me_2SO$ solution leaves both photosolvation modes of each complex entirely unquenched, also excludes pathway a. Thus in these species, as in $Cr(CN)_6^{3-}$ [29,36], all of the photochemistry must be concluded to proceed from the quartet state(s): the excitation energy ‘trapped’ in the doublet is not utilized chemically.

It is tempting to state the converse, i.e. the doublet excitation energy may be utilized chemically only when it ‘escapes’ via bisc. It may not be fortuitous that for various simple ammine complexes (having overall photolysis efficiencies of 0.3–0.5) the unquenchable yields are around 0.1 [3–7], just like the total (and unquenchable) yields of cyano complexes. Other factors being equal, the photochemistry ‘missing’ in the cyanides would be that occurring when pathway b is allowed. This would provide a photophysical explanation for the lower photoreactivity of cyanochromates(III).

### 6.6. UV photolyses

Only in two pentacyanochromates(III) has the photochemistry been explored upon 254-nm excitation (Table 4).

Irradiation of the CT band of $Cr(CN)_5(OH)^{3-}$ in 1 M KOH solution saturated with oxygen, results in the appearance of chromate ion with a quantum yield of 0.025. The same kind of reactivity is exhibited by $Cr(CN)_6^{3-}$. In both cases, a primary photoredox process generates Cr(II) species that are then thermally oxidized to $CrO_4^{2-}$ [42]. Formation of Cr(II) was regarded as evidence for the theoretically deduced $CN \rightarrow Cr$ direction of the CT transition [41,57]. The redox reaction is accompanied by more than a doubling of the apparent $CN^-$ photoaquation quantum yield with respect to LF photolysis: such an increase was attributed to the catalytic effect of Cr(II) [22].

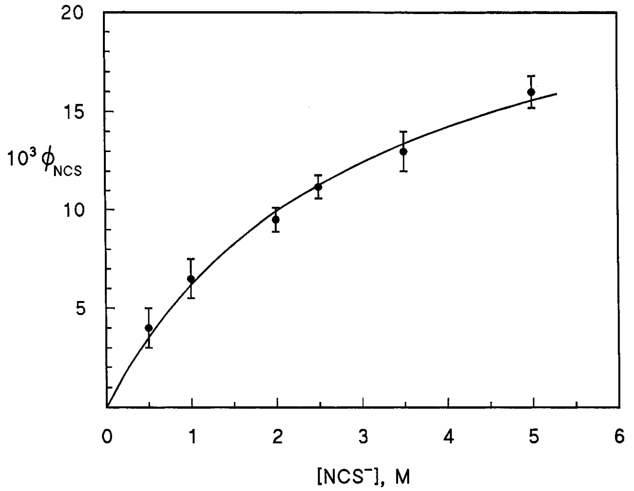


Fig. 2. Dependence of the photoanation quantum yields of $Cr(CN)_5(H_2O)^{2-}$ on the concentration of $NCS^-$ at 7°C, pH 5.0, and at a constant ionic strength of 5.00 ($NaClO_4$).

For aqueous $Cr(CN)_5(py)^{2-}$, the outcome of UV excitation is an analogous increase by 30% of both $\Phi_{py}$ and $\Phi_{CN}$, that indicates the participation of higher-energy states, other than LF states [30]. The UV absorption of this complex is due to superimposition of $\pi \rightarrow \pi^*$(py) and cyanide-related CT transitions. For the higher $\Phi_{py}$ value, a reactive contribution by the py-localized excited-state was proposed, in as much as population of $\pi^*$(py) orbitals involved in back-bonding may well induce Cr-py bond weakening. For the increase of $\Phi_{CN}$, a redox step was assumed, followed by back transfer of the optically driven electron prior to escape of the primary fragments from the solvent cage; the details of this possible path were, however, not investigated.

## *6.7. Photoanation*

The rate of anation of $Cr(CN)_5(H_2O)^{2-}$ by $NCS^-$ (Eq. (4)) is enhanced by LF excitation of the complex, showing that the thermal process is superimposed by a photoreaction of the same stoichiometry. We have quantitatively examined the system [15] for various thiocyanate concentrations (up to 5 M) and various ionic strengths (2.00–5.00, $NaClO_4$), at the temperature of 7°C chosen to minimize the thermal contribution. Also in this case, the intense CT band of $Cr(CN)_5(NCS)^{3-}$ ensured kinetic accuracy: photoanation yields, $\Phi_{NCS}$, were obtained from differences between rates of $NCS^-$ entry in irradiated and dark solutions for low extents ($<3\%$) of total reaction. The results are graphically presented in Fig. 2: the dependence of $\Phi_{NCS}$ on $[NCS^-]$ can be expressed by the equation:

$$\Phi_{NCS} = 0.026[NCS^-]/(3.5 + [NCS^-]) \qquad (10)$$

Chromium(III) photoanation studies have not been numerous, and have, thus far, involved only cationic complexes [3,7]. The proposed mechanism has been an inner–outer sphere exchange within ion-paired reactants, consistent with the associative character of Cr(III) photosubstitution and with lifetimes of the photoreacting quartet states too short to allow bimolecular processes. In this framework, the present anion–anion photointeraction (the exclusive mediator of the photochemistry is the excited quartet; see Section 6.5) can be understood in terms of ligand interchange taking place in ion triplets or higher associates where the cations hold together the negatively charged photoreacting species:

$$\mathrm{Cr(CN)_5(H_2O)^{2-} + Na^+ + NCS^- \overset{K}{\rightleftarrows} \{Cr(CN)_5(H_2O)^{2-}\cdot Na^+\cdot NCS^-\}} \quad (11)$$

$$\mathrm{\{Cr(CN)_5(H_2O)^{2-}\cdot Na^+\cdot NCS^-\} \xrightarrow{\Phi_{an}} Cr(CN)_5(NCS)^{3-} + H_2O + Na^+} \quad (12)$$

Schemes (11) and (12) are compatible with Eq. (10) which gives a limiting anation quantum yield $\Phi_{an} = 0.026$ at $\mu = 5.00$. Of course, photoanation must compete with water photoexchange, that could not be measured. The $\Phi_{an}$ value may then be taken as a lower limit for the efficiency of $H_2O$ exchange in the absence of $NCS^-$, considering that this photoprocess is also likely to affect non-associated complex molecules.

From Eq. (10), an apparent association constant $K = 0.28$ is evaluated at $\mu = 5.00$ and t = 7°C, to be compared with the value of 0.17 obtained from thermal anation data at the same ionic strength, but at the higher temperature of 40°C, on the assumption of a similar interchange mechanism for the ground-state anation reaction. The likeness of the plots of Figs. 1 and 2 would support such a conclusion.

The role of ion association is also evident in Fig. 3. When at constant thiocyanate concentration the ionic strength is increased by the addition of inert electrolyte, that

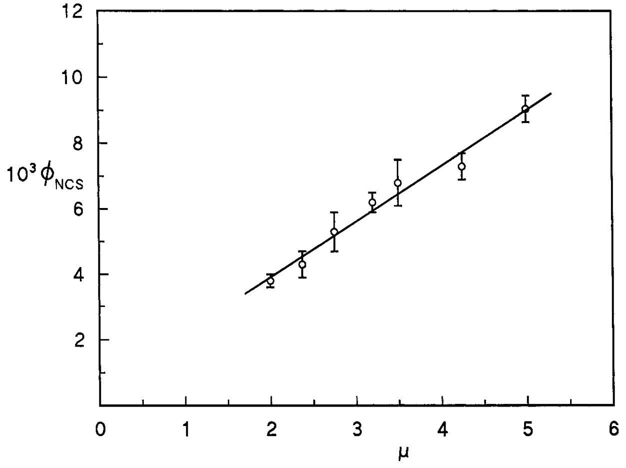


Fig. 3. Effect of added $NaClO_4$ on the photoanation quantum yields of $Cr(CN)_5(H_2O)^{2-}$ at a constant $NCS^-$ concentration of 2.00 M, 7°C and pH 5.0.

is, by addition of extra $Na^+$ cations, a virtually linear increment of the apparent photoanation quantum yield is observed.

The effect of the complex charge on the photoanation efficiency has preliminarily been explored by analogous experiments with $Cr(CN)_6^{3-}$. In this system, photoinduced entry of $NCS^-$

$$Cr(CN)_6^{3-} + NCS^- \xrightarrow{\Phi_{NCS}} Cr(CN)_5(NCS)^{3-} + CN^- \tag{13}$$

occurs in competition with cyanide photoaquation:

$$Cr(CN)_6^{3-} + H_2O \xrightarrow{\Phi_{H_2O}} Cr(CN)_5(H_2O)^{2-} + CN^- \tag{14}$$

Since process (14) is largely dominant, secondary thermal anation of photoproduced $Cr(CN)_5(H_2O)^{2-}$ (Eq. (4)) must be allowed for even at 7°C. At a given $[NCS^-]$, the time concentration of the isothiocyanato complex generated by reactions (4) and (13) is given by:

$$[Cr(CN)_5(NCS)^{3-}] = I\{(\Phi_{NCS} + \Phi_{H_2O})t - \Phi_{H_2O}(1 - e^{-kt})/k\} \tag{15}$$

where $I$ is the absorbed light intensity, and $k$ and $\Phi_{H_2O}$ denote the known pseudo-first-order rate constant of reaction (4) and quantum yield of photoreaction (14), respectively. Under the same conditions, the anation quantum yields $\Phi_{NCS}$ of the trinegative $Cr(CN)_6^{3-}$ complex evaluated by Eq. (15) are, in fact, about half of those of the dinegative $Cr(CN)_5(H_2O)^{2-}$ ion, in agreement with an increased repulsion between reactants.

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