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Theoretical Interpretation of the Photochemical Behaviour of $[Cr(CN)_6]^{3-}$ Ion by the SINDO/FEMP Method

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Photochemical behaviour of the hexacyanochromate(III) ion has been widely studied. Irradiation within band I ($\nu = 26.5 \times 10^3$ cm^{-1}) and band II ($\nu = 32.6 \times 10^3$ cm^{-1}) leads to photosubstitution of one cyano ligand [1, 2]

$$[Cr(CN)_6]^{3-} \xrightarrow[S]{h\nu\,(I,\,II)} [Cr(CN)_5S]^{2-} + CN^-$$

$S = H_2O, OH^-$, DMSO, DMF, MeCN

whereas irradiation within band III ($\nu = 38 \times 10^3$ cm^{-1}) causes, in alkaline solution, photoreduction [3].

$$[Cr(CN)_6]^{3-} \xrightarrow[S]{h\nu\,(III)} [Cr(CN)_6]^{4-} + \cdot S$$

$S = H_2O, CH_3OH$

Such photochemical properties are not well explained by the known assignments of the electronic spectra of the $[Cr(CN)_6]^{3-}$ complex. According to CFT [4] the first two bands are spin allowed dd transitions ($t_{2g} \rightarrow e_g$). The same interpretation follows from the results of SCCC MO [5], DV Xα [6] as well as *ab initio* SCF calculations [7] and in agreement with experiment predictions no photoredox reaction upon irradiation occurs within this region. Under these circumstances band III has to be the charge transfer one. The question is whether electron transfer is L → M or M → L. The only theoretical assignment of this band was given by Alexander and Gray [5] on the basis of the SCCC MO method. They attributed band III to ($t_{2g} \rightarrow t_{1u}\pi^*$) transition leading to photooxidation of the chromium atom (CTML). Such interpretation is inconsistent with the recent experimental data [3] and from the theoretical point of view is also questionable. The SCCC MO method based on an effective one-electron Hamiltonian is too simple and the transition energies are estimated as the differences between eigenvalues of orbitals obtained for the ground state. Such a procedure which neglects the changes of the character and energy of the orbitals caused by the excitations is known to be invalid [8, 12]. Moreover in the case of the $[Cr(CN)_6]^{3-}$ complex the SCCC MO method does not give a univocal answer whether band III is CTLM or CTML because the differences in the molecular orbital energies are almost the same, *i.e.* $E(t_{1u}\sigma \rightarrow t_{2g}) \approx E(t_{2g} \rightarrow t_{1u}\pi^*)$.

In the present work an attempt is made to interpret the photochemical behaviour of the $[Cr(CN)_6]^{3-}$ complex by the more advanced SINDO/FEMP method which has already been applied with success to other related problems [9–12]. For example this method gives, in contrast to the older treatments, a reasonable explanation of the photochemical reactivity of the nitrosylopentacyanoferrate(II) ion [12].

The SINDO/FEMP method, free of empirical parameters, is fitted to the electronic spectrum in the SCCC MO method [13]. The transition energies are taken as the differences in total energies obtained from the SCF procedure applied for ground and all excited states separately [9].

The geometry of the $[Cr(CN)_6]^{3-}$ ion was taken from X-ray data [14].

According to SINDO and other methods the ground state of $[Cr(CN)_6]^{3-}$ is of the $^4A_{2g}$ symmetry which follows from the $2t_{2g}{}^3$ configuration. Concerning the LUMO orbital the SINDO method predicts its π^* CN character. This does not prevent ($2t_{2g} \rightarrow 4e_g$) transitions having the lowest energies because the excitations cause changes of energy and of character of the molecular orbitals. Thus in agreement with previous assignments band I and band II are of the same origin ($2t_{2g} \rightarrow 4e_g$) leading to the final terms $^4T_{2g}$, $^4T_{1g}$, respectively.

As follows from the SINDO calculations the next transitions are due to electron transfer from the occupied $4t_{1u}$ orbital to the partly occupied $2t_{2g}$ orbital (CTLM). Such orbital excitation splits into four quartet–quartet transitions from which transition ($^4A_{2g} \rightarrow {}^4T_{1u}$) is allowed by Laport's rule and by symmetry. Thus this transition is mainly assigned to the intense band III. The CTLM character of band III was earlier suggested by Schläfer *et al.* [15]. The estimated next transitions are also connected with electron transfer from the occupied orbitals to the $2t_{2g}$ orbital (CTLM). The energies of transition (CTML) from the partly occupied $2t_{2g}$ to the lowest unoccupied orbital, $5t_{1u}$ and to other unoccupied orbitals are much higher.

Table I summarizes the characteristics of the ground and excited states of $[Cr(CN)_6]^{3-}$. The transitions I and II cause a very small change in the atomic charges, however they weaken the bond between chromium and the cyano ligand. Both σ and π bond orders p^{σ}(Cr–C), p^{π}(Cr–C) decrease. The two center contributions to the total energy E(Cr–NO) which can be also taken as a measure of the strength of the bond increases ($\Delta = +3.16$ eV) suggesting strong destabilization of the Cr–C bond.

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TABLE I. Characteristics of Ground and Excited States of the $[Cr(CN)_6]^{3-}$ Complex According to the SINDO/FEMP Method

Quantity	Ground state	Excited states	
	$^4A_{2g}$ $(2t_{2g}^3)$	$^4T_{2g}$(I) $^4T_{1g}$(II) $(2t_{2g}^2\ 4e_g^1)$	$^4A_{1u}$ $^4E_{1u}$ $^4T_{1u}$(III) $^4T_{2u}$ $(4t_{1u}^5\ 2t_{2g}^4)$
q_{Cr}[a]	+0.056	+0.092	−0.258
q_C[a]	+0.378	+0.323	+0.442
q_N[a]	−0.887	−0.838	−0.899
$p_{Cr—C}$	2.430	2.244	2.405
$p_{Cr—C}$	0.819	0.720	0.830
$E^{cov}_{Cr—CN}$[b]	×	+1.98	−0.39
$E^{tot}_{Cr—CN}$[b]	×	+3.16	+0.12

[a] Net atomic charges. [b] Two centre contribution to the total energy, with one center referring to Cr and the other to CN.

On the contrary the transition III results in significant changes in atomic charges. The net charge of chromium becomes negative (+0.056 → −0.258). In spite of that fact the bond between chromium and the cyano group remains almost unchanged, the bond orders p^σ(Cr–C), p^π(Cr–C) and E(Cr–NO) change only slightly.

Based on the presented results one can postulate that irradiation within band III should lead to photoreduction of chromium without any ligand exchange. Photosubstitution can be expected upon irradiation in the region of band I and II. In this case the bond between chromium and the cyano ligand is weakened which enables substitution of the cyano ligand by the molecule of solvent. These results seem to explain the photochemical properties of the $[Cr(CN)_6]^{3-}$ complex.

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