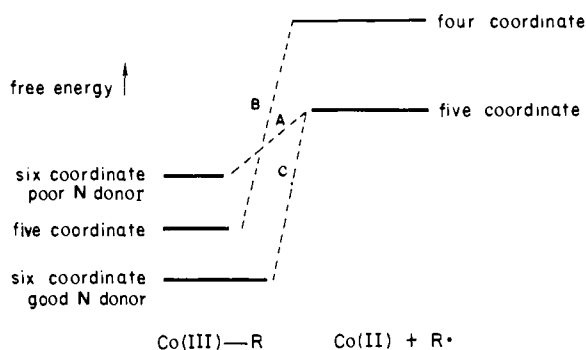the Co–C cleavage process would be most facile in a situation where the Co–N bond changes from being a relatively long bond (weak donor) in the still six-coordinate ground state to a relatively stronger bond leading to a five-coordinate Co(II) species, as illustrated schematically below:

The minimum barrier would involve path A, where the 5,6-dimethylbenzimidazole supports formation of the five-coordinate Co(II) species (B_{12r}) without stabilizing the six-coordinate Co(III) relative to the five-coordinate Co(III) species. In a six-coordinate species with a weakly bound 5,6-dimethylbenzimidazole, the Co is maintained in the plane defined by the four corrin N atoms, thereby maintaining steric repulsions between the 5′-deoxyadenosyl and the corrin. These steric interactions could be made more severe in the holoenzyme if the protein distorts the corrin.[41-51]

(50) A detailed discussion of the relationship between the structure and Co–C bond energy for cobalamins as well as relevant references can be found in ref 22.

Path B, between a five-coordinate cobalt(III) and a four-coordinate cobalt(II) species, is probably the most unfavorable pathway both because the five-coordinate species is stabilized somewhat by the reduction in steric interaction and also because a four-coordinate cobalt(II) species should be relatively unstable. Path C corresponds to free-energy changes expected in models and in cobalamins in the absence of enzymes.

The above qualitative picture requires further investigation of both the energetics and structural changes in models and cobalamins. However, if it represents a reasonable approximation of the interrelationship between structure, coordination number, and axial bond strengths, then the intermediacy of five-coordinate $Co^{III}R$ species in the enzymic process appears unlikely.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and structure factors (41 pages). Ordering information is given on any current masthead page.

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Control of the Photochemical Reactivity of Coordination Compounds by Formation of Supramolecular Structures: The Case of the Hexacyanocobaltate(III) Anion Associated with Polyammonium Macrocyclic Receptors

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Abstract: The photochemical behavior of free Co(CN)$_6^{3-}$ and of the adducts obtained from the association of Co(CN)$_6^{3-}$ with diethylammonium ion (Et$_2$NH$_2^+$), a linear polyammonium ion (L-21-N$_6$H$_6^{6+}$), and three polyammonium macrocycles (24-N$_6$H$_6^{6+}$, 32-C$_9$-N$_6$H$_6^{6+}$, and 32-N$_8$H$_8^{8+}$, Figure 1) has been studied in aqueous solution at room temperature. In all cases a simple photoaquation reaction takes place, with substitution of one CN$^-$ ligand by H$_2$O. The quantum yield of the photoaquation reaction (Φ = 0.30 for the free Co(CN)$_6^{3-}$ complex) is not affected by the presence of Et$_2$NH$_2^+$ but decreases when Co(CN)$_6^{3-}$ is associated with polyammonium ions. Specifically, the photoaquation quantum yield drops to 0.15, 0.11, and 0.10 when Co(CN)$_6^{3-}$ is associated with 24-N$_6$H$_6^{6+}$, 32-C$_9$-N$_6$H$_6^{6+}$, and 32-N$_8$H$_8^{8+}$, respectively. The reduction of the quantum yield is interpreted by assuming that only a discrete number of CN$^-$ are allowed to dissociate in the adducts. This agrees with the formation of adducts of defined molecular structure, in which some of the CN$^-$ ligands are bound to the polyammonium receptor and are thus prevented from escaping when the Co-CN bonds are temporarily broken as a consequence of light excitation. These adducts may be considered as complexes of complexes (or supercomplexes) since the ligands coordinated in the first coordination sphere of the metal in their turn coordinate a macrocyclic ligand. The results obtained indicate that it is possible to protect coordination compounds against ligand photodissociation by using appropriate receptors and they are also promising for other applications related to the control of photochemical reactions.

The photochemical behavior of Werner-type transition-metal complexes has been extensively investigated in the last 25 years,

and the results obtained have given important information on the reactivity of the various types of electronically excited states.[2-4]
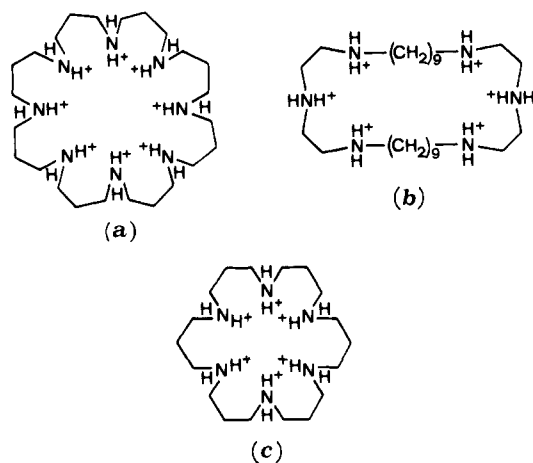
Figure 1. Structures of the macrocyclic polyammonium ions: (a) 32-$N_8H_8^{8+}$; (b) 32-C_9-$N_6H_6^{6+}$; (c) 24-$N_6H_6^{6+}$.

While further investigations on simple Werner-type complexes are required in order to arrive at a complete understanding of their photochemical and photophysical behavior, there is also the need to study more complex species to extend our knowledge of basic photochemical processes and to find systems which might be useful for practical photochemical applications. One way to proceed along this direction is to study the photochemical and photophysical behavior of polynuclear coordination compounds.[5] Another way is to study the perturbations caused on the photochemical and photophysical behavior of simple coordination compounds by specific interactions with other chemical species. Since coordination compounds are usually charged species, the most common perturbation means is via formation of ion-pair adducts.[6-11]

In this paper we report results concerning the perturbation of the photochemical behavior of $Co(CN)_6^{3-}$ upon association with some selected polyammonium macrocyclic ions (Figure 1).[12] For the sake of comparison, the photochemical behavior of $Co(CN)_6^{3-}$ in the presence of $Et_2NH_2^+$ or of a linear polyammonium ion (the fully protonated form of 4,8,12,16-tetraaza-1,19-diaminononadecane, abbreviated as L-21-$N_6H_6^{6+}$) has also been investigated. $Co(CN)_6^{3-}$ was chosen as the cyanide complex to be studied because it shows the simplest and best understood pho-

Table I. Acidity Constants, K_1 to K_8, for the Macrocyclic and Linear Polyammonium Ions and Stability Constant, K_s, of Their Complexes with $Co(CN)_6^{3-}$ (from References 14 and 15)[a]

constant	polyammonium ions			
	32-$N_8H_8^{8+}$	32-C_9-$N_6H_6^{6+}$	24-$N_6H_6^{6+}$	L-21-$N_6H_6^{6+}$
pK_1	6.45	3.55	6.60	7.05
pK_2	6.95	4.15	7.15	7.65
pK_3	7.50	9.25	7.90	8.70
pK_4	8.05	9.60	9.05	9.50
pK_5	9.00	9.65	10.35	10.35
pK_6	9.65	>9.7	10.45	10.40
pK_7	10.45			
pK_8	10.70			
K_s^b	1×10^6	c	8×10^3	1×10^3

[a] H_2O; 25 °C; μ = 0.1 M (NMe_4Cl). [b] Stability constant of the complex formed by $Co(CN)_6^{3-}$ with the fully protonated form of the polyammonium ligands. [c] Value not determined. To evaluate the fraction of $Co(CN)_6^{3-}$ involved in the complex, we have assumed K_s = 1×10^3, by analogy with the polyammonium ions that have the same ionic charge.
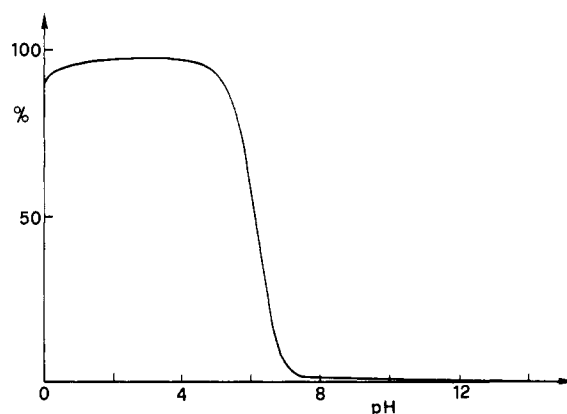

Figure 2. Calculated fraction of $Co(CN)_6^{3-}$ associated with 32-$N_8H_8^{8+}$ as a function of pH. $[Co(CN)_6^{3-}] = [32$-$N_8H_8^{8+}] = 2 \times 10^{-3}$; μ = 0.1 M (NMe_4Cl). Complexes involving partially protonated ligands 32-$N_8H_n^{n+}$ which appear as pH increases have not been considered.

tochemical behavior among the various cyanide complexes.[2,3,13] On the other hand, the polyammonium macrocycles a, b, and c in Figure 1 were known to act as molecular receptors binding a number of organic and inorganic anions and forming especially stable complexes with the anionic metal–hexacyanides.[14,15]

Experimental Section

Materials. $K_3[Co(CN)_6]$ was prepared according to Bigelow[16] and purified by recrystallization from aqueous alcoholic solutions. The polyammonium ions (as chloride salts) used were those prepared by Lehn and co-workers.[14,15] Solid diethylamine hydrochloride, $Et_2NH·HCl$, was obtained by bubbling gaseous HCl in an ether solution of diethylamine and washed with acetone. The other chemicals used were of reagent grade.

Apparatus. Light excitation at 313 nm was carried out by a medium-pressure Hg lamp as previously described.[17] The incident light intensity (of the order of 10^{-7} N$h\nu$ min^{-1}) was measured by the ferric oxalate actinometry.[18] Spectrophotometric measurements were performed with a Cary 219 spectrophotometer. The pH of the solutions was measured by a Knick KpH 350 pH meter.

Procedures. All the experiments were carried out at room temperature ($\sim$22 °C) on aqueous solutions containing 2.0×10^{-3} M $K_3[Co(CN)_6]$

(1) (a) Istituto Chimico "G. Ciamician", Universita' di Bologna. (b) Istituto di Scienze Chimiche, Universita' di Bologna. (c) Istituto FRAE-CNR, Bologna. (d) Institut LeBel, Universite' Luis Pasteur, Strasbourg.

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and 0.1 M NaClO$_4$. The pH of the solution (adjusted with HClO$_4$) and the concentration of the polyammonium ion are reported in Table II. Irradiation was performed in spectrophotometric cells (optical path 1 cm, capacity 3 mL). After appropriate irradiation periods the absorption spectrum of the solution in the spectral range 250–500 nm was recorded. Quantum yields were obtained from the changes in absorbance at 380 nm, taking into account the decrease in the fraction of light absorbed by the reactant as the reaction proceeds. After such correction, linear plots of the absorbance at 380 nm vs. number of photons absorbed by the reactant were always obtained (zero-order reactions). Before and after each photochemical experiment on the adducts, a blank test on "free" Co(CN)$_6$$^{3-}$ was performed under the same conditions, in order to provide an internal reference for quantum yield determinations.
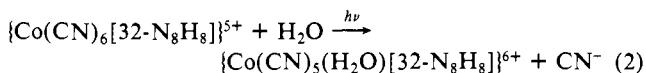
Results

The Co(CN)$_6$$^{3-}$ ion shows ligand field absorption bands at 260 and 312 nm.[19] Excitation with 313-nm light of a 2.0×10^{-3} M aqueous solution of K$_3$[Co(CN)$_6$] containing 0.1 M NaClO$_4$ and 3.0×10^{-3} M HClO$_4$ at room temperature caused spectral changes in the near-UV region as previously described by Moggi et al.[13] Two isosbestic points at 286 and 333 nm were maintained throughout the photoreaction, which is known to involve the substitution of one CN$^-$ ligand by solvent water:[13,20]

$$Co(CN)_6^{3-} + H_2O \xrightarrow{h\nu} Co(CN)_5(H_2O)^{2-} + CN^- \quad (1)$$
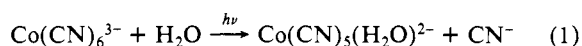
Co(CN)$_5$(H$_2$O)$^{2-}$ shows an absorption band with λ_{max} = 380 nm and is substantially photoinert upon irradiation in the visible or UV spectral region under the experimental conditions used.[13,20] The quantum yield of reaction 1, measured from the change in absorbance at 380 nm, was 0.30 ± 0.02, in full agreement with the results previously reported.[13] The qualitative and quantitative features of the photoreaction were not affected by the acidity of the solution (pH 1.2–2.5) or by the presence of Et$_2$NH$_2$$^+$ up to 0.1 M (pH 2.5).

The ionization constants (Table I) show that the polyammonium ions used in this work are completely undissociated in sufficiently acidic solutions. The stability constants of the complexes which they form with Co(CN)$_6$$^{3-}$ are also given in Table I. On the basis of the data of Table I and of the protonation constant of Co-(CN)$_6$$^{3-}$,[21] one can calculate the percent of cyanide complex which is associated with the fully protonated forms of the polyammonium ions. An example of such a calculation is shown in Figure 2 for binding of Co(CN)$_6$$^{3-}$ to 32-N$_8$H$_8$$^{8+}$; of course, as pH increases complexes involving partially protonated ligands also participate in the equilibrium mixture according to the pK_a values and the corresponding stability constants.[14,15] In all our solutions, the concentrations of Co(CN)$_6$$^{3-}$, polyammonium ions, and H$^+$ were such that more than 95% of Co(CN)$_6$$^{3-}$ was involved in the adduct with 24-N$_6$H$_6$$^{6+}$ and more than 99% with the other fully protonated polyammonium ions. Above 265 nm, the absorption spectra of the adducts were practically equal to the sum of the spectra of the parent compounds. A slight increase in absorption was, however, observed at shorter wavelengths.

When solutions containing the adducts between Co(CN)$_6$$^{3-}$ and the polyammonium ions were excited with 313-nm light, the observed spectra changes were qualitatively the same as those obtained upon irradiation of solutions containing Co(CN)$_6$$^{3-}$ alone.[22] These results indicate that the adducts undergo the same photoaquation reaction as "free" Co(CN)$_6$$^{3-}$, e.g.

$$\{Co(CN)_6[32-N_8H_8]\}^{5+} + H_2O \xrightarrow{h\nu}$$
$$\{Co(CN)_5(H_2O)[32-N_8H_8]\}^{6+} + CN^- \quad (2)$$

The quantum yield of photoaquation of the Co(CN)$_6$$^{3-}$ adducts

Table II. Experimental Conditions and Quantum Yields^a for the Photoaquation of Co(CN)$_6$$^{3-}$ and Its Adducts with Polyammonium Ions

polyammonium ion (M)	pH^b	Φ	n^c
	1.2–2.5	0.30 ± 0.02^d	
32-N$_8$H$_8$$^{8+}$ (2×10^{-3})	2.5	0.10 ± 0.01	1.7–2.4
32-C$_9$-N$_6$H$_6$$^{6+}$ (6×10^{-3})	1.2	0.11 ± 0.01	1.9–2.6
24-N$_6$H$_6$$^{6+}$ (4×10^{-3})	2.5	0.15 ± 0.01	2.6–3.4
L-21-N$_6$H$_6$$^{6+}$ (6×10^{-3})	2.5	0.22 ± 0.01	3.9–4.9

^{a} Excitation at 313 nm; [Co(CN)$_6$$^{3-}$] = 2×10^{-3}; 0.1 M NaClO$_4$; room temperature. ^{b} Adjusted with HClO$_4$. $^c n = 6(\Phi/\Phi_f)$, where Φ_f is the quantum yield for "free" Co(CN)$_6$$^{3-}$; see also the text. ^{d} Not affected by addition of 1×10^{-1} M Et$_2$NH$_2$$^+$.

with the various polyammonium ions was determined from the change in absorbance at 380 nm.[23] In the case of the adduct with 24-N$_6$H$_6$$^{6+}$, appropriate correction (<7%) was made for the contribution of "free" Co(CN)$_6$$^{3-}$ photoaquation. The values reported in Table II are average values of at least three experiments.

Discussion

Complexation of Co(CN)$_6$$^{3-}$. The formation of ion-pair complexes between anions of various types (including cyanide complexes) and the polyammonium macrocycles shown in Figure 1 was unequivocally demonstrated on the basis of pH titrations[14,15] and cyclic voltammetry measurements.[24] The adducts of complex anions like the metal hexacyanides may be considered as complexes of complexes (supercomplexes) since the ligands coordinated in the first coordination sphere of the metal are themselves coordinated by the polyammonium macrocycles. The M(CN)$_6$$^{n-}$ substrates may be bound into the macrocycle cavity via multiple N—H$^+$···$^-$NC—M hydrogen bonds.[14,15] The strong complexation of M(CN)$_6$$^{n-}$ affects the electrochemical properties of these anions, stabilizing the more highly charged form (i.e., the lower oxidation state of the central metal).[24]

Adduct formation, however, does not affect the spectroscopic properties. The absorption spectra of the adducts between Co-(CN)$_6$$^{3-}$ and the polyammonium macrocycles used in this work are substantially identical to the summation of the spectra of the two components for $\lambda > 265$ nm, as expected for partners which cannot give rise to low-energy charge-transfer transitions.

Photochemical Reactivity. The spectroscopy and photochemistry of the Co(CN)$_6$$^{3-}$ ion have been extensively investigated. In aqueous solution the absorption spectrum in the near-UV region shows $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ ligand field absorption maxima at 312 and 260 nm.[19] In other protic solvents the low-energy absorption falls at $\sim$312 nm, whereas in aprotic solvents it is near 320 nm.[25] The shift of the second ($^1A_{1g} \rightarrow {}^1T_{2g}$) ligand field band is analogous. The blue shift in proton-donor solvents is attributed to strong hydrogen bonding to the nitrogen end of cyanide.[26] The reactive excited state of Co(CN)$_6$$^{3-}$ is thought to be the lowest triplet ($^3T_{1g}$).[27,28] The lifetime of the $^3T_{1g}$ excited state is about 20 μs in EPA rigid matrix at 94 K[29,30] and decreases strongly with increasing temperature.[31] Forster and co-workers reported that Co(CN)$_6$$^{3-}$ exhibits a weak emission with 3–5 ns lifetime in various

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(22) For the adducts with 32-N$_8$H$_8$$^{8+}$ and 32-C$_9$-N$_6$H$_6$$^{6+}$, a very slight red shift ($\sim$3 nm) of the isosbestic point around 286 nm was observed with increasing irradiation time. This shift was found[12] to be due to the thermal anation of the pentacyanoaquo adduct by Cl$^-$ ion, which is present in the solutions as counterion of the polyammonium salts.

(23) In the calculations of the quantum yields we have used the same extinction coefficient values as for the photoaquation of Co(CN)$_6$$^{3-}$, namely ϵ_{313} = 162 and ϵ_{380} = 1.5 for Co(CN)$_6$$^{3-}$, and ϵ_{380} = 235 for Co(CN)$_5$(H$_2$O)$^{2-}$.

(24) Peter, F.; Gross, M.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *J. Chem. Soc., Chem. Commun.* **1981**, 1067. Peter, F.; Gross, M.; Hosseini, M. W.; Lehn, J. M. *J. Electroanal. Chem.* **1983**, *144*, 279.

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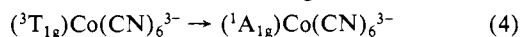
(30) Viaene, L.; Ceulemans, A.; Vanquickenborne, L. G. *Inorg. Chem.* **1985**, *24*, 1713 (footnote 5).

(31) D'Olieslager, J.; Viaene, L.; Vanquickenborne, L. G., private communication.

Photochemical Reactivity of Supramolecular Structures

J. Am. Chem. Soc., Vol. 107, No. 24, 1985 6891

solvent mixtures at room temperature;[32] however, we and others have not been able to observe any emission in aqueous solutions[33] and in EPA or ethylene glycol–water solvents.[31] The quantum yield of population of the $^3T_{1g}$ state via the spin-allowed $^1T_{2g}$ and $^1T_{1g}$ levels has been estimated to be ~0.4 from photosensitization studies[27] and ~0.9 from direct irradiation experiments.[28] In aqueous solution $Co(CN)_6^{3-}$ undergoes a photoaquation reaction (eq 1) with $\Phi = 0.30 \pm 0.02$,[13] independent of the excitation wavelength.[13,28] Photosolvation also takes places in a variety of solvents,[25,26] with practically the same quantum yield (0.30 ± 0.02) in all cases. This behavior has led to the conclusion[26] that the quantum yield of $Co(CN)_6^{3-}$ is a "molecular" characteristic, only weakly (if at all) affected by any solvent parameters. The simplest explanation of this behavior is that the primary photochemical process is in all cases a CN^- photodissociation

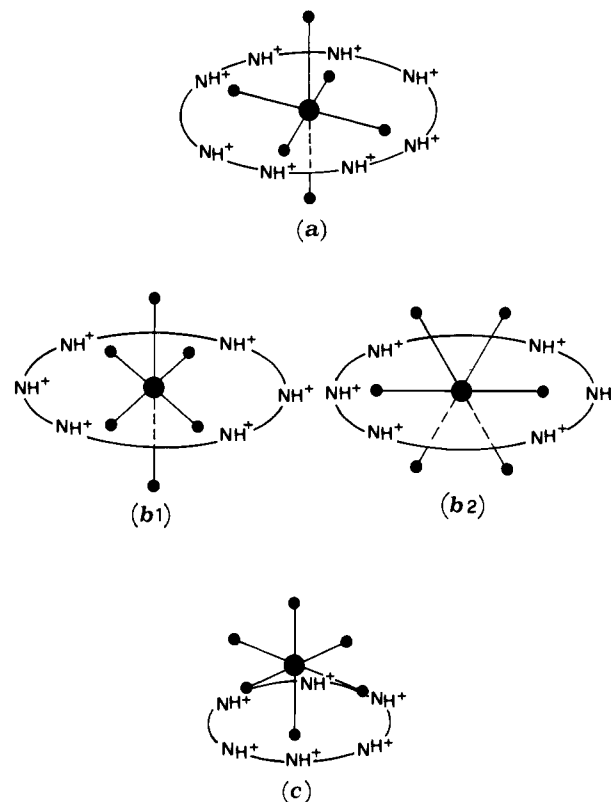$$(^3T_{1g})Co(CN)_6^{3-} \rightarrow Co(CN)_5^{2-} + CN^- \qquad (3)$$
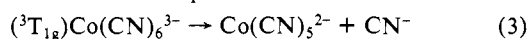
which competes with deactivation to the ground state:

$$(^3T_{1g})Co(CN)_6^{3-} \rightarrow (^1A_{1g})Co(CN)_6^{3-} \qquad (4)$$

A simple dissociative initial step without any significant concerted rearrangement of the five-coordinated fragment has also been taken as a basis for a general interpretation of the ligand field photochemistry of d^6 coordination compounds.[34–37] It should also be noted that the $Co^{II}(CN)_5^{3-}$ ion, which is a good model for the excited $Co^{III}(CN)_6^{3-}$ ion because of the presence of a $\sigma^*(e_g)$ electron, is known to have a square-pyramidal structure.[38] In high viscosity media, evidence for cage recombination effects in the photochemistry of $Co(CN)_6^{3-}$ has been reported.[39]

The results obtained in this work show that the ion-pair complexes formed by $Co(CN)_6^{3-}$ with the polyammonium ions undergo the same photoaquation reaction as the "free" $Co(CN)_6^{3-}$ ion (eq 1). Since adduct formation does not cause any spectral change in the ligand field bands of $Co(CN)_6^{3-}$, it seems fair to assume that the reactive excited state of the adduct is the same as that of "free" $Co(CN)_6^{3-}$. Nevertheless, the reaction quantum yields of the adducts with L-21-$N_6H_6^{6+}$, 24-$N_6H_6^{6+}$, 32-C_9-$N_6H_6^{6+}$, and 32-$N_8H_8^{8+}$ are considerably smaller than the quantum yield of "free" $Co(CN)_6^{3-}$ (Table II). The presence of $Et_2NH_2^+$ in a concentration up to 0.1 M (i.e., 17 to 50 times higher than that of the polyammonium ions) does not affect the quantum yield, showing that a compound having a single ammonium site (which is expected to be very weakly bound) has no effect.

The observed decrease of the quantum yield in going from "free" $Co(CN)_6^{3-}$ to its adducts may be due to (i) changes in the rate constants of the intramolecular steps of the excited complex which affect the quantum yield (e.g., radiative and nonradiative deactivation of the $^3T_{1g}$ state) or (ii) some cage recombination effect due to the presence of the receptor in the second coordination sphere. Changes in the intramolecular rate constants seem unlikely, since the photochemistry of $Co(CN)_6^{3-}$ is not affected by the solvent or by addition of $Et_2NH_2^+$ and the presence of the receptor does not cause any significant change in the absorption spectrum of the complex.[40] We suggest, therefore, that the polyammonium receptors are responsible for the quantum yield decrease by restraining escape of CN^- ligands out of the adducts, when Co–CN bonds are temporarily broken as a consequence of

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(40) Definite evidence in this regard could be obtained, in principle, from emission intensity and lifetime measurements. However, as we have seen above, no emission is detectable in fluid solution at room temperature.

Figure 3. Possible supramolecular structures of the adducts between $Co(CN)_6^{3-}$ and 32-$N_8H_8^{8+}$ (a), 32-C_9-$N_6H_6^{6+}$ (b), or 24-$N_6H_6^{6+}$ (c).

light excitation. Space-filling models of the supercomplexes show that the receptors can bind via hydrogen bonds some of the six ligands of the complex, and it seems probable that such ligands are subjected to a cage recombination. In other words, in the supercomplexes some of the CN^- ligands might have the same probability to undergo photosubstitution as in "free" $Co(CN)_6^{3-}$, while others (those involved in the hydrogen bonds) might be prevented to escape. According to this hypothesis, the number of "free" ligands in the supercomplexes should be $n = 6(\Phi/\Phi_f)$, where Φ and Φ_f are the photoaquation quantum yields for the supercomplex and "free" $Co(CN)_6^{3-}$, respectively. Lower and upper limits for n (calculated taking into account the experimental uncertainties of the quantum yields) are reported in Table II.

Definite evidence for our reaction model could only be obtained from independent elucidation of the structures of the supercomplexes. However, we wish to note that structures inferred from space-filling models are in agreement with the above-discussed interpretation of the photochemical results. Adduct formation between $Co(CN)_6^{3-}$ and 32-$N_8H_8^{8+}$ is likely to involve enclosure of $Co(CN)_6^{3-}$ into the 32-atom ring of the polyammonium macrocycle, with strong hydrogen bonds between the nitrogen atoms of the four equatorial CN^- ligands and the ammonium groups of the macrocycle (Figure 3a). Accordingly, only the two axial ligands should contribute to the photodissociation reaction, in agreement with the value of n reported in Table II. For the adduct with 32-C_9-$N_6H_6^{6+}$, space-filling models indicate that the two limiting structures shown in Figure 3b are possible. The first one involves strained hydrogen bonds between four coplanar CN^- ligands of $Co(CN)_6^{3-}$ and four ammonium groups of the macrocycle. The second one allows hydrogen bonding between two axial CN^- ligands and the ammonium groups. The value of n (Table II) is in agreement with the structure shown in Figure 3b1. For the smaller 24-$N_6H_6^{6+}$ macrocycle, encircling of $Co(CN)_6^{3-}$ by the ring is no longer possible, and the most stable structure is likely that shown in Figure 3c, where three CN^- ligands of an octahedral face are hydrogen bonded to the macrocycle. The value of n close to 3 (Table II) is in agreement with this structure. For the adduct with the linear L-21-$N_6H_6^{6+}$, no specific structure can be predicted because of the flexibility of the polyammonium ion;

the photochemical results suggest that 1-2 CN⁻ ligands are prevented to escape.

The observed effects for the polyammonium macrocyclic receptors can thus be accounted for by the formation of complexes of defined geometry although, of course, one cannot exclude that such effects result from the coexistence of several adducts having various geometries.

Conclusions

The results obtained in this paper show that the photoreactivity of transition-metal complexes can be controlled by adduct formation. Furthermore, they agree with structural considerations on relative shape, size, and binding site arrangements, suggesting that the adducts formed by $Co(CN)_6^{3-}$ with polyammonium macrocyclic receptors have defined supramolecular structures. In particular, the complexes of $Co(CN)_6^{3-}$ with 32-$N_8H_8^{8+}$ and 32-C_9-$N_6H_6^{6+}$ (a and b1 in Figure 3) may be considered as complexes of complexes (or supercomplexes) since the hexacyano cobaltate anion should be contained inside the macrocyclic ligand, which substantially constitutes the second coordination sphere of

the central metal. These results suggest that in favorable cases photochemistry may be a probe for supramolecular structures. Besides offering a generic protection against photodissociation, adduct formation might find interesting application in the case of complexes containing mixed ligands: on one hand it could provide information on the site of ligand release and on the other hand it can orient photosubstitution reactions toward specific products. These results and perspectives further extend the scope and applications of anion coordination chemistry.

Dual Stereoselectivity in the Nucleophilic Attack on (π-Allyl)palladium Complexes
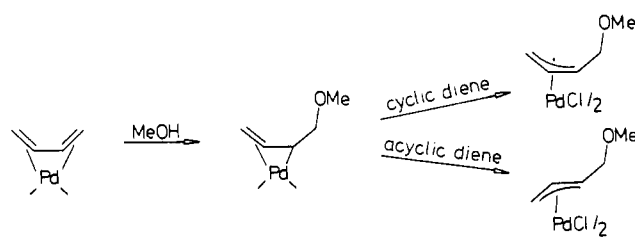
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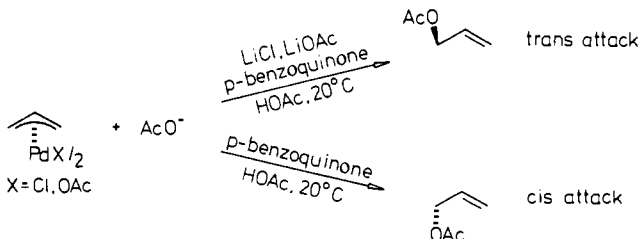
Abstract: Stereochemical studies of nucleophilic addition to (π-allyl)palladium complexes **1-5** and **10** show that carboxylates, e.g., acetate, can be directed toward cis or trans attack depending on the ligand environment. This dual stereoselectivity was obtained in both cyclic and acyclic systems. The acetate attack was induced by the addition of *p*-benzoquinone, which most likely coordinates to the metal. Accordingly, maleic anhydride was shown in one case to induce a cis migration of acetate in bis[(4-methoxy-η³-1,3-cyclohexenyl)palladium acetate]. Attempts to induce a cis migration of a stabilized carbon nucleophile (acetylacetonate) in a (π-allyl)palladium complex led only to a cis/trans addition ratio of 20:80. The cis migration of carboxylates probably occurs via a (σ-allyl)palladium complex, whereas the trans attack takes place directly on the (π-allyl)palladium complex.

Nucleophilic addition to unsaturated hydrocarbons coordinated to a transition metal is an important type of reaction in organic synthesis. In these reactions, the question concerning the regio- and stereoselectivity plays a central role (Figure 1). Although many studies have addressed the question of altering the regioselectivity for a given nucleophile (i.e., full regiocontrol),[1-3] relatively little work has been aimed at altering the stereoselectivity (i.e., full stereocontrol).[1b,2b,c,4] A dual stereocontrol is of great

Scheme I

Scheme II

importance in organic synthesis since it allows a choice in stereochemistry in the creation of new asymmetric centers.

We have recently reported palladium-catalyzed 1,4-additions to conjugated dienes involving stereo- and regioselective additions

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