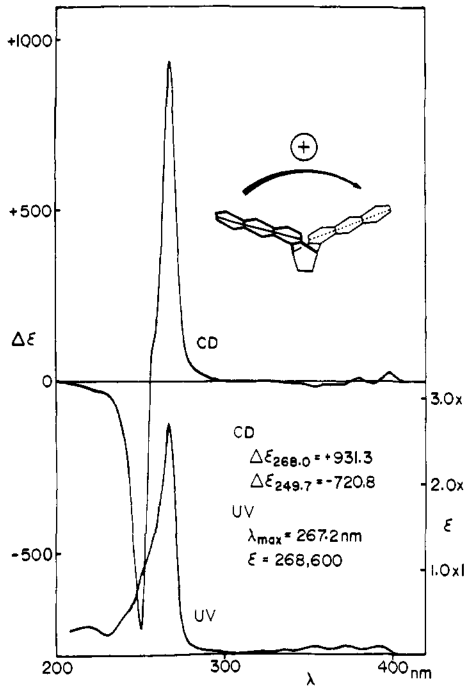

Figure 1. Uv and CD spectra of (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (**1**) (see text for the solvent systems).

of **7** with zinc powder in alkaline medium gave a strong fluorescent hydrocarbon **1** in solid masses:[12] $[\alpha]_{\mathrm{D}}$ +1157° (*c* 0.034, dioxane); mass spectrum *m/e* 406 (M^+), 378 ($M - C_2H_4$); NMR ($CDCl_3$) δ 1.79 (br s, 4 H), 5.41 (br s, 2 H), 6.8–8.1 (m, 12 H), 8.22 (s, 2 H), 8.75 (s, 2 H); ir (KBr) ν_{max} 3040, 1615, 1150, 874, 740, 467 cm^{-1}; uv (0.08% dioxane in EtOH) λ_{max} 391.0 (ϵ 9100), 371.2 (ϵ 11 200), 352.7 (ϵ 9000), 267.2 nm (ϵ 268 600); CD (0.18% dioxane in EtOH) $\Delta\epsilon_{397.2} = +26.4$, $\Delta\epsilon_{388.1} = -2.3$, $\Delta\epsilon_{378.0} = +6.3$, $\Delta\epsilon_{362.9} = -9.7$, $\Delta\epsilon_{352.8} = -14.5$, $\Delta\epsilon_{268.0} = +931.3$, $\Delta\epsilon_{249.7} = -720.8$.

The CD spectrum of **1** clearly exhibits very strong positive first and negative second Cotton effects due to coupling of the ^1B_b transitions ($\Delta\epsilon_{268.0} = +931.3$ and $\Delta\epsilon_{249.7} = -720.8$; $A (= \Delta\epsilon_1 - \Delta\epsilon_2) = +1652.1$), the positive sign of the A value being in accord with the positive exciton chirality,[2,7] i.e., the clockwise screwness, between the two long axes of the anthracene moieties in **1** (see Figure 1).

The related homologues **2a**, mp 209.5–211.0 °C, and **2b**, mp 124–126 °C, synthesized[9] from **3** also show clearly split Cotton effects arising from the ^1B_b transition of naphthalene chromophores ($\Delta\epsilon_{240.6} = +371.5$, $\Delta\epsilon_{227.0} = -149.4$ for **2a** and $\Delta\epsilon_{242.0} = +340.3$, $\Delta\epsilon_{212.5} = -139.3$ for **2b**).[13] The present data thus demonstrate ideal cases of chiral exciton coupling in CD spectra, and provide the most unambiguous evidence which demonstrates the consistency between nonempirical circular dichroic and x-ray Bijvoet methods. The quantitative calculation of the chiral exciton coupling in these compounds is now in progress.

Acknowledgments. One of the authors (N.H.) thanks Professor Koji Nakanishi, Columbia University, for invaluable discussions during his stay in New York.

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(12) Since the hydrocarbon **1** solidified as masses instead of crystals, it was purified by preparative thin layer chromatography on silica gel.
(13) A similar CD spectrum was reported for 7,14-dihydro-7,14-ethanodibenz[*a,h*]anthracene-15,16-dicarboxylic acid, the absolute configuration of which was determined by kinetic resolution methods; see ref 8a.

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Received March 12, 1976

Laser Excitation of Spin Forbidden Bands. Triplet Photochemistry of Cobalt(III) Ammines

Sir:

States related to the ground state by a spin forbidden band play a very large role in the attempt to account for reaction pathways in transition metal photochemistry. Since phosphorescence is not generally observed, it is often difficult to develop experimental tests of hypotheses concerning "spin forbidden states". Direct population of such states by light absorption is highly desirable but requires a light source meeting two limiting characteristics: (1) the source must be intense; (2) the source must be highly monochromatic so that irradiation can be at a well-defined wavelength which allows for precise determination of the absorbance in the spin forbidden band with a limited and calculable contribution from absorbance in the tails of more intense spin allowed bands. A laser can meet these criteria and should find important uses.

In this report, we describe the direct population of ^3T (O_h approximate microsymmetry) states of the d^6 Co(III) complexes $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ using the 647.1-nm line of a Spectra Physics krypton ion laser. In these experiments, we have used a Perkin-Elmer polarimeter cell as an irradiation vessel and absorbance matched ammonium reineckate for actinometry. Dark controls were run in the thermostat bath used to circulate water around the polarimeter cell. The methodology is very close to that of ref 1, and we find good agreement for the experiments which overlap ref 1 as a check on our approach. Radiation times ranged up to 8 h and involved approximately 3% conversion. In the reaction with $Fe(CN)_6^{4-}$, there is no correction for absorbance by $Fe(CN)_6^{4-}$ at 647 or 514 nm, but correction for product absorption was carried out by both graphical approximation and rigorous calculation.

The population of spin allowed ligand field singlets $^1T_{1g}$ and $^1T_{2g}$ (O_h approximate microsymmetry) of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ leads to a substitutional photochemistry which is to be contrasted to other d^6 systems mainly in respect of the low total quantum yield (near 10^{-3}).[1] The singlet and triplet excited states of Co(III) correspond to the ligand field electron configurations $t_{2g}{}^5e_g{}^1$ and are thought to be appropriate for efficient photosubstitution[2] in consequence of the population of a single σ antibonding orbital. The low quantum yield following irradiation of singlet bands has been attributed by some

Table I. Quantum Yields for Ligand Field Irradiation of Co(III) Complexes (T = 25 °C)

Complex	Wavelength (nm)	Reaction mode	Quantum yield[a]
$Co(NH_3)_6^{3+}$	488	NH_3 loss	$(3.2 \pm 0.3) \times 10^{-4}$
	514		$(2.1 \pm 0.1) \times 10^{-4}$
	647		$(1.3 \pm 0.4) \times 10^{-4}$
$Co(NH_3)_5Cl^{2+}$	514		$(50.7 \pm 1.3) \times 10^{-4}$
	647		$(1.1 \pm 0.2) \times 10^{-4}$
	514	Cl^- loss	$(17.2 \pm 1.0) \times 10^{-4}$
	647		$(9.6 \pm 0.9) \times 10^{-4}$
$Co(en)_3^{3+}$	514	Redox[b]	0.23 ± 0.03
	647		0.60 ± 0.10[c]

[a] Yields reported at 488 and 514 are in good agreement with those reported in ref 1. Reference 1 should be consulted for analytical methods. The intensity of the 647.1-nm laser line was fairly stable near 10^{-7} einstein s^{-1} throughout this work. [b] The redox reaction is that with $Fe(CN)_6^{4-}$ in 1.5 M NaCl described in ref 6. It is not a reaction with the ammine serving as reducing agent. [c] This result is corrected for product absorption according to ref 7. The red product has an extinction coefficient at 647 nm of 56 whereas the $Co(en)_3^{3+}$ ion has an extinction coefficient of 1.13 at 647 nm. In all experiments, the initial concentration of $Co(en)_3^{3+}$ was near 0.05 M. The final concentration of the red product ranged from 6 to 18 × 10^{-4} M corresponding to absorbance changes at the analytical wavelength of 440 nm of 0.061 to 0.171.

authors to a rapid radiationless deactivation of ^1T states to the $^1A_{1g}$ ground state.[2] (It has been suggested that the rapid relaxation is mediated by mixing of the nearby ^5T state of the configuration $t_{2g}^4e_g^2$ which becomes the ground state for Co(III) in a weak ligand field.[3])

If the lifetime of the triplet is crucial to quantum yield, it might reasonably be predicted that direct population of the triplet would lead to increased quantum yields.[4] Argument for very simplified MO theory would suggest that the singlet and triplet should have very similar reactivity since the one-electron MO configurations are the same. A more sophisticated MO treatment[5] shows that the σ antibonding character is somewhat larger in the triplet than in the singlet so that one might predict higher substitution yield. (It is also possible[5] that the theory predicts an increase of Cl^- loss relative to NH_3 loss from the lowest triplet of $Co(NH_3)_5Cl^{2+}$.)

Contrary to all of these predictions, our main observation is that *substitution quantum yields are significantly reduced* on shifting from initial population of a singlet with 514-nm irradiation to population of a triplet with 647-nm irradiation. As Table I indicates, yields for replacement of NH_3 and Cl^- by H_2O fall by a factor of about two or more. It is, however, observed that the ratio of release of NH_3 to Cl^- which has a value of 3.1 in the case of singlet irradiation of $Co(NH_3)_5Cl^{2+}$ is inverted to 0.11 on changing to triplet region irradiation. The reaction from the singlet has been characterized as *antithermal*[1] because Cl^- is the more labile ligand in thermal substitution. The reaction from the triplet appears to be qualitatively *thermal*. The irradiation wavelength is in a region where a significant tail of the singlet band is still present in the spectrum of $Co(NH_3)_5Cl^{2+}$. This means that the value of the quantum yield for NH_3 release must be regarded as an upper limit and the ratio, 0.11, similarly regarded *only* as an upper limit.

In order to elucidate the mechanism further, a study was made of the photoreaction between $Co(en_3)^{3+}$ and $Fe(CN)_6^{4-}$ which is known to have a high quantum yield on irradiation in the singlet region.[6] This is a bimolecular reaction which leads to a red cyanide bridged product and is thought to be initiated by an electron transfer between Fe(II) and Co(III).[6] At 514 nm in 1.5 M NaCl medium (see ref 6 for the significance of the high salt concentration), the quantum yield for the red product was 0.23 at 25 °C. The corresponding yield at 647 nm, was estimated to be 0.60 ± 0.10. Both values are corrected for product absorption.[7] Runs were carried out at 25 and 40 °C but the temperature dependence was not large enough to measure reliably.

A mechanistic theory, now, must account for the following summarized facts. (1) Substitution yields are *low* and *decrease* with increasing wavelength. (2) Substitution patterns can change on passing to longer wavelength from, e.g., antithermal toward thermal. (3) The alternative reaction with $Fe(CN)_6^{4-}$ is much more efficient than substitution at all wavelengths. An attractive possibility, which is not much more speculative than most mechanisms but by no means unique, is an additional state model. If one assumes that substitution occurs in competition with relaxation to a lowest lying state which is not reactive in substitution one can easily understand the low yields and the wavelength dependence of yields. The differences of pattern of reactivity of $Co(NH_3)_5Cl^{2+}$ can be explained by the theory developed in ref 5. The lowest lying state would then be considered responsible for reaction with $Fe(CN)_6^{4-}$. Such a lowest lying state could be in ^5T. A recent calculation of potential surfaces shows this to be a reasonable possibility for some related d^6 complexes,[8] and Beattie and Sutin[9] have shown that singlet-quintet intersystem crossing in a d^6 Fe(II) complex can be rapid. It has also recently been argued that photosubstitution can occur on a very short time scale. Kane-Maguire and his collaborators argue that Cr(III) substitutions (not unrelated theoretically to the present case) occur in competition with vibrational relaxation.[10] Finally, the electron configuration of the quintet ($t_{2g}^4e_g^2$) is related to the reduction product $Co(NH_3)_6^{2+}$ which is high spin d^7. If it is correct that the reaction with $Fe(CN)_6^{4-}$ is a redox mediated process, there is appeal in assigning it to the quintet. (An example of an alternative approach to developing a mechanism for the present results might be to follow the considerations developed by Endicott et al.[11])

We wish to conclude with a more concrete observation emphasized by the present study. The majority of studies of metal complex photochemistry have required (because of the experimental design) that the complex either react unimolecularly or with only the solvent as a reaction partner. No other reaction partners were supplied. This study, in common with two other recent ones,[6,12] *indicates an opportunity, largely unexploited, to develop a bimolecular photochemistry of ligand field states.* The reaction with $Fe(CN)_6^{4-}$ had a quantum yield two orders of magnitude higher than solvolysis.

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Received February 3, 1976