

of whether *unsupported* actinide-transition-metal bonds can be synthesized. This goal has been achieved recently by Marks and co-workers.³¹

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Supplementary Material Available: Crystal data, tables of distances and angles, positional and thermal parameters, observed and calculated structure factors, and selected theoretical results (25 pages). Ordering information is given on any current masthead page.

(31) (a) Professor Tobin Marks has informed us of the synthesis and structural characterization of $\text{Cp}_2^*\text{Th}(\text{I})[\text{RuCp}(\text{CO})_2]$, a complex with an unbridged thorium-ruthenium bond.^{31b} (b) Sternal, R. S.; Brock, C. P.; Marks, T. J. *J. Am. Chem. Soc.*, submitted for publication.

Cation-Directed Photochemistry of an Anthraceno-Crown Ether

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We report on a system, bis(anthraceno)-crown ether I, designed to direct intramolecular photophysics and photochemistry by complexation with cations.

The interplay between ion complexation and spectroscopic properties of chromophores has aroused considerable interest. Vögtle¹ recently reviewed the topic with emphasis on molecules called "chromoionophores" showing ion-specific color changes resulting from the perturbation of electronic absorption spectra by cation insertion into a neutral ligand cavity. *Luminescence is also susceptible to such effects.*^{2a-3}

Relationships between photoreactivity and complexation have been examined from two standpoints: (i) the modification of complexing ability as a result of a photochemical reaction; (ii) the change of photochemistry as a result of cation complexation. The first of these has been well illustrated by Shinkai's photoresponsive³ systems based on cis-trans isomerization of the azo-

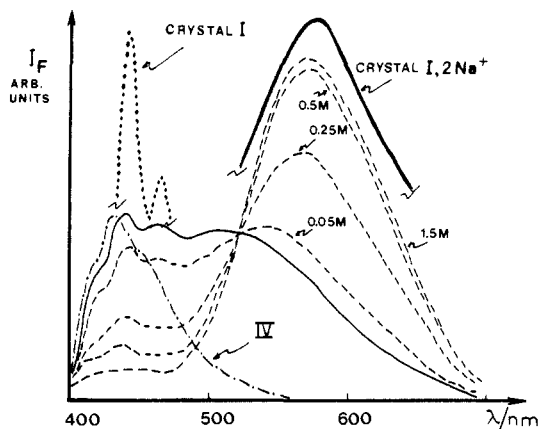


Figure 1. Corrected fluorescence spectra ($\lambda_{\text{exc}} = 380$ nm, room temperature, degassed solutions) of I (5×10^{-6} M): (i) in methanol (—), (ii) in methanol + NaClO_4 0.05, 0.25, 0.5, 1.5 M (---), and of IV in methanol (- - -). Fluorescence spectra ($\lambda_{\text{exc}} = 366$ nm) of microcrystals of I (···) and of $\text{I}, 2\text{Na}^+$ (—), represented, in part, at a different scale.

benzene chromophore as well as by related molecules,^{4a-e} such as the "photoresponsive molecular tweezers".^{4e} Cation complexation with crown ethers has often been reported to enhance the rates of photochemical reactions^{5a-e} and, in one case, to favor the photochemical reaction of one excited state at the expense of another state.^{5f}

We sought a system with the potential to give a highly sensitive response to variations in conformations which arise from cation complexation. A good candidate was the anthracene ring because of its dual (monomer/excimer) fluorescence and its versatile photoreactivity. Therefore we designed new bisanthracenic anthracenophanes such as I; their synthesis has already been described.⁶

In this paper, we will demonstrate that important alterations of conformations of 1,4,7,10,13,28,31,34,37,40-decaoxa-[13.13](9,10)-anthracenophane (I) are induced by metal cation complexation and these greatly affect fluorescence emission and photochemical regioselectivity. (Part of this study was presented at the 7th Symposium on Macrocyclic Compounds, Provo, UT, Aug 1983, and at the 10th IUPAC Symposium on Photochemistry, Interlaken, Switzerland, July 1984.)

*Electronic absorption spectra⁷ of the bichromophore I were examined in order to elucidate intramolecular ground-state interactions.*⁸ A comparison of the UV absorption spectra in methanol between I and the monochromophoric reference compound IV (9,10-bis[(1-methoxy-3,6-dioxaoctyl)oxy]anthracene) shows hypochromism for the first transition ($^1\text{L}_a$)⁹ and intensity redistribution for the second transition ($^1\text{B}_u$).⁹ These features are an indication of some weak interactions between the two rings; strong interactions are known to produce pronounced red shifts.¹⁰

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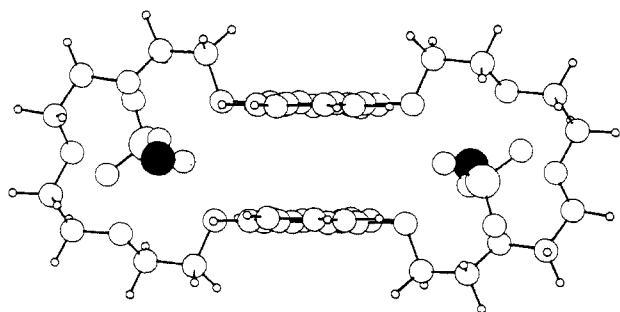
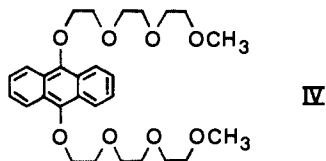


Figure 2. View of the complex $I,2Na^+$ in the crystalline state. Atoms of carbon are represented by open circles, atoms of oxygen by stippled circles, atoms of chlorine by large open circles, and sodium by heavy dark circles.

In the presence of a large excess of $NaClO_4$ (1 M) further hypochromic (but no bathochromic) effects appear for the 1L_a band whereas the 1B_g transition undergoes further intensity modifications and a new band, blue shifted, is in accord with the presence of a complex.

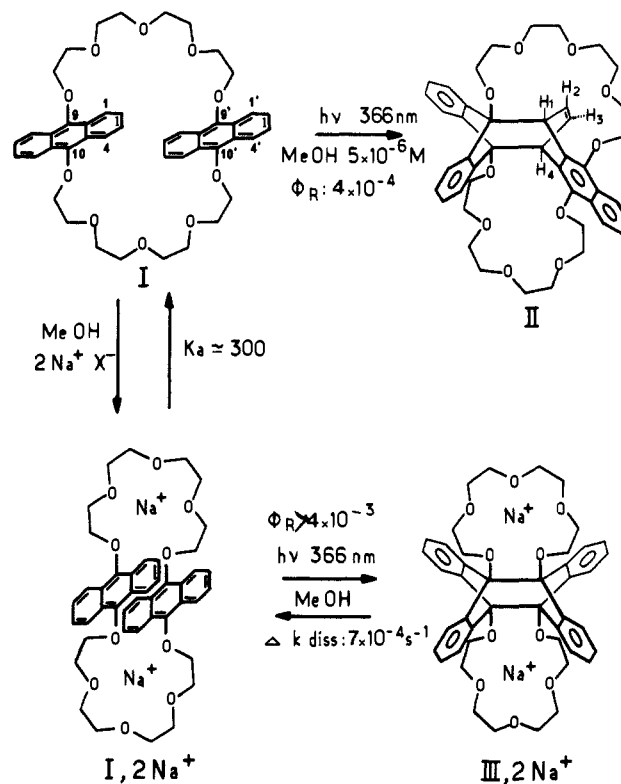
The anthracene ring is an efficient fluorophore and the dual fluorescence emission (monomer and excimer) is particularly suited to reflect intramolecular interactions in the excited state related to conformational mobility.¹¹ Both structured monomer and unstructured excimer ($\lambda_{max} \approx 510$ nm) fluorescence emissions are observed in pure methanol solutions of I (concentration, 5×10^{-6} M; total quantum yield 0.13) whereas IV exhibits a monomer



emission (Figure 1); this is an indication that I in methanol is a mixture of conformers in which the anthracene rings experience diverse mutual relationships: in some of these conformers, the rings behave independently and, in others, they can partially overlap to form an excimer.¹² Contrary to IV whose fluorescence remains unchanged, progressive addition of $NaClO_4$ ¹³ (from 0.05 to 1.5 M) to the solution of I greatly alters the spectrum and the excimer band is gradually shifted to the red ($\lambda_{max} \rightarrow 570$ nm) at the expense of the monomer band. These results are paralleled by the effect of the salt on the excitation spectra of the solution of I. In the absence of the salt, the spectrum is independent of the emission wavelengths and similar to the absorption spectrum. In contrast, the spectrum in the presence of the salt displays two distinct excitation profiles related to the monomer (which appeared similar to the absorption spectrum of IV) and excimer (which is similar to the solution of I with $NaClO_4$) emissions.

X-ray structural analysis¹⁴ of a monocrystal grown from a $NaClO_4$ saturated solution of I shows that the complex $I,2Na^+$

consists of two five-oxygen cavities each of which contains a sodium cation (Figure 2); the two anthracene rings are aligned forming a slightly staggered sandwich with an interplanar distance of ca. 3.4 Å (van der Waals distance). At room temperature, the crystal



displays a nonstructured fluorescence with $\lambda_{max} \approx 580$ nm (Figure 1). The absence of fine structure implies that the ground state is dissociative as in an excimer; the enforced arrangement of the two anthracene rings is presumably the last observable step on the pathway toward the staggered sandwich excimer where the interring distance should be less than in the ground state. Our results are in accord with and further substantiate Ferguson's observations¹⁵ of similar fluorescence from an anthracene "broken dimer" in hard matrices, at very low temperature. The bimolecular association in $I,2Na^+$ is also reminiscent of the pairing of pyrene rings in crystals of pyrene¹⁶ or in pyrenophanes¹⁷ which suggests a staggered sandwich geometry for these excimers. As expected from the above results, the fluorescence spectra of crystals of I and of $I,2Na^+$ display respectively monomer and sandwich excimer fluorescence.

The change in excimer geometry with Na^+ complexation is expected to induce a modification of photoreactivity. UV irradiation ($\lambda \geq 330$ nm) of a degassed methanol solution of I ($c \leq 10^{-4}$ M) cleanly yields the photocyclomer II (mp 142–145 °C, $\Phi_R \approx 4 \times 10^{-4}$) as the single photoproduct;¹⁸ this type of ring closure between positions 9,1' and 10,4' has already been encountered^{8b} when the classical 9,9'-10,10' cycloaddition is unfavorable; in the present case, failure to isolate the classical photocyclomer is attributed to an electronic repulsion between the lone pairs of the oxygen atoms located in positions 9,10, 9', and 10'; this is in agreement with the observed thermal instability of the related

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(13) (a) The sodium cation was selected as less important effects were noted with Li^+ and Mg^{2+} ; no influence of the counter-anion was detected by replacement of ClO_4^- by CH_3COO^- . (b) Assuming that two sodium cations are involved in the complex as shown in the crystal, the association constant $K_a \approx 300$ M⁻² was estimated from a plot of fluorescence intensity vs. salt concentration.

(14) The crystals (transparent needles; mp 250 °C) are octahedral (acetone-methanol-water, 1/1/1), space group *Pbca* orthorhombic N. 61, $a = 16.805$ (4) Å, $b = 13.222$ (3) Å, $c = 20.708$ (5) Å, $\alpha = \beta = \gamma = 90^\circ$, and $Z = 8$. The structure was solved by direct methods (Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. *MULTAN* 80, 1980; a system of computer programs for the automatic solution of crystal structures from x-ray diffraction data, University of York, York, U.K.) and refined to $R = 0.053$ and $R_w = 0.062$ by using 951 independent reflections of Cu $K\alpha$ radiation. Additional details will be published later.

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(18) II has the following spectral characteristics: 1H NMR ($CDCl_3$, 90 MHz) δ 3.90 (m, 32 H, OCH_2CH_2O), 4.55 (AA'XX' pattern, 2 H, H_1 and H_4 $J_{H_1H_2} = 5, 6$, $J_{H_1H_3} = 3, 3$ Hz), 5.84 (AA'XX' pattern, 2 H, H_2 and H_3), 6.75 (m, 2 H, β naphthalenic protons), 7.2–7.9 (m, 10 H, other aromatic protons); IR (KBr pellet) $\bar{\nu}$ (cm^{-1}) 2925, 1460, 1100–1050 (br), 800; UV (ethyl ether) λ_{nm} ($\log \epsilon$) 335 (3.04), 320 (3.18), 305 (3.51), 296 (3.63), 282 (3.74), 271 (3.88), 252 (4.48).

9,9'-10,10' bisanthracenic photocyclomers V linked by a poly-(oxyethylene) chain.^{4c,19} In contrast, in the complex $I, 2Na^+$ the interaction of the oxygen lone pairs with the cation may be expected to decrease the repulsion experienced in the free ligand and, in so doing, to restore the normal regioselectivity of the photoprocess. This aspect was examined by irradiation of a $NaClO_4$ -saturated methanolic solution of I, under the same conditions as above, and although no photoproduct was isolated, evidence for the formation of essentially the photocyclomer 9,9'-10,10' III, $2Na^+$ is obtained from the following observations: (i) the anthracenic 1L_a band (310–420 nm) disappeared without any significant growing in of a naphthalenic absorption, (ii) the disappearance quantum yield of I was at least 1 order of magnitude greater ($\phi_R > 4 \times 10^{-3}$) than that observed from the cation free solution, and (iii) in the dark, the photoproduct underwent an almost quantitative fast thermal back reaction with a rate ($k_{diss} \approx 7 \times 10^{-4} s^{-1}$) close to that recorded for compounds V,¹⁹ this last feature can be explained by a competition between MeOH and I to solvate Na^+ ; the desolvated photocyclomer III then is thermally unstable and reverts to the anthracenophane I.

A greater understanding of such systems in which fluorescence and photochemistry can be cation directed and an improvement of their physical properties are under current investigation.

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Insertion of the Nitrosonium Ion into a Chromium–Methyl Bond^{1,2}

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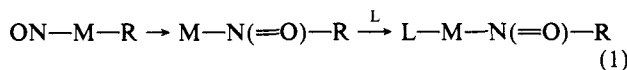
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Insertion reactions of metal–carbon σ bonds are an integral and important part of transition-metal organometallic chemistry.³ Of these reactions, the conversions involving the thermodynamically spontaneous migratory insertion of coordinated nitric oxide, i.e.,⁴



(where R = alkyl and L = Lewis base) are of particular interest since they lead to the formation of new carbon–nitrogen bonds.

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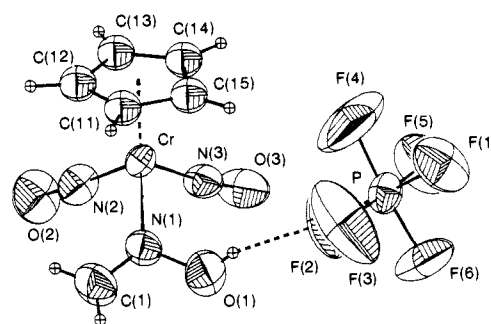
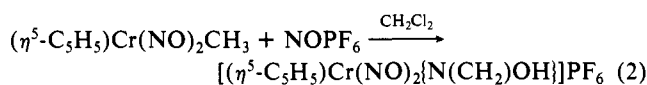


Figure 1. Molecular structure of $[(\eta^5-C_5H_5)Cr(NO)_2\{N(CH_2OH)\}]PF_6$. Selected bond lengths (Å) and angles (deg): C(1)–N(1) = 1.253 (9), N(1)–O(1) = 1.392 (7), Cr–N(1) = 2.034 (5), Cr–N(2) = 1.702 (6), Cr–N(3) = 1.709 (5), N(2)–O(2) = 1.163 (6), N(3)–O(3) = 1.152 (6), Cr–C₅H₅(centroid) = 1.843, H(10)–F(2) = 2.14 (8), Cr–N(1)–C(1) = 128.9 (5), C(1)–N(1)–O(1) = 111.5 (6), O(1)–N(1)–Cr = 119.6 (4), N(2)–Cr–N(3) = 93.5 (3), O(2)–N(2)–Cr = 174.5 (6), O(3)–N(3)–Cr = 172.2 (5).

We now wish to report the first instance of the formation of a C–N linkage by the insertion of NO⁺ into a transition-metal–carbon bond. Specifically, we present the conditions for effecting the transformation



and describe in detail the characterization of the novel product, a rare organometallic formaldoxime complex.

In a typical experiment, a green solution of $(\eta^5-C_5H_5)Cr(NO)_2CH_3$ ⁵ (0.384 g, 2.00 mmol) in CH_2Cl_2 (20 mL) was treated with solid $NOPF_6$ (0.280 g, 1.60 mmol), and the mixture was stirred at room temperature under N_2 . After 1 h, a dark green, microcrystalline solid began to precipitate. This solid was collected by filtration after 3.5 h and was recrystallized from CH_2Cl_2 to obtain 0.260 g (44% yield based on $NOPF_6$) of analytically pure⁶ $[(\eta^5-C_5H_5)Cr(NO)_2\{N(CH_2OH)\}]PF_6$ as green, diamagnetic crystals. The crystals are moderately air-stable and are most soluble in solvents such as nitromethane.⁷

A single-crystal X-ray crystallographic analysis of the formaldoxime complex⁸ established the cation as a normal "three-legged piano stool" (Figure 1). Within the cation, the $(\eta^5-C_5H_5)Cr(NO)_2$ fragment closely resembles that found in $(\eta^5-C_5H_5)Cr(NO)_2Cl$.⁹ Furthermore, the $H_2CN(OH)Cr$ portion is essentially planar, and the intramolecular dimensions of the formaldoxime ligand resemble

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