with the absence of deuterium scrambling (racemization) in **4**-OH. These data also exclude significant "leakage" from **3** to **11**. The structure(s) of the intermediate(s) en route to **4** and **5** will be discussed in a forthcoming full paper.[15] The **4**-OH/**6**-OH ratios of **4**-NH_2 and **6**-NH_2 (Table I) indicate that solvolytic displacement (k_s) contributes to the formation of **4**-OH from **6**-N_2^+.

The generation of **3** from **6**-N_2^+, but not from **6**-OBs, deserves comment. The small activation energy of nitrogen extrusion from diazonium ions brings the rates of several competing processes (k_s, k_c, k_Δ) closer together.[16] As a rule, k_Δ processes provide low-energy reaction paths and are therefore more prominent in solvolysis than in deamination. The present case is thought to be exceptional because bridging is associated with increased strain energy. Thus k_Δ is accentuated by the better leaving group. Our observations with **6**-NH_2 parallel previous reports on *endo*-2-norbornylamine[14] and add a new species to the $C_7H_{11}^+$ manifold.[17]

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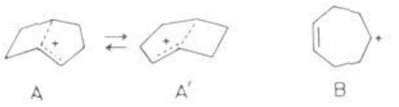
[15] The symmetrical 7-norbornyl cation (**12**), drawn here for the sake of simplicity, is not an adequate representation; see: Sunko, D. E.; Vancik, H.; Deljac, V.; Milun, M. *J. Am. Chem. Soc.* **1983**, *105*, 5364 and references cited therein.

[16] Streitwieser, A. *J. Org. Chem.* **1957**, *22*, 861.

[17] A referee has pointed out that our data do not distinguish the bishomocyclopropenyl cation **3** from a pair of rapidly equilibrating homoallylic ions, A ⇄ A′. The open 4-cycloheptenyl cation (B), although not a precursor



to the bicyclo[3.2.0]heptan-2-ols,[7] may intervene on the reaction path from **3** to **7**.

Photoactivated Stereospecific Cleavage of Double-Helical DNA by Cobalt(III) Complexes

Jacqueline K. Barton* and Adrienne L. Raphael

Department of Chemistry, Columbia University
New York, New York 10027

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There has been considerable interest in DNA endonucleolytic cleavage reactions that are activated by metal ions,[1,2] both for the preparation of "footprinting" reagents[3] and as models for the reactivity of some antitumor antibiotics, notably bleomycin[4] and streptonigrin.[5] The features common to these complexes are that the molecule has a high affinity for double-stranded DNA and that the molecule binds a redox-active metal ion cofactor. The delivery of high concentrations of metal ion to the helix, in locally generating oxygen or hydroxide radicals, yields an efficient DNA cleavage reaction. We have demonstrated[6] that tris(phenanthroline) complexes of zinc(II) and ruthenium(II) display enantiomeric selectivity in binding to DNA. This chiral discrimination is enhanced markedly in the case of tris(diphenylphenanthroline)ruthenium(II) isomers, which serve as spectroscopic probes in solution to distinguish right- and left-handed DNA helices.[7] It occurred to us that a *stereospecific* DNA nicking agent might be prepared by using tris(diphenylphenanthroline) complexes with the suitable choice of a redox-active metal; metallointercalation reagents[8] offer that flexibility. Our work has been prompted also by the finding[9] that cobalt(III) bleomycins cleave DNA in the presence of light.[10] We report here that tris(phenanthroline)cobalt(III)[11] at low concentrations cleaves

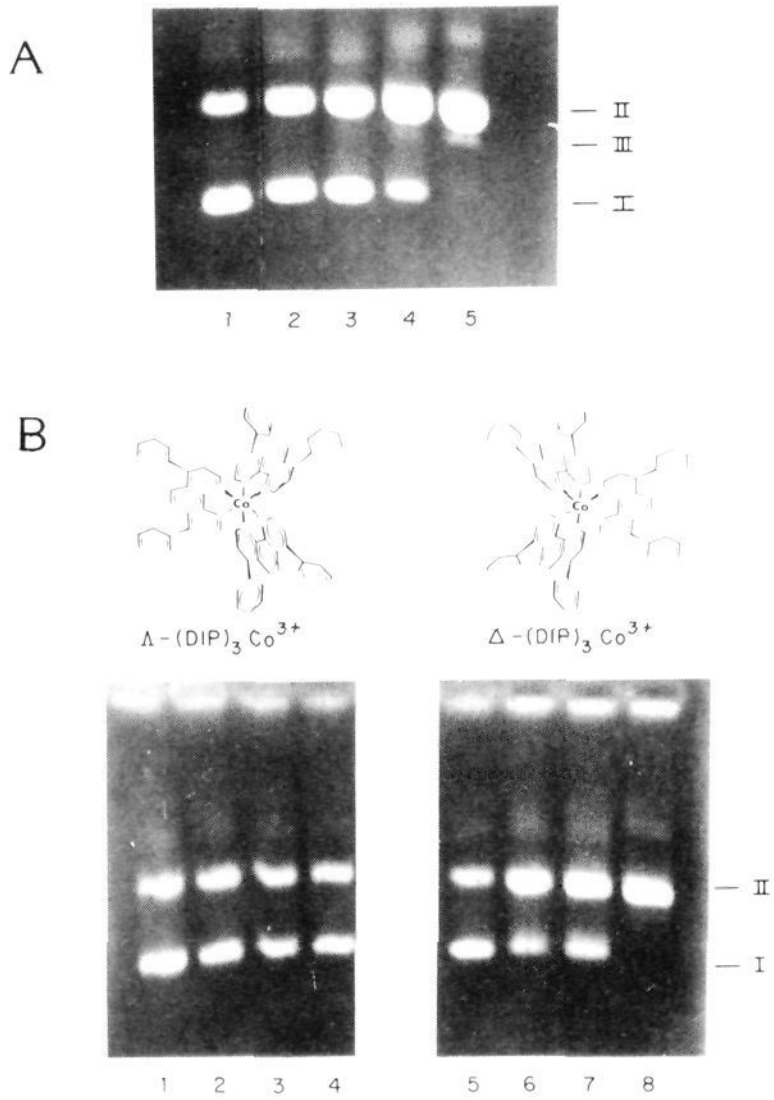

Figure 1. (A) Cleavage of plasmid ColE1 DNA in the presence of $(phen)_3Co^{3+}$ and light. The 1% agarose gel shows the distribution of DNA forms (100 μM nucleotide) initially without cobalt (lane 1) and after irradiation at 254 nm (4-W mercury lamp) in the presence of 10 *μM $Co(phen)_3^{3+}$ for 0, 20, 40, and 60 min (lanes 2–5, left to right)*. The samples were incubated in 50 mM Tris acetate buffer, pH 7.0, and 18 mM NaCl and then electrophoresed for 1 h at 60 V and stained with ethidium. (B) The cleavage is also stereoselective. Plasmid ColE1 DNA (100 μM) was incubated with Λ- (left) or Δ-$Co(DIP)_3^{3+}$ (right) (5 μM) and irradiated for 0, 0.5, 1.0, or 1.5 h (lanes 1–4 and 5–8 for the Λ and Δ isomers, respectively). Incubation of this DNA with Λ-$Co(DIP)_3^{3+}$ in light has no effect, while incubation with Δ-$Co(DIP)_3^{3+}$ in light causes complete conversion of form I to form II.

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DNA when irradiated at 254 nm. Furthermore the high stereospecificity of the tris(diphenylphenanthroline) (DIP) metal isomers[12] with DNA helices is preserved in these cleavage reactions.

Figure 1 shows gel electrophoretic separations of plasmid ColE1 DNA after incubation with cobalt complexes and irradiation for variable times. DNA cleavage is followed by monitoring the conversion of supercoiled (form I) closed circular plasmid DNA to the nicked circular (form II) and linear (form III) species.[13] Figure 1A reveals the complete conversion of form I to II after a 1-h irradiation in the presence of 10 μM Co(phen)$_3^{3+}$. Neither irradiation of the DNA at these low intensities without cobalt nor incubation with cobalt without light yielded significant strand scission.[14] It is likely that the reduction of Co(III) is the important step leading to DNA cleavage and not that irradiation provides a means to generate cobalt(II) in situ. DNA incubation with the tris(phenanthroline) complex initially in the cobaltous form yielded no reaction unless irradiated. Presumably the cobaltous complex is oxidized in solution to the cobaltic species, since it is the +3 oxidation state in cobalt polyamine complexes that is photochemically active. Also dithiothreitol inhibits activity of Co(phen)$_3^{3+}$, perhaps by precluding regeneration of an active cobalt(III) species.[15] Interestingly, electrophoresis also reveals with increasing irradiation a small reproducible increase in the mobility of form II; this may reflect some short-range radical-induced DNA cross-linking.[16]

The cleavage reaction is furthermore strongly stereospecific. Figure 1B shows pColE1 DNA after incubation with either Λ-Co(DIP)$_3^{3+}$ or Δ-Co(DIP)$_3^{3+}$ [17,18] and irradiation with ultraviolet light. Incubation of pColE1 DNA with the Λ isomer, which cannot bind to a right-handed duplex owing to steric constraints, yields no appreciable reaction,[19] whereas incubation with Δ-Co(DIP)$_3^{3+}$, which is able to associate closely with right-handed B-DNA, shows efficient nicking activity comparable to that seen with Co(phen)$_3^{3+}$. This different cleavage efficiency by each enantiomer is consistent with our earlier finding[7] of conformational discrimination by the ruthenium(II) isomers; one enantiomer of Ru(DIP)$_3^{2+}$ binds to B-DNA, but both Δ- and Λ-Ru(DIP)$_3^{2+}$ bind to the left-handed Z-DNA helix. These results underscore the importance of an intimate association of the metal with the duplex. In Figure 1B the overall concentrations of the cobalt isomers are equal,[20] yet the Λ trication, if it cannot intercalate, does not yield DNA strand scission.

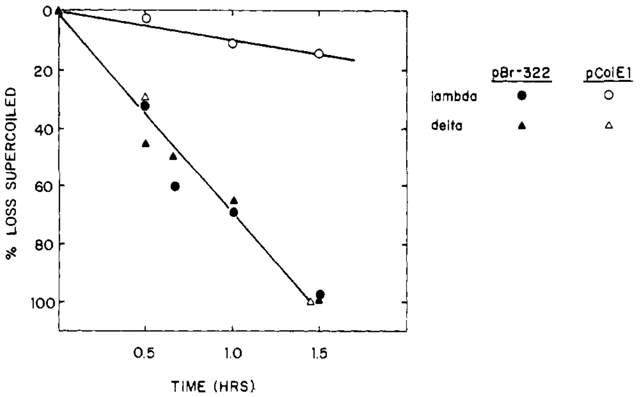

Figure 2. Plot showing the percent reduction in form I band intensity for pBR322 DNA (closed symbols) and pColE1 DNA (open symbols) incubated with either Δ- (triangles) or Λ-Co(DIP)$_3^{3+}$ (circles) (5 μM) as a function of time irradiated. Extensive strand scission is evident in pBR322 with both isomers.

The Λ-tris(phenanthroline) metal complexes do, however, bind to left-handed Z-DNA.[21,22] We examined the plasmid pBR322 containing a 42-base-pair alternating guanine–cytosine insert (pLP42)[23] and which was shown[23,24] to adopt the Z-conformation in 4 M NaCl. Under these conditions, cleavage by *both* Co(DIP)$_3^{3+}$ enantiomers is obtained. Hence the Λ isomer may recognize and cleave left-handed helices. More interesting, however, is the finding, plotted in Figure 2 as percent loss of supercoiled form, that the plasmid pBR322 at physiological salt concentrations and without extreme superhelix underwinding also is significantly cleaved by the Λ isomer. Given our other results of differential binding based on DNA helicity[7] and the differential cleavage of ColE1 described above, it is tempting to suggest that Λ-Co(DIP)$_3^{3+}$ binds to and cleaves a natural left-handed segment in pBR322 DNA in normal salt concentrations. These observations support the findings by Rich and co-workers[25] of anti-Z antibody binding to the 14-base-pair alternating purine–pyrimidine segment in pBR322.[26]

We think these experiments are important in several respects. The photoactivated DNA cleavage reaction with Co(phen)$_3^{3+}$ illustrates with a simple inorganic complex the notion of DNA strand scission mediated by a locally generated redox reaction. We suspect here it is a *reduction* of Co(III) with perhaps con-

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(13) The original ColE1 preparation contained 60% form I and 40% form II molecules.

(14) Irradiation at 310 nm where there are strong ligand transitions also leads to cleavage.

(15) This finding is in contrast to the iron and copper systems where thiols are thought to stimulate activity by generating the metal species in the reduced form.[1-5]

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(17) Tris(diphenylphenanthroline)cobalt(III) (Co(DIP)$_3^{3+}$) tritartrate was prepared as follows: 4,7-diphenyl-1,10-phenanthroline (Aldrich) was dissolved in a minimum volume of ethanol to which one third stoichiometric CoCl$_2$·6H$_2$O was added. The green brown solution was oxidized by using Br$_2$/H$_2$O, and a heavy orange precipitate formed immediately. The solution was refluxed for 1 h, and concentrated hydrochloride acid was added. The bromine oxidation was then repeated. The crude chloride salt was used directly for enantiomeric separations. With either *l*- or *d*-tartaric acid (Aldrich), the deep red tartrate (Tar) diastereomeric salts [Λ-Co(DIP)$_3$]·(*l*-Tar)$_3$ and [Δ-Co(DIP)$_3$]·(*d*-Tar)$_3$, were prepared by several successive recrystallizations in 50% ethanol, pH 7.0.

(18) Chemical and spectroscopic data for these complexes are as follows: Anal. Calcd for [Co(DIP)$_3$](Tar)$_3$·H$_2$O (CoC$_{84}$N$_6$O$_{19}$H$_{65}$) C, 66.32; H, 4.32; N, 5.52. Found: C, 65.87; H, 4.46; N, 5.78. Absorption spectra showed λ_{max} at 278 and 312 nm (shoulder). The circular dichroic spectra resemble those of enantiomers of Ru(DIP)$_3^{2+}$, and absolute configurations have been assigned on that basis.

(19) After a 1-h irradiation, a 15% reduction in the supercoiled band intensity is found on incubation with the Λ isomer. Cleavage by the Λ isomer could result from a small amount of Δ-Co(DIP)$_3^{3+}$ in the preparation or photoracemization. No change in the supercoiled band intensity on irradiation without cobalt is evident during this time period.

(20) Presumably the rate of photodecomposition of each isomer is also equal, unless photosensitization of the bound complex occurs through DNA absorption.

(21) Racemic Co(DIP)$_3^{3+}$ and Co(phen)$_3^{3+}$, despite the high concentration of positive charge, do not promote a B → Z transition in poly(dGC) as judged by circular dichroism.

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(26) The statistically significant 14 base pair sequence (CACGGGTGCGCATG) in pBR322 shows alternation of purine and pyrimidine with one base out of register.[27] Alternating purine–pyrimidine sequences tend to adopt the Z conformation.[22,28] The plasmid pColE1 sequence contains no comparable stretch of alternation.[29]

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comitant hydroxide oxidation that is responsible for cleavage. With regard to applications, this photoactivated reaction should make possible "footprinting" as a function of time. Most importantly, the differential cleavage of ColE1 DNA by enantiomers of $Co(DIP)_3^{3+}$ represents a clear example of a *conformation-specific* DNA cleaving molecule. This molecule will be useful in determining regions of Z-DNA conformation within long segments of native DNA. Moreover the high level of recognition of DNA conformation by these chiral inorganic complexes suggests to us the powerful application of stereospecificity in DNA drug design.

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Nature of the Emissive Excited State of Quadruply Bonded $Mo_2X_4(PMe_3)_4$ Complexes

Michael D. Hopkins and Harry B. Gray*

Contribution No. 6957, Arthur Amos Noyes Laboratory
California Institute of Technology
Pasadena, California 91125
Received December 7, 1983

A totally convincing interpretation of the electronic emission spectra of quadruply bonded transition-metal dimers has not yet been achieved.[1-6] This is in contrast to the increasingly detailed understanding of the absorption spectra of these complexes that has been realized in recent years.[7,8] Conclusive assignment of the emissive state and establishment of its geometry have been hindered in these systems by the general observation of a lack of mirror symmetry between the emission and lowest energy absorption band. The sole unambiguous example of prompt fluorescence from the singlet $\delta\delta^*$ excited state to the δ^2 ground state was observed for $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ and was attributed to the fact that the arrangement and steric bulk of the ligands imposed a considerable barrier to certain geometrical distortions generally available to this excited state.[3] Our interest in determining the extent of ligand participation in these formally metal-localized excited states has led us to examine the electronic spectra of a number of derivatives of the $M_2X_4(PR_3)_4$ type.[9]

The electronic absorption spectrum of $Mo_2X_4(PMe_3)_4$ (X = Cl, Br, I)[10] exhibits a band attributable to the singlet $\delta^2 \rightarrow \delta\delta^*$ ($^1B_2 \leftarrow {}^1A_1$; D_{2d}) transition[3,7,11] as its lowest energy feature. This band both red shifts and increases in intensity according to Cl < Br < I (X = Cl, λ_{max} = 585 nm, f = 0.026; X = Br, λ_{max} = 598 nm, f = 0.032; X = I, λ_{max} = 636 nm, f = 0.040; 300 K, 2-methylpentane). Upon excitation of this transition, crystals and hydrocarbon solutions of $Mo_2X_4(PMe_3)_4$ display an intense red luminescence. The radiative efficiency of this luminescence is, by an order of magnitude, the highest yet observed for a quadruply bonded system (X = Cl, λ_{max} = 673 nm, ϕ = 0.26, τ = 140 ns; X = Br, λ_{max} = 671 nm, ϕ, = 0.16, τ = 90 ns; X = I, λ_{max} = 715 nm, ϕ = 0.12, τ = 30 ns; 300 K, 2-methylpentane).[12] The close agreement of the radiative rate constant with that calculated from the oscillator strength[13] of the $^1B_2 \leftarrow {}^1A_1$ transition, in addition to the substantial overlap of the emission spectrum with this band, strongly suggests assignment of the emission to $^1B_2 \rightarrow {}^1A_1$ fluorescence for all three complexes.

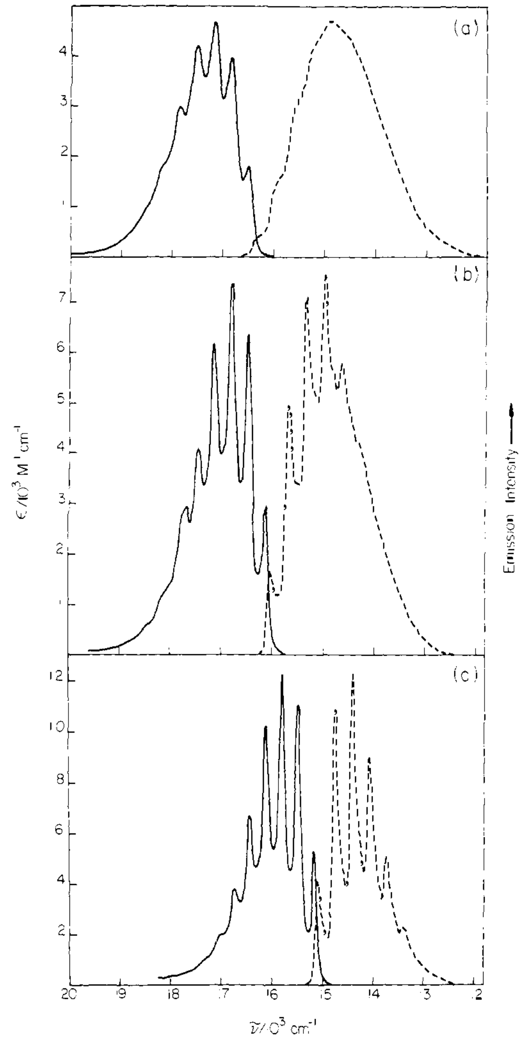

Figure 1. Absorption (—) and corrected emission (---) spectra of $Mo_2X_4(PMe_3)_4$ in 2-methylpentane at 77 K: (a) X = Cl; (b) X = Br; (c) X = I.

Vibrational fine structure is resolved in both the $^1B_2 \leftarrow {}^1A_1$ and $^1B_2 \rightarrow {}^1A_1$ bands of $Mo_2X_4(PMe_3)_4$ at low temperature. At 77 K the absorption and emission spectra (Figure 1) progress in a single mode, with spacings corresponding to the metal-metal stretching frequencies of the excited and ground states, respectively.[14] In the absorption spectra of all three complexes, the Franck-Condon factors calculated from the relative intensities

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[10] The complexes were prepared by treating $Mo_2(O_2CCH_3)_4$ with excess trimethylphosphine and halotrimethylsilane, following the route to $Mo_4X_8(PR_3)_4$ (Ryan, T. R.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 2072-2079).

[11] Spectroscopic studies on single crystals of $Mo_2Br_4(PMe_3)_4$ have been performed (Miskowski, V. M., unpublished results). The 598-nm band is found to be polarized parallel to the Mo-Mo axis, consistent with the $^1B_2 \leftarrow {}^1A_1$ assignment.

[12] The origin of the unexpected increase of the emission lifetime and quantum yield of $Mo_2Cl_4(PMe_3)_4$ relative to the electronically similar $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$[3] has been investigated through variable-temperature lifetime measurements of the complexes $Mo_2Cl_4(PR_3)_4$ (R = Me, Et, *n*-Pr, *n*-Bu)[9] (Hopkins, M. D.; Gray, H. B., unpublished results). The nonradiative rate constants (k_{nr}) of all complexes follow the expression

$$k_{nr} = k_0 + k_1 \exp(-E_a/kT)$$

and appear to have very similar values of E_a and k_0. The trimethylphosphine complex differs from the other three by having a smaller value of k_1. An interpretation of the "phosphine sensitivity" of k_1 is not yet available.

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