Although the bond distances in rings II and IV are similar, the latter is significantly less planar than ring II, with a dihedral angle about the Cβ–Cβ bond of 14.5 (4)° as compared to 5.4 (4)° in ring II. Deviations of the 26 atoms of the macrocycle from the plane defined by the four nitrogens are presented in Figure 2b; the largest displacement, 0.263 Å, occurs at C17 in the distorted ring IV.

As previously observed,[11] the MeBPheo *a* molecules stack to form one-dimensional chains in which rings I and III of successive molecules overlap with perpendicular separations of 3.59 Å and center-to-center distances of 8.07 Å. The benzene rings sit between rings II in the chains. The chains further associate to form two-dimensional layers with a closest approach of 7.18 Å between the centers of the macrocycles in neighboring layers.

Recent structural data clearly demonstrate the skeletal distortions that crystal packing, steric, or protein constraints can impose on porphyrin derivatives.[2,4,10,12,18] Such conformational variations provide an attractive mechanism for fine-tuning the redox, optical, and charge-transfer properties of the chromophores in vitro and in vivo.[14,18] We are therefore attempting to obtain different crystal forms of MeBPheo in a search for different conformers.

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Supplementary Material Available: Experimental details, tables of bond angles, positional and anisotropic thermal parameters for the non-hydrogen atoms, positional parameters for the hydrogen atoms, contact distances, and some least-square planes and torsion angles, a view of the one-dimensional chains with the benzenes, and a packing diagram (10 pages); table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Light-Induced Nicking of DNA by a Synthetic Analogue of Cobalt(III)-Bleomycin

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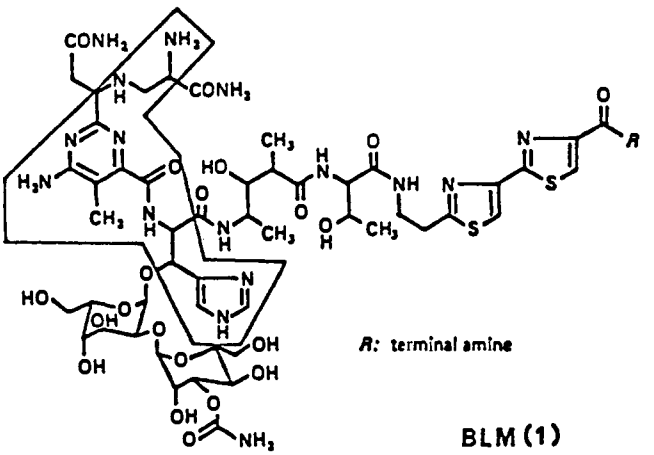
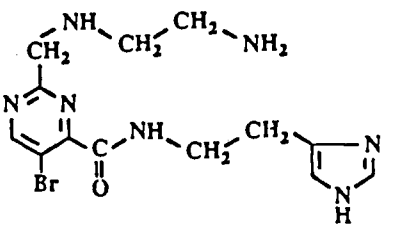
Bleomycins (BLM, **1**) are a family of glycopeptide antitumor drugs that inflict single and double strand breaks in cellular DNA in the presence of metal ions like Fe^{2+} and molecular oxygen.[1] The strand scission reaction is brought about by oxygen-based free radicals like •OH and/or hypervalent metal-oxo species that are formed in the vicinity of the DNA helix. Cobalt(III)–BLMs[2] are however exceptions in this regard—the kinetically inert cobalt(III) chelates of the drug cleave DNA only when illuminated with UV[3,4] or visible[5] light, and this photoinduced cleavage reaction is insensitive to dioxygen.[6] The light-driven DNA degradation reaction of Co^{III}–BLMs has raised renewed interest in the structure(s) and photochemistry of the cobalt(III) complexes of BLM.

Aerobic oxidation of Co^{II}–BLM[7] results in at least three different products two of which appear to contain a superoxide and a hydroperoxide group bound to cobalt(III) (the brown[7,8] and the green[9] Co^{III}–BLM, respectively), while the thermodynamically stable orange Co^{III}–BLM is devoid of any "active" form of dioxygen in the coordination sphere of the metal. More recent



BLM (1)



PMAH
(2)

works have also reported a brown Co^{III}–BLM with water as a ligand on cobalt.[6,9] Unfortunately, no crystallographic information is available on any Co^{III}–BLM at the present time. Spectroscopic studies indicate that in the brown aquo-Co^{III}–BLM as well as in the cobalt(III) complex of pseudotetrapeptide A,[10] BLM employs five nitrogen donor centers located in the primary and secondary amines, pyrimidine and imidazole rings, and the amide moiety (the boxed area in **1**) to bind cobalt(III). The sixth coordination site is filled by a water molecule in both of the *proposed* structures.

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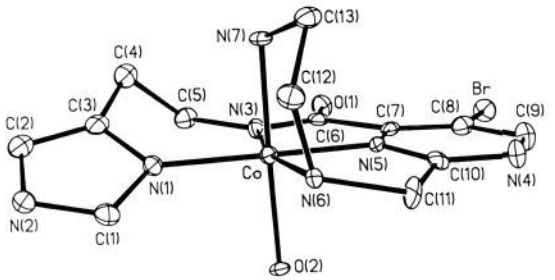

Figure 1. Computer-generated thermal ellipsoid (probability level 50%) plot of $[Co(PMA)(H_2O)]^{2+}$ (cation of **4**) with the atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances in Å, Co–N(1) 1.912 (5), Co–N(3) 1.917 (4), Co–N(5) 1.865 (4), Co–N(6) 2.004 (4), Co–N(7) 1.933 (5), Co–O(2) 1.945 (4). Selected bond angles in deg, N(1)–Co–N(3) 93.4 (2), O(2)–Co–N(1) 91.5 (2), N(3)–Co–N(5) 82.4 (2), N(5)–Co–N(6) 83.9 (2), O(2)–Co–N(6) 89.7 (2), O(2)–Co–N(7) 175.3 (1), N(3)–Co–N(7) 92.1 (2), N(6)–Co–N(7) 85.6 (2).

Recently, we have reported the synthesis of a ligand PMAH (**2**), that mimics the entire metal-chelating locus of the drug (boxed area in **1**).[11,12] The copper(II) complex of PMAH[12,13] has clearly established the coordination structure of Cu^{II}–BLM at physiological pH. We now report the structure of the cobalt(III) complex of PMAH namely, $[Co(PMA)(H_2O)](NO_3)_2$ (**4**), that serves as a model for the socalled aquo-brown Co^{III}–BLM.[14] This synthetic analogue of Co^{III}–BLM does cleave DNA under illumination by UV light.

A slurry of 572 mg (1.6 mmol) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$[15] and 700 mg (1.9 mmol) of PMAH in 10 mL of water was stirred at room temperature for 3 h. The pH of the reaction mixture was maintained at 5 with 0.5 N HBF_4. The deep red solution thus obtained was loaded on a SP-C50 sephadex column (6 × 20 cm)[16] and eluted with 0.1 N aqueous KCl solution. The first band was collected and evaporated to dryness, and the excess KCl was removed by extracting the residue with ethanol. The green ethanolic extract on evaporation afforded a green solid which was washed with 3 × 10 mL of acetonitrile to remove a blue-green impurity. A batch of 500 mg (0.93 mmol) of green solid that analyzes as $[Co(PMA)Cl_2\cdot HCl]$ (**3**)[17] was obtained. Next, the entire amount of **3** was dissolved in 5 mL of water, and to the orange-brown solution[19] was added a solution of 480 mg (2.8 mmol) of $AgNO_3$ in 5 mL of water. The mixture was stirred vigorously at 50 °C for 10 min, and the precipitate of AgCl was filtered off. The orange filtrate was then stored at room temperature for 3 h. Finally, 300 mg of $NaNO_3$ was added to the filtrate, and it was evaporated to dryness. The orange-brown residue was quickly washed with 5 mL of cold water followed by 5 mL of methanol. The batch of 250 mg of solid thus obtained was recrystallized from 10 mL of water that also contained 200 mg of $NaNO_3$. The yield of crystalline **4** was 20% based on $Na_3[Co(CO_3)_3]\cdot 3H_2O$.[20]

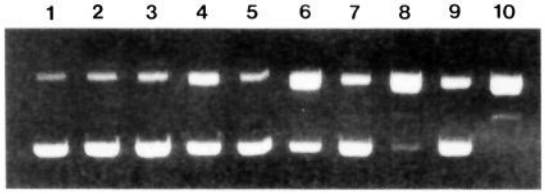

Figure 2. Plasmid ($\phi X174$ rf) DNA cleavage experiment with $[Co(PMA)(H_2O)](NO_3)_2$ (**4**) in 25 mM Tris-borate, 190 μM EDTA, pH 8.1 buffer at 298 K. Each reaction mixture contained 1 μg of DNA in a total volume of 40 μL. Concentration of **4** used = 5×10^{-4} M. Lane 1, DNA, dark, 3 h; lane 2, DNA + **4**, dark, 3 h; lane 3, DNA, UV light, 15 min; lane 4, DNA + **4**, UV light, 15 min; lane 5, DNA, UV light, 1 h; lane 6, DNA + **4**, UV light, 1 h; lane 7, DNA, UV light, 2 h; lane 8, DNA + **4**, UV light, 2 h; lane 9, DNA, UV light, 3 h; lane 10, DNA + **4**, UV light, 3 h.

The structure[21] of $[Co(PMA)(H_2O)]^{2+}$ in **4** is shown in Figure 1. The coordination geometry around cobalt is octahedral. Four nitrogens from the pyrimidine, imidazole, secondary amine, and the deprotonated amide group form the basal plane of coordination, while the primary amine nitrogen and a water molecule occupy the axial positions. Interestingly, spectroscopic data led Dabrowiak et al. to assign a coordination structure to the cobalt(III) complex of pseudotetrapeptide A of BLM[10a] that is identical with the one shown in Figure 1. The Co^{III}–N distances range from 1.865 (4) to 2.004 (4) Å and are comparable to those found in related compounds.[14,22]

Like green and brown Co^{III}–BLM, the present synthetic analogue **4** induces strand breaks in DNA under UV illumination.[23] This is shown in Figure 2. Irradiation of supercoiled covalently closed circular (form I) $\phi X174$ DNA[24] in the presence of submillimolar **4** results in progressive appearance of nicked circular (form II) and linear duplex (form III) DNA in lanes 4, 6, 8, and 10.[25] No strand scission is observed with **4** in the dark (lane 2). The UV light alone causes no significant nicking (lanes 3, 5, 7, and 9) either. The extent of DNA damage is also indifferent to the concentration of dissolved oxygen in the reaction medium. That **4** is stable in the reaction mixture under prolong UV irradiation has been confirmed. Unlike Co^{III}–BLM, **4** is devoid of functionalities that assist binding of the complex to DNA. Consequently, the concentration of **4** needed to observe significant

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(16) The strongly acidic cation exchanger SP-C50-120 was purchased from Sigma Chemical Co.

(17) The electronic absorption spectrum of $[Co(PMA)Cl_2\cdot HCl]$ (**3**) is very similar to that of *trans*-$[Co(py)_4Cl_2]Cl$.[18] Also, the ^1H NMR (300 MHz) spectrum of **3** in $(CD_3)_2SO$ shows that the primary amine nitrogen N7 is not coordinated to the metal center. We propose that in **3**, N1, N3, N5, and N6 of PMAH (Figure 1) constitute the basal coordination plane of cobalt(III), while two Cl^- ions occupy the two axial positions. The primary amine group of PMAH is present as the HCl salt in **3**. Attempts to obtain single crystals of **3** are in progress.

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(19) In aqueous solutions, most *trans*-$[Co(amine)_4Cl_2]^+$ complexes (green) are hydrolyzed to orange *trans*-$[Co(amine)_4(H_2O)_2]^{3+}$: Basolo, F.; Pearson, R. G. In *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: 1967; p 162.

(20) Chemical Anal. Calcd for $[Co(PMA)(H_2O)](NO_3)_2$, $CoC_{13}H_{19}N_9O_8Br$: C, 27.46; H, 3.37; N, 22.19. Found: C, 27.40; H, 3.29; N, 22.24. Spectral data ν_{CO} 1618 cm^{-1}; electronic spectrum, water, λ_{max} nm (ϵ, M^{-1} cm^{-1}) 540 sh (90), 375 sh (1800), 325 sh (3300), and 280 sh (5500); NMR ($(CD_3)_2SO$, 298 K, 300 MHz, ppm from TMS) ^1H NMR δ 1.94 (2 H, m, CH_2, C13), 2.51 (1 H, t, J = 12 Hz, +solv), 2.82 (1 H, t, J = 12 Hz), 3.05 (2 H, m, CH_2, C12), 3.26 (1 H, d, J = 14 Hz), 3.39 (2 H, s, H_2O), 4.17 (1 H, d, J = 14 Hz), 4.2 (2 H, NH_2), 4.67 (1 H, d, J = 19 Hz, CH_2, C11), 5.10 (1 H, m, CH_2, C11), 7.59 (1 H, s, Im), 8.16 (1 H, s, NH), 8.83 (1 H, s, Im), 9.52 (1 H, S, H9 of Pm), 13.47 (1 H, s, NH of Im); ^{13}C NMR δ 25.65, 40.78, 43.25, 54.20, 57.60, 116.13, 116.37, 138.31, 139.05, 157.14, 165.45, 168.83, 172.59.

(21) X-ray analysis: orange-brown blocks from water: $CoC_{13}H_{19}N_9O_8Br$ (**4** triclinic space group $P\bar{1}$, a = 7.608 (3) Å, b = 10.542 (3) Å, c = 13.116 (4) Å, α = 71.14 (2)°, β = 74.59 (3)°, γ = 81.66 (3)°, V = 957.7 (6) Å^3, Z = 2, d_{calcd} = 1.97 g/cm^3, d_{obsd} = 1.96 (1) g/cm^3, R = 0.049, R_w = 0.053. The structure was solved by Patterson methods (SHELXTL, revision 5.1). Full details will be reported elsewhere.

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(23) The samples were placed into a multiple-well tissue culture cluster plate (volume of wells = 40 μL) and covered with a quartz plate. A Transilluminator (UVP-TM-36, λ_{max} = 302 nm, intensity 7 mW/cm^2) was placed face-down on the plate. The distance between the light source and the samples was 4 cm. At the end of 3 h, the samples were loaded onto a 1% agarose gel (TAE running buffer) and electrophoresed for 3 h.

(24) $\phi X174$ rf DNA was purchased from Bethesda Research Laboratories and contained >95% form I.

(25) The DNA cleavage efficiency of **4** is enhanced by the presence of $NaBH_4$ in such reaction mixture (see ref 3a). The "green complex" **3** inflicts more damage to DNA under similar experimental conditions (Figure S3, Supplementary Material).

strand breaks within a certain period of time is higher than that of brown (or green) Co^{III}-BLM used in previous reports.[3,6] Details of the DNA cleavage reaction will appear elsewhere.

Acknowledgment. Financial assistance of a grant from the Cancer Research Coordination Committee of UC is gratefully acknowledged.

Supplementary Material Available: ^1H and ^{13}C NMR spectra (300 MHz, 298 K) (Figure S1) and ^1H-^{13}C (J = 140 Hz) COSY spectrum (Figure S2) of **4** in $(CD_3)_2SO$, plasmid DNA cleavage experiment with **3** and **4** in Tris-borate buffer (Figure S3), and tables of atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances and bond angles, and the H-atom coordinates for **4** (9 pages); table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

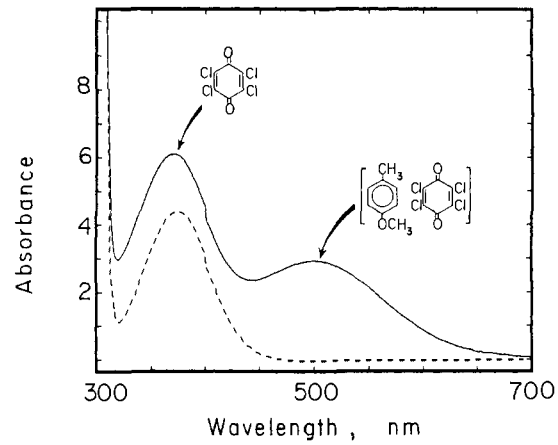

Figure 1. Absorption spectra of 2.0×10^{-3} M CA alone (---) and with 0.4 M MT (—) in dichloromethane.

Efficient Charge-Transfer Photochemistry via Fragmentable Cation Radicals with Variable Lifetimes. Direct Comparison with Chloranil Sensitization

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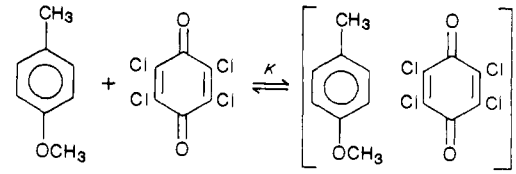
Electron transfer from various donors (D) to different acceptors (A) occurs upon the specific irradiation of the charge-transfer band ($h\nu_{CT}$) of the EDA precursor complex, i.e.[1,2]

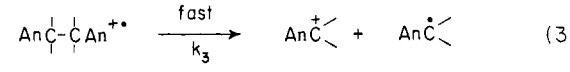
$$D + A \overset{K}{\rightleftharpoons} [D, A] \underset{k_2}{\overset{h\nu_{CT}}{\rightleftharpoons}} [D^{\bullet+}, A^{\bullet-}] \xrightarrow{k_1} \text{products} \quad (1)$$

Although such a direct process for photoinduced electron transfer does not depend on diffusional quenching that complicates the kinetics analysis of the more conventional sensitization methods,[3,4] its exploitation is often frustrated by an efficient back electron transfer (k_2).[5,6] This limitation can be addressed with labile acceptor moieties ($A^{\bullet-}$) such as that from tetranitromethane[7] and donor cations ($D^{\bullet+}$) derived from strained hydrocarbons,[8] which undergo unimolecular decomposition with rate constants comparable to k_2. Indeed the latter underscores the need for a related series of highly labile donor cations to enhance the efficiency of charge-transfer photochemistry. Accordingly, we report the use of arene donors derived from *p*-methoxytoluene (MT)[7c] in which the presence of the common chromophore also allows the direct comparison of charge-transfer and sensitized photochemistry as described by Jones, Farid, and co-workers.[9,10]

The absorption spectrum in Figure 1 shows the simultaneous appearance of two resolved bands—one arising from the local excitation of the chloranil acceptor (CA) and the other from the CT excitation of the 1:1 EDA complex, i.e.



The spectrophotometric determination of the formation constant in eq 2 according to the Benesi-Hildebrand procedure[11] indicated $K = 0.3\ M^{-1}$ in dichloromethane.[12] In such weak EDA complexes, the previous photophysical and photochemical studies by time-resolved spectroscopy[13] as well as Mulliken theory[14] point to $[MT^{\bullet+}, CA^{\bullet-}]$ as the pertinent ion-radical pair in eq 1. In order to promote the CT photochemistry in eq 1, we utilize the methoxytoluene chromophore in various dimeric structures DMT that are known to yield highly unstable cation radicals,[15-18] i.e.



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