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Cleavable Double-Chain Surfactant Co(III) Complexes

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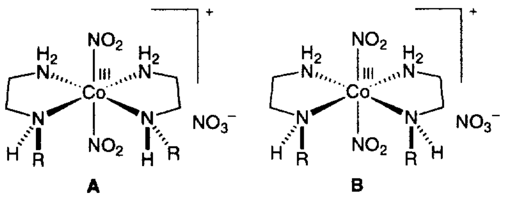
Abstract: Double-chain surfactant Co(III) complexes **1** and **2** have been cleaved in H_2O by reduction with $Na_2S_2O_4$ under mild conditions or by irradiation at 354 nm or with sunlight. In each case, cleavage derives from the reduction of substitutionally inert Co(III) to substitutionally labile Co(II).

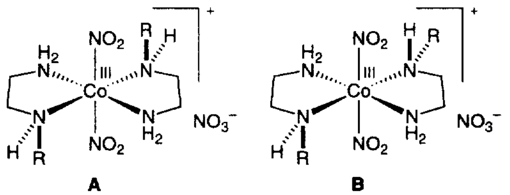
Keywords: Cleavage reactions; Cobalt and compounds; Photochemistry; Surfactants

There have been numerous reports of a variety of cleavable surfactants.[1] Such surfactants can be converted into nonsurfactants or into daughter surfactants with different aggregation properties, generally by cleavage at a labile functional group. But there are only a few examples[2] of cleavable surfactants based on a transition metal complex as the labile unit. Herein we report the cleavable nature of surfactants **1** and **2**, which contain Co(III)-based head groups. The stability/lability characteristics of **1** and **2** derive from the substitutional inertness and lability of Co(III) and Co(II) complexes, respectively.[3] We previously reported the synthesis of **1** and **2** and several homologues.[4] The former was likely obtained as a mixture of (±)-**1A** (only one enantiomer shown) and *meso* **1B**, and the latter as a mixture of (±)-**2A** (only one enantiomer shown) and *meso* **2B**.[4] Surfactants **1** and **2** have been cleaved in H_2O by reduction with $Na_2S_2O_4$ under mild conditions or by irradiation at 354 nm or with sunlight. There have been only a few reports of photocleavable surfactants of any type.[5]



A **B**

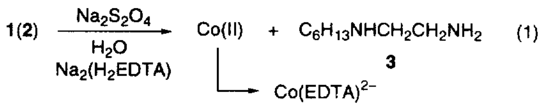
1, R = C_6H_{13}



A **B**

2, R = C_6H_{13}

The reduction of **1** and **2** in aqueous solutions gave Co(II) and *N*-hexylethylenediamine (**3**) (eq 1), and presumably NO_2^-. The reaction mixtures also contained disodium dihydrogen ethylenediaminetetraacetate [$Na_2(H_2EDTA)$], which formed a complex with Co(II) and thereby allowed its quantitation as $Co(EDTA)^{2-}$.



$$1(2) \xrightarrow[\substack{H_2O \\ Na_2(H_2EDTA)}]{Na_2S_2O_4} \underset{\downarrow\ Co(EDTA)^{2-}}{Co(II)} + \underset{\mathbf{3}}{C_6H_{13}NHCH_2CH_2NH_2} \quad (1)$$

The following is a procedure for reductive cleavage of **2**, and that for **1** was analogous. To a transparent deep yellow solution of 100 mg (0.199 mmol) of **2** in 125 mL of H_2O containing 93 mg (0.25 mmol) of $Na_2(H_2EDTA)$ at 25 °C was added, in one portion, a solution of 173 mg (0.995 mmol) of $Na_2S_2O_4$ in 5.0 mL of

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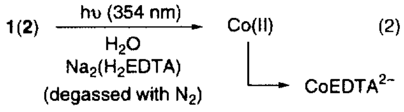
H_2O. While the reaction mixture was stirred at 25 °C for 30 min, its color changed to pale purple, and its pH deceased to 5.4 from 7.0. To ensure complete chelation of Co(II) by $Na_2(H_2EDTA)$ to give $Co(EDTA)^{2-}$,[6] the reaction mixture was adjusted to pH 13.5 with aqueous 3 M KOH. Then it was extracted with three 25-mL portions of CH_2Cl_2, and the combined extracts were dried (Na_2SO_4) and rotary evaporated. The residue was column chromatographed on silica gel with 1:5 (v/v) MeOH-CH_2Cl_2 as eluant to give **3**,[7] identified by ^1H and ^{13}C NMR and identical with authentic material. The average yield of **3** in three runs was (85 ± 2)%.

The formation of Co(II) in the reduction was confirmed and quantitated as follows. After the above extraction, the reaction mixture was stirred for 12 h at 25 °C to allow complete chelation of Co(II). Then it was concentrated to just below 25 mL by rotary evaporation and diluted to 25.00 mL with H_2O. The UV-vis spectrum of this solution contained an absorption maximum at 490 nm, consistent with $Co(EDTA)^{2-}$ at pH 13.5.[6,8] The absorbance at 490 nm and a calibration curve for the analysis were used to determine the concentration of $Co(EDTA)^{2-}$ and thus the yield of Co(II), which was (98 ± 2)% in three runs. In the reductive cleavage of **1**, the average yields of **3** and Co(II) in three runs were (84 ± 2) and (99 ± 2)%, respectively.

Photochemical cleavage of **1** and **2** in H_2O gave Co(II) (eq 2) and presumably NO_2^- and NO_3^- (see below) and a complex mixture of organic products containing some **3**, as determined by ^1H NMR. The following is the photolysis procedure for **2**, and that for **1** was analogous. A transparent solution of 5.0 mg (0.010 mmol) of **2** and 4.1 mg (0.011 mmol) of $Na_2(H_2EDTA)$ in 3.5 mL of H_2O within a quartz cuvette (1 cm × 1 cm × 4.8 cm) was degassed with a stream of N_2 for 2 min. Then the cuvette was sealed with a cap and parafilm, and the solution, thermostatted at 22 ± 0.5 °C, was irradiated for 3 min at 354 nm with a 1000 W Hg lamp.[9] During this time the color of the solution changed from deep yellow to pale purple, indicating the destruction of **2**. The loss of **2** was followed by UV-vis spectroscopy; see Figure 1. With irradiation, the absorbance at ca. 450 nm decreased significantly as that at >500 nm increased modestly. Thereafter, the reaction mixture was adjusted to pH 13.5 with 3 M KOH, stirred for 12 h at 25 °C, and diluted to 5.00 mL with H_2O. The absorbance at 490 nm and a calibration curve were used as above to determine the concentration of $Co(EDTA)^{2-}$ and the yield of Co(II), which was (89 ± 7)% in three runs. In the photochemical cleavage of **1**, the average yield of Co(II) in three runs was (93 ± 2)%. Controls demonstrated that $Na_2(H_2EDTA)$ by itself does not effect cleavage under the conditions of the above reductive and photochemical processes.[10]



(2)

Photochemical cleavages of **1** and **2** were also effected with sunlight, to demonstrate that they can be cleaved under very mild conditions. A solution of **1**(**2**), prepared as for the above photolyses, was exposed to window glass-filtered sunlight at 25 °C. The destruction of **1**(**2**) was complete after 90 min, as determined by UV-vis spectroscopy.

The UV-vis spectra of both **1** and **2**, recorded in MeOH, displayed three absorption bands. For **1**: λ_{max} (log ε_{max}) = 252 (4.36), 351 (3.65), and 453 nm (2.38); for **2**: 256 (4.46), 353 (3.66), and 447 nm (2.33). The parent compound *trans*-dinitro-bis(ethylenendiamine)cobalt(III) nitrate[11] in MeOH gave comparable absorption bands at somewhat lower wavelengths: 250 (4.06), 340 (3.50), and 416 nm (2.51). The bathochromic shifts on going from the 340-nm absorption for the parent compound to the 351 and 353-nm absorptions for **1** and **2**, respectively, are consistent with results for other Co(III) complexes.[7a,12a]

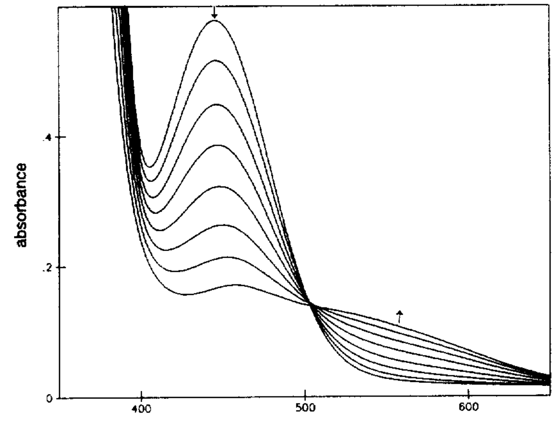


Figure 1. Changes in absorption spectra of a degassed aqueous solution containing 0.0029 M **2** and 0.0031 M $Na_2(H_2EDTA)$ with irradiation at 354 nm. Spectra were obtained at 20-sec intervals; the top spectrum corresponds to time = 0.

The first and second absorption bands of the complexes are due to electronic transitions within the metal center,[13] and the third, at the shortest wavelength, is most likely associated with the *trans* dinitro groups.[12b] For an octahedral Co(III) complex the metal transitions are $^1A_{1g} \rightarrow {}^1T_{1g}$ (first) and $^1A_{1g} \rightarrow {}^1T_{2g}$ (second), while the highest energy band is most likely ligand-to-metal charge-transfer in character. Within the local D_{2d} symmetry imposed by the staggered nitro π-interactions[4] the molecular orbitals corresponding to these transitions are symmetry-forbidden $B_2 \rightarrow E_g{}^*$ (first) and symmetry-allowed $E_{2g} \rightarrow E_{2g}{}^*$ (second) and $E_g \rightarrow E_g{}^*$ (third).[14]

In the photochemical cleavages of **1** and **2**, an $E_{2g} \rightarrow E_{2g}{}^*$ transition, resulting from irradiation at 354 nm, increases the electron density in the antibonding orbital localized between Co(III) and a nitro ligand, with resultant homolysis of the Co(III)-N bond to give Co(II) and nitrogen dioxide, which then undergoes hydrolytic disproportionation to yield NO_2^- and NO_3^-.[15] On the other hand, the cleavage by $Na_2S_2O_4$ involves direct reduction of the metal center since the LUMO for **1**(**2**) is predominantly metal-centered.[14]

Solutions of **1** and **2** identical to those used in the photochemical cleavages were irradiated at 440 nm with the 1000 W Hg lamp[9] for 60 min. By UV-vis spectroscopy, there was no decomposition of **1**(**2**). Analogous runs with **1** and **2** with irradiation at 254 nm were not made, since excitation at this wavelength could result in cross-population of the photochemically active states associated with their absorptions at 351 and 353 nm, respectively.

The solubility limits of **1** and **2** in H_2O at 25 °C are 0.0028 (1.4) and 0.0034 M (1.7 mg/mL), respectively. The surface tensions (du Noüy ring) of 0.0028 M solutions of **1** and **2** in H_2O are 54 and 60 mN/m, respectively. Since the Krafft temperatures (T_k)[16] of **1** and **2** in H_2O are 42 and 38 °C, respectively, their solutions can contain only surfactant monomers at 25 °C. Aggregation of a surfactant can occur only above its T_k value and above its critical aggregation concentration.[16] But solutions of monomeric surfactant below its T_k display detergency.[17]

The lack of aggregation of **1** and **2** at 25 °C is consistent with cryo-transmission electron microscopy (cryo-TEM)[18] results for a 1% (w/w) solution of the dioctyl homologue of **2** in a pH 7.0 Tris buffer ($I = 0.007$) vitrified from 55 °C, which is below its T_k value of 71 °C. No micellar or larger aggregates were observed in the cryo-TEM micrograph. Also consistent with the absence of aggregates larger than micelles are the high resolution ^1H NMR spectra obtained for saturated solutions of **1** and **2** in D_2O at 25 °C.

In summary, we have demonstrated the cleavable nature of surfactants **1** and **2** by their reductive and photochemical conversion to Co(II) and other fragments.

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(8) The UV-vis spectrum of an aqueous solution at pH 13.5 (KOH) containing 0.0250 M $Co_2NO_3 \cdot 6H_2O$ and 0.0283 M $Na_2(H_2EDTA) \cdot 2H_2O$ displays three absorption bands: λ_{max} (log ε_{max}) = 617 (0.15), 520 (1.13), and 490 nm (1.18).

(9) Radiation from the lamp (Oriel Model 6287) was passed through a long pass filter (Oriel Model 59460) to remove radiation 350 nm, and then through a monochromator (Oriel 59450) set at 354 nm.

(10) In runs identical to the reductive and photochemical cleavages, except for the absence of $Na_2S_2O_4$ or lack of irradiation, respectively, there was no reaction of **1(2)**, even after 2 days.

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